

# Rubber-Modified Epoxy Resins Containing High Functionality Acrylic Elastomers

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## Synopsis

The effect of the functionality of *n*-butylacrylate/acrylic acid copolymers upon the impact resistance of epoxy resins modified with these rubbery copolymers as a second phase was investigated using a high speed tensile test and scanning electron microscopy. It was found that an optimum functionality of copolymer existed for maximum impact resistance. This optimum value was the result of the competition between the amount of rubber-matrix reaction, an increase in which tended to increase toughness, and solubility of the rubber in the epoxy matrix, which eventually decreased toughness.

## INTRODUCTION

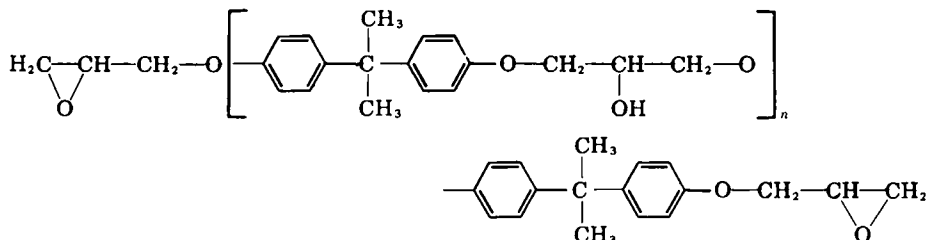
Epoxy resins have excellent adhesion, mechanical, and electrical properties, and are widely utilized in the fields of coatings, adhesives, castings, etc. However, it is well known that the commonly used epoxy resins when cured with stoichiometric amounts of polyfunctional amines are rather brittle, and their low impact resistance limits the use of these resins in structural applications. Improvement of the impact strength of epoxy resins, without loss of thermal resistance, is therefore a significant goal.

Since it was shown by McGarry and Willner<sup>1</sup> that the carboxy-terminated copolymer of butadiene and acrylonitrile (CTBN) is useful for the improvement of the fracture toughness of epoxy resins, much work has been done in this field.<sup>2-8</sup> In these researches, the effect of the acrylonitrile content of copolymer,<sup>2</sup> copolymer concentration,<sup>3,4</sup> and the types and the concentration of curing agents<sup>5,6</sup> on the fracture toughness or on the impact strength of the epoxy resin have been studied. In this paper we report a study of the effect of degree of interphase bonding on impact strength, changed by increasing the rubber functionality.

In previous studies<sup>9-11</sup> Bell and Gazit showed that carboxy-terminated poly(*n*-butylacrylate) liquid rubber (CTPnBA) is effective as a modifier for improving the impact resistance of amine cured epoxy resins, and suggest that (CTPnBA) has advantages over CTBN. CTPnBA was chosen for the present work and the *n*-butylacrylate was copolymerized with acrylic acid to vary the rubber functionality. The resulting *n*-butylacrylate-acrylic acid copolymer has both end and pendant carboxyl groups.

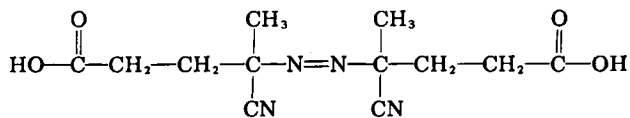
## EXPERIMENTAL

**Materials.** The epoxy resin used was liquid bisphenol-A-type epoxy resin (Epon\* 828) with an equivalent weight per epoxide group of  $180 \pm 5$ . The structure is shown below, where  $n$  is approximately 0.2:

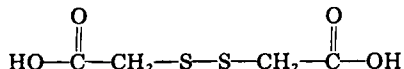


Methylenedianiline (MDA) was used as a curing agent. Tetrabutylammonium iodide (TBAI) was used as a catalyst for the carboxyl-epoxy group reaction, at a concentration of 1% by weight of the epoxy resin. *n*-Butylacrylate (nBA) and acrylic acid (AA) were used as monomers.

4,4'-azobis-(4-cyanovaleric acid) (ABCVA)



and dithiodiglycolic acid (DTDGA)



were used as an initiator and chain transfer agent, respectively. The curing agent, catalyst, monomers, and chain transfer agent were reagent grade materials and were used without further purification. The initiator was purified by freeze-drying, since as supplied it contains water.

nBA/AA copolymers were bulk polymerized using a previously described polymerization procedure.<sup>9,11</sup> The AA/nBA volumetric ratio was changed from 0/50 to 10/50 (Table I). After completion of polymerization the products were washed by an acetone and water method (Appendix). It was confirmed by GPC that the method removes the excess initiator and chain transfer agent, as well as any small amounts of residual monomers.

**Epoxy Resin Curing.** The curing of the epoxy resin was carried out by a two-step curing process. In the first step, 10 parts by weight of nBA/AA copolymer were added to 90 parts of epoxy + TBAI, and the mixture was placed

TABLE I  
The Concentrations of Carboxyl Group of nBA/AA Copolymers and Their Prereaction Products with Epon 828

AA/nBA (cc/cc)	Conc of -COOH group (meq/g rubber)	
	Copolymers	Products
0/50	0.215	0.0152
4/50	1.130	0.0100
10/50	2.130	0.0168

\* Trade mark of Shell Chemical Co.

in the oven for 2 h at 120°C. During this stage the carboxyl groups on the copolymers reacted with the epoxide groups on the Epon 828, with the aid of the TBAI catalyst. Titration of this mixture after the reaction showed practically no carboxyl groups in the solution, as shown in Table I. The reaction products in this stage were still liquid; no gel was observed. The large excess of epoxy resin made it possible for each carboxyl group to react with an unreacted epoxy molecule.

In the second step, the prescribed amount of curing agent was added to this compound and the mixture was poured into glass molds which were coated with a thin film of a release agent (tetrafluoroethylene oligomer: MS-136 by Miller-Stephenson) and cured at 120°C for 1 h followed by 150°C for 2 h. The various samples for the mechanical tests were machined from these cured epoxy plates.

**Measurements.** The carboxyl content of the carboxyl-terminated nBA/AA copolymers was determined by a titration method: 0.5–1.0 g of copolymer was accurately weighed into a 150-cc flask, into which were then pipetted 10 cc of methanol and 20 cc of acetone. 0.1N KOH solution was continuously added into the sample solution at a rate of about 0.01 cc/min by use of a constant rate syringe pump. The inflection end point occurred at about pH 10.5.

The molecular weight of nBA/AA copolymers was determined by vapor pressure osmometry (VPO) and gel permeation chromatography (GPC). The experimental conditions for both methods have been described in detail elsewhere.<sup>11</sup>

Tensile impact strength and elongation of cured epoxy resins were measured at a crosshead speed of 3500 ± 500 mm/s with the Plastechon Universal Tester (Plas-Tech).<sup>10</sup> Load and displacement were read via a digital oscilloscope (Explorer III, Nicolet Instrument Corporation). Tensile strength, Young's modulus, and sample elongation were simultaneously obtained by this test. The impact strength (energy) was calculated from the area under the stress-strain curve. Merits of the method have been discussed previously.<sup>10,11</sup>

The morphology of fracture surfaces of samples broken in the tensile impact test was observed by using the scanning electron microscope (SEM). The fracture surfaces were coated with a layer of gold about 200 Å thick. Magnifications of about 1500× and 3800× were used.

TABLE II  
Some Properties of nBA-AA Copolymers

AA/nBA (cc/cc)	Concn of COOH group (meq/g)	$\bar{M}_n^a$	$\bar{M}_n^b$	$\bar{M}_w^b$	$\bar{M}_w/\bar{M}_n^b$	Function- ality (eq/mol)
0/50	0.216	9000	6530	31,700	4.9	1.94
2/50	0.816	10,000	6070	37,900	6.2	8.16
4/50	1.13	10,300	6700	33,100	4.9	11.6
6/50	1.40	9000	7070	32,800	4.6	12.6
8/50	1.80	12,400	7300	36,700	5.0	22.4
10/50	2.13	12,300	7570	40,600	5.4	26.2

<sup>a</sup> Measured by VPO.

<sup>b</sup> Measured by GPC.

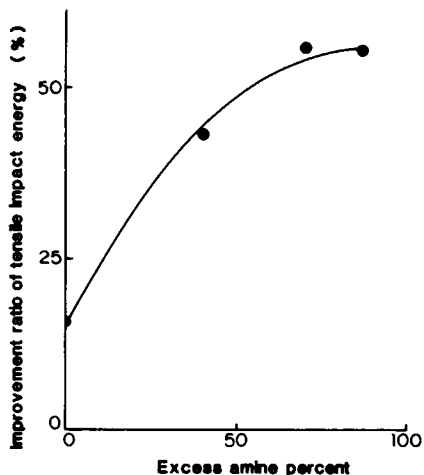


Fig. 1. Improvement in tensile impact energy vs. stoichiometric excess amine percent. Epoxy resin: diglycidyl bisphenol A (Epon 828). Curing agent: methylene dianiline. Functionality of nBA/AA copolymer: 12.6 eq/mol. Rubber concentration: 10 parts rubber/100 parts epoxy resin.

## RESULTS AND DISCUSSION

**Characterization of the nBA/AA Copolymers.** The number and weight average molecular weight ( $\overline{M}_n$ ,  $\overline{M}_w$ ), concentration of COOH groups, and functionality of the nBA/AA copolymers are shown in Table II. The concentration of COOH groups in the copolymers increased from 0.216 to 2.13 meq/g with an increase of AA added, and the functionality estimated from the product of the COOH concentration and  $\overline{M}_n$  (VPO), was changed from 2.0 to 26.1, i.e., the lowest and highest functionality copolymer have one carboxyl group per about 330 and 34 methylene units, respectively. Accordingly, it is expected that the prereaction product from the first stage of cure has one epoxy molecule per 330 and 34 methylene units in the lowest and highest carboxyl content systems, respectively.

The average molecular weights and their distribution ( $\overline{M}_w/\overline{M}_n$ ) for the copolymers remained at about the same level, even though the concentration of carboxyl groups changed.

**The Effects of Functionality of Copolymer on the Impact Resistance of Modified Epoxy Resins.** The effect of the concentration of curing agent on percent improvement in the tensile impact energy of modified epoxy resins is shown in Figure 1. The improvement is the percentage improvement in tensile impact energy of the rubber-modified sample relative to a control (no rubber) at the same percent excess amine as the rubber-modified sample. The amount of impact energy improvement increased as the concentration of curing agent increased, up to 86% excess amine.

Bell<sup>12,13</sup> showed that as the molecular weight between crosslinks ( $M_c$ ) of an epoxy resin increased with increasing the concentration of MDA, the Izod impact strength of these systems also increased to a maximum and then decreased. Figure 1 shows that the network structure of the epoxy matrix has an important

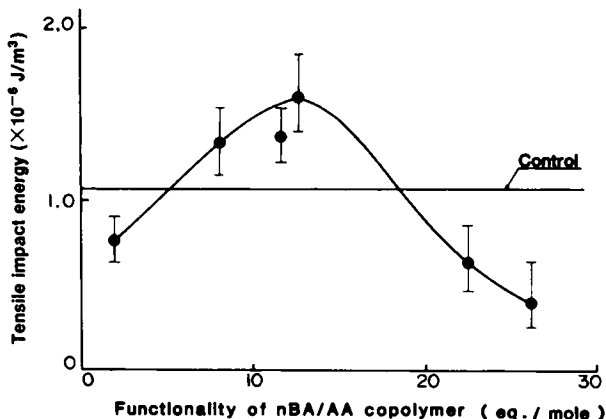


Fig. 2. Tensile impact energies of modified epoxy resins vs. functionality of nBA/AA copolymers. Epoxy resin: bisphenol A DGE (Epon 828). Curing agent: methylene dianiline. Excess amine %:  $86 \pm 1$ . Crosshead speed:  $3500 \pm 500$  mm/s.

additional effect on the impact strength in the nBA/AA copolymer-modified system (in addition to the effect in the nonmodified system), and that a loosely crosslinked matrix is more suitable for rubber modification than a tightly crosslinked matrix. Unfortunately, this implies that a lower  $T_g$  polymer (e.g., 100–130°C) is more easily toughened by rubber modification than a high  $T_g$  polymer (e.g., 150–200°C). To maximize the rubber modification effect, subsequent tensile impact energies were measured at 86% excess of MDA.

Tensile impact energies of epoxy resins modified with a series of nBA/AA copolymers are shown in Figure 2. With increasing COOH content the impact energy increased, but showed a maximum value in the region where the functionality of the copolymer was about 12. The toughest sample had a tensile impact strength 50% greater than that of the control. This shows that an optimum functionality of copolymer exists for improving the tensile impact strength of cured epoxy resins; the magnitude of this optimum value is expected to vary with rubber-matrix compatibility.

Izod impact strength measurements, when plotted as a function of carboxyl functionality, gave a curve of the same shape and relative improvement as the tensile impact data. Data for another curing agent (2,4-dimethyl, 2,4-diaminohexane, at 70% stoichiometric excess) gave the same curve shape and relative impact energy improvement.

In addition, the modified epoxy resins were opaque in the region where the functionality was less than 12, but the samples which had a functionality of higher than about 12 were clear. This observation suggests that the copolymers of functionality greater than 12 dissolve in the matrix and were therefore not effective as a separate phase. Elongation at break of the modified epoxy systems is shown in Figure 3. The elongation at break of these systems shows a maximum value analogous to the tensile impact energy. This result also shows an optimum functionality of copolymer exists.

To examine the situation further, the morphology of the fracture surface,  $T_g$ , and the weight loss by solvent extraction were studied. The morphology of the

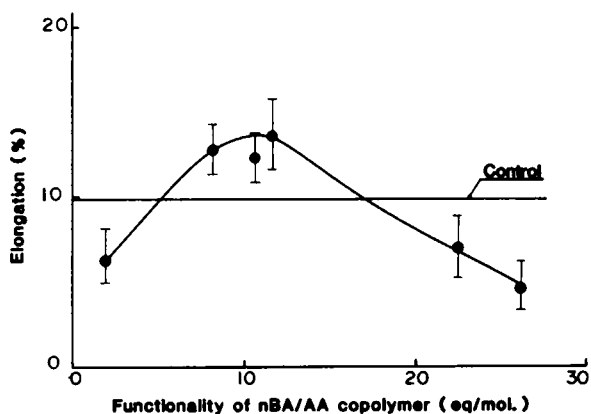


Fig. 3. Ultimate elongation of modified epoxy resins vs. functionality of nBA/AA copolymers. Epoxy resin: bisphenol A DGE (Epon 828). Curing agent: methylene dianiline. Excess amine (%):  $86 \pm 1$ . Crosshead speed:  $3500 \pm 500$  mm/s.

fracture surfaces, observed by SEM, are shown in Figures 4 and 5. Two size particle distributions can be clearly seen in the epoxy resin modified with nBA/AA copolymer for which the functionality is 1.9 eq/mol [Fig. 4(b)]. In this system, the rubber-epoxy solution before mixing with the curing agent was not completely clear. This shows that this  $f = 1.9$ ,  $\overline{M}_n = 6.5 \times 10^3$  to  $9.0 \times 10^3$  co-

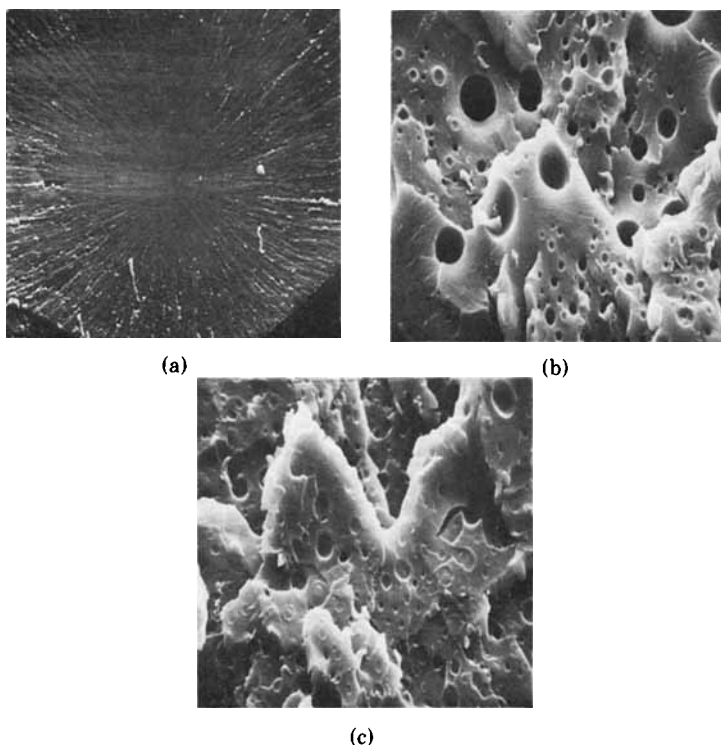


Fig. 4. Morphology of fracture surfaces from the tensile impact test. Magnification 1500 $\times$ . (a) control (nonmodifying); (b) functionality 1.94 eq/mol (1500 $\times$ ); (c) functionality 8.16 eq/mol (1500 $\times$ ).

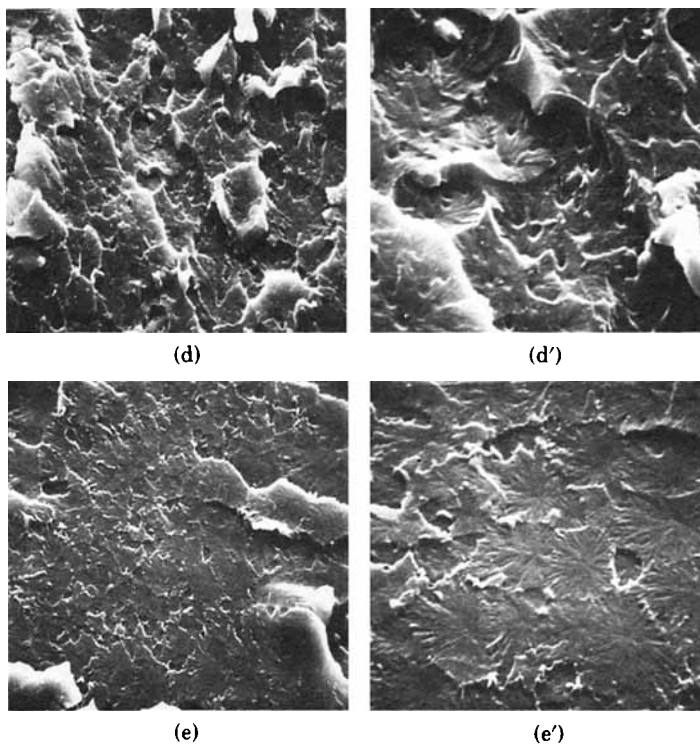


Fig. 5. Morphology of the fracture surface broken in the Tensile impact test: (d) functionality 12.6 eq/mol (1500 $\times$ ); (d') functionality 12.6 eq/mol (3800 $\times$ ); (e) functionality 26.2 eq/mol (1500 $\times$ ); (e') functionality 26.2 eq/mol (3800 $\times$ ).

polymer is noncompatible in the epoxy matrix, and is not completely dissolved in the matrix before curing. With higher functionality copolymers, the size of the copolymer particles is smaller than that of the lower functionality copolymer [Figs. 4(c) and 5(d,d')]. In the ca. 28 functionality copolymer, the copolymer particles are not observed at even higher magnification [ $\times 3800$ , Fig. 5(e')]. It can be concluded from these observations that by increasing the COOH content of the copolymer, the compatibility between the copolymer and epoxy matrix is increased. The copolymer of functionality about 28 eq/mol is completely dissolved in the matrix.

On the other hand, in the large size particles in Figure 4(b), rubber particles are not observed, only holes. That is, the particles have already fallen away from the matrix. This observation suggests that the reaction between the large copolymer particles and epoxy matrix is not sufficient in this system. In the higher COOH content copolymers, the copolymer phase is observed in the SEM micrographs [Figs. 4(c) and 5(d')]. In these systems the failure crack has propagated through the particles. This shows that the reaction between the copolymer phase and the epoxy matrix increased with an increase of the COOH content of the copolymer.

We can conclude from these SEM micrographs that both solubility and extent of reaction between the copolymer phase and epoxy matrix increased as the COOH content of the copolymers increased.

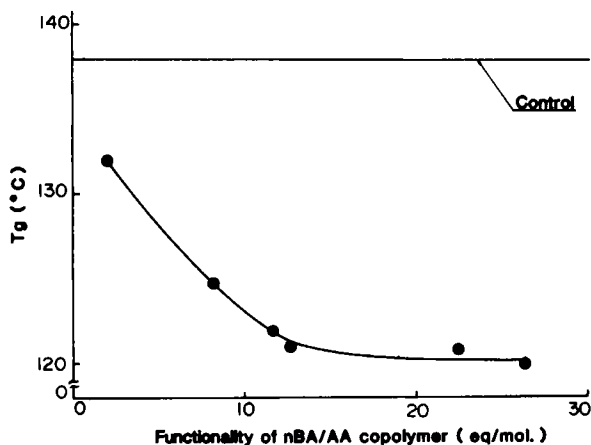


Fig. 6.  $T_g$  of cured epoxy resins vs. functionality of nBA/AA copolymer. Epoxy resin: bisphenol A DGE (Epon 828). Curing agent: methylene dianiline. Excess amine (%):  $86 \pm 1$ .

The glass transition temperatures ( $T_g$ ) of the modified epoxy resins are shown in Figure 6. The  $T_g$  of these systems decreased as the COOH content of copolymers increased. This result means that a greater amount of copolymer dissolved in the epoxy matrix as the COOH content increased, in harmony with the size decrease of the copolymer phase observed in the fracture surfaces by SEM (Figs. 4 and 5).

The weight loss of modified and nonmodified (control) epoxy resin by Soxhlet extraction is shown in Figure 7. The weight loss of the control is only about 5%, but in the low-functionality rubber, about 15% of the sample was lost by the extraction. The weight loss decreased with increasing of COOH content of the copolymer. In addition, it was confirmed by IR analysis that the soluble portions were composed primarily of copolymer rubber.

This result again shows that the reaction between the rubber particles and the epoxy matrix was insufficient in the low functionality copolymer, and that reaction increased as the functionality of copolymer increased. This is consistent with the observation that the copolymer phase did not appear to separate from the fracture surface in the high carboxyl content systems (Figs. 4 and 5).

It is well known<sup>1,3,14</sup> that, in order to toughen an epoxy resin by the addition of a liquid polymer, (a) the liquid polymer should form a rubbery second phase which is dispersed throughout the matrix and (b) the rubbery second phase should be bonded to the matrix through the functional groups on the liquid polymer. We can explain the effect of the functionality on the impact strength (Fig. 2) elongation (Fig. 3) on the basis of these principles as follows: With an increase of the functionality of the copolymers, the reaction between the copolymers and epoxy matrix increases so that the copolymer phase becomes more strongly bonded to the matrix [e.g., Fig. 4(c) vs. Fig. 4(b)], and the toughness of these systems therefore increases. However, when the functionality becomes higher than 10–15, the compatibility of the copolymers with the matrix is too great to form a separate copolymer phase [Figs. 5(e) and 5(e')]. These systems become homogeneous, and their toughness decreases. We conclude that the toughness of epoxy resins modified with high functionality nBA/AA copolymers



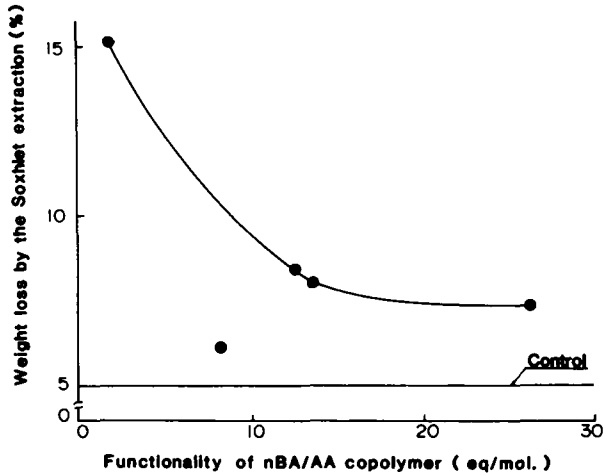


Fig. 7. Weight loss by the soxhlet extraction vs. functionality of nBA/AA copolymer. Solvent: acetone. Extraction time: 24 h. Drying conditions: 60°C, 15 h (in a vacuum oven).

is determined by the competition between the amount of reaction at the particle-matrix interface, and the compatibility of the copolymer with the epoxy matrix.

**Other Mechanical Properties of Epoxy Resins Modified with nBA/AA Copolymers.** Tensile strength and Young's modulus of epoxy resins modified with nBA/AA copolymers are shown in Figure 8. The solid lines in this figure show data for the same composition without copolymer. Tensile strength and Young's modulus of the modified epoxy resins remained at approximately the same value as that of the corresponding control. These results show that the

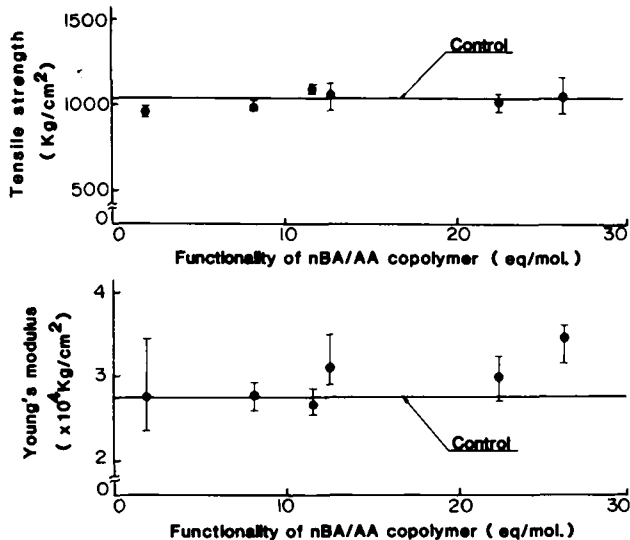


Fig. 8. Tensile strength and Young's modulus of cured epoxy resins vs. functionality of nBA/AA copolymers. Epoxy resin: bisphenol A DGE (Epon 828). Curing agent: methylene dianiline. Excess amine (%):  $86 \pm 1$ . Crosshead speed:  $3500 \pm 500$  mm/s.

addition of the copolymers (less than 10 parts) increased the impact resistance of the cured epoxy resin without a significant decrease in tensile properties.

### CONCLUSIONS

The bisphenol A type epoxy resin cured with methylene dianiline was modified with a series of *n*-butylacrylate-acrylic acid copolymers. The effect of the functionality of the copolymers on the impact resistance of cured epoxy resins was investigated in detail from the standpoint of the reactivity and compatibility between the copolymers and epoxy matrix. From these results, the following conclusions are obtained:

(i) An optimum functionality of nBA/AA copolymer for tensile impact strength and elongation exists in epoxy resins modified with the copolymers.

(ii) This optimization is the result of the competition between the reactivity and compatibility of copolymer with the epoxy matrix.

(iii) The addition of nBA/AA copolymers (less than 10 parts) improved the impact resistance of the cured epoxy resin without a major decrease of other mechanical properties.

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### APPENDIX: WASHING PROCEDURE FOR nBA HOMOPOLYMER AND nBA/AA COPOLYMER IN ACETONE AND WATER

The PnBA and nBA/AA copolymer were bulk-polymerized.<sup>9,11</sup> The rubber after cooling was removed from the reaction vessel by adding 80 mL of boiling acetone. All products, including the initiator and chain transfer agent, dissolved. The solution was transferred to a 150-mL flask, and 80 mL of distilled H<sub>2</sub>O was added to this solution. Immediately a thick viscous white precipitate formed. The liquid and precipitate were poured into centrifuge tubes and centrifuged at 2800 rpm for 25 min. The brown clear acetone layer and viscous white rubber layer formed at the top and bottom of the tube, respectively. The acetone layer was removed.

80 mL of fresh acetone was added to the rubber in the centrifuge tubes and stirred. The rubber dissolved completely. 70 mL of distilled H<sub>2</sub>O was added to this solution. Again, a viscous white precipitate formed. The mixture was centrifuged for 25 min. The rubber and acetone layers formed again. The acetone layer was removed.

80 mL of fresh acetone was added to the rubber. Again, the rubber dissolved completely. To this, 60 mL of distilled H<sub>2</sub>O was added and stirred. The mixture was centrifuged for 25 min. The resultant top acetone layer formed a nonviscous cloudy white emulsion. The rubber has a brown hazy color. The acetone layer was removed and rubber was placed overnight in a vacuum oven at 80°C.

The final product was transparent with a slight brown color.

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