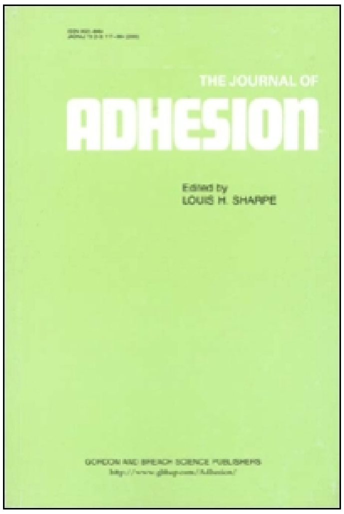

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Elastomers Formed *In-Situ* in Epoxy Resins: Chemistry and Toughening*

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The chemistry of the *in-situ* formation of elastomer particles in epoxy resins is described. Under normal synthetic conditions, if one polymerizes an acrylic monomer in an epoxy resin, the resulting polymer is soluble in the epoxy resin or it grossly phase separates, depending upon the solubility parameter difference between the acrylic polymer and the epoxy resin. This work shows that with the use of a specifically tailored material (which we believe operates as a "polymeric surfactant") in the reaction mixture, a free-flowing, stable suspension of acrylic elastomer particles in epoxy resin can be obtained. Thus, the reaction product of isocyanatoethylmethacrylate and EPON™ 1009 can be used as the polymeric surfactant in a reaction mixture containing hexyl acrylate, azo-bis(isobutyronitrile) and the diglycidyl ether of bisphenol A. The resulting dispersion is stable to settling even after exposure to 150°C. When properly formulated, the resulting modified epoxy resins are improved in their fracture resistance after cure over a similar resin without the elastomeric particles. The effect of the following parameters on the fracture resistance of the cured epoxy resin are discussed: chemistry of the polymeric surfactant, chain extension in the cure of the epoxy resin, type of acrylic monomer and the level of the elastomer. The physical properties of several adhesive formulations based upon these modified epoxy resins are also discussed.

KEY WORDS epoxy; acrylic; adhesive; toughening; resin; fracture; phase separation.

INTRODUCTION

Cured epoxy resins are brittle materials. The technology of epoxy resins as adhesives took a great stride forward when it was realized that certain elastomers could be used to impart fracture resistance to epoxy resins without a substantial reduction in their other important properties, such as modulus and glass transition temperature. The work of McGarry[1] on telechelic nitrile-butadiene copolymers signaled the

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*One of a Collection of papers honoring A. J. Kinloch, the recipient in February 1992 of *The Adhesion Society Award for Excellence in Adhesion Science, Sponsored by 3M.*

beginning of the greater applicability of epoxy resins as adhesives. McGarry and Willner[1a] showed that toughening of epoxy resins could be achieved using telechelic nitrile butadiene "reactive liquid polymers" (RLP's) when:

- the RLP contained about 20% acrylonitrile,
- the RLP was telechelic with end-groups reactive with epoxy resins,
- the RLP phase separated from the epoxy resin during cure, and
- the second phase formed particles of elastomer large enough to scatter light.

Riew, Rowe and Siebert[2] clearly demonstrated the effect of epoxy matrix ductility in showing the importance of adding bis-phenol A to the reaction mixture. Pearson and Yee[3] showed the importance of the cross-link density on the toughenability of epoxy resins. Sultan and McGarry[1b] showed the effect of the size of the elastomer particles on the mechanism of toughening. Kinloch[4] and concurrently Yee[5] well described the polymer physics of the mechanism by which phase-separated elastomers increased the fracture resistance of cured epoxy resins. In particular, the work of Kinloch and Hunston[6] showed a model by which one could predict the properties of toughened epoxy resins from a series of simple measurements.

The data and the phenomena described in the literature on toughening of epoxy resins does not indicate that the toughener must be an "RLP." The data and the mechanisms presented indicate only that it is necessary that a second phase be formed, that this second phase is substantially different in physical properties from the cured epoxy resin and that the second phase is "well-connected" with the epoxy resin matrix. For example, Cunliffe and co-workers[7] have described the generation of rubber-modified epoxies based upon the anionic polymerization of monomers such as isoprene, butadiene and acrylonitrile. Their method guaranteed the reaction of the anionic functional rubber with an epoxy group, which then guaranteed reaction of the epoxy end-capped rubber to the matrix. The main problem, which is addressed in our work, was the instability of the formed rubber particles upon standing. Meeks[8] showed that preformed ABS (acrylonitrile-butadiene-styrene) powder could be used as a toughening agent and reported fracture energy values which equalled or surpassed those of an RLP-toughened epoxy.

Acrylic elastomers were first examined by Riew, Rowe and Siebert[2] and were found to provide toughening when the elastomer was carboxyl terminated. Gazit and Bell[9] have studied the use of carboxyl terminated n-butyl acrylate rubber and found that the addition of this rubber with the appropriate choice of curative led to substantial improvements in impact strength. These authors also indicated that successful use of this rubber required that its molecular weight be about 4000, which allowed solubility of the rubber in epoxy resins before cure. Ochi and Bell[10] extended the study to include further acrylic acid functionality in the n-butyl acrylate and also found that there was an optimum amount for maximum epoxy resin toughness.

The above-described literature is thus mixed with respect to the overall chemical criteria for obtaining toughness in epoxy resins by the addition of elastomers. It may be supposed from some part of the above discussion, that it is *necessary* to have the elastomer such that its chemical constitution provides solubility in the uncured epoxy resin but insolubility in the cured resin. However, the mechanisms of action put forth by McGarry, Kinloch and Yee make no such requirement. Indeed, it may be apparent that if cure conditions are not optimum, a system which requires cure for phase separation may give irreproducible effects.[11]

Particles, including elastomeric particles, can be held in suspension in an **organic** medium by means of steric stabilization. In such a system, the stabilization is provided by favorable thermodynamics. Thus, if polymer chains, which we will call "stabilizers," are attached to the surface of the particle and this stabilizer has a more negative Gibbs free-energy change of interaction with the medium than it does with itself, the coalescence of particles will be inhibited by thermodynamics. This is due to the fact that removal of stabilizer-medium interactions and their replacement with stabilizer-stabilizer interactions would result in a positive Gibbs free-energy change. This phenomenon has been used to provide detergency for automotive lubricants as well as other industrially useful effects. We have used this phenomenon to provide an alternative means for toughening epoxy resins.

The purpose of this article is to describe the chemistry by which we have obtained an alternative method of toughening epoxy resins. This article also describes some of the parameters which we investigated which control the phenomenon of toughening with these pre-phase-separated elastomers. The work done to support this article does not constitute a complete mechanistic study of the toughening effect but rather provides guidelines to some of the important parameters which govern the phenomenon of toughening. We also describe some work on the use of these resins as the base for structural adhesives and we compare them with simple formulations based upon RLP's.

EXPERIMENTAL

Stabilizer Solution Synthesis

The stabilizer used most in this work is the adduct of isocyanatoethylmethacrylate and a higher molecular weight epoxy resin. The synthesis proceeded as follows: A reaction flask was dried and into that flask was placed 95 g of EPON™ 1009 (A product of Shell Chemical Co.). The molecular weight as determined by titration was 4040. (The titration method was based upon perchloric acid.) 200 g of tetrahydrofuran were added as well as 5 g of isocyanatoethylmethacrylate. The reaction mixture was agitated and heated at 80°C for five hours. The resulting solution was 33% solids and had an average of 2.7 pendant methacrylate groups per epoxy polymer chain. The solids in this solution are considered to have the structure shown as "Stabilizer A" in Figure 1.

Elastomer Dispersion Synthesis

A 500 ml reaction vessel was equipped for distillation. In that vessel was placed 78 g of EPON™ 828 (a product of Shell Chemical Co.). This epoxy resin has an epoxy equivalent weight of 185 to 191. In this paper, this material is denoted "DGEBPA." 6 g of the above-described stabilizer solution (*i.e.*, the adduct of EPON™ 1009 with isocyanatoethylmethacrylate in tetrahydrofuran solvent) was added to the reaction

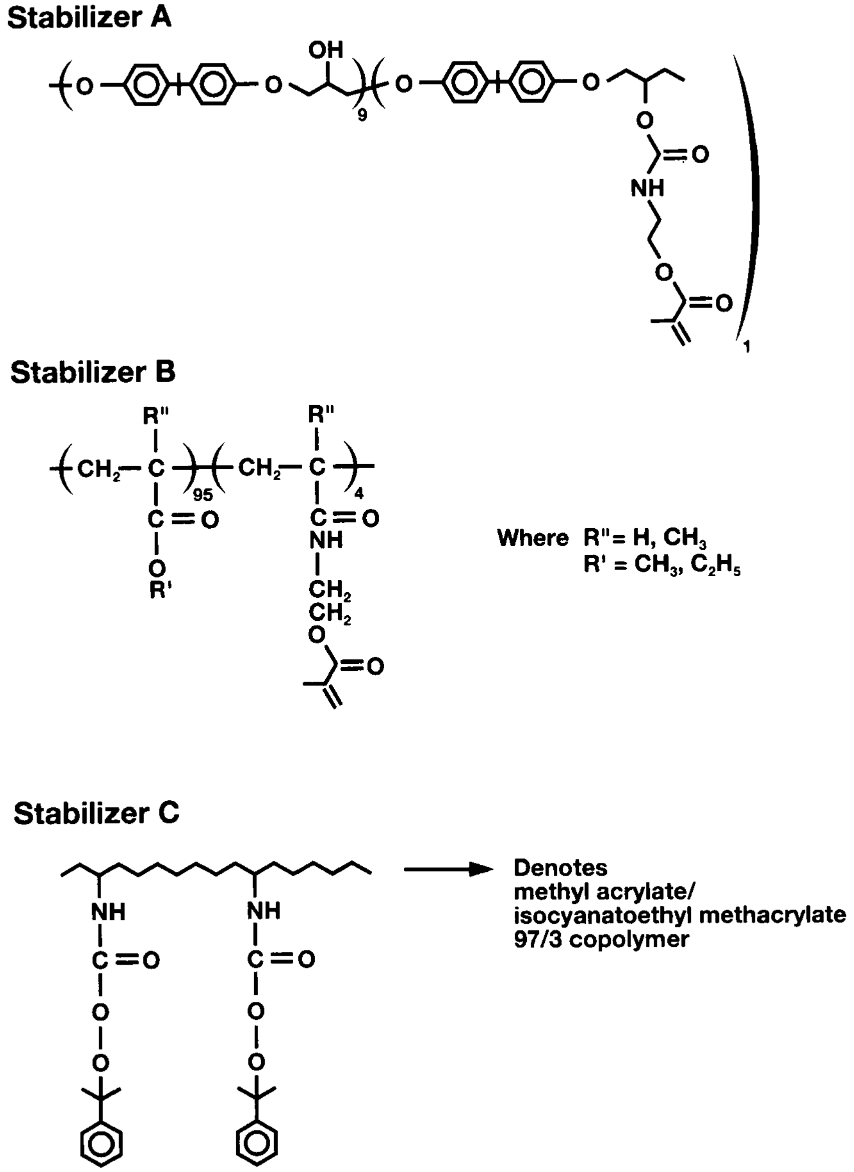

FIGURE 1 Chemical structures of stabilizers synthesized as part of this work. Stabilizer A was used to generate all of the dispersions for which physical properties were measured. Stabilizers B and C were synthesized to show that stabilizers having a structure substantially different from A but meeting the amphiphile/reactivity criteria described in the text could also be used to generate dispersions of acrylic elastomers in epoxy resins.

vessel. A vacuum was applied to the reaction vessel and the vessel was heated to 100°C at a pressure of less than 1 torr. The tetrahydrofuran was distilled. 20 g of hexyl acrylate and 0.1 g of azobis(isobutyronitrile) was added. A nitrogen gas purge was added to the reaction vessel as was an agitator. The reaction mixture was vigorously agitated and heated to 65°C and the reaction continued under these conditions for 16 hours. A moderately viscous, milky white dispersion of poly(acrylate) particles in epoxy resin was obtained. Essentially the same synthetic procedure was used for all of the dispersions described in this article, regardless of the monomer.

Characteristics of the Dispersions

All of the stable dispersions of acrylic elastomers in epoxy resins formed during this work were milky white materials. The Brookfield viscosity of the dispersions ranged from 17,000 centipoise to several hundred thousand centipoise depending upon the monomer and reaction conditions. The epoxy equivalent weight of the dispersion was measured using the perchloric acid method. In general, for an elastomer content of 20%, the epoxy equivalent weight was about 240. All of the dispersions which used stabilizers of the type shown in Figure 1 were stable to exposure of the dispersion to 150°C for an hour.

The morphology of the pre-phase-separated rubber particles was examined in the case of the use of hexyl acrylate as the monomer. In this instance, mostly spherical, discrete acrylic particles of diameter 2–5 microns were observed using optical microscopy. Examination by scanning electron microscopy of fracture surfaces of this dispersion cured using 2-ethyl-4-methyl imidazole showed that the discrete character of the particles was retained in that "pock marks" signifying rupture of the particle were observed. However, the volume fraction of rubber particles, as calculated from examination of the electron micrograph, did not agree with that expected from the volume of acrylate monomer used. This is not unexpected. In general, the cavities resulting from fracture are larger than those of the original particle due to dilatation effects. Transmission electron microscopy of cross sections was not done due to the lack of contrast between the acrylate and epoxy domains.

Synthesis of Alternative Stabilizers

Although Stabilizer A (described above and in Figure 1) was used for all of the resins utilized in the physical properties tests described in this article, other stabilizers with essentially the same efficacy could be generated by alternative means. The following are examples of alternative stabilizers.

Stabilizer B A reaction flask was dried and into it was weighed 79 g of methyl acrylate, 10 g of acrylic acid, 300 g of tetrahydrofuran and 0.4 g of azobis(isobutyronitrile). The mixture was flushed with dry nitrogen and heated to 60°C. The reaction was allowed to proceed for 16 hours under these conditions. The reaction mixture was cooled to 35°C. 11 g of isocyanatoethylmethacrylate was added and the reaction mixture was allowed to react for an additional 24 hours. Infrared spectra of the product demonstrated that all of the isocyanate groups had been reacted. The resulting moderately viscous solution contained 25% poly(methyl acrylate-co-N-(2-methacryloylethyl) acrylamide). This stabilizer is called Stabilizer B and is believed to have the structure shown in Figure 1. Stabilizer B was used in like manner to Stabilizer A (described above) such that when hexyl acrylate was polymerized in DER™ 332 (a product of Dow Chemical Company), a stable milky white moderately viscous resinous dispersion of acrylic particles in epoxy resin was obtained.

Stabilizer C A sample of DER™ 332 was dried by agitating at 50°C with 1.63 g of phenyl isocyanate followed by vacuum distillation of the unreacted phenyl isocyanate. This provided an epoxy resin that was thoroughly dry and also free of hydroxyl groups. 67 g of this treated epoxy resin was placed in a dried reaction vessel. To this vessel was also added 30 g of methylacrylate, 3 g of isocyanatoethylmethacrylate and 0.3 g of azobis(isobutyronitrile). Under a nitrogen atmosphere, this reaction mixture was held at 65°C for 24 hours. A clear viscous solution resulted. 6 g of this solution were placed in another reaction vessel along with 20 g of hexylacrylate, 74 g of DER™ 332 and 0.2 g of cumene hydroperoxide. The reaction mixture was agitated under a nitrogen atmosphere at 75°C for 24 hours. The resulting milky dispersion was checked for volatile content and it was found that the acrylic monomer had reacted to 75% conversion. 0.1 g of azobis(isobutyronitrile) was added and the reaction was allowed to continue for another 8 hours. The resulting milky white dispersion was stable to settling. The stabilizer in this reaction is considered to have the structure shown as Stabilizer C in Figure 1. This synthesis demonstrates that attachment of the stabilizer onto the particle can take place by means of having a radical initiator on the stabilizer chain.

Synthesis of Poly(oxyhydrocarbolene) Diamines

The poly(oxyhydrocarbolene)diamine based upon diethylene glycol was purchased from the Union Carbide Co. as hardener "H-221." The remainder of the poly(oxyhydrocarbolene)diamines were synthesized as follows: The glycol was converted to its disodium salt by addition of sodium methoxide. The salt was cooled to 10°C followed by slow addition of acrylonitrile. The reaction was allowed to proceed at room temperature for 16 hours. The reaction mixture was acidified with aqueous hydrochloric acid and then extracted with 1,2-dichloroethane. The dinitrile was isolated by fractional distillation. The diamine was prepared by reducing the nitrile in an acetic anhydride reaction medium with hydrogen catalyzed by Raney nickel. The resulting amide was isolated from the reaction solution and then hydrolyzed with potassium hydroxide to form the diamine. The diamine was isolated by fractional distillation.

Double Torsional Fracture Energy

One of the two primary means used to gauge the fracture resistance of the cured epoxy resins generated in this work is the double torsional fracture energy test.[12] In this test, the epoxy resin formulation is mixed and deaerated. In general, the curing agent was 2-ethyl-4-methyl imidazole. Epoxy matrix crosslink density, and hence ductility, was varied by means of the addition of resorcinol at various levels. After deaeration, the curable epoxy resin mixture was placed in a Teflon® mold. The cure schedule was 1 hour at 60°C then 1 hour at 90°C followed by 16 hours at 120°C. After cure, the specimen was removed from the mold and a track was routed down the center of the sample. A sharp crack was placed at the tip of one of the ends of the routed groove by means of a razor blade. The sample was placed in an Instron tensile testing machine in a four-point bending mode. The geometry and the loading conditions for each sample were made as identical as possible to every other sample. A quantity which we call "T" was measured for each sample. "T" is the area under the force-displacement curve measured on the Instron testing machine divided by the crack length plus crack thickness. It is an energy dissipated per unit area of crack growth. Thus "T" can be considered to be a relative resistance to fracture that is useful only to compare the data in this paper. During the measurement of "T," the force-displacement curve was observed. The crack propagation was considered "stable" when the force-displacement profile was monotonic with increasing displacement. The crack propagation was considered "unstable" when the force-displacement profile exhibited discontinuities as a function of increasing displacement. This condition is also known as "stick-slip."

These measurements can be related to normal fracture mechanics parameters such as the critical stress intensity factor (K_I) by means of the following expression:

$$K_I = PW_m\left[\frac{3(1+\nu)}{Wt^3t_n}\right]$$

where P is the load, W_m is the moment arm, ν is Poisson's ratio, W is the sample width, t is the sample thickness and t_n is the groove thickness. This was not done in this work because we did not have the means to measure Poisson's ratio.

Gel Swell Measurements

The gel swell of acrylic elastomers in DGEBPA was measured by generating samples of elastomer by means of UV photopolymerization. Thus, the acrylic monomer (see Table II) was mixed with 0.5% by weight butanedioldiacrylate and 0.25% by weight Irgacure 651 as photoinitiator. The mixture was placed in a Petri dish and exposed to UV radiation. After cure, the sample was cut in half and accurately weighed. Each half of the sample was placed in DER™ 332 DGEBPA. One half was exposed to 60°C while the other half was exposed to 100°C while immersed in the DGEBPA. After two days the samples were removed from the DGEBPA and quickly rinsed with acetone and wiped with a paper towel. The samples were dried to remove any excess acetone and then reweighed. The results are reported as a % weight gain.

Adhesive Properties

T-Peel This test is the other major method of gauging resistance to fracture. The T-peel test was conducted according to ASTM D1876-72 with the following modifications:

1. 0.635 mm thick adherends were used instead of 0.81 mm thick adherends. The adherends were 2024-T3 bare aluminum.
2. The aluminum was surface prepared by means of the FPL etch procedure.[13]
3. The components of the adhesive were weighed and mixed by hand. The mixed adhesive was deaerated before use by means of a vacuum pump.
4. Bondline thickness was controlled by the strategic placement of shims in the bonded joint. 0.20 mm shims were employed. The shims were placed at the edges of the specimen and these portions of the bond were cut away before testing.

Lap Shear The lap shear tests were conducted according to ASTM D1002-72 with the following modifications:

1. Adherends were 2024-T3 bare aluminum, 1.57 mm thick.
2. The aluminum was surface prepared by means of the FPL etch procedure.
3. The components of the adhesive were weighed and mixed by hand. The mixed adhesive was deaerated before use by means of a vacuum pump.
4. Bondline thickness was controlled by the inclusion of glass thread of diameter 0.1 mm in the bondline.

Both the T-peel and lap shear specimens were cured at room temperature under steel plates which were meant to provide a reasonably uniform pressure across the bonded area. The adhesive was allowed to cure for 7 days at room temperature before the samples were cut into specimens by means of a band saw. The width of the specimens for both T-peel and lap shear was 2.54 cm. The specimens were placed in an Instron environmental chamber and allowed to equilibrate at temperature for at least 10 minutes before they were destructively tested.

RESULTS AND DISCUSSION

Stabilizer Chemistry and Requirements

Figure 1 shows the types of chemistry which were evaluated as stabilizers. The chemistry ranges from higher molecular weight epoxy resins modified to be reactive with acrylics, to epoxy soluble acrylates retaining some acrylic reactivity to an acrylic polymer functionalized as a free radical initiator. The measurement of fracture characteristics of cured resins was made on dispersions prepared using Stabilizer A. Stabilizers B and C were used to demonstrate that different chemical compositions having the requisite chemical characteristics could be used to prepare stable resinous dispersions. The key features which were discovered by the exercise of synthesizing various stabilizers are:

- the stabilizer must be amphiphilic, *i.e.* partially soluble in the epoxy resin and partially soluble in the acrylic elastomer,
- the stabilizer, if it is based upon bis-phenol A chemistry, must be at least the molecular weight of EPON™ 1004 and
- the stabilizer should be reactive with the acrylic phase.

If any of these criteria are not met, the dispersion will be unstable or will not have good fracture resistance properties. All of the fracture data and adhesive properties data described in this article was generated using Stabilizer A.

It is more than likely that the reason why the higher molecular weight is necessary for the phenoxy resin is for it to be able to intertwine with the epoxy resin to form, as much as possible, an interpenetrating polymer network with the epoxy resin. Attempts were also made to follow the work of Hoffman, Kolb, Arends and Stevens[14] in which they attempt to generate acrylic dispersions in epoxy resins by means of a much lower molecular weight stabilizer. Invariably, these attempts gave dispersions which were metastable at room temperature but unstable when exposed to elevated temperatures. We believe that this is due to the lower molecular weight of the stabilizer.

Monomer Requirements

Using Stabilizer A, dispersions of elastomers were generated in DGEBPA. Table I shows a list of monomers which were used in an attempt to form dispersions. As can be seen in Table I, monomers which have a solubility parameter less than 8.8 $cal^{1/2}/cm^{3/2}$ form dispersions in DGEBPA while those which have solubility parameters greater than 8.8 $cal^{1/2}/cm^{3/2}$ tend to form solutions in DGEBPA. These data provide some of the criteria for the formation of stable dispersions of acrylic elastomers formed *in-situ* in epoxy resins. That is, the elastomer which is formed must come from a monomer whose solubility parameter is less than that of the epoxy resin. Inherently, the elastomer must be polymerized by a mechanism which does not interact with the epoxy resin. Thus, if the epoxy resin is modified to remove all hydroxyl groups (as described above for Stabilizer C), the elastomer could also be formed from urethane precursors.

TABLE I
Monomers evaluated for forming dispersions in DGEBPA

Those which formed solutions	Those which formed dispersions
methyl acrylate	butyl acrylate
ethyl acrylate	hexyl acrylate
methyl methacrylate	octyl acrylate
ethyl methacrylate	pentyl methacrylate
	octyl methacrylate
	lauryl methacrylate
$\delta > 8.8$ $cal^{1/2}/cm^{3/2}$	**$\delta < 8.8$ $cal^{1/2}/cm^{3/2}$**

In another experiment, dispersions of acrylic elastomers were generated in DGEBPA at a level of 15% (based upon the total weight of the dispersion) using Stabilizer A (2% based upon the total weight of the dispersion). Cured resin was generated using 21 pph resorcinol and 3 pph 2-ethyl-4-methyl imidazole as the curing agent (based upon 100 parts of DGEBPA). Cure was carried out as described in the Experimental section. Fracture resistance measurements were done using the double torsion specimen. Table II shows the results of those measurements.

TABLE II
Fracture toughness as a function of elastomer chemical constitution

Elastomer identity	Elastomer T_g (°C)	Gel swell in DGEBPA at 60°C	Gel swell in DGEBPA at 100°C	T (10^6 ergs/cm^2)	Type of crack extension
Butyl Acrylate	−54	54	108	2.4	Unstable
Hexyl Acrylate	−57	23	44	9.7	Stable
Octyl Acrylate	−62	22	11	2.1	Unstable
Butyl Acrylate/Octyl Acrylate (60:40) Copolymer	−58	47	26	9.4	Stable
Hexyl Methacrylate	−7	38	19	12.2	Stable
Lauryl Methacrylate	−67	18	8	2.8	Unstable

The data shown in Table II provide an interesting correlation of the fracture resistance with the chemical constitution of the elastomer. All of these monomers provided dispersions that were stable to settling. The table provides a listing of the elastomers used as well as their T_g. In the folklore of this type of technology, it was once thought that the T_g of the elastomer in some way controlled the level of toughening that was possible. As can be seen, within the range of monomers investigated in this system, there is no correlation between T_g of the elastomer and the resulting fracture toughness of the cured resin. Closer examination of Table II, however, shows an odd correlation between the swellability of the elastomer in DGEBPA and the fracture resistance. In this measurement, the equilibrium swelling weight of DGEBPA in the elastomer was measured at both 60°C and 100°C. Table II shows that excessive swelling of the elastomer in DGEBPA as well as little swelling of the elastomer by DGEBPA both lead to poor fracture resistance. However, a moderate amount of swelling provides optimum fracture resistance. There is evidence in the literature that there is some degree of solubility of epoxy in RLP toughened systems[14] and *vice versa*. It is apparent that in our system not only does some solubility occur but it is also necessary for optimum toughness. It is possible that part of the mechanism for toughening in this system is due to a graded interphase between the epoxy and the elastomer, but this is just conjecture.

Table III shows the effect of the level of rubber in the epoxy resin. The fracture resistance data presented in this table were taken from double torsion tests of samples made using resorcinol at the levels cited as well as 3 pph 2-ethyl-4-methyl imidazole as the curing agent (based upon 100 parts of the DGEBPA). The epoxy resin was as described in the Experimental section using Stabilizer A at a level of 2 pph based upon the total weight of the dispersion. Cure was carried out as described in the Experimental section.

The data in this table indicate two interesting phenomena. First, the degree of fracture resistance obtained from the system is dependent upon both the level of resorcinol as well as the level of elastomer in the epoxy. In general, the higher the level of elastomer, the greater the resistance to fracture. The effect is mediated by the amount of resorcinol present in the system. This matter will be discussed below. Although not listed in this table, it was found that the level necessary for best

TABLE III
Effect of the level of elastomer in the epoxy resin

% Hexyl acrylate[1]	% Resorcinol[2] (pph)	T (10^6 ergs/cm^2)
7.5	24	5.5
10	24	16.5
12.5	24	11.7
15	24	11.8
7.5	20	3.7
10	20	—
12.5	20	5
15	20	5.7

[1] based upon the total weight of the epoxy/acrylic elastomer dispersion
[2] based upon 100 parts of DGEBPA

utilization of this resin system in room temperature curing adhesive formulations was in excess of 20%.

Effect of Epoxy Crosslink Density

The effect of resorcinol on the toughness of cured epoxy resins containing phase-separated elastomers is apparent from Table III. Another experiment was run in which the level of resorcinol was varied in order to study systematically the effect of epoxy resin crosslink density on fracture resistance. Table IV shows the result of varying the resorcinol content from 0 to 24 pph in the epoxy. In this experiment, the level of 2-ethyl-4-methyl imidazole was 3 pph (based upon the weight of the DGEBPA). The cure was carried out as described in the Experimental section.

TABLE IV
Effect of crosslink density

DGEBPA level	Elastomer level[1] (%)	Resorcinol level[2] (pph)	M_c	T (10^6 ergs/cm^2)
100	15	0	380	0.2
100	16.5	10	600	2.6
100	17.6	17.25	1,050	4.2
100	18	20	1,380	5.7
100	18.3	22	1,850	16.2
100	18.6	24	2,380	11.8

[1] based upon the total weight of the epoxy resin/acrylic elastomer dispersion
[2] based upon the 100 parts of the DGEBPA

M_c is the molecular weight between crosslinks and was calculated from the stoichiometry in the system. The data in Table IV clearly indicate that there seems to be an optimum level of M_c for obtaining maximum properties. Unfortunately, due to the method by which these samples were made the level of elastomer was not held exactly constant. Although not apparent from the data in Table IV, samples having M_c less than 1050 gave fracture propagation which was unstable. The morphology of the particles was not investigated as part of this study due to the contrast restrictions mentioned above. However, the reader should be aware that the dispersions were milky white before cure and were milky white after cure. The fact that chain extension and control of crosslink density are important with respect to toughenability of epoxy resins has been described in the literature in work on RLP's. This phenomenon was also investigated in the formulation of two-part room temperature curing adhesives.

2-Part Room Temperature Curing Adhesives

One application of the above-described resin technology is the formulation of 2-part room temperature curing adhesives. It was thought that the unique character of having a pre-phase-separated elastomer could provide benefits to the technology of room temperature curing epoxies since the cure schedule in such epoxies is uncontrolled. That is, since materials like the RLP's relied on the cure mechanism of the epoxy for phase separation, it seemed likely that there would be cure conditions under which phase separation of the elastomer would be hampered. In our resin system, the elastomer is pre-phase separated and would thus be likely to be more resistant to such vagaries in cure.

The results shown in Table IV indicate that crosslink density should play an important role in the performance of an epoxy adhesive based upon this technology. The cases described above were cured at elevated temperatures. Under those circumstances, materials such as resorcinol or bis-phenol A can be used to control the crosslink density of the matrix. In room temperature curing epoxies, such an option is not available. Thus, we must look to the chemistry of the curative and the inherent crosslink density that is generated by the chain length between the reactive groups in the curative.

Table V shows a list of the curatives which were synthesized or purchased. It also shows a listing of the adhesive physical properties that were measured using a resin system based upon DGEBPA and 20% of elastomer particles based upon hexyl acrylate. The curative was added at a stoichiometric ratio to the epoxy resin and 12% (based upon the level of curative) imidazole was also added as a curing accelerator. As can be seen from the table, the room temperature lap shear performance is essentially insensitive to the type of curing agent. However, the room temperature T-peel performance is extremely sensitive to the chemical composition (and hence the M_c) of the curing agent. Of particular note is the series of increasing polyethylene oxide chains as the center portion of the poly(oxyhydrocarbolene)diamines. In those cases, the room temperature T-peel performance is maximized at the diethylene glycol center link. With the ethylene glycol link, the room temperature T-peel performance is somewhat lower than that for the diethylene glycol link but is substantially decreased at −55°C. For the triethylene glycol center link, the room temperature T-peel performance was reduced in comparison with diethylene glycol but the −55°C performance is improved. The importance of crosslink density is further exemplified in that a mixture of equal amounts of the ethylene glycol center segment containing curative and the triethylene glycol center segment containing curative gave results similar to those for the diethylene glycol center segment containing curative.

TABLE V
Correlation of curative with adhesive bond performance

Curative no.	Formula	−55° T-peel (N/25 mm)	RT T-peel (N/25 mm)	RT Lap shear (MPa)	82°C Lap shear (MPa)
1	$H_2N—C_3H_6—O—C_3H_6—NH_2$	0	8.9	28	3.4
2	$H_2N—C_3H_6—O—C_2H_5—O—C_3H_6—NH_2$	45	160	33	4.6
3	$H_2N—C_3H_6—O—(C_2H_5—O)_2—C_3H_6—NH_2$	110	210	33	3
4	$H_2N—C_3H_6—O—(C_2H_5—O)_3—C_3H_6—NH_2$	160	190	31	3
5	50% of 2 + 50% of 4	58	200	32	2

A comparison was also made with the RLP's. Using a formula in which the level of RLP used was identical to the level of pre-phase-separated n-hexyl acrylate based elastomer and the curative used was the same combination of diethylene glycol bis-propylamine with imidazole described above. The results are shown in Table VI. The RLP was pre-reacted with the epoxy resin as described by Paul, *et. al.*[15] The viscosity of the RLP-epoxy reaction product prepared by the method of Paul *et. al.*[15] was increased over that of the epoxy. The reaction product was opalescent when stirred, but no further characterization of the reaction product was done. The T_g of the cured epoxy based upon the pre-phase-separated acrylic elastomer used as the adhesive in these tests was 60°C while that made from the HYCAR™ 1300X8 was 56°C. As can be seen from the table, improved performance at all temperatures was obtained using the pre-phase-separated elastomer system. Electron micrographs of the failure surfaces of the T-peel specimens showed that the adhesive made using the pre-phase-separated elastomer provided a surface which was heavily plastically deformed and exhibited much cavitation due to rupture of the elastomer. The failure surface of the T-peel specimen made from the HYCAR™ 1300X8 showed some plastic deformation but little cavitation due to elastomer particle rupture. It may be construed that the RLP did not properly phase separate under these room temperature curing conditions, thus leading to the less than desireable performance. It should not be construed that this performance is that which is typical of RLP-based adhesives. Rather, this is meant to be a one-on-one comparison in a simple adhesive formulation which has not been optimized for the RLP.

TABLE VI
Adhesive bond performance as a function of type of phase separated elastomer

Elastomer type	−55° T-Peel (N/25 mm)	RT T-peel (N/25 mm)	RT Lap shear (MPa)
Hexyl Acrylate Based Elastomer	110	210	33
HYCAR™ 1300X8	108	145	27
HYCAR™ 1300X15	62	95	33
HYCAR™ 1300X13	130	87	30

HYCAR™ materials are products of B. F. Goodrich and are the so-called "RLP"s

CONCLUSIONS

We have described a novel concept for providing a toughened epoxy-based resin system which can be used to formulate adhesives. This resin system is based upon an *in-situ* formation of pre-phase-separated elastomer particles. The stability of this dispersion in the epoxy resin is heavily dependent upon an amphiphilic "polymeric stabilizer" which is specially designed to be reactive with the forming elastomer particle and soluble in the epoxy matrix. We have shown that the toughening effect is dependent upon the level of elastomer in the epoxy resin, the chemical constitution of the elastomer (especially in providing the right level of solubility in the epoxy matrix) and the crosslink density of the cured epoxy matrix. The resin was used to formulate 2-part room temperature curing epoxy adhesives. The properties of adhesive bonds made with those adhesives were shown to be dependent upon parameters similar to those that the heat curing epoxies were dependent upon. Adhesive formulas were described in which performance was higher than similar formulations based upon RLP's.

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