Poly(ether urethane) Flexible Cyanate Ester Resins: Synthesis, Characterization, and Performance in Commercial Epoxy and Polyurethane Applications

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ABSTRACT: A poly(ether urethane)-based cyanate ester resin (PEUCER) with a biphenyl polyether backbone obtained from polymeric 4,4′-diphenylmethanediisocyanate, bisphenol A, polyether polyols of three different molecular weights, and cyanogen bromide was synthesized to obtain a polymer with better functional and physical properties, such as adhesion, flexibility, and thermal stability. The synthesis of the poly(ether urethane)-based 4,4′-(oxybiphenyl propane) cyanate ester involved three steps: the formation of the poly(ether urethane) NCO-terminated prepolymer, the formation of the OH-terminated poly(ether urethane) prepolymer (PEU–PP), and the esterification reaction of cyanate to produce PEUCER. PEUCER was cyclotrimerized to yield a triazine-ring-containing polymer, which possessed better adhesion at high temperatures and better impact resistance. PEU–PP and PEUCER were characterized with wet chemical analysis, spectral methods, and thermal methods. PEUCER showed better performance with respect to thermal and adhesion properties with a single-part polyurethane lamination adhesive and also showed better performance as a toughening agent in a two-part epoxy laminate system. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 193–202, 2008

Key words: adhesion; blends; esterification; glass transition; impact resistance

INTRODUCTION

Poly(ether urethane)-based polymers are more flexible but have low thermal and chemical resistance.[1,2] In contrast, cyanate esters have high thermal and chemical resistance but are brittle.[3–5] A number of attempts are currently being made to incorporate the thermal advantages of cyanate esters into polyurethane[6] and to incorporate the processing advantages of polyurethane into cyanate esters. Cyanate ester resins are tougher[7] than comparable thermosets, such as high-performance epoxies and bismaleimides. Control of the heterophase morphological structure is necessary to achieve significant toughening of the thermosetting cyanate ester.[8] Incorporating a bisphenol moiety[9] into poly(ether urethane) imparts compatible toughening to a cyanate ester system. Most of these cyanate resins do not soften on heating even at high temperatures, and this limits their use in other applications such as adhesives.[10] The development of an oligomeric cyanate ester resin with enhanced processability[11] is aimed at reducing the manufacturing cost.[12] Cyanate esters are grafted with a polyhydroxyl polymer for a flexible die-attached adhesive in semiconductor devices such as smart cards.[13] Oligodimethylsiloxanes with molecular weights of 1000–10,000 linked with aromatic cyanate ester resins have been reported.[14,15] Designing poly(ether urethane) thermosetting polymers for high-performance applications in electrical insulation, adhesives, coatings, and electronic encapsulation through the incorporation of cyanate groups[16] into a poly(ether urethane) network is of current interest. Grigoryeva et al.[17] reported that polycyanurates modified with polyurethane could be used as high-temperature heating melt adhesives, coatings, and sealants. Commercial cyanate ester resins[18] are used in high-temperature resistance applications such as composites and adhesives. Aryl cyanates are cyclotrimerized by heating at 175–400°C to form aryloxy-*s*-triazine, which possesses high thermal stability.[19]

The objective of this study was to synthesize and characterize a poly(ether urethane)-based cyanate ester resin (PEUCER) with a linear aromatic ester backbone. A three-step preparation of poly(ether urethane) prepolymerization and esterification was carried out for PEUCER. The effect of the polyether molecular weight of PEUCER was also studied. The performance of PEUCER in the epoxy laminate system was optimized as a toughening agent and flame retardant. Similarly, the amount of PEUCER for increasing the adhesion of the polyurethane laminating system at higher temperatures was also optimized.

OCN·C₆H₄·CH₂·C₆H₄·NCO + HO· CH₂·CH·O·(CH₂·CH·O)n·H + OCN·C₆H₄·CH₂·C₆H₄·NCO
| |
CH₃   CH₃

Diphenylmethane diisocyanate   polypropylene glycol   Diphenylmethane diisocyanate

↓ Dbtdl

OCN·C₆H₄·CH₂·C₆H₄·NHCOO·CH₂·CH·O·(CH₂·CH·O)n·OCHN·C₆H₄·CH₂·C₆H₄·NCO
| |
CH₃   CH₃

NCO Terminated polyether-urethane prepolymer

↓ + 2 HO· C₆H₄·C(CH₃)₂·C₆H₄·OH
Bisphenol A

OCHN·C₆H₄·CH₂·C₆H₄·NHCOO·CH₂·CH·O·(CH₂·CH·O)n·OCHN·C₆H₄·CH₂·C₆H₄·NHCO

O·C₆H₄·C(CH₃)₂·C₆H₄·OH   CH₃   CH₃   HO·C₆H₄·C(CH₃)₂·C₆H₄·O

OH Terminated polyether-urethane prepolymer (PEU-PP)

+ N(CH₃)₃   ↓   + 2 Br·C≡N
Cyanogen bromide

N≡C·O·**PEU-PP**·O·C≡N   + BrN(CH₃)₃

Polyether-urethane cyanate ester resin (PEUCER)   Ammonium salt

Scheme 1 Synthesis of a polyether-based polyurethane cyanate ester.

EXPERIMENTAL

Materials

Bisphenol A, tetrahydrofuran (THF; Qualigens Chemicals, Mumbai, India), modified polymeric 4,4′-diphenyl methane diisocyanate (Rubinate 9433, Huntsman, Geismar) with an isocyanate equivalent weight of 132 and an NCO content of 31.90%, cyanogen bromide (S.D. Fine Chemical, Mumbai, India), triethylamine (TEA; S.D. Fine Chemical), a cobalt octate solution, nonyl phenol (Qualigens), poly(propylene glycol)s (PPGs) with molecular weights of 1000, 2000, and 4000 (Dow Chemical), and dibutyl tin dilaurate (DBTDL) were used as received. THF was purified by distillation under reduced pressure just before use. TEA was dried over anhydrous calcium chloride and distilled. Bisphenol A, modified polymeric methylenediphyenylisocyanate (MDI) polyether polyols (PPGs), a diglycidyl ether of bisphenol A (DGEBA) epoxy resin (LY556, Huntsman), epoxy hardener diaminodiphenylmethane (HT972; Huntsman), and a solvent-based, single-part polyurethane aluminum (Al) foil/flexible foam lamination adhesive (Anabond 745), all commercial-grade, were used as received.

Synthesis of PEUCER

PEUCER was synthesized in three stages. In the first stage, the NCO-terminated prepolymer was prepared in a three-necked flask fitted with a mechanical stirrer, nitrogen inlet, and water condenser. One mole of the difunctional polyether polyol was degassed under reduced pressure for 1–2 h at 90–100°C and reacted with 2.0 mol of modified 4,4′-diphenyl methane diisocyanate at 95–105°C. The reaction was continued for 3 h with the DBTDL catalyst. The NCO-terminated prepolymer was characterized by a chemical method for the free isocyanate content. That process was adopted for the preparation of NCO-terminated prepolymers based on polyether polyols with molecular weights of 1000, 2000, and 4000 (Scheme 1).

In the second stage, the OH-terminated poly(ether urethane) prepolymer (PEU–PP) was prepared through the reaction of 2 mol of bisphenol A with 1 mol of the NCO-terminated poly(ether urethane) prepolymer (dissolved in THF) placed in a three-necked flask fitted with a mechanical stirrer, nitrogen inlet, and water condenser. The reaction mixture was made homogeneous through stirring at about 50°C. The reaction was carried out at about 105°C with constant stirring for about

4 h. The reaction mixture was dried at 50°C for 4 h to yield a highly viscous semisolid of PEU–PP. PEU–PP was characterized by a chemical method for the hydroxyl value and free isocyanate content. The same method was adopted for the preparation of NCO-terminated prepolymers of PPGs with molecular weights of 1000, 2000, and 4000 (Scheme 1), which are called PEU–PP 1000, PEU–PP 2000, and PEU–PP 4000.

In the third stage, the cyanate ester was prepared by the reaction of 1 mol of PEU–PP with 2 mol of cyanogen bromide in a THF medium with TEA as a catalyst. The reaction mixture, placed in a three-necked flask, was initially maintained at −70 to −60°C under a nitrogen atmosphere for about 1 h with constant stirring. The temperature was then raised to −10 to +10°C and maintained there for about 2 h. The temperature was raised to the final temperature of about +30°C and maintained there for 3 h. The reaction mixture was poured into an ice bath to isolate the semisolid, which was collected on a filter and washed repeatedly with ice-cold water to remove the ammonium salts. The semisolid was dried at about 50–60°C for about 4 h. PEUCER was subjected to instrumental and chemical methods of analysis. The same process was adopted for the OH-terminated prepolymers of PPGs with molecular weights of 1000, 2000, and 4000 (Scheme 1), which are called PEUCER 1000, PEUCER 2000, and PEUCER 4000.

The PEUCER was subjected to curing in the presence of the hydrogen cocatalyst (nonyl phenol) and transition-metal carboxylate (cobalt octate). The trimerization reaction[20] was carried out in two temperature ranges: 120–130°C for about 2 h and 200–210°C for about 1 h. The trimerized product was also subjected to an instrumental method of analysis. The same process was adopted for PEUCER 1000, PEUCER 2000, and PEUCER 4000. The trimerized product was also subjected to an instrumental method of analysis.

Characterization

Wet chemical analysis

The prepared NCO-terminated prepolymer, PEU–PP, and PEUCER were subjected to a wet chemical analysis to determine the hydroxyl value by titration with a standard solution of NaOH. The free NCO content of PEU–PP was determined by a reaction with a known excess of n-butyl amine titration with HCl acid.

Infrared (IR)/Fourier transform infrared (FTIR) spectra

A Hitachi IR spectrometer model 270–50 (Tokyo, Japan) and a Thermomaltson FTIR spectrophotometer were used for studying the IR spectra (400–4000 cm^{-1}) of the NCO-terminated prepolymer, PEU–PP, PEUCER, and trimerized PEUCER samples. Solid KBr pellets were prepared for the analysis. The spectral resolution was ±1 cm^{-1}.

^{1}H- and ^{13}C-NMR spectroscopy

The ^{13}C- and ^{1}H-NMR spectra of the synthesized PEUCER compounds were taken with a JEOL GS X 400-MHz NMR spectrometer (Tokyo, Japan) at room temperature with CDCl$_3$ as a solvent and tetramethylsilane as an internal standard.

Thermal analysis

Differential scanning calorimetry (DSC) thermograms were carried out with a TA Instruments Q600/Q10. The sample (4.0 ± 0.2 mg), placed in an alumina crucible, was heated in a nitrogen atmosphere (flow rate = 100 mL/min) at a heating rate of 20°C/min.

Mechanical properties

The tensile strength, elongation, and flexural strength were tested with a universal testing machine (Houns Field, United Kingdom) at a crosshead speed of 5 mm/min, and the impact strength was tested in an impact tester in the R3 mode for epoxy–PEUCER blends. The tensile strength and elongation were tested according to ASTM Standard D 638. The flexural strength and impact strength were tested according to ASTM Standard D 790 and ASTM Standard D 256.

Adhesive properties

The lap shear strength (LSS) was characterized for the polyurethane adhesive–PEUCER blend system. LSS was determined according to ASTM Method D 1002. The bonded specimens were tested with a universal testing machine (Houns Field) at a crosshead speed of 50 mm/min. For determining LSS at higher temperatures, the specimens were thermostated for 15 min at the desired temperature and then tested at that temperature.

Moisture absorption properties

The moisture absorption was characterized for the epoxy–PEUCER blends. It was determined with the following formula: $(W_2 - W_1)/(2\pi \times r^2 + 2\pi \times r \times T)$, where W_2 and W_1 are the weights (mg) after and before the test, respectively, T is the thickness of the specimen, and r is the radius of the specimen. A sample 30 mm in diameter was soaked in water for 24 h at 70°C for observation.

RESULTS AND DISCUSSION

Wet chemical analysis

The free hydroxyl values of PEU–PP 1000, PEU–PP 2000, and PEU–PP 4000 were determined to be 42,
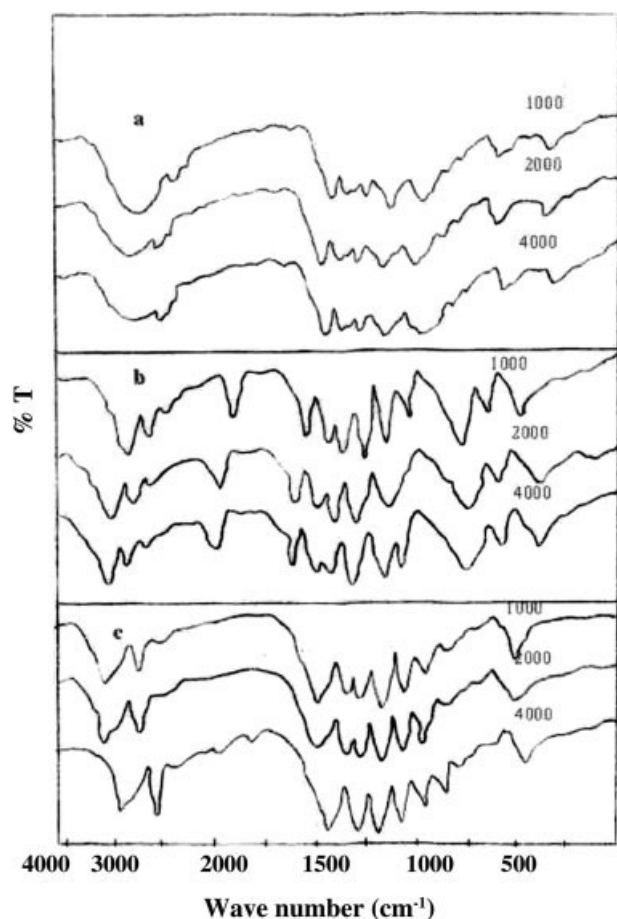
Figure 1 FTIR spectra of (a) PEU–PPs, (b) PEUCERs, and (c) trimerized PEUCERs with molecular weights of 1000, 2000, and 4000.

25, and 15 mg of KOH/g of prepolymer, respectively. The PEU–PP hydroxyl values were much lower than those of the respective polyether polyols (112, 56, and 28 mg of KOH/g for PPG 1000, PPG 2000, and PPG 4000), and this confirmed that the PEU–PP molecular weights were higher than those of the basic polyols. The free hydroxyl value of the prepared PEUCER was determined to be close to zero, indicating the absence of free OH groups in PEUCER. This confirmed that the PEU–PP hydroxyl groups completely reacted with cyanogen bromide. The free NCO content of PEU–PP was close to zero, indicating the absence of free isocyanate groups and confirming the complete reaction of polymeric isocyanate with bisphenol A.

Spectroscopy analysis

IR/FTIR spectroscopy analysis

The IR spectra of PEU–PP 1000, PEU–PP 2000, and PEU–PP 4000 [Fig. 1(a–c)] indicate the presence of hydroxyl groups as a broad absorption band at 3600–3300 cm^{-1}. The characteristic peak at 1730 cm^{-1}

was assigned to the urethane (—NHCOO—) group in PEU–PP. Other IR absorption bands due to NH stretching (3050–3200 cm^{-1}), a phenyl ring (1640–1770 cm^{-1}), an ether linkage (1080–1120 cm^{-1}), and —CH$_2$— (2900–3000 cm^{-1}) can also be observed. The absence of a peak around 2220 cm^{-1} for the free NCO group indicated the conversion of the free isocyanate group into the corresponding urethane group.[21,22]

The FTIR spectra of PEUCER 1000, PEUCER 2000, and PEUCER 4000 [Fig. 1(a–c)] show a characteristic peak at 2200–220 cm^{-1} assigned to a cyanate ester (—OCN) group. Other FTIR absorption bands due to urethane —NHCOO— (1750–1760 cm^{-1}), NH stretching (2900–3500 cm^{-1}), —CH$_2$— (2900–3000 cm^{-1}), and NH and CH bending (1200–1450 cm^{-1}) can also be observed. The absence of a peak around 3500 cm^{-1} for the free OH group indicates the conversion of the free hydroxyl group into the corresponding cyanate ester group.[23]

The IR spectra of trimerized PEUCERs [Fig. 1(a–c)] show a characteristic peak at 1500–1600 cm^{-1} assigned to a triazine ring and also at 1350–1380 cm^{-1} assigned to triazine. Another characteristic peak at 1100–1200 cm^{-1} was assigned to asymmetric stretching of Ph—O—C. The C—O—C stretching was confirmed by a peak at 1025–1045 cm^{-1}. The absence of a peak around 2220 cm^{-1} for the free OCN group indicates the conversion of the cyanate group into the corresponding triazine/aryloxy ring.

^{1}H- and ^{13}C-NMR spectroscopy analysis

The ^{1}H-NMR spectra of PEUCER 1000, PEUCER 2000, and PEUCER 4000 [Fig. 2(a–c)] show absorption peaks at δ = 7.1–7.3 ppm, indicating the presence of the phenyl group. The peak at δ = 6.7 ppm was assigned to the urethane group. The NMR spectra of these polymers exhibited signals at δ = 1.0–4.0 ppm corresponding to the rest of the carbon-bearing proton. The absence of a peak at δ = 9.10 ppm indicates the absence of a hydroxyl group in the PEUCER polymer.[17]

The ^{13}C-NMR spectra of PEUCER 1000, PEUCER 2000, and PEUCER 4000 [Fig. 3(a–c)] show peaks for isopropyl carbons at δ = 18–20 ppm. Absorption peaks at δ128–130 ppm indicate the presence of OCN carbon. The peak at δ = 115 ppm was assigned to the aromatic group. Other NMR absorption peaks for urethane carbonyl at δ = 155 ppm, for diphenyl carbon at δ = 78 ppm, and for aliphatic carbon at δ = 30–32 ppm can also be observed.

DSC thermogram analysis

The DSC curves of PEUCER 1000, PEUCER 2000, and PEUCER 4000 [Fig. 4(a–c)] show glass-transition
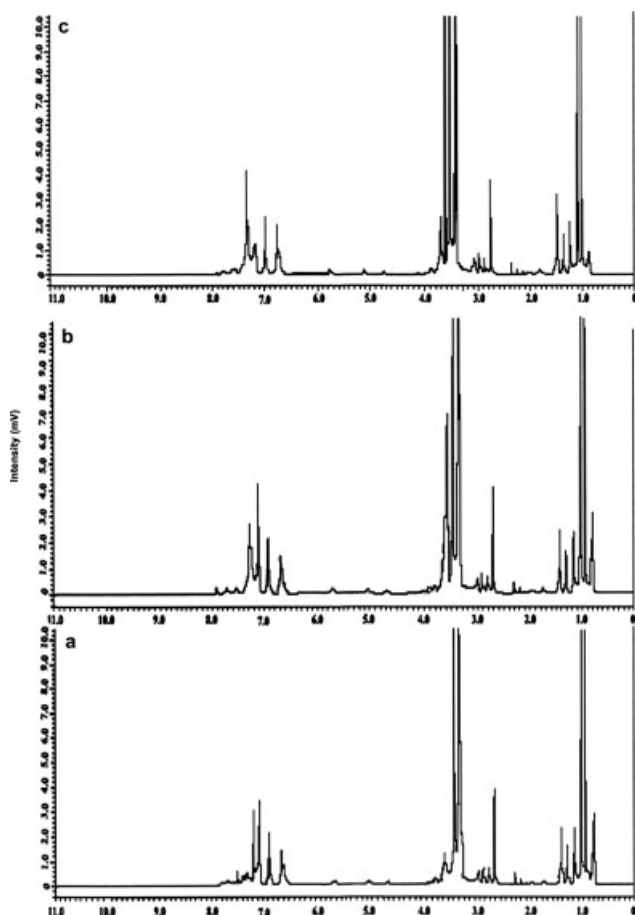
Figure 2 ^{1}H-NMR spectra of PEUCERs with molecular weights of 1000, 2000, and 4000.
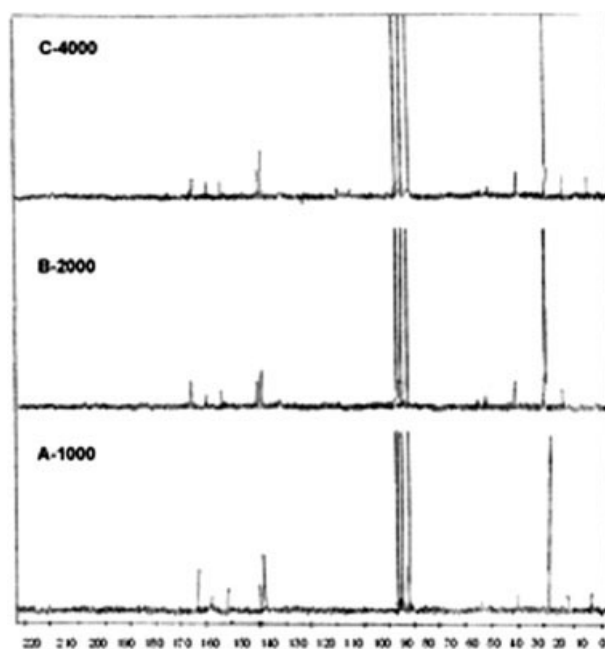

Figure 3 ^{13}C-NMR spectra of PEUCERs with molecular weights of 1000, 2000, and 4000.

DSC curves of trimerized PEUCER 1000, PEUCER 2000, and PEUCER 4000 [Fig. 5(a–c)] show T_g values of 80.2, 84.4, and 93.3°C, respectively. PEUCER 1000 and PEUCER 2000 had the same T_g values before and after the addition of the trimerization catalyst,
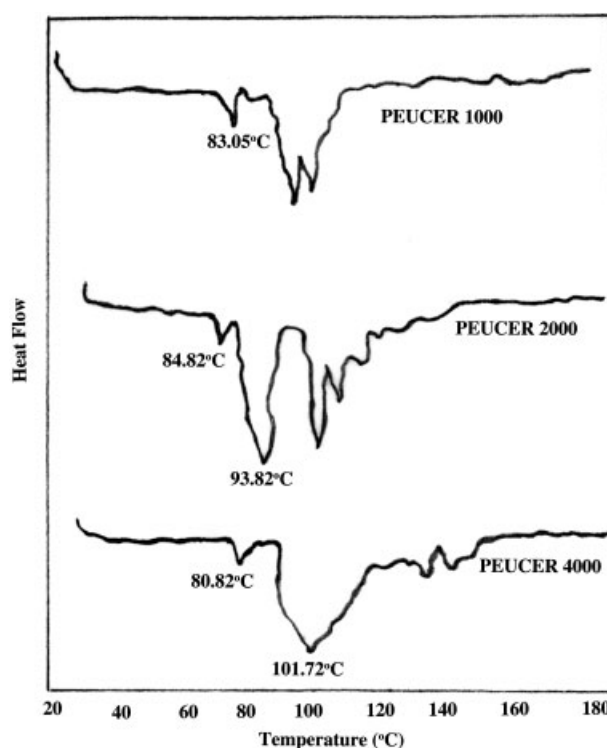
temperature (T_g) values of 80, 84, and 83°C. T_g of PEUCER was much lower than that of commercial bisphenol A cyanate ester (AroCy B; 289°C) and tetramethyl bisphenol F cyanate ester (AroCy M; 252°C) because of the presence of long, flexible aliphatic ether chains. 1,3-Bis[3′-(2-cyanato phenyl)-propyl]-1,1,3,3-tetramethyldisiloxane and 1,3-bis[3′-(2-cyanato phenyl)propyl]-1,1,3,3,5,5,7,7-octamethyl-disiloxane have T_g values of + 15°C and −43°C, respectively, according to Maya et al.[14] A slight variation in the molecular weight led to a drastic reduction in T_g, but the variation of the molecular weight of PPG (1000–4000) in PEUCER did not have much impact on T_g. The PEUCER thermograms showed broader melting endothermic peaks that may been due to the impurities and noncrystalline polymer behavior of PEUCER, as indicated by Lin[24] for phosphorous cyanate esters. PEUCER thermograms showed large endothermic curves that may have been due to the large processing window between the melting transition temperatures and the onset of the exothermic polymerization reactions of the long-chain polymer.

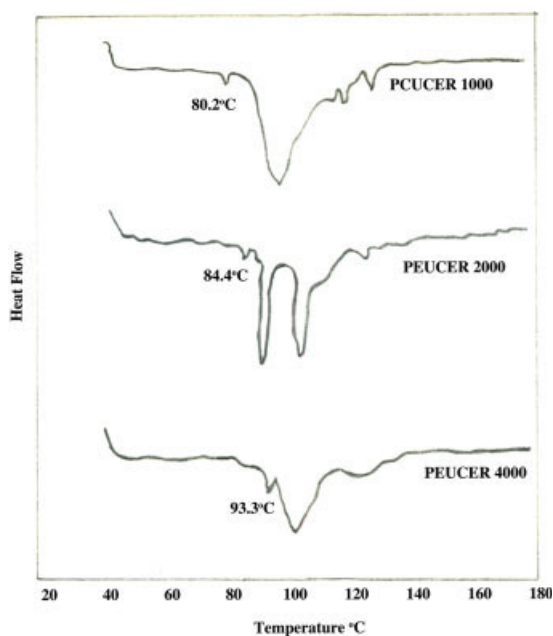**Figure 4** DSC thermograms of PEUCERs with molecular weights of 1000, 2000, and 4000.

Figure 5 DSC thermograms of trimerized PEUCERs.

but PEUCER 4000 had a higher T_g value after the addition of the trimerization catalyst, perhaps because of the higher molecular weight. The DSC curves of PEUCER 1000 and PEUCER 4000 reflect the chemical uniformity and homogeneity of the system by a single derivative of weight loss, but the curve for PEUCER 2000 shows double derivatives of weight loss by its nonhomogeneity, as stated by Fainleib et al.[25] DBTDL might have acted as a trimerization catalyst in PEUCER 1000 and PEUCER 2000 and produced T_g just as a nonyl phenol trimerization catalyst.

PEUCER in commercial applications

Blend of PEUCER with a neat two-part epoxy laminate system

The PEUCER resin prepared in this study was tested for improving the mechanical properties of a two-part epoxy laminate system in a blend. The neat two-part epoxy system and blends containing 3, 6, or 9% PEUCER 1000, PEUCER 2000, or PEUCER 4000 were subjected to stress to evaluate the tensile strength, flexural strength, and so forth. The effect of the presence or absence of a trimerization catalyst on the mechanical properties of the blends was also investigated. A commercially available epoxy resin (LY556), with an equivalent weight per epoxide of 190 ± 5, was mixed with the hardener diaminodiphenylmethane (HT972) in a weight ratio of 100 : 27, degassed at room temperature, and poured into mold made up of mild steel (MS) mold 3 mm thick. It was initially
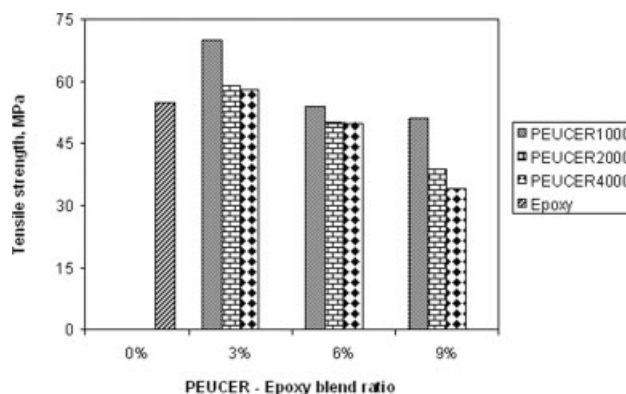
Figure 6 Tensile strength of epoxy–PEUCER blends.

cured at 120°C for 2 h and finally at 150°C for 1 h. PEUCER 1000, PEUCER 2000, and PEUCER 4000 were blended with the epoxy system at concentrations of 3, 6, and 9% with 5 phr trimerization catalyst. *Tensile strength and elongation.* The tensile strength of the neat two-part epoxy system was determined to be 55 kg/cm^2. The tensile strength of the epoxy blend of 3% PEUCER 1000 (Fig. 6) was increased to 70 kg/cm^2 (27% increase), but for a 9% blend, the tensile strength remained the same; this may be attributed to the mobility of the polymer chain and microplasticity, as stated by Kripotou et al.[26] for a hybrid of polycyanurate and a poly(oxytetramethylene glycol) (1000 equiv mol) network. However, the tensile strengths of 3% PEUCER 2000 and PEUCER 4000 were found to be similar to that of the neat epoxy system and less than that of PEUCER 1000; this might be attributed to the cooperative rearrangements of the polymer chains with the epoxy matrix. The tensile strength of the 6 and 9% blends of PEUCER 1000 decreased as the content of soft segments increased. The tensile strengths of blends containing 3% PEUCER 2000 and PEUCER 4000 were less than that of the neat two-part epoxy system,
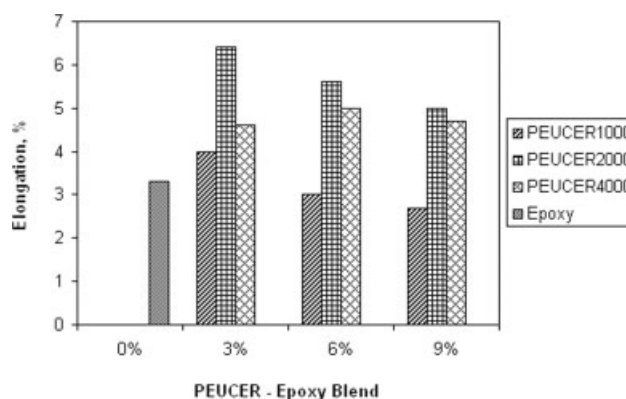

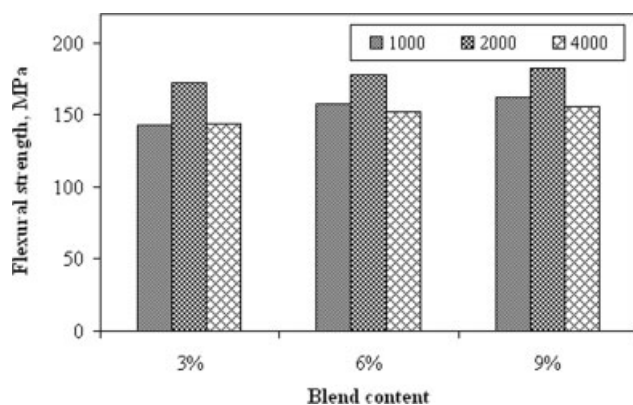**Figure 7** Elongation of epoxy–PEUCER blends.

Figure 8 Flexural strength of epoxy–PEUCER blends.

TABLE I
Water Absorption of Epoxy–PEUCER Blends

Epoxy–PEUCER blend	Water absorption (mg)		
	3%	6%	9%
PEUCER 1000	2.00	2.16	3.01
PEUCER 2000	1.42	1.45	1.96
PEUCER 4000	1.18	1.39	2.06

and this may once again be attributed to the increase in the soft segments in the blends. A similar decreasing trend was exhibited in the blends of PEUCER 2000 and PEUCER 4000 containing a higher percentage of PEUCER (6 or 9%). The optimum concentration of PEUCER 1000 in the epoxy blend was 3% for achieving a higher tensile strength.

The elongation percentages of epoxy–PEUCER 1000 blends with 3, 6, and 9% were determined to be 5.4, 5.6, and 5.5%, respectively, that is, 60% higher than that of the neat epoxy matrix. This may be attributed to the chain mobility[26] of PEUCER 1000. The elongation percentages of the epoxy–PEUCER 2000 and 4000 blends were less, being in the range of 3.4–3.5% (Fig. 7).

Flexural strength and impact strength. The flexural strength of the neat epoxy system was determined to be 74 MPa. The flexural strength (Fig. 8) of the PEUCER 1000–epoxy blend with 3% increased to 148 MPa (200% increase), and this may be attributed to flexible soft segments. The blending of PEUCER 2000 had a similar effect of increasing the flexural strength of the blend, which was observed to be quite high and also comparable to those of other cy-
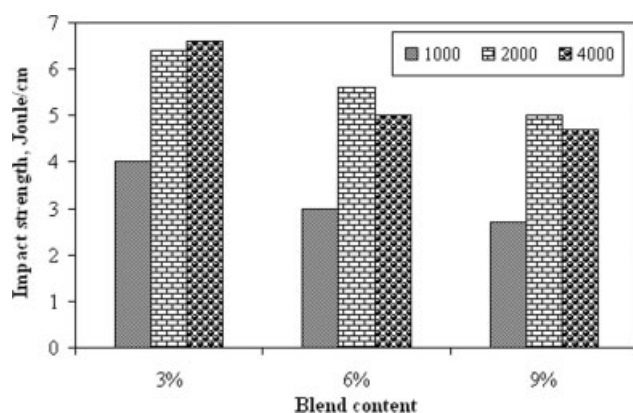
anate esters, as reported by Alagar and Dinakaran,[27] because of the lower crosslink density of the cyanate esters with the epoxy matrix. However, a further increase in the chain length through the blending of PEUCER 4000 reduced the flexural strength. Thus, an optimum chain length of PEUCER and an optimum concentration of the resin seem to be necessary for achieving a higher flexural strength (246%).

The impact strength of the neat two-part epoxy system was determined to be 0.75 J/cm. The impact strength (Fig. 9) of the epoxy blend of 3% PEUCER 1000 increased to 4.0 J/cm (a 533% increase), and this may be attributed to the higher flexibility and lower crosslink density.[27] However, a downward trend of the impact strength was noted for a higher percentage of the same PEUCER blends, and this may have been due to poorly crosslinked polymer networks. In contrast, increasing the chain length from PEUCER 1000 to PEUCER 4000 had a positive effect on the impact strength, perhaps because of more free volume.

Water absorption. The water absorption characteristic of the neat epoxy system (30.4 mg) was drastically reduced (ca. 90%) by an epoxy–PEUCER blend (Table I) to about 1.18–3.01 mg, and this may have been due to the hydrophobic formation of PEUCER with the epoxy system.[27] When the percentage of the PEUCER blends increased, the water absorption also increased, and this may have been due to the increase in the polarity of the polymer network per Jones and Karad.[28] PEUCER reduced the moisture sensitivity and enhanced the environmental durability and viscoelastic properties of the epoxy matrix.

DSC thermal analysis. T_g of the neat epoxy system was determined to be 143°C. PEUCER 1000 and PEUCER 2000 blends (Table II) showed that there

Figure 9 Impact strength of epoxy–PEUCER blends.

TABLE II
DSC Thermograms of Epoxy–PEUCER Blends

	T_g (°C)		
	3%	6%	9%
Epoxy–PEUCER 1000	145.3	142.3	138.5
Epoxy–PEUCER 2000	140.9	136.2	128.9
Epoxy–PEUCER 4000	154.5	158.7	163.4

TABLE III
Fire Retardancy of Epoxy–PEUCER Blends

Epoxy–PEUCER blend	Flame extinguishing time (s)		
	3%	6%	9%
Epoxy–PEUCER 1000	25	30	56
Epoxy–PEUCER 2000	33	45	60
Epoxy–PEUCER 4000	60	62	72

was a marginal difference in T_g (145.3 and 140.9°C) with respect to the epoxy system, for which the crosslink density was not much affected. T_g of the PEUCER–epoxy blends at 6% was lower than that of the neat epoxy matrix (144°C), and this may be attributed to changes in the miscibility of the PEUCER and epoxy segments. Hamerton et al.[29] made a similar observation for cyanate ester blends. T_g decreased linearly with increasing percentages of PEUCER 1000 and PEUCER 2000 in the blends. A similar trend was observed by Alagar et al.[30] for a cyanate ester epoxy blend that may have been due to the formation of an aliphatic oxazolidinone reaction of epoxy with cyanurate. However, an opposite trend was observed in the case of PEUCER 4000, for which T_g increased with its increasing content in the blend, and this may have been due to the high molecular weight of the polymer backbone.

Flame retardancy. The flame retardancy decreased with an increasing percentage of PEUCER in the epoxy blends (Table III). Moreover, these systems were not eligible for the UL 94 V0 grade; for that, these blend systems might be required to incorporate some other fire retardants, such as melamine and phosphorus. PEUCER 1000 exhibited an extinguishing time of 25 s for a 3% blend with epoxy, but other blends exhibited times around 60 s because of the thermal stability and flammability of the cyanate ester resin structures. The neat epoxy laminate had a self-extinguishing time of 80 s, and that may have been due to the aliphatic moieties of the epoxy, which exhibited lower thermal stability.

Performance of polyurethane laminate adhesives with PEUCER

PEUCER blend with a single-part polyurethane lamination adhesive system

The PEUCER resin prepared in this study was tested for improving the adhesion properties of a one-part polyurethane laminate for a high-temperature (100°C) application. A single-part polyurethane solvent-based lamination adhesive was cured at 120°C for 2 h; it is used for bonding flexible polyurethane foams with Al foil in automotive industries. This system is based on a modified poly(ester urethane) prepolymer. The adhesive strength of the polyurethane system was evaluated with LSS, which was applied to MS and Al strips. The neat single-part polyurethane system and the poly(ether urethane) cyanate ester systems of PEUCER 1000, PEUCER 2000, and PEUCER 4000 were subjected to stress to evaluate the LSS. The effect of the presence or absence of the trimerization catalyst on the adhesion properties of the blends was also investigated. PEUCER 1000, PEUCER 2000, or PEUCER 4000 was blended with the polyurethane adhesive at a concentration of 50%, applied to MS and Al strips with and without trimerization catalysts, and characterized.

Polyurethane system and poly(ether urethane) cyanate resins: LSS

The LSS values of single-part polyurethane flexible lamination adhesives were determined to be 72 and 81.5 KPa at room temperature on MS and Al substrates, but at 100°C, LSS was reduced by 65% for both substrates. LSS of PEUCER 1000 (Table IV) by itself in the absence of a trimerization catalyst was about 3–4 times higher (250 KPa) for MS–MS adhesion at the ambient temperature. The same trend was maintained for binding MS–MS at 100°C, although the adhesion strength was less at 100°C. This clearly shows the high-temperature adhesion capability of PEUCER 1000. Similar behavior was shown by PEUCER 1000 in binding with Al–Al.

TABLE IV
LSS Values of Neat PEUCER Systems

Substrate (polyurethane system and PEUCER)	MS–MS at 25 ± 1°C (KPa)	MS–MS at 100 ± 2°C (KPa)	Al–Al at 25 ± 1°C (KPa)	Al–Al at 100 ± 2°C (KPa)
Cyanate resin without a trimerization catalyst				
PEUCER 1000	250.0	87.0	188.0	88.0
PEUCER 2000	48.0	18.0	67.0	25.6
PEUCER 4000	12.5	04.0	12.0	02.0
Cyanate resin with a trimerization catalyst				
PEUCER 1000	271.0	74.0	160.7	58.7
PEUCER 2000	58.0	21.0	62.0	23.0
PEUCER 4000	18.5	08.0	20.6	07.6

Substrate (polyurethane system and cyanate blend)	MS–MS at 25 $\pm$ 1°C (KPa)	MS–MS at 100 $\pm$ 2°C (KPa)	Al–Al at 25 $\pm$ 1°C (KPa)	Al–Al at 100 $\pm$ 2°C (KPa)
Cyanate resin blend with a polyurethane system without a trimerization catalyst				
PEUCER 1000, 50 wt %	146.0	62.0	160.6	67.0
PEUCER 2000, 50 wt %	54.0	14.5	66.0	23.5
PEUCER 4000, 50 wt %	21.0	05.0	24.0	04.0
Cyanate resin blend with a polyurethane system with a trimerization catalyst				
PEUCER 1000, 50 wt %	54.0	18.0	61.0	21.0
PEUCER 2000, 50 wt %	23.0	10.0	24.0	09.0
PEUCER 4000, 50 wt %	22.0	04.5	27.0	06.0

Increasing the polyether chain length in PEUCER 2000 and PEUCER 4000 drastically reduced the LSS for both MS–MS and Al–Al adhesion. The addition of a trimerization catalyst (nonyl phenol) to PEUCER 1000 improved the adhesion strength in MS–MS binding marginally at the ambient temperature. However, at 100°C, the LSS decreased, possibly because of greater brittleness of trimerized PEUCER 1000. A similar trend was found for both PEUCER 2000 and PEUCER 4000. However, the LSS was very poor and would have no industrial significance, particularly in the case of PEUCER 4000.

Polyurethane system blend with poly(ether urethane) cyanate resins: LSS

The blending of different PEUCERs with polyurethane adhesive systems showed drastic reductions in the LSS, which might have been caused by the diffusion of water through cyanate linkages, as stated by Lin,[24] because some of the cyanate groups did not have enough mobility to form triazine. However, for a PEUCER 1000–polyurethane adhesive blend, the LSS (Table V) was almost doubled at the ambient temperature and at high temperatures for both MS–MS and Al–Al, possibly because of the secondary forces of hydrogen bonding and dipole–dipole interactions of cyanate ester adding more cohesion within the polyurethane adhesive and PEUCER than the adhesion at the MS or Al interface, as stated by Voss et al.[31] Thus, blending PEUCER 1000 with the commercially available polyurethane adhesive improved both low- and high-temperature adhesion for MS–MS and Al–Al substrates.

CONCLUSIONS

Flexible PEUCERs with a biphenyl backbone were synthesized and characterized chemically, spectroscopically, and mechanically. Lower T_g and higher T_g polyurethane cyanate esters were obtained by the choice of soft and hard segments of dihydroxy compounds. These studies show that poly(ether urethane) cyanate esters could be used to enhance the thermal resistance of polyurethane adhesives and to toughen the epoxy matrix. The molecular weights of the polyether polyol have a significant influence on the adhesive strength in polyurethane adhesives and a significant influence on the toughening of epoxy laminates. The incorporation of a lower T_g urethane linkage into cyanate ester might be beneficial to a cyanate ester prepreg application process.

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