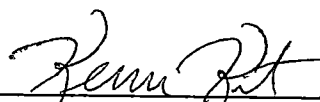


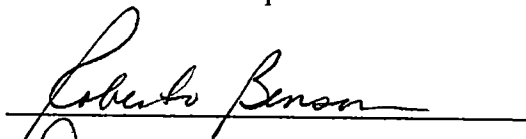
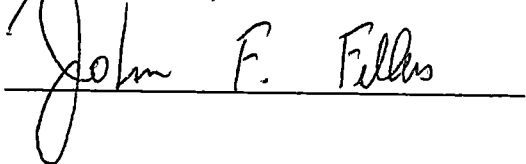
To the Graduate Council:

I am submitting herewith a thesis written by Stephanie Lynn Evans entitled "Phase Separation Behavior in a Rubber-Toughened Epoxy System." I have examined the final 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 Polymer Engineering.



Dr. Kevin Kit, Major Professor

We have read this thesis and
recommend its acceptance:

Accepted for the Council:



Interim Vice Provost and
Dean of The Graduate School

Phase Separation Behavior in a
Rubber-Toughened Epoxy System

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Stephanie Lynn Evans
May 2001

DEDICATION

To my wonderful parents and sisters, who always kept me on
the right track, no matter how difficult that proved to be.

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ABSTRACT

Four series of epoxy resins were cured in the presence of a carboxyl-terminated butadiene acrylonitrile (CTBN). The first two series consisted of 7 components, in which the epoxy, hardener, and rubber form one network and two methacrylates form a second interpenetrating, interconnected network. The variables explored are the initial composition of rubber and the ratio of the two methacrylates. The last two series consist of only 3 components, epoxy, hardener, and rubber. The only variable in each is the rubber concentration. The cure schedule for all the samples was the same. The final size of the rubber particles in each sample were measured using optical microscopy (OM) and scanning electron microscopy (SEM). The impact strength of the seven component samples was measured using an Izod impact tester. Particles were not seen in OM for the first two series and only one rubber concentration value in the second two. SEM on etched samples confirmed the presence of particles formed by nucleation and growth in all the samples. The SEM confirmed the OM results of 8.5 and 9 μm domain sizes for the two samples that showed optically. Phase separation was seen in the 7 component series up to 16% rubber in the first and 10% in the second and rubber particles were measured at 0.75-3 μm in size. The Izod results showed an apparent increase in toughness with increasing rubber concentration and no clear dependence on particle size or size distribution, though the error was so large that the true effect of the presence of particles cannot be confirmed.

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CHAPTER 1

INTRODUCTION

Epoxies have many different applications, but it is well known that adding small amounts of rubber to the system will temper the properties and increase the toughness so that the range of material uses increases. The presence of the rubber particles that phase separate from the epoxy resin are the important controlling factor in how much the rubber benefits the resin. It is therefore significant to study both how large these particles grow and their effect on impact strength.

Epoxy resins are strong thermosets but brittle. The addition of rubber into the system decreases the strength but also increases the toughness to make the resin useable in more applications. This increase is only accomplished when the rubber phase separates from the resin and forms particles. These particles improve the deformation mechanics by causing shear yielding or crazing in the resin matrix and thus increasing the toughness.¹ The size and shape of the rubber particles affects how well they enhance the resin properties.

There are multiple techniques for measuring the size of small particles. Two of them are optical microscopy (OM) and scanning electron microscopy (SEM). OM can detect particles as small as a fraction of a micron, in the region of the wavelength of visible light. SEM detects particles smaller still. Relating particle size to the

mechanical properties is also important. Simple Izod impact tests measure the impact strength of the resins. This impact strength can then be correlated with both rubber concentration and particle size.

There are two types of epoxies, one part and two part. The two part type is formulated so that the epoxy and hardener monomers are in separate containers and curing occurs upon mixing. The one part type is formulated so that all the components are mixed in a single container but curing does not occur until initiated. Initiation can be thermal, electron beam, or radiation. There is a strong motivation for developing this type of epoxy for use in cases where application time or storage are factors in the use of the material.

This study will examine a two part rubber-toughened epoxy system where the weight fraction of rubber is varied. Both of the detection methods (OM and SEM) will be used to measure the size of rubber particles that phase separate in the resins. Izod tests will be performed on all the samples and conclusions drawn regarding the effect of rubber concentration and particle size on impact strength.

CHAPTER 2

LITERATURE REVIEW

2.1 Epoxies

The term epoxy refers to a large range of materials that contain an epoxy, or oxirane, ring in their chemical structure. The ring consists of two carbon atoms and one oxygen atom all bonded with single bonds and either or both of the carbons can be bonded to other chain groups. The most standard epoxies are formed by the reaction of bisphenol A and epichlorohydrin to form a liquid polymer with epoxy end-groups. This type of epoxy has a good balance of chemical, physical, and electrical properties, which makes it practical for uses from coatings and adhesives to composites.² A curing agent must be chosen to initiate crosslinking of the epoxy and the formation of a thermoset network. There are many choices of curing agent including amines, anhydrides, and acids.³ The choice of curing agent affects the properties of the epoxy. Table 2.1 lists some typical properties of an epoxy cured with different curing agents. Table 2.2 gives the impact strengths for a number of different materials and shows that epoxies have a brittle nature.

There are two different types of epoxy systems that can be used. The most common is a two part epoxy. In this system, the epoxy molecules and the curing molecules are contained separately and mixed just prior to use. The curing begins

Table 2.1: Properties for epoxy cured with different hardeners.

Curing Agent	Impact Strength (kJ/m ²)	Tensile Strength (MPa)	Tensile Modulus (GPa)
Aliphatic amine	0.46	42.7	3.4
BF ₃ MEA	0.57	58.6	--
Anhydride	1.5	82.7	3.1
Aromatic amine	--	80	2.7

Source: *Engineering Materials Handbook Vol. 2: Engineering Plastics*; ASM International; 1988.

Table 2.2: Impact strength values for some rigid plastics.

Plastic	Notched Impact Strength (J/m)
Polystyrene	13.3-21.3
Nylon 6/6	53.3-160
Polyoxymethylene	107-160
Polypropylene	27-107
Polytetrafluoroethylene	107-215
Polyphenylene oxide, 25% glass fibers	74.6-80
Epoxy, glass fiber filled	10-30

Source: *Engineering Materials Handbook Vol. 2: Engineering Plastics*; ASM International; 1988.

almost immediately and the epoxy must be applied quickly before the onset of gelation. The second type is the one part epoxy, where both the epoxy and curing molecules are mixed together and stored in the same container but do not fully cure until initiated.

A one part epoxy system is formulated in such a way that only partial curing occurs after initial mixing. The mixture can then be stored for some length of time before use. When it is finally applied, the epoxy must then be given a final cure by some kind of initiation. It should be noted that the epoxy has a finite shelf life, as it continues to cure slowly while on the shelf, but this life can be lengthened slightly by controlling both mixture composition and storage conditions.

It is possible to improve epoxies through the use of a second, interpenetrating network (IPN). An IPN, in general, is different from a copolymer in that the system will swell in the presence of a solvent but not dissolve and both creep and flow behaviors are suppressed.⁴ In the case of thermoset networks, IPNs allow for a larger degree of softening of the material at high temperatures than single networks.

2.2 Rubber Toughening

Epoxies and many other thermoset materials have a brittle nature. This limits the uses for which these polymers can be employed. One common way to extend their uses is to use a process called rubber toughening. Rubber toughening is the inclusion of particles, either rubber or some thermoplastic with a very low glass transition temperature, into the brittle polymer matrix. The effect of the particle addition is an increase in the toughness of the polymer, which results in an increase of applications,

while the overall strength and stiffness of the matrix is reduced. Rubber toughening has been used on many sorts of brittle polymers including epoxies,^{1,3,5-15} poly(methyl methacrylate) (PMMA),^{1,16} and polystyrene (PS),^{1,17} as well as some ductile ones like polycarbonate (PC),¹⁸ and poly(vinyl chloride) (PVC).¹

There are three key elements that must be taken into account when choosing which type of toughening agent is to be used in each particular case. The first is that the glass transition temperature of the rubber or thermoplastic must be much lower than that of the matrix polymer and the temperature of use so that the particles retain their rubbery behavior. The second is that the rubber must not be soluble in the matrix so that a two phase system is formed. The third is that good adhesion is created between the particles and the matrix to prevent debonding from occurring.¹ The best adhesion can be achieved when there is chemical bonding between the rubber and matrix components.

The reason that rubber toughening is effective is that it enhances the deformation mechanics of the matrix polymer.¹ Brittle materials can deform by both shear yielding and crazing. Shear yielding results in a permanent change in shape without a change in volume of the material.¹⁹ A craze is a microcrack in the material that nucleates at a stress concentrator, a porosity or a scratch.¹⁷ Rubber particles increase toughness by inducing shear yielding or multiple crazing in the matrix, or by rubber particle stretching or tearing.^{1,19} There are a number of factors that influence which toughening mechanism controls the matrix deformation, including the type of

rubber and matrix, the size and distribution of particles, the overall rubber content, the adhesion between particles and the matrix, and the use temperature.²⁰

The first mechanism proposed to explain rubber toughening was rubber stretching and tearing. The belief was that as a crack propagated through the matrix, the rubber particles bridged the opposite sides, slowing the crack growth. The toughness was seen as a measure of the energy needed to stretch and tear the particle apart, in addition to the energy to fracture the matrix. Though this mechanism can be present in the matrix, it has been shown to account for only one tenth of the total amount of fracture energy under normal conditions.¹⁹ Kunz showed rubber stretching and tearing to be the primary mechanism of toughening in tests at very low temperatures (-110°C).²¹

Shear yielding is the second toughening mechanism. In this mechanism, the rubber particles act as stress concentrators which initiate yielding in the matrix. This mechanism is believed to be responsible for increasing toughness in more ductile matrices like PVC.²⁰ It has been proposed that a critical value of inter-particle distance exists, below which yielding occurs. This critical value, τ_c , is a characteristic of the matrix for a given temperature and testing rate and does not depend on the rubber.¹⁹ This inter-particle distance, τ , is defined in equation 2.1 as a function of volume fraction (V_f) and particle diameter (d_p) of the rubber.

$$\tau = d_f \left[\left(\frac{\pi}{6V_f} \right)^{\frac{1}{3}} - 1 \right] \quad (2.1)$$

Thus, for any given volume fraction of rubber, smaller particles will increase toughness more than larger ones and shear yielding will be the mechanism of toughening. It has been reported that particles 0.12-1.0 μm are most effective at inducing shear yielding in ductile resins.²

The third toughening mechanism is massive crazing. This mechanism is usually the dominant one in cases of glassy matrix polymers, such as PS, styrene-acrylonitrile copolymers (SAN), and PMMA.¹⁹ Once again, the rubber particles act as stress concentrators that initiate crazing in the matrix. The crazes grow normal to the direction of stress and are stopped when they reach another particle.¹⁷ The particles must be larger than a minimum value so that they can initiate and terminate the crazes without being so large as to cause cracking instead of crazing.¹⁹ This mechanism works because the particles cause a large number of small crazes, instead of the small number of large crazes that generally occur in non-toughened brittle polymers.²⁰ Particles of 0.3-4 μm have been seen to be most effective at improving crazing in brittle matrices.²

Rubber toughening increases the impact strength of the matrix while a decrease is generally seen in the strength and modulus. Table 2.3 shows the toughening effect of the addition of acrylonitrile-butadiene-styrene (ABS) to PC on some properties of the material. Greco showed that the yield strength and Young's modulus decreased with the addition of ABS, while the total fracture energy (G_T) increased to a peak at 20% and then decreased.¹⁸ Table 2.4 gives information on the toughening effect of rubber modified PS. A decrease in the tensile modulus and a peak in the impact strength at

Table 2.3: Toughening data for a PC-ABS system.

ABS Content (wt%)	Yield Stress (MPa)	Young's Modulus (GPa)	G _T (kJ/m ²)
0	63	0.995	3
10	63.5	0.855	22
20	61	0.855	26
30	58	0.845	20
40	52	0.813	4

Source: Greco, R.; Iavarone, M. *Polymer Engineering and Science* **2000**, *40*, 1701-1715.

Table 2.4: Toughening data for a rubber modified PS.

Rubber Content (volume fraction)	Tensile Modulus (GPa)	Impact Strength (MJ/m ³)
0.06	2.8	0.42
0.12	2.4	1.90
0.22	1.9	11.6
0.30	1.0	5.6
0.78	0.55	1.2

Source: Osswald, T. A.; Menges, G. *Materials Science of Polymers for Engineers*; Hanser: Munich, 1996.

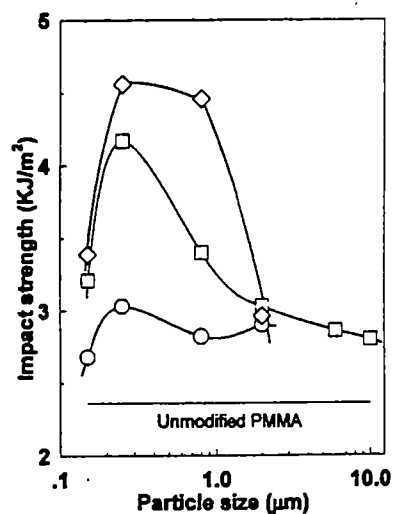
22% rubber was observed by Osswald.¹⁷ Cho plotted the change in impact strength against both particle size and rubber phase content in a PMMA toughened with poly(n-butyl acrylate) (PBA).¹⁶ These plots are seen in figure 2.1.

2.3 Phase Separation

Phase separation is a key element of rubber toughening because, as previously mentioned, toughening only works when the addition of rubber produces a second phase of small particles in the brittle polymer matrix. Good adhesion between the particles and the matrix is also important, as debonding can cause as much damage to the strength of the polymer as a crack. There are two signs that phase separation has occurred. The first is that the material has a milky white coloring. This works if the indices of refraction for the 2 phases are different. The second is that the material exhibits two glass transition temperatures (T_g), one for each of the two phases. This works if the T_g s of the two phase are not too similar.⁴

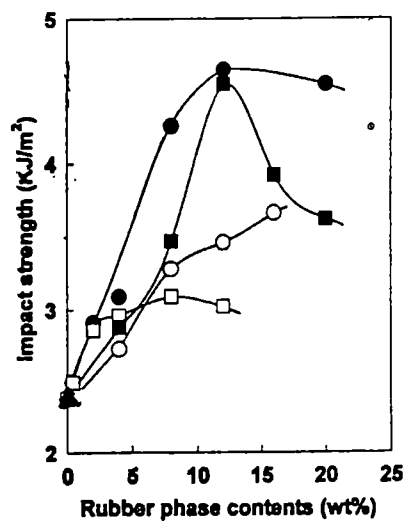
Initially, the rubber and matrix monomers exist in a single, liquid phase. Phase separation occurs when polymerization of the matrix starts and molecular weight (MW) increases. Equations 2.2 define the free energy of the system, ΔG_m , in terms of the enthalpy, ΔH_m , and the entropy, ΔS_m .⁴

$$\begin{aligned}\Delta G_m &= \Delta H_m - T\Delta S_m \\ \Delta H_m &= RT(V_A + V_B)\chi\phi_A\phi_B \\ \Delta S_m &= -R(V_A + V_B)\left(\frac{\phi_A}{\tilde{V}_A}\ln\phi_A + \frac{\phi_B}{\tilde{V}_B}\ln\phi_B\right)\end{aligned}\tag{2.2}$$



(a) Impact strength v. particle size.

Rubber phase contents: ○, 4 wt%; □, 8 wt%; ◇, 12 wt%.



(b) Impact strength v. rubber content.

Rubber particle size: ○, 0.15 μm; ●, 0.25 μm; ■, 0.8 μm; □, 2 μm; ▲, neat PMMA.

Figure 2.1: Impact strength data for a PMMA-PBA system.
Source: Cho, K.; Yang, J.; Park, C. E. *Polymer* 1998, 39, 3073-3081.

where $\tilde{V}_i \propto MW_i$. When ΔG_m is negative, the two phases are miscible. As the molecular weight of the network increases during polymerization, the entropy term becomes smaller and the ΔH_m term begins to dominate. If the ΔS_m term becomes small enough, part of the ΔG_m v. ϕ_B curve will become concave downward and partial phase separation will occur over a certain composition range. As the molecular weight continues to increase (and ΔS_m to decrease), phase separation occurs to greater extents.

There are generally two ways in which the second phase develops in the polymer matrix, nucleation and growth and spinodal decomposition. Both occur because phase separation causes a decrease in the free energy of the system making a two phase state more stable than a single phase state. In nucleation and growth the most common type of nucleation is heterogeneous, where the nuclei form at impurities in the sample or along the container walls.²² There is an energy barrier for this type of phase separation which causes the formation of nuclei to occur slowly. The free energy of the sample is affected by both the interfacial energy between particles and the matrix and the volumetric free energy of a particle. The formation of a nuclei creates an interface with the polymer and increases the free energy of the sample, but the nuclear formation also causes a decrease in free energy by the reduction in volumetric free energy when phase separation occurs.

The molecules in the polymer move around and cluster in small groups, then move apart and cluster in a different location. When one of these clusters forms with a large enough volume, so that the reduction in volumetric free energy is more than the

interfacial creation free energy, a stable nuclei is formed. Since the sphere has the smallest surface area to volume ratio, most nuclei that form will be spherical. Once formed, the nuclei will grow until an equilibrium state is reached or molecular movement is no longer possible due to quenching, molecular weight increase, or the formation of a 3D network. Figure 2.2 shows a picture of a nucleation and growth type phase structure in an epoxy-CTBN system.¹¹ Residual stresses develop during this phase separation and the polymerization of the matrix due to the change in volume of the network. These stresses can contribute to the failure of the material. The presence of a second, interpenetrating network decreases the amount of volumetric change that occurs overall, thereby reducing the amount of residual stress.

The second way phase separation can occur is by spinodal decomposition. This type has no energy barrier to formation and occurs relatively rapidly and spontaneously. It is a feature of certain systems which have free energy curves with regions of negative curvature ($\partial^2 G / \partial^2 \phi_B < 0$).⁹ For sample compositions which fall in this region, the energy of the mixed, one phase material, is unstable and the sample will decompose into two phases with the lowest energy whenever any fluctuation in concentration, no matter how small, results.^{4,22} In the first stage of spinodal decomposition, a periodic structure develops instantaneously, driven by diffusion, with a characteristic domain size of λ_m , the spinodal wavelength. This wavelength is a constant for any system that falls in the spinodal region of the phase diagram, regardless of actual sample composition. Over time, λ_m increases and the growth rate decreases. This coarsening of the structure is the second phase of decomposition, where concentration gradients cause smaller

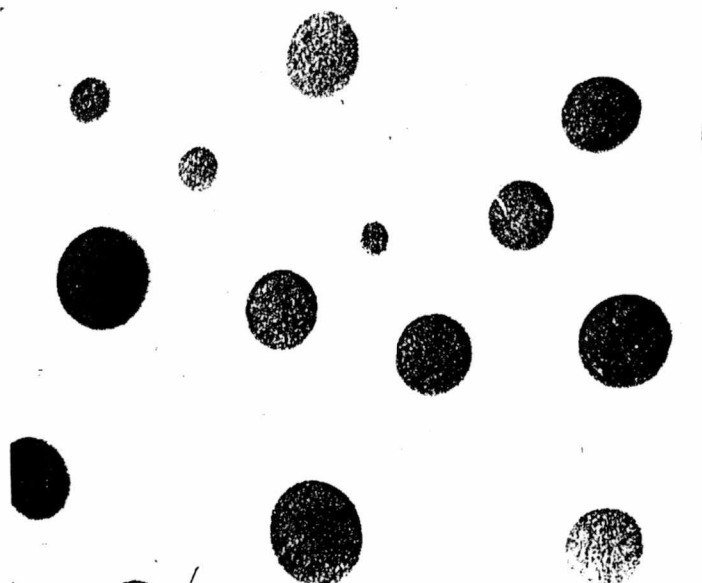


Figure 2.2: Nucleation and growth type phase structure.

TEM micrograph of OsO_4 -stained epoxy-CTBN resin.

Source: Lee, W. H.; Hodd, K. A.; Wright, W. W. *Phase-Separation and Transition Phenomena in Toughened Epoxies*; Riew, C. K., Ed.; American Chemical Society: Washington, D.C., 1989; Vol. 222, pp 263-287.

regions to be incorporated into larger ones.⁹ The structure thus formed by spinodal decomposition has a worm-like, interconnected appearance as opposed to the particle spheres of nucleation and growth. Figure 2.3 shows, conceptually, the appearance of a spinodal decomposition phase separated system.⁴

The increase in molecular weight and the degree of crosslinking in the network affect the phase separation behavior of the system by reducing the mobility of the rubber molecules. The presence of an IPN also affects the mobility, depending on whether the IPN is cured after the phase separating network or simultaneously. It has been seen that most epoxy-rubber systems show a lower critical solution temperature (LCST) behavior in their phase diagrams due to the nature of the network formation and the molecular weight.^{5,6,15} Figure 2.4 shows a plot of extent of reaction v. rubber content for an epoxy-ETBN system.⁵ The critical volume fraction of rubber is 0.24, the system for which only spinodal decomposition will occur as the reaction progresses. For the other rubber fractions, it is seen that as the reaction progresses and molecular weight of the network increases, the system goes from a homogenous phase state to a phase separated state. A similar plot could be constructed using cure temperature instead of extent of reaction. The presence of the LCST shows that phase separation occurs with increasing rubber content to a point, then a single phase region is again seen. It follows that particle size that develops before gelation of the matrix in the phase separated region should increase to a maximum as well and then decrease before the system returns to a single phase state.

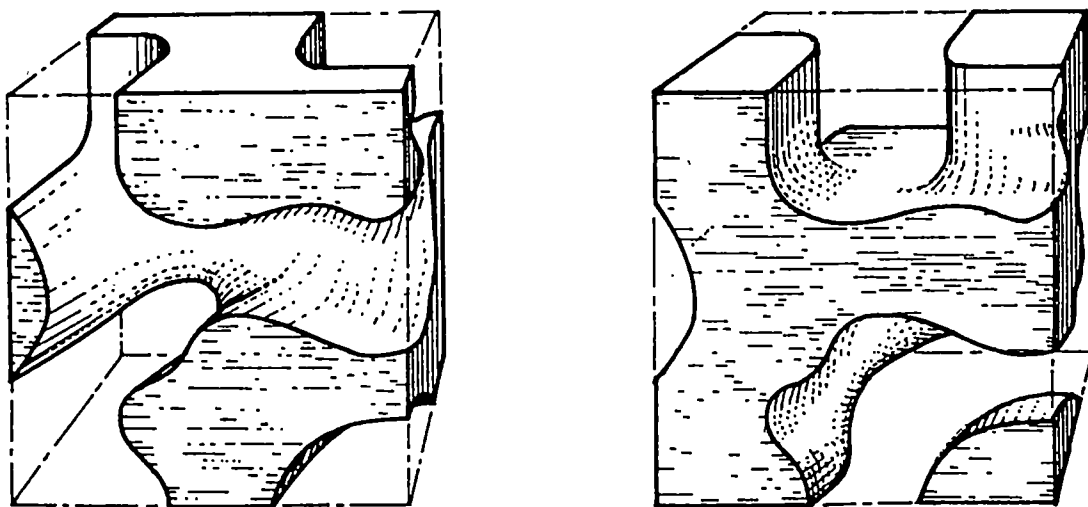


Figure 2.3: Spinodal decomposition type phase structure.
Source: *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; John Wiley & Sons: New York, 1988.

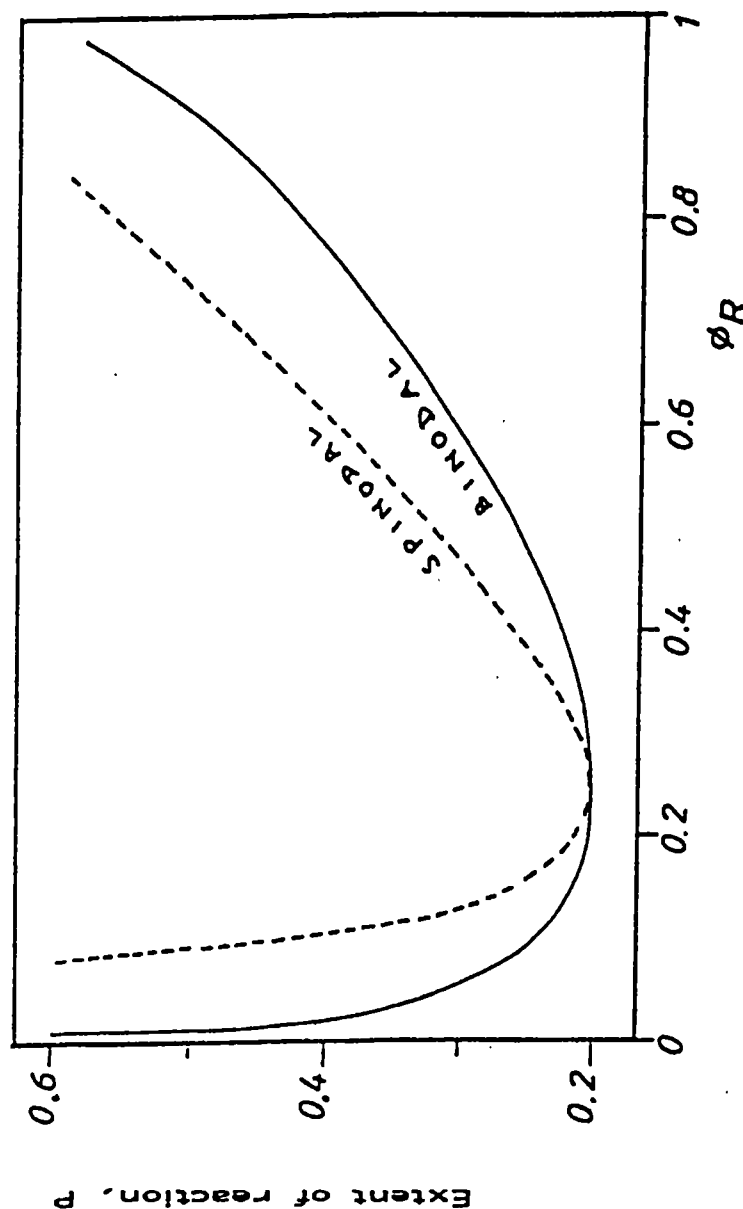


Figure 2.4: Typical phase diagram for epoxy-rubber systems.

Extent of reaction v. rubber content for an epoxy-ETBN resin.

Source: Verchere, D.; Sautereau, H.; Pascault, J. P.; Moschiar, S. M.; Riccardi, C. C.; Williams, R. J. J. *Rubber-Modified Epoxies: Analysis of the Phase-Separation Process*; Riew, C. K., Ed.; American Chemical Society: Washington, D. C., 1993; Vol. 233, pp 335-363.

2.4 Rubber Toughened Epoxies

The toughening of epoxies by a rubber phase was first proposed in 1968.⁴ Since then, much research has been done on rubber toughened epoxies, studying aspects from phase separation to particle morphology to properties of the material. There are an overwhelming number of variables and combinations of variables that every study can focus on and many different detection methods that can be used to obtain results. There are many different types of rubbers that can be chosen, among them are carboxyl-terminated butadiene acrylonitrile (CTBN),¹¹⁻¹³ amine-terminated butadiene acrylonitrile (ATBN),⁷ and epoxy-terminated butadiene acrylonitrile (ETBN),^{5,14} as well as some thermoplastics, including poly(ether sulphone) (PES).⁶ Detection apparatuses generally include light scattering, optical microscopy and electron microscopy equipment as well as calorimetry and other thermal analyzers.

It is generally agreed upon that it is not one variable in a system that will determine if or how phase separation will occur, but a complex and subtle combination of all involved factors.¹¹ The interaction parameter between the rubber phase and the matrix, χ , has been shown to be temperature dependent. Vazquez reports values for χ between 0.52 and 0.54, while Verchere cites 0.63 as the value for an epoxy-CTBN system.^{5,15} Some of the most important elements in phase separation behavior are the compatibility of the rubber and matrix components, the type of curing agent(s) used, the cure schedule (both time and temperature), and the amount of rubber added.^{11,13} When it does occur, phase separation has been observed to be completed well before the gelation point of the matrix is reached.^{13,14} The increase in molecular weight of the

matrix results in reduced mobility of the toughening molecules and halts morphological development before the final structure is frozen at gelation.

The two types of phase separation structure development, nucleation and growth and spinodal decomposition, are both found throughout the literature. The structure development appears to be a function of all involved parameters and it is not possible to predict beforehand which type of separation will occur. It has been noted that at higher rubber concentrations, 20-30%, a phase inversion is generally seen in the material from an epoxy matrix with rubbery occlusions to a rubbery matrix with epoxy occlusions.^{11,13}

The literature includes many citations of particles sizes and detection methods for measuring them. Particles are seen to be either 0.2 to 0.5 μm or between 1 and 5 μm , size being most dependent on the type of curing agent used and the properties of the rubber (molecular weight, acrylonitrile content). OM detected particles in the range of 1 to 4 μm .^{11,13} Particles in both size ranges were detected by SEM.^{5,7,9,14,15}

The effects of toughening on the mechanical properties of the epoxy have been seen to rely on three major factors.^{7,12} The first is the size and distribution of rubber particles in the matrix, which are controlled mostly by the cure schedule. The second is the volume fraction of rubbery domains in the sample, which is tied to the initial weight fraction of rubber added.¹⁴ The third factor is the adhesion between the particles and the matrix, so that fracture by debonding can be avoided. Kim found that for an epoxy-ATBN hardened with triethylene tetramine the optimum fracture toughness was recorded for particles of 1-5 μm and a volume fraction of 10% rubber.⁷

In all cases that study mechanical properties, it is seen that the strength of the epoxy is decreased by the inclusion of rubber particles.^{5,7} Verchere et al. found a decrease in Young's modulus from 2.4 to 1.3 GPa and a decrease in the yield strength from 128 to 69 MPa when the ETBN content in epoxy was increased from 0 to 20%.⁵ Yamanaka found an increase in shear strength from 225 to 260 kg/cm² and in T-peel strength from 0.35 to 1.36 kg/in upon addition of 19% PES to epoxy.⁶

The toughness of the epoxy is seen to increase with the addition of rubber. The degree of toughening, however, is related to the acrylonitrile content of the rubber (%AN), the cure temperature, and the rubber content. Table 2.5 shows the relation of impact strength to the rubber content. Butta recorded that increasing the ATBN content to 20% nearly tripled the impact strength. At 30% ATBN, the toughness was five times that of the neat epoxy, but the samples were too soft to be useful.⁸ Figure 2.5 shows the relationship between impact energy and both cure temperature and rubber type. It is seen that higher cure temperatures make toughening less effective and higher %AN is more effective at lower cure temperatures than lower %AN.⁴

Table 2.5: Toughening data for an epoxy-ATBN system.

Rubber Content (wt%)	Impact Strength (kJ/m ²)
0	1.5
5	2.1
10	3.9
20	4.0
30	7.6

Source: Butta, E.; Levita, G.; Marchetti, A.; Lazzeri, A. *Polymer Engineering and Science* **1986**, 26, 63-73.

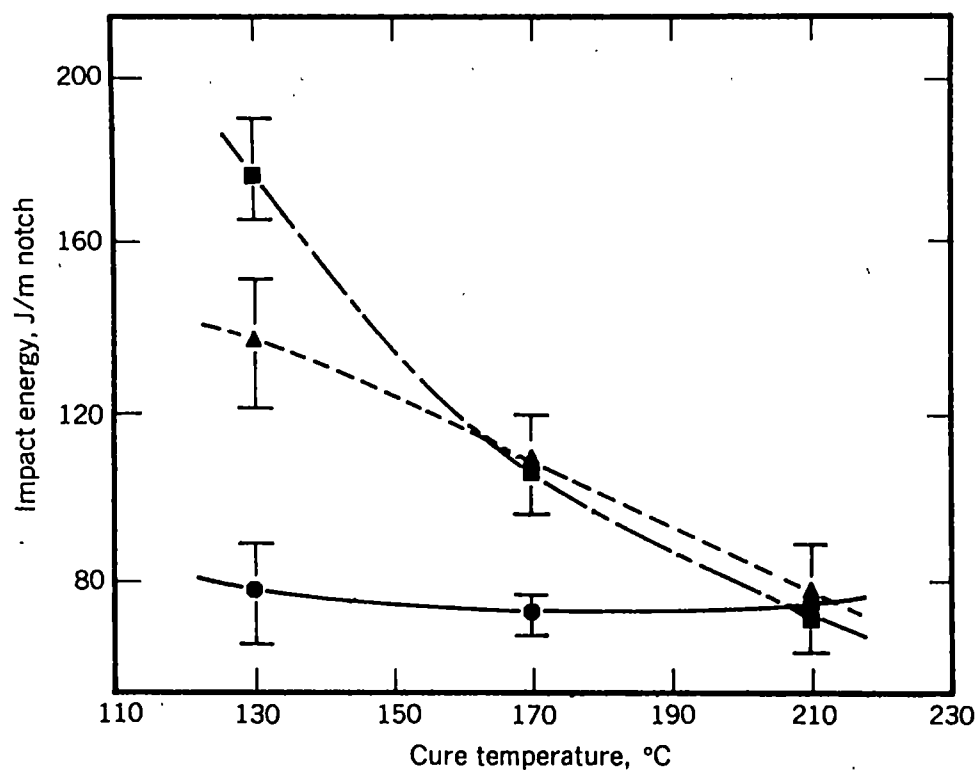


Figure 2.5: Impact strength data for a CTBN toughened epoxy.

%AN in CTBN: ■, 17%; ▲, 27%; ●, no rubber.

Source: *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; John Wiley & Sons: New York, 1988.

CHAPTER 3

EXPERIMENTAL METHODS

3.1 Introduction to Epoxy System

The epoxy system under study can be considered a one or two part epoxy depending on the adjustment of a compositional variable. After curing, it consists of two interpenetrating networks of epoxy/hardener units and methacrylate units. The two networks are connected through some molecules which have epoxy bonds on one end and methacrylate on the other. The epoxy molecules react with the amine curing agent upon mixing, but the methacrylate molecules do not react fully until an initiator is used. This initiator can be electron beam, light, or thermal. Addition of different amounts of rubber molecules to the mixture alters the mechanical properties of the final product. In order to prove useful, the rubber must react and phase separate during the first part of the curing process, when the epoxy network forms, and before the methacrylates react.

The use of the methacrylate network not only allows for extended storage of a partially cured mixture, in which the epoxy network is kept below the gelation point, but also for some control of the viscosity of the mix. By incorporating two different methacrylate monomers of very different viscosity into the initial mixture, the storage viscosity can be increased or decreased to aid in application for final use.

3.2 Materials

The composition of a radiation curable epoxy is generally more complex than that of a standard two part resin. Following is a list of the materials used in this epoxy system. The weight per epoxide (WPE) is the molecular weight of the monomer divided by the functionality of the monomer. Figure 3.1 shows the chemical structures of the components.

Epoxides

Epon 828 Resin: This is a diepoxide monomer based on bisphenol A provided by Shell Chemical. It has a WPE of 187 and will be referred to as 828.

Heloxy modifier 63: This is a monoepoxide of phenyl glycidyl ether supplied by Shell Chemical. It acts as a chain-ender and decreases the viscosity of the mix. It has a WPE of 150 and will be known as PGE.

Amine Curing Agent

Amicure PACM Curing Agent: This is a tetra-functional monomer known as bis(para-aminocyclohexyl)methane. It is supplied by Air Products & Chemicals, Inc. as PACM-20. It has a WPE of 52.5 and will be referred to as PACM.

Methacrylates

CN151: This is an aromatic dimethacrylate. It is bisphenol A epoxy that has

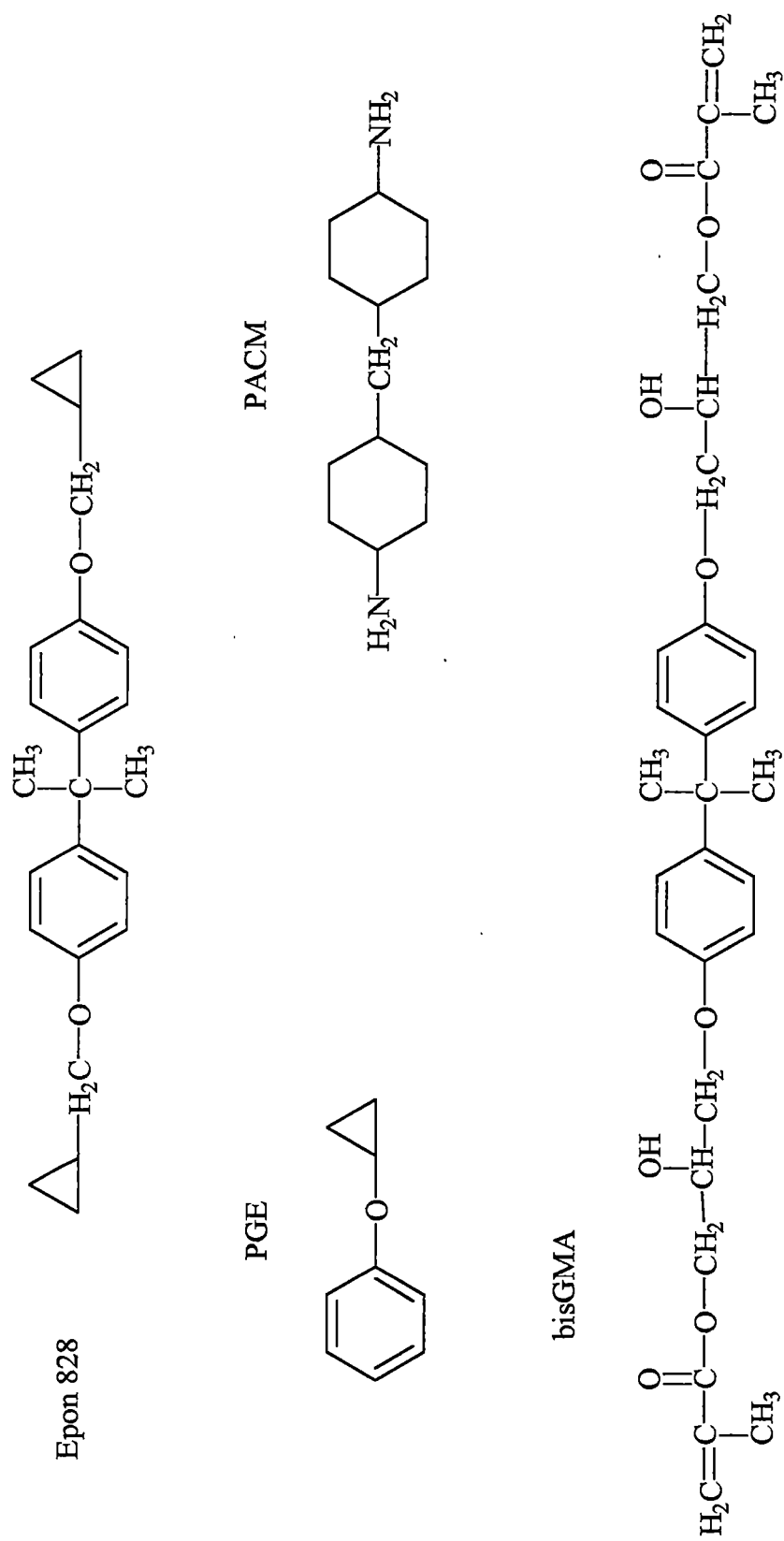


Figure 3.1: Chemical structures of components.

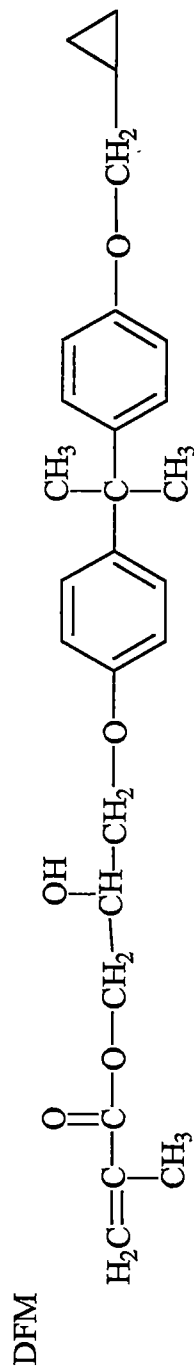
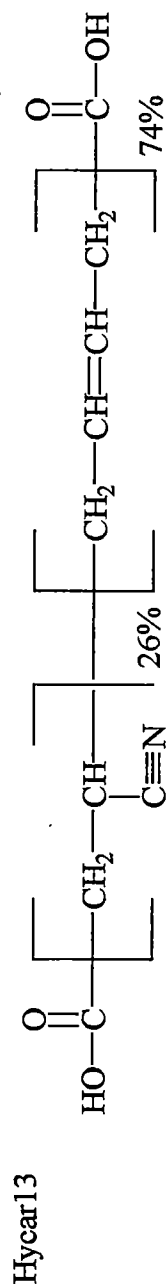
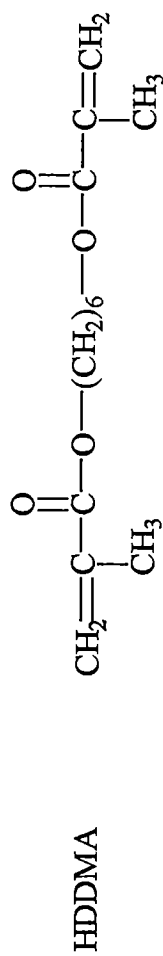


Figure 3.1 (cont.)

been fully methacrylated. It is provided by Sartomer Company and will be called bisGMA.

SR239: This is an aliphatic dimethacrylate of 1,6 hexanediol dimethacrylate. It is supplied by Sartomer Company and will be known as HDDMA.

Rubber

Hycar CTBN 1300x13: This is a carboxyl-terminated butadiene acrylonitrile random copolymer provided by BF Goodrich Co. It contains 26% acrylonitrile. It has a WPE of 1750 and will be known as Hycar13.

Dual Functional Monomer

ARL1: This compound was synthesized and provided by the US Army Research Laboratory. It is created by reacting methacrylic acid and Epon 828, with a mole ratio of 1:1, in the presence of a catalyst.²³ The reaction produces three species: 25% (by mole) unreacted Epon 828 monomers, 25% fully reacted monomers equivalent to bisGMA, and 50% partially reacted dual functional monomers (DFM) with one epoxide and one methacrylate end group. The DFM has a WPE of 466 and the mixture will be called ARL.

Other agents

Epon 58005 Resin: This resin is supplied by Shell Chemical. It is a mixture of

60% Epon 828 and 40% Hycar 1300x13, which has been reacted to have epoxide end groups. It has a WPE of 340 and will be called 58005.

Phenol: This molecular biology grade phenol is provided by Fisher Biotech. It aids in the quick cure of the epoxy network.

Tert-Butyl peroxide, 98%: This peroxide is provided by Aldrich. It is used to allow for thermal free radical curing of the methacrylate network.

3.3 Variables

There are several variables that control the properties of the mixed resins. These may be changed to alter the system, but must be set for the proportions of mixing to be calculated for any one sample.

ARL Weight Fractions

The composition of the ARL is given in mole fractions. For the purposes of mixing, it is more convenient to use weight fractions. These can be calculated as follows with an R value of one (from the mole ratio 1:1).

$$x_{828} = \frac{374(1 - R/2)^2}{374(1 - R/2)^2 + 466R(1 - R/2) + 542(R/2)^2} = 0.2024 \quad (3.1)$$

$$x_{DFM} = \frac{466R(1 - R/2)}{374(1 - R/2)^2 + 466R(1 - R/2) + 542(R/2)^2} = 0.5043 \quad (3.2)$$

$$x_{bisGMA} = \frac{542(R/2)^2}{374(1 - R/2)^2 + 466R(1 - R/2) + 542(R/2)^2} = 0.2933 \quad (3.3)$$

Rubber Fraction

This is the total weight fraction of the rubber in the system. It is represented as

W_{rubber}

Branching Coefficient

The branching coefficient, α , is the probability that a multi-functional monomer is connected to another multi-functional monomer by a chain of covalent bonds. The critical branching coefficient α_c is defined as $1/(f-1)$ where f is the functionality of the curing agent. If $\alpha > \alpha_c$, then the epoxy will fully cure upon mixing and be considered a two part. If $\alpha < \alpha_c$, the epoxy will be a one part because it will remain below the gelation point after mixing. In order for the partially cured resin to remain useable, it must not reach the gelation point before being applied. Since PACM has $f = 4$, the critical value for α is $1/3$.

Matrix Composition

This is the weight of the epoxides (excluding the DFM) divided by the total weight of the resin (excluding the DFM and the rubber). This is the variable that controls the relative amounts of the two networks. It is defined as

$$\beta = \frac{WPACM + W828 + X828W_{ARL} + WPGE}{WPACM + W828 + (X828 + X_{bisGMA})W_{ARL} + WPGE + W_{bisGMA} + WHDDMA} \quad (3.4)$$

Monoepoxide Composition

This is the weight of the PGE divided by the total weight of monoepoxides (the PGE and the DFM). It is defined as

$$\gamma = \frac{W_{PGE}}{W_{PGE} + X_{DFM}W_{ARL}} \quad (3.5)$$

Dimethacrylate Composition

This is the total weight of the bisGMA divided by the total weight of the dimethacrylates (the bisGMA and the HDDMA). This is the variable that controls the viscosity of the partially cured resin. It is defined as

$$\delta = \frac{W_{bisGMA} + X_{bisGMA}W_{ARL}}{W_{bisGMA} + X_{bisGMA}W_{ARL} + W_{HDDMA}} \quad (3.6)$$

3.4 Development of Solution Matrix

There are seven components in the resin system, which means that there must be seven equations solved simultaneously to determine the weight fraction of each in the mixture (w_{828} , w_{PACM} , $w_{HYCAR13}$, w_{ARL} , w_{PGE} , w_{bisGMA} , w_{HDDMA}). Five variables have so far been defined (α , β , γ , δ , and w_{rubber}). Epoxy-amine stoichiometry and mass balances must also be incorporated. This provides seven equations.

Stoichiometric Balance

It is important to have a stoichiometric balance between the epoxide monomers and the amine and carboxyl monomers. Each PACM unit can react with four other

monomers. This defines the following equation.

$$\frac{WP_{ACM}}{WPE_{ACM}} + \frac{WHYCAR13}{WPE_{HYCAR13}} - \frac{(W_{828} + X_{828}W_{ARL})}{WPE_{828}} - \frac{WP_{GE}}{WPE_{PGE}} - \frac{X_{DFM}W_{ARL}}{WPE_{ARL}} = 0 \quad (3.7)$$

Rubber Fraction

This is a simple specification of the amount of rubber desired in the sample. It is represented as

$$WHYCAR13 = W_{rubber} \quad (3.8)$$

Branching Coefficient

The branching coefficient α is a non-linear function of the weight fractions. Using statistical analysis and a few good assumptions, it is possible to simplify its definition to the following linear equation.²⁴

$$\frac{WP_{ACM}}{WPE_{ACM}} + \frac{WHYCAR13}{WPE_{HYCAR13}} - \frac{1}{\alpha} \frac{(W_{828} + X_{828}W_{ARL})}{WPE_{828}} = 0 \quad (3.9)$$

Matrix Composition

Equation 3.4 is rewritten as

$$\begin{aligned} &(\beta - 1)WP_{ACM} + (\beta - 1)W_{828} + (\beta - 1)WP_{GE} + \beta W_{HDDMA} + \beta W_{bisGMA} \\ &+ [(\beta - 1)X_{828} + \beta X_{bisGMA}]W_{ARL} = 0 \end{aligned} \quad (3.10)$$

Monoepoxide Composition

Equation 3.5 is rewritten as

$$(\gamma - 1)WPGE + \gamma XDFMWARL = 0 \quad (3.11)$$

Dimethacrylate Composition

Equation 3.6 is rewritten as

$$(\delta - 1)W_{bisGMA} + (\delta - 1)X_{bisGMA}WARL + \delta WHDDMA = 0 \quad (3.12)$$

Mass Balance

The sum total of all the weight fractions must be equal to one.

$$\begin{aligned} WPACM + WHYCAR13 + W828 + WARL + WPGE + W_{bisGMA} \\ + WHDDMA = 1 \end{aligned} \quad (3.13)$$

Solution Matrix

Equations 3.7 - 3.13 are most easily solved in matrix form. They can be written as

$$\mathbf{A} \begin{Bmatrix} W828 \\ WPACM \\ WHYCAR13 \\ WARL \\ WPGE \\ W_{bisGMA} \\ WHDDMA \end{Bmatrix} = \begin{Bmatrix} 0 \\ W_{rubber} \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{Bmatrix} \quad (3.14)$$

where

$$\mathbf{A} = \begin{bmatrix} \frac{-1}{WPE_{828}} & \frac{1}{WPE_{PACM}} & \frac{1}{WPE_{HYCAR13}} & \frac{-x_{828}}{WPE_{828}} - \frac{x_{DFM}}{WPE_{ARL}} & \frac{-1}{WPE_{PGE}} & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ -1 & 1 & 1 & -x_{828} & 0 & 0 & 0 \\ \frac{\alpha WPE_{828}}{\beta - 1} & \frac{WPE_{PACM}}{\beta - 1} & \frac{WPE_{HYCAR13}}{0} & \frac{\alpha WPE_{828}}{(\beta - 1)x_{828} + \beta x_{bisGMA}} & \beta - 1 & \beta & \beta \\ 0 & 0 & 0 & \gamma x_{DFM} & \gamma - 1 & 0 & 0 \\ 0 & 0 & 0 & (\delta - 1)x_{bisGMA} & 0 & \delta - 1 & \delta \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 \end{bmatrix}$$

This equation can then be solved using a spreadsheet to determine the mixing proportions of all seven components.

3.5 Three Component Trial System

A second, simpler system is useful for trying mixing procedures and checking equipment functions. This resin is composed of only three components (828, 58005, and PACM), which makes the calculations more manageable. This resin is considered a two part epoxy since it cures fully upon mixing no matter what composition is chosen. The only variable in this case is the weight fraction of rubber in the system, w_{rubber} . The three necessary equations are reached by combining this with the stoichiometric and mass balances.

Stoichiometric Balance

It is important to have a balance between the epoxides and the amine groups. The resulting equation is

$$\frac{W_{58005}}{WPE_{58005}} + \frac{W_{828}}{WPE_{828}} - \frac{WPACM}{WPE_{PACM}} = 0 \quad (3.15)$$

Rubber Fraction

This is the amount of rubber desired in the sample. It is represented as

$$0.4 W_{58005} = W_{rubber} \quad (3.16)$$

Mass Balance

The sum of all the weight fractions must equal one.

$$W_{58005} + W_{828} + WPACM = 1 \quad (3.17)$$

Solution Matrix

Equations 3.15 - 3.17 are combined into a matrix equation for solution. This is written as

$$\begin{bmatrix} \frac{1}{WPE_{58005}} & \frac{1}{WPE_{828}} & \frac{-1}{WPE_{PACM}} \\ 0.4 & 0 & 0 \\ 1 & 1 & 1 \end{bmatrix} \begin{Bmatrix} W_{58005} \\ W_{828} \\ WPACM \end{Bmatrix} = \begin{Bmatrix} 0 \\ W_{rubber} \\ 1 \end{Bmatrix} \quad (3.18)$$

The solution to this matrix provides the composition for the simple epoxy resin.

3.6 Sample Preparation

The formulations of all the samples are calculated using equations 3.14 and 3.18 above. Three different sets of compositions of samples are mixed and prepared for the different detection apparatus. The optical microscopy requires thin samples prepared on glass slides. The scanning electron microscopy requires a fracture surface of a more substantial sample. The Izod impact requires a sample of very specific size and shape. All actual sample compositions and curing times are given in the Appendix.

In preparing samples for testing, it is necessary to determine which aspects of the composition will be studied and then to set the possible variables to those qualifications. It is unknown at the start what range of rubber compositions will produce phase separations, so a trial must be performed to determine the appropriate study range. Attention can then be focused on the region where phase separation occurs.

The samples were mixed using mostly disposable equipment for ease of clean-up. This includes 150 mL plastic beakers to mix in, small glass pipettes to measure out the liquid components (PACM, HDDMA, peroxide), and the wooden end of cotton tipped swabs to mix with. The balance used to measure the weights was a Mettler Toledo balance model PB153. The higher viscosity components (ARL, Hycar13, 828, bisGMA) were heated for about 30 minutes at 60°C to lower their viscosities to usable levels before mixing. They were measured out using small metal spatulas, which were then cleaned up with acetone. The mixing process created bubbles in the samples, so

degassing was done in a Fisher Scientific 281A Vacuum Oven with a Fisher Scientific Maxima C Plus Corrosion Resistant Labor Vacuum Pump model M2C.

Each group of samples was prepared in a different form. The glass slides used were Fisherbrand Microscope Cover Glass 12-545M, 24 mm*60 mm*1 mm. The smooth bottom aluminum pans, Fisher #087325A, have a 4 cm diameter and are 1 cm deep. The samples for the Izod test require more specific size and geometry. Molds were made with 3120 RTV silicon using steel Izod bars, 57 mm*10 mm*10 mm, as templates. The notch is 2 mm across and 2 mm deep. The silicon both holds its shape at high temperatures and easily releases the epoxy samples. The samples were cured in a Fisher Scientific Isotemp Programmable Oven model 825f.

Three Component Group

The first group of samples is the simple three component trial system. Its purpose is to check equipment and mixing methods. The only variable is w_{rubber} which is varied from 0 to 0.2 in 0.05 increments. Two series were mixed. The first, 58005 series, included only the three components while the second, 58005' series, contained 1.49wt% phenol mixed with the 828 component. The phenol acts to cure the resin faster and should produce smaller rubber particle sizes. Sample identification was given as the % rubber without and with an apostrophe to indicate the series, for example, 0, 5, 5', 10', etc. All were prepared in the same way. Ten grams of sample were mixed by hand for about 5 minutes to ensure good mixing. Then slide samples were mounted and pan samples were poured. The sample pans were degassed at 60°C

for 5 minutes and all samples were then cured at 60°C for approximately 22.5 hours. The degassing process did not remove all the bubbles from the samples, but most of them floated to the surface of the sample. The center region, which is the more important area of the sample, was then bubble-free. The resulting thickness of the pan samples was around 5 mm.

Seven Component Trial Group

The second group of samples consists of two separate series. This group is the test group of the seven component samples to determine the range of rubber concentrations where phase separation occurs. The samples were all mixed and cured and then a visual inspection determined whether separation had occurred or not. It was assumed that cloudy samples indicated phase separation and clear samples indicated no phase separation. For this study it is unnecessary to have the epoxy network remain below the gelation point. Gelation must occur to ensure that maximum phase separation occurs. Therefore the value of α , the branching coefficient, is set well above 1/3 and there is no PGE included in the composition. This means that the study epoxy is in fact a two part epoxy system. For all of these samples, the epoxy network cures and reaches the gelation point which makes them solid, but the methacrylate network does not cure. The samples were identified consecutively as they were mixed, not by rubber concentration, and with a letter indicating the series, for example, 1A, 2A, 2B, 3B, etc.

A Series

The compositional variables are first set for the series. They are $\alpha = 0.75$, $\beta = 0.5$, $\gamma = 0$, $\delta = 0.6$, and w_{rubber} varied from 0 to 0.3 in 0.05 increments. Ten grams of sample were mixed for each composition for about 5 minutes. The samples were created using both slides and pans. The amount of sample placed between the slides was not measured, but was kept small enough to keep material from oozing out. The remainder of the mixture was poured into an aluminum pan and degassed at 60°C for 20 minutes. All the samples were placed in a 60°C oven and cured for approximately 21 hours.

When the samples were removed from the oven, they were examined for phase separation. To further develop the phase diagram, more samples were prepared, with w_{rubber} of 1%, 3%, 6%, 8%, 11%, 12%, 13%, and 14%, in the same manner as before. Figure 3.2 is a phase diagram for the system showing the lines of composition along which samples of both this A series and the following B series are created. The ARL component is ignored in the creation of the phase diagram giving apparent rubber fractions which are larger than the actual values.

B Series

The compositional variables for this series are $\alpha = 0.75$, $\beta = 0.5 - w_{\text{rubber}}$, $\gamma = 0$, $\delta = 0.6$, and w_{rubber} is varied from 0.05 to 0.3 in 0.05 increments. (The 0% rubber sample is the same for both the A series and the B series so it was not repeated.) Ten grams of each composition were mixed for about 5 minutes and both slide and pan samples were

Phase Diagram at 60°C

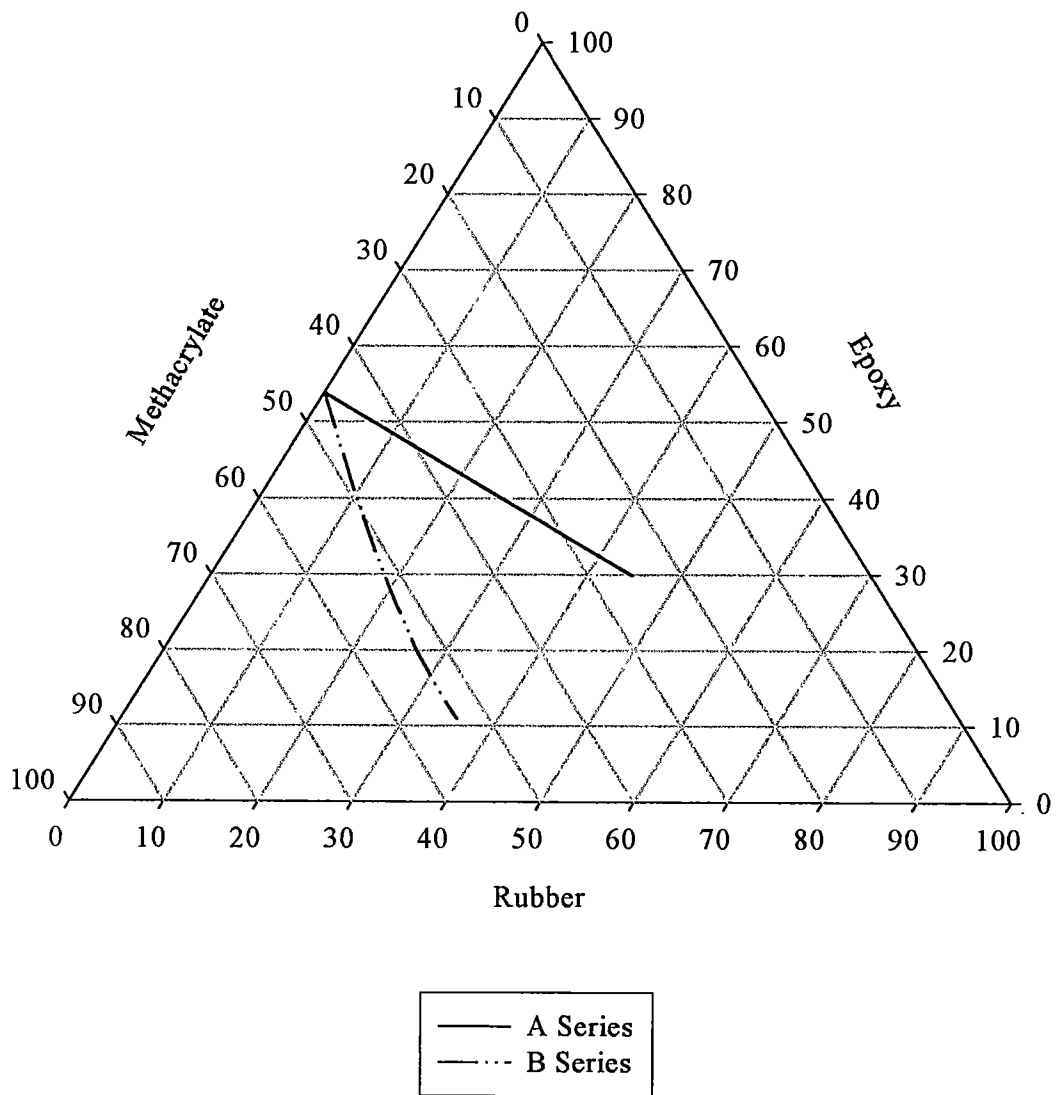


Figure 3.2: Phase diagram of study compositional lines.
ARL composition disregarded.

created in the same manner as the A series. The pans were degassed at 60°C for 20 minutes and cured for approximately 21 hours at 60°C.

As with the A series, the B series was also examined visually for phase separation after curing. More samples were created with w_{rubber} of 1%, 3%, 6%, 7%, 8%, and 9%. Figure 3.2 shows the compositional line for the B series.

Seven Component Group

The third group of samples is the important one. These are the samples of seven components that will be tested and provide the results for this study. The variables of mixing and the rubber compositions are the same as for the second group samples with one important change. One additional component, peroxide, is added to these samples. The peroxide is necessary so that a free radical cure of the methacrylate network can be thermally initiated. The second group of samples, without having the peroxide, consists only of a fully gelled epoxy network swelled by unreacted methacrylates. For the purposes of determining the phase separation region, this was not important, but for Izod testing it is. The third group can be fully cured and will be harder than the first. The samples were identified by the letter of the series and the % rubber, for example, $\alpha 0$, $\alpha 2$, $\beta 2$, $\beta 4$, etc.

α Series

This series uses the same variable values as the A series. The w_{rubber} is varied from 0 to 0.16 in 0.02 increments. The peroxide is added as 3.5% of the total

methacrylate weight (bisGMA and HDDMA). For the Izod tests, it is important that the samples be bubble free. When the samples were mixed, they were degassed in the plastic beakers, which gave more room than the pans to get all the air out. They were degassed for 10 minutes at 60°C. They were then poured into the Izod molds to fill them first and the remainder into pans, creating pan samples approximately 7 mm thick. The pans were then degassed for 5 more minutes. Both the molds and pans were cured in the oven first for about 21.5 hours at 60°C and then for 3 hours at 150°C to initiate free radical polymerization of the methacrylate network. More Izod samples of each composition were prepared following the same procedure, for a total of four Izod samples.

β Series

The compositional variables for this series are the same as the B series. The w_{rubber} is varied from 0.02 to 0.12 in 0.02 increments. Peroxide is also added to this series in the same proportion as the α series. The samples were degassed in the beakers and poured into the molds and pans in the same manner as the α series. They were cured at 60°C for about 22 hours and then at 150°C for 3 hours.

3.7 Optical Microscopy

The first detection method used is optical microscopy. Light is transmitted through a thin sample on a glass slide and provides a picture of the sample. Hoffman modulation contrast microscopy (HMC) was used to obtain these images. Figure 3.3

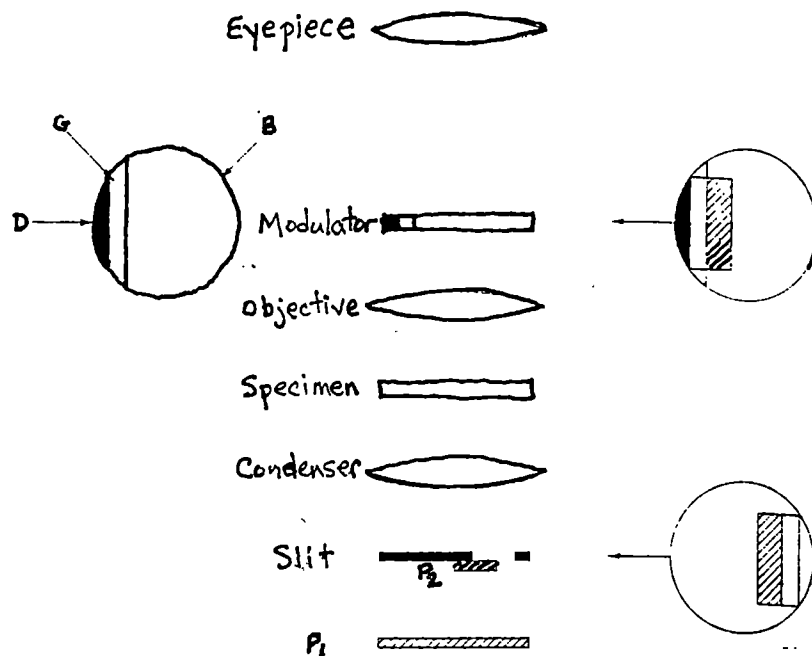


Figure 3.3: Schematic of Hoffman Modulation Contrast microscope.

The left plan view shows the modulator regions, dark (D), grey (G), and bright (B). The right plan view shows the slit and slit image correctly registered and superimposed on the modulator. P_1 and P_2 are polarizers.

Source: Hoffman, R. *Journal of Microscopy* 1977, 110, 205-222.

shows a schematic view of the components of HMC.²⁵ A slit aperture is placed below the condenser and a modulator is placed in the objective plane to modify a standard bright field microscope. The modulator causes no phase changes to the light, but affects the intensity of the transmitted light. There are three regions: dark, with <1% transmission, grey, with 15% transmission, and bright, with 100% transmission. Optimal image contrast is achieved when the polarizers are uncrossed and maximum resolution occurs when the plane of the optical gradient is parallel to the length of the slit.

HMC works when there is a difference between the refractive index of the particles and that of the matrix. These differences can be considered as a series of optical gradients around the boundaries of a round object. Figure 3.4 is an illustration of how the intensity is varied by the optical gradients.²⁵ Light passing only through the matrix material will be undeflected and will pass through the grey region of the modulator (figure 3.4c). The boundaries between the particles and matrix will cause the light to refract and pass through the bright or dark regions of the modulator. Since the optical gradients on either side of the particle are opposite in sign, one side of the particle will appear darker and the other brighter than the background. This produces a 3D effect which makes details easier to see. Another advantage to using HMC is the ability to focus on different levels through the thickness of the sample without interference from other levels.²⁵

The microscope is a Nikon Optiphot2-pol polarized transmitted light microscope. It is connected to a viewing monitor which is connected to a computer.

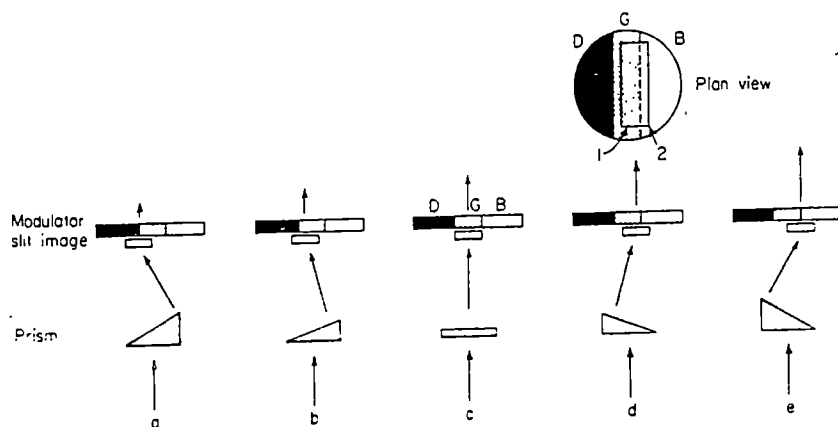


Figure 3.4: Illustration of intensity variation production in HMC.
 Length of arrow after modulator indicates intensity. The sum of the intensity of area 1 and 2 is the intensity after the modulator.

Source: Hoffman, R. *Journal of Microscopy* 1977, 110, 205-222.

The monitor must be calibrated using a stage micrometer. The program Image/VGA 400 Demo for Windows NT version 1.5 is used to capture a bitmap image of the sample. This image is then loaded into Macromedia xRes 3 where calculations of particle size can be determined by direct measurement based on the calibration. The slide samples of the 58005, 58005', A, and B series were examined using OM.

3.8 Scanning Electron Microscopy

Scanning electron microscopy is the second detection method. An SEM operates by having a focused beam of electrons scan across the surface of a sample. The sample must be electrically conductive so, for most polymers, this means that the surface must be coated with a thin layer of conductive metal, usually gold. As the electron beam scans, both secondary and backscattered electrons are emitted from the surface. The backscattered electrons were collected in this SEM work and provide a signal which is transformed into the picture that shows on the monitor. Magnification with this method can reach 100,000 times, though 5,000-10,000 times is the usual working condition.²⁶ A scale is shown on the screen so particle sizes can be directly measured from the picture on the monitor or by taking photos and measuring from them.

The equipment used was a Hitachi S-3500N. It is operated with a computer, so photos of the samples are digitally captured directly onto zip disks. The accelerating voltage used was 20 kV. The equipment was operated in the low vacuum mode with a pressure of 20-60 Pa in the chamber. This pressure, as opposed to a high vacuum

situation, is useful when examining polymer samples as it helps to lessen the amount of sample charging that occurs, but with the effect that the focus on the sample is decreased.

The pan samples of the 58005, 58005', α , and β series were examined using SEM. The samples required special preparation for this equipment. The 58005 and 58005' series samples were removed from the aluminum pans they were cured in. A strip approximately 1 cm wide was cut with a hacksaw from the center of each sample. The strips were placed in a vise and broken with a hammer at room temperature. There was no surface treatment. One fracture surface of each was coated by gold sputtering. The α and β series samples were given 4 different surface treatments. Strips were cut from the pan samples in the same method as above. The strips were cooled in liquid nitrogen for 10 minutes. They were then removed and quickly placed in the vise and broken with a hammer. One fracture surface with no etching was coated by gold sputtering. The other fracture surface was etched in an aqueous acid solution of 120 mL of H_2SO_4 and 57.5 mL of 10% CrO_3 (in H_2O) at 75°C for 25 minutes.¹⁸ The etched surface was rinsed in hot water for 20 minutes then coated by gold sputtering. One Izod bar of each sample composition was broken in the Izod tester at room temperature. One fracture surface was treated with the same acid solution for 50 minutes at 75°C , rinsed for 20 minutes and gold coated. The other fracture surface was etched in 10% CrO_3 (in H_2O) for 30 minutes, rinsed in hot water for 10 minutes, and coated by gold sputtering.²⁶

3.9 Izod Impact

The Izod impact test measures the impact resistance of a material when it is struck by a swinging weight. Testing was done following ASTM standard D256. In the Izod test, the sample is placed vertically in the clamp with the notched side facing the weight. The weighted arm is dropped from a standard height, breaks the sample, and rises to a lower height. The height difference is due to the energy absorbed by the sample in the breaking process, the impact resistance.¹⁷ The value is read directly off the scale on the front of the machine. Figure 3.5 shows the setup of the Izod. The tester used is an Olsen Model 66 Plastic Impact Testing Machine. The weight of the arm provided a full scale impact resistance of 2.825 J. Additional weight can be placed on the arm, but is not necessary in this case. The samples were placed in the machine with the notch even with the top of the vise so that the sample is extending 28.5 mm from the top of the clamp. The weight strikes the sample 6.35 mm from the top.

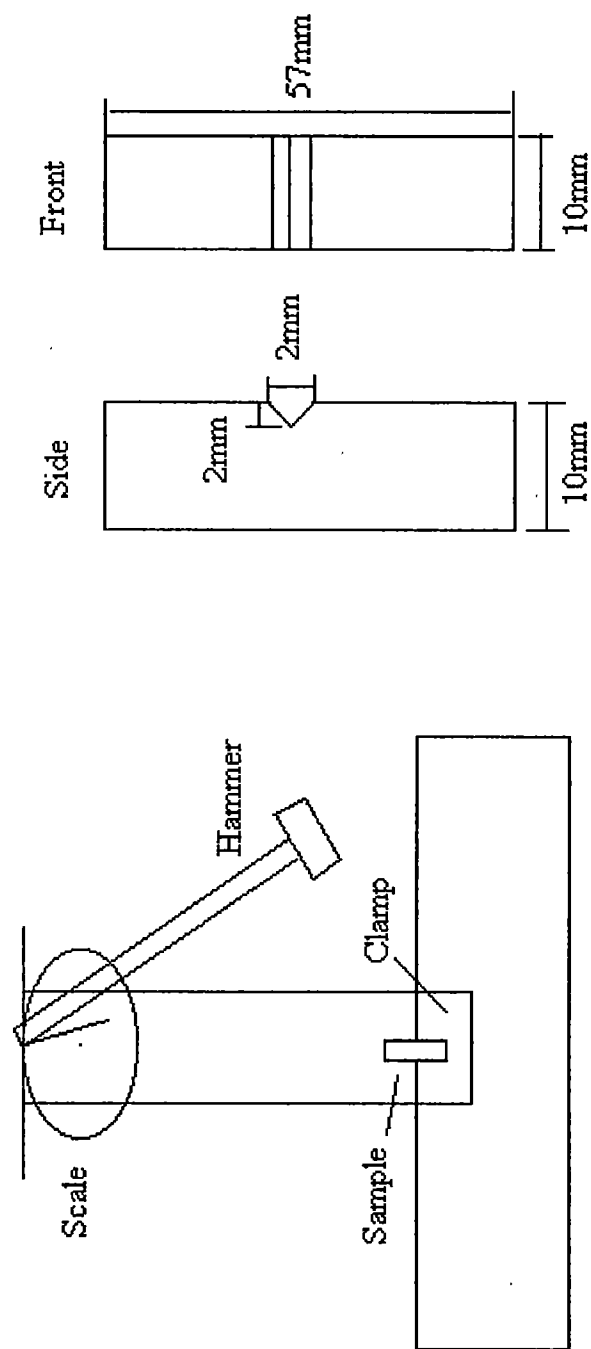


Figure 3.5: Izod Impact Tester equipment setup.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Compositions for Study

The determination of the appropriate rubber composition ranges was provided by the A series and B series samples. After mixing and curing, visual inspections were performed to decide which samples were cloudy and which were clear. Cloudiness is an indication of phase separation.

For the A series, samples were made with rubber compositions of 0% to 30% at 5% intervals. It was determined that the 5% and 10% rubber samples were cloudy, but the 15% and higher were clear. More samples were mixed at 1%, 3%, 6%, 8%, 11%, 12%, 13%, and 14%. All of these samples were cloudy upon curing. So it was determined that the study range for the A series was 0% to 15% rubber content. This shows that this system exhibits an LCST behavior typical of epoxy-rubber systems.

The B series range was determined in the same manner. Samples were prepared with rubber compositions of 5% to 30% at 5% intervals. The 5% rubber sample was the only one that was cloudy. More samples were mixed with compositions of 1%, 3%, 6%, 7%, 8%, and 9%. All of these samples appeared cloudy upon curing. The study range for the B series was therefore set at 0% to 10% rubber.

Figure 4.1 is a phase diagram which shows the regions of phase separation for both series of samples based on visual inspection.

4.2 Optical Microscopy

Optical microscopy was performed on all of the samples of the first and second groups. The object was to determine the sizes of the particles in the samples. The sample slides were observed using HMC with the highest magnification, 400X. Figure 4.2 shows a photo of a stage micrometer with divisions of 10 μm for calibration purposes.

None of the samples with seven components showed particles and only the 20% rubber samples of the three component group did. The samples 20 and 20' both clearly showed large particles. However, the particles were not round or oval, but worm-like and S-shaped in appearance, an indication that spinodal decomposition is responsible for particle growth in these samples. Figure 4.3 shows digital photos taken of both samples so that particle size measurements could be taken. Because of the nature of the particle shapes, measurement of the particle dimensions is difficult. A number of measurements were taken on many different particles in the sample. Table 4.1 gives the average values of these measurements for particles.

As previously stated, the A series samples up to 15% rubber and the B series to 10% rubber were visually cloudy. This indicates that the index of refraction for the rubber particles is different than that of the epoxy. If the particles are large enough (i.e. greater than $\sim 1 \mu\text{m}$, they should be seen using HMC microscopy. Another detection

Phase Diagram at 60°C

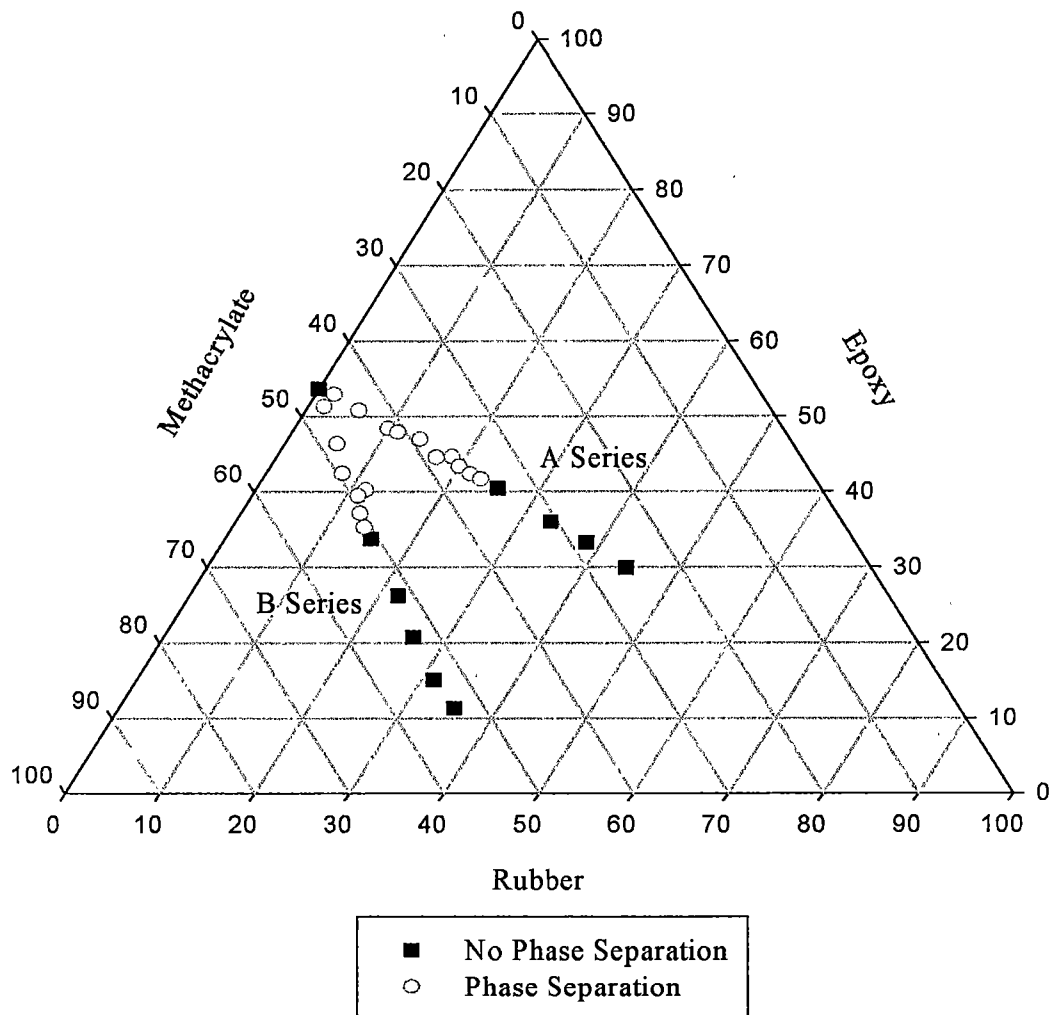


Figure 4.1: Phase diagram based on visual inspection.
ARL composition disregarded.

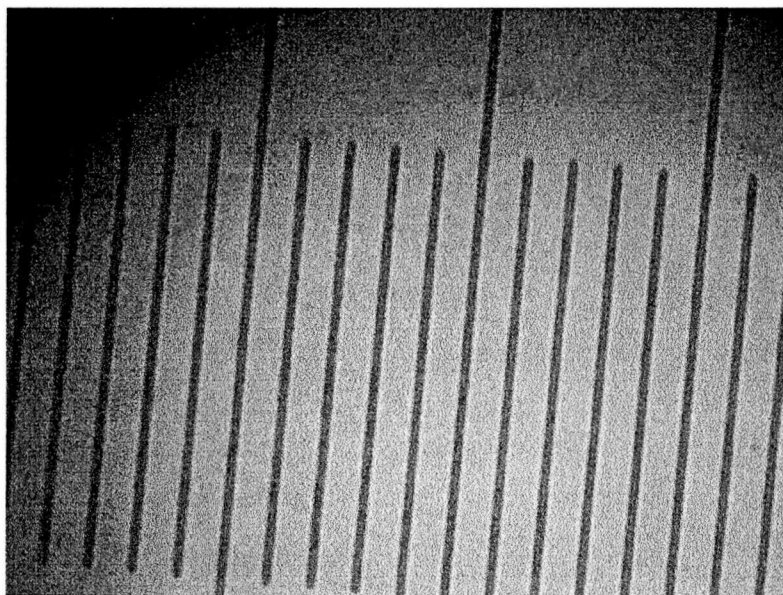
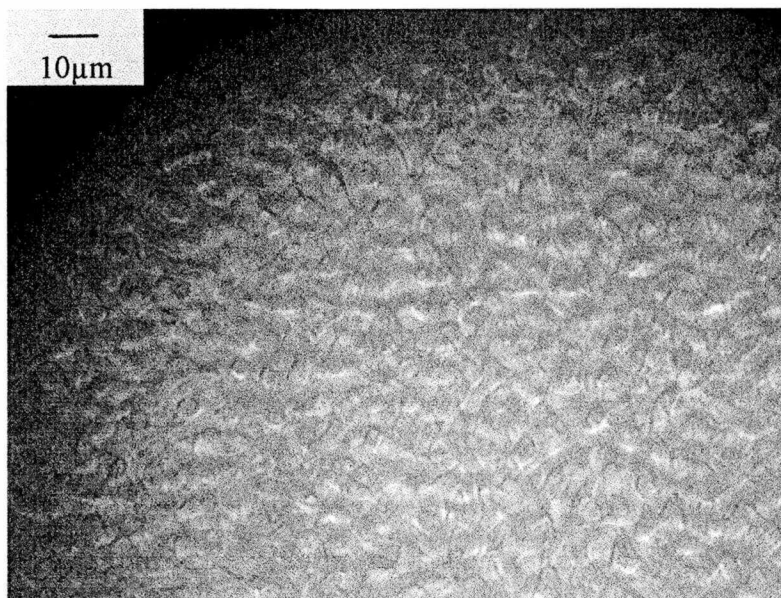


Figure 4.2: OM photo of stage micrometer.
Each division is $10\mu\text{m}$.



(a) Sample 20, 19.93% rubber.



(b) Sample 20', 19.89% rubber.

Figure 4.3: OM photos of three component samples.

Table 4.1: OM results for the three component samples.

Sample Number	Average Measured Particle Sizes	Average
20	13 μm * 4 μm	8.5 μm
20'	14 μm * 4 μm	9.0 μm

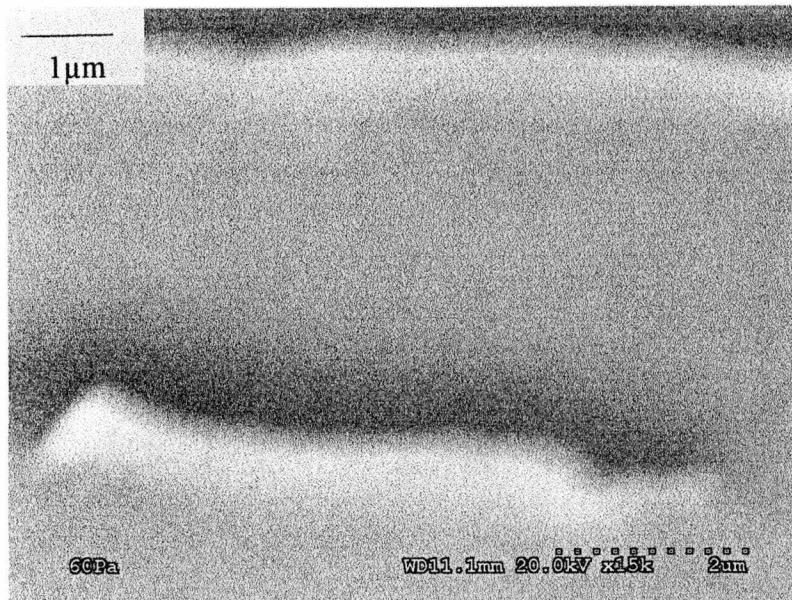
method is necessary for determining the size of the particles in the seven component samples since they were not seen optically.

4.3 Scanning Electron Microscopy

The third group of samples was mixed so that fully cured samples could be achieved. Peroxide was added so that free radical initiation of the methacrylate network formation would occur. The cure was done in two steps, at two different temperatures, so that fully cured samples resulted. These samples had the same compositions as the trial group samples, and are expected to have the same particle sizes. These samples were examined using SEM. The three component group was examined again to confirm the results of OM. The equipment captured digital pictures of all the samples from which particle sizes were measured.

Figures 4.4 and 4.5 are photos of the samples of the three component group. The samples were not etched, but were gold coated. There are no particles seen in the 0% rubber sample, indicating that any particles seen are not a matrix feature. All the other samples clearly showed particles. It can be seen that there are both particles and holes on the surface of the samples. This indicates that when the samples were broken, the rubber particles separated from the matrix and the fracture did not go through the particles. Table 4.2 lists the values of particle size determined from the photos.

The particles of the 0-15% samples were small and round, an indication that nucleation and growth is the method of phase separation for small rubber concentrations in the three component system. For 0% and 5% rubber contents, the

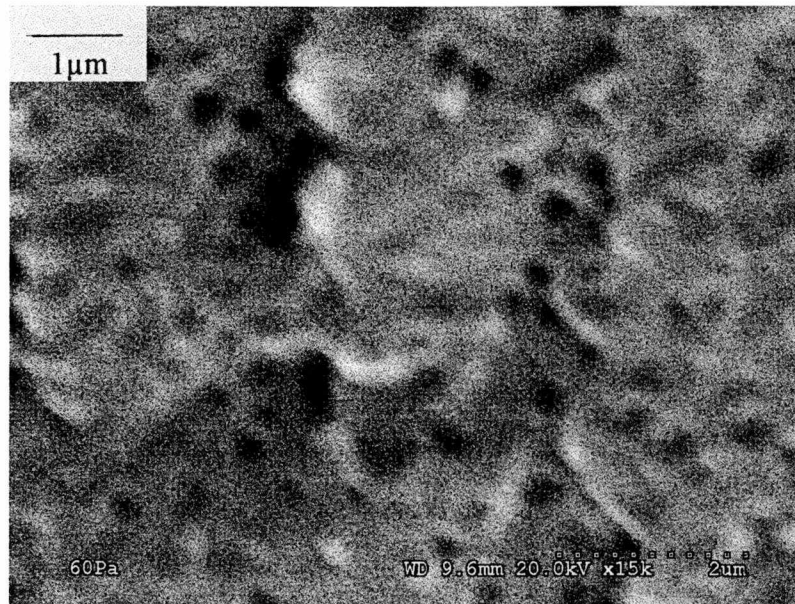


(a) Sample 0, 0% rubber.

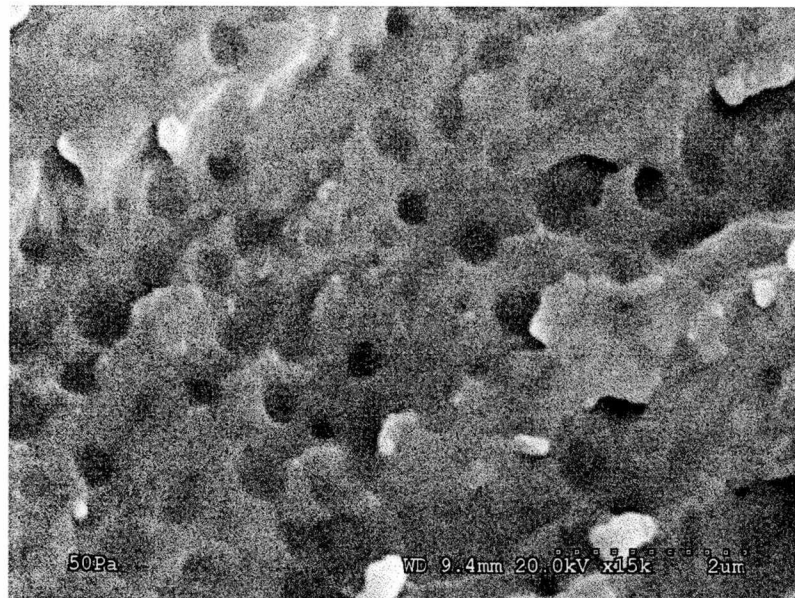


(b) Sample 5, 5.07% rubber.

Figure 4.4: SEM photos of 58005 series samples.

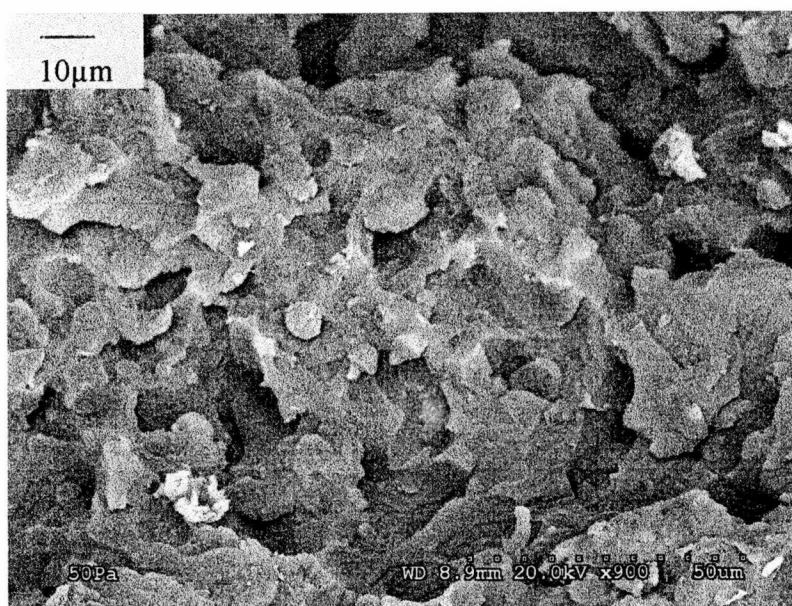


(c) Sample 10, 10.04% rubber.



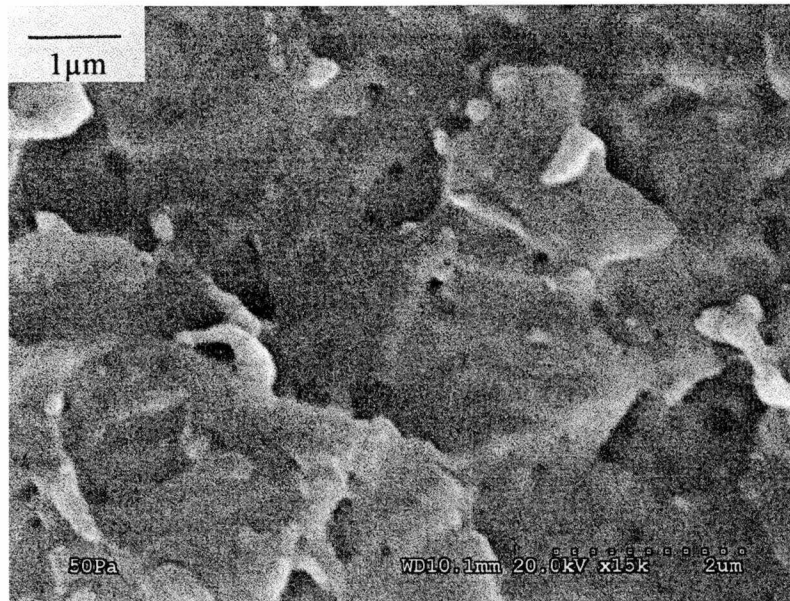
(d) Sample 15, 15.07% rubber.

Figure 4.4 (cont.)

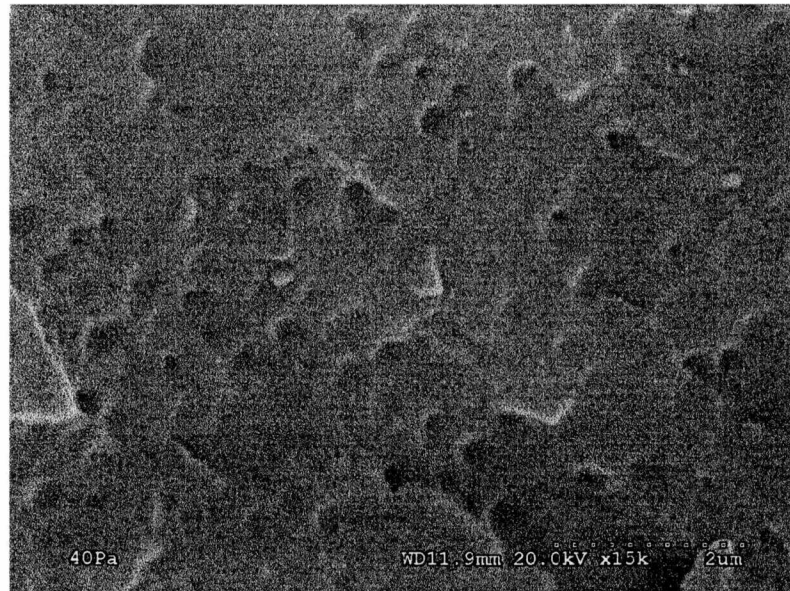


(e) Sample 20, 19.93% rubber.

Figure 4.4 (cont.)

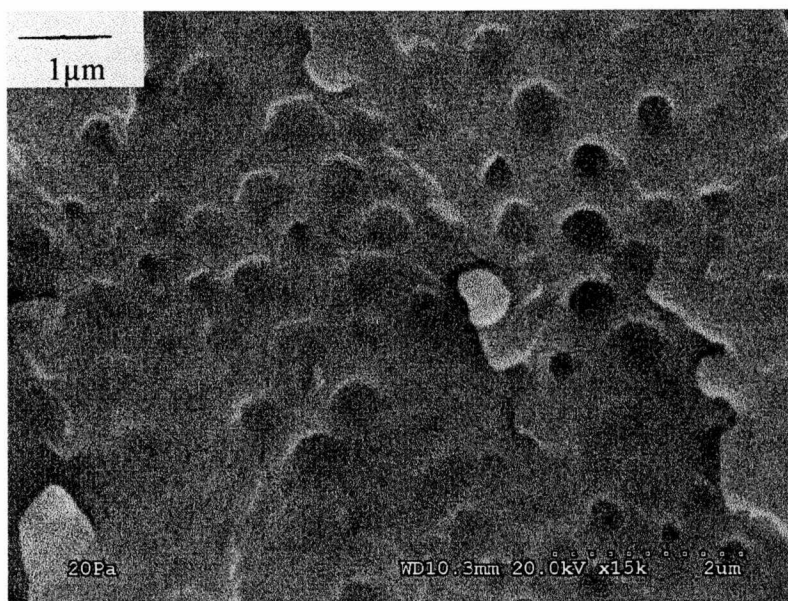


(a) Sample 5', 5.01% rubber.

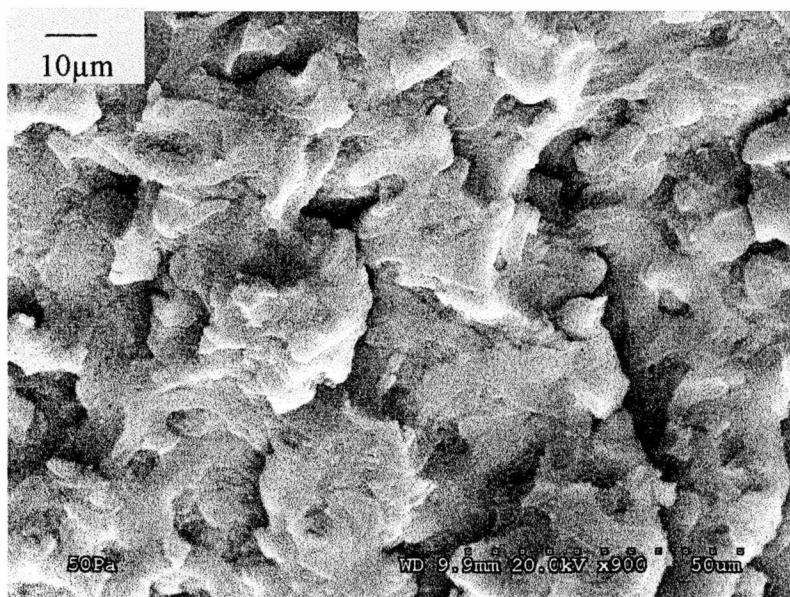


(b) Sample 10', 9.91% rubber.

Figure 4.5: SEM photos of 58005' series samples.



(c) Sample 15', 14.92% rubber.



(d) Sample 20', 19.89% rubber.

Figure 4.5 (cont.)

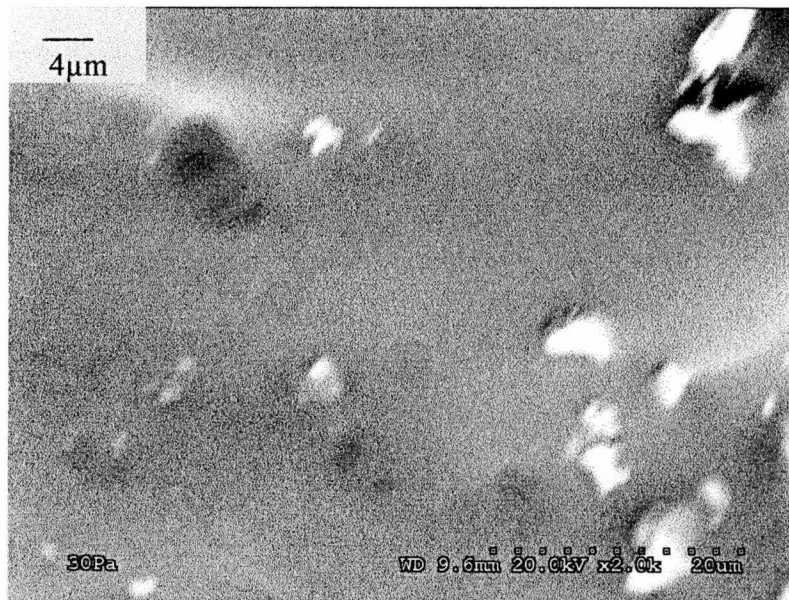
Table 4.2: SEM results for the three component samples.

Sample Number	Average Particle Diameter (μm)	Sample Number	Average Particle Diameter (μm)
0	none		
5	0.32	5'	0.28
10	0.36	10'	0.32
15	0.44	15'	0.44
	Average Domain Size (μm)		Average Domain Size (μm)
20	8.28	20'	8.97

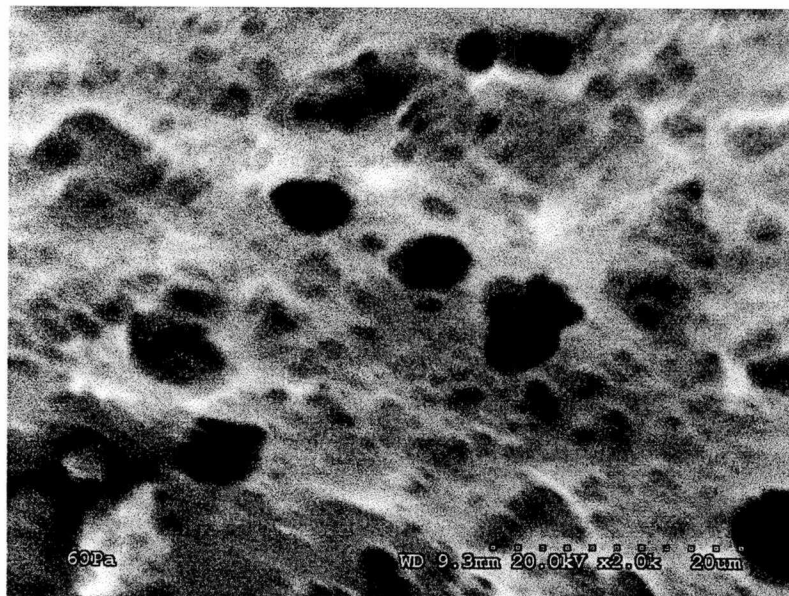
samples containing phenol had smaller particles, as was the expected result. The particles in the samples with 15% rubber did not appear to be affected by the presence of phenol, as they were the same size. The features in the 20% rubber samples were much, much larger, and the phenol containing sample had a greater domain size than that without. The structure is representative of the spinodal decomposition and coarsening type of phase separation. This observation in the SEM photos confirms what was seen in the optical micrographs of the 20% samples.

Four different surface treatments were tried on the seven component samples. The samples that were not etched did not present particles. The samples etched with the aqueous acid solution also did not show particles. Etching with the 10% CrO_3 acid did allow the particles to be seen by dissolving the rubber out of the matrix and leaving holes on the surface. Figures 4.6 and 4.7 are photos of the seven component samples. Table 4.3 lists the values of particle sizes measured. Figure 4.8 shows histograms of particle size distribution in all of the seven component samples.

Particles were not seen in either the sample with 0% rubber or the sample β_{12} , with 12% rubber, again indicating that any particles seen are not matrix features. The rest of the samples showed small, round particles, indicating that nucleation and growth was the mechanism of phase separation in the seven component samples. There is no evidence of spinodal decomposition present in these samples. There is evidence of air bubbles in many of the photos, so it was necessary to ensure that the particle holes were measured in the photos and not the bubbles. In the α series, the particle sizes increased with the addition of rubber to a maximum of $\sim 3 \mu\text{m}$ at 4% and then

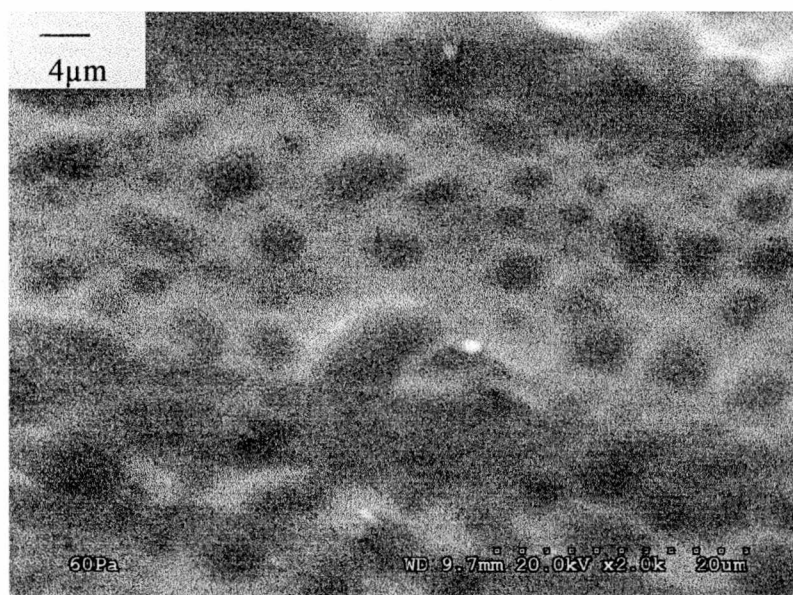


(a) Sample α_0 , 0% rubber.

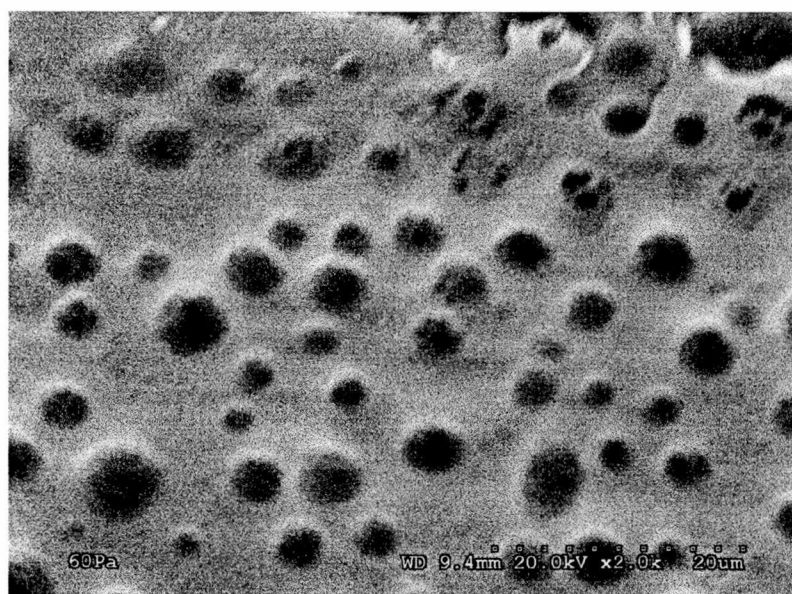


(b) Sample α_2 , 2.05% rubber.

Figure 4.6: SEM photos of α series samples.

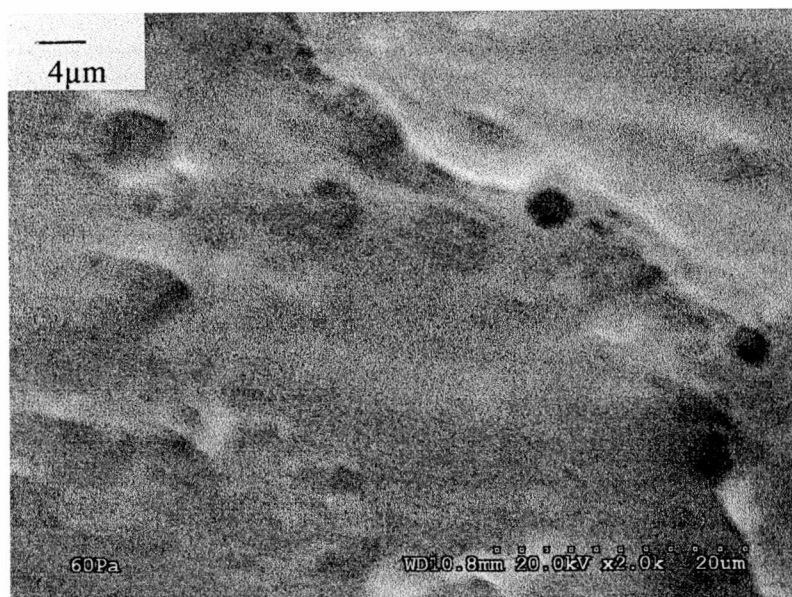


(c) Sample α_4 , 4.12% rubber.

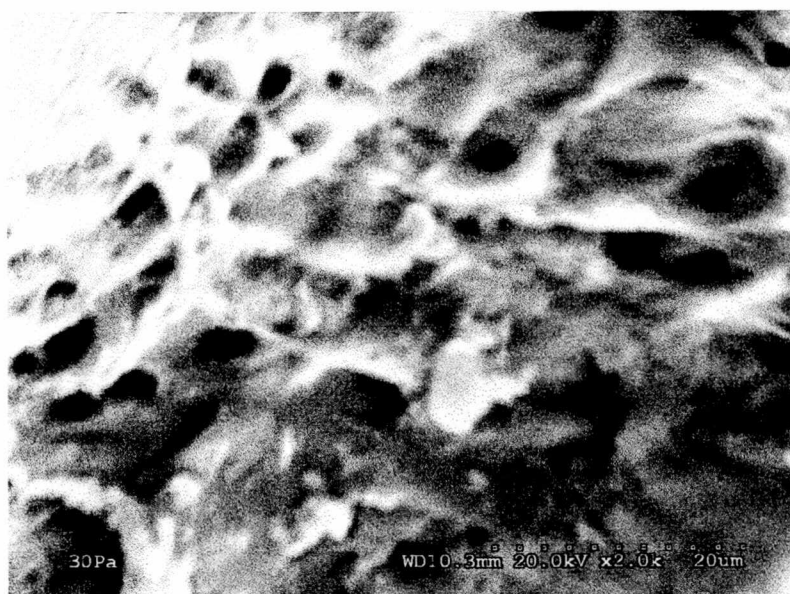


(d) Sample α_6 , 6.02% rubber.

Figure 4.6 (cont.)



(e) Sample α 8, 7.95% rubber.

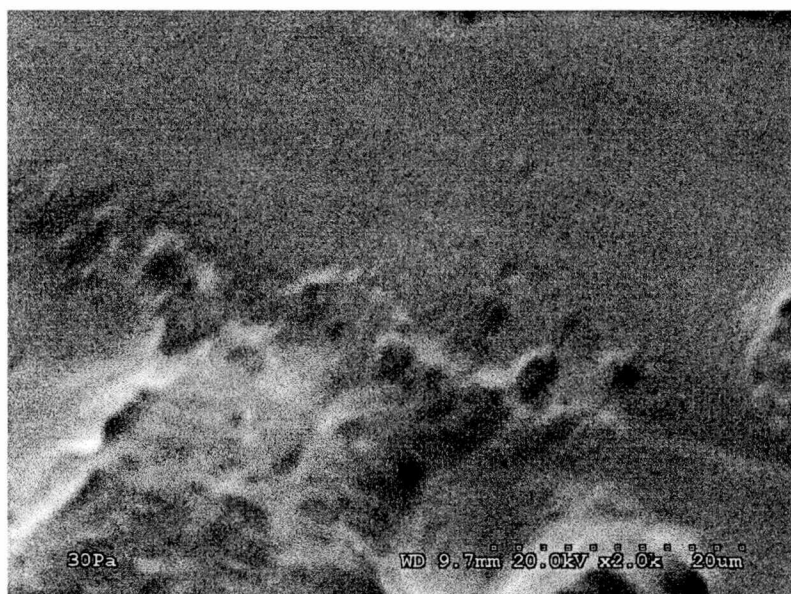


(f) Sample α 10, 10.01% rubber.

Figure 4.6 (cont.)

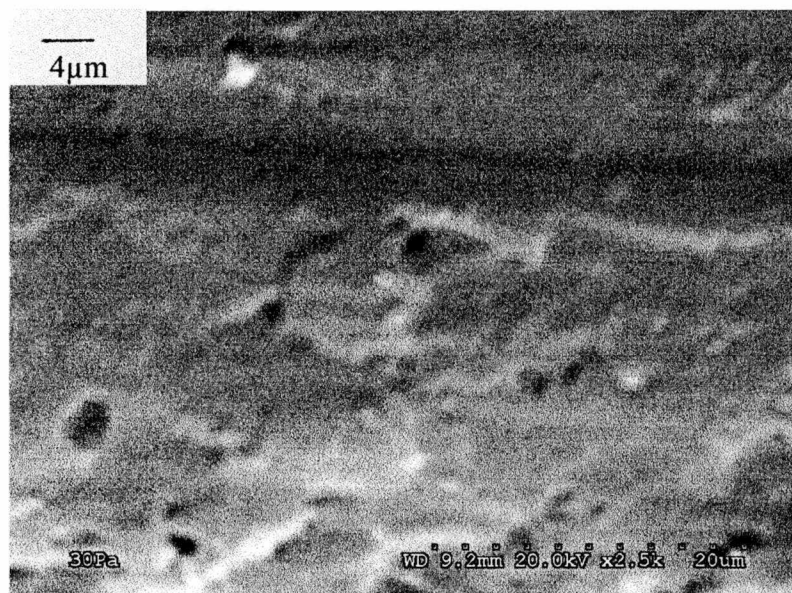


(g) Sample α 12, 11.97% rubber.



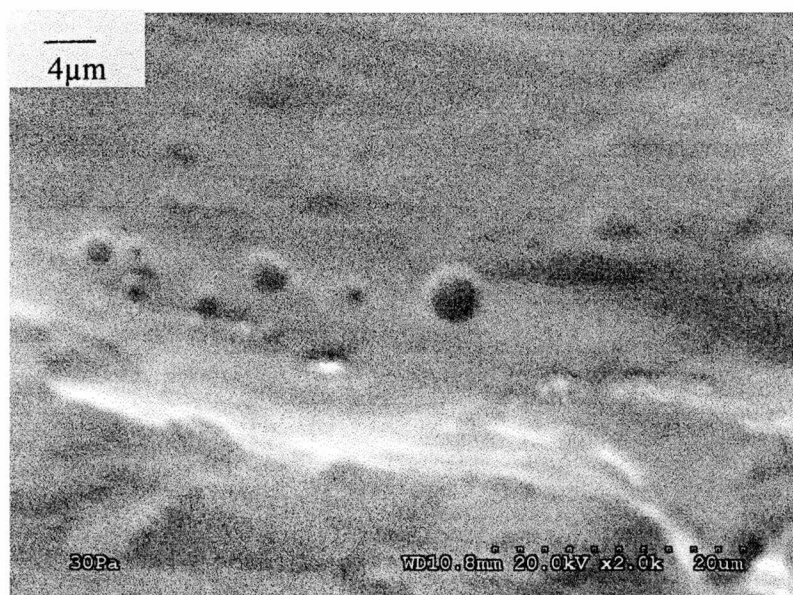
(h) Sample α 14, 13.86% rubber.

Figure 4.6 (cont.)

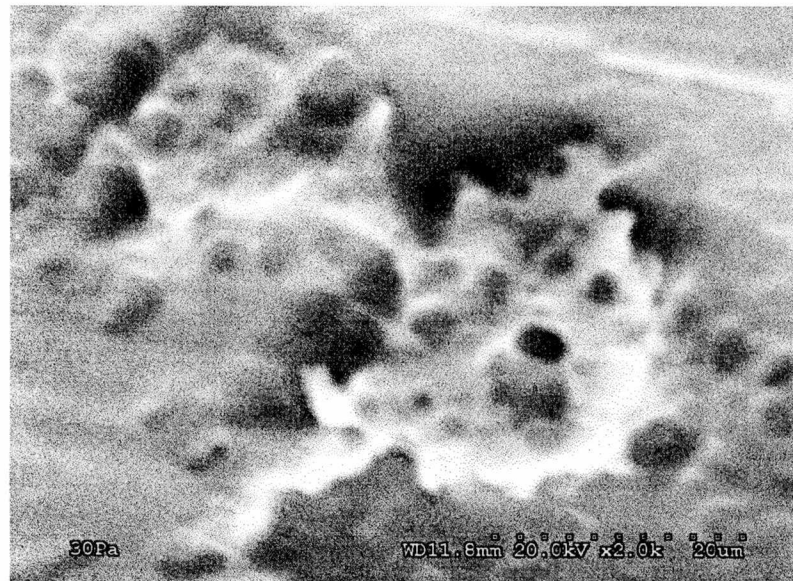


(i) Sample $\alpha 16$, 15.97% rubber.

Figure 4.6 (cont.)

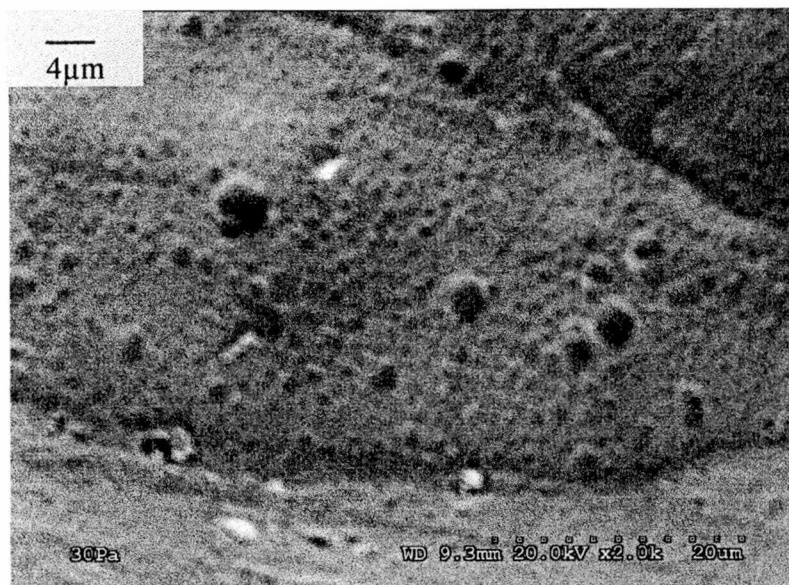


(a) Sample β_2 , 2.03% rubber.

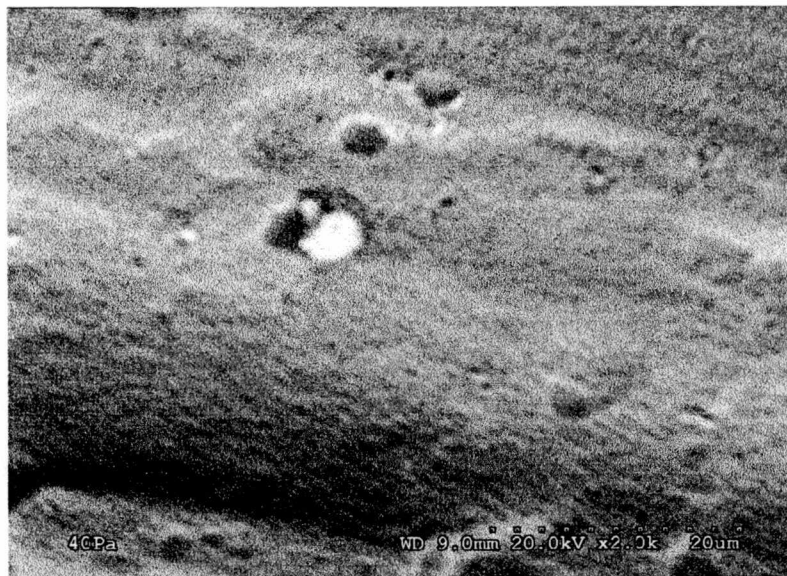


(b) Sample β_4 , 3.97% rubber.

Figure 4.7: SEM photos of β series samples.



(c) Sample β_6 , 6.04% rubber.



(d) Sample β_8 , 7.88% rubber.

Figure 4.7 (cont.)



(e) Sample β_{10} , 10.03% rubber.

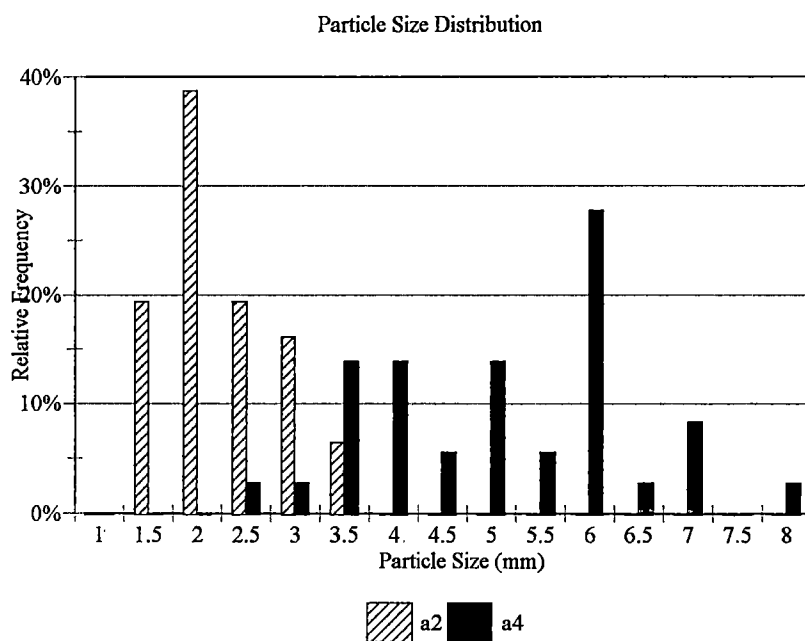


(f) Sample β_{12} , 12.11% rubber.

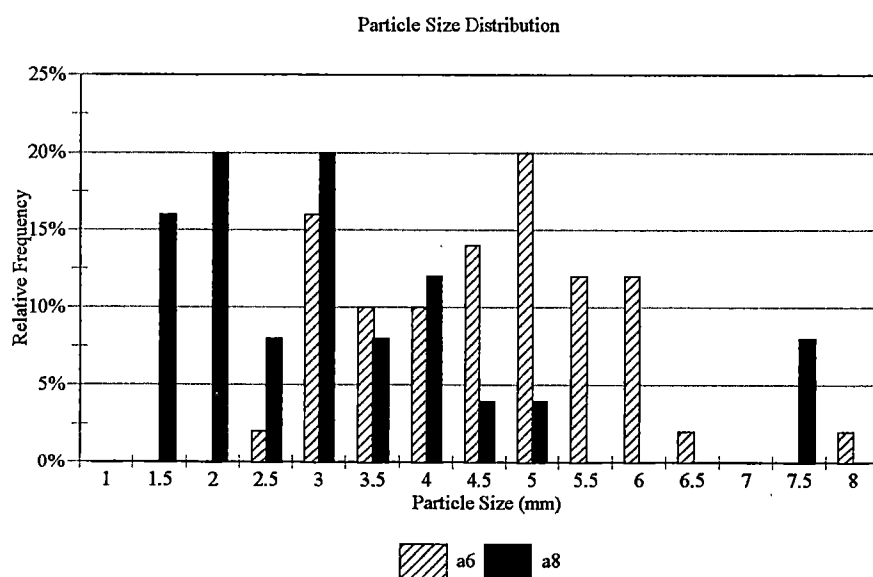
Figure 4.7 (cont.)

Table 4.3: SEM results for the seven component samples.

Sample Number	Average Particle Size (μm)	Sample Number	Average Particle Size (μm)
$\alpha 0$	none, dirt		
$\alpha 2$	1.37	$\beta 2$	1.39
$\alpha 4$	3.10	$\beta 4$	1.55
$\alpha 6$	2.79	$\beta 6$	1.07
$\alpha 8$	1.94	$\beta 8$	0.76
$\alpha 10$	1.75	$\beta 10$	0.76
$\alpha 12$	0.86	$\beta 12$	none, dirt
$\alpha 14$	1.28		
$\alpha 16$	1.20		

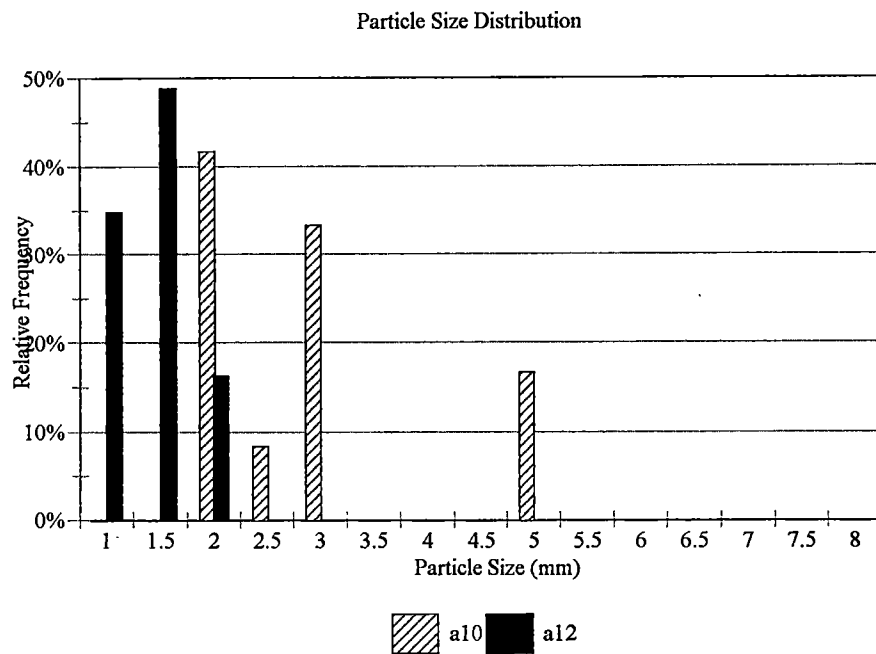


(a) Samples $\alpha 2$ & $\alpha 4$.

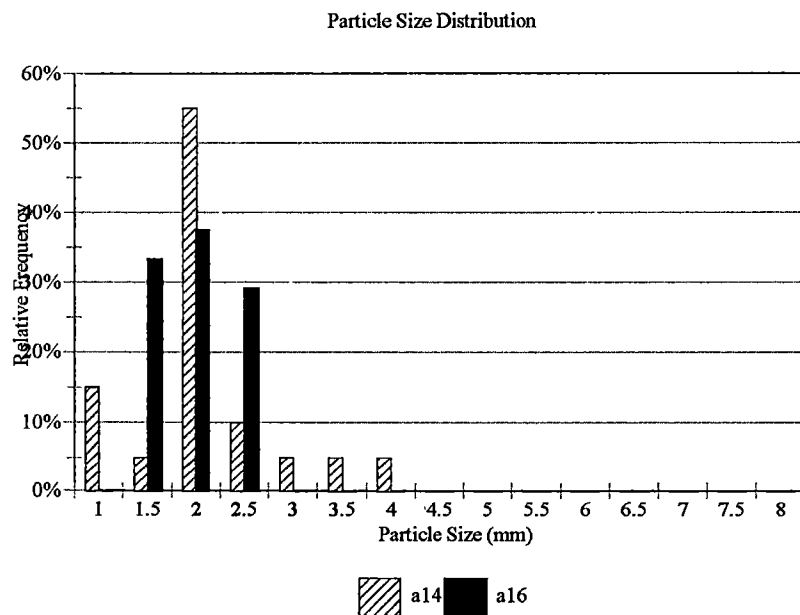


(b) Samples $\alpha 6$ & $\alpha 8$.

Figure 4.8: Particle size distributions for seven component samples.
Multiply mm by 14/23 to convert to actual size in μm .

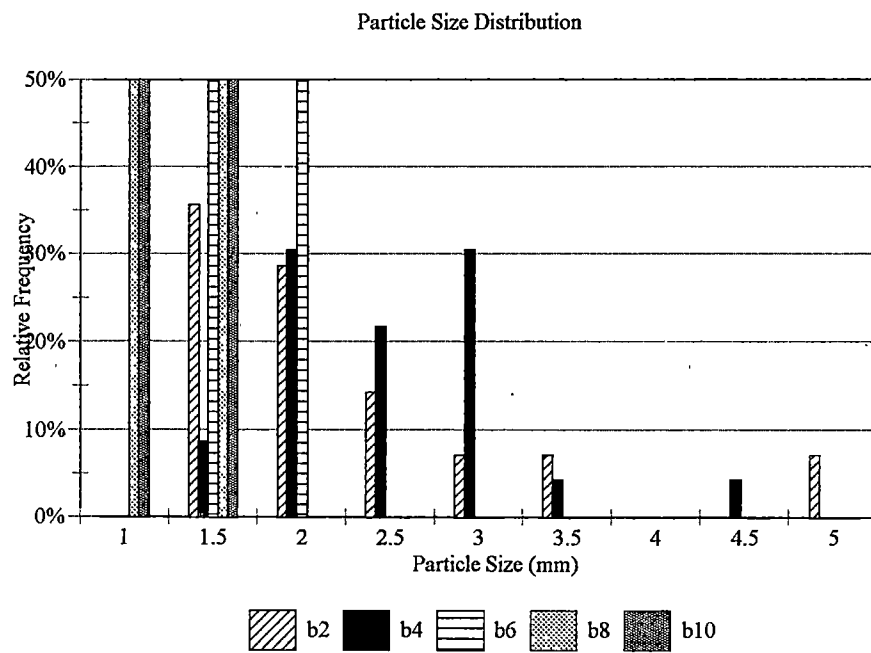


(c) Samples $\alpha 10$ & $\alpha 12$.



(d) Samples $\alpha 14$ & $\alpha 16$.

Figure 4.8 (cont.)



(e) β samples.

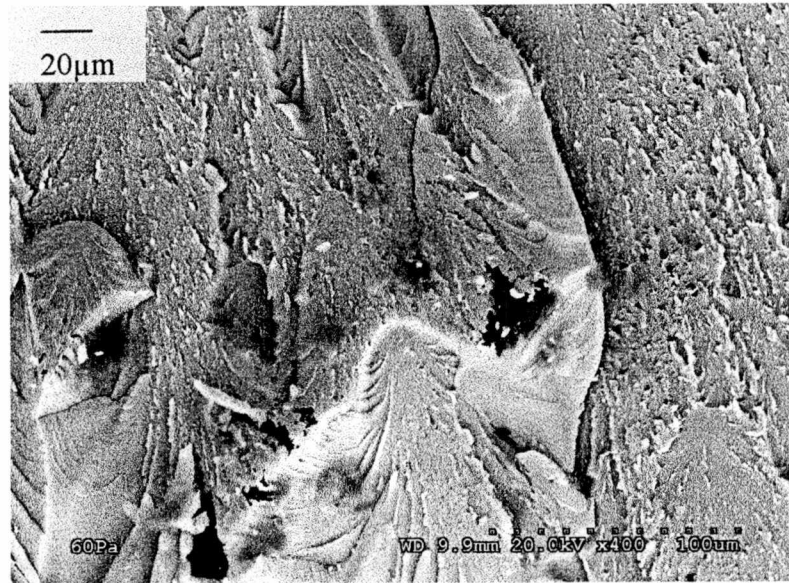
Figure 4.8 (cont.)

decreased through 16% rubber. The maximum particle volume occurred at 12% rubber. In the β series, the particles reached a maximum size of $\sim 1.5 \mu\text{m}$ at 4% rubber and decreased through 10% rubber. The volume of particles was a maximum at 6% rubber content. From figure 4.8 it can be noted that, in the α series, the rubber concentrations from 2-10% had relatively wide distributions in particle size. The higher concentrations, 12-16% rubber, showed narrow size distributions. The same was observed in the β series, where 2 and 4% rubber had wide distributions and 6-10% showed very narrow distributions.

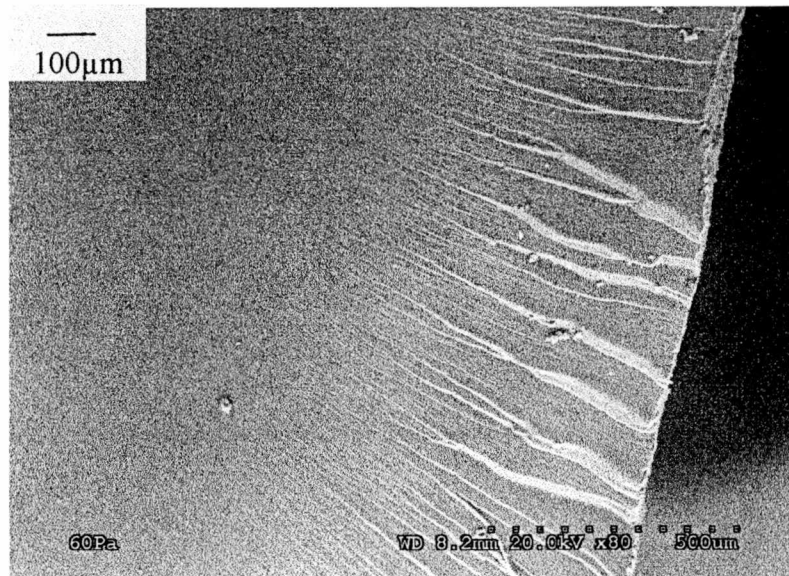
Figure 4.9 shows SEM photos of some of the unetched samples of the seven component group. The fracture patterns and the deformations do not appear related to the rubber concentrations in each sample. There is evidence of air bubbles in these as well, but no evidence of particles. Figure 4.10 is a phase diagram which shows the range of phase separation for the α and β series based on the SEM results. The areas of phase separation correspond with those determined by the visual inspection of the samples for cloudiness.

4.4 Izod Impact

Izod impact tests were performed on the seven component samples so that a correlation could be made between both rubber concentration and the particle size and the impact strength of the samples. Four samples of each composition were tested in the apparatus and the impact energy recorded for each. Table 4.4 lists the values for these samples. The error calculated is the standard deviation. Figures 4.11 and 4.12



(a) Sample α_0 , 0% rubber.

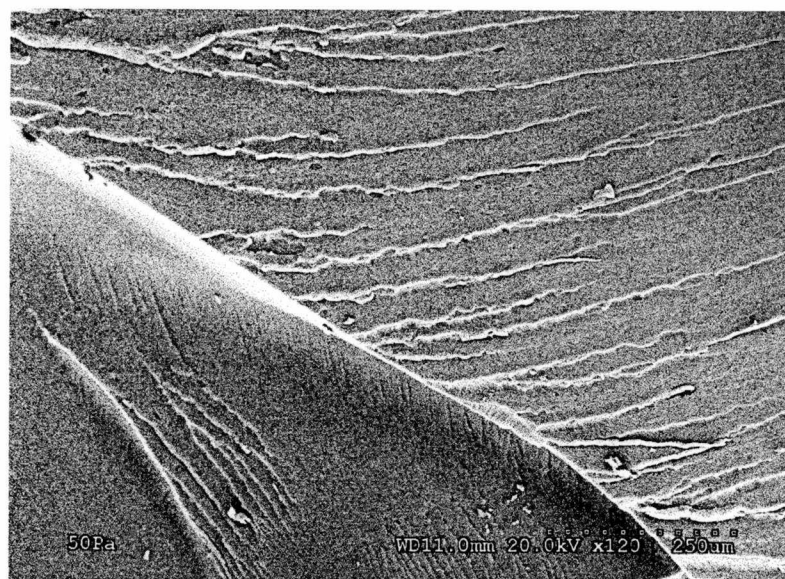


(b) Sample α_6 , 6.02% rubber.

Figure 4.9: SEM photos of unetched seven component samples.



(c) Sample β_6 , 6.04% rubber.



(d) Sample β_{12} , 12.11% rubber.

Figure 4.9 (cont.)

Phase Diagram at 60°C

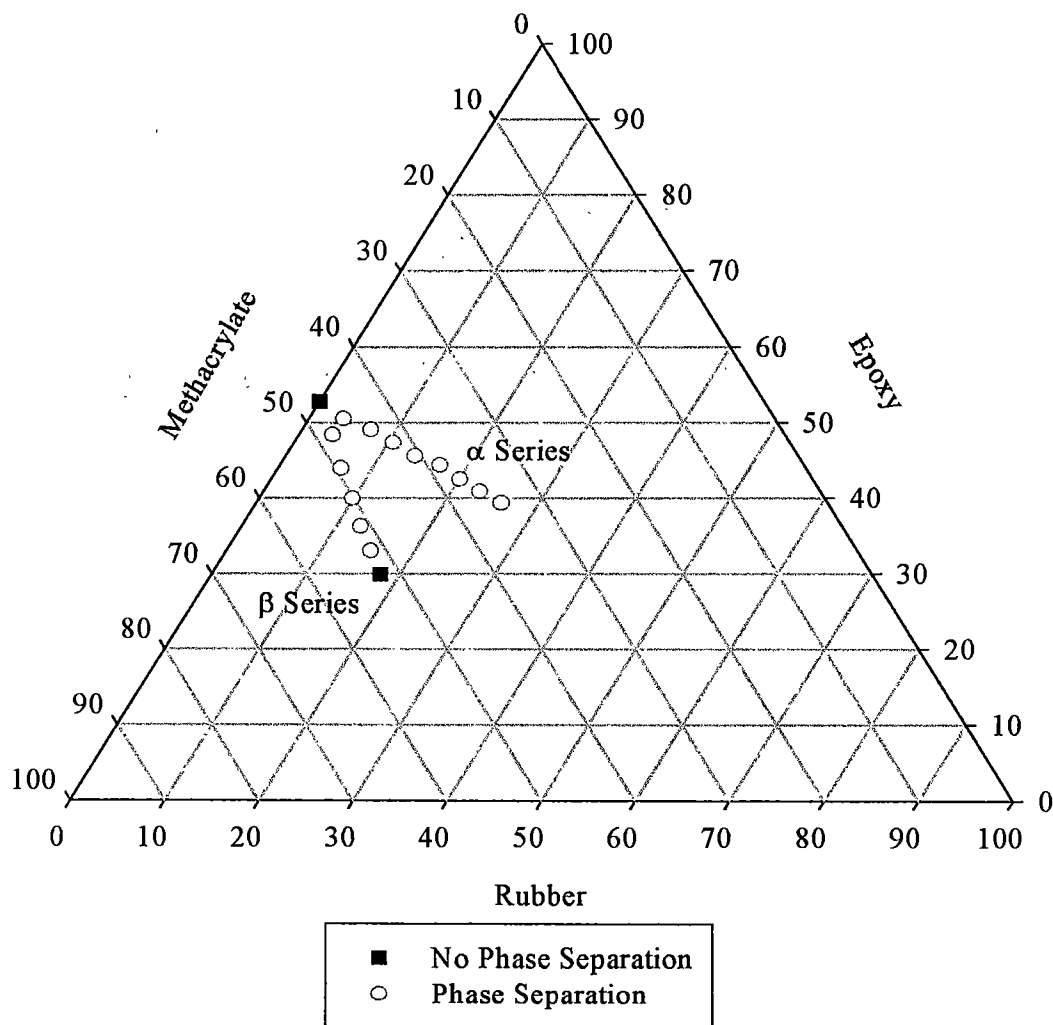


Figure 4.10: Phase diagram based on experimental data.
ARL composition disregarded.

Table 4.4: Izod impact results for the seven component samples.

Sample Number	Impact Strength (J/m ²)	Sample Number	Impact Strength (J/m ²)
$\alpha 0$	33.8 ± 4.2		
$\alpha 2$	30.2 ± 2.5	$\beta 2$	27.1 ± 1.8
$\alpha 4$	29.9 ± 3.9	$\beta 4$	29.1 ± 2.1
$\alpha 6$	41.3 ± 15.3	$\beta 6$	39.3 ± 15.1
$\alpha 8$	44.4 ± 15.4	$\beta 8$	47.4 ± 19.4
$\alpha 10$	60.9 ± 26.3	$\beta 10$	49.3 ± 24.0
$\alpha 12$	43.0 ± 12.3	$\beta 12$	29.0 ± 4.1
$\alpha 14$	57.8 ± 15.5		
$\alpha 16$	55.2 ± 12.8		

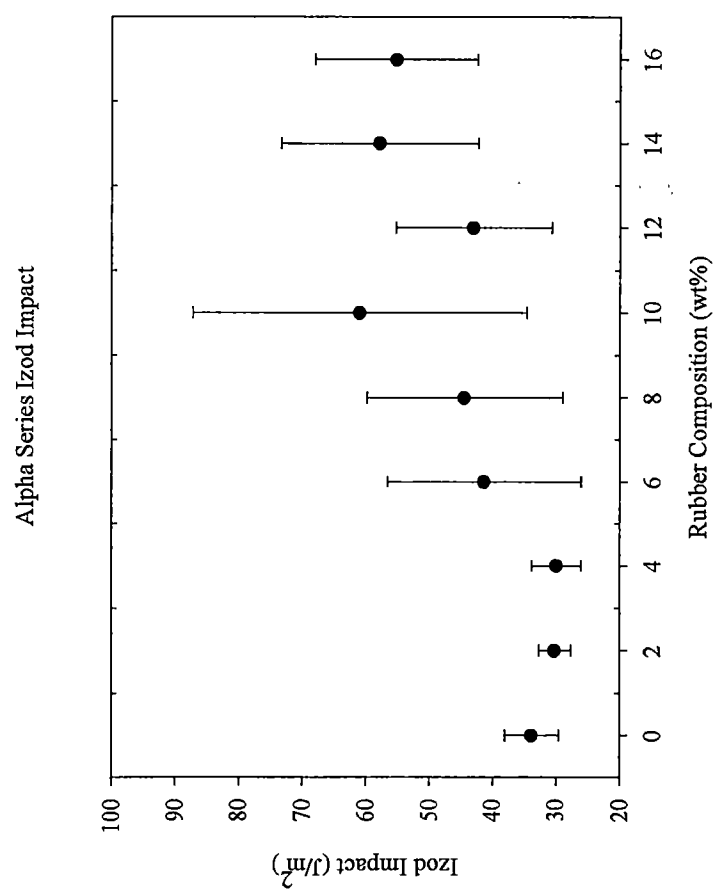


Figure 4.11: Plot of Izod strength v. rubber content for α series.

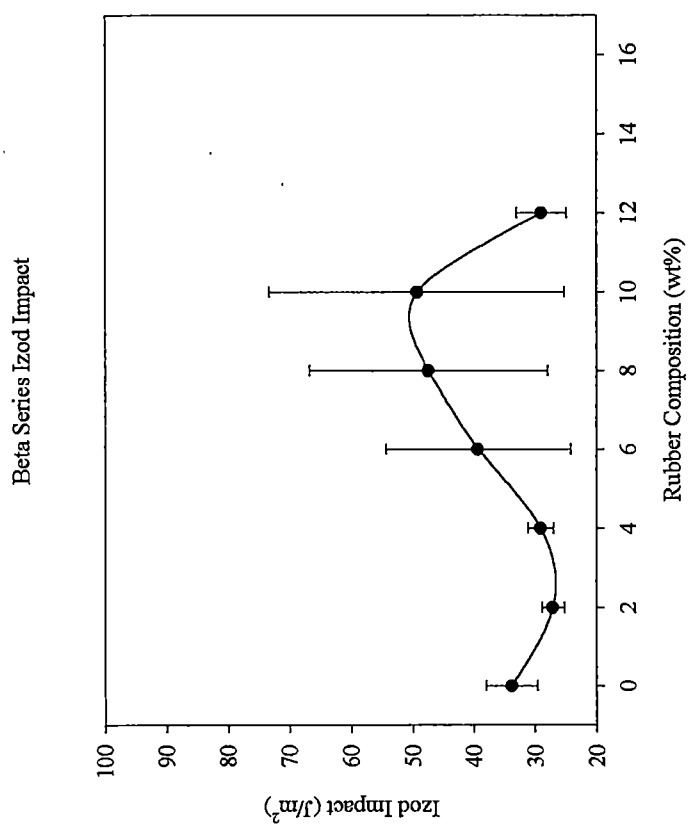


Figure 4.12: Plot of Izod strength v. rubber content for β series.

plots of impact strength v. rubber concentration. Figures 4.13 and 4.14 are plots of impact strength v. particle size.

It can be seen from figures 4.11 and 4.12 that there is a small amount of error in the samples with no particles (both $\alpha 0$ and $\beta 12$) and those with very low rubber concentrations (2% and 4%). The samples with 6% and greater rubber concentrations (up to 10% in the β series) showed a very large amount of scatter in the impact results. The error appears to have some correlation to the volume fraction of rubber in the samples, when phase separation occurs. The peak value of impact strength for the α series occurs at about 10% rubber, between the concentration with the largest particles (4%) and that with the greatest concentration of particles (12%). For the β series, the peak value is also at 10% rubber, the greatest concentration for which particles formed. There is an apparent increase in Izod strength with the increase in rubber concentration up to 15% for the α series and 10% for the β series, the same values seen in the initial visual inspection of the samples, though the error makes a definite conclusion difficult to state.

Examination of figure 4.13 shows that there is no apparent connection between particle size and Izod strength in the α series. Particles in the 1.4 μm range showed both low and high values of impact strength. Large scatter was seen for particle sizes over the whole range of recorded sizes. Figure 4.14 shows that the β series does not follow this trend. The largest particle sizes were associated with the smallest degree of scatter in Izod results and the smaller particles had the most degree of scatter.

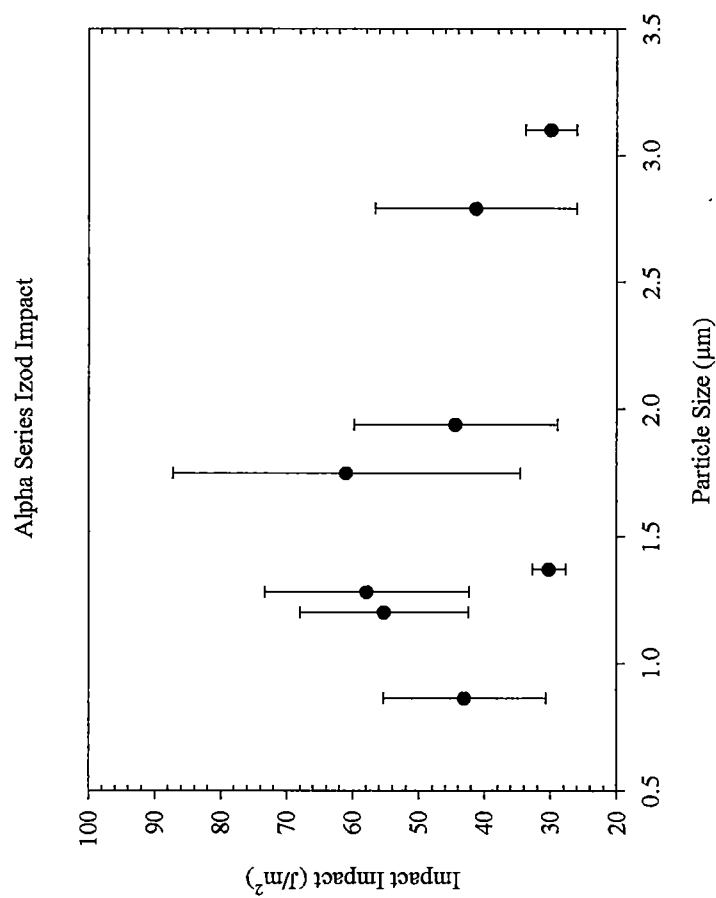


Figure 4.13: Plot of Izod strength v. particle size for α series.

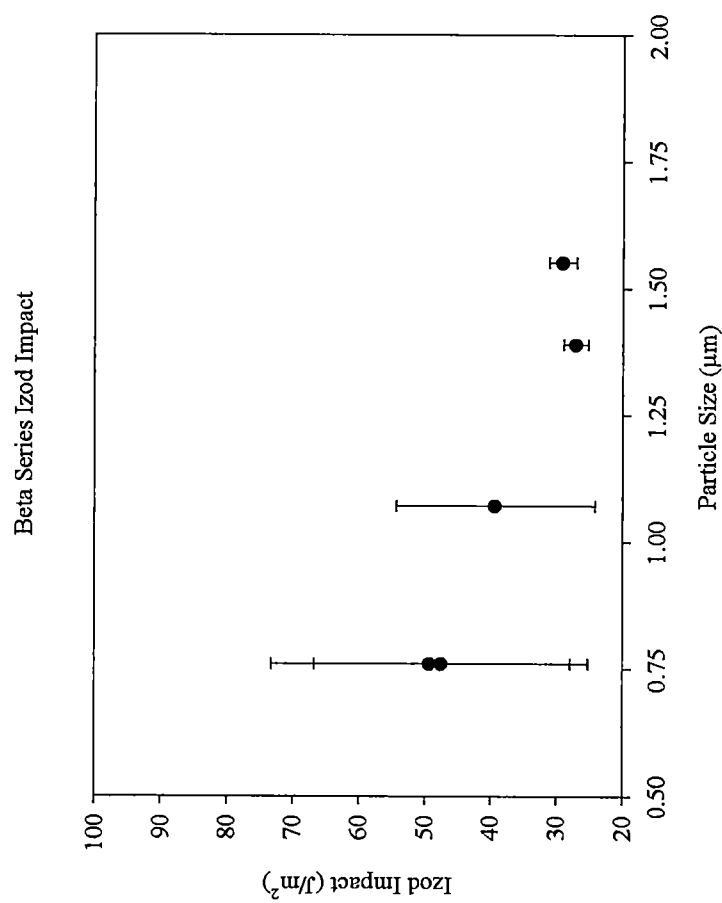


Figure 4.14: Plot of Izod strength v. particle size for β series.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The collection of data for this experiment proved to be more difficult than originally expected. Whereas it is assumed that nucleation and growth is the mechanism of particle growth in these epoxy systems, the type of structure seen in the optical micrographs is more representative of spinodal decomposition. The data from the OM showed periodic structures of domain size $8.5\text{ }\mu\text{m}$ for sample 20 and $9.0\text{ }\mu\text{m}$ for sample 20'. Since spinodal decomposition has no barrier to formation, this may explain why the domain sizes did not appear to depend on the presence of phenol in the sample.

The SEM provided information on all the samples of the three and seven component groups. The photos for the 58005 and 58005' samples showed that both the size and concentration of particles increase with increasing rubber content. The samples with low rubber concentrations had particles that were small and round, indicating that nucleation and growth is the mechanism of phase separation in these cases while spinodal decomposition occurs at 20%. For both the 5% and 10% rubber samples, those containing phenol showed particles that were smaller than those

without, but at 15% there was no difference in size. At sizes of 0.28-0.44 μm , the particles are too small to have been seen in OM.

The photos for both the α and β series showed round particles, again an indication that nucleation and growth is the mechanism of phase separation. The peak in particle size for the α series samples was about 4% rubber concentration, while the highest density of particles appeared around 12% rubber. Wide distributions in particle size were seen for rubber concentrations from 2% to 10% and narrow distributions for 12-16%. The β series presented a similar split between the rubber concentration with the largest particles, about 4%, and that with the most particles, about 6%. Again, wide distributions were seen for the smaller rubber concentrations, 2% and 4%, and narrow for the 6-10% concentrations. The particle sizes, between 0.76 and 3.10 μm , are in the range where OM should have detected them. The samples were visually cloudy, indicating that the indices of refraction of the particles and matrix are different enough that HMC should have easily detected the particles. There are two possible explanations for the lack of optical data. The first is that the seven component trial samples did not develop particles as large as those in the bulk samples of the third group due to the sample thickness between the glass slides upon which they were mounted, which was not regulated and could have been too small for particle growth. This could explain why the smaller particles were not detected. The second explanation is that the microscope was used incorrectly.

The results of the Izod testing proved quite inconclusive. The amount of error was small in samples with no particles and those with very low rubber content. The

error was quite large in the samples with 6% and greater rubber concentrations, which may indicate a relationship between the volume fraction of rubber and the impact strength. There appears to be an increase in measured toughness as rubber concentration increases with a decrease after 15% in the α series and after 10% in the β series, which coincides with the range of the initial visual inspection of the samples. However, the error is so large that this increase is lost in the detail. There is no clear correlation between particle size distribution and scatter in the α series. The $\alpha 2$ and $\alpha 4$ samples showed as wide of distributions as $\alpha 6$, $\alpha 8$, and $\alpha 10$, yet they recorded very small amounts of scatter compared to these. The correlation is better in the β series. The $\beta 2$ and $\beta 4$ samples have wide distributions and large particles compared to $\beta 6$, $\beta 8$, and $\beta 10$ and they had a small degree of scatter compared with these.

Plotting impact strength v. particle size for the α series did not provide further clarification. There was no clear correlation between particle size and toughness seen in the graph, 1.4 μm particles gave both low and high toughness values for example. If the rubber concentration is taken into account, the sample with the lower concentration but the same particle size gives a lower impact strength. But this explanation again relies on rubber concentration and not particle size. The information for the β series is clearer. The smaller particle sizes resulted in greater toughness, and larger scatter, than the larger particles.

Particles were seen to develop in both the α and β series in a manner indicative of an LCST in the phase diagram. The particle sizes, 0.75-3 μm , were seen to fall in the size range where optimum toughening should occur as noted in the literature. The

degree of toughening that results from the addition of rubber to this epoxy-methacrylate system appears to depend the most on the rubber composition and not on the particle sizes or size distributions that develop during phase separation. The high degree of scatter in the Izod results is still a problem. The equipment may be partially to blame, as it was difficult to find and keep a zero point of reference during testing. The presence of air bubbles in the samples may also have had an effect, because bubbles were present in all the samples, but the concentration of them varied from sample to sample.

5.2 Recommendations

There are many things in the study of this epoxy-rubber-methacrylate system that could be altered to provide more conclusive results. A more reactive rubber would have been more effective at both forming particles and strengthening the matrix through better adhesion. Better Izod results could be obtained by greatly increasing the number of samples tested to reduce the amount of error. Other mechanical properties could also be explored, such as yield strength and Young's modulus, by changing the prepared sample dimensions to provide a more complete picture of the effect of the rubber toughening on the system.

There are also many variations of the epoxy-rubber-methacrylate system itself that could be explored. Additional research could include variations in the cure schedule of the samples or changes in the variables that lead to the initial solution matrix. Changes

in the materials themselves, the type of rubber or the curing agent used, could also provide a better overall picture of the system.

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APPENDIX

			All weights are in grams.			
58005 Series	0	5	10	15	20	
w58005=	0.000	1.271	2.513	3.769	5.064	
w828=	7.827	6.681	5.550	4.417	3.395	
wPACM=	2.189	2.068	1.947	1.819	1.707	
Rubber content	0.00%	5.07%	10.04%	15.07%	19.93%	
Curing Time	23 h	22.5 h	22.5 h	22 h	22 h	
58005' Series	5'	10'	15'	20'		
w58005=	1.267	2.494	3.763	5.015		
w828=	6.784	5.626	4.496	3.370		
wPACM=	2.070	1.949	1.828	1.699		
%phenol=	1.00%	0.83%	0.66%	0.50%		
Rubber content	5.01%	9.91%	14.92%	19.89%		
Curing Time	23 h	22.5 h	22.5 h	22 h		

Appendix: Compositions of samples.

A Series	1A	2A	3A	4A	5A	6A	7A	8A
w828=	1.862	1.783	1.719	1.625	1.527	1.440	1.359	1.875
wPACM=	1.053	0.993	0.922	0.849	0.798	0.724	0.673	1.047
wHYCAR13=	0.000	0.570	1.008	1.559	2.150	2.510	3.008	0.113
wARL=	4.600	4.392	4.189	3.948	3.748	3.522	3.373	4.596
wPGE=	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
wbisGMA=	0.974	0.925	0.900	0.796	0.760	0.694	0.676	0.962
wHDDMA=	1.541	1.463	1.383	1.292	1.226	1.151	1.074	1.528
Rubber content	0.00%	5.63%	9.96%	15.48%	21.06%	25.00%	29.60%	1.12%
Curing Time	21 h	21 h	21 h	21 h	22 h	22 h	22 h	22 h
	9A	10A	11A	12A	13A	14A	15A	
w828=	1.853	1.780	1.821	1.803	1.703	1.666	1.636	
wPACM=	1.013	0.984	0.975	0.910	0.914	0.877	0.887	
wHYCAR13=	0.321	0.645	0.837	1.126	1.204	1.300	1.399	
wARL=	4.473	4.390	4.298	4.195	4.173	4.064	4.012	
wPGE=	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
wbisGMA=	0.957	0.912	0.902	0.860	0.852	0.822	0.810	
wHDDMA=	1.500	1.448	1.419	1.373	1.360	1.345	1.328	
Rubber content	3.17%	6.35%	8.16%	10.97%	11.80%	12.90%	13.89%	
Curing Time	21 h	21 h	21 h	21 h	21 h	21 h	21 h	

Appendix (cont.)

B Series	2B	3B	4B	5B	6B	7B	8B
w828=	1.664	1.443	1.233	1.054	0.845	0.690	1.837
wPACM=	0.917	0.769	0.633	0.520	0.387	0.272	1.017
wHYCAR13=	0.492	1.014	1.567	2.001	2.557	3.014	0.097
wARL=	4.165	3.512	2.985	2.504	2.025	1.620	4.497
wPGE=	0.000	0.000	0.000	0.000	0.000	0.000	0.000
wbisGMA=	1.370	1.592	1.862	2.114	2.408	2.539	1.045
wHDDMA=	1.640	1.746	1.814	1.894	1.955	1.998	1.568
Rubber content	4.80%	10.06%	15.52%	19.84%	25.13%	29.74%	0.96%
Curing Time	21 h	21 h	21 h	21 h	47.5 h	47.5 h	24.5 h
	9B	10B	11B	12B	13B		
w828=	1.727	1.627	1.604	1.530	1.483		
wPACM=	0.963	0.888	0.867	0.833	0.795		
wHYCAR13=	0.321	0.731	0.702	0.804	0.907		
wARL=	4.290	3.941	3.831	3.730	3.620		
wPGE=	0.000	0.000	0.000	0.000	0.000		
wbisGMA=	1.158	1.346	1.404	1.500	1.567		
wHDDMA=	1.635	1.662	1.684	1.700	1.719		
Rubber content	3.18%	7.17%	6.96%	7.96%	8.99%		
Curing Time	21 h	21 h	21 h	21 h	21 h		

Appendix (cont.)

alpha Series	a0	a2	a4	a6	a8	a10	a12	a14	a16
w828=	3.744	3.676	3.590	3.513	3.459	3.464	3.311	3.260	3.193
wPACM=	2.115	2.056	1.998	1.952	1.894	1.846	1.811	1.735	1.688
wHYCAR13=	0.000	0.418	0.834	1.218	1.618	2.036	2.419	2.807	3.233
wARL=	9.217	9.035	8.855	8.699	8.610	8.358	8.147	8.030	7.821
wPGE=	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
wbisGMA=	1.915	1.885	1.831	1.797	1.789	1.697	1.673	1.627	1.594
wHDDMA=	3.144	3.148	2.975	2.889	2.829	2.763	2.695	2.631	2.569
wPeroxide=	0.184	0.175	0.170	0.171	0.162	0.167	0.157	0.168	0.145
Rubber content	0.00%	2.05%	4.12%	6.02%	7.95%	10.01%	11.97%	13.86%	15.97%
Curing Time	21+3 h	21+3 h	21+3 h	21+3 h	21.5+3 h	21.5+3 h	21.5+3 h	21.5+3 h	21.5+3 h
beta Series	b2	b4	b6	b8	b10	b12			
w828=	3.576	3.360	3.181	3.004	2.840	2.682			
wPACM=	1.988	1.867	1.758	1.645	1.544	1.427			
wHYCAR13=	0.412	0.802	1.226	1.618	2.035	2.459			
wARL=	8.756	8.310	7.896	7.689	6.999	6.574			
wPGE=	0.000	0.000	0.000	0.000	0.000	0.000			
wbisGMA=	2.181	2.423	2.680	2.932	3.161	3.372			
wHDDMA=	3.165	3.251	3.328	3.410	3.473	3.545			
wPeroxide=	0.191	0.209	0.213	0.224	0.232	0.245			
Rubber content	2.03%	3.97%	6.04%	7.88%	10.03%	12.11%			
Curing Time	22+3 h	22+3 h	22+3 h	22+3 h	21.5+3 h	21.5+3 h			

Appendix (cont.)

alpha Izod Serie	a0'	a2'	a4'	a6'	a8'	a10'	a12'	a14'	a16'
w828=	7.063	5.845	5.735	5.628	5.527	5.400	5.288	5.178	5.062
wPACM=	3.976	3.267	3.178	3.104	3.027	2.937	2.852	2.780	2.691
wHYCAR13=	0.000	0.652	1.277	1.927	2.566	3.208	3.839	4.503	5.222
wARL=	17.478	14.441	14.168	13.898	13.616	13.358	13.061	12.802	12.522
wPGE=	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
wbisGMA=	3.640	2.979	2.922	2.852	2.790	2.710	2.634	2.583	3.261
wHDDMA=	5.835	4.815	4.713	4.615	4.518	4.416	4.315	4.217	4.119
wPeroxide=	0.331	0.270	0.266	0.260	0.255	0.250	0.241	0.238	0.233
Rubber content	0.00%	2.02%	3.96%	5.97%	7.94%	9.94%	11.91%	13.94%	15.77%
Curing Time	24+3 h	22.5+3 h	23.5+3 h	22+3 h	24+3 h	23.5+3 h	22+3 h	23+3 h	23+3 h
beta Izod Series	b2'	b4'	b6'	b8'	b10'	b12'			
w828=	5.668	5.378	5.092	4.815	4.539	4.266			
wPACM=	3.162	2.985	2.801	2.623	2.453	2.284			
wHYCAR13=	0.648	1.287	1.926	2.569	3.231	3.867			
wARL=	14.005	13.290	12.590	11.898	11.214	10.545			
wPGE=	0.000	0.000	0.000	0.000	0.000	0.000			
wbisGMA=	3.518	3.882	4.287	4.667	5.054	5.406			
wHDDMA=	5.053	5.185	5.315	5.434	5.559	5.664			
wPeroxide=	0.300	0.317	0.345	0.354	0.370	0.388			
Rubber content	2.00%	3.98%	5.95%	7.94%	9.97%	11.93%			
Curing Time	23+3 h	23.5+3 h	22+3 h	23+3 h	23+3 h	22.5+3 h			

Appendix (cont.)

VITA

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