

CHARACTERIZATION OF RUBBER EPOXY BLENDS BY THERMAL ANALYSIS

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Abstract

Differential scanning calorimetry (DSC), thermogravimetric analysis (TG) and dynamic mechanical analysis (DMA) of the blends of epoxy cresol novolac (ECN) resin toughened with liquid carboxy terminated butadiene-co-acrylonitrile (CTBN) rubber have been carried out. Exothermal heat of reaction (ΔH) due to crosslinking of the resin in presence of diaminodiphenyl methane (DDM, as amine hardener) showed a decreasing trend with increasing rubber concentration. Enhancements of thermal stability as well as lower percentage mass loss of the epoxy–rubber blends with increasing rubber concentration have been observed in TG. Dynamic mechanical properties reflected a monotonic decrease in the storage modulus (E') with increasing rubber content in the blends. The loss modulus (E'') and the loss tangent ($\tan\delta$) values, however, showed an increasing trend with rise of the temperature upto a maximum (peak) followed by a gradual fall in both cases. Addition of 10 mass% of CTBN resulted maximum E'' and $\tan\delta$.

Keywords: carboxy terminated butadiene-co-acrylonitrile rubber, DMA, DSC, epoxy cresol novolac resin, TG

Introduction

Use of varieties of rubber toughened epoxy resins have become a common place as structural and load bearing materials, in adhesives, encapsulants for electrical and electronic components [1–5]. In these applications thermal stability and structural integrity of the materials at elevated temperatures are of primary importance especially when the products undergo long-term serviceability in dynamic conditions. Conventional methods viz., Fourier transform infrared spectroscopy (FTIR), physico-mechanical properties, failure mechanism through scanning electron microscopy (SEM) and wide angle X-ray scattering (WAXS) for varied rubber–epoxy systems have been reported recently [6–8]. Despite the influence of volume fraction, particle size and particle size distribution were also found to play a significant role in toughening [3, 9, 10]. Setua *et al.* [11] also reported on the characterization and compatibility of elastomer blends using various thermo-physical, microscopic and ultrasonic tech-

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niques. In the present paper we report results of our investigations on thermal analysis of ECN–CTBN blends with the help of several thermal techniques viz., differential scanning calorimetry (DSC), thermogravimetric analysis (TG) and dynamic mechanical analysis (DMA).

Experimental

Differential scanning calorimetry studies were carried out in DSC 2910 of TA Instruments Inc. USA in the temperature range from ambient to +350°C in nitrogen atmosphere.

Thermogravimetric analysis were made in high resolution TG 2950 of TA Instruments Inc. USA at a heating rate of 10°C min⁻¹ and in the temperature range from ambient to +800°C.

Dynamic mechanical analysis was conducted on a DuPont's 983 dynamic mechanical analyser in nitrogen atmosphere at a heating rate of 10°C min⁻¹. The temperature range was between ambient to +350°C. The analysis was carried out in a resonance mode.

Results and discussion

Characteristics of ECN (synthesized in the laboratory) and CTBN (obtained from trade) are given in Tables 1 and 2 respectively. Compositions of the blends are depicted in Table 3.

Table 1 Typical properties of ECN

No.	Property	Value
1	Molecular mass, (M_n/M_w)/g mol ⁻¹	850, 1000
2	Softening point/°C	40–45
3	Epoxy equivalent mass/g mol ⁻¹	220
4	Physical state	viscous fluid

Table 2 Typical properties of CTBN

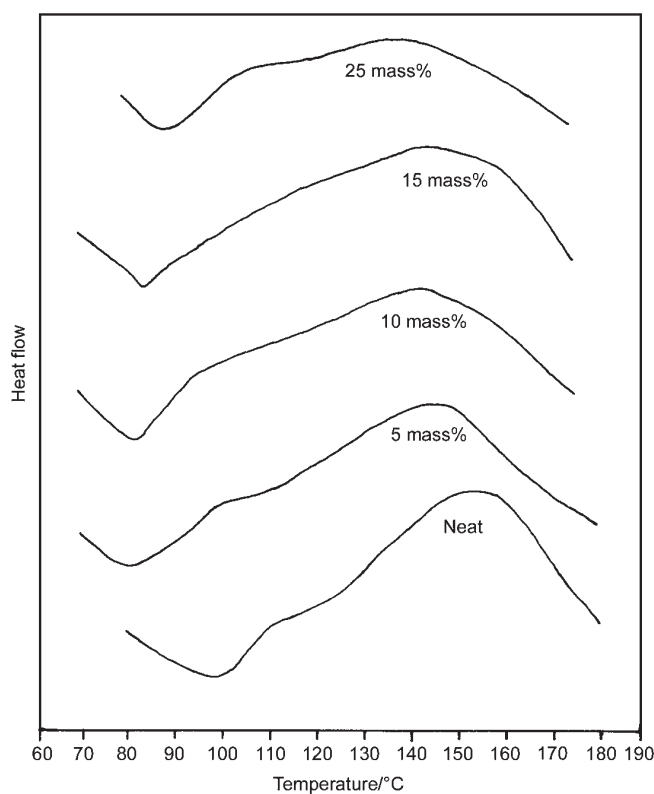
No.	Property	Values
1	Brookfield viscosity at 27°C/mPa s	60000
2	Carboxyl content/%	2.37
3	Specific gravity at 25°C/g cm ⁻³	0.948
4	Acrylonitrile content/%	17
5	Functionality/%	1.85

Table 3 Composition of ECN with CTBN blends containing DDM

No.	Nomenclature of the blends	ECN/	CTBN/	DDM/
		g		
1	EBN ₀	100	0	23.0
2	EBN ₅	95	5	21.5
3	EBN ₁₀	90	10	20.0
4	EBN ₁₅	85	15	19.2
5	EBN ₂₅	75	25	17.1

Differential scanning calorimetry

Figure 1 shows curing of ECN and CTBN in presence of DDM. Presence of a weak endotherm prior to onset of curing was noticed in all cases. In case of neat epoxy system (EBN₀), the negative ΔH value obtained was 28.08 J g^{-1} . Addition of rubber and rubber-resin adhesion restrained isomerization of resin and thereby resulted a corresponding decrease in the ΔH values in accordance to the rubber concentration.

**Fig. 1** DSC curves of ECN-CTBN blends

Further, it showed that curing started around $80\pm 10^\circ\text{C}$ irrespective of the CTBN content in the blends and the presence of rubber did not affect either the cure rate or the final cure state of the resin. A gradual decrease in the peak exotherm temperature and ΔH with increasing CTBN concentration in the blends was also evident. They were due to two factors, the compatibility of ECN and CTBN which resulted adduct formation between the polymers and a concomitant decrease in the net volume fraction of ECN with increasing CTBN which caused reduction of ΔH values for epoxy crosslinking.

Thermogravimetric analysis

Figure 2 shows the TG graphs of the blend systems. TG analysis of pure ECN resin and blends with varied CTBN concentrations confirms the occurrence of degradation in stages during elevation of temperatures in the path of complete degradation of the samples. Implications of the addition of the liquid rubber which is more thermally stable than novolac itself was envisaged in the offspring of better thermal stability for the composites compared to neat resin. The degradation was found to occur in three stages (I, II & III) in all cases.

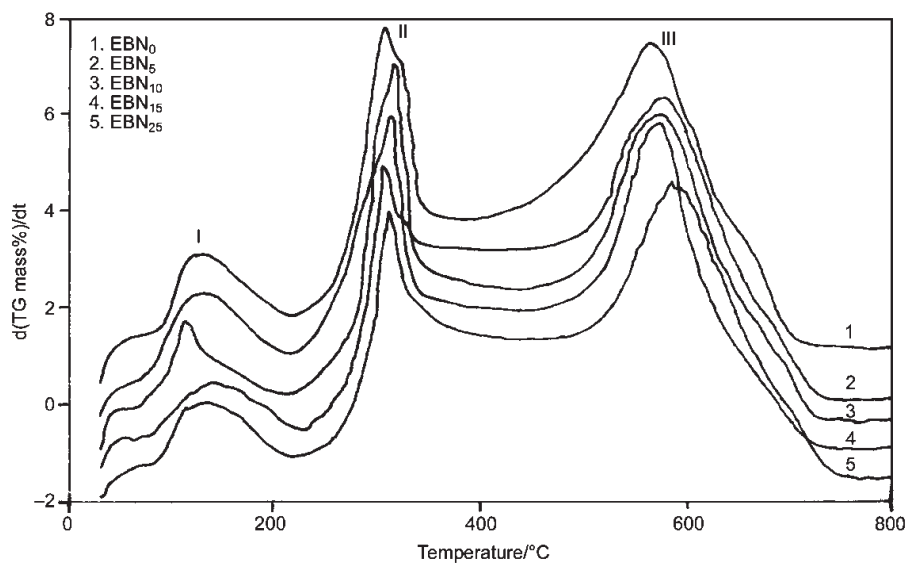


Fig. 2 TG curves of ECN-CTBN blends

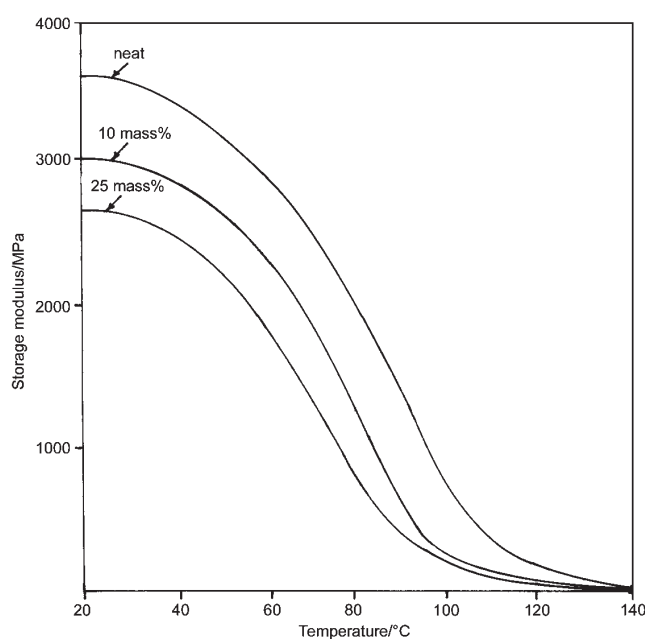
Positioning of these peaks, and the corresponding percent mass losses are depicted in Table 4. At elevated temperatures, the rubber started functioning as a thermal stabiliser and resulted in an increase in the thermal stability of ECN-CTBN blends from 547°C (for neat resin) to 575°C (for blend containing 25 mass% CTBN).

Table 4 Percentage mass loss in ECN–CTBN blends

No.	Temperature/percentage mass loss of degradation stage		
	I	II	III
EBN ₀	131/4.23	307/23.92	547/68.10
EBN ₀	135/3.84	323/32.96	590/60.79
EBN ₀	135/3.93	328/33.00	575/62.81
EBN ₀	126/3.84	328/34.61	587/60.83
EBN ₀	140/3.50	316/31.17	575/64.99

Dynamic mechanical analysis

Figure 3 shows the plots consisting of the storage modulus (E'), of the composites containing different proportions of CTBN as a function of temperature. In all cases E' decreased with increasing temperatures. Also at any given temperature, the storage moduli decreased with increasing rubber loading which is due to lowering of the stiffness of the matrix.

**Fig. 3** Storage modulus plots of ECN–CTBN blends

Both the loss modulus (E'' , Fig. 4) and the loss tangent ($\tan\delta$, Fig. 5) for the composites increased with increasing temperatures upto a peak maximum followed by a reversion with further temperature rise. The differences in E'' and $\tan\delta$ values between the filled and the neat epoxy polymer at lower temperatures are only marginal.

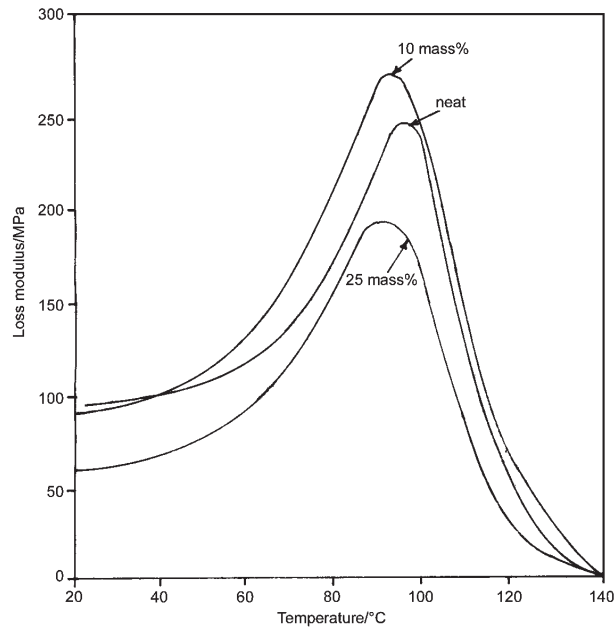


Fig. 4 Loss modulus plots of ECN-CTBN blends

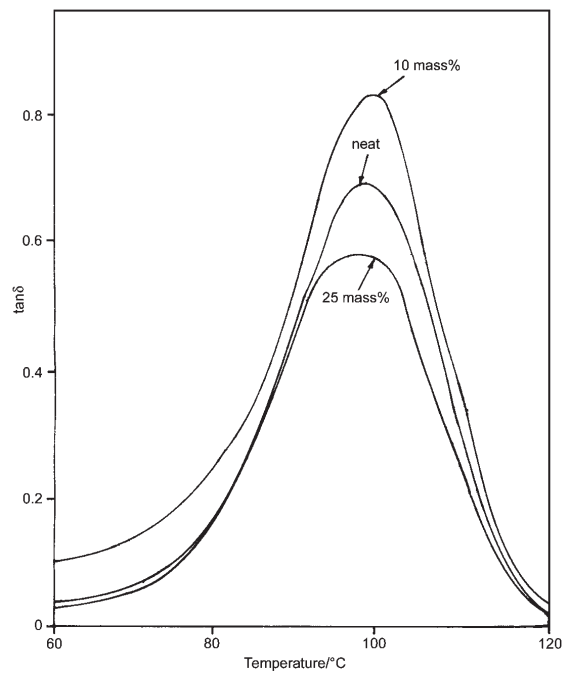


Fig. 5 Tan δ plots of ECN-CTBN blends

Upto 10 mass% rubber, the peak maximum of both the E'' and $\tan\delta$ showed shifts towards lower temperature which is due to compatibility and enhancement of rubber-matrix interaction. At higher rubber content, however, the matrix is less restrained by the presence of rubber globules with sizes increased by rubber particles coalescence, cavitation and inhomogeneity of the system. SEM studies published earlier [6–8] give evidences in support of above statement. Incidentally, 10 mass% CTBN filled epoxy system has also been found, in these studies, to offer a best match between the optimum physico-mechanical properties e.g., tensile strength, tensile modulus and impact strengths compared to blends containing otherwise lower or higher rubber concentrations.

Conclusions

- a) DSC studies showed reductions of the extent of isomerization as well as exothermal heat of reaction of epoxy crosslinking due to addition of rubber into epoxy resin.
- b) TG studies showed enhancement of the thermal stability with increasing rubber concentration in the blends.
- c) DMA analysis, signified that a 10 mass% rubber filled epoxy composites can behave as a better damping material in dynamic applications compared to brittle epoxy resin.

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