# Epoxy–Imide Resins Based on Bis(carboxyphthalimide)s

K. ADHINARAYANAN, S. PACKIRISAMY,* REENA S. GEORGE,† V. LAKSHMANA RAO, and R. RAMASWAMY

Polymers and Special Chemicals Division, Propellants and Special Chemicals Group,
Vikram Sarabhai Space Centre, Trivandrum 695022, India

**SYNOPSIS**

Epoxy–imide resins have been obtained through the reaction of Araldite GY 250 (diglycidylether of bisphenol-A and epichlorohydrin; difunctional) and Araldite EPN 1138 (Novolac-epoxy resin; polyfunctional) with bis(carboxyphthalimide)s derived from 4,4′-diaminodiphenylsulfone, 3,3′-diaminodiphenylsulfone, 4,4′-diaminodiphenylether, and 4,4′-diaminodiphenylmethane and trimellitic anhydride. For each epoxy-imide resin system, epoxy equivalent to carboxy equivalent ratio has been optimised to obtain the maximum tensile lap shear adhesive strength on stainless steel substrates at room temperature. The lap shear strength at 100, 150, and 175°C has been determined for the optimum ratio. Araldite EPN-1138-based systems give the lap shear strength of 141–182 kg/cm$^2$ at room temperature for the optimum compositions and retain about 84–100% of the lap shear strength at 150°C. Araldite GY-250-based systems have lap shear strength of 183–193 kg/cm$^2$ and retain 76–84% of the lap shear strength at 150°C except for the one cured with bis(carboxyphthalimide) prepared from 4,4′-diaminodiphenylmethane, which retains only 17% of the lap shear strength. Among the systems studied, Araldite GY 250 cured with bis(carboxyphalimide) synthesized from 3,3′-diaminodiphenylsulfone appears to be the best, retaining 75% (138 kg/cm$^2$) of the lap shear strength at 175°C.

## INTRODUCTION

Epoxy resins find extensive applications as reinforced plastics, surface coatings, adhesives, encapsulation of electronic components, castings, etc.[1,2] Amines, polyamides, anhydrides, $BF_3$: amine complexes, etc. have been commonly used as curators for epoxy resins.[3] In recent years, attention has focused on the development of novel curators containing imide group for epoxy resins with a view to improving the performance at elevated temperatures. A patent by Lee[4] describes the synthesis of anhydride-terminated polyimide through the reaction of 2,4-toluidinediamine and 3,3′,4,4′-benzophenone tetracarboxylic dianhydride and the use of this compound as a curator for epoxy resins for making composites. Another patent, by Seraffini et al.,[5] deals with the preparation of composites from epoxy resins using bisaminoimides as curators. Of late, Ichino and Hasuda[6] studied the curing of epoxy resin with bis(hydroxyphthalimide)s obtained through the reaction of aromatic/aliphatic diamines and 4-hydroxyphthalic anhydride and evaluated the adhesive properties.

In the present work, we report the adhesive properties of epoxy–imide resins obtained through the reaction of epoxy resins, namely Araldite GY 250 (diglycidylether of bisphenol-A and epichlorohydrin; difunctional) and Araldite EPN1138 (Novolac-epoxy resin; polyfunctional) with bis(carboxyphthalimide)s. The bis(carboxyphthalimide)s, viz., sulfuryl-bis[*N*-(4-phenylene)-4′-(carboxy)phthalimide] (BCPI-1), sulfuryl-bis[*N*-(3-phenylene)-4′-(carboxy)phthalimide] (BCPI-2), methylene-bis-[*N*-(4-phenylene)-4′-(carboxy)phthalimide] (BCPI-3), and oxy-bis[*N*-(4-phenylene)-4′-(carboxy)phthalimide] (BCPI-4), have been synthesized through the reaction of corresponding aromatic diamines with trimellitic anhydride followed by chemical imidization. The curing behaviour of the epoxy resins with these bis(carboxyphthalimide)s

* To whom correspondence should be addressed.
† Project student, Cochin University of Science and Technology, Cochin, India.

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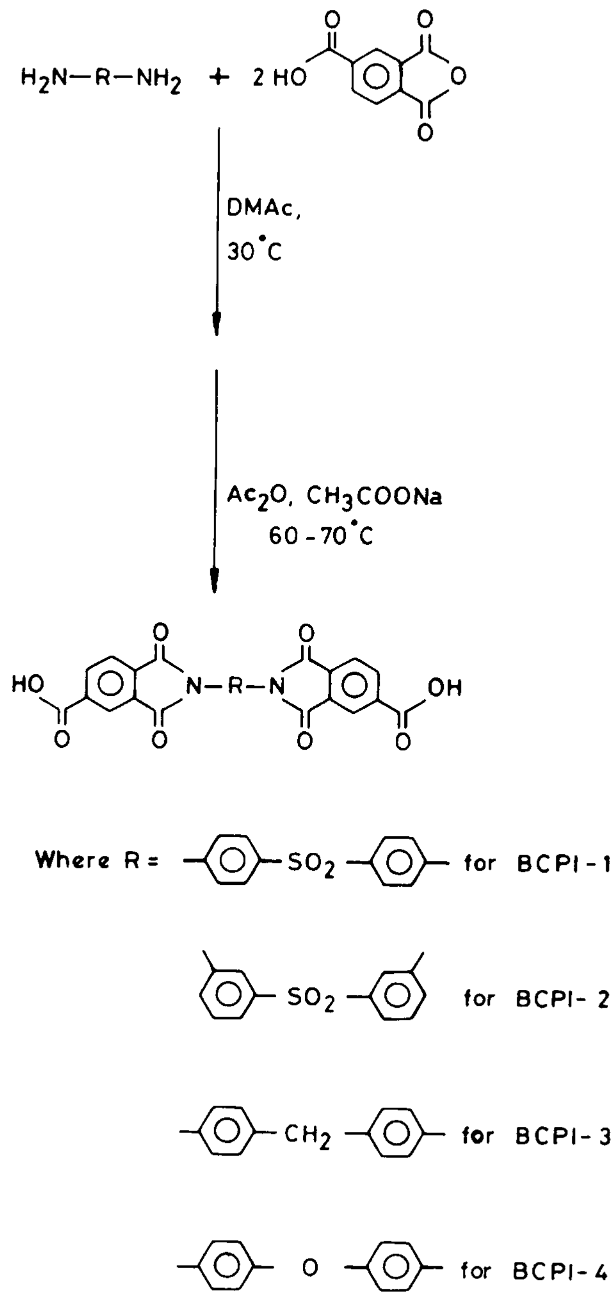
have been studied. For each epoxy–BCPI system, epoxy equivalent to carboxy equivalent ratio has been optimised to obtain the maximum tensile lap shear adhesive strength on stainless steel substrate at room temperature. For these systems, the tensile lap shear adhesive strength at 100, 150, and 175°C has been evaluated for the optimum composition. The thermal properties of these epoxy–imide resins have also been studied.

## EXPERIMENTAL

### Synthesis of Bis(carboxyphthalimide)s

Bis(carboxyphthalimide)s have been synthesized through the reaction of aromatic diamines such as 4,4′-diaminodiphenylsulfone,3,3′-diaminodiphenylsulfone, 4,4′-diaminodiphenylmethane and 4,4′-diaminodiphenylether with trimellitic anhydride in dimethyl acetamide followed by chemical imidization adopting the procedure similar to that of Wrasidlo and Augl[7] (Scheme I).

These bis(carboxyphthalimide)s have been characterized by elemental analysis and acid value. The observed values were in good agreement with the calculated values. The characteristic imide absorption peaks were observed at 1,780, 1,730, and 720 $cm^{-1}$. The broad band around 3,500 $cm^{-1}$ is attributed to the —OH of carboxylic acid groups.




**Scheme I** Synthesis of bis(carboxyphthalimide)s.

### Epoxy Resins

Araldite GY 250 (DGEBA; epoxy value 5.0–5.5 eqv/kg) and Araldite EPN 1138 (Novolac-epoxy; epoxy value 5.5–5.7 eqv/kg) (Fig. 1) manufactured and supplied by M/s Hindustan Ciba-Geigy India Ltd. have been used.

### Surface Preparation of SS Test Specimen

Stainless steel (AISI 304 SS cold roll) test pieces of dimension 100 × 25.4 × 1.6 mm were cut from a large SS sheet as per procedure of ASTM 1002-72. These test pieces were first abraded followed by chemical etching at 50°C for 15 min in chromic acid solution (saturated sodium dichromate solution, 3.5 g and concentrated sulfuric acid, 100 mL). After etching, carbon residues were removed with a nylon brush while rinsing and cleaned pieces were dried at 70°C in an air oven.

### Curing of Epoxy Resins with Bis(carboxyphthalimide)s

Known quantities of epoxy resin and BCPI were mixed thoroughly in a pestle and mortar and the cure reactions were followed by DSC and IR spectra.

The epoxy–BCPI mixture was applied on SS substrate and bonded test specimens were kept in an air oven under contact pressure and the temperature of the oven raised to 170°C. They were kept

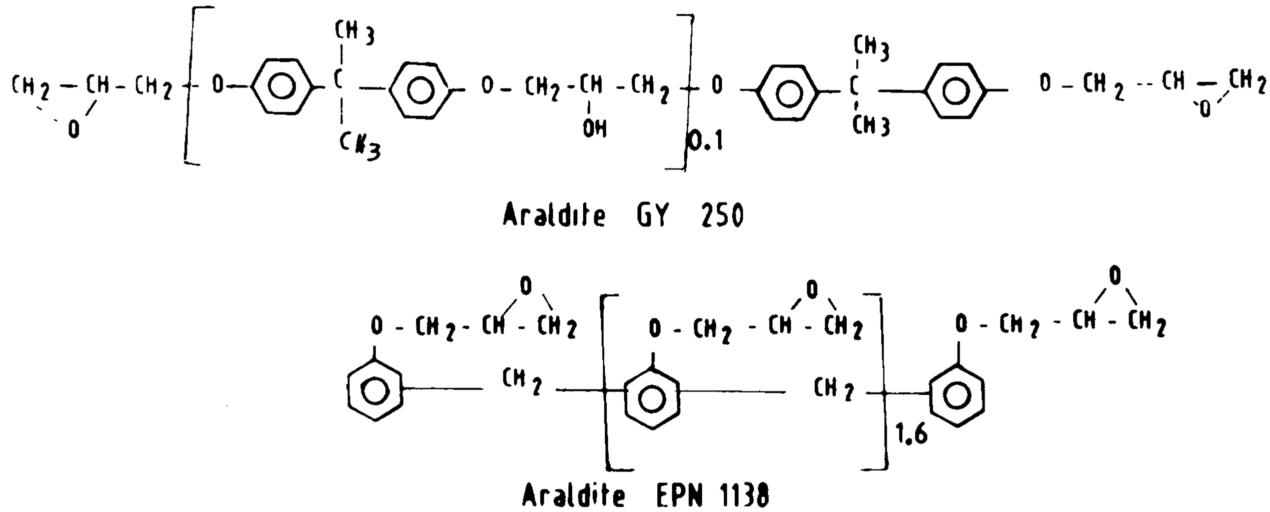



**Figure 1** Chemical structures of Araldite GY 250 and Araldite EPN 1138.

at this temperature for 1 h followed by 220°C for 1 h and finally at 250°C for 1 h.

### Measurements

IR spectra were recorded on a Perkin-Elmer 283 spectrometer in KBr pellets. DSC studies were made with a Mettler DSC Model No. TA 3000 at a heating rate of 10°C/min. TGA curves were recorded with a Dupont 900 thermal analyzer in conjunction with 951 thermogravimetric analyzer at a heating rate of 10°C/min in nitrogen atmosphere. Tensile lap shear strength of bonded SS specimens was measured using Instron Model No. 4202 at a crosshead speed of 10 mm/min. Tensile lap shear strength at 100, 150, and 175°C was measured using Instron after equilibrating the test specimen in a hot chamber attached to the Instron for a period of 10 min.

**Table I Curing of Epoxy Resins with Bis(carboxyphthalimide)s: DSC Studies**

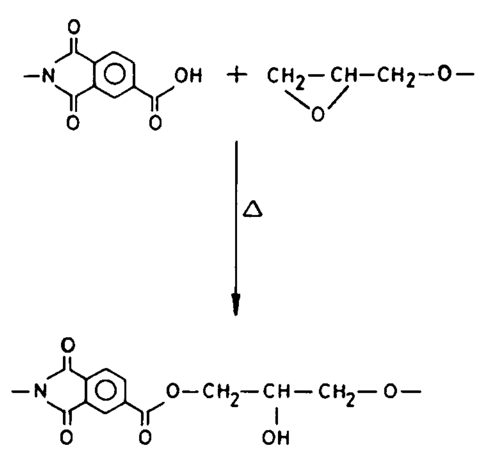
| Systems[a] | $T_i$ (°C) | $T_{max}$ (°C) | $T_f$ (°C) |
|---|---|---|---|
| BCPI-1-EPN 1138 | 128 | 210 | 231 |
| BCPI-2-EPN 1138 | 125 | 185 | 200 |
| BCPI-3-EPN 1138 | 120 | 195 | 217 |
| BCPI-4-EPN 1138 | 165 | 225 | 265 |
| BCPI-1-GY 250 | 151 | 208 | 245 |
| BCPI-2-GY 250 | 150 | 184 | 198 |
| BCPI-3-GY 250 | 130 | 186 | 211 |
| BCPI-4-GY 250 | 180 | 229 | 272 |

$T_i$, initial cure temperature; $T_{max}$, maximum cure temperature; $T_f$, final cure temperature.
[a] BCPI:epoxy (acid equivalent to epoxy equivalent) = 1:2.

## RESULTS AND DISCUSSION

### Curing of Epoxy Resins with Bis(carboxyphthalimide)s

Curing of epoxy resins, Araldite EPN 1138, and Araldite GY 250 with BCPIs have been studied using DSC for the composition 1 : 0.5 (epoxy equivalent to acid equivalent ratio). The results of this study are summarized in Table I. The curing reaction is shown in Scheme II. It is observed that, in general, the initiation of curing is at a lower temperature for the EPN 1138 system compared to the GY 250 system, indicating that the BCPIs probably have better reactivity with the former than the latter. It is in-



**Scheme II** Curing of epoxy resin with bis(carboxyphthalimide).

teresting to note that the initial cure temperature is relatively higher for GY 250–BCPI-4 and EPN 1138–BCPI-4 systems. Except for these two systems, all other systems undergo complete curing below 250°C.

Following the cure schedule discussed in the Experimental section, epoxy resin–BCPI ratios have been optimised to obtain the maximum room temperature adhesive lap shear strength; the details of this study will be discussed later. For all these systems, acid equivalent to epoxy equivalent ratio is less than one to obtain the maximum adhesive strength. If the curing proceeds through the —COOH–epoxy addition reaction only, it is expected that the cured product should contain unreacted epoxy groups. The IR spectra of the cured resins for the optimum ratios indicate the complete disappearance of the peak at 910 $cm^{-1}$ corresponding to epoxy group. The above observation suggests that in addition to acid–epoxy reaction as indicated in Scheme II, additional cure reaction involving the dangling —OH group present in the growing polymer chain and epoxy group probably takes place.[6,8] The IR spectra of the cured resins show absorptions at 1,780, 1,720, 1,370, and 720 $cm^{-1}$ arising due to imide group. The broad band around 3,500 $cm^{-1}$ is due to associated —OH group obtained as a result of the esterification reaction. The characteristic ester peak is probably merged with the imide absorption at 1,720 $cm^{-1}$ (Figs. 2 and 3).

## Effect of BCPI–Araldite GY 250/EPN 1138 Ratio on the Adhesive Strength of SS Substrates

Initial attempts have been made to study the adhesive strength of BCPI–GY 250/EPN 1138 systems for BCPI–epoxy ratio (acid equivalent to epoxy equivalent) of 1 : 1. As the adhesive strength was considerably low, it was necessary to optimise the BCPI–epoxy ratio to obtain a reasonably good strength. The variation in adhesive strength with the variation of BCPI–epoxy ratio is presented in Figures 4 and 5.

It is observed that, in general, the adhesive strength at room temperature of BCPI–EPN 1138 systems is lower than that of BCPI–GY 250 systems. The lower adhesive strength of EPN-1138-based systems is probably caused by the increase in crosslinking and correspondingly brittle character arising due to the polyfunctional nature of EPN 1138 resin. It is interesting to note that the optimum ratio to obtain the maximum adhesive strength for BCPI–EPN 1138 systems varies over a narrow range, 0.37–0.40. For BCPI-1–EPN 1138 and BCPI-2–EPN 1138 systems, adhesive strength of 141 and 127 $kg/cm^2$ have been obtained, which are lower than those of BCPI-3–EPN 1138 and BCPI-4–EPN 1138 systems. The higher adhesive strength for the latter two systems may be attributed to the presence of flexible groups such as $—CH_2—$ and —O—.

Unlike the case of BCPI–EPN 1138 systems for

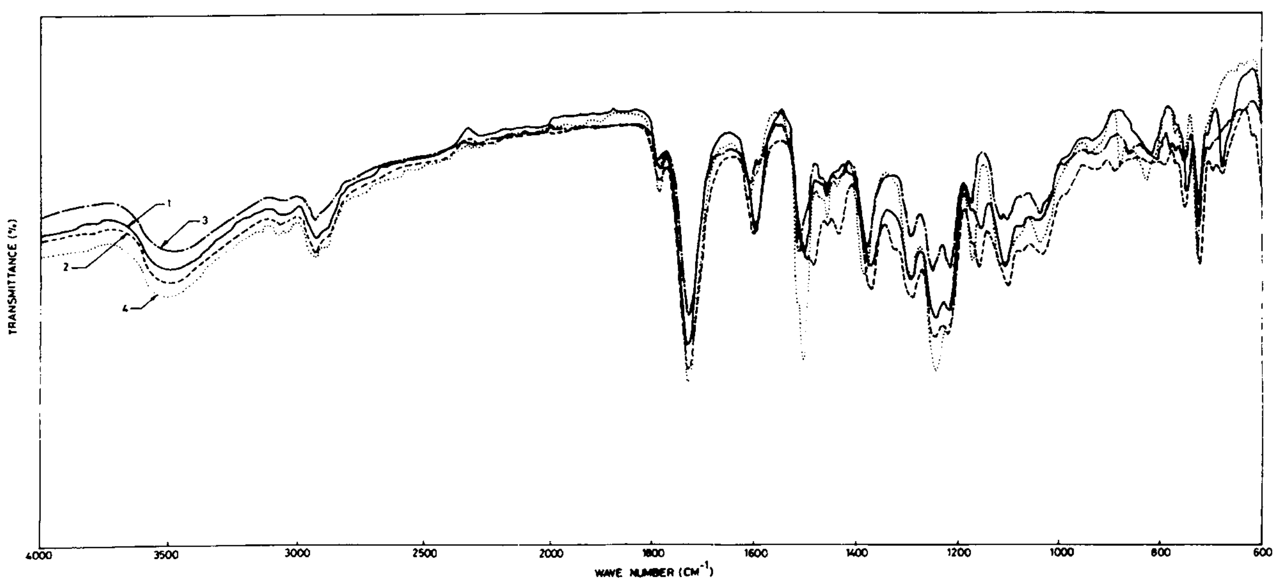



**Figure 2** IR spectra of epoxy-imide resins based on Araldite EPN 1138. 1, BCPI-1; 2, BCPI-2; 3, BCPI-3; 4, BCPI-4.

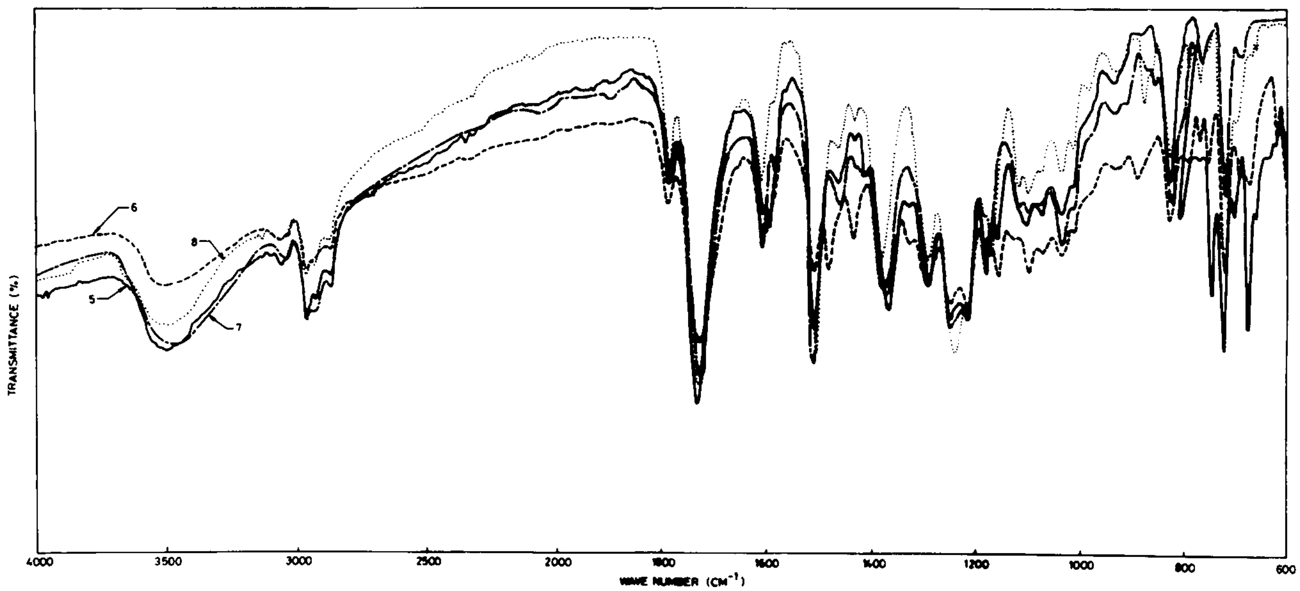



**Figure 3** IR spectra of epoxy–imide resins based on Araldite GY 250. 5, BCPI-1; 6, BCPI-2; 7, BCPI-3; 8, BCPI-4.

BCPI–GY 250 systems, the optimum ratio to obtain the maximum room temperature adhesive strength varies from 0.25–0.75. The maximum adhesive strength of 185 kg/cm$^2$ is obtained when BCPI-1–GY 250 ratio is 0.30. For the same ratio, BCPI-2–GY 250 gives only 80 kg/cm$^2$ and the maximum strength of 183 kg/cm$^2$ is achieved only when the ratio is 0.70. It is known that the parasubstituted compound has better packing than the metasubstituted compound. Thus, it is expected that a greater quantity of BCPI-2, a metasubstituted compound, would be needed to achieve the required stiffness of the polymer.

## Thermal Properties

The TGA curves of BCPI–EPN 1138 and BCPI–GY 250 systems for the optimum ratios are given in Figures 6 and 7, respectively. It is observed that all the systems are stable up to 370–380°C, above which they undergo rapid degradation. The char residues of BCPI–EPN 1138 systems at 900°C fall in the range of 33–45%, whereas for BCPI–GY 250 systems char residues are in the range of 24–28%, except for BCPI-3–GY 250. BCPI-2–EPN 1138 and BCPI-4–EPN 1138 systems having acid equivalent to epoxy

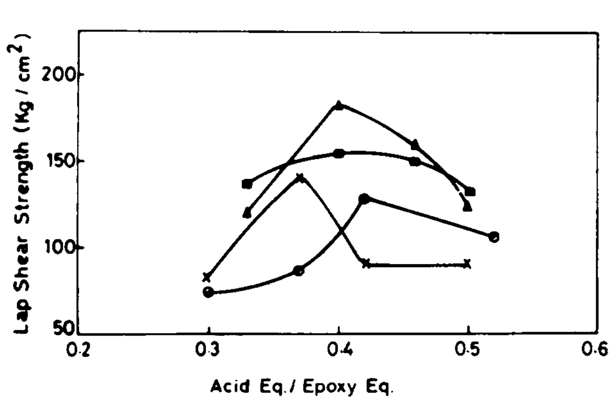



**Figure 4** Effect of BCPI content on adhesive strength of epoxy–imide resins based on Araldite EPN 1138. ×, BCPI-1; ⊙, BCPI-2; △, BCPI-3; ⊡, BCPI-4.

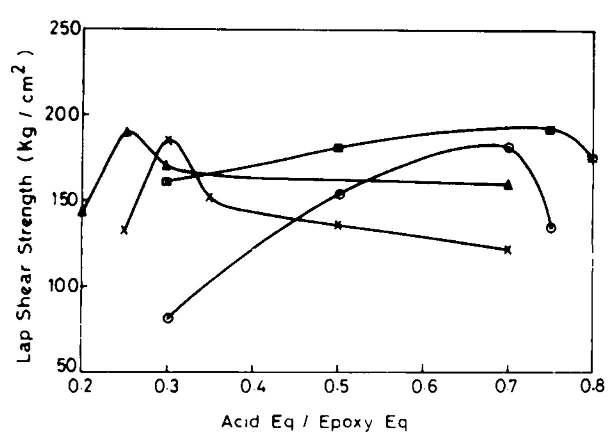



**Figure 5** Effect of BCPI content on adhesive strength of epoxy–imide resins based on Araldite GY 250. ×, BCPI-1; ⊙, BCPI-2; △, BCPI-3; ⊡, BCPI-4.

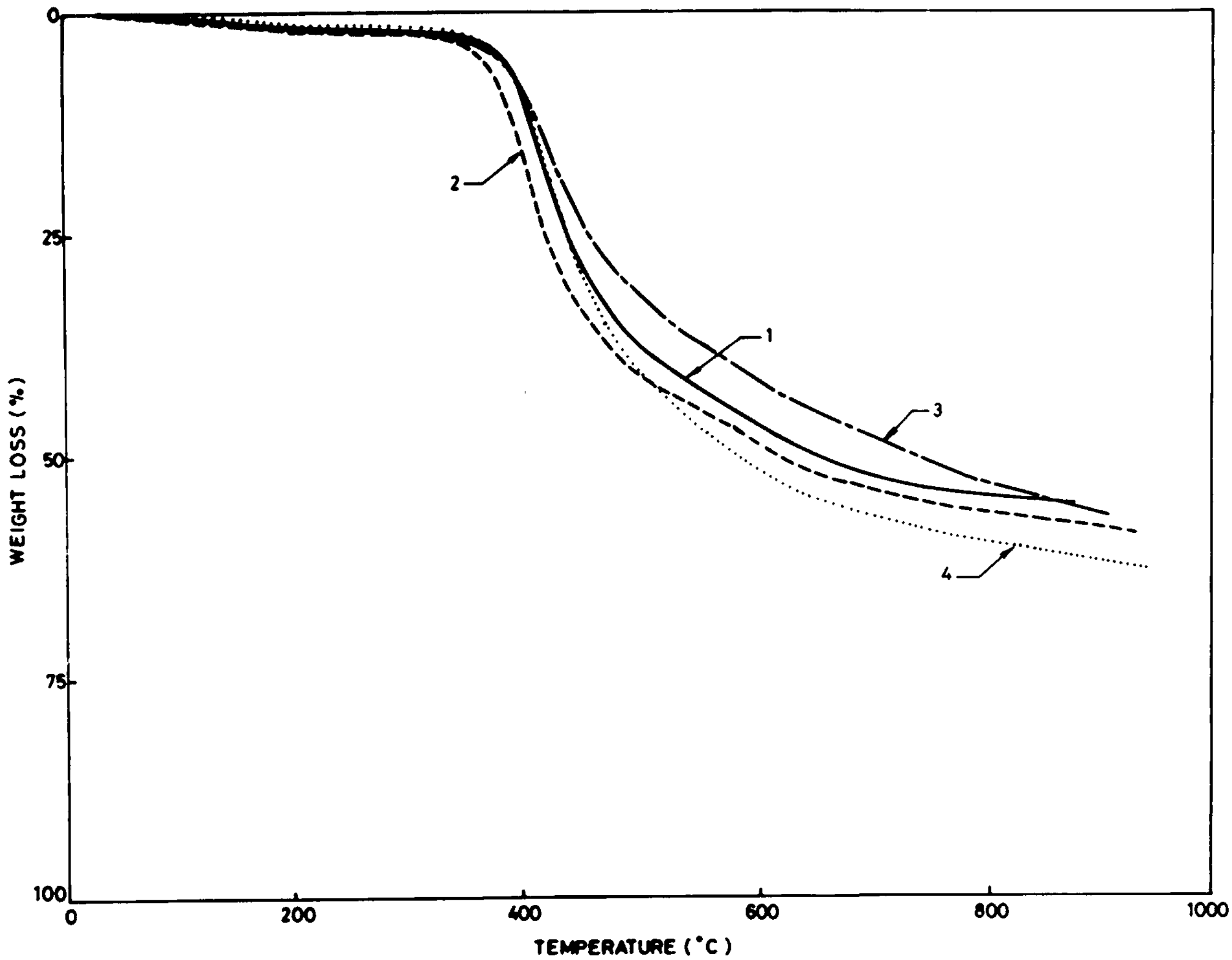



**Figure 6** TGA curves of epoxy–imide resins based on Araldite EPN 1138. 1, BCPI-1; 2, BCPI-2; 3, BCPI-3; 4, BCPI-4.

equivalent ratios of 0.42 : 1 and 0.4 : 1 give char residues of 41.3 and 33.8%, respectively. However, BCPI-2–GY 250 and BCPI-4–GY 250 having acid equivalent to epoxy equivalent ratios of 0.7 : 1 and 0.75 : 1 give char residues of 24.4 and 28.5%, respectively. Though the imide content is less in the above two EPN-1138-based systems, the char residues are higher than the GY-250-based systems with higher imide content. This observation may be attributed to the high crosslinking possible for the former systems compared to the latter systems. In the case of BCPI-1–GY 250 having acid to epoxy ratio of 0.3 : 1 gives a char residue of 24.4%, whereas BCPI-2–GY 250 having acid to epoxy ratio of 0.7 : 1 gives a char residue of 26.3%. Though the imide content is much less in the former system, the char residue is almost equal to that of the latter, which may be explained by the anticipated close packing and higher thermal stability of parasubstituted diimide-diester moieties present in the system. The char residue of BCPI-3–GY 250 is the lowest (4.4%) of all the systems. It is interesting to observe that for this system when the acid to epoxy ratio is increased from 0.25 : 1 to 0.7 : 1, the char residue at 900°C increases from 4.4 to 32%.

The glass transition temperatures ($T_g$) of BCPI–EPN 1138 and BCPI–GY 250 systems for the optimum ratios are compared in Table II. It is observed that, in general, BCPI–EPN 1138 systems have $T_g$ higher than that of BCPI–GY 250 systems. This observation is understood in view of the high crosslinking possible in the case of the former systems.

## Effect of Temperature on Adhesive Strength

The adhesive strength of BCPI–EPN 1138 and BCPI–GY 250 systems at different temperatures are

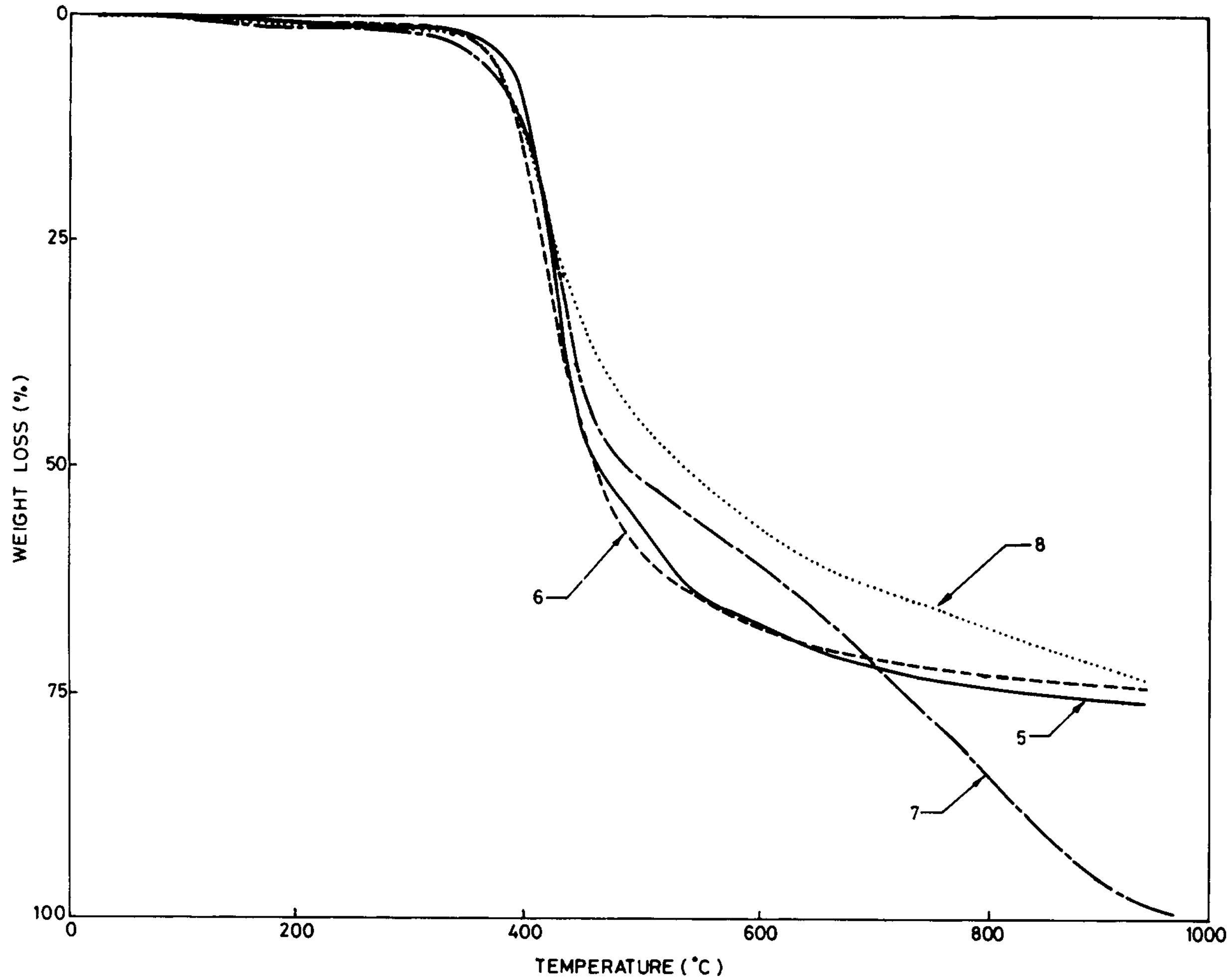



**Figure 7** TGA curves of epoxy–imide resins based on Araldite GY 250. 5, BCPI-1; 6, BCPI-2; 7, BCPI-3; 8, BCPI-4.

compared in Figures 8 and 9, respectively. It is observed that BCPI-1-EPN 1138 and BCPI-2-EPN 1138 retain the adhesive strength up to 150°C. For BCPI-4–EPN 1138, a decrease in strength of 15 kg/$cm^2$ is noticed when the temperature is increased from ambient to 150°C. In the case of BCPI-3–EPN 1138, an increase in adhesive strength of 30 kg/$cm^2$ is observed when the temperature is increased from ambient to 100°C; with further increase in temperature to 150°C, a decrease in strength of 50 kg/$cm^2$ is noticed. Though there is a drop in adhesive strength for this system, the adhesive strength obtained at 150°C is 153 kg/$cm^2$, comparable to the adhesive strength obtained for the other systems at this temperature. For BCPI–EPN 1138 systems, a drastic reduction in adhesive strength is observed above 150°C.

BCPI-1–GY 250 and BCPI-2–GY 250 systems have the adhesive strength of about 185 kg/$cm^2$ at room temperature and the adhesive strength is almost retained up to 100°C; with further increase in temperature to 150°C, these systems lose their strength by 20 and 30 kg/$cm^2$, respectively. In the case of BCPI-3–GY 250, adhesive strength is retained up to 100°C and the strength drops by 155 kg/$cm^2$ when the temperature is raised to 150°C. It is observed that BCPI–GY 250 systems, except for BCPI-3–GY 250, have the adhesive strength of about 150 kg/$cm^2$ at 150°C, comparable to that of BCPI–EPN 1138 systems at this temperature.

It is seen that though the acid to epoxy ratio for BCPI-1–GY 250 and BCPI-3–GY 250 are close to each other (*ca.,* 0.25–0.3 : 1) the latter retains only 17% of its adhesive strength when the temperature is raised to 150°C, whereas the former retains 82% of its adhesive strength under this condition. The

**Table II Glass Transition Temperature of Epoxy–Imide Resins**[a]

| System | $T_g$ (°C) |
|---|---|
| BCPI-1–EPN 1138 | 156 |
| BCPI-2–EPN 1138 | 157 |
| BCPI-3–EPN 1138 | 134 |
| BCPI-4–EPN 1138 | 127 |
| BCPI-1–GY 250 | 118 |
| BCPI-2–GY 250 | 114 |
| BCPI-3–GY 250 | 95 |
| BCPI-4–GY 250 | 117 |

[a] Glass transition temperatures were measured using DSC for the optimum composition, i.e., for the composition that gives the maximum adhesive strength at room temperature.

better high-temperature properties of BCPI-1-GY 250 may be attributed to the presence of polar $-SO_2-$ groups.

## Effect of Acid to Epoxy Ratio on the Adhesive Strength at Elevated Temperatures

From Figure 9, it is seen that BCPI-3-GY 250 having the acid to epoxy ratio of 0.25 : 1 retains the adhesive strength up to 100°C and the strength drops from 188 to 33 kg/cm$^2$ when the temperature is increased to 150°C. An attempt was made to study the effect of increasing the imide content of this system on the high-temperature adhesive property. The adhesive strength at elevated temperatures for BCPI-3-GY 250 system for the acid to epoxy ratios of 0.25 : 1 and 0.7 : 1 is compared in Figure 10. When the acid to epoxy ratio is 0.7 : 1, 88% of the adhesive strength is retained at 150°C, whereas only 17% of the adhesive strength is retained at this temperature when the acid to epoxy ratio is 0.25 : 1. Moreover,

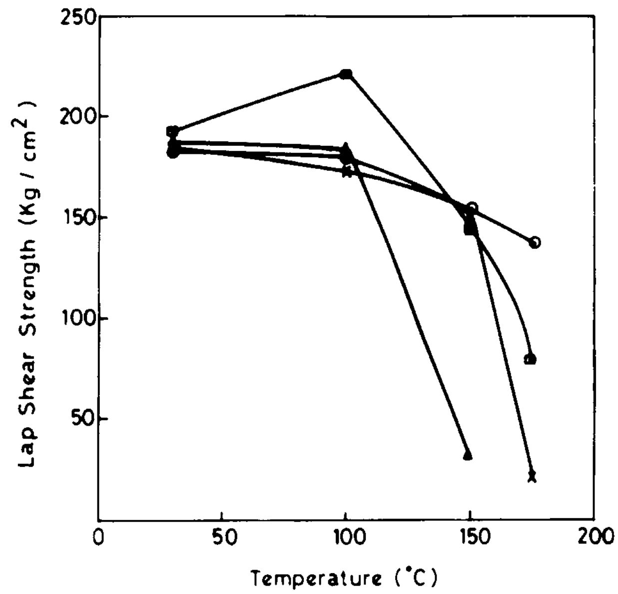



**Figure 9** Effect of temperature on adhesive strength of epoxy–imide resins based on Araldite GY 250. ×, BCPI-1; ⊙, BCPI-2; △, BCPI-3; ⊡, BCPI-4.

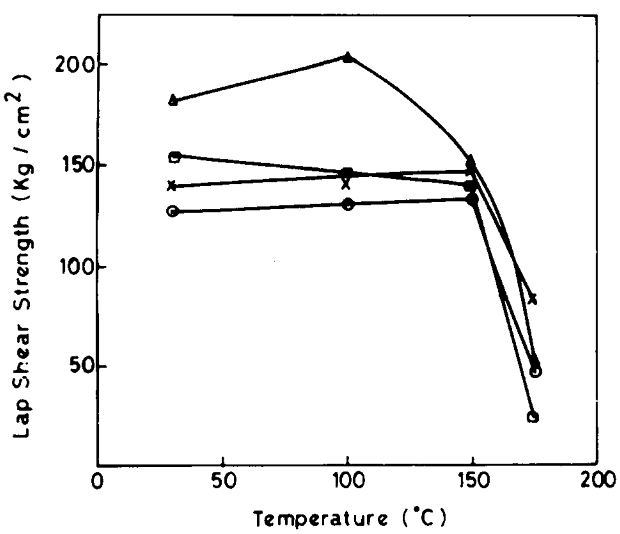



**Figure 8** Effect of temperature on adhesive strength of epoxy–imide resins based on Araldite EPN 1138. ×, BCPI-1; ⊙, BCPI-2; △, BCPI-3; ⊡, BCPI-4.

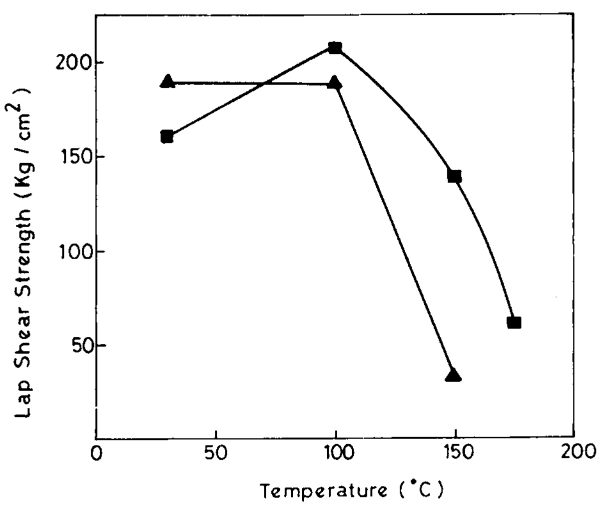



**Figure 10** Effect of imide content of BCPI-3-GY 250 system on adhesive strength at elevated temperatures. ▲, acid to epoxy ratio = 0.3 : 1; ■, acid to epoxy ratio = 0.7 : 1.

when the acid to epoxy ratio is 0.7 : 1 about 37% of the adhesive strength is retained at 175°C, whereas no strength is obtained at this temperature when the acid to epoxy ratio is 0.25 : 1. Thus, it is observed that increasing the imide content of BCPI-3–GY 250 system improves the high-temperature adhesive properties. It is also noticed that increasing the acid to epoxy ratio from 0.25 : 1 to 0.7 : 1 for this system increases the char residue at 900°C from 4.4 to 32% and the $T_g$ from 95 to 125°C.

The effect of imide content on the high-temperature adhesive property is also evident for BCPI-2–GY 250 and BCPI-1–GY 250 systems (Fig. 9). BCPI-2–GY 250 retains about 75% of its adhesive strength when the temperature is raised to 175°C, whereas BCPI-1–GY 250 retains only 10% of its adhesive strength at this temperature. The acid to epoxy ratio of the former is 0.7 : 1 and that of the latter 0.3 : 1. The better performance of the former may be attributed to the higher imide content.

## CONCLUSIONS

The main conclusions that may be drawn from this study are:

1. The optimum ratio (acid equivalent to epoxy equivalent) of BCPI–EPN 1138 systems to obtain the maximum room temperature adhesive strength varies over a narrow range (0.37–0.40), whereas for BCPI–GY 250 systems the optimum ratio varies over a wide range (0.25–0.75).
2. BCPI–EPN 1138 and BCPI–GY 250 systems are stable up to 370–380°C (in nitrogen atmosphere) and undergo rapid degradation above this temperature. In general, the overall thermal stability and $T_g$ of BCPI–EPN 1138 systems are higher than those of BCPI–GY 250 systems; this has been attributed to high crosslinking possible for the former systems.
3. BCPI–EPN 1138 systems give adhesive strength of 141–182 kg/cm$^2$ at room temperature and retain about 84–100% of the adhesive strength at 150°C. BCPI–GY 250 systems have room temperature adhesive strength of 183–193 kg/cm$^2$. Except for BCPI-3–GY 250 systems, other systems based on GY 250 retain *ca.,* 76–84% of room temperature adhesive strength at 150°C. BCPI-3–GY 250 system retains only 17% of their room temperature adhesive strength at 150°C; the poor performance of this system at 150°C is attributed to the low imide content.
4. BCPI–EPN 1138 and BCPI–GY 250 systems except for BCPI-2–GY 250 system lose their strength drastically above 150°C. BCPI-2–GY 250 system retains *ca.,* 75% (138 kg/cm$^2$) of the room temperature adhesive strength at 175°C. Thus, this system appears to be the best of all the systems as far as overall performance is concerned. The better performance of this system has been attributed to the high imide content and the presence of $-SO_2-$ group.
5. For BCPI-3–GY 250 system, when the acid to epoxy ratio is increased from 0.25 to 0.7 the adhesive strength retention at 150°C is improved from 17 to 88%. The improvement in adhesive strength retention at 150°C is attributed to the increase in imide content.

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