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I am submitting here a thesis written by Say Lee Teh entitled “The Impact of Non-Covalent Interactions on the Dispersion of Fullerenes and Graphene in Polymers.” I have examined the final electronic copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemistry

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**Impact of non-covalent interactions on the dispersion of
fullerenes and graphene in polymers**

A Thesis

Presented for the

Master of Science Degree

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Abstract

The work presented in this dissertation attempts to form an understanding of the importance of polymer connectivity and nanoparticle shape and curvature on the formation of non-covalent interactions between polymer and nanoparticles by monitoring the dispersion of nanoparticles in copolymers containing functionalities that can form non-covalent interactions with carbon nanoparticles.

The first portion of this study is to gain a fundamental understanding of the role of electron donating/withdrawing moieties on the dispersion of the fullerenes in copolymers. UV-Vis spectroscopy and x-ray diffraction were used to quantify the miscibility limit of C₆₀ fullerene with the incorporation of electron donor-acceptor interactions (EDA) between the polymer and fullerene. The miscibility and dispersion of the nanoparticles in a polymer matrix are interpreted to indicate the extent of intermolecular interactions, in this case non-covalent EDA interactions. Experimental data indicate that the presence of a minority of interacting functional groups within the polymer chains leads to an optimum interaction between polymer and fullerene. This is further affirmed by density functional theory (DFT) calculations that specify the binding energy between interacting monomers and fullerenes.

The second portion focuses on the impact of sample preparation on the dispersion of graphene nanocomposites. Visualization and transparency are used to quantify the dispersion of graphene in the polymer matrix. In addition, differential scanning Calorimetry (DSC) also provides insight into the efficiency of the preparation process in forming a homogeneous sample, where rapid precipitation and solvent evaporation are studied. Examining the change in glass transition temperature, T_g, with nanoparticle addition also provides insight into the level of

interaction and dispersion in the graphene nanocomposites.

The approach of utilizing non-covalent interactions to enhance the dispersion of polymer nanocomposites is realized by varying the functional group in the copolymer chains, while the impact of nanoparticle shape is also examined. The optimum enhancement of dispersion is interpreted in terms of the improvement of interaction between polymer and nanocomposites. This interpretation leads to the conclusion that chain connectivity and the ability of the polymer to conform to the nanoparticle shape are two important factors that govern the formation of non-covalent interactions in polymer nanocomposites.

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CHAPTER 1: INTRODUCTION

1.1 Background

In 1959, Richard Feynman first described nanotechnology in a lecture entitled “There’s Plenty of Room at the Bottom” as a process to manipulate individual atoms and molecules using a set of precise tools to build and control another proportionally smaller set.¹ However, it is only during the past decade that nanotechnology has spread through a variety of disciplines. Nanotechnology is the study of the design and synthesis of functional materials with a nanometer scale dimension (from 1nm to 100 nm) and the exploitation of the resultant properties. The importance of this technology has been realized by a tremendous enhancement of applications in many branches of science. Furthermore, the National Science Foundation has forecast that \$1 trillion worth of nanotechnology-enabled products will be on the market by 2015.²

A particular driving force in the area of nanotechnology research in the field of polymer science is to produce lighter, stronger and more cost efficient materials.² Due to continuous demand from different end-use sectors, research institutions and companies are engaged in the exploration of efficient methods to develop nanocomposites in large volume and at lower cost. Traditionally, automotive and packaging industries have driven development in polymer science due to the unique mechanical and electronic properties of polymeric materials. Polymers can provide materials with tailored properties for various applications. Polymer blends and composites broaden the range of materials and properties available, where the properties can be controlled by the composition of each component in the system.³ Properties of new polymers can also be tailored by changing the monomer structure to produce a novel material. The physical properties of polymers, such as strength and flexibility, depend on a number of molecular level

structural characteristics, such as the chain length, cross linking density, side group structure and branching.^{4,5} Other properties of polymers such as impact resistance, melt viscosity, toughness, processibility and dimensional stability can be varied to produce the desired product.^{4-6,7} For example, the rigidity and brittleness of polystyrene can be improved by blending it with polybutadiene rubber to create high impact polystyrene (HIPS).³ This new material, HIPS, has good impact strength at low temperatures and cost and is utilized for engineering prototypes and architecture.

When there are two or more different monomers joined in the same polymer chain, the polymer is called a copolymer. The monomers in a copolymer can be distributed randomly (random copolymer), in alternating fashion (alternating copolymer) or in blocks (block copolymer) as shown below:⁸

Random copolymer :AAAABBBBBBBBAAAABBBBBBABBBBBBBBBB

Alternating copolymer : ABABABABABABABABABABABABABABA

Block copolymer : AAAAAAAAAAABBBBBBBBBBBBBBBBBBBBBB

The different connectivity of copolymers has a great impact on their solubility properties and alignment at interfaces. In these systems, the backbone chain connectivity dictates the flexibility of the polymer as well as the formation of interactions between a polymer matrix and fillers.

Although polymer blends or composites can improve polymer properties such as cost and weight that cannot be achieved by a single polymer, but there are certain properties that cannot be improved by blending two different types of polymers due to the nature of the polymers themselves. For instance, plastic is recognized as flexible and lightweight, but generally exhibits

less robust mechanical properties such as low strength and low elastic modulus as compared to metals or ceramics.⁹ Thus, by incorporating fillers into a polymer, a new material that maintains the desirable properties of the polymer with the addition of optimal mechanical properties from the filler can be achieved.

1.2 Polymer Nanocomposites (PNCs)

Polymer nanocomposites (PNCs) are a class of hybrid material composed of polymers with well defined nanoparticles (NPs) which have at least one dimension in the range of 1 to 100 nanometers.^{10,11} PNCs open a new horizon for polymeric materials with properties that are a synergistic combination of both components; with polymer based components, it is possible to make product that are lightweight, strong, environmentally inert and cost efficient,^{2,5} while nanoparticles enhance the mechanical, electrical and thermal properties.¹⁰

Nanocomposite technology can be described as a new frontier of material science because with a minimal addition of filler (~ 1 wt%), a property increase in the order of ~10% can be achieved.¹² Experimental testing on PNCs shows a more significant improvement in mechanical reinforcement, even with a filler content as low as one weight percent as compared to traditional composites.^{2,11} For example, Pleximer reports that for a chair back product, a small amount (~2 wt%) of nanoparticles filler is needed to produce the same quality of product as traditional filler such as glass fiber at 17 wt%.² As a result, a lighter product can be achieved with a lower cost and higher quality because it has fewer defects and less waste generated. Inclusion of nanoparticles confers significant property improvements with very low loading level as compared to traditional microparticle additives. The resulting weight reduction is crucial in

various military and aerospace applications.¹³ Thus, polymer nanocomposites are slowly replacing conventional micro-composites in the automobile industry.

Numerous studies have shown that improving bonding between a polymer matrix and the reinforcing phase leads to improved mechanical properties.¹⁰ Lee and coworkers found that the addition of 0.1 wt% single-wall carbon nanotube (SWNT) will increase the storage modulus of the final product by 8 GPa, and as the temperature increases, this modulus increases further.¹⁴ Another unique feature of polymer nanocomposites is that the small size of fillers leads to an increase in interfacial area. It is well known that the performance of a polymer nanocomposite depends significantly on the interfacial adhesion between the nanoparticle and the polymer matrix. Zhu et al. found that with stronger hydrogen bonding interaction at the interface between the polyurethane and epoxy resin, the resultant polymer nanocomposites exhibit better miscibility and efficient chain packing.¹⁵

In addition, nanoparticles provide a high surface area to volume ratio, which can alter the stiffness of the polymers. Due to the high interfacial area and very short distance between reinforcing particle surface and the polymer, the shape factor of the nanoparticles plays an important role in determining the final type of network, either stiffer or softer. Mackay et al. reported that the dispersion of nanoparticles will swell the polystyrene and reduce the viscosity of the polymer below that of a traditional composite.¹⁶ The swelling of the polymer results in an increase by 10-20% in the radius of gyration of d-polystyrene as NPs are added and homogeneously dispersed in the polymer.

Polymer-based nanocomposites have been studied to achieve particle spatial dispersion by intermolecular interaction between the polymer matrices with the nanoparticles either covalently

or non-covalently bound. Electron donor acceptor (EDA) interactions of fullerenes involve electron transfer from one ‘electron rich’ component to the other ‘electron deficient’ component.¹⁷ The weak attractive non-covalent interaction between the donor and the acceptor create an interactions complex (Figure 1.1). This type of interaction is a non-covalent interaction because it does not involve bond destruction or formation. This technique has been used to improve the dispersion of nanoparticles because it creates an enthalpic attraction between the nanoparticles and the polymer matrix. Thus, it can enhance the miscibility and dispersion of the nanoparticles in the polymer matrix. With a fine dispersion, the resulting polymer nanocomposites should exhibit the beneficial properties of both polymer and nanoparticles. Thus, electron acceptor–donor interactions have been reported as one method to creating a miscible polymer nanocomposite system.¹⁸

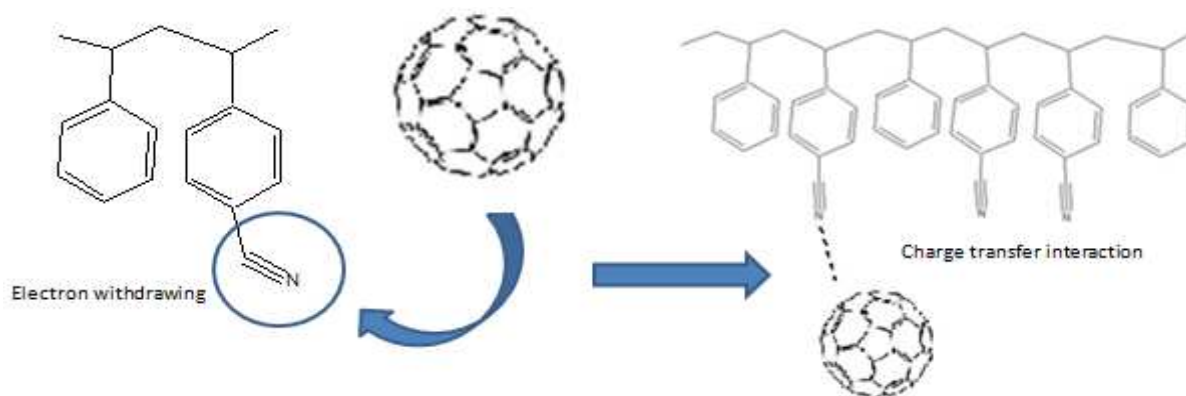


Figure 1.1: An illustration of the formation of an electron acceptor donor (EDA) interaction.

1.3 Nanoparticles (NPs)

Typical examples of carbon-based nanoparticles such as fullerenes, carbon nanotubes (CNTs) and graphene are shown in Figure 1.2. The various types of carbon-based nanoparticles offer different sizes and shape with high precision characterization capabilities to better understand the impact of shape and size on the properties of PNCs. Their incorporation in polymer nanocomposites can extend the function and utility of carbon based material while maintaining the processing flexibility inherent to plastics. Understanding nanoparticle dispersion and interfacial interactions with the polymer matrix are essential to achieving the desired material properties. In addition, it is known from the polymer composite field that a strong interaction between the nanoparticles and polymer matrix is required for polymer nanocomposite to be effective.^{17,18}

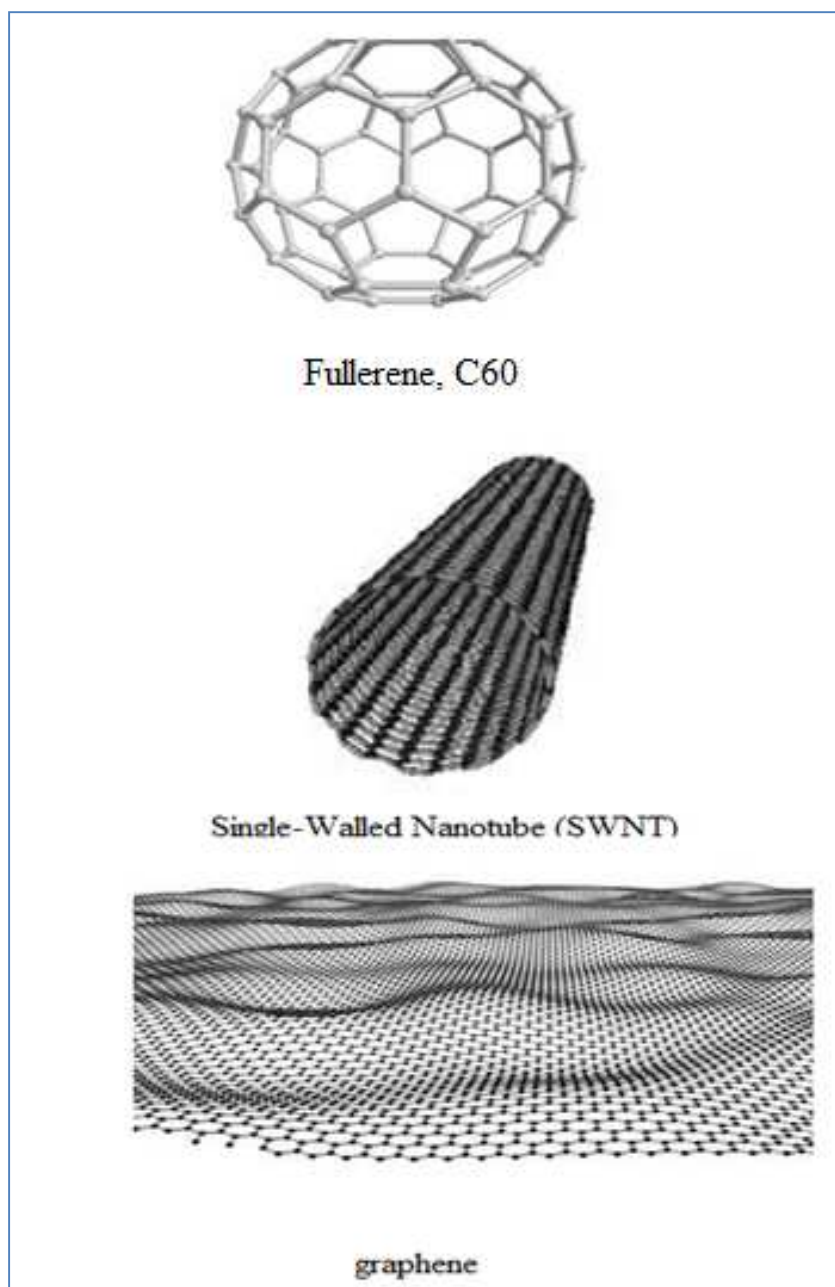


Figure 1.2: Various types of carbon based nanoparticles^{19,20,21}

(i) Fullerene

A fullerene is a well-characterized and common NP with a diameter of approximately 0.71 nm, is model spheres that exhibit outstanding properties.²² Though first discovered in 1985 by Kroto and coworkers,²³ the major breakthrough of fullerene chemistry occurred in 1990 when Kratchmer et al. found a method to prepare macroscopic quantities of fullerenes.²⁴ The availability of much larger quantities of fullerenes provided a great incentive to the study of C₆₀-related materials. The unique combination of fullerenes with polymers has given rise to a new interdisciplinary field. Fullerenes are a closed cage of 60 carbon atoms known as C₆₀ arranged in interconnected hexagons and pentagons, forming a two dimensional pi-system. The pentagon structures gives rise to the curvature of the nanoparticle to form a close surface.²⁵ This 3D geometry of fullerenes with a convex surface offers possibilities of new interactions with geometrical constraints on carbon atoms.

C₆₀ are known to behave as semiconductor materials. Fullerene derivatives can exhibit superconductivity when reacted with an alkaline-metal. The first observation of superconductivity in a fullerene was in K₃ C₆₀ with T_c ~ 19K.²⁶ This superconducting field effect can produce a material with promising magnetic properties. Thus, the design of polymer composites filled by fullerenes to create a material with high electrical conductivity has been a research focus in recent years.^{26,22} Wong and coworkers showed that with an increase in fullerene content, the glass transition temperature (T_g) increases, indicating a slowdown of the alpha relaxation of the polymers.²⁷ This effect can be understood as the particle modifying the polymer packing and increasing the fragility of glass formation. In addition, the increase of T_g indicates the reduction of polymer mobility or free volume between the polymer and fullerene.²⁷ The T_g of both polymer nanocomposites and polymers can be used as a tool to understand the

impact of the incorporation of the nanoparticle on the thermal properties of the polymer. The introduction of fullerenes also may yield significant improvement in tensile strength of a thermoplastic by 30-40% upon addition of 0.02-0.08 wt % C₆₀.²⁸ This enhancement shows the effectiveness of the nanoparticles to create a novel material. Additionally, conjugated polymer – fullerene nanocomposites are one of the most promising materials in organic photovoltaics.

Fullerenes are well known to be excellent electron acceptors with an activation energy of 2.6-2.9 eV, capable of taking on as many as six electrons to form charge transfer interactions with a variety of strong donors.²⁹ However, fullerenes have low solubility in both polymeric and small molecule solvents, which creates a stumbling block for practical applications. Ruoff et al., first attempted to correlate the solubility of C₆₀ with the properties of a solvent using the Hildebrand solubility parameter ($\delta = 20.5 \text{ MPa}^{1/2}$).³⁰ In addition, Hansen et al., found that C₆₀ dissolves well in polycyclichydrocarbons or aromatic hydrocarbons with halogenated substituents.³¹ The solubility of C₆₀ plays an important role in obtaining optimal properties of polymer nanocomposites. Rashidov and coworkers showed that the mechanical properties of low density polyethylene(LDPE) with C₆₀ prepared from dichlorobenzene (DCB) solution yields a significant increase in its Young modulus, E, as compared to samples prepared from toluene solution.³² The authors report that strength of the polymer- C₆₀ nanocomposite increases up to 30MPa with an increase in C₆₀ concentration.

Much of the current research focused on improving dispersion in polymer nanocomposites focuses on introducing functionalities to the polymer or the NP.^{33,34} Modified fullerenes with covalently attached organic groups have been synthesized to enhanced the solubility of the fullerene in both solvent and polymer. For example, C₆₀ has been incorporated covalently into

polymer, by a variety of reactions; as part of the main chain, at the end of the main chain as end groups, as branch point of stars and as junctions of a network.^{34-35,36} Geckeler and coworkers first attempted to use soluble amino polymers to covalently bond to C₆₀ to form a strong connecting chain between poly(alkylene imine)s and C₆₀.³⁷ Similarly, Wudl reported the nucleophilic addition of amines to C₆₀ via direct polymerization, either anionic or free radical, where species react randomly with the double bonds of the fullerene.³⁵ A commonly used functionalized fullerene to incorporate the fullerenes into a polymer matrices [6]-phenyl-61-butyl acid methyl ester (PCBM).

Yet, the problem of solubility of C₆₀ has not been resolved through fullerene functionalization due to the additional complexity of the fullerene synthesis. Thus, the effect of non-covalent interactions on the solubility of C₆₀ has been of significant focus by various research groups.^{17,18} Wang et al., first discovered that weakly bound charge transfer complexes form between C₆₀ and the carbozole group of poly(N-vinylcarbozole), PVK.³⁸ Lailo et al., found charge transfer complex formation between fullerenes and the block copolymer polystyrene-b-poly(4-vinylpyridine), PS-P4VP, resulting from an interaction with the pyridine group to form charge transfer complexes.¹⁷ The change in morphology with C₆₀ addition to PS-P4VP block copolymer provides evidence of the role of the electron donor-acceptor interaction. We have taken the electron donor-acceptor interaction approach in our investigation to quantify the extent of this non-covalent interaction and correlate the interactions presence to the miscibility and dispersion of nanoparticles in a polymer matrix.

(ii) Carbon Nanotubes (CNTs)

The development of fullerenes indirectly brought about the introduction of carbon nanotubes in 1991 when Ijima discover the arrangement of carbon as a tiny tube.³⁹ The nanotubes that were first synthesized were in the form of multi-walled nanotubes (MNWT) made by involved an arc-evaporation of graphite. However, a major breakthrough in nanotube synthesis occurred in 1993 when Ijima successfully discovered single-walled nanotubes (SWNTs) by addition of metal to graphite electrodes.⁴⁰ Structurally, a SWNT is a sheet of graphene rolled into a hollow cylindrical tube, whereas multi-walled carbon nanotubes (MWNTs) are composed of multiple concentric tubes.⁴⁰

The mechanical and optical properties, as well as electrical and thermal conductivity, of CNTs hold great promise for utility in the field of polymer science. The tensile strength and Young's modulus of an individual SWNT can be as high as 1TPa with a surface area of 1180 m²/g.⁴¹ The high surface area of a carbon nanotube can provide a large interfacial area between the nanotube and polymer matrix. Based on these properties, numerous applications or potential applications have been reported for CNTs, such as conductive and high strength composites, energy storage and energy conversion devices.^{42,43,44} CNTs have an exceptional thermal conductivity, ~6000 Wm⁻¹K⁻¹, and electrical conductivity on the order of ~10,000S/cm.⁴³ Coleman and coworkers have reported an increase in Young's modulus and hardness of poly(vinyl alcohol), by factor of 1.8 and 1.6, respectively, when doped with 1 wt% of CNTs.⁴⁵

Several studies show that interfacial interactions of CNTs can be improved by functionalization and preconditioning of CNTs prior to composite fabrication.^{42,44,46} CNTs can be covalently functionalized by oxidizing CNTs in an acid to formcarboxylic or hydroxyl groups

and subsequently grafting a polymer chain. Lee et al., showed that by treating with nitric acid, SWNTs show drastic improvement in dispersion and resulted in significant increase in the storage modulus of nanocomposites.¹⁴ In addition, Zhu et al. reported improvement in the mechanical properties of a polymer nanocomposites with SWNT covalently bound to an epoxy polymer.¹⁵ These results indicate improved compatibility between SWNT and polymer matrix, resulting in a better dispersion of SWNT and consequently better mechanical properties of the polymer nanocomposites.

Yet, in many cases, non-covalent modification is preferable to produce a novel material with CNT spatial uniformity in polymer matrices.⁴⁷ The advantage of non-covalent interactions is that it preserves the desired properties of nanoparticle while improving the solubility of nanoparticle in the polymer. Non-covalent interaction can be accomplished through interactions with delocalized π bonds on the CNTs. For example, nanotubes can be helically wrapped by polymers such as poly(phenylacetylenes) to improve their solubility.⁴⁸ Linton and coworkers showed that SWNTs form an electron donor-acceptor interaction with strong electron donor or electron acceptor functional groups, improving dispersion.⁴⁹ These non-covalent interactions are utilized in our investigation, where the extent of intermolecular interaction correlates to the dispersion in polymer nanocomposites.

(iii) Graphene

Another popular carbon based nanoparticle is graphene. Graphene is commonly prepared as individual flakes by micromechanical cleavage of graphite.⁵⁰ This method was discovered in 2004 when Geim and coworkers first successfully isolated single layer samples from graphite.⁵⁰ The single graphene sheet is a one atom thick, two dimensional layer of carbon, with a thermal

conductivity of 5000 W/mK and an electrical conductivity up to 6000 S/cm.^{51,52} With a Young's modulus of 1 TPa and mechanical stiffness of approximately 130 GPa, graphene can be considered as the strongest carbon based NP.⁵² Graphene has been viewed as the building block of all other graphitic carbon allotropes of different dimensionality. For example, nanotubes are made by rolling and slicing graphene sheets into one-dimensional carbon allotropes.⁵³

Research involving graphene is in its early stages, but with significant improvement of mechanical and electrical properties of PNCs, graphene has been a popular topic as of late. For instance, Stankovich et al. reported that a polystyrene-graphene composite showed significantly improved electric conductivity with as low as 0.1 vol.% loading, which is the lowest report for any carbon based composite.⁵⁴ In addition, like most carbon-based composites, the addition of graphene can improve the thermal conductivity and raise T_g significantly. Ramanathan and coworkers observed an unprecedented shift in T_g of nearly 30 °C with only 0.05 wt % loading of graphene added to a sample of poly(methylmethacrylate)(PMMA).⁵⁵

1.4 Miscibility Issues

The simplest method for preparing polymer nanocomposites involves mixing nanoparticles with solutions of the polymer and then evaporating the solvents or precipitating into a non-solvent. A fine dispersion of the NPs within the polymer matrix is necessary to achieve most desired enhancement of properties. Traditionally, the dispersion of NPs in polymeric materials has proven difficult because NPs have a strong tendency to agglomerate. For example, a well-aligned composite of 1wt% nanotubes in a polymer matrix yields only a 6 % increase in the modulus due to the insufficient load transfer resulting from agglomeration of nanotubes.⁵⁶ Therefore, methods to improve the miscibility of NPs and polymers are needed. In

order to gain full insight into the miscibility of PNCs, a close look at the basic thermodynamics of polymer blends are discussed.

The concept of miscibility can be quantified by the free energy of mixing,

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (\text{equation 1.1})$$

Where ΔG_m is the free energy of mixing, ΔH_m and ΔS_m are the enthalpy and entropy of mixing, respectively, and T is the absolute temperature.⁵⁷ The enthalpy of mixing ΔH_m , summarizes the change in the interaction between members of the mixture, while the entropy change, ΔS_m results from the degree of disorder of the polymer chain upon mixing. In general, an interplay of entropic and enthalpic factors in the mixing process determines the structure of the ultimate mixture, thus affecting the dispersion of nanoparticles in a polymer matrix. One way to create a thermodynamically miscible system is to include attractive intermolecular interactions between components, which creates a favorable enthalpy of interaction, potentially leading to a negative free energy of mixing ($\Delta G_m < 0$).⁵⁸ Due to the degree of disorder in a long polymer chain, the addition of a second component does not produce a substantial gain in entropy, ΔS_m . Thus, a miscible system is primarily controlled by the enthalpy of mixing (ΔH_m) to attain favorable free energy of mixing. One method to achieve a negative free energy mixing is to form efficient intermolecular interactions between the two components in the system to attain a favorable enthalpic interaction. These interactions may range from strongly ionic to weak interactions, from covalent to non-covalent interactions, such as hydrogen bond, ion-dipole, dipole-dipole and electron acceptor-donor pair interactions.

In order to understand the role of the electron donor acceptor complex in governing the homogeneity in polymer nanocomposites, Flory Huggins theory can be used to calculate the

enthalpy of mixing of a polymer mixture by accounting for interaction energies between neighboring segments of different types. This statistical approach relates the enthalpy and entropy of mixing to the free energy of mixing and molecular properties, such as the interaction between the molecules, denoted by the interaction parameter χ . Equation 1.2 gives the expression for the Flory Huggins free energy of mixing a polymer and solvent:

$$\Delta G_m = kT [\phi_1 \ln \phi_1 + \phi_2 / N \ln \phi_2 + \phi_1 \phi_2 \chi] \quad (\text{equation 1.2})$$

where ϕ_1 and ϕ_2 are the volume fractions of component A and B, respectively, N is the degree of polymerization, T the temperature in Kelvin, χ is the Flory-Huggins interaction parameter between polymer and solvent and k is Boltzmann's constant.⁵⁷ Immiscible systems tend to have a positive χ parameter that results from a positive ΔH_m , which results in $\Delta G_m > 0$. This is due to the repulsive interaction between segments of different components, which is significantly larger than the change in entropy. Consequently, a small or negative value of the χ parameter is needed to promote miscibility.

Flory-Huggins theory is widely used among researchers to understand the relationship between the interaction parameter (χ) and the miscibility behavior of polymer solutions and blends.⁵⁹ Although, NPs are not polymers, the physical interpretation of Flory-Huggins theory can be applied analogously to understand polymer nanocomposites. If the nanoparticles are dispersed in the polymer blend, then they gain molecular contacts on their entire surface, which results in a negative χ parameter.⁶⁰ However due to the simplicity of the Flory Huggins theory, it may not be adequate to explain every experimental results.

Other factors that dictate the miscibility of PNCs are entropic factors such as geometrical constraints resulting from the arrangement of the monomers, the chain connectivity, shape and

size of the NPs, etc. These entropic parameters control the formation of interaction in polymeric mixtures due to the fact that the motion and geometrical structure of a given interacting group along the chain is influenced by the proximity of other functional groups.⁶¹ The role of chain connectivity to induce EDA interaction between polymer and NPs has been well studied by Linton and coworkers.⁴⁹ Their work has shown that the participation of one functional group in an intermolecular interaction inhibits the mobility of neighboring groups and thus, limit their ability to access and orient correctly to form additional interfacial interactions. Similarly, Coleman and Painter have reported that the miscibility of polymer blend systems can be controlled by the extent of intermolecular interaction between components.⁶¹ The authors claimed that chain connectivity is important in this process, as the formation of one hydrogen bond restricts the mobility of a nearby functional group to form an intermolecular interaction with the corresponding group, a consequence of rotational bond angle restriction found in polymer chains. Therefore, the variation of functional group packing in a copolymer chain is used in this study to optimize and control the extent of interactions between polymer and nanoparticle, which impacts the miscibility of the resultant polymer nanocomposite.

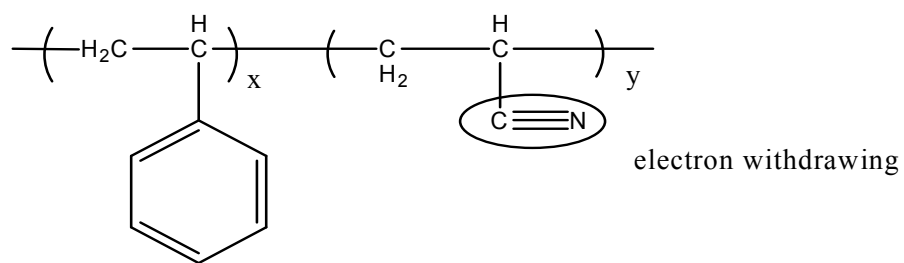
1.6 Objective of this thesis

Experimental evidence of interactions between nanoparticles and molecules containing various functional groups via formation of electron donor acceptor complexes has been reported.⁴⁹ This thesis will describe results that study the role of electron donor acceptor interactions between copolymers and nanoparticles in defining the dispersion of the resultant nanocomposite. To realize this, different functional groups are introduced into copolymers with the goal of creating non-covalent interactions between the polymer and nanoparticle to enhance their dispersion, with the goal of creating a homogeneous product. The electron accepting

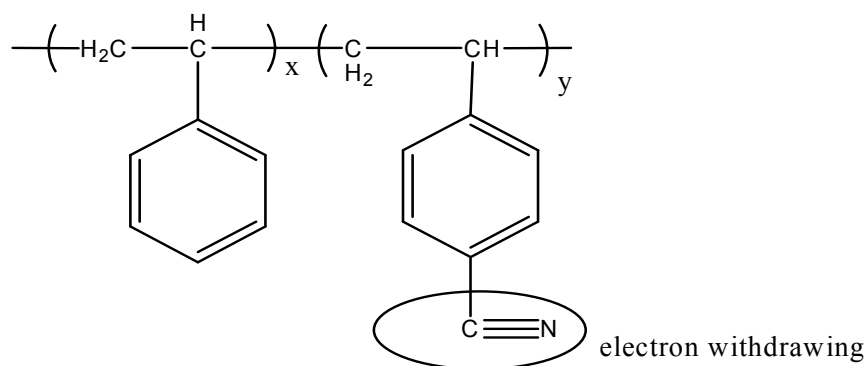
functional group –CN is introduced in poly(cyanostyrene-*ran*-styrene)(PSCN) and poly (styrene-*ran*-acrylonitrile) (PSAN) copolymers and the electron donating amino group is introduced in poly(dimethylaminoethylmethacrylate-*ran*-methylmethacrylate)(PDMA) copolymers, and used in this study. Figure 3 shows the structure of the copolymers used in this thesis, while Table 2 lists the composition of each.

Table 1: The composition of each component of the copolymers

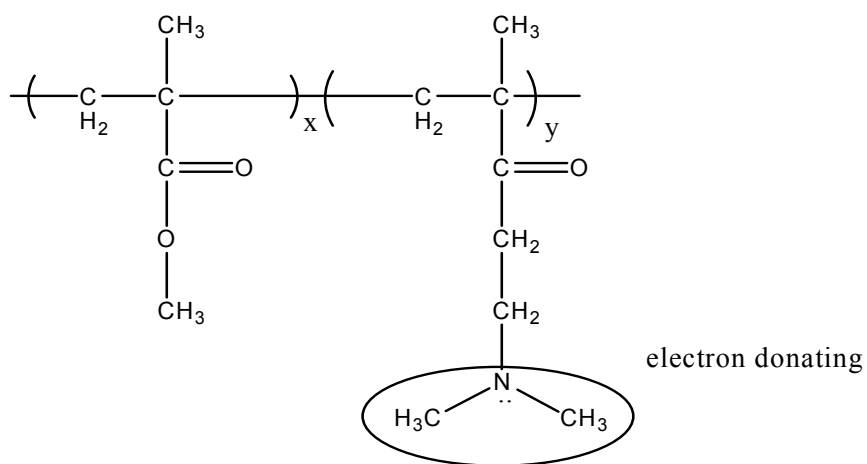
<u>PSAN</u>		<u>PSCN</u>		<u>PDMA</u>	
St mol%	AN mol%	CNSt mol%	St mol%	PDMAEMA mol%	MMA mol%
70.5	29.5	16.0	84.0	12.2	87.8
63.2	36.8	22.3	77.7	26.3	73.7
55.0	45.0	28.5	71.5	30.4	69.6
51.2	48.8	43.1	56.9	49.2	50.8
43.77	56.23				



Poly(styrene-r-acrylonitrile) - PSAN



Poly(styrene-r-cyanostyrene)- PSCN



Poly(methylmethacrylate-r-2-(dimethylamino)ethylmethacrylate)-PDMA

Figure 1.3 Structure of the copolymers with different functional groups

Currently, there is little information that details the impact of changing the copolymer connectivity or sequence distribution on the ability of the functional groups in a copolymer to interact with nanoparticles. Rasheed and coworkers have shown that when incorporating hydrogen bonding between vinyl phenol and an oxidized CNT into nanocomposites, steric effects or the ability of the functional groups on the polymers to access and orient to the functional group on the nanotube are key to controlling the miscibility of the system.⁶² From these experiments, it was discovered that a 20 moles % phenol copolymer exhibited maximum interaction with the oxidized CNT. Similarly, Linton et al. recently reported that chain connectivity and steric effects are important factors that determine the maximum non-covalent electron donor-acceptor interaction between polymer bound functional groups and SWNTs.⁴⁹ As a result, they found that 23 mole % of the –CN group in PSCN forms the most homogenous single-walled nanotubes PNC.

Thus, to more thoroughly understand the ability to use EDA interactions between nanoparticles and polymers in nanocomposites, the same set of copolymers as Linton et al., are used in this study to examine the effect of nanoparticle size and shape on the formation of homogeneous nanocomposites.⁴⁹ Due to the potential to place a large fraction of polymers at the nanoparticle interface, the strength of the polymer-nanoparticle interactions can dominate the macroscopic properties. In our study, the amount of electron donating (DMAEMA) or electron withdrawing (AN and CNSt) moieties in three sets of copolymers were varied between ~10 to 50 mol% to control the extent of EDA complex formation with C₆₀. Similarly, NPs are added in different fractions (mass percent) to determine the miscibility limit of NPs in each copolymer.

Since the performance of nanocomposites is largely governed by the nanoparticles dispersion, the miscibility of C₆₀ in copolymer nanocomposites is studied using UV-Visible

spectroscopy and X-ray diffractometry. It is generally accepted that favorable interaction between the polymer and NPs is of substantial importance in improving dispersion.

The Beer-Lambert law is used in the UV-Visible experiments to determine the concentration where the sample deviates from Beer's law indicate the heterogeneity,

$$\text{Beer's law: } A = \epsilon bc \text{ (equation 1.3)}$$

where A is the absorption, ϵ is the molar absorption coefficient, b is the length/thickness of the sample and c is the concentration of fullerene in the samples.

X-Ray diffractometry (XRD) is also used to monitor solubility, by identifying the presence of fullerene crystals. X-rays have relatively short wavelengths and this electromagnetic radiation can be focused into a fine beam onto the sample. The X-ray are scattered by the sample, where crystal formation results in Braggs peaks.⁶³ Using XRD, the size, type and distribution of various NP crystals present inside polymers can be determined. In XRD, crystalline C₆₀ gives peaks at scattering angles, 2θ of 11°, 17°, 21°. No scattering peaks are observed when no crystals exist. Together, this information is used to determine when the PNCs precipitate crystalline nanoparticles, by observing the appearance of the crystalline peaks.

The glass transition, characterized by an appropriately defined glass transition temperature, is also monitored in this study. Within the transition region, many macroscopic properties such as viscosity, dielectric and mechanical properties, which may have great practical importance, change their values. In this study, the primary objective of monitoring T_g is to determine the effect of the extent of interaction between a polymeric matrix and NPs on composite properties when compare with the T_g of the polymer itself. In general, the addition of NPs can directly affect the flexibility and mobility of the polymer chain, which shifts the T_g of

composites. Separate reports on Tg of various nanocomposites indicate that Tg may increase or decrease upon addition of NPs.^{64,65,66} With the addition of NPs, the confinement and altered polymer packing play a part in increasing the Tg of the resultant nanocomposite. On the other hand, if the NPs did not disperse well in the polymer matrix, Tg may decrease due to an increase in mobility of the polymer chain resulting from an increase in free volume, as in the addition of a plasticizer.⁶⁷ Density functional theory (DFT) was also completed to provide additional insight into the extent of molecular interaction between polymers and NPs from the calculation of binding energies of optimized geometries.

Finally, an investigation of the relationship between sample preparation processes on the miscibility and dispersion of PNCs is presented. A review of the literature reveals that the dispersion of NPs, the interfacial strength between fillers and polymers, and consequently the mechanical properties of nanocomposites can be altered by varying the sample preparation method.⁷³ For instance, Lee et al. showed that nanocomposites composed of poly(styrene-co-vinyl phenol) and multi-wall nanotubes prepared by melt-mixing lead to a more reproducible mechanical properties than solution casting.⁶⁸

PNCs prepared by solvent evaporation exhibit a slower evolution of structure, which may result in a less homogeneous blend. As the solvent evaporates, the polymer density at the film interface can increase sharply, creating a polymer density gradient, which acts as a barrier for further solvent evaporation. The evaporation rate therefore may decrease when the volume of solvent in the film surface regions drop to a critical level. Conversely, rapid precipitation tends to form a more homogeneous blend of polymers and NPs, when compared to solvent evaporation.

The introduction of solvent and non-solvent interactions is a relatively fast process that enables the formation of dispersed polymer and NPs at first encounter.⁶⁹

In Chapter 3, the miscibility limits of fullerenes in copolymers are presented as studied by UV-Visible Spectroscopy, X-Ray Diffractometry and Differential Scanning Calorimetry. These experiment data are correlated to the DFT calculations, which quantify the interaction between the interacting monomers with fullerenes. The discussion in Chapter 4 focuses on comparison of sample preparation techniques by transparency tests and Tg monitoring.

CHAPTER 2: EXPERIMENTAL TECHNIQUES

This chapter describes the reaction procedures and experimental details used in this research program. The polymer and nanocomposites preparations are presented with the corresponding techniques and characterizations.

2.1 Materials

Styrene, dichloromethane and 4-cyanostyrene monomers were purchased from Acros Organics and 2,2'-azobisisobutyronitrile (AIBN), 1,1,2,2-tetrachloroethane and N,N-dimethylacetamide were purchased from Sigma Alrich. N-hexane and methanol were purchased from Fisher Scientific. Poly-2-(dimethylamino ethyl methacrylate) (PDMAEMA), polystyrene (PS) and polyacrylonitrile were obtained from Scientific Polymer Products, Inc. Styrene-*ran*-acrylonitrile copolymer (PSAN) with 29.4, 36.8, 45.05, 48.8, 56.2 mol% AN were obtained from an industrial source. Methyl methacrylate-*ran*-DMAEMA was synthesized by Dias Linton via atom transfer radical polymerization. The fullerenes were used without further treatment and were purchased from Bucky USA (99.5% purity).

2.2 Synthesis of random copolymer of styrene and cyanostyrene

Free radical polymerization is a one-pot synthesis where the reaction mixture contains monomer, solvent and initiator. This technique is a key synthetic method for obtaining a wide variety of polymers due to its versatility with respect to reaction conditions and its compatibility with many monomers. Statistics show that in 2001, approximately 36% of polymeric goods in the United States were produced by free radical polymerization.⁷⁰ The disadvantage of this polymerization technique is little or no control over the chain morphology, tacticity or molar

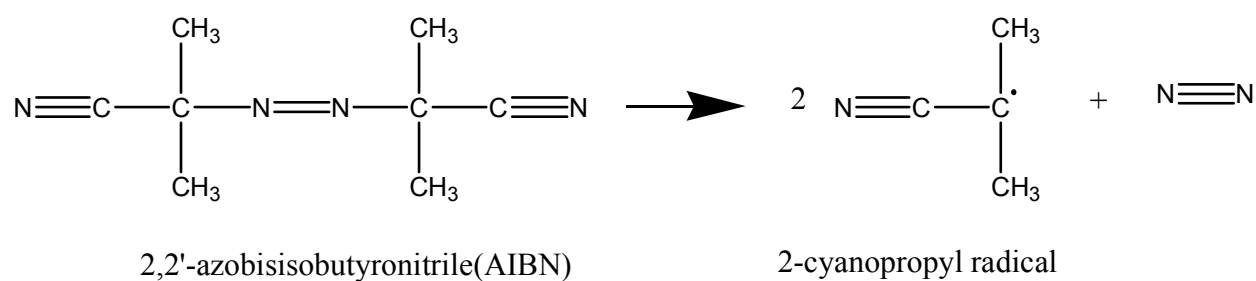
mass distribution of the product. However, polymers with high molecular weight are easily formed due to the formation of radical centers that increase the chain length in a chain reaction.

In this study, free radical polymerization was used to copolymerize styrene and cyanostyrene. The main steps for free radical polymerization that occur are initiation, propagation, and termination, as described below:^{3,8}

Initiation:

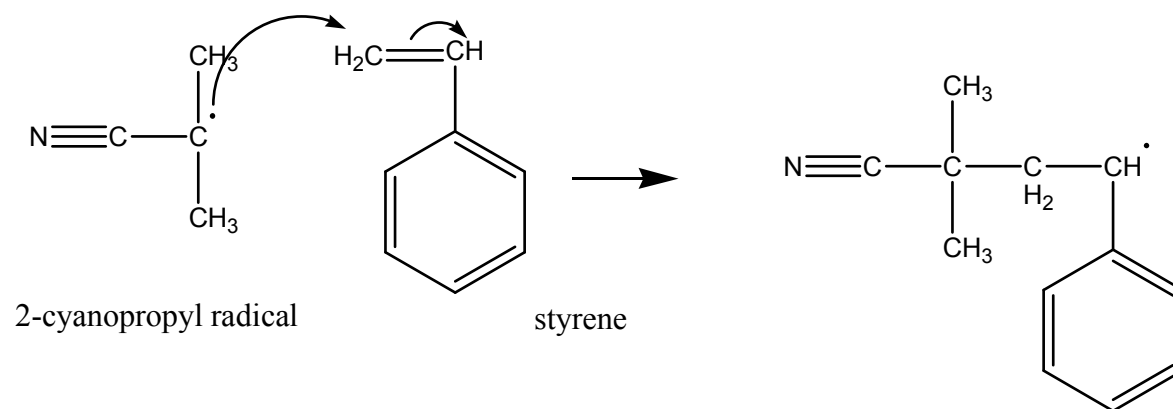
The first part of the initiation step is the homolytic dissociation of the AIBN initiator species, yielding a pair of 2-cyanopropyl radicals and nitrogen.

AIBN is a common free radical thermal initiator that is commonly used at 50-70 °C



Scheme 2.1: Dissociation of AIBN forming 2-cyanopropyl radicals and nitrogen

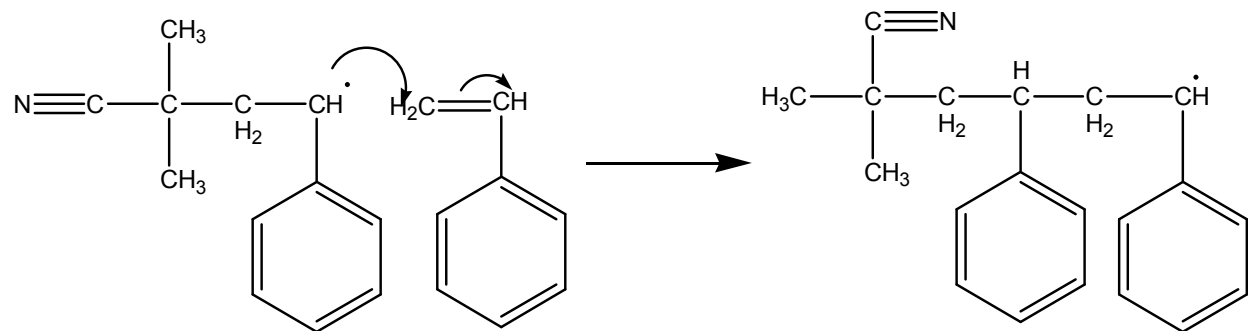
In the next step, the initiator reacts with one of the monomers (either styrene or cyanostyrene) from its unreactive state to its reactive state generating another radical



Scheme 2.2: Initiation of monomer by the 2-cyanopropyl radical

Propagation

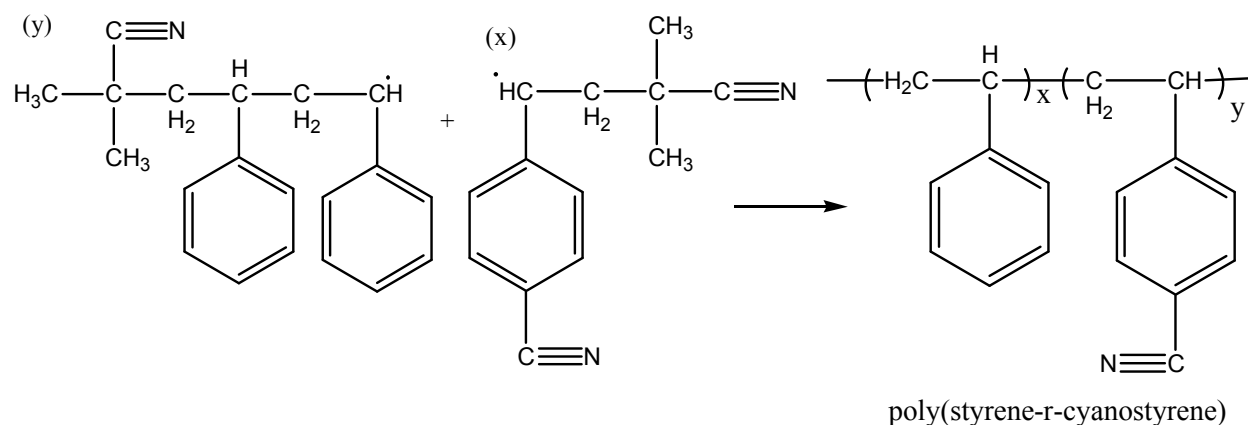
Chain growth occurs in the propagation step, which includes the reaction of an initiating species with another monomer and this successive addition continues. The reactive monomer will react with other monomers (either adding to itself or other monomers) to increase the length of the chain. This process continues until a termination reaction occurs.



Scheme 2.3: Propagation step of polystyrene reaction

Termination:

When two reactive chains combine, the chain lengthens but is also turned back into its unreactive state.



Scheme 2.4: Termination by coupling of two reactive monomer chains.

A 1:1 volume ratio of solvent to monomer is used for the polymerization. The purpose of the solvent was to reduce the viscosity of the reacting polymer. For this study, the solvent was N,N-dimethylacetamide (DMAc).

A typical reaction procedure for the preparation of the 20% cyanostyrene copolymer is described here. In this reaction, styrene (19.2756 g), 4-cyanostyrene(1.8082g), AIBN (0.07652 g) and DMAc (21.0838 mL) were used as starting materials. Different compositions were synthesized by varying the ratio of 4-cyanostyrene to styrene in the flask. All chemicals were combined in a two neck round bottom flask, under nitrogen flow and equipped with a reflux condenser and stir bar. The mixture was subjected to three “freeze-pump-thaw” cycles using dry ice to ensure that all air was removed from the flask. The temperature of the flask was raised by submersion in a hot oil bath at 65 °C for approximately 20 hours with continuous stirring and nitrogen flow. The polymer was precipitated in a ten-fold excess of cold methanol with rapid stirring. The polymer was then dried in a vacuum oven overnight to remove any remaining solvent.

2.3 Preparation of polymer nanocomposites

The copolymer PSAN and C₆₀ composite samples were prepared from toluene solutions. The copolymer PDMA and PSCN with C₆₀ composite samples were prepared from 1,1,2,2-tetrachloroethane (TCE) solutions. In the preparation of these nanocomposites, C₆₀ was added to solvent (2 mg/ml concentration) and the mixture was sonicated until a purple solution was produced, which indicates fullerene dispersion. The copolymer (~0.5 g) was then added to the solvent (0.1 g/ml) and the mixture was vortexed to form a solution without any remaining solid. The solution containing C₆₀ was added dropwise to the copolymer solutions to achieve the

required C₆₀ concentration relative to copolymer: 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0 and 5.0 weight % (wt%) respectively. The combined solutions were homogenized by further sonication for approximately one hour. The resulting solutions were added to a five-fold excess of cold methanol with continuous stirring and the resulting mixture was left in the refrigerator at 4 °C for 12 h. The product was then collected by vacuum filtration and the composite was dried under vacuum at room temperature overnight.

The dried composite was compressed onto a thin aluminum mold (1 cm x 2 cm x 0.05 cm) with Kapton sheets sandwiched between two plates. These samples were compression molded above the glass transition temperature, T_g, of the polymer at a pressure of ~10,000 lbs/.at 135 °C for a duration of about 5 minutes on the Carver press. The press was gently compressed until the sample was flattened without deformation.

2.4 Polymer Characterization

(A) Gel Permeation Chromatography (GPC)

GPC, also called size exclusion chromatography (SEC), separates analytes on the basis of their size by passing the molecules, in a solvent, through a densely packed column of porous materials. Size separation is realized by varying degree of pore permeation of the molecules, where the smaller molecules are retained longer in the column relative to the larger molecules.⁷¹ Thus, a larger size polymers will elute first, as they are excluded from the smaller size pores of the gel in the column. The larger the polymer molecular weight, the fewer beads that are penetrated and the faster the transport through the interstitial volume (volume between beads). Gel permeation chromatography was used to determine the number average molecular weight (M_n), weight

average molecular weight (Mw), and polydispersity index (PDI) of the polymers used in this study. Measurements were carried out on a Polymer Lab GPC-20 instrument with 300 mm x 7.5 mm Polymer Labs 5 μ m Mixed C columns, a 50 mm x 7.5 mm Polymer Labs 5 μ m guard column, and a Knauer K-2301 differential refractometer as a detector. Samples were prepared at 1mg/ml concentration in HPLC grade THF, stabilized with 100 ppm butylated hydroxyl toluene (BHT) as mobile phase. In addition, the samples were filtered through a 0.45 μ m syringe filter under vacuum prior to injection. The copolymers, SAN and St-*ran*-CNSt, were characterized by this method.

(B) Nuclear Magnetic Resonance (NMR)

Nuclear Magnetic Resonance (NMR) was used to determine the composition of the St-*ran*-CNSt. Samples were prepared as 7 mg/ml in deuterated chloroform and the chemical shift scale was referenced to the tetramethylsilane peak at 0 ppm. The measurements were carried out on Varian 250 MHz and Varian 400 MHz NMR spectrometers.

The ^1H NMR peak assignment for poly(styrene-*ran*-cyanostyrene) are;

7.08-7.43ppm	multiplet	9H	aromatic protons
2.76-2.94ppm	singlet	2H	-CH
1.58ppm	doublet	1H	-CH ₂

The ^{13}C NMR spectrum confirmed the incorporation of the nitrile group from cyanostyrene in the copolymer with a characteristic peak at chemical shift, δ = 119.1 ppm. The ^{13}C spectrum of poly(styrene-*ran*-cyanostyrene) is given in Figure 2.1.

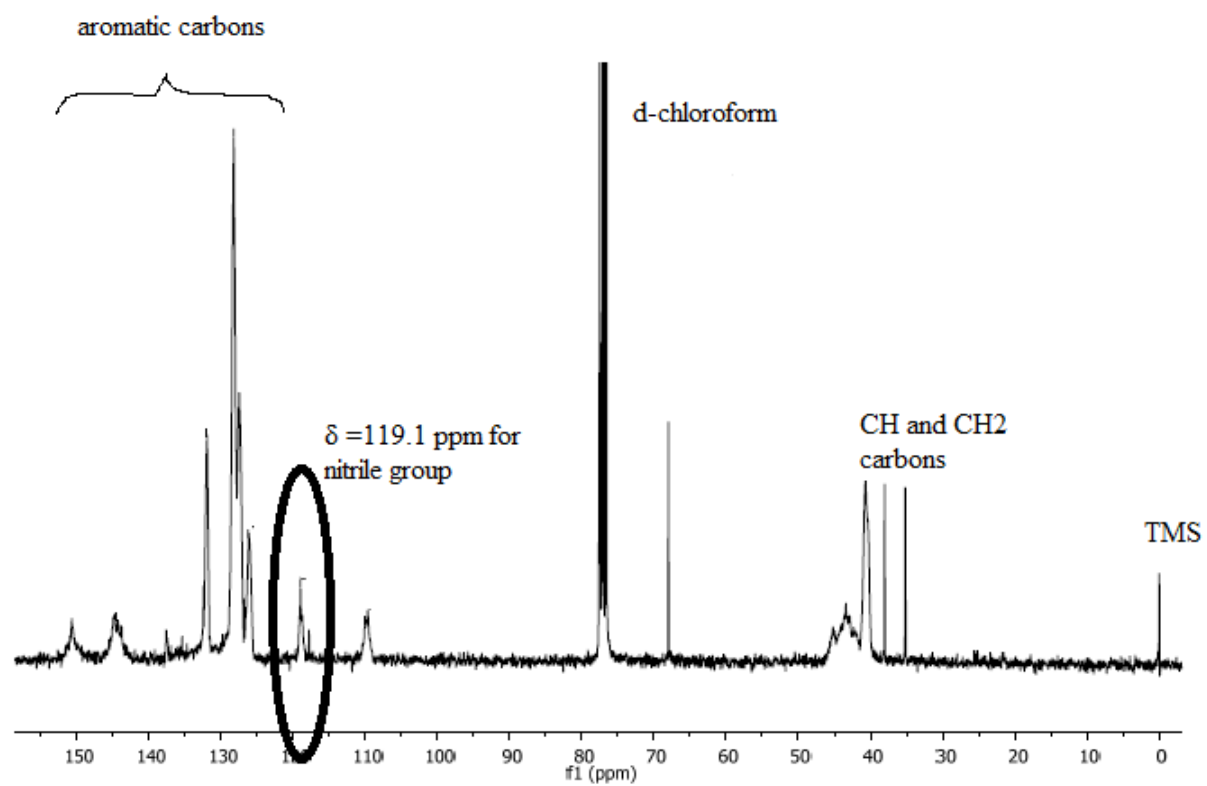


Figure 2.1. ^{13}C NMR spectrum of styrene-*ran*-cyanostyrene

(C) Elemental Analysis

Elemental analysis was completed by Atlantic Microlab Incorporated, Norcross GA to determine the composition of St-*ran*-CNSt and PSAN copolymers. An automatic analyzer was used to determine the C, H, N percentage in the sample by weight with an error of $\pm 0.3\%$ for both accuracy and precision. The molar composition of each functional group monomer was calculated as follows:

Average molecular weight of monomer = $\{ (a) \text{ MW of styrene, } 129.16 \text{ g/mol} \} + \{ (1-a) \text{ MW of cyanostyrene, } 104.151 \text{ g/mol} \}$

$a = \% \text{ nitrile/cyanostyrene in copolymer}$

$b = \% \text{ nitrogen in copolymer (determined from elemental analysis)}$

thus, $b = \frac{\text{Atomic mass of nitrogen, } 14.0 \text{ g/mol}}{\text{Average MW of monomer}}$

Therefore, mol % cyanostyrene in the random copolymer can be determined.

From error analysis, an error limit of $\pm 0.3 \text{ mass\%}$ of nitrogen translates to an error of $\pm 3.5 \text{ mol\%}$ of nitrile.

2.5 Characterization of the PNCs

(A) UV-Vis Spectroscopy

The spectroscopy measurements were carried out with a scanning spectrometer with dual light beams and dual sample holders for simultaneous measurement of I and I_o , as shown in Figure 2.2.

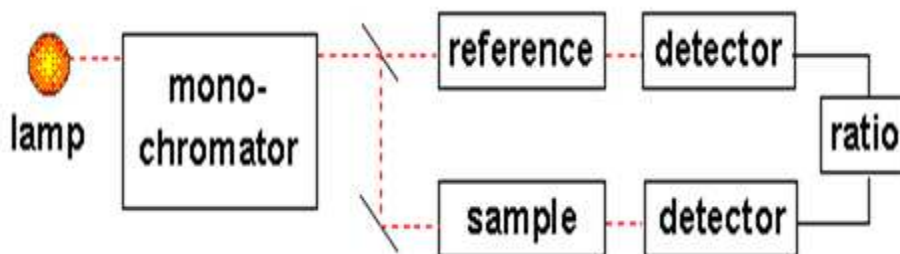


Figure 2.2: A diagram showing the set-up of a dual beam UV-Vis⁷²

The light passing through the reference cell for each wavelength is measured and referred to I_0 . Meanwhile, the intensity of light passing through the sample is defined as I .

These intensities are related to the absorbance, A of the sample:

$$A = \log I_0/I$$

The change in absorption with nanocomposite composition provides information on the homogeneity and dispersion of polymer nanocomposites. Thin film polymer nanocomposites with thickness of approximately 0.1 mm were scanned from wavelength 350 nm to 700 nm to measure the UV-Vis absorbance at room temperature. The miscibility limit of nanoparticles in the polymer nanocomposites were determined from this information using the method discussed in Chapter 3.

The UV-Vis absorption spectroscopy measurements were carried out on an Evolution 600 Thermo Scientific instrument. The light sources were deuterium and halogen lamps. Double beam spectroscopy was used, where a beam of light was separated into its component wavelengths by a prism and then split into two equal intensity beams through the sample and reference cells, respectively.

(B) X-ray Diffraction (XRD)

XRD was used to study the miscibility of the nanocomposites in polymer matrix. The combination of intense x-ray sources, high-speed detectors and efficient methods of analyzing data permit the analysis at high spatial resolution and small time scales.⁶³

The XRD patterns were obtained using a Rigaku, Inc XRD instrument at room temperature, using monochromatic $\text{CuK}\alpha$ radiation operated at 45 kV and 0.66 mA. Using a mirror to focus the radiation through the pinholes on to the sample can compensate for this small wattage. Normally, XRD utilizes a line focus or a line source of the tube.

In our study, the line source was used to emit radiation in all directions, together with a divergence slit of 0.1° in the direction along the focus line. This small slit was used to obtain better angular resolution at low angle. Data were collected with 2θ ranging from 5 to 35 degrees. The diffractogram of the sample was analyzed by comparing it with a “standard” pattern.

(C)Differential Scanning Calorimetry (DSC)

DSC monitors the thermal properties of a sample in a given temperature range. The calibration of the DSC was completed using indium as a standard (m.p. 156.6°C and heat of fusion= 28.45 J/g).⁷³ DSC measurements were carried out on a Mettler Toledo DSC 821 and TA Instruments DSC with nitrogen as the purging gas. Heating the furnace produces equal heat flow into the sample and a reference. Samples, weighing 10-15 mg, were heated from 60°C to 160°C at a rate of 10°C/min , with a nitrogen flow rate of 200 ml/min. To verify reproducibility, thermal properties of the polymers and polymer nanocomposites were determine by running multiple sets of measurements. The midpoint of the heat capacity change of the second

consecutively identical scan was recorded as the glass transition temperature. This step is necessary to eliminate the influence of thermal history.

The sample was heated to a range of 10-15 K above T_g . The samples are annealed at the highest temperature for a short period of time (3-5 minutes) in order to establish thermodynamic equilibrium and erase the thermal history of the system. This was followed by a rapid cooling to a temperature to at least 40K below the glass transition and immediate reheating at a constant rate.

The main parameters used to characterize T_g are shown in Figure 2.3.

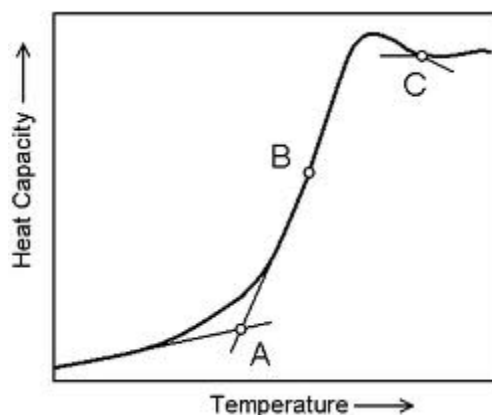


Figure 2.3: Definition of the quantities for characterization of T_g .⁷³

(A- Extrapolated onset temperature, C-extrapolated offset temperature, B- T_g)

The temperature at which the long-range segmental motion of the polymer chains starts is termed the glass transition temperature, T_g . T_g can be altered by the presence of attractive interactions between the polymer and nanoparticles such as EDA interactions which reduces or increases the mobility of polymeric chains and increases/decreases the glass transition temperature.

CHAPTER 3: OPTIMIZING THE MISCIBILITY OF FULLERENES IN COPOLYMERS

3.1 Introduction

This chapter presents experimental data that provides information on the miscibility of fullerenes in copolymers. The copolymers studied were synthesized according to the procedures described in Chapter 2. The exact copolymer composition, molecular weights and polydispersity are listed in Tables 3.1, 3.2 and 3.3. The dispersion of fullerenes in copolymers is determined by UV-Vis spectroscopy and X-Ray diffraction, while differential scanning calorimetry provides information on the impact of fullerene addition on the polymer thermal properties. Density functional theory (DFT) calculations will be discussed to provide insight into the role of binding energies between copolymers and C₆₀ and optimized geometries on the formation of polymer-fullerene interactions.

3.2 Materials

Fullerenes were used without further treatment and were purchased from Bucky USA (99.5% purity). The copolymers used in the study are illustrated in Figure 3.1 with pertinent functional group compositions listed in Tables 3.1, 3.2, 3.3. The Poly(MMA-*ran*-DMAEMA) or PDMA copolymers used were provided by a coworker, Dias Linton, while poly(styrene-*ran*-acrylonitrile) or PSAN copolymers were obtained from an industrial source. Poly(styrene-*ran*-cyanostyrene) or PSCN copolymers were synthesized via free radical polymerization as outlined in Chapter 2. The nanocomposites preparation procedures are also described in Chapter 2.

Table 3.1: PSAN copolymer composition and molecular weight characteristics.

Polymer Label	Molecular weight (g/mol)	PDI	mol % AN	Mol % PS
PSAN10	83000	2.28	29.5	70.5
PSAN20	79000	2.35	36.8	63.2
PSAN30	55000	2.04	45.0	55.0
PSAN40	67000	2.12	48.8	51.2
PSAN50	55000	2.37	56.2	43.8

*note: mol % monomer is determine by elemental analysis

Table 3.2: PSCN copolymer composition and molecular weight characteristics.

Polymer Label	Molecular weight (g/mol)	PDI	mol % AN	mol % PS
PSCN 10	62000	1.47	16.0	84.0
PSCN 30	79000	1.55	22.3	77.7
PSCN 40	66000	1.51	28.5	71.5
PSCN 50	89000	1.57	43.1	56.9

*note: mol % monomer is determine by elemental analysis

Table 3.3: PDMA copolymer composition and molecular weight characteristics.

Polymer Label	Molecular weight (g/mol)	PDI	mol % DMAEMA	Mol % MMA
PDMA10	88000	1.40	13.2	86.8
PDMA20	54000	1.15	24.2	75.8
PDMA30	46000	1.08	30.4	69.6
PDMA40	33000	1.24	40.0	60.0
PDMA50	32000	1.12	53.5	46.5

*note: the copolymer is synthesized by co-worker, Dias Linton.

3.3 Experimental Results and Discussion

A. UV-Visible Spectroscopy

UV-Vis absorption spectroscopy is a widely used analytical technique. This method compares the attenuation of a beam after it passes through a blank and an absorbing species. The UV-Vis spectrum has broad features that are of limited use for sample identification but are very useful for quantitative measurements. The wavelength of the UV-Vis spectra ranges from approximately 190 nm to 900 nm.

The intensity of the reference beam is defined as I_0 . The intensity of the beam that passes through the sample is defined as I . The incident light has intensity I_0 , and if it passes through a sample that absorbs light at the wavelength λ , the light intensity I leaving the sample is attenuated. If the sample compound does not absorb light of a given wavelength, $I = I_0$. However, if the sample compound absorbs light then I is less than I_0 . These two quantities can be related to the absorption ($A = \log I_0/I$), or transmittance ($T = I/I_0$). If no absorption has occurred, $T = 1.0$ and $A = 0$. Most spectrometers display absorbance on the vertical axis, and the commonly observed range is from 0 (100% transmittance) to 2 (1% transmittance).⁷²

Several investigators have used UV-visible spectroscopy to study the dispersion of nanocomposites by varying the dispersing agents.^{74,72} For example, Romyen et al, utilized UV-Visible spectroscopy to study the level of dispersion of carbon black in nanocomposites with addition of surfactant.⁷²

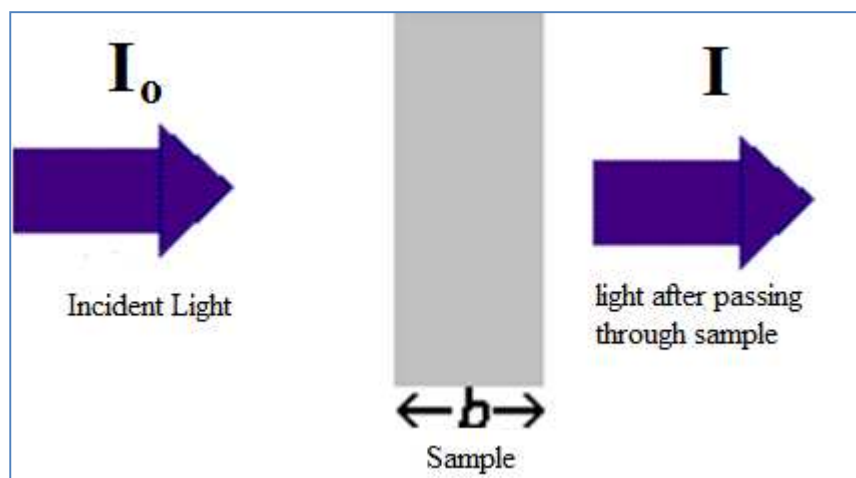


Figure 3.1: Illustration depicting the process of absorption

The absorption of light by the sample is described by the Beer-Lambert Law,

$$A = \epsilon bc \quad (\text{equation 3.1})$$

where b is the length of the sample or path that the light traverses through the sample, c is the concentration of the absorbing species within the sample and ϵ is the molar extinction coefficient.⁷² Meanwhile, the absorbance can be expressed as,

$$A = \log I_0/I \quad (\text{equation 3.2})$$

$$\text{Thus, } \epsilon bc = \log I_0/I \quad (\text{equation 3.3})$$

From the equations above, the concentration of the sample is inversely proportional to the light intensity, I , leaving the sample. According to Beer's law, when the concentration of the absorbing species increases, the absorbance will proportionally increase, resulting in a decrease in measured intensity, I . Consequently, a system which does not follow this concentration-light intensity relationship indicates one that is non-homogeneous or immiscible.

In order to verify the ability of UV-vis to accurately monitor the homogeneity of a system, solutions of fullerene in toluene with different concentration of fullerene ranging from 1mg/mL to 5mg/mL were analyzed. In these particular experiments, the blank or solution of toluene was used as the reference. Figure 3.2 shows the absorbance of the fullerene solution as a function of C₆₀ concentration in toluene solution. According to Beer's law, $A = \epsilon bc$ where ϵ , and b are constant in this case, a direct proportional relationship between the absorbance and concentration is expected, and observed up to ~ 4 mg/ml. Thus, the miscibility limit of C₆₀ in is 4mg/mL as illustrated in the figure below. This is exemplified by the plateau of the absorption of the fullerenes in toluene above 4 mg/ml.

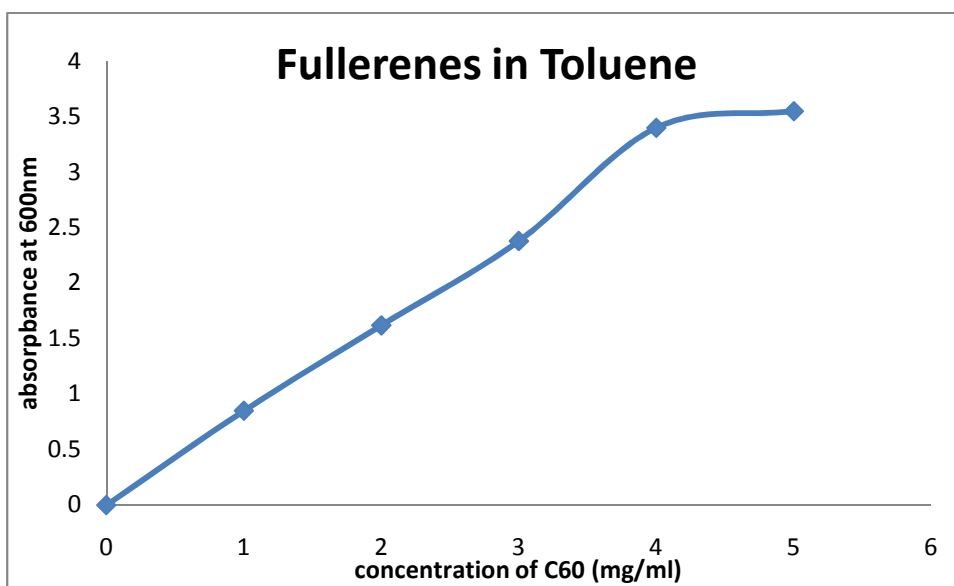


Figure 3.2 Plot of optical density as a function of concentration of C₆₀ for fullerenes in toluene

In a similar manner, the miscibility of fullerenes in polymers can be studied. For example, Figure 3.3 shows the spectra of polystyrene/ C_{60} nanocomposites with fullerene concentrations ranging from 1 -5 wt%. Upon addition of C_{60} , two peaks at 540nm and 600nm appear in the spectra, where the intensity of these peaks increase with C_{60} concentration. Figure 3.4 shows the absorbance of the polystyrene/ C_{60} nanocomposites as a function of fullerene concentration, showing a similar trend to the solution studies, indicating the suitability of using UV-vis to monitor the miscibility limit of the samples.

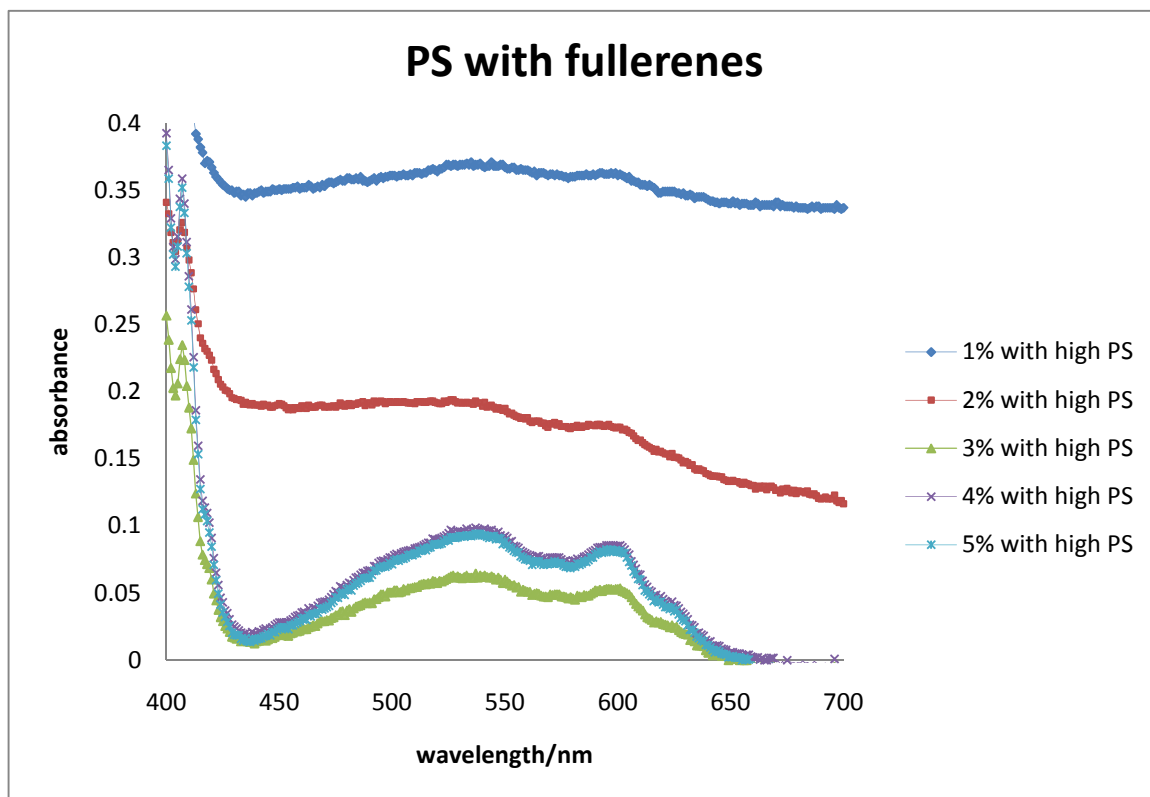


Figure 3.3: Spectra for polystyrene(PS) with fullerene (1wt%, 2wt%, 3wt%, 4wt%, 5wt%)

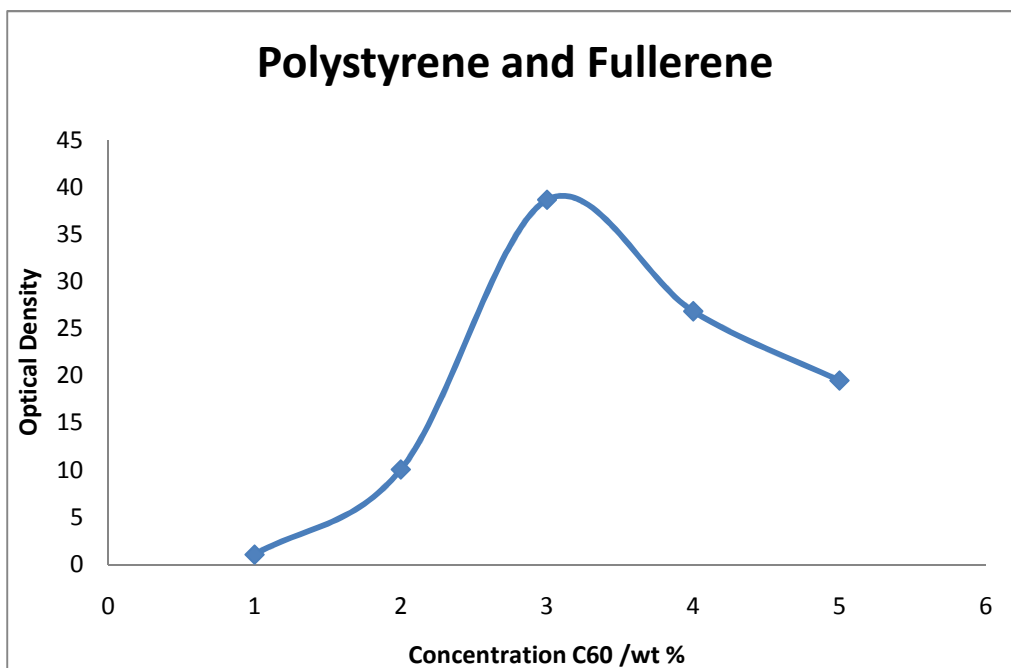


Figure 3.4: Optical density as a function of wt% C60 for polystyrene and fullerene in solution.

In the graph above, the absorption behavior of the fullerene in polystyrene mimics the behavior of the fullerene in toluene solution. This confirms that UV-vis of polymer nanocomposites will exhibit a deviation from the Beer-Lambert law upon reaching the miscibility limit, and can thus be used to monitor the mixing behavior of polymer-fullerene nanocomposites. This may be due to the precipitation or aggregation of the excess fullerene. Tomiyama et al. described that after the solubility limit of fullerene in solvent such as carbon disulfide, fullerene tends to form various forms of clusters which are proven to be present after centrifuging the sample.⁷⁵

In our study of polymer nanocomposite thin films, each sample was analyzed three times at different positions (top, middle, and bottom) for a range of wavelengths (300-700nm). The graph of absorbance as a function of wavelength as shown in Figure 3.5, were obtained to search for a suitable wavelength for film analysis as the concentration of C₆₀ increases. At the wavelength of 650nm, the polymer nanocomposites film produces significant variation with fullerene concentration. However, the synthesized film had various thicknesses ranging from 5-15μm. A description of the optical density calculation and associated error are included in the Appendix. Therefore, to include the effect of the film thickness, the optical density is calculated for each sample.

$$\text{Optical density, OD} = A/b = \epsilon c \text{ (Equation 3.4)}$$

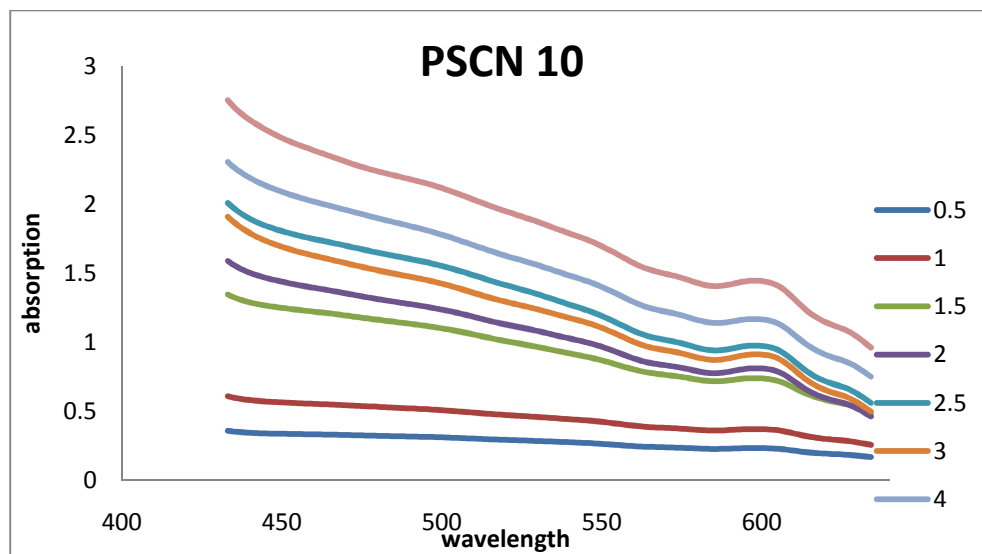


Figure 3.5. The UV-Vis spectrum of PSCN 10 nanocomposites with different C₆₀ loadings (0.5,1.0,1.5,2.0,2.5,3.0,4.0,5.0 wt%)

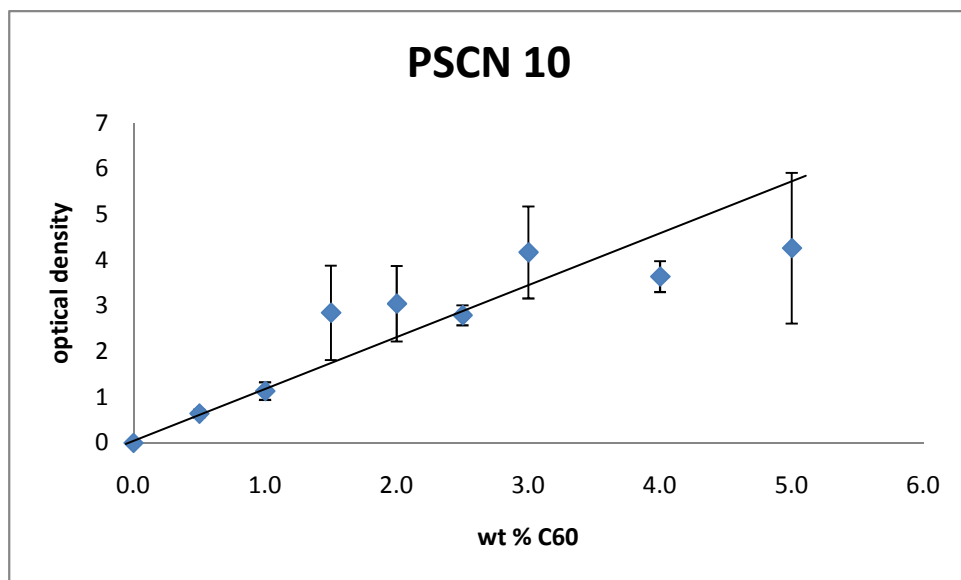


Figure 3.6. The optical density as a function of wt % C₆₀ for the PSCN 10 nanocomposites at 650 nm

To evaluate the miscibility of the fullerene in each copolymer, the optical density of each sample is calculated and plotted as a function of wt% C₆₀. A line is drawn through the origin (0,0) and fit to the low wt% C₆₀, and the fullerene concentration that deviates from the linear fit breaks Beer's law, and is denoted as the beginning of heterogeneity of the sample, i.e. the miscibility limit. Figure 3.6 shows the plots of the optical density as a function of wt% C₆₀, for the PSCN30 nanocomposites. From this graph, 3.0wt% C₆₀ is identified as the miscibility limit of C₆₀ for this particular copolymer, or the maximum amount that can be dispersed into the polymer before heterogeneity began to appear. This process is repeated for each copolymer to determine the miscibility limit of C₆₀ for each polymer matrix.

The miscibility limit of each copolymer is then plotted as a function of the wt % of the functional group (AN, CNSt, DMAEMA) to identify the impact of copolymer composition on fullerene dispersion. Figure 3.7 displays the fullerene miscibility limit as a function of the copolymer composition of each functional group, AN, CNSt, and DMAEMA respectively. Miscibility and dispersion can be interpreted to indicate the extent of interaction; therefore this analysis provides insight into the interactions that exist between fullerenes and copolymers for each copolymer. Thus, the compositions with the highest miscibility limit are interpreted to indicate the presence of optimal interactions with C₆₀.

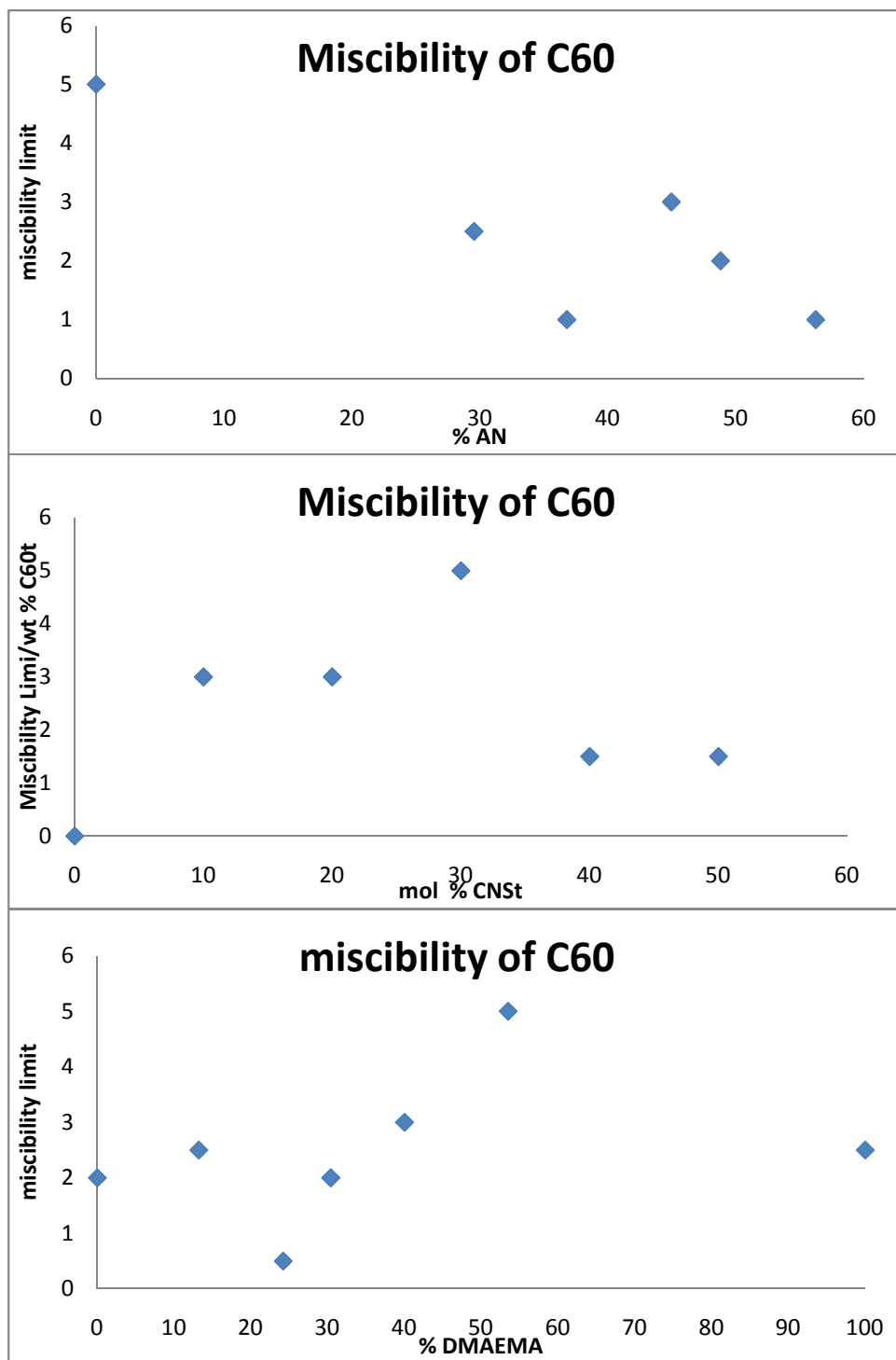


Figure 3.7. Plots of miscibility limit with mol % of functional groups

(a) AN (b) CNSt (c) DMAEMA

As can be seen in Figure 3.7 (a), for PSAN composites, the 45.0mol%AN composite has the highest miscibility limit. At higher AN content than 45.0mol%AN, the miscibility limit for fullerenes decreases steadily. This is interpreted to indicate that 45.0mol% AN copolymer is optimal for the formation of intermolecular interaction between the polymer matrix and C₆₀, leading to improved C₆₀ dispersion. The optimal composition may be due to polymer chain connectivity, sterics and the conformation between the NPs and polymer.

In addition, the spacing between the interacting functional groups along a polymer chain may affect the formation of electron donor-acceptor complex with fullerene. For example, Rasheed et al. report that a moderate amount of vinyl phenol content along a polymer chain allows the optimum hydrogen bonding formation with carboxyl-functionalized single-walled carbon nanotubes.⁶⁸

PSCN exhibits a different trend as PSAN, the PSCN10 or 16.0% CNSt copolymer composition shows the highest miscibility limit at 5wt%. Further addition of cyanostyrene functional group resulted in the decreased in the miscibility of fullerene. This clearly demonstrates that fullerenes tend to agglomerate when the concentration of fullerenes increases. The existence of an optimum amount of interacting functional group is crucial to obtain a homogeneous polymer nanocomposite with high fullerene concentration. The ability of SAN and CNSt to form pi-pi(π - π) stacking between the phenyl ring of the polymer and the curved π surface of the C₆₀ cage maybe an important key in determining the miscibility limits of C₆₀. Yu and coworkers report that π - π stacking is the dominant interaction between the C₆₀ cage and the phenyl ring of poly(methylphenylsilane-*co*-methylsilane) (PMPS-*co*-MS).⁷⁹ Thus, π - π stacking

between spherical C_{60} and the phenyl ring of polystyrene-containing copolymers can improve the miscibility of C_{60} in these copolymers.

As discussed above, the miscibility of fullerenes are favorable with the presence of a certain amount of interacting functional group in the polymer chain because the distance between the interacting functional group along a polymer chain in the random copolymer is crucial to the formation of electron donor-acceptor complexes with fullerenes. At a certain distance or spacing, the rotational freedom of each interacting functional group is increased. As a result, the formation of non-covalent interactions increases, since this affects the ability of a polymer chain to conform itself favorably to the curved surface of C_{60} . This helps to explain why PSAN 30 with 45.0 mol% AN have the highest miscibility limit among these series.

The extent of interaction also correlates very well with the observed dispersion of SWNT in these polymer matrices. In our group's previous work, it was reported that the strongest interaction between monomer and SWNT occurred at CNSt 23 mol% and AN 45mol %.⁴⁹ The importance of chain connectivity in the copolymer in the formation of non-covalent interactions between SWNTs and the interacting groups in polymers has been explained. In addition, the loss of the aromatic rings of the styrene in SAN also leads to a more flexible chain that can wrap around the SWNT more easily, creating EDA interactions at higher AN composition.

On the other hand, the DMAEMA exhibits the highest miscibility limit of C_{60} at 53.5 mol% DMAEMA. As shown in Figure 3.7(c), with the addition of DMAEMA on the polymer chain, the miscibility of C_{60} increases, from 2 wt% C_{60} for PMMA homopolymer to 2.5wt% for 13.2mol% DMAEMA. However, the miscibility limit shows a decrease at 24.2mol%

DMAEMA before a consistent increase in miscibility from 24.2 mol% DMAEMA composition to 53.5 mol% DMAEMA composition.

The introduction of DMAEMA moieties, an electron-donating group, into PMMA enhances the formation of EDA interactions. In addition, DMAEMA does not have any aromatic groups, which leads to a significantly more flexible chain, which is able to adopt a favorable conformation with C_{60} . This can explain the consistent increase in miscibility limit from 24.2-53.5mol% DMAEMA. Moreover, the miscibility limit of the homopolymers, PMMA and PDMAEMA, are not as high as the 50:50 copolymer. In polymer-nanocomposite systems, geometrical constraints are very important parameters that limit the formation of non-covalent interactions by polymers on the nanoparticle. The conformation of the polymer chain near the spherical surface of the nanoparticle is crucial to create effective non-covalent interactions and produce miscible polymer nanocomposites.

Thus, these results appear to indicate that increased flexibility of the polymer chain increases the propensity to form non-covalent EDA interactions between the polymer and fullerene. This can be quantified by estimating the Kuhn length of each copolymer studied, a quantitative measure of polymer chain flexibility. The Kuhn length, l_k , is often employed to characterize the stiffness of the polymer chain and understand the flexibility of the polymer, and can be used to determine the importance of this parameter in the interaction with other polymer or particles.⁷⁶ The simplest model for understanding the flexibility of the polymer chain is the freely jointed chain model. In this model, the contour length of the molecules is given by $L = Nb$, where b is the Kuhn length and N is the number of Kuhn segments in the molecule. Kuhn length is defined as the distance along the chain contour over which the chain orientation becomes

statistically uncorrelated. In order to utilize the freely jointed chain, this value is equated to the known molecular weight/chain length dependence of a Gaussian chain,

$$\langle r^2 \rangle_0 = N l_k^2 = C n l^2 \quad (\text{equation 3.5})$$

In this equation, C is the characteristic ratio, $\langle r^2 \rangle_0$ is the end to end distance, n is the number of bonds, and l is the length of the backbone bond (in our case, $1.54 \text{ \AA}$ for a C-C bond).⁷⁷

Additionally, the contour length R of the real chain is equivalent to that of the Kuhn chain,

$$R_{\max} = N l_k = n l \quad (\text{equation 3.6})$$

From equation 1 and equation 2, the traditional definition of a Kuhn length is defined as:

$$l_k = C l \quad (\text{equation 3.7})$$

Thus, the characteristic ratio, C can be determined, and inspected to describe the effect of local steric constraints and monomer structure on the chain dimension. C can be expressed as a function of polymer molecular weight, M as.

$$C = m_b [\langle r^2 \rangle_0 / l^2 M] \quad (\text{equation 3.8})$$

The value of $\langle r^2 \rangle_0 / M$ can be readily obtained from reference [79], where $(\langle r^2 \rangle_0 / M)$ for poly(methylmethacrylate) = $0.39 \text{ \AA}^2$ and $(\langle r^2 \rangle_0 / M)$ for polystyrene = $0.437 \text{ \AA}^2$.⁷⁸ The characteristic ratios of poly(cyanostyrene) (PCNSt) and poly(dimethylaminoethylmethacrylate) (PDMAEMA) are not as readily available, but are estimated to be similar to those of poly(α -methyl styrene) and poly(ethylbutyl methacrylate) respectively, due to the similarity in structure.

The characteristic ratio of the copolymers used in this study can then be calculated by assuming that the characteristic ratio of the copolymer is the sum of the weighted average of the characteristic ratios of the two homopolymers as

$$C^{\text{copolymer}} = C_A \times n_A + C_B \times n_B \quad (\text{equation 3.9})$$

Where n_i is the molar composition of monomer i in the copolymer. The value of C calculated by using equation 3.10, where x is the monomer molar mass.

$$C = \frac{x \langle r^2 \rangle_0}{2 l^2 M} \quad (\text{equation 3.10})$$

Table 3.4 shows the calculated characteristic ratios, C and Kuhn length, b , of the PDMA, PSAN and PSCN copolymers used in the study. The plots of Kuhn length as a function of functional group composition in the copolymers are shown in Figure 3.8.

Table 3.4 Characteristic ratio and Kuhn length of copolymer used

	MOL% AN	MOL% St	C	b
PSAN 10	0.295	0.705	8.381868	15.5519
PSAN 20	0.368	0.632	8.081536	14.99466
PSAN 30	0.45	0.55	7.744177	14.36871
PSAN 40	0.488	0.512	7.58784	14.07864
PSAN 50	0.562	0.438	7.283395	13.51377
	MOL% CNS	MOL% St	C	b
PSCN 10	0.16	0.84	9.985996	18.52823
PSCN 20	0.223	0.777	10.13974	18.81349
PSCN 30	0.285	0.715	10.29104	19.09422
PSCN 50	0.431	0.569	10.64734	19.7553
	MOL % DMAEMA	MOL%MMA	C	b
PDMA 10	0.132	0.868	7.477757	13.87439
PDMA 20	0.242	0.758	8.168341	15.15572
PDMA 30	0.304	0.696	8.55758	15.87792
PDMA 40	0.4	0.6	9.160272	16.99617
PDMA 50	0.535	0.465	10.00781	18.5687

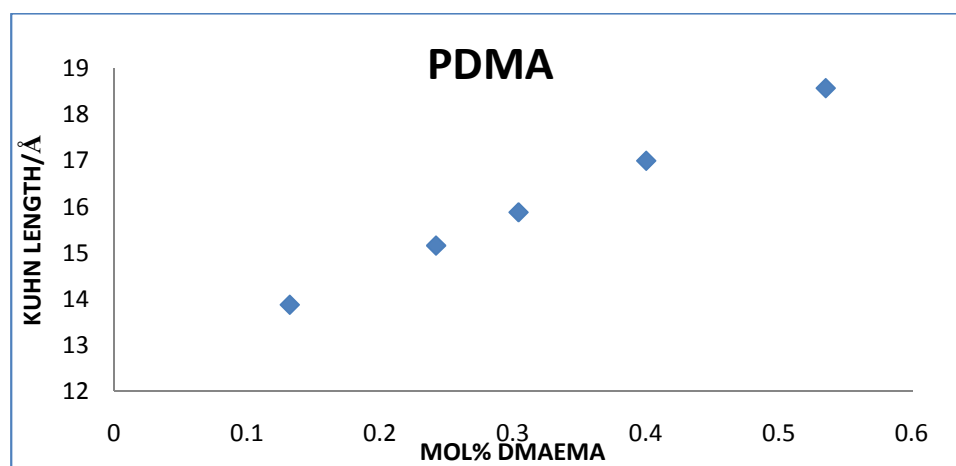
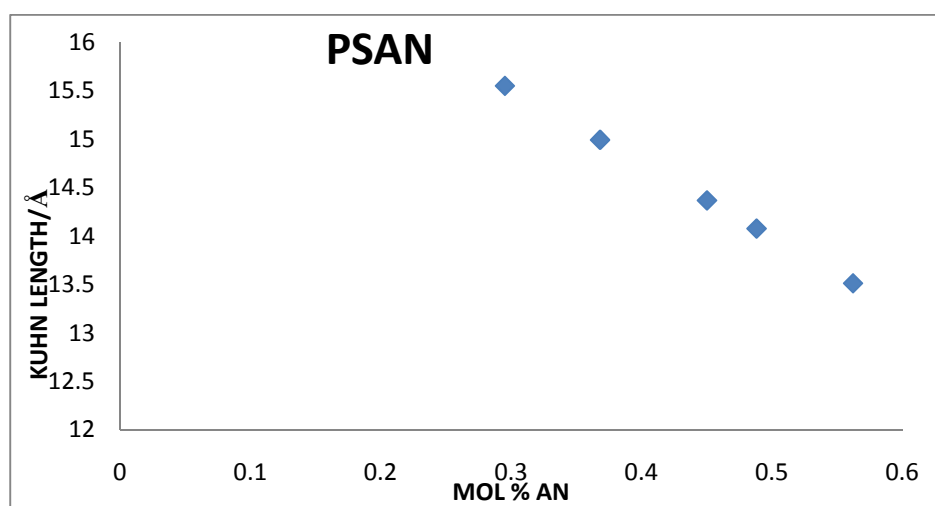
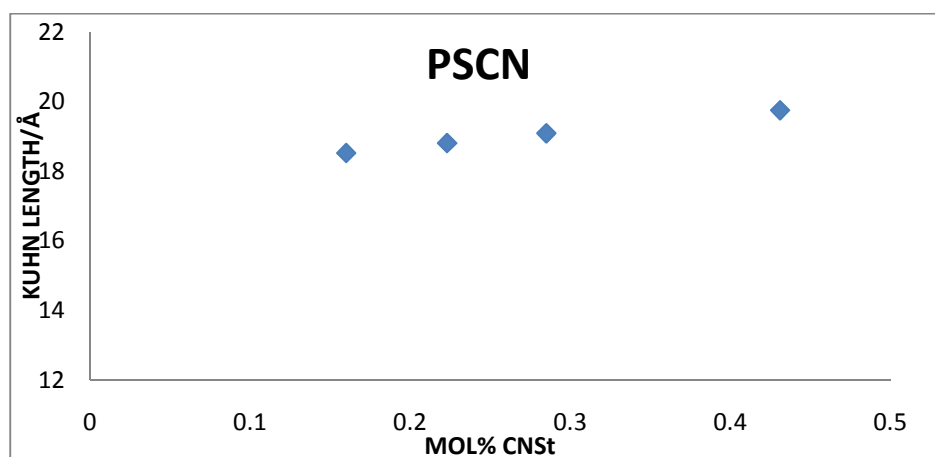


Figure 3.8 Plots of Kuhn length as the function of functional monomer in copolymers

From Figure 3.8, the dependence of Kuhn length on the composition of the functional group in the copolymer provides insight into the flexibility of the polymer chains. The stiffness of the copolymers can be classified as , PS>PAN, PCNSt> PS and PMMA> PDMAEMA. Therefore, for both DMAEMA and AN, the Kuhn length decreases as the composition of functional group increases, while the incorporation of CNSt into polystyrene increases the Kuhn length of the polymer chain. This makes sense, as the AN and DMAEMA monomers are less bulky than the styrene and MMA monomers, respectively. Clearly the cyano group on the styrene ring increases its bulkiness, increasing the polymer chain rigidity. Moreover, the absolute values of this measure of chain flexibility corroborates the importance of chain flexibility in the formation of EDA interactions, as the DMAEMA containing polymers are significantly more flexible than the styrene containing polymers, with smaller Kuhn lengths.

In conclusion, the results presented in this section indicate that the electron donating DMAEMA is more effective than the electron withdrawing acrylonitrile or CNSt in the formation of electron donor-acceptor complexes with fullerene, where one factor that controls the formation of the interaction is the flexibility of the polymer chain. Further experiments such as X-Ray diffraction (XRD) and differential scanning calorimetry (DSC) will be discussed below to provide additional information that provides additional insight into the fundamental parameters that control EDA formation between polymer bound functionalities and fullerenes.

B. X-Ray Diffractometry (XRD)

X-ray diffraction is a technique primarily used for phase identification of crystalline materials. X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation and focused into a fine beam that impinges on a solid sample. Some of the X-ray beam is scattered and some adsorbed by the sample, where the scattered beam can lead to a phenomenon called diffraction.⁶³ The interaction of the incident rays with the atoms in the sample produces constructive and destructive interference of the x-rays which can be described by Bragg's Law ($n\lambda = 2d\sin\theta$).⁶¹ This equation describes the relationship between wavelength of electromagnetic radiation (λ) to the diffraction angle (θ) and the lattice spacing in a crystalline sample(d) as illustrate in Figure 3.9. In our experiments, each diffractogram was recorded from $2\theta = 5^\circ$ to 35° at scanning speed of 1° /min.

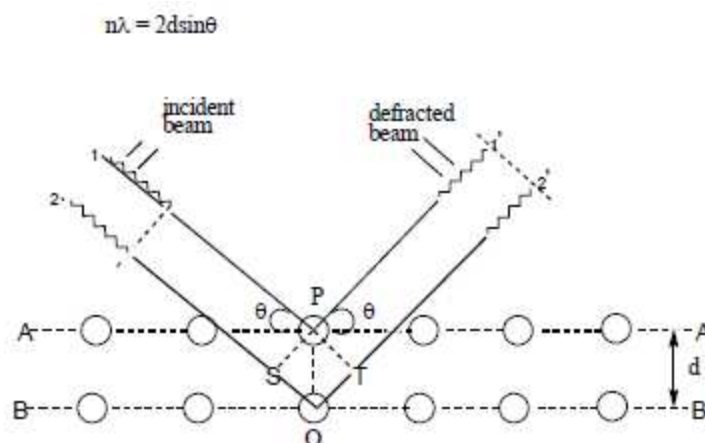


Figure 3.9. Diffraction of X-Rays by planes of atoms (A-A' and B-B')⁷⁹

X-ray diffraction by the polymer nanocomposites is analyzed to evaluate the miscibility of C_{60} in the copolymers. Figure 3.10 shows the XRD pattern of pure C_{60} which exhibit crystalline peaks at $2\theta = 11.0^\circ$, 17.8° , 21.1° , 21.9° , 27.5° , and more. The thin films nanocomposites are analyzed to identify the miscibility limit of C_{60} in the polymer. If C_{60} is homogeneously dispersed in the polymer matrix, no diffraction peaks are observed. However, the appearance of diffraction peaks clearly indicates the phase separation of C_{60} from the polymer matrix. Thus, the highest C_{60} concentration that exhibits an amorphous peak are consider the miscibility limit of fullerene in that particular composition of the copolymer.

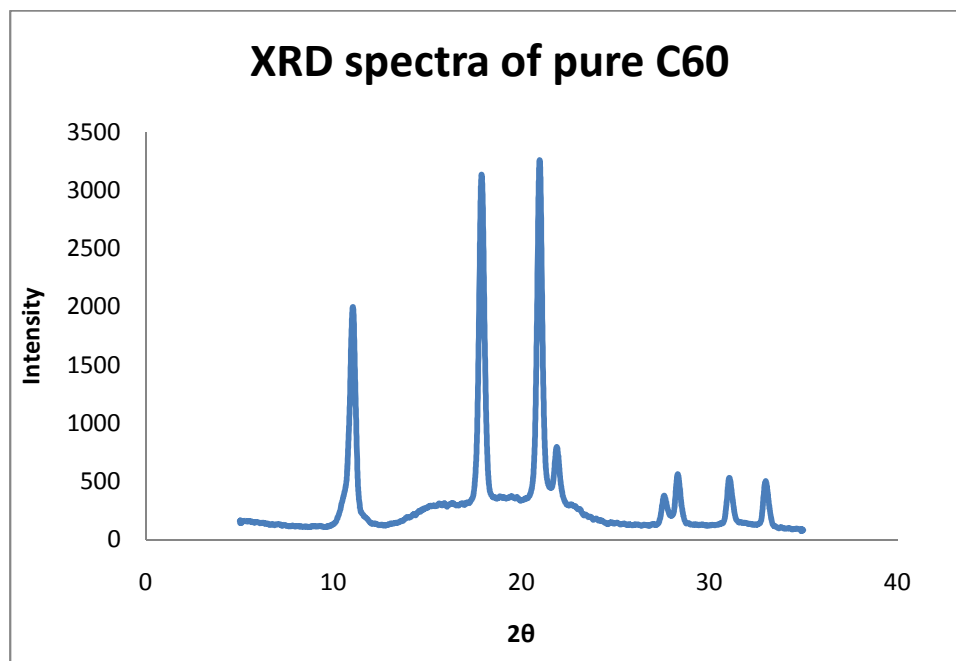


Figure 3.10. XRD spectra for pure C_{60} powder

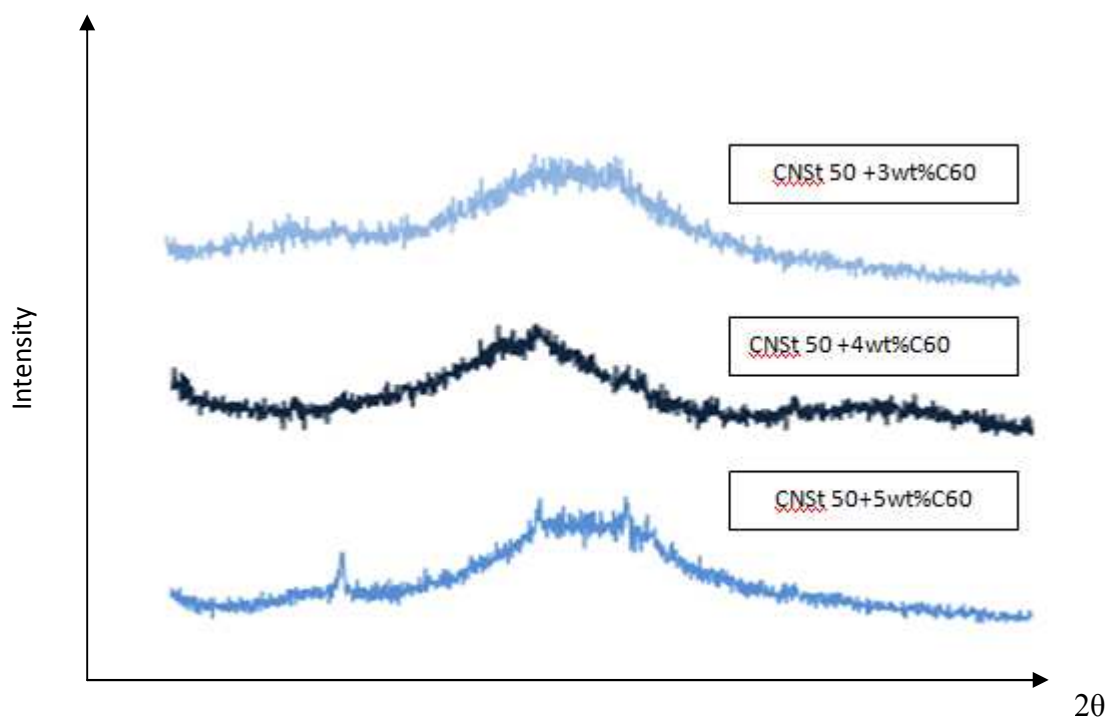


Figure 3.11. Comparison of spectra of CNSt 50 nanocomposites with increasing C_{60}

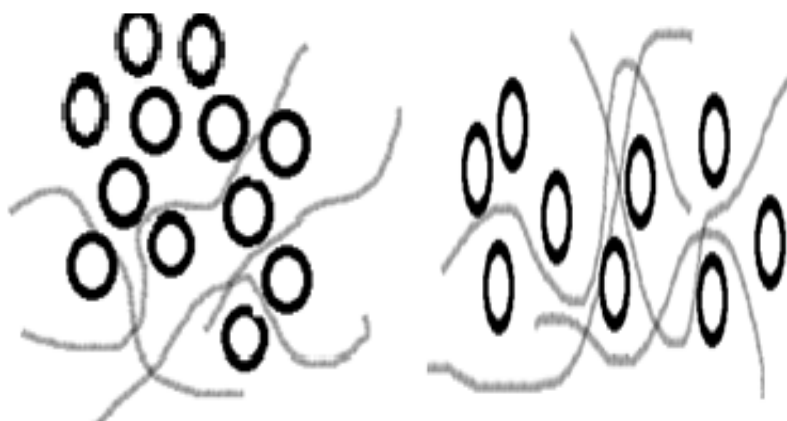


Figure 3.12. Diagram showing the different cluster formations

A broad peak in XRD spectra represents the miscible sample, which could result from a strong interaction between the copolymer and C₆₀. Meanwhile, sharp crystalline peaks appear when there is crystalline C₆₀ present in the samples. For this study, the appearances of crystalline peaks are used to indicate the miscibility limit of C₆₀ and the copolymers. Itoh et al. indicate that C₆₀ are easily crystalline due to its closed packed structure.⁸⁰ Thus, miscibility of nanocomposite can be quantified by the absence of XRD crystalline peaks.

Figure 3.11 shows the XRD patterns of PSCN50 with an increase of C₆₀ concentration, from 3wt% to 5wt% C₆₀. The diffractogram of 3wt% and 4wt% C₆₀ only exhibit a broad peak similar to that of the pure polymer. However, the crystalline peaks begin to appear at 5wt % C₆₀. As a result, repeating the same process can identify the miscibility limit of each copolymer.

The quality of the nanoparticle dispersion in the polymer matrices directly correlates to the formation of the C₆₀ clusters in the blend. Samples that exceed the miscibility limit produce sharp diffractions peaks. However, XRD can only detect periodically stacked or clusters of nanoparticles, which requires sufficiently large aggregates of fullerenes to exhibit diffraction peaks. To better understand this result, Figure 3.12 illustrates the phenomena that might occur in a nanocomposite and its impact on the XRD. The left figure shows an obvious cluster or agglomeration of C₆₀ that may produce a crystalline peak while the right figure shows a system with a smaller C₆₀ clusters that are not large enough to produce crystalline peaks. Similarly, Manias reported that the XRD can only detect the periodically stacked montmorillonite layers; disordered (bunched together but not parallel stacked) or exfoliated layers are not detected.⁸¹ In addition, Rashidov et al. also mentioned that XRD will produce a broad peak when the aggregation of C₆₀ is no more than 100 molecules.³² The disordered aggregates of C₆₀ are smaller

in cluster size, exceeding the sensitivity of the XRD instrument. As a consequence of this detail, the UV-Vis , which also monitors immiscibility due to the formation of C_{60} clusters, may be more sensitive to the presence of smaller clusters than XRD.

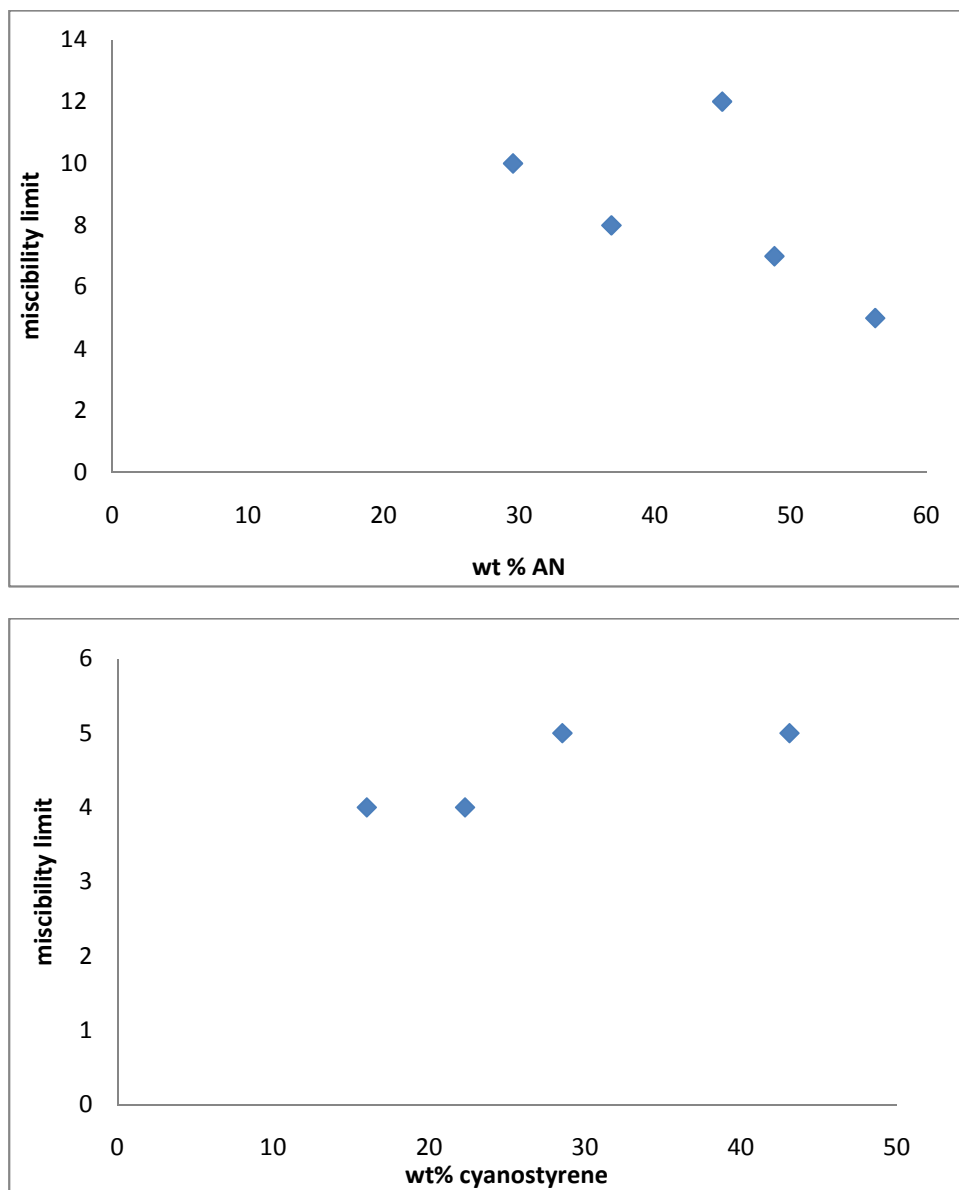


Figure 3.13. Graphs of miscibility limit of AN (a) and CNSt(b) as a function of copolymer composition

A plot of the miscibility limit of C_{60} as a function of copolymer composition is shown in Figure 3.13. In this figure, PSAN 30 corresponding to 45.0mol%AN, shows the highest miscibility limit of approximately 12 wt% C_{60} . This result agrees qualitatively with UV-Vis, but implies a higher miscibility limit, demonstrating the variation in sensitivity of the techniques. For PSCN, there is no clear optimal copolymer composition, as the miscibility limit does not change much with composition. This implies that XRD is not sufficiently sensitive to observe a variation while UV-Vis is.

Likewise, the miscibility of the PDMA copolymer was examined to observe the crystalline peak by XRD spectrum. The results show that no crystalline peak is present up to 20wt% C_{60} in PDMA50 in the XRD spectrum. This indicates that the PDMA copolymer exhibits a better C_{60} dispersion relative to the PSAN and PSCN copolymer.

The results from both XRD and UV-Vis are utilized to quantify the dispersion of polymer nanocomposites. It is clearly evident that fullerenes disperse well in PSAN 30 copolymer, as indicated by both techniques. Even though not all PDMA copolymers are analyzed with XRD, the results simply demonstrate that the dispersion of fullerene in DMAEMA copolymer is better than in AN and CNSt.

As shown in the result, the miscibility of C_{60} is enhanced at a certain composition of interacting functional group, demonstrating that the polymer chain connectivity is important in the formation of non-covalent interactions between C_{60} and polymer. Thus, further investigation with DSC and density functional theory was completed to more thoroughly test this interpretation.

C. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry is a technique used to measure the thermal properties of a sample. In this experiment, a small quantity of sample is confined to an aluminum pan and subjected to controlled temperature variation. An equivalent reference pan is heated together with the sample pan as illustrated in Figure 3.14. The temperature/heat flow to the sample can be determined by monitoring the heat flow rates into the sample and into the reference. The inflection point of the heat flow was taken as the glass transition temperature, T_g .⁷³ T_g for both polymer and polymer nanocomposites are compared to understand how the introduction of the nanoparticles into the sample alters its thermal properties.

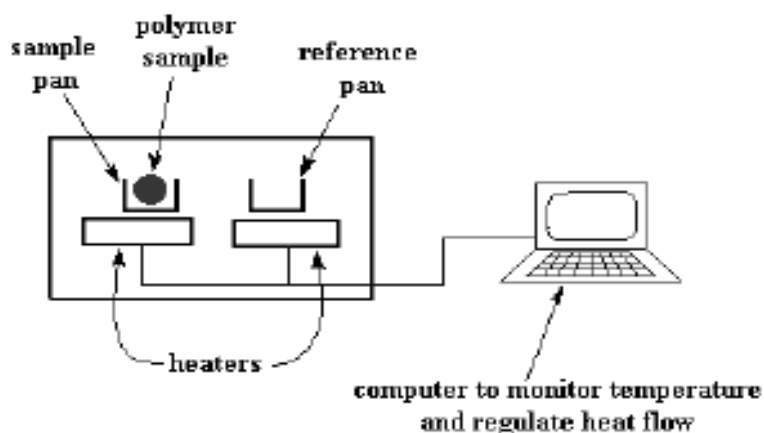


Figure 3.14. A schematic representation of DSC experimental setup

An enhancement in the Tg is interpreted as the result of the presence of an interaction between the nanoparticles and the polymer, which reduces molecular mobility and flexibility of the polymer chain in the vicinity of the NP. However separate reports on the Tg of various nanocomposites demonstrates that Tg may increase or decrease with the addition of nanoparticles.^{82, 62-64} For instance, Starr et al., reported that for a nanocomposite with an attractive interaction between components, Tg increased by approximately 6% for particle loading of 8 wt%, while for a nanocomposites with no attractive interactions between components, the Tg decreases by a similar amount.⁶⁵ Similarly, Lu and Weiss demonstrated that an increase in Tg represent strong interactions, while a decrease in Tg is the result of weak interactions.⁸³ The authors explained that particles with a strongly attractive polymer-particle interactive gives rise to an increase in Tg, reflecting its immobilization. In addition Wong et al. reported that the presence of C₆₀ alters the high frequency local dynamics of a polymer with an increase in Tg and slower chain dynamics.²⁸ The polymer-particle interaction manifests as dynamics that differ from those of the neat polymer. Therefore, an increase of Tg is interpreted to indicate the presence of a strong interaction between the copolymer and C₆₀. The quality of nanoparticle dispersion in the polymer matrix also correlates with its changes in Tg.

DSC analysis shows that the incorporation of fullerene into the copolymer changes the Tg. The interpretation that strong interactions between the copolymer and nanoparticle alter the mobility of the polymer matrix resulting in a variation in Tg is used to explain the behavior of each copolymer.

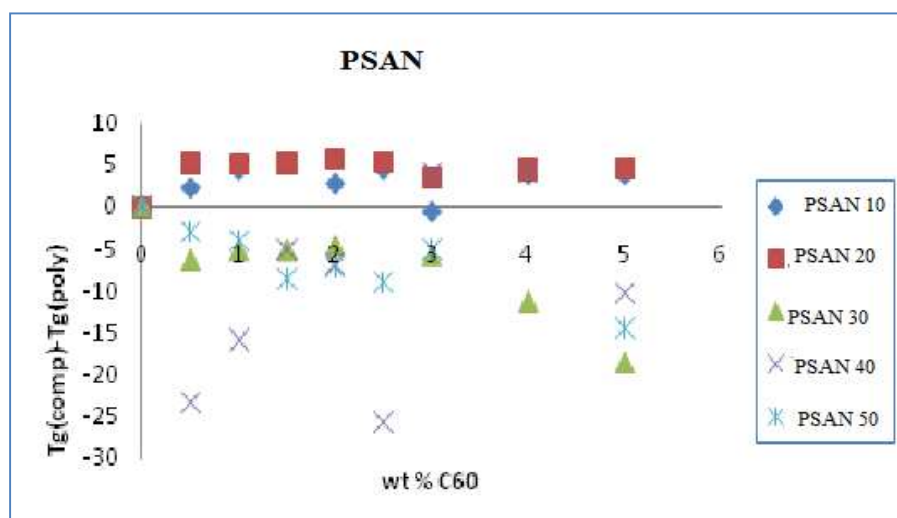
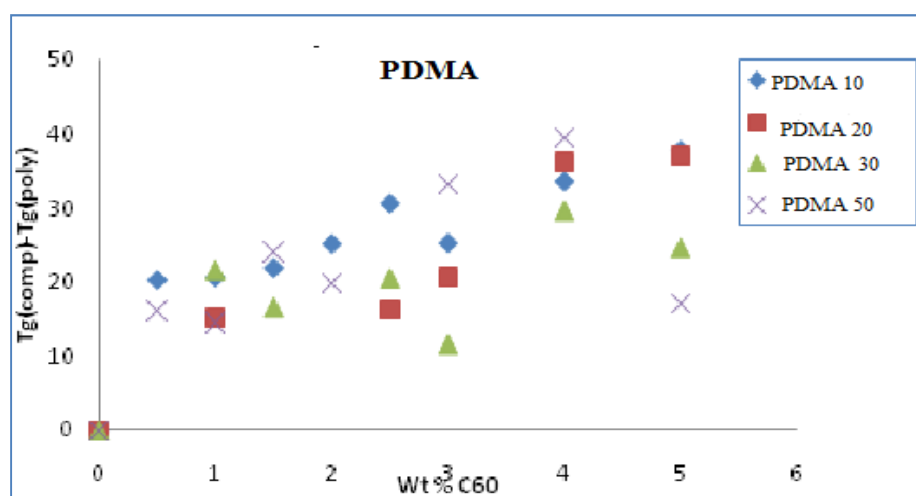
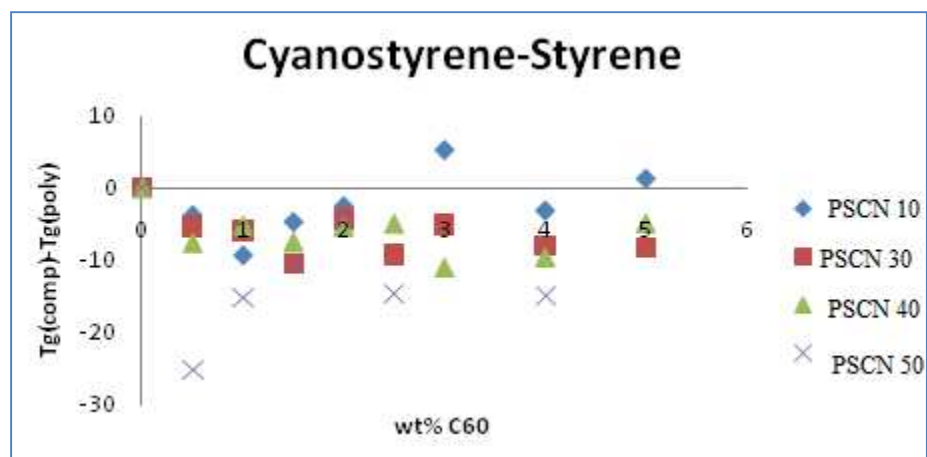


Figure 3.15. Graphs show the $T_g(\text{composite}) - T_g(\text{poly})$ with wt% C₆₀ for

(a) CNSt (b) DMAEMA (c) AN

As shown in Figure 3.15, the PSAN, PSCN and PDMA copolymers exhibit different changes in T_g with incorporation of C_{60} . An increase of T_g in the DMAEMA- C_{60} nanocomposites is observed, the T_g of the CNSt- C_{60} nanocomposites generally decreases, while the T_g of the AN- C_{60} nanocomposites exhibit both an increase and decrease in T_g . The changes in T_g can be correlated to the polymer nanocomposite dispersion and interaction between fullerene and functional groups in each copolymer. This result is critical to understand the role of the interacting functional group in copolymers on improving the dispersion of fullerenes in polymers.

Figure 3.15 plots the change of T_g , ΔT_g ($\Delta T_g = T_{g(\text{nanocomposite})} - T_{g(\text{copolymer})}$) as a function of copolymer composition for the different copolymers. The steady increment of T_g with the addition of DMAEMA as shown in Figure 3.13(a) can be interpreted as the result of strong interactions between the copolymer and C_{60} . Along with the XRD results, where fullerene readily dispersed in DMAEMA up to 20wt%, DSC analysis confirms the presence of strong interactions between DMAEMA and C_{60} .

CNSt exhibits an opposite trend to that of DMAEMA, showing a consistent decrease in T_g for every copolymer composition. As mentioned above, this negative deviation of T_g can be interpreted as indicating the presence of weak interactions between polymer and nanoparticle, which can increase the mobility of the polymer chain in the nanocomposite. The increased mobility in a nanocomposites can be associated with the formation of clusters of nanoparticles in the PNCs. Consequently, CNSt displays a drop of T_g when fullerene are added.

The SAN nanocomposites trend is more complex, with an increase in T_g for copolymers with low AN content and a decrease in T_g at higher AN compositions. EDA complexes are

created when the electron withdrawing nitrile group of AN on a polymer chain is in close proximity to the carbon cage of C₆₀. These results appear to indicate that for copolymers with low AN content, strong intermolecular interactions exist that limit polymer mobility. After an optimal amount of AN groups has been incorporated into the copolymer matrix, further increasing AN concentration results in a decrease of T_g, indicating a decrease in the extent of strong interactions between the polymer and fullerene. Thus, π - π stacking, polymer chain flexibility and steric limitations may explain the difference in the behavior of the CNSt and SAN nanocomposites. The CNSt matrix contains a bulky phenyl ring on every monomer, presumably inhibiting the ability of sufficient functional groups to orient and position to form EDA or π - π interactions, resulting in an increase in free volume and a decrease in the measured T_g. With an increasing amount of smaller, more flexible acrylonitrile groups in the polymer chain, the chain is able to form more π - π and EDA interactions. However, increasing the AN content further lowers T_g, which implies that the loss of the styrene and π - π interactions dominates the response of the system. This can be further interpreted to indicate that the π - π interactions are stronger than the EDA interaction between the fullerene and the nitrile group, a conclusion that is verified below in the density functional theory results. This interpretation is consistent with both the CNSt and AN results, exemplifying the role of π - π and EDA interactions between fullerenes and copolymers in determining their dispersion.

3.4 Computational Study: Density Functional Theory (DFT)

Density functional theory (DFT) is a molecular-based statistical thermodynamic theory, which relates the adsorption isotherm to the microscopic properties of the system. For this study, this theory provides information on the binding energy between monomers and C₆₀. The binding

energies of monomers to C_{60} are compared with those of binding energies to SWNT with the same monomers to understand the role of size and curvature of NPs on the formation of this interaction. Our collaborator, Dr Bobby Sumpter, completed this work and one calculation is illustrated in Figure 3.16, which shows the potential energy curve of C_{60} -acrylonitrile as a function of distance between C_{60} and the monomer.

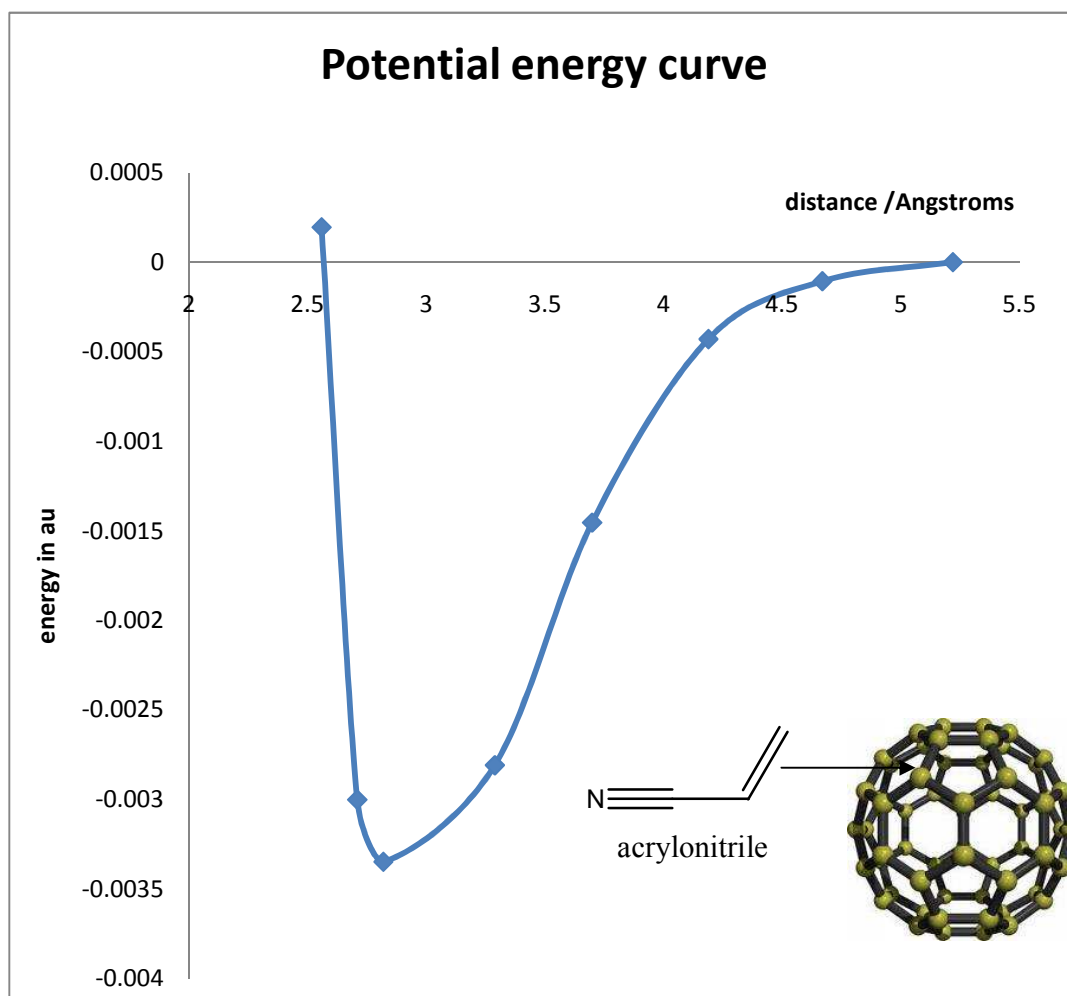
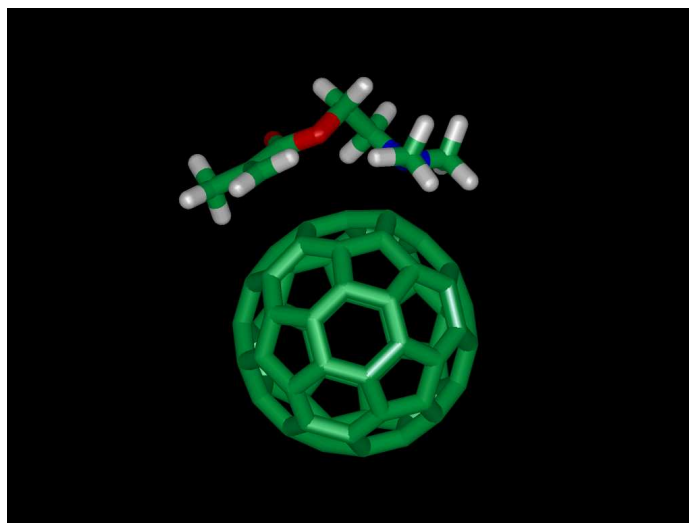
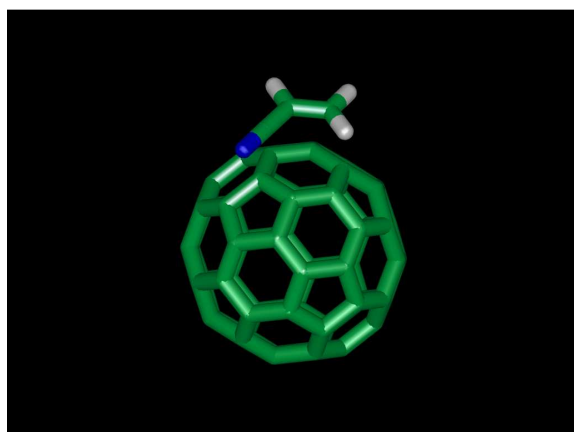


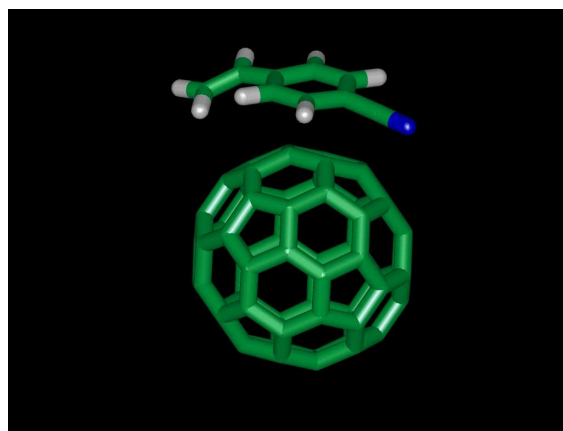
Figure 3.16. The potential energy curve of AN- C_{60} with C-C bond of AN aligned to the center of the hexagon on C_{60}



(a) Binding of DMAEMA monomer and C₆₀



(b) Binding of AN monomer and C₆₀



(c) Binding of CNSt monomer and C₆₀

Figure 3.17. Optimized geometries of monomers that contain electron donating or accepting moieties interacting with C₆₀

Brief details of the calculation are discussed to understand the analysis of the EDA interaction between monomer and nanoparticles. Geometries of the complexes were optimized at the density functional theory (DFT) level, using both the local density approximation (LDA) and generalized gradient approximation (GGA).⁸⁴ These approximations are utilized to obtain an accurate calculation by considering the local density and gradient of the density at the same coordinate. Figure 3.16 shows the graph of the potential energy curve for the acrylonitrile (AN) – C₆₀ interaction using the Gaussian basis set, 3-21G.⁷⁹ These calculations of intermolecular interactions have been reported with basis set superposition error (BSSE) and deformation energy correction.⁸⁵ The binding energy for the optimal interaction between monomer and C₆₀ are in au (Hartree, 1 au=27.2 eV) and plotted as a function of distance between monomer and C₆₀ in angstroms in the graph.⁸⁶ As the center C-C bond on AN is aligned to the center of the hexagon on C₆₀, the energy level decreases with distance, favoring the interaction until it reaches the minimum energy called the binding energy. After the binding energy is reached, the energy rises when distances are decreased.

Figure 3.17 (a) shows the optimized geometry for DMAEMA- C₆₀, where the alignment of the N-atom on DMAEMA with the C atom on C₆₀ produces a strong interaction. In order to validate the relative strength and trends of the intermolecular interaction as computed, Figure 3.17 can be used to better illustrate the close distance between the monomers and C₆₀. The geometries of the C₆₀ are optimized with different monomers to obtain their binding energies.

Meanwhile, in Figure 3.17(c), the alignment of the phenyl ring on CNSt is neither face-to-face tangential nor parallel with a hexagon on C₆₀. This odd angle alignment results in a larger distance between the C on CNSt and C on C₆₀, as well as a larger distance between the CN group

to C on C₆₀. Due to these large distances, the binding energy of CNSt with C₆₀ is significantly lower than CNSt with SWNT.

Table 3.5. Closest distance between monomer and C₆₀ in the optimized geometry

Monomer	Distance C(monomer)-C (C ₆₀) /(Å)	Distance C ₆₀ – functional group (Å)
Acrylonitrile	3.02	(C->N)=3.27
Cyanostyrene	2.67	(C->N)=3.79
DMAEMA	2.91	(C->N)=1.87
Methyl methacrylate	3.13	C=O->C)=2.64
Styrene	2.63	N/A

Table 3.6. Binding energy of monomer and nanoparticles (SWNT and C₆₀)

Monomer	SWCNT kcal/mol	C ₆₀ kcal/mol
Acrylonitrile	4.5	2.10
Cyanostyrene	10	2.40
DMAEMA	0.31	4.73
Methyl methacrylate	0.6	1.44
Styrene	1.9	3.21

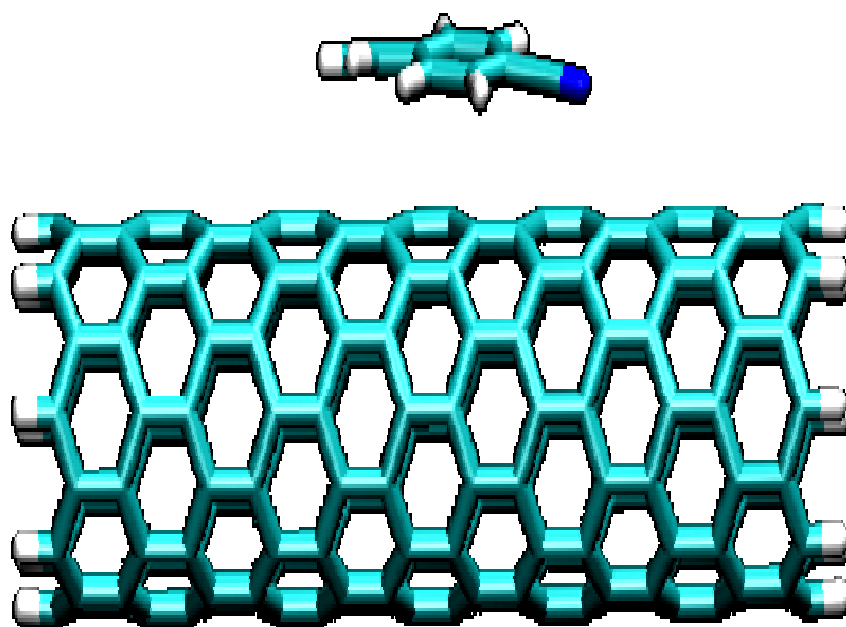


Figure 3.18: Interaction between SWNT and CNSt with aromatic structure facing the
SWNT π network

Table 3.5 shows the distance between monomers and C₆₀ at an optimized geometry for both the C-C and C-functional group pairs. These values quantify the level of interaction between fullerene with each monomer, as the smaller the distance between the polymer and fullerene, the stronger the intermolecular interactions in the polymer nanocomposites. It is worth noting that the distance between the carbon of styrene and the carbon in C₆₀ are relatively close, which may be associated with the π - π interaction. Similarly, the distance between carbon in C₆₀ and carbon in cyanostyrene which consist of the aromatic phenyl ring and a nitrile group are the second shortest after styrene. This indicates that the shape and conformation of the nanoparticle with the polymer matrix impact the formation and strength of the interaction.

Due to the different curvature of the nanoparticles, SWNT and C₆₀ display different geometries and strengths of interaction with these monomers. Table 3.6 shows the values of the binding energies for these monomers with both C₆₀ and SWNT. For example, the CNSt monomer has an intermolecular binding energy of 10 kcal/mol with SWNT at the preferred orientation. The aromatic structure of CNSt interacts well with SWNT in a flat position with its sp² resonance facing the π network structure between monomer and SWNT, as show in Figure 3.18. On the other hand, C₆₀ has a smaller binding energy with CNSt at 2.40 kcal/mol as a result of the odd alignment geometry; a result of the curvature of the C₆₀ sphere.

Computation results show that the interaction between C₆₀ and the amine group in the DMAEMA monomer has a binding energy of 4.73 kcal/mol, twice that of CNSt (Figure 3.14(a)). The optimized geometry of the DMEAMA monomer and C₆₀ shows that the N atom is directly above a carbon on the C₆₀ and creates a relatively strong interaction. Thus, the distance between the N atom on DMAEMA and C on C₆₀ is short at 1.87 Å. This is clearly a result of the

flexibility of the DMAEMA monomer allowing the DMAEMA to conform to the shape of the C_{60} considerably better than the CNSt can.

Interestingly, styrene exhibits a relatively high binding energy with C_{60} among the monomers listed in Table 3.6. The binding energy of 3.21 kcal/mol between fullerene and styrene is stronger than that between C_{60} and AN or between C_{60} and CNSt. Styrene is able to interact with C_{60} via π - π stacking between the curved π surface of the C_{60} cage and the flat π surface of the phenyl ring of polystyrene. In addition, the distance between C_{60} and PS is also relatively small ~ 2.63 Å, as shown in Table 3.5, indicating the strong interaction between the nanoparticle and the monomer. This is also valid for the CNSt monomer due to the presence of the phenyl ring. As a result, CNSt is the third strongest binding monomer with a binding energy of 2.4 kcal/mol. The result reveals that π - π stacking interactions occur in the polymer nanocomposites with the phenyl ring on the polymer chains and play a significant role in the dispersion of C_{60} in these polymers.

The correspondence between our experimental results and the DFT computational results indicate that the extent of electron donor-acceptor interaction varies with the distribution of interacting functional groups along the polymer chain and their specific structures. The role of chain flexibility and realization of an optimized geometry even when the functional group is bound to a polymer leads to the conclusion that DMAEMA binds more efficiently with C_{60} to form homogeneous polymer nanocomposites.

3.5 Conclusion

The experiments described in this chapter show that the level of dispersion is optimal when a minority of non-covalent interacting functional groups is present in a copolymer matrix. This implies that polymer chain connectivity is critical to obtain an optimal dispersion of a nanoparticle in a polymer matrix. In addition, the π - π stacking interactions with phenyl rings on the polymer chains play a key role in determining the dispersion of the fullerene in the copolymers. In the first portion of this study, the miscibility limit of the fullerene in the copolymers was examined by evaluating the homogeneity of the nanocomposite with UV-Vis and XRD. Then, the dynamic behavior of the polymer nanocomposites is quantified with DSC. Lastly, theoretical calculations are utilized to provide further insight into the experimental results.

The formation of the EDA interactions is optimal with a certain interacting functional group composition, the exact value of which is dependent on geometrical constraints, flexibility, and structure of the monomers in the copolymer. UV-Vis results indicate that PSCN 10 and PSAN 30 have the highest miscibility with C_{60} , which can be interpreted to indicate the presence of the strongest interaction with C_{60} . The Kuhn length of the copolymers quantifies the chain flexibility, indicating that a decrease in allows the monomer to wrap around the fullerene. PSAN and PDMA demonstrate good compatibilizer with fullerene as the Kuhn length decrease as more functionality group are added. These results agree with previous work in our group on the dispersion of SWNT in these same copolymers. Among the three different copolymers (PSAN, PSCN and PDMA), the DMAEMA copolymer exhibits the most homogeneous nanocomposites with C_{60} . However, as compare with UV-Vis, XRD is less sensitive to the presence of small

C₆₀ clusters in monitoring the heterogeneity of the polymer-C₆₀ nanocomposites. The results clearly indicate that UV-Vis can monitor the miscibility limit of fullerenes with copolymers.

The binding energies and distance between monomers and C₆₀ in its optimized binding geometry that are obtained from density functional theory calculation corroborates our experimental data. These results indicate that DMAEMA forms the strongest intermolecular interaction with C₆₀, followed by styrene, acrylonitrile and CNSt. This further affirms our conclusion that C₆₀ forms strong π - π interactions and prefers to act as an electron-acceptor in the formation of electron donor acceptor complexes, as demonstrated by the preferable interaction with DMAEMA to those with AN or CNSt. Thus, these results indicate that in order to form effective interactions between polymer-bound functional groups and fullerenes, the effect of steric restrictions of the polymer backbone, chain connectivity and the ability to coordinate the interacting functional group with the fullerene near its optimized geometry play critical roles in the extent of intermolecular interactions that can be realized between polymer- C₆₀, which further impacts the dispersion and properties of polymer-fullerene nanocomposites.

CHAPTER 4: THE IMPACT OF SAMPLE PREPARATION ON THE DISPERSION OF GRAPHENE IN COPOLYMERS

4.1. Introduction

In this chapter two different techniques of polymer nanocomposites preparation are examined to understand the role of sample preparation on the homogeneity of graphene-polymer nanocomposites and their thermal properties. Sample preparation methods that are examined are solvent evaporation (SE) and rapid precipitation (RP). The copolymers used in this study contain styrene and acrylonitrile (AN) with varying AN content, as listed on Table 4.1. The transparency tests are determined by laser transmittance as shown in Figure 4.2. The thermal properties are studied by differential scanning calorimetry (DSC).

4.2. Material

Graphene was provided by a collaborator, Dr Humberto Terrones and coworkers, from the Instituto Potosino de Investigación Científica y Tecnológica (IPICYT) in Mexico and used without further treatment. The synthesis and characteristics of graphene are briefly discussed in Chapter 4.3. The specifications of the as-received graphene and a typical SEM image of the nanoparticle are given in Figure 4.1. The poly(styrene-*ran*-acrylonitrile) or SAN copolymers are obtained from an industrial source and used as received. The detail composition and characteristics of SAN are listed in Table 4.1.

Table 4.1: SAN copolymer composition and characteristic.

Polymer Label	Molecular weight (g/mol)	PDI	mol % AN	Mol % PS
PS	77,000	1.04	0.0	100.0
Sparkle	81,000	2.28	29.6	70.4
DN 52	79,000	2.35	37.8	62.2
DN 59	56,000	1.98	45.0	55.0
DN 77	57,000	2.00	48.5	51.5
CN 40	36,000	2.24	56.4	43.6
PAN	102,700	1.35	100.0	0.0

*mol% AN are determined by elemental analysis as described in Section 2.4 (C)

4.3. Experimental

(I) Synthesis of Graphene nanoribbons

Graphene ribbons were obtained from collaborators at the Instituto Potosino de Investigación Científica y Tecnológica (IPICYT), and their preparation is summarized below based on reference 82.

Grapheneribbons are prepared via chemical vapor deposition (CVD)from bulk carbon. In this process, mixtures of ferrocene and thiophene in ethanol were prepared and then dispersed ultrasonically at 1223Kwith an argon flow (0.8L/min). After 30 minutes, the ultrasonic sprayer was turned off and the rate of argon gas is adjusted to 0.2-0.3L/min. The final product, which is in the form of a black powder, is found to be sticking on the wall of the tube. After scraping off the graphene from the wall of the tube, it is characterized by SEM. Figure 4.1 shows SEM images of the graphene nanoribbons at different magnifications. The resulting graphene has a width of 20-300 nm, thickness less than 15nm and occur as two different structures; zig-zag and arm chair edge.

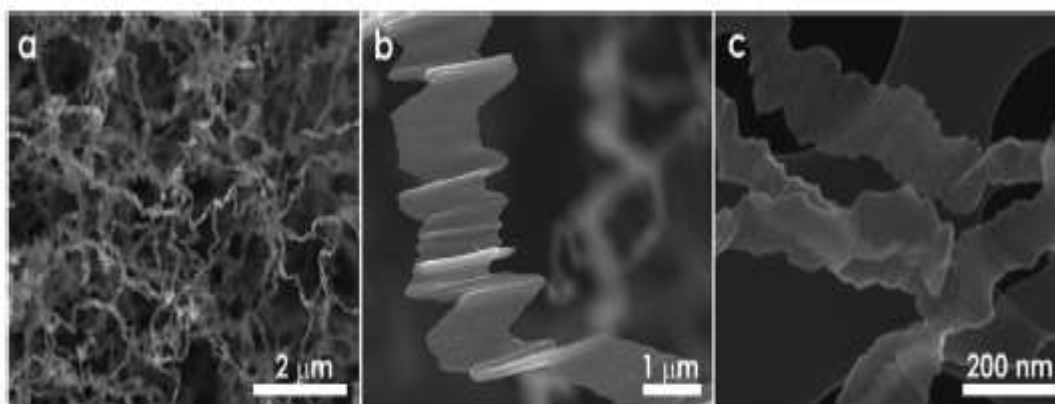


Figure 4.1. SEM images of graphene ribbon at different magnifications⁸⁷

(II) Composite Preparation

(A) Solvent Evaporation

A high school student, Kelsey Dadmun, prepared and evaluated the solvent evaporation samples as part of her summer internship. In this study, SAN and graphene were weighed out to form 1%, 0.1%, 0.05% and 0.01% nanocomposites. Graphene in dimethylformamide (DMF) was sonicated for an hour in a sonicator bath at room temperature. Appropriate amounts of polymer were added to the DMF/Graphene solution and heated to 130°C, above T_g, until the solution was reduced to half its original volume. The polymer/graphene composite films were formed by casting the prepared suspension onto a mold and by evaporating the DMF in vacuum at 130 °C. The mixture was kept in the oven for 72 hours to remove trace solvent. Finally the nanocomposites were gently pressed to form a uniform thin film at 150 °C and a pressure of 10,000 lbs.

(B) Rapid Precipitation

The thin films obtained from technique (i) are re-dissolved in 5mL of DMF. The mixtures are vortexed until completely dissolved. The solutions are sonicated for an hour in a sonicator bath (Branson 3510) operated at a frequency of 40Hz. The solutions were then precipitated into 20-folds excess of cold methanol with rapid stirring. The nanocomposites were slowly dried in the oven overnight and then pressed to thin films with the hot press at 150 °C and pressure of 10,000lbs.

4.4. Transparency Test

The work presented in this chapter seeks to understand and obtain quantitative and qualitative data of the dispersion of polymer-graphene nanocomposites fabricated by solvent evaporation and precipitation. The composition of acrylonitrile (AN) in the copolymer is varied to determine the importance of this parameter on the dispersion of graphene in the SAN copolymer. In order to assess the effect of the presence of the electron withdrawing acrylonitrile (AN) on the formation of electron donor acceptor interactions and its correlation to the dispersion of graphene in a polymer matrix, a visualization evaluation was performed on the thin film composites SAN. Photographs of thin films are taken to qualitatively analyze the dispersion of nanoparticles in the polymer matrix both as the composition of the AN varies and composition of graphene increases. Poor dispersion will result in a darker or less homogeneous thin film. This means, a strong dispersion will be expected to be clearer and have less defects in the thin film.

As a preliminary assessment in this study, thin films of graphene and SAN nanocomposites with increasing graphene concentration, as shown in Figure 4.2, were visually analyzed. As expected, the color of the thin film gets darker as the concentration of graphene increases. This trend shows that with the increased amount of nanoparticles, the dispersion of the nanoparticles decreases. However, this trend cannot be used to quantify the miscibility or dispersion limit of the graphene in the copolymer.

Thus, photographs of thin film of nanocomposites for a particular graphene concentration were taken to characterize the range of dispersions in the copolymer nanocomposites, as displayed in Figure 4.3.

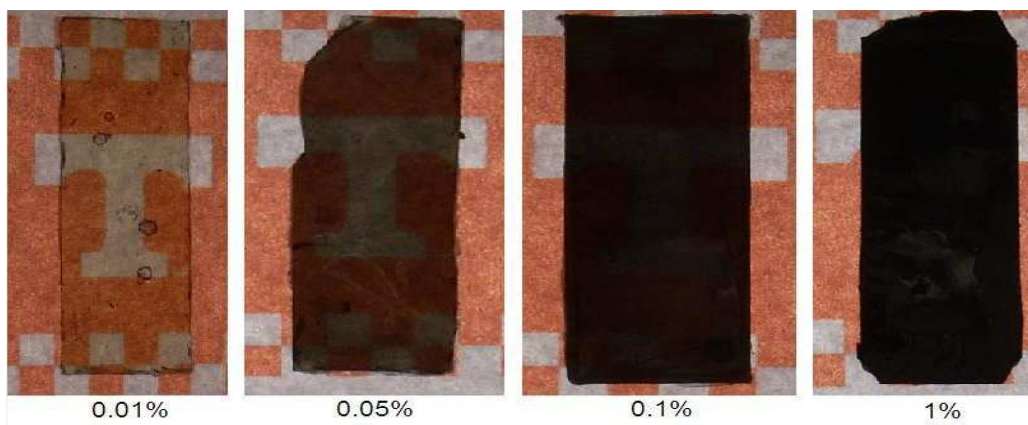


Figure 4.2. Photograph image of DN 59 with increasing graphene
Via solvent evaporation (0.01, 0.05, 0.1 and 1.0wt%)

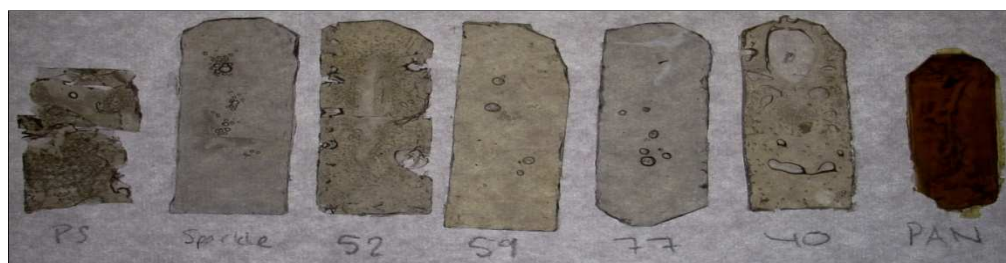


Figure 4.3 (a): Photograph of SAN series with 0.01wt% graphene
from solvent evaporation



Figure 4.3 (b): Photograph of SAN series at 0.05wt% graphene from solvent evaporation

From Figure 4.3, it is clearly evident that the DN59, corresponding to 45.0mol% AN, nanocomposites attains optimal homogeneity and transparency among the SAN copolymers for 0.05wt% graphene. On the other hand, samples with poor miscibility appear darker and opaque.

In order to assess the effect of the presence of electron withdrawing acrylonitrile(AN) functionality on the dispersion of graphene in a polymer matrix, and thus the formation of electron donor-acceptor interactions, this evaluation was performed on the graphene nanocomposites of the neat polymers, PS and PAN, as well as copolymers of SAN with different AN composition. Qualitatively, this inspection shows that the PAN composite appears heterogeneous even for small loadings of graphene (0.01wt %), indicated by the darkest thin films for a given graphene loading. This poor dispersion indicates minimal interactions between the polymer and nanoparticles. When the phenyl group of polystyrene is incorporated into the polymer matrix, a dramatic enhancement of the nanocomposite dispersion is observed, as shown in Figure 4.3. The existence of the aromatic ring on PS and nitrile functional group moieties allow the formation of non-covalent π - π interaction as well as electron donor-acceptor interaction between graphene and copolymer. Interestingly, the conditions observed are opposite those with SWNT which exhibits better dispersion in PAN than PS.⁴⁹ This implies that the shape and curvature of the nanoparticles is important in the realization of strong non-covalent interactions between the polymer and nanoparticles.

Even though these photographs of thin film composites provide a qualitative characterization of the level of dispersion, a quantitative analysis is needed to provide additional insight into the role of copolymer composition and sample preparation technique on the extent of dispersion in the SAN-graphene system.

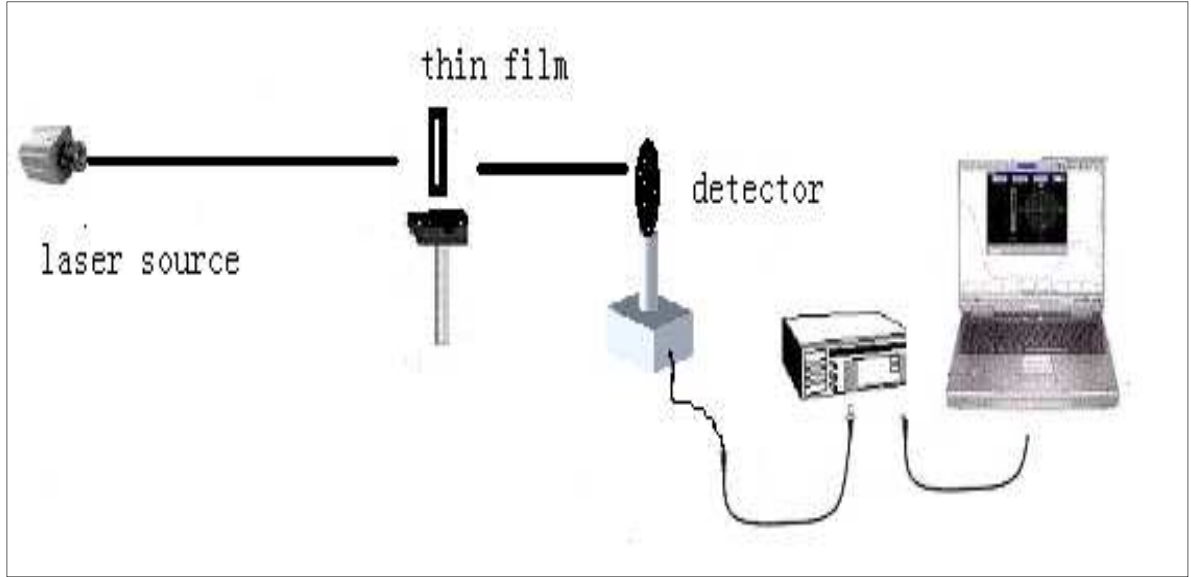


Figure 4.4: A schematic representation of the experimental setup to quantify transparency

In order to quantify the transparency of the thin films, the transmission of light through each sample is monitored. The experiments are carried out as illustrated in Figure 4.4, where the laser source, sample and detector are aligned to detect the intensity of light that passed through each sample, I_s . When no sample is present, the intensity of the laser is defined as I_L . In addition, the background light measured at the detector without the laser beam is also measured and defined as I_o . These quantities then are used to calculate the transmittance of the sample as,

$$\text{Transmittance, } T = \frac{I_s - I_o}{I_L - I_o} \quad (\text{equation 4.1})$$

The detector is connected to a data acquisition system to record the light intensity on a computer and analyzed using DT Open-Layer software supplied by Data Translation, Inc.

As expected, the sample with the lowest graphene concentration absorbed little light and has transmittance close to 1. Similarly, the sample with the highest graphene concentration has

the lowest transmittance, approaching zero. It is a general trend that when the concentration of graphene increases the transmittance value decreases for each copolymer composition (Figure 4.5).

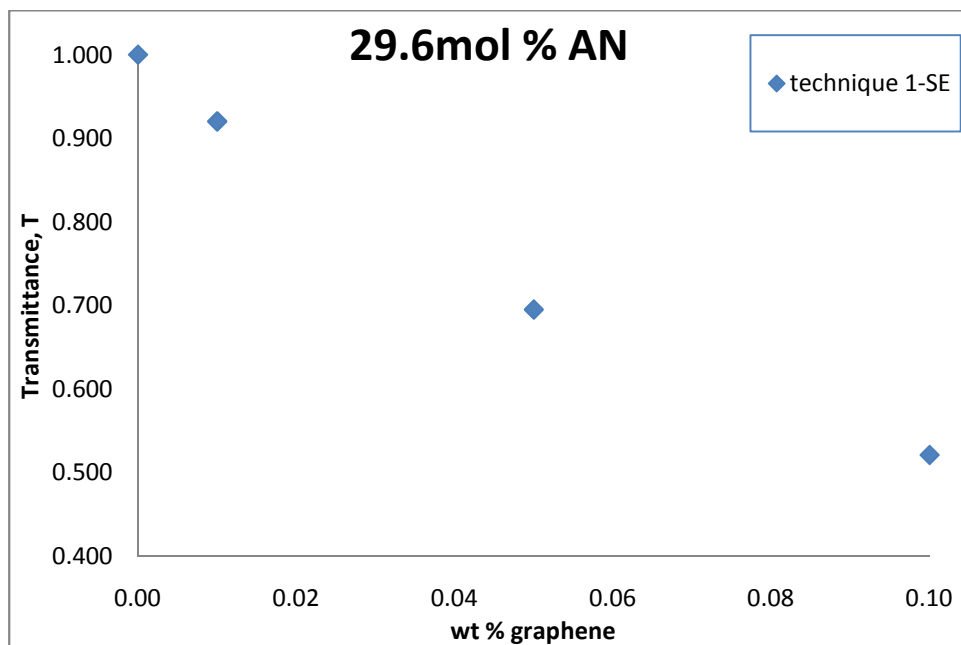


Figure 4.5: Plot of transmittance against wt% graphene for SAN 29.6 mol% AN with solvent evaporation

In order to assess the importance of the sample preparation technique, a correlation between the dispersion of graphene with copolymer composition is determined by completing the transparency test for both rapid precipitation and solvent evaporation samples. The combination of image analysis and transparency test provides a tool to quantify the homogeneity of the graphene nanocomposites. This approach provides insight into how the spatial dispersion of graphene in the polymer matrix changes with the variation of copolymer composition and sample preparation technique.

The plot of transmittance as a function of mol% AN for the 0.01wt% and 0.05wt% graphene nanocomposites are shown in Figure 4.6. These graphs show the amount of light transmitted through each SAN copolymer at low loading of graphene nanoparticles. From these data, there is very little difference in transparency of the samples created by the two techniques, solvent evaporation and rapid precipitation. Thus, at this low loading of nanoparticles, the sample preparation does not appear to influence the dispersion as measured optically, however further DSC experiments will indicate a variation in their thermal properties.

Graphs in Figure 4.6 are utilized to determine the dispersion of the polymer nanocomposite. The homogeneity of the samples are indicated by the highest transmittance value, where minimal light is absorbed.

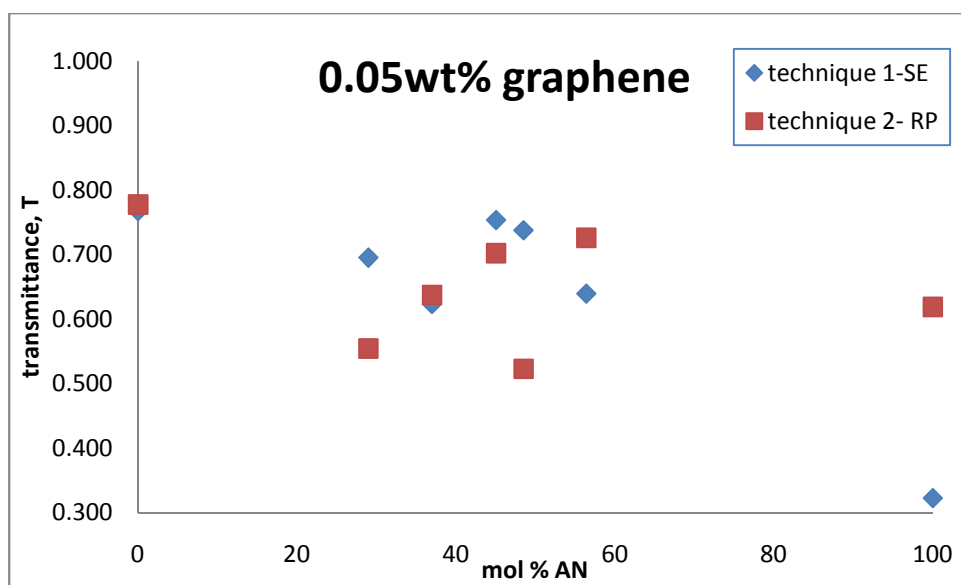
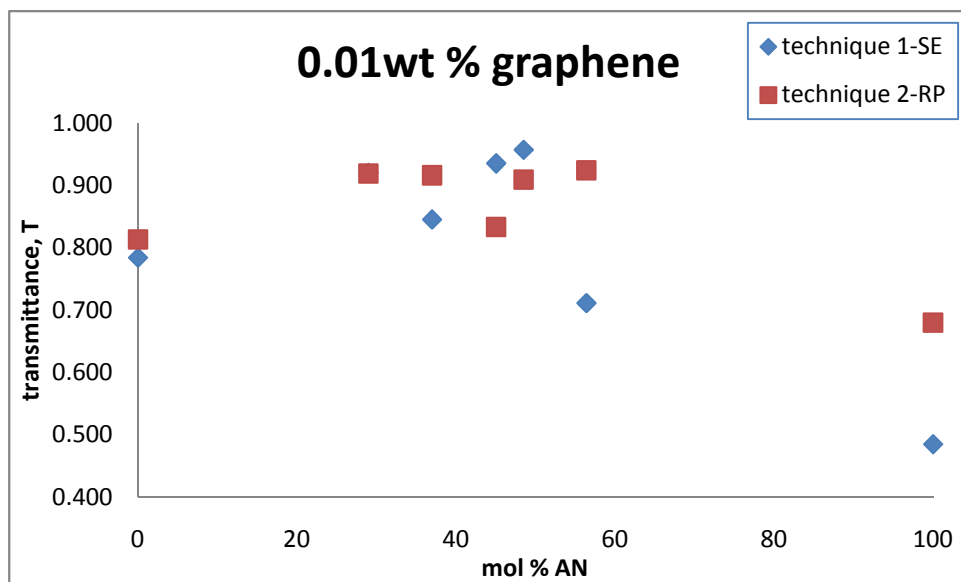


Figure 4.6. Graphs of transmittance versus mol% AN for

(a) 0.01wt% graphene (b) 0.05wt% graphene

This transmittance data indicate that the copolymer composition affects the dispersion of the nanoparticles in the polymer matrix. It appears that DN59 which corresponds to 45.0mol% AN, exhibits the highest transmittance for both sample preparation techniques. This quantitative result confirms the qualitative visual inspection of the thin film, where these samples appear to be the clearest films for both 0.01 and 0.05wt %. Similarly, Linton et al. demonstrated that optical microscopy and image analysis can be used to quantify the dispersion of nanoparticles on the micron level, where this result was further affirmed with Raman mapping analysis.⁴⁹ As the amount of AN in the copolymer increases, the level of transparency does not further increase. This shows that the presence of more interacting moieties on the polymer chain does not correspond to improved dispersion in the polymer nanocomposite. Thus, the chain connectivity impacts the formation of non-covalent interactions between graphene and SAN copolymer, as in the fullerene and SWNT nanocomposites.

Qualitative and quantitative observations indicate that at 45.0mol% AN, the graphene has the best dispersion, which could be a result of the presence of significant intermolecular interactions. This observation is consistent with the result from fullerenes (discussed in chapter 3) and SWNT.⁴⁹ As discussed in Chapter 3.5, chain connectivity and the occurrence of π - π interactions dominate the formation of non-covalent interactions.

4.5. Differential Scanning Calorimetry (DSC)

DSC was utilized to determine the T_g of the polymer and polymer nanocomposites to provide insight in to the homogeneity of the NP- polymer system. Samples (~10-15mg) are weighed in an aluminum pan and scanned over a range of temperatures on a Mettler Toledo DSC 821 Instrument. To insure that thermal history does not influence the result, the midpoint of the

heat change is obtained from two consecutive identical measurements and recorded as the glass transition temperature, T_g . The difference between the T_g of the nanocomposite and the T_g of the pure polymer, ΔT_g is calculated as

$$\Delta T_g = T_{g(\text{nanocomposites})} - T_{g(\text{polymer})} \quad (\text{equation 4.2})$$

The glass transition temperature quantifies the thermal properties of the polymer in the nanocomposite. Incorporating the nanoparticles in the polymer matrices can reduce the free volume and increase the T_g of the nanocomposite. The free volume is associated with the space between molecules in a sample, including in this case the space between polymer matrix and the nanoparticles. Subsequently, the optimum enhancement in the T_g indicates that there exists a significant restriction on polymer chain mobility, which can be interpreted as the inhibition of polymer chain motion by close proximity and significant interaction with nanoparticles.

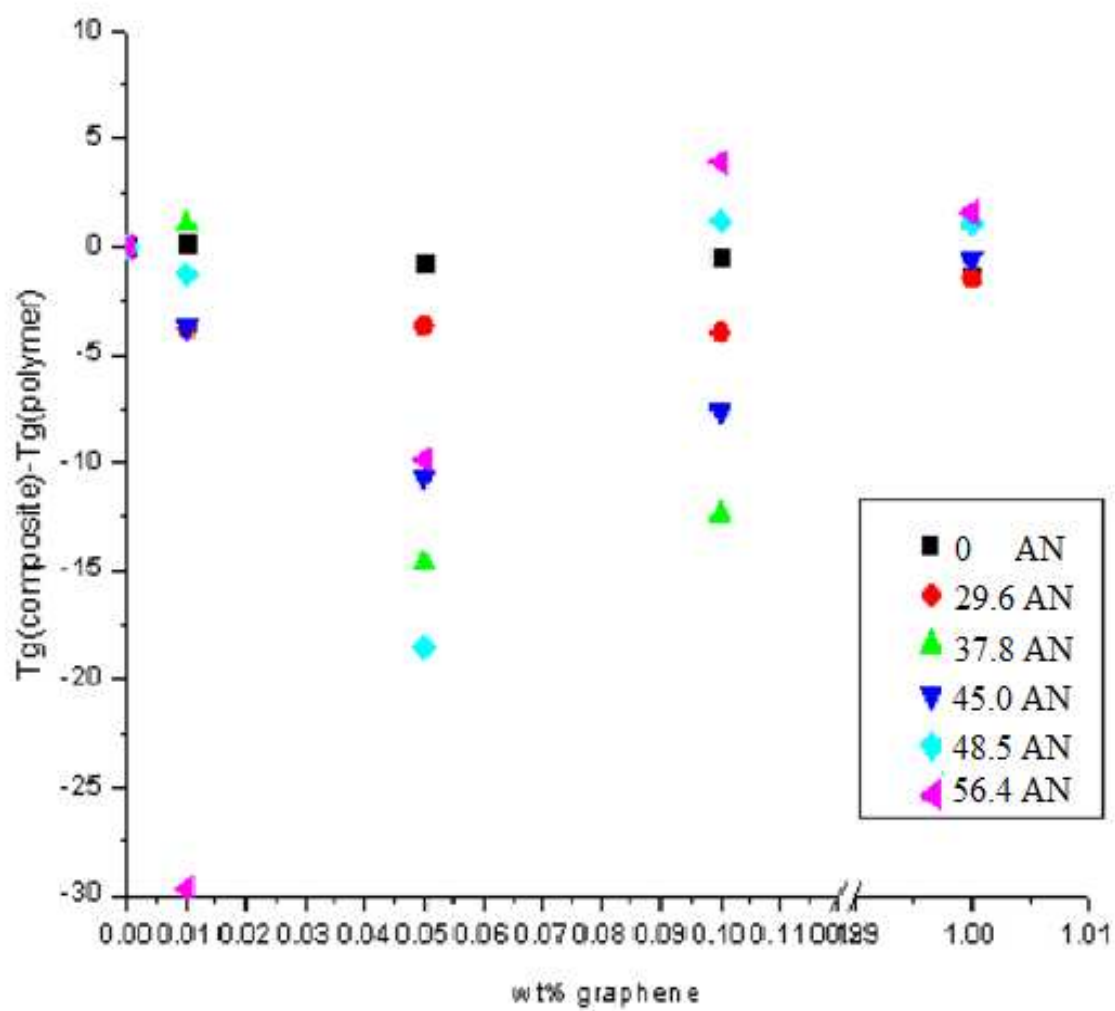


Figure 4.7. Plot of $\Delta T_g = T_g(\text{composite}) - T_g(\text{polymer})$ vs. wt % graphene
for nanocomposites prepared by solvent evaporation (SE)

Figure 4.7 displays ΔT_g as a function of wt % graphene for all nanocomposites prepared by solvent evaporation, which shows a decrease in T_g when small amounts of graphene are added (at 0.01-0.05wt%). With further loading of graphene (up to 1wt%), T_g increases and continues to rise for most of the SAN copolymers. The glass transition temperature, T_g is directly related to the molecular mobility of the polymer chain. According to Starr and Douglas, particles with a strongly attractive polymer-particle interaction give rise to an increase in T_g reflecting the immobilization of the segments near the polymer surface, while polymer with neutral or repulsive interaction cause T_g to drop.¹¹

Therefore, these results suggest that the addition of graphene initially increases the mobility and free volume of the sample at low loadings of nanoparticles, resulting in a lower T_g than the neat polymer. As the loading of graphene increases, the interaction with the nanoparticles increases, resulting in a decrease of polymer mobility. An increase in T_g at 0.1wt% graphene loading indicates the reduction of free volume due to an increase in the interaction between the graphene and polymer. In addition, the confinement of the polymer by the nanoparticle and its packing may play a part in changing the T_g of the polymer nanocomposites, together with the change in cohesive interaction strength.

In the solvent evaporation (SE) process, the gradual solvent evaporation initially results in a significant decrease in solvent concentration, but it remains sufficiently high to retain significant polymer mobility. Due to the lower solubility of nanoparticles in the solvent than that of the copolymer, the NP tends to precipitate out from the solution before the polymer, leading to the formation of a phase separated polymer nanocomposite. Consequently, the nanoparticles can begin to agglomerate into clusters in the sample, separate from the polymer chain. Space that is

created between the nanoparticles clusters and the polymer chain results in more free volume in the nanocomposite.

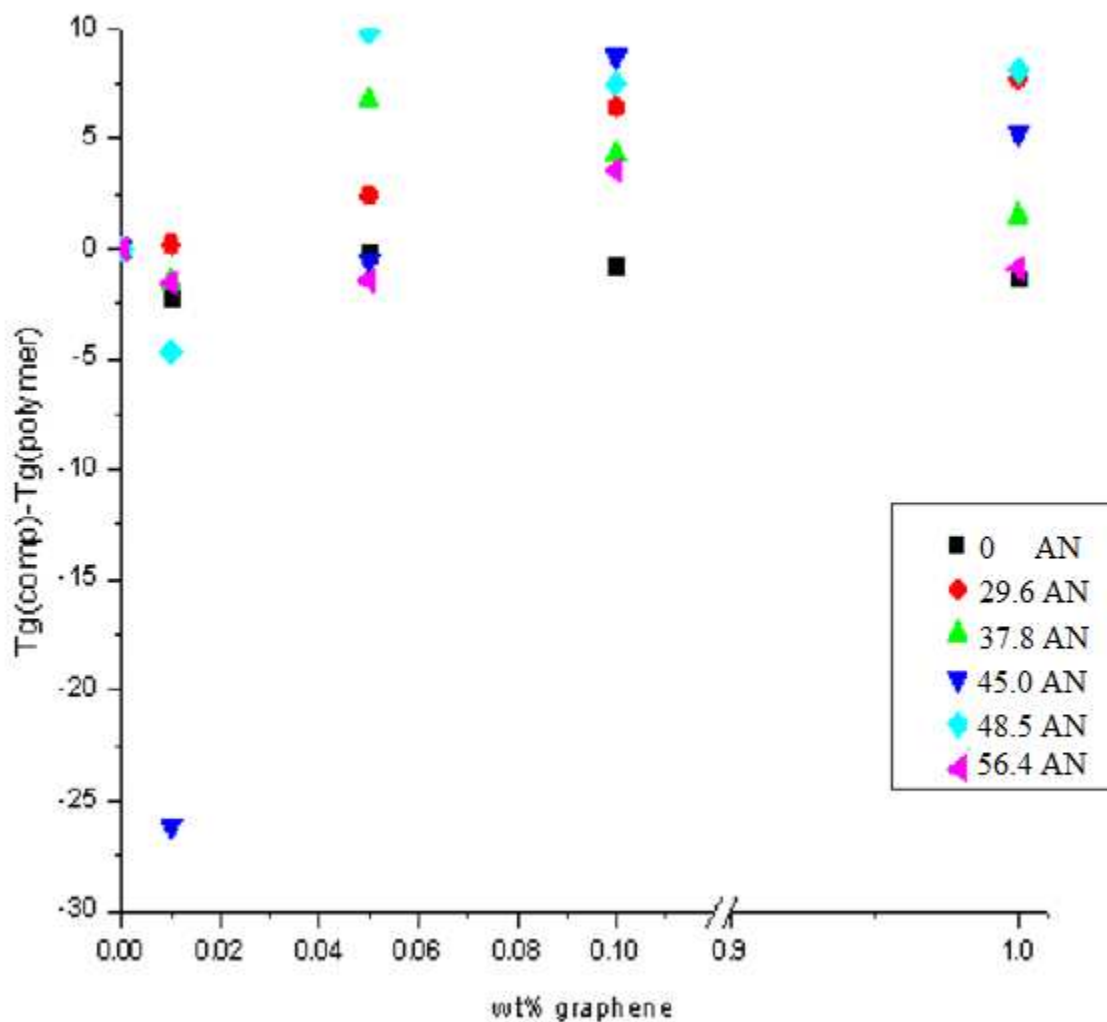


Figure 4.8. Plot of $\Delta T_g = T_g(\text{composite}) - T_g(\text{polymer})$ vs. wt % graphene for technique 2- rapid precipitation (RP)

The results for the samples formed by rapid precipitation are displayed in Figure 3.8 as a graph of ΔT_g as a function of wt % graphene. This plot shows a decrease in T_g when a small amount of graphene was added (at 0.01wt%). With further loading of graphene (up to 1wt%), T_g increases and continues to rise for most of the SAN composition.

As mentioned above, the mobility of the polymer chains is affected by the presence of strong interactions between the polymer and nanoparticles. Thus with the initial loading of graphene, the small quantity of nanoparticles increases the mobility of the polymer chain. As the quantity of graphene increases, the mobility and free volume of the sample decreases, resulting in an increase in T_g of the nanocomposites. The well-dispersed polymer-nanoparticle blends reduce the free volume of the polymer due to increasing molecular contacts between the polymer and nanoparticle. Consequently, higher temperatures are needed to allow polymer mobility and change the nanocomposite from a hard, glassy state to a rubbery state.

This can be explained by envisioning the rapid precipitation (RP) process, which is an instantaneous process that forces the NPs and polymer to arranged into a morphology that mimics that which existed in solution at the moment when the solvent was added to the non-solvent. This technique clearly produces a product that has less mobility than those fabricated with SE. The non-solvent induces rapid precipitation (RP) where the precipitates consist of intimately mixed polymer-nanoparticle blends. Mackay et al. reported that rapid precipitation can be used to produce miscible fullerene-polystyrene nanocomposites up to a maximum concentration of $\sim 2\text{vol}\%$.⁸⁸ In the RP method the NP and copolymer separate out of solution simultaneously, enabling formation of more well dispersed and more strongly

interacting polymer-nanoparticle nanocomposites, and is not influenced by the differing solubilities of the two components.

4.6. Conclusion

A scheme to compare the dispersion of graphene in a polymer matrix when fabricated by two different techniques; solvent evaporation(SE) and rapid precipitation(RP) has been studied, and a synopsis of the results is shown in Figure 4.9.

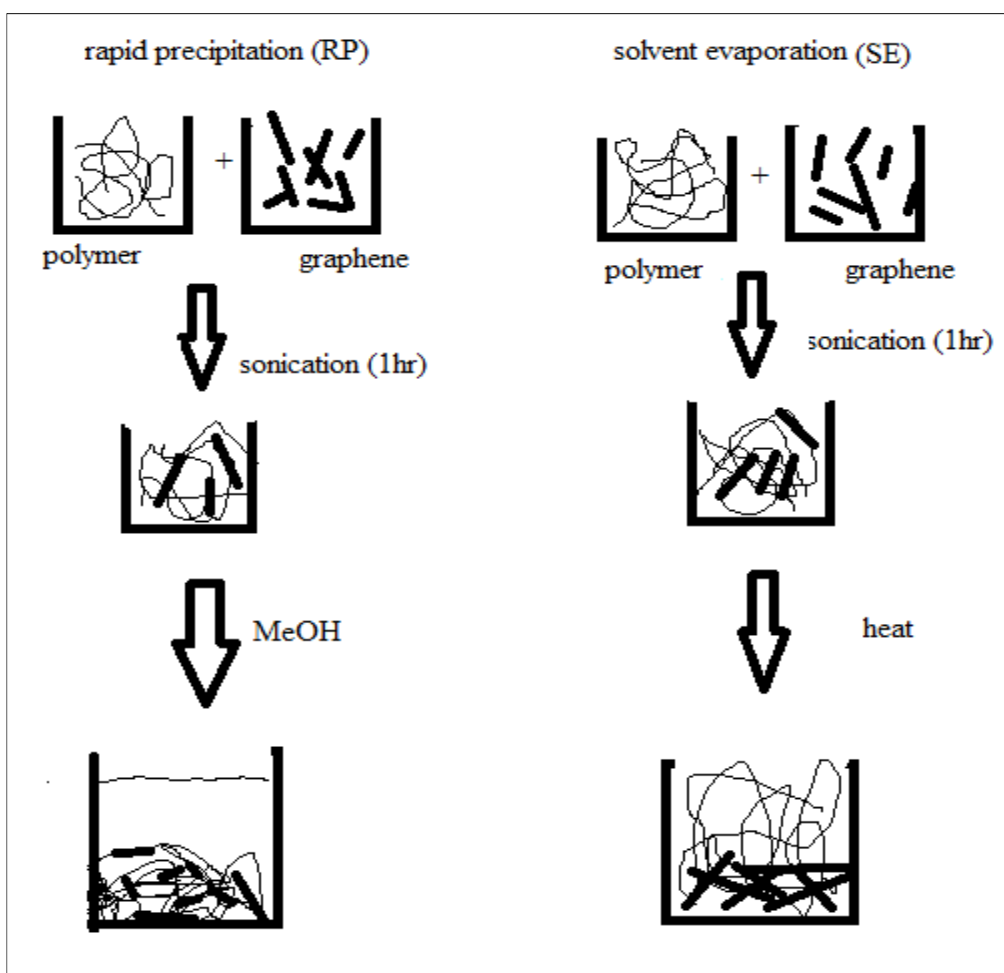


Figure 4.9. Scheme of sample preparation processes for polymer nanocomposites

The experiments described in this chapter have shown that the preparation technique is important in obtaining an optimal dispersion in a polymer nanocomposite. More specifically, DSC quantitatively indicates that rapid precipitation (RP) produce a more homogenous dispersion with more intermolecular interactions than those created with solvent evaporation (SE). DSC was used to measure the thermal properties of the neat copolymer and polymer nanocomposites to determine the change in glass transition with addition of nanoparticle. Additionally, the glass transition temperature (T_g) provides information on the extent of interaction between nanoparticles and the copolymer in the nanocomposites. The data show that the SE produces a negative ΔT_g , implying a higher free volume with little polymer-nanoparticle interactions in the resultant nanocomposite, while RP exhibits a positive ΔT_g , indicating significant polymer-graphene interactions. This result further affirms the importance of the preparation in enhancing the dispersion of nanoparticles in polymer nanocomposite.

Transparency results clearly indicate that graphene is optimally dispersed in the copolymer with 45.0mol% nitrile group. The clear and homogeneous dispersion of the thin film nanocomposites indicate an interaction between the copolymer and graphene. The formation of the interaction is optimal when a certain amount of interacting functional groups is present in the copolymer matrix. This confirms that chain connectivity and steric constraints are important in controlling the extent of intermolecular interaction between polymer and nanoparticles. Optimizing the intermolecular interaction between a polymer and nanoparticle leads to improved dispersion and properties in polymer nanocomposites as discussed in chapter 3. Thus, it is logical to interpret the result in this chapter in a similar manner.

CHAPTER 5: CONCLUSION AND FUTURE WORK

5.1 Final Conclusion

This thesis presents experimental efforts to study the dispersion of nanoparticles in a polymer matrix to determine the importance of the formation electron donor-acceptor (EDA) interactions between nanoparticles and polymers with different interacting functional groups in the formation of homogeneous polymer nanocomposites. The homogeneous dispersion of nanoparticles in the polymer matrix is interpreted to indicate the presence of intermolecular interactions in the polymer nanocomposites. This indicates the need to understand the fundamentals of interfacial adhesion between the polymer and nanoparticles in order to develop strategies to produce homogeneously dispersed polymer nanocomposites.

Through experimental work that is presented in this thesis, we have clearly established a protocol to optimize the dispersion of carbon nanoparticles in polymer matrices by understanding the extent of intermolecular interactions that occurs between a polymer and fullerenes. In the first portion of this thesis, the miscibility of fullerenes in copolymers containing different electron donating/withdrawing moieties are determined to examine their impact on the extent of dispersion in the nanocomposites. UV-Vis spectroscopy is used to measure the light transmittance of each sample, and deviation from the Beer Lambert law is interpreted to indicate the miscibility limit or identify the beginning of heterogeneity. From the dependence of the miscibility limit on the copolymer composition using XRD and UV-Vis spectroscopy, it is shown that the presence of a minority of interacting functional group within a polymer chain leads to optimum dispersion. The results indicate that 45.0mol% AN and 16.0 mol% CNSt have the highest miscibility with fullerene, which can be understood by invoking the importance of chain connectivity and

π - π interactions between the phenyl group in PS and aromatic rings in the fullerene in the formation of non-covalent interactions. In addition, we report that the tertiary amino group in DMAEMA has the strongest interaction with fullerene. This is further affirmed by density functional theory (DFT) calculations that were performed by our collaborator, Dr Bobby Sumpter. The DFT calculations reveal that the binding energies between the fullerene and the monomers are ranked as:

DMAEMA (4.73 kcal/mol) > St (3.21kcal/mol) >CNSt (2.40kcal/mol) > AN
(2.10kcal/mol) >MMA(1.44kcal/mol)

As a conclusion, chain flexibility and polymer conformation critically impact the formation of optimal intermolecular interactions and particle dispersion in the PNC.

In the second portion of this thesis, the impact of sample preparation on the dispersion of graphene nanoparticles in a polymer matrix is examined. The measured thermal properties of the nanocomposites suggest that rapid precipitation leads to more dispersed nanocomposite relative to solvent evaporation. In addition, the importance of chain connectivity in the dispersion of nanoparticles is also discussed as both visualization and transparency tests indicate that 45.0mol% AN has the clearest/most homogeneous mixture. This result correlates reasonably well with the SWNT and fullerene data. However, further experiments are required to gain a complete understanding of the governing parameters that control nanoparticles dispersion in terms of nanoparticles' size and shape.

5.2 Future Work

In order to more fully understand the miscibility of nanoparticles in polymers and copolymers, further experiments will be beneficial. One possible study would be to investigate the morphologies of the polymer nanocomposites to observe the interfacial structure between the polymers and nanoparticles. In Chapter 4, the impact of the sample preparation process was analyzed to quantify its impact on the extent of dispersion. The measured thermal properties of the nanocomposites suggest that rapid precipitation leads to a more homogeneous system than solvent evaporation. With the aid of morphology analysis, the structure of the nanocomposite can be obtained. In addition, Raman or IR spectroscopy can be utilized to provide insight into the extent of interactions.

As for now, the series of experimental studies that were completed to understand the miscibility of nanoparticles in copolymers have been analyzed to achieve an understanding of the role of non-covalent interactions between the polymers and the nanoparticles on its dispersion. Due to the different size and shape of nanoparticles that have been studied, the influence of the nanoparticle's interface and geometrical constraints of the polymer chain have been shown to impact the extent of interaction. The underlying question that still needs to be better understood is the role of the size and shape of the nanoparticles on the formation of intermolecular interactions between the polymer and nanoparticle. Figure 5.1 illustrates possible interactions between polymer and fullerene that can be formed by accommodating the structure/curvature of fullerene in the design of the matrix molecule. Therefore, an interesting study would be to determine if these different non-covalent interactions and conformations can translate to improved interactions and dispersion, as well as enhanced mechanical, electrical and thermal

properties of the polymer nanocomposites? In addition, how does this molecular level control impact the miscibility limit as compared to traditional micro-fillers?

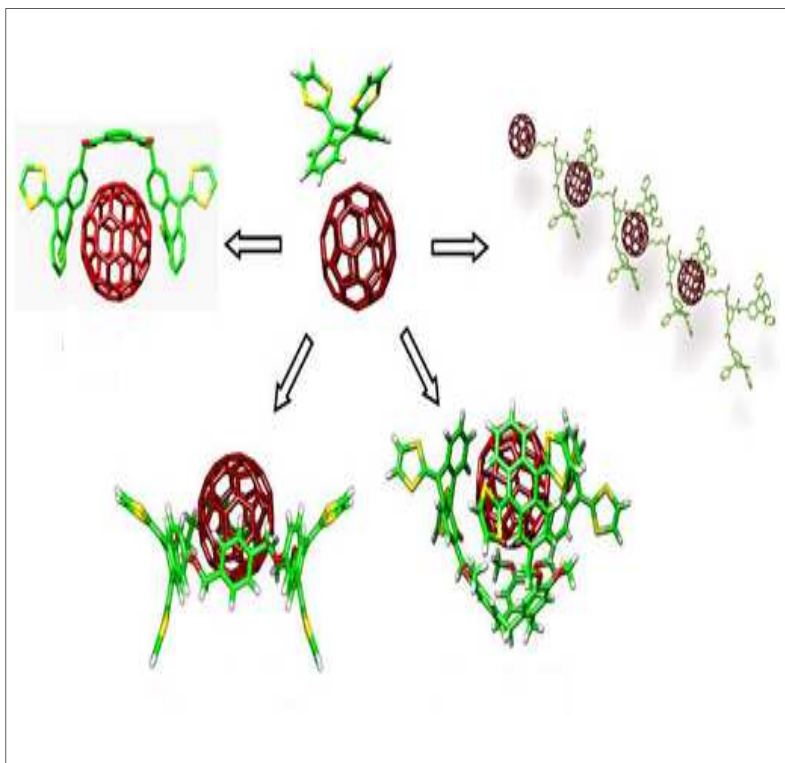


Figure 5.1. Different non-covalent interaction that occurred between C₆₀ and polymer⁸⁹

In Chapter 3, preliminary density functional theory (DFT) calculations of the binding energy between an interacting monomer and a fullerene particle performed by Dr. Bobby Sumpter were discussed. These calculations show that a spherical C₆₀ forms a relatively strong interaction with the tertiary amino group in DMAEMA relative to the SAN and CNSt monomers. However, these results differ from the DFT calculation performed on SWNT. Thus, it is also interesting to investigate the origin of the increased interaction of these functional groups with C₆₀ relative to those with SWNT.

Another important question is the role of π - π interactions between the monomer and π -electron of carbon nanoparticles on the extent of intermolecular interaction? In Chapter 4, the transparency visualization results illustrate that the incorporation of an aromatic ring in the copolymer enhances the dispersion of the nanoparticles. Likewise, the DFT calculations also indicate that styrene has a relatively high binding energy with fullerene, second to the strongly interacting DMAEMA monomer. Consequently, studies of the details of the interaction between the π -electron of the aromatic ring and the π -electrons of the nanoparticles needs further validation to provide insight into the formation of non-covalent interaction between monomers and nanoparticles.

A long-term goal of this project is to understand the impact of non-covalent intermolecular interactions between copolymers and nanoparticles on the dispersion of various carbon nanoparticles in polymer matrices. This study is designed such that the electron donating or electron withdrawing functional group are varied to form EDA interaction with carbon nanoparticles. In future work, it would be intriguing to investigate the mechanical properties of

the nanocomposites to understand the impact of the improved dispersion and intermolecular interactions between the polymers and nanoparticles on these properties.

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Appendix

A.1. Reproducibility and Estimation of Error

To improve statistics in the UV-Vis experiments, each thin film was examined twice at three different positions. Table A.1, A. 2, and A. 3 show the thickness of the thin film nanocomposites at three different positions using a caliper. The unit of measurement of the caliper is inches and the average value of the thickness is converted to millimeter

Table A.4, A.5 and A.6 show the calculated value of the optical density of the sample together with the average and error calculations. The errors are calculated based on the standard deviation of the optical density(OD) as below;

$$standard\ deviation = \sqrt{\frac{(average - OD1)^2 + (average - OD2)^2 + (average - OD3)^2}{2}}$$

The values obtained from Table A.4, A.5 and A.6 are used to plot the optical density as a function of weight percent (wt%) fullerenes as shown in Figure A.1, A.2, and A.3. In order to determine the miscibility limit, the data is fit to a line, where the last data point that remains on this fit is defined as the miscibility limit of that particular sample.

Table A.1. Thickness of PSCN+ fullerene nanocomposites thin film

PSCN 10

film sample	0.5	1	1.5	2	2.5	3	4	5
#1	0.0085	0.009	0.01	0.011	0.008	0.01	0.009	0.009
#2	0.0075	0.011	0.0075	0.0101	0.009	0.009	0.009	0.01
#3	0.0105	0.01	0.008	0.0085	0.0085	0.0105	0.008	0.01
average (inch)	0.0088	0.0100	0.0085	0.0099	0.0085	0.0098	0.0087	0.0097
Mm	0.2244	0.2540	0.2159	0.2506	0.2159	0.2498	0.2201	0.2455

PSCN 30

film sample	0.5	1	1.5	2	2.5	3	4	5
#1	0.012	0.005	0.005	0.0105	0.008	0.01	0.006	0.008
#2	0.01	0.006	0.006	0.01	0.009	0.011	0.006	0.008
#3	0.0105	0.0055	0.006	0.0095	0.009	0.012	0.006	0.008
average (inch)	0.0108	0.0055	0.0057	0.0100	0.0087	0.0110	0.0060	0.0080
mm	0.2752	0.1397	0.1439	0.2540	0.2201	0.2794	0.1524	0.2032

PSCN 40

film sample	0.5	1	1.5	2	2.5	3	4	5
#1	0.013	0.0105	0.011	0.0125	0.015	0.0135	0.013	0.006
#2	0.0135	0.0085	0.0105	0.0085	0.011	0.011	0.009	0.007
#3	0.01	0.008	0.011	0.008	0.0105	0.0135	0.0095	0.007
average (inch)	0.0122	0.0090	0.0108	0.0097	0.0122	0.0127	0.0105	0.0067
mm	0.3090	0.2286	0.2752	0.2455	0.3090	0.3217	0.2667	0.1693

PSCN 50

film sample	0.5	1	1.5	2	2.5	3	4	5
#1	0.016	0.0155	0.01	0.0065	0.009	0.0075	0.009	0.014
#2	0.012	0.0105	0.01	0.007	0.012	0.008	0.012	0.0125
#3	0.013	0.013	0.0085	0.0075	0.0125	0.0085	0.0135	0.012
average (inch)	0.0137	0.0130	0.0095	0.0070	0.0112	0.0080	0.0115	0.0128
mm	0.3471	0.3302	0.2413	0.1778	0.2836	0.2032	0.2921	0.3260

Table A.2 Thickness of PDMA +fullerenes nanocomposites thin film

PDMA 10

film sample	0.5	1	1.5	2	2.5	3	4	5
#1	0.024	0.014	0.018	0.012	0.011	0.019	0.012	0.013
#2	0.0185	0.0145	0.014	0.013	0.0115	0.0165	0.0125	0.0135
#3	0.016	0.016	0.0255	0.013	0.0145	0.0105	0.012	0.013
average (inch)	0.020	0.015	0.019	0.013	0.012	0.015	0.012	0.013
mm	0.495	0.377	0.487	0.322	0.313	0.389	0.309	0.334

PDMA 20

film sample	0.5	1	1.5	2	2.5	3	4	5
#1	0.0105	0.01	0.015	0.0165	0.024	0.01	0.018	0.021
#2	0.011	0.012	0.015	0.0175	0.02	0.0105	0.021	0.024
#3	0.012	0.013	0.0175	0.0165	0.0185	0.021	0.0165	0.0255
average (inch)	0.011	0.012	0.016	0.017	0.021	0.014	0.019	0.024
mm	0.284	0.296	0.402	0.428	0.529	0.351	0.470	0.597

PDMA 30

film sample	0.5	1	1.5	2	2.5	3	4	5
#1	0.0125	0.015	0.014	0.01	0.0145	0.01	0.0145	0.018
#2	0.0135	0.0155	0.0175	0.012	0.014	0.012	0.0115	0.018
#3	0.0145	0.0155	0.019	0.014	0.02	0.0105	0.0075	0.018
average (inch)	0.014	0.015	0.017	0.012	0.016	0.011	0.011	0.018
mm	0.343	0.389	0.428	0.305	0.411	0.275	0.284	0.457

PDMA 40

film sample	0.5	1	1.5	2	2.5	3	4	5
#1	0.012	0.0185	0.009	0.017	0.0125	0.0105	0.015	0.012
#2	0.0135	0.023	0.009	0.019	0.0115	0.01	0.0155	0.0115
#3	0.017	0.0145	0.009	0.0145	0.019	0.0125	0.0135	0.0115
average (inch)	0.014	0.019	0.009	0.017	0.014	0.011	0.015	0.012
mm	0.360	0.474	0.229	0.428	0.364	0.279	0.373	0.296

PDMA 50

film sample	0.5	1	1.5	2	2.5	3	4	5
#1	0.0135	0.012	0.008	0.0085	0.02	0.0105	0.0115	0.008
#2	0.014	0.0105	0.0085	0.0075	0.018	0.0065	0.0075	0.008
#3	0.0105	0.0145	0.012	0.008	0.0115	0.006	0.01	0.011
average (inch)	0.013	0.012	0.010	0.008	0.017	0.008	0.010	0.009
mm	0.322	0.313	0.241	0.203	0.419	0.195	0.246	0.229

Table A.3 Thickness of PSAN + fullerenes nanocomposites thin film

PSAN 10

film sample	0.5	1	1.5	2	2.5	3	4	5
#1	0.0245	0.01	0.013	0.01	0.015	0.008	0.0145	0.012
#2	0.0125	0.017	0.0055	0.0085	0.0075	0.0085	0.0075	0.0155
#3	0.012	0.0155	0.006	0.007	0.0095	0.006	0.007	0.01
average (inch)	0.0163	0.0142	0.0082	0.0085	0.0107	0.0075	0.0097	0.0125
mm	0.4149	0.3598	0.2074	0.2159	0.2709	0.1905	0.2455	0.3175

PSAN 20

film sample	0.5	1	1.5	2	2.5	3	4	5
#1	0.0095	0.009	0.011	0.0095	0.008	0.0075	0.012	0.0065
#2	0.01	0.0105	0.01	0.009	0.009	0.0085	0.009	0.0075
#3	0.011	0.01	0.009	0.0075	0.011	0.01	0.008	0.006
average (inch)	0.0102	0.0098	0.0100	0.0087	0.0093	0.0087	0.0097	0.0067
mm	0.2582	0.2498	0.2540	0.2201	0.2371	0.2201	0.2455	0.1693

PSAN 30

film sample	0.5	1	1.5	2	2.5	3	4	5
#1	0.011	0.0135	0.006	0.008	0.008	0.009	0.007	0.0055
#2	0.0085	0.018	0.007	0.009	0.007	0.007	0.009	0.006
#3	0.007	0.013	0.008	0.01	0.0055	0.0065	0.0095	0.008
average (inch)	0.0088	0.0148	0.0070	0.0090	0.0068	0.0075	0.0085	0.0065
mm	0.2244	0.3768	0.1778	0.2286	0.1736	0.1905	0.2159	0.1651

PSAN 40

film sample	0.5	1	1.5	2	2.5	3	4	5
#1	0.006	0.013	0.008	0.0085	0.007	0.005	0.01	0.015
#2	0.0065	0.009	0.0085	0.006	0.007	0.005	0.0095	0.013
#3	0.006	0.008	0.008	0.0075	0.006	0.005	0.009	0.017
average (inch)	0.0062	0.0100	0.0082	0.0073	0.0067	0.0050	0.0095	0.0150
mm	0.1566	0.2540	0.2074	0.1863	0.1693	0.1270	0.2413	0.3810

PSAN 50

film sample	0.5	1	1.5	2	2.5	3	4	5
#1	0.017	0.017	0.009	0.015	0.007	0.0075	0.0135	0.006
#2	0.018	0.007	0.014	0.013	0.008	0.008	0.009	0.0055
#3	0.0125	0.008	0.0085	0.012	0.011	0.009	0.014	0.007
average (inch)	0.0158	0.0107	0.0105	0.0133	0.0087	0.0082	0.0122	0.0062
mm	0.4022	0.2709	0.2667	0.3387	0.2201	0.2074	0.3090	0.1566

Table A. 4 The calculation of optical density for PDMA nanocomposite

PSCN 10

Sample	ABS 1	thickness	OD 1	ABS 2	Thickness	OD 2	ABS 3	Thickness	OD 3	Average	StdDev
0.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.5	0.1960	0.0130	0.5936	0.2250	0.0135	0.7382	0.1950	0.0100	0.5906	0.6408	0.0844
1.0	0.3400	0.0105	1.2748	0.3240	0.0085	1.2148	0.3020	0.0080	0.9146	1.1348	0.1930
1.5	0.5600	0.0110	2.0043	0.6450	0.0105	2.5394	0.8640	0.0110	4.0019	2.8485	1.0340
2.0	0.6870	0.0125	2.1638	0.6760	0.0085	3.8020	0.6050	0.0080	3.1759	3.0472	0.8267
2.5	0.9770	0.0150	2.5643	0.8600	0.0110	2.8215	0.9530	0.0105	3.0016	2.7958	0.2198
3.0	1.0350	0.0135	3.0184	0.9930	0.0110	4.8868	0.9950	0.0135	4.6086	4.1713	1.0081
4.0	1.3230	0.0130	4.0067	1.0180	0.0090	3.3399	1.2270	0.0095	3.5783	3.6416	0.3379
5.0	0.9400	0.0060	6.1680	1.0530	0.0070	3.3165	1.0070	0.0070	3.3038	4.2628	1.6500

PSCN 30

Sample	ABS 1	thickness	OD 1	ABS 2	Thickness	OD 2	ABS 3	Thickness	OD 3	Average	StdDev
0.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.5	0.1990	0.0850	0.0922	0.2350	0.0075	1.2336	0.2410	0.0105	0.9036	0.7431	0.5874
1.0	0.5060	0.0090	2.2135	0.4400	0.0110	1.5748	0.4270	0.0100	1.6811	1.8231	0.3422
1.5	0.5700	0.0100	2.0401	0.5330	0.0075	2.7979	0.4270	0.0080	2.1014	2.3131	0.4209
2.0	0.7150	0.0110	3.5187	0.5920	0.0105	2.2197	0.5850	0.0085	2.7096	2.8160	0.6560
2.5	0.7290	0.0080	2.8701	0.6560	0.0090	2.8696	0.6910	0.0085	3.2006	2.9801	0.1909
3.0	1.0560	0.0100	4.6194	1.0620	0.0090	4.6457	1.1260	0.0105	4.2220	4.4957	0.2374
4.0	1.0240	0.0090	4.4794	1.0510	0.0090	4.5976	1.0560	0.0080	5.1969	4.7579	0.3847
5.0	1.2670	0.0090	5.5424	1.2440	0.0100	4.8976	1.3180	0.0100	5.1890	5.2097	0.3229

PSCN 40

Sample	ABS 1	thickness	OD 1	ABS 2	Thickness	OD 2	ABS 3	Thickness	OD 3	Average	StdDev
0.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.5	0.2750	0.0160	0.6767	0.2370	0.0120	0.7465	0.4600	0.0130	1.5748	0.9993	0.4996
1.0	0.3450	0.0155	0.8763	0.3520	0.0105	1.7323	0.5270	0.0130	2.9640	1.8575	1.0495
1.5	0.4710	0.0100	1.8543	0.4670	0.0100	3.0643	0.4040	0.0085	1.3255	2.0814	0.8914
2.0	0.3800	0.0065	2.3016	0.4000	0.0070	0.7158	0.3860	0.0075	0.6754	1.2310	0.9275
2.5	0.7850	0.0090	3.4339	0.6980	-0.0120	1.8952	0.7880	0.0125	2.2160	2.5150	0.8118
3.0	0.6630	0.0075	3.4803	0.6620	0.0080	2.3694	0.6780	0.0085	2.2244	2.6914	0.6871
4.0	1.7960	0.0090	7.8565	1.7540	0.0120	11.5092	1.9360	0.0135	11.7262	10.3640	2.1742
5.0	2.6680	0.0140	7.5028	3.0600	0.0125	15.0591	2.6740	0.0120	15.0394	12.5337	4.3569

PSCN 50

Sample	ABS 1	thickness	OD 1	ABS 2	Thickness	OD 2	ABS 3	Thickness	OD 3	Average	StdDev
0.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.5	0.5600	0.0105	2.0997	0.3660	0.0125	1.1528	0.3340	0.0115	1.1434	1.4653	0.5494
1.0	0.9350	0.0070	5.2587	0.6930	0.0080	3.4104	0.6440	0.0070	3.6220	4.0971	1.0116
1.5	1.0300	0.0060	6.7585	0.7370	0.0060	4.8360	1.0990	0.0120	3.6056	5.0667	1.5891
2.0	0.9090	0.0200	1.7894	0.9180	0.0220	1.6428	0.9420	0.0225	1.6483	1.6935	0.0831
2.5	1.3250	0.0145	3.5976	1.4280	0.0145	3.8773	1.3920	0.0140	3.9145	3.7965	0.1732
3.0	1.1300	0.0120	3.7073	1.0860	0.0110	3.8869	1.1360	0.0120	3.7270	3.7738	0.0985
4.0	1.5450	0.0060	10.1378	0.6110	0.0060	4.0092	1.6210	0.0065	9.8183	7.9884	3.4498
5.0	2.7900	0.0085	12.9226	3.8850	0.0080	19.1191	3.7830	0.0070	21.2767	17.7728	4.3367

Table A.5: The calculation of optical density for PDMA nanocomposite

PDMA 10

Sample	ABS 1	thickness	OD 1	ABS 2	thickness	OD 2	ABS 3	thickness	OD 3	Average	StdDev
0.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.5	0.3830	0.6096	0.6283	0.3410	0.4699	0.7257	0.2950	0.4064	0.7259	0.6933	0.0563
1.0	0.4340	0.3556	1.2205	0.3640	0.3683	0.9883	0.5110	0.4064	1.2574	1.1554	0.1459
1.5	0.6300	0.3048	2.0669	0.6050	0.3556	1.7013	0.8220	0.6477	1.2691	1.6791	0.3994
2.0	0.4510	0.2794	1.6142	0.5980	0.3302	1.8110	0.6110	0.3302	1.8504	1.7585	0.1266
2.5	0.7610	0.4826	1.5769	0.8170	0.2921	2.7970	0.8160	0.3683	2.2156	2.1965	0.6103
3.0	0.7410	0.3048	2.4311	0.7180	0.4191	1.7132	0.7410	0.2667	2.7784	2.3076	0.5432
4.0	1.1530	0.3048	3.7828	0.9510	0.3175	2.9953	0.9730	0.3175	3.0646	3.2809	0.4361
5.0	1.6410	0.3302	4.9697	1.5960	0.3429	4.6544	1.6440	0.3429	4.7944	4.8062	0.1580

PDMA 20

Sample	ABS 1	thickness	OD 1	ABS 2	thickness	OD 2	ABS 3	thickness	OD 3	Average	StdDev
0.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.5	0.5050	0.2667	1.8935	0.6150	0.2794	2.2011	0.5590	0.3048	1.8340	1.9762	0.1971
1.0	0.4350	0.2540	1.7126	0.4540	0.3048	1.4895	0.4160	0.3302	1.2598	1.4873	0.2264
1.5	1.1600	0.4191	2.7678	1.0150	0.3810	2.6640	1.0770	0.4445	2.4229	2.6183	0.1769
2.0	2.0310	0.6096	3.3317	1.7730	0.4445	3.9888	2.0240	0.4191	4.8294	4.0499	0.7507
2.5	1.0060	0.2540	3.9606	1.0290	0.5080	2.0256	1.0160	0.4699	2.1622	2.7161	1.0799
3.0	0.8690	0.4572	1.9007	0.8920	0.2667	3.3446	0.9180	0.5334	1.7210	2.3221	0.8900
4.0	1.6170	0.5334	3.0315	1.8830	0.5334	3.5302	1.8610	0.4191	4.4405	3.6674	0.7144
5.0	2.2250	0.5334	4.1714	2.1400	0.6096	3.5105	2.2550	0.6477	3.4816	3.7211	0.3902

PDMA 30

Sample	ABS 1	thickness	OD 1	ABS 2	thickness	OD 2	ABS 3	thickness	OD 3	Average	StdDev
0.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.5	0.2690	0.3175	0.8472	0.2770	0.3429	0.8078	0.2910	0.4318	0.6739	0.7763	0.0908
1.0	0.6520	0.3810	1.7113	0.6590	0.5842	1.1280	0.4450	0.3683	1.2083	1.3492	0.3161
1.5	1.2890	0.3556	3.6249	0.7550	0.2286	3.3027	1.0940	0.2286	4.7857	3.9044	0.7800
2.0	0.6760	0.2540	2.6614	0.9810	0.4826	2.0327	0.7670	0.3683	2.0825	2.2589	0.3495
2.5	0.6880	0.3683	1.8680	0.6640	0.2921	2.2732	0.7250	0.4826	1.5023	1.8812	0.3856
3.0	2.9700	0.2540	11.6929	3.3380	0.2540	13.1417	3.0240	0.3175	9.5244	11.4530	1.8206
4.0	1.0780	0.3683	2.9270	1.0460	0.3937	2.6568	1.0990	0.3429	3.2050	2.9296	0.2741
5.0	1.4700	0.4572	3.2152	1.3220	0.2921	4.5258	1.3000	0.2921	4.4505	4.0639	0.7359

PDMA 40

Sample	ABS 1	thickness	OD 1	ABS 2	thickness	OD 2	ABS 3	thickness	OD 3	Average	StdDev
0.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.5	0.4020	0.3048	1.3189	0.3130	0.3556	0.8802	0.3390	0.2667	1.2711	1.1567	0.2407
1.0	0.4850	0.4699	1.0321	0.5050	0.2667	1.8935	0.5230	0.3683	1.4200	1.4486	0.4314
1.5	0.4430	0.2286	1.9379	0.4160	0.2184	1.9044	0.4380	0.3048	1.4370	1.7598	0.2800
2.0	0.7390	0.4318	1.7114	0.7450	0.1905	3.9108	0.7520	0.2032	3.7008	3.1077	1.2137
2.5	0.9470	0.3175	2.9827	0.8510	0.4572	1.8613	0.9040	0.2921	3.0948	2.6463	0.6821
3.0	0.7630	0.2616	2.9164	0.7130	0.1651	4.3186	0.7280	0.1524	4.7769	4.0040	0.9693
4.0	1.0090	0.3810	2.6483	1.0900	0.1905	5.7218	0.9590	0.2540	3.7756	4.0486	1.5548
5.0	2.0010	0.3048	#REF!	3.2210	0.2032	15.8514	2.9001	0.2794	10.3797	10.9320	4.6678

PDMA 50

Sample	ABS 1	thickness	OD 1	ABS 2	thickness	OD 2	ABS 3	thickness	OD 3	Average	StdDev
0.0	0.0000	0.0000	0.0000	0.2960	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.5	0.2570	0.3429	0.7495	0.5060	0.3556	1.4229	0.3760	0.2667	1.4098	1.1941	0.3851
1.0	0.3800	0.3048	1.2467	0.4010	0.2667	1.5036	0.4440	0.3683	1.2055	1.3186	0.1615
1.5	0.3810	0.2032	1.8750	0.6670	0.2184	3.0535	0.3760	0.3048	1.2336	2.0540	0.9231
2.0	0.5770	0.2159	2.6725	1.3530	0.1905	7.1024	0.6690	0.2032	3.2923	4.3557	2.3987
2.5	1.2920	0.5080	2.5433	2.5700	0.4572	5.6212	1.2050	0.2921	4.1253	4.0966	1.5391
3.0	2.4500	0.2667	9.1864	0.5860	0.1651	3.5494	2.5630	0.1524	16.8176	9.8511	2.0000
4.0	0.7300	0.2921	2.4991	3.0640	0.1905	16.0840	0.5270	0.2540	2.0748	6.8860	2.0000
5.0	3.8270	0.2032	18.8337	1.5840	0.2032	7.7953	3.1740	0.2794	11.3601	12.6630	2.0000

Table A.6: The calculation of optical density for PSAN nanocomposite

PSAN 10

Sample	ABS 1	thickness	OD 1	ABS 2	thickness	OD 2	ABS 3	thickness	OD 3	Average	StdDev
0.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.5	0.7480	0.6223	1.2020	0.5970	0.3175	1.8803	0.6730	0.3048	2.2080	1.7634	0.5131
1.0	1.2850	0.2540	5.0591	1.3390	0.4318	3.1010	1.3670	0.3937	3.4722	3.8774	1.0400
1.5	0.6260	0.3302	1.8958	0.9000	0.1397	6.4424	0.7130	0.1524	4.6785	4.3389	2.2922
2.0	1.5750	0.2540	6.2008	2.0170	0.2159	9.3423	1.5930	0.1778	8.9595	8.1675	1.7140
2.5	1.6470	0.3810	4.3228	1.1120	0.1905	5.8373	1.3930	0.2413	5.7729	5.3110	0.8564
3.0	2.3050	0.2032	11.3435	2.4070	0.2159	11.1487	2.4670	0.1524	16.1877	12.8933	2.8547
4.0	1.4510	0.3683	3.9397	1.4900	0.1905	7.8215	1.4500	0.1778	8.1552	6.6388	2.3434
5.0	2.3330	0.3048	7.6542	3.1110	0.3937	7.9020	2.4560	0.2540	9.6693	8.4085	1.0989

PSAN 20

Sample	ABS 1	thickness	OD 1	ABS 2	thickness	OD 2	ABS 3	thickness	OD 3	Average	StdDev
0.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.5	0.9070	0.2413	3.7588	0.8330	0.2540	3.2795	0.9370	0.2794	3.3536	3.4640	0.2580
1.0	1.6130	0.2286	7.0560	1.4330	0.2667	5.3731	1.5400	0.2540	6.0630	6.1640	0.8460
1.5	1.7940	0.2794	6.4209	1.9450	0.2540	7.6575	1.9040	0.2286	8.3290	7.4691	0.9679
2.0	1.8910	0.2413	7.8367	1.7960	0.2286	7.8565	1.9570	0.1905	10.2730	8.6554	1.4009
2.5	1.5980	0.2032	7.8642	1.6170	0.2286	7.0735	1.6910	0.2794	6.0523	6.9966	0.9084
3.0	2.6360	0.1905	13.8373	2.5700	0.2159	11.9037	2.8010	0.2540	11.0276	12.2562	1.4376
4.0	2.9000	0.3048	9.5144	3.1000	0.2286	13.5608	2.9000	0.2032	14.2717	12.4490	2.5661
5.0	3.1200	0.1651	18.8976	3.3000	0.1905	17.3228	3.0330	0.1524	19.9016	18.7073	1.2999

PSAN 30

Sample	ABS 1	thickness	OD 1	ABS 2	thickness	OD 2	ABS 3	thickness	OD 3	Average	StdDev
0.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.5	0.4750	0.2794	1.7001	0.6080	0.2159	2.8161	0.5260	0.1778	2.9584	2.4915	0.6891
1.0	2.5710	0.3302	7.7862	1.9370	0.4572	4.2367	2.1630	0.3302	6.5506	6.1911	1.8019
1.5	1.5760	0.1524	10.3412	1.5680	0.1778	8.8189	1.5840	0.2032	7.7953	8.9851	1.2811
2.0	3.3600	0.2032	16.5354	2.8130	0.2286	12.3053	3.1840	0.2540	12.5354	13.7921	2.3786
2.5	2.1230	0.2032	10.4478	2.3800	0.1778	13.3858	2.1720	0.1397	15.5476	13.1271	2.5597
3.0	2.6760	0.2286	11.7060	2.9680	0.1778	16.6929	2.9830	0.1651	18.0678	15.4889	3.3474
4.0	0.9300	0.1778	5.2306	1.0790	0.2286	4.7200	1.1070	0.2413	4.5877	4.8461	0.3395
5.0	1.4210	0.1397	10.1718	1.6810	0.1524	11.0302	1.6920	0.2032	8.3268	9.8429	1.3814

PSAN 40

Sample	ABS 1	thickness	OD 1	ABS 2	thickness	OD 2	ABS 3	thickness	OD 3	Average	StdDev
0.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.5	0.3430	0.1524	2.2507	0.4190	0.1651	2.5379	0.4340	0.1524	2.8478	2.5454	0.2986
1.0	1.0940	0.3302	3.3131	1.0770	0.2286	4.7113	1.1750	0.2032	5.7825	4.6023	1.2383
1.5	1.3860	0.2032	6.8209	1.0980	0.2159	5.0857	1.3150	0.2032	6.4715	6.1260	0.9177
2.0	1.6740	0.2159	7.7536	1.3160	0.1524	8.6352	1.6000	0.1905	8.3990	8.2626	0.4563
2.5	0.6780	0.1778	3.8133	0.6950	0.1778	3.9089	0.7110	0.1524	4.6654	4.1292	0.4668
3.0	1.8560	0.1270	14.6142	1.7980	0.1270	14.1575	1.7320	0.1270	13.6378	14.1365	0.4885
4.0	2.3340	0.2540	9.1890	2.3310	0.2413	9.6602	2.1300	0.2286	9.3176	9.3889	5.4811
5.0	4.8890	0.3810	12.8320	1.9800	0.3302	5.9964	3.1100	0.4318	7.2024	8.6769	3.8576

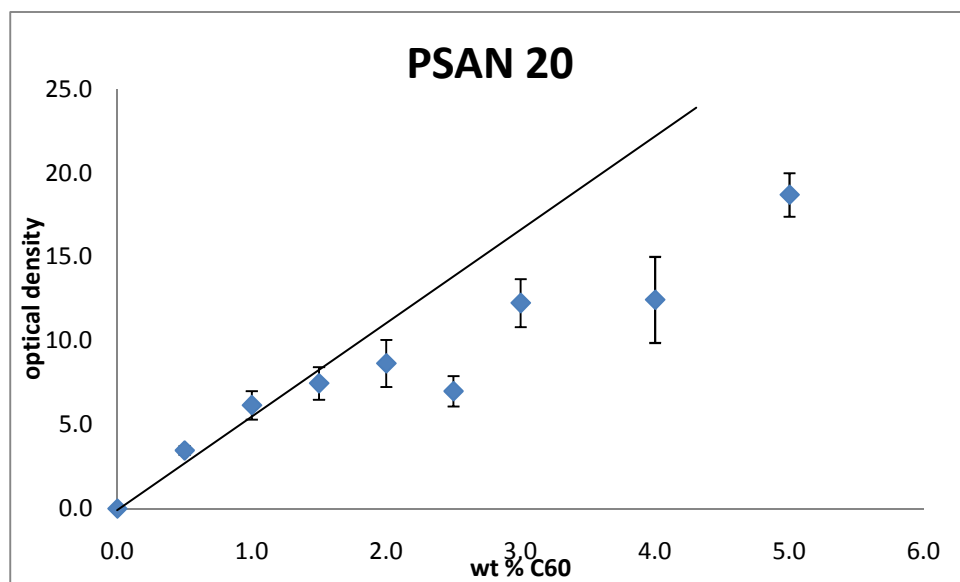
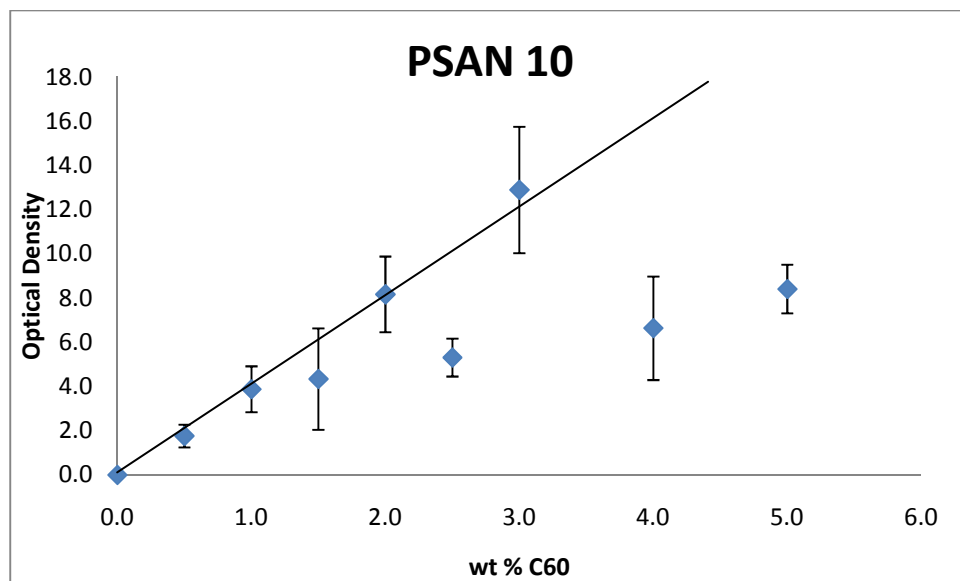
PSAN 50

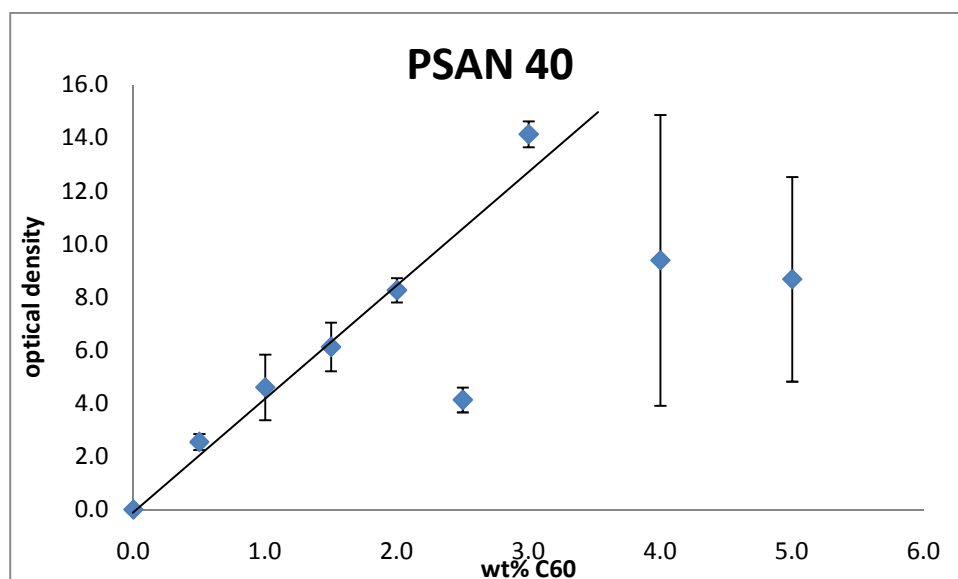
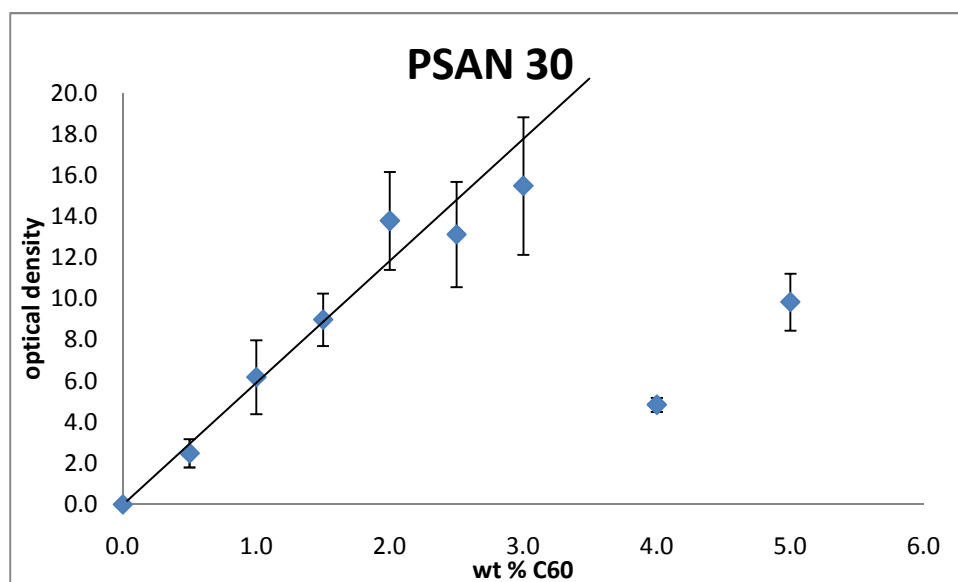
Sample	ABS 1	thickness	OD 1	ABS 2	thickness	OD 2	ABS 3	thickness	OD 3	Average	StdDev
0.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.5	0.8390	0.4318	1.9430	0.8370	0.4572	1.8307	0.9000	0.3175	2.8346	2.2028	0.5501
1.0	0.4890	0.4318	1.1325	0.6870	0.1778	3.8639	0.5500	0.2032	2.7067	2.5677	1.3710
1.5	0.7720	0.2286	3.3771	0.5700	0.3556	1.6029	0.7650	0.2159	3.5433	2.8411	1.0755
2.0	0.9600	0.3810	2.5197	1.1440	0.3302	3.4646	0.8880	0.3048	2.9134	2.9659	0.4746
2.5	0.6670	0.1778	3.7514	0.6560	0.2032	3.2283	0.5880	0.2794	2.1045	3.0281	0.8415
3.0	0.8100	0.1905	4.2520	0.7850	0.2032	3.8632	0.7910	0.2286	3.4602	3.8584	0.3959
4.0	2.2150	0.3429	6.4596	1.7610	0.2286	7.7034	2.0760	0.3556	5.8380	6.6670	0.9498
5.0	2.0100	0.1524	13.1890	1.5840	0.1397	11.3386	2.0120	0.1778	11.3161	11.9479	1.0749

(I) UV-Visible Spectroscopy

From the calculated values in Table A.4, A.5 and A.6, the plots of optical density as the function of weight percent fullerenes are drawn to identified the miscibility limit of fullerene in each samples.

(a) PSAN





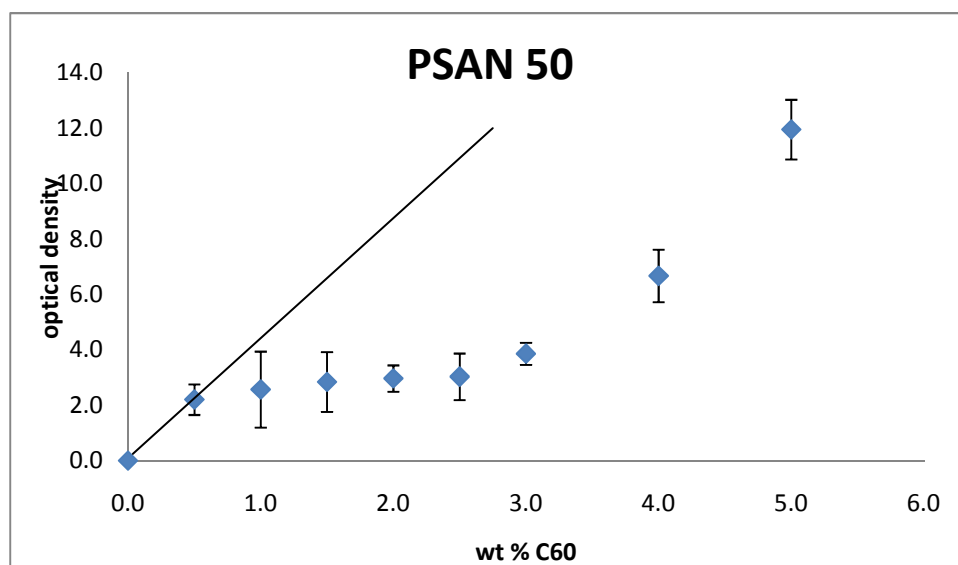
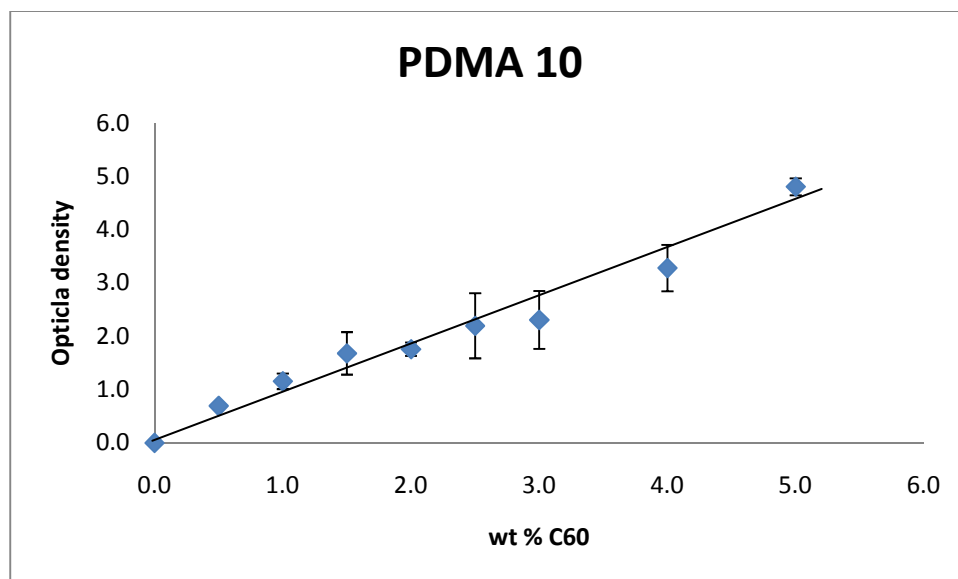
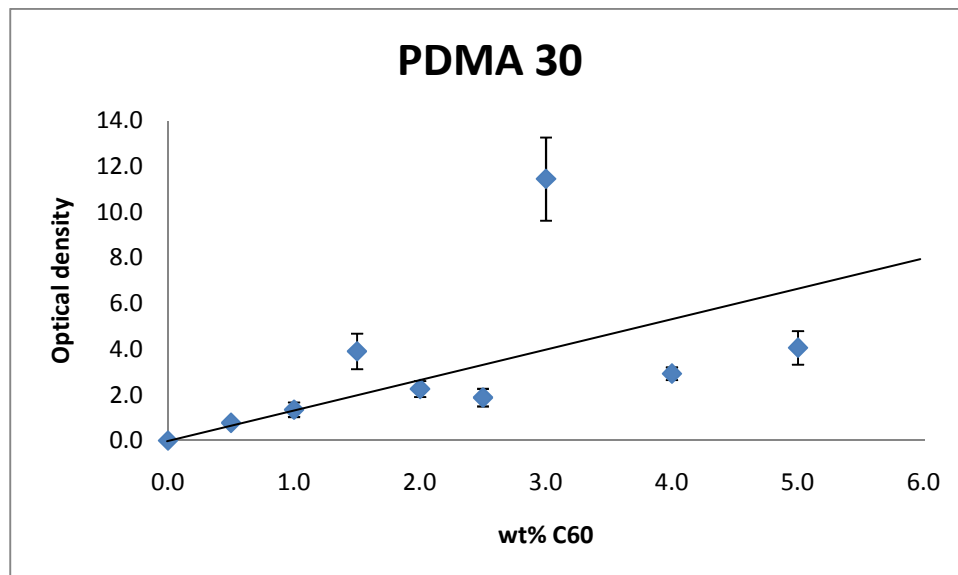
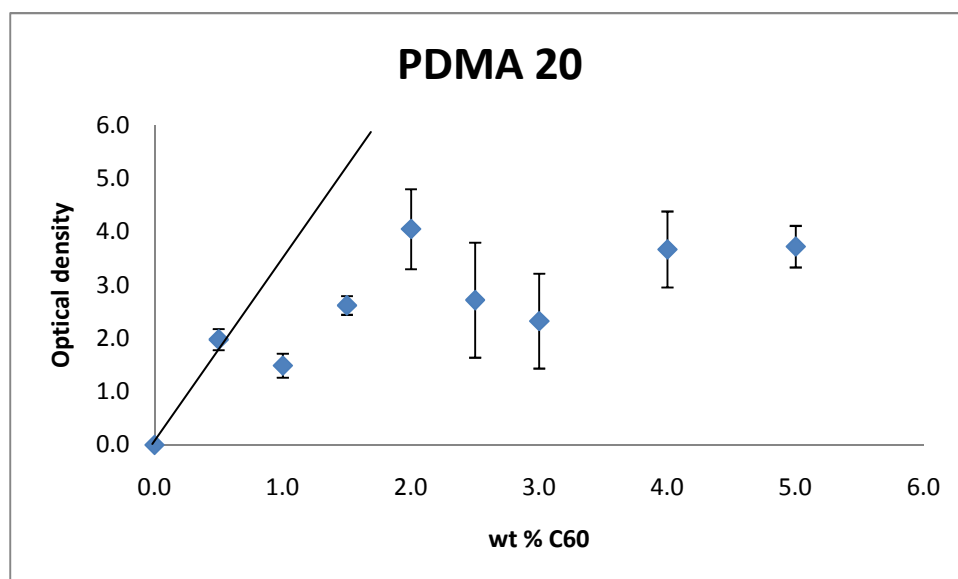


Figure A.1 Plots of optical density as a function of wt% C60 for PSAN nanocomposite

(b) PDMA





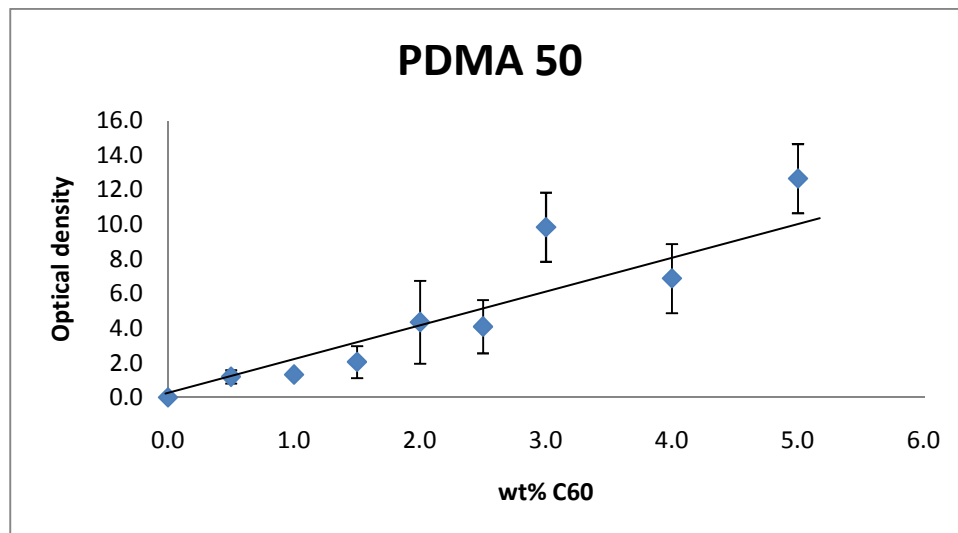
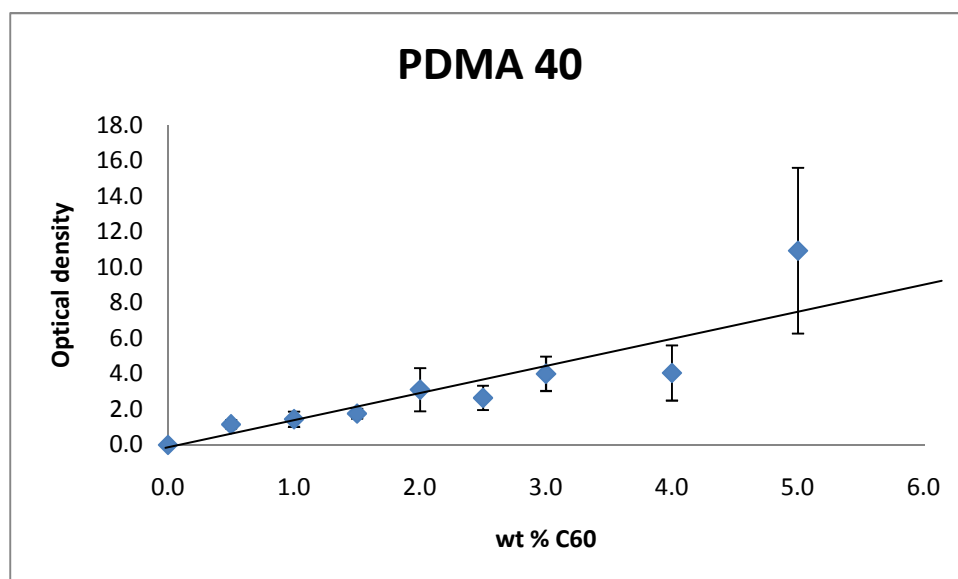
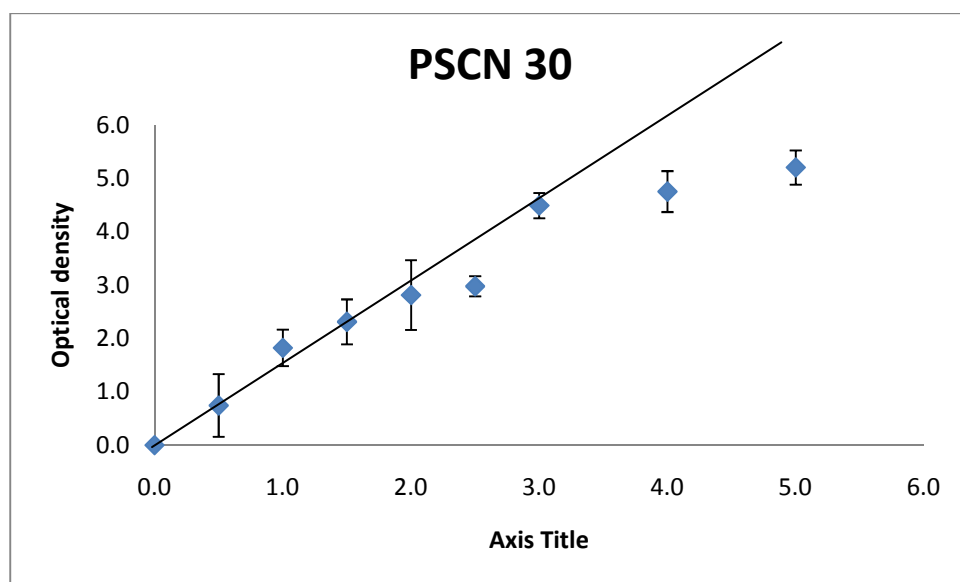
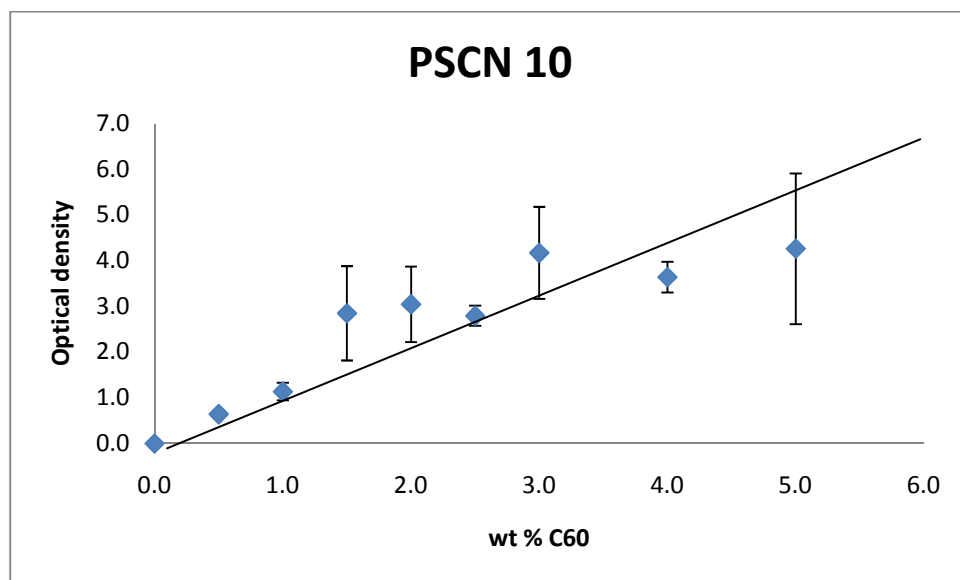


Figure A.2 Plots of optical density as a function of wt% C60 for PDMA nanocomposite

(C) PSCN



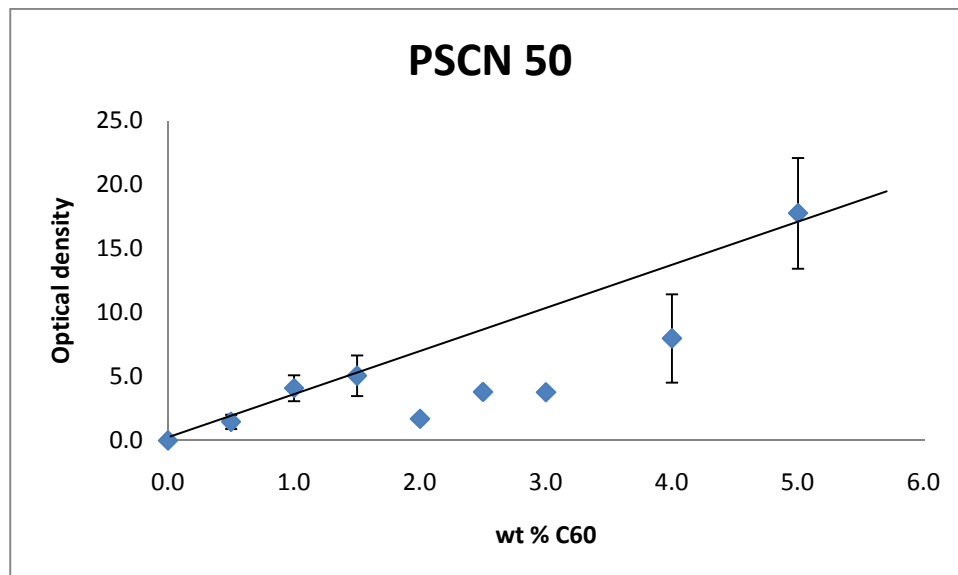
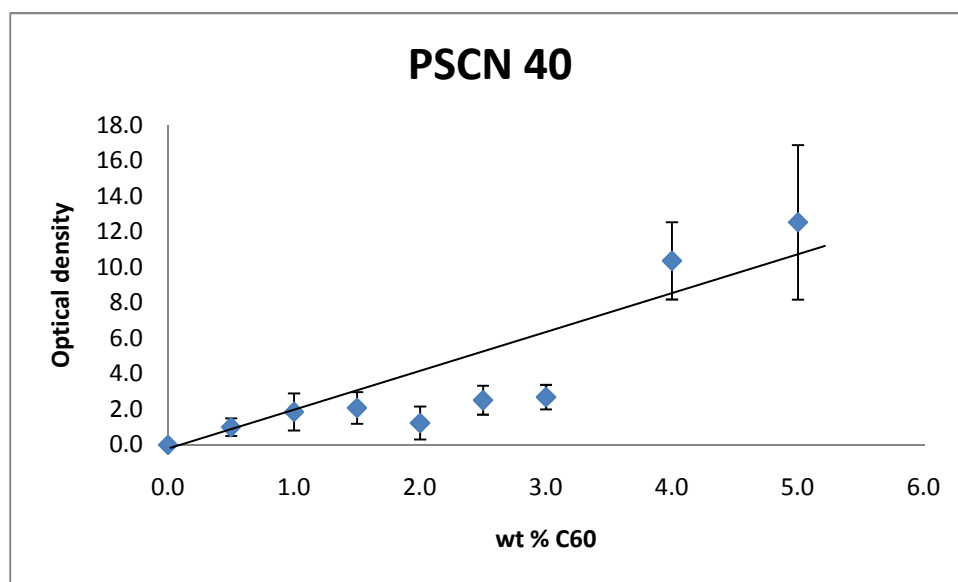


Figure A.3 Plots of optical density as a function of wt% C60 for PSCN nanocomposite

(II) X-Ray Diffraction (XRD)

The XRD spectrum of (a) homopolymers, (b) PSAN (c) PSCN and (d) PDMA are presented to show the reproducibility and method to utilize X-ray diffraction to determine the solubility limit of fullerenes in a polymer matrix. For each polymer nanocomposite, the miscibility limit of the fullerene is identified as the sample with the lowest fullerene loading that do not exhibit sharp crystalline fullerene peaks in the spectrum.

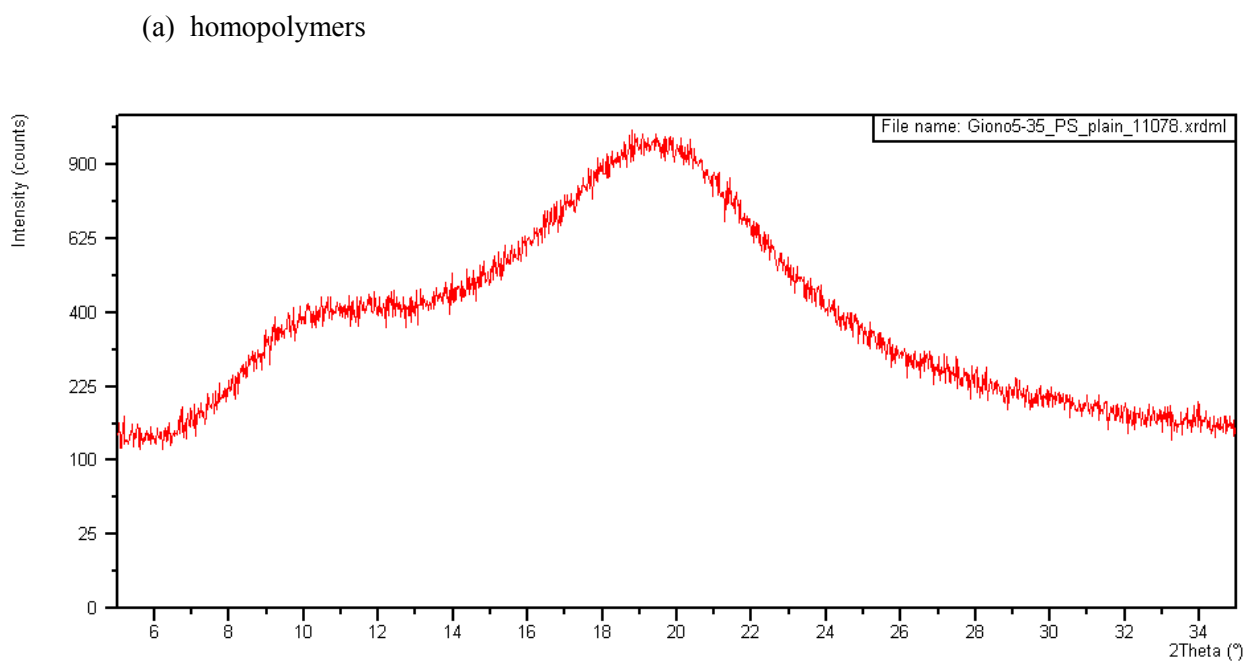


Figure A.4: Spectra of pure polystyrene

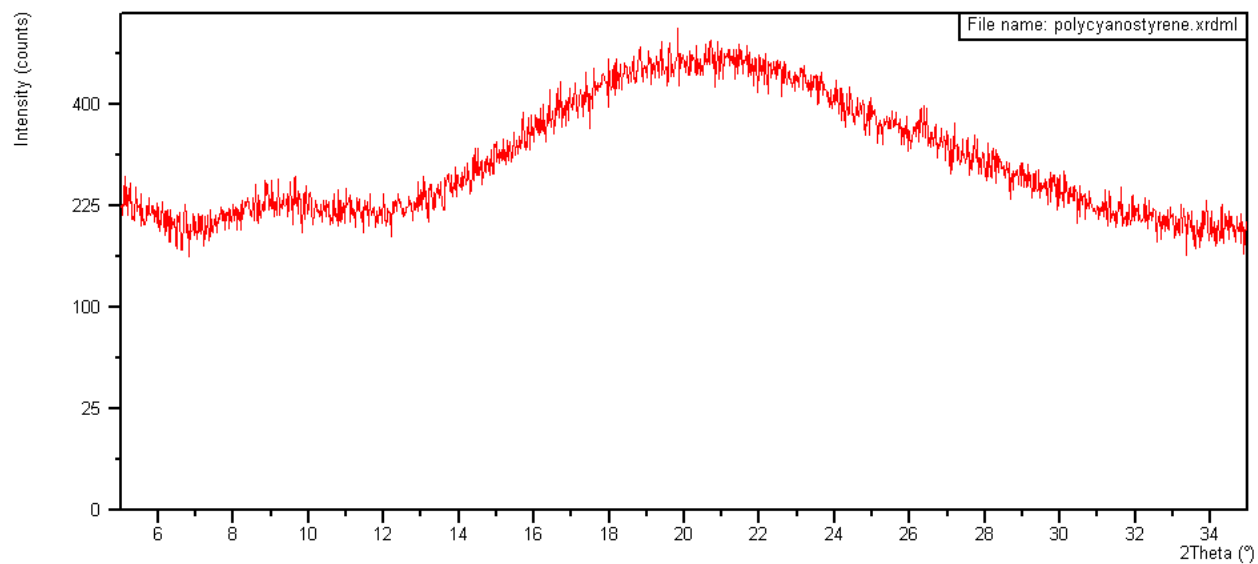


Figure A.5: Spectra of polycyanostyrene

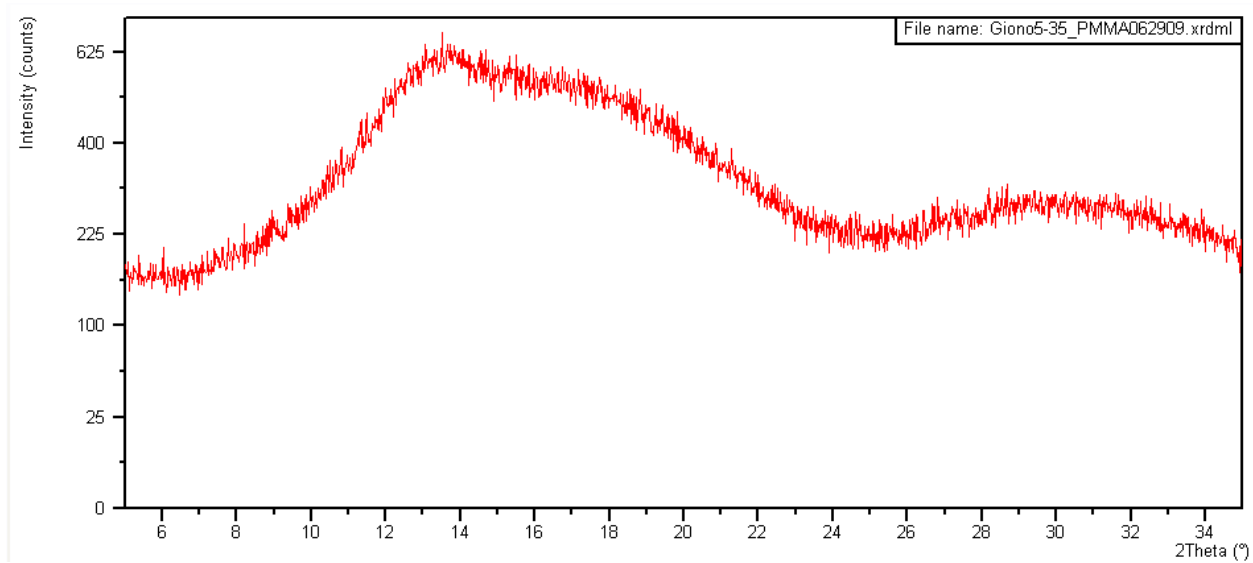
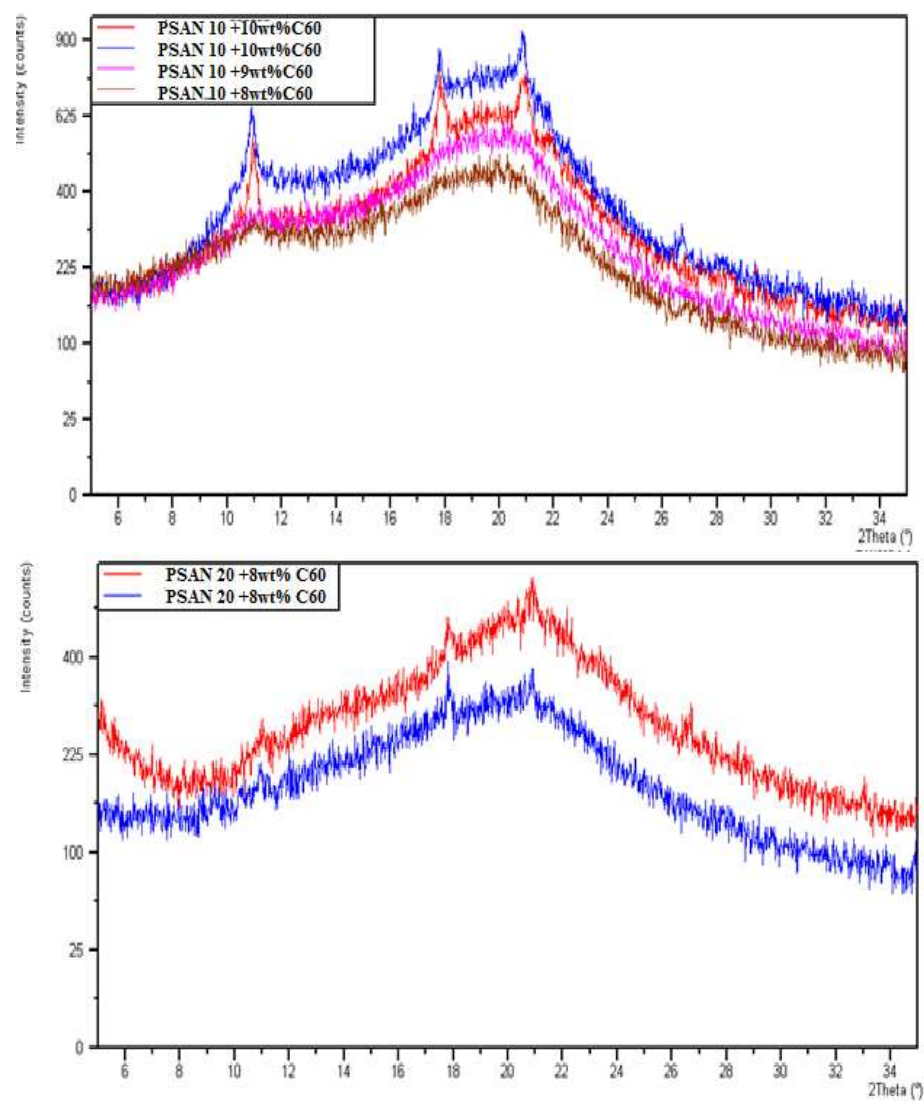
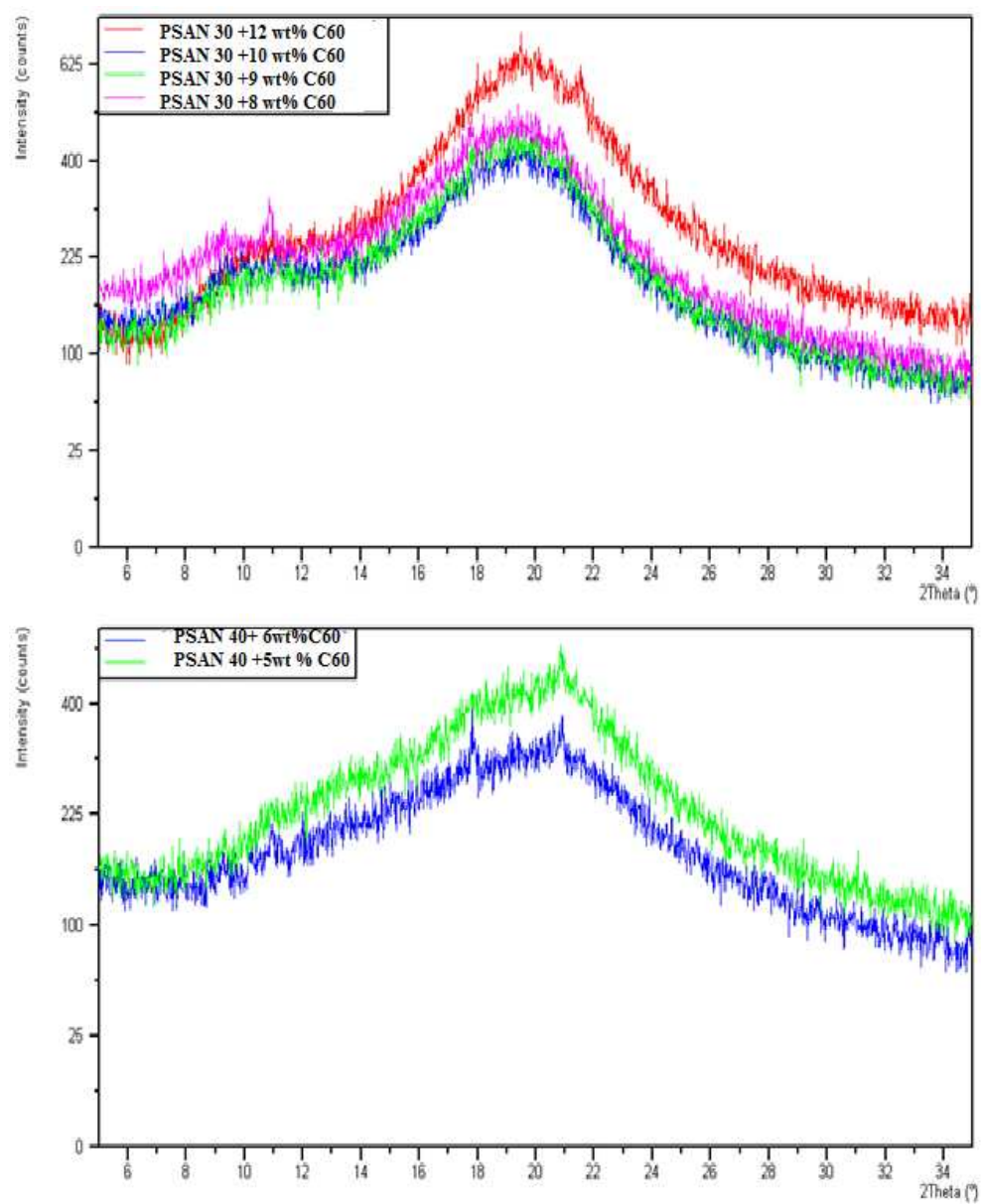


Figure A.6 Spectra of poly(methylmethacrylate)

(a) PSAN Data





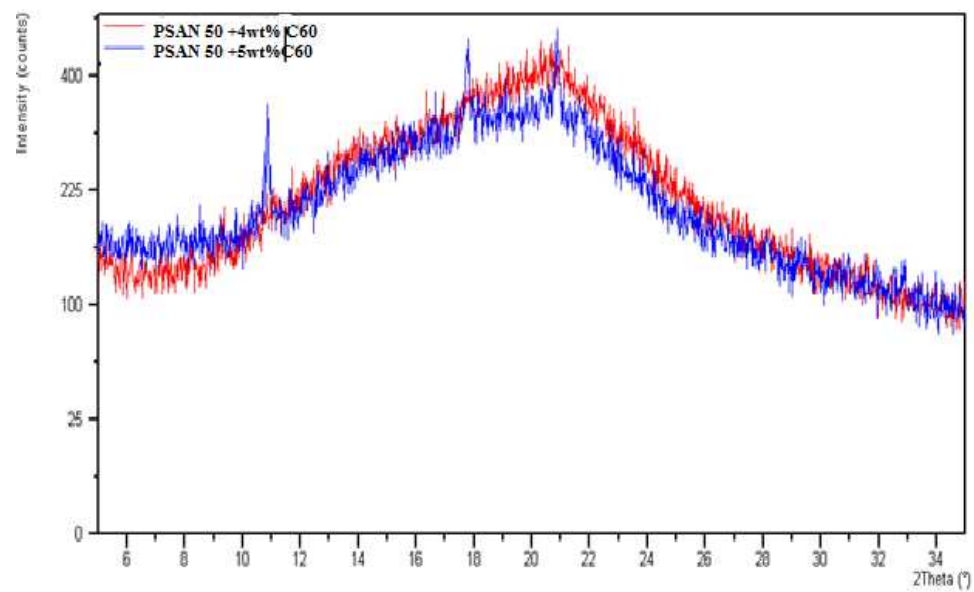
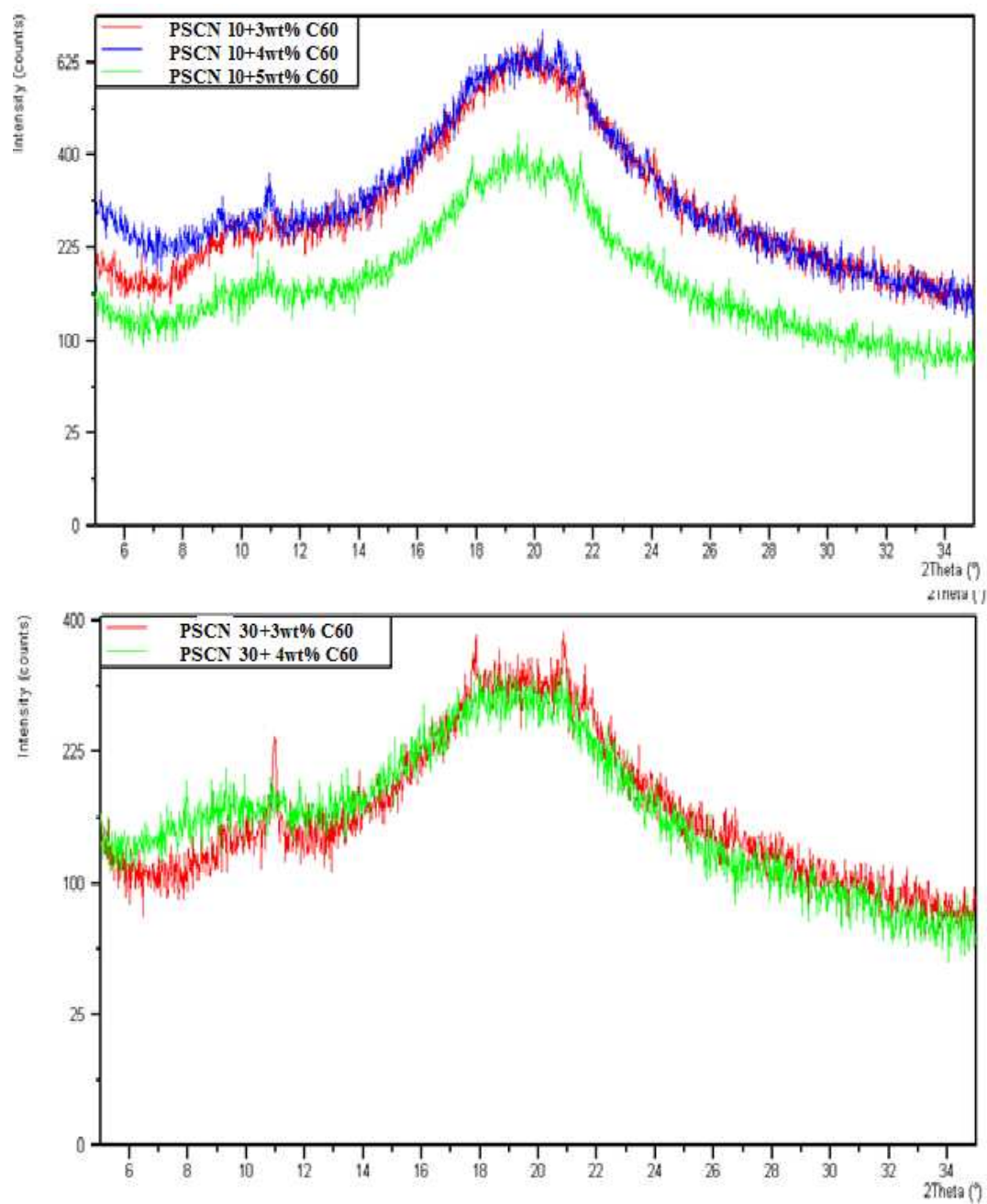


Figure A.7 Spectrum of PSAN nanocomposites

(b) PSCN



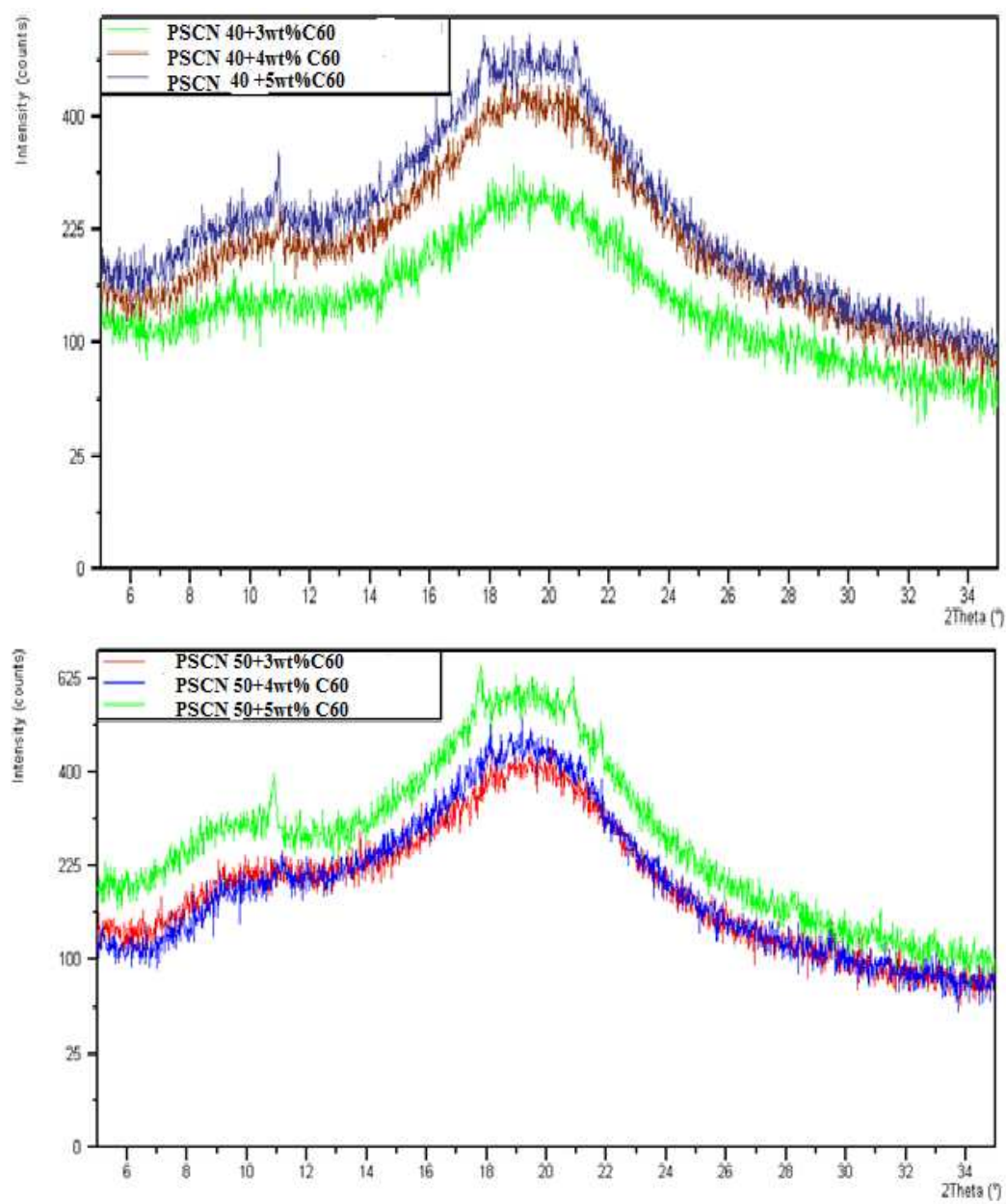


Figure A.8 Spectrum of PSCN nanocomposites

(c) PDMA

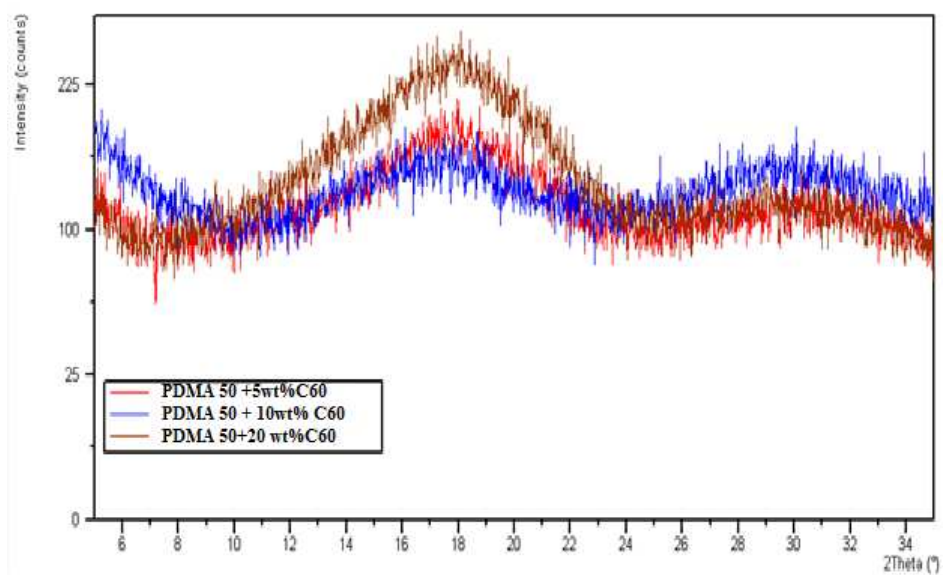


Figure A.9 Spectrum of PDMA nanocomposites

Vita

Say Lee Teh was born on February 28, 1983 in Klang Selangor, Malaysia. She attended junior and high school in Klang. In July of 2004, she moved to the United States of America, to begin her undergraduate studies at Berea College, Kentucky. In the spring of 2008, she received a B.A. degree in Chemistry with a minor in Business Administration from Berea College, Kentucky.

She began pursuing her Masters degree in Chemistry with a specialization in Polymer Chemistry under the direction of Professor Mark D. Dadmun at the University of Tennessee Knoxville in the fall of 2008. She successfully defended her dissertation in December 2010.