Carboxyl-Terminated Poly(propylene Glycol) Adipate-Modified Room Temperature Curing Epoxy Adhesive for Elevated Temperature Service Environment

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SYNOPSIS

An investigation was carried out into the effect of modification of an epoxy resin with carboxyl-terminated poly(propylene glycol) adipate (CTPPGA) liquid rubber, on room temperature and elevated temperature adhesive joint strengths, after curing at room temperature (25°C) with tris-2,4,6-(*N,N*-dimethyl amino methyl) phenol hardner. CTPPGA prepared by the esterification of poly(propylene glycol) (PPG) and molar excess of adipic acid was incorporated into the epoxy resin by the prereact method. CTPPGA modification showed significant enhancement of adhesive joint strengths over the unmodified epoxy and the joint strengths were found to depend on the molecular weight of CTPPGA and its content in the epoxy resin. The elevated temperature lap shear strength measurement made for the CTPPGA-modified epoxy adhesive showed that the adhesive formulation has a temperature service capability up to 120°C. The results are discussed in terms of the data obtained from the tensile tests, DSC analysis, and SEM observations of the fractured surfaces.

INTRODUCTION

Reactive liquid rubber-modified epoxy resins are finding increasing use as structural adhesives because of their better durability[1] and ability to prevent catastrophic failure of structural bonds. When the low modulus rubber is dispersed and bonded to the brittle epoxy network, the toughness of the system is improved with a minimal decrease in thermal and mechanical properties.[2,3] In adhesives, this produces enhancement in lap shear strength and peel strength[4,5] without the loss of glass transition temperature (T_g).

Rubber-modified epoxy adhesives that produce high joint strength with good elevated temperature service capability have been available for many years, but they all suffer from the problem of heat cure. Heat curing is difficult or impractical in the repair and fabrication of certain structures and requires a significant amount of energy. Curing at ambient conditions saves energy and considerable research effort has been made recently to develop room temperature curing liquid rubber-modified epoxy adhesives that possess good elevated temperature service capability.[6,7]

As a part of the development program of a room temperature curing epoxy adhesive with elevated temperature service capability, we studied the room temperature and elevated temperature adhesive joint strengths of an experimental epoxy resin, modified with carboxyl-terminated polypropylene glycol adipate (CTPPGA) and cured at room temperature with tris-2,4,6-(*N,N*-dimethyl aminomethyl) phenol. The room temperature curing of a CTBN toughened epoxy adhesive with elevated temperature service capability has been reported by us recently.[7] The highly unsaturated structure of CTBN makes it unsuitable for use at elevated temperature. Also there is some limitation in its use due to the presence of traces of carcinogenic acrylonitrile.[8] Because of the absence of unsaturation, CTPPGA can exhibit better oxidative stability. The carboxyl group of CTPPGA provides a site for linking the epoxy resin, whereas the poly(oxy propylene) moiety

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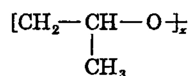


in the backbone provides low cohesive energy between the chains and imparts elastomeric properties. Further, it is reported that polypropylene oxide elastomers have good low temperature and high temperature properties.[9] Misaki et al.[10] found that poly(propylene glycol) diglycidyl ether is an effective modifier for improving the fracture toughness of an epoxy resin with a minimal decrease of the heat deflection temperature.

Carboxyl-terminated poly(propylene glycol) adipate (CTPPGA) can be prepared in various controlled molecular weights by the esterification of different ratios of poly(propylene glycol) (PPG) and adipic acid. But we decided to restrict our studies only to viscous liquid polymers. The liquid CTPPGA was incorporated into epoxy resin as a prereact concentrate containing 50% CTPPGA and 50% epoxy resin, prepared by a reported procedure.[11] The modification of epoxy resin with CTPPGA showed significant enhancement of joint strength both at room temperature and at elevated temperature over the unmodified epoxy resin. The variables that were investigated include concentration of one of the liquid rubbers (CTPPGA) and the molecular weight of CTPPGA (varied from 3500 to 6500) at a particular concentration. The best adhesive joint strength was obtained for the composition containing 15 parts CTPPGA per 100 parts epoxy resin. The molecular weight of CTPPGA was also found to influence the joint strengths. To explain the observed results, morphology, thermal and mechanical properties of CTPPGA-modified epoxy adhesive were also measured and the correlation between the adhesive joint strength and bulk mechanical properties discussed.

EXPERIMENTAL

Materials

The poly(propylene glycol) used in this work was Desmophen 7750, obtained from Bayer (FRG). Adipic acid was obtained from SD Fine Chem Pvt. Ltd., Bombay, India, and *p*-toluene sulfonic acid from Sisco Laboratories, Bombay, India. The epoxy resin and hardner used were liquid glycidyl ether of bisphenol A (trade name GY 250) and tris-2,4,6-(*N*,*N*-dimethyl amino methyl) phenol (Trade name HY 960) respectively, supplied by Hindustan Ciba Geigy Ltd., Bombay, India. CTPPGA was synthesized in our laboratory.

CTPPGA, Synthesis, and Characterization

CTPPGA with different number average molecular weights were synthesized by reacting different mole ratios of PPG ($\bar{M}_n$ by VPO 3300) and adipic acid with 1% by weight of *p*-toluene sulfonic acid catalyst. The water formed during the esterification reaction was removed continuously from the reaction mixture under atmospheric pressure using toluene as an azeotropic agent. The reactants along with 25% by weight of toluene were charged into a three-necked flask equipped with a stirrer, N_2 inlet, and Dean and Stark condenser. The flask was heated in an oil bath and the bath temperature was maintained at 165 ± 2°C with a contact thermometer. The reaction was monitored from the amount of water collected. After the completion of the reaction (reaction time was about 3 h), the solution was cooled to room temperature, washed with water to neutral pH and then the solvent distilled out at 60–70°C under reduced pressure until the product weight remained constant. The yield of the CTPPGA was about 90% and was characterized by number average molecular weight $\bar{M}_n$, viscosity, acid value, hydroxyl value, and T_g.

The mole ratios of PPG and adipic acid used for the synthesis of four carboxyl-terminated poly(propylene glycol) adipates and their chemical and physical characteristics are listed in Table I.

CTPPGA-Modified Epoxy Resin Preparation and Curing

All carboxyl-terminated poly(propylene glycol) adipates (100 pbw) were prereacted with epoxy resin (100 pbw) via triphenyl phosphine (0.25 pbw) catalyzed alkyl hydroxyl esterification reaction, carried out under N_2 atmosphere at 80°C till all carboxyl groups were completely reacted. The reaction was monitored by titration in a toluene/methanol (1 : 1) mixture with 0.1 *N* alcoholic KOH. The epoxy resin endcapped poly(propylene glycol) adipate was then diluted with appropriate amounts of epoxy resin to get various concentrations of CTPPGA in the formulations.

All formulations were cured with 6 phr of tris-2,4,6-(*N*,*N*-dimethyl amino methyl) phenol. Curing at room temperature (25°C) for 7 days was used for the determination of adhesive properties, mechanical properties, thermal properties, and morphology.

Measurement of Adhesive Properties

Single lap shear strength and T-peel strength were determined on a B51 SWP aluminum substrate as

Table I Chemical and Physical Characteristics of Carboxyl-Terminated Poly(propylene Glycol) Adipates Prepared by the Esterification of PPG and Adipic Acid

Sample Designation	PPG : Adipic Acid Mole Ratio Used for the Synthesis	Mol Wt $\bar{M}_n$ by VPO	Viscosity (Brookfield) at 25°C (cps)	Acid Value (mg KOH/g)	Hydroxyl Value (mg KOH/g)	Glass Transition Temperature (T_g)
CTPPGA(a)	1 : 3	3530	3000	43.8	1.4	−59.5
CTPPGA(b)	1 : 2	4200	8110	36.5	Nil	−60.7
CTPPGA(c)	1 : 1.75	5060	13270	31.6	1.8	−61.9
CTPPGA(d)	1 : 1.5	6330	36860	20.9	Nil	−61.2

per ASTM-D-1002 and ASTM-D-1876, respectively. The aluminum specimens were etched with chromic acid, washed in running water, and dried. The adhesive formulation was applied uniformly on both sides over the area to be bonded and mated using contact pressure and cured. The joint strength was measured in an Instron 4202 at a crosshead speed of 10 mm/min. Joint strength at elevated temperature was determined after soaking the specimens for 10 min at that temperature.

Measurement of Tensile Properties

Tensile properties of the adhesive formulations were measured from the cured dumbbells, using an Instron 4202 at a crosshead speed of 10 mm/min, keeping 45 mm gauge length.

Measurement of Thermal Properties

DSC-20-Mettler TA 3000 instrument, at a heating rate of 10°C/min, was used for glass transition temperature (T_g) determination. The T_g value was calculated automatically through the interactive DSC program by using inflection point for the break in the heat flow curve.

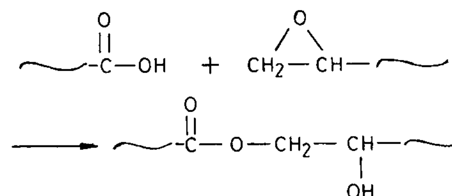
The thermal degradative stability of the cured adhesive formulation was checked by a DuPont 951 thermogravimetric analyzer at a heating rate of 10°C/min.

Scanning Electron Micrographs (SEM)

SEM was obtained on the fractured surface of the tensile test specimen with a stereoscan 250 MK-3 Cambridge instrument.

RESULTS AND DISCUSSION

Liquid rubber if not chemically bound to the epoxy resin can act as a weak boundary layer in the adhesive joint of a rubber-modified epoxy adhesive.[12] This might be the reason for the reduction in joint strength observed compared to the control (lap shear strength 47 kg/cm^2) when poly(propylene glycol) (Desmophen-7750) was added to epoxy resin and cured at room temperature with tris-2,4,6-(*N,N*-dimethyl amino methyl) phenol. Lap shear strength of 31.7 kg/cm^2 was obtained for the formulation containing 15 parts PPG per 100 parts epoxy. Under ambient cure conditions PPG cannot chemically bind to the epoxy resin, due to the poor reactivity of the —OH group with epoxide. An improvement in adhesive joint strength was accomplished by the addition of carboxyl-terminated poly(propylene glycol) adipate (CTPPGA), which is due to the increased chemical bonding between the epoxy resin and the rubber element by the following base catalysed monoesterification reaction:



Therefore, bonding between the epoxy and the rubber element is necessary to improve the adhesive properties of the rubber-modified epoxy resin. For this reason, before mixing with the hardner, CTPPGA was end-capped with epoxy resin by the triphenyl-phosphine-catalyzed epoxide–carboxyl reaction. The possible mechanism of the reaction proposed by Romanchick et al.[13] is shown in Figure 1. Epoxy resin end-capped poly(propylene glycol) adipate intermediate is capable of reacting with the hardner in the same manner as epoxy resin and can be crosslinked into the epoxy matrix by the cure reaction.

CTPPGA-epoxy prereacted intermediate, mixed with appropriate amounts of epoxy resin, was cured

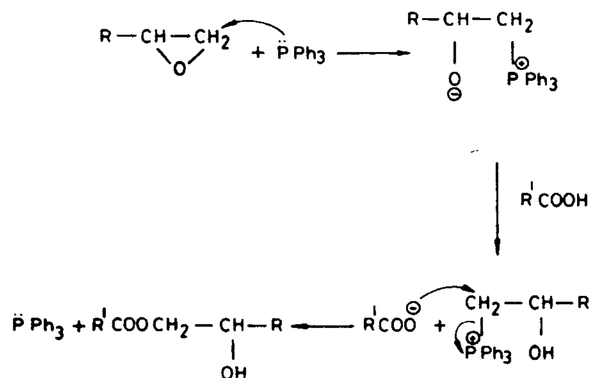


Figure 1 Triphenyl phosphine catalyzed epoxide-carboxyl reaction.

at room temperature (25°C) with 6 phr tris-2,4,6-(*N,N*-dimethyl amino methyl) phenol. After a cure time of 7 days at room temperature, the lap shear strength and bulk tensile strength of the adhesive reached their maximum values. Therefore, this cure condition was kept throughout the study. The cure reaction is the homopolymerization of the epoxide by the *t*-amine resulting in a polyether network.[14] The DSC curve [Fig. 2(a)] of the one week ambient temperature cured sample showed that the cure reaction is not completed, even though lap shear strength and bulk tensile strength reached their maximum values. The DSC curve of a similar sample after soaking at 120°C for 10 min, showed no residual cure exotherm peak [Fig. 2(b)] and the ET_g was found to be shifted to higher temperature, due to post-curing.

Effect of CTPPGA Modification on the Joint Strength of the Epoxy Adhesive

An initial study was conducted to determine the effect of CTPPGA concentration on the joint strength of epoxy resin cured at room temperature with tris-2,4,6-(*N,N*-dimethyl amino methyl) phenol. CTPPGA prepared from 1 mol PPG and 2 mol adipic acid [CTPPGA(b) $\bar{M}_n$ 4200] was used for this investigation. The dependence of joint strength on the CTPPGA concentration is presented in Figure 3(a). As the CTPPGA concentration increased, the T-peel strength and lap shear strength, tested at room temperature (25°C) and at 120°C increased initially, passed through a maximum, and then decreased with further CTPPGA content. The best combination of lap shear and T-peel strengths was obtained for the adhesive formulation prepared with 15 parts CTPPGA content per 100 parts epoxy resin which was adopted for further studies.

Incorporation of CTPPGA at a concentration of 15 parts per 100 parts epoxy resin resulted in two- to threefold increase in lap shear strength and four- to fivefold increase in T-peel strength. The increase in joint strengths by the incorporation of low levels of CTPPGA can be attributed to the toughening effect accomplished by CTPPGA. The dispersed CTPPGA elastomer reduces the local stress concentration in the adhesive joint by the dissipation of mechanical energy, which increases the external load required to break the joint. A decline in joint strength was observed for higher concentrations of CTPPGA [Fig. 3(a)], which can be attributed to the flexibilization or softening effect. A higher concentration of dissolved CTPPGA elastomer in the cured epoxy matrix can act as a flexibilizer and result in decreased joint strength especially at higher temperatures. The toughening and flexibilization effects are further evidenced from the tensile properties and glass transition temperature (discussed later).

The lap shear strength of CTPPGA-modified epoxy adhesive (15 parts CTPPGA content per 100 parts epoxy resin) for various molecular weights of CTPPGA are shown in Figure 3(b). All the CTPPGA-modified epoxy formulations showed much higher joint strengths compared to the unmodified epoxy, indicating that the toughness of the epoxy is improved by the CTPPGA modification. Epoxy adhesive formulations modified with CTPPGA(c) $\bar{M}_n$ 5060 and CTPPGA(d) $\bar{M}_n$ 6330 gave marginally superior lap shear strength compared to CTPPGA(b) $\bar{M}_n$ 4200-modified epoxy system. On the other hand, CTPPGA(a) $\bar{M}_n$ 3530-modified epoxy formulation produced lower lap

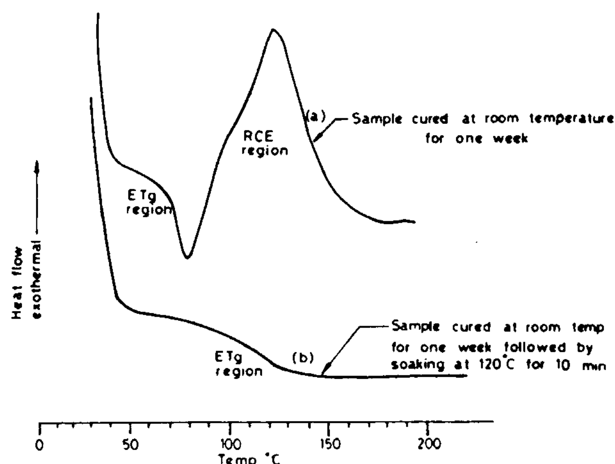


Figure 2 DSC scans of CTPPGA-modified epoxy adhesive (15 parts CTPPGA $\bar{M}_n$ 4200 per 100 parts epoxy resin).

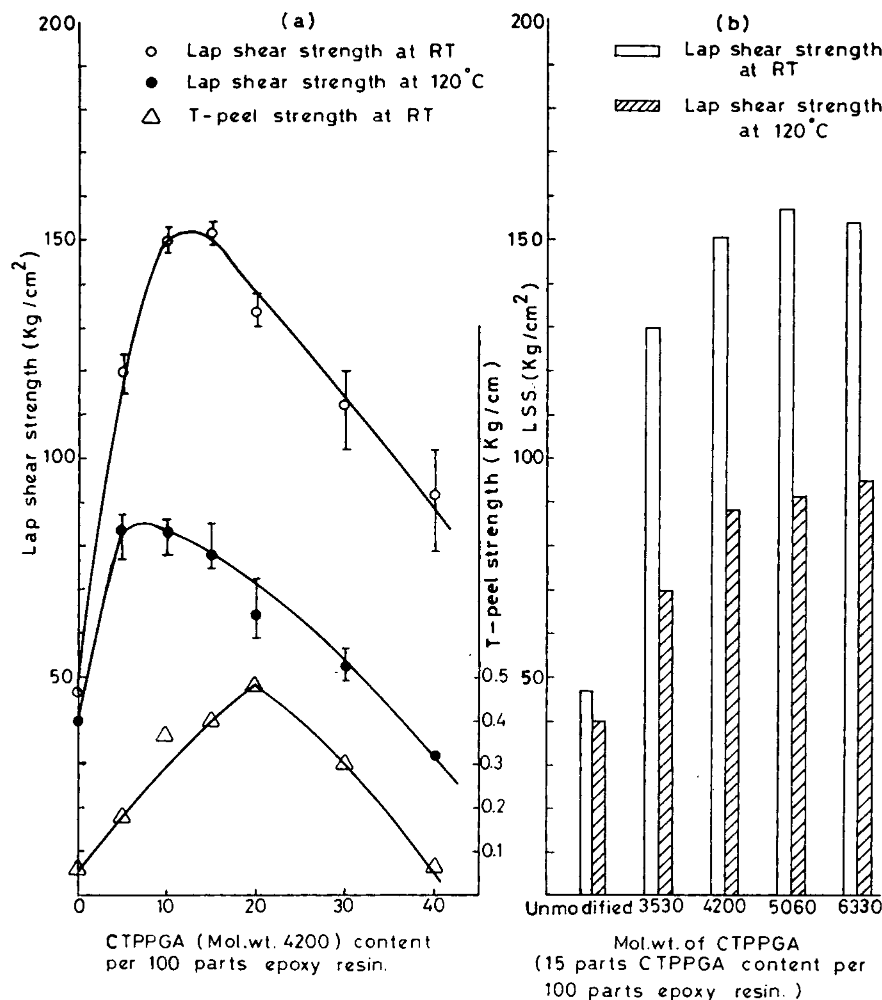


Figure 3 Effect of CTPPGA modification on the joint strength of the epoxy adhesive: (a) effect of CTPPGA ($\bar{M}_n$ 4200) concentration; (b) effect of molecular weight of CTPPGA at a particular concentration.

shear strengths, which is due to the increased miscibility of CTPPGA in the epoxy matrix, as evidenced from the T_g and SEM observations (discussed later), causing flexibilization effect.

One major drawback of room temperature curing epoxy adhesive is the poor elevated temperature resistance.[15] Figure 4 shows the influence of test temperatures on the lap shear strength of a CTPPGA-modified epoxy adhesive formulation [15 parts CTPPGA(d) $\bar{M}_n$ 6330 per 100 parts epoxy resin], cured at room temperature. The results indicate a decline in lap shear strength on increasing the test temperature. However, Figure 4 indicates that the adhesive formulation can be used for elevated temperature environment up to 120°C, since the lap shear strength obtained up to 120°C is reasonably good for many applications. The high temperature capability of the system might be due to the shifting of ET_g to higher values due to the post-curing taking place when the specimen is soaked at the test temperature [Fig. 2(b)]. The temperature (120°C) at which the adhesive begins to lose strength drastically is the T_g region, which was clearly indicated by the DSC thermogram.

Effect of CTPPGA Modification on the Tensile Properties of the Epoxy Adhesive

Figure 5 shows the results of tensile tests of CTPPGA-modified epoxy adhesive formulations cured at room temperature with tris-2,4,6-(N,N-dimethyl amino methyl) phenol. The toughness, implied by the area under the stress strain curve, was higher for CTPPGA-modified formulations than the

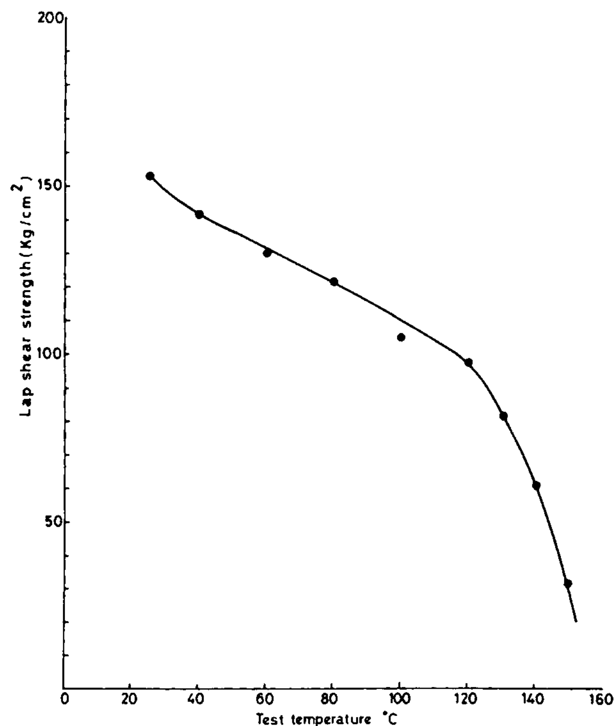


Figure 4 Variation of lap shear strength of CTPPGA ($\bar{M}_n$ 6330)-modified epoxy adhesive with test temperature (CTPPGA content 15 parts per 100 parts epoxy resin).

control. The ultimate tensile strength (σ) showed an increase upon incorporation of CTPPGA, passed through a maximum at about 15 parts CTPPGA content per 100 parts epoxy resin, then decreased [Fig. 5(a)]. Such synergistic improvements in certain properties are observed in immiscible polymers with slight solubility, which form a solid solution of minor polymer in the major polymer and are well bonded to each other.[16] The increase of elongation at break (e_b) and the decrease of ultimate tensile strength (σ) above 15 parts CTPPGA content per 100 parts epoxy resin can be attributed to the softening effect of the epoxy matrix by the dissolved CTPPGA.

We believe that, because of the increase in bulk mechanical strength of the cured epoxy resin by the incorporation of CTPPGA, the adhesive joint strength was improved. Although the direct correlation between the mechanical properties and the adhesive joint strength is not well established, it is recognized at least qualitatively that if a satisfactory interfacial state of adhesion is achieved, the mechanical properties of the adhesive material control the adhesive joint strength.[17-19] The plot of all the room temperature lap shear strength data (taken from Fig. 3) and the corresponding bulk tensile

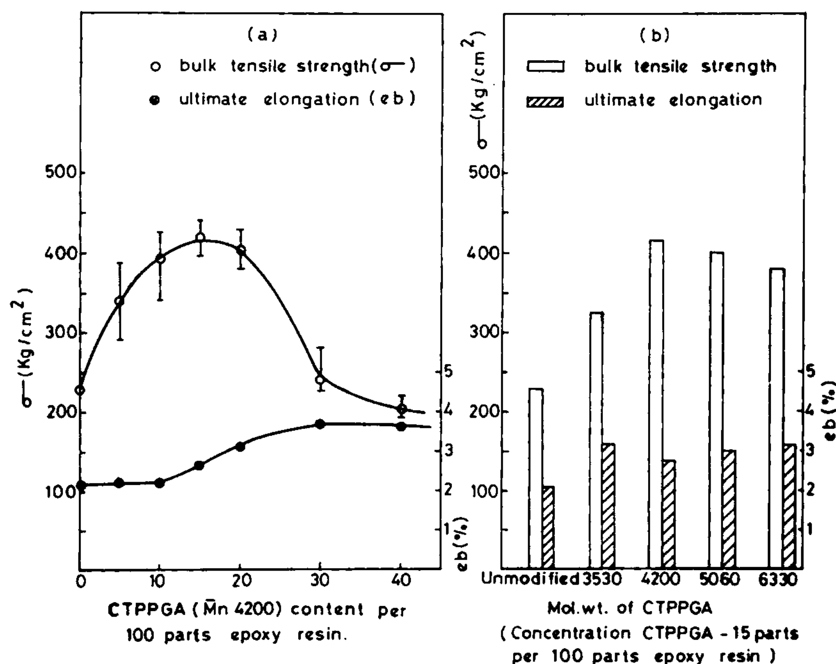


Figure 5 Effect of CTPPGA modification on the bulk tensile strength (σ) and breaking elongation (e_b) of the epoxy adhesive: (a) effect of CTPPGA (mol wt 4200) concentration; (b) effect of molecular weight of CTPPGA at a particular concentration.

strength (taken from Fig. 5) displayed a linear relationship with a correlation factor of 0.86.

Effect of CTPPGA Modification on the Elevated Temperature Stability of the Epoxy Adhesive

DSC analysis showed that, for the cured CTPPGA-modified epoxy adhesive, two distinct T_g's corresponding to CTPPGA and epoxy matrix were present. This finding indirectly implies that phase separation has occurred in the CTPPGA-modified epoxy adhesive (2 T_g = 2-phase criterion). The T_g (−64.3°C) of CTPPGA in the modified epoxy was lower than that of pure CTPPGA. This lowering can be due to the differences in coefficient of thermal expansion between the glassy epoxy matrix and the rubber phase.[2] The glass transition temperature of the epoxy matrix (ET_g) decreased with CTPPGA concentration and more drastically for higher concentrations [Fig. 6(a)]. The decrease of ET_g with CTPPGA concentration is the consequence of the plasticization of the epoxy matrix by the dissolved rubber element. From Figure 6(b), we can see that for constant CTPPGA content (15 parts CTPPGA per 100 parts epoxy resin), the ET_g increases with the molecular weight of CTPPGA. Epoxy formulations modified with CTPPGA(a) $\bar{M}_n$ 3530 and CTPPGA(b) $\bar{M}_n$ 4200 showed ET_g depression with respect to the unmodified epoxy, indicating partial miscibility of CTPPGA in the epoxy matrix. On the other hand, compared to the control, ET_g values remained unchanged or marginally improved for the epoxy formulations modified with CTPPGA(c) $\bar{M}_n$ 5060 and CTPPGA(d) $\bar{M}_n$ 6330, indicating more immiscibility for higher molecular weight CTPPGA. Epoxy adhesive formulations modified with higher molecular weight CTPPGA exhibited higher ET_g, hence better high temperature (120°C) lap shear strength [Fig. 3(b)].

The thermal degradation of the cured CTPPGA-modified epoxy adhesive was investigated by means of TGA. TGA data indicates that the thermal degradative stability of CTPPGA-modified epoxy adhesive formulations are marginally higher than or equal to the unmodified epoxy adhesive. The weight loss data, T_i (initial decomposition temperature), T_{max} (the temperature where the rate of weight loss is maximum), and T_f (the temperature up to which the decomposition continues) are compiled in Table II.

SEM Observation of Fractured Surfaces

In Figure 7, SEMs of fractured surfaces of tensile test specimens of the epoxy adhesive, unmodified

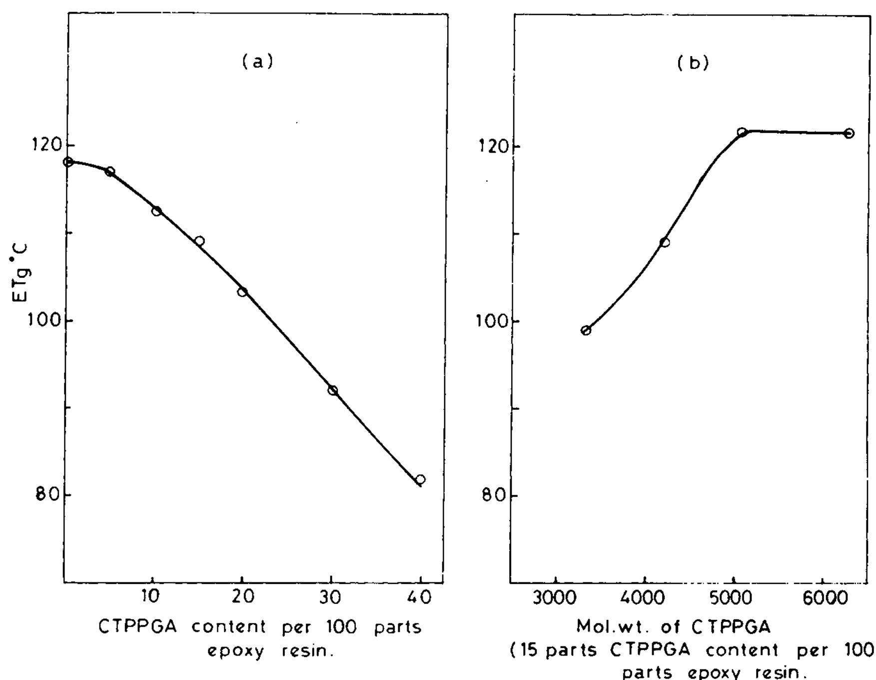


Figure 6 Effect of CTPPGA modification on the ET_g of the epoxy adhesive: (a) effect of CTPPGA concentration ($\bar{M}_n$ 4200); (b) effect of CTPPGA molecular weight at a particular concentration.

Table II Effect of CTPPGA Modification on the Thermal Degradative Stability of the Cured Epoxy Adhesive (CTPPGA Content 15 Parts Per 100 Parts Epoxy Resin)

	T_i (°C)	T_{max} (°C)	T_f (°C)	Temperature (°C) of Various Percentage of Weight Loss				
				10%	20%	40%	60%	80%
1. Unmodified epoxy resin	320	420	470	375	395	415	430	445
2. Modified with CTPPGA(a) $\bar{M}_n$ 3530	320	435	490	395	415	435	450	465
3. Modified with CTPPGA(b) $\bar{M}_n$ 4200	325	435	480	385	405	425	435	455
4. Modified with CTPPGA(d) $\bar{M}_n$ 6330	335	435	490	395	405	420	435	450

and modified, with CTPPGA of different molecular weights are shown (CTPPGA content 15 parts per 100 parts epoxy resin). The smooth, glassy fractured surface with cracks in different planes shows brittle fracture for the unmodified epoxy [Fig. 7(a)]. CTPPGA modification changed the fractured surface from smooth to rugged and deformed surface. The fractured surface of most of the rubber-toughened epoxy systems has a rigid continuous epoxy matrix with a dispersed rubbery phase as isolated

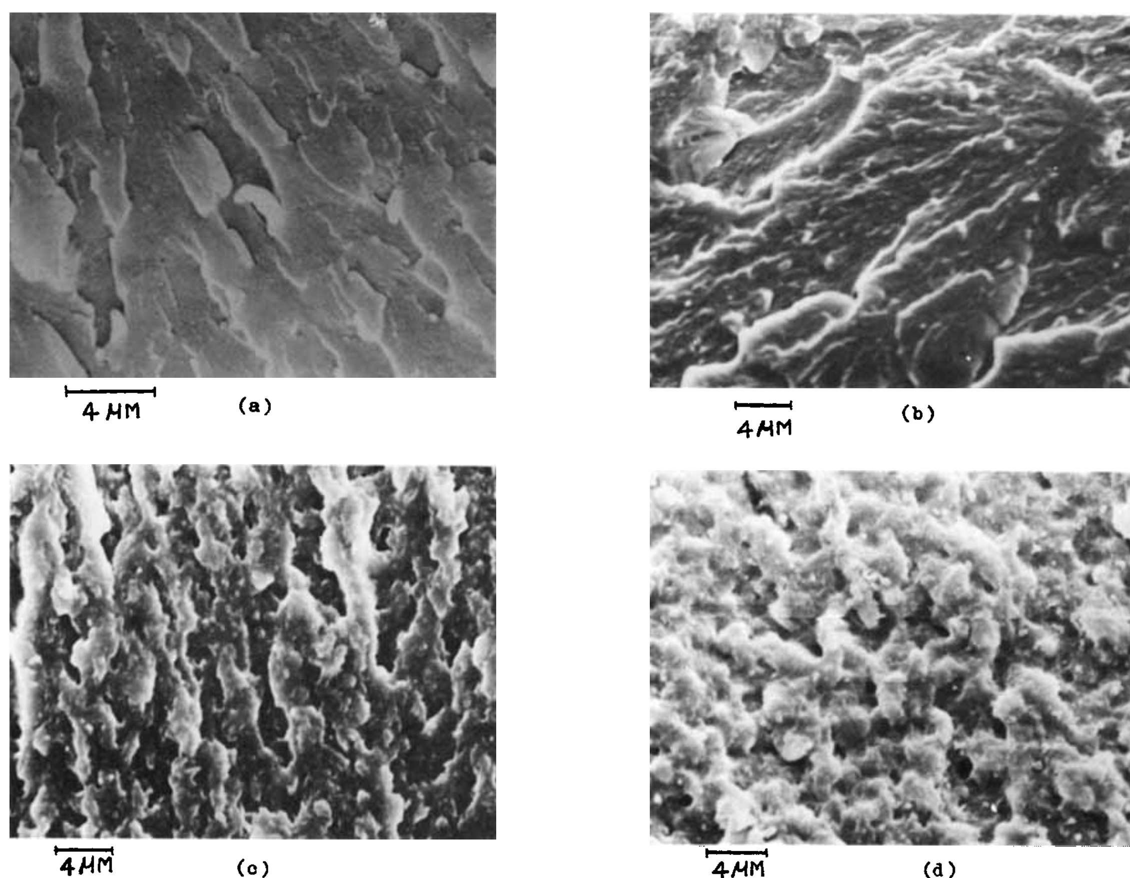


Figure 7 SEMs of tensile fractured surfaces of ambient temperature cured epoxy adhesive (a) unmodified and (b), (c), and (d) modified with CTPPGA $\bar{M}_n$ 3530, $\bar{M}_n$ 4200, and $\bar{M}_n$ 6330, respectively (CTPPGA content 15 parts per 100 parts epoxy resin).

particles. The CTPPGA-modified epoxy has less obvious two-phase morphology, although the properties are favourably affected. From SEM micrographs of CTPPGA-modified epoxy adhesives, shown in Figures 7(b), 7(c), and 7(d), it is clear that, as the molecular weight of CTPPGA is increased, there is progressive increase of roughening of the fractured surface due to the local ductile deformation. It is clear that 7(c) and 7(d) have more local ductile deformation (evident from the microvoids and roughness of the fractured surface) than 7(b), giving rise to higher toughness, hence higher adhesive joint strength.

CONCLUSIONS

Liquid carboxyl-terminated poly(propylene glycol) adipates (CTPPGA) of various molecular weights in the range 3500–6500 were synthesized, and the effect of CTPPGA modification on the room temperature and elevated temperature adhesive joint strengths of an epoxy resin, cured at room temperature with tris-2,4,6-(*N,N*-dimethyl amino methyl) phenol, was studied. The effect of CTPPGA modification on the bulk tensile properties, thermal stability and morphology was also investigated. The following conclusions were drawn from the present study.

1. CTPPGA-modified epoxy formulation containing 15 parts CTPPGA content per 100 parts epoxy resin showed two- to threefold increase in lap shear strength and four- to fivefold increase in T-peel strength over the unmodified epoxy resin and exhibited elevated temperature service capability up to 120°C.
2. The CTPPGA content in the epoxy resin and the molecular weight of CTPPGA had significant influences on the joint strength, which was attributed to the variation in the bulk mechanical strength. There was an increase in joint strength up to a CTPPGA level of 15 parts per 100 parts epoxy resin, but further increase in CTPPGA content decreased the joint strength. For a concentration of 15 parts CTPPGA per 100 parts epoxy resin, it was found that, for obtaining best results, the molecular weight of CTPPGA must be above 5000.
3. DSC analysis and SEM observations indicated that phase separation had occurred in the CTPPGA-modified epoxy adhesive. The CTPPGA-modified epoxy adhesive displayed a separate T_g for the CTPPGA phase at low temperature and a T_g at high temperature due to the epoxy matrix (ET_g). However, the low molecular weight CTPPGA and higher concentration of CTPPGA in the epoxy resin decreased the ET_g; thus partial miscibility was implied.
4. Based on the results, it could be concluded that CTPPGA-modified epoxy resin, cured with tris-2,4,6-(*N,N*-dimethyl amino methyl) phenol is a potential room temperature curing structural adhesive which can be used for elevated temperature environment up to 120°C.

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