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CTBN rubber phase precipitation in model epoxy resins

C.W. Wise, W.D. Cook*, A.A. Goodwin

Department of Materials Engineering, Cooperative Research Centre for Polymers, Monash University, Clayton, Vic. 3168, Australia

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Abstract

This study investigated the precipitation of three types of end-functionalised liquid rubber (two CTBN and one ATBN) from two homologous series of amine-cured epoxy polymers with variable cross-link density. The CTBN carboxyl endgroups strongly enhanced the curing rate through the impurity catalysis mechanism, however, the amino-terminated ATBN only retarded the reaction, possibly by dilutional effects or owing to changes in the dielectric constant of the reacting medium. The glass transition temperature (T_g) of the epoxy phase was depressed by CTBN rubber dissolved in the epoxy matrix and the T_g of the CTBN rubber was also lowered. The height of the DMTA rubber peak was a linear function of the level of CTBN and suggested that ca. 3% of the rubber was dissolved in the cured epoxy matrix. The microstructure of the rubber particles was studied by SEM and related to the kinetics and thermodynamics of phase separation.

Keywords: Epoxy resins; Curing; Phase precipitation

1. Introduction

Epoxy resins are reactive monomers, which are commonly cured with amine to form thermosetting polymers. If the epoxy is cured with an aromatic amine of sufficient functionality, the result is a highly cross-linked network with relatively high stiffness, glass transition temperature (T_g) and chemical resistance. Unfortunately, the inherent toughness of tightly cross-linked polymer networks is relatively low. It is therefore desirable to enhance toughness without adversely affecting the other useful properties of the polymer. Aside from inorganic reinforcement, elastomer modification is one of the most frequently used methods of toughening rigid network polymers [1–4].

The principle mechanism of rubber toughening for network polymers is thought [1,2,4] to be the enhancement of shear yielding at the crack tip through a change in stress state in the region around a rubber particle. For optimal shear banding to occur, the stress fields around the particles must overlap, thus the particle diameter and inter-particle spacing are important in determining the toughness of the material.

The most common methods of rubber toughening are by the use of liquid rubbers or preformed rubber particles. In the former method, the rubber is initially dissolved into the epoxy resin [5,6], but during cure the rubber phase separates as a discrete particulate phase. Extensive studies [7–10] have shown that the phase separation process is a result of the decrease in configurational entropy due to the increase in molecular weight as the epoxy cures. This changes the free energy of mixing leading to a decrease in the solubility of the rubber that provides the driving force for phase separation. Thus the functionality of the matrix monomers, which control the development of the network and the cross-link density of the epoxy matrix, has an effect on the phase precipitation process. The particle size and concentration of the precipitated rubber also depends on the curing process and the interaction between the rubber and the epoxy resin. With butadiene-based rubbers the solubility may be increased by forming a copolymer with the more polar acrylonitrile monomer. Another way that the liquid rubber may be modified to alter their interaction with the matrix is by functionalising the chain ends with carboxyl, amine or epoxide groups that may couple with the reacting matrix [4,8,11].

Previous studies of the phase precipitation have varied the chemical nature of the rubber [12] or of the network resin structure [13]. In the present work, the effects of cross-link density and rubber polarity on the rubber precipitation is studied by DSC, dynamic mechanical thermal analysis (DMTA) and scanning electron microscope (SEM). For these studies a model amine–epoxy resin system is used,

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* Corresponding author. Tel.: +61-03-99054926; fax: +61-03-99054926.
E-mail address: wayne.cook@eng.monash.edu.au (W.D. Cook).

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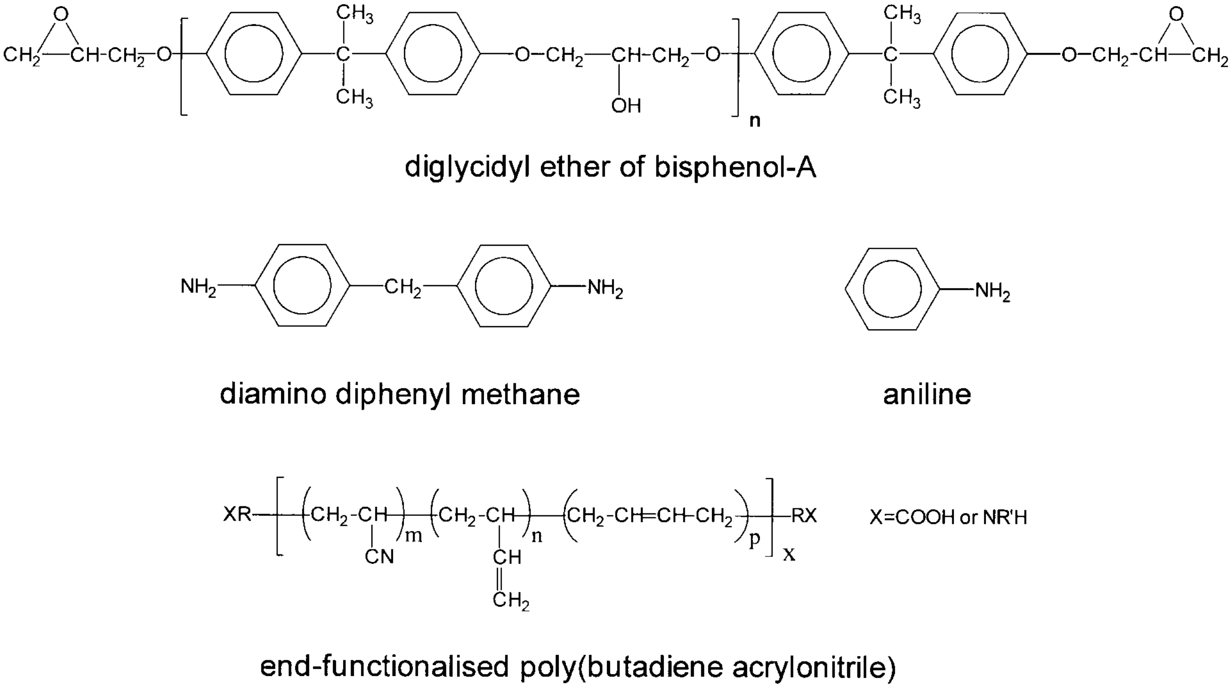

Fig. 1. Chemical structures of materials used.

which has variable cross-link density but virtually constant chemical composition. The phase precipitating rubbers investigated are butadiene–acrylonitrile copolymers of varying polarity and end-functionality but with similar molecular weight.

2. Experimental

The epoxy monomer used was diglycidyl ether of bisphenol-A (DGEBA) (Epikote 828, supplied by Shell Chemicals, Australia). The DGEBA was titrated using the HBr technique [14] and the average molecular weight was found to be 360 g/mol (assuming a di-epoxide structure) which compares with 340 g/mol for pure DGEBA. Two related amines were used as curing agents. Diamino diphenyl methane (DDM, supplied by Ciba–Geigy) is a solid, difunctional aromatic primary amine with a molecular weight of 198 g/mol. Aniline (Mallinckrodt Chemical Works) is a liquid monofunctional aromatic primary amine with a molecular weight of 93 g/mol. The reaction of DGEBA with the amines results in a fully cross-linked structure (with DDM) or a linear structure (with aniline), thus yielding polymers of totally different molecular architecture but very similar chemical composition (see Fig. 1).

Two classes of end-functionalised liquid rubbers were used. The first class of rubber consisted of carboxyl terminated butadiene-acrylonitrile copolymers, Hycar CTBN 1300X8 and CTBN 1300X13 (BF-Goodrich) with 18 and 26% acrylonitrile content and with nominal molecular weights of 3550 and 3150 g/mol, respectively (from manufacturer's data sheet). The second class consisted of an amine terminated butadiene–acrylonitrile copolymer, ATBN 1300X16 (BF-Goodrich) with 18% acrylonitrile content and with a nominal molecular weight of 1760 g/mol. The structures of these polymers are shown in Fig. 1.

Rubber-filled samples were produced by first dissolving the CTBN or ATBN into the DGEBA at approximately 60°C and with thorough stirring. DDM/DGEBA samples with an equal stoichiometric ratio of epoxide and amino-hydrogen groups were prepared by melting DDM at approximately 90°C and mixing with the rubber/DGEBA blend heated to the same temperature. The resultant mixture was thoroughly stirred and then cooled rapidly to room temperature to minimise any cure reaction during preparation. For aniline/DGEBA mixtures, the amine was dissolved in the rubber/DGEBA blend at room temperature to produce an analogous stoichiometric mixture.

A differential scanning calorimeter (Perkin–Elmer DSC-7) was used to monitor the cure kinetics. The DSC enthalpy was calibrated using a high purity indium sample; a high purity zinc sample was also used to calibrate the temperature scale. Resin samples of approximately 10 mg were used in sealed pans for all experiments to prevent evaporation of the amines. Measurements of the aniline/DGEBA mixture at the highest curing temperature revealed no measurable mass loss. Experiments were performed in temperature ramping mode by scanning the temperature of the sample at 5°C/min from room temperature to 250°C. Further information of the curing kinetics was obtained by using the DSC in isothermal mode at 120°C.

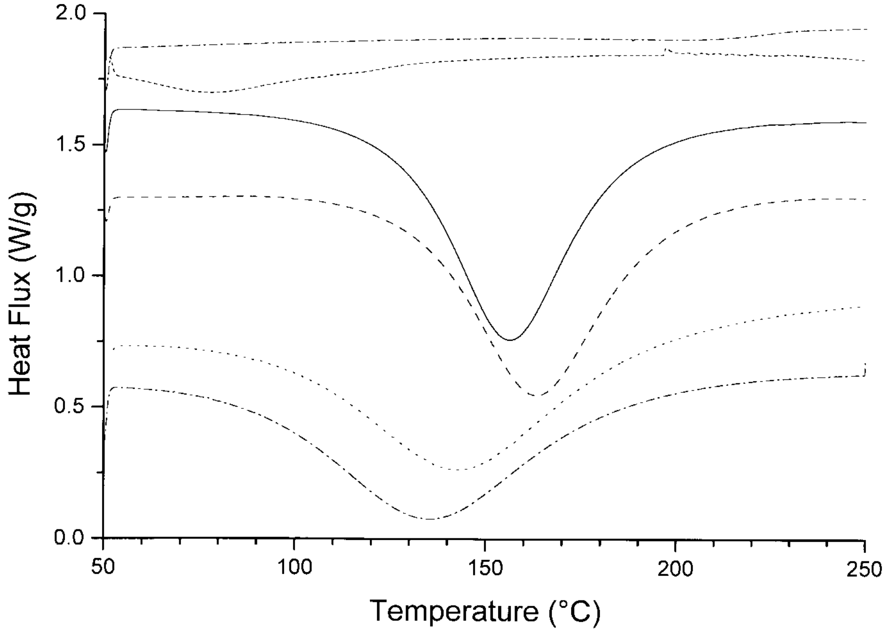

Fig. 2. Scanning DSC of aniline/DGEBA, unfilled (solid curve), with 10 wt% X13 CTBN (···), 20 wt% X13 CTBN (–·–·–) and 10 wt% X16 ATBN (– – –). Also shown are 25 wt% X13 CTBN in DGEBA (–··–··–) and 55 wt% X16 ATBN in DGEBA (---).

Dynamic mechanical thermal analysis (DMTA) at 1 Hz was performed using a Rheometric Scientific Mk II DMTA for the fully cured samples. The testing mode was dual cantilever bending with samples having a cross-section of 6 × 2 mm and a length of 16 or 22 mm between the clamps. Experiments were performed using a temperature scan rate of 2°C/min starting from −100°C and ending just above the glass transition temperature of the test material. To obtain comparable data for the neat CTBN components, dynamic mechanical analysis was also performed on a glass braid that was saturated with the CTBN liquid.

In order to observe the microstructure of the rubber precipitates, fracture surfaces were prepared from several selected specimens. The fracture surfaces were gold coated and examined in a JEOL JSM 840A SEM.

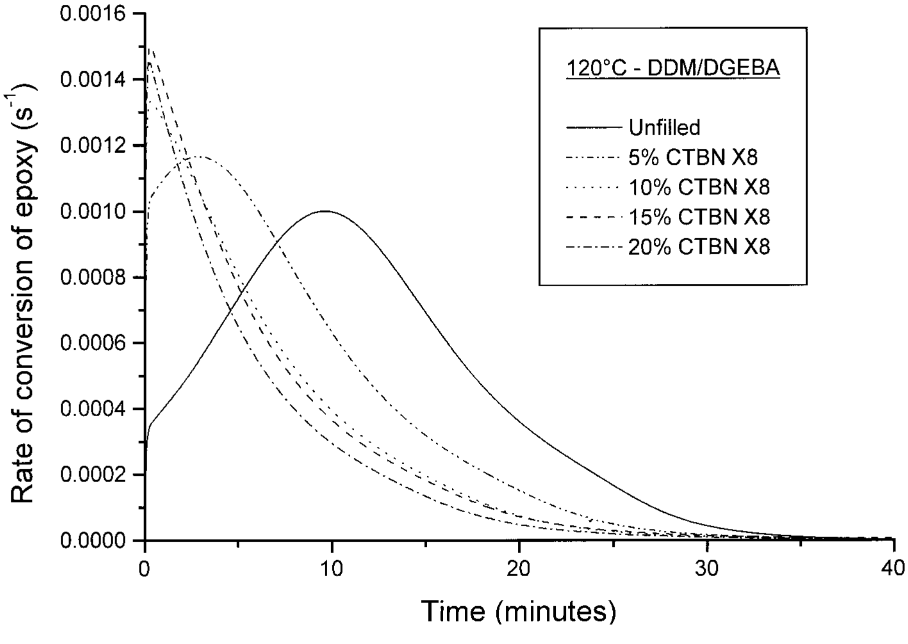

Fig. 3. Isothermal DSC for the cure of DDM/DGEBA with 0 (solid curve), 5 (–··–··–), 10 (···), 15 (– – –) and 20 (–·–·–) wt% CTBN X8 at 120°C.

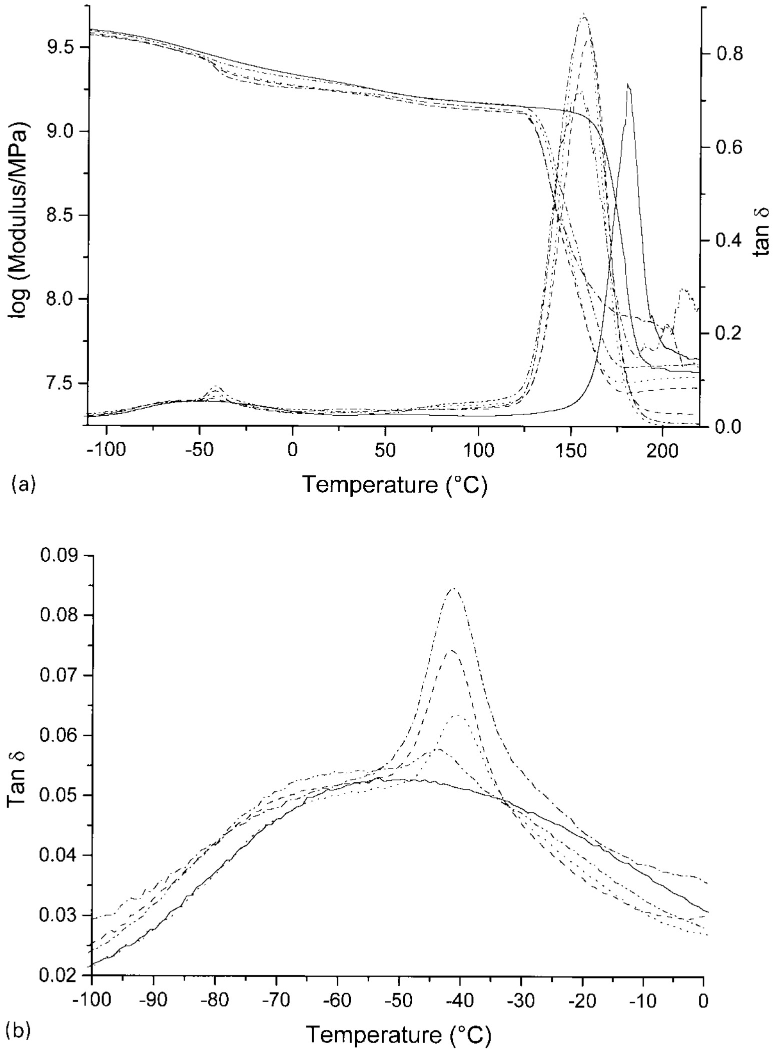

Fig. 4. (a) Flexural modulus and tan δ for the cured specimens of DDM/DGEBA with various levels of CTBN X13: 0 (solid curve), 5 (–··–··–), 10 (···), 15 (– – –) and 20 (–·–·–) wt%. (b) Detail of the low temperature region of the tanδ spectrum showing the glass transition of the CTBN X13 phase.

3. Results and discussion

Fig. 2 shows the accelerating effect of the CTBN carboxyl groups on the cure of aniline/DGEBA—with increasing levels of CTBN the peak exotherm is shifted to lower temperatures due to the enhanced reaction rate. This behaviour can be interpreted in terms of the intermolecular transition state for the epoxy–amine reaction—according to this mechanism [15–17], strong hydrogen-bonding species, such as acids and alcohols, stabilise the transition state and strongly accelerate the reaction. In contrast, the heat of polymerisation (ΔH_p) was virtually independent of rubber content—ΔH_p ranged from 99.9 J/mol (441 J/g) for unfilled aniline/DGEBA to 95.4 J/mol (421 J/g, expressed in terms of the mass of epoxide/amine mixture) for 25 wt% CTBN confirming that the final reaction state is not significantly affected by the presence of the CTBN. The ΔH_p was previously found to be 98.9 J/mol for DDM/DGEBA and 99.1 J/mol for aniline/DGEBA [18]. This compares with 91.4 J/mol found by Barton [19] for the DDM/DGEBA system and values ranging from 100–118 J/mol for phenyl glycidyl ether type epoxy–amine reactions tabulated in a review by Rozenberg [17].

A mixture containing 10% ATBN rubber is also included in Fig. 2 for comparison with the effect of the CTBN on the kinetics. The ATBN does not catalyse the aniline–DGEBA reaction; rather it is somewhat retarded. This may be due to the effect of dilution on the concentration of reacting species. Alternatively this retardation may be caused by a destabilisation of the polar transition state as a result of the reduction in the dielectric constant when the less polar rubber is added to the mixture. Also included in Fig. 2 are DSC traces of DGEBA without the amine and with 25% X13 CTBN (which is equivalent in concentration to the 20% CTBN DDM/DGEBA system) or 55% X16 ATBN. The reaction between the DGEBA and CTBN is small relative to the epoxy–amine reaction, while there

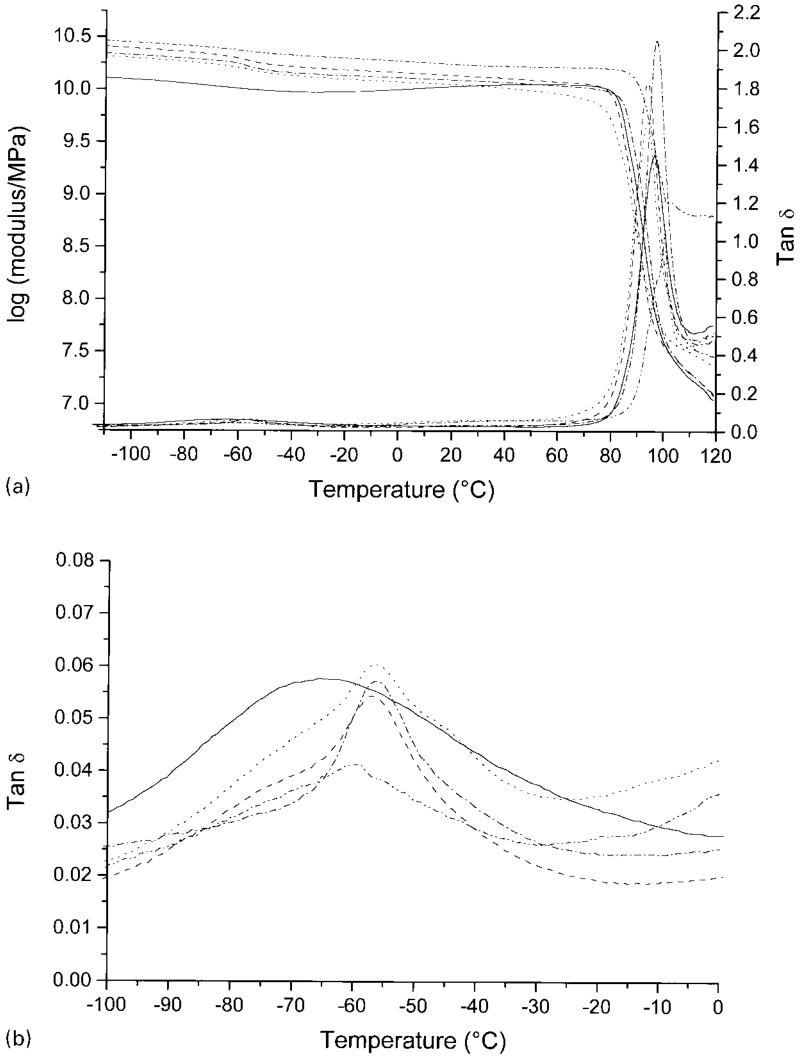

Fig. 5. (a) Flexural modulus and tan δ for the cured specimens of aniline/DGEBA with various levels of CTBN X8: 0 (solid curve), 5 (–··–··–), 10 (···), 15 (– – –) and 20 (–·–·–) wt%. (b) Detail of the low temperature region of the tan δ spectrum showing the glass transition of the CTBN X8 phase.

is a measurable reaction between the ATBN and DGEBA.

Similar accelerating effects to those shown in Fig. 2 were found by isothermal DSC (Fig. 3). The commonly accepted kinetic rate expression for amine cured epoxy reaction can be expressed as [15,18]

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = K_1(1-\alpha)^2\left(\alpha + \frac{K_{1c}}{K_1}\right) \tag{1}$$

where α is the conversion and K_1 and K_{1c} are the rate constants associated with auto-acceleration (due to the hydroxy groups formed in the reaction) and external catalysis (such as the CTBN carboxyl groups), respectively. In contrast to the mainly autocatalytic reaction (i.e. $K_1 > 2K_{1c}$) previously observed [18] for this system in the absence of CTBN, Fig. 3 shows that at high CTBN levels, the reaction is dominated by the external catalyst (i.e. $K_{1c} > (1/2)K_1$). This external catalysis causes the rate to be at a maximum initially followed by a rate decrease throughout the remaining reaction—compared with the pure DDM/DGEBA, the initial rate is increased by more than a factor of four at 20 wt% CTBN. Thus it is difficult to accurately determine the conversion from these isothermal experiments because of the uncontrolled reaction that occurs before the isothermal section of the DSC experiment. As suggested above, the impurity catalysis appears to be principally caused by the carboxyl end-groups on the CTBN molecules. In experiments on a similar system where the CTBN rubber was pre-reacted with the epoxy, Verchere et al. [8] reported that there was only a relatively small change in the epoxy–amine reaction rate of the rubber containing systems, compared with the unfilled system.

Fig. 4 shows the DMTA data for DDM/DGEBA with varying amounts of X13 CTBN while Fig. 5 has similar data for aniline/DGEBA with varying amounts of X8 CTBN. Each of the filled materials exhibits three relaxational processes. At high temperatures, the glass transition is observed as a large maximum in the tan δ curve and a

Table 1
Glass transition temperatures (°C) of the matrix phase in CTBN/epoxy resins

	Material: DDM/DGEBA		Material: aniline/DGEBA	
	X13 CTBN	X8 CTBN	X13 CTBN	X8 CTBN
Unfilled	180	180	96	96
5% CTBN	157	158	96	101
10% CTBN	155	155	89	94
15% CTBN	157	166	91	93
20% CTBN	154	166	91	97

corresponding drop in the flexural modulus curve. The glass transition temperature (taken as maximum of the tan δ curve at 1 Hz) is 180°C for DDM/DGEBA and 96°C for aniline/DGEBA, which agrees well with the results of other workers [20,21]. Owing to the similar chemical nature of DDM/DGEBA and aniline/DGEBA (Fig. 1), the differences in their T_gs are purely due to the differences in cross-link density [18]. The T_g of the unfilled DDM/DGEBA resin is higher than that of the filled materials—this observation was confirmed in the DDM-cured resins containing X8 CTBN (Table 1). This suggests that either the filled materials are not fully cured or that some of the rubber is dissolved in the epoxy phase and is plasticising the glass transition. A related trend may also occur for the aniline/DGEBA systems with either X8 or X13 CTBN, but here the data is more scattered.

At low temperatures, the tan δ curves (Figs. 4 and 5) reveal a broad peak centred at ca. −60°C in the DDM/DGEBA and aniline/DGEBA systems and an additional sharper peak at ca −40°C for DDM/DGEBA/X13 CTBN and at ca −55°C for aniline/DGEBA/X8 CTBN. As a result of the narrowness of the latter tan δ peak, this relaxation is also revealed in the flexural modulus plot, which shows a corresponding step at ca −40 and −50°C, respectively. The broad peak at −60°C in the unfilled network can be identified as the β relaxation of the epoxy resin, which is often attributed to the crankshaft motion of the glyceryl-like groups in DGEBA [22]. The sharper relaxation peak at ca −40°C for DDM/DGEBA/X13 CTBN and at ca. −55°C for aniline/DGEBA/X8 CTBN can be assigned to the glass transition of the CTBN X13 and X8 rubbers because the magnitude of the tan δ peak increases when the rubber level is raised.

The T_g of the CTBN (Table 2) when precipitated from the epoxy matrix is lower than when in its pure form. Similar results have been reported by Verchere et al. [9] for epoxy terminated butadiene/acrylonitrile rubber in an aliphatic-amine cured DGEBA. Three effects may be responsible for this observation. One possibly is that this is due to the presence of a small amount of unreacted monomer that plasticises the CTBN. The T_g of DGEBA is −11°C (by DSC) which is higher than the T_g of the CTBN, so this affect cannot be attributed to plasticisation by DGEBA alone. On basis of the correlation between melting points and glass transition temperatures $-T_g/T_m = 0.6$ [23]—the T_g of aniline and DDM would be expected to be of the order of ca. −113 and −55°C, which is consistent with our previously measured DSC T_gs of −40 and −12°C for unreacted aniline/DGEBA and DDM/DGEBA mixtures, respectively [18]. Thus the presence of aniline or DDM in the CTBN phase could lead to the observed plasticisation of the CTBN rubber's T_g. The greater solubility of DDM in the polar X13 CTBN should cause a greater depression of T_g than for the less polar X8 CTBN as is observed. However this argument does not fully explain the shift in the CTBN T_g by aniline.

Alternatively, the lowering of the CTBN rubber T_g may be due to compositional heterogeneity of acrylonitrile in the copolymer chains, which causes compositional fractionation of the acrylonitrile–butadiene copolymer during the phase precipitation process. This could cause the non-polar, butadiene-rich component of the CTBN copolymer to be preferentially expelled from the more polar matrix thus leading to a reduction in the T_g of the dispersed phase because the butadiene-rich CTBN has a lower T_g. A third explanation, offered by Verchere et al. [9], is that after curing at elevated temperatures and subsequent cooling, thermal hydrostatic stresses are applied to the rubber inclusions due to differences in the thermal expansion coefficients of the rubber and matrix phases. This is believed [9] to raise the free volume in the rubber phase and hence increase T_g.

The glass transition peak of the CTBN rubber in Figs. 4 and 5 was separated from the underlying epoxy β relation and background damping by fitting curved baselines to the tan δ peaks by inspection, which is similar to the approach used by Bucknall and Yoshii [24]. More elaborate methods, including the resolution of the tan δ curves by fitting

Table 2
Glass transition temperatures (°C) of the rubbery phase in CTBN/epoxy resins

	Material: DDM/DGEBA		Material: aniline/DGEBA	
	X13 CTBN	X8 CTBN	X13 CTBN	X8 CTBN
CTBN on glass braid	−27	−43	−27	−43
5% CTBN	−43	−60	−39	−59
10% CTBN	−41	−47	−37	−56
15% CTBN	−42	−46	−40	−57
20% CTBN	−41	−46	−38	−57

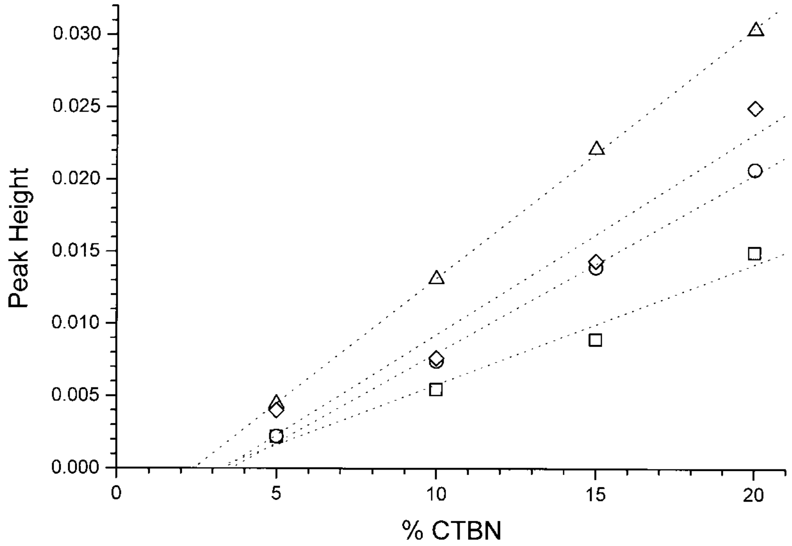

Fig. 6. Resolved tan δ peak height (tan δ(max)) of the rubber transition versus the wt% CTBN added to the polymer. (△) DDM/DGEBA/CTBN X13, (◇) DDM/DGEBA/CTBN X8, (○) aniline/DGEBA/CTBN X8, (□) aniline/DGEBA/CTBN X13.

Gaussian or Lorentzian curves to the tan $\delta - 1/T$ data, as employed by Charlesworth [25], did not improve the analysis. In Fig. 6, the height of the tan δ peak due to the CTBN rubber transition is plotted against the wt% CTBN added to the resin mixture. In agreement with its assignment as a rubber peak, a linear relation is observed. Interestingly, the tan δ(max) extrapolates to zero at ca. 3% CTBN, suggesting that the epoxy matrix contains some dissolved rubber and that the CTBN rubber is precipitated only at levels higher than 3 wt%. This is consistent with the depression in T_g of the epoxy phase, noted above. This result is also consistent with the observed fracture surfaces of the DDM cured DGEBA and aniline cured DGEBA samples containing 5% CTBN, shown in Fig. 7, which suggest only small amounts of precipitated rubber particles in the epoxy resin's matrix.

Typical microstructures for rubber filled epoxies are revealed by the fracture surfaces in Fig. 8. The particles in the X8 CTBN filled systems (see Fig. 8(c) and (d)) are of the order of 1 μm or larger. In the X13 CTBN filled epoxies, (see Fig. 8(a) and (b)) rubber is more finely distributed, with particles being sub-micron in size. This may result from the greater solubility of X13 CTBN in the epoxy; X13 CTBN has a greater level of the polar acrylonitrile units thus requiring a higher degree of cure before phase precipitation of a CTBN phase occurs. Presumably this results in a smaller particle size because at higher degrees of cure the viscosity of the epoxy phase is higher, which would reduce the ease of CTBN diffusion and of particle agglomeration. The DDM cured systems (see Fig. 8(a) and (c)) show larger particles than the corresponding aniline cured systems (see Fig. 8(b) and (d)). This may be associated with the tetrafunctional nature of DDM which initiates the CTBN precipitation at a lower conversion than for the aniline/DGEBA systems.

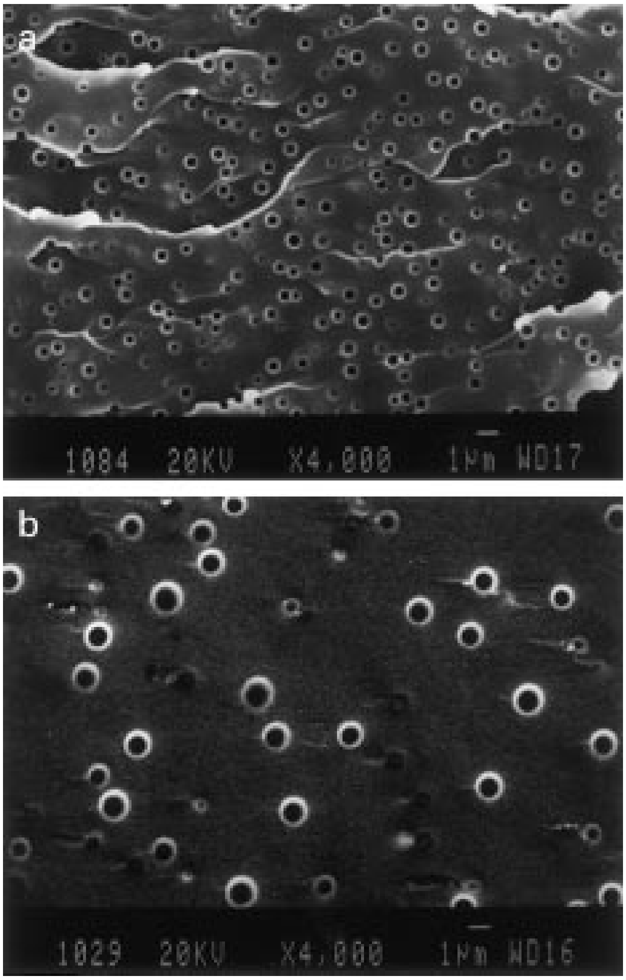

Fig. 7. SEM micrographs of fracture surfaces containing 5 wt% CTBN: (a) 5 wt% X13 CTBN in DDM/DGEBA; (b) 5 wt% X8 CTBN in aniline/DGEBA.

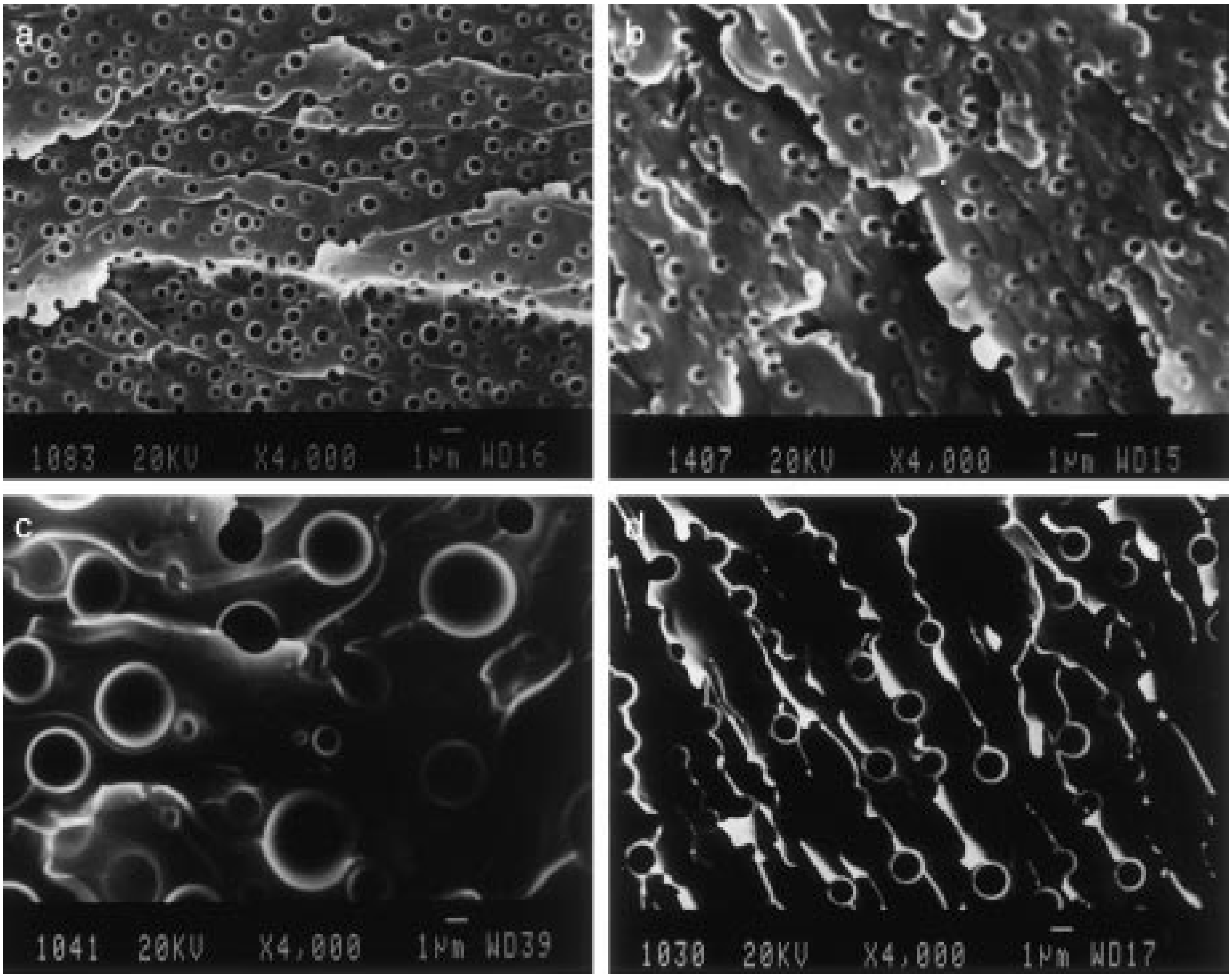

Fig. 8. SEM micrographs of fracture surfaces of materials containing 10 wt% CTBN: (a) DDM/DGEBA/X13 CTBN; (b) aniline/DGEBA/X13 CTBN; (c) DDM/DGEBA/X8 CTBN; and (d) aniline/DGEBA/X8 CTBN.

4. Conclusions

The addition of carboxyl terminated butadiene–acrylonitrile rubbers to aromatic amine cured epoxy resins has been shown to increase the rate of the epoxy–amine reaction, due to the catalytic effect of the CTBN carboxyl groups on the cure process. In contrast, amine terminated rubber slowed the curing reaction, possibly resulting from the dilution of the reacting species or due to destabilisation of the transition state due to reduction in the dielectric constant.

The T_g of the epoxy matrix was slightly depressed for the CTBN-filled systems, probably due to the plasticising action of small levels of rubber dissolved in the matrix. The glass transition of the rubbery CTBN phase was also lower than the glass transition temperature of the neat CTBN. The magnitude of the depression of T_g varies from 3 to 17°C; the cause of this depression of T_g has not been determined although several possible reasons were discussed.

The height of the DMTA rubber glass transition loss peak was used as an indication of the proportion of CTBN that was contained in the precipitate particles. Determination of this peak height was complicated by the coincidence of a secondary relaxation of the epoxy in the same temperature range. The solubility of CTBN in the epoxy matrix was estimated to be between 2 and 4% for the four combinations of CTBN and matrix examined. Related fracture surfaces of epoxy samples with 5% rubber clearly show a spherical second phase when examined by SEM. The size of the rubber particles was smaller for the more polar CTBN rubber possibly due its greater solubility in the matrix.

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