

**Improving Polymer Recycling Through Understanding Passive
Compatibilization of Semicrystalline Polymer Blends from Waste
Streams**

**A Dissertation Presented for the
Doctor of Philosophy
Degree
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DEDICATION

I dedicate my work to my family: my mom, dad, siblings, and various pets.

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ABSTRACT

Recycling plastics is not an optimized process, as only 9% of plastic waste is repurposed each year. Products from recycling streams have diminished mechanical properties, which makes them fiscally undesirable. These diminished properties are due to plastic sorting limitations resulting in immiscible polymer mixtures, which phase separate in the melt during mechanical recycling. Compatibilizers can be added to the melt to stabilize the interface between immiscible polymer blends. While the important molecular-level interactions of effective compatibilizers for blends composed solely of amorphous polymers are well established, the equivalent molecular-level processes that are needed in blends that consist of semicrystalline homopolymers remain less understood. This dissertation focuses on understanding the dominating mechanisms that enable effective compatibilizers for immiscible blends containing a semicrystalline polymer component.

The first system evaluated is an immiscible blend of amorphous polyvinyl chloride (PVC) and semicrystalline polyolefin elastomer (POE). Chapter II looks at the individual interactions between commercially available chlorinated polyethylene compatibilizers and each homopolymer. This study determined that semicrystalline compatibilizers that optimized entanglement with the semicrystalline phase showed the best improvement in interfacial adhesion and the most significant evidence of co-crystallization. Chapter III expanded on these results using synthesized dichlorinated cyclooctene/cyclooctene gradient copolymers as compatibilizers with varying monomer feed ratios and molecular weight. Chapter V uses dechlorinated PVC as a compatibilizer

for PVC/POE systems. These materials exhibit similar trends to those previously observed but have improved interfacial adhesion due to increased miscibility with the PVC phase, facilitated by the presence of vinyl chlorine groups. Chapter IV examined a semicrystalline/semicrystalline polymer blend system composed of high-density polyethylene and isotactic polypropylene. These blends were compatibilized with ethylene-propylene rubbers and an ethylene/1-octene random copolymer. In these compatibilizers, only the ethylene component is crystalline, and improved overall mechanical properties were found by optimizing the miscibility and entanglement between the semicrystalline components. Overall, in blends containing a semicrystalline homopolymer, the compatibilizer will entangle between the phases based on the miscibility of the segments and block lengths. If these segments are crystalline, then a co-crystal between the compatibilizer and homopolymer can form at the entangled sites, anchoring the interface.

TABLE OF CONTENTS

CHAPTER I: INTRODUCTION.....	1
Polymer Recycling.....	2
Polymer Blends.....	3
Polymer Thermodynamics	5
Compatibilization of Polymer Blends.....	11
Importance of Copolymer Sequence Distribution in Compatibilization	13
Impact of Polymer Sequence on the Ability to Entangle between Polymer Phases .	14
Role of Polymer Crystallization in Blend Compatibilization	18
Elucidating Compatibilizer Efficiency	25
Determination of Morphology in Phase-Separated Blends	27
Objective and Outline	35
CHAPTER II: MOLECULAR DESIGN OF EFFECTIVE COMPATIBILIZERS OF A	
CRYSTALLINE POLYMER BLEND.....	38
Abstract.....	39
Introduction.....	40
Experimental	46
Materials	46
Nuclear Magnetic Resonance Spectroscopy:.....	47
Size Exclusion Chromatography:	47
Interfacial Adhesion of Trilayer Samples:.....	47
Interfacial Adhesion of Bilayer Samples:	48

Crystallinity Analysis Sample Preparation:	50
Differential Scanning Calorimetry (DSC):	50
X-ray scattering:.....	51
Results and Discussion	52
Characterization of Commercial c-PE:	52
Interfacial Adhesion (Ga) of PVC/POE Interface with c-PE Compatibilizers:	55
Interfacial Adhesion for PVC/c-PE and c-PE/POE Bilayer Interfaces:.....	58
Thermal Behavior and Crystalline Structure of Crystalline Polymer Blends:.....	67
Conclusion	76
Acknowledgements	77
CHAPTER III: CORRELATING CHLORINATED POLYETHYLENE MOLECULAR	
STRUCTURE TO COMPATIBILIZATION EFFICIENCY FOR MIXED POLYMER	
WASTE.....	78
Abstract	79
Introduction.....	80
Experimental	83
Materials and Methods.....	83
Formation of Compatibilized Trilayer Films.....	85
Characterization of Materials.....	86
Results and Discussion	88
Characterization of c-PE Homopolymers and Copolymers.....	88
Determination of Copolymer Sequence Distribution.	88

Ability of Synthesized Copolymers to Strengthen the POE/PVC Interface	93
Comparing the Compatibilization Effectiveness of Synthesized Copolymers and Commercial Materials.....	97
Conclusion	106
Acknowledgement	107
CHAPTER IV: IMPACT OF COMMERCIAL POLYOLEFIN ARCHITECTURE AND COMPOSITION ON ITS ABILITY TO COMPATIBILIZE HIGH-DENSITY POLYETHYLENE/ISOTACTIC POLYPROPYLENE BLENDS	
	109
Abstract	110
Introduction.....	111
Experimental	116
Materials	116
Dog Bone Sample Prep.....	116
Micro-compounding and Injection Molding.....	118
Tensile Testing.....	118
Differential Scanning Calorimetry.....	118
Nuclear Magnetic Resonance	119
High-Temperature Size-Exclusion Chromatography	120
Results and Discussion	120
Mechanical Properties of the HDPE Rich Blends	120
Determination of Compatibilizer Molecular Structure	125
Impact of Compatibilizer Molecular Structure on Compatibilization	131

Mechanical Properties of the i-PP Rich Blends	136
Conclusion	145
Acknowledgement:	146
CHAPTER V: COMPATIBILIZATION OF PVC/POLYOLEFIN ELASTOMER	
BLENDS WITH DECHLORINATED PVC	147
Abstract	148
Introduction	149
Experimental	154
Materials	154
Nuclear Magnetic Resonance Spectroscopy:	155
Interfacial Adhesion of Trilayer Samples:	155
Differential Scanning Calorimetry (DSC):	157
Results and Discussion	157
Impact of Chain Length on Interfacial Adhesion	159
Possible Impact of Copolymer Architecture and Composition on Interfacial	
Adhesion	159
Determination and Impact of Compatibilizer Block Length	162
Comparison of Dechlorinated PVC and Commercial Materials.....	165
Conclusion	170
Acknowledgement:	170
CHAPTER VI: CONCLUSION AND FUTURE OUTLOOKS	
Conclusions	172

Future Outlooks	174
REFERENCES	176
APPENDICES	201
Appendix A: Chapter II Supporting Information.....	201
¹ H NMR Spectra for Commercial c-PE	201
¹³ C NMR Spectra for Commercial c-PE	206
Relative Blockiness Calculations.....	210
Peel Test Example.....	211
DSC Curves	212
WAXS/SAXS	215
Appendix B: Chapter III Supporting Information	217
¹ H NMR Spectrum.....	217
Quantitative ¹³ C NMR Spectrum	223
GPC Chromatograms of c-PE Compatibilizers:	229
DSC Chromatograms of c-PE Compatibilizers:	229
Determination of Chlorine Content:	247
Determination of Reactivity Ratios:	248
Appendix C: Chapter IV Supporting Information	251
Structure assignments for ethylene-propylene random copolymers:.....	251
Differential scanning calorimetry (DSC).....	253
High temperature ¹ H NMR	258
High temperature quantitative ¹³ C NMR	261

Stress-Strain Curves:.....	264
Toughness vs. Homopolymer Crystallinity for iPP-rich blends.	267
Appendix D: Chapter V Supporting Information	269
¹ H NMR spectrum for dechlorinated PVC	269
Peel Test Curves for dechlorinated PVC.....	277
VITA	284

LIST OF TABLES

Table 2.1. Molecular characteristics of seven commercial chlorinated polyethylene compatibilizers as well as interfacial adhesion of PVC/POE interfaces compatibilized with the c-PE.	54
Table 2.2. Melt temperature and heat of fusion of the 16-day annealed samples of the three c-PE/POE blends.	68
Table 3.1. Representative examples of c-PE homopolymers and copolymers synthesized via ROMP. ^a	90
Table 4.1. ExxonMobil VistaMaxx Ethylene-Propylene Rubbers of Interest. Ethylene content determined by quantitative ¹³ C NMR. Percent crystallinity is calculated from DSC.	117
Table 4.2. Overall mechanical properties for the injection molded samples using the ASTM 1708D standard. Average and standard deviations are presented for each mechanical property.	123
Table 4.3. Secondary and tertiary carbon assignments for ethylene-propylene random copolymers.	127
Table 4.4. Ethylene and propylene triad contents for VistaMaxx EPR samples as determined from quantitative ¹³ C NMR.	129
Table 4.5. Crystallization characteristics for HDPE/iPP blends normalized based on composition.	141

Table 5.1. Overview of d-PVC samples from USC. D-PVC chlorine content was calculated based on ^1H NMR spectra. Starting M_n and initiator concentration provided by collaborators. All other data was collected at UTK.....	158
Table 5.2. Hansen solubility parameters for the materials relevant to this study. All solubility parameters are in $(\text{MPa})^{1/2}$	166
Table 5.3. Commercially available c-PE spin-coated with either THF or toluene solutions to get interfacial adhesion.	168
Table 5.4. Characterization of dechlorinated waste PVC and its efficiency as a compatibilizer.	168
Table S2.1. Bernoullean Probabilities obtained from Chang et. al. ⁵¹	210
Table S2.2. ^{13}C NMR integrations for 23/R which has a chlorine content of 23 mol% Cl.	210
Table S2.3. ^{13}C NMR integrations for 19/43B, which has a chlorine content of 19 mol% Cl.....	210
Table S4.1. Structure assignments for ethylene-propylene random copolymers.....	251

LIST OF FIGURES

Figure 1.1. Representation of high interfacial tension between immiscible phases and stress transfer across a phase-separated interface with the presence of a compatibilizer.	4
Figure 1.2. Filled 2-d lattice model with each site occupied by polymer species 1 or 2. Image obtained from Reference 17.....	7
Figure 1.3. Morphology of an immiscible polymer blend.	10
Figure 1.4. Representation of how reactive and passive compatibilizers interact at the interface of polymer blends. Reactive compatibilizers will form block copolymers in situ, while passive compatibilizers are already formed copolymers added to the melt.	12
Figure 1.5. Impact of polymer sequence on the ability to entangle between polymer phases.....	15
Figure 1.6. Model of entanglement and co-crystallization mechanisms at the interface between two polymer phases.	20
Figure 1.7. DSC thermogram of 54% crystalline isotactic polypropylene run at 10 °C/min. (Exo Up).....	22
Figure 1.8. SAXS (top) and WAXS (bottom) spectra for polyolefin elastomers (POE) and three 50:50 POE: chlorinated polyethylene (c-PE) blends. C-PE can be used as a compatibilizer for POE and polyvinyl chloride polymer blends.	24
Figure 1.9. Stress-Strain curve for high-density polyethylene using ASTM D1708 standard.	28

Figure 1.10. Simplified diagram showing the differences between secondary and backscattered electrons in scanning electron microscopy.	31
Figure 1.11. TEM image of an 80/20 wt% HDPE/iPP immiscible blend that was embedded in epoxy and ultra-microtomed at room temperature. The sample was stained with RuO ₄ vapors for 2 hours.	33
Figure 2.1. Model of phase separation driving droplet coalescence in an immiscible polymer blend.	43
Figure 2.2. Model of compatibilizer stabilizing the interface between immiscible polymers to prevent droplet coalescence from occurring.	43
Figure 2.3. Model of how different copolymer structures interact as compatibilizers at the interface between two domains.	43
Figure 2.4. Structure of Mark 1900 thermal stabilizer, methyltin mercaptide.	46
Figure 2.5. Combination T+U peel test with the flexible polymer pulled from the more rigid polymer.	49
Figure 2.6. Variable temperature ¹ H NMR of 5 wt% 23/9B c-PE dissolved in TCE-d ₂ at 90 °C.	53
Figure 2.7. Quantitative ¹³ C NMR for a random (top) and blocky (bottom) c-PE. The peak at ~29 ppm that corresponds to non-chlorinated carbon pentads is more prevalent in the blockier sample.	53
Figure 2.8. Relationships between interfacial adhesion and crystallinity (top) and blockiness (bottom) for the trilayer compatibilized system. Error bars represent one standard deviation from the average.	56

Figure 2.9. Impact of composition (top) and number-average molecular weight (bottom) of compatibilizers on the strength of the PVC/c-PE interface. Error bars represent one standard deviation from the average.	59
Figure 2.10. Relationship between blockiness and adhesion for the highest chlorine content at the PVC/c-PE interface. Error bars represent one standard deviation from the average.	60
Figure 2.11. Impact of crystallinity (top) and sequence structure (bottom) on the interfacial adhesion in the PVC/c-PE bilayer interfaces. Error bars represent one standard deviation from the average.	62
Figure 2.12. Impact of crystallinity (top) and sequence structure (bottom) for c-PE/POE. Error bars represent one standard deviation from the average.	63
Figure 2.13. Comparison of the individual bilayers to the overall trilayer system regarding the extent of crystallinity (left) and mol% chlorination (right). Error bars represent one standard deviation from the average.....	66
Figure 2.14. Overall (left) and zoomed (right) DSC spectra of the three chlorinated polyethylene/polyolefin elastomer blends and the pure components after annealing at 47°C for 16 days. The figures on the left highlight the shift in the c-PE melting peaks and the figures on the right highlight shifts in the POE melting peaks	69
Figure 2.15. Comparison of normalized DSC integrations for the POE or c-PE components for three c-PE/POE systems.	71
Figure 2.16. SAXS (top) and WAXS (bottom) spectra for three c-PE/POE systems.....	73

Figure 2.17. Relationship between d-space values from WAXS spectra with c-PE/POE bilayer adhesion and heat of fusion for 23/R, 23/27B (worst performing) and 19/43B (best performing).	74
Figure 3.1. Mechanisms of entanglement and co-crystallization between polymer chains.	84
Figure 3.2. Combination T+U peel test with the flexible polymer pulled from the more rigid polymer.....	89
Figure 3.3. Monitoring comonomer conversion of Cl ₂ COE (M _A , red) and COE (M _B , blue) using the Beckingham-Sanoja-Lynd (BSL) model to determine reactivity ratios. The black dotted line is representative of a true random copolymerization. .	92
Figure 3.4. Interfacial adhesion strength of the compatibilized PVC/c-PE/POE trilayer interface as a function of the heat of fusion for the S25, S50, and S75 series of compatibilizers. Error bars represent one standard deviation from the average.	95
Figure 3.5. Maximum trilayer interfacial adhesion of the compatibilized PVC-POE interface for each of the COE compositions of the synthesized Cl ₂ COE-r-COE copolymers. Error bars represent one standard deviation from the average.	95
Figure 3.6. Average interfacial adhesion plotted against molecular weight for homopolymer of Cl ₂ COE and synthesized c-PE copolymers of (a) homopolymers of Cl ₂ COE (labeled as S100), (b) copolymers of Cl ₂ COE and COE in a 75:25 ratio (labeled as S75), (c) copolymers of Cl ₂ COE and COE in a 50:50 ratio (labeled as S50), (d) copolymers of Cl ₂ COE and COE in a 25:75 ratio (labeled as S25). Error bars represent one standard deviation from the average.	96

Figure 3.7. Plots reporting the relative blockiness, as determined by quantitative ^{13}C NMR, and interfacial adhesion of commercial c-PEs (top) and synthesized c-PEs (bottom). The gray line at 20% represents the maximum relative blockiness observed for the synthesized samples. Error bars represent one standard deviation from the average.	100
Figure 3.8. Depiction of random, gradient, and block copolymers at a polymer blend interface.....	102
Figure 3.9. Polymer percent blockiness vs. heat of fusion of synthesized copolymers (solid dots) and commercial c-PEs (open squares).	102
Figure 3.10. Average interfacial adhesion of the compatibilized PVC/POE interface as a function of the heat of fusion of commercial c-PEs. Error bars represent one standard deviation from the average.....	104
Figure 3.11. Average interfacial adhesion vs. molecular weight of commercial c-PEs. Error bars represent one standard deviation from the average.	104
Figure 4.1. Illustration of phase separation in an immiscible polymer blend.....	112
Figure 4.2. Structure of ethylene-propylene rubber (EPR) and ethylene/1-octene polyolefin elastomers (POE).....	115
Figure 4.3. Stress-Strain curves for the pure components and 80/20 mass ratio of HDPE/iPP.	121
Figure 4.4. Change in elongation at break of the compatibilized 80/20 HDPE/i-PP blends at different compatibilizer loadings. HDPE has an elongation at break of 973%,	

which is significantly greater than that of the compatibilized blends or i-PP. Error bars represent one standard deviation from the average.	124
Figure 4.5. Quantitative ^{13}C NMR assignments for ethylene/1-octene copolymers.....	130
Figure 4.6. Quantitative ^{13}C NMR peak assignments for Engage 8180 run in 1,1,2,2-tetrachloroethane-d ₂	130
Figure 4.7. Toughness of 5 wt% compatibilizer blend as a function of weight-average molecular weight (M_w) (top) and the relationship between the molecular weight characteristics and toughness for the five VistaMaxx (VM) compatibilizers loaded at 5 wt% (bottom). Error bars represent one standard deviation from the average. ...	132
Figure 4.8. Change in toughness as a function of the mol% ethylene content of the VistaMaxx (VM) compatibilizers at 5 wt% compatibilizer loading. HDPE has a toughness of 253 MPa and iPP has a toughness of 198 MPa. Error bars represent one standard deviation from the average.	134
Figure 4.9. Change in toughness with the mol% of PPP triads in VistaMaxx (VM) compatibilizers at 5 wt% compatibilizer loading. HDPE has a toughness of 253 MPa and iPP has a toughness of 198 MPa. Error bars represent one standard deviation from the average.	134
Figure 4.10. Change in toughness with the mol% of EEE triads in VistaMaxx (VM) compatibilizers at 5 wt% compatibilizer loading. HDPE has a toughness of 253 MPa and iPP has a toughness of 198 MPa. Error bars represent one standard deviation from the average.	135

- Figure 4.11.** Comparison of compatibilizer efficiency for ethylene-propylene copolymers against an Engage POE for (a.) ethylene content in mol% as well as (b.) the mol% of EEE triads. Error bars represent one standard deviation from the average. 137
- Figure 4.12.** Comparison of compatibilizer efficiency at 5 wt% compatibilizer loading in 30/70 HDPE/iPP blends compared to the 80/20 HDPE/iPP blends (a) based on mol% EEE triad (b) and PPP triad (c) compositions as well as against number-average molecular weight (d). Error bars represent one standard deviation from the average. 138
- Figure 4.13.** Percent crystallinity of HDPE (a) and iPP (b) phases in the 80/20 HDPE/iPP samples determined by integrating the corresponding melting peak from DSC. Total crystallinity reflects the sum of both melting processes for both the 80/20 HDPE/iPP (c) and 30/70 HDPE/iPP (d) samples. Normalized by composition using Eqns 4.1-4.3. All compatibilized samples are at 5 wt% loading. Error bars represent one standard deviation from the average. 143
- Figure 5.1.** Mechanisms of entanglement and co-crystallization..... 151
- Figure 5.2.** Relationship between the extent of crystallinity (heat of fusion) and the chlorination of d-PVC. Open shapes were dechlorinated at 40 °C. Patterned filled samples have a starting M_n of 46 kDa. All other samples have a starting M_n of 99 kDa and were dechlorinated at 80 °C. Diamonds represent unpublished samples. 160
- Figure 5.3.** Impact of chlorine content of d-PVC compatibilizer on the overall interfacial adhesion. Open shapes were dechlorinated at 40 °C. Patterned filled samples have a starting M_n of 46 kDa. All other samples have a starting M_n of 99 kDa and were

dechlorinated at 80 °C. Diamond samples are unpublished data. Error bars represent one standard deviation from the average. 160

Figure 5.4. Impact of block number (left) and theoretical block length (right) on interfacial adhesion for d-PVC. Theoretical block lengths based on the starting M_n and the average block number for d-PVC. Open shapes were dechlorinated at 40 °C. Patterned filled samples have a starting M_n of 46 kDa. All other samples have a starting M_n of 99 kDa and were dechlorinated at 80 °C. Diamond samples are unpublished data. Error bars represent one standard deviation from the average. . 163

Figure 5.5. Interfacial adhesion for both c-PE and d-PVC spin-coated in THF and c-PE in toluene. Open shapes were dechlorinated at 40 °C. Patterned filled samples have a starting M_n of 46 kDa. All other samples have a starting M_n of 99 kDa and were dechlorinated at 80 °C. Diamond samples are unpublished data. Error bars represent one standard deviation from the average. 169

Figure 5.6. Dechlorinated waste PVC fits the plot containing the dechlorinated virgin PVC in respect to chlorine content and interfacial adhesion. Error bars represent one standard deviation from the average. 169

Figure S2.1. ^1H NMR spectrum of 23/R dissolved in 1,1,2,2-tetrachloroethane- d_2 201

Figure S2.2. ^1H NMR spectrum of 10/27B dissolved in 1,1,2,2-tetrachloroethane- d_2 . 202

Figure S2.3. ^1H NMR spectrum of 14/19B dissolved in 1,1,2,2-tetrachloroethane- d_2 . 202

Figure S2.4. ^1H NMR spectrum of 19/43B dissolved in 1,1,2,2-tetrachloroethane- d_2 . 203

Figure S2.5. ^1H NMR spectrum of 18/36B dissolved in 1,1,2,2-tetrachloroethane- d_2 . 203

Figure S2.6. ^1H NMR spectrum of 23/9B dissolved in 1,1,2,2-tetrachloroethane- d_2 . .. 204

Figure S2.7. ^1H NMR spectrum of 23/27B dissolved in 1,1,2,2-tetrachloroethane- d_2 .	204
Figure S2.8. Quantitative ^{13}C NMR of 23/R dissolved in 1,1,2,2-tetrachloroethane- d_2 .	
.....	206
Figure S2.9. Quantitative ^{13}C NMR of 10/27B dissolved in 1,1,2,2-tetrachloroethane- d_2 .	
.....	207
Figure S2.10. Quantitative ^{13}C NMR of 14/19B dissolved in 1,1,2,2-tetrachloroethane- d_2 .	
.....	207
Figure S2.11. Quantitative ^{13}C NMR of 19/43B dissolved in 1,1,2,2-tetrachloroethane- d_2 .	
.....	208
Figure S2.12. Quantitative ^{13}C NMR of 18/36B dissolved in 1,1,2,2-tetrachloroethane- d_2 .	
.....	208
Figure S2.13. Quantitative ^{13}C NMR of 23/9B dissolved in 1,1,2,2-tetrachloroethane- d_2 .	
.....	209
Figure S2.14. Quantitative ^{13}C NMR of 23/27B dissolved in 1,1,2,2-tetrachloroethane- d_2 .	
.....	209
Figure S2.15. Example of the raw data collected from a combination T+U peel test (trial 3 for sample 14/19B).	
.....	211
Figure S2.16. DSC curves of pure POE, cPE, melted and separated 19/43B blends. ...	212
Figure S2.17. DSC curves of pure POE, cPE, melted and separated 23/R blends.	213
Figure S2.18. DSC curves of pure POE, cPE, melted and separated 23/27B blends. ...	214
Figure S2.19. SAXS curves for the three cPEs of interest with the individual cPE scattering curves.	
.....	215

Figure S2.20. WAXS curves for the three cPEs of interest with the individual cPE scattering curves.....	216
Figure S3.1. ^1H NMR spectrum of Cl_2COE monomer in CDCl_3	217
Figure S3.2. ^1H NMR spectrum of S100-3 prior to hydrogenation in CDCl_3	218
Figure S3.3. ^1H NMR spectrum of S75-3 prior to hydrogenation in CDCl_3	219
Figure S3.4. ^1H NMR spectrum of S50-1 prior to hydrogenation in CDCl_3	219
Figure S3.5. ^1H NMR spectrum of S25-1 prior to hydrogenation in CDCl_3	220
Figure S3.6. ^1H NMR spectrum of S100-3 dissolved in 1,1,2,2-tetrachloroethane- d_2	220
Figure S3.7. ^1H NMR spectrum of S75-3 dissolved in 1,1,2,2-tetrachloroethane- d_2	221
Figure S3.8. ^1H NMR spectrum of S50-1 dissolved in 1,1,2,2-tetrachloroethane- d_2 . ..	221
Figure S3.9. ^1H NMR spectrum of S25-1 dissolved in 1,1,2,2-tetrachloroethane- d_2 . ..	222
Figure S3.10. Quantitative ^{13}C NMR of PCOE dissolved in 1,1,2,2-tetrachloroethane- d_2	223
Figure S3.11. Quantitative ^{13}C NMR of S100-3 dissolved in 1,1,2,2-tetrachloroethane- d_2	224
Figure S3.12. Quantitative ^{13}C NMR of S75-3 dissolved in 1,1,2,2-tetrachloroethane- d_2	224
Figure S3.13. Quantitative ^{13}C NMR of S75-4 dissolved in 1,1,2,2-tetrachloroethane- d_2	225
Figure S3.14. Quantitative ^{13}C NMR of S75-5 dissolved in 1,1,2,2-tetrachloroethane- d_2	225

Figure S3.15. Quantitative ^{13}C NMR of S50-2 dissolved in 1,1,2,2-tetrachloroethane- d_2	226
Figure S3.16. Quantitative ^{13}C NMR of S50-3 dissolved in 1,1,2,2-tetrachloroethane- d_2	226
Figure S3.17. Quantitative ^{13}C NMR of S50-5 dissolved in 1,1,2,2-tetrachloroethane- d_2	227
Figure S3.18. Quantitative ^{13}C NMR of S25-1 dissolved in 1,1,2,2-tetrachloroethane- d_2	227
Figure S3.19. Quantitative ^{13}C NMR of S25-3 dissolved in 1,1,2,2-tetrachloroethane- d_2	228
Figure S3.20. Quantitative ^{13}C NMR of S25-4 dissolved in 1,1,2,2-tetrachloroethane- d_2	228
Figure S3.21. DSC spectrum for S100-1.	230
Figure S3.22. DSC spectrum for S100-2.	230
Figure S3.23. DSC spectrum for S100-3.	231
Figure S3.24. DSC spectrum for S100-4.	231
Figure S3.25. DSC spectrum for S100-5.	232
Figure S3.26. DSC spectrum for S100-6.	232
Figure S3.27. DSC spectrum for S100-7.	233
Figure S3.28. DSC spectrum for S100-8.	233
Figure S3.29. DSC spectrum for S100-9.	234
Figure S3.30. DSC spectrum for S75-1.	234

Figure S3.31. DSC spectrum for S75-2.	235
Figure S3.32. DSC spectrum for S75-3.	235
Figure S3.33. DSC spectrum for S75-4.	236
Figure S3.34. DSC spectrum for S75-5.	236
Figure S3.35. DSC spectrum for S75-6.	237
Figure S3.36. DSC spectrum for S50-1.	237
Figure S3.37. DSC spectrum for S50-2.	238
Figure S3.38. DSC spectrum for S50-3.	238
Figure S3.39. DSC spectrum for S50-4.	239
Figure S3.40. DSC spectrum for S50-5.	239
Figure S3.41. DSC spectrum for S50-6.	240
Figure S3.42. DSC spectrum for S25-1.	240
Figure S3.43. DSC spectrum for S25-2.	241
Figure S3.44. DSC spectrum for S25-3.	241
Figure S3.45. DSC spectrum for S25-4.	242
Figure S3.46. DSC spectrum for S25-5.	242
Figure S3.47. DSC spectrum for S25-6.	243
Figure S3.48. DSC spectrum for 23/R.	243
Figure S3.49. DSC spectrum for 23/9B.	244
Figure S3.50. DSC spectrum for 10/27B.	244
Figure S3.51. DSC spectrum for 18/36B.	245
Figure S3.52. DSC spectrum for 19/43B.	245

Figure S3.53. DSC spectrum for 14/19B.	246
Figure S3.54. DSC spectrum for 23/27B.	246
Figure S3.55. ¹ H NMR spectrum of S50-1 dissolved in 1,1,2,2-tetrachloroethane-d ₂ with integrations of S ₁ , S ₂ , and S ₃ identified.....	247
Figure S3.56. ¹ H NMR of copolymerization ran for 10 seconds with trimethoxy benzene as internal standard in deuterated chloroform.....	249
Figure S4.1. DSC spectrum for VistaMaxx (VM) 3588 (ExxonMobil).	253
Figure S4.2. DSC spectrum for VistaMaxx (VM) 6202 (ExxonMobil).	254
Figure S4.3. DSC spectrum for VistaMaxx (VM) 3980 (ExxonMobil).	254
Figure S4.4. DSC spectrum for VistaMaxx (VM) 3020 (ExxonMobil).	255
Figure S4.5. DSC spectrum for VistaMaxx (VM) 8880 (ExxonMobil).	255
Figure S4.6. DSC spectrum for Engage 8180 (DOW Chemical).	256
Figure S4.7. DSC spectrum for all 80/20 HDPE/iPP blends with 5 wt% compatibilizer loading.....	257
Figure S4.8. DSC spectrum for all 80/20 HDPE/iPP blends with 5 wt% compatibilizer loading.....	257
Figure S4.9. ¹ H NMR Spectrum for VistaMaxx (VM) 3588 dissolved in 1,1,2,2- tetrachloroethane-d ₂	258
Figure S4.10. ¹ H NMR spectrum for VistaMaxx (VM) 6202 dissolved in 1,1,2,2- tetrachloroethane-d ₂	259
Figure S4.11. ¹ H NMR spectrum for VistaMaxx (VM) 3020 dissolved in 1,1,2,2- tetrachloroethane-d ₂	259

Figure S4.12. ^1H NMR spectrum for VistaMaxx (VM) 3980 dissolved in 1,1,2,2-tetrachloroethane- d_2 .	260
Figure S4.13. ^1H NMR spectrum for VistaMaxx (VM) 8880 dissolved in 1,1,2,2-tetrachloroethane- d_2 .	260
Figure S4.14. Quantitative ^{13}C NMR spectrum for VistaMaxx (VM) 3588 dissolved in 1,1,2,2-tetrachloroethane- d_2 .	261
Figure S4.15. Quantitative ^{13}C NMR spectrum for VistaMaxx (VM) 6202 dissolved in 1,1,2,2-tetrachloroethane- d_2 .	262
Figure S4.16. Quantitative ^{13}C NMR spectrum for VistaMaxx (VM) 3020 dissolved in 1,1,2,2-tetrachloroethane- d_2 .	262
Figure S4.17. Quantitative ^{13}C NMR spectrum for VistaMaxx (VM) 3980 dissolved in 1,1,2,2-tetrachloroethane- d_2 .	263
Figure S4.18. Quantitative ^{13}C NMR spectrum for VistaMaxx (VM) 8880 dissolved in 1,1,2,2-tetrachloroethane- d_2 .	263
Figure S4.19. Stress-strain curve for Engage 8180 at 1, 2.5, and 5 wt% compatibilizer loading in an 80/20 HDPE/iPP blend.	264
Figure S4.20. Stress-strain curve for VistaMaxx 3020 (VM3020) at 1, 2.5, and 5 wt% compatibilizer loading in an 80/20 HDPE/iPP blend.	264
Figure S4.21. Stress-strain curve for VistaMaxx 3588 (VM3588) at 1, 2.5, and 5 wt% compatibilizer loading in an 80/20 HDPE/iPP blend.	265
Figure S4.22. Stress-strain curve for VistaMaxx 8880 (VM3588) at 1, 2.5, and 5 wt% compatibilizer loading in an 80/20 HDPE/iPP blend.	265

Figure S4.23. Stress-strain curve for VistaMaxx 6202 (VM6202) at 1, 2.5, and 5 wt% compatibilizer loading in an 80/20 HDPE/iPP blend.	266
Figure S4.24. Stress-strain curve for VistaMaxx 3980 (VM3980) at 1, 2.5, and 5 wt% compatibilizer loading in an 80/20 HDPE/iPP blend.	266
Figure S4.25. Stress-strain curve for all compatibilizers tested at 5 wt% compatibilizer loading in a 30/70 HDPE/iPP blend.....	267
Figure S4.26. HDPE crystallization in 30/70 HDPE/iPP blends and their observed toughness. Error bars represent one standard deviation from the average.	268
Figure S4.27. iPP crystallization in 30/70 HDPE/iPP blends and their observed toughness. Error bars represent one standard deviation from the average.	268
Figure S5.1. ^1H NMR spectrum of sample d-PVC44.	269
Figure S5.2. ^1H NMR spectrum of sample d-PVC42.	270
Figure S5.3. ^1H NMR spectrum of sample d-PVC40.	270
Figure S5.4. ^1H NMR spectrum of sample d-PVC37.	271
Figure S5.5. ^1H NMR spectrum of sample d-PVC32.	271
Figure S5.6. ^1H NMR spectrum of sample d-PVC32(2).....	272
Figure S5.7. ^1H NMR spectrum of sample d-PVC22.	272
Figure S5.8. ^1H NMR spectrum of sample d-PVC17.	273
Figure S5.9. ^1H NMR spectrum of sample d-PVC16.	273
Figure S5.10. ^1H NMR spectrum of sample d-PVC12.	274
Figure S5.11. ^1H NMR spectrum of sample d-PVC6.	274
Figure S5.12. ^1H NMR spectrum of sample d-PVC3.	275

Figure S5.13. ^1H NMR spectrum of sample d-PVC3(2).....	275
Figure S5.14. ^1H NMR spectrum of sample d-PVC2.	276
Figure S5.15. ^1H NMR spectrum of sample d-PVC0.	276
Figure S5.16. Peel strength measurements for sample d-PVC44.	277
Figure S5.17. Peel strength measurements for sample d-PVC42.	277
Figure S5.18. Peel strength measurements for sample d-PVC40.	278
Figure S5.19. Peel strength measurements for sample d-PVC37.	278
Figure S5.20. Peel strength measurements for sample d-PVC32.	279
Figure S5.21. Peel strength measurements for sample d-PVC32(2).....	279
Figure S5.22. Peel strength measurements for sample d-PVC22.	280
Figure S5.23. Peel strength measurements for sample d-PVC17.	280
Figure S5.24. Peel strength measurements for sample d-PVC16.	281
Figure S5.25. Peel strength measurements for sample d-PVC12.	281
Figure S5.26. Peel strength measurements for sample d-PVC6.	282
Figure S5.27. Peel strength measurements for sample d-PVC3.	282
Figure S5.28. Peel strength measurements for sample d-PVC2.	283
Figure S5.29. Peel strength measurements for sample d-PVC0.	283

CHAPTER I: INTRODUCTION

Polymer Recycling

Plastic recycling has been of great concern in recent years as plastic waste continues to pile up and polymer production exponentially grows.^{1,2} There are several problems with the current recycling systems, which have resulted in approximately 80% of plastic sent to recycling plants cannot be repurposed and is either burned for power or sent to landfills.³ There is also a deficiency of available recycling plants since recycled material products are not fiscally desirable compared to virgin material.⁴ Recycled plastics are less desirable since polymers can only be remelted with like plastics to form a stable product and this is nearly impossible with current recycling sorting techniques.⁵ Consumer plastics typically are composed of multiple components, such as polyethylene terephthalate soda bottles with polypropylene caps and a label composed of either polyethylene or polyvinyl chloride, so it is difficult to ensure no other type of polymer is in a batch without costly sorting techniques.^{6,7} Recycling plants use near-infrared scanning (NIR) and sink-float processes to separate different types of plastics, but there are limits to this technology.^{6,7} For example, polyolefins have similar NIR peaks due to the carbon-only backbones, but polymer blends of polyethylene and polypropylene form compromised phase-separated materials. Polyvinyl chloride is also particularly difficult to separate in recycling streams.⁶ Several techniques have been implemented at the industrial scale to sort PVC from other polymers. Manual sorting can produce streams with 80% homogeneity, but this is a time-consuming and costly process. Selective density processes have successfully removed common olefins from a recycling stream based on their specific gravities.⁵ Unfortunately, PVC and PET are common polymers

with almost identical specific densities of approximately 1.35 g/cm³.³ PVC can be sorted using x-ray fluorescence detectors which can indicate the chlorines off the carbon backbone, but these are expensive to implement.⁸

Polymer Blends

Inefficient sorting leads to the formation of mixed plastic waste. Due to the inherent immiscibility of most polymers, the remelting and reprocessing of this feedstock will result in a phase-separated product. Phase-separated materials have high interfacial tension and weak interfaces, which prevents the transfer of applied stress across the interface, **Figure 1.1**. This minimizes the amount of applied force the polymer blend can withstand before reaching failure, resulting in a brittle material with low tensile strength. Some amorphous polymer pairs are miscible and do not suffer from this phenomenon. These polymer blends will exhibit thermal and mechanical properties that are directly proportional to their composition. For example, the Fox equation predicts that the glass transition temperature (T_g) of these blends is dependent on the T_g of the homopolymers normalized by composition, as shown in Eqn (1.1).⁹ The presence of the single T_g near the predicted Fox equation T_g is used as an indicator that a blend is miscible.^{10, 11} Miscible blends will also follow the concept of mechanical property additivity.^{11, 12} For example, poly(methyl methacrylate) (PMMA) exhibits good chemical resistance and a relatively high tensile strength; however, it has very low ductility. Since PMMA has good compatibility with polycarbonate (PC), a more ductile polymer, blends of the two materials exhibit higher toughness than the pure PMMA material, thereby improving the material's desirability.¹²

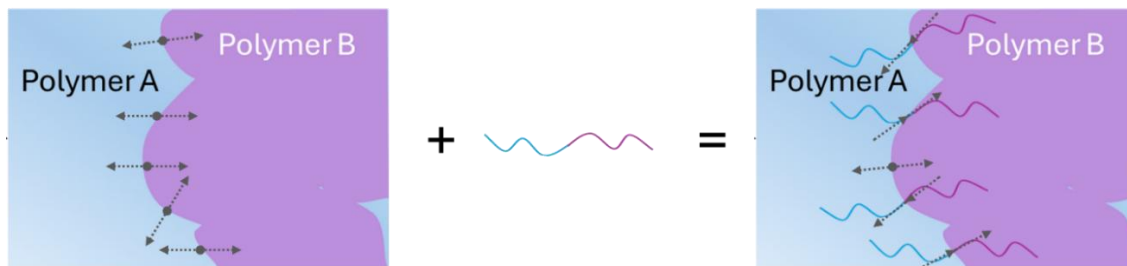


Figure 1.1. Representation of high interfacial tension between immiscible phases and stress transfer across a phase-separated interface with the presence of a compatibilizer.

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad \text{Eqn (1.1)}$$

A compatibilizer can be added to an immiscible polymer blend to stabilize the interface, minimizing phase separation. This allows the transfer of stress across the interface as the presence of compatibilizers can reduce interfacial tension and improve interfacial adhesion, as shown in **Figure 1.1**. A successfully compatibilized blend will therefore exhibit improved mechanical property that approaches the ideal additivity model and therefore exhibits properties that are more similar to those observed in miscible polymer blends. Therefore, the objective of this research is to provide a fundamental understanding of the molecular characteristics of a compatibilizer that make it an effective interfacial modifier to improve the desirability of immiscible polymer blends from recycling streams.

Polymer Thermodynamics

Polymer miscibility can be quantified using thermodynamic principles. A miscible polymer blend will spontaneously mix the polymer chains on a molecular level, resulting in a homogeneous system. The Gibbs free energy equation, Eqn (1.2), defines the change in free energy of mixing (ΔG_m) to be equal to the enthalpy of mixing (ΔH_m) minus the entropy of mixing (ΔS_m) multiplied by the temperature (T).^{13, 14} Polymer blends have a very low/negligible entropy of mixing due to high molecular weights or degrees of polymerization, N .¹⁴ So, for mixing to be favorable and $\Delta G_m < 0$, a negative/or very slightly positive enthalpy of mixing (ΔH_m) is required.¹³

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad \text{Eqn (1.2)}$$

The Flory-Huggins model is a lattice model that defines the free energy of mixing a polymer and a solvent or a polymer-polymer blend and thus can be used to predict miscibility. This theory provides insight into polymer blend thermodynamics, in which polymer segments fully occupy a lattice site, as shown in **Figure 1.2**.¹⁵⁻¹⁷ Based on this model, Eqn (1.3-1.5), the Gibbs free energy of mixing of two polymers, 1 and 2, is defined as dependent on the Flory-Huggins binary interaction parameter (χ_{12}), the Boltzmann constant (k_B), as well as the volume fraction (ϕ) and chain length (N_i) of each component in the blend.¹⁶⁻¹⁸ Using this equation, a polymer blend is considered miscible when the Flory-Huggins interaction parameter is negative or slightly positive, as this results in a ΔG_m less than 0.^{14, 16} The Flory-Huggins lattice theory assumes that molecular interactions are only dependent on nearest neighbors and relies on the mean-field assumption, where a local concentration is representative of the overall bulk material.¹⁷ In experimental systems, polymer-polymer interaction parameters are impacted by intermolecular interactions, molecular weights, functionalization, branching, crystallinity, etc., of the specific materials.

$$\Delta H_m = \chi_{12} k_B T \phi_1 \phi_2 \quad \text{Eqn (1.3)}$$

$$\Delta S_m = -k_B \left(\frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 \right) \quad \text{Eqn (1.4)}$$

$$\Delta G_m = k_B T \left(\frac{\phi_1}{N_1} \ln \phi_1 + \frac{\phi_2}{N_2} \ln \phi_2 + \phi_1 \phi_2 \chi_{12} \right) \quad \text{Eqn (1.5)}$$

The Flory-Huggins interaction parameter (χ_{12}) between two polymers can also be correlated to their solubility parameters (δ). This relationship is shown in Eqn (1.6), where V_{ref} is the reference/mixing volume.^{5, 16, 18} This approach, however, does not take

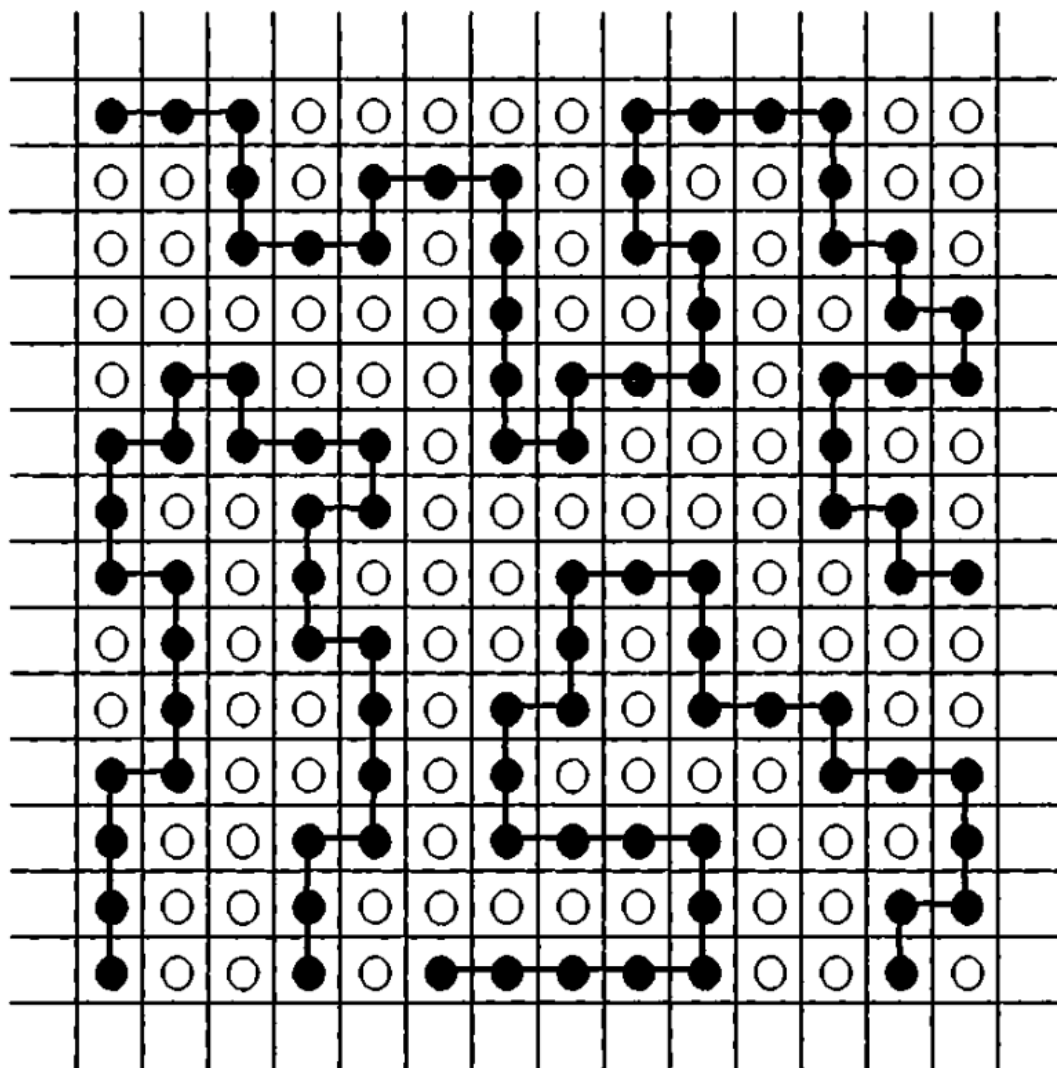


Figure 1.2. Filled 2-d lattice model with each site occupied by polymer species 1 or 2.
Image obtained from Reference 17.

specific polymer characteristics such as molecular weight and dispersity into account when using reference solubility parameters.

$$\chi_{12} \approx \left(\frac{V_{ref}}{RT} \right) (\delta_1 - \delta_2)^2 \quad \text{Eqn (1.6)}$$

χ_{12} can be determined experimentally from the melting point of a polymer in a polymer blend from isothermal differential scanning calorimetry (DSC). In this case, the melting point depression of the blend is analyzed using the Nishi-Wang equation presented in Eqn 1.7.¹⁹⁻²¹ In this equation, $T_m^{0'}$ and T_m^0 are the equilibrium melting temperatures of the blend and pure semicrystalline polymer, respectively. V is the volume fraction of the amorphous diluent (subscript 1) or the semicrystalline component (subscript 2) and ΔH_f^0 is the heat of fusion of the semicrystalline component in the polymer blend. Inputting this information as well as $T_m^{0'}$ and T_m^0 from DSC experiments as a function of the composition of the amorphous component, ϕ_1 , enables the determination of the binary interaction parameter, χ . This only applies to systems with the crystalline component as a minor phase in an amorphous matrix.²²

$$\frac{1}{T_m^{0'}} - \frac{1}{T_m^0} = - \frac{V_2}{V_1} \frac{R}{\Delta H_f^0} \chi_{12} \phi_1^2 \quad \text{Eqn (1.7)}$$

Other techniques to determine χ utilize small-angle neutron scattering (SANS), light scattering (LS), and cloud point determinations which are dependent on the impact phase separation has on the interaction of the polymer sample with neutrons or light.^{16, 18, 23-26} In amorphous systems, light scattering can be used to determine miscibility, as an immiscible blend will be turbid, causing scattering to occur.^{16, 27, 28} SANS has been used to understand the degree of phase separation in binary polymer blends when one of the polymer components contains a deuterated analog. The scattering curve can be fitted

using the random phase approximation to determine χ_{12} . It is important to keep in mind the impact of deuteration on molecular interactions in the polymer blend when using this method. It is also necessary to specify which experimental method is used to determine χ , as the determined χ_{12} varies based on the specific polymer-polymer interactions under investigation and assumptions made during the analyses.¹⁸

The morphology of a phase-separated blend is dependent on the composition of the polymer blend, as shown in **Figure 1.3**, and will also play a role in determining the thermal and mechanical properties of the blend. When one of the components is a majority phase, the morphology will form as droplets of the minority phase in a matrix of the majority phase.¹⁴ When the volume fractions of the components are close to equal, neither can form a minor phase, and the blend forms a co-continuous phase structure.^{14, 29} The co-continuous structure is believed to exhibit effective yield stress transfer due to its interconnected and interpenetrated nature of the network, which prevents a drastic loss of mechanical strength that is typically observed with droplet morphologies.¹⁴

The morphologies represented in **Figure 1.3** are not at equilibrium due to the fact that they evolve during the demixing process to form a heterogeneous morphology. As a blend transitions between the co-continuous and droplet morphologies, it may form a fiber-like lamellar phase.³⁰⁻³² A miscible polymer blend will not exhibit these morphologies and is homogeneous down to the molecular length scale. In the case of polymer blends formed in recycling streams, the minor component is formed from a contaminating polymer, which is present in small concentrations. For this reason, the morphology of most polymer blends that emerge from incomplete sorting in the waste

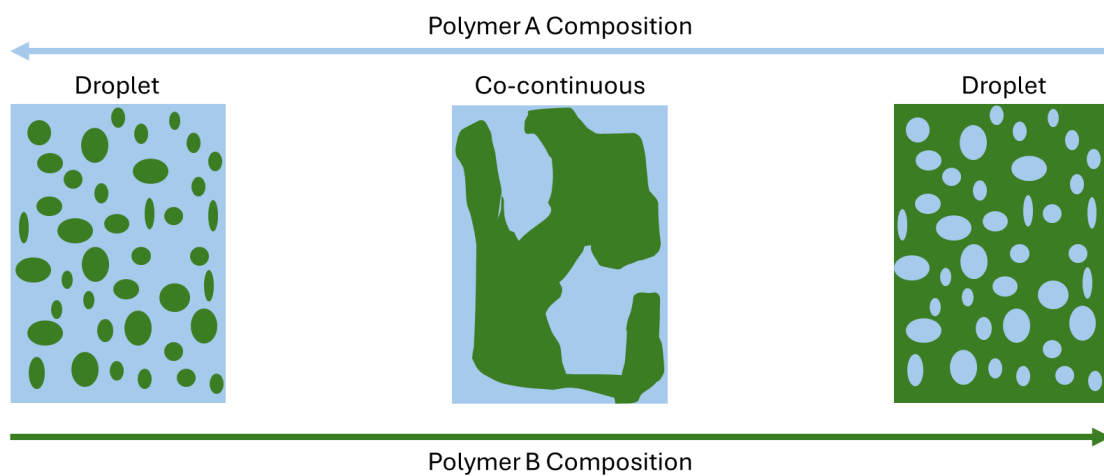


Figure 1.3. Morphology of an immiscible polymer blend.

stream is a droplet dispersion in matrix morphology.

Compatibilization of Polymer Blends

To minimize the impact of immiscibility, interfacial modifiers known as compatibilizers can be added to the polymer blend at low weight percentages. Compatibilizers behave similarly to surfactants, which will travel to the interface of two phases due to their amphiphilic nature.³³⁻³⁵ They can then interact at the interface between dissimilar polymers to stabilize a phase-separated blend by decreasing interfacial tension, minimizing droplet coalescence, and enhancing interfacial adhesion.¹⁴ Compatibilization can be either passive or reactive, as represented in **Figure 1.4**. Passive compatibilization involves adding copolymers directly to the polymer blend that can interact and entangle with both phases to “stitch” the interface. These compatibilizers have segments that are miscible with either component, allowing them to interact at the interface. Reactive compatibilizers have a molecular structure that is miscible with one of the phases, but contain functional end groups that can react with similar end-functionalized reactive components that are in the other phase, where these two components can come together at the interface to react and form multiblock copolymers.^{14, 36} Either reactive or passive compatibilizers can minimize the impact of phase-separation on the blend properties, but cannot change the inherent immiscibility of the polymers.

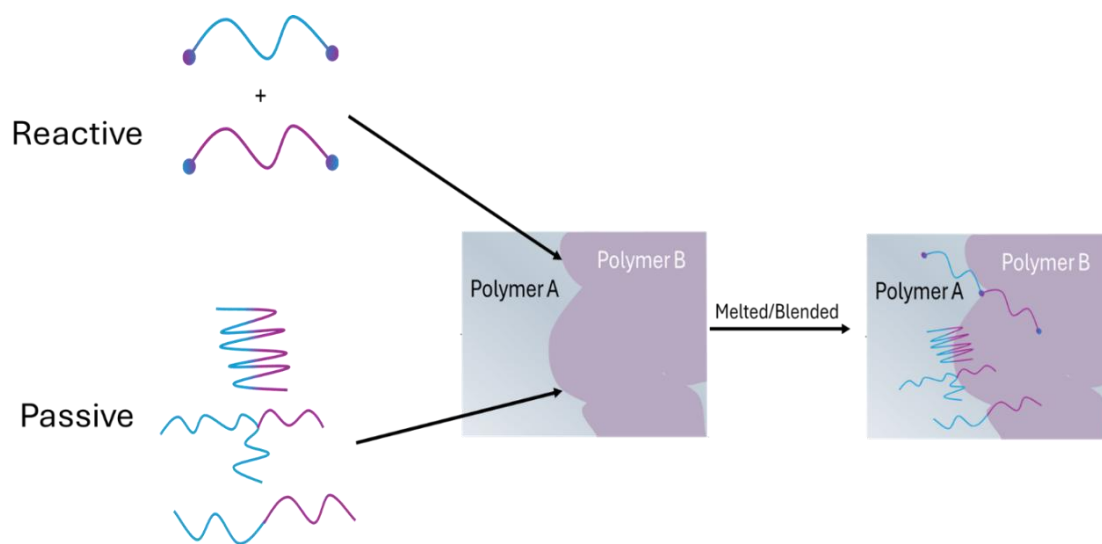


Figure 1.4. Representation of how reactive and passive compatibilizers interact at the interface of polymer blends. Reactive compatibilizers will form block copolymers in situ, while passive compatibilizers are already formed copolymers added to the melt.

Importance of Copolymer Sequence Distribution in Compatibilization

Copolymers are composed of at least two components or monomer species.^{37, 38} The connectivity of the components in the polymer chain determines its sequence distribution. An alternating copolymer switches between monomers *a* and *b* at every bond, resulting in an *ababab* sequence.³⁹ Multi-block copolymers will have repeating segments composed of consecutive identical monomers, resulting in sequences such as *aaaaabbbbbbaaaabbbbbbbbaaaabbbbbbb*, where each run of a given monomer can be denoted as *A* for the *..aaaaa..* block and *B* for the *..bbbbb..* block.³⁸ The block length denotes the number of repeating monomers of the same identity within a block. The block number is the number of blocks, or approximately the number of covalent bonds between *a* and *b* monomers. Block copolymers are labeled be named based on the number of blocks in the copolymer, where diblock, tetrablock, and hexablock copolymers contain 2, 4, and 6 blocks, respectively.⁴⁰ Other copolymer sequences include random and gradient copolymers. A statistically random copolymer will have just as many *a-a* bonds as *a-b* bonds, but a random copolymer can also have blockier or more alternating sequence distributions, where this change in molecular structure can influence its thermal, mechanical, and interfacial properties

Research into the compatibilization of amorphous polymer blends has shown that interfacial strength depends on the architecture and sequence distribution of the compatibilizer.¹⁴ This is because the efficiency of compatibilizers in amorphous-amorphous systems depends on the formation of entanglements between the phases by the compatibilizer. Both architecture and polymer sequence impact entanglement, where graft and linear multi-block copolymers can form effective entanglements at amorphous-

amorphous polymer blend interfaces. Linear compatibilizers will be the focus of the work in this thesis.

The ability to form entanglements between a compatibilizer and homopolymer is dependent on the molecular weight of the compatibilizer. To maximize the probability of entanglements forming between a compatibilizer and homopolymer, the molecular weight of the copolymer blocks in the compatibilizer must be greater than twice the molecular weight of entanglement (M_e) or the critical molecular weight (M_c), Eqn (1.8).⁴¹ The molecular weight of entanglement is the molecular weight between two chain intertangles.¹⁷ This is because it requires approximately two entanglements per chain to form a “loop”. **Figure 1.5** illustrates how multi-block copolymers are effective at maximizing entanglements, when compared to alternating, random, and gradient copolymers. Alternating copolymers do not have long enough segments to effectively form entanglements between the copolymer and the homopolymer, so they will sit at the interface and form a barrier between the two phases, increasing interfacial tension and promoting phase separation.

$$M_c = 2M_e \quad \text{Eqn (1.8)}$$

Impact of Polymer Sequence on the Ability to Entangle between Polymer Phases

Previous research by Dadmun et al. has shown that blockier random copolymers are significantly better-performing compatibilizers than copolymers that tend towards an alternating chain sequence.^{42, 43} Research by Shull et al. and Genzer et al. elucidate how the sequence distribution of the copolymer compatibilizer directly influences the strength of the interface.^{44, 45} They specifically focused on gradient copolymers, which are similar

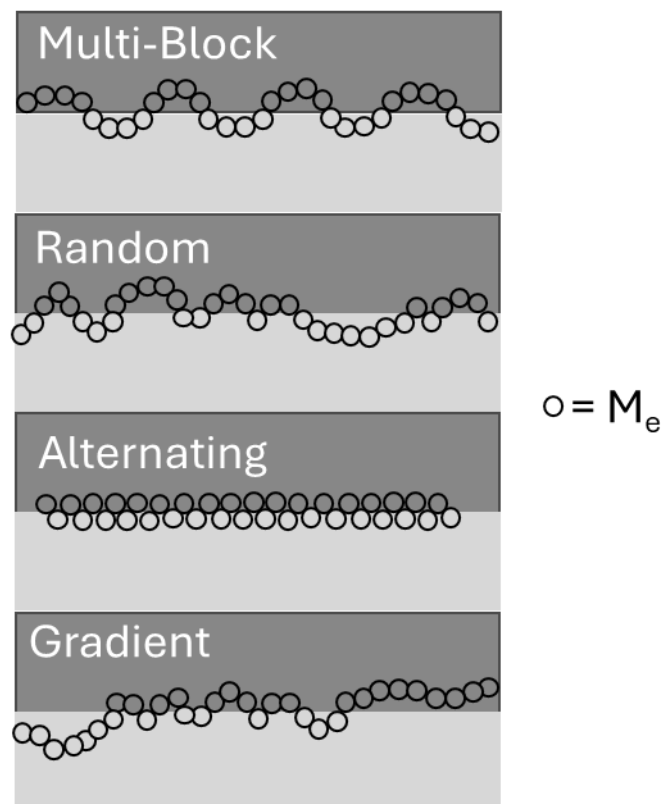


Figure 1.5. Impact of polymer sequence on the ability to entangle between polymer phases.

in structure to diblock copolymers, with a transition that mirrors that of random copolymers. Diblock copolymers are less effective compatibilizers than multi-blocks, as chain pull-out can occur when the system is under stress since there is not a second crossing at the interface to entrap chains.¹⁷ In gradient copolymers, it appears that the transition random sequence between blocks in gradient copolymers hinders chain pullout from dominating. Thus, gradient copolymers stabilize the interface between immiscible polymer phases more effectively than diblocks.

Significant research has been accomplished to understand the role of molecular structure on the effectiveness of multi-block copolymers as compatibilizers. Coates et al. investigated tetra- and di-block copolymers as compatibilizers of isotactic polypropylene (iPP) and high-density polyethylene (HDPE) blends.⁴⁰ They found that tetrablock copolymers significantly outperformed diblock copolymers with similar block lengths as compatibilizers, since there are at least three interface crossings, preventing chain pullout. Bates et al. expanded this work to focus on the impact of copolymer sequence distribution on compatibilization effectiveness, focusing on the importance of diblock and tetrablock block lengths, including an iPP-PE hexablock copolymer.^{40, 46} Overall, they found that increasing the number of blocks in the compatibilizer increases the overall toughness of the compatibilized blend. Also, increasing the block length of the diblock copolymers significantly improved the compatibilizer efficiency. This is likely due to the ability of long-chain diblock copolymers to entangle and co-crystallize with the homopolymer and minimize chain pullout. Changes in wide-angle x-ray scattering (WAXS) and small-angle x-ray scattering (SAXS) spectra support this conclusion, where peak shifts indicate changes in crystal structures. The copolymers with four or more

blocks didn't improve the blend toughness with increasing block length if the block lengths were above the critical molecular weight.⁴⁶ Extending these studies to include compatibilizers with high block numbers is difficult, as these multi-block copolymers require a very controlled polymerization, making the synthesis of such copolymers difficult.

Given the importance of copolymer sequence distribution, determining the structure and the sequence distribution of the compatibilizers of interest is crucial to correlate compatibilizer molecular structure to its effectiveness as a compatibilizer. This is especially important when analyzing commercial materials since the composition and polymerization conditions are not readily available.

Nuclear magnetic resonance (NMR) can provide the molecular level information needed to characterize copolymer composition and structures, specifically for the compatibilizers of interest in these studies. For chlorinated polyethylene investigated in Chapters II and III, the chlorine content can be determined by ^1H NMR as there are proton peak shifts that correlate to the presence of chlorine.^{47, 48}

Quantitative ^{13}C NMR provides crucial information to determine polyolefin compositions and the sequence distribution.⁴⁹⁻⁵² This technique uses an angled pulse and longer relaxation times between scans to ensure that residual excitation doesn't artificially increase the intensity of the peaks.⁵³ Preventing residual signals between scans enables the NMR spectra to be quantitatively integrated to determine the concentration of carbon sequences, providing sequence distribution information. This type of NMR peak analysis was previously reported by Hiltner et al to determine the molecular structure of chlorinated polyethylene.^{51, 54} It has also been used to determine the sequence

distributions of ethylene/ α -olefin copolymers by Randall et al and of ethylene-propylene copolymers by Carman et al.^{49, 50} Determining the sequence distribution of the compatibilizers of interest in our studies is crucial to provide fundamental insight into the correlation of compatibilizer molecular structure to its effectiveness as a compatibilizer.

Role of Polymer Crystallization in Blend Compatibilization

Polymer crystallization may play an important role in the compatibilization of a blend that contains crystalline polymers. Thus, it is crucial to understand the processes that impact polymer crystallization to provide thorough insight into the compatibilization of semicrystalline polymer blend systems. There are two processes that occur in the crystallization of polymers: nucleation and crystal growth. Nucleation occurs first and is the formation of new crystal structures or spherulites. In nucleation, a crystal structure is formed as local areas of the polymer chain become ordered on the molecular level.⁵⁵ Crystal growth is the growth of crystals from the nuclei to form larger crystal sizes. The nucleation rate can be impacted by the material's properties and the addition of additives that can function as nucleating agents.⁵⁶ A nucleating agent is a well-ordered structure that promotes the formation of new crystals and increases the rate of crystallization.⁵⁷⁻⁶⁰

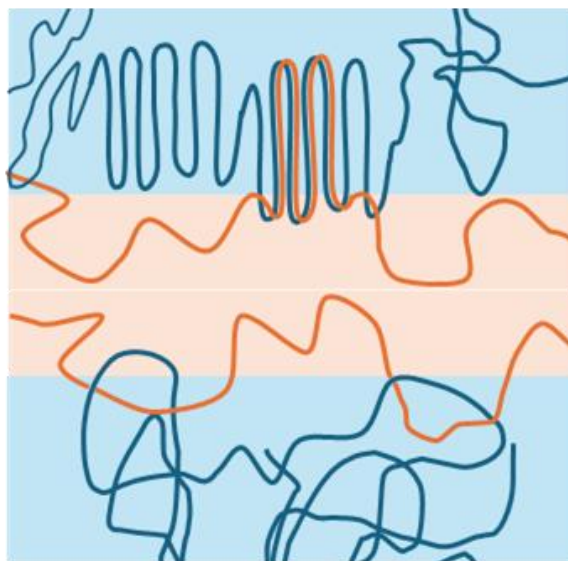
The kinetics of the crystallization of a polymer at a given temperature can be understood using the Avrami equation in Eqn (1.9), which considers both nucleation and growth processes.^{55, 61, 62} In this equation, the relative crystallinity ($\phi_c(t)$) at time t is shown to be dependent on the crystallization rate constant (k_a) and the Avrami exponent (n).⁵⁵ Unfortunately, the crystallization kinetics of polymer blends and compatibilized polymer blends as a whole are not well defined by the Avrami Equation, as the Avrami

model doesn't account for how additional components can either hinder or promote crystallization, where the specific impact of an additive is dependent on component crystallization properties, molecular diffusion, and miscibility.⁶³

$$\phi_c(t) = 1 - e^{-k_a t^n} \quad \text{Eqn (1.9)}$$

Polymer co-crystallization involves a crystal structure formed with two types of polymer chains. It is hypothesized that semicrystalline compatibilizers can co-crystallize with a semicrystalline component and create a strong anchor, as visualized in **Figure 1.6**.^{62, 64-67} This co-crystallization will increase the interfacial adhesion between the immiscible polymers since pulling apart that interface requires more energy to break a crystal network than a polymer entanglement.^{67, 68} This is experimentally supported by the formation of stronger polymer-polymer interfaces that is reported when evidence of co-crystallization across the interface is present.^{46, 64, 68, 69} There are several methods to determine if there is evidence of co-crystallization between two polymers, but for the scope of this manuscript, we will focus on differential scanning calorimetry (DSC) and x-ray scattering.⁷⁰ Analyses of the blends and pure components using these techniques can be compared for variations, where differing results for the blend than the individual components could suggest that the compatibilizers impact the crystal structures and are forming co-crystals.⁷¹

Co-Crystallization



Entanglement

Figure 1.6. Model of entanglement and co-crystallization mechanisms at the interface between two polymer phases.

Differential scanning calorimetry (DSC) can monitor the changes in the crystallinity of a polymer blend with the addition of compatibilizers, as DSC measures the amount of heat/energy required to increase the temperature of the whole sample. This method provides insight into the individual crystallization of multiple semicrystalline components on the same DSC curve if each component has a separate melting temperature. An example of a DSC thermogram for pure isotactic polypropylene is presented in **Figure 1.7**, showing the melting temperature (T_m) at *ca.* 160 °C on heating and the crystallization temperature (T_c) at *ca.* 120 °C on cooling. In DSC, changes in melting temperature (T_m) could indicate changes in the size of the crystals or the presence of newly formed crystals or crystal structures. For instance, smaller crystals will shift the melting temperature down as they require less heat to melt. The opposite will occur for the formation of larger crystals. The area under the melting peak provides a method to monitor changes in polymer crystallinity, as the area under the melting peak measures the sample's heat of fusion (ΔH_f).⁷² As this value increases, so does the overall crystallinity of the material, as shown in Eqn (1.10).

Cold crystallization occurs when there is sufficient energy to allow chain mobility, where the polymer chains can move onto a growing crystal and form new crystal structures. The presence of this process is characterized by the appearance of a peak between the glass transition temperature and the melting point on the heating DSC curve. This formation of a new crystal must be accounted for in the analysis of the DSC curve to determine the percent crystallinity of a polymer chain. Thus, in a sample that undergoes cold crystallization during the DSC scan, the percent crystallinity is determined by subtracting the enthalpy of a cold crystallization peak (ΔH_{cc}), from the

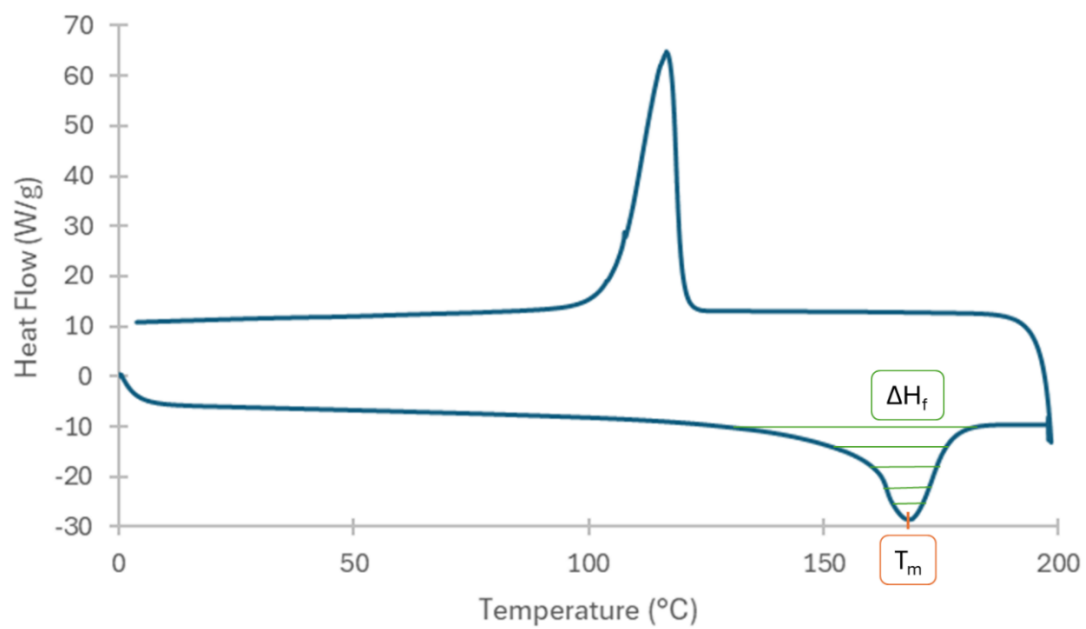


Figure 1.7. DSC thermogram of 54% crystalline isotactic polypropylene run at 10 °C/min. (Exo Up)

ΔH_f and dividing this value by the reference heat of fusion of a 100% crystalline sample ($\Delta H_{100\%}$).

$$\% \text{ crystallinity} = \frac{\Delta H_f - \Delta H_{cc}}{\Delta H_{100\%}} * 100\% \quad \text{Eqn (1.10)}$$

Moreover, when analyzing DSC curves of a sample that contains multiple components, the heat of fusion collected must be normalized by the composition of the mixture to separately determine changes in crystallinity for each component in the sample.^{62, 73} This calculation is shown in Eqn (1.11) for a sample where the percent crystallinity of a component (X_1) is the heat of fusion of the corresponding melting peak ($\Delta H_{f,1}$) divided by the reference heat of fusion of a 100% crystalline sample ($\Delta H_{100\%}$) normalized by the mass composition (ϕ_1) of the component in the blend. This value can be compared to the percent crystallinity of the pure material to evaluate any changes in crystallization caused by interactions in the polymer blend.

$$X_1 = \frac{\Delta H_{f,1} - \Delta H_{cc,1}}{\phi_1 * \Delta H_{100\%}} \times 100\% \quad \text{Eqn (1.11)}$$

Small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) provide information about the structure of the sample, including the crystal structure.⁷⁴ This can be used to characterize the chemical assembly of semicrystalline polymers, which have crystalline and amorphous regions. Well-ordered crystalline regimes produce constructive interference when the scattering of X-rays is measured as a function of angle. This is represented by a peak on the plot of intensity vs q (which is proportional to scattering angle)⁷⁴, an example of which is shown in **Figure 1.8**.^{74, 75} SAXS provides information on the size of lamellae and the crystal structure on the nanometer length scale. On the other hand, WAXS probes the structure of the crystal ordering on the

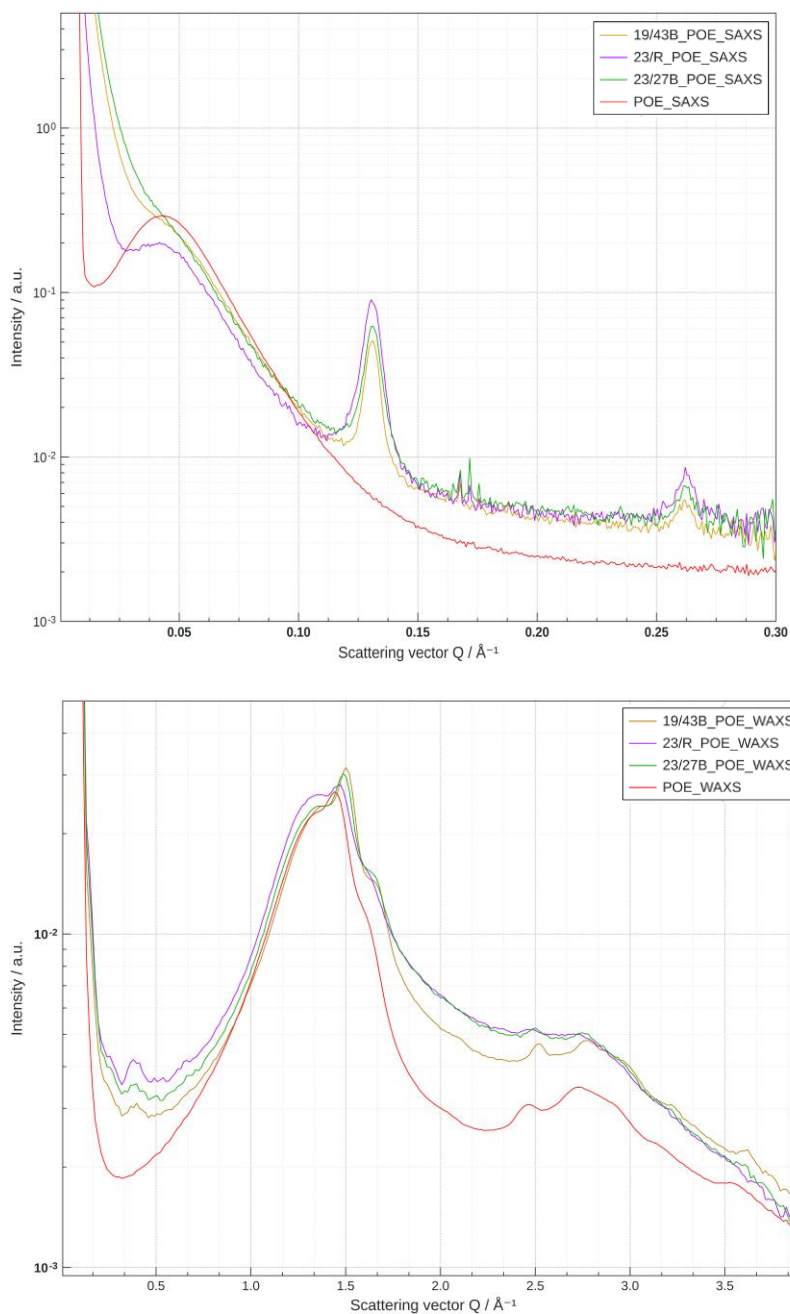


Figure 1.8. SAXS (top) and WAXS (bottom) spectra for polyolefin elastomers (POE) and three 50:50 POE: chlorinated polyethylene (c-PE) blends. C-PE can be used as a compatibilizer for POE and polyvinyl chloride polymer blends.

angstrom scale and therefore provides information about the atomic arrangement in the crystal unit cells.^{74, 76} The length scale of the crystal structure is inversely related to the q value of the peak position as shown in Eqn (1.12).^{46, 77} The scattering pattern of the polymer blend can be compared to that of the individual components to identify changes to the crystal size and atomic spacing in the crystal, which may be a signature of co-crystallization between the homopolymer and compatibilizer. **Figure 1.8** shows such a variation, where the peaks in the WAXS spectra of the compatibilized sample are shifted to the right relative to the scattering pattern of the pure components, indicating that the crystal unit cell is more compact with the addition of a compatibilizer.

$$q = \frac{2\pi}{d} = \frac{4\pi}{\lambda} \sin (\theta/2) \quad \text{Eqn (1.12)}$$

Elucidating Compatibilizer Efficiency

A successful compatibilizer increases interfacial adhesion, lowers interfacial tension, and minimizes droplet coalescence in a phase-separated blend. The efficiency of compatibilizers to stabilize an immiscible polymer blend can be determined through adhesion testing, mechanical testing, crystallography, viscometry, and droplet size distributions from microscopy.⁶⁵ Adhesion testing provides a measure of how effectively a compatibilizer improves the interfacial adhesion between an immiscible polymer pair. The strength of a polymer/polymer interface can be characterized by its interfacial adhesion (G_a) or interfacial fracture toughness (G_c). In both tests, a thin coating of the compatibilizer is sandwiched between sheets of the immiscible polymer pair. Interfacial adhesion is then determined through peel tests, where the force required to pull the

homopolymers apart at a specific crosshead speed is measured. This force (F) is divided by the width (w) of the strips to get the interfacial adhesion (G_a) as shown in Eqn (1.13).

$$G_a = \frac{F}{w} \quad \text{Eqn (1.13)}$$

Fracture toughness is determined by an asymmetric double cantilever beam (ADCB) test.⁷⁸ In this test, a razor blade is driven at the interface between the two polymers, forming a crack. The crack length (a), razor blade thickness (Δ), the height of homopolymer strips (h_1 and h_2), and Young's moduli of the homopolymers (E_1 and E_2) are needed to correlate the measured crack length to the interfacial fracture toughness (G_c)^{63, 64, 79} as shown in Eqn (1.14). G_c is typically monitored when the interfacial strength is weak, and G_a is used to determine the adhesion of more efficient compatibilizers.⁶⁴ This is because the crack formed from samples with a high adhesion will be small and difficult to measure accurately.

$$G_c = \frac{3\Delta^2 E_1 h_1^3 E_2 h_2^3}{8a^4} \frac{E_1 h_1^3 C_2^2 + E_2 h_2^3 C_1^2}{[E_1 h_1^3 C_2^3 + E_2 h_2^3 C_1^3]^2}; \quad C_x = 1 + \frac{0.64h_x}{a} \quad \text{Eqn (1.14)}$$

Compatibilizer efficiency can also be determined by monitoring the tensile properties of the uncompatibilized blends and comparing them to those of the compatibilized blend using ASTM D1708 or ASTM D638 mechanical testing standards. These are common ASTM tensile testing protocols for analyzing small polymer samples. In this procedure, an immiscible blend is compounded with a small weight percent of a compatibilizer. The sample is either injected into a mold or pressed into a sheet with coupons that are then cut out using an ASTM D1708 or D638 shaped die. The stress-strain behavior of the sample can then be monitored at a specific crosshead speed. The resultant stress-strain curves can be analyzed to obtain tensile strength, elongation at

break, toughness, and Young's modulus, where the relationships between these parameters and the stress-strain curve are shown in **Figure 1.9**. A more effective compatibilizer will form a blend that attains properties that resemble those of a miscible mixture of the pure components, which can be estimated by the theory of additive properties as previously outlined.

Determination of Morphology in Phase-Separated Blends

Phase-separation in immiscible polymer blends also drives droplet coalescence as the phase-separated blend attempts to minimize the amount of polymer-polymer interface. Droplet coalescence occurs when domains of a component-rich phase merge, resulting in larger droplets. These phase domain droplets can be visualized using microscopy techniques to determine droplet size and distribution. An effectively compatibilized blend will have smaller droplets than the non-compatibilized system since the improved interfacial adhesion and reduced interfacial tension will minimize droplet coalescence that can occur during processing in the melt.³⁴ The morphology of the phase-separated blend has been visualized by optical microscopy (OM), atomic force microscopy (AFM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM).^{13, 70}

Polarized Optical microscopy (POM) will visualize differences between crystalline phases.^{62, 72} In POM, a polarizer is aligned in the path of the light before it reaches the specimen. A polymer crystal will rotate the direction of the polarized light due to its birefringence from the oriented polymer chains.⁸⁰ Birefringence is the

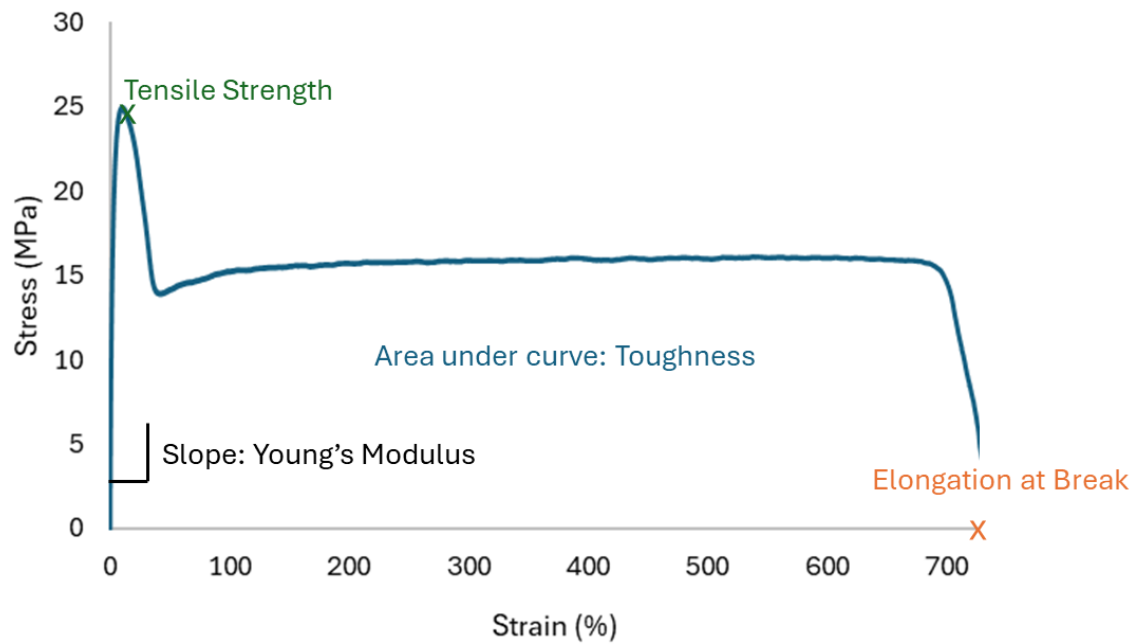


Figure 1.9. Stress-Strain curve for high-density polyethylene using ASTM D1708 standard.

formation of two refractive indices that results from light refracting as it passes through a material with molecular chain orientation, such as in a spherulite.⁸¹ This means that crystalline segments will rotate the plane of the polarized light, while amorphous material will not.⁸² Thus, when the light from a birefringent sample passes through an analyzer located below the sample and is rotated 90° from the polarizer, it can pass through the analyzer and will appear light.^{83, 84} Light that passes through an amorphous material will not pass through the orthogonally oriented analyzer and thus appear dark.. This will lead to a visualization of crystalline segments in POM, while the amorphous segments will remain dark. The drawback is that the resolution of optical microscopy is limited.

AFM uses a scanning probe to analyze the interactions between the probe tip and the surface of a sample. The tip is equipped with a force sensor/cantilever.⁸⁵ AFM is typically used for polymer blends if there is a significant difference in hardness between the materials, as AFM provides an image based on the tip-sample force.⁸⁶ AFM, however, is also limited to the morphology of the sample surface and, therefore, doesn't necessarily provide characterization of the polymer bulk morphology. This technique is also limited by the need to make a very smooth sample for analysis, which can be challenging with immiscible polymer blends as they have compromised mechanical properties.

SEM can be advantageous in determining the morphology of a phase-separated blend, as it does not require a thin specimen. There are several methods to visualize phase-separation in polymer blends by SEM. These include solvent extraction, backscattering electrons, differences in surface roughness, and staining. Scanning electron microscopy (SEM) applies an electron beam to a sample and detects the

secondary and backscattering electrons to form an image.⁸⁷ **Figure 1.10** provides a visual representation of the differences between the topological information gleaned from secondary electrons and the compositional information from backscattered electrons, which interact with the nucleus of an atom and the electrons in the innermost electron shell.⁸⁸ The secondary electrons scattered from the surface of the material can be detected to form an image of the sample. A small concentration of backscattered electrons can also be detected by the secondary electron detector (SED), which provides some compositional information.⁸⁷ SEM that uses a secondary electron detector can be implemented to examine the fracture surface of an immiscible polymer blend. If the two homopolymers have different mechanical strength or hardness, then at the fracture, there will be a variation of roughness based on the composition and distribution of the matrix and minor phase. The fracture surface can then be analyzed to determine the roughness at the fracture site. This technique is more qualitative, as it does not distinguish between microscopic phase-separated structures and the roughness of a material. Solvent extraction can be used to retrieve quantitative morphological information using secondary electron SEM. This is realized by dissolving the minor phase from the bulk polymer sample using a selective solvent. Solvent extraction can be used when there is a significant difference in solubility between the two immiscible polymeric materials.⁸⁹ The solvent must be a good solvent for the minor phase and a very poor solvent for the matrix. As the solvent dissolves one of the phases, it will leave pores in the sample that can be visualized and measured via SEM. The concern with this method is that it is challenging to verify that the selected solvent has completely removed one phase from

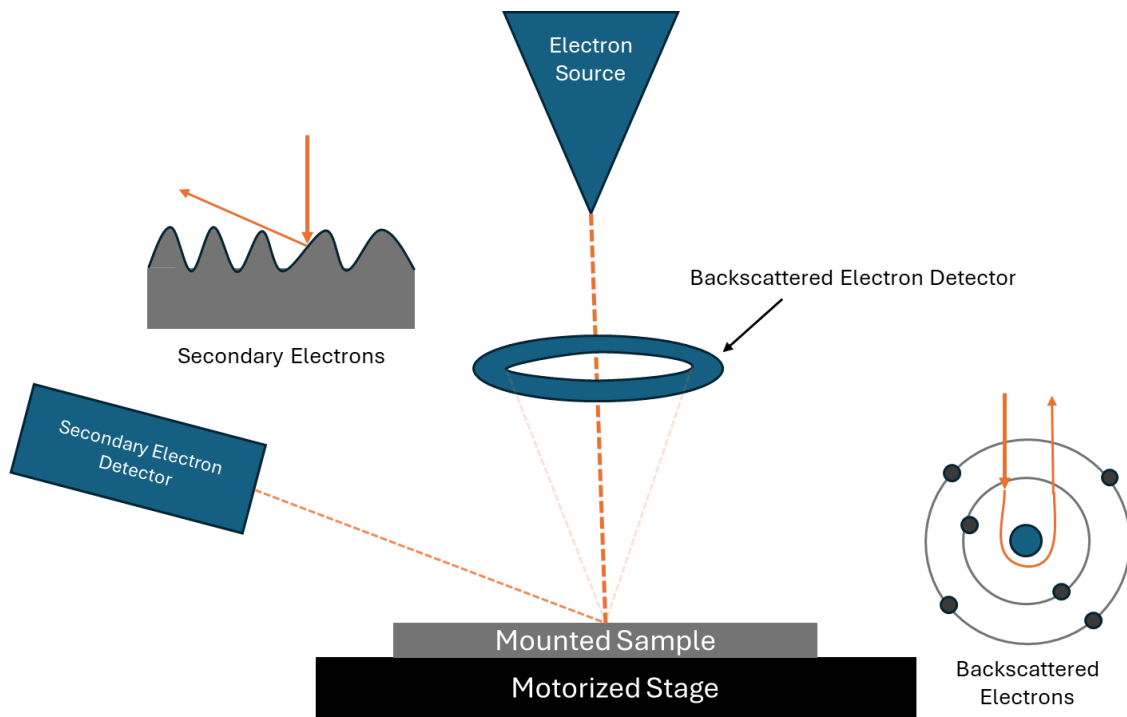


Figure 1.10. Simplified diagram showing the differences between secondary and backscattered electrons in scanning electron microscopy.

the material or that it has not modified the morphology of the matrix.

Backscattered electrons can also be collected in SEM to obtain information about surface composition.^{88, 90} However, defects in the surface often prevent the structure of the phase domain droplets from being resolved, so a very smooth surface is required for this technique. A backscattering detector (BSD) is sensitive to the contrast between phases with different elements. This is particularly useful when examining blends where one of the homopolymers contains another, non-hydrocarbon, element along the polymer chain, for instance, with a larger atomic radius than carbon. Another technique to visualize polymer phases in SEM involves staining a polymer blend for SEM backscattering analysis. This typically involves exposing the sample to oxidation by RuO₄ or OsO₄ vapors.⁹¹ Staining is used if there are significant differences in reactivity or vapor diffusion of the penetrant between the two polymer phases to ensure adequate contrast.⁹¹ For example, the vapor diffusion of RuO₄ into polypropylene is significantly slower than its diffusion into polyethylene. Using a backscattering detector, the RuO₄ stained PE phase will appear bright in the SEM of a PP/PE blend.⁸⁹

Transmission electron microscopy (TEM) is another microscopy technique; however, this geometry detects electrons as they transmit through the sample. TEM is also a common technique to visualize phases that can be differentiated through RuO₄ or OsO₄ staining.^{89, 92} In this process, a sample is ultra-microtomed (less than 100 nm thick) and placed on Cu grids for imaging.^{86, 93} **Figure 1.11** shows the phase-separation of an 80:20 mass ratio of high-density polyethylene (HDPE) and isotactic polypropylene (iPP) that was stained with RuO₄ vapors for 2 hours, according to the standard procedure by Brown and Butler.^{46, 89} Since RuO₄ stains polyethylene at a higher rate than

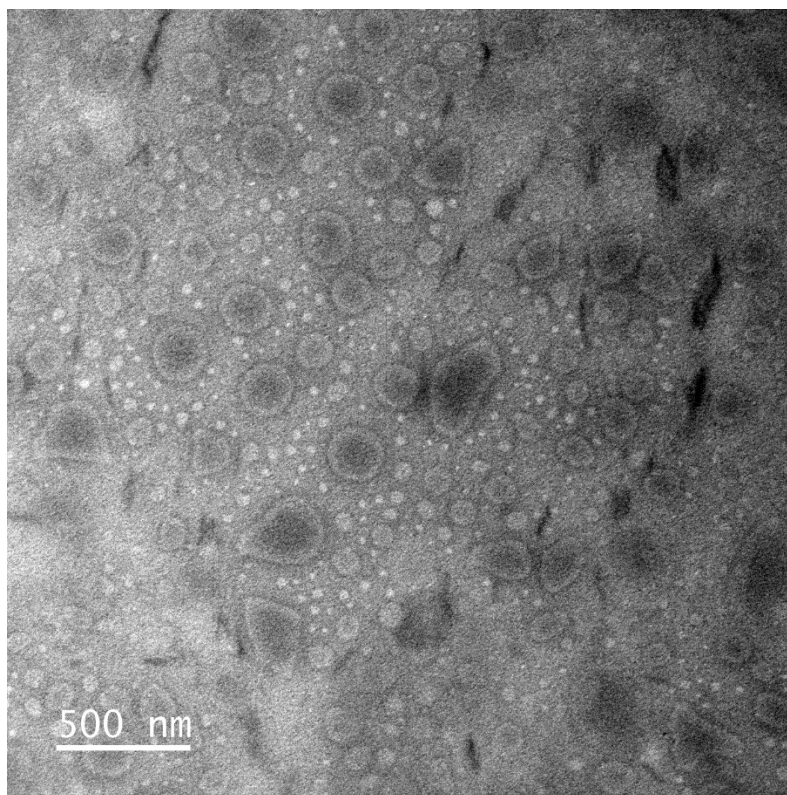


Figure 1.11. TEM image of an 80/20 wt% HDPE/iPP immiscible blend that was embedded in epoxy and ultra-microtomed at room temperature. The sample was stained with RuO_4 vapors for 2 hours.

polypropylene, the polyethylene phase appears dark as RuO₂ nanoparticles block the electrons from transmitting to the detector through the sample.

Choosing the best microscopy technique to visualize the morphology of a phase-separated blend to monitor droplet coalescence depends on the specific polymer blend being studied. Each technique has drawbacks, and it is essential to determine which one best aligns with the properties of the sample being investigated. In some cases, it is better to focus on other techniques to determine the compatibilizer efficiency, as reliable images may be difficult to obtain for analysis.

In summary, an immiscible polymer blend will exhibit diminished mechanical properties due to high interfacial tension and a phase-separated morphology. The properties of the blend may approach those of a miscible blend by adding a compatibilizer to the blend, which will increase interfacial adhesion, reduce interfacial tension, and reduce droplet coalescence. NMR is a robust technique to determine the composition and sequence distribution of the compatibilizers that are of interest. DSC and SAXS/WAXS can be used to understand the crystallization behavior of the polymers in the blends. Several techniques exist that can provide insight into how effective a compatibilizer is at successfully compatibilizing a specific polymer blend. Overall, this chapter provides the foundation and background to elucidate the molecular level processes, such as crystallization and entanglement, that are crucial in determining the efficiency of semicrystalline interfacial modifiers in compatibilizing immiscible semicrystalline polymer blends.

Objective and Outline

Plastic recycling remains inefficient, with only about 9% of plastic waste recycled annually. Recycled polymeric materials often exhibit reduced mechanical properties, limiting their economic viability. These property losses largely result from impure waste streams that induces phase separation of two polymers in the melt during mechanical recycling. Incorporating compatibilizers into the polymer blend melt can stabilize the interfaces between the two components in the immiscible polymer blend. While the important molecular level interactions of effective compatibilizers for blends composed solely of amorphous polymers are well established, the equivalent molecular level processes that are needed in blends that consist of semicrystalline homopolymers remains less understood. This dissertation investigates the dominating mechanisms that enable effective compatibilizers of blends that contain semicrystalline homopolymers to provide insight that can be used to rationally improve compatibilizer efficiency in immiscible blends containing a semicrystalline component.

To tackle this goal, we first analyzed a system with semicrystalline compatibilizers in an immiscible polymer blend containing a semicrystalline and an amorphous homopolymer. The specific system under investigation is a blend of amorphous polyvinyl chloride (PVC) and semicrystalline polyolefin elastomers (POE), where the interfacial adhesion between these two polymers is monitored. Chapter II looked at the molecular level interactions between commercially available chlorinated polyethylene (c-PE) and each homopolymer. Six of the c-PEs investigated were suspension chlorinated and blocky in structure, while one randomly chlorinated PE

sample was also analyzed. The molecular structure of these compatibilizers were characterized using ^1H NMR, quantitative ^{13}C NMR, DSC, and high-temperature gel permeation chromatography. The interfacial adhesion between the compatibilizers at the interface of PVC/POE, as well as the interfacial adhesion between each compatibilizer and each homopolymer, was analyzed as a function of the molecular structure of the compatibilizer. This study determined that semicrystalline compatibilizers that optimized entanglement with the semicrystalline phase showed the best improvement in interfacial adhesion and the greatest evidence of co-crystallization according to SAXS, WAXS, and DSC.

Chapter III builds on this understanding, but shifting to examining the effectiveness of synthesized dichlorinated cyclooctene (Cl_2COE)/cyclooctene (COE) copolymers as compatibilizers for the PVC/POE system. These compatibilizers have a gradient sequence distribution, and their synthesis by ring-opening metathesis polymerization allows for control of molecular weight and composition. While these gradient copolymers resulted in lower interfacial adhesion compared to their blocky counterparts, there was an improvement in interfacial adhesion between PVC and POE with COE, or polyethylene-like, content in the synthesized chlorinated polyethylenes. The data also showed that at higher COE content, there is a greater dependence on compatibilizer efficiency with molar mass. This indicates that the entanglement of the semicrystalline segment of the compatibilizer into the semicrystalline phase is a crucial molecular level process in strengthening the PVC/POE interface.

Chapter IV examined the compatibilization of a semicrystalline/semicrystalline polymer blend composed of high-density polyethylene and isotactic polypropylene.

These blends were compatibilized with olefinic random copolymers, either ethylene-propylene rubber (EPR) or an ethylene/1-octene random copolymer. Only the ethylene component in the EPR can crystallize copolymers as the synthesis catalyst doesn't control tacticity in the propylene segments. This is important to note as there was improved toughness in polymer blends containing either HDPE or iPP as the major phase as the ethylene content increased in the compatibilizer. It is also observed that there is an improvement in mechanical properties by optimizing the miscibility and entanglement with the polyethylene phase with the homopolymers.

The last chapter in this dissertation focuses on optimizing the miscibility of the compatibilizer into both homopolymer phases. To realize this, broader control of the c-PE structure was needed, thus dechlorinated PVC is used as the compatibilizer for PVC/POE. The dechlorination of PVC using silylium ions results in a block copolymer with PVC and PE-like segments and a broad range of chlorine content in the compatibilizer. These materials exhibit similar trends to those previously observed but have improved interfacial adhesion due to increased miscibility with the PVC phase, facilitated by the presence of more vinyl chlorine groups. This material also resulted in a maximum interfacial adhesion of the PVC/POE interface when the copolymer contained ~66 mol% polyethylene, which is consistent with the importance of optimizing the entanglement between the compatibilizer and the homopolymers, which in turn can also improve the possibility of co-crystallinity occurring between the semicrystalline homopolymer phase and the compatibilizer.

CHAPTER II:
MOLECULAR DESIGN OF EFFECTIVE COMPATIBILIZERS OF A
CRYSTALLINE POLYMER BLEND

A version of this chapter was originally published by Bailey Eberle, Timothy Taylor, and Mark Dadmun:

Eberle, B.; Taylor, T.; Dadmun, M. “Molecular design of effective compatibilizers of a crystalline polymer blend.” *Polymer* **2025**, 327, 128385. DOI: <https://doi.org/10.1016/j.polymer.2025.128385>.

Bailey Eberle performed all sample preparation, peel tests, DSC measurements, and collected and analyzed NMR spectra. Timothy Taylor performed WAXS and SAXS measurements and helped with scattering analysis. The document was revised by Dr. Mark Dadmun.

Abstract

Managing the end-of-life of plastics is a challenging problem for a variety of reasons, including the complexity of recycling mixed waste streams. This is due to the inherent immiscibility of different polymers. One method to improve the properties of immiscible polymer pairs is through compatibilization. This study is designed to provide insight into the molecular mechanisms that result in the effective compatibilization of immiscible polymer blends that contain crystalline polymers, as crystalline polymers are a dominant fraction of the waste stream. In this study, the immiscible polymer pair examined contains polyvinyl chloride (PVC) and a polyolefin, as this pair of polymers is difficult to sort and make up a significant portion of commercial polymers in the waste stream. In these studies, the strength of the interface between amorphous poly(vinyl)

chloride (PVC) and semicrystalline polyolefin elastomer (POE) compatibilized with chlorinated polyethylene (c-PE) are monitored as well as the strength of the interface between each homopolymer-compatibilizer pair. The results of this research show improvement in the interfacial adhesion at the c-PE/POE, c-PE/PVC and PVC/c-PE/POE interfaces as the blockiness of c-PE increases, which is interpreted to indicate that the entanglement of the compatibilizer with both the amorphous and semicrystalline phases is necessary to effectively compatibilize the biphasic interface. Further DSC, SAXS, and WAXS data provide evidence that semi-crystalline compatibilizers can co-crystallize with the polyolefin elastomers, indicating that the co-crystallization can further strengthen the biphasic interface. Thus, this research provides insight into the molecular design of effective compatibilizers and the molecular level mechanisms that occur in compatibilized phase separated amorphous/crystalline polymer blends.

Introduction

Plastic pollution is a worldwide concern as an estimated 13 to 25 million metric tons of plastic waste is annually released into the environment globally per year through littering and overfilled landfills.^{1, 94} Approximately 55% of the 360 million tons of plastic produced globally in 2020 ended up in landfills, and this continues to grow as plastic production increases.^{1, 94} The preferred choice to deal with the plastic accumulation is mechanical recycling as it requires less energy and produces lower carbon dioxide emissions compared to landfills and incineration for energy recovery.^{5, 94} Unfortunately, current recycling systems are far from optimal and are not equipped to prevent overflowing landfills as plastic production continues to increase. There are several

problems with the current recycling systems, especially since approximately 80% of plastic sent to recycling plants cannot be repurposed and is either burned for power or sent to landfills.³ A major contributor to the limited mechanical recycling of plastics is that it is not fiscally practical to produce plastics from recycled waste streams since the secondary products have less desirable mechanical properties compared with those produced from the virgin material.⁹⁵ One contribution to the inferior properties of recycled plastic materials is the limited ability to successfully sort plastics in the waste stream into homogeneous categories. This is a problem because most polymers are immiscible with other polymers and polymer mixtures phase separate when processed together. This immiscibility leads to phase separated structures that have fragile interfaces between phases, which results in a material with weak mechanical strength.

One common method to separate polymers into homogeneous streams in recycling plants uses near-infrared (NIR) scanning to separate different types of plastics, but there are limits to this technology.⁶ For example, polyolefins, such as polypropylene and polyethylene typically share distinguishing NIR peaks.⁸ There are also packaging materials composed of multiple components in a single piece of plastic, such as multi-layer films, that cannot be separated by the current technology. In general, it is difficult to ensure homogeneous waste streams without costly sorting techniques.⁶ If an immiscible polymer blend is formed from a heterogeneous waste stream, the resultant material will have weak interfaces and the plastic will structurally fail. Moreover, as phase separated polymer blends are processed in the melt, the phase separated domains may coalesce via droplet coalescence as illustrated in **Figure 2.1**, further deteriorating the properties.

Polyvinyl chloride (PVC) is a polymer that is particularly difficult to separate in recycling streams. Several techniques have been implemented at the industrial scale to sort PVC from other polymers.⁶ Manual sorting can produce streams with 80% homogeneity, but this is a costly process. X-ray fluorescence can detect chlorinated polymers for sorting, but this technology is expensive and not widely implemented.

The lack of an efficient and effective sorting system in recycling plants means the plastics that emerge from the recycling process are likely immiscible polymer blends. Immiscibility is the result of the low entropies of mixing inherent to polymer blends due to long chain lengths.^{9, 14} The addition of compatibilizers to a phase-separated polymer blend may improve its mechanical properties. Compatibilizers are amphiphilic polymers that are molecularly designed to reside at the interface between the two phases, strengthen the interface, lower interfacial tension, and inhibit droplet coalescence, as illustrated in **Figure 2.2**.

The composition of plastic waste is dominated by semi-crystalline polymers such as polyethylene, polypropylene, and polyethylene terephthalate (PET), where these three polymers make up nearly 61% of the waste stream.^{5, 95} Another important component in the plastic waste stream is PVC which is an amorphous polymer that makes up ~5% of plastic waste.⁹⁵ Blends of any of these polymers are immiscible, and thus the resultant mixtures of polymers in the waste stream would benefit from the rational development of effective compatibilizers. An understanding of the important molecular characteristics and processes that effectively compatibilize amorphous polymer blends has been well documented.^{41, 43, 45, 96-98} Previous research has emphasized the importance of the molecular structure of a compatibilizer to improve the strength of an amorphous phase

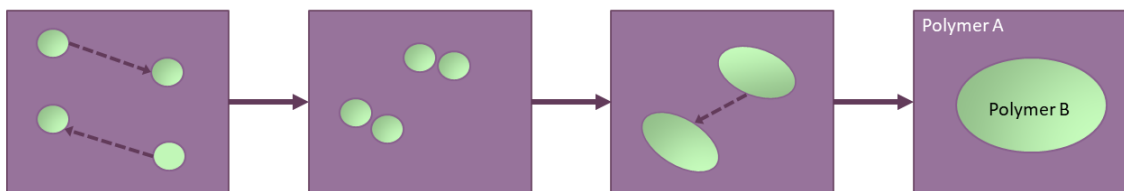


Figure 2.1. Model of phase separation driving droplet coalescence in an immiscible polymer blend.



Figure 2.2. Model of compatibilizer stabilizing the interface between immiscible polymers to prevent droplet coalescence from occurring.

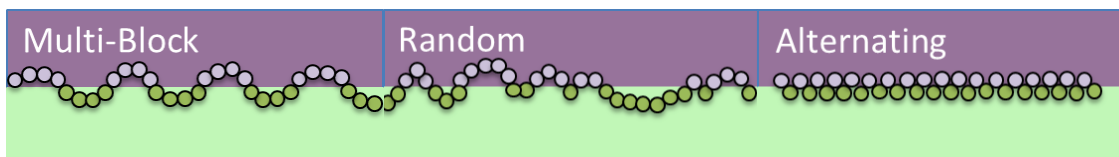


Figure 2.3. Model of how different copolymer structures interact as compatibilizers at the interface between two domains.

separated blend interface, which relies on chain entanglements to strengthen interfaces.^{41,}
^{42, 44, 99-101} Alternating copolymers tend to be the least effective linear copolymer, where the alternating copolymer tends to lay flat at the polymer-polymer interface. This conformation does not significantly extend into either homopolymer phase to successfully form entanglements with either homopolymer, and thus does not strengthen the interface and “stitch” the phases together, as illustrated in **Figure 2.3**.⁴² Block and blocky copolymers tend to more effectively strengthen the interface than random copolymers, as the random copolymers may assemble along the interface similar to the alternating copolymer. Blocky copolymers with block lengths that are greater than twice the molecular weight of entanglement (M_e) tend to form entanglements with the homopolymer phases, as the blocks can form loops at the biphasic interface.^{41, 43} Unfortunately, the identification of the crucial processes and molecular characteristics of effective compatibilizers in polymer blends that contain a crystalline polymer is less well understood.⁴³ Thus, there is a need to develop this foundational information in order to rationally design effective compatibilizers for immiscible polymer blends containing a crystalline component since this is most applicable to recycling of polymer waste streams.

Thus, an interesting system to develop this understanding is a blend composed of polyvinyl chloride (PVC) and polyolefin elastomers (POE).^{64, 102-104} Previous research in the Dadmun group tested commercially available chlorinated polyethylene (c-PE) as compatibilizers for polyvinyl chloride (PVC) and polyolefin elastomer (POE) blends. These studies found that suspension chlorinated polyethylene creates blockier compatibilizers, where blockier copolymers form stronger interfacial adhesion between

PVC and POE. The blocky compatibilizers are also superior to more randomly chlorinated polyethylene, that are chlorinated in solution. This is consistent with previous studies that show that blocky copolymeric compatibilizers form better entanglements at a biphasic interface.^{41-45, 101} It was also noted that co-crystallization could occur at the semicrystalline interface, which is a mechanism for interfacial reinforcement that remains of interest.

In this research, we evaluate the impact of the sequence distribution of 6 blocky chlorinated polyethylenes (c-pes) and one randomly chlorinated polyethylene sample on its ability to strengthen the biphasic interface between a polyolefin elastomer and poly(vinyl chloride), with the goal of providing insight into the important molecular characteristics of the compatibilizer that will effectively compatibilize the biphasic interface between a crystalline and an amorphous polymer. These compatibilizers are named based on their sequence distribution, chlorine content, and heat of fusion. For example, 23/9b is a blocky copolymer with 23 mol% cl, and a heat of fusion of 9 J/g.

The heat of fusion is used to quantify the extent of crystallinity of these samples, since the heat of fusion for 100% crystalline chlorinated polyethylene is unknown. For this reason, the heat of fusion and extent of crystallinity will be used interchangeably, but neither of these values can be compared to the percent crystallinity of other polymers.

This manuscript describes a research program that is designed to provide insight into the important molecular-level characteristics and processes that drive the compatibilization of blends containing a crystalline polymer. These studies focus on the ability of chlorinated polyethylenes (c-PEs) to strengthen the interface between amorphous PVC and crystalline polyolefin elastomers. This is accomplished by

monitoring the strength of these compatibilized interfaces with peel tests as well as experiments that monitor the interfacial adhesion between the c-PE and PVC as well as between the c-PE and POE. Combining these mechanical properties with differential scanning calorimetry (DSC) and x-ray scattering studies that document the crystalline melting behavior and structure of component pairs provides molecular level insight into the importance of polymer chain entanglement, polymer co-crystallization, and molecular design on the effectiveness of chlorinated polyethylene as compatibilizers in these crystalline polymer blends.

Experimental

Materials

The materials for this research program were obtained from commercial sources. Polyvinyl chloride (PVC) (233 kDa) was obtained from Sigma Aldrich. The PVC was thermally stabilized with 4 phr Mark 1900 methyltin mercaptide (Galata Chemicals), the structure of which is shown in **Figure 2.4**. Engage polyolefin elastomer (POE) 7270 was obtained from Dow Chemicals. All chlorinated polyethylenes (c-PE) were provided by Showa Denko (Japan).

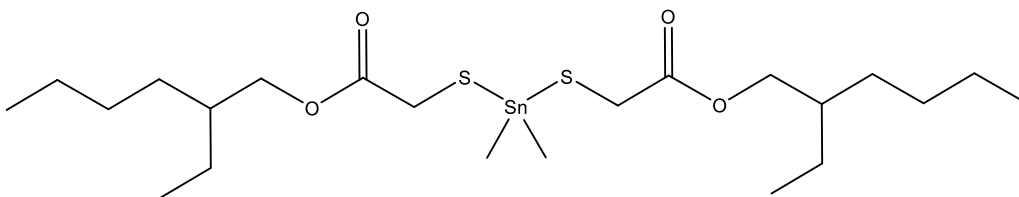


Figure 2.4. Structure of Mark 1900 thermal stabilizer, methyltin mercaptide.

Nuclear Magnetic Resonance Spectroscopy:

The compositions of the chlorinated polyethylenes were determined by ^1H NMR, while the sequence distributions of the c-PEs are determined by quantitative ^{13}C NMR. In both of these experiments, samples of 5 wt% c-PE dissolved in 1,1,2,2-tetrachloroethane- d_2 (Cambridge Isotope Labs) were prepared at 110 °C for NMR analysis.¹⁰⁵ ^1H NMR and quantitative ^{13}C NMR were run on a Bruker Avance 400 MHz at 90 °C to prevent precipitation

Size Exclusion Chromatography:

The molecular weight characteristics of the commercial c-PE samples (5 mg/mL) were determined using a Malvern Viscotek 350A High-Temperature Gel Permeation Chromatography (GPC) run in 1,2,4-trichlorobenzene (TCB) at 150 °C using polystyrene standards.

Interfacial Adhesion of Trilayer Samples:

PVC (20 g) powder is stabilized with 4 phr of methyltin mercaptide (Mark 1900).^{106, 107} This powder is added to a preheated mold that is placed in a Carver Laboratory Press Model C set to 200 °C. The sample is left in the melt press for 3 minutes without pressure then for 2 min with an applied pressure of 1 metric ton. This PVC sheet is left to cool below its T_g (~85 °C) in the mold to prevent curling. Polyolefin elastomer (POE) is separately melted into a strip mold with dimensions 10 mm x 65 mm x 2.3 mm at 200 °C for 5 minutes in the Carver Press.⁶⁴

Chlorinated polyethylene (2.5 wt%) is then dissolved in toluene overnight at 85 °C to make a 2 g homogeneous solution.¹⁰⁸ The c-PE solution is then spin-coated onto the

PVC sheet at 2500 rpm for 20 seconds. The coated sheet is left overnight for the toluene to evaporate. The coated PVC is then cut into 4-5 strips with dimensions 10 mm x 65 mm x 2.3 mm using a Dremel 4300.

The POE strip is then laid on top of the c-PE coated PVC in a mold at 200 °C. The trilayer is left in the Carver melt press for 15 minutes. At times longer than 15 minutes, the PVC will begin to show evidence of thermal degradation. The mold is removed from the melt press but left on the hot metal plate until the temperature of the sample is below the T_m of the POE (~ 60 °C). The samples are then removed from the mold and left to cool to room temperature. The cooled samples are peeled using a combination T+U peel test illustrated in **Figure 2.5** on an Instron Model 5965 Universal Tester 5kN at 10 mm/min.⁶⁴ The results reported are the average of 8-10 trials for each c-PE analyzed.

Interfacial Adhesion of Bilayer Samples:

To make c-PE/PVC bilayer samples, individual strips of each c-PE and stabilized PVC were prepared by melting 2.5 g of powder in a preheated mold in the Carver melt press at 200 °C for 3 min uncovered followed by 5 min with 1 metric ton of applied pressure. Two c-PE or two PVC strips were combined and placed back in the melt press for another 5 min under pressure to ensure the entirety of the polymer had melted. In total, the individual PVC and c-PE strips have a mass of ~5 g. To make the POE/c-PE bilayer samples, POE strips were made by melting 2 g of pellets for 5 min in the Carver melt press under 1 metric ton of pressure. Bilayer samples of POE/c-PE and c-PE/PVC are made using the same procedure. Strips of c-PE and either POE or PVC were placed in

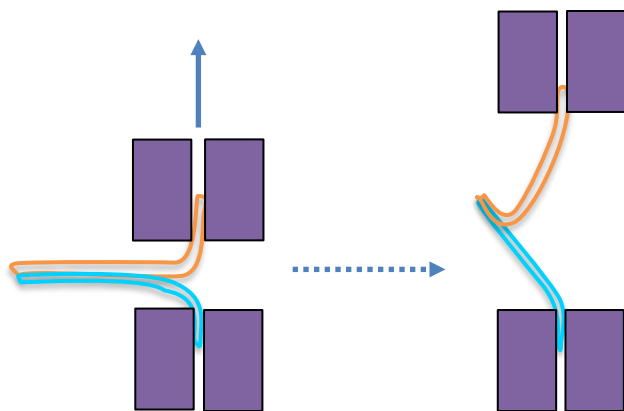


Figure 2.5. Combination T+U peel test with the flexible polymer pulled from the more rigid polymer.

the same mold used for the trilayer samples for 15 minutes at 200 °C. The same cooling and peel test procedure was used with the bilayer samples as with the trilayer samples.

Crystallinity Analysis Sample Preparation:

The melting behavior and crystalline structure of POE/c-PE blends was examined to provide molecular level insight into possible changes in crystalline structure and interactions between components. In these studies, pure samples of POE and c-PE were prepared by melt-pressing the samples into thin films at 200 °C for 5 min in a Carver Laboratory Press to mimic the thermal history of the sample preparation of the bilayer and trilayer samples. Similarly, binary blends of mass ratios of 50:50 were formed of POE and each of the analyzed c-PE through solution mixing in toluene and precipitation in methanol. These samples were dried in a vacuum oven for 24 hrs at 75 °C. A portion of these were melt-pressed at 200 °C for 5 minutes and are labeled as c-PE/POE melted. To further analyze the crystalline structure and melting behavior of the POE/c-PE blends, the pure POE, pure c-PE and POE/c-PE binary blends were annealed at 45 °C for 16 days.

Differential Scanning Calorimetry (DSC):

Crystallinity and thermal transitions of the commercial c-PE, POE, stabilized PVC, and binary blends were analyzed using a TA Instruments Q-2000 DSC. To determine the thermal characteristics of the individual components, 5-10 mg of material was run through two heating and cooling cycles at 10 °C/min. The first cycle was run to remove the thermal history of the pure material. The chlorinated polyethylene was scanned from 20 - 150 °C, while the POE scanned from -20 - 120 °C and PVC was

scanned from 20 - 240 °C. The DSC curve that emerges from the second cycle of each sample was analyzed to determine heat of fusion (ΔH_f), T_g , and T_m of the sample.⁶⁴

The simultaneous DSC of both components in the same DSC pan but separated by aluminum foil were obtained to use as a baseline of the blend if the two components did not interact on the molecular level. To make these samples, both POE and c-PE were placed in the DSC pan but were physically separated from each other with aluminum foil. The DSC curves of the annealed blend samples were analyzed by scanning from 0-150 °C. Since we wanted to characterize crystallization behavior due to the processing of the samples, the first heating/cooling cycle is needed.

X-ray scattering:

POE, c-PE, melted blend samples, and annealed blend samples were analyzed by small- and wide-angle x-ray scattering (SAXS and WAXS). The SAXS and WAXS curves of these samples were analyzed to provide information on their crystalline structure. The SAXS and WAXS curves were obtained on a Xenocs Xeuss 3.0 X-ray scattering instrument. The data was collected using a copper source and a PILATUS3 detector. The sample to detector distances were 0.9 m for SAXS and 0.045 m for WAXS. The data were analyzed using gaussian curves fitted over specific peaks to yield peak positions in scattering vector (q). These peak positions were then translated to real space d-spacings (d) using the relationship $d = \frac{2\pi}{q}$.

Results and Discussion

Characterization of Commercial c-PE:

The chlorine content of the commercial chlorinated polyethylenes (c-PE) is determined by analysis of ^1H NMR spectra as shown in **Figure 2.6** and Eqn 2.1.⁴⁸ Chlorine content, as mol% chlorine, is determined by dividing the integration of the chloromethylene (S_{CHCl}) peak by the sum of the ^1H NMR peak integrations normalized by the number of hydrogens for chloromethylene, methylene (S_{CH_2}) and the methyl (S_{CH_3}) end groups.

$$\text{mol\% Cl} = \frac{S_{\text{CHCl}}}{S_{\text{CHCl}} + S_{\text{CH}_2}/2 + S_{\text{CH}_3}/3} \quad \text{Eqn (2.1)}$$

The relative blockiness of a c-PE copolymer is determined by integrating quantitative ^{13}C NMR based using the method designed by Chang et. al.⁵¹ In this analysis, the relative blockiness is quantified by determining the percent difference in the integration of the non-chlorinated carbon pentad peak at ~29 ppm of the commercial copolymers relative to the identical integration of a statistically randomly chlorinated polyethylene copolymer.⁵¹ **Figure 2.7** shows an example spectra and analysis, where the sum of the peak integrations in the ^{13}C NMR are normalized to 1. Example model integrations and calculations for 23/R and 19/43B can be found in Tables S2.2 and S2.3 in Appendix A. The greater the difference between the integration of the non-chlorinated carbon pentad peak in the commercial copolymer relative to that of an ideal random copolymer, the more the structure of the c-PE reflects a multi-block copolymer rather than a randomly chlorinated polyethylene. The results of this analysis are shown in **Table 2.1**.

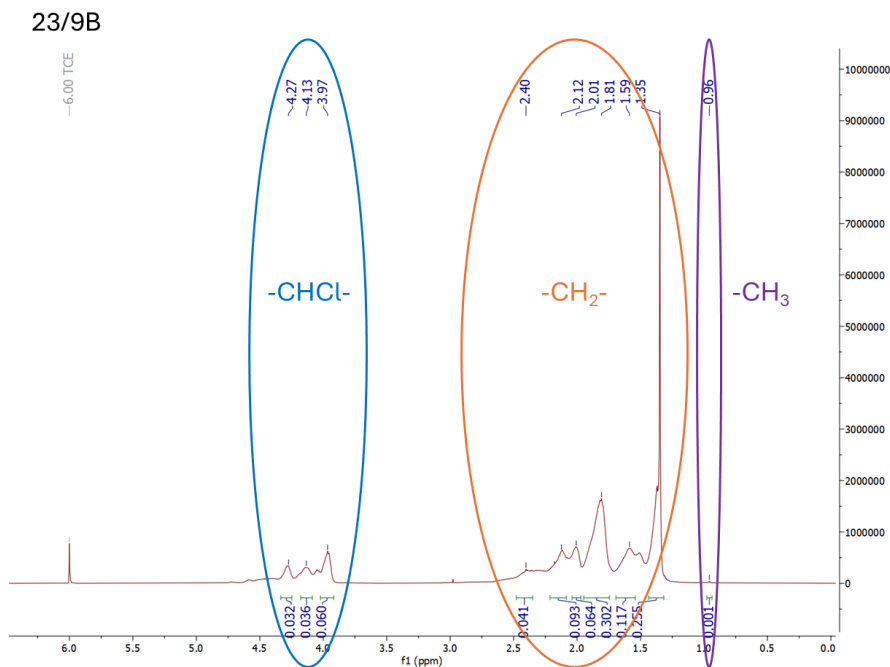


Figure 2.6. Variable temperature ${}^1\text{H}$ NMR of 5 wt% 23/9B c-PE dissolved in TCE- d_2 at 90°C .

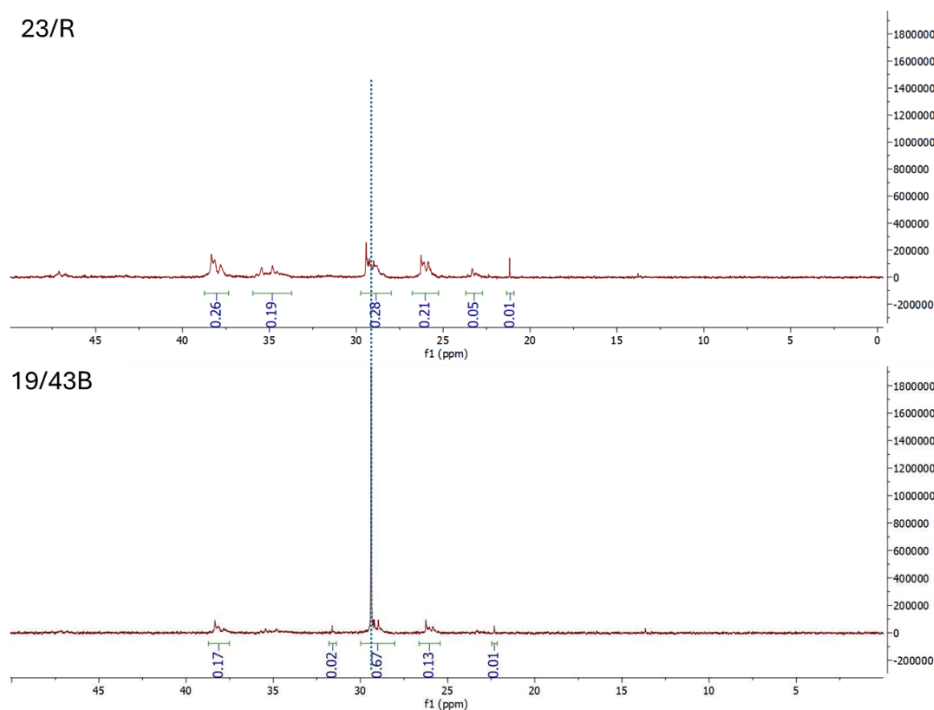


Figure 2.7. Quantitative ${}^{13}\text{C}$ NMR for a random (top) and blocky (bottom) c-PE. The peak at ~ 29 ppm that corresponds to non-chlorinated carbon pentads is more prevalent in the blockier sample.

Table 2.1. Molecular characteristics of seven commercial chlorinated polyethylene compatibilizers as well as interfacial adhesion of PVC/POE interfaces compatibilized with the c-PE.

Sample	Average G_a (J/m²)	M_n (kDa)	Chlorine Content (mol%)	Heat of Fusion (J/g)
23/27B	2971	24	22.7%	27
23/9B	4397	87	22.6%	9
19/43B	5564	31	19.3%	43
18/36B	4870	36	17.7%	36
14/19B	3159	63	13.8%	19
10/27B	3759	67	10.5%	27
23/R	4244	128	23.1%	33

Interfacial Adhesion (G_a) of PVC/POE Interface with c-PE Compatibilizers:

The interfacial adhesion (G_a) of the neat PVC/POE interface and those compatibilized with the chlorinated polyethylenes were determined from peel test experiments and Eqn 2.2. In Eqn 2.2, F is the force measured during the peel test and w is the width of the sample that is measured using calipers.⁶⁴ This value for interfacial adhesion presented in **Figure 2.8**, quantifies how the strength of the interface between the incompatible polymers increases with the addition of compatibilizers.

$$G_a = \frac{F}{w} \quad \text{Eqn (2.2)}$$

Figure 2.8 plots the interfacial adhesion of the compatibilized interfaces as a function of the extent of crystallinity of the c-PE (left) and as a function of the blockiness of the c-PE (right). This figure shows that the interfacial adhesion does not change much with the extent of crystallinity up to ~ 25 J/g, but the interfacial adhesion increases with extent of crystallinity above that value. The plot of interfacial adhesion with copolymer blockiness also shows an increasing trend in interfacial adhesion with blockiness.

The commercial c-PE with the highest interfacial adhesion (19/43B) has a chlorine content of 19 mol% Cl as recorded in **Table 2.1**. This is in line with previous studies by Dadmun et. al. which showed that c-PEs with chlorine contents above 20% limits the compatibility of the chlorinated polyethylene with POE, hindering the ability of the copolymer to compatibilize the interface.⁶⁴ The 23/27B compatibilizer produces an interface that is weaker than the one compatibilized by 10/27B, yet has similar crystallinity to 10/27B, but as shown in **Table 2.1**, it has a higher chlorine content and the lowest molecular weight of the compatibilizers tested. We interpret this adhesion data to

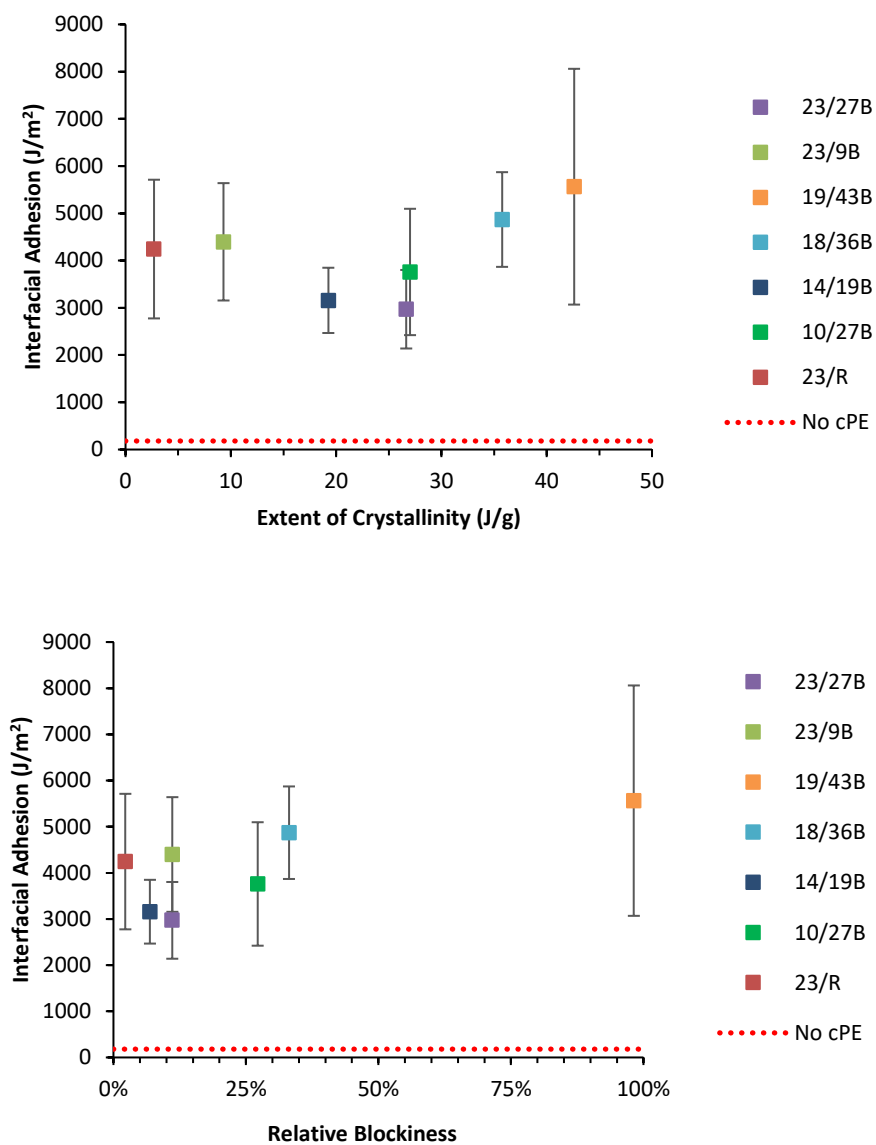


Figure 2.8. Relationships between interfacial adhesion and crystallinity (top) and blockiness (bottom) for the trilayer compatibilized system. Error bars represent one standard deviation from the average.

show that the higher chlorine content of this c-PE limits the chain compatibility with the POE homopolymer phase, and the low molecular weight limits the number of entanglements that can be formed between the compatibilizer and the homopolymers, leading to a weaker compatibilized interface. The compatibilizer that forms the strongest interface, 19/43B c-PE, has the highest extent of crystallinity and relative blockiness of the commercial c-PE assessed and a balanced chlorine content of 19 mol%. The variation in the behavior of these compatibilizers with crystallinity, blockiness, and %Cl indicates that optimizing entanglement between the compatibilizer and PVC phase is an important process in strengthening interfacial adhesion between the amorphous and crystalline polymers. It is important to note that all of the c-PEs tested improved the interface by at least 15 times that of the un-compatibilized PVC/POE interface.

In **Figure 2.8**, the interface that is compatibilized with the 19/43B copolymer has the strongest interfacial adhesion and the highest extent of crystallinity of the analyzed c-PE. Previous research has shown that more crystalline compatibilizers may form a stronger interface via co-crystallization than polymer/polymer interfaces compatibilized with other copolymers.^{62, 64, 67} This suggests that co-crystallization of the compatibilizer and the POE may occur with this commercial c-PE, which in turn significantly strengthens the PVC/POE interface. To individually investigate the importance of the entanglement of the compatibilizer and the PVC as well as the co-crystallization of the c-PE with the POE, the system was simplified to examine the interfaces that exist between the PVC/c-PE pair and the c-PE/POE pair.

Interfacial Adhesion for PVC/c-PE and c-PE/POE Bilayer Interfaces:

Monitoring the strength of the bilayer interfaces allows us to determine how the molecular structure of c-PE impacts its adhesion to the POE and PVC individually. These experiments were completed for the seven commercial c-PEs under the same interface formation conditions as the trilayer study. Investigation of the PVC/c-PE bilayer interface provides insight into the interactions between the compatibilizer and the amorphous layer, while the POE/c-PE bilayers offer information on the interactions between the compatibilizer and the crystalline phase. Observations from this pair of systems are combined to provide insight into the importance of the potential mechanisms that may strengthen the trilayer interface.

Figure 2.9 plots the interfacial adhesion of the bilayers between PVC and each c-PE as a function of compatibilizer chlorine content (left) and number-average molecular weight, M_n , (right). These figures show an increase in interfacial adhesion with copolymer chlorine content to a maximum at $\sim 20\%$ and a decrease in interfacial adhesion with increasing molecular weight. The stark variation in interfacial adhesion with the 3 compatibilizers of similar chlorine content at ~ 23 mol% Cl content in **Figure 2.9** suggests that there are aspects of these three copolymers beyond the chlorine content that impact its ability to strengthen the interface. To investigate this further, **Figure 2.10** plots the strength of the interfaces that are strengthened with these three c-PEs as a function of relative blockiness (left) and extent of crystallinity (right). Inspection of **Figure 2.10** shows that the interfacial adhesion of PVC/c-PE also depends on the sequence distribution and crystallinity of the copolymer, where an increase in blockiness and crystallinity corresponds to an increase in interfacial adhesion. These results strongly

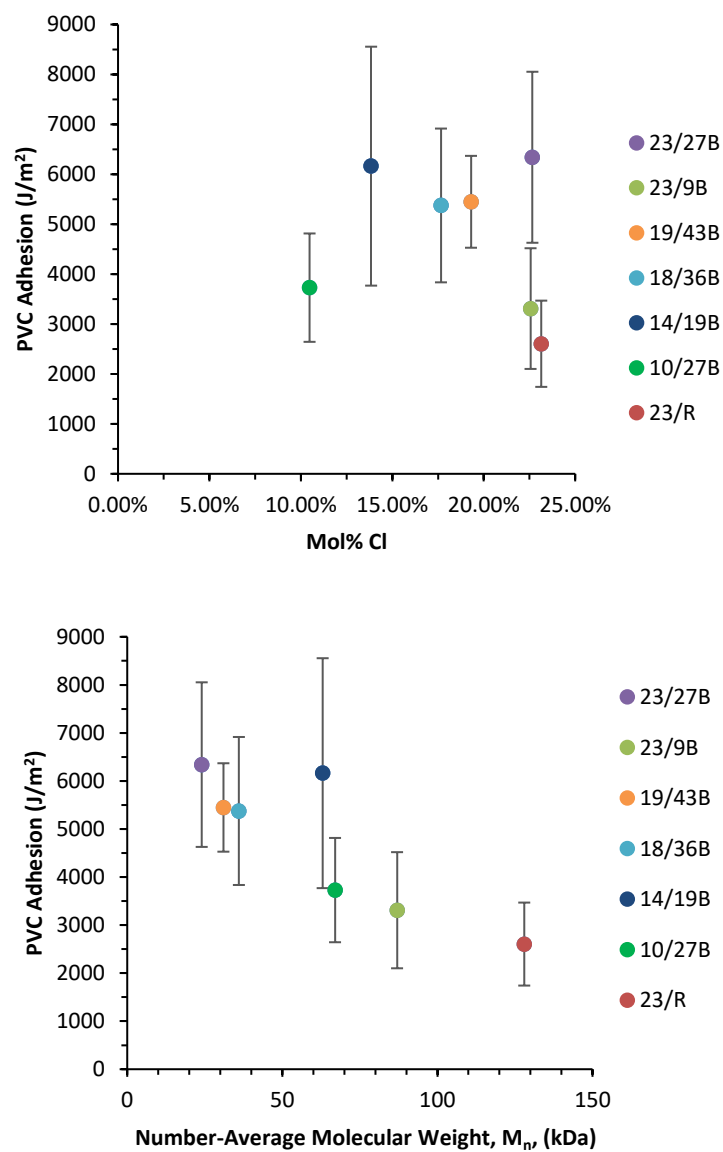


Figure 2.9. Impact of composition (top) and number-average molecular weight (bottom) of compatibilizers on the strength of the PVC/c-PE interface. Error bars represent one standard deviation from the average.

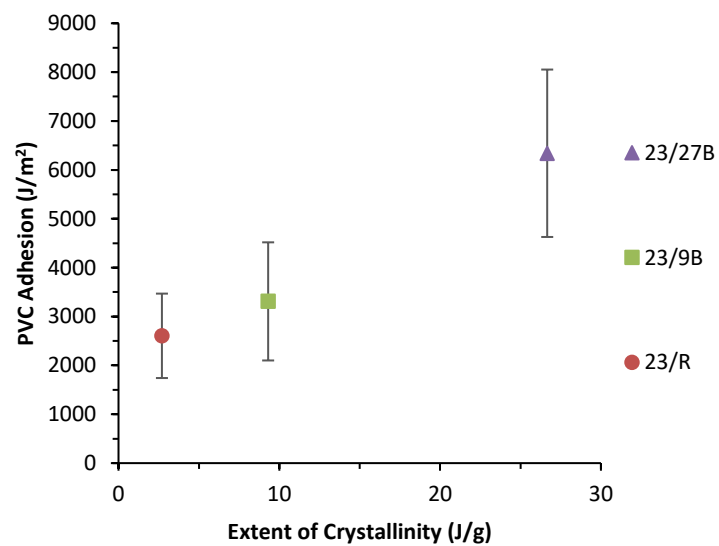
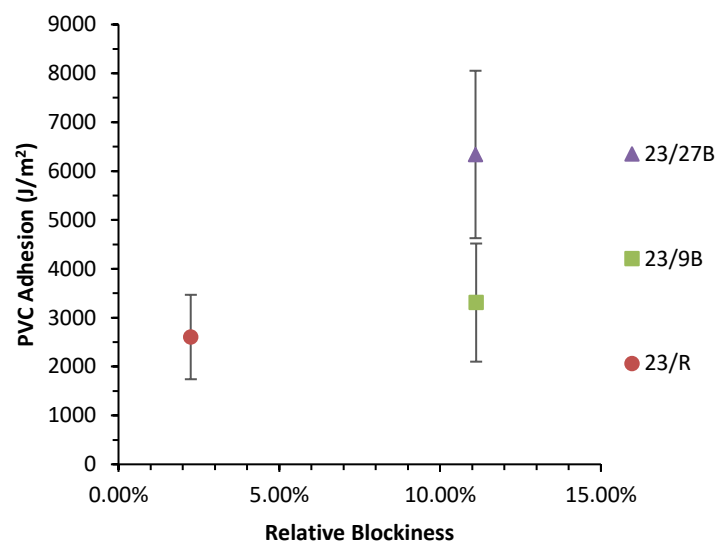


Figure 2.10. Relationship between blockiness and adhesion for the highest chlorine content at the PVC/c-PE interface. Error bars represent one standard deviation from the average.

suggest that the blockiness of the distribution of the -Cl along the chain is an important molecular characteristic of the compatibilizer in forming a strong interface with the amorphous polymer.

In this amorphous-semicrystalline interface, the compatibilizer with the highest adhesion (23/27B) also has the highest mol% chlorination (**Figure 2.9**). The Cl content of this copolymer is the closest to the composition of PVC, which is ~50 mol% or 50 chlorinated carbons per 100 carbons in a chain. There is a decrease in interfacial adhesion with increasing molecular weight, where this may be due to the slower equilibration of the larger chains. **Figure 2.10** reveals the dependence of the interfacial strength of the compatibilized interface on the copolymer sequence distribution, where the best performing compatibilizer for the PVC/c-PE interface has a higher blockiness of the c-PE which indicates that the copolymer contains longer runs of chlorinated carbons which will entangle better with the PVC chains than copolymers with randomly dispersed chlorination.

Figure 2.11, which plots the interfacial adhesion of the compatibilized PVC/c-PE interface as a function of the extent of crystallinity (left) and relative blockiness (right) of all c-PE compatibilizers is consistent with this interpretation. There is a general improvement in interfacial adhesion in **Figure 2.11** with an increasing heat of fusion and a higher blockiness of the compatibilizer. In summary, the amorphous/semicrystalline PVC/c-PE interfaces attain a higher adhesion and interfacial stability with increased compatibilizer blockiness and compatibility with the amorphous phase.

Figure 2.12 presents a plot of interfacial adhesion (G_a) of the semicrystalline/semicrystalline c-PE/POE bilayer interface as a function of the extent of

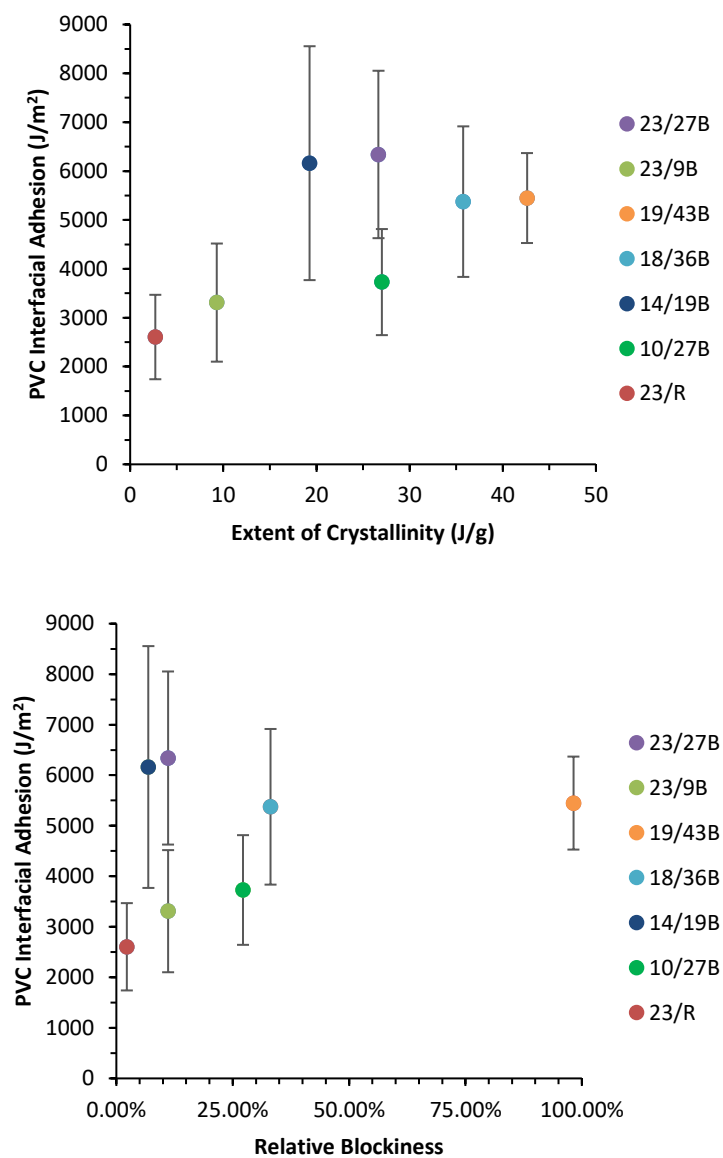


Figure 2.11. Impact of crystallinity (top) and sequence structure (bottom) on the interfacial adhesion in the PVC/c-PE bilayer interfaces. Error bars represent one standard deviation from the average.

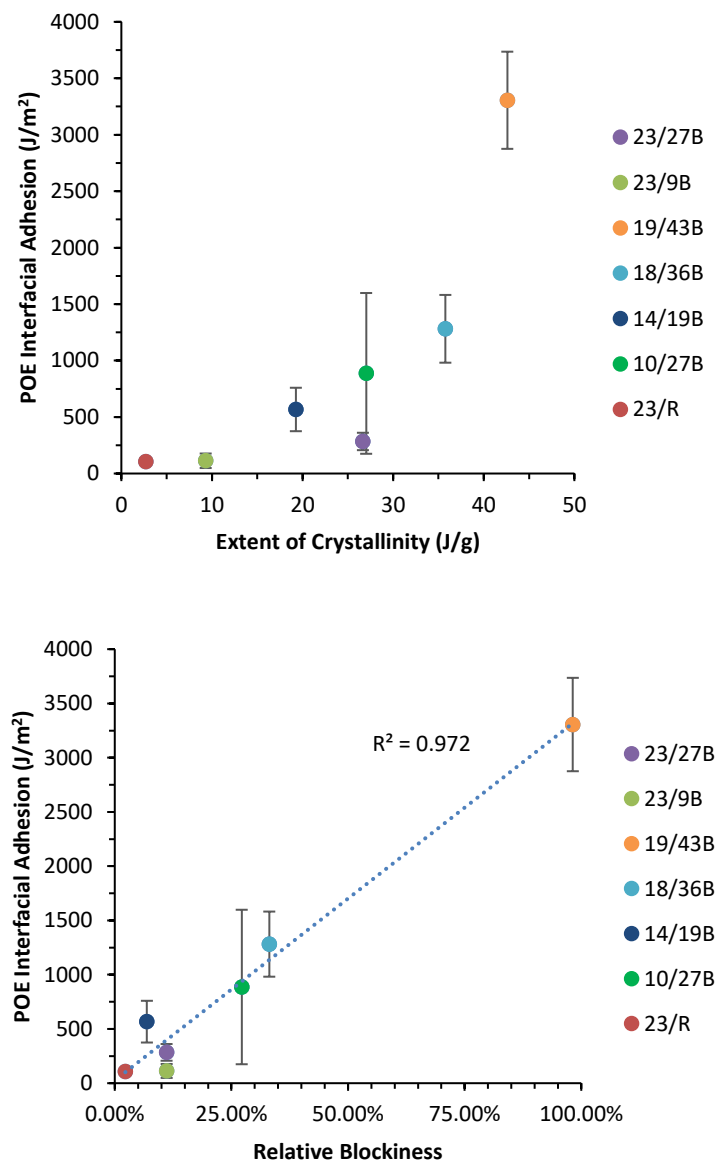


Figure 2.12. Impact of crystallinity (top) and sequence structure (bottom) for c-PE/POE. Error bars represent one standard deviation from the average.

crystallinity (top) and relative blockiness of the compatibilizer (bottom). There is a significant increase in interfacial adhesion with crystallinity from the least crystalline compatibilizer (23/R), which forms an interface with a G_a of 107 J/m^2 , to the best performing compatibilizer (19/43B), which forms a bilayer with an adhesion of 3306 J/m^2 . This is an approximately 30 times improvement in adhesion with a 40 J/g increase in extent of crystallinity. Moreover, there appears to be a linear increase in bilayer interfacial adhesion with relative blockiness of the c-PE compatibilizer. It is interesting to note that the 23/27B and 10/27B copolymers have the same extent of crystallinity but the 23/27B interface is less than half as strong as the 10/27B interface. The difference between the molecular structure of these two copolymers is that the 23/27B is less than half as blocky as the 10/27B copolymer. A blockier structure has previously been shown to entangle better with the homopolymers than copolymers with a more random architecture.⁴² 23/27B also has a chlorine content that is twice that of 10/27B, where this high chlorine content further prevents significant entanglement between the phases due to a decrease in compatibility of the c-PE with the POE. We therefore interpret the improvement in interfacial strength in the c-PE/POE interface with copolymer blockiness of compatibilizers with similar crystallinity to indicate that entanglement remains an important process in strengthening the semicrystalline/semicrystalline interface.

In **Figure 2.12**, the linear increase in adhesion with relative blockiness indicates that there is a correlation with chain sequence distribution and the successful compatibilization of the semicrystalline-semicrystalline interface. The bilayer adhesion significantly increases with compatibilizer crystallinity, which is consistent with a co-crystallization mechanism between the two crystalline components at the interface. It is

also interesting that the best performing c-PE/POE bilayer interface contains 19/43 B, which is also the compatibilizer that forms the trilayer interface with the highest adhesion. These results strongly suggest that the blockiness of the c-PE and its ability to form crystalline domains is an important molecular characteristic of an effective compatibilizer of semi-crystalline/semi-crystalline interfaces.

The bilayer study provides direct insight into how each homopolymer interacts with the semicrystalline compatibilizers. To visualize how these pairwise interactions impact the trilayer adhesion, **Figure 2.13** plots both the bilayer and the trilayer interfacial adhesion as a function of the extent of crystallinity (left) and chlorine content (right) of the c-PE compatibilizer. It is clear from **Figure 2.13** that the majority of the trilayer adhesion strengths are similar to the strength of the corresponding PVC/c-PE bilayer interface. Overall, the POE/c-PE bilayer interfaces are weaker than the PVC/c-PE bilayer interfaces. Conversely, the increasing trends exhibited by the POE bilayers match that of the trilayer system, including the improvement in interfacial adhesion with increasing crystallinity. Since the trends of the adhesion strength of the semicrystalline/semicrystalline bilayer interface seem to be integral to the performance of the c-PE compatibilizers in the PVC/POE compatibilization, the potential for co-crystallization between the POE and c-PE was investigated further. The importance of crystallization on the compatibilization process was therefore investigated for c-PEs based on the results from the trilayer studies. The three compatibilizers examined are the worst performing trilayer blocky compatibilizer (23/27 B), the overall best performing blocky trilayer compatibilizer (19/43B), as well as the randomly chlorinated compatibilizer (23/R).

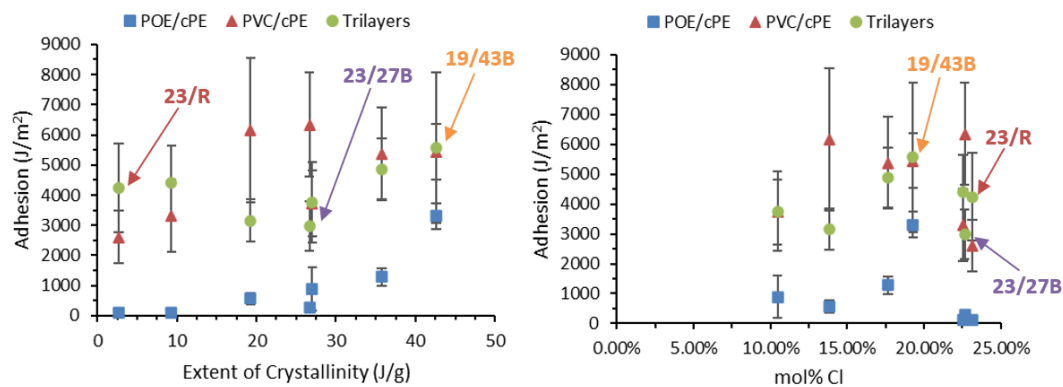


Figure 2.13. Comparison of the individual bilayers to the overall trilayer system regarding the extent of crystallinity (left) and mol% chlorination (right). Error bars represent one standard deviation from the average.

Thermal Behavior and Crystalline Structure of Crystalline Polymer Blends:

POE/c-PE blends were fabricated as described in the experimental section, where their thermal behavior was monitored by DSC, while the crystalline structure of these blends was analyzed by SAXS and WAXS, to look for evidence that these two polymers may co-crystallize. The melting behavior of the pure components, the three mixed blends, as well as the physically separated samples, where the two components are both in the DSC hematic pan but separated by aluminum foil, are determined by DSC. All samples are annealed for 16 days at 45 °C to allow the crystallization of the blends to develop extensively.

The melting behavior of the separated blends provide a baseline to determine how changes to the melting peaks of the melted blends are due to direct interactions between the components and their DSC curves can be found in **Figure S2.3** in Appendix A.⁶⁴ In **Table 2.2** and **Figure 2.14**, the ‘melted’ sample refers to a 1:1 mass ratio of c-PE and POE blend that is prepared by solution mixing in toluene and precipitation in methanol. The heat of fusions of the separated components reported in **Table 2.2** are normalized to the mass composition in the sample and match the heat of fusion of each corresponding pure component. Thus, any changes to the heat of fusion of either component in the ‘melted’ blends must be driven by the impact of the presence of the other component.

The differential scanning calorimetry (DSC) spectra of the three compatibilizers of interest and the corresponding binary blends are displayed in **Figure 2.14** to reveal changes to the melting behavior of the components when they are blended. The DSC spectra (**Figure 2.14**) of the each melted blend shows the loss of two distinct POE melting peaks between 50 °C and 80 °C, which we interpret to indicate that the crystal

Table 2.2. Melt temperature and heat of fusion of the 16-day annealed samples of the three c-PE/POE blends.

Sample		T _m (°C)	Normalized H _f (J/g)
POE		61.0	38
19/43 B c-PE		122	34
Separated	POE	57.2	40
	c-PE	70.2	33
Melted	POE	120	43
	c-PE	61.6	20
23/R c-PE		-	-
Separated	POE	58.8	33
	c-PE	72.3	-
Melted	POE	-	37
	c-PE	62.6	-
23/27 B c-PE		117	15
Separated	POE	57.3	33
	c-PE	71.6	15
Melted	POE	116	40
	c-PE	60.6	16

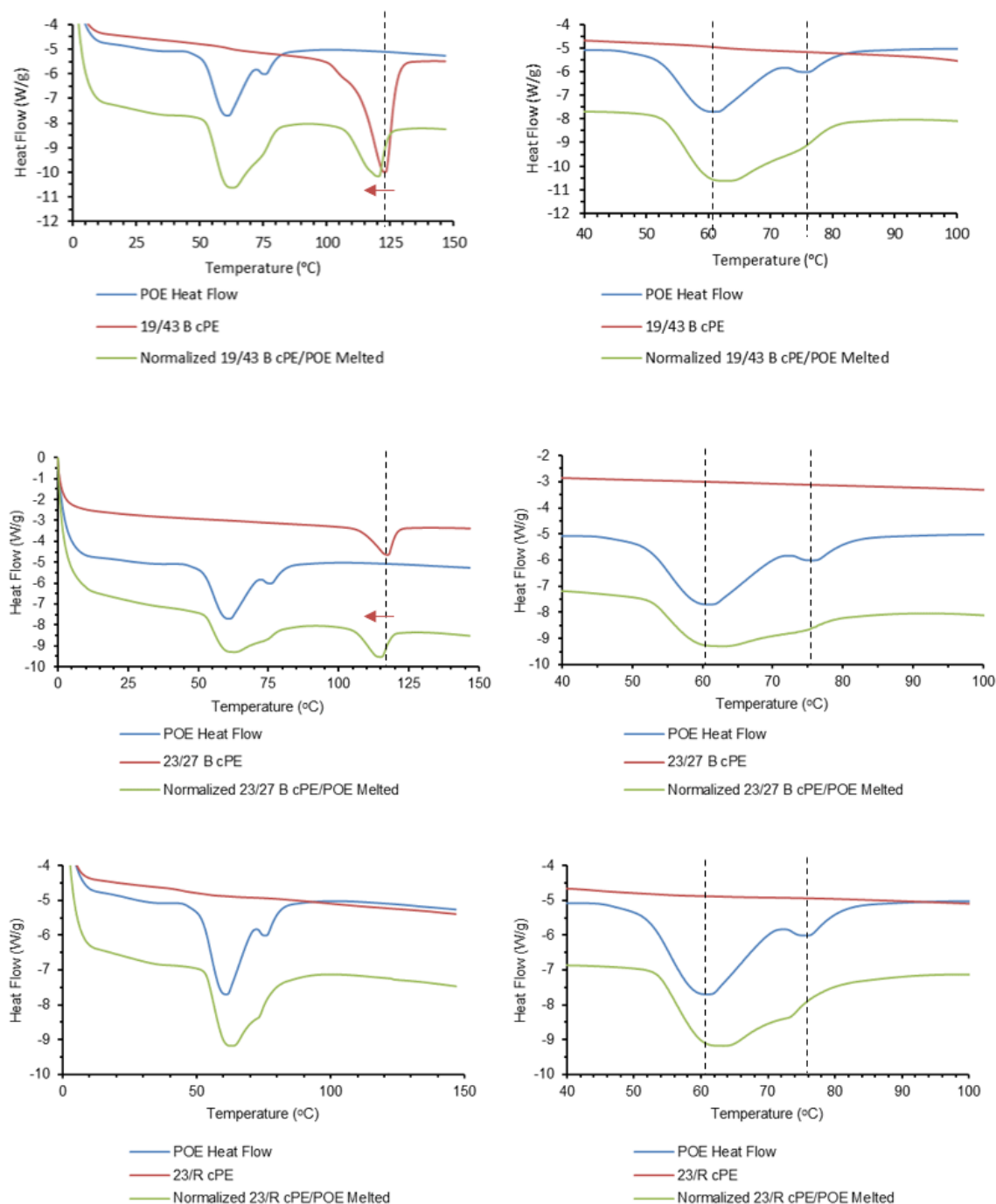


Figure 2.14. Overall (left) and zoomed (right) DSC spectra of the three chlorinated polyethylene/polyolefin elastomer blends and the pure components after annealing at 47°C for 16 days. The figures on the left highlight the shift in the c-PE melting peaks and the figures on the right highlight shifts in the POE melting peaks

structure of the POE is different when crystalized in the presence of the c-PE than in the pure melt. There is also a decrease in the temperature of the c-PE melting peak in the blends that contain 19/43B or 23/27B. The randomly chlorinated c-PE (23/R) is amorphous and does not have a melting peak. There is also an increase in the temperature of the POE melting peaks in the ‘melted’ blends samples. The shifts of the melting peaks to a higher temperature may indicate larger or more robust POE crystals. It is further noted that the increase in the melting point of the POE and a decrease in the c-PE melting point is consistent with co-crystallization occurring between the c-PE and POE, forming crystals that melt between that of the two pure components. Thus, it is clear that the melting behavior of both components in the blend is significantly impacted by the presence of the other component.

The changes in the normalized heat of fusion in the DSC spectra of the POE and c-PE melting peaks are plotted in **Figure 2.15** to provide insight into how the presence of the other component impacts the extent of crystallization of each polymer in the blend. For the 1:1 blend of the POE and the best performing compatibilizer (19/43 B), the POE is more crystalline than in the pure POE sample. On the other hand, the heat of fusion of the c-PE at ~120 °C decreased significantly in this blend. The randomly chlorinated c-PE is amorphous, so does not have a melting peak to analyze, however the POE melting peak in the blend with the random c-PE is very similar to that of the pure component. The melting peaks of the c-PE and POE in the blend containing the worst performing compatibilizer (23/27 B) are slightly larger than the melting peaks in the pure components. compatibilizer (23/27 B) are slightly larger than the melting peaks in the pure components.

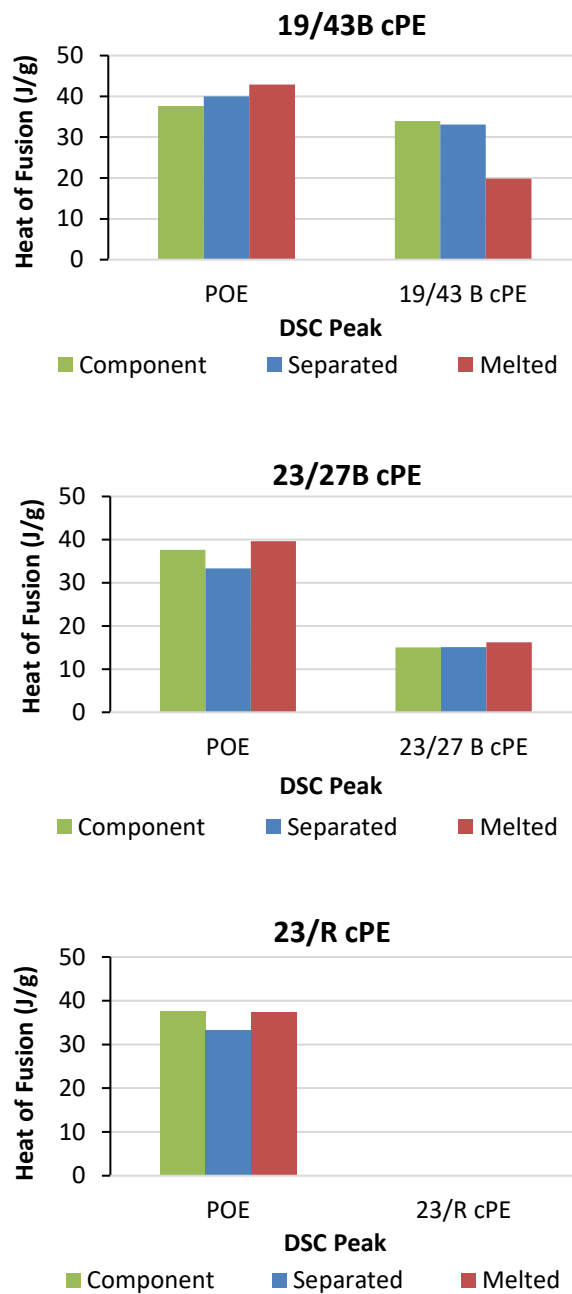


Figure 2.15. Comparison of normalized DSC integrations for the POE or c-PE components for three c-PE/POE systems.

The decrease in the heat of fusion in the DSC associated with the c-PE peak in the 19/43B/POE blend presented in **Figure 2.15** is consistent with the interruption of the homogeneous crystallization of c-PE by the presence of the POE.⁶¹ Meanwhile, the heat of fusion of the normalized POE peaks in this blend shows an increase in crystallinity, suggesting that the c-PE is likely promoting crystal growth in the POE. We interpret this to indicate that the best-performing compatibilizer (19/43B) is the most likely to co-crystallize with the POE.

Small- and wide-angle x-ray scattering curves of the pure annealed POE and 1:1 melted compatibilizer/POE binary blends are presented in **Figure 2.16** to provide insight into the local crystalline structure of these blends. The SAXS data shows a different lamellar structure in the blend samples than in the pure POE and the pure c-PE, as exemplified by the well-defined SAXS peaks at $Q \sim .125 \text{ \AA}^{-1}$. The formation of this new assembly is independent of the extent of crystallinity of the compatibilizer since all three compatibilizers of varying crystallinity formed the same peak at the same Q position. Further examination of the WAXS curves also shows a variation in the local packing of the polymer in the unit cell of the three c-PE/POE blends from that of the pure POE. This manifests as a shift of the POE peak at $Q \sim 1.5 \text{ \AA}^{-1}$.

This variation in the WAXS curve indicates a change in the packing of the polymers in the unit cell of polyethylene. This peak corresponds to the b -length of the orthorhombic unit cell of crystalline polyethylene.¹⁰⁹ This X-ray data shows that the distance between chains decreases from $4.32 \text{ \AA}$ in the pure polyolefin elastomer (POE) crystal to $4.17 \text{ \AA}$ in the POE/c-PE blend crystal containing the best performing compatibilizer (19/43 B). Moreover, in **Figure 2.17**, the d -space distance in the three

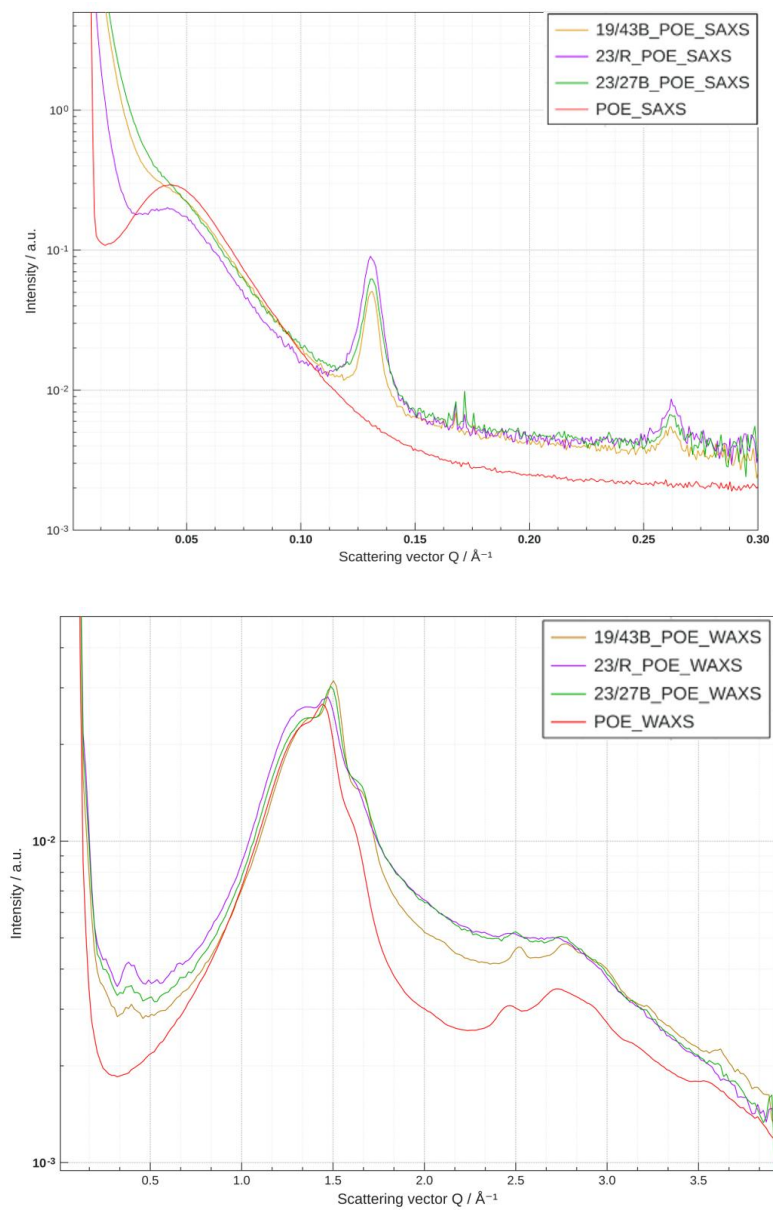


Figure 2.16. SAXS (top) and WAXS (bottom) spectra for three c-PE/POE systems.

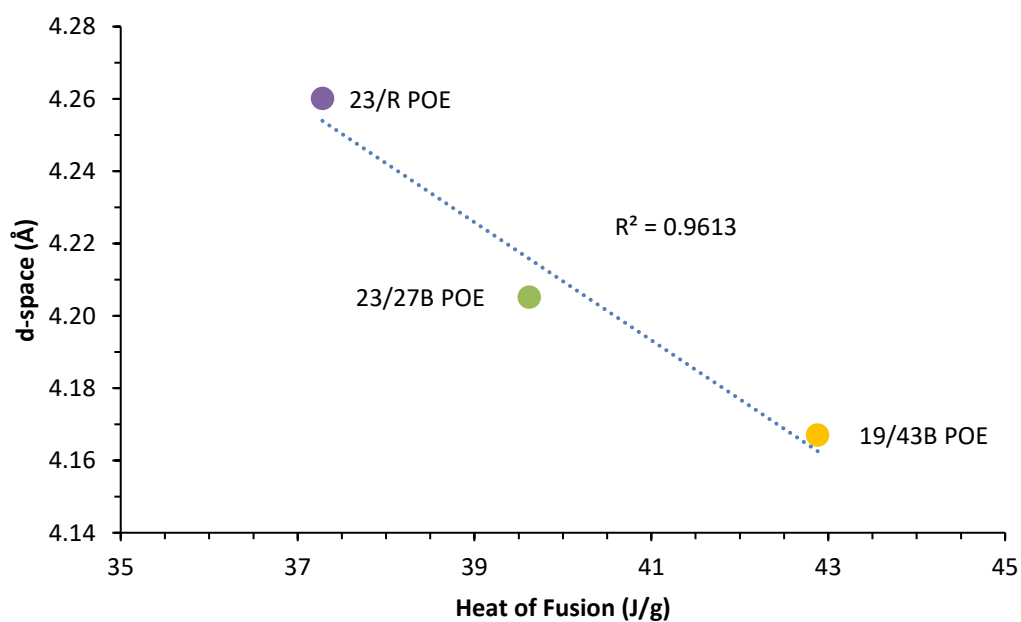
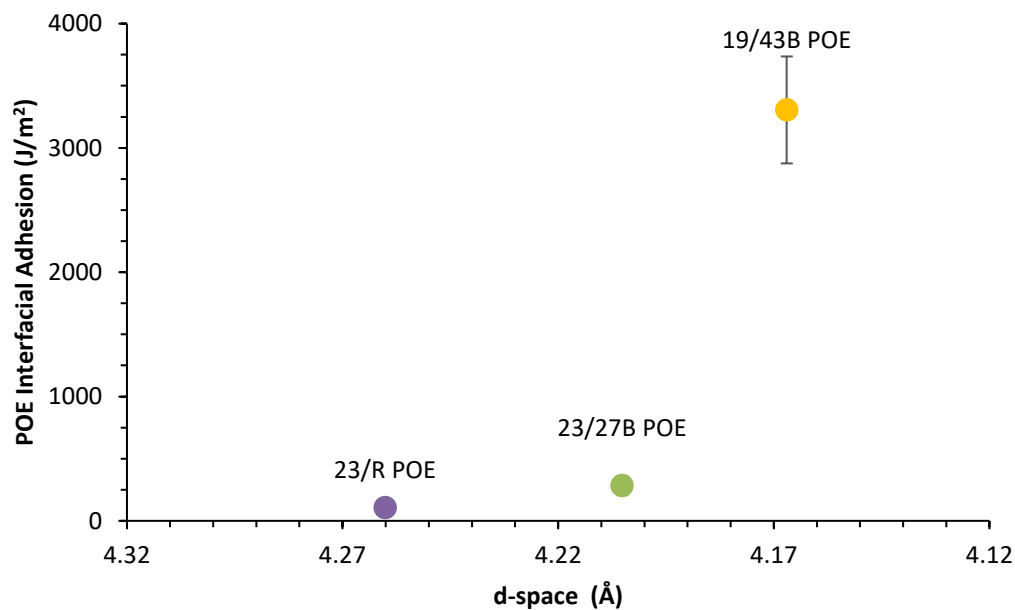


Figure 2.17. Relationship between d-space values from WAXS spectra with c-PE/POE bilayer adhesion and heat of fusion for 23/R, 23/27B (worst performing) and 19/43B (best performing).

compatibilizer blends is plotted as a function of the POE bilayer adhesion (left) and heat of fusion of the c-PE component (right). These plots show that the crystalline unit cell becomes more compact as the crystallinity of the compatibilizer increases, where the more compact unit cell also results in an improvement to the interfacial adhesion at the semicrystalline-semicrystalline interface (**Figure 2.17**). The change in the crystal structure in the blends as observed by the presence of a new peak in SAXS, a shift in the POE peak domain in WAXS as well as the change in normalized heat of fusion of the c-PE/POE blends is consistent with co-crystallization. These observations are more pronounced for 19/43B, which is the best performing compatibilizer in the c-PE/POE bilayers and the PVC/c-PE/POE trilayer peel tests. This strongly suggests that the co-crystallization of the components contributes to the additional strength of the PVC/c-PE/POE interface compatibilized by 19/43B.

A holistic interpretation of these results provides a comprehensive picture of the most beneficial molecular characteristics of an effective compatibilizer in amorphous/crystalline polymer blends. These results show that the compositions of the compatibilizers studied here are sufficient to form strong entanglements with *both phases*, where a blockier sequence distribution provides more effective pathways to form molecular entanglements. At the same time, the blocky sequence distribution of the compatibilizer provides routes for co-crystallization of the compatibilizer and crystalline homopolymer that will further enhance the strength of the compatibilized interface. Thus, these studies reveal that an optimal molecular design of the compatibilizer has a composition that allows entanglement with both phases and a blocky sequence distribution that fosters stronger entanglements and promotes co-crystallization, which in

turn augments the strength of the compatibilized interface. It is important to emphasize that our results indicate that the formation of entanglements with both phases appears to be a crucial and necessary process, and that any co-crystallization that may occur between the compatibilizer and homopolymer phase augments the compatibilizing effectiveness and provides further strengthening of the interface.

Conclusion

The strength of the interface of a compatibilized immiscible amorphous/semicrystalline blend is dependent on the molecular architecture of the compatibilizer and its ability to crystallize. The composition dependence and role of copolymer blockiness on the interfacial strength of the compatibilized interface as well as of both bilayer indicates that blockier copolymers are more effective compatibilizers than random copolymers since they can diffuse and entangle with both homopolymers upon heating. The co-crystallization of c-PE and POE at the interface, which would strongly anchor the entangled chains, is supported by shifts in the SAXS, WAXS, and DSC data. Particularly, WAXS shows that stronger c-PE/POE interfaces have a more compact polyethylene unit cell and there is a change in crystal structure from that of either of the pure components. Holistically, this data indicates that the molecular design of a compatibilizer for an immiscible crystalline blend should account for the ability of the copolymer to both entangle and co-crystallize in the interface with the homopolymer domains. This leads to the suggestion that semi-crystalline blocky copolymers can bias the formation of stronger interfaces and are more likely to entangle and co-crystallize making them an effective compatibilizer for amorphous/semicrystalline blends.

Acknowledgements

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CHAPTER III:
CORRELATING CHLORINATED POLYETHYLENE MOLECULAR
STRUCTURE TO COMPATIBILIZATION EFFICIENCY FOR
MIXED POLYMER WASTE

A version of this chapter was submitted to Polymer Chemistry for publication by Bailey Eberle, Christine W. Barker, Dr. Brian Long, and Dr. Mark Dadmun:

Bailey Eberle and Christine Barker are co-first authors on the manuscript for publication. Bailey performed sample preparation, peel tests, DSC measurements, and collected and analyzed NMR spectra. Christine Barker synthesized all Cl₂COE copolymers and performed all reactivity experiments. The document was revised by Dr. Mark Dadmun and Dr. Brian Long.

Abstract

End-of-life plastics pose a significant threat to the environment due to a lack of recycling of these materials into valuable products. This is, in part, due to the limitations of recycling caused by immiscibility between difficult-to-sort plastics. Mixtures of these immiscible polymer components have poor properties due to weak interfaces, driven by phase separation. To address this, compatibilizers are often used to strengthen the interface between phases and stabilize the blend morphology. Previous research by our group has examined the ability of chlorinated polyethylene (c-PE) to compatibilize polyvinyl chloride (PVC) and polyolefin elastomers (POE). However, the specific molecular level processes that improve the interface of these amorphous-semicrystalline materials are not fully understood. To address this knowledge gap, a series of gradient c-PE copolymers were polymerized via Ring Opening Metathesis Polymerization (ROMP) with varying incorporations of dichlorinated cyclooctene and cyclooctene monomers. The

ability of these polymers, with molar masses ranging from ~25-150 kg/mol, to strengthen the PVC/POE interface were compared to that of commercial blocky c-PEs. The results of this study elucidates the role of crystallinity and molecular sequence distribution of the compatibilizer on its efficacy as a compatibilizer. Here we show that the blocky commercial samples improve interfacial adhesion with increased c-PE crystallinity and blockiness whereas the synthesized gradient compatibilizers improve the interfacial adhesion with increased PE-like segment block length. This indicates that while co-crystallization between semicrystalline components is important in compatibilization, entanglement between polymer phases is also necessary. These studies provide insight into the molecular design and crucial molecular-level processes that drive the development of morphology and properties of compatibilized phase-separated amorphous-semicrystalline polymer blends, including those that are most relevant for mixed waste streams in polymer recycling.

Introduction

While polymers have become indispensable in modern society, the absence of effective end-of-life management for these materials poses an environmental concern.^{5, 95,}
¹¹⁰ As of 2022, it was estimated that 9.2 billion metric tons of plastic have been produced since 1950, yet it is estimated that only 9% of the total plastic produced has ever been recycled.^{110, 111} Modern mixed polymer waste streams consist of a variety of polymers that differ in molecular structure and thermomechanical properties, which ideally could be melt-processed as a blend to generate new recycled materials.³ However, most polymers are immiscible with one another due to their low entropy of mixing, resulting in blended

materials with macrophase-separated structure and inferior thermal and mechanical properties. This fact necessitates advanced sorting methods for mechanical recycling that greatly limits recycling for the majority of post-consumer polymeric waste.^{3, 34} To address this challenge, alternative recycling methods are being explored that include chemical recycling of waste polymers back to their monomeric form, as well as the development of compatibilizers for mixed polymer waste blends. Chemical recycling to monomer (or other usable feedstocks) is an attractive route to ensure polymer circularity; however, it encompasses many challenges related to the ease and efficiency by which common polymer classes (e.g. polyolefins) may be depolymerized. Alternatively, compatibilizers may be accessed via known chemistries and have been shown to stabilize immiscible polymer blends by mitigating phase separation and enhancing the final mechanical properties (e.g. tensile strength and elongation) of blended polymer products.^{40, 42, 64, 112-114}

Much of the research in the field of polymer blend compatibilization using synthesized copolymers has focused on amorphous polymer blends, such as those containing polystyrene (PS) and poly(methyl methacrylate) (PMMA).^{42, 43, 79, 115} These studies have established that both compatibilizer structure and (co)monomer sequence play a critical role in reinforcing and stabilizing interfaces within the immiscible polymer blend. These compatibilizers form chain-entanglements with both polymer phases, which promotes adhesion at their interface, provides a mechanism to inhibit droplet coalescence, and lowers the interfacial tension in phase-separated polymer blends.^{42, 64, 79} In contrast, fewer studies have investigated the passive compatibilization of semicrystalline polymers, a class of materials that make up the majority of commercial

polymer waste.¹¹⁶ As examples, Ellison, Bates, and Mohammadi have each shown that multi-block copolymers with blocky segments exceeding the entanglement molar mass of the homopolymer are essential to successfully form “loops” and “tie” together the phases of semicrystalline polymer blends.^{46, 98, 117} However, they also suggest that co-crystallization occurs within these materials – a phenomenon that remains insufficiently understood within the field of compatibilization.^{64, 68, 118}

We are interested in a blend of amorphous polyvinyl chloride (PVC) and semicrystalline polyolefins, which together form an immiscible polymer blend and are both of great concern to polymer recycling. PVC alone is very brittle, has low impact resistance, and is prone to thermal degradation that releases HCl gas.⁶ We hypothesize that its processability can be improved by blending the material with an elastomer, in this case, polyolefin elastomer (POE). Prior research by Dadmun and coworkers has shown that commercially available c-PEs are effective compatibilizers for PVC and POE, wherein blocky c-PE copolymers were found to perform better as compatibilizers than their random copolymer analogues.⁶⁴ In this study, we seek to further these investigations to provide more detailed insight into the impacts that synthesized c-PE compatibilizers with controlled molecular structure (i.e., copolymer sequence distribution, molar mass, chlorine content, and crystallinity) have on the ability of the c-PE copolymer to compatibilize PVC and POE blends. Our research aims to elucidate the molecular level structural characteristics of the compatibilizer that are crucial to effectively compatibilize polymer blends containing mixtures of amorphous and semicrystalline components, including compatibilizer sequence distribution, molar mass, and chemical composition, as

well as how these features influence chain-entanglement and co-crystallization between the compatibilizer and each homopolymer (**Figure 3.1**).

To accomplish this, we measured the interfacial strength of the PVC/POE interfaces that are compatibilized by either synthesized or commercially available c-PE copolymers. The synthesized c-PE compatibilizers were found to be predominantly gradient copolymers in nature due to inherent comonomer reactivity ratio differences, and their efficacy as compatibilizers was compared to those of both random and blocky commercially available c-PE samples. Our results show that the blocky commercial samples improve interfacial adhesion as a function of c-PE crystallinity and blockiness, whereas the synthesized gradient copolymer compatibilizers increase interfacial adhesion as a function of increasing PE-like segment block length. This indicates that while co-crystallization between semicrystalline components is important in compatibilization, entanglement between polymer phases is also necessary and may be notably impacted by the comonomer sequence distribution along the compatibilizer backbone.

Experimental

Materials and Methods

Cyclooctene (COE) and ethyl vinyl ether (stabilized with KOH) were purchased from TCI America, dried, and degassed prior to use. 1,5-Cyclooctadiene (COD), lithium chloride, copper(II) chloride, (1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro (phenylmethylene)-(tricyclohexylphosphine)ruthenium (**G2**), 3-bromopyridine, p-toluenesulfonyl hydrazide (TSH), xylenes and acetonitrile were purchased from Thermo Fisher Scientific, Inc. and used as received. 1,1,2,2-

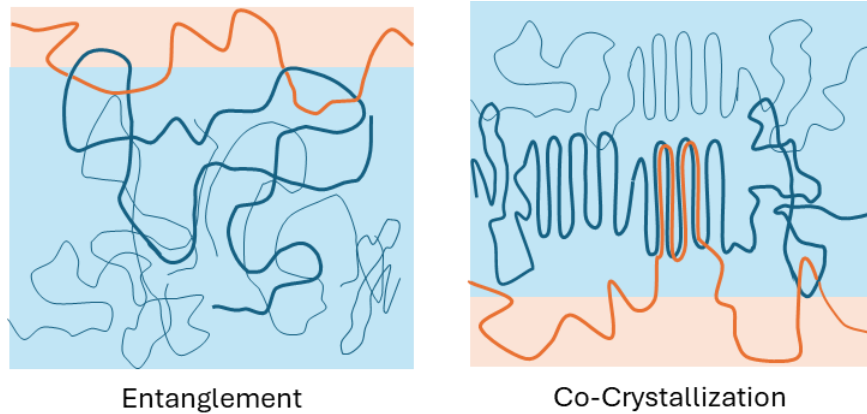
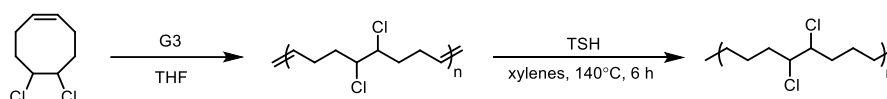


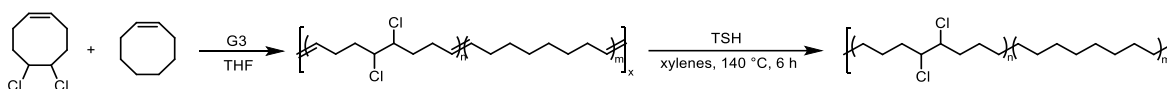
Figure 3.1. Mechanisms of entanglement and co-crystallization between polymer chains.

tetrachloroethane-d₂ (TCE-d₂) was purchased from Cambridge Isotope Laboratories. Tetrahydrofuran (THF) was purchased from Thermo Fisher Scientific, Inc., dried, and degassed prior to use. Polyvinyl chloride (PVC) (M_w: 233 kDa), was purchased from Sigma Aldrich. Methyl tin mercaptide (Mark 1900) was provided by Galata Chemicals. Engage POE 7270 (DOW Chemical) was purchased from Avient Corporation. Commercially available c-PEs (401AY, 404B, 402B, 352GB, 303BS, 202KB and 252B) were provided as a gift from Showa Denko (Japan). The dichlorocyclooctene/cyclooctene ring opening metathesis polymerization (ROMP) copolymerizations were performed by Christine W. Barker in Dr. Brian Long's lab at UTK using **Schemes 3.1** and **3.2**.

Scheme 3.1. Synthesis of chlorinated polyethylene homopolymers via ROMP.



Scheme 3.2. Synthesis of chlorinated polyethylene copolymers via ROMP.



Formation of Compatibilized Trilayer Films.

Polyvinyl chloride (Sigma Aldrich; M_w: 233 kg/mol) was thermally stabilized with 4 phr (parts per hundredth rubber) of methyl tin mercaptide (Mark 1900).^{106, 107} The polymer powder (20 g) was then added to a preheated mold that was placed in a Carver Laboratory Press Model C equilibrated at 200 °C. The sample was held in the melt press for 3 min without pressure, then 1 metric ton of pressure was applied for 2 min. The PVC

was cooled below its T_g (~ 85 °C) in the mold to avoid deformation. Engage POE 7270 was melted into a rectangular mold with dimensions 10 mm x 65 mm x 2.3 mm at 200 °C for 5 min.⁶⁴

Trilayer samples were formed using a modified literature procedure, as follows.⁶⁴ Each compatibilizer (2.5 wt%) was dissolved in toluene at 85 °C to make a homogeneous solution (2 g of polymer solution).¹⁰⁸ The c-PE solution was spin-coated onto the prepared PVC sheet at 2500 rpm for 20 s and the toluene was allowed to evaporate overnight to produce a ~ 150 nm thick coating. The coated PVC sheet was then cut into strips with dimensions of 10 mm x 65 mm x 2.3 mm using a Dremel 4300 Series Rotary Tool. In a mold, POE strips of the same dimensions were stacked on top of the coated PVC to form a trilayer (PVC/c-PE/POE) sample stack. The mold was sandwiched by two 10 lb. iron metal plates and placed in the melt press at 200 °C for 15 min with no additional applied pressure. The mold was then removed from the melt press and cooled on the hot metal plates at a rate of 9 °C/min until the temperature of the sample fell below the T_m of POE (~ 60 °C). The samples were then removed from the mold and cooled to room temperature.

Characterization of Materials.

High-temperature ^1H NMR spectroscopy was performed using a Bruker AVANCE NEO 500 MHz spectrometer in *d*-chloroform to determine chlorine content, which is reported as number of chlorines per 100 carbons or mol% Cl. High-temperature, quantitative ^{13}C NMR spectroscopy was obtained using either a Bruker AVANCE NEO 500 MHz or a Varian 500 MHz NMR spectrometer in 1,1,2,2-tetrachloroethane- d_2

(Cambridge Isotope Labs). These spectra were analyzed to quantify the percent blockiness of the commercially available polymers.⁵¹ Heat of fusion is used as a representation of the extent of crystallinity, as there is no known theoretical 100% crystalline value to compare with. The heat of fusion and melting temperatures of each polymer were determined using a TA Instruments Q-2000 differential scanning calorimeter (DSC) at a 10 °C/min ramp rate. Only the second heating cycle was collected and analyzed to ensure previous thermal history is removed. Additional DSC details are found in Appendix B. Polymer molar mass and dispersity were measured using either a Malvern 350A HT-GPC system operating at 150 °C in 1,2,4-trichlorobenzene equipped with triple detection (used for all commercial c-PEs) or a Tosch EcoSEC GPC system equipped with RI detection using tetrahydrofuran as the eluent and reported relative to polystyrene standards (used for all ROMP polymers before reduction of alkenes).¹¹⁹ It should be noted that the molar masses and dispersities of the synthesized c-PEs samples were only obtained of their olefin containing precursors due to their reduced forms being isorefractive with the 1,2,4-trichlorobenzene eluent used in the HT-GPC system. It is assumed that the molar masses of these synthesized polymers remained constant following diimide reduction as has been shown in prior literature reports.^{120, 121} The interfacial adhesion strength (G_a) of all compatibilizers were analyzed via a combination T+U peel testing as seen in **Figure 3.2** using an Instron Model 5965 Universal Tester (5 kN) with a crosshead rate of 10 mm/min.⁶⁴ Interfacial adhesion (G_a) is calculated by dividing the force required to peel the sample by the width of the sample.

Results and Discussion

Characterization of c-PE Homopolymers and Copolymers.

For each homopolymer or copolymer series, molar masses ranging from 50-150 kg/mol and chlorine contents ranging from 5-25 mol% Cl were synthesized to provide insight into how copolymer chain length, sequence distribution, and composition impact their ability to compatibilize PVC/POE blends. Each copolymer was characterized via ^1H NMR spectroscopy, gel permeation chromatography (GPC), and differential scanning calorimetry (DSC) to assess their comonomer incorporation ratios, chlorine contents, molar masses, and heats of fusion (correlated to percent crystallinity), respectively (representative examples are shown in **Table 3.1** and full list of all samples is provided in Table S3.3). Synthesized compatibilizers are labeled as S100, S75, S50, and S25, respectively, wherein the “S” indicates a statistical copolymer, the number is indicative of the mole percent Cl_2COE in the $\text{Cl}_2\text{COE}:\text{COE}$ comonomer feed ratio. Lastly, because each homopolymer and copolymer was synthesized in three molar mass regimes (i.e. $\sim 25\text{-}75$, $\sim 75\text{-}125$, and $\sim 125\text{-}175$ kg/mol), each sample is also denoted with an “L,” “M,” or “H,” respectively, indicating a sample of low, medium or high molar mass. For example, sample S50-L is a statistical copolymer made with a 50:50 $\text{Cl}_2\text{COE}:\text{COE}$ comonomer feed ratio that has a molar mass in the $\sim 25\text{-}75$ kg/mol regime (**Table 3.1**, entry 7).

Determination of Copolymer Sequence Distribution.

Though the copolymers described in **Table 3.1** each achieved a final comonomer

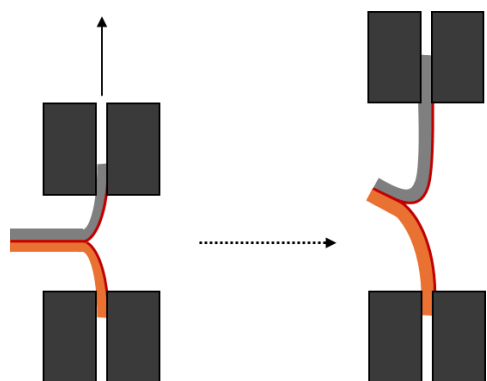


Figure 3.2. Combination T+U peel test with the flexible polymer pulled from the more rigid polymer.

Table 3.1. Representative examples of c-PE homopolymers and copolymers synthesized via ROMP.^a

entry	sample	monomer feed (Cl ₂ COE:COE)	monomer incorp. (Cl ₂ COE:COE) _b	M _n (kg/mol) ^c	Đ ^c	mol% Cl ^b
1	S100-L	100:0	100:0	69	1.8	22.2
2	S100-M	100:0	100:0	100	1.8	23.5
3	S100-H	100:0	100:0	140	2.1	24.1
4	S75-L	75:25	73:27	79	2.1	17.9
5	S75-M	75:25	77:23	102	2.1	18.5
6	S75-H	75:25	76:24	128	2.1	18.5
7	S50-L	50:50	54:46	57	2.9	12.5
8	S50-M	50:50	48:52	91	2.3	11.6
9	S50-H	50:50	48:52	137	2.3	11.7
10	S25-L	25:75	25:75	66	2.4	6.0
11	S25-M	25:75	25:75	100	2.2	6.0
12	S25-H	25:75	24:76	149	2.4	5.7

^a. A full list of polymer samples and replicates, as well as their characterization, can be found in Table S3.1. General homopolymerization conditions: total monomer = 2.79 mmol, catalyst = 0.01 mmol, 1.4 mL THF, T_{rxn} = r.t., and t = 4 min. General copolymerization conditions: total monomer = 3.36 mmol, catalyst = 0.01 mmol, 1.68 mL THF, T_{rxn} = r.t., and t = 4 min. All polymers were then reduced using tosyl hydrazide (3 eq) in xylenes (81 mmol) for 6 h at 140 °C.

^b Determined via ¹H NMR spectroscopy. ^c M_n and Đ were measured using GPC equipped with RI detection and THF as the eluent.

incorporation ratio nearly identical to that of the feed, we observed that the homopolymerization of COE proceeded more quickly than analogous polymerizations of Cl₂COE:COE (**Figure 3.3**). Because of this, we suspected that the comonomer sequence distribution within the S75, S50, and S25 c-PEs copolymer series may not be truly random but may instead be statistical or gradient in nature. To assess this, we estimated the reactivity ratios of each comonomers using both the Beckingham-Sanoja-Lynd (BSL) and Mayo-Lewis (ML) models (see Appendix B for additional details), where the model parameters were refined using the measured conversion of each comonomer within the first minute of the reaction. Only the first minute was observed because COE is completely consumed in one minute and conversion at longer times deviated from the model after this monomer consumption. The reactivity ratios were found to be 0.26 ± 0.01 for Cl₂COE and 3.75 ± 0.13 for COE using the BSL method, and 0.30 ± 0.04 for Cl₂COE and 3.99 ± 0.23 for COE using the ML model.¹²²⁻¹²⁴ The BSL model is a non-terminal model that is particularly useful for distinguishing random and gradient copolymers, whereas the Mayo Lewis model is terminal model. The reactivity ratios determined from both models agree closely and indicate that the c-PE copolymers synthesized via ROMP are predominantly gradient in nature with COE being more likely to homopropagate than Cl₂COE which tends to cross-propagate with COE preferentially before the conversion of both monomers converges late in the reaction. This indicates that there is a higher percentage of non-chlorinated COE repeat units at the start of the polymer chain growth, whereas the polymer chain is enriched in chlorinated Cl₂COE repeat units at the end of the polymerization, as opposed to a random distribution which was initially targeted.

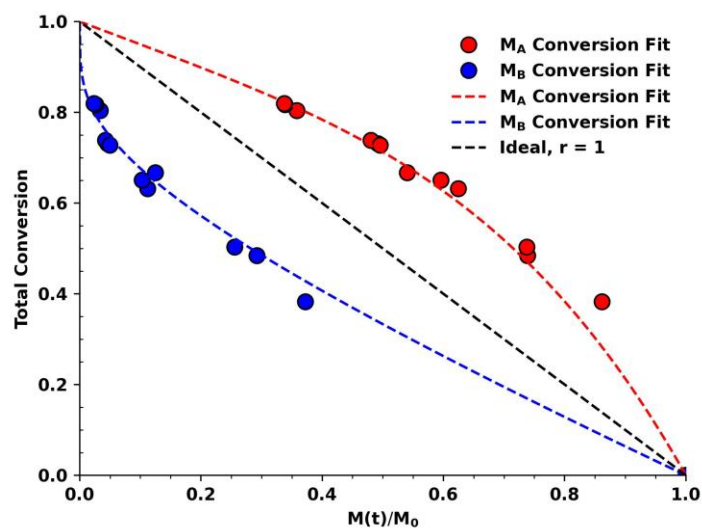


Figure 3.3. Monitoring comonomer conversion of Cl_2COE (M_A , red) and COE (M_B , blue) using the Beckingham-Sanoja-Lynd (BSL) model to determine reactivity ratios. The black dotted line is representative of a true random copolymerization.

These partially chlorinated c-PEs present a unique opportunity to provide additional insight into the importance of monomer sequence distribution in a copolymer on the effectiveness of the copolymer in blend compatibilization. For example, gradient copolymers have been shown to compatibilize mixed polymer systems better than their random copolymer analogues, but not as well as blocky or block copolymers.^{44, 64} Though the impact of a gradient type sequence distribution on compatibilization has been studied for amorphous polymer blends, the impact of the gradient copolymer sequence distribution on the compatibilization of blends containing both amorphous and semicrystalline components has not been as extensively studied.⁴⁴

Ability of Synthesized Copolymers to Strengthen the POE/PVC Interface

Previous studies have shown that gradient copolymers more effectively increase the interfacial adhesion between two dissimilar polymers than a random copolymer.⁴⁴ This is believed to be due to the presence of longer sequences of each comonomer at opposite ends of gradient copolymer, which can effectively entangle with both phases, which in turn mimics some aspects of the behavior of a block copolymer as a compatibilizer. These studies provide additional information on the performance of gradient polymers in amorphous/semicrystalline blends. The variation in the interfacial adhesion strength (G_a) of the compatibilized PVC/c-PE/POE interface was then correlated to the molecular characteristics of the c-PE compatibilizer, including molar mass, copolymer composition, and crystallinity (semi-quantitatively catalogued with the

experimentally determined heat of fusion), as well as referenced to an uncompatibilized PVC/POE interface as a control.

First, to provide insight into the role of c-PE compatibilizer crystallinity on the compatibilization of the PVC/POE interface, the interfacial adhesion strength is plotted as a function of compatibilizer heat of fusion (J/g), which is used here as a relative proxy for c-PE crystallinity, in **Figure 3.4**. These results show that compatibilizer crystallinity increases with molar percentage of COE repeat units along the copolymer, and that interfaces with c-PE compatibilizers with increased COE loading and crystallinity tend to exhibit increased interfacial adhesion, shown in **Figure 3.5**. These results suggest that compatibilizers having longer PE-like runs along their backbones exhibit slightly enhanced interfacial adhesion strength at the PVC/POE blend interface. Previous research by our group supports that this is likely attributable to a combination of compatibilizer/POE chain entanglement and co-crystallization.

To evaluate the role of copolymer chain length on compatibilized interfacial adhesion strength, each compatibilizer was synthesized in three molar mass regimes (i.e. ~25-75, ~75-125, and ~125-175 kg/mol) for each copolymer series with varied chlorinated comonomer content, where **Figure 3.6** plots the interfacial adhesion of the compatibilized interface as a function of copolymer chain length for each c-PE composition. **Figure 3.6a** plots the strength of the PVC-POE interface for the interfaces compatibilized with the Cl₂COE homopolymers (S100 series), where these results show virtually no change in interfacial adhesion with polymer chain length for these compatibilized interfaces. A similar trend was found for the S75 series of copolymer compatibilizers as shown in **Figure 3.6b** where virtually no change in interfacial

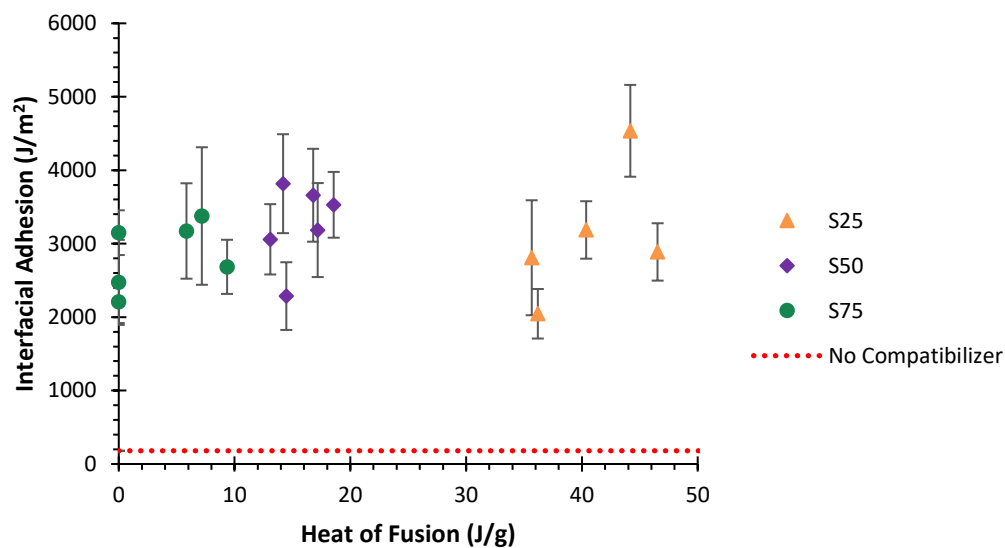


Figure 3.4. Interfacial adhesion strength of the compatibilized PVC/c-PE/POE trilayer interface as a function of the heat of fusion for the S25, S50, and S75 series of compatibilizers. Error bars represent one standard deviation from the average.

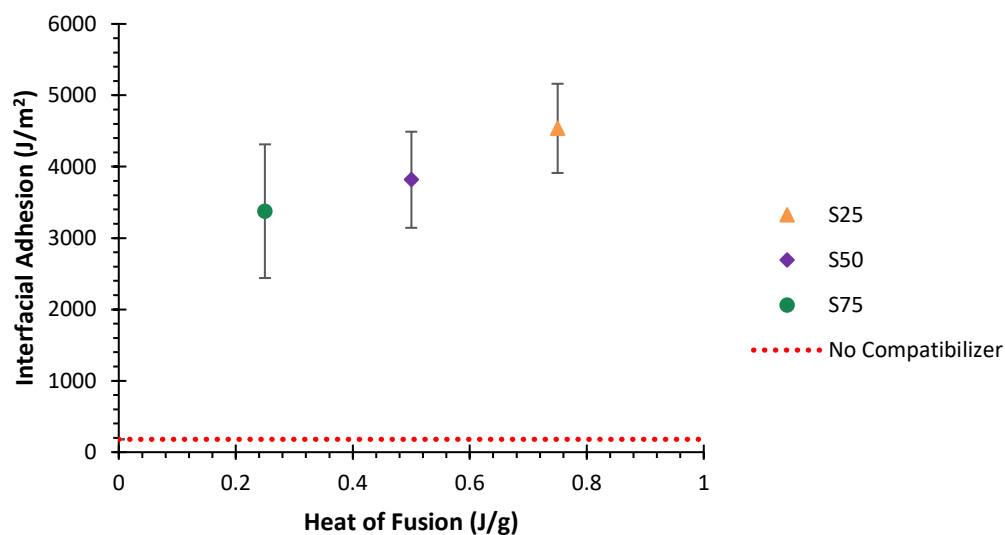


Figure 3.5. Maximum trilayer interfacial adhesion of the compatibilized PVC-POE interface for each of the COE compositions of the synthesized Cl2COE-r-COE copolymers. Error bars represent one standard deviation from the average.

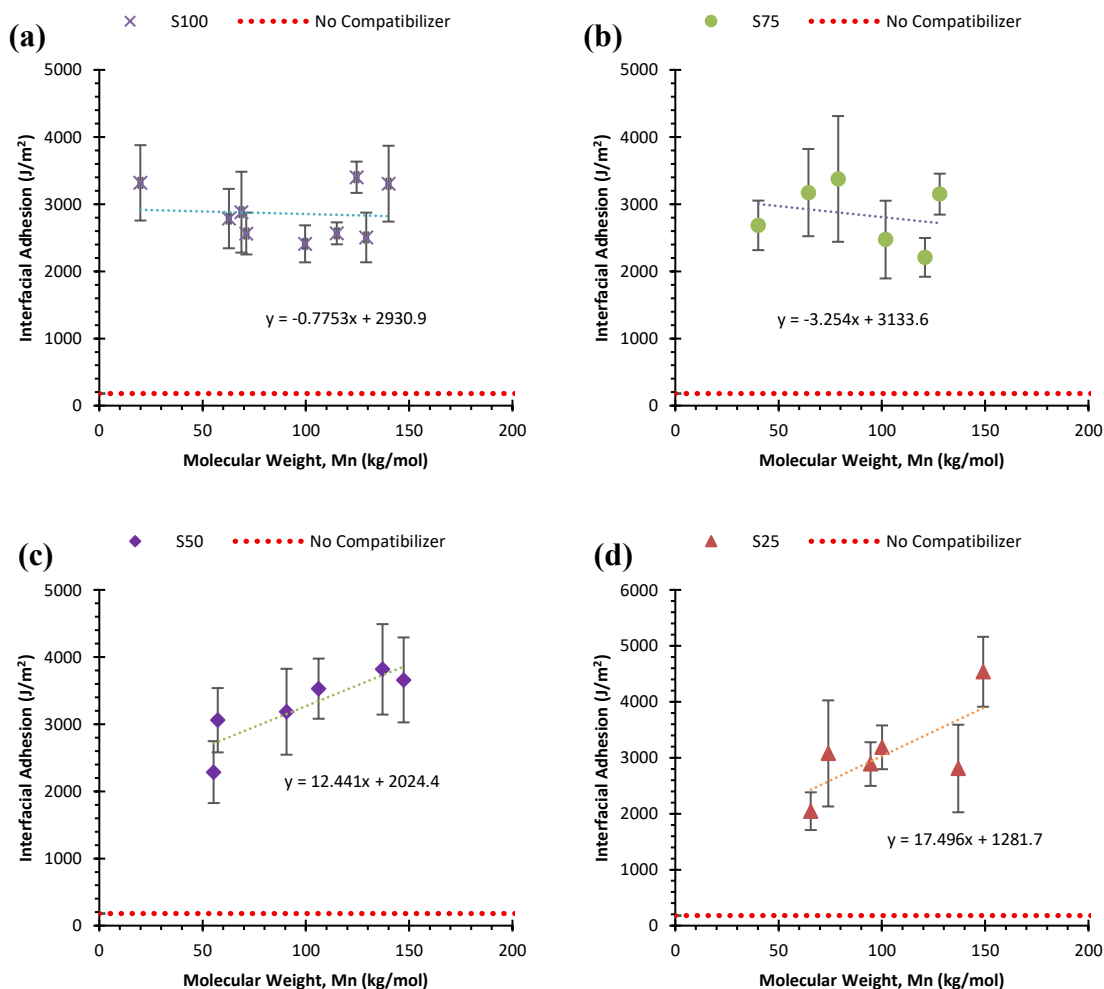


Figure 3.6. Average interfacial adhesion plotted against molecular weight for homopolymer of Cl₂COE and synthesized c-PE copolymers of (a) homopolymers of Cl₂COE (labeled as S100), (b) copolymers of Cl₂COE and COE in a 75:25 ratio (labeled as S75), (c) copolymers of Cl₂COE and COE in a 50:50 ratio (labeled as S50), (d) copolymers of Cl₂COE and COE in a 25:75 ratio (labeled as S25). Error bars represent one standard deviation from the average.

adhesion strength is observed with increased compatibilizer chain length. These c-PE copolymers have the least amount of ethylene like COE repeat units, which translates to longer chlorinated segments. This sequence distribution may inhibit entanglement of the compatibilizer with the POE phase and obstructing possible co-crystallization.^{46, 125, 126} In contrast, **Figures 3.6c-d** show the change in the strength of the compatibilized PVC/POE interface the S50 and S25 series of copolymer compatibilizers, which have 50 and 75 mol percent PE-like repeat units (i.e. arising from COE incorporation), respectively. In these systems, the adhesion strength of the compatibilized PVC/POE interface increases as a function of compatibilizer chain length. This shows that increasing the chain length of compatibilizers having 50 mol% or more PE-like repeat units along the copolymer backbone increases compatibilization of the PVC/POE interface.⁶⁶ This effect, coupled with the slight correlation of interfacial adhesion with compatibilizer crystallinity, indicates that the PE-like components play an important role in strengthening the interface, where these copolymers may both entangle and co-crystallize with the POE phase and promote compatibilization. This interpretation is also consistent with the gradient sequence distribution of these copolymer compatibilizers, where this sequence distribution contains longer stretches of PE-like units at one end of the polymer chain.

Comparing the Compatibilization Effectiveness of Synthesized Copolymers and Commercial Materials.

The ability of our synthesized gradient copolymers to compatibilize the POE/PVC interface was also compared to that of both random and blocky commercial c-PE samples. To accomplish this, the ability of a series of commercially sourced c-PEs to

strengthen the POE/PVC interface under identical conditions was also studied. These commercially sourced samples were produced either via suspension or solution-state chlorination of polyethylene using chlorine gas. Samples that are chlorinated using solution-state methods allow chlorination to occur randomly along the polymer chain, resulting in randomly chlorinated polyethylene. In contrast, a suspension method facilitates chlorination only at amorphous accessible reaction sites along the PE chain, ultimately leading to polymer chains in which multiple chlorines may be installed on neighboring repeat units and resulting in materials that are “blockier” in nature. These compatibilizers are named based on their sequence distribution, chlorine content, and heat of fusion. For example, 23/9B is a blocky copolymer with 23 mol% Cl, and a heat of fusion of 9 J/g. Quantitative ^{13}C NMR spectroscopy was used to quantify the randomness or blockiness of these commercial c-PEs. This analysis compares the monomer connectivity to that of a statistically random chlorinated polyethylene model as previously described in the literature. This analysis provides a measure of the blockiness of each c-PE (additional details of this analysis are provided in Appendix B).^{51, 66}

Quantitative ^{13}C NMR spectroscopy of the commercially sourced c-PE materials confirmed that one copolymer is randomly chlorinated (23/R) and six samples are blocky. Sample 23/R, which is provided by the supplier as a random copolymer, indeed fits the random chlorination statistical model with only a 2.25% difference in the expected ^{13}C NMR spectroscopic integrations for a truly random copolymer. Analysis of the remaining samples all revealed some degree of blockiness, with differences from an ideal random sequence distribution ranging from a 6.9% difference to a 98.2% difference. For example, the compatibilizer with the highest percent difference (19/43B) is significantly blocky in

structure. In the same manner, and for ease of comparison, quantitative ^{13}C NMR spectroscopy was also used to analyze the blockiness of the synthesized gradient c-PEs within the three molar mass ranges (~ 50 , ~ 100 , and ~ 150 kg/mol). These analyses revealed that all synthesized gradient c-PEs have less than 20% relative blockiness, which is lower than half of the suspension chlorinated commercial samples, but notably higher than the random commercial samples 23/R and 14/19B, 23/27B, 23/9B.

Figure 3.7 plots the relative blockiness and interfacial adhesion of the commercial samples, showing that the interfacial adhesion of samples increases with the blockier copolymers, reaching an average interfacial adhesion energy of 5600 J/m^2 .^{42, 64} In contrast, a comparable trend is not observed for the synthesized c-PEs, which may be due to their predominantly gradient sequence distribution of the copolymer. We hypothesize that the gradient sequence distribution of the synthesized c-PEs will allow the copolymer to entangle with both the PVC and POE polymer phases more effectively than the commercial copolymers as they have longer PVC-and PE- like segments along the polymer chain.

Indeed, previous research has shown that chain entanglement between compatibilizers and homopolymers is optimized when blocks exist that are longer than the critical molar mass (M_c) of the specific polymer (PE: ~ 2.5 kg/mol; PVC: ~ 10.8 kg/mol), as a “loop” can be formed in the homopolymer phase by these blocks.^{65, 127, 128} The gradient sequence distribution provides a molecular structure where these longer stretches of PVC- or PE-like segments exist and increases the likelihood of forming entanglements between the homopolymer and compatibilizer. These analyses also show that the synthesized c-PEs do not strengthen the PVC/POE interface as well as the

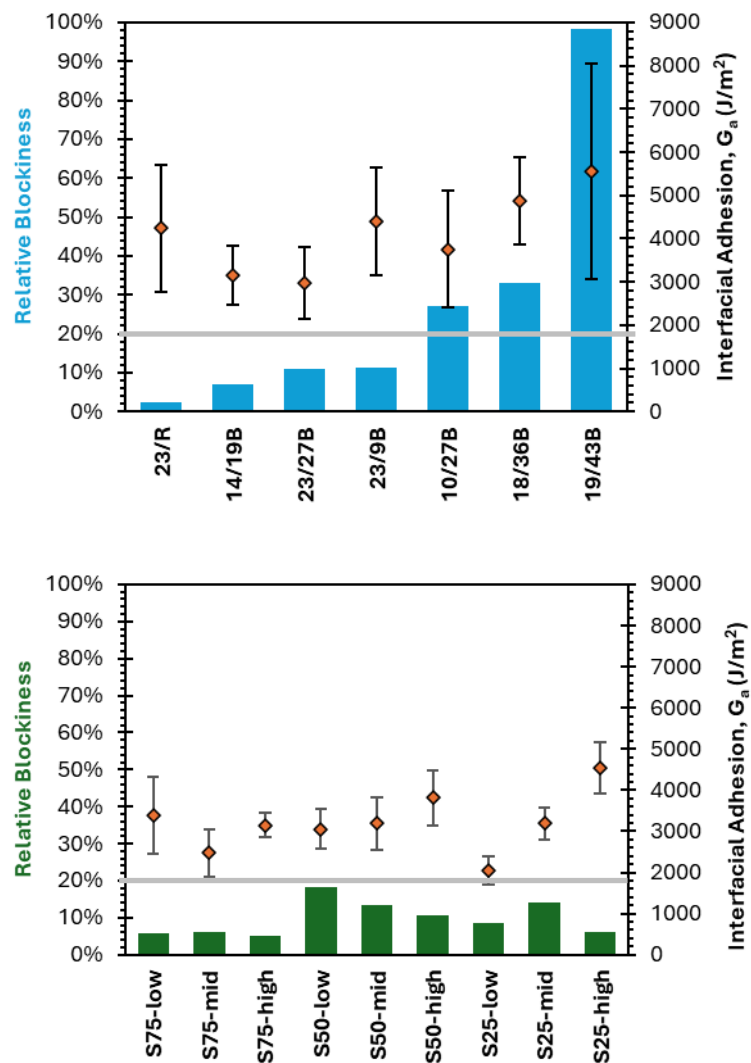


Figure 3.7. Plots reporting the relative blockiness, as determined by quantitative ^{13}C NMR, and interfacial adhesion of commercial c-PEs (top) and synthesized c-PEs (bottom). The gray line at 20% represents the maximum relative blockiness observed for the synthesized samples. Error bars represent one standard deviation from the average.

blockier commercial materials (18/36B and 19/43B), where we attribute this to formation of fewer and shorter loops formed at PVC/POE interface by the gradient copolymers. The formation of these loops for random, gradient and blocky compatibilizers is illustrated in **Figure 3.8** to underscore the importance of molecular design of the compatibilizer.^{42, 44, 99, 129} Such loops are believed to inhibit chain pullout for well-defined block copolymers with block segments exceeding the M_c for each polymer phase.^{44, 98} To further understand how polymer sequence distribution of the compatibilizer may influence the strengthening of the PVC/POE interface, the interfacial adhesion as a function of c-PE compatibilizer crystallinity and blockiness. **First** inspection of Figure 3.9 shows that the blockiness of the commercial c-PEs can be directly correlated to its crystallinity, which is likely due to improvements in chain ordering that occurs within a copolymer with a more block-like sequence. Essentially, the blockier samples have longer stretches of the crystallizable component that is not interrupted by chlorinated carbon segments that will disrupt polymer crystallization from occurring.^{130, 131} The synthesized gradient c-PE materials, however, do not show a correlation between interfacial adhesion and heat of fusion, further suggesting that despite their relative crystallinity observed, that c-PEs with gradient structures may decrease the potential of these materials to co-crystallize with the POE phase of the mixed polymer blend.¹³²

To further probe this, the interfacial adhesion of the compatibilized PVC/POE interfaces are plotted as a function of the heat of fusion of each commercially sourced c-PE (**Figure 3.10**).¹¹⁹ The commercial compatibilizer with the highest average interfacial adhesion commercial compatibilizer in **Figure 3.10** has the highest heat of fusion and is more likely to co-crystallize with POE chains. We suspect this is due to the crystalline

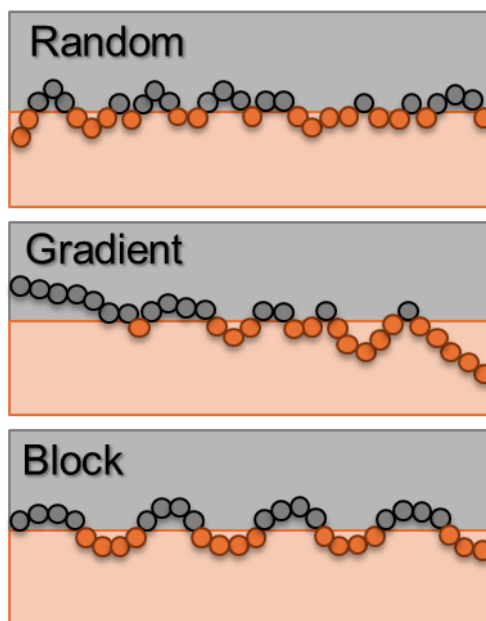


Figure 3.8. Depiction of random, gradient, and block copolymers at a polymer blend interface.

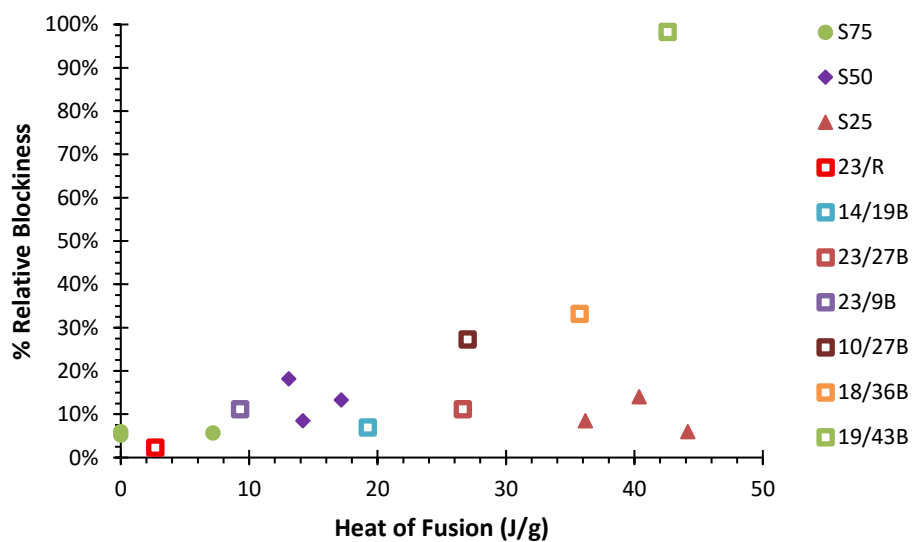


Figure 3.9. Polymer percent blockiness vs. heat of fusion of synthesized copolymers (solid dots) and commercial c-PEs (open squares).

PE-like segments of the compatibilizer co-crystallizing with the POE, which becomes a crucial mechanism in increasing interfacial adhesion of the compatibilized PVC/POE interface. These results further support that interactions between the PE-like segments of the c-PE and the POE are important for strengthening the interface in this system. Moreover, previously published research by Dadmun and coworkers found that commercial c-PE compatibilizers with increased crystallinity exhibit evidence of co-crystallization with the POE, as indicated by wide-angle x-ray scattering (WAXS) and differential scanning calorimetry (DSC) studies.⁶⁶

Additionally, the impact of compatibilizer chain length on the interfacial adhesion was examined for each commercial sample, as shown in **Figure 3.11**. This data shows that the impact of compatibilizer chain length on the interfacial strength in the commercial c-PEs differs from that which was observed for the synthesized gradient copolymers, as shown in **Figure 3.6**. Inspection of **Figure 3.11** reveals that the strength of the compatibilized interfaces does not vary with compatibilizer chain length for the commercial c-PEs. If only chain entanglements determined the strength of the interface, the c-PE with the highest chain length would form the most entanglements between the phases and have the highest interfacial adhesion. However, the commercial samples 23/R and 23/9B have the two highest chain lengths among the commercial materials, but exhibit lower interfacial adhesion. We interpret this to be due to their lower relative blockiness and crystallinity compared to the blockier samples 18/36B and 19/43B, which have lower chain lengths but the highest interfacial adhesion.⁶⁴ These considerations suggest that the compatibilizer blockiness is dominant in determining the effectiveness of the copolymer in its ability to increasing interfacial adhesion due to the effects of co-

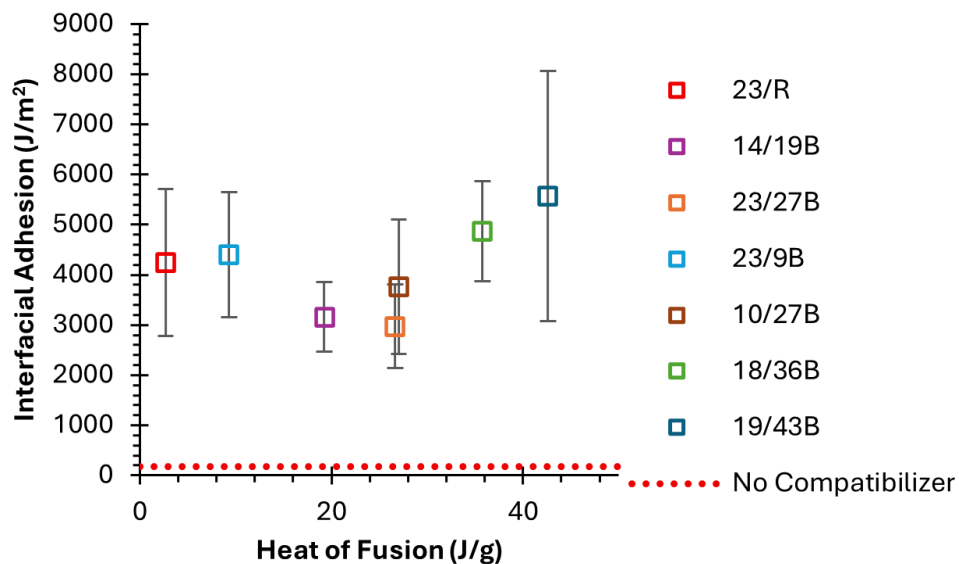


Figure 3.10. Average interfacial adhesion of the compatibilized PVC/POE interface as a function of the heat of fusion of commercial c-PEs. Error bars represent one standard deviation from the average.

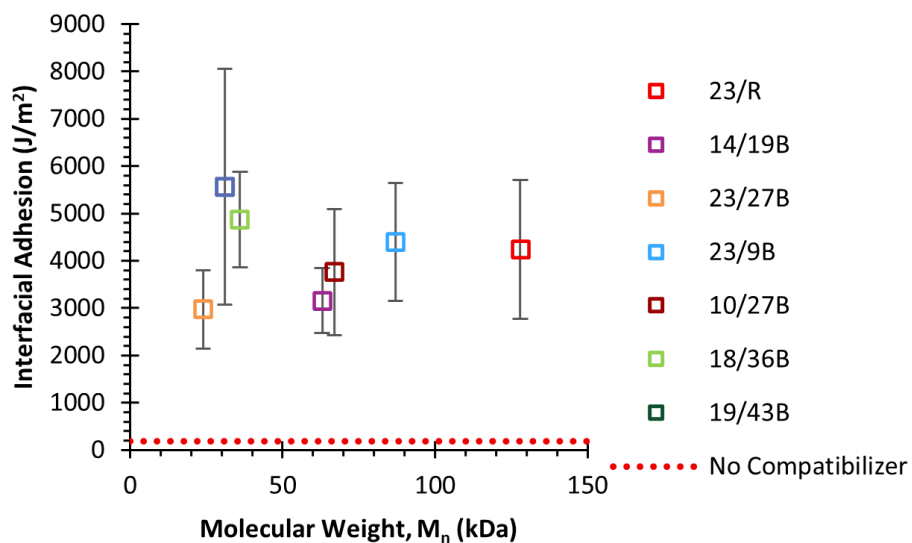


Figure 3.11. Average interfacial adhesion vs. molecular weight of commercial c-PEs. Error bars represent one standard deviation from the average.

crystallization; however, copolymer chain length still contributes to in the compatibilization of PVC/POE blends for less blocky materials that are rich in PE-like segments.

The results of the commercial c-PE samples indicate that the increase in interfacial adhesion is mainly influenced by increased crystallinity and blockiness of the compatibilizer, allowing for co-crystallization to occur, while the results of the synthesized gradient compatibilizers show improvement in interfacial adhesion that is driven by optimized entanglement between the homopolymers and the copolymer, engendered by semicrystalline PE-like blocky segments. The variation in the dependence of the interfacial adhesion on compatibilizer crystallinity between the synthesized samples and the commercial c-PE is presumably due to their differences in sequence distribution, as the commercial samples are blocky, whereas the synthesized copolymers are predominantly gradient. Simplistically, the gradient structures of the synthesized c-PEs are more akin to di-block copolymers, whereas the commercial blocky compatibilizers are comparable to multi-block copolymers.^{44, 45} There is literature evidence that multi-block copolymers are better compatibilizers than di-blocks, as these polymer chains can cross the interface between phases multiple times, optimizing entanglement.^{40, 43, 46, 114} We hypothesize that the compatibilizer and homopolymer may co-crystallize where the blocky segments of the copolymer extend into the homopolymer, wherein more blocky segments results in more possible sites for co-crystallization anchors to occur.¹¹⁴ The lack of a significant trend between interfacial adhesion and crystallinity for the synthesized gradient compatibilizers, compared to the commercially

sourced blocky samples, indicates that while co-crystallization may aid compatibilization, entanglement drives adhesion at the interface.¹³³

Conclusion

Characterization of commercial and synthesized chlorinated polyethylene (c-PE) compatibilizers through GPC, NMR, and DSC provides the foundation for an in-depth analysis of the specific molecular-level processes that control the ability of the c-PEs to improve the interfacial adhesion at an amorphous/semicrystalline interface. The synthesized c-PEs, polymerized via ROMP and with molecular weights ranging from 25-150 kg/mol, resulted in a predominantly gradient sequence distribution as determined by reactivity ratios and statistical relative blockiness analysis. The results of this study show that the interfacial adhesion of a compatibilized poly(vinyl chloride) (PVC)/polyolefin elastomer (POE) interface increased with the PE-like content in the gradient copolymer compatibilizers. This is interpreted to indicate that this dependence is due to longer PE like chain length blocks in the gradient copolymers, which can readily entangle and potentially co-crystallize with the semicrystalline POE phase.

Alternatively, the commercially available blocky c-PE compatibilizers, ranging in blockiness from 6.9-98.2%, exhibited improved interfacial adhesion with an increase in both blockiness and crystallinity of the c-PE, which is consistent with the presence of both entanglement and co-crystallization between the compatibilizers and the homopolymers. These multiblock-like structures allow for more “loops” to be formed at the interface between the compatibilizer and the homopolymers relative to those that can form with gradient copolymers. This explains why the commercial blocky

compatibilizers slightly outperform the synthesized gradient counterparts in strengthening the PVC/POE interface. For instance, the maximum interfacial adhesion of the PVC/POE interface with the commercial blocky copolymers is 5600 J/m² while the maximum interfacial adhesion of the PVC/POE interface compatibilized with the gradient copolymers is only 4500 J/m².

Overall, this research offers insight into how compatibilizer sequence distribution, crystallinity, and chain length impact the ability of that copolymer to compatibilize phase-separated crystalline/amorphous polymer blends, particularly those that are applicable to mixed polymer waste streams. This study offers evidence that the molecular design of a compatibilizer for a semi-crystalline/amorphous interface may bias the formation of entanglements and offer pathways for co-crystallization between the compatibilizer and the homopolymer phases. Therein, a copolymer with a more blocky sequence distribution is more effective in catalyzing these molecular level processes than one with a gradient sequence distribution.

Acknowledgement

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CHAPTER IV:
IMPACT OF COMMERCIAL POLYOLEFIN ARCHITECTURE
AND COMPOSITION ON ITS ABILITY TO COMPATIBILIZE
HIGH-DENSITY POLYETHYLENE/ISOTACTIC
POLYPROPYLENE BLENDS

A version of this chapter is being prepared to be submitted for publication.

Abstract

Recycling of polyolefins is a growing concern as these materials make up approximately 50% of plastic waste. This research focuses on elucidating the relationship between the sequence distribution of commercially available ethylene-propylene random copolymers and an ethylene/1-olefin copolymer and their effectiveness as a compatibilizer of high-density polyethylene (HDPE)/isotactic polypropylene (iPP) blends. The compatibilization of both HDPE-rich and iPP-rich blends were examined to determine the impact of matrix composition on the ability of these compatibilizers to enhance mechanical properties of the phase separated blend. Overall, the results show that increasing the concentration of the semicrystalline ethylene content and ethylene-ethylene-ethylene triad components in the copolymer compatibilizer improved the tensile toughness of both blends. The toughness of the HDPE-rich blend was improved by a maximum of a factor of 20, while the toughness of the iPP-rich blend doubled in the presence of 5 wt% compatibilizer loading. These findings indicate that the compatibilization of these blends with random copolymers is entanglement-dependent; however, the presence of semicrystalline segments can greatly increase the compatibilizer efficiency. Additionally, ethylene-1-olefin copolymers appear to improve the toughness of the compatibilized blends the most in the HDPE-rich blends, whereas the ethylene-propylene rubbers are the most effective compatibilizer in the iPP-rich blends.

Introduction

The accumulation of plastics in the world poses a significant problem as landfills continue to fill up and plastic production shows no signs of slowing down.^{3, 95, 111} In 2017, the global annual production of plastics was estimated to be 438 Mt and is expected to reach 1.1 billion metric tons by 2050.¹¹¹ This is in large part due to plastic being used once and then discarded, which became prevalent as plastics are cheap to produce and market. Polyolefins are among the most common single-use plastics, which include plastic bags, straws, and plastic wrap. Mechanical recycling is one process that can bring recycled waste streams back into the commercial market, but products that emerge from the mechanical recycling of polyolefins create products that often have reduced mechanical properties and are not economically competitive with the virgin material.^{3, 111}

One of the reasons that mechanically recycled materials have compromised mechanical properties is due to the inherent immiscibility between different polymers, as illustrated in **Figure 4.1**.³ Even within the category of polyolefins, high-density polyethylene, low-density polyethylene, and polypropylene have been shown to be immiscible – even though they have very similar molecular structures. The similarity of molecular structure also makes these polymers difficult to sort as they have very similar densities and near-infrared (NIR) spectroscopy curves, which are primary techniques that recycling plants use to purify waste streams.^{3, 134-136} This is concerning as polyolefins make up ~50% of the waste streams.^{111, 137} They are the main component in prescription pill bottles, plastic bags, food storage containers, and much more.¹¹¹ Polyolefins are chemically inert, have good barrier properties, and have tunable mechanical properties

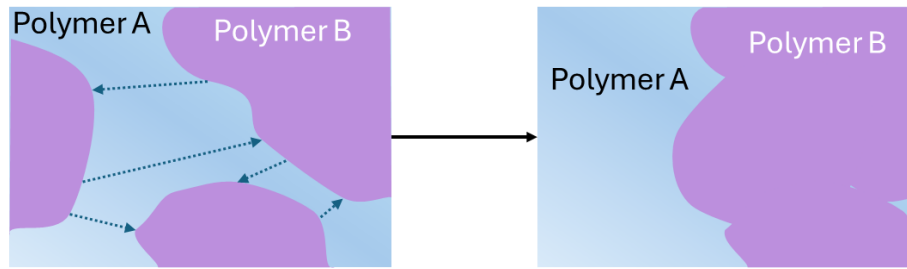


Figure 4.1. Illustration of phase separation in an immiscible polymer blend.

based on the molecular structure of the products, including its molecular weight, tacticity, branching, and crystallinity, among others, making them a very desirable material. On the other hand, these variations in molecular structure result in the formation of immiscible systems when different grades are blended and lead to difficulty producing valuable and comparable products from mechanical recycling.

Most polymer pairs are immiscible due to a low/negligible entropy of mixing (ΔS_m) caused by their high molecular weights.¹³⁸ This means that for a polymer blend to be miscible, or to have mixing be favored, the enthalpy of mixing (ΔH_m) must be negative or very slightly positive in order for the Gibbs free energy of mixing for the system to be spontaneous (negative) based on the Gibbs free energy equation (Eqn 4.1).¹⁶

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad \text{Eqn (4.1)}$$

$$\Delta H_m = \chi k_B T \phi_1 \phi_2 \quad \text{Eqn (4.2)}$$

The extent of immiscibility can be quantified by the Flory-Huggins binary interaction parameter (χ) between two polymers, which is related to inherent differences in composition, molecular weights, branching, and crystallinity, among other material properties.^{36, 100} In thermodynamics, the enthalpy of mixing is related to the interaction parameter, the Boltzmann constant (k_B) as well as the volume fraction (ϕ) of component 1 and 2. The interaction parameter is directly related to the enthalpy of mixing as represented by Eqn 4.2.¹⁶⁻¹⁸ Therefore, spontaneous mixing will occur if χ is negative or very slightly positive.^{14, 16} Unfavorable mixing leads to phase separation, where droplet coalescence is an important process in the morphological development of phase-separated polymer blends, as illustrated in **Figure 4.1**. To inhibit droplet coalescence, the interface

between polymer components in a phase-separated blend can be stabilized by adding a small amount of a compatibilizer. Compatibilizers can improve the interface through either reactive or passive mechanisms by increasing interfacial adhesion and decreasing interfacial tension.⁴¹ Reactive compatibilizers have functional groups that can react with the components within the polymer blend melt to form compatibilizers during processing, while passive compatibilizers are already formed copolymers that are added to the melt during processing and can stabilize the interface through entanglement or co-crystallization.

Some interfacial modifiers that have shown to be effective in the passive compatibilization of polyethylene/polypropylene blends, including ethylene-propylene rubbers (EPR) and polyolefin elastomers (POE), whose structures are depicted in **Figure 4.2**.^{134, 135, 139} EPRs and POEs are synthesized through the random copolymerization of ethylene and 1-alkene monomers with single-site metallocene or Ziegler-Natta catalysts.^{137, 140} The POE of focus in this study is a random copolymer composed of ethylene and 1-octene monomers, however there are commercially available POEs that contain a variety of olefin branch lengths, including 1-hexene and 1-butene monomers.¹³⁷ Block copolymers of ethylene/1-olefin are also commercially available, where these are synthesized using chain shuttling catalyst technology spearheaded by Dow Chemical.^{137, 141} The chain shuttling catalyst process, however, requires two catalysts and a chain-shuttling agent which limits its application.¹³⁷ Coates et al used a chain shuttling polymerization to synthesize tetrablock copolymers of PE-iPP that are effective compatibilizers of HDPE/iPP blends at only 1 wt% loading, but this synthesis is complex

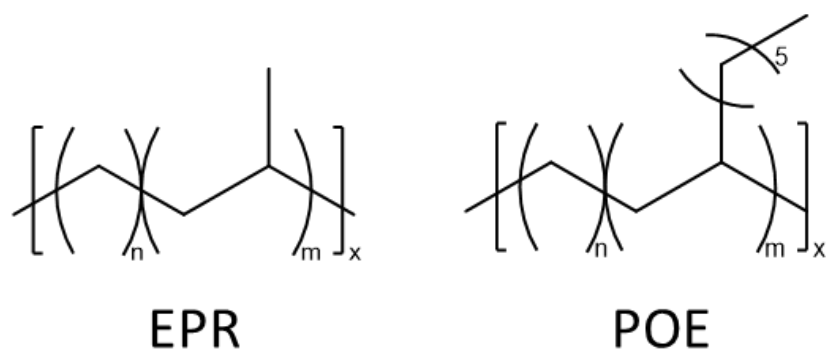


Figure 4.2. Structure of ethylene-propylene rubber (EPR) and ethylene/1-octene polyolefin elastomers (POE).

and difficult to implement on a large scale.^{46, 86}

In this paper, the structure, composition, and sequence distribution of commercially available ethylene-propylene random copolymers are characterized to determine the correlation of molecular level characteristics of the copolymer on its ability to effectively compatibilize isotactic polypropylene/high density polyethylene semicrystalline polymer blends with industrially prevalent materials. The five EPRs studied were supplied by ExxonMobil and vary in molecular weight, dispersity, and ethylene content. The compatibilizing effectiveness of the EPRs are compared to that of a Dow Chemical POE material that has been shown to be more miscible with polyethylene when compared to the propylene-rich EPRs from ExxonMobil.¹³⁴

Experimental

Materials

High-density polyethylene (HDPE) ALATHON H5234 was purchased from APSX; this grade has a relatively low dispersity, making it suitable for injection molding. Isotactic polypropylene (iPP) was obtained from Sigma Aldrich (Mw: 250 kDa). **Table 4.1** displays the molecular characteristics of the five EPR VistaMaxx (VM) samples supplied by ExxonMobil. The polyolefin elastomer, Engage 8180 (Dow Chemical), was provided by Troy University.

Dog Bone Sample Prep

Blends are prepared that contain high-density polyethylene (HDPE) and isotactic polypropylene (iPP) pellets at an 80/20 mass ratio at a 1-gram scale. The compatibilizer

Table 4.1. ExxonMobil VistaMaxx Ethylene-Propylene Rubbers of Interest. Ethylene content determined by quantitative ^{13}C NMR. Percent crystallinity is calculated from DSC.

Sample	Ethylene Content (mol%)	% Crystallinity	T_m (°C)
VM6202	32%	0.15%	110
VM8880	27%	4.8%	98
VM3980	30%	7.9%	78
VM3020	56%	4.7%	64
VM3588	24%	13.5%	108

is then weighed out to either 1, 2.5 or 5 wt% loading and added to the blends. Samples that are 30/70 HDPE/iPP with 5 wt% compatibilizer loading are also prepared by a similar method. The samples are dried at 80 °C overnight under vacuum.

Micro-compounding and Injection Molding

To make samples suitable for mechanical tensile testing, the dried samples are fed into a DSM Xplore 5mL micro-compounder at 190 °C. The sample is mixed at this temperature at 100 rpm for 8 minutes under nitrogen before transferring to the transfer chamber.^{46, 92} The DSM Injection Molding Machine has a transfer chamber and a mold holder preheated to 194 °C and 110 °C, respectively. A 1 g scale ASTM D1708 mold was machined to fit the instrument. The injection molder applies 60 psi of pressure for injection of the polymer material into the heated mold. For each compatibilizer and composition, 5 ASTM D1708 dog bones are prepared for testing.

Tensile Testing

Stress-Strain curves are collected with an Instron 5kN Universal Tester using a set crosshead speed of 10 mm/min following ASTM D1708. The stress-strain curves are analyzed for tensile strength, elongation at break (ϵ_b), and toughness.

Differential Scanning Calorimetry

Crystallinity and thermal transitions of the materials were determined using a TA Instruments Q-2000 DSC. To determine the thermal characteristics of the individual components, 5-10 mg of material was heated and cooled from 0 to 200 °C at 10 °C/min for two cycles. To ensure the thermal history is not impacting the thermal properties, the

DSC curve from the second cycle of each sample was analyzed to determine heat of fusion (ΔH_f) and melting temperature (T_m) of the sample.⁶⁴ Percent crystallinity is determined using a 100% crystalline polyethylene heat of fusion of 293 J/g.

The DSC curves for the blended samples are similarly collected on the first DSC cycle, which was run from 40 – 180 °C. This data was analyzed to quantify the crystallinity of the materials during mechanical testing. The normalized percent crystallinity (X) of the blends are calculated using Eqns 4.3-4.5, where ϕ_x and $\Delta H_{f,x}$ are the mass ratio and heat of fusion of component x , respectively.^{62, 142} The percent crystallinity is determined using $\Delta H_{100\%iPP} = 207$ J/g and $\Delta H_{100\%HDPE} = 293$ J/g.

$$X_{HDPE} = \frac{\Delta H_{f,HDPE}}{\phi_{HDPE} * \Delta H_{100\%HDPE}} \times 100\% \quad \text{Eqn (4.3)}$$

$$X_{iPP} = \frac{\Delta H_{f,iPP}}{\phi_{iPP} * \Delta H_{100\%iPP}} \times 100\% \quad \text{Eqn (4.4)}$$

$$X_{Total} = \frac{\Delta H_{f,HDPE} + \Delta H_{f,iPP}}{\phi_{HDPE} \Delta H_{100\%HDPE} + \phi_{iPP} \Delta H_{100\%iPP}} \times 100\% \quad \text{Eqn (4.5)}$$

Nuclear Magnetic Resonance

The composition of the ethylene-propylene rubbers and Engage 8180 POE as well as the sequence distribution of the polyolefins is determined by quantitative ¹³C NMR.⁵³ Samples of 5 wt% compatibilizer were dissolved in 1,1,2,2-tetrachloroethane-d₂ (Cambridge Isotope Labs) at 110 °C and transferred to preheated NMR tubes using preheated pipettes.^{49, 50, 143, 144} ¹H NMR and quantitative ¹³C NMR were run on a Bruker Avance 400 MHz at 110 °C to prevent precipitation. The high temperature ¹H NMR is run to verify the polymer is dissolved before running the longer carbon experiment.

High-Temperature Size-Exclusion Chromatography

The molecular weight characteristics of the commercial EPR samples (5 mg/mL) were determined using a Malvern Viscotek 350A High-Temperature Gel Permeation Chromatography (GPC) run in 1,2,4-trichlorobenzene (TCB) at 150 °C using polystyrene standards.

Results and Discussion

Mechanical Properties of the HDPE Rich Blends

The high-density polyethylene (HDPE) used in this study is designed for injection molding, has a low dispersity of 2.19, and a low M_w of 32 kDa according to GPC.¹⁴⁵ The pure material has a tensile strength of 25 MPa and an elongation at break of 973%. The isotactic polypropylene (iPP) is also specified for injection molding. This material has an average tensile strength of 35 MPa and an elongation at break of 341%. One stress-strain curve for the HDPE and iPP samples is plotted in **Figure 4.3**, as well as a stress-strain curve of the immiscible blend of 80 wt% HDPE and 20 wt% iPP is. This polymer blend has an average tensile strength of 26 MPa and an elongation of only 10% before breaking. The brittle behavior of the polymer blend highlights the problem of creating robust materials from phase-separated polymer blends, where the weak interface between phases serves as a weak point in their ability to sustain an applied stress. Compatibilizers can be added to an immiscible blend to strengthen this interface between phases and improve the overall mechanical properties of the immiscible HDPE/iPP polymer blend.

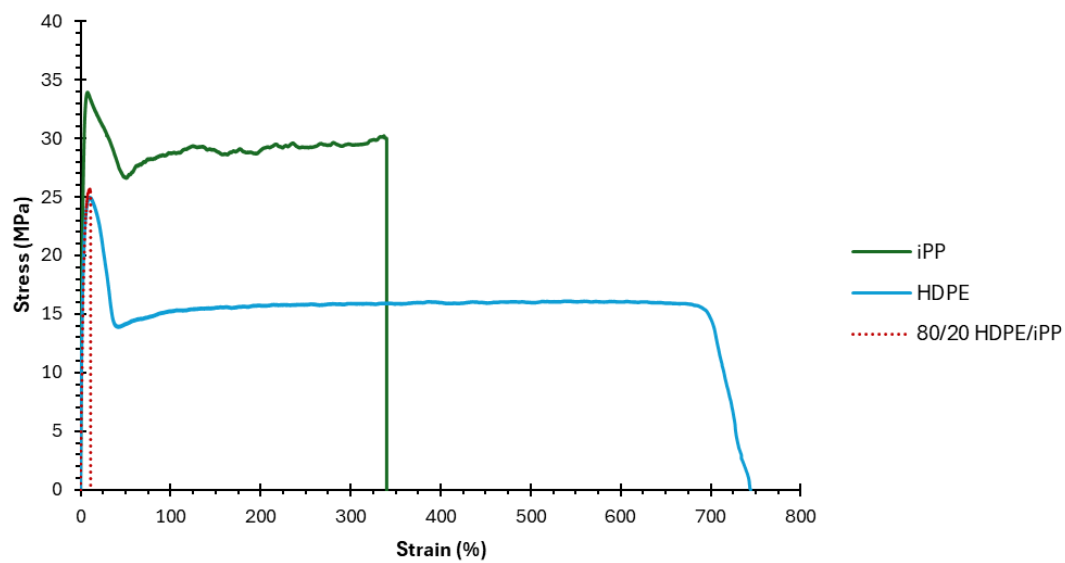


Figure 4.3. Stress-Strain curves for the pure components and 80/20 mass ratio of HDPE/iPP.

Table 4.2 displays the mechanical properties of the pure components, the 80/20 blend without a compatibilizer and with compatibilizer at 1, 2.5, and 5 wt% compatibilizer loading for all the compatibilizers studied. The tensile strength provides a measure of the maximum stress that the sample can sustain, while elongation at break denotes the extension of the material before failure, which is a measure of the materials ductility. The loss of ductility in the compatibilized blend is improved by the incorporation of any of the compatibilizers at any of the tested compatibilizer loadings. There is, however, a significant variation in the ability of the compatibilizer to improve this property, where the elongation at break increases from a factor of 2 to 26 improvement in ductility, where the maximum improvement occurs for the sample that includes 5 wt% of Engage 8180 as the compatibilizer.

The change in the elongation at break with increasing compatibilizer loading is presented in **Figure 4.4**. The incorporation of a 5 wt% compatibilizer loading creates materials with the highest elongation at break for all samples studied, except those with VM8880 and VM6202 as the compatibilizer. Since samples with 5 wt% compatibilizer loadings have the best elongation at break with the majority of the compatibilizers, this compatibilizer loading is chosen to examine the impact of compatibilizer molecular structure on the effectiveness of the compatibilizer to improve the mechanical properties of semicrystalline/semicrystalline HDPE/*i*-PP blends.

Table 4.2. Overall mechanical properties for the injection molded samples using the ASTM 1708D standard. Average and standard deviations are presented for each mechanical property.

Sample	Compatibilizer Content (wt%)	Tensile Strength (MPa)		Elongation At Break (%)		Young's Modulus (MPa)		Toughness (MPa)	
80/20 HDPE/IPP	0	26	±1.7	10	±2	992	±264	4.2	±0.7
IPP	0	35	±2.2	341	±148	1276	±117	198	±87
HDPE	0	25	±0.17	973	±206	1128	±159	253	±20
ENGAGE 8180	1%	26	±0.59	100	±14	809	±97	27.3	±3.3
	2.5%	27	±1.1	112	±14	918	±181	36.1	±3.6
	5%	25	±0.67	263	±49	734	±197	93.4	±18.5
	1%	25	±1.5	26	±29	815	±153	7.7	±6.5
VM3020	2.5%	23	±2.2	24	±15	715	±114	6.8	±4.0
	5%	23	±1.3	238	±123	661	±50	73.2	±36.4
	1%	28	±1.6	72	±29	1131	±82	21.1	±28.6
VM3588	2.5%	27	±2.2	114	±35	1038	±255	32.6	±15.4
	5%	27	±1.5	153	±25	1162	±67	48.6	±9.1
	1%	26	±1.6	82	±22	994	±117	18.7	±4.5
VM3980	2.5%	25	±1.4	20	±16	1019	±135	5.3	±2.3
	5%	28	±1.6	146	±29	1042	±59	51.5	±19.6
	1%	27	±1.1	121	±33	1142	±92	34.5	±14.0
VM8880	2.5%	26	±0.56	56	±13	1126	±45	15.3	±4.3
	5%	24	±2.1	75	±42	952	±272	21.1	±16.1
	1%	27	±1.8	93	±23	1135	±52	24.7	±9.0
VM6202	2.5%	24	±1.4	147	±84	982	±104	36.6	±22.2
	5%	23	±1.0	103	±51	1113	±41	26.5	±16.8

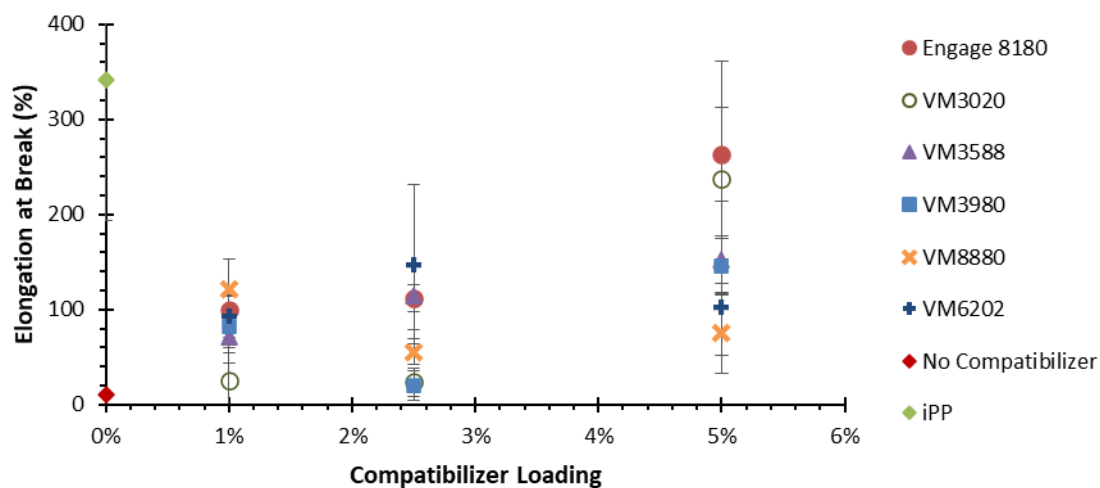


Figure 4.4. Change in elongation at break of the compatibilized 80/20 HDPE/i-PP blends at different compatibilizer loadings. HDPE has an elongation at break of 973%, which is significantly greater than that of the compatibilized blends or i-PP. Error bars represent one standard deviation from the average.

Determination of Compatibilizer Molecular Structure

A primary goal of this study is to correlate the molecular structure of the commercial polyolefin copolymers to their effectiveness at compatibilizing a blend of HDPE and i-PP. Thus, quantitative carbon NMR (^{13}C NMR) was implemented to determine the composition and sequence structure of the random copolymers of ethylene and propylene units in the VistaMaxx samples. Eqns 4.6-4.9 show the analysis of the NMR peaks that are used to determine the mole percent of propylene (*mol% P*) and ethylene (*mol% E*) in the copolymers. The peak assignments and calculations in Eqns 4.6-4.9 are based on work by Carman et al and Sun et al.^{49, 52, 53, 144, 146} In these analyses, the sum of all the NMR peak integrations is normalized to 1. The mol% ethylene content is calculated for the VistaMaxx samples since they are ethylene-propylene copolymers. The secondary $\alpha\alpha$ ($S_{\alpha\alpha}$) carbon peaks are present in propylene-propylene dyad sequences and show a peak in the NMR at 46.2 – 45.2 ppm. $S_{\alpha\gamma}$ and $S_{\alpha\delta}$ peaks emerge from a propylene unit linked to an ethylene unit and appear in the NMR spectrum at 37.3 - 37.0 ppm. The areas of these peaks are divided by two in Eqn 4.6 to monitor the presence of propylene units since these peaks represent a structure that contains both an ethylene and a propylene repeat unit. Thus, summing the areas of the $S_{\alpha\alpha}$ and $\frac{1}{2} S_{\alpha\gamma}$ and $\frac{1}{2} S_{\alpha\delta}$ peaks accounts for the contribution of the propylene repeat units to the NMR curve. The second set of peaks that are analyzed to determine the composition of ethylene (E') repeat units in the copolymer is based on the $S_{\gamma\delta}$, $S_{\beta\delta}$, and $S_{\alpha\delta}$ structures, which contain a propylene-ethylene-ethylene sequence, as well as $S_{\delta\delta}$, $S_{\beta\delta}$, and $S_{\alpha\gamma}$. $S_{\beta\delta}$ and $S_{\alpha\gamma}$ structures that include junctions between propylene-ethylene segments, and $S_{\delta\delta}$ structures that emerge from an ethylene-ethylene-ethylene triad.¹⁴⁴ Thus, Eqn 4.7 elucidates the relationship between the

amount of ethylene repeat units in the copolymer and the peaks in the NMR curve. Eqns 4.8 and 4.9 combine P' and E' to normalize the NMR spectra analysis to provide the mol% of propylene and ethylene segments in the examined EPR.

$$P' = S_{\alpha\alpha} + \frac{1}{2}(S_{\alpha\gamma} + S_{\alpha\delta}) \quad \text{Eqn (4.6)}$$

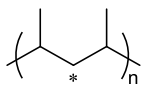
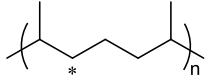
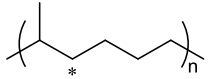
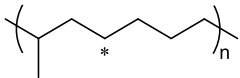
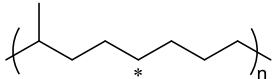
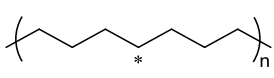
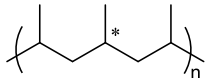
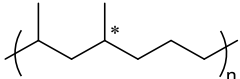
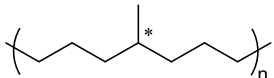
$$E' = \frac{1}{2}[S_{\delta\delta} + S_{\beta\delta} + S_{\alpha\gamma} + \frac{1}{2}(S_{\gamma\delta} + S_{\beta\delta} + S_{\alpha\delta})] \quad \text{Eqn (4.7)}$$

$$\text{mol\% } P = \frac{P'}{P' + E'} \times 100\% \quad \text{Eqn (4.8)}$$

$$\text{mol\% } E = \frac{E'}{P' + E'} \times 100\% \quad \text{Eqn (4.9)}$$

The determination of the triad sequences that exist in the copolymers are also based on the ^{13}C NMRs as shown in Eqns 4.10 and 4.11.¹⁴⁴ The tertiary carbons (T) are only present at the propylene segments of the polymer chain. $T_{\beta\beta}$ is a tertiary carbon that has a propylene unit preceding and following it as represented in **Table 4.3**.^{49, 53} The amount of PPP triads in the copolymer is calculated by dividing peak integration associated with $T_{\beta\beta}$ by the integration of tertiary carbon peaks for $T_{\beta\beta}$, $T_{\beta\delta}$, and $T_{\delta\delta}$, which represent triads with 3, 2, and 1 propylene units, respectively. This calculation is normalized by the mol% of polypropylene in the copolymer to determine the mol% of propylene-propylene-propylene (PPP) triads in the commercial ethylene-propylene random copolymers. The mol% of EEE triads in the copolymer is calculated based on the analysis of the NMR curve that accounts for the segments in the copolymer that contain the ethylene-ethylene-ethylene triad. Since secondary carbons are present in both propylene and ethylene units, this calculation is normalized by both these units in

Table 4.3. Secondary and tertiary carbon assignments for ethylene-propylene random copolymers.

Structure	Carbon Assignment Secondary (S) or Tertiary (T)	Composition
	$S_{\alpha\alpha}$	2 propylene units
	$S_{\alpha\gamma}$	2 propylene units 1 ethylene unit
	$S_{\alpha\delta+}$	≥ 1 propylene unit ≥ 1 ethylene units
	$S_{\beta\delta+}$	≥ 1 propylene unit ≥ 2 ethylene units
	$S_{\gamma\delta+}$	≥ 1 propylene unit ≥ 2 ethylene units
	$S_{\delta+\delta+}$	≥ 3 ethylene units
	$T_{\beta\beta}$	3 propylene units
	$T_{\beta\delta+}$	≥ 2 propylene units ≥ 1 ethylene units
	$T_{\delta+\delta+}$	≥ 1 propylene unit ≥ 2 ethylene units

+ the last carbon in these sequences can be a part of a propylene or ethylene unit

Eqn 4.11. The results of these calculations are tabulated in **Table 4.4**.

The compatibilizing ability of the ethylene-propylene random copolymers in the HDPE/*i*-PP blend is also compared to that of an ethylene/ α -octene random copolymer, Engage 8180. The molecular structure of the Engage 8180 copolymer is determined using quantitative ^{13}C NMR, where this spectrum is shown in **Figure 4.6**. NMR peaks were assigned to specific carbons in the copolymer based on work by Liu et al and Randall et al according to **Figure 4.5**.^{50, 143, 147} This POE sample doesn't have any $S_{\alpha\alpha}$ NMR peaks present at 40.2-41.9 ppm, which indicates that there are no sequential octene units,¹⁴³ where these secondary carbons at the $\alpha\alpha$ position are methylenes neighbored by carbon branches similar to the $S_{\alpha\alpha}$ structure presented in **Table 4.3**. If there are no O-O links along the copolymer chain, then the remaining triads can be either EEO/OEE, EEE, or EOE. The difficulty with characterizing poly(ethylene-*co*-1-octene) is that the $4B_6$ carbon and the ethylene backbone carbons are both secondary carbons in the delta-delta position, which have a characteristic peak in the NMR curve at 29.4-29.5 ppm. Eqn 4.12 presents the solution for this concern as the integration of another secondary carbon in the branch ($3B_6$) can be subtracted from the total integration of $S_{\delta\delta}$ carbons ($S_{\delta\delta}$ and $4B_6$) to determine the mol% of ethylene in the backbone.¹⁴³ Determining the ratio of ethylene-octene-ethylene triads is more straightforward as the EOE content is represented by the tertiary carbon (T), $6B_6$, and $5B_6$ as shown in Eqn 4.13. The branch carbons are normalized by possible resonances.¹⁴³ Each of these three contributions to Eqn 4.13 are equivalent, as shown by integration of the NMR spectra (**Figure 4.6**), but taking the average improves accuracy. In this copolymer, the octene units appear to be surrounded

Table 4.4. Ethylene and propylene triad contents for VistaMaxx EPR samples as determined from quantitative ^{13}C NMR.

Sample	Ethylene Content (mol%)	EEE Content (mol%)	PPP Content (mol%)
VM6202	32%	12%	22%
VM8880	27%	18%	34%
VM3980	30%	17%	23%
VM3020	56%	45%	8.9%
VM3588	24%	19%	34%

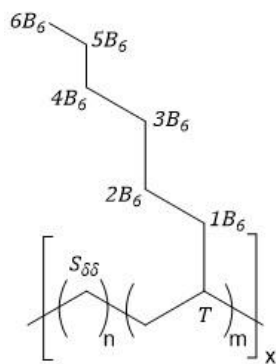


Figure 4.5. Quantitative ^{13}C NMR assignments for ethylene/1-octene copolymers.

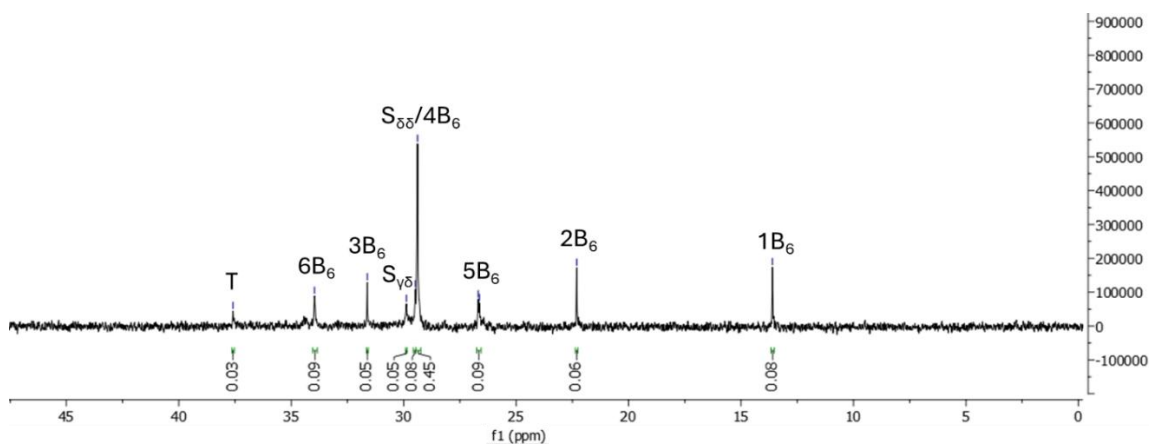


Figure 4.6. Quantitative ^{13}C NMR peak assignments for Engage 8180 run in 1,1,2,2-tetrachloroethane- d_2 .

by ethylene segments longer than 2 units, as the peaks associated with EEO/OEE at ~35.5 ppm and ~25.4 ppm are not differentiable from the baseline in the q¹³C NMR.^{49, 50, 144} Thus, the mol% octene and ethylene content is calculated from the analysis of the peaks that are associated with the EEE and EOE triads, as shown in Eqns 4.14 and 4.15. From these formulae, the composition of Engage 8180 can be shown to be 85.5 mol% ethylene.

$$EEE' = [(S_{\delta\delta} + 4B_6) - 3B_6]/2 \quad \text{Eqn (4.12)}$$

$$EOE' = \frac{T + \frac{6B_6}{3} + \frac{5B_6}{3}}{3} \quad \text{Eqn (4.13)}$$

$$\text{mol\% } O = \frac{EOE'}{EOE' + EEE'} \times 100\% \quad \text{Eqn (4.14)}$$

$$\text{mol\% } E = 100\% - \text{mol\% } O \quad \text{Eqn (4.15)}$$

Impact of Compatibilizer Molecular Structure on Compatibilization

Toughness is the area under the stress-strain curve and documents the total amount of energy that the sample absorbs before fracturing. **Figure 4.7** plots the change in toughness with M_n and M_w for the blends with the five VistaMaxx compatibilizers at 5 wt% compatibilizer loading. This data shows that there is an increase in toughness with compatibilizer chain length, where the correlation is stronger with M_w than with M_n . As M_w is more dependent on the high molecular weight tail of the distribution curve, this suggests that the longer chains in the EPR samples dominate the physics of the strengthening. This is consistent with the random copolymers stabilizing the interface with entanglements, as longer chains will form more entanglements.

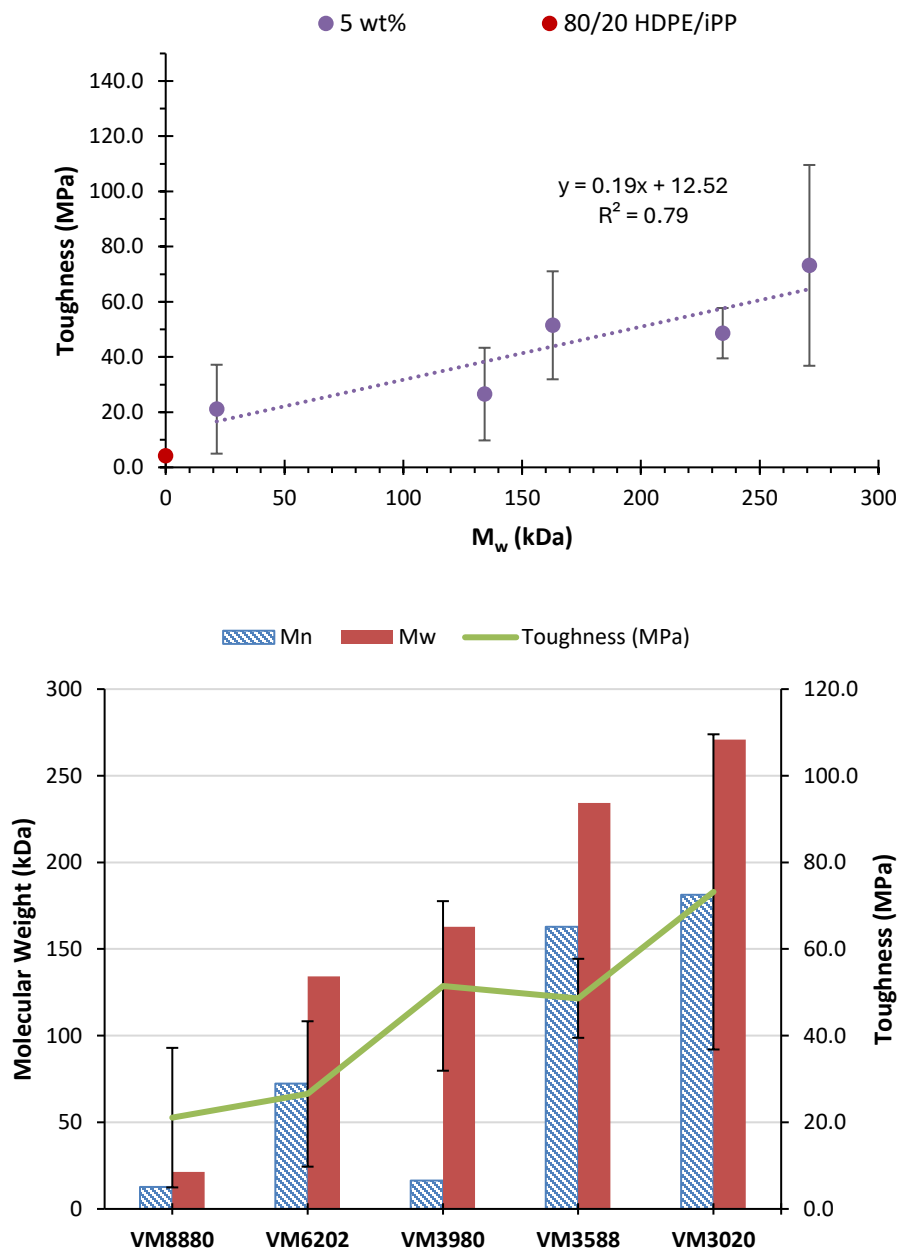


Figure 4.7. Toughness of 5 wt% compatibilizer blend as a function of weight-average molecular weight (M_w) (top) and the relationship between the molecular weight characteristics and toughness for the five VistaMaxx (VM) compatibilizers loaded at 5 wt% (bottom). Error bars represent one standard deviation from the average.

Figure 4.8 presents the change in toughness with the copolymer composition quantified by the mol% ethylene in the copolymer as determined with $q^{13}\text{C}$ NMR. The toughness of the compatibilized blends is always below that of the iPP (198 MPa) and the HDPE (253 MPa); however, the toughness of the compatibilized blends are a factor of ten greater than that of the uncompatibilized blend (4.2 MPa). **Figure 4.8** shows that there is an increase in toughness with an increase in ethylene content in the EPR compatibilizer. Thus, the incorporation of ethylene repeat units in the compatibilizers is an important molecular characteristic of effective compatibilizers of these blends of HDPE and polypropylene.

Figure 4.9 plots the change in polymer blend toughness with the mol% of propylene-propylene-propylene (PPP) triads for 5 wt% VistaMaxx compatibilizer loading. This data shows a decrease in toughness with an increasing concentration of propylene triads in the compatibilizer. We ascribe this to the composition of the blend that is 80 wt% polyethylene and 20 wt% polypropylene, where the lower PP content leads to compatibilizers that can more readily diffuse to the PP/HDPE interface through the major HDPE phase.¹⁴⁸

Figure 4.10 displays the increase in blend toughness with an increasing concentration of EEE triads in the compatibilizer. This is consistent with the importance of the entanglement of the compatibilizer with the HDPE major phase between the EPR ethylene runs and the HDPE phase in determining the effectiveness of the compatibilizer in the 80/20 HDPE/iPP blend. This indicates that improving the compatibility of the copolymer with the semicrystalline polyethylene phase will improve the mechanical

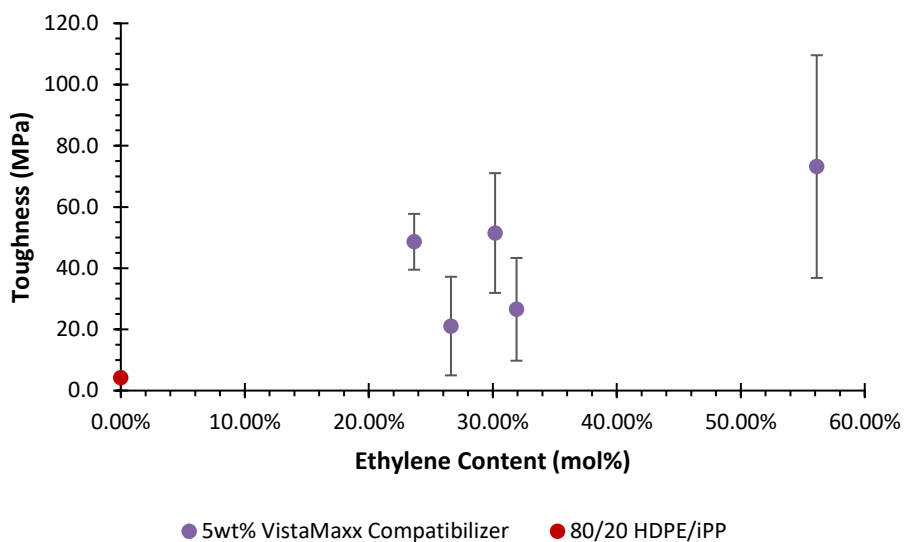


Figure 4.8. Change in toughness as a function of the mol% ethylene content of the VistaMaxx (VM) compatibilizers at 5 wt% compatibilizer loading. HDPE has a toughness of 253 MPa and iPP has a toughness of 198 MPa. Error bars represent one standard deviation from the average.

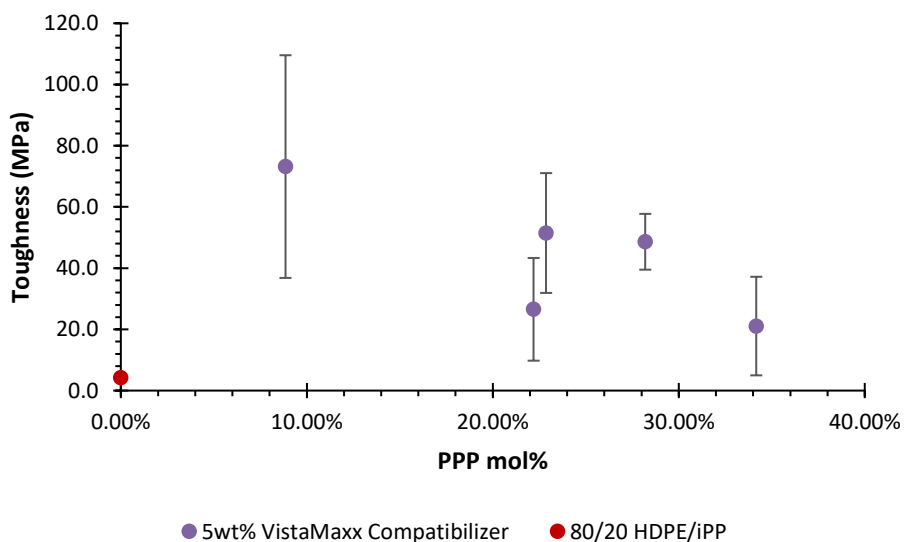


Figure 4.9. Change in toughness with the mol% of PPP triads in VistaMaxx (VM) compatibilizers at 5 wt% compatibilizer loading. HDPE has a toughness of 253 MPa and iPP has a toughness of 198 MPa. Error bars represent one standard deviation from the average.

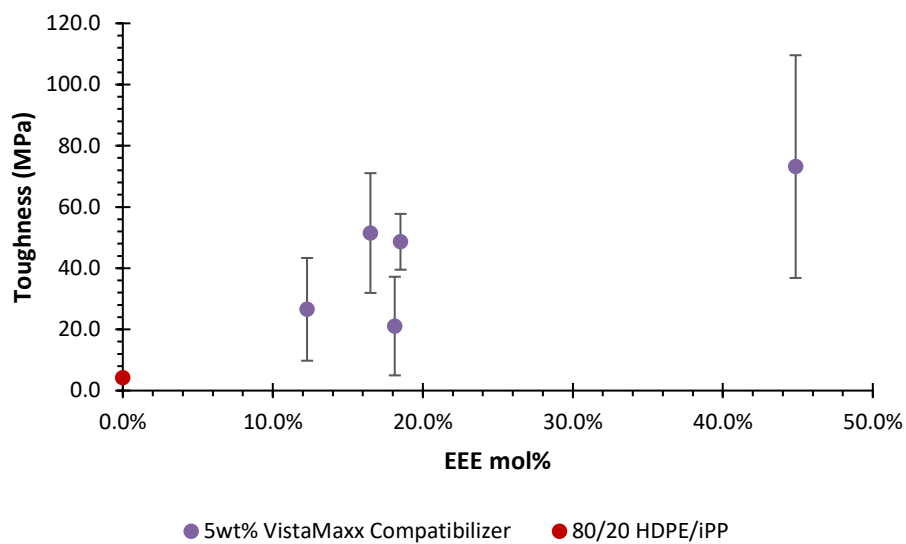


Figure 4.10. Change in toughness with the mol% of EEE triads in VistaMaxx (VM) compatibilizers at 5 wt% compatibilizer loading. HDPE has a toughness of 253 MPa and iPP has a toughness of 198 MPa. Error bars represent one standard deviation from the average.

properties of the blend.

The toughness of the compatibilized blends as a function of ethylene content and EEE triad content are plotted for all of the compatibilizers tested, both Vistamaxx and Engage, in **Figure 4.11**. The ethylene/1-octene Engage copolymer has a better toughness at 5 wt% compatibilizer loading compared to the VistaMaxx samples, but it still follows the trends with higher ethylene content and EEE sequences leading to a better compatibilized polymer blend.

Mechanical Properties of the i-PP Rich Blends

Figure 4.12 provides a comparison of how effective these compatibilizers are in an isotactic polypropylene-rich blend relative to their behavior in the HDPE-rich blend with 5 wt% compatibilizer loading. Inspection of this data shows that the VM6202, VM3020, and VM3588 copolymers provide the strongest improvement in toughness. Vistamaxx 8880 is the worst-performing compatibilizer in both the iPP- and HDPE-rich blends. This could be due to its low molecular weight, preventing adequate entanglement between the phases. The compatibilizer with the greatest improvement in overall toughness (VM3020) has the largest number-average molecular weight (M_n), which supports the interpretation that optimizing possible entanglements in both phases is crucial. Interestingly, the uncompatibilized 80/20 HDPE-rich blend has a toughness of 4.2 MPa, while the 30/70 iPP-rich blend has a toughness of 15.3 MPa without compatibilization. Yet, most of the compatibilizers tested result in a tougher material in the 80/20 HDPE/iPP blends than in the compatibilized 30/70 HDPE/iPP blend, despite the fact that the uncompatibilized 30/70 HDPE/iPP blend has a higher starting toughness.

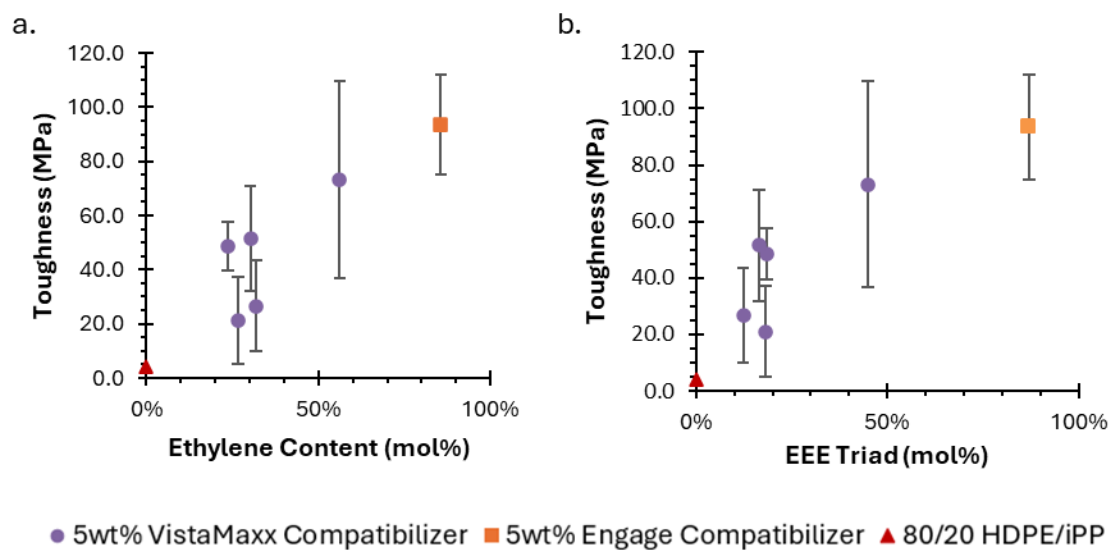


Figure 4.11. Comparison of compatibilizer efficiency for ethylene-propylene copolymers against an Engage POE for (a.) ethylene content in mol% as well as (b.) the mol% of EEE triads. Error bars represent one standard deviation from the average.

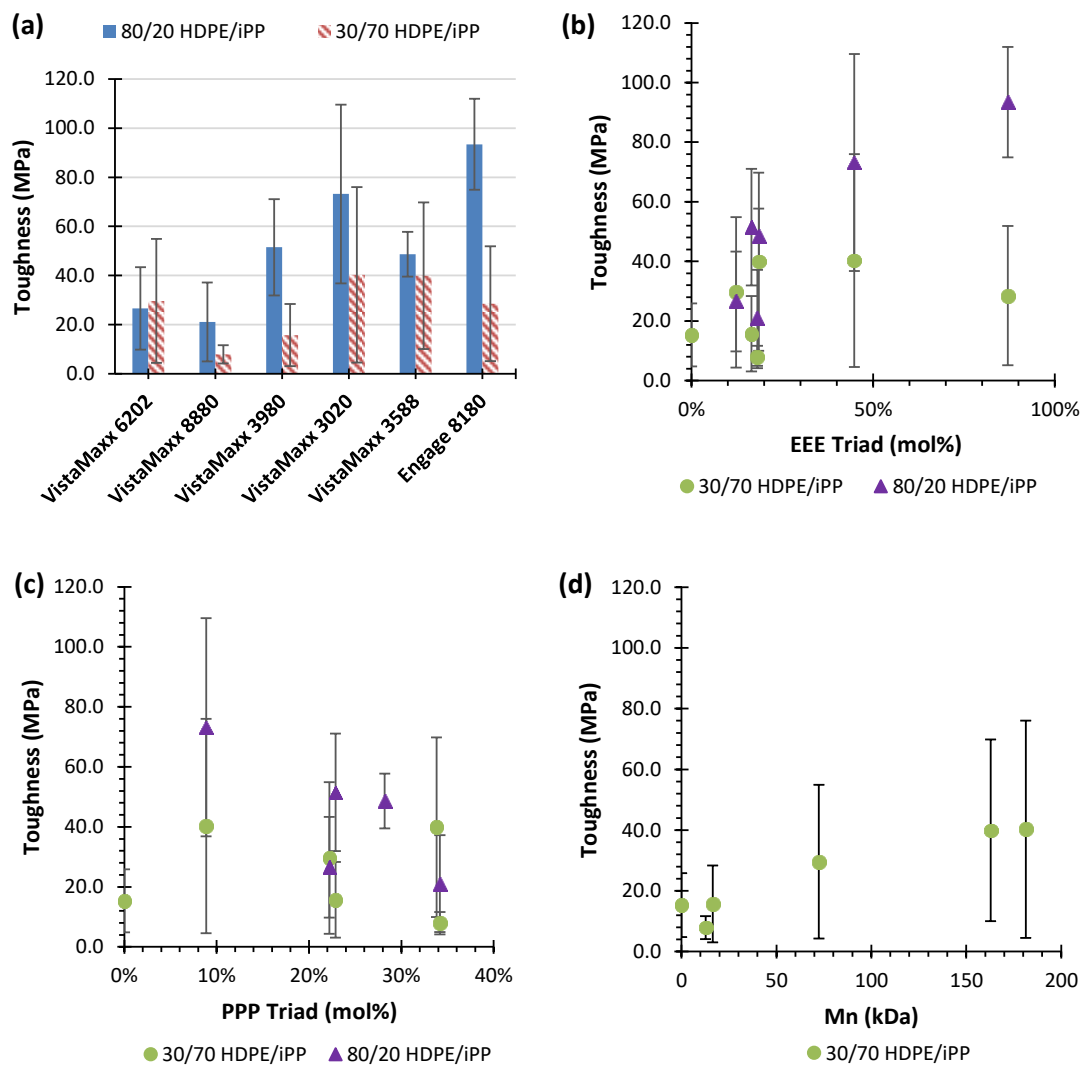


Figure 4.12. Comparison of compatibilizer efficiency at 5 wt% compatibilizer loading in 30/70 HDPE/iPP blends compared to the 80/20 HDPE/iPP blends (a) based on mol% EEE triad (b) and PPP triad (c) compositions as well as against number-average molecular weight (d). Error bars represent one standard deviation from the average.

The exception to this trend is the blend compatibilized with VM6202, which has similar properties at both blend compositions.

Inspection of **Figure 4.12b** and **4.12c** shows that the toughness of the iPP-rich blends lacks a strong dependence on compatibilizer sequence. This is specifically interesting in **Figure 4.12c** where there is a slight decrease in toughness as the concentration of PPP sequences increases even though polypropylene is the major phase. There is also a slight increase in the average toughness of the compatibilized blend with ethylene content in the ethylene-propylene rubber copolymers. However, the ethylene/1-octene copolymer (Engage 8180; square data points in **Figure 4.12b**) doesn't follow this slight trend noted for the EPRs in the iPP-rich blend, even though it follows EPR trends in the HDPE-rich blends. Overall, the change in the toughness of the compatibilized blend with EEE and PPP loading in the compatibilizer exhibit similar trends for both iPP-rich and HDPE-rich blends.

In the synthesis of EPR, there is a lack of tacticity control by the catalyst, which results in atactic propylene segments. This is supported by DSC analysis (Appendix C) of the compatibilizers, where there is no melting peak corresponding to polypropylene, verifying that the atactic segments form amorphous segments in the polymer chains. Su and coworkers determined that the Flory-Huggins interaction parameter for iPP/atactic PP blends is -0.21, indicating they are miscible.^{149, 150} Therefore, the limited effectiveness of the compatibilizer with the polypropylene phase relative to the polyethylene phase is due to another factor other than entanglement and miscibility. One thing to note is that while the polypropylene-like segments of EPR are amorphous, the ethylene segments are

crystallizable. This suggests that crystallization interactions between the crystalline ethylene “blocks” and the semicrystalline polyethylene homopolymer could be improving the compatibilization of these blends.

The improvement in toughness for the non-compatibilized 30/70 HDPE/iPP blend relative to the HDPE-rich blend may be due to changes in HDPE crystallization in the blends. **Table 4.5** presents the melting temperatures and percent crystallinity calculated using Eqns 4.3-4.5. The crystallinity of HDPE increases from 58% in the pure sample to 62% in the presence of 20 wt% iPP. In the iPP major phase sample, the HDPE percent crystallinity increases to 74%. The increase in HDPE phase crystallinity with iPP composition is consistent with iPP acting as a nucleating agent for HDPE. Previous studies have shown that the iPP lamellae can promote nucleation of HDPE crystals due to epitaxy crystallization in blends of HDPE/iPP with high iPP content.^{151, 152} This is a surface-induced crystallization where HDPE segments align perpendicular to iPP lamellae in the space between methyl chains.¹⁴² This epitaxial crystallization can only occur in blends with a majority iPP and well-defined iPP lamellae are already formed during the cooling process.¹⁵¹ This process is promoted during injection molding when shear aligns the iPP chains, and its crystallization rate increases.^{142, 151, 153} This process leads to the formation of small, dispersed droplets as the epitaxial HDPE crystals are oriented to the iPP matrix, and this ordering improves the mechanical properties of the blend.^{152, 153} DSC analysis of the samples studied here further supports this interpretation as the crystallinity of the HDPE phase of the 30/70 HDPE/iPP blends is significantly greater than in the 80/20 blends, as shown in **Table 4.5**. The crystallinity of the iPP phase

Table 4.5. Crystallization characteristics for HDPE/iPP blends normalized based on composition.

Sample	T_m(HDPE)	Normalized % Crystallinity (HDPE)	T_m(iPP)	Normalized % Crystallinity (iPP)	Total % Crystallinity
iPP	-	-	168 °C	54%	54%
HDPE	129 °C	58%	-	-	58%
80wt% HDPE/ 20wt% iPP	133 °C	62%	165 °C	28%	57%
30wt% HDPE/ 70wt% iPP	133 °C	74%	168 °C	30%	47%

decreases from 54% in the pure material to ~30% in the blends. Previous research has noted that the crystallization of isotactic polypropylene is disrupted in blends containing a component with a significantly lower crystallization temperature, such as polyethylene.^{71,}

154, 155

DSC was used to monitor the change in the crystallinity of the polyethylene and isotactic polypropylene homopolymer phases with the addition of a compatibilizer.

Figure 4.13 shows how these crystallinities impact the blend toughness. The melting points of the compatibilizers are lower than those of HDPE (129 °C) and iPP (168 °C), ranging from 59 °C to 104 °C (**Table 4.1**), thus the melting behavior of the pure phases can be readily monitored. The changes in crystallinity of the individual iPP and HDPE phases in the compatibilized 30/70 HDPE/iPP blends are included in the Supplemental Information. The toughness of these iPP rich blends show no correlation to the specific homopolymer crystallinities (Figure S4.26 and S4.27), but there is a decrease in toughness with an overall increase in crystallinity (**Figure 4.13d**). Inspection of **Figure 4.13a** shows that the 80/20 HDPE/iPP compatibilized blends exhibit better toughness at lower crystallinity of the HDPE homopolymer relative to the uncompatibilized sample. This indicates that better-performing compatibilizers also have a greater disruption in the crystallization of the HDPE. In **Figure 4.13b**, the POE compatibilized sample is represented by a square data point. The blends compatibilized with these ethylene-propylene copolymers also exhibit a higher toughness with a decrease in the crystallization of the iPP phase. However, **Figure 4.13b** also shows that the presence of Engage slightly increases the crystallinity of the iPP phase. Thus, these data show that the total crystallinity is dependent on the composition of the blends. Therefore, the HDPE-

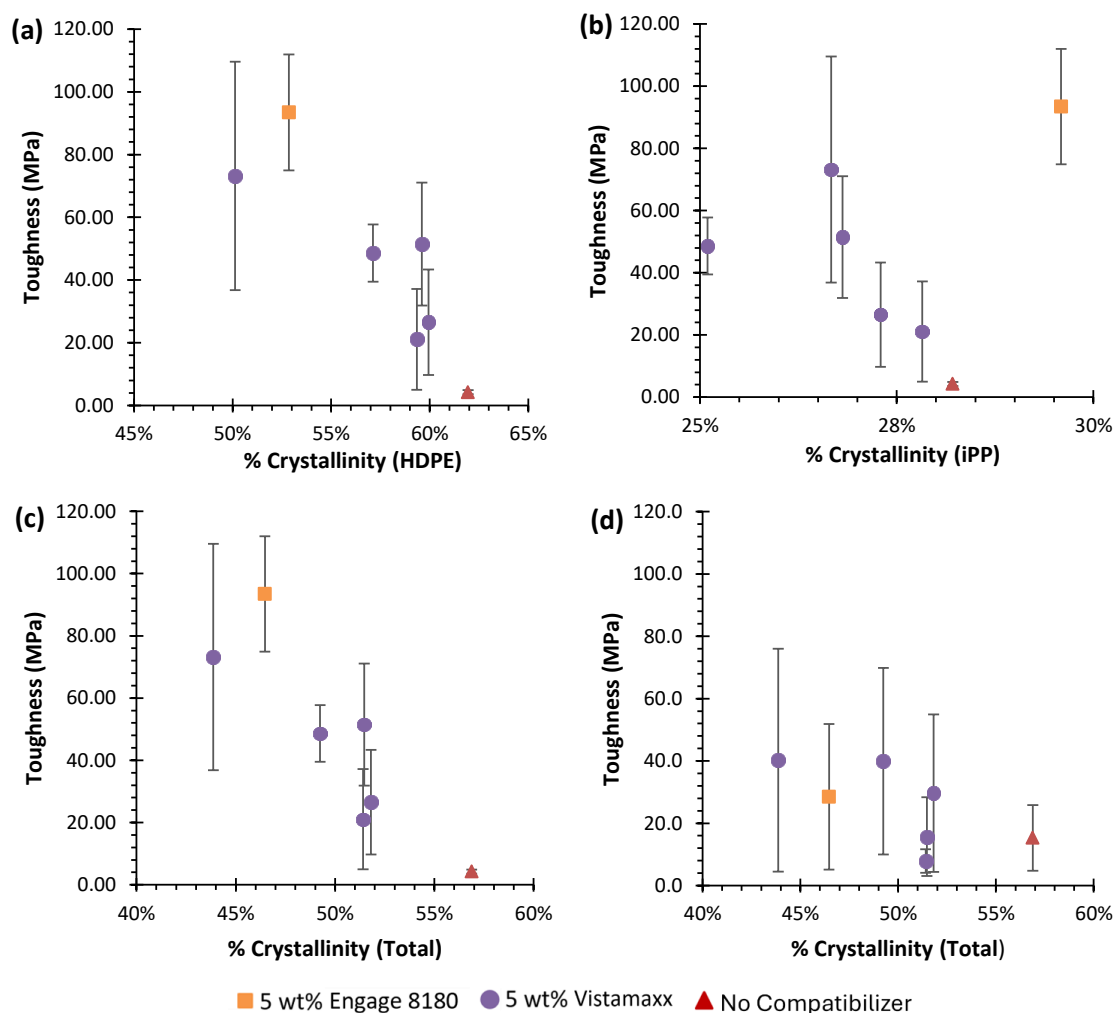


Figure 4.13. Percent crystallinity of HDPE (a) and iPP (b) phases in the 80/20 HDPE/iPP samples determined by integrating the corresponding melting peak from DSC. Total crystallinity reflects the sum of both melting processes for both the 80/20 HDPE/iPP (c) and 30/70 HDPE/iPP (d) samples. Normalized by composition using Eqns 4.1-4.3. All compatibilized samples are at 5 wt% loading. Error bars represent one standard deviation from the average.

rich samples are more significantly impacted by changes in HDPE crystallization, while the properties of the iPP-rich blends are most impacted by the iPP crystallinity. Regardless of composition, the HDPE-rich and iPP-rich blends exhibit a decrease in toughness with increasing overall crystallinity.

Literature has shown that changes in polymer crystallinity of a sample can slightly impact its stress-strain behavior, but not to the extent observed.^{156, 157} For low molecular weight polyethylene, a ductile-brittle crystallinity barrier exists, which, when exceeded, results in a drastic loss of elongation and tensile toughness in the material.^{156, 158, 159} This is not, however, a gradual process as observed in **Figure 4.13**. It is therefore more likely that samples with better mechanical performance exhibit more favorable interactions between the compatibilizer and homopolymers. These interactions could also be disrupting homogeneous crystallization in the phases.

Overall, the dependence of the toughness of the compatibilized blends on the compatibilizer molecular structure in both the HDPE- and iPP- rich blends indicate that entanglement between the copolymer and the homopolymers is necessary to improve the blend properties. The data that supports this interpretation includes the dependence of the blend toughness on the molecular weight and sequence structure of both ethylene-propylene random copolymers and polyolefin elastomers. The more effective compatibilizers are copolymers with longer stretches of EEE and PPP segments, suggesting their blockier structure impacts the ability of the copolymer to compatibilize the blend. This is consistent with previous studies that “blockier” copolymer compatibilizers are more effective compatibilizer as the compatibilizer can entangle between phases.^{42, 44, 65, 118} An improved compatibilizer efficiency with molecular weight

is consistent with longer chains forming more entanglements, “stitching” the phases in the immiscible polymer blend.^{40, 98, 148} For these commercially available random copolymers, it appears beneficial to limit the amorphous propylene/octene component and promote semicrystalline contributions of the compatibilizers in both iPP-rich and HDPE-rich blends. This suggests future studies should focus on isotactic polypropylene/ethylene copolymers as possible compatibilizers for this semicrystalline polymer blend.^{160, 161} Additionally, increasing molecular weight of the compatibilizers can improve entanglement, thereby enhancing the stabilization of the phase-separated blend.

Conclusion

The ability of commercially available ethylene-propylene rubbers (EPRs) and a polyolefin elastomer (POE) to compatibilize high-density polyethylene (HDPE) and isotactic polypropylene (i-PP) blends was examined in this study. These results show that these copolymers improve the toughness of polyethylene/isotactic polypropylene blends by a factor of ~20 at 5 wt% compatibilizer loading in an HDPE-rich blend and doubled the overall toughness in iPP-rich blends. The sequence distribution of the sourced compatibilizers was determined using quantitative ¹³C NMR to elucidate the impact of the molecular structure of the compatibilizer on its ability to improve the toughness of the blends. In both blends, there is an improvement in toughness with an increasing molecular weight of the compatibilizer. There is also a significant improvement in mechanical properties with ethylene content and an increasing composition of ethylene-ethylene-ethylene triad structures. This indicates that optimizing

the semicrystalline component of the compatibilizer and entanglement of the compatibilizer with the homopolymers in the blends is crucial for an effective compatibilization of these blends. These results also indicate that commercially prevalent materials can be used as compatibilizers for polyethylene and polypropylene, which make up approximately half of the plastic waste stream.

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CHAPTER V:
COMPATIBILIZATION OF PVC/POLYOLEFIN ELASTOMER
BLENDS WITH DECHLORINATED PVC

Data presented in this chapter were originally published by Dr. Megan Fieser and Dr.

Mark Dadmun:

Wood, Zachary[‡]; Sapp, Tyeshia[‡]; Eberle, Bailey; Wang, Xuchun; Hunt, Samuel; Barber, Sarah; Cheng-Tan, Mary Dana Czarinah; Zhao, Tommy; Perras, Frédéric; Delferro, Massimiliano; Lee, Byeongdu; Dadmun, Mark; Fieser, Megan. “Synthesis and properties of poly(vinyl chloride)-b-polyethylene multiblock copolymers through the hydrodechlorination of PVC with silylium ions.” *J. Am. Chem. Soc.* **2025**, *147* (30), 26267-26276.

Bailey Eberle performed all peel tests, DSC measurements, and analyzed NMR spectra.

Dechlorinated PVC samples were synthesized by Zachary Wood and Tyeshia Sapp.

Analysis of interfacial adhesion data was performed by Bailey Eberle. The document was revised by Dr. Mark Dadmun.

Abstract

Previous research has examined using chlorinated polyethylene as a compatibilizer for polyvinyl chloride (PVC) and polyolefin elastomer (POE) polymer blends. We wanted to expand on this knowledge to determine how having a compatibilizer with improved miscibility with PVC would impact the importance of entanglement and cocrystallization to strengthen the interface. This was accomplished by analyzing PVC dechlorinated using silylium ions, which produce block-like copolymers with polyethylene-like segments. These compatibilizers outperformed their chlorinated polyethylene (c-PE) counterparts with a maximum average interfacial adhesion

improvement of 6300 J/m^2 , compared to 5600 J/m^2 obtained from c-PE. The synthesis of these materials also allows for control over composition and sequence based on reaction time and temperature, as well as the ability to dechlorinate any PVC, including waste materials. This will allow for compatibilizers to be used in mechanical recycling that are sourced from chemically recycled material.

Introduction

Polymer recycling has become an area of great interest due to the growing concern over plastic waste accumulation. A primary recycling avenue is mechanical recycling, where a plastic product is remelted and reprocessed into recycled material. While this process is straightforward, the recycled material has diminished mechanical properties compared to the virgin material. One cause of this is the difficulty in attaining completely pure waste streams due to the limitations of plastic sorting. When mechanically recycled, mixed plastic waste forms immiscible polymer blends. An immiscible polymer blend occurs when the free energy of mixing (ΔG_m) is positive.^{16, 162} In this case, the blend will phase separate rather than form a homogeneous mixture. This phase separated structure has poor stress transfer across the polymer-polymer interface, which will cause brittleness and a deterioration of toughness.

Passive or nonreactive compatibilizers are copolymer additives that can be introduced into the immiscible polymer blend to reduce interfacial tension and facilitate stress transfer across the polymer-polymer interface. Compatibilizers will also enhance interfacial adhesion between the phases, preventing phase-separation by inhibiting droplet coalescence in the polymer melt. In order for the compatibilizer to interact

between both phases, there must be segments of the copolymer that are miscible with both phases.

Two possible mechanisms by which passive compatibilizers can stabilize the interface are entanglement and co-crystallization, as visualized in **Figure 5.1**.

Maximizing entanglements requires the copolymer to diffuse between the phases and successfully form entanglements, which must occur during the processing of the blend. As the polymer blend is cooled after processing, it cools to below the T_m , where crystallization begins to occur. When the temperature is below the T_m of both components, co-crystallization may occur between the compatibilizer and a semicrystalline homopolymer. A co-crystal is a crystal structure with two polymer species present. Previous research has shown evidence that co-crystallization can occur between chlorinated polyethylene and polyethylene.^{64, 66}

Polyvinyl chloride (PVC) and polyolefins form an immiscible polymer blend, and both materials are of great concern to polymer recycling. PVC alone is prone to thermal degradation that releases HCl gas.⁶ It is also very brittle and has low impact resistance. Overall, its processability can be improved by blending the material with an elastomer. Previous research has shown that compatibilizers synthesized from chlorinating polyethylene can be used for blends of PVC and polyolefin elastomers.^{64, 66} To expand the options for the source of chlorinated polyethylene, we are interested in understanding the effectiveness of dechlorinated PVC (d-PVC) from the waste stream as compatibilizers for PVC/POE blends. d-PVC can be formed with higher chlorination content, and thus will have improved miscibility with the PVC phase due to the presence of vinyl chlorine groups and control over blockiness. The dechlorination of PVC can also be performed on

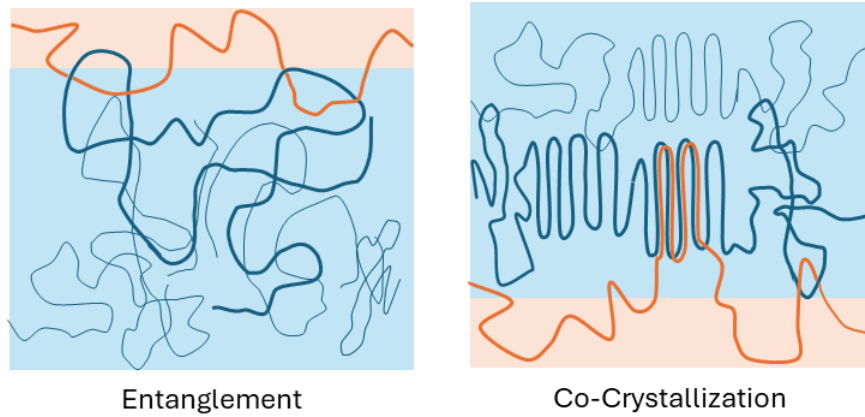
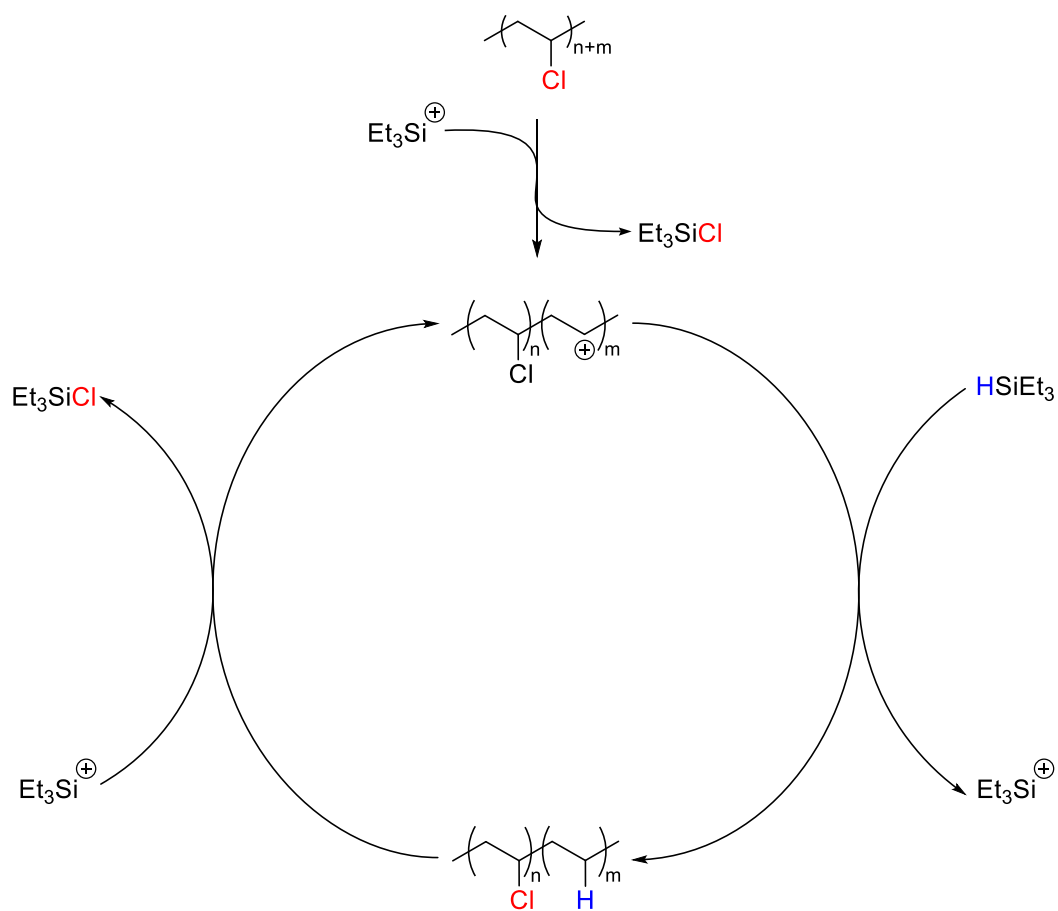


Figure 5.1. Mechanisms of entanglement and co-crystallization.

waste PVC material, which could allow for the compatibilizer to also be derived from recycling streams.

Analysis of dechlorinated PVC as a compatibilizer will also provide further insight into the impact of molecular structure on the ability of a c-PE to compatibilize a PVC/POE interface. In fact, the range of chlorination that is available from c-PE that is produced by the suspension chlorination of polyethylene is less than 30 mol% Cl. On the other hand, by dechlorinating PVC, a broader range of chlorine content in the c-PE is accessible. Our collaborators at USC have developed a synthetic protocol to synthesize hydrodechlorinated PVC with chlorine contents that range from 2 - 44 mol% Cl (4 to 88 mol% PVC repeat units) using the procedure shown in **Scheme 5.1**. In this reaction to hydrodechlorinate PVC, the initiator, $[\text{Ph}_3\text{C}] [\text{B}(\text{C}_6\text{F}_5)_4]$, is added at either 0.5 or 0.75 mol% to form the initial Et_3Si cation from $\text{Et}_3\text{Si-H}$ starting catalyst. The reaction may be performed at either 40 °C or 80 °C, where changing these conditions has been shown to impact the architecture of d-PVC; a lower reaction temperature leads to “blockier” copolymer structures i.e., one that consists of longer runs of dechlorinated carbons. The hydrodechlorination reaction time controls the chlorine content of the c-PE, where a longer reaction time results in a greater dechlorination, i.e., lower chlorine content.

We have thus completed peel test experiments on the ability of 25 dechlorinated polyvinyl chloride (d-PVC) samples of varying compositions and block lengths and 7 commercially available chlorinated polyethylene (c-PE) samples to strengthen PVC/POE interfaces. Ten of the d-PVC samples were derived from common PVC waste, including a vinyl record, credit cards, and a shower curtain, among others. Overall, it was found that d-PVC from virgin sources outperformed commercial c-PE as PVC/POE



Scheme 5.1. Hydrodechlorination of PVC mechanism proposed by Fieser et al.⁴⁷

compatibilizer at similar chlorine contents. The waste PVC was not as effective as a compatibilizer, likely due to impurities of the PVC that result in limitations of the success of the dechlorination process. However, it still improved the interfacial adhesion of the PVC/POE interface relative to the strength of the uncompatibilized interface.

Experimental

Materials

Polyvinyl chloride (PVC) (233 kDa) was obtained from Sigma Aldrich. The PVC was thermally stabilized with 4 phr Mark 1900 methyltin mercaptide (Galata Chemicals). Engage polyolefin elastomer (POE) 7270 (Dow Chemicals) was obtained from Avient. All chlorinated polyethylenes (c-PE) were provided by Showa Denko (Japan).

Dechlorinated PVC (d-PVC) was provided by the Fieser group at the University of Southern California (USC). Dechlorination reactions were performed using commercial poly(vinyl) chloride (PVC) (Sigma Aldrich: $M_n = 46$ kDa, $M_w = 80$ kDa; $M_n = 99$ kDa, $M_w = 233$ kDa) as reactant. In this hydrodechlorination reaction of PVC, triphenylmethylium tetrakis(pentafluoroethyl)borate ($[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$) was purchased from Fisher Chemical, triethylsilane (Et_3SiH) (Chem-Impex International, Inc.) was purchased from Fisher, and both were used as received.^{47, 163} ($[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$) stored in a glove box under an N_2 atmosphere and transferred to a desiccator 1 hour to 14 days before use. Et_3SiH was stored under atmospheric conditions.

Nuclear Magnetic Resonance Spectroscopy:

The composition of the chlorinated polyethylenes was determined by ^1H NMR, and the sequence distributions were determined by quantitative ^{13}C NMR. In both experiments, samples of 5 wt% c-PE dissolved in 1,1,2,2-tetrachloroethane- d_2 (Cambridge Isotope Labs) were prepared at 110 °C for NMR analysis.¹⁰⁵ ^1H NMR and quantitative ^{13}C NMR were run on a Bruker Avance 400 MHz at 90 °C to prevent precipitation. For d-PVC, ^1H NMR spectra from USC were recorded using a Varian VNMRs-600 3-Channel NMR spectrometer at 373 K. Deuterated chloroform or tetrachloroethane solvent was added to reach a concentration of 1.5 mg/mL and heated to 80 °C for 1 hour. All NMRs are referenced against residual solvent resonances.

Interfacial Adhesion of Trilayer Samples:

To create the trilayer sample for compatibilizers, the polyolefin elastomer (POE) DOW Engage 7270 (20 g) was melt-pressed in a Carver Model C Laboratory press at 200 °C with 1 metric ton applied pressure for 5 minutes in a 2.3 mm thick sheet mold. This POE sheet was removed and left to cool under a heavy weight to acquire a smooth surface. The compatibilizer was dissolved in tetrahydrofuran (THF) at 2.5 wt%. The solution was then spin-coated onto the POE sheets at 2500 rpm for 20 seconds and left to dry overnight to ensure the THF solvent evaporated, leaving a thin layer (~350 nm) of d-PVC. PVC powder (20 g) and 4 phr Mark 1900 methyltin mercaptide thermal stabilizer (Galata Chemical) were mixed in a beaker with a spatula until homogeneous. This powder was transferred to a preheated 2.3 mm thick sheet mold and placed in the Carver melt press set to 200 °C. The sample was heated for 3 minutes without applied pressure

and then another 2 minutes with 2 metric tons of applied pressure. The PVC sheet was left to cool down below its T_g ($\sim 85^\circ\text{C}$) in the mold to prevent curling. The PVC and coated POE sheets were cut into 4-5 strips of dimensions 10 mm x 65 mm using a Dremel 4300 or shears, respectively. The spin-coated POE is laid on top of the PVC strip in a mold at 200°C with a small Kapton tab between strips for gripping during peel testing.

This procedure is modified as some compatibilizers needed to be dissolved in toluene. Because POE is soluble in toluene, this solution could not be spin-coated onto POE. In this case, the c-PE or d-PVC samples dissolved in toluene are spin-coated onto PVC sheets following the procedure used in Chapters II and III. To make PVC sheets, PVC (20 g) powder was stabilized with 4 phr of methyltin mercaptide (Mark 1900).^{106, 107} This powder was added to a preheated mold and placed in a Carver Laboratory Press Model C set to 200°C . The sample was left in the melt press for 3 minutes without pressure, then for 2 min with an applied pressure of 1 metric ton. This PVC sheet was left to cool below its T_g ($\sim 85^\circ\text{C}$) in the mold to prevent curling. The polyolefin elastomer (POE) was separately melted into a strip mold with dimensions 10 mm x 65 mm x 2.3 mm at 200°C for 5 minutes in the Carver Press.⁶⁴

The compatibilizer (2.5 wt%) was then dissolved in toluene overnight at 85°C to make a 2 g homogeneous solution.^{66, 108} The solution was then spin-coated onto the PVC sheet at 2500 rpm for 20 seconds. The coated sheet was left overnight for the toluene to evaporate. The coated PVC was then cut into 4-5 strips with dimensions 10 mm x 65 mm x 2.3 mm using a Dremel 4300. The POE strip was laid on top of the coated PVC in a trilayer mold at 200°C .

For both the THF and toluene solvent procedures, the trilayers were heated in the Carver melt press for 15 minutes under minimal pressure. This mold was removed from the melt press but left to slowly cool on the hot metal plate until the temperature of the sample was below the T_m of POE ($\sim 60^\circ\text{C}$). The samples were then removed from the mold and left to cool to room temperature. The cooled trilayer samples were peeled using a combination T+U peel test on an Instron Model 5965 Universal Tester (5KN) at 10 mm/min. Interfacial adhesion (G_a) is calculated using the force (F) required to peel the layers divided by the width (w) of the sample at the point of data collection, $G_a = \frac{F}{w}$.⁶⁴ The results reported are the average of 6-10 trials for each compatibilizer analyzed.

Differential Scanning Calorimetry (DSC):

Crystallinity and thermal transitions of d-PVC and c-PE were analyzed using a TA Instruments Q-2000 DSC. To determine the thermal characteristics of the individual components, 5-10 mg of material was heated and cooled through two cycles from 20 - 150 $^\circ\text{C}$ at 10 $^\circ\text{C}/\text{min}$. The first cycle was completed to remove the thermal history of the pure material. The DSC curve that emerges from the second cycle of each sample was analyzed to determine the heat of fusion (ΔH_f) of the polymer, T_g , and T_m .⁶⁴

Results and Discussion

The characteristics of the dechlorinated PVCs provided by the Fieser group at the University of Southern California (USC) are listed in **Table 5.1**. The number following d-PVC refers to the chlorine content determined by ^1H NMR using the same procedure shown in Figure 2.6 and Eqn 2.1 in Chapter II.⁶⁶ The crystallinity of the semicrystalline

Table 5.1. Overview of d-PVC samples from USC. D-PVC chlorine content was calculated based on ^1H NMR spectra. Starting M_n and initiator concentration provided by collaborators. All other data was collected at UTK.

Sample	Chlorine Content	ΔH_f	Block Number	Starting M_n	Initiator Conc.	Reaction Temp.	Average Interfacial Adhesion (G_a)	
	per 100 Carbons	(J/g)		(kDa)	mol ratio	($^{\circ}\text{C}$)	THF (J/m 2)	
d-PVC44	44	0	54	99	0.75	80	1213	± 313
d-PVC42	42	0	23	99	0.5	80	4635	± 1207
d-PVC42*	42	0		99	0.75	80	3110	± 896
d-PVC41*	41	0	28	99	0.75	40	2898	± 604
d-PVC40	40	0	29	46	0.5	80	4430	± 519
d-PVC37	37	0	30	99	0.5	80	4558	± 485
d-PVC35*	35	0	44	99	0.75	40	4054	± 354
d-PVC32	32	0	25	99	0.5	80	5559	± 512
d-PVC32 (2)	32	0	70	99	0.75	80	5380	± 869
d-PVC26*	26	1.79	48	99	0.75	80	5640	± 1243
d-PVC22	22	8.26	54	99	0.75	80	6108	± 1069
d-PVC17	17	8.80	24	99	0.5	80	6289	± 446
d-PVC16	16	-	18	46	0.5	80	5407	± 637
d-PVC14*	14	10.9	18	99	0.5	80	2803	± 500
d-PVC12	12	11.6	17	99	0.5	80	4180	± 761
d-PVC9*	9	29.1	18	99	0.75	40	1625	± 344
d-PVC6	6	39.0	19	99	0.75	80	3616	± 514
d-PVC3	3	40.0	7	99	0.5	80	3640	± 973
d-PVC3 (2)	3	39.3	12	99	0.75	80	1908	± 734
d-PVC2	2	50.7	5	99	0.75	80	2834	± 353

*Not previously published

PE regions of the d-PVC increases with the extent of dechlorination as shown in **Figure 5.2**, which plots the extent of crystallinity of the d-PVC as a function of mol% Cl. This relationship was also observed for the polymerized chlorinated cyclooctenes investigated in Chapter III. The ^1H NMRs of the d-PVCs can be found in the appendix.

Impact of Chain Length on Interfacial Adhesion

Two of the d-PVC compatibilizers, d-PVC40 and d-PVC16, have a starting number-average molecular weight (M_n) of 46 kDa PVC, while the rest of the samples have a starting M_n over twice that, at 99 kDa. d-PVC37 is dechlorinated under comparable conditions to d-PVC40, but with the 99 kDa PVC starting molecular weight. The interfaces that are compatibilized with this higher M_n material have an interfacial adhesion that is 128 J/m^2 greater than the interface that is compatibilized with the lower d-PVC40. The d-PVC16 sample is dechlorinated under similar conditions as d-PVC17, but has a lower molecular weight. The interface that is compatibilized with d-PVC-17 has an interfacial adhesion that is 882 J/m^2 , greater than that of the interface that is compatibilized with the lower molecular weight d-PVC-16 compatibilizer. Both these results indicate that an increase in compatibilizer chain length improves the effectiveness of the compatibilizer to strengthen the PVC/POE interface. This is consistent with entanglement of the compatibilizer with the homopolymer is an important process in strengthening these interfaces.^{41, 133}

Possible Impact of Copolymer Architecture and Composition on Interfacial Adhesion

Figure 5.3 presents the interfacial adhesion as a function of chlorine content of the d-PVC, which comes from **Table 5.1**. In **Figure 5.3**, the purple dots represent d-PVC

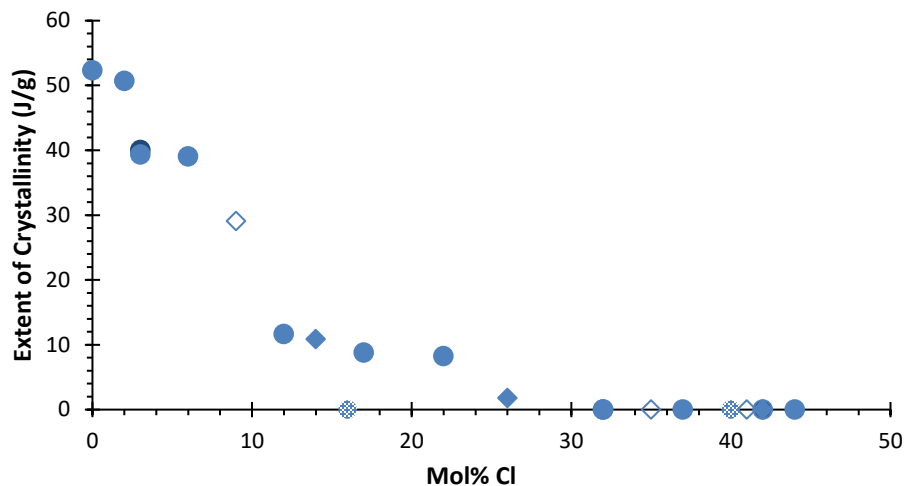


Figure 5.2. Relationship between the extent of crystallinity (heat of fusion) and the chlorination of d-PVC. Open shapes were dechlorinated at 40 °C. Patterned filled samples have a starting M_n of 46 kDa. All other samples have a starting M_n of 99 kDa and were dechlorinated at 80 °C. Diamonds represent unpublished samples.

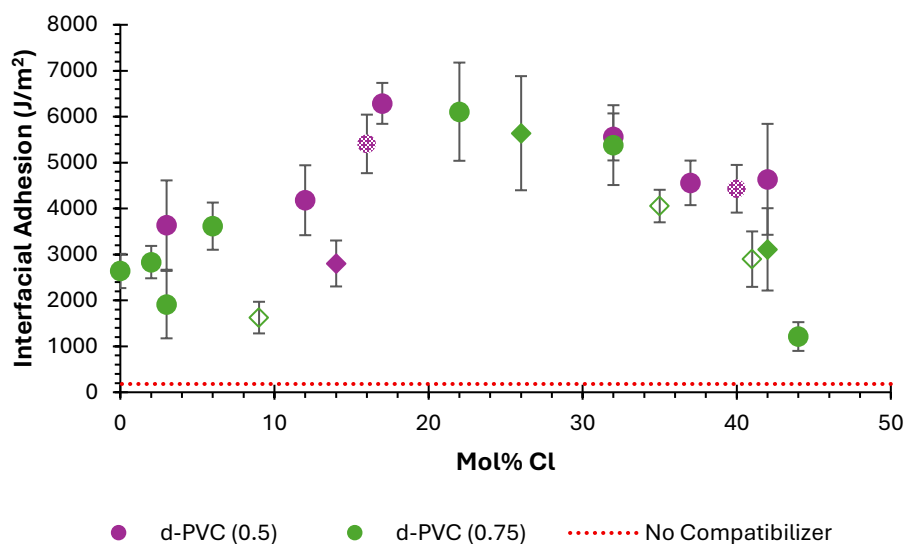


Figure 5.3. Impact of chlorine content of d-PVC compatibilizer on the overall interfacial adhesion. Open shapes were dechlorinated at 40 °C. Patterned filled samples have a starting M_n of 46 kDa. All other samples have a starting M_n of 99 kDa and were dechlorinated at 80 °C. Diamond samples are unpublished data. Error bars represent one standard deviation from the average.

that is formed with 0.5 mol% initiator concentration, and the green dots represent d-PVC that is formed with 0.75 mol% initiator concentration. Samples that have the same chlorine content, but were synthesized using either 0.5 or 0.75 mol% initiator concentration have a (2) assigned to the sample with the higher initiator concentration in **Table 5.1**. These are d-PVC32(2) and d-PVC3(2). For the compatibilizers d-PVC32 and d-PVC32(2), the interfacial adhesion difference is only 179 J/m² of the two d-PVC, which is within the standard deviation of both samples. For the sample that was dechlorinated to only 3 mol% Cl, there is a significant difference in compatibilizer efficiency with the d-PVC that is formed with 0.5 mol% initiator concentration creating an interface that is nearly twice the interfacial adhesion of the d-PVC that synthesized with the 0.75% initiator concentration. This indicates that the amount of initiator in the dichlorination reaction may have an impact on the structure of the compatibilizer, as a d-PVC synthesized with a higher concentration of initiator leads to reduced interfacial adhesion.

In a previous study by Dr. Fieser, they found that at ~100% dechlorination, the branching content increased with an increase in initiator concentration.⁴⁷ This was determined to be due to carbocation rearrangement, resulting in 40 out of 49 branches per 1000 carbons consisting of methyl groups according to ¹³C NMR. Further studies will need to be performed on the branching content and molecular weight of d-PVC at different reaction times to more thoroughly determine the impact of initiator content on the polymer structure. This initial data indicates that d-PVC3(2) has a higher branching content and undergoes greater carbocation rearrangement than d-PVC3, where this

change in molecular structure to negatively impact the compatibilizer efficiency of the polymer.

Figure 5.3 also shows that when evaluating the impact of chlorine content, the d-PVC with ~17 mol% Cl creates the strongest interface. This is consistent with previous studies that examined the ability c-PE to strengthen PVC/POE interfaces.^{64, 66} This is interpreted to indicate that there is the minimum required miscibility of the compatibilizer with PVC to maximize the miscibility with the POE phase. This is interesting as it was expected that the chlorinated segment of d-PVC may have better miscibility with PVC compared to the chlorinated segments of c-PE.

Determination and Impact of Compatibilizer Block Length

The ability of a compatibilizer to form strong entanglements at the interface is dependent on both block length and block number of the copolymer. The block number represents the possible number of “stitches” or chains crossing the interface that can form at the POE/PVC interface. As the number of stitches increases, so does the strength of the interface, thus one would expect the interfacial adhesion to increase with block number. This trend is generally observed for the d-PVCs as shown in **Figure 5.4**. The one outlier is the interface that is strengthened with d-PVC44, which has a high block number but a low PE composition. Thus, it appears that the composition of the compatibilizer is a more important molecular characteristic than the block number in determining the effectiveness of a d-PVC molecule as a compatibilizer. The block number of the d-PVC compatibilizers is determined using Eqn (5.1) using the concentration of C-C(Cl)-C-C (VE) as determined by ¹H NMR, where this signature indicates a transition from PVC-

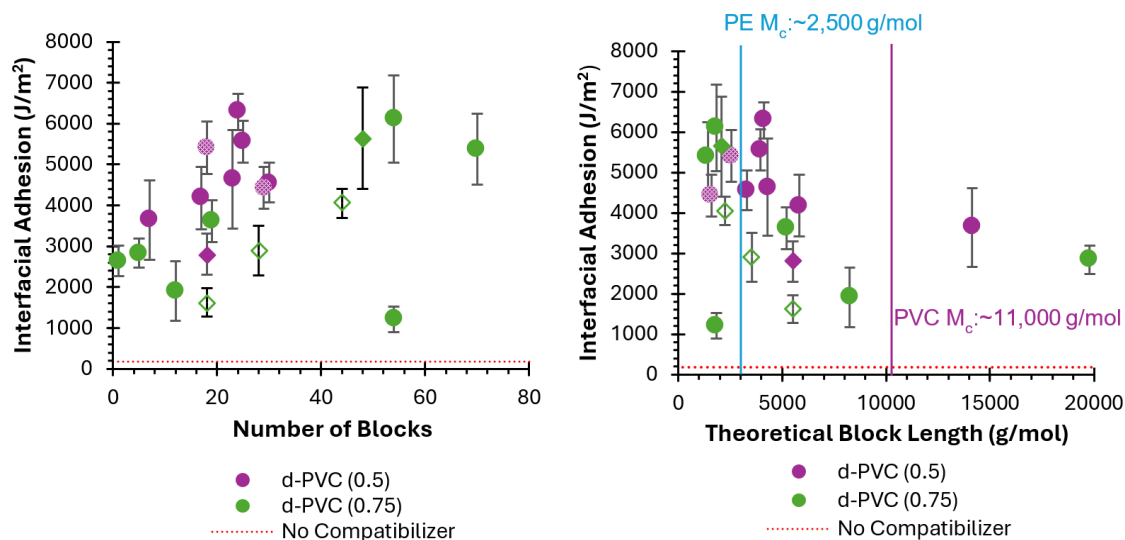


Figure 5.4. Impact of block number (left) and theoretical block length (right) on interfacial adhesion for d-PVC. Theoretical block lengths based on the starting M_n and the average block number for d-PVC. Open shapes were dechlorinated at 40 °C. Patterned filled samples have a starting M_n of 46 kDa. All other samples have a starting M_n of 99 kDa and were dechlorinated at 80 °C. Diamond samples are unpublished data. Error bars represent one standard deviation from the average.

like to PE-like monomer runs.¹⁶⁴ The initial molecular weight (M_n) is then divided by the block number to give a theoretical block length. Previous research has found that blocks that are at least twice the molecular weight of entanglement (M_e), or the critical molecular weight (M_c), fully entangle with the homopolymer. The M_e for polyethylene is approximately 1,250 g/mol, and the M_e for PVC is ~5,400 g/mol.^{65, 128, 165} All of the samples tested have a theoretical block length greater than the molecular entanglement of PE. Due to the significant majority of the samples having the same starting molecular weight, as the theoretical block length increases, the block number decreases. An increase in interfacial adhesion is observed in **Figure 5.4** once the block length of the d-PVC passes the threshold for PVC molecular entanglement. These results further support that it is necessary to prioritize the entanglement capabilities of compatibilizers in this amorphous/semicrystalline system to form an effective compatibilizer .

$$\# \text{ blocks} = \frac{M_n \text{ PVC}}{MW \text{ PVC monomer}} * \frac{\frac{VE}{EV}}{VV + \frac{VE}{EV} + EE} + 1 \quad \text{Eqn (5.1)}$$

Samples where the hydrodechlorination of PVC was performed at the lower reaction temperature of 40 °C include d-PVC41*, d-PVC35*, and d-PVC9*. The interfacial strengths of the PVC/POE interface strengthened with these copolymers are designated with open diamonds in **Figure 5.3**. Overall, the interfaces formed from these samples seem to have a slightly lower interfacial adhesion relative to those that are strengthened with d-PVC that is dechlorinated at the higher reaction temperature of 80 °C. This change in reaction temperature creates copolymers that vary in structure, where for materials with a starting M_n of 46 kDa, there is an increase in block length (or

blockiness) with decreasing reaction temperature. However, the block length of the 99 kDa samples studied in this paper do not vary at similar reaction conditions.¹⁶⁴ We theorize that this loss of control of blockiness with reaction temperature is due to solubility differences in the reaction solvent dichloromethane (DCM), since the lower molecular weight PVC is significantly more soluble in DCM. This indicates that future studies should focus on lower molecular weight materials to obtain better control over block length and determine their specific impact on compatibilizer efficiency.

Comparison of Dechlorinated PVC and Commercial Materials

To further explore these results, we referred to the ability of commercially available chlorinated polyethylenes to strengthen the PVC/POE interface that is previously described in this document. This comparison is a bit complicated, because of the difference in the solubility of the commercial c-PEs and the d-PVC. The dechlorinated PVCs are not soluble in toluene, while only the c-PEs with higher chlorination are soluble in THF. This difference in solubility can be understood by examining the Hansen solubility parameters (δ) of these components that collected from literature and reported in **Table 5.2**. Studies by Huang et al have shown that as the chlorine content in c-PE increases, so does the solubility parameter.¹⁶⁶ PVC is soluble in THF at room temperature and has similar solubility parameters: 21.55 and 19.5 (J/cm^3)^{1/2}, respectively.^{16, 167}

As the chlorination of c-PE increases, the solutions required more heat to dissolve in toluene at 2.5 wt%. As the d-PVC loses chlorination and becomes closer in structure to PE from PVC, the solutions also requires higher temperatures to dissolve in THF. The

Table 5.2. Hansen solubility parameters for the materials relevant to this study. All solubility parameters are in (MPa)^{1/2}.

Material	Total Hansen Solubility Parameter, δ_{tot}
PVC	21.55 ¹⁶
LLDPE	17.35 ¹⁶
c-PE	18.66 - 26.01 ¹⁶⁶
Toluene	18.2 ¹⁶⁷
THF	19.5 ¹⁶⁷

~100% dechlorinated PVC sample is not soluble in THF but can dissolve in toluene. This is important to keep in mind when analyzing the interfacial adhesion values in **Table 5.3** for the c-PEs that were spin-coated in either THF or toluene as the solubility of the polymer can impact compatibilizer film thickness, where thicker films for stronger interfaces. This translates to samples that are spin-coated from a better solvent will exhibit a higher interfacial adhesion.

Figure 5.5 presents the interfacial adhesion of all the compatibilized interfaces examined in this study. These films are fabricated from both solvents for both the commercial c-PE and the synthesized d-PVC. Regardless of the solvent from which the compatibilizer is deposited, the change in interfacial adhesion as a function of %Cl remains constant, even though the interfacial adhesion of the samples deposited from THF is significantly lower. None of the c-PEs dissolved in either solvent reached the same average interfacial adhesion as the interfaces that are compatibilized with dechlorinated PVC. This indicates that the improved miscibility of the d-PVC with PVC creates a stronger interface and attains a better compatibilizer efficiency than the interfaces that are compatibilized with suspension chlorinated PE.¹⁶⁸

The collaborators at USC also attempted to use plastic waste to synthesize d-PVC compatibilizers. In **Table 5.4** and **Figure 5.6**, it is observed that the interfaces that are compatibilized with these d-PVC improved the interfacial adhesion by at least 5x over that of the uncompatibilized interface. However, these materials were not pure, and particles were found to remain on the POE sheet after spin coating, thereby increasing surface roughness and artificially enhancing interfacial adhesion. For example, the d-PVC that emerged from the vinyl record retained the carbon black additive, leaving black

Table 5.3. Commercially available c-PE spin-coated with either THF or toluene solutions to get interfacial adhesion.

Sample	Chlorine Content mol% Cl	ΔH_f (J/g)	Average Interfacial Adhesion			
			THF (J/m ²)		Toluene (J/m ²)	
23/9B	23	9.31			4397	±1242
23/27B	23	26.7	2918*	±432	2970	±831
18/36B	18	35.8	3342*	±870	4870	±1002
19/43B	19	42.6			5564	±2496
14/19B	14	19.3	2057*	±545	3158	±691
10/27B	10	27.0			3759	±1337
23/R	23	2.70	2440*	±324	4244	±1468

*Not previously published

Table 5.4. Characterization of dechlorinated waste PVC and its efficiency as a compatibilizer.

Sample	Chlorine Content per 100 Carbons	ΔH_f (J/g)	Initiator Conc. mol ratio	Reaction Temp. (°C)	Average Interfacial Adhesion	
					THF (J/m ²)	
Vinyl Record	40	0	0.5	80	1202	±179
Stadium Bag	44	0	0.5	80	1309	±289
Shower Curtain	48	0	0.5	80	1344	±228
Chase Credit Card	39	4.98	0.5	80	2194	±644
Saline Bag	49.5	0	0.75	80	1078	±258
USC Credit Card	44	0	0.75	80	1049	±269
Toy Lizard	11	12.97	0.75	80	1976	±231
Toy Hippo	8	13.94	0.75	80	1976	±600

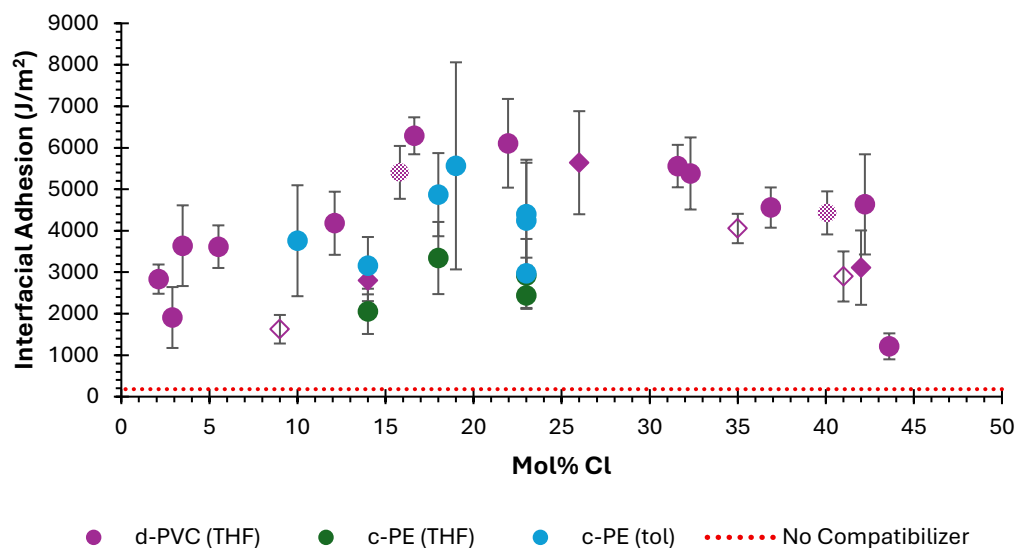


Figure 5.5. Interfacial adhesion for both c-PE and d-PVC spin-coated in THF and c-PE in toluene. Open shapes were dechlorinated at 40 °C. Patterned filled samples have a starting M_n of 46 kDa. All other samples have a starting M_n of 99 kDa and were dechlorinated at 80 °C. Diamond samples are unpublished data. Error bars represent one standard deviation from the average.

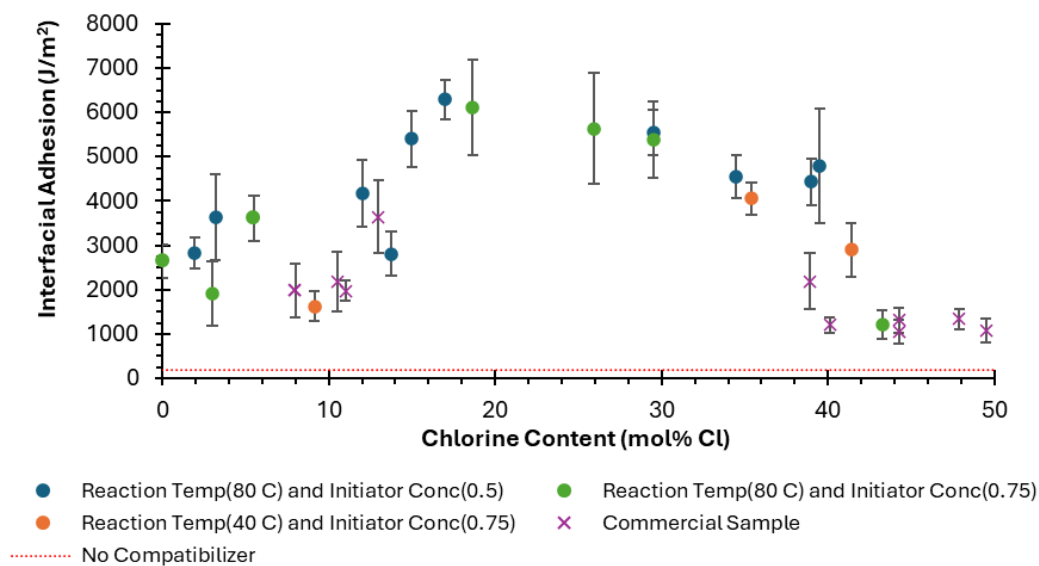


Figure 5.6. Dechlorinated waste PVC fits the plot containing the dechlorinated virgin PVC in respect to chlorine content and interfacial adhesion. Error bars represent one standard deviation from the average.

specks on the POE after coating.¹⁶⁹ These results suggest that waste materials could be repurposed as compatibilizers for the mechanical recycling of immiscible polymer blends, but care must be taken to consider the heterogeneity of the sample.

Conclusion

In this study, poly(vinyl) chloride (PVC) was hydrodechlorinated to form dechlorinated poly(vinyl) chloride (d-PVC). The ability of these materials to act as compatibilizers of the PVC/polyolefin elastomer (POE) interface was studied. These results shows that the d-PVC were slightly more efficient compatibilizers relative to commercially available chlorinated polyethylenes (c-PE) even though these c-PE have evidence of co-crystallization occurring in the POE phase. This is interpreted to indicate that improving miscibility and therefore entanglement of the compatibilizer with the homopolymers in an amorphous/semicrystalline blend is crucial to performing as an effective compatibilizer. These d-PVCs can also reach a significantly wider range of chlorination compared to c-PEs, which provides a wider parameter space to create effective compatibilizers for this system.

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CHAPTER VI: CONCLUSION AND FUTURE OUTLOOKS

Conclusions

Chapter II focused on how the individual interactions between the compatibilizer and the homopolymers could influence the overall system. It was determined that interfacial adhesion between a semicrystalline chlorinated polyethylene (c-PE) compatibilizer and amorphous polyvinyl chloride (PVC) was improved by modifying the composition and blockiness. Essentially, samples with higher chlorination and a blocky structure exhibited the best performance. If either structure or composition wasn't optimized, then there was a diminishment in the strength of the interface. The semicrystalline polyolefin elastomer (POE)/compatibilizer interfaces, however, exhibited a maximum chlorine content at ~19 mol% Cl, followed by a sharp drop-off. This indicates that a high chlorine content impacts miscibility with POE and explains why the overall system also experiences a decrease in interfacial adhesion beyond this point. The POE/c-PE bilayer system does see a significant improvement in interfacial adhesion with increasing relative blockiness and crystallinity. The impact of crystallinity on the semicrystalline/semicrystalline interface was investigated further using x-ray scattering and differential scanning calorimetry (DSC). Both wide-angle x-ray scattering and DSC curves showed shifts in polyethylene crystallization with the addition of compatibilizers. These changes became more pronounced as the efficiency of the compatibilizer increased. This is consistent with co-crystallization occurring in the POE phase. Overall, Chapter II provides evidence that entanglement into both the PVC and POE phases is required to improve interfacial adhesion. It is hypothesized that the compatibilizer will

entangle with the phases during heating, and this entanglement is required for co-crystallization to occur during cooling of the samples.

Chapter III expanded on this by investigating synthesized gradient chlorinated cyclooctene/cyclooctene copolymers ($\text{Cl}_2\text{COE-r-COE}$) as compatibilizers instead of commercially available chlorinated polyethylene (c-PE). This allowed for direct control over composition, structure, and molecular weight. While gradient copolymers are not as effective compatibilizers as block copolymers, they have been shown to demonstrate better performance than random or diblock copolymers. There was an increase in interfacial adhesion of samples with 75 mol% cyclooctene as the molecular weight increased. This study concluded that increasing the PE-like content resulted in the best interfacial adhesion. This is further evidence that optimizing entanglement with POE is necessary before optimizing the ability to co-crystallize.

A fully semicrystalline polymer blend system is investigated in Chapter IV. In this system, high-density polyethylene and polypropylene polymer blends are compatibilized with commercially available ethylene-propylene random copolymers (EPR) and an ethylene/1-octene random copolymer (POE). These copolymers are widely available due to their commercial use as thermoplastic polyolefins (TPOs) in applications such as roofing and car parts. It was determined that there was an improvement in overall toughness with increasing polyethylene-like segments and molecular weight in both the HDPE- and iPP-rich samples. These materials are synthesized without control over tacticity, so the polypropylene segments in these EPRs are not able to readily crystallize. This indicates that there needs to be optimization of entanglement in the phase that has the potential to co-crystallize.

Chapter V revisits the PVC/POE system to investigate whether enhancing miscibility with the amorphous phase affects interfacial adhesion. In this study, dechlorinated PVC (d-PVC) was used as the compatibilizer. This study revealed similar trends to those found with c-PE but exhibited higher interfacial adhesion at the same chlorine content. The commercially available c-PEs showed no evidence of vinyl chlorine groups, as determined by NMR, which is the functional group that PVC is composed of. Since d-PVC has PVC as its base, all chlorinated segments should be more favorable to mix with PVC.

While examining several different compatibilizers for amorphous/semicrystalline polymer blends, we have determined that the most important characteristics are improving miscibility with both phases and optimizing entanglement in the phase where co-crystallization can occur. Without entanglement, the compatibilizer will be unable to successfully diffuse and co-crystallize with the homopolymer component. This was also found to be true for a semicrystalline/semicrystalline polymer blend. Overall, significant improvement in interfacial adhesion and overall polymer blend toughness can be achieved with block/blocky semicrystalline copolymer compatibilizers of higher molecular weights.

Future Outlooks

Studies into the amorphous/semicrystalline polyvinyl chloride (PVC)/polyolefin (POE) system could be expanded to include the compounding and extrusion of polymer blends and the testing of their mechanical properties. PVC is difficult to compound, and additives such as plasticizers and lubricants, in addition to thermal stabilizers, are

required to facilitate mixing and prevent the screws from clogging. This problem can be minimized through successful compatibilization, but it will require testing and a standardized procedure. Additionally, block copolymers composed of Cl₂COE and COE monomers are being synthesized by the Long group to determine how block length and block number affect interfacial adhesion between PVC and POE.

Future studies will also focus on other semicrystalline systems using synthesized copolymer compatibilizers with well-defined architectures. Specifically, multiblock copolymers that have the ability to cocrystallize with both phases will be of great interest. These studies will also expand to use compatibilizers derived from waste streams.

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APPENDICES

Appendix A: Chapter II Supporting Information

¹H NMR Spectra for Commercial c-PE

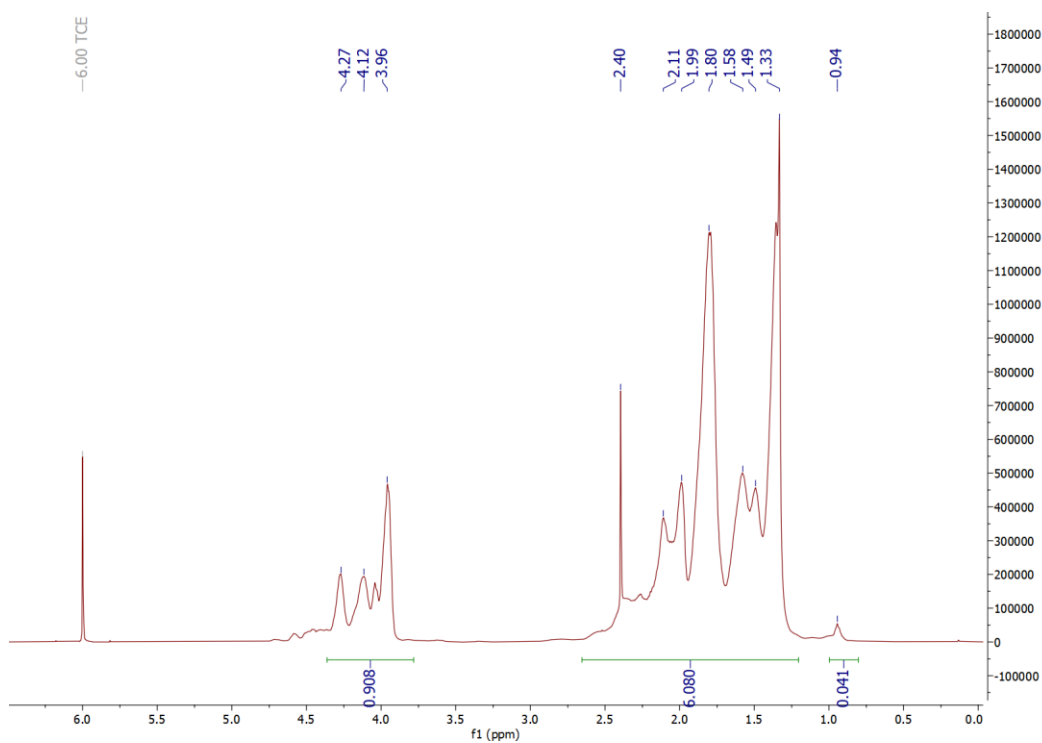


Figure S2.1. ¹H NMR spectrum of 23/R dissolved in 1,1,2,2-tetrachloroethane-d₂.

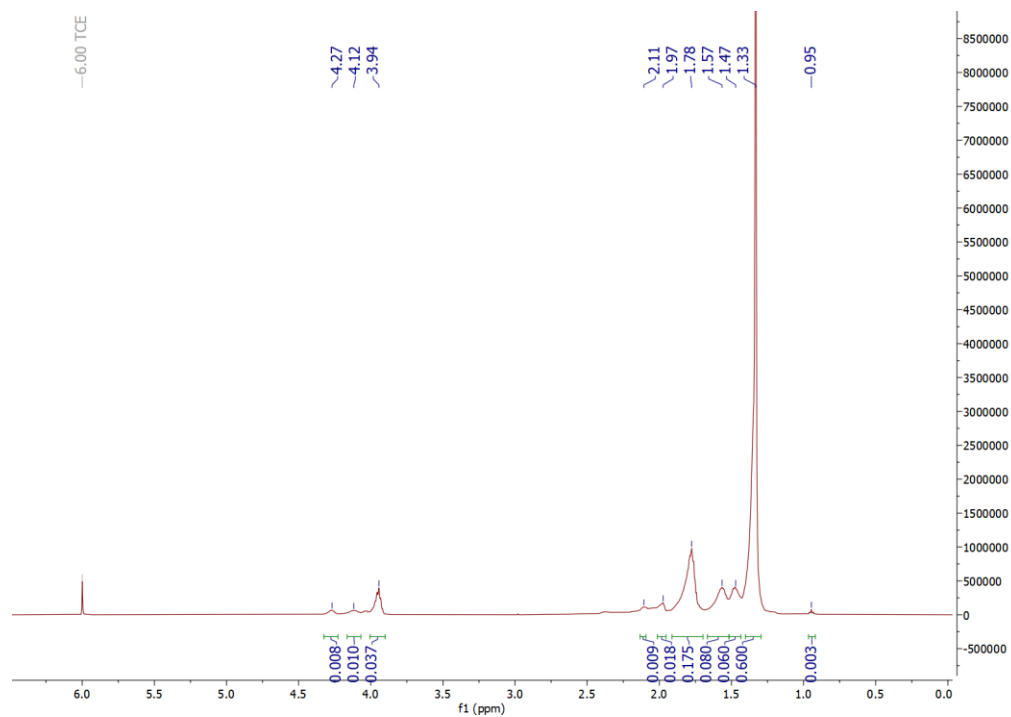


Figure S2.2. ^1H NMR spectrum of 10/27B dissolved in 1,1,2,2-tetrachloroethane- d_2 .

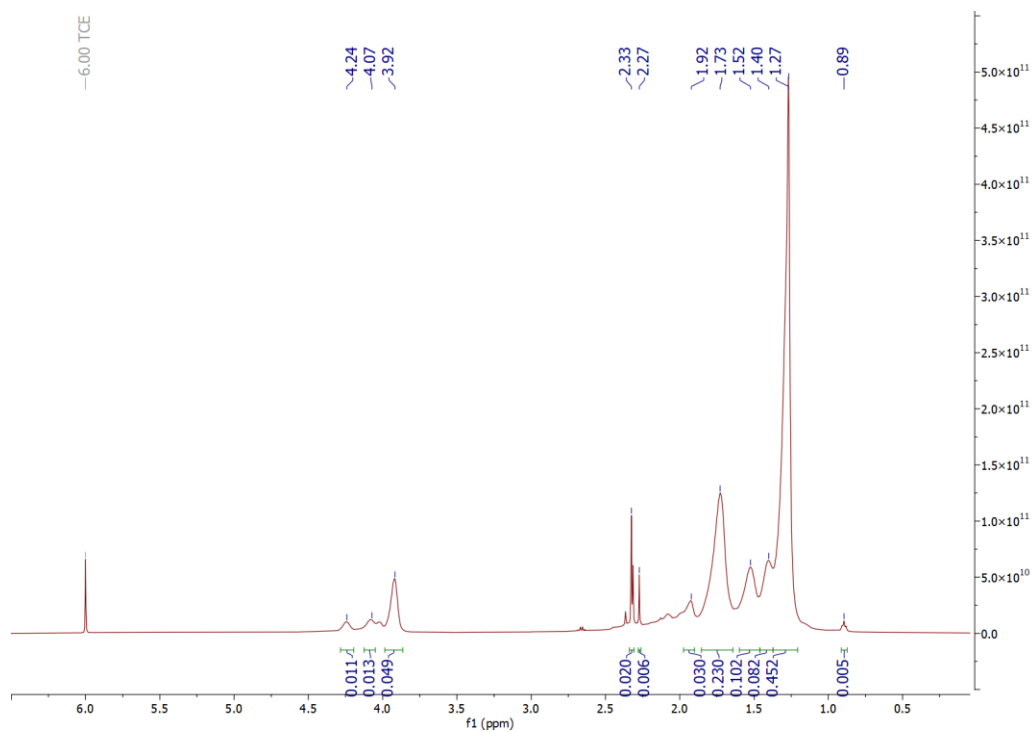


Figure S2.3. ^1H NMR spectrum of 14/19B dissolved in 1,1,2,2-tetrachloroethane- d_2 .

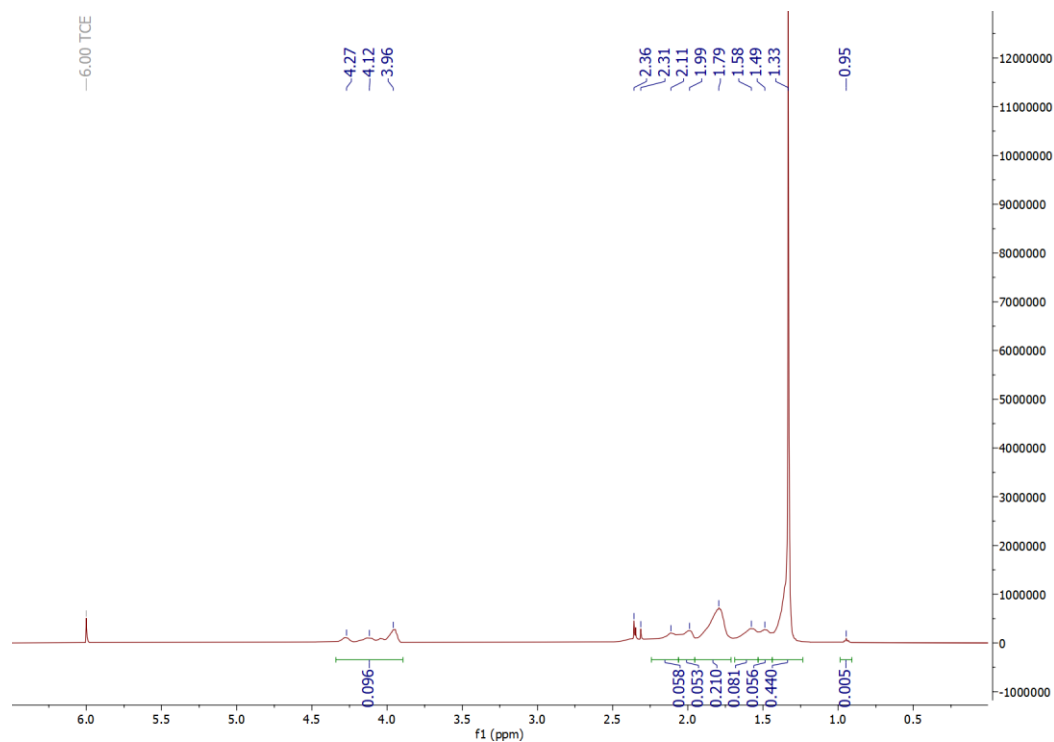


Figure S2.4. ^1H NMR spectrum of 19/43B dissolved in 1,1,2,2-tetrachloroethane- d_2 .

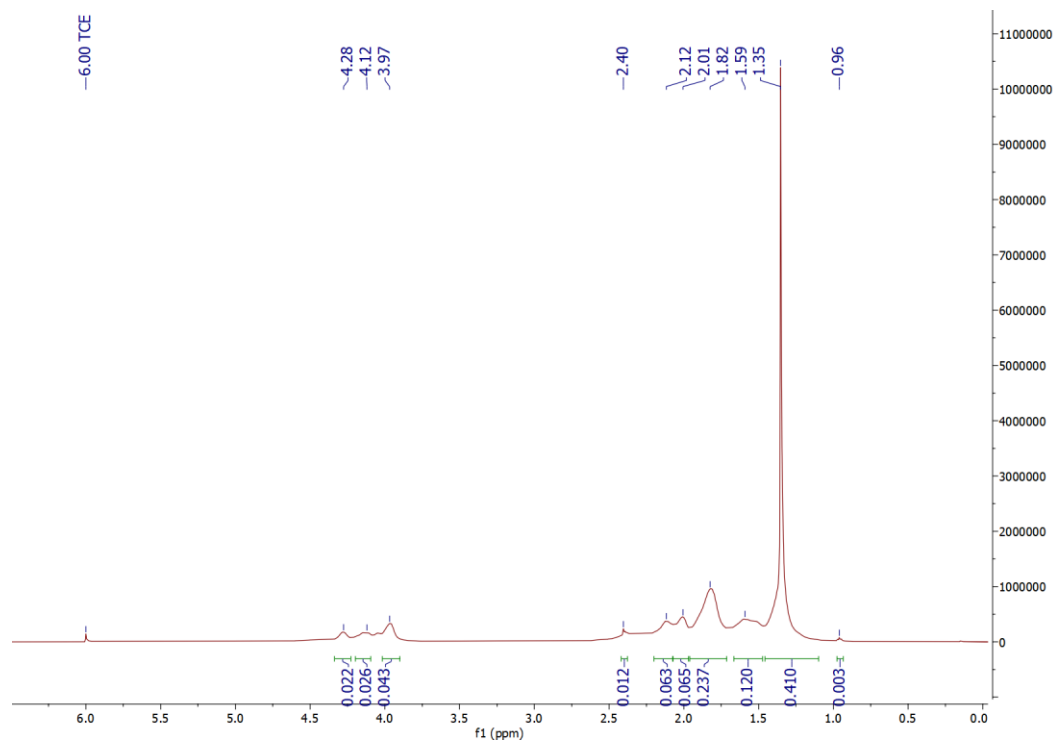


Figure S2.5. ^1H NMR spectrum of 18/36B dissolved in 1,1,2,2-tetrachloroethane- d_2 .

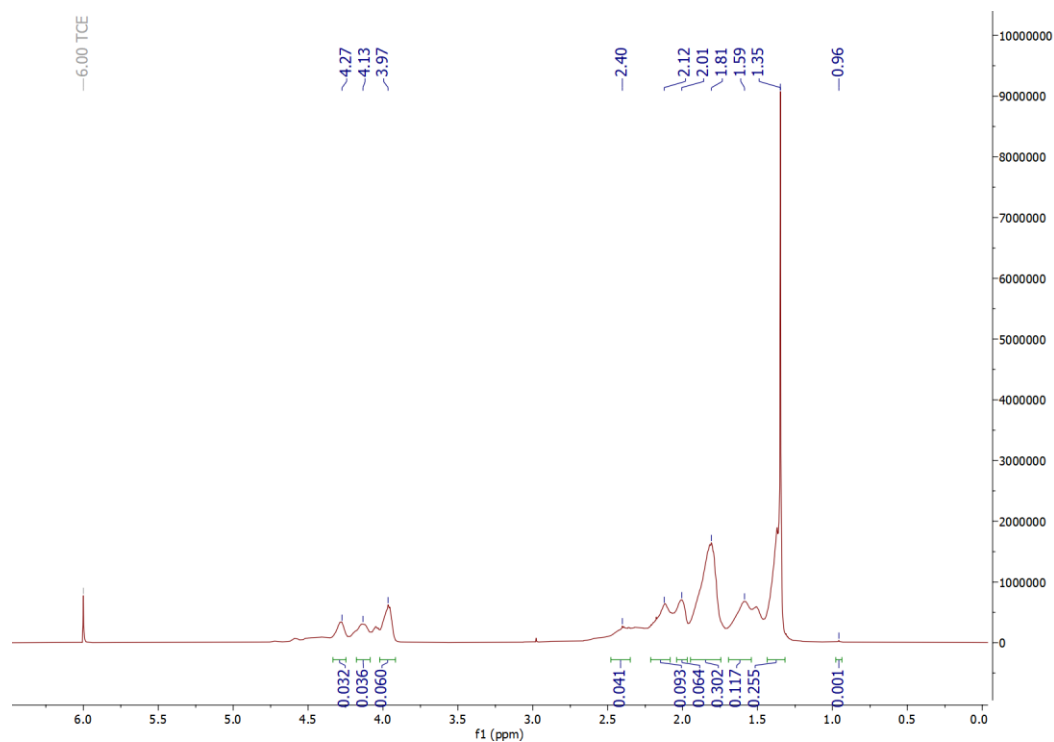


Figure S2.6. ^1H NMR spectrum of 23/9B dissolved in 1,1,2,2-tetrachloroethane- d_2 .

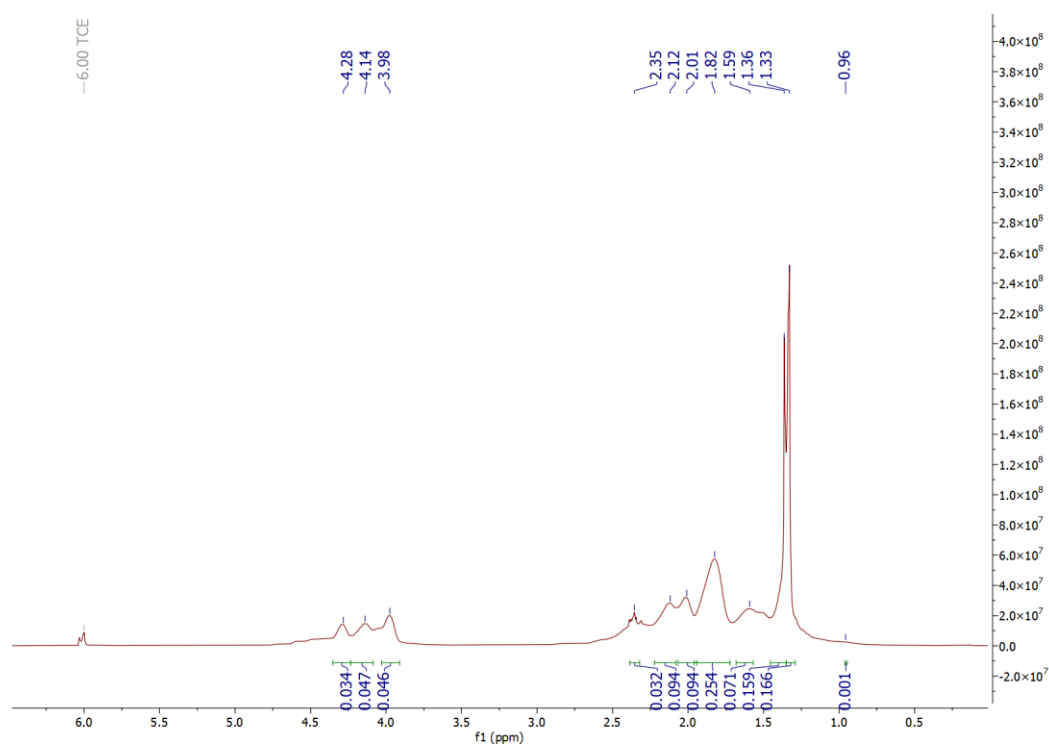


Figure S2.7. ^1H NMR spectrum of 23/27B dissolved in 1,1,2,2-tetrachloroethane- d_2 .

Chlorination calculations based on ^1H NMR integrations

$$23/\text{R}: \frac{0.908}{0.908 + 6.080/2 + 0.041/3} * 100\% = 23 \text{ mol\% Cl}$$

$$10/27\text{B}: \frac{0.055}{0.055 + 0.946/2 + 0.003/3} * 100\% = 10 \text{ mol\% Cl}$$

$$14/19\text{B}: \frac{0.073}{0.073 + 0.865/2 + 0.005/3} * 100\% = 14 \text{ mol\% Cl}$$

$$19/43\text{B}: \frac{0.096}{0.096 + 0.898/2 + 0.005/3} * 100\% = 19 \text{ mol\% Cl}$$

$$18/36\text{B}: \frac{0.091}{0.091 + 0.843/2 + 0.003/3} * 100\% = 18 \text{ mol\% Cl}$$

$$23/9\text{B}: \frac{0.127}{0.127 + 0.872/2 + 0.001/3} * 100\% = 23 \text{ mol\% Cl}$$

$$23/27\text{B}: \frac{0.128}{0.128 + 0.871/2 + 0.001/3} * 100\% = 23 \text{ mol\% Cl}$$

¹³C NMR Spectra for Commercial c-PE

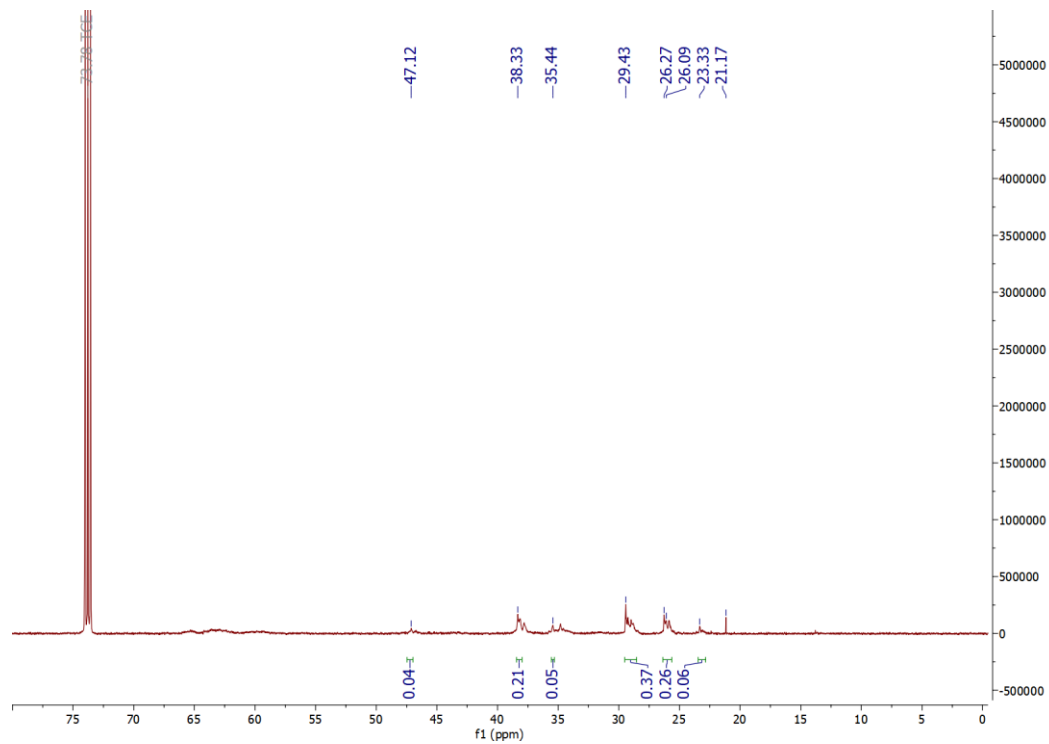


Figure S2.8. Quantitative ¹³C NMR of 23/R dissolved in 1,1,2,2-tetrachloroethane-d₂.

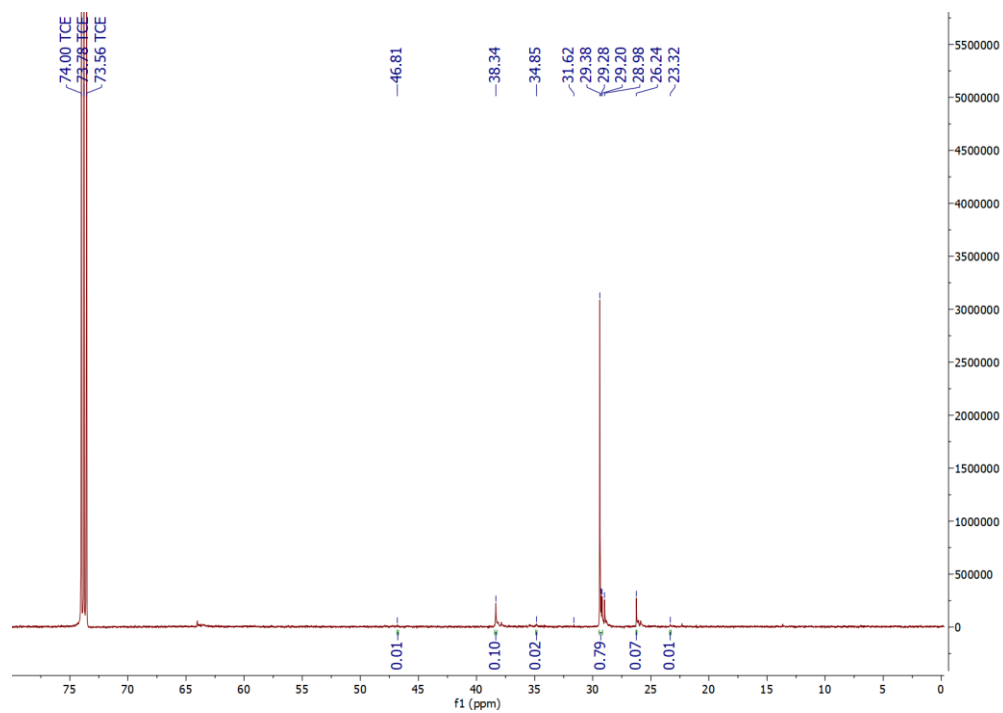


Figure S2.9. Quantitative ^{13}C NMR of 10/27B dissolved in 1,1,2,2-tetrachloroethane-d₂.

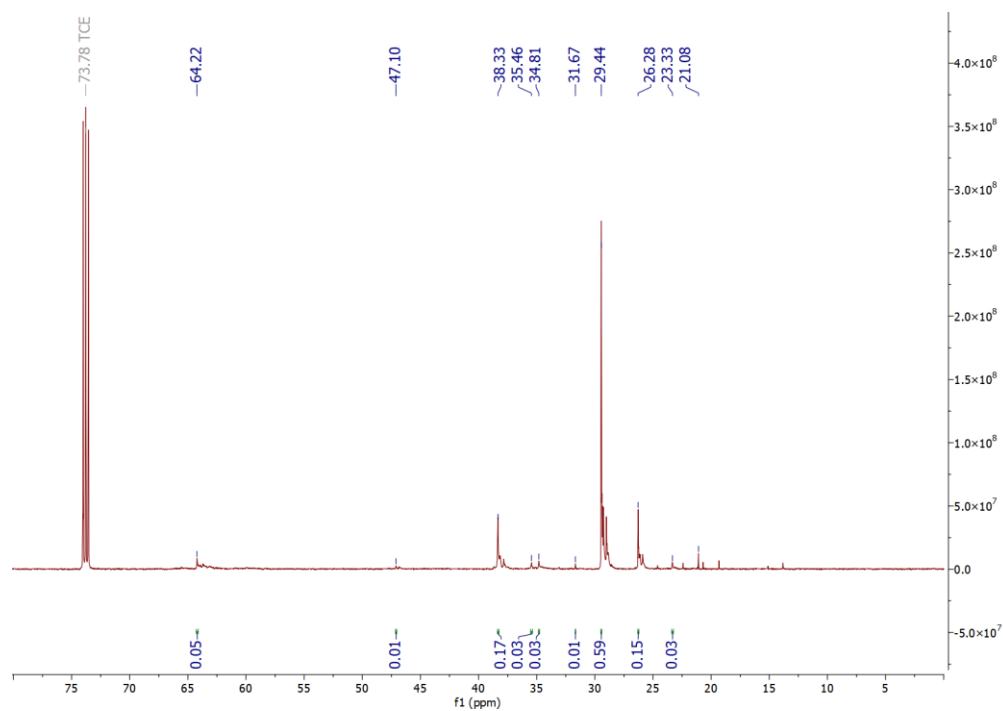


Figure S2.10. Quantitative ^{13}C NMR of 14/19B dissolved in 1,1,2,2-tetrachloroethane-d₂.

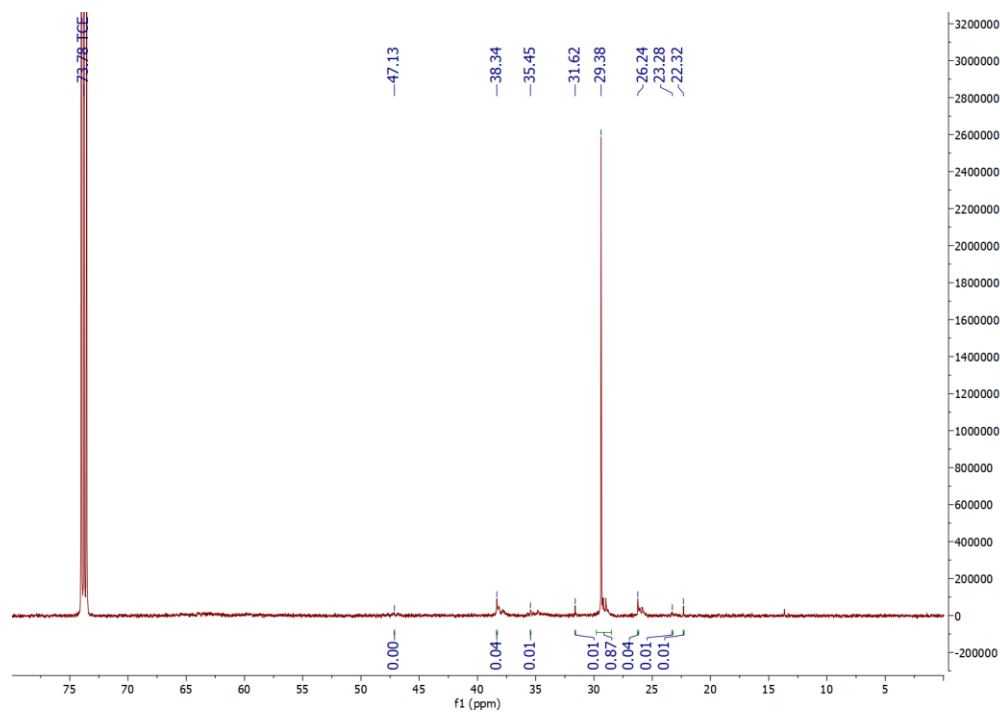


Figure S2.11. Quantitative ^{13}C NMR of 19/43B dissolved in 1,1,2,2-tetrachloroethane- d_2 .

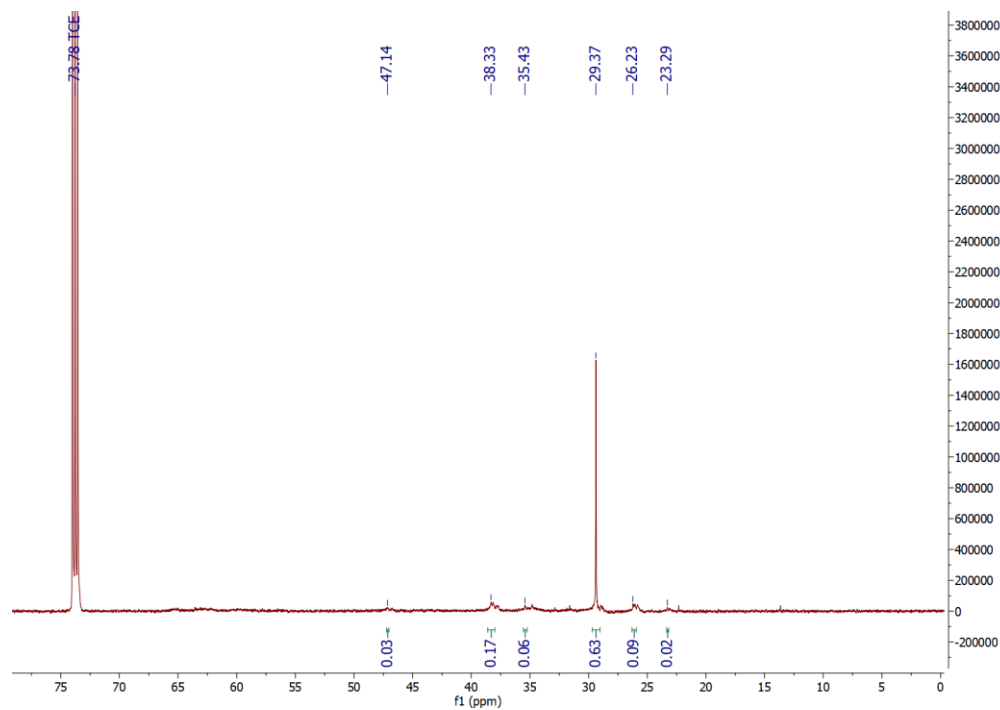


Figure S2.12. Quantitative ^{13}C NMR of 18/36B dissolved in 1,1,2,2-tetrachloroethane- d_2 .

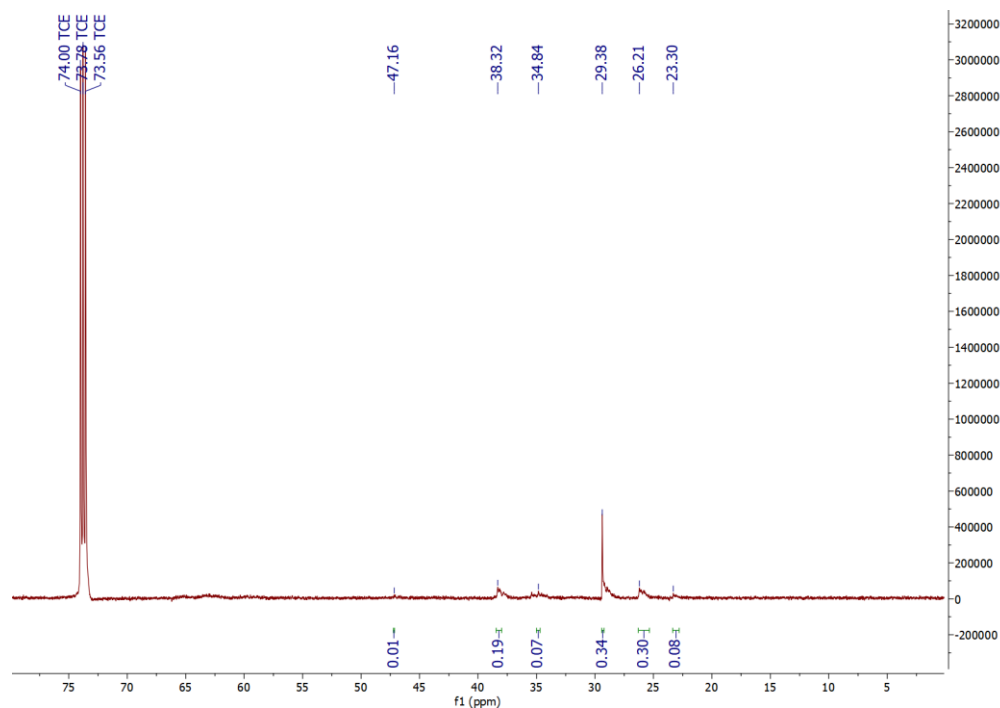


Figure S2.13. Quantitative ^{13}C NMR of 23/9B dissolved in 1,1,2,2-tetrachloroethane- d_2 .

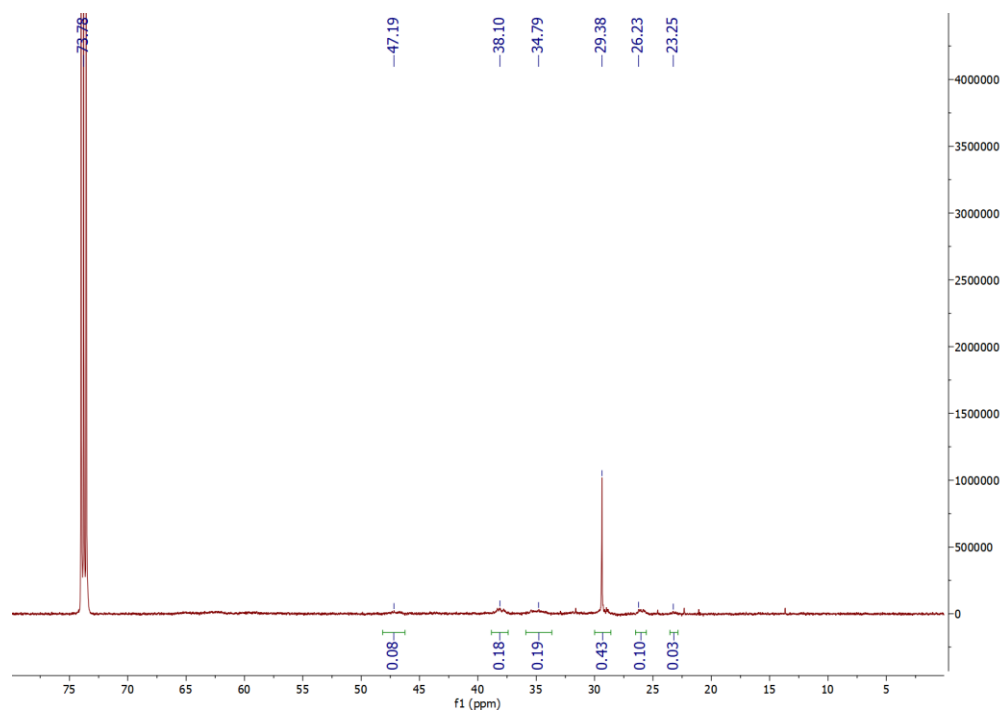


Figure S2.14. Quantitative ^{13}C NMR of 23/27B dissolved in 1,1,2,2-tetrachloroethane- d_2 .

Relative Blockiness Calculations

Peak identification and bernoullean probabilities based on Chang et. al. (Reference 51).

Chemical shifts relative to 1,1,2,2-tetrachloroethane.

Table S2.1. Bernoullean Probabilities obtained from Chang et. al.⁵¹

Pentad	Chemical Shift (ppm)	Bernoullean Probabilities
α	64	-
$\beta\beta$	47	$6x^2(1-x/2)^6$
β	38	$4x(1-x/2)^7$
$\beta\gamma$	35	$6x^2(1-x/2)^6$
ISO	29	$(1-x/2)^8$
γ	26	$4x(1-x/2)^7$
$\gamma\gamma$	23	$6x^2(1-x/2)^6$

x = mol ratio of chlorine

$$\text{Relative Blockiness(ISO)} = \frac{[\text{Expected} - \text{Observed}]}{\text{Expected}} \times 100\%$$

Sample calculation for 23/R

Table S2.2. ¹³C NMR integrations for 23/R which has a chlorine content of 23 mol% Cl.

Integrations	ISO	γ	β	$\gamma\gamma$
Expected	0.377	0.193	0.193	0.040
Observed	0.368	0.262	0.214	0.064

$$\text{Relative Blockiness(ISO)} = \frac{[0.377 - 0.368]}{0.377} \times 100\% = 2.25\%$$

Sample calculation for 19/43B

Table S2.3. ¹³C NMR integrations for 19/43B, which has a chlorine content of 19 mol% Cl.

Integrations	ISO	γ	β	$\gamma\gamma$
Expected	0.441	0.192	0.192	0.031
Observed	0.874	0.044	0.045	0.009

$$\text{Relative Blockiness} = \frac{[0.441 - 0.874]}{0.441} \times 100\% = 98.2\%$$

Peel Test Example

The interfacial adhesion of the compatibilizer is determined using a combination T+U Peel Test. An example of the raw data collected from an Instron Universal Tester (5 kN load cell) at a 10 mm/min crosshead speed is presented in **Figure S2.15**.

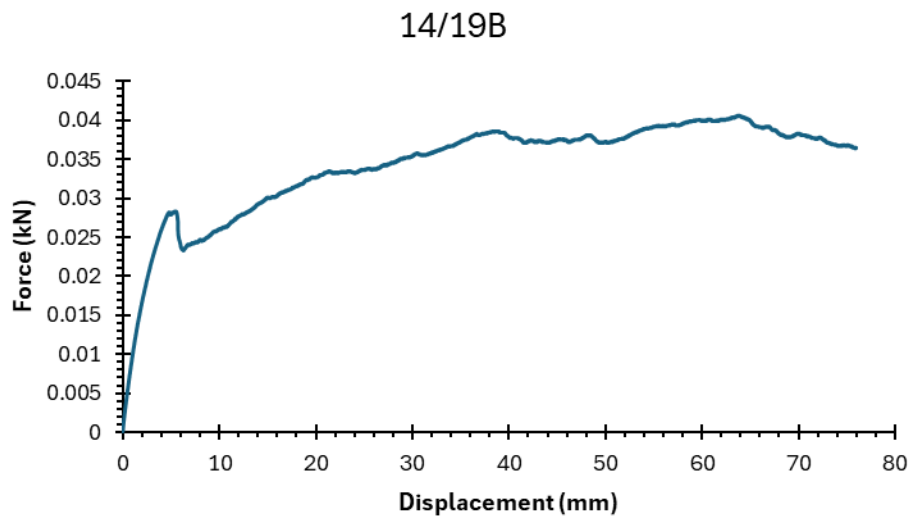


Figure S2.15. Example of the raw data collected from a combination T+U peel test (trial 3 for sample 14/19B).

DSC Curves

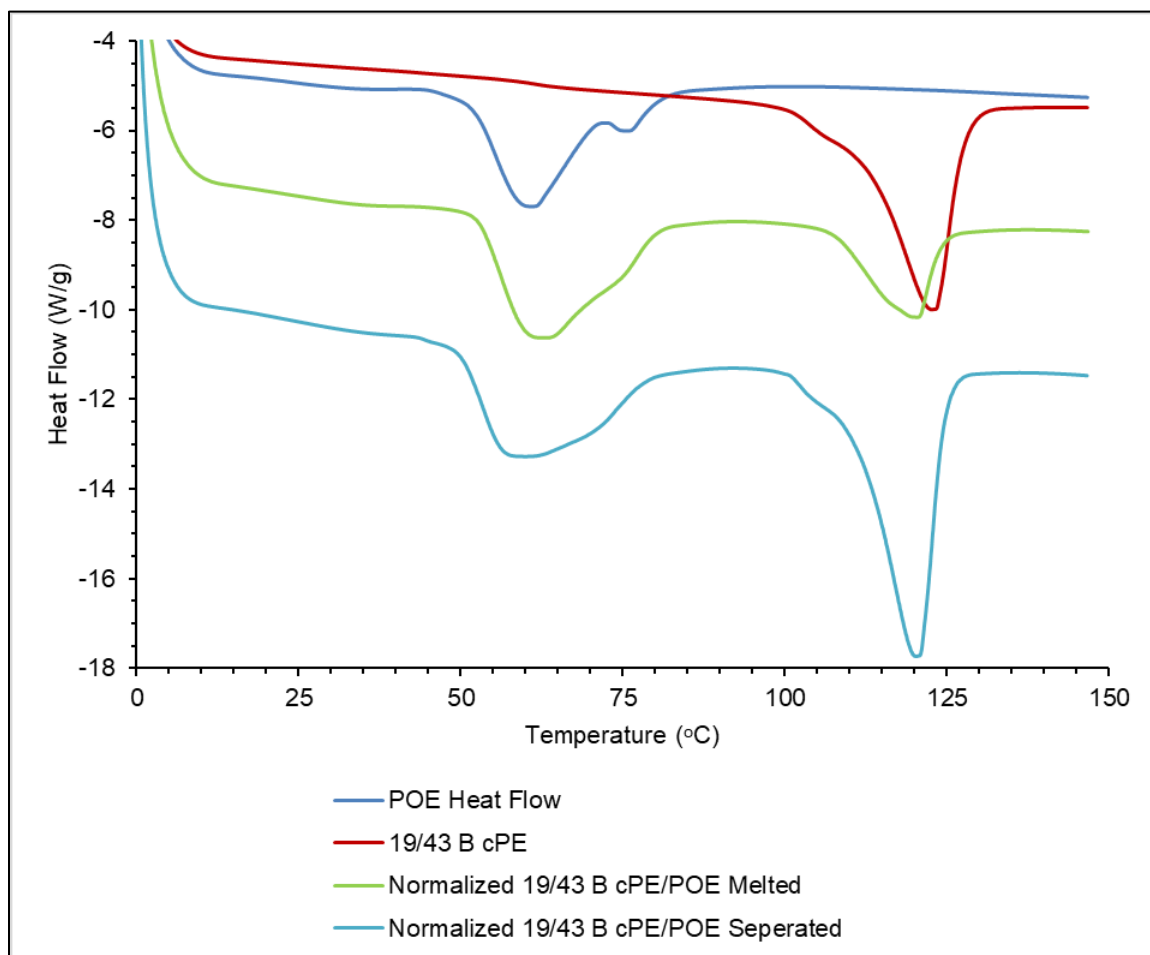


Figure S2.16. DSC curves of pure POE, cPE, melted and separated 19/43B blends.

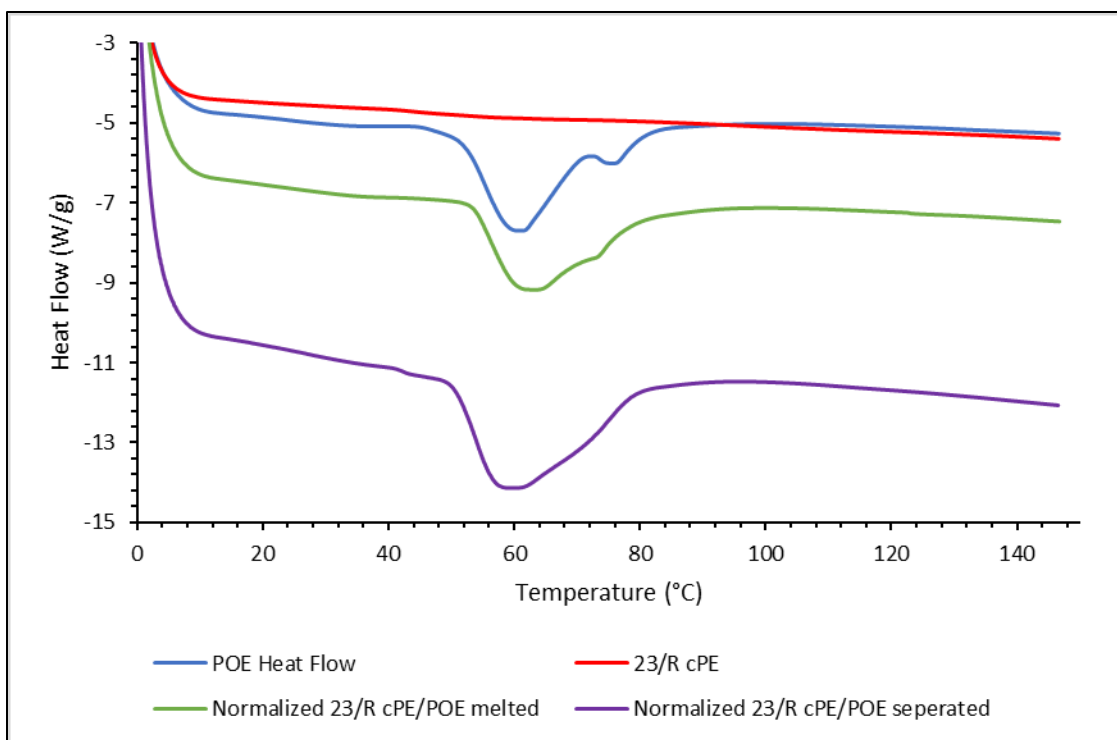


Figure S2.17. DSC curves of pure POE, cPE, melted and separated 23/R blends.

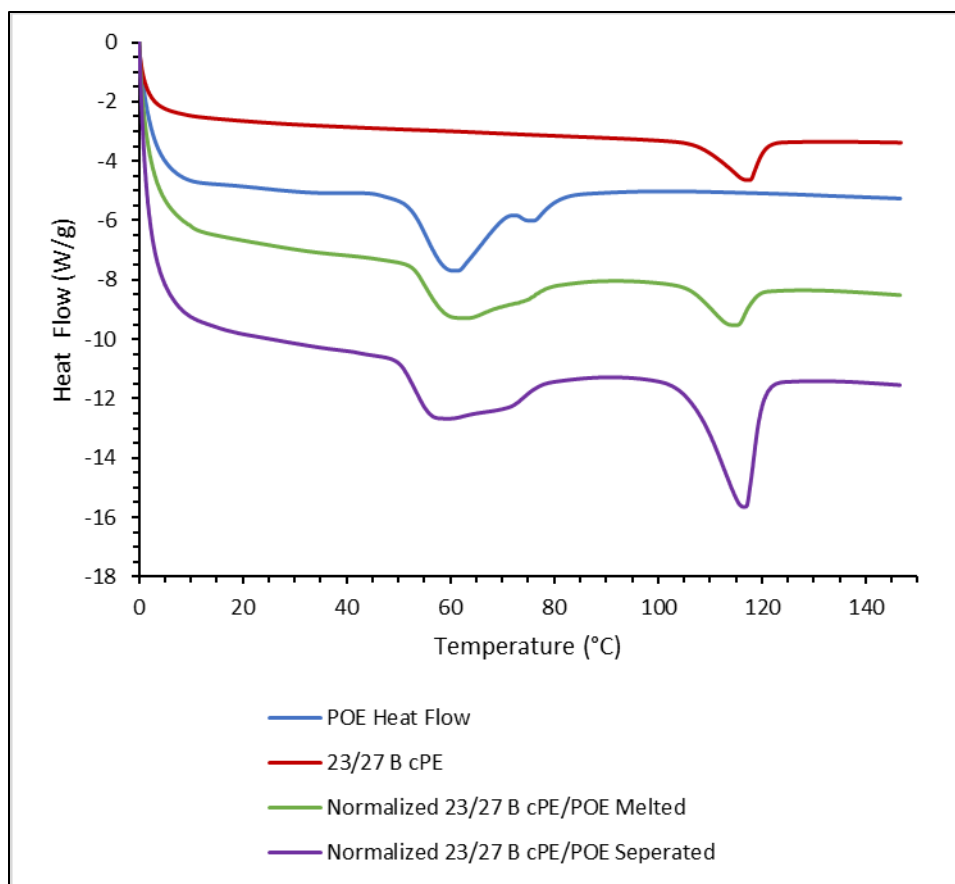


Figure S2.18. DSC curves of pure POE, cPE, melted and separated 23/27B blends.

WAXS/SAXS

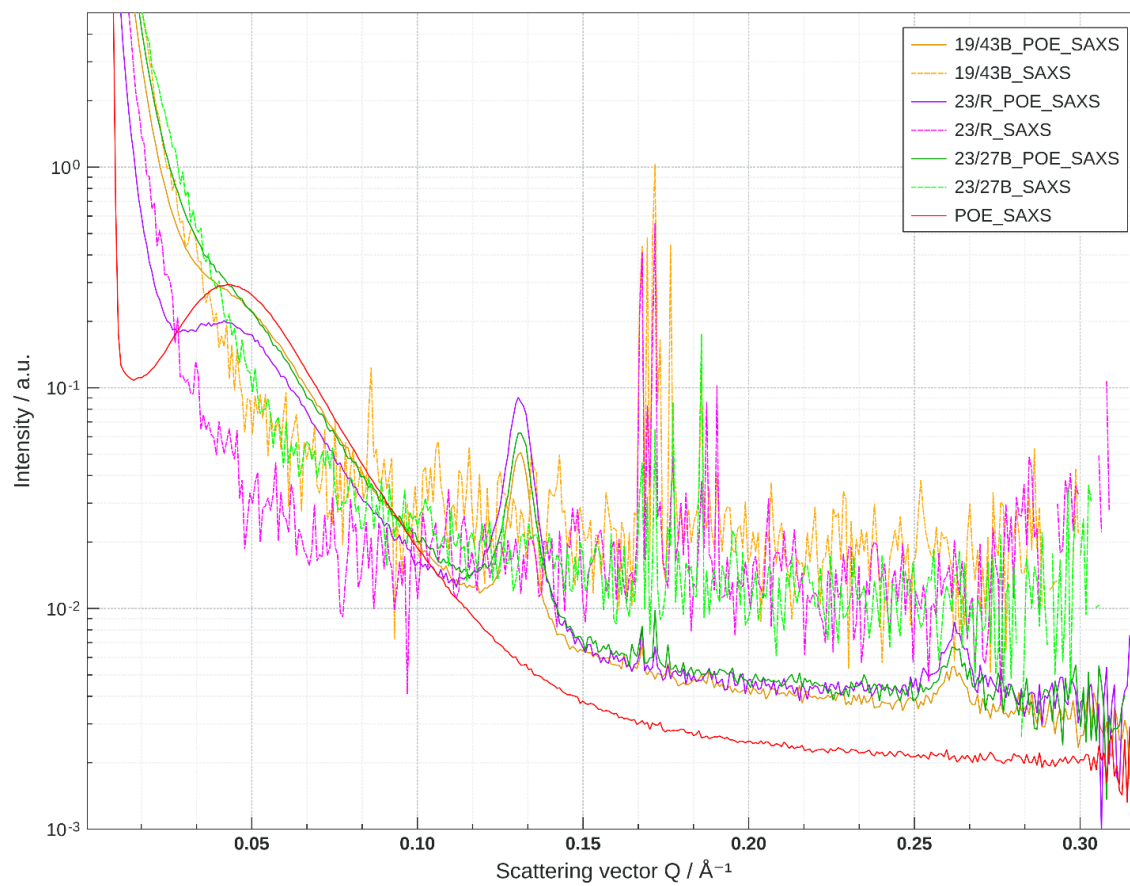


Figure S2.19. SAXS curves for the three cPEs of interest with the individual cPE scattering curves.

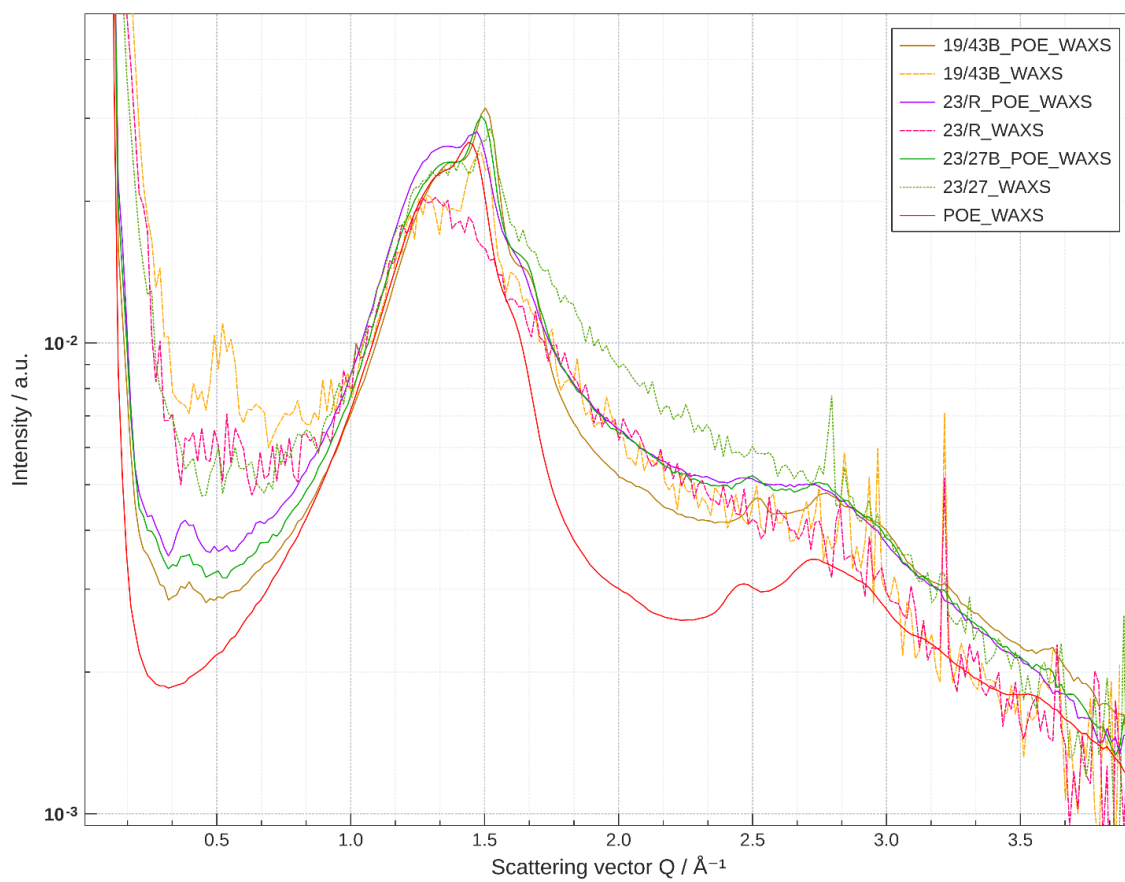


Figure S2.20. WAXS curves for the three cPEs of interest with the individual cPE scattering curves.

Appendix B: Chapter III Supporting Information

¹H NMR Spectrum

¹H NMR Spectra of Cl₂COE Monomer:

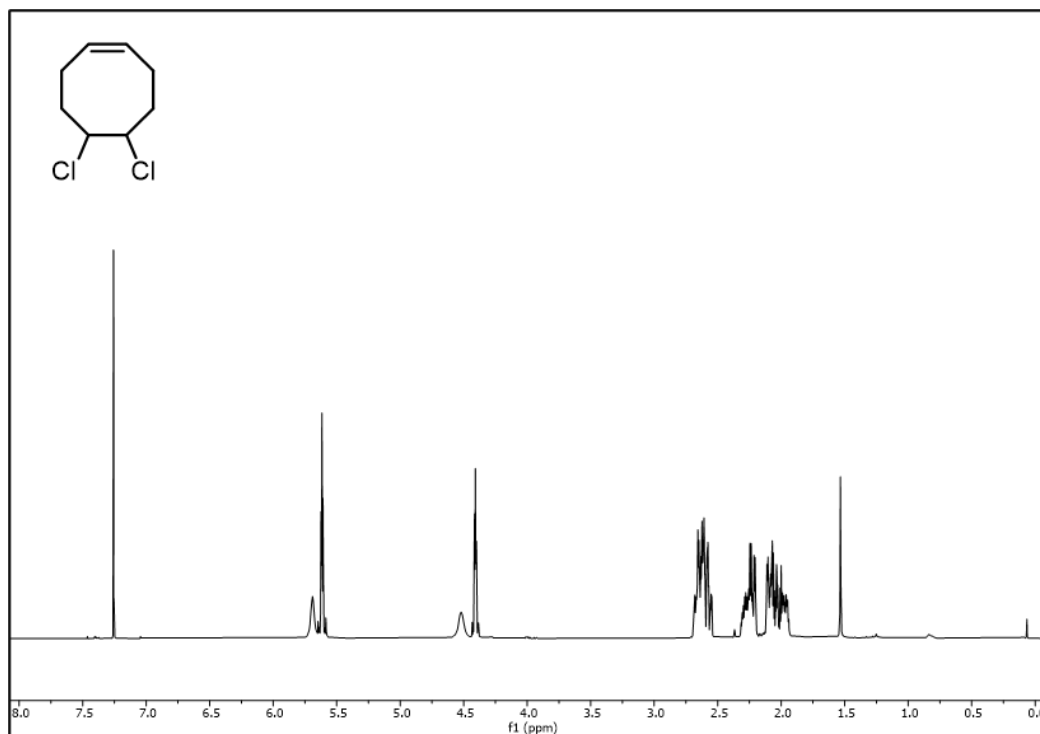


Figure S3.1. ¹H NMR spectrum of Cl₂COE monomer in CDCl₃.

^1H NMR Spectra of Synthesized c-PE Compatibilizers:

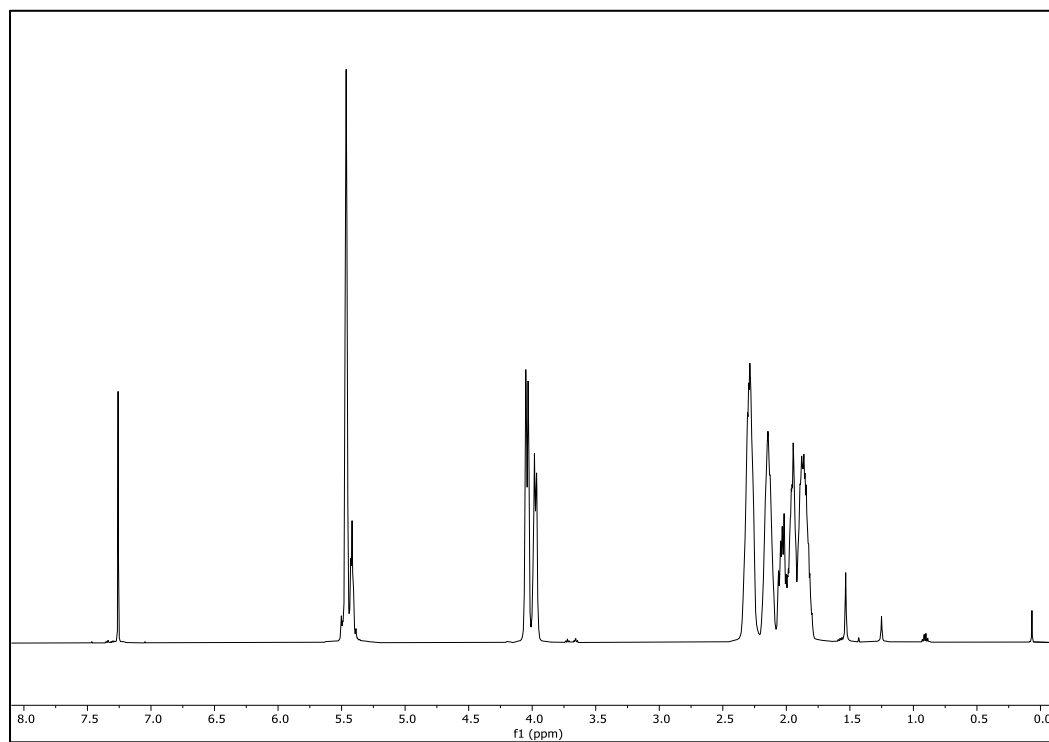


Figure S3.2. ^1H NMR spectrum of S100-3 prior to hydrogenation in CDCl_3 .

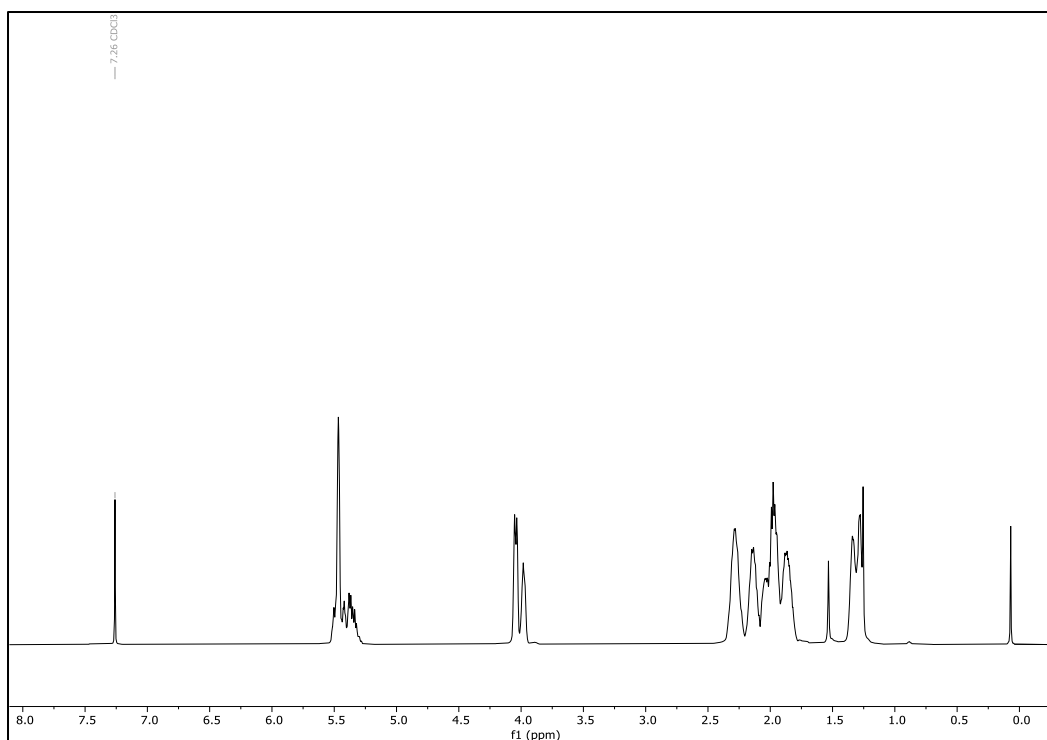


Figure S3.3. ^1H NMR spectrum of S75-3 prior to hydrogenation in CDCl_3 .

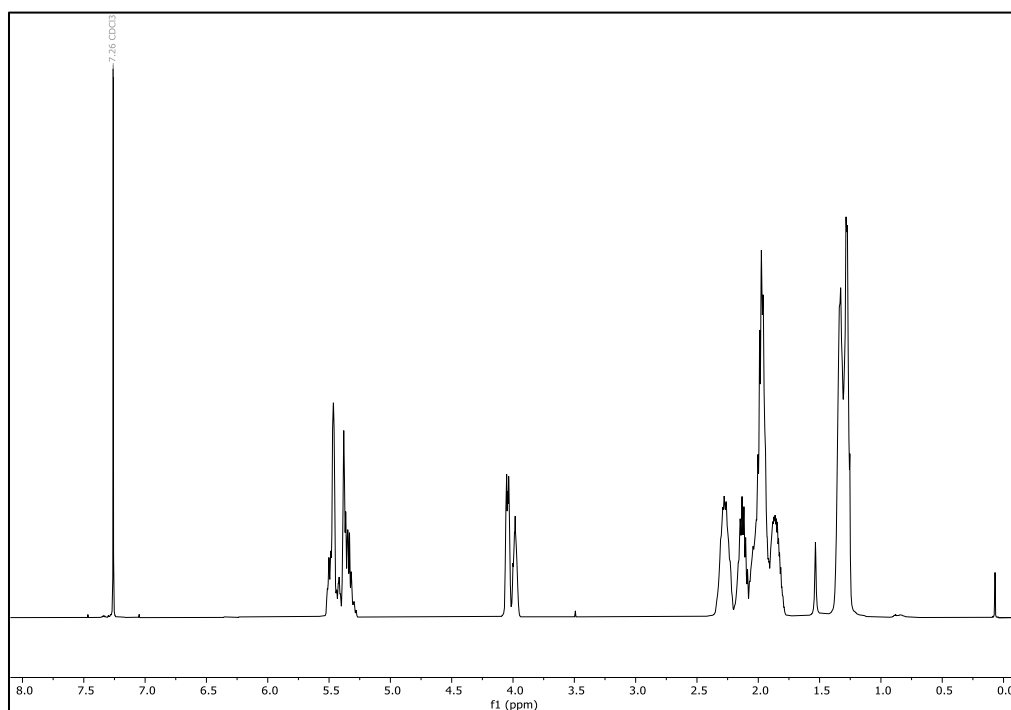


Figure S3.4. ^1H NMR spectrum of S50-1 prior to hydrogenation in CDCl_3 .

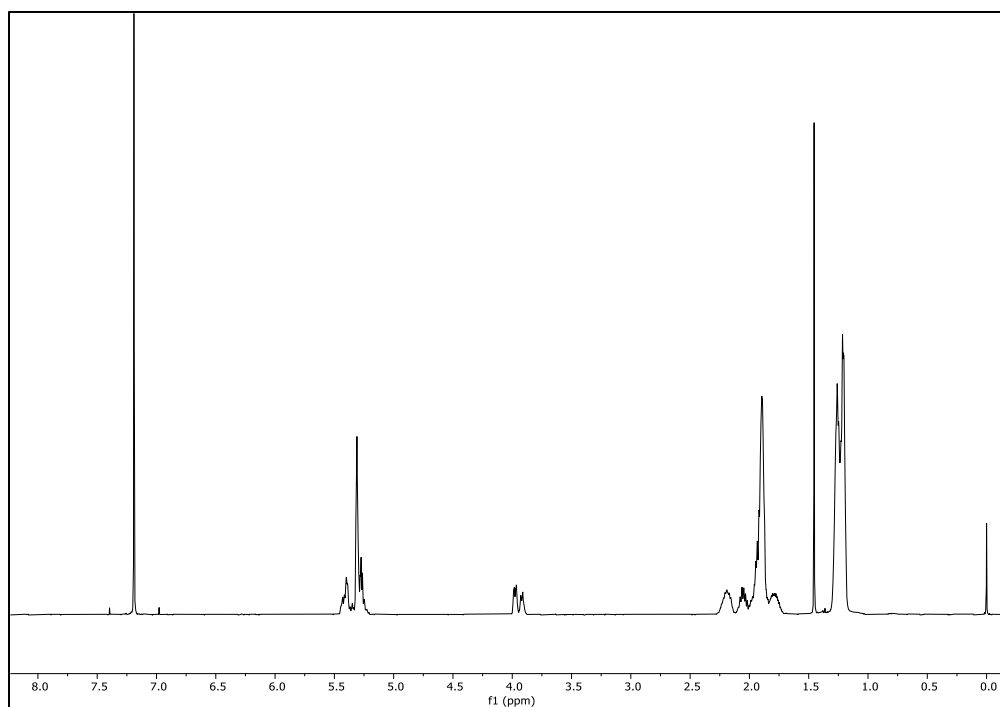


Figure S3.5. ^1H NMR spectrum of S25-1 prior to hydrogenation in CDCl_3 .

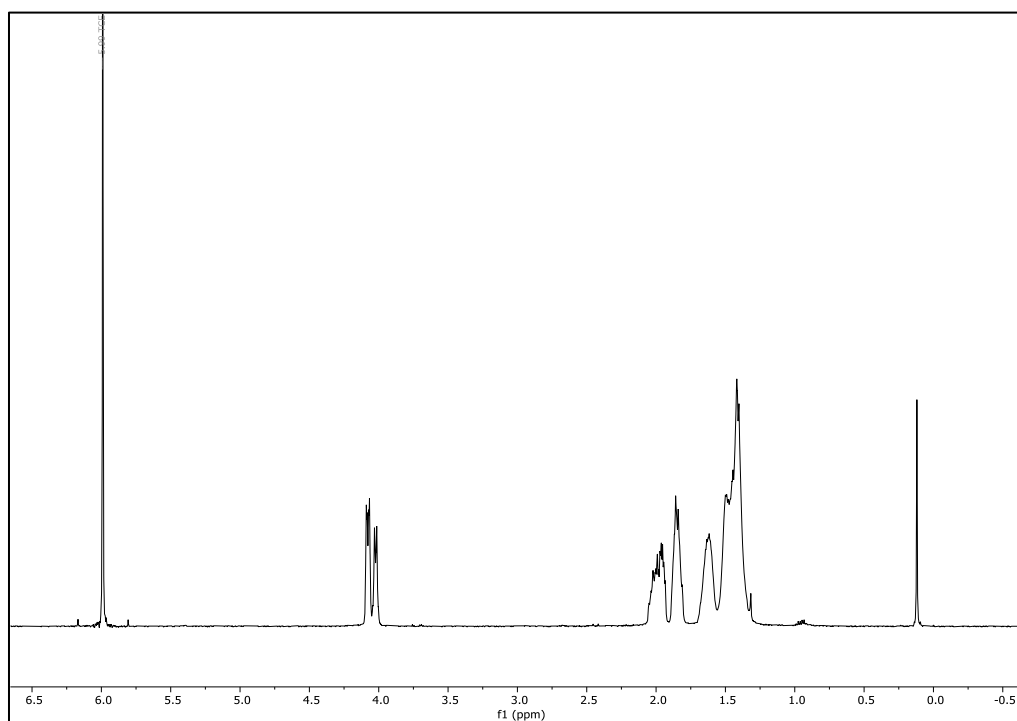


Figure S3.6. ^1H NMR spectrum of S100-3 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

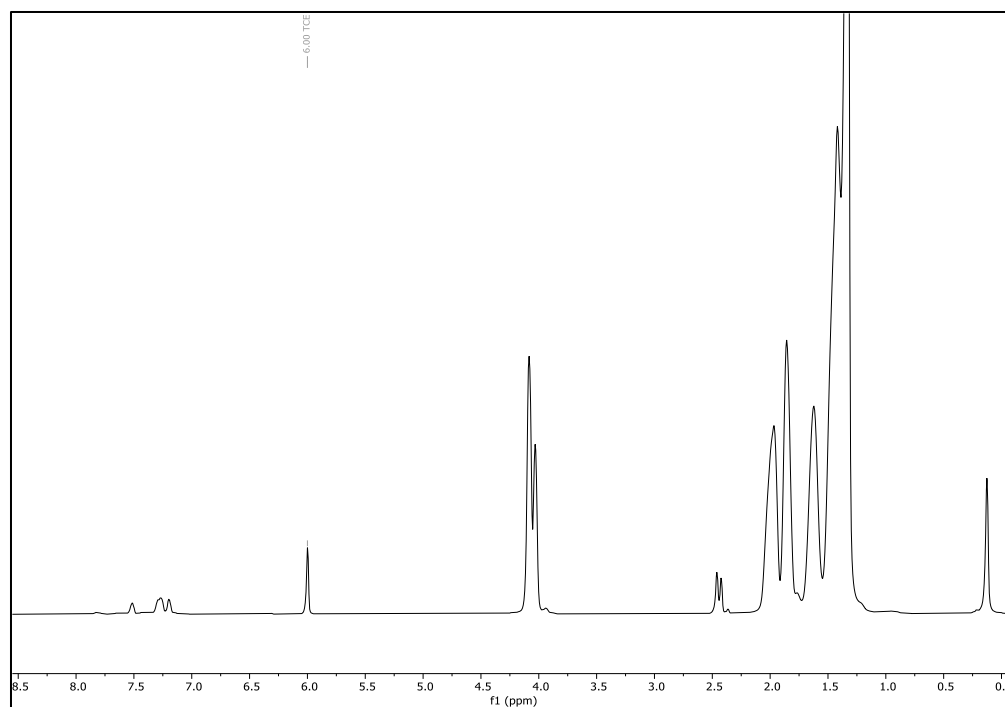


Figure S3.7. ^1H NMR spectrum of S75-3 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

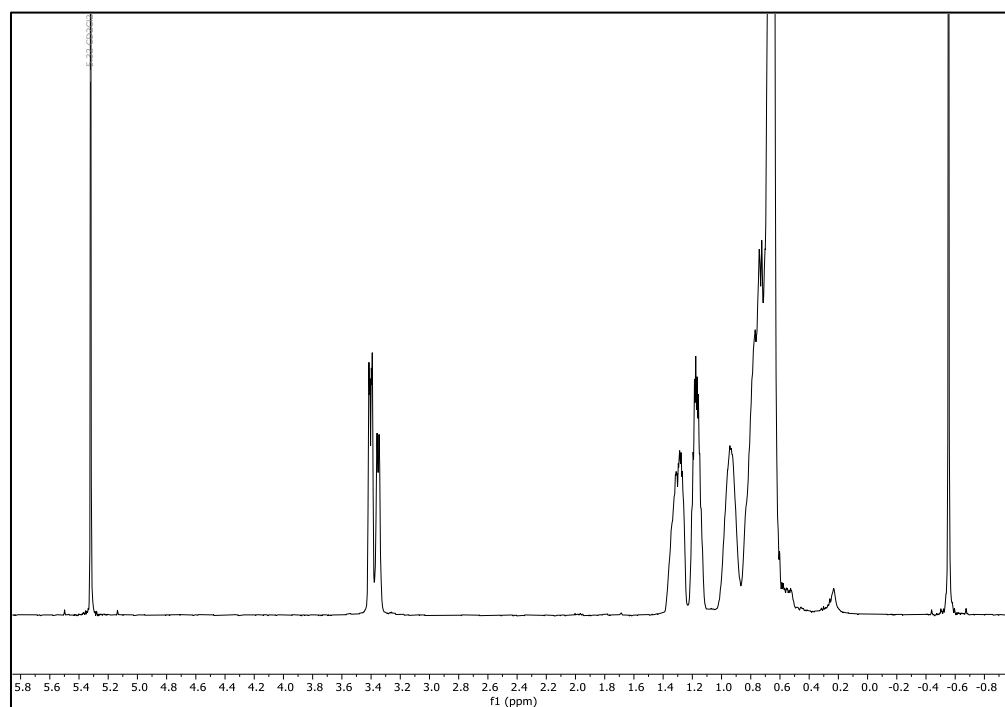


Figure S3.8. ^1H NMR spectrum of S50-1 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

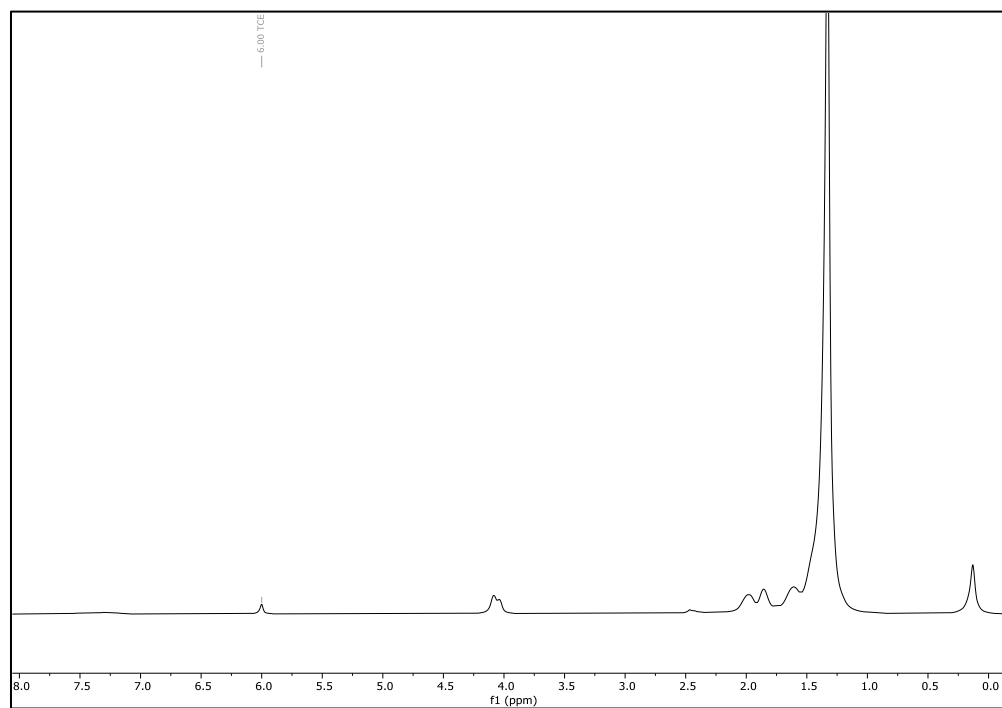


Figure S3.9. ^1H NMR spectrum of S25-1 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

Quantitative ^{13}C NMR Spectrum

Quantitative ^{13}C NMR Spectra of c-PE Compatibilizers:

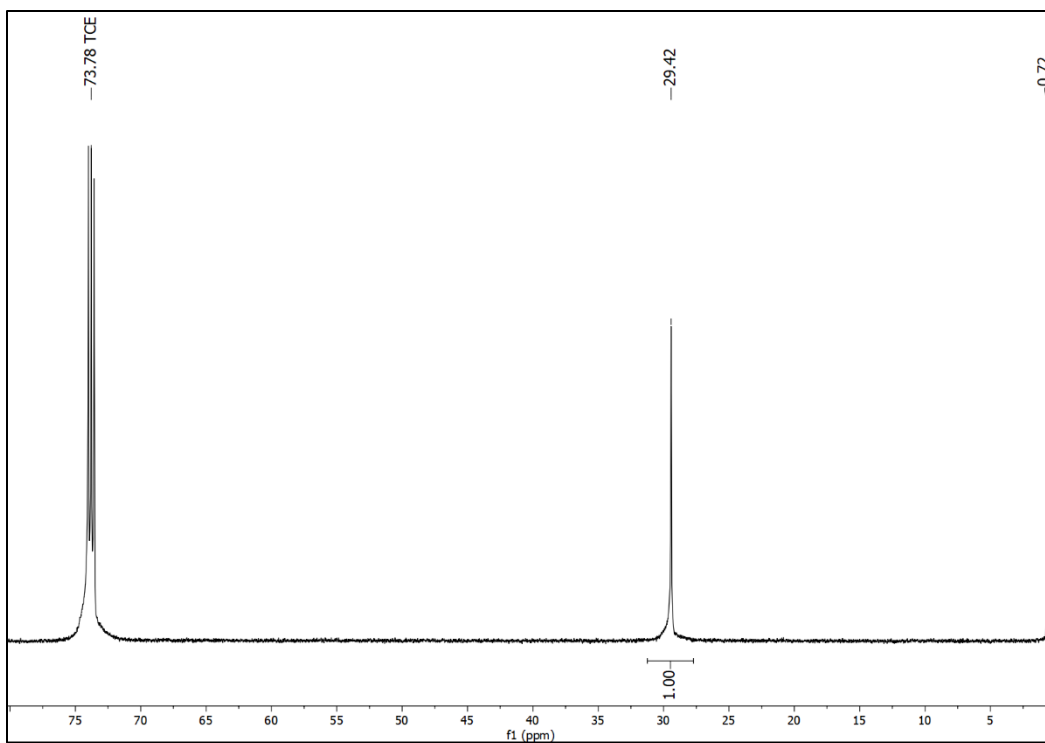


Figure S3.10. Quantitative ^{13}C NMR of PCOE dissolved in 1,1,2,2-tetrachloroethane- d_2 .

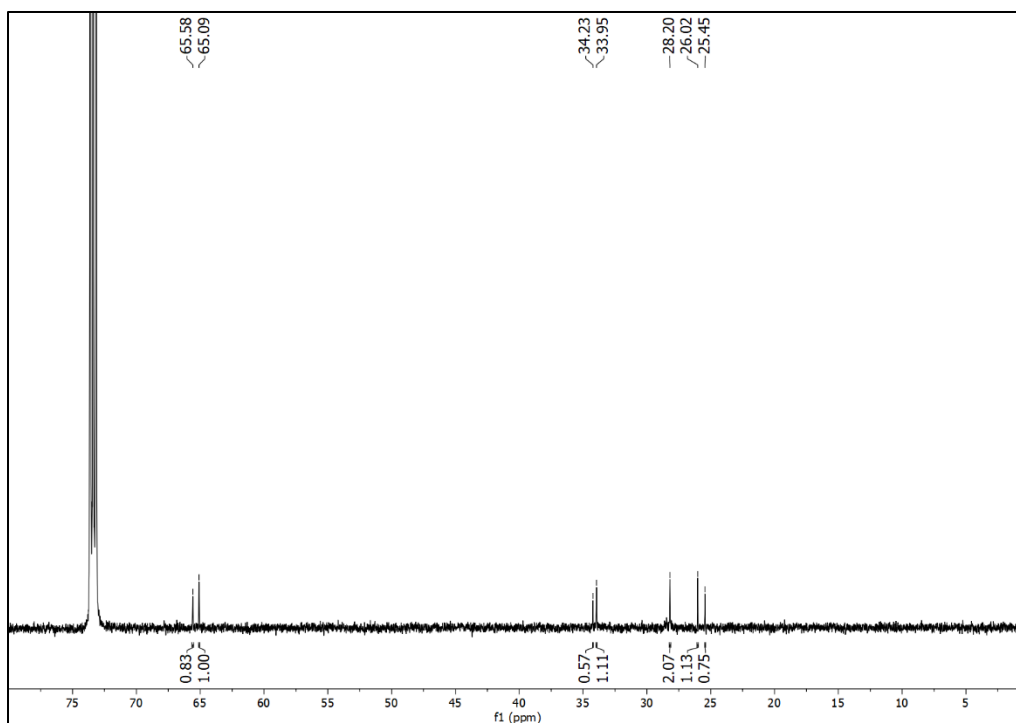


Figure S3.11. Quantitative ^{13}C NMR of S100-3 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

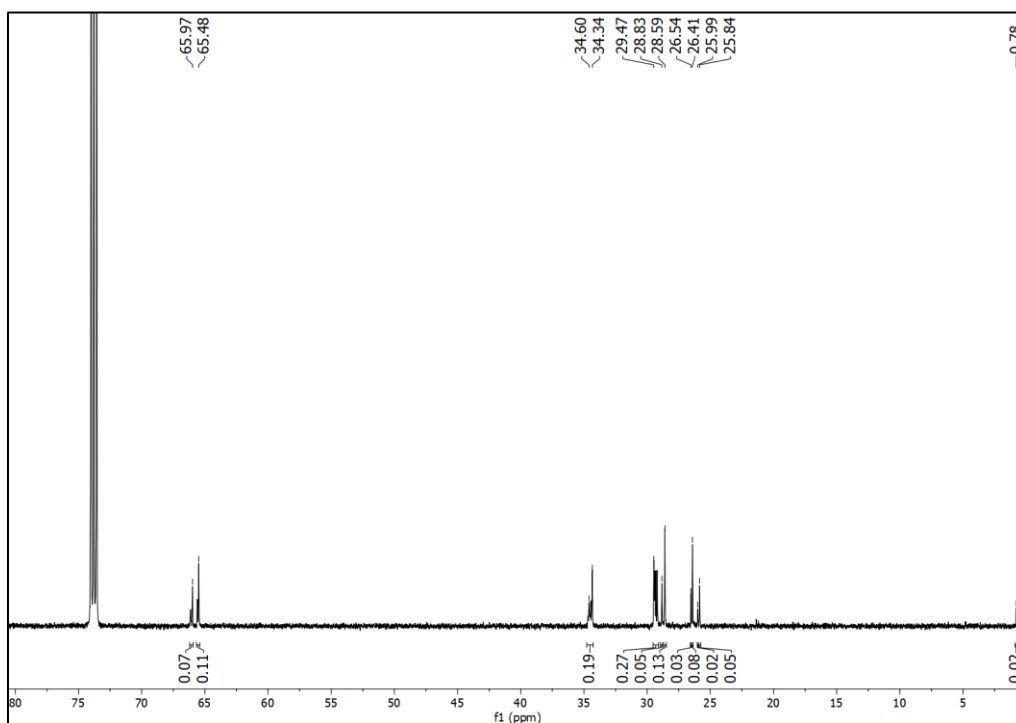


Figure S3.12. Quantitative ^{13}C NMR of S75-3 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

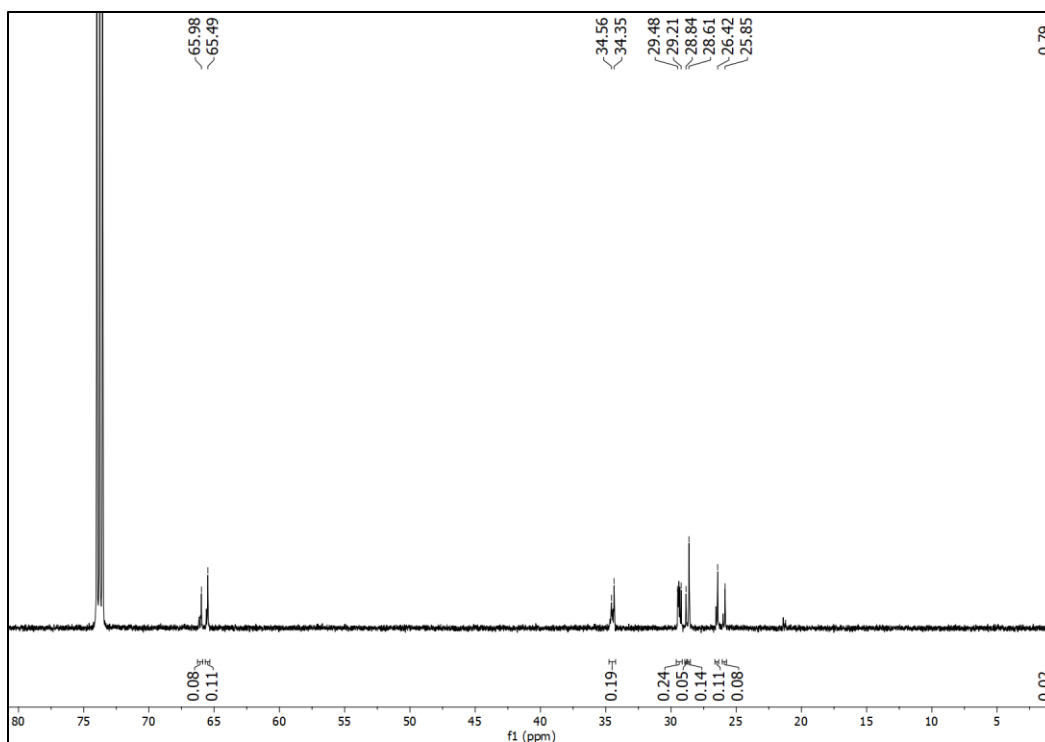


Figure S3.13. Quantitative ^{13}C NMR of S75-4 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

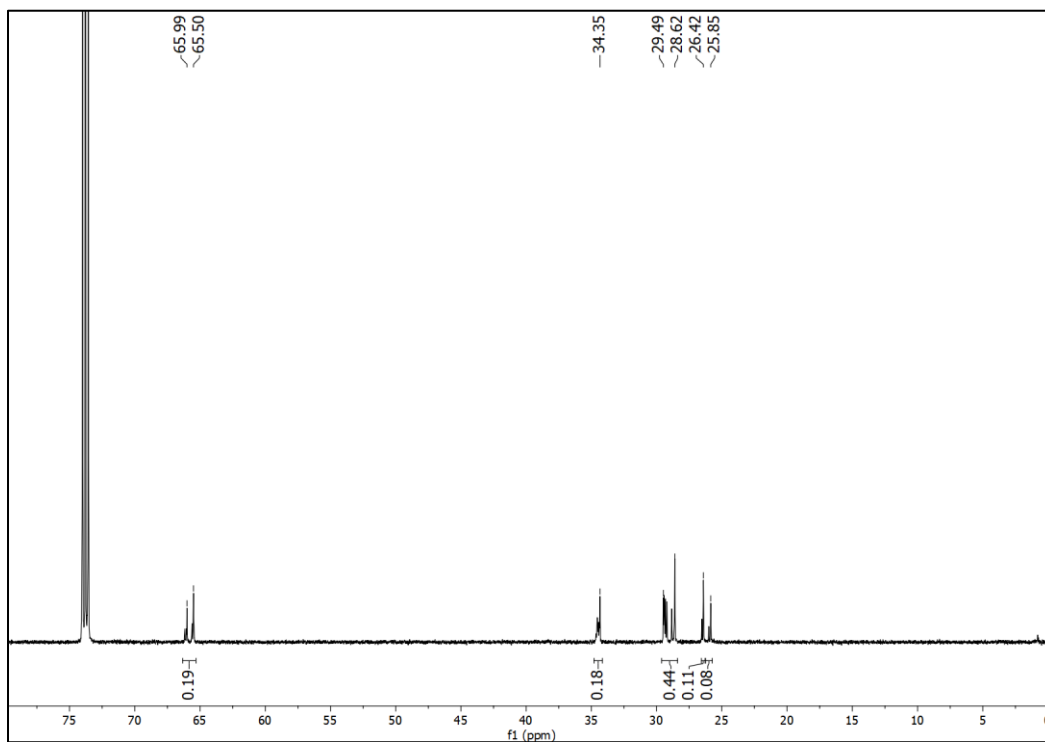


Figure S3.14. Quantitative ^{13}C NMR of S75-5 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

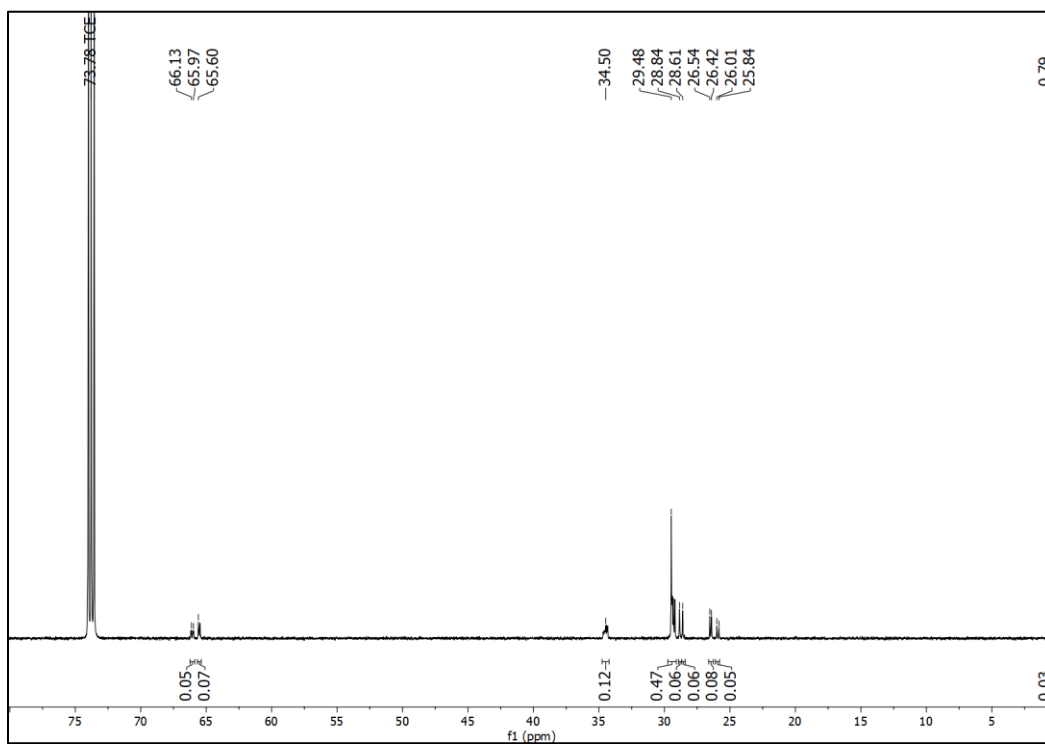


Figure S3.15. Quantitative ^{13}C NMR of S50-2 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

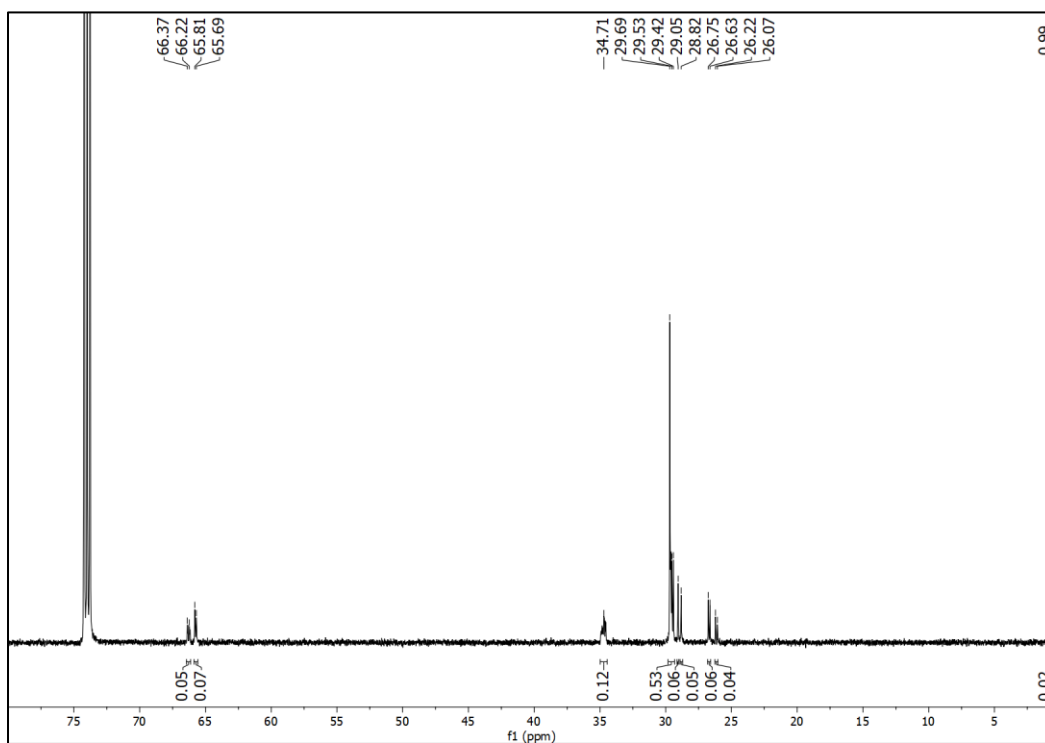


Figure S3.16. Quantitative ^{13}C NMR of S50-3 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

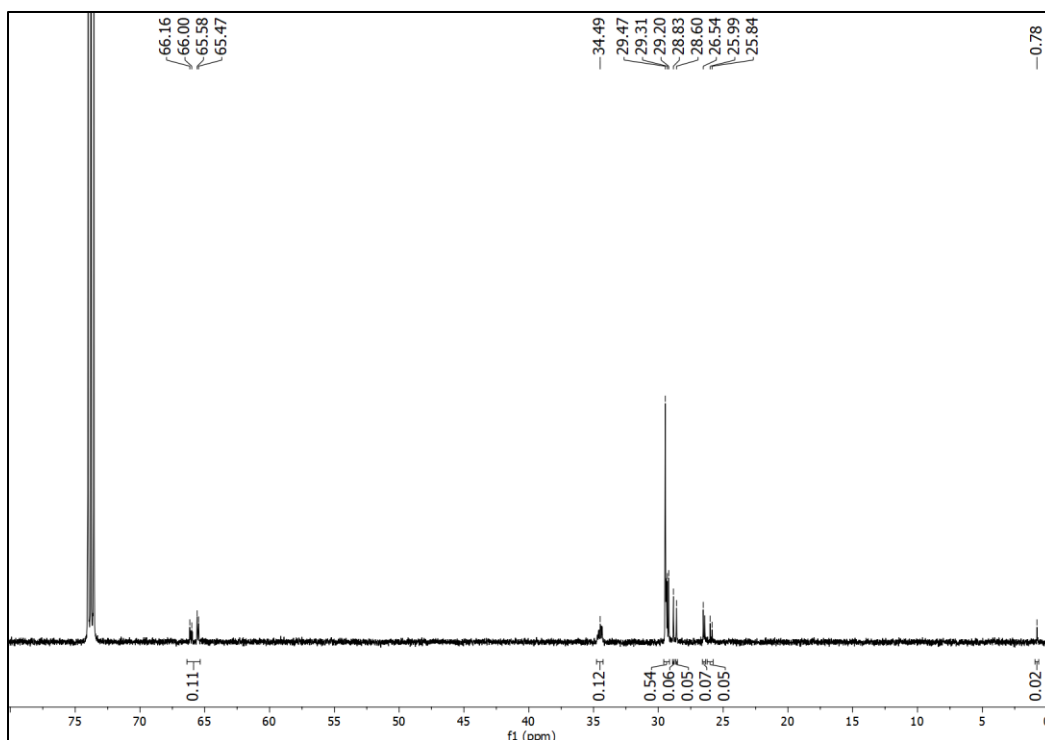


Figure S3.17. Quantitative ^{13}C NMR of S50-5 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

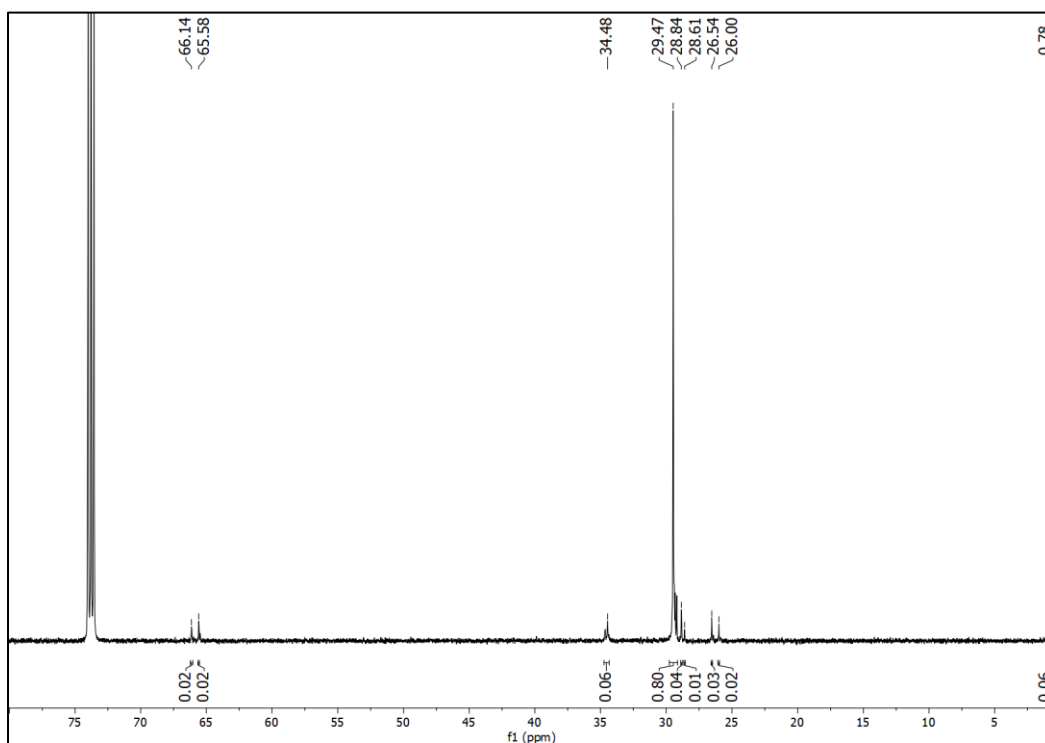


Figure S3.18. Quantitative ^{13}C NMR of S25-1 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

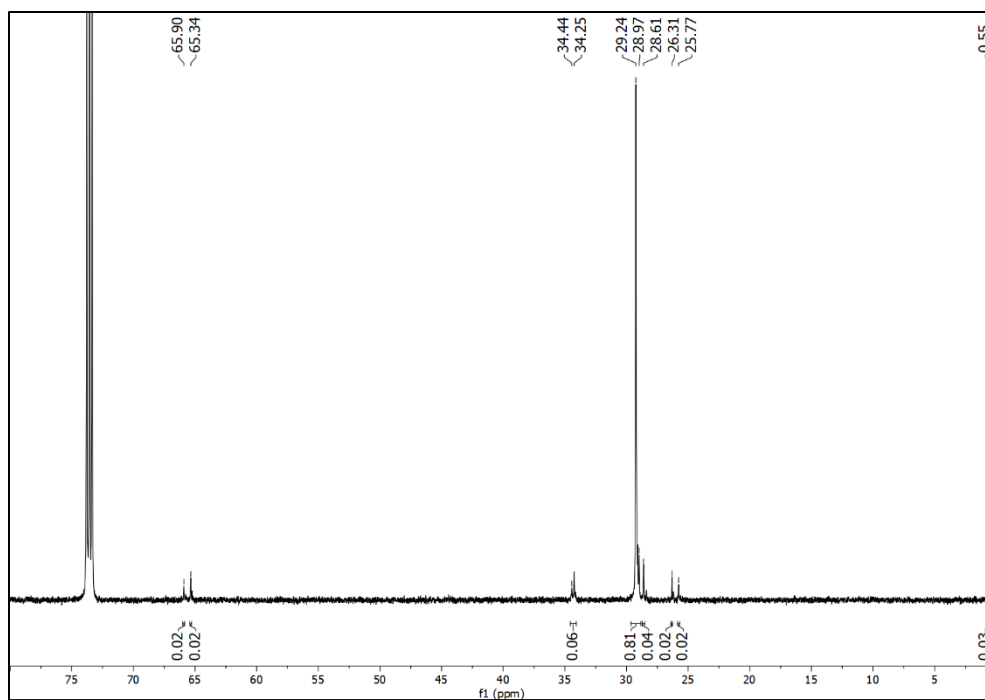


Figure S3.19. Quantitative ^{13}C NMR of S25-3 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

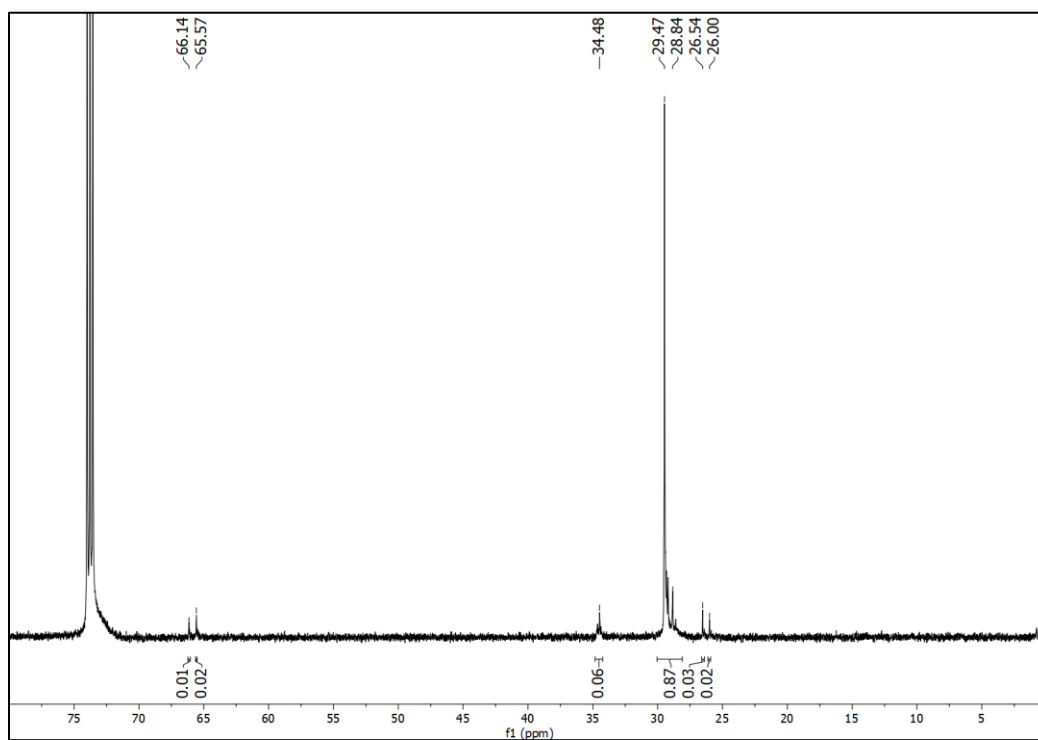


Figure S3.20. Quantitative ^{13}C NMR of S25-4 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

GPC Chromatograms of c-PE Compatibilizers:

Molecular weights were obtained from gel permeation chromatography (GPC). The synthesized compatibilizers were tested in their pre-hydrogenated form. The material was run on a Tosch EcoSEC GPC system equipped with RI detection in tetrahydrofuran. The post-hydrogenated samples were not tested by GPC due to their insolubility in THF and the fact that they are isorefractive with 1,2,4-trichlorobenzene. We assume their molecular weight stays the same post hydrogenation due to the nature of the diimide reduction they undergo and therefore only obtained molecular weight of the initial polymer materials. The commercial c-PEs were run on a Viscotek 350A HT-GPC system at 150 °C in 1,2,4-trichlorobenzene.

DSC Chromatograms of c-PE Compatibilizers:

Differential scanning calorimetry (DSC) was used to obtain heat of fusion and melting temperatures using a TA Instruments Q-2000 DSC. C-PE samples of 5 – 10 mg were run through two cycles at 10 °C/min, with the second heating cycle collected for analysis. Integrations of the melting peak are used to calculate the heat fusion, which is a representation of the extent of crystallinity.¹¹⁹

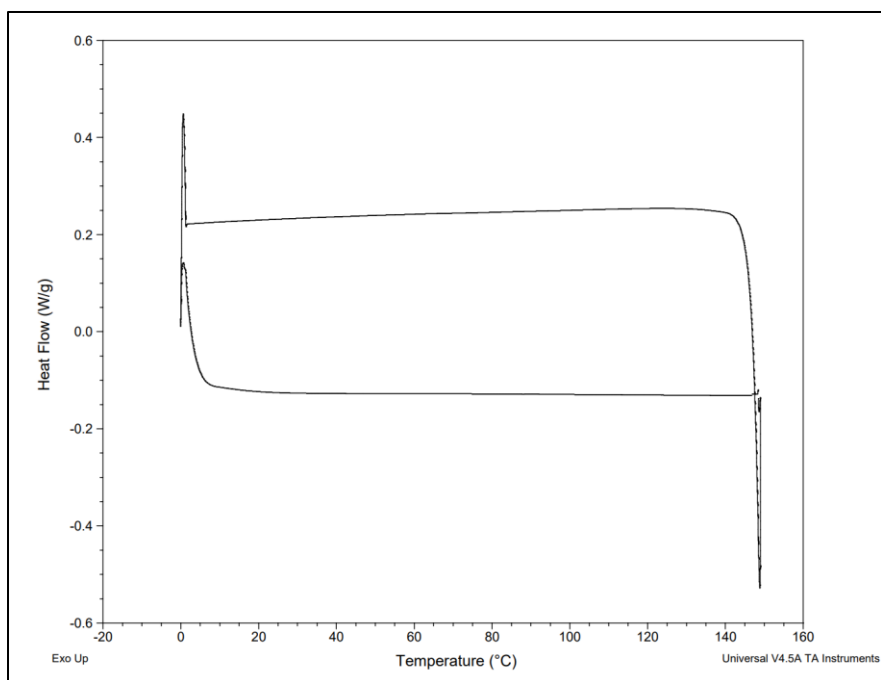


Figure S3.21. DSC spectrum for S100-1.

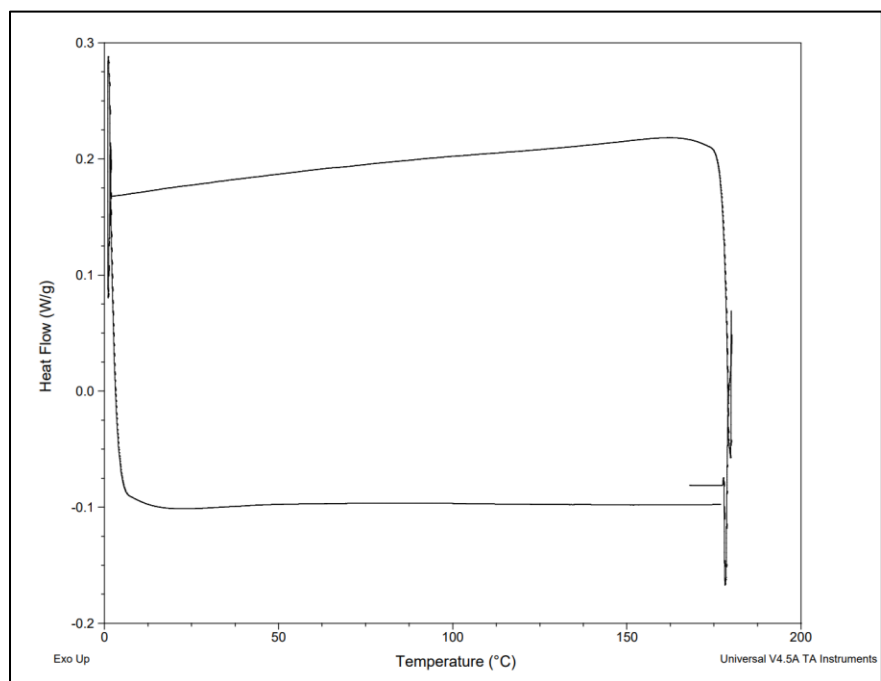


Figure S3.22. DSC spectrum for S100-2.

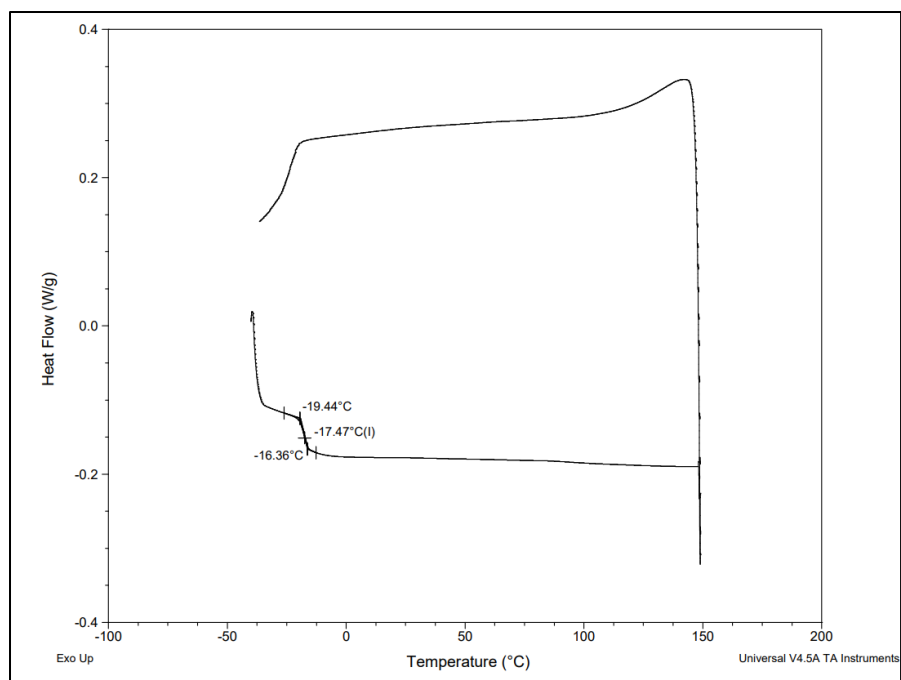


Figure S3.23. DSC spectrum for S100-3.

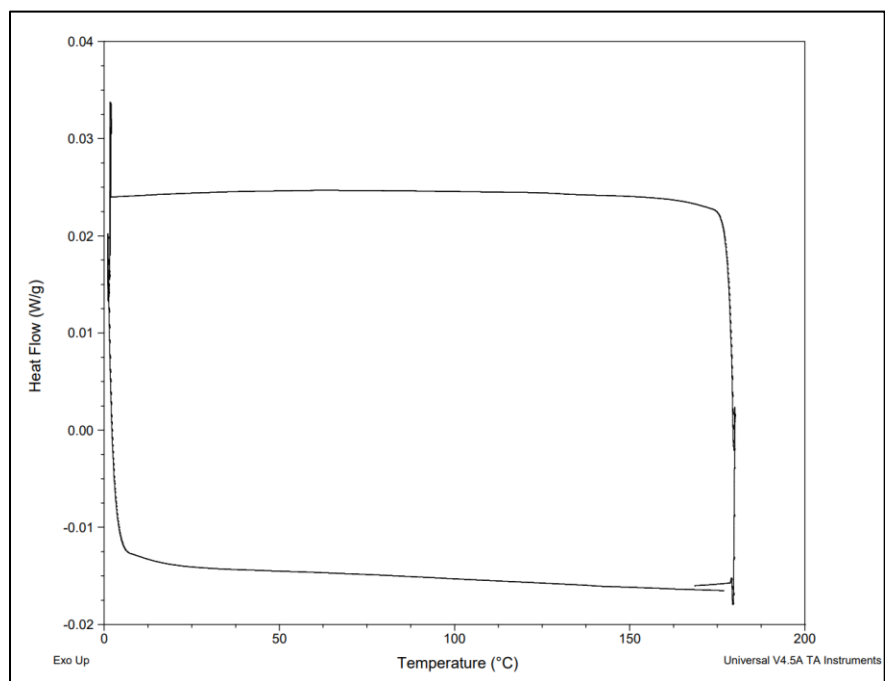


Figure S3.24. DSC spectrum for S100-4.

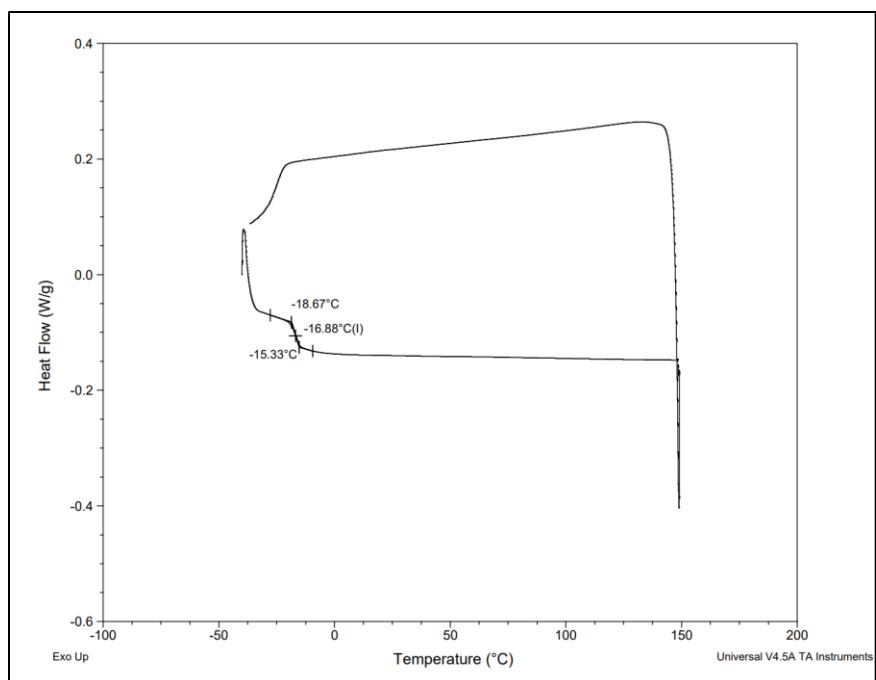


Figure S3.25. DSC spectrum for S100-5.

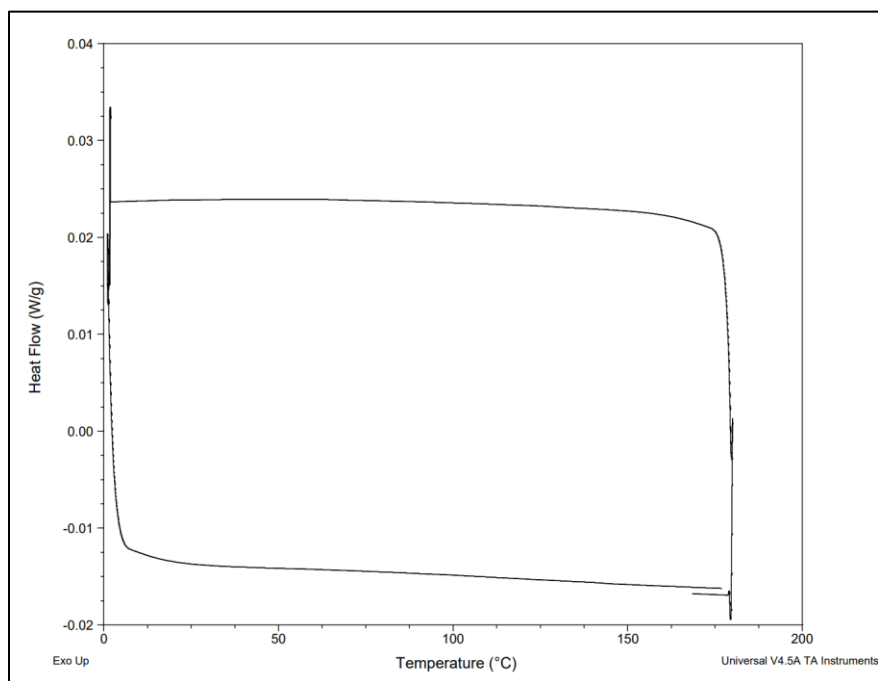


Figure S3.26. DSC spectrum for S100-6.

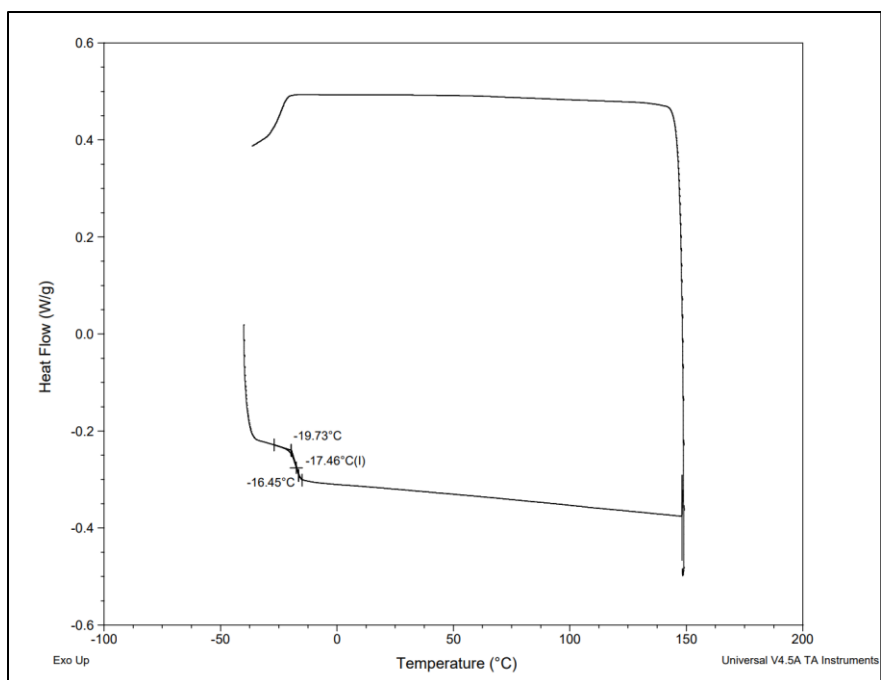


Figure S3.27. DSC spectrum for S100-7.

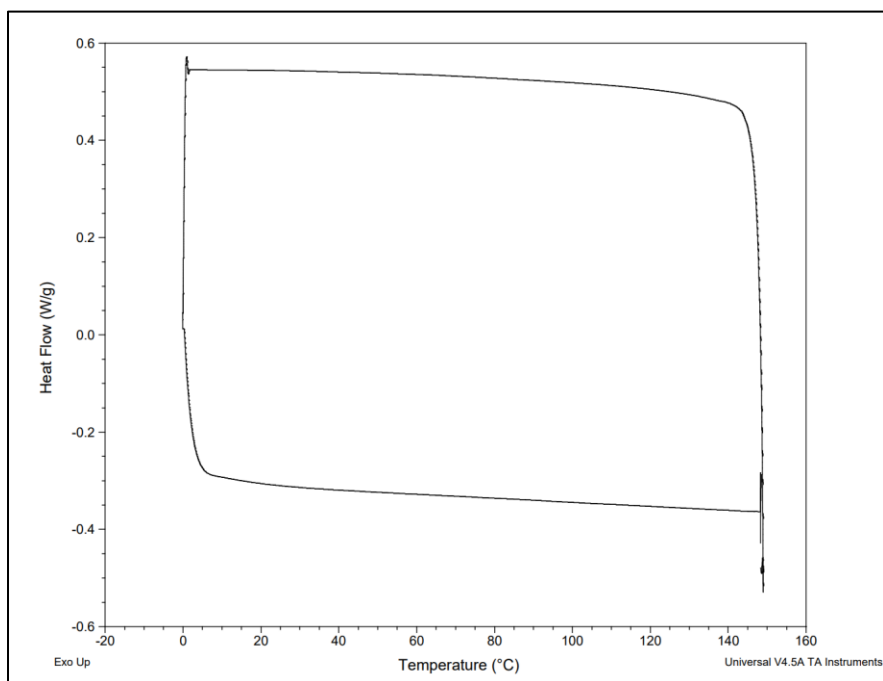


Figure S3.28. DSC spectrum for S100-8.

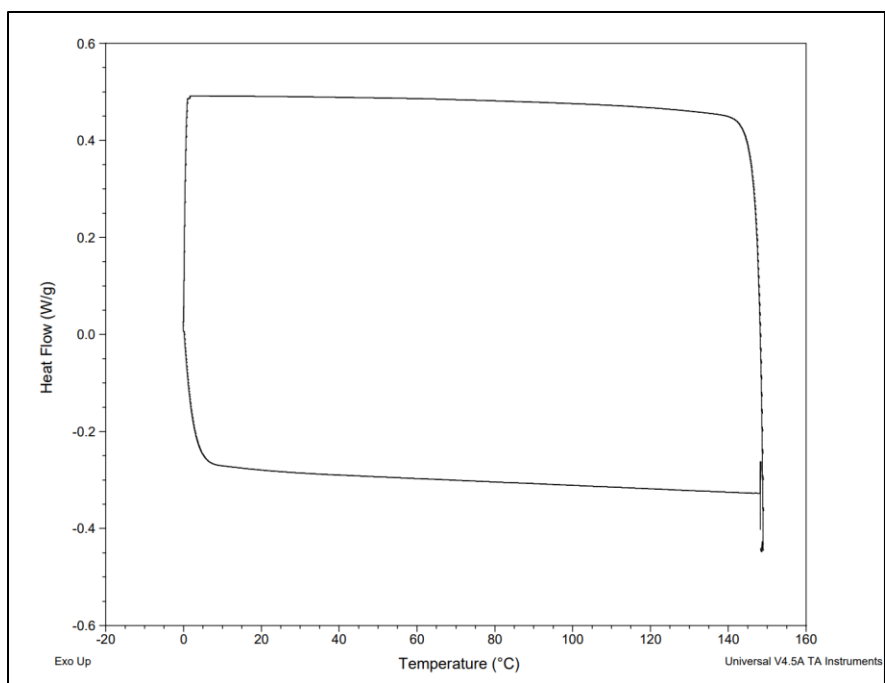


Figure S3.29. DSC spectrum for S100-9.

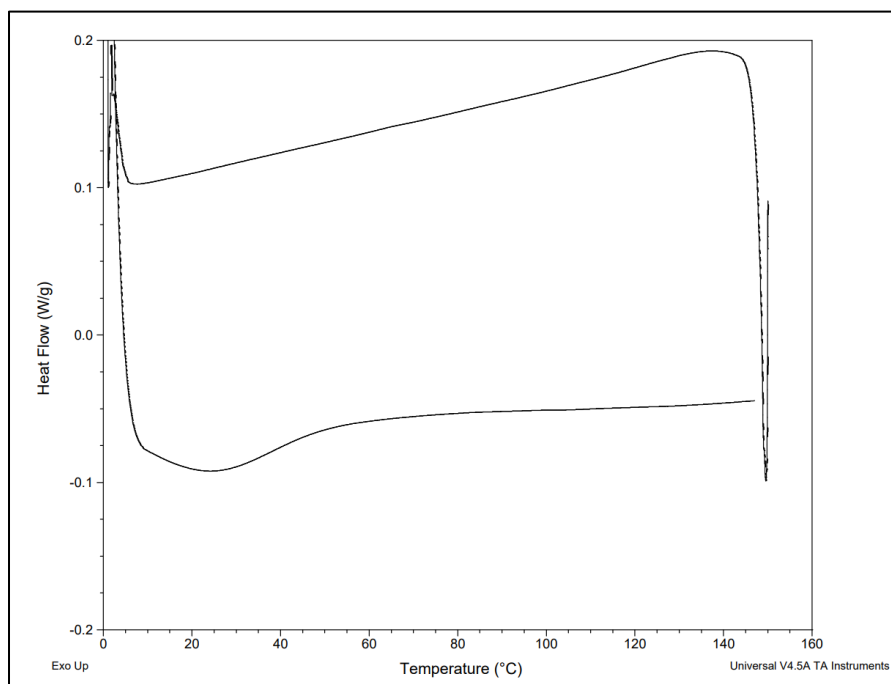


Figure S3.30. DSC spectrum for S75-1.

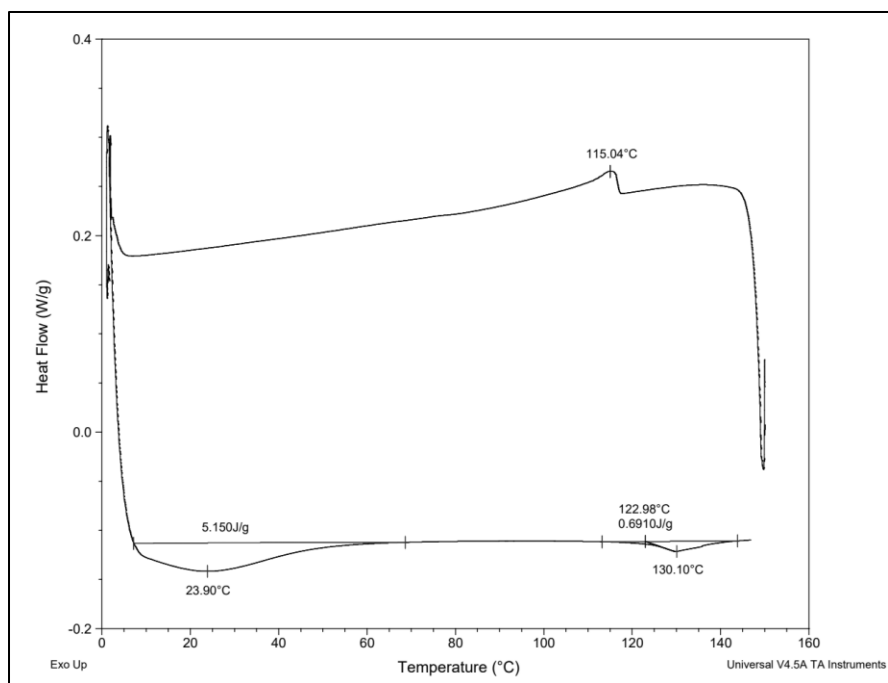


Figure S3.31. DSC spectrum for S75-2.

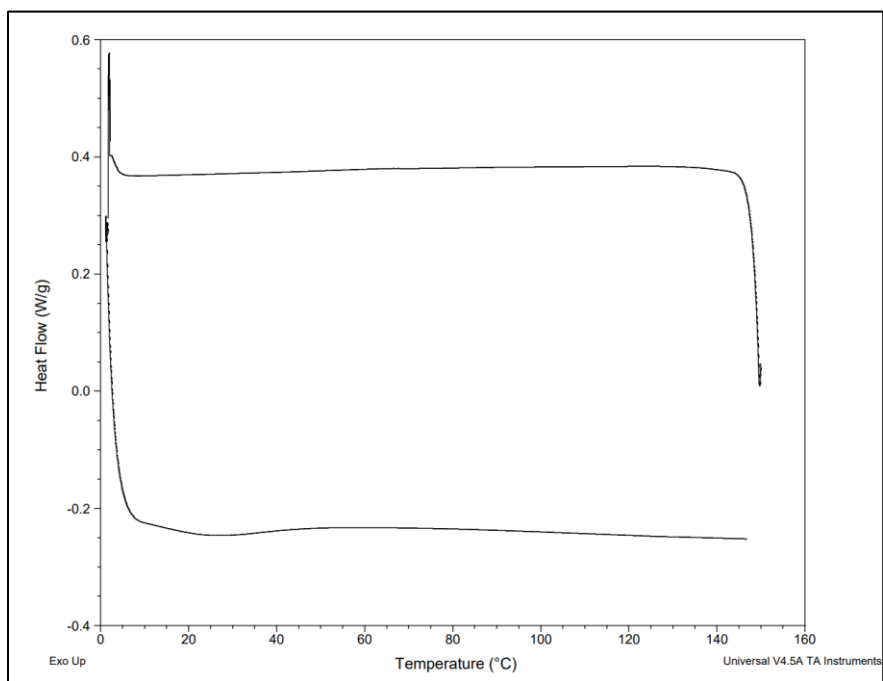


Figure S3.32. DSC spectrum for S75-3.

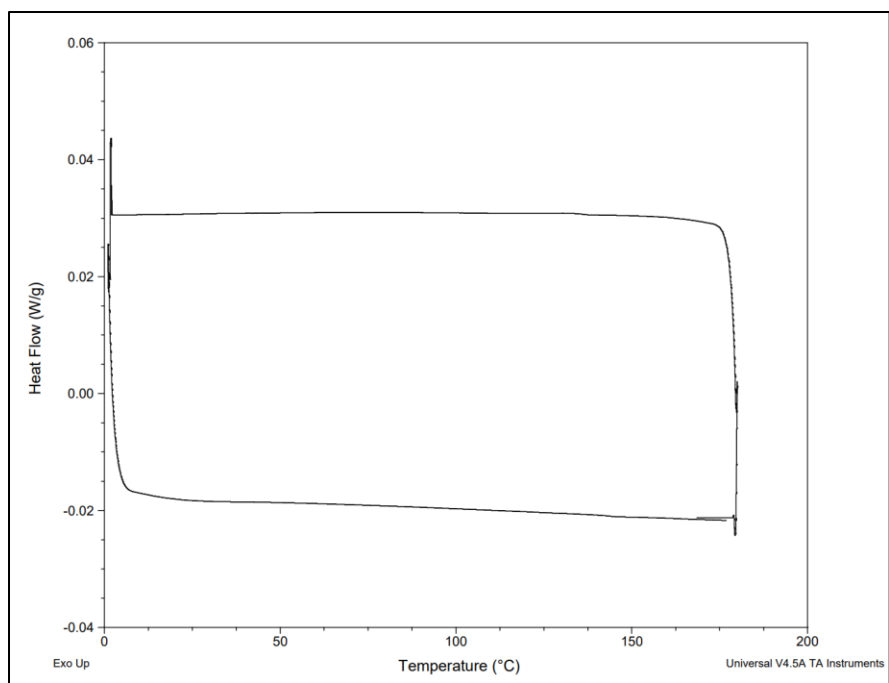


Figure S3.33. DSC spectrum for S75-4.

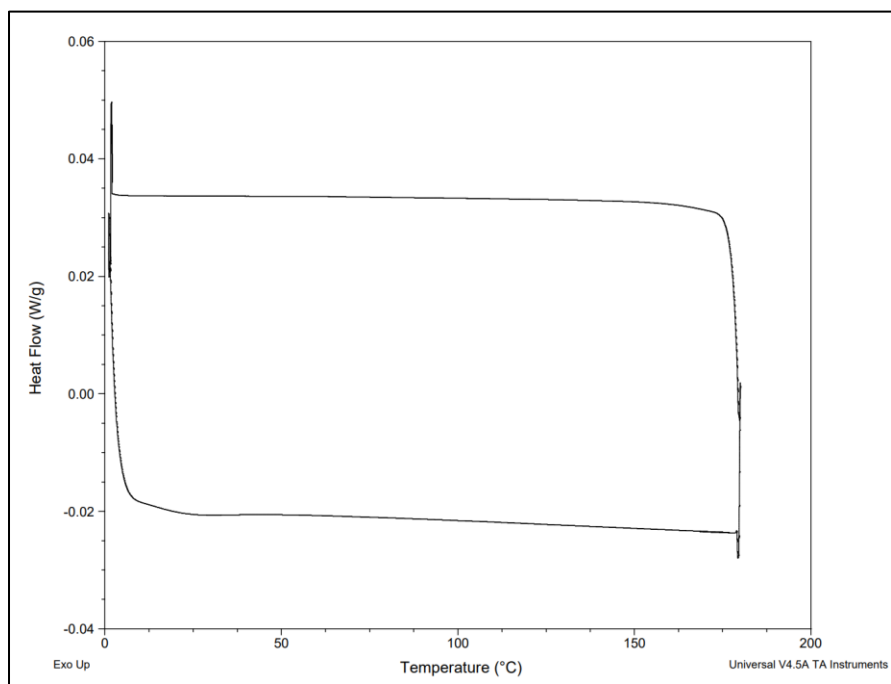


Figure S3.34. DSC spectrum for S75-5.

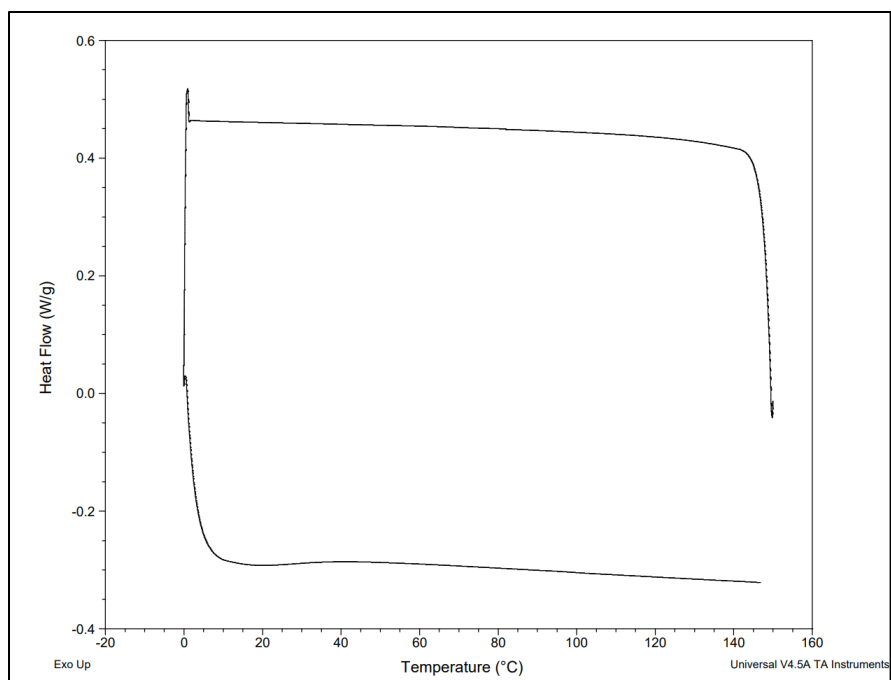


Figure S3.35. DSC spectrum for S75-6.

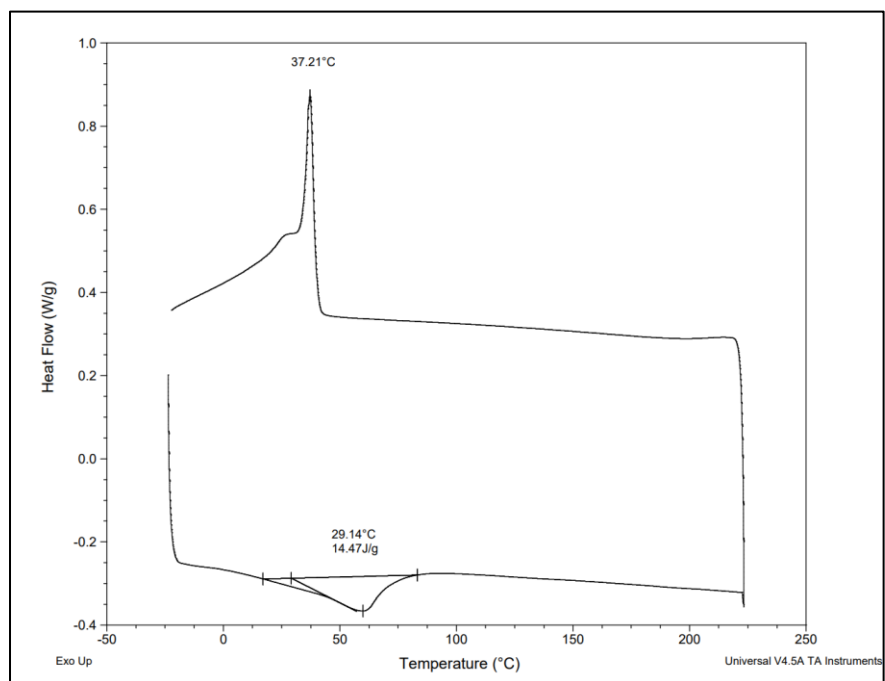


Figure S3.36. DSC spectrum for S50-1.

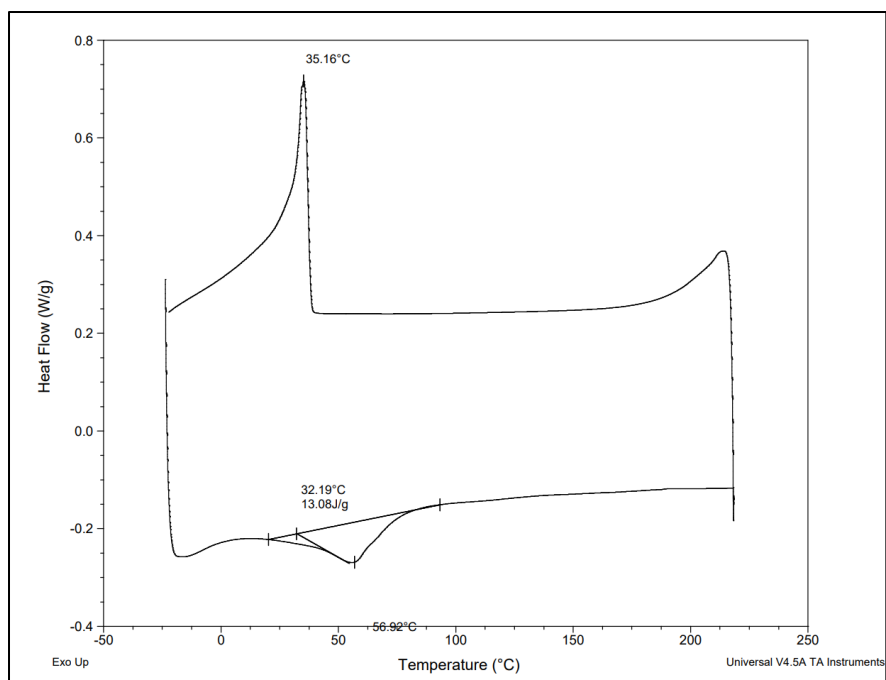


Figure S3.37. DSC spectrum for S50-2.

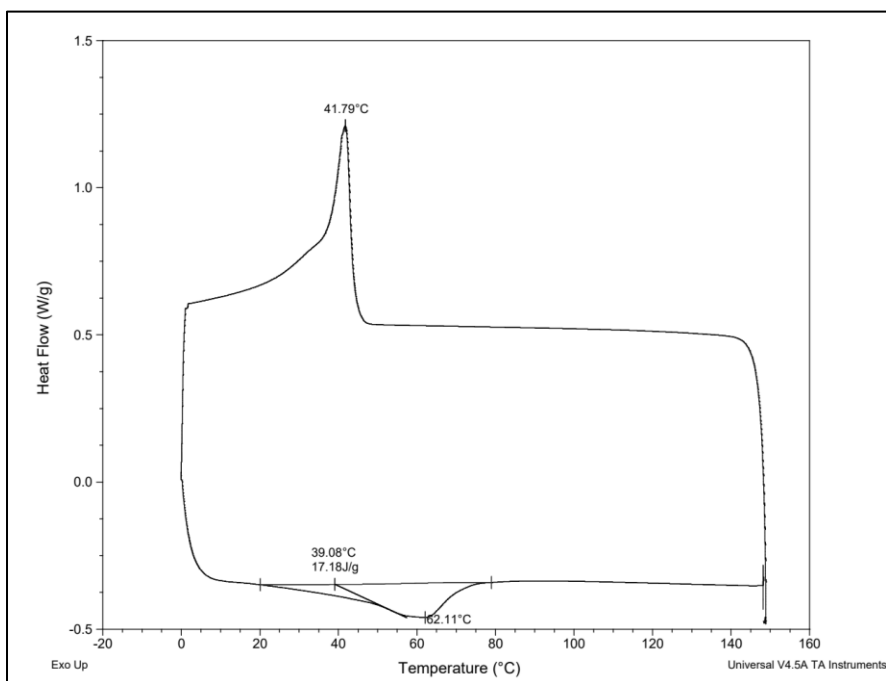


Figure S3.38. DSC spectrum for S50-3.

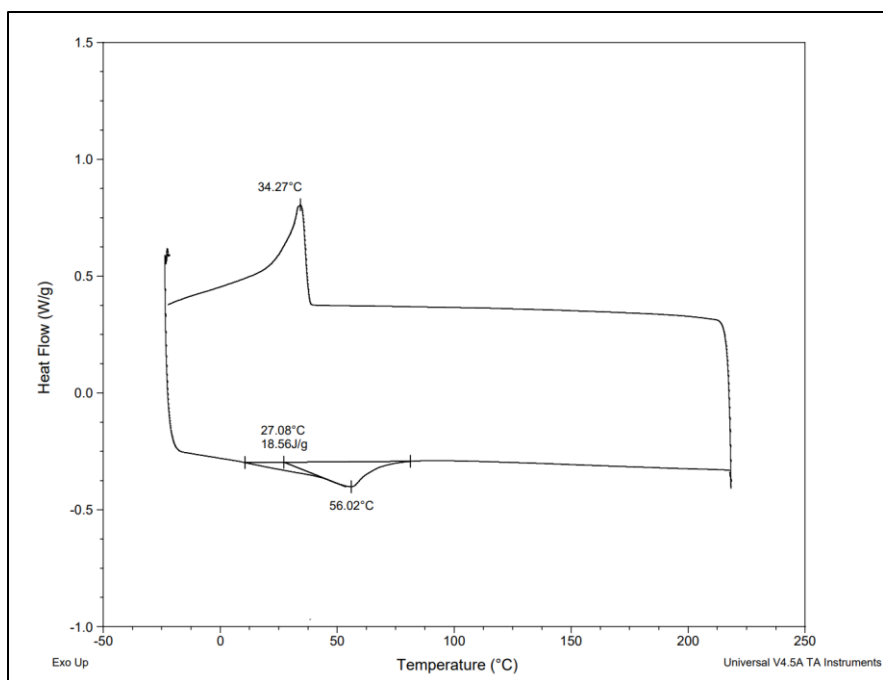


Figure S3.39. DSC spectrum for S50-4.

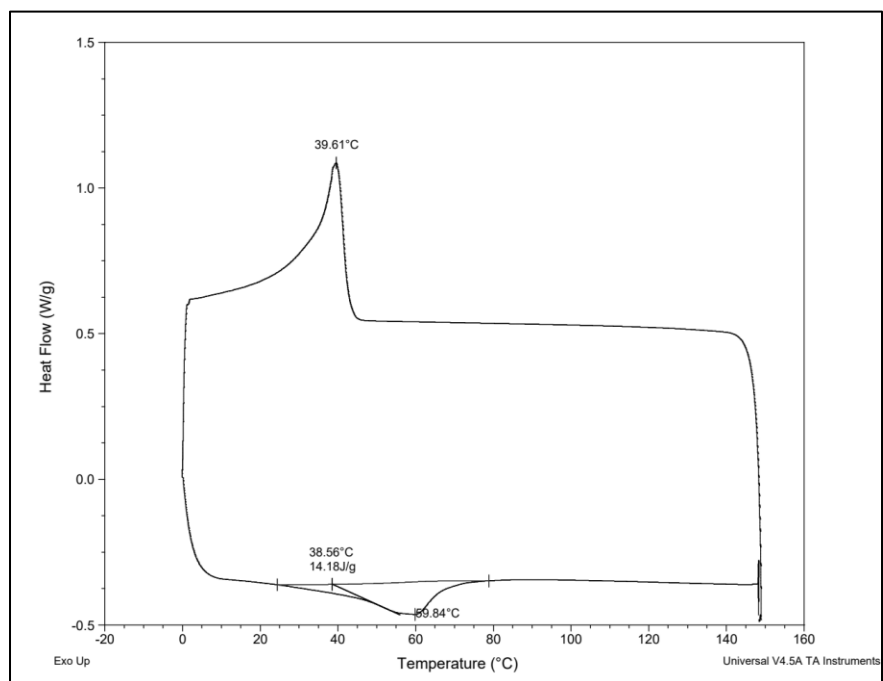


Figure S3.40. DSC spectrum for S50-5.

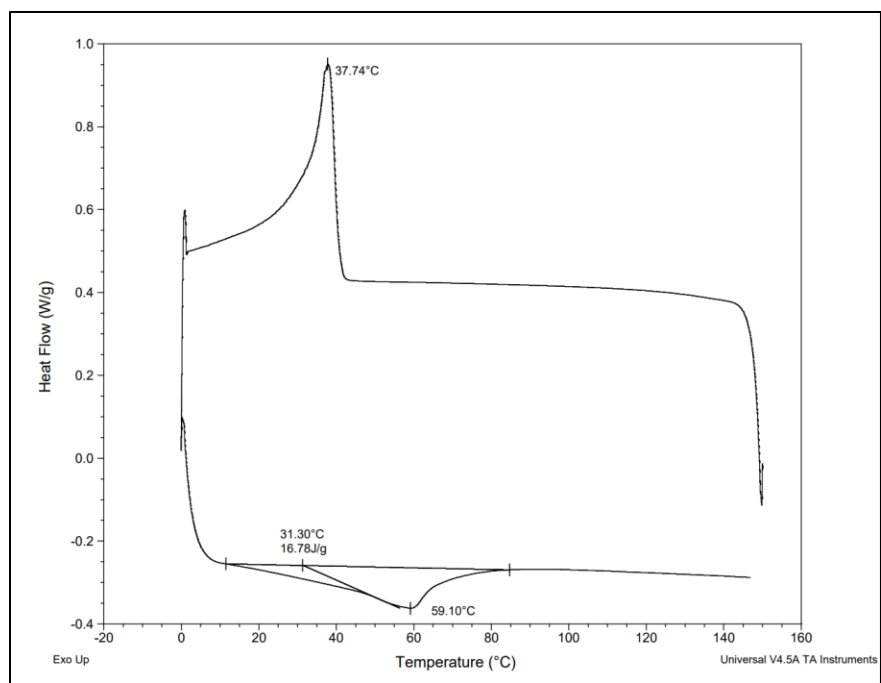


Figure S3.41. DSC spectrum for S50-6.

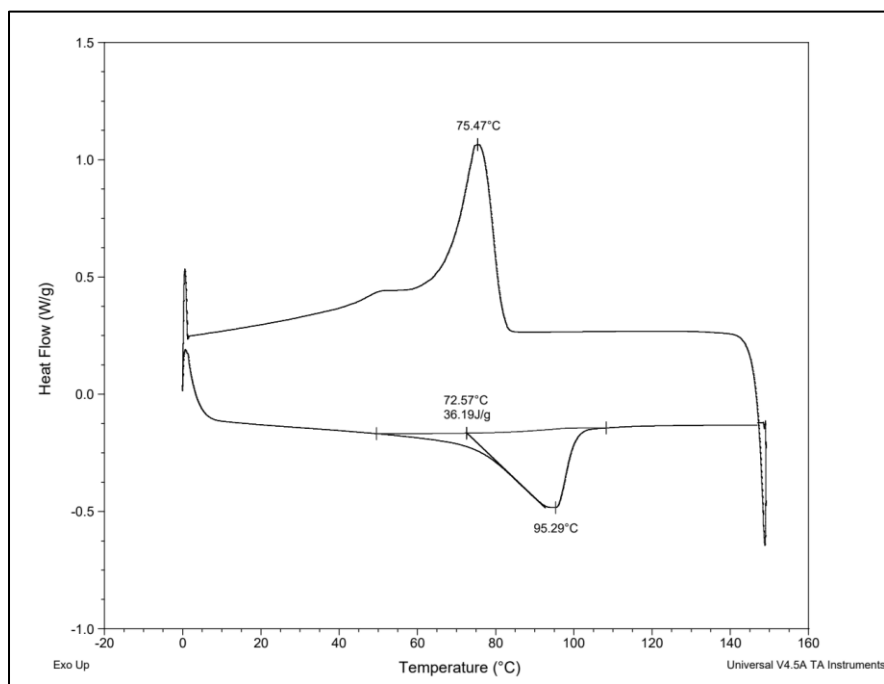


Figure S3.42. DSC spectrum for S25-1.

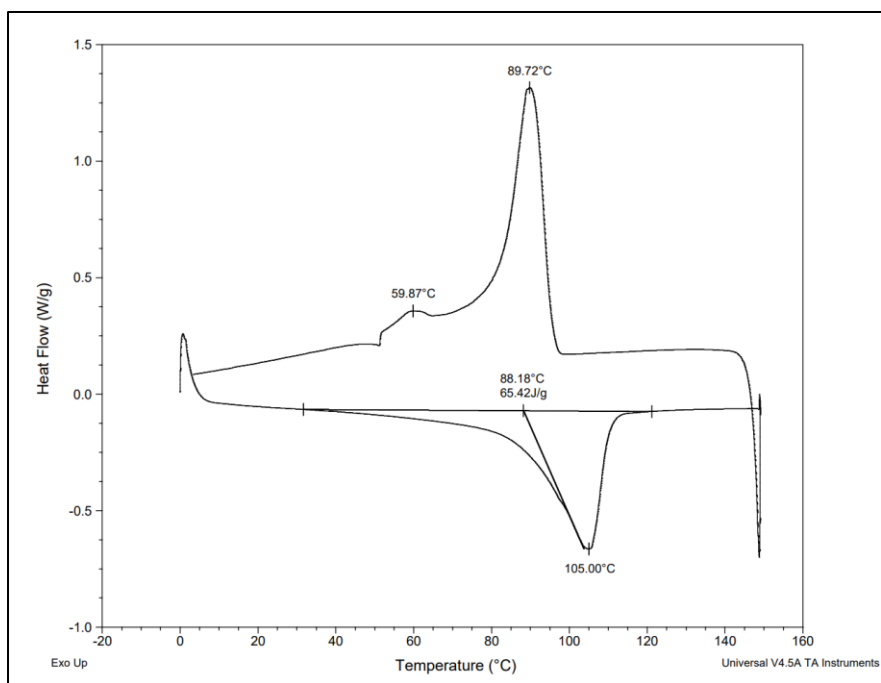


Figure S3.43. DSC spectrum for S25-2.

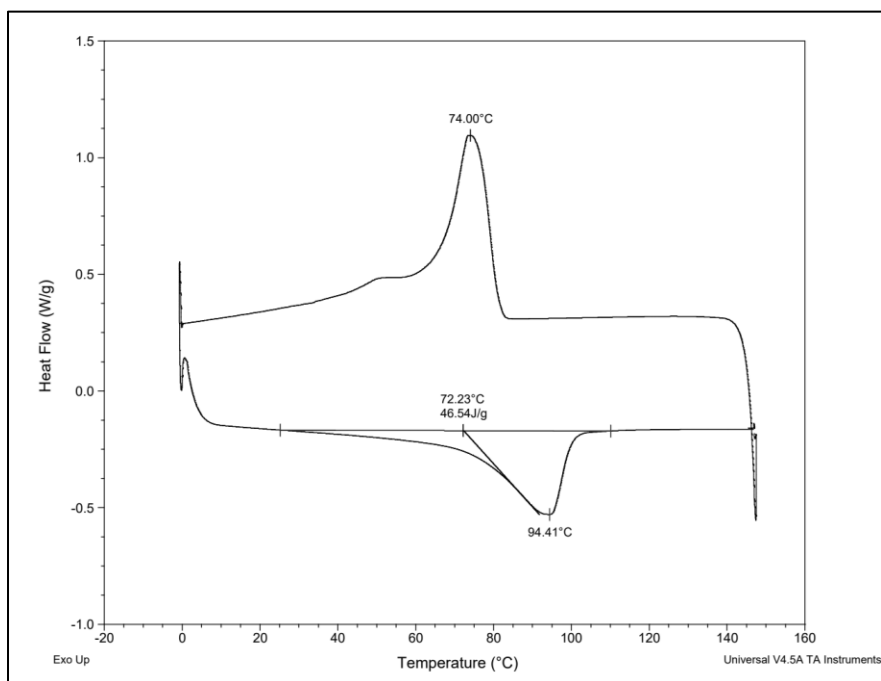


Figure S3.44. DSC spectrum for S25-3.

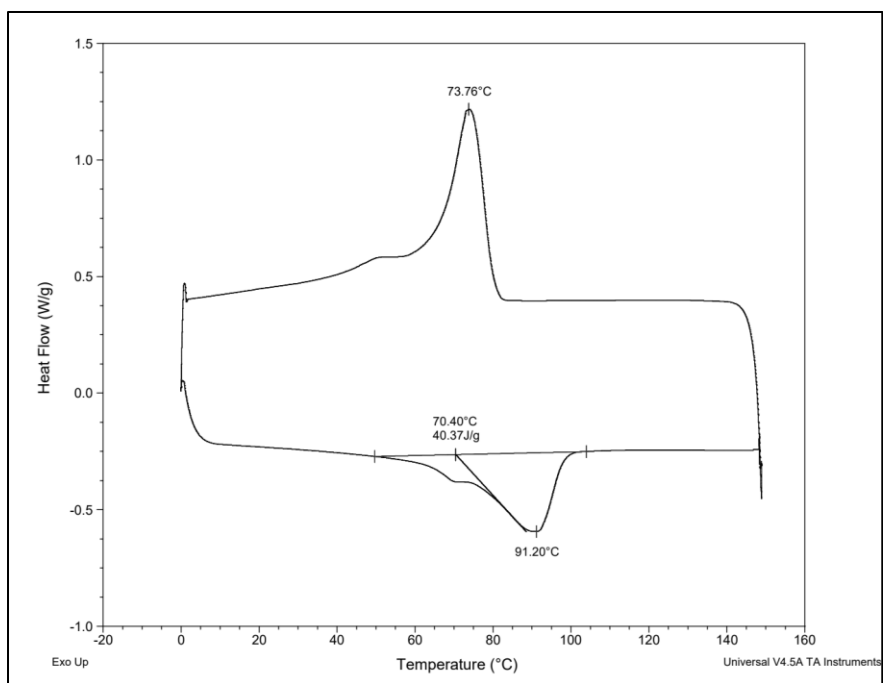


Figure S3.45. DSC spectrum for S25-4.

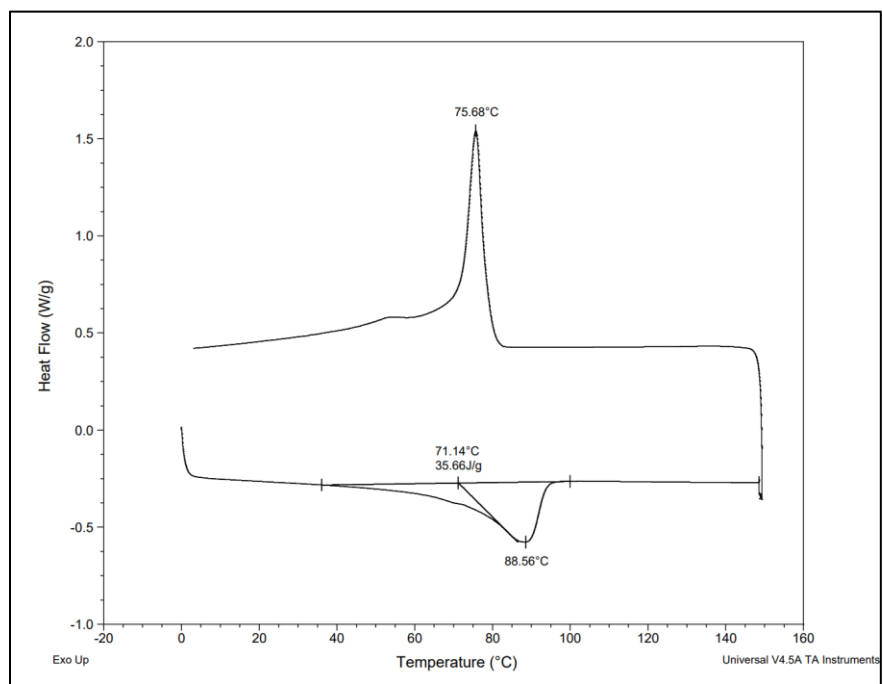


Figure S3.46. DSC spectrum for S25-5.

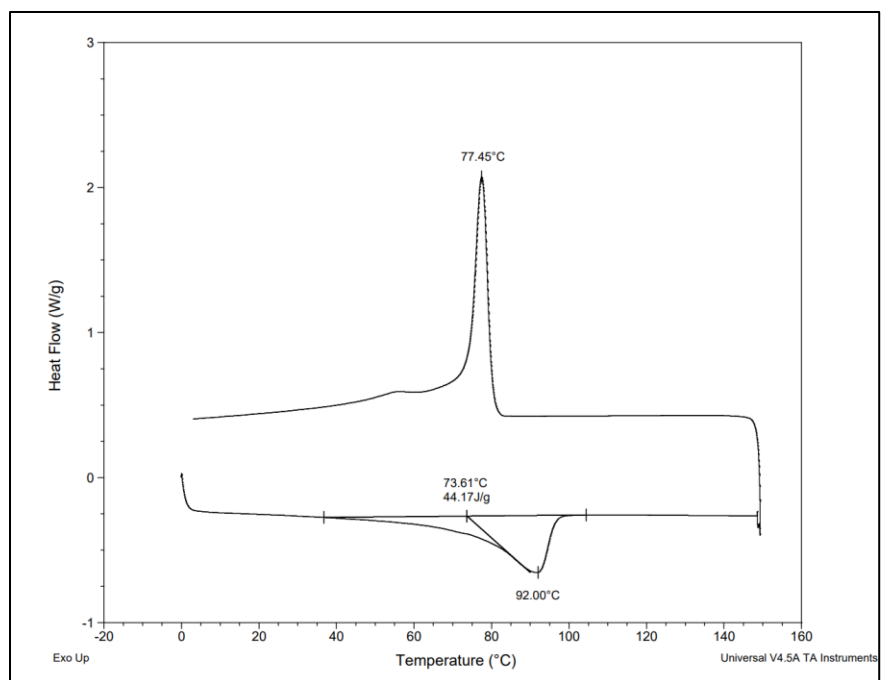


Figure S3.47. DSC spectrum for S25-6.

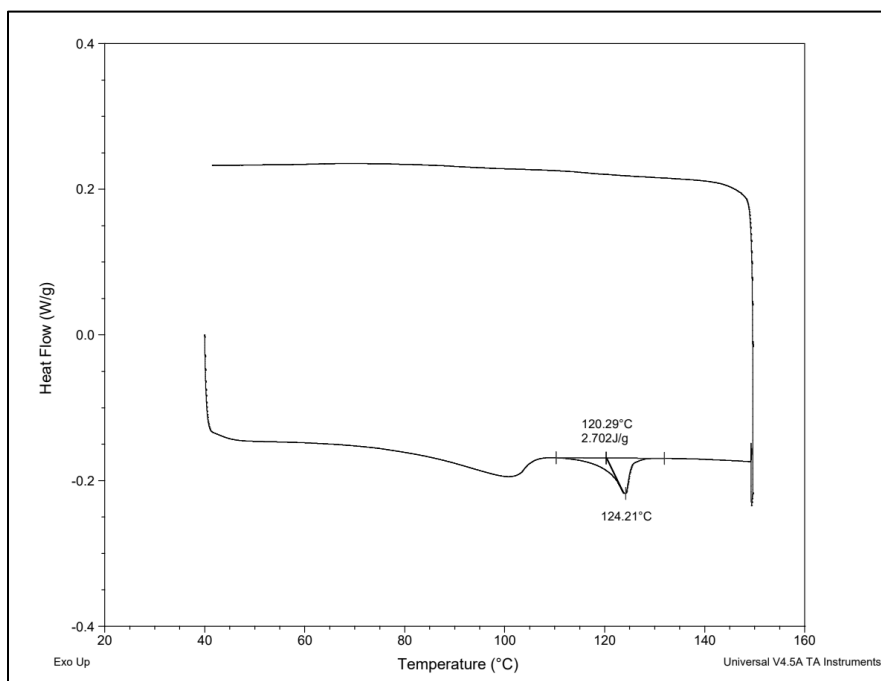


Figure S3.48. DSC spectrum for 23/R.

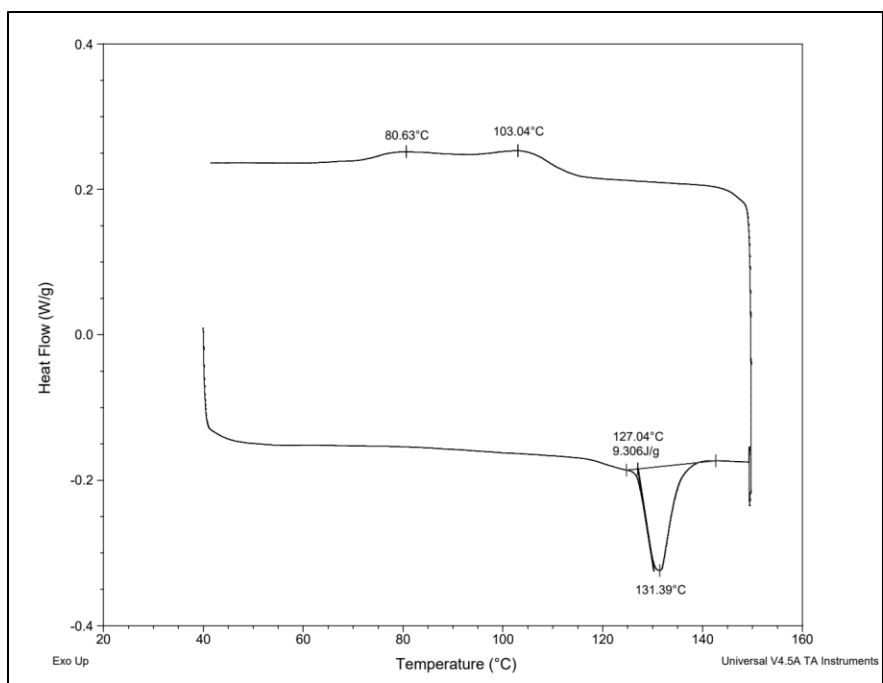


Figure S3.49. DSC spectrum for 23/9B.

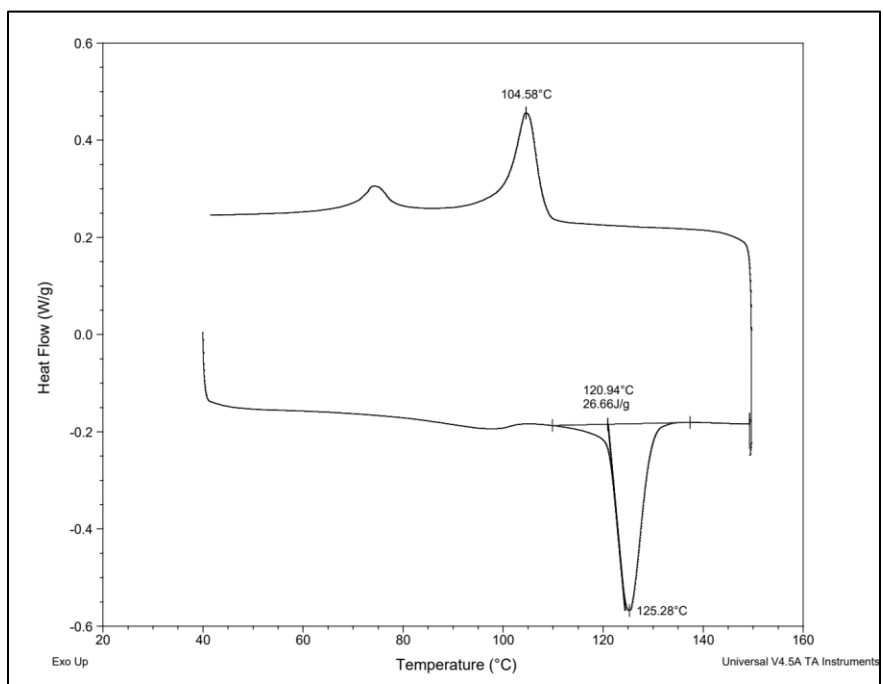


Figure S3.50. DSC spectrum for 10/27B.

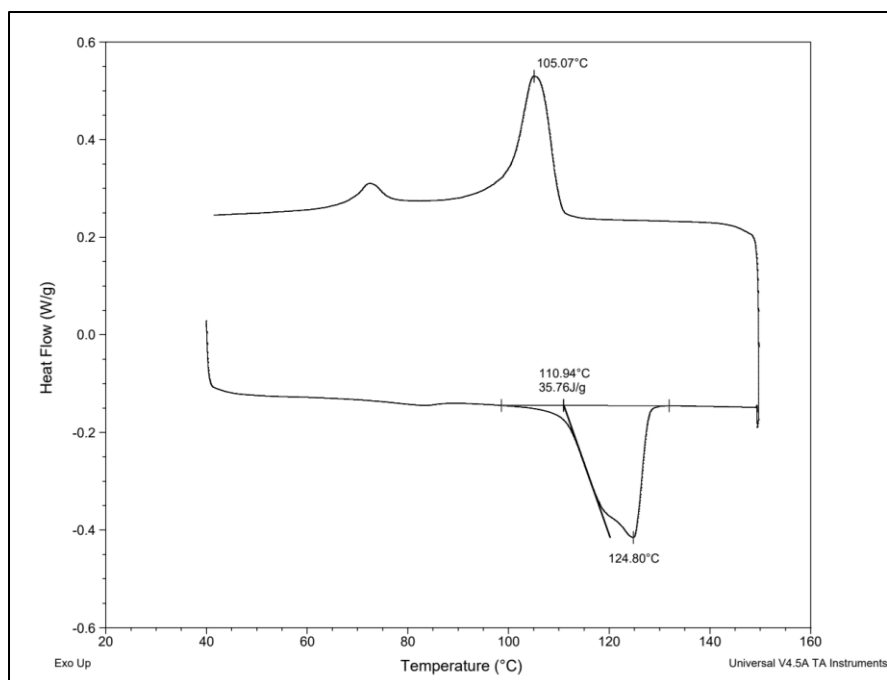


Figure S3.51. DSC spectrum for 18/36B.

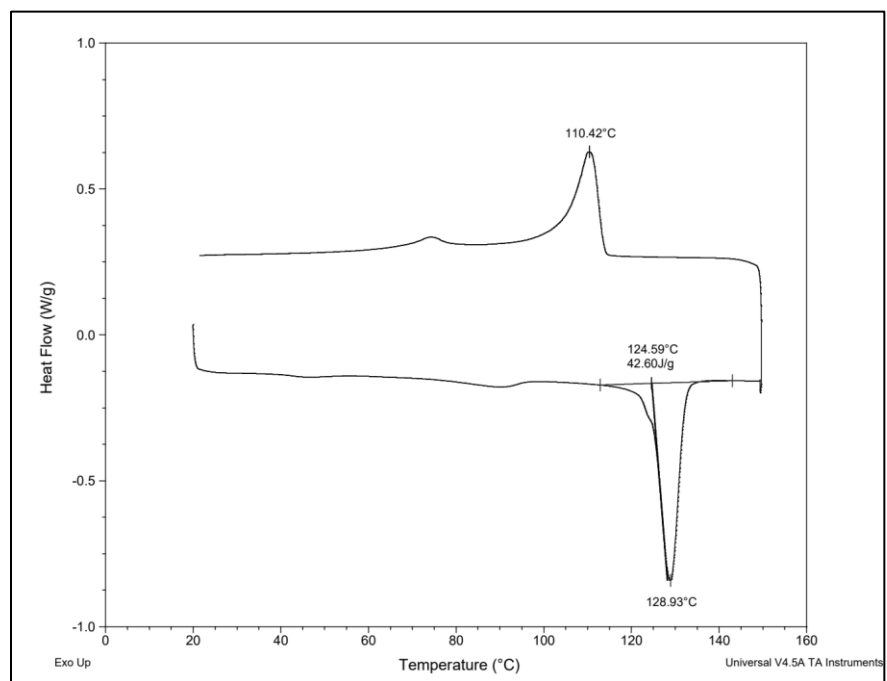


Figure S3.52. DSC spectrum for 19/43B.

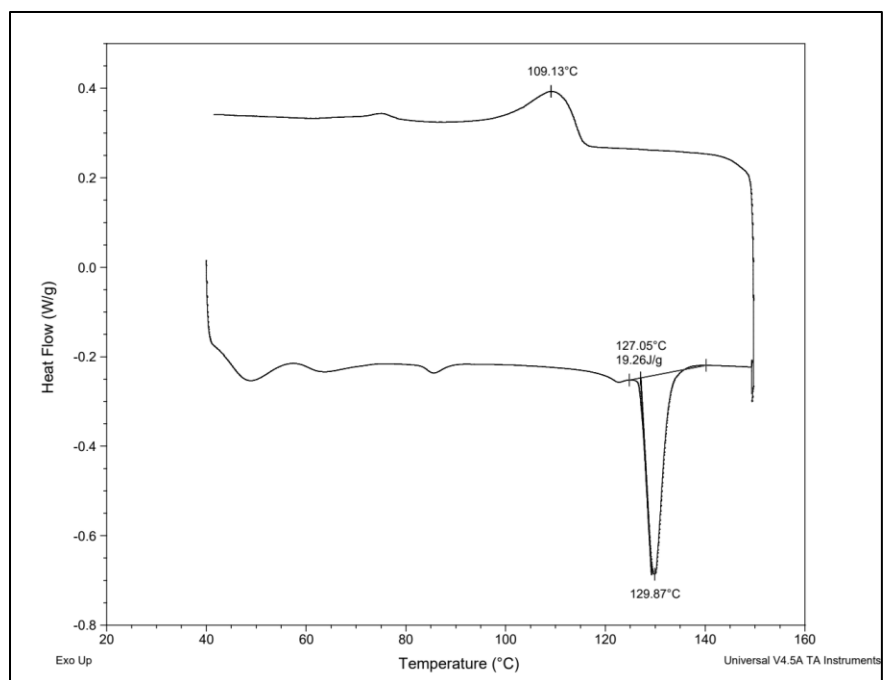


Figure S3.53. DSC spectrum for 14/19B.

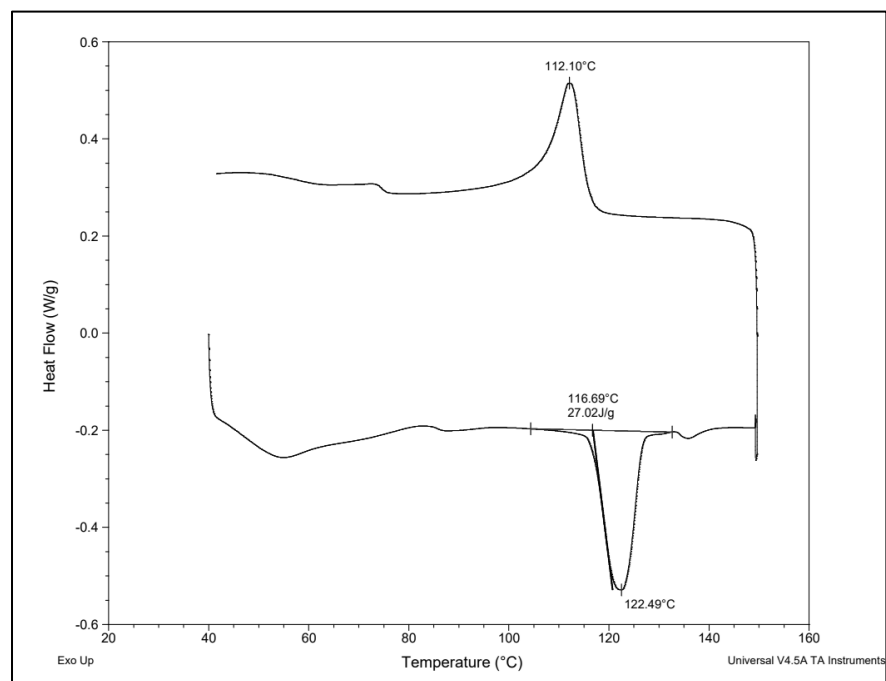


Figure S3.54. DSC spectrum for 23/27B.

Determination of Chlorine Content:

To determine chlorine content per 100 carbons, high-temperature ^1H NMR of all c-PEs was obtained using a Bruker AVANCE NEO 500 MHz at 60-80 $^\circ\text{C}$. Eqn S3.1 is used, where S_1 is the integration of the methyl protons, S_2 is the integration of the methylene protons, and S_3 is the methine protons geminal to the chlorine atoms.⁴⁸ An example spectra can be found in **Figure S3.55**.

$$\text{Chlorines per 100 carbons} = \frac{(S_3)}{(S_3/1) + (S_2/2) + (S_1/3)} \times 100 \quad \text{Eqn (S3.1)}$$

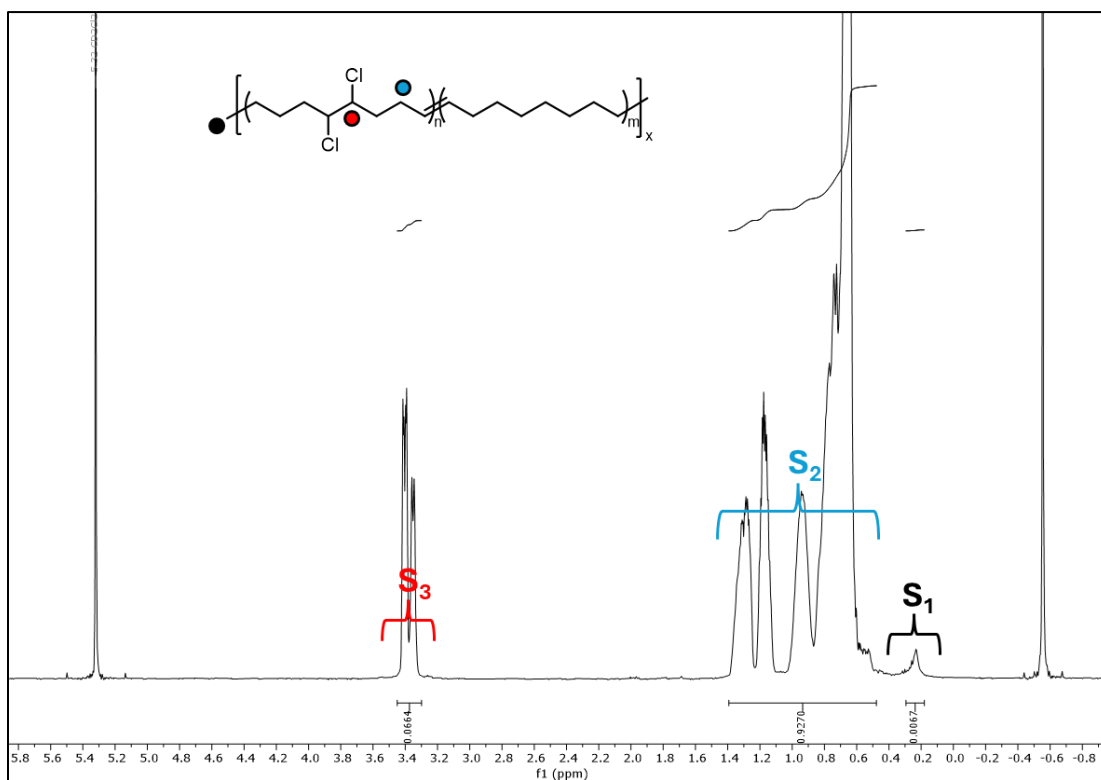


Figure S3.55. ^1H NMR spectrum of S50-1 dissolved in 1,1,2,2-tetrachloroethane- d_2 with integrations of S_1 , S_2 , and S_3 identified.

Determination of Reactivity Ratios:

To determine reactivity ratios of these monomers, the nonterminal or Beckingham-Sanoja-Lynd (BSL) model was then used to determine reactivity ratios due to the nature of the monomers used.¹²³ These copolymerizations are classified as “ideal,” meaning they depend on the chemistry of the monomer, and in this case, the interaction with the ruthenium metal center of **G3**, not the polymer chain end, to determine which monomer will add next. This method of determining reactivity ratios was chosen because of the BSL model’s ability to distinguish between random and gradient copolymers.¹²³ To do this, ¹H NMR was used to monitor conversion over time, and total monomer conversion versus individual monomer conversion was plotted. A standard polymerization reaction was set up where both monomers were added to a vial in a 1:1 mixture with deuterated chloroform as the solvent and trimethoxybenzene as an internal standard added in 1 equivalent. ¹H NMRs were obtained on a Varian 500 MHz NMR of the initial monomer mixture before Grubbs 3rd generation catalyst was added and of aliquots over a period of several minutes (0 s, 10 s, 20 s, 30 s, 1 min, 2 min, 3 min, 4 min, 5 min, and 6 min) after the catalyst was added. All samples were quenched with ethyl vinyl ether, including the initial time point, before taking NMR to ensure consistency. A sample ¹H NMR of a 10s timepoint is included in **Figure S3.56**.

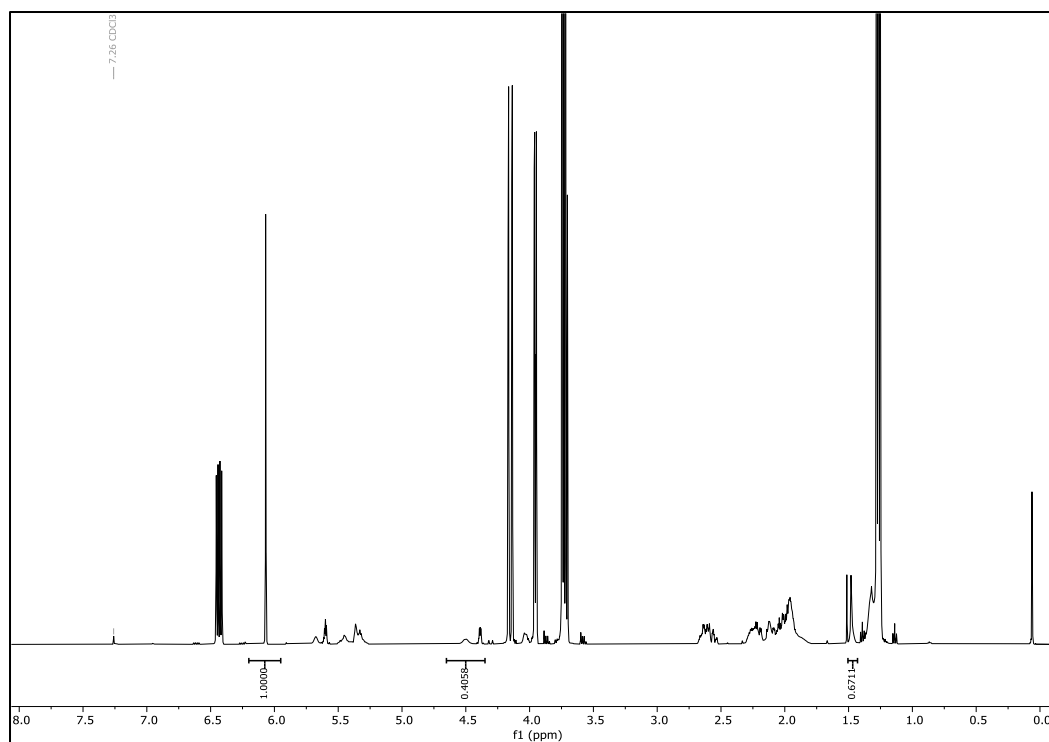


Figure S3.56. ^1H NMR of copolymerization ran for 10 seconds with trimethoxy benzene as internal standard in deuterated chloroform.

Trimethoxy benzene was integrated from 6.01-6.14 ppm and set to 1 for the other integrations to be referenced against. Cl₂COE (monomer A) was integrated from 4.35-4.63 ppm, as this encompasses both protons geminal to the chlorine in both isomers, and COE (monomer B) was integrated from 1.44-1.51 ppm. These integrations were monitored over time and the monomer conversion (p_A and p_B) was calculated over a period of 6 minutes. The rate of conversion over time for each monomer (k_A and k_B) was determined and used to solve for the reactivity ratios (r_A and r_B) using equations S3-S6 where A_0 , B_0 , and X_0 are the initial concentrations of monomer A, B, and initiator X.¹²³ Total monomer conversion was found using Eqn S3.7 where n_A and n_B are the mole fractions of each respective monomer.¹²⁴ Eqns S3.8 and S3.9 were then used to plot total monomer conversion versus individual monomer conversion.¹²³

$$A(t) = A_0 e^{-k_A X_0 t} \quad \text{Eqn (S3.3)}$$

$$B(t) = B_0 e^{-k_B X_0 t} \quad \text{Eqn (S3.4)}$$

$$\left(\frac{B(t)}{B_0}\right)^{r_A} = \frac{A(t)}{A_0} \quad \text{Eqn (S3.5)}$$

$$\left(\frac{A(t)}{A_0}\right)^{r_B} = \frac{B(t)}{B_0} \quad \text{Eqn (S3.6)}$$

$$p_{AB} = 1 - n_A \times (1 - p_A) - n_B \times (1 - p_B) \quad \text{Eqn (S3.7)}$$

$$p_{AB}(p_A) = 1 - n_A \times (1 - p_A) - (1 - n_A) \times (1 - p_A)^{r_B} \quad \text{Eqn (S3.8)}$$

$$p_{AB}(p_A) = 1 - n_A \times (1 - p_B)^{r_A} - (1 - n_A) \times (1 - p_B) \quad \text{Eqn (S3.9)}$$

Appendix C: Chapter IV Supporting Information

Structure assignments for ethylene-propylene random copolymers:

Table S4.1. Structure assignments for ethylene-propylene random copolymers

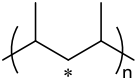
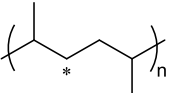
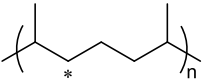
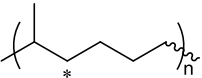
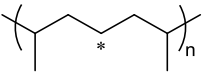
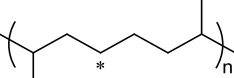
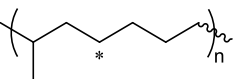
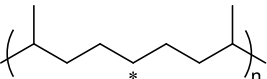
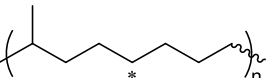
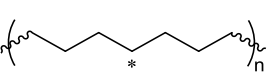
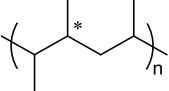
Structure	Carbon Assignment Secondary (S) or Tertiary (T)	Composition
	$S_{\alpha\alpha}$	2 propylene units
	$S_{\alpha\beta}$	2 propylene units
	$S_{\alpha\gamma}$	2 propylene units 1 ethylene unit
	$S_{\alpha\delta+}$	≥ 1 propylene unit ≥ 1 ethylene units
	$S_{\beta\beta}$	2 propylene units 1 ethylene unit
	$S_{\beta\gamma}$	2 propylene units 1 ethylene unit
	$S_{\beta\delta+}$	≥ 1 propylene unit ≥ 1 ethylene units
	$S_{\gamma\gamma}$	2 propylene units 2 ethylene unit
	$S_{\gamma\delta+}$	≥ 1 propylene unit ≥ 2 ethylene units
	$S_{\delta+\delta+}$	≥ 3 ethylene units
	$T_{\alpha\beta}$	3 propylene units

Table S4.1.: Continued

	$T_{\beta\beta}$	3 propylene units
	$T_{\beta\gamma}$	3 propylene units
	$T_{\beta\delta+}$	≥ 2 propylene units ≥ 1 ethylene units
	$T_{\gamma\gamma}$	3 propylene units
	$T_{\gamma\delta+}$	≥ 2 propylene units ≥ 1 ethylene unit
	$T_{\delta+\delta+}$	≥ 1 propylene unit ≥ 2 ethylene units

+ the last carbon in these sequences can be a part of a propylene or an ethylene unit.
Only one resonance is presented for each triad sequence.

Differential scanning calorimetry (DSC) for the 5 VistaMaxx ethylene-propylene rubber samples provided by ExxonMobil, as well as the Engage polyolefin elastomer ethylene 1-octene sample. Samples of 5-10 mg of the material are run on a TA Q-2000 DSC at a 10 °C/min ramp rate. The second heating/cooling curve is collected for analysis to ensure thermal history isn't impacting results.

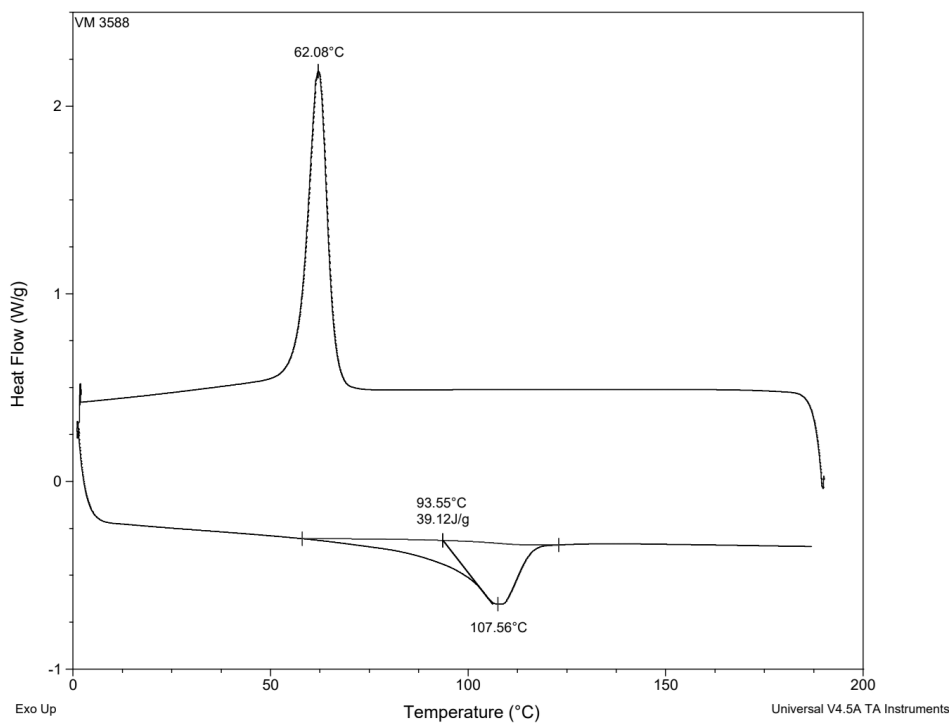


Figure S4.1. DSC spectrum for VistaMaxx (VM) 3588 (ExxonMobil).

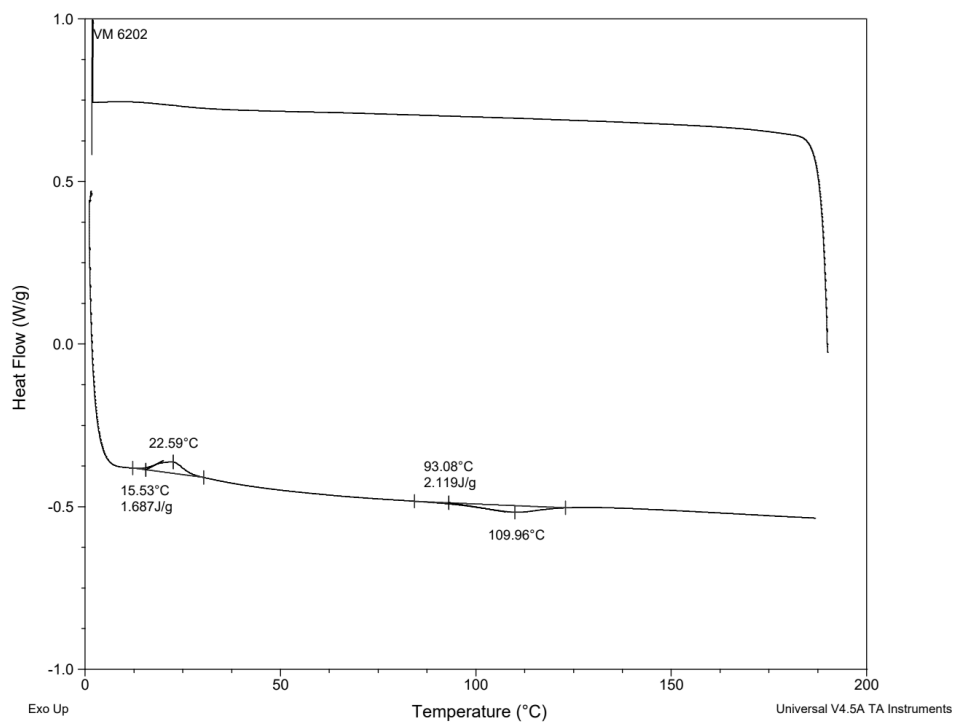


Figure S4.2. DSC spectrum for VistaMaxx (VM) 6202 (ExxonMobil).

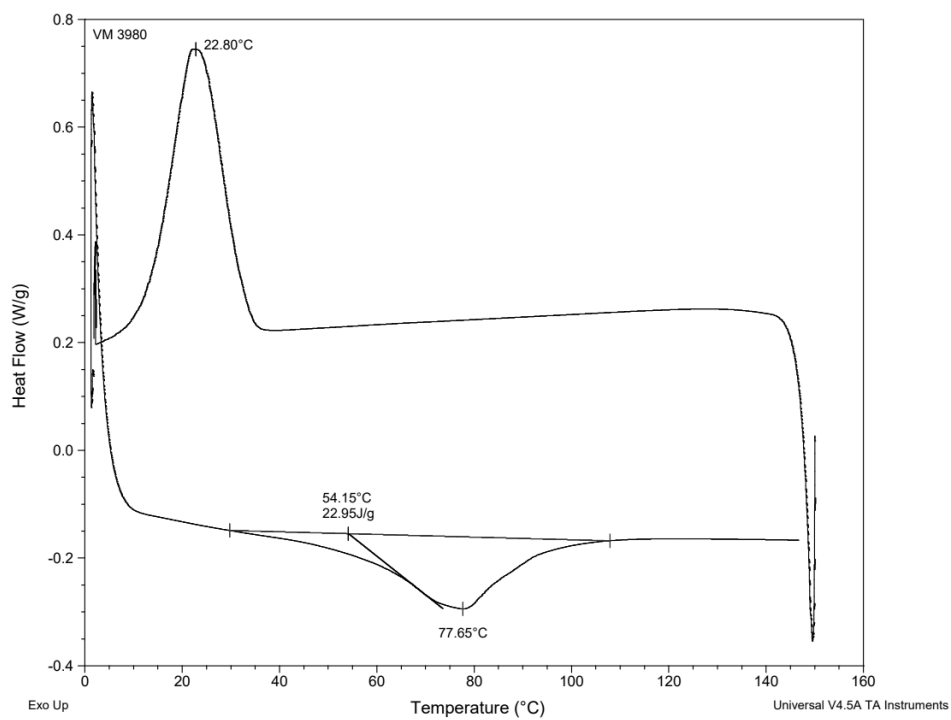


Figure S4.3. DSC spectrum for VistaMaxx (VM) 3980 (ExxonMobil).

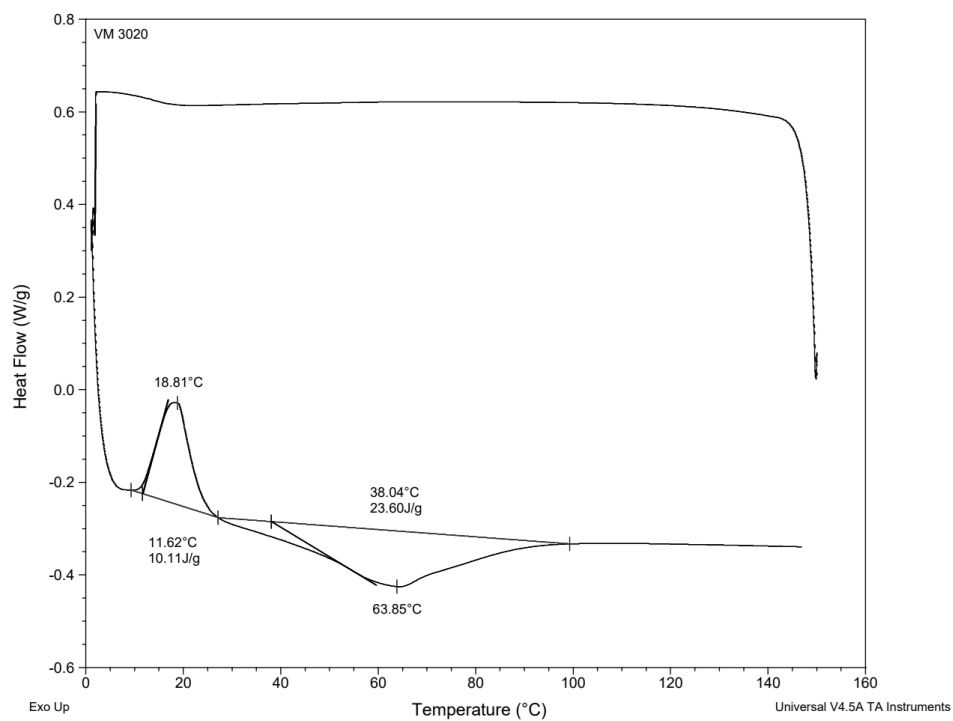


Figure S4.4. DSC spectrum for VistaMaxx (VM) 3020 (ExxonMobil).

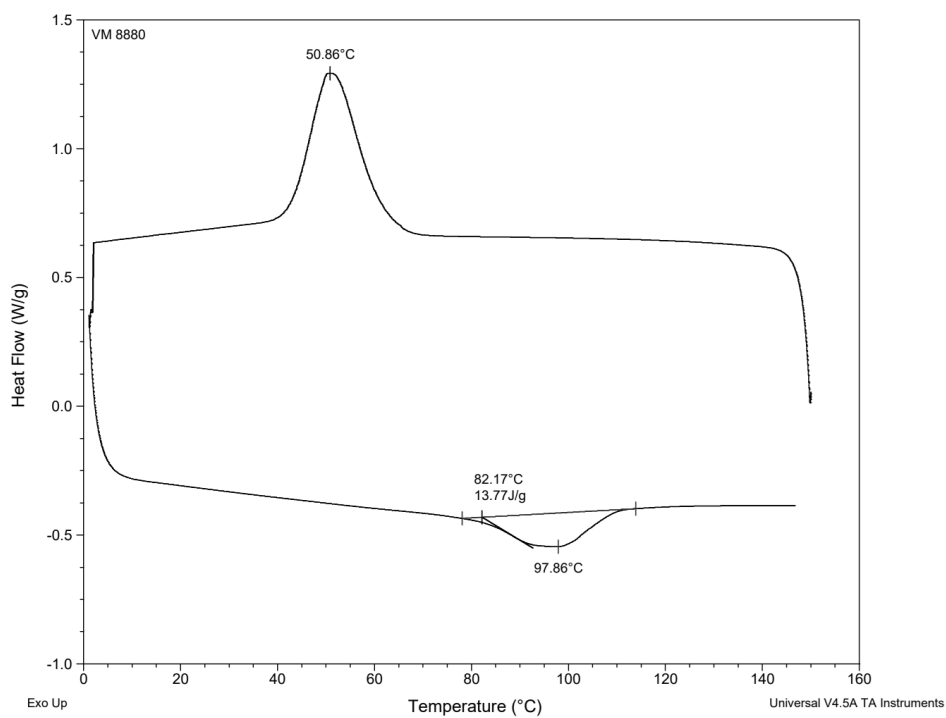


Figure S4.5. DSC spectrum for VistaMaxx (VM) 8880 (ExxonMobil).

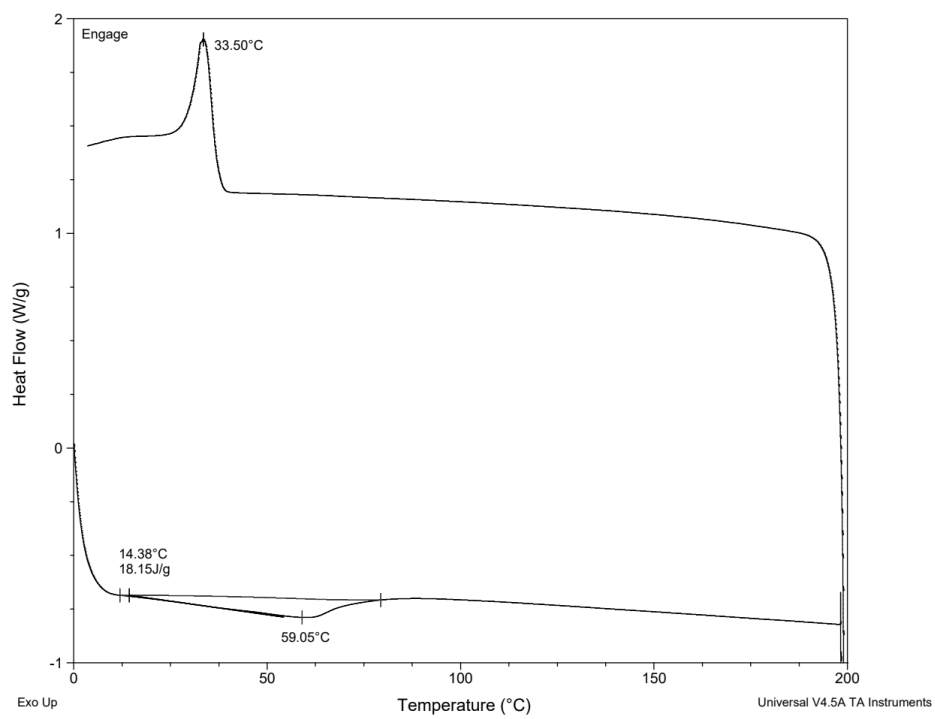


Figure S4.6. DSC spectrum for Engage 8180 (DOW Chemical).

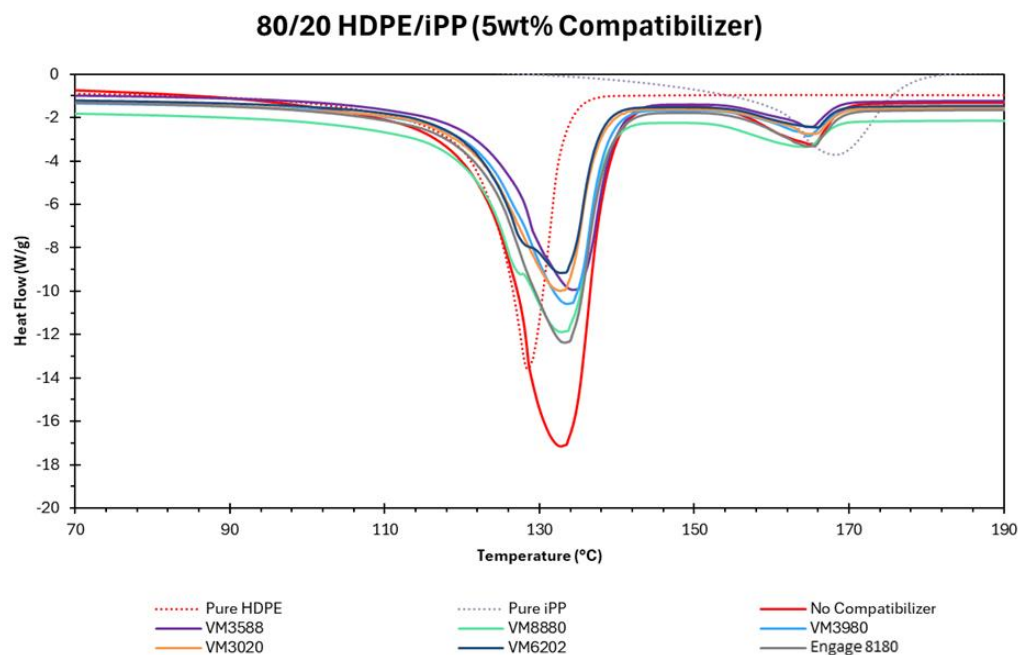


Figure S4.7. DSC spectrum for all 80/20 HDPE/iPP blends with 5 wt% compatibilizer loading.

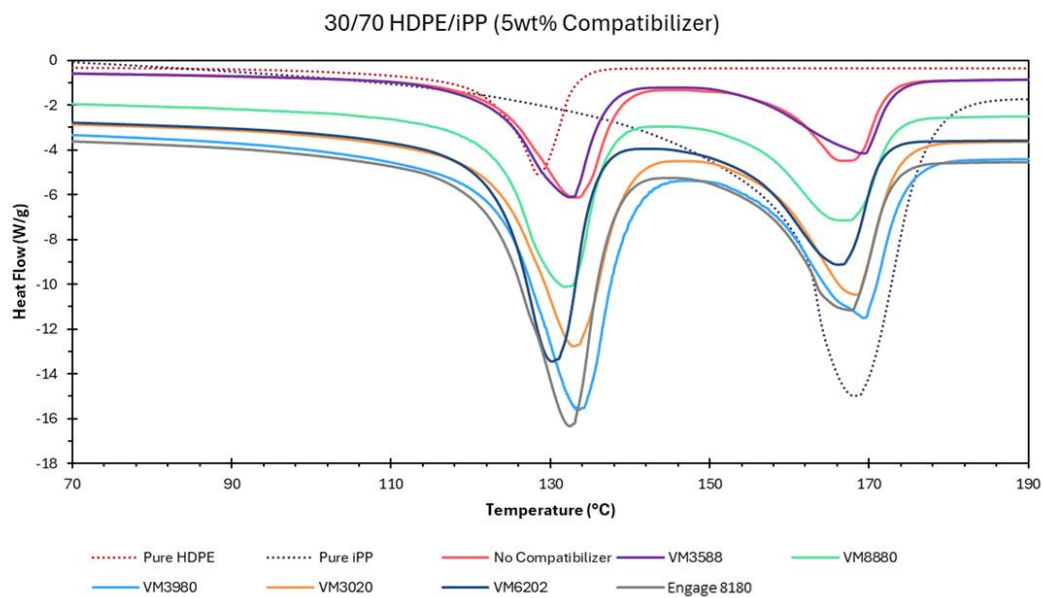


Figure S4.8. DSC spectrum for all 80/20 HDPE/iPP blends with 5 wt% compatibilizer loading.

High temperature ^1H NMR spectra for the VistaMaxx (VM) samples at 5 wt% dissolved in 1,1,2,2-tetrachloroethane- d_2 .

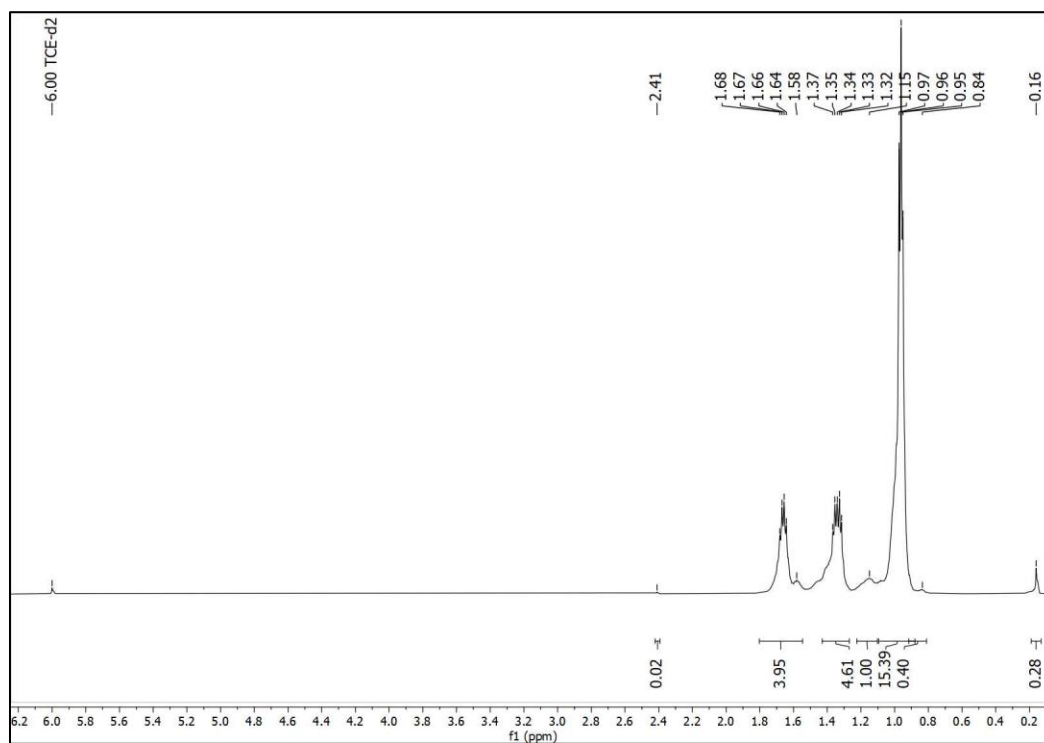


Figure S4.9. ^1H NMR Spectrum for VistaMaxx (VM) 3588 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

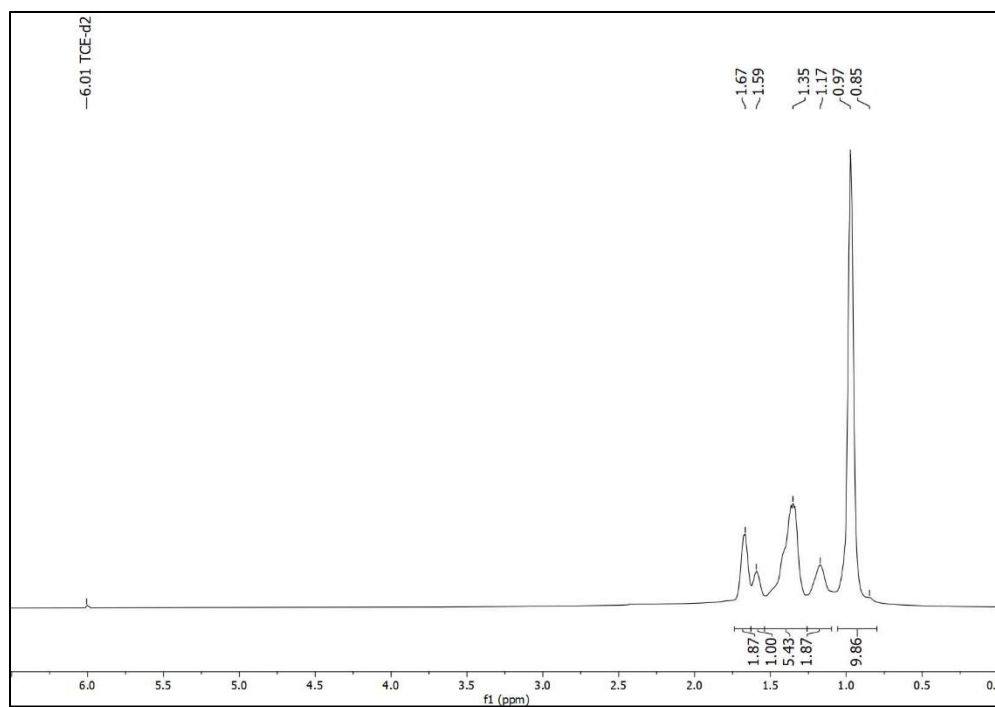


Figure S4.10. ^1H NMR spectrum for VistaMaxx (VM) 6202 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

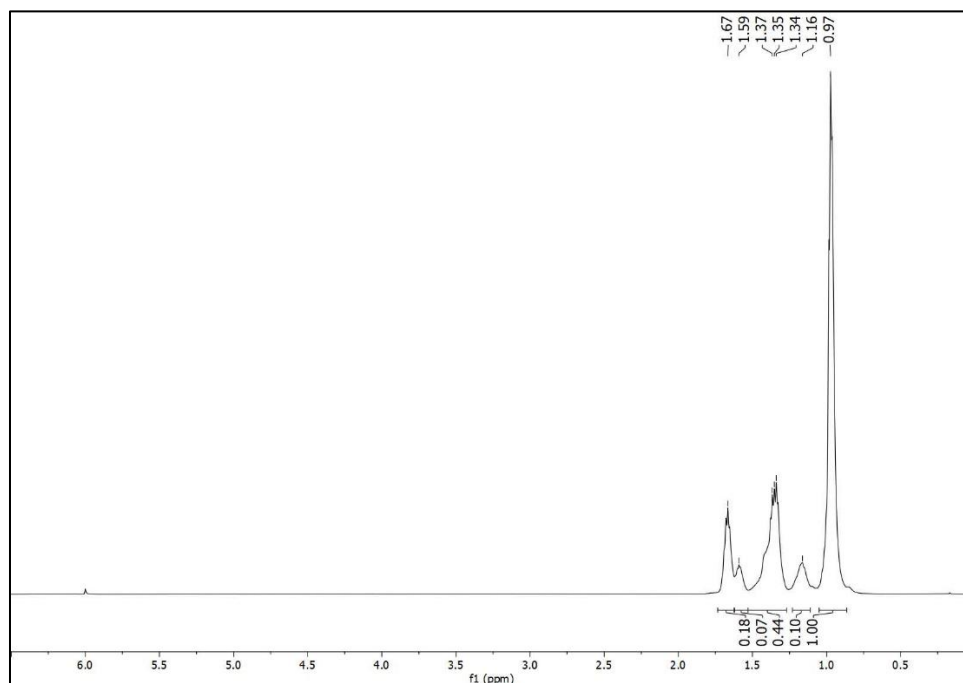


Figure S4.11. ^1H NMR spectrum for VistaMaxx (VM) 3020 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

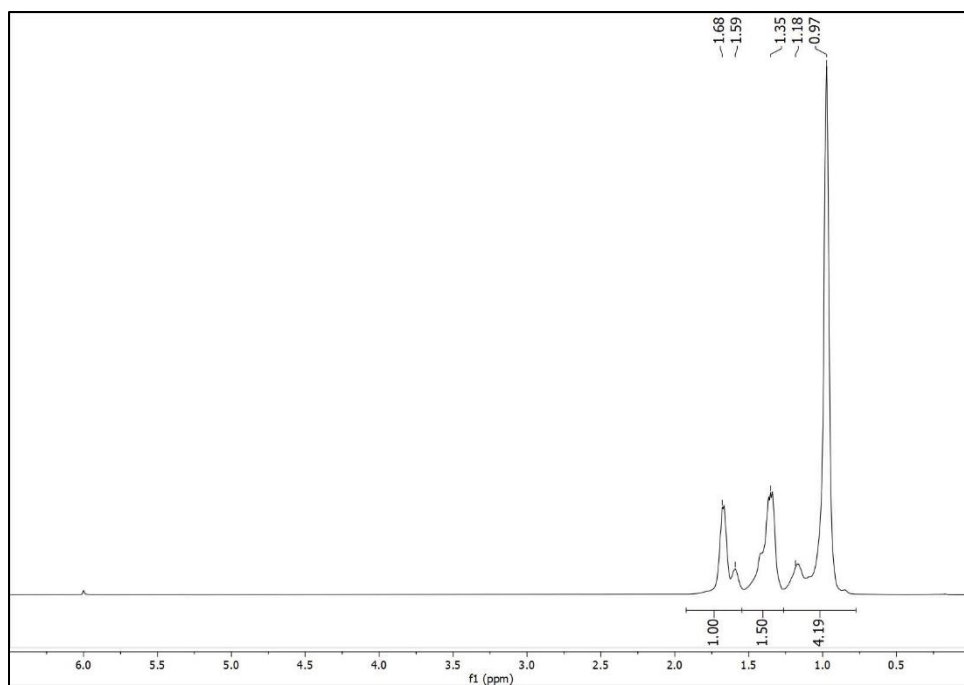


Figure S4.12. ^1H NMR spectrum for VistaMaxx (VM) 3980 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

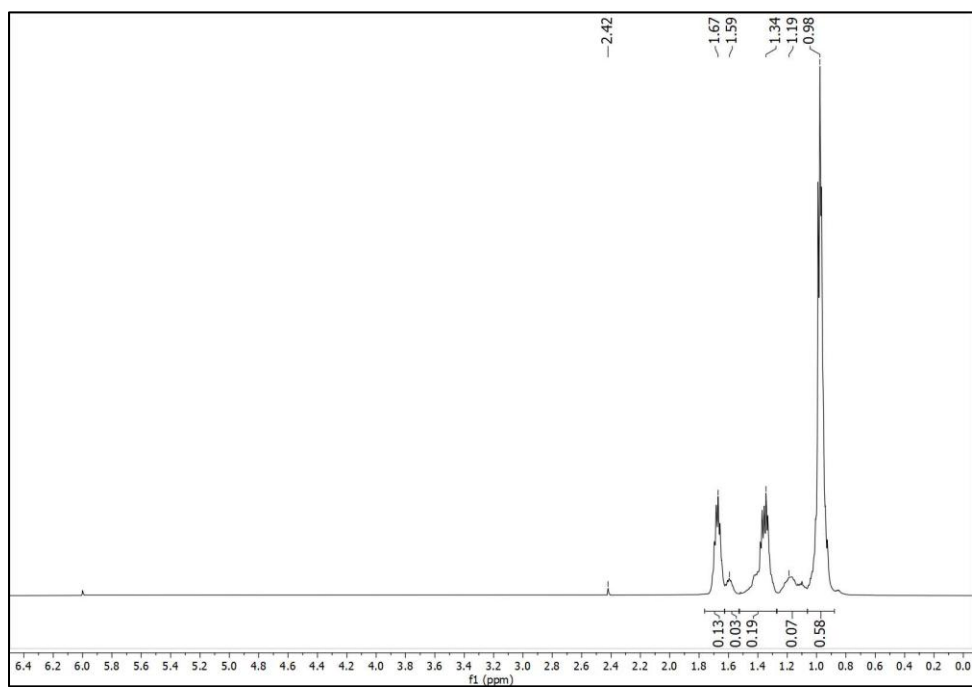


Figure S4.13. ^1H NMR spectrum for VistaMaxx (VM) 8880 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

High temperature quantitative ^{13}C NMR spectra for the VistaMaxx (VM) samples at 5 wt% dissolved in 1,1,2,2-tetrachloroethane-d₂.

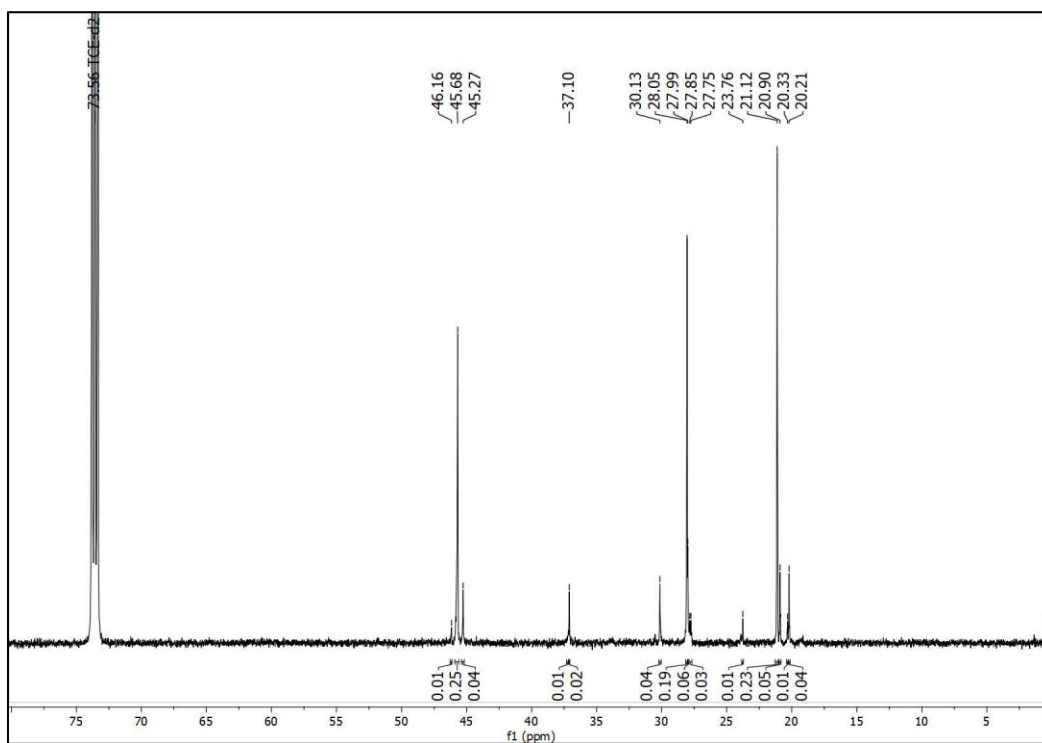


Figure S4.14. Quantitative ^{13}C NMR spectrum for VistaMaxx (VM) 3588 dissolved in 1,1,2,2-tetrachloroethane-d₂.

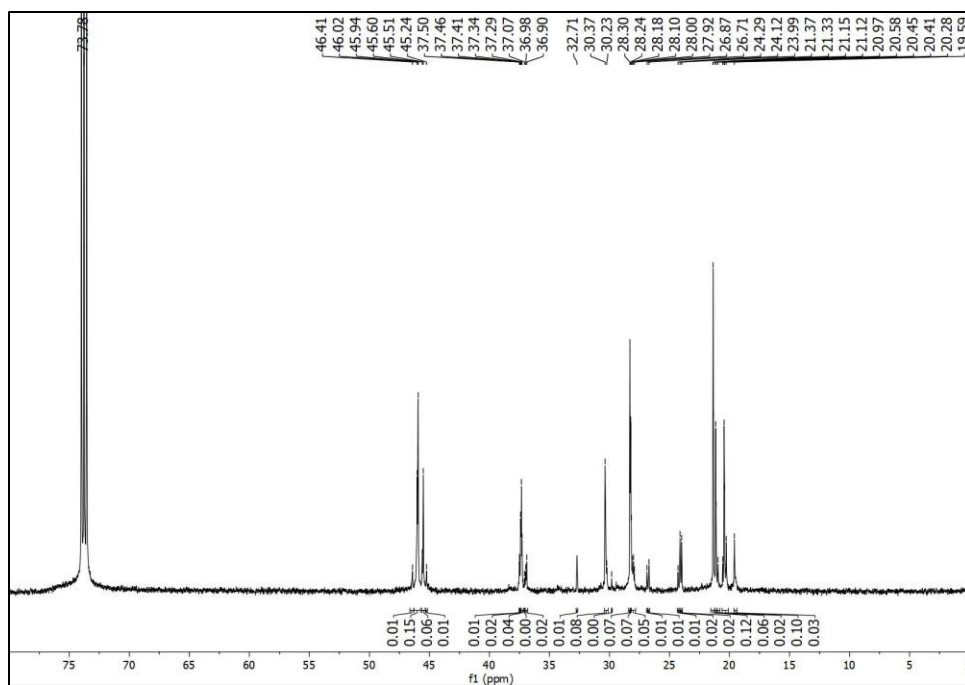


Figure S4.15. Quantitative ^{13}C NMR spectrum for VistaMaxx (VM) 6202 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

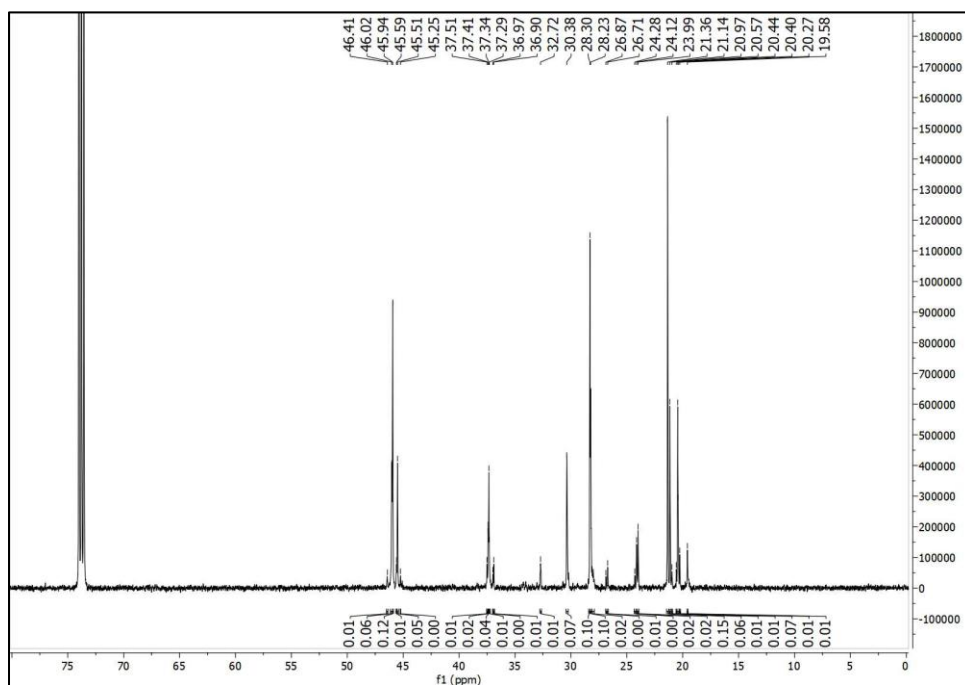


Figure S4.16. Quantitative ^{13}C NMR spectrum for VistaMaxx (VM) 3020 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

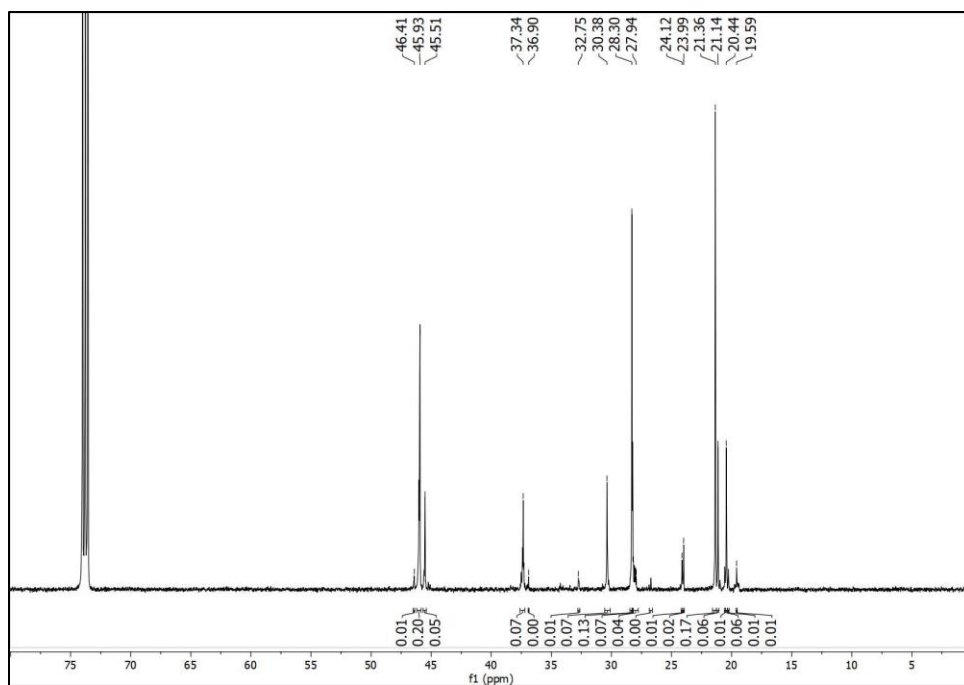


Figure S4.17. Quantitative ^{13}C NMR spectrum for VistaMaxx (VM) 3980 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

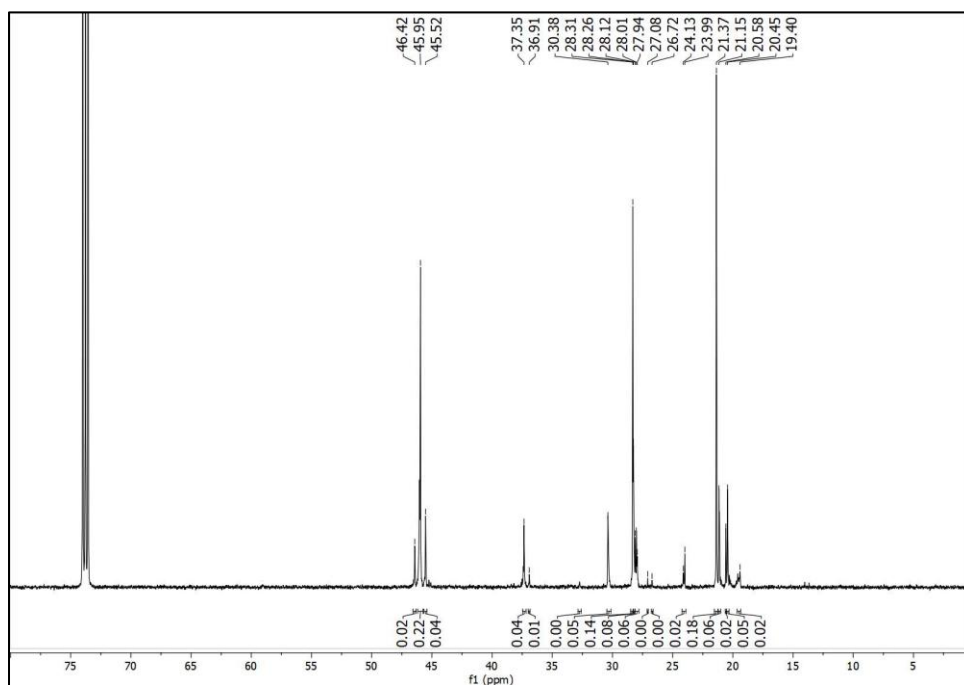


Figure S4.18. Quantitative ^{13}C NMR spectrum for VistaMaxx (VM) 8880 dissolved in 1,1,2,2-tetrachloroethane- d_2 .

Stress-Strain Curves: ASTM 1708 samples collected using an Instron 5kN Universal Tester at a crosshead rate of 10 mm/min. The curve plotted is the trial with data closest to the average of all five trials for each compatibilizer analyzed.

80/20 HDPE/iPP Blends:

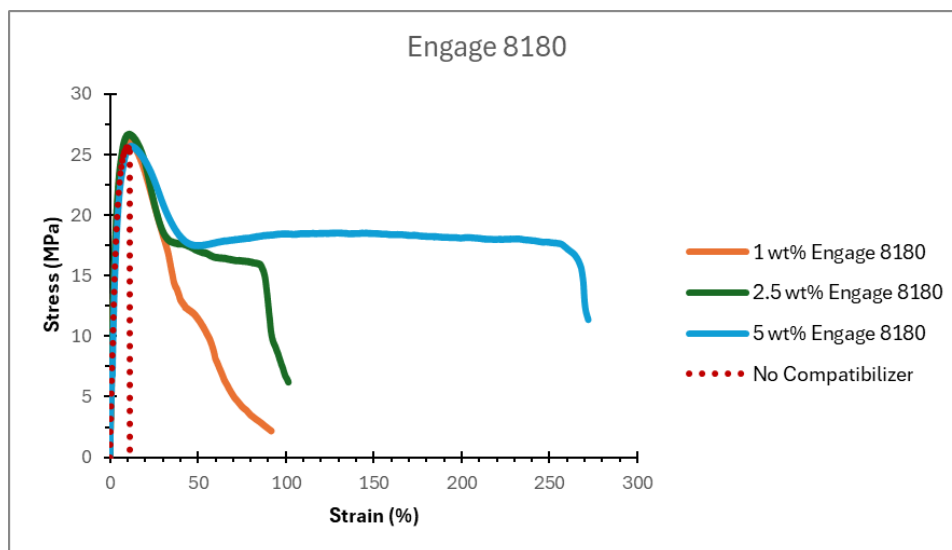


Figure S4.19. Stress-strain curve for Engage 8180 at 1, 2.5, and 5 wt% compatibilizer loading in an 80/20 HDPE/iPP blend.

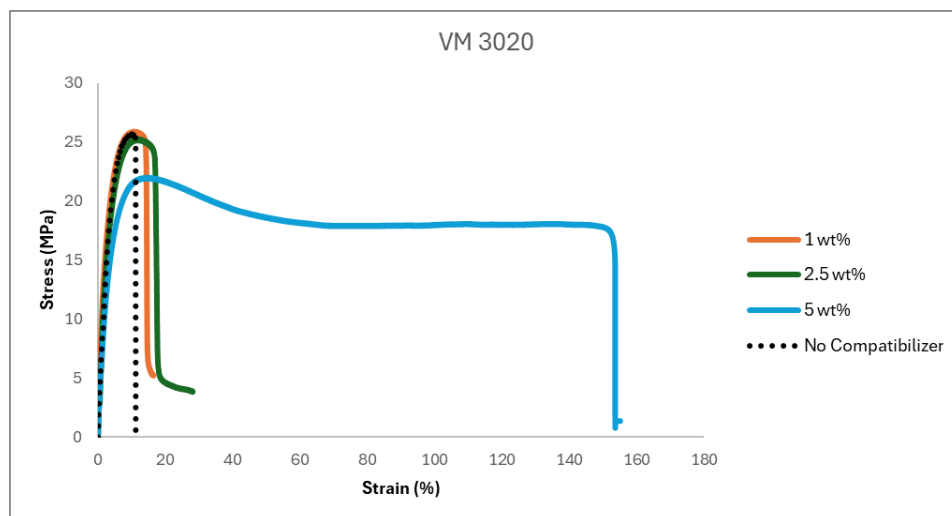


Figure S4.20. Stress-strain curve for VistaMaxx 3020 (VM3020) at 1, 2.5, and 5 wt% compatibilizer loading in an 80/20 HDPE/iPP blend.

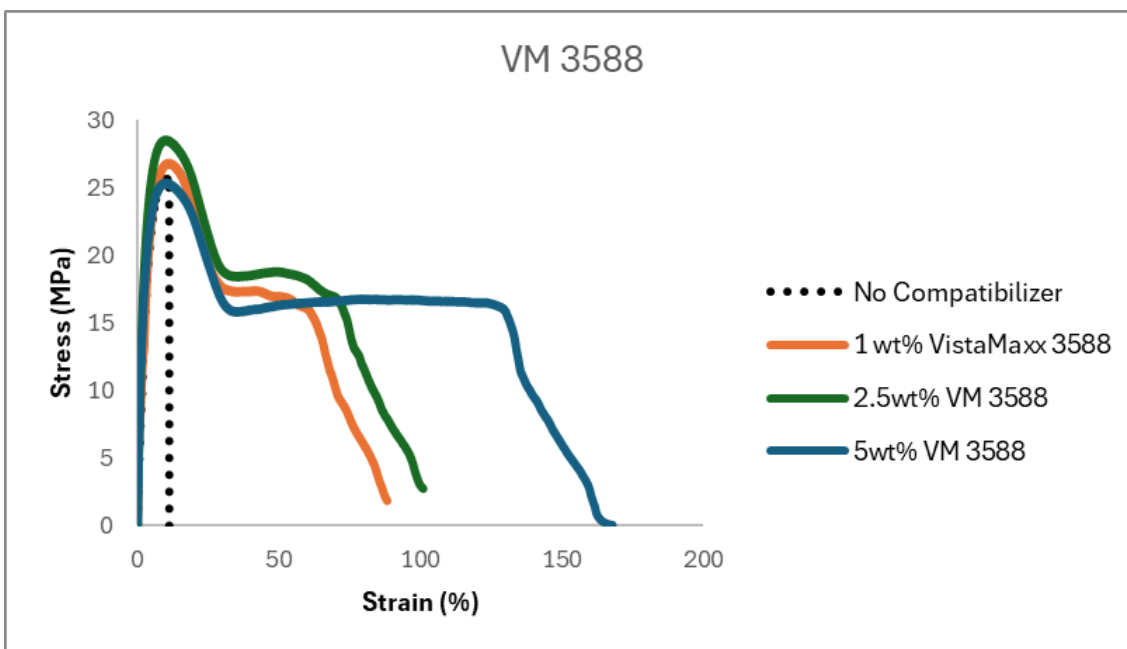


Figure S4.21. Stress-strain curve for VistaMaxx 3588 (VM3588) at 1, 2.5, and 5 wt% compatibilizer loading in an 80/20 HDPE/iPP blend.

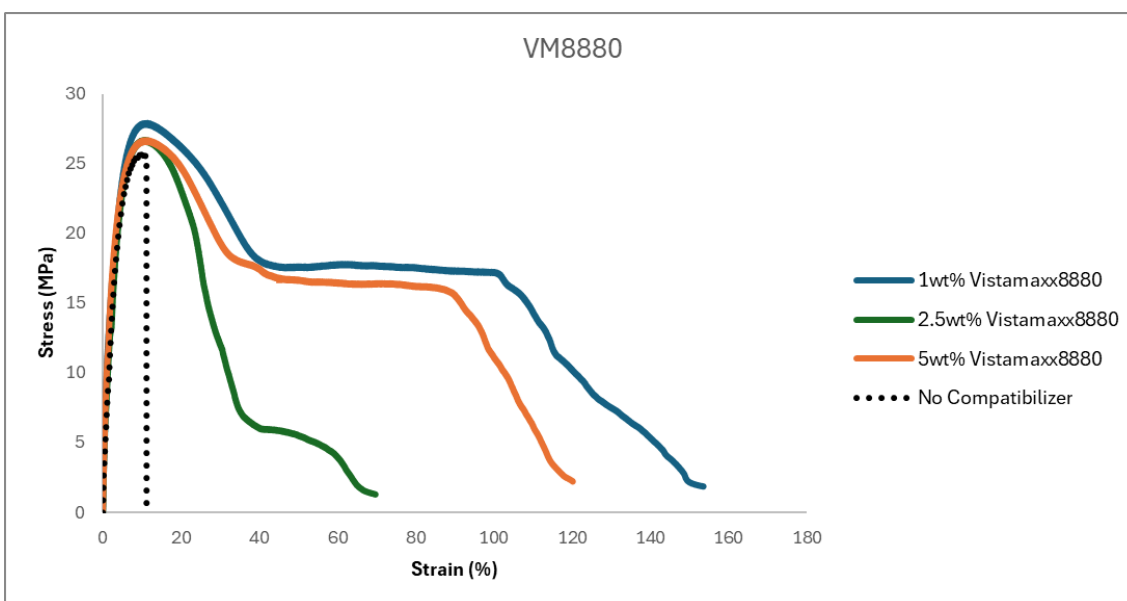


Figure S4.22. Stress-strain curve for VistaMaxx 8880 (VM3588) at 1, 2.5, and 5 wt% compatibilizer loading in an 80/20 HDPE/iPP blend.

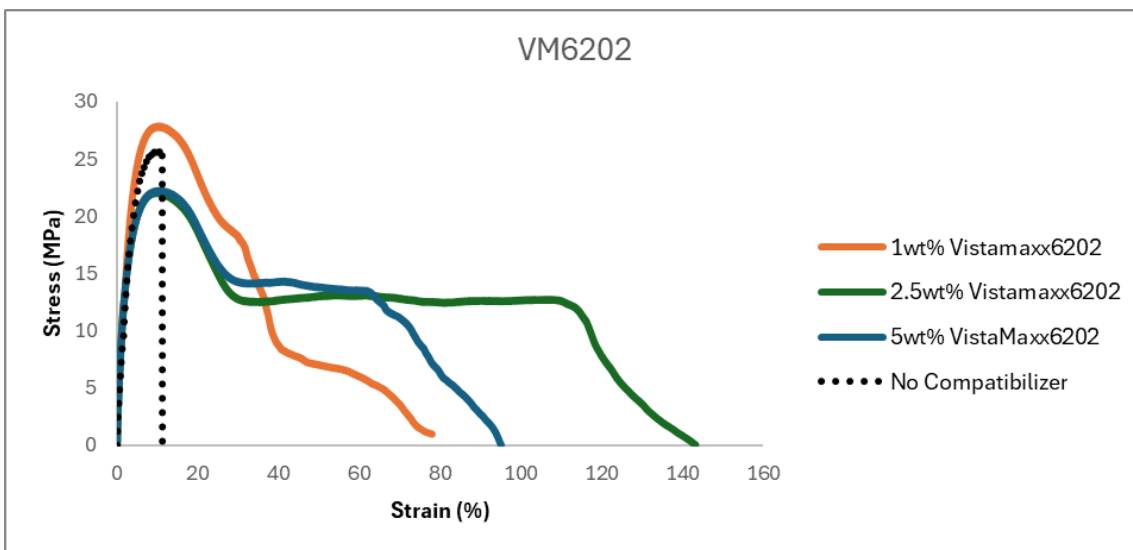


Figure S4.23. Stress-strain curve for VistaMaxx 6202 (VM6202) at 1, 2.5, and 5 wt% compatibilizer loading in an 80/20 HDPE/iPP blend.

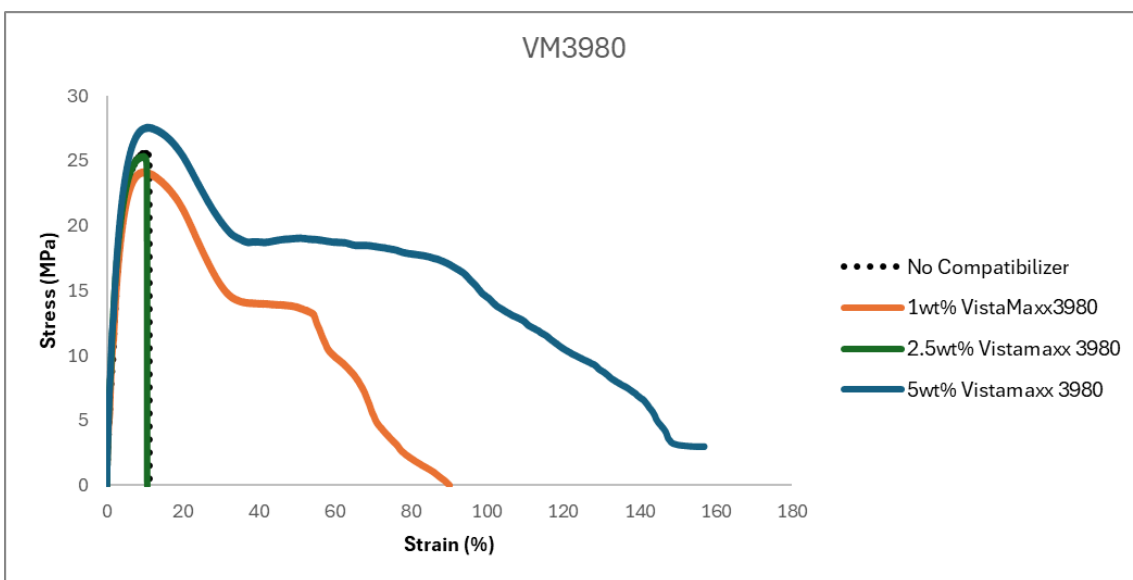


Figure S4.24. Stress-strain curve for VistaMaxx 3980 (VM3980) at 1, 2.5, and 5 wt% compatibilizer loading in an 80/20 HDPE/iPP blend.

30/70 HDPE/iPP Blends: Only examined at 5 wt% compatibilizer loading.

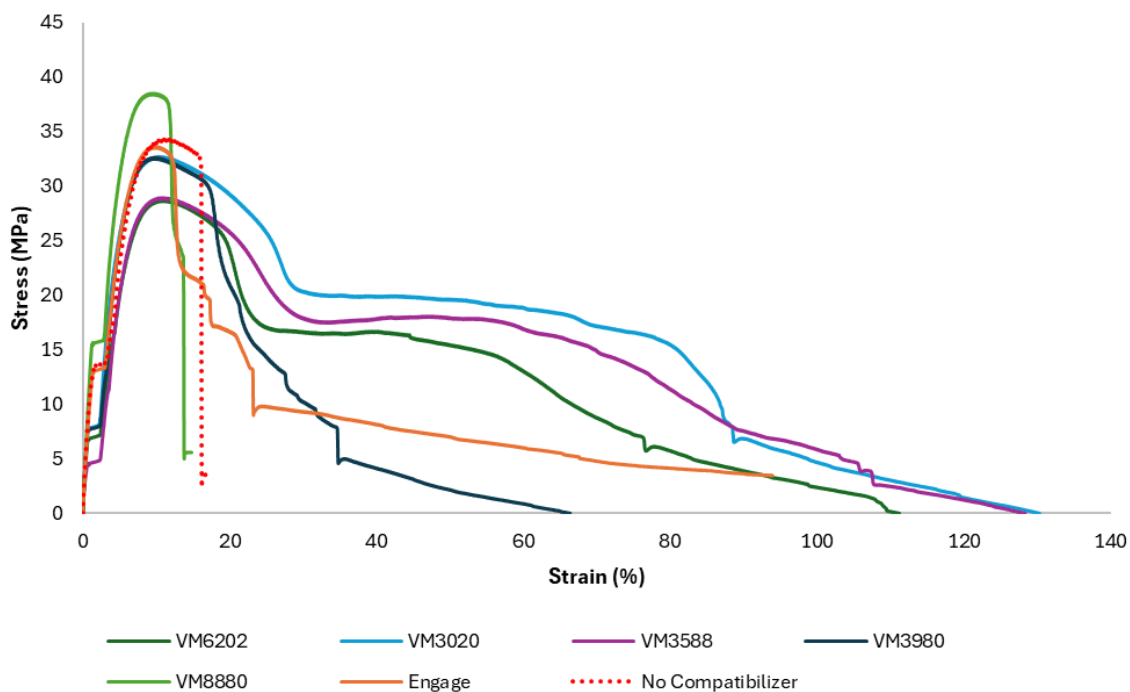


Figure S4.25. Stress-strain curve for all compatibilizers tested at 5 wt% compatibilizer loading in a 30/70 HDPE/iPP blend.

Toughness vs. Homopolymer Crystallinity for iPP-rich blends. Toughness is determined from the area under the stress-strain curve. Crystallinity is determined from integrating blend DSC spectra and is normalized based on composition.

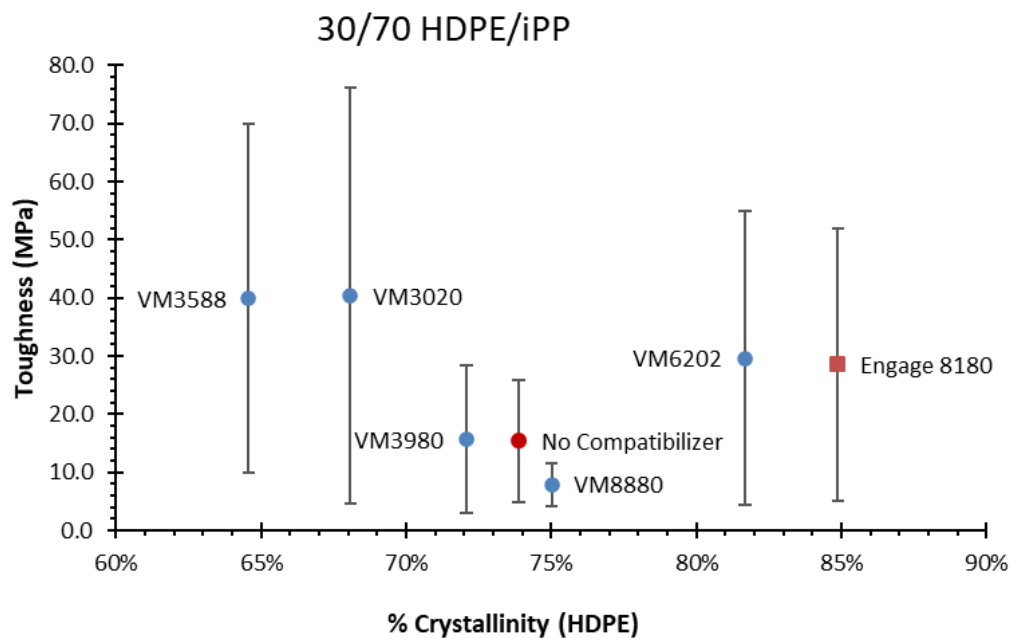


Figure S4.26. HDPE crystallization in 30/70 HDPE/iPP blends and their observed toughness. Error bars represent one standard deviation from the average.

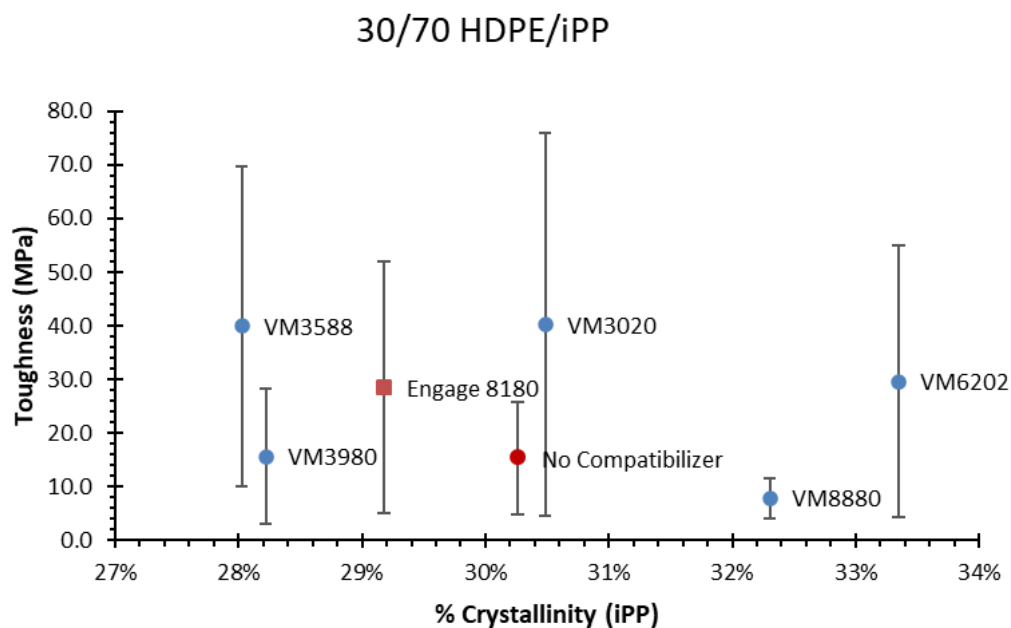


Figure S4.27. iPP crystallization in 30/70 HDPE/iPP blends and their observed toughness. Error bars represent one standard deviation from the average.

Appendix D: Chapter V Supporting Information

¹H NMR spectrum for dechlorinated PVC

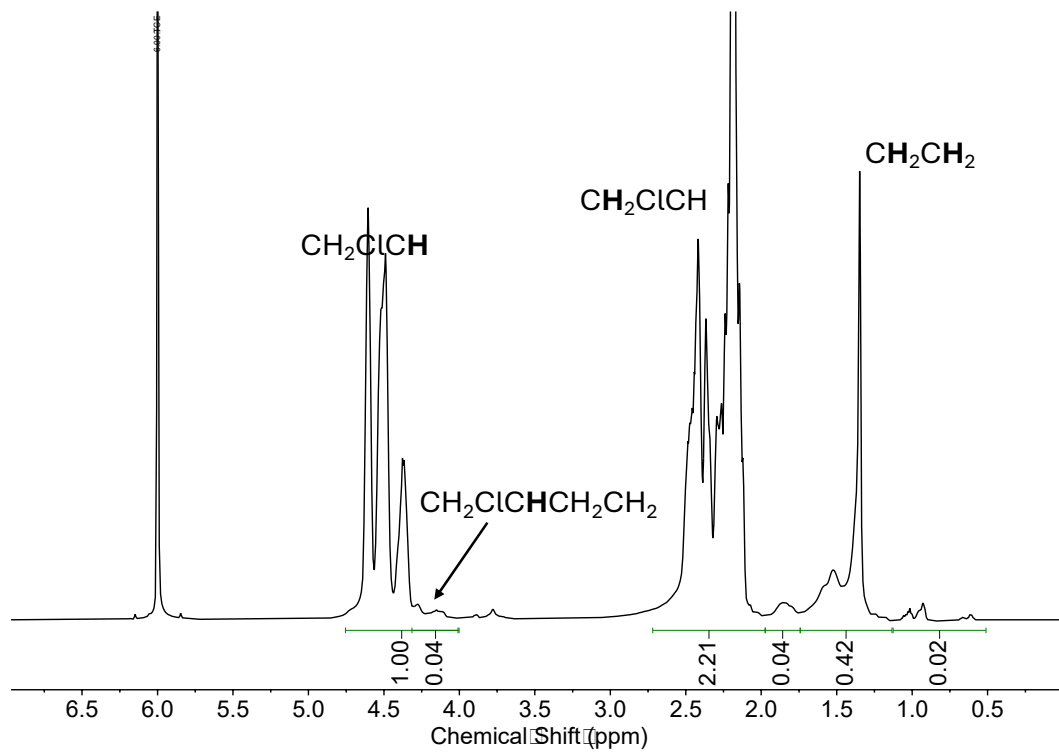


Figure S5.1. ¹H NMR spectrum of sample d-PVC44.

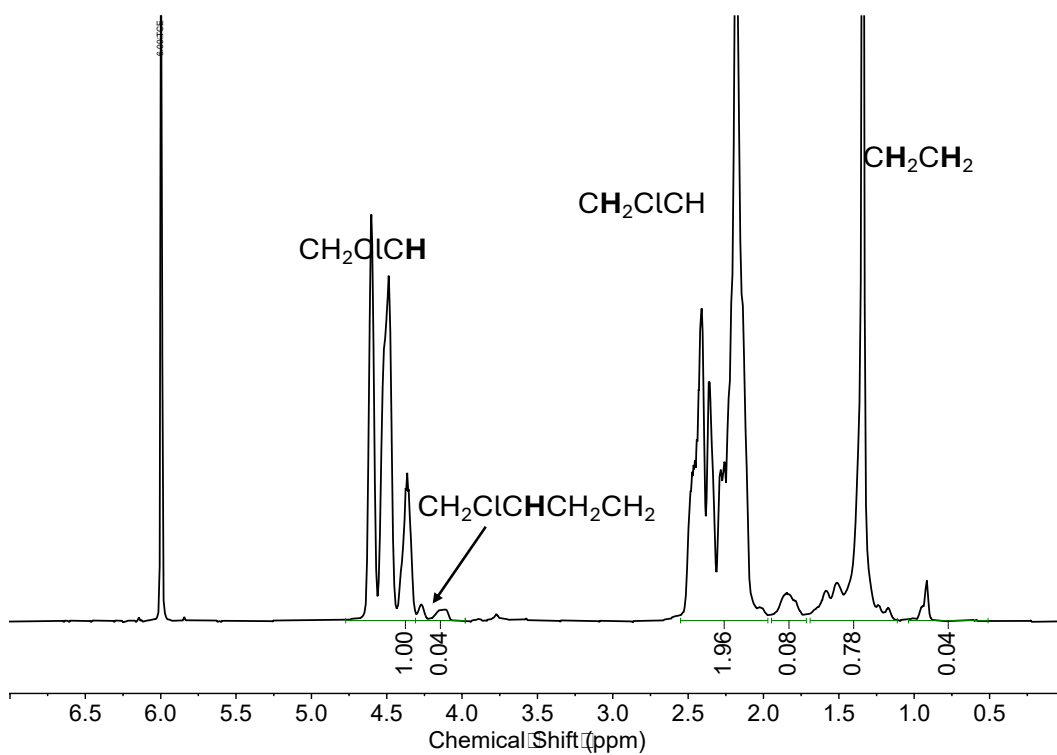


Figure S5.2. ¹H NMR spectrum of sample d-PVC42.

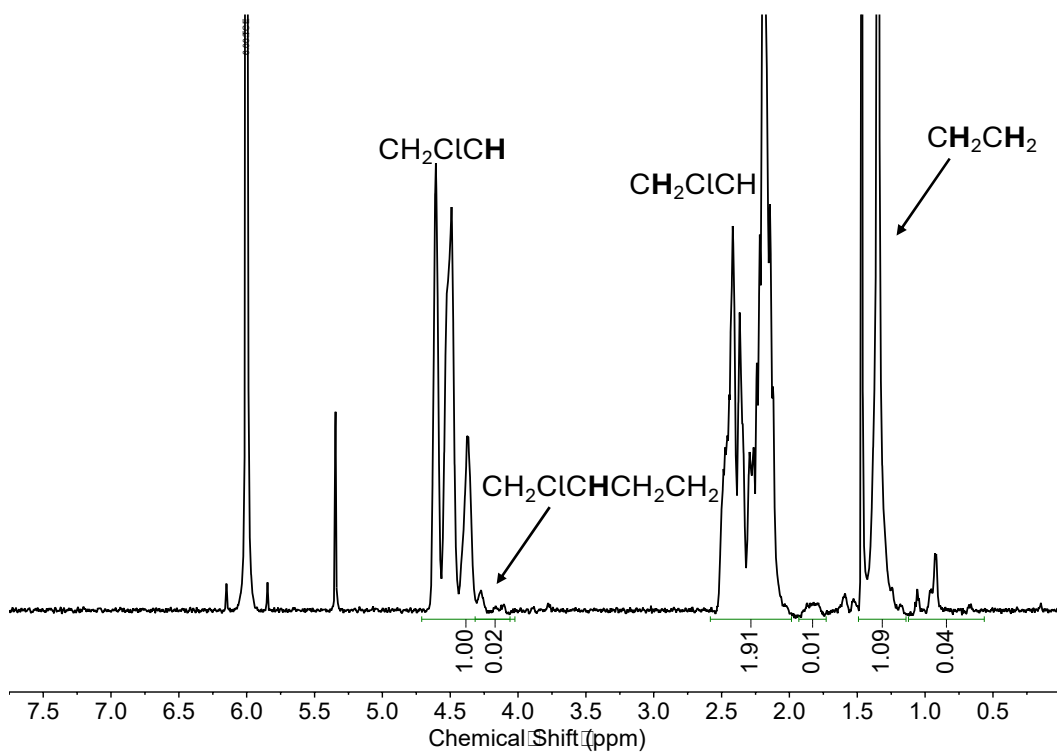


Figure S5.3. ¹H NMR spectrum of sample d-PVC40.

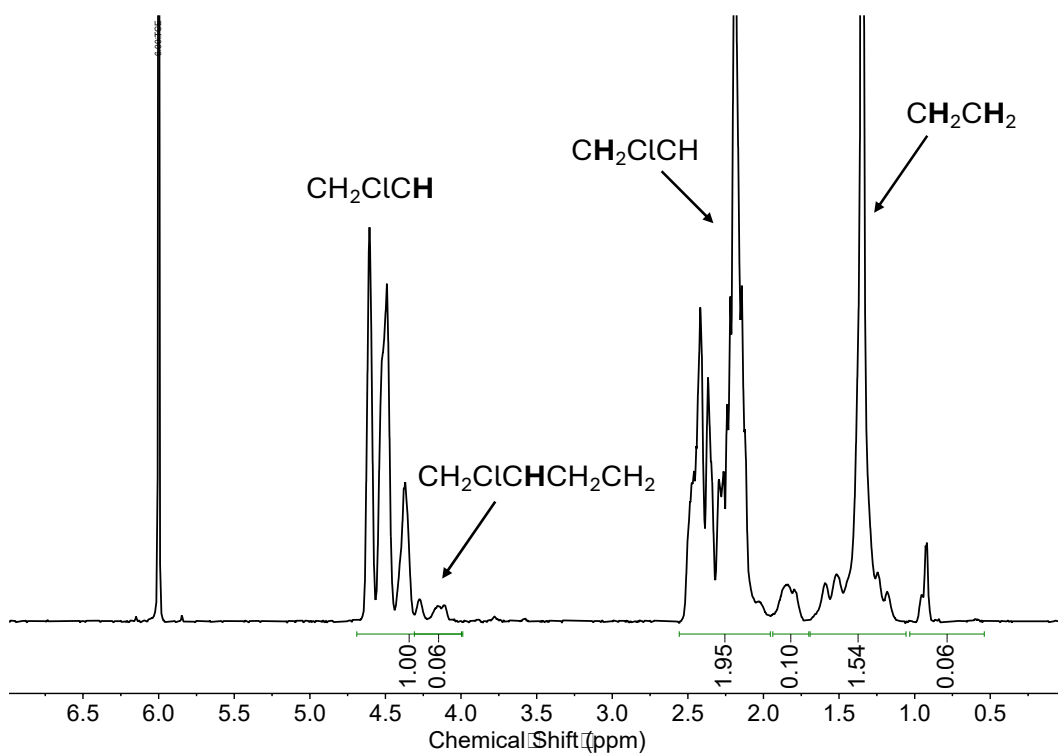


Figure S5.4. ^1H NMR spectrum of sample d-PVC37.

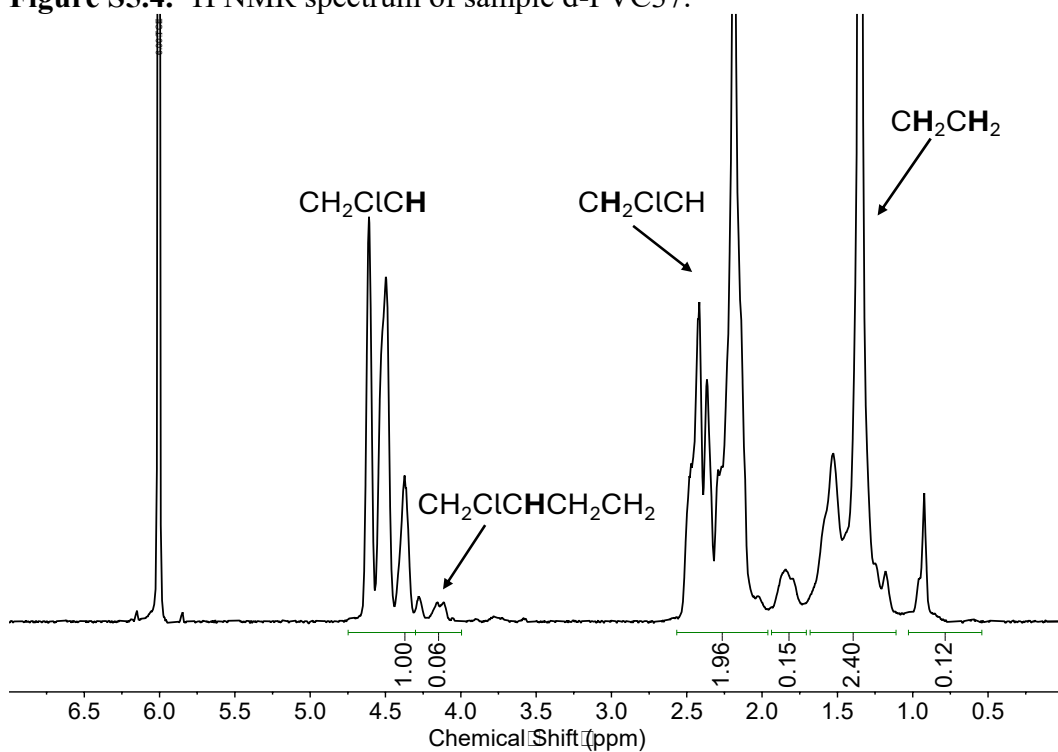


Figure S5.5. ^1H NMR spectrum of sample d-PVC32.

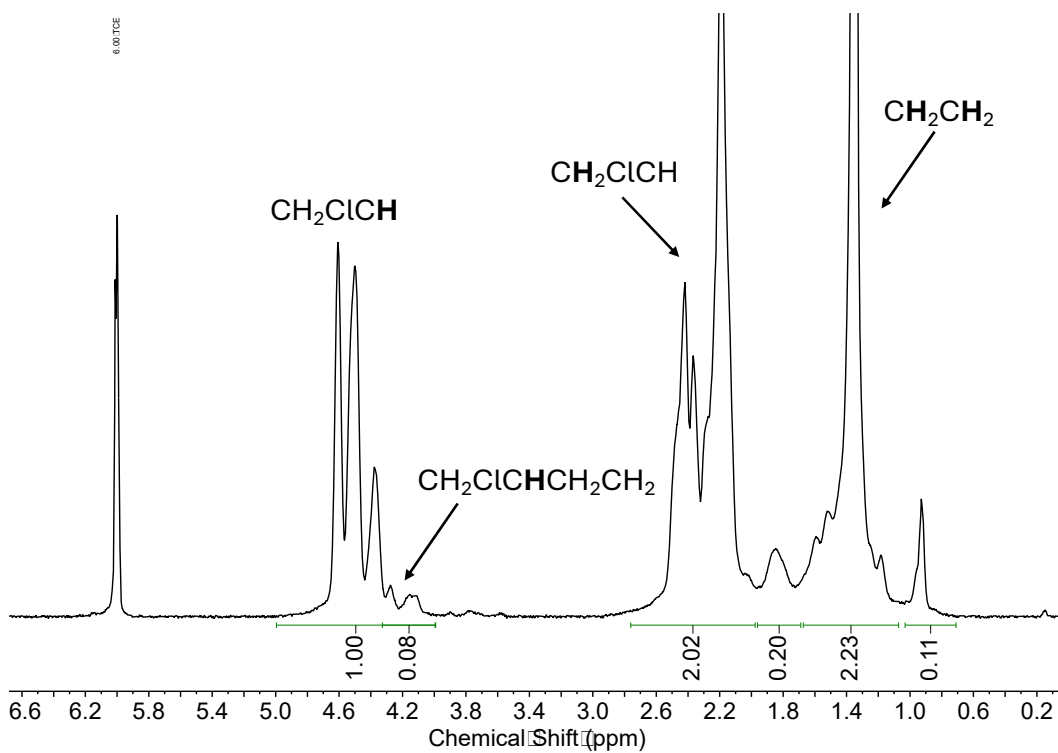


Figure S5.6. ¹H NMR spectrum of sample d-PVC32(2).

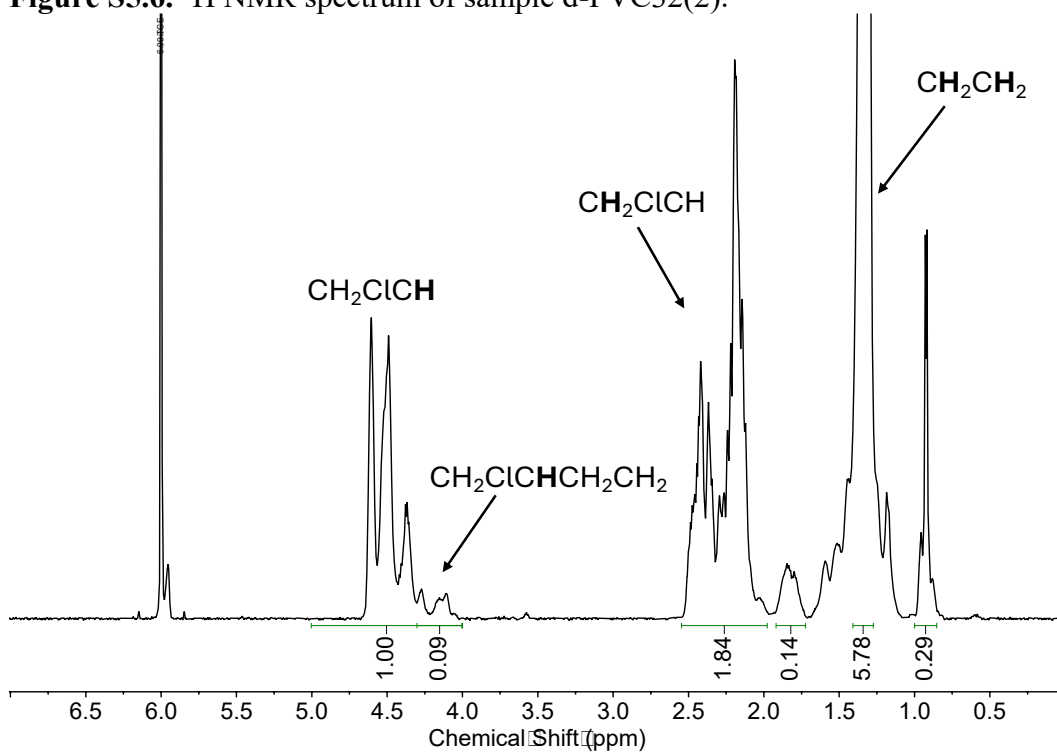


Figure S5.7. ¹H NMR spectrum of sample d-PVC22.

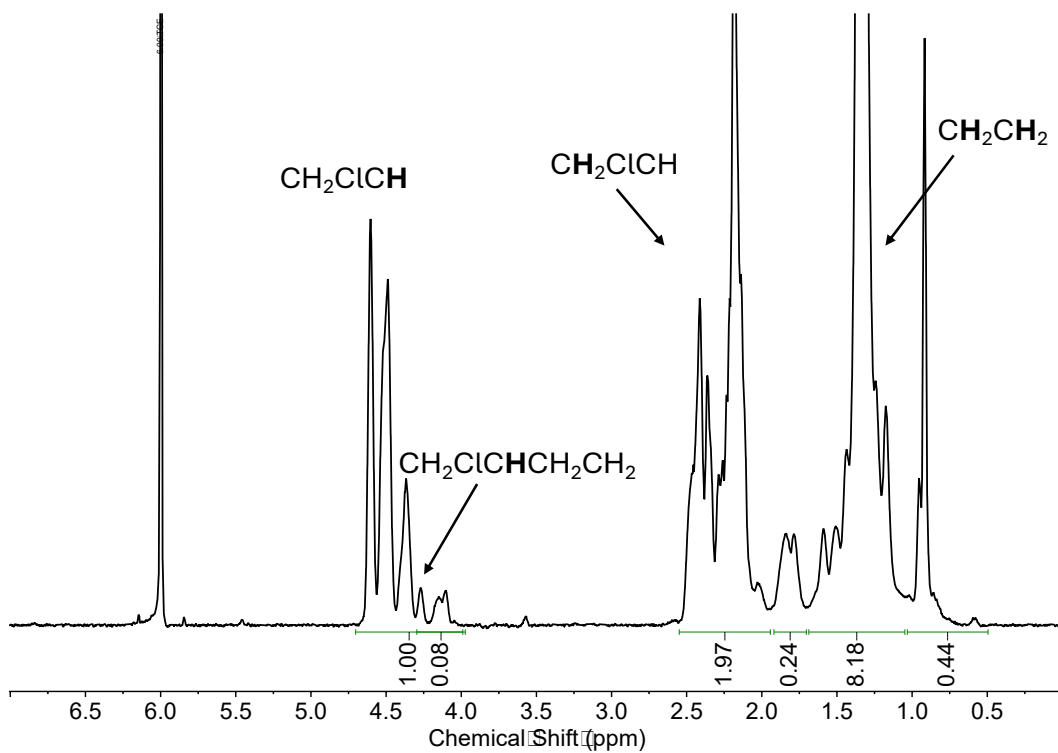


Figure S5.8. ^1H NMR spectrum of sample d-PVC17.

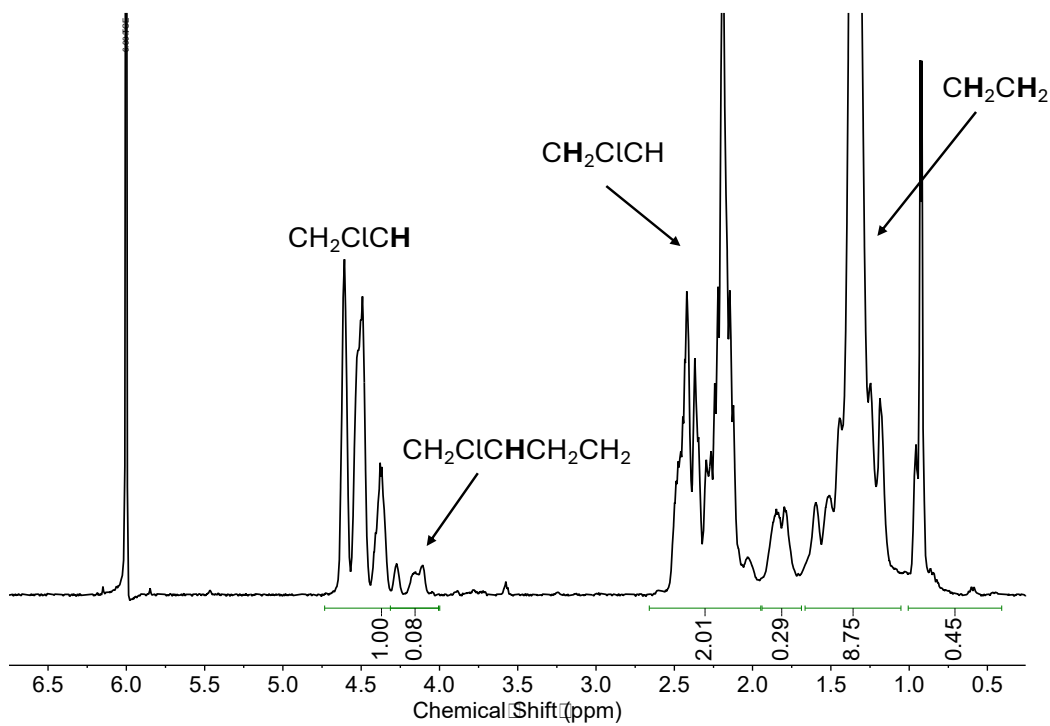


Figure S5.9. ^1H NMR spectrum of sample d-PVC16.

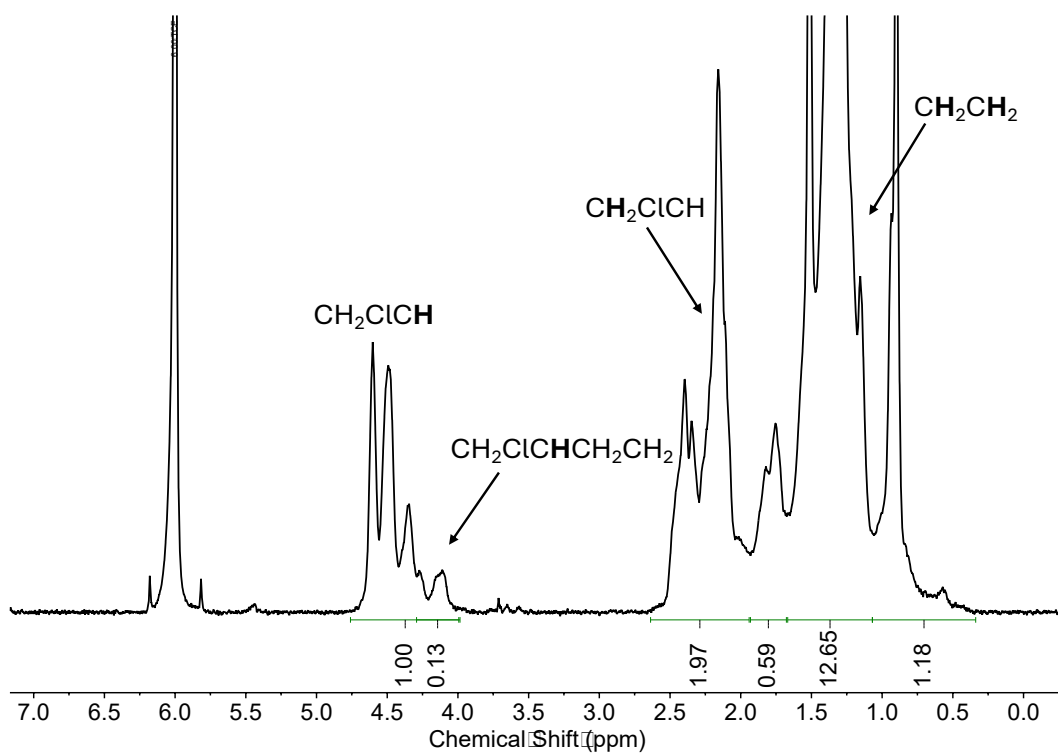


Figure S5.10. ¹H NMR spectrum of sample d-PVC12.

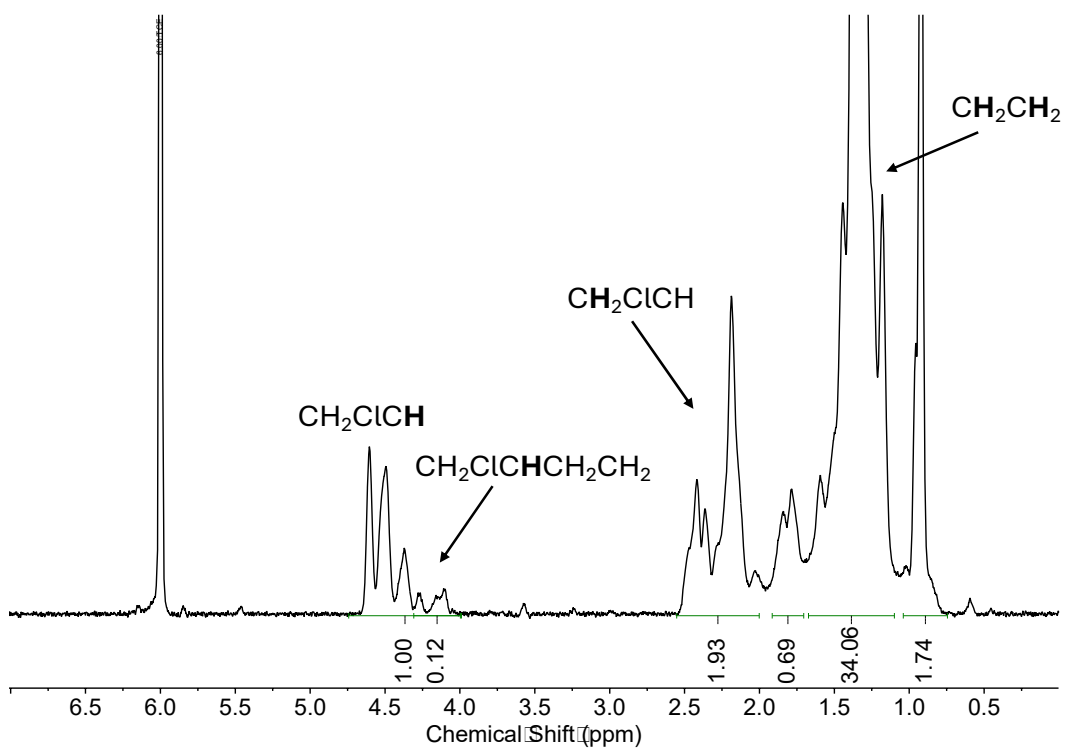


Figure S5.11. ¹H NMR spectrum of sample d-PVC6.

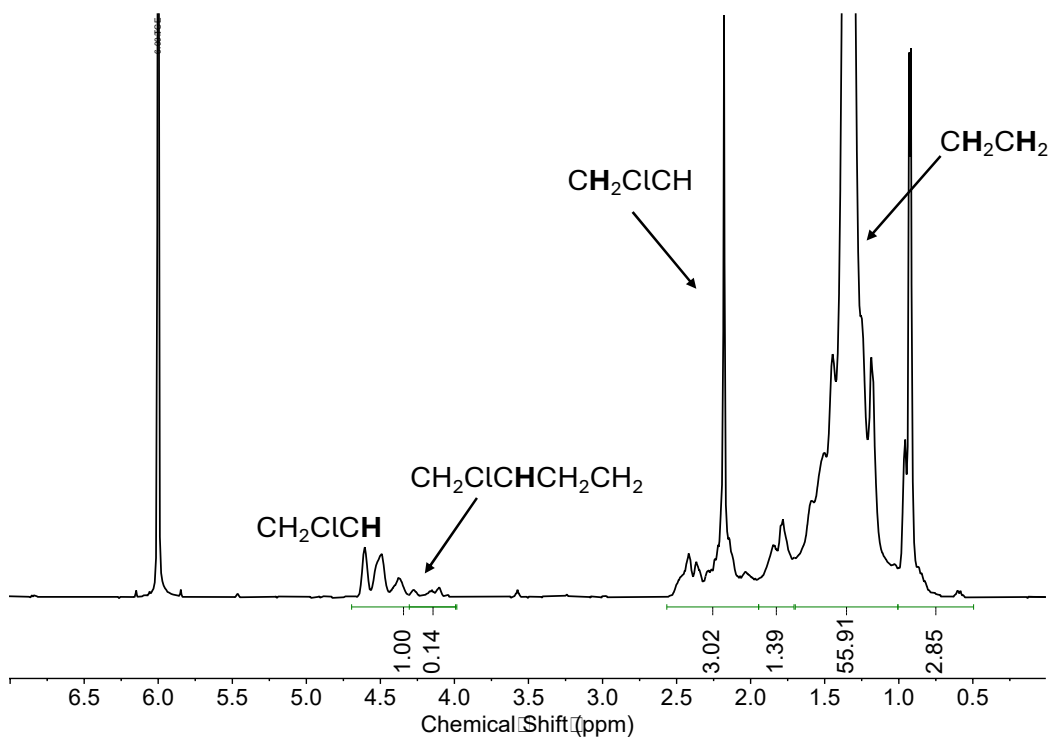


Figure S5.12. ^1H NMR spectrum of sample d-PVC3.

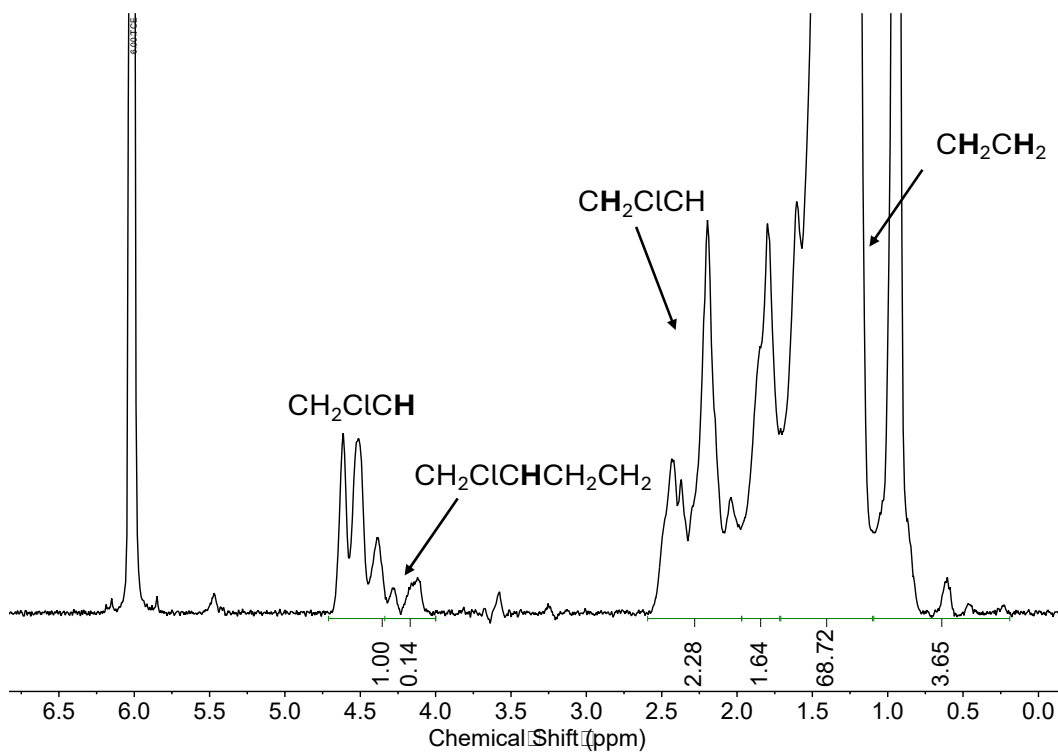


Figure S5.13. ^1H NMR spectrum of sample d-PVC3(2).

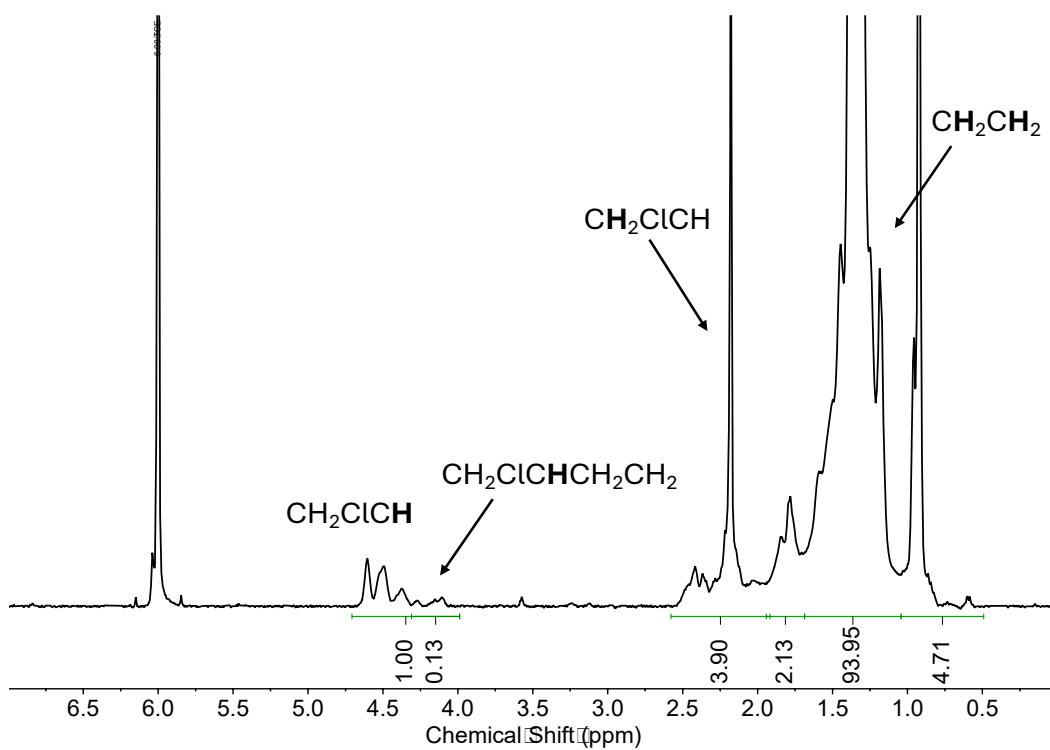


Figure S5.14. ¹H NMR spectrum of sample d-PVC2.

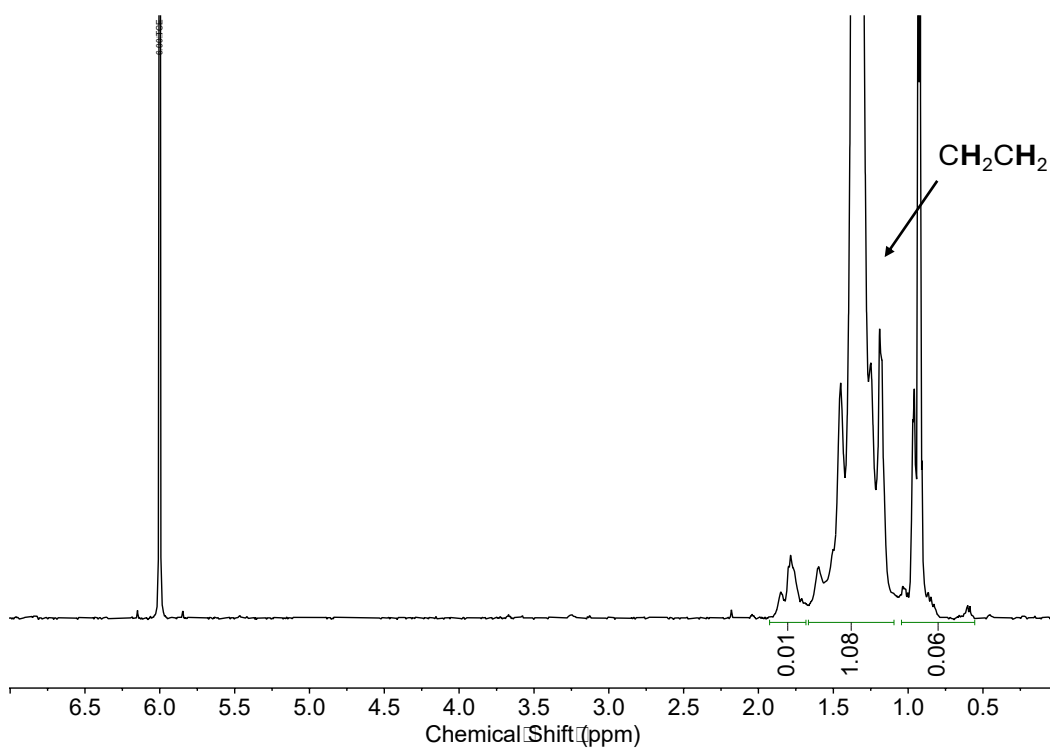


Figure S5.15. ¹H NMR spectrum of sample d-PVC0.

Peel Test Curves for dechlorinated PVC

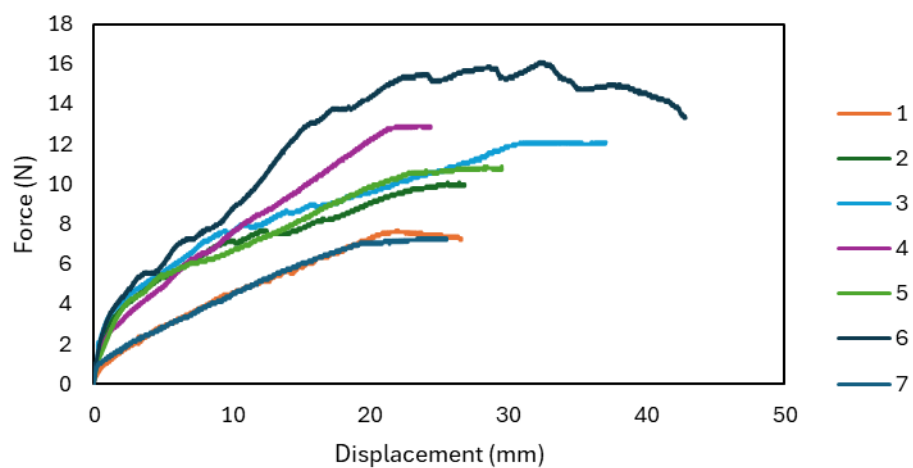


Figure S5.16. Peel strength measurements for sample d-PVC44.

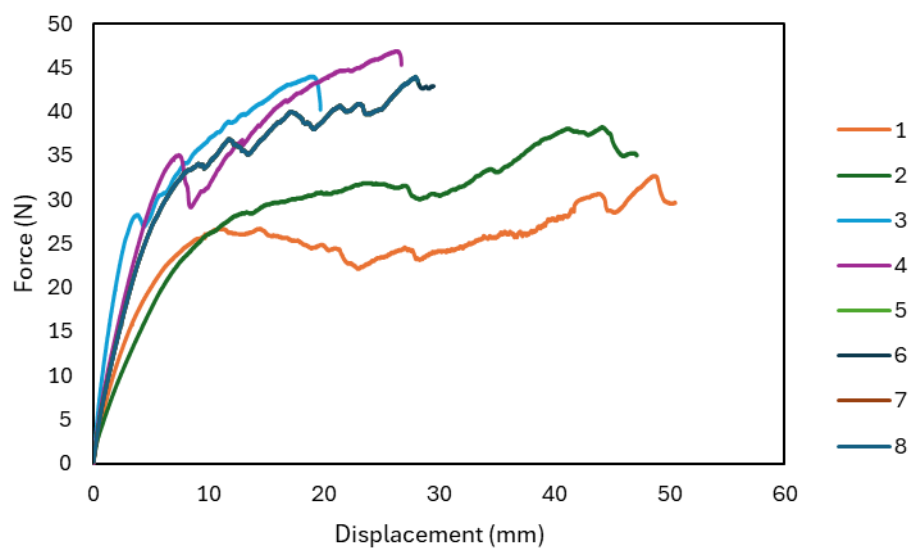


Figure S5.17. Peel strength measurements for sample d-PVC42.

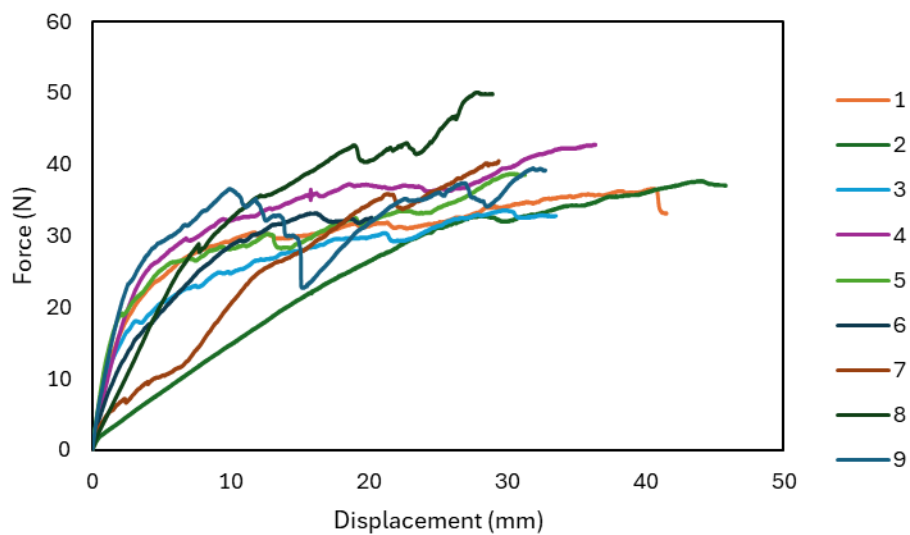


Figure S5.18. Peel strength measurements for sample d-PVC40.

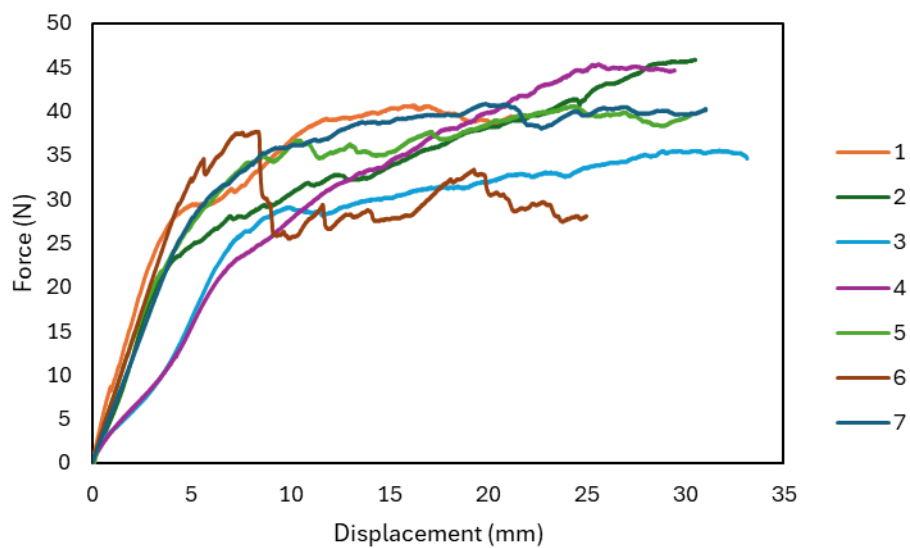


Figure S5.19. Peel strength measurements for sample d-PVC37.

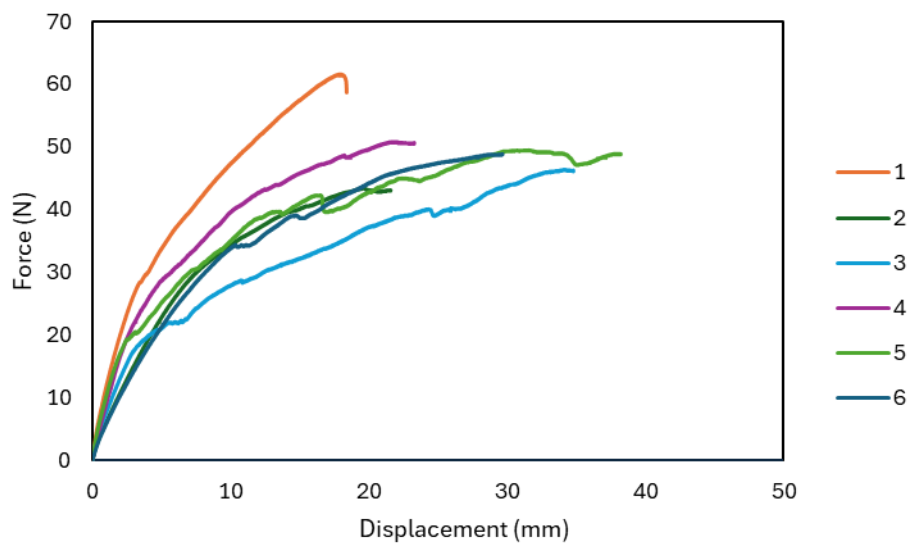


Figure S5.20. Peel strength measurements for sample d-PVC32.

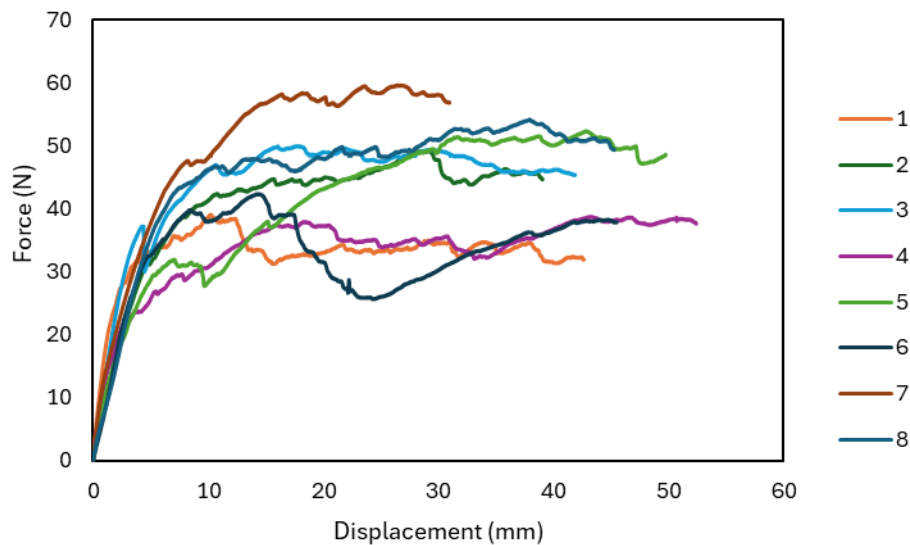


Figure S5.21. Peel strength measurements for sample d-PVC32(2).

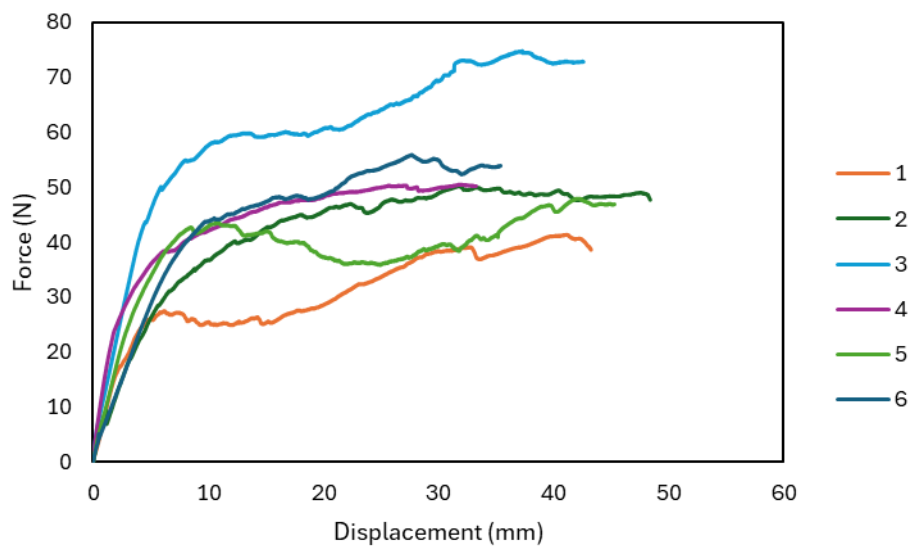


Figure S5.22. Peel strength measurements for sample d-PVC22.

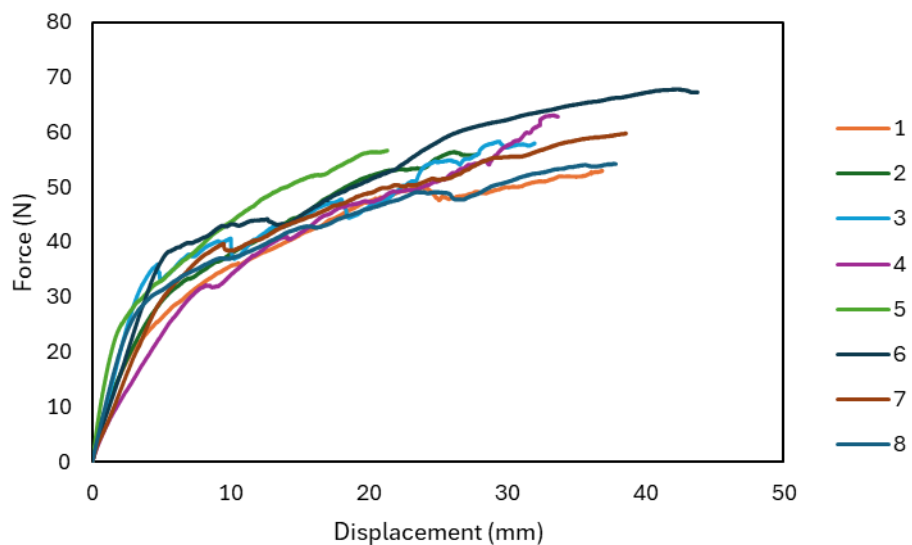


Figure S5.23. Peel strength measurements for sample d-PVC17.

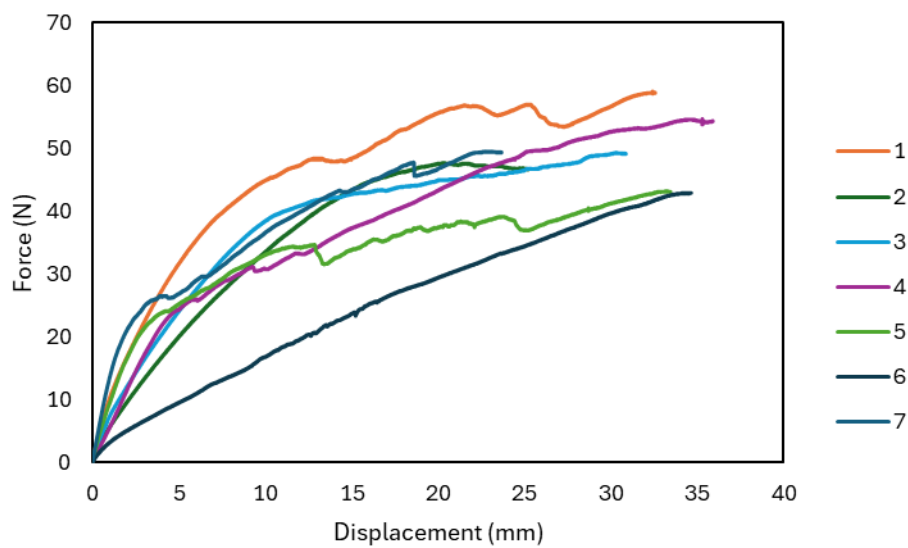


Figure S5.24. Peel strength measurements for sample d-PVC16.

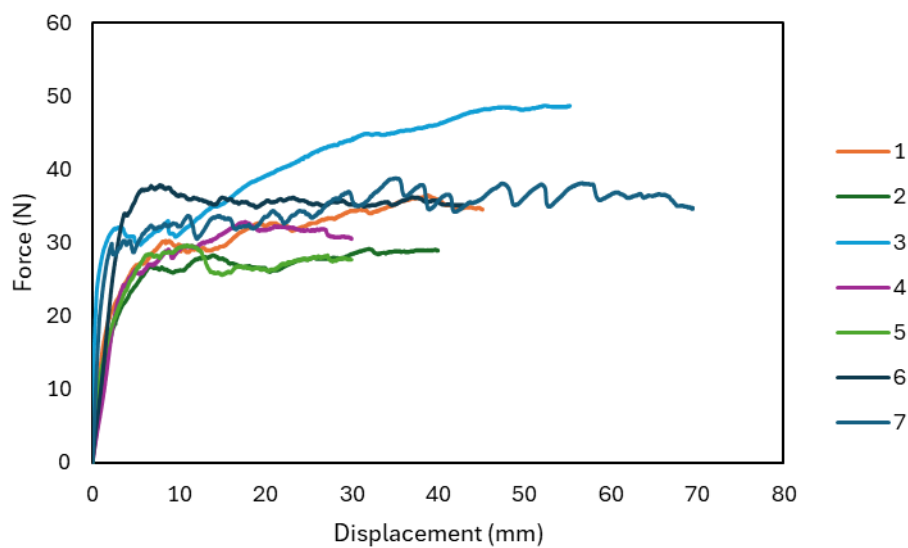


Figure S5.25. Peel strength measurements for sample d-PVC12.

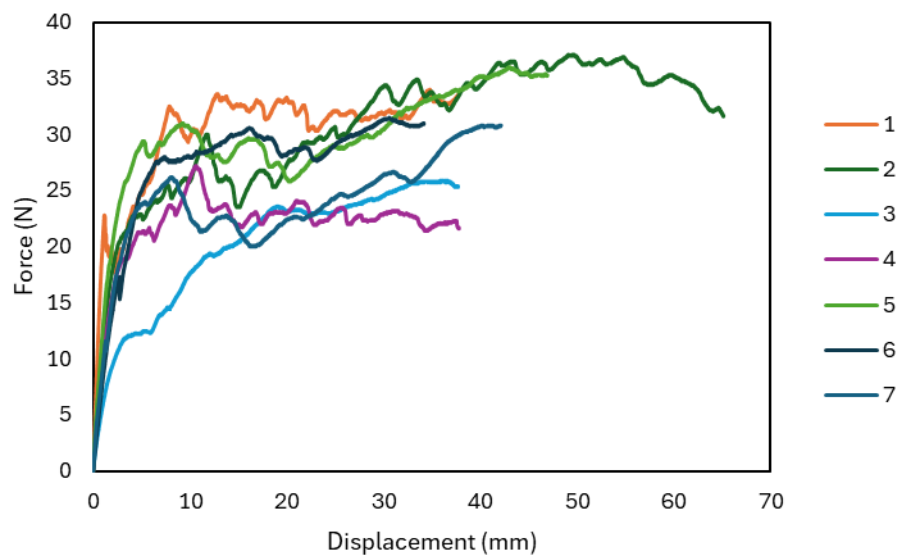


Figure S5.26. Peel strength measurements for sample d-PVC6.

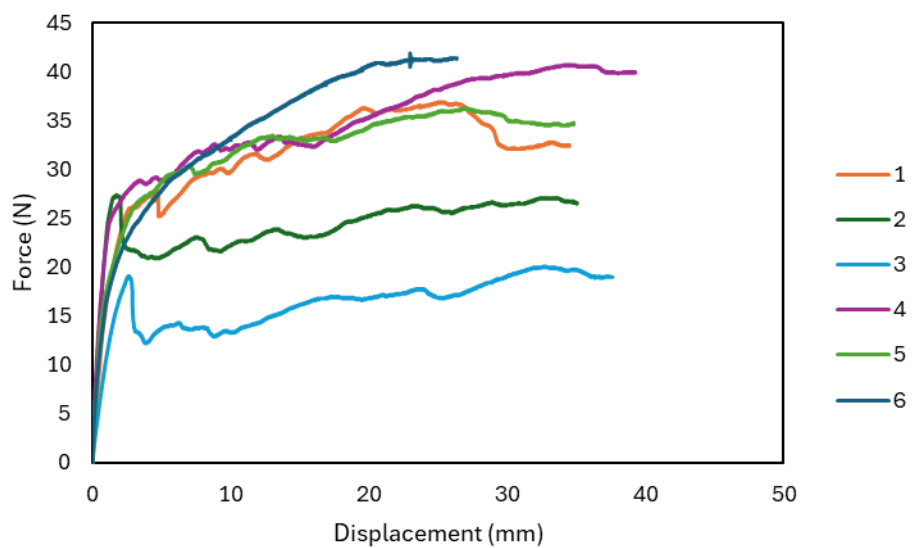


Figure S5.27. Peel strength measurements for sample d-PVC3.

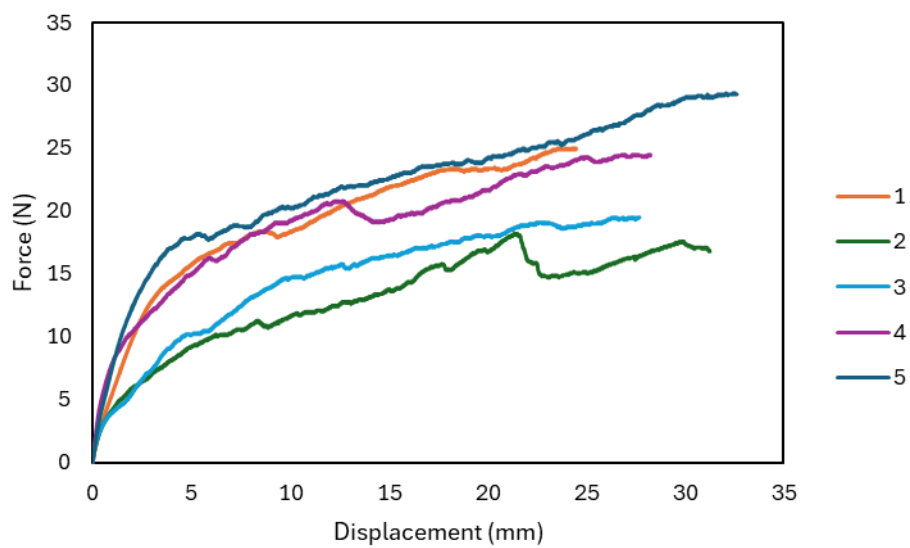


Figure S5.28. Peel strength measurements for sample d-PVC2.

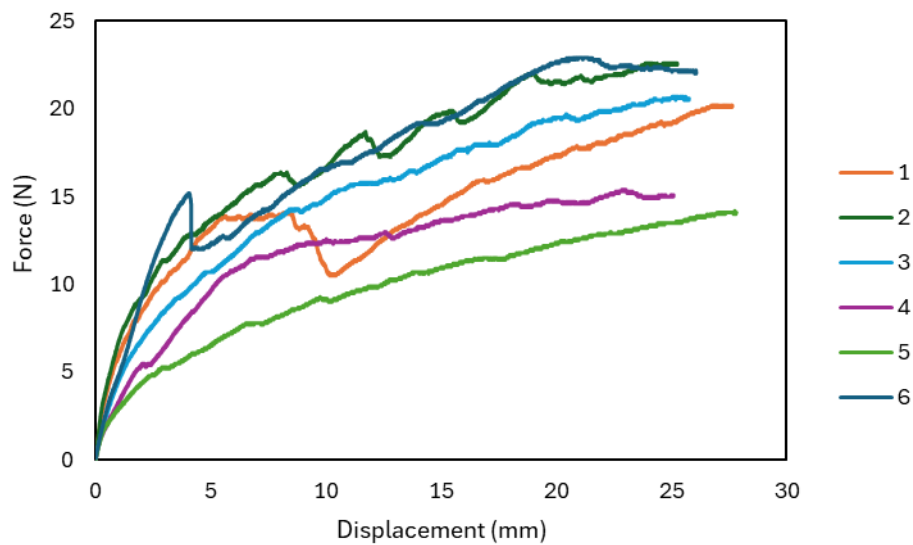


Figure S5.29. Peel strength measurements for sample d-PVC0.

VITA

Bailey Eberle was born and raised in San Antonio, TX. She has two siblings born two years after her. She was raised by Kristen and Douglas Eberle, a chemical engineer and a mechanical engineer, who supported and fostered a love of STEM. They encouraged her to seize the opportunity to attend Joseph Baldwin Academy at Truman State University while in middle school, where she took college-level math and chemistry courses and obtained college credits. The experiences she had here sparked her love for understanding and applying chemistry.

She began her undergraduate studies at Texas A&M University in 2016 as a chemical engineering major. While in the engineering department, she was a part of a team that won third place at the Engineering Showcase. Due to her high academic performance, she was placed into the Engineering Honors program. In 2018, she realized that while she was successful in engineering, she found her fundamental chemistry courses more intriguing and changed her major to chemistry. After her sophomore year, she joined Dr. Jamie Grunlan's Nanomaterials Lab, where she worked on gas barriers and flame-resistant coatings. She continued working in this lab until she graduated in May 2020, and during this time, she contributed to four published papers. Dr. Grunlan and the graduate students in the group (specifically Dr. Shuang Qin, Dr. Simone Lazar, Dr. Henry Chiang, and Dr. Thomas Kolibaba) urged her to continue her education and obtain a Ph.D. in Chemistry with a focus on polymers. This prompted her to attend the University of Tennessee due to its polymer chemistry program. Here, she joined Dr. Mark Dadmun's group and began working on the research presented in this thesis. Her experiences in both

her undergraduate and graduate research labs have reaffirmed her desire to work in the research and development of polymer materials at the industrial level.