

Phase Separation in Rubber-Modified Thermoset Resins: Optical Microscopy and Laser Light Scattering

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Synopsis

Phase separation of a prereacted rubber in di-, tri-, and tetrafunctional epoxy systems is discussed. Optical microscopy and laser light scattering are used to characterize the morphology and dimensions of the rubbery domains. Systems without rubber are transparent while systems containing 2%, 4%, 6%, and 8% and rubber exhibit distinct phase separation. The average domain size is about 1 μm . In the 8% systems the particles are larger and in the trifunctional system the rubbery domains are in the shape of shell and core. Laser light scattering proves that the scattering particles are in the core observed in the optical micrographs. The difference in morphologies is explained by the difference in the chemical structure of the epoxy resin and the rubber content. Thermodynamic considerations and solubility parameters show that the di- and tetrafunctional systems have similar enthalpies of mixing while the trifunctional system is much more incompatible with the rubber.

INTRODUCTION

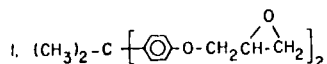
The improvement in the toughness of elastomer-modified thermosetting systems has been attributed to elastomer domains dispersed in the cross-linked network.^{1,2} Telechelic reactive butadiene-acrylonitrile polymers are the most popular elastomers used in epoxy and styrenated polyester resins.³ It has been shown that chain extenders such as bisphenol A^{4,5} and brominated epoxy resins⁶ which serve as spacers in the thermoset network, also increase the toughness of the material. Bucknall and Yoshii⁵ summarize the factors which affect the mechanical properties of such systems. These factors include: (a) rubber type and content, (b) type and concentration of the curing agent, (c) solubility parameter of the rubber, (d) rubber end group, (e) cure temperature, and (f) concentration of chain extender. A correlation between size and shape of the rubbery domains, which phase-separate well before gelation, and mechanical properties of the material has been suggested.^{2,7,8} Understanding of phase separation mechanisms may therefore lead to better design of toughened materials.

Scanning (SEM) and transmission (TEM) electron microscopy have been used to study the morphology of the rubber particles. SEM samples are examined as fractured surfaces while TEM samples are prepared from thin slices of the quenched material. In both techniques one has to use a vacuum chamber so that experiments in real time on the material are excluded.

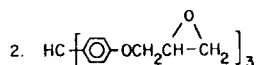
We would like to report in this paper on the effect of the rubber content and the nature of the major epoxy resin on phase separation as seen by optical microscopy and laser light scattering.

EXPERIMENTAL

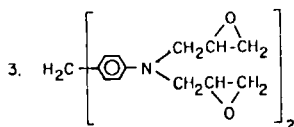
Materials Diglycidyl ether of Bisphenol A (DR) (DER 332) and triglycidyl ether of tris hydroxyphenyl methane (TEN) (XD 7342.00L), both of the Dow Chemical Co., and tetraglycidyl diamino diphenyl methane (TGDDM) (MY 720), Ciba-Geigy, were the epoxy resins. A brominated difunctional epoxy resin, F2001P (Makhteshim Chemical Works) was the chain extender. The brominated epoxy resin (BER) was prereacted with carboxyl-terminated acrylonitrile-butadiene rubber, CTBN (Hycar 1300×13), B.F. Goodrich Chemical Co., to form a 50% epoxide (w/w). Diamino diphenyl sulfone (DDS) (Aldrich) was the curing agent. No catalyst was added. Formulations were prepared to obtain 19% bromine and 0%, 2%, 4%, 6%, and 8% rubber (w/w). DDS was added to form stoichiometric compositions (1 mol epoxy with 1 mol amine hydrogen). Each formulation was dissolved in 1:10 w/v in methyl ethyl ketone (MEK). Formulae of raw materials are shown in Figure 1. Thin layers (5–50 μm) were prepared by mechanically dip coating on



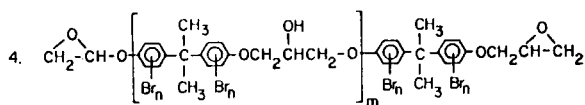
DIGLYCIDYL ETHER OF BISPHENOL A, DR



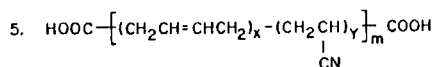
TRIGLYCIDYL ETHER OF TRIS (HYDROXY PHENYL) METHANE, TEN



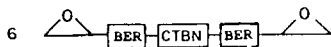
TETRAGLYCIDYL 4,4' DIAMINO DIPHENYL METHANE, TGDDM



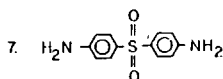
BROMINATED EPOXY RESIN, BER



CARBOXYL TERMINATED BUTADIENE ACRYLONITRILE COPOLYMER, CTBN



BER-CTBN DIEPOXIDE



DIAMINO DIPHENYL SULFONE, DDS

Fig. 1. Formulae of raw materials.

precleaned glass slides and cured according to the following cure cycle: 45 min at 80°C, 8 min at 125°C, and 2 h at 177°C. After cooling to room temperature, the specimens were further cured for 4 h at 192°C.

Microscopy. Morphology was examined using a Zeiss Optical Microscope.

Laser Light Scattering. A classical diffraction arrangement was set. Measurements were performed with a 1 mW Spectra Physics 162A 5145 Å CW Argon Laser. The beam was focused on the sample, and the scattered light pattern was projected on a translucent screen and photographed. It was shown⁹ that in films thicker than 1–5 μm, phase separation is independent of thickness.

RESULTS AND DISCUSSION

To ensure that the polymerization mechanism is limited to epoxy/amine reactions, we chose a prereacted rubber, end-capped with a difunctional brominated epoxy resin (BER). The BER and the CTBN-BER serve therefore as chain extenders in the epoxy matrix. Hycar 1300×13 was chosen since its acrylonitrile content (26%) renders the initial compatibility with the epoxy system. Three epoxides were chosen—a difunctional (DR), trifunctional (TEN), and tetrafunctional (TGDDM)—in order to compare the effect of their functionality and chemical structure on phase separation.

Optical microscopy has the advantage of looking at the sample without quenching or fracture, but has the disadvantage of a relative lower magnification and the fact that the light forms a projected picture of all the layers through the thickness of the sample. Representative optical micrographs of the three major epoxy systems containing 4% and 8% rubber are shown in Figure 2. The dimensions of the rubbery domains are summarized in Table I.

Systems which include the major epoxy resin and the brominated epoxy without rubber are transparent and do not show phase separation. Phase separation is evident from all optical micrographs of samples which include even 2% rubber. The difunctional resin shows homogeneously dispersed rubber particles in the epoxy matrix. The homogeneous dispersion of the rubber particles is a result of its initial good compatibility with the epoxy matrix. Upon cure, as the network is formed, the rubber phase separates due to the difference in solubility parameters but remains attached to the matrix through the BER segments. In the difunctional system, the chemical structure of the chain extender is similar to that of the major epoxy resin. It was expected that the effect of the chain extender on the morphology would be smaller than in the other two epoxy systems. It is interesting to note that the rubbery domains are of the same order of magnitude (about 1 μm) for all four rubber concentrations. However, in the 8% system the rubbery domains are somewhat bigger. SEM micrographs of a system containing a DGEBA type epoxy resin cured with trimethylene glycol di-*p*-aminobenzoate, which was modified with carboxyl-terminated and amine-terminated butadiene-acrylonitrile copolymer, each designed to contain 9.7% rubber,⁸ show a similar morphology with average dimensions of 0.6–3.1 μm.

In the tri- and tetrafunctional systems, the rubbery domains are in the shape of a shell and core. This shape is apparently formed since the BER

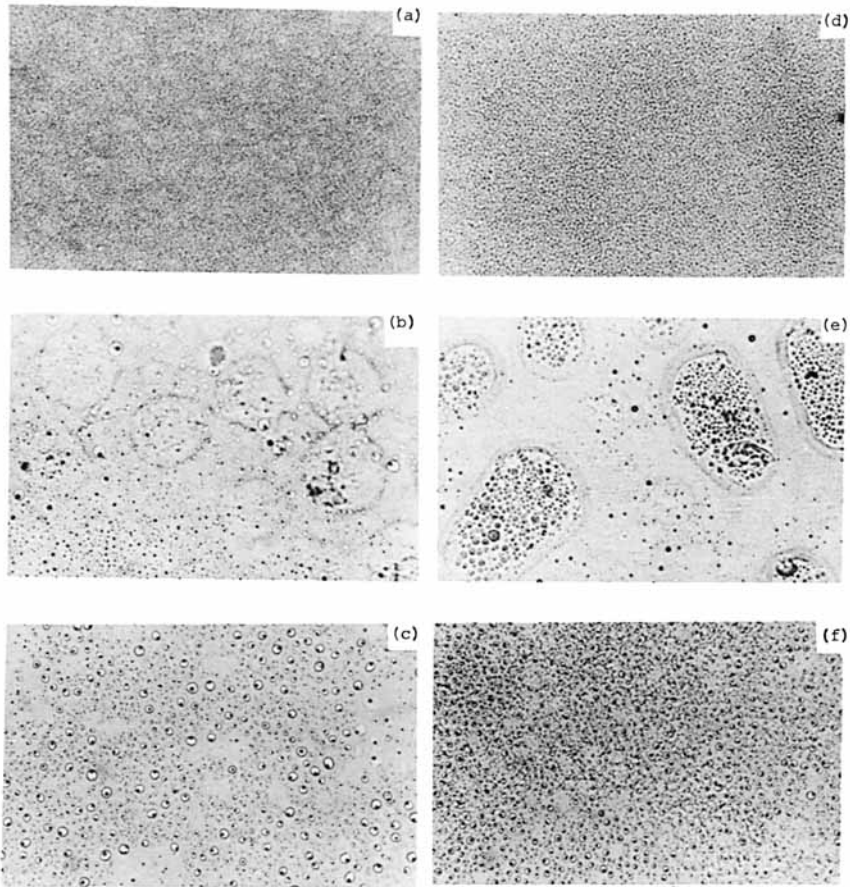


Fig. 2. Representative optical micrographs: (a) DR, 4% rubber; (b) TEN, 4% rubber; (c) TGDDM, 4% rubber; (d) DR, 8% rubber; (e) TEN, 8% rubber; (f) TGDDM, 8% rubber.

segments are attached to the prereacted rubber and therefore surround the rubber droplets. Another possibility is that this shape is formed due to the difference in the thermal expansion coefficients of the rubber and the epoxy matrix. This morphology has been found in SEM and TEM microscopy,^{10,11} and it was shown¹¹ that most of the rubber is in these "holes" by using a solvent which causes the rubber to swell. It was suggested that microvoids are produced during ductile stable crack growth by cavitation in the rubbery particles and that the rubber collapses back into the hole to give a cavity lined with rubber. In our case, the morphology is that of the cured system without any fracture and also exhibits the shape of a shell and core. This implies that the morphology is determined during the cure cycle rather than at a later stage such as mechanical fracture. However, the question still remains whether the rubber is concentrated in the core or fills the shell as well. From volume fraction considerations it is suggested that the rubber occupies mainly the core. Romanchick et al. studied the effect of a chain extender in rubber-modified epoxy systems.⁴ They concluded also that

TABLE I:
Dimensions of Phase-Separated Rubber Particles

System	%Rubber	\bar{d} (OM)(μm)		\bar{d} (laser) (μm)
		Core	Shell	
DR/DDS/BER	2	0.76	—	—
	4	1.14	—	1.22
	6	0.91	—	1.40
	8	2.07	—	1.94
TEN/DDS/BER	2	1.82	—	—
	4	2.68	9.09	2.25
	6	2.27	7.17	2.33
	8	3.33	8.58	3.24
TGDDM/DDS/BER	2	2.73	6.59	—
	4	2.58	7.05	2.93
	6	3.64	9.47	2.87
	8	3.21	8.16	3.24

the morphology is determined during the cure cycle and depends on the compatibility of the rubber and the epoxy, and the temperature and time of cure. An increase in elastomer concentration resulted in larger rubber domains. In their system, however, the core-shell structure is a result of the rubber being depleted by the epoxy matrix to form domains in which the interior of the domain is rich in epoxy and the shell is rich in elastomer. In our systems, the core dimensions and shape are similar in the tri- and tetrafunctional systems to those found in the difunctional system, regardless of the rubber content. Since all these systems were cured at the same cure cycle, this indicates that the size and shape are mainly determined by the cure conditions and the compatibility of the rubber with the epoxy system.

A bimodal distribution is observed in the trifunctional and tetrafunctional systems. Particles of average dimensions, which are about half the dimensions of the cores, are dispersed homogeneously as a background to the shell and core shapes. These may be projections of rubbery domains from different layers which are not in focus. However, in the tetrafunctional systems different regions are observed: Those with sharp shell and core structure (as in Fig. 2) and those which do not have a definite structure and look like the rubbery domains are absorbed in the matrix without sharp boundaries. A significant difference in the morphology of the rubbery domains is observed in the trifunctional system containing 8% rubber. Most of the rubber particles, still having the same average dimension as the core particles, are concentrated inside larger shells (20–180 μm) forming "cells." The particles outside these agglomerates still have the shell and core structure. This agglomeration occurs due to the dimensions of the network formed by the trifunctional system which apparently cannot accommodate more than 6% rubber in it and therefore rejects the rubber to form the observed cells.

If the rubber in the network is ordered or has a unique dimension, laser light scattering may produce a pattern from which the dimensions of the rubbery domains may be extended. This dimension should correlate with either the core or the shell dimensions. The advantages of using a laser

light scattering apparatus are in its coherent, monochromatic light and its simple and convenient operation. Stein et al.¹² have shown that light scattered from spherulites in crystalline polymers produces a unique pattern from which the size of the spherulites may be calculated. Visconti and Marchessault¹³ used laser light scattering to study phase separation in rubber-modified cycloaliphatic epoxy resins cured with hexahydrophthalic anhydride. They used an expression similar to that introduced by Stein et al.¹² to characterize the dimensions of the phase-separated particles. No scattering was observed below 5% rubber while the dimensions of the particles in systems containing 9% and 14% rubber were about 4 μm . At about 15% rubber, a second maximum in the scattered light was observed, indicating that the small particles are packed in larger domains. However, the dimensions of the same samples, as seen in electron micrographs, were much smaller and the particle diameter was bigger the higher the rubber content. The particles, either in this system or in the present study, are spherical rubber particles dispersed in a matrix (see Fig. 2). The diffraction pattern produced by a random array of N identical spherical particles is the same as that produced by one particle alone, but N times brighter. Any deviation from randomness would produce enhancement of the intensity of the scattered light in certain directions. Similar patterns have been observed in polymer blends.^{9,14} The size of the particles can be calculated using Bragg's equation:

$$2d \sin \theta/2 = n\lambda$$

where d is the dimension of the particle, θ is the scattering angle, n is an integer, and λ is the light wavelength. Representative diffraction patterns from systems containing 4% and 8% rubber are shown in Figure 3. The dimensions of the rubber particles are summarized in Table I.

All samples scatter the light significantly. The most intense and sharp diffraction rings were obtained from the trifunctional system. The intensity of the ring is a measure of the arrangement (order) of the particles while the width of the ring is a measure of their dimension distribution. Hence, the most ordered system is the trifunctional, and the least ordered is the difunctional one. The trifunctional system has also the narrowest dimension distribution while the tetrafunctional one has the broadest dimension distribution. The dimensions of the particles in the difunctional systems are smaller than those found in the other systems. This may be due to better solubility of the rubber in the epoxy in earlier stages of polymerization.

The dimensions of the scattering particles as seen by laser light scattering correlate well with observations by optical microscopy and prove that it is the core rather than the shell that scatter the light. Therefore, it is assumed that most of the rubber is concentrated in the core. It is interesting to note that since the particles are homogeneously dispersed in the matrix, 2% rubber content (in all three systems) is too low to produce a visible enhancement of the scattered light to form diffraction patterns. Four percent rubber content is already sufficient in these systems to enhance the scattered light to obtain the diffraction rings. However, if one scans the sample in the beam, the pattern is not of a unique size but has a certain statistical

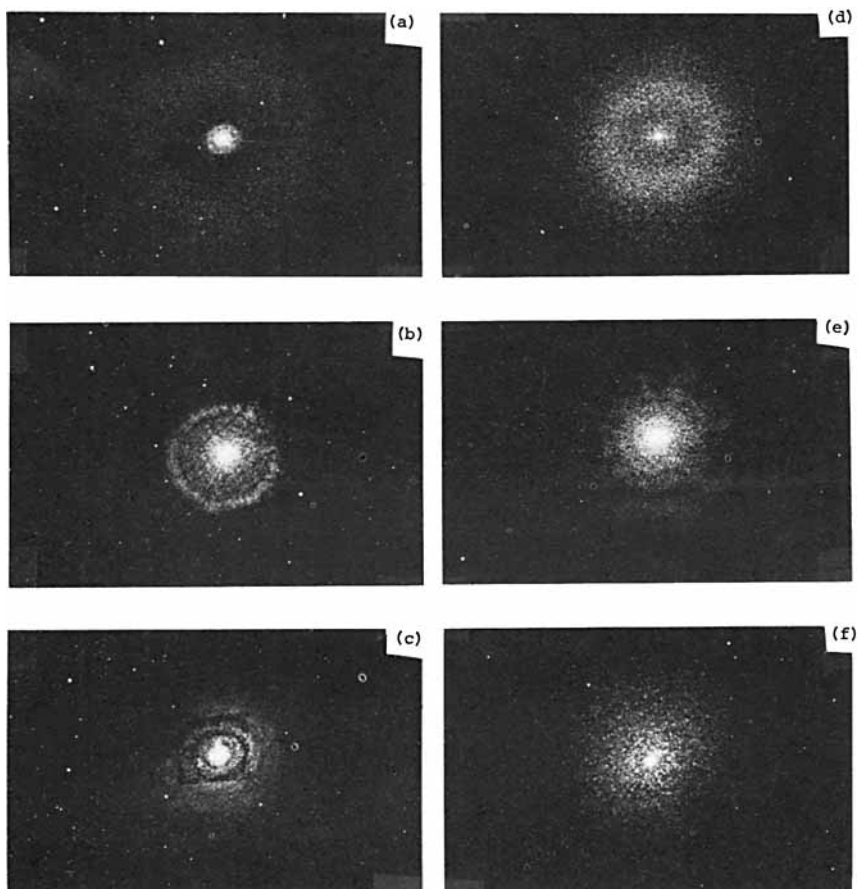


Fig. 3. Representative diffraction patterns; (a) DR, 4% rubber; (b) TEN, 4% rubber; (c) TGDDM, 4% rubber; (d) DR, 8% rubber; (e) TEN, 8% rubber; (f) TGDDM, 8% rubber.

distribution. This is a result of the fact that the rubber particles do not have a unique size but rather a statistical distribution. In some cases, several rings are observed, indicating a local higher degree of ordered particles, as seen in the diffraction pattern of the four functional system containing 4% rubber. A similar pattern is observed more frequently in the trifunctional system containing 8% rubber. Moreover, in this system another feature is observed: The scattered light pattern has higher intensity in certain directions. Such patterns point out that the particles are arranged in a highly ordered array. This system also produces diffraction rings of smaller diameter, which indicate that the small particles are packed inside a bigger structure of average size of about 30 μm . This higher degree of order was already pointed out by Visconti and Marchessault.¹³ These particles may correspond to the cells observed in SEM and optical micrographs.

Since the rubber is chemically bonded to the matrix through the epoxide end group, the following mechanism for the formation of the rubbery domains is suggested: The BER-rubber diepoxide reacts, together with the major component, with the curing agent to form the chain extended network. At the beginning of polymerization the system behaves like a solution

in which all the components are compatible. As the network grows, one can visualize that the rubbery segments are aligned outside the main chain. As long as these deviations are local and the network is in its initial stages of growth, the material is transparent. As more and more crosslinks are formed, there are sites in the network where there is a relative higher concentration of the rubber. These sites are the spheres observed in the scanning electron microscope and the optical micrographs. If the crosslinks are relatively close to each other, many rubbery segments are formed out of the main matrix and result in agglomerates. These agglomerates are in the form of "cells" which include a high concentration of rubber particles inside. Such agglomerates are seen in the trifunctional system (Fig. 2). A schematic representation of this mechanism is shown in Figure 4.

The shape and size of the rubbery domains are determined by the kinetics of nucleation of the rubbery segments and thermodynamic considerations of phase separation. Since phase separation occurs already in early stages of polymerization, we may assume that the rules which apply in mixtures of small molecules are the same in mixtures of growing networks. A similar assumption has led to the development of theoretical considerations in polymer blends.^{15,16} Since all the components, except the rubber segments, are miscible in each other, we treat the rubber segments as one type of material and all the other components as a second type. Therefore, a total weighted property is attached to all nonrubber components and a specific property is attached to the rubber segments. The Gibbs free energy of mixing will therefore be:

$$\Delta G_{\text{mix}} = \frac{RTV}{V_r} \left[\frac{V_A}{X_A} \ln V_A + \frac{V_R}{X_R} \ln V_R + \chi_{AR} V_A V_R \right] \quad (1)$$

where V is the total volume of the mixture, V_r is a reference volume taken as the molar volume of a repeat unit in the network, V_A is the total volume fraction of all the components except rubber, V_R is the rubber volume fraction, X_A is the degree of polymerization of the growing network (considered as a random copolymer at this stage), and X_R is the degree of polymerization of the rubber units. χ_{AR} is the interaction parameter between

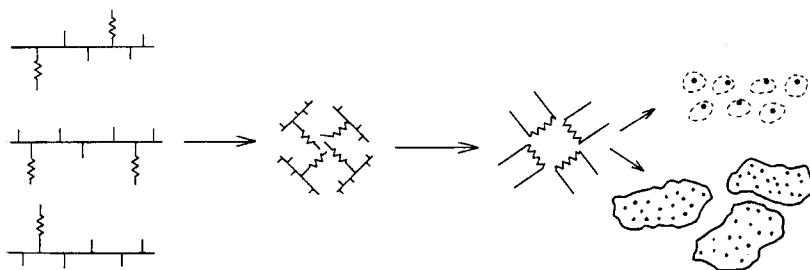


Fig. 4. Schematic representation of phase separation.

the network and the rubbery segments. χ_{AR} is calculated from the solubility parameters d_i of the components:

$$\chi_{AR} = \frac{V}{RT} (d_A - d_R)^2 \quad (2)$$

where

$$d_A = \Sigma d_i V_i \quad (3)$$

$$d_i = \Sigma F_j / M_i \quad (4)$$

$$d_R = \Sigma F_j / M_R \quad (5)$$

Since the molecular weight of the network increases rapidly during polymerization, X_i increases rapidly. Thus, the dominant factor in eq. (1) is the interaction parameter. The value of the solubility parameters may be estimated using group attraction constants¹⁵ to calculate ΣF_j . Values of these parameters for each component in the systems discussed are shown in Table II. Calculated values for d_A are 11.0 for the trifunctional system, 10.4 for the difunctional system, and 10.3 for the tetrafunctional system. It is already clear at this point that the major consideration in estimating the extent of phase separation is the difference between the solubility parameters of the epoxy system and the rubber. The trifunctional system is significantly more incompatible with the rubber while the di- and tetrafunctional systems are almost similar in their compatibility with the rubber. It is interesting to note that since the solubility parameter is the same in a given system, the higher the volume fraction of the rubber, the higher the free energy of mixing. Therefore, phase separation is preferred the higher the rubber concentration. These two considerations are illustrated in Figure 5 which shows the enthalpy of mixing as a function of the rubber content for the three epoxy systems. These trends are, indeed, evident from the optical micrographs and from the laser light scattering from these systems. The effects of cure temperature and time are currently being studied.

CONCLUSIONS

The different morphologies of rubbery domains which phase-separate during cure are formed as a result of the difference in the chemical structure of the epoxy resins in addition to other factors such as the rubber content

TABLE II
Material Properties for the Calculation of Solubility Parameters

Material	Molecular weight	Density	ΣF_j	Solubility parameter
DR	352	1.16	3035	10.00
TGDDM	486	1.17	3883	9.05
TEN	502	1.22	4444	11.16
DDS	248	1.54	2177	13.52
BER	1090	1.83	5542	9.30
CTBN	3500	0.96	34097	9.35

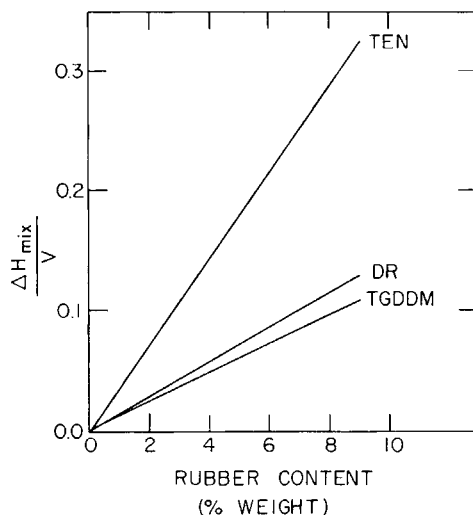


Fig. 5. Enthalpy of mixing as a function of rubber content.

and the cure temperature. It is shown that different morphologies develop at the same cure cycle as a function of the compatibility of the epoxy system and the rubber. A relationship between the chemical structure and the free energy of mixing enables us to predict the compatibility of the epoxy and the rubber if one assumes the same rules which apply for polymer mixtures. Thus, the most incompatible system is that containing a trifunctional epoxy while the di- and tetrafunctional systems are about the same. This conclusion is in contrast to that expected from conversion calculations, which consider the functionality as the main factor.

The average dimension of the rubbery domains is about the same for all systems (about 1 μm). This implies that the extent of phase separation depends on the compatibility while the size of the phase-separated domains depends on the cure conditions. However, at rubber content higher than 8%, agglomeration may occur. In the trifunctional system the rubber particles form cells which may cause mechanical failure of the material. Optimal cure conditions should therefore be designed to avoid such agglomeration.

Optical microscopy is a convenient and simple technique to characterize phase separation, and its use together with laser light scattering may lead to better characterization of the size and distribution of the rubbery domains. Laser light scattering proves that the scattering particles coincide with the core observed in the optical micrographs and may be used to study the degree of order of these particles.

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