

Thermophysical Properties of CTBN and HTPB Liquid Rubber Modified Epoxy Blends

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ABSTRACT: Thermal conductivity and diffusivity of carboxyl-terminated copolymer of polybutadiene and acrylonitrile (CTBN) and hydroxyl-terminated polybutadiene (HTPB) liquid rubber-modified epoxy blends were investigated. A good agreement was observed between the calculated values of the specific heat estimated from thermal conductivity, diffusivity, and density measurements and the DSC results. Measurements of the thermal conductivity values of HTPB/Epoxy blends were in good agreement with three simple theoretical models, which have been used thereafter for the estimation of the unknown value of

the thermal conductivity of CTBN ($k_{\text{CTBN}} = 0.24 \text{ Wm}^{-1}\text{K}^{-1}$). The morphology of the rubber-modified epoxy blends has been quantified and indicate a tendency towards co-continuous phase upon the inclusion of higher weight percentage of rubber ($\geq 30 \text{ wt } \%$). Moreover, we notice a significant enhancement of the thermal conductivity during this morphological shift. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 3232–3241, 2010

Key words: thermal conductivity; thermophysical properties; blends; CTBN; HTPB

INTRODUCTION

Epoxy resins are widely used as coatings, structural adhesives, electronic and electrical materials, and advanced composite materials in many applications, because of their excellent mechanical, thermal, and electrical properties.¹ However, one of the most undesirable property of these materials is their very poor fracture toughness. The cured neat epoxy matrices are often very brittle and show poor resistance to crack propagation and this adversely affects most physico-mechanical properties. To overcome this problem, modifiers are often incorporated during cure of the epoxy matrices because of their potential to toughen thermosetting matrices. Among the modifiers are engineering thermoplastics^{2–5} and functionalized polysiloxanes.⁶ Rubbery modification of epoxy resins has been found to be a most successful method. This is achieved by the use of functionally terminated liquid rubbers⁷ or preformed rubber particles.⁸ Low molecular weight liquid rubbers are preferred to toughen the thermoset matrix to avoid an excessive increase of viscosity and thus to enhance the easiness of the process ability of the sys-

tem.⁹ During the cure polymerization reaction, the molecular weight increases, and the rubber gets phase separated, leading to the formation of a two-phase morphology¹⁰ and this has been shown to be the result of the decrease in configurational entropy.¹¹ It is now well established that rubber domains act as stress concentrators and toughen the epoxy matrix to obtain excellent mechanical and electrical properties.¹² Synthetic rubbers having reactive functionalities, such as methylol, hydroxyl, carboxyl, anhydride, amine, or thiol groups that potentially react with epoxy resins, are employed as modifiers. Barcia et al.¹³ have modified the carbon fiber reinforced epoxy matrix composite using hydroxyl-terminated polybutadiene (HTPB). Hydroxyl-terminated internally epoxidized polybutadiene has been used to modify the mechanical properties of an epoxy resin matrix.¹⁴ In another interesting study,^{15,16} epoxidized polybutadiene rubber has been found to be an effective modifier for epoxy system. Carboxyl-terminated polybutadiene (CTPB) has also been studied as an effective toughening agent for epoxy matrix.¹⁷ Among the liquid rubbers, carboxyl-terminated copolymer of acrylonitrile and butadiene (CTBN) has been largely used as a modifier for epoxy resin. Most of the works in the literature that are dedicated to toughening of epoxy network have been related to characterization in terms of different parameters, such as morphology, cure kinetics, mechanical properties, particle size

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distribution, interparticle distance, matrix to particle adhesion, etc. that defines the structure–property relationship of toughened epoxies.^{18–22}

Previous studies by the authors^{21–23} have revealed the versatile behavior of the liquid rubbers, CTBN, and HTPB, in toughening the epoxy matrix. Being a polar rubber, contributed by the acrylonitrile content, CTBN is miscible with epoxy resin, and the phase separated cure network was found to show enhanced mechanical properties. From DMA studies it was revealed that the phase separated rubber domains are not pure, but contain some dissolved epoxy. On the other hand, HTPB is immiscible with epoxy. However, being a reactive hardener, the anhydride reacts with the rubber to a certain extent, which in turn reacts with the epoxy, thus extending the dimension of the rubber-hardener-epoxy matrix. DMA studies revealed only a slight shift in the T_g values, which has been explained as due to the lowering in crosslinking density, attributed to the occupation of rubber particles in between the reactive sites of the resin.

Literature survey revealed a number of versatile methods to determine physical properties of polymer blends and composites. In a study by Sabzi et al.²⁴ physical properties of polymer mixtures and blends were studied by predicting an analytical equation of state. The study was based on surface tension and liquid state density at room temperature as two parameters that were correlated and predicted the behavior of polymer solutions and blends. The thermomechanical properties of aqueous solutions-cast films of chitosan (C), starch–chitosan (SC), and pullulan–chitosan (PC) blends were examined by dynamic mechanical thermal analysis (DMTA) and large deformation tensile testing.²⁵ Calorimetric methods have also been reported to study the optical and thermophysical properties of polymer dispersed liquid crystals (PDLC).²⁶ Thermophysical properties, such as thermal conductivity and thermal diffusivity and specific heat of polyester/natural fiber (banana/sisal) composites were investigated as a function of fiber concentration and for several fiber surface treatments.²⁷ A number of analytical models have been proposed to predict thermal conductivity of short fiber composites.^{28–31}

The aim of this work is to study the physical properties of CTBN and HTPB toughened epoxy materials, and more specifically their thermophysical behavior. However, it is a problem to achieve a reasonable and reliable prediction of the properties of the blends based on the nature and the concentration of individual components. In a filler-modified composite material, most of the physical properties and more particularly thermal properties depend on factors, such as filler particles size, shape and dispersion, and filler–matrix interactions.^{24–26} Such fac-

tors are prevailing in rubber dispersed - epoxy matrices as well. With a view to investigate the influence of particle size, shape, and distribution of the dispersed phase on the thermophysical properties, the morphological parameters of blends have been quantified. Determination of thermal conductivity and diffusivity of materials is necessary in the processing stage and in applications.

In this article, the thermophysical properties of CTBN and HTPB dispersed rubber particles filled epoxy systems are characterized for several concentrations. The thermal conductivity values are compared to models based on electrical analogy. Such thermophysical studies on rubber toughened epoxy systems are not yet widely understood. Therefore the present analysis becomes very important and novel.

EXPERIMENTAL

Materials

The epoxy resin used was a diglycidyl ether of bisphenol-A (DGEBA, Gy-250) with an epoxy equivalent value of 5.3 eq.kg⁻¹. The curative was an anhydride, nadic methyl anhydride, under the trade name (Hy-906). A tertiary amine, *N,N*-dimethyl benzylamine (Dy-062) was used as an accelerator. The liquid rubbers used were of two types: carboxyl-terminated butadiene-*co*-acrylonitrile (CTBN) under the trade name Hycar 1300*8 and HTPB. All the chemicals, except HTPB, were kindly supplied by Huntsmann and were used as received without purification. The rubber, HTPB, was supplied by Vikram Sarabhai Space Center, Thiruvananthapuram, India. Figure 1(a–e) show structures of the materials used in the study. The characteristics of CTBN and HTPB liquid rubbers are reported in Tables I and II.

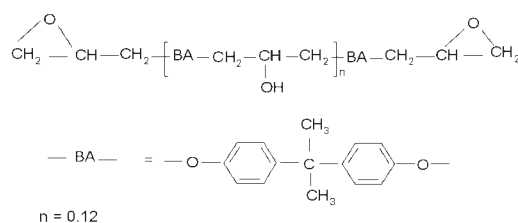
Preparation of samples

Solutions of various CTBN and HTPB concentrations in the epoxy resin were prepared using a mechanical stirrer at room temperature. Stoichiometric amount of anhydride was added followed by the tertiary amine accelerator. Small amounts of samples taken from freshly prepared blends were used for DSC analysis. For thermophysical measurements and SEM investigations, blend samples were prepared by pouring the mixture into a preheated silicone mold. It was then precured for 30 min at 120°C and then post cured for 2 h at 200°C.

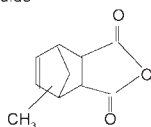
Phase-morphology studies

Fractured surfaces of the samples were examined at various magnifications by using JEOL JSM 5800

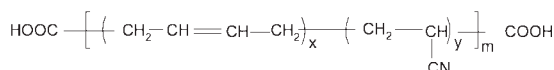
(a) epoxy resin



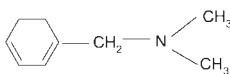
(b) nadic methyl anhydride



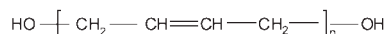
(c) CTBN



(d) N,N-dimethyl benzylamine



(e) Hydroxyl-terminated poly butadiene (HTPB)

**Figure 1** (a–e) Structure of components.

model scanning electron microscope (SEM) to analyze the rubber domains dispersed in the matrix. The samples were fractured under liquid nitrogen, and the dispersed rubber phase was extracted using toluene for 10 h at ambient temperature. The dried samples were sputter-coated with gold before SEM examination to provide a conductive surface. Several micrographs were analyzed for each sample.

Density measurements

A density balance was used to know the volume fraction of the blend plates studied for the thermal conductivity and diffusivity measurements. Measurements were achieved for square plate samples with a Mettler–Toledo AT61 delta range balance. According to Archimedes' principle, a body

TABLE I
Characteristics of CTBN

Properties ^a CTBN	(1300*8)
Molecular weight, M_n (g mol ⁻¹)	3500
Acrylonitrile content (wt %)	18
Viscosity, Brookfield, cp (300 K)	570
Specific gravity	0.96
Solubility parameter, δ (cal/cm ³) ^{1/2}	9.14
T_g^b (K)	215

^a Material and data supplied by Huntsman Co.

^b Glass transition temperature determined by DSC.

TABLE II
Characteristics of HTPB

Properties ^a HTPB	
Molecular weight (VPO) g mol ⁻¹	2710
Hydroxyl value (mg KOH g ⁻¹)	42.40
Acid Value (mg KOH g ⁻¹)	0.30
Viscosity at 30°C, Brookfield (CP)	6160
Specific gravity	0.96
T_g^b (K)	215
Thermal conductivity (Wm ⁻¹ K ⁻¹) ^{31,32}	0.22

^a Data provided by manufacturer.

^b Glass transition temperature determined by DSC.

immersed in a liquid receives a pressure equal to the displaced liquid. Therefore, by knowing the density of the liquid, it is simple to calculate the volume of the sample and its specific mass.

Thermal conductivity and diffusivity measurements

A periodical method developed by Boudenne et al.³⁴ was used to estimate simultaneously thermophysical values of polymer composite materials at room temperature. This method is based on the use of a small temperature modulation in a parallelepiped-shape sample (44 mm of side and 4 mm of thickness) and allows obtaining the thermal conductivity and diffusivity parameters in only one measurement with their corresponding statistical confidence bounds. The blend sample was fixed between two metallic plates. The front side of the first metallic plate was heated periodically and the temperature was measured on both two metallic plates using thermocouples. The sample temperature during experiments was equal to $25 \pm 5^\circ\text{C}$. The thermophysical parameters of the blend were identified iteratively by comparison of the experimental and theoretical heat transfer functions using the Levenberg–Marquardt method.^{34,35}

Specific heat measurements

In this study, two different ways were used for the characterization of the specific heat. First, calorimetric measurements were performed with a Perkin Elmer Pyris DSC 6 differential scanning calorimeter. The instrument was calibrated with indium and dry cyclohexane standards. Specific heat capacity, C_p , measured using DSC is obtained using the expression:

$$C_p = \frac{(dH/dt)}{mq_H} \quad (1)$$

where dH/dt is the heat flow rate as a function of temperature, m is the mass of the sample and q_H is the temperature scanning rate. Errors due to the

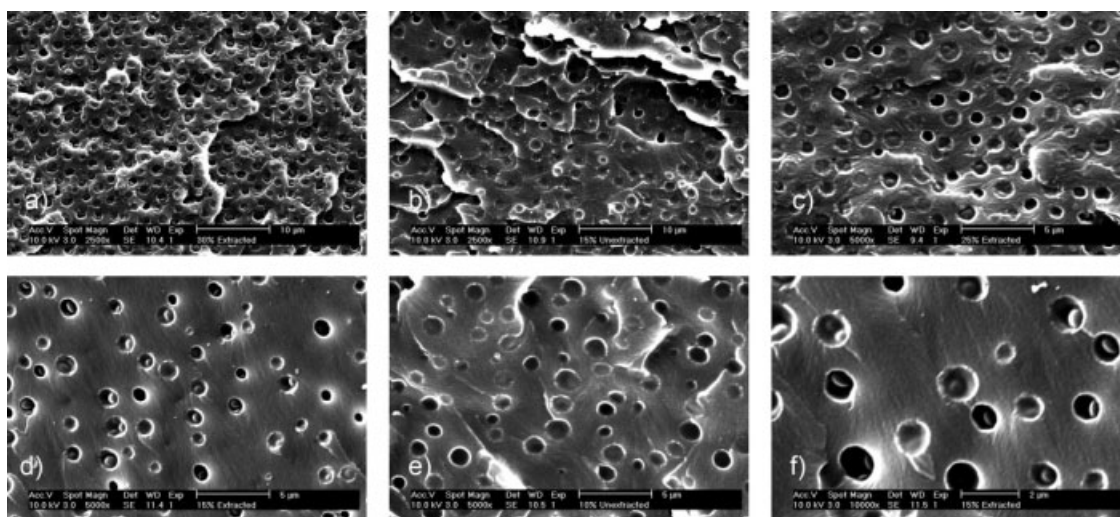


Figure 2 SEM micrographs of CTBN-modified epoxy network: (a) 5 phr, (b) 10 phr, (c) 15 phr, (d) 20 phr, (e) 25 phr, and (f) 30 phr of CTBN.

drift of the signal were adjusted using a standard sapphire disk of known heat capacity, studied in the same experimental conditions and at all temperatures. The sample and the sapphire weights are approximately 14 and 28 mg, respectively. The heating rate q_H was fixed to $10^\circ\text{C}/\text{min}$. The temperature range of measurement is between -50 and 200°C .

Secondly, the specific heat capacity (C_p) values were determined using the density (ρ), thermal conductivity (k), and diffusivity (a) values:

$$C_p = \frac{k}{\rho a} \quad (2)$$

RESULTS AND DISCUSSION

Morphological analysis

Figures 2(a–f) and 3(a–d) show typical SEM micrographs of each formulation of CTBN and HTPB-modified epoxies. Considering more than 500 domains from a large number of SEM samples, it is observed that spherical rubber domains are uniformly distributed in the epoxy matrix. Dimensions of the dispersed phases were analyzed by image analyzer. The number-average diameter (\overline{D}_n), weight-average diameter (\overline{D}_w), and volume-average diameter (\overline{D}_v) diameters were calculated from the following relationship.²¹

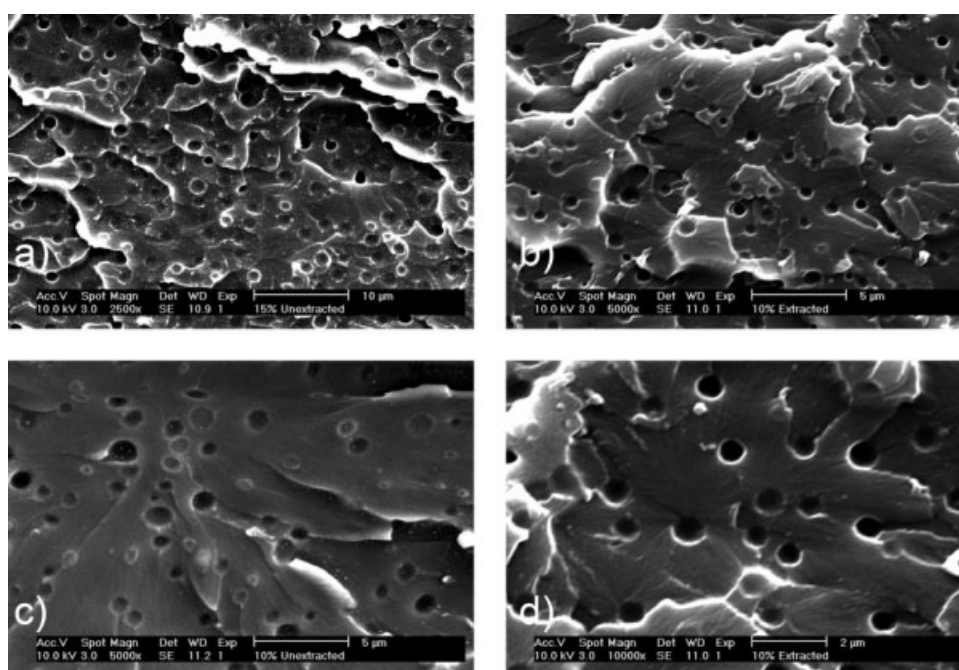


Figure 3 SEM micrographs of HTPB-modified epoxy network: (a) 5 phr, (b) 10 phr, (c) 15 phr, (d) 20 phr of HTPB.

$$\overline{D}_n = \frac{\sum n_i D_i}{\sum n_i} \quad (3)$$

$$\overline{D}_w = \frac{\sum n_i D_i^2}{\sum n_i D_i} \quad (4)$$

$$\overline{D}_v = \frac{\sum n_i D_i^4}{\sum n_i D_i^3} \quad (5)$$

where n_i is number of particles within the diameter range i .

The volume fraction of dispersed phase (V_D) may be calculated as:

$$V_D = \frac{\pi}{4} \left(\frac{\sum n_i D_i^2}{A_\tau} \right) \quad (6)$$

where A_τ is the area of micrographs region under analysis. The isotropic property of volume fraction is assumed by the earlier equation. Hence, the values measured in the micrograph plane are the same as those in the real volume. The volume fraction is regarded as an effective value because it is measured in the plane of crack propagation. As expected the volume fraction of the dispersed phase increased with elastomer concentration. The micrographs have been quantified based on above equations and the distributions of morphological parameters are given in Table III. The values are found to increase with an increasing amount of rubber content. Initially, CTBN is miscible in the epoxy resin. During the cure polymerization reaction of the rubber-epoxy blends, the molecular weight of the epoxy system increases and as a consequence, the rubber phase separates from the epoxy matrix. The elastomer phase forms domains of different sizes. We have observed from DMTA presented in another study that the phase separated rubber domains and the epoxy matrix after curing, are not pure rubber and epoxy, instead, they contain some dissolved epoxy and CTBN, respectively.²² It was observed that the addition of liquid rubber lowered the T_g of the cured network; however, this became more significant when the weight percentage of CTBN was higher. This is due to the incorporation of the low modulus liquid rubber phase in to the epoxy matrix where it

acts as a flexibilizer. The CTBN addition resulted in a slight change in the β -transition temperature. As the weight content of rubber increased, the T_g transition of the rubber phase moved slightly towards high temperature region. This shows that the rubber domains have epoxy dissolved within the system in a molecular scale. Similarly, the continuous epoxy phase has dissolved rubber phase miscible in a molecular scale. The increase in the morphological domain parameters with rubber content is attributed to the coalescence of particles, which is more prominent in higher rubber-modified epoxies. Of course, viscosity and elasticity ratio of the components are the deciding factors of the extent of segregation. The volume fraction, V_D , measures the compatibility of rubber with epoxy. The sub-micron sizes of the phase separated rubber particles in Figure 2(a,b) shall be due to the higher solubility of CTBN in epoxy at a low level concentration. The CTBN elastomer has a large level of polar acrylonitrile units, thus acquiring a higher degree of cure before phase separation of rubber occurs. Accordingly, this results in the formation of smaller particles because at higher degrees of curing the viscosity of the epoxy phase is higher, which would reduce the easiness of CTBN diffusion and of particle coalescence. Presumably the volume fraction of the dispersed rubber domains in the modified epoxy network is low. But, as the concentration of the rubber content in the system increases, the cure reaction becomes delayed, principally due to dilution and viscosity factors, which results in the segregation of small rubber particles leading to the formation of bigger domains. This state of affairs is depicted in Figure 2(c,d). Addition of still higher weight percentage of rubber leads to increase domains size depicted by Figure 2(e,f). Also one can notice a tendency of shift in the morphology from dispersed to a continuous nature at 25 and 30 phr elastomer modified epoxies. It is important to note that the rubber is not fully continuous in nature. One can see both dispersed and continuous rubber particles. Of course continuous rubber phase morphology is expected in higher concentration of rubber-modified epoxies and is reported in our earlier studies.²¹

TABLE III
Dispersed Particle Size of CTBN/HTPB-Modified Epoxy Network

Composition (phr)	CTBN			HTPB		
	\overline{D}_n (μm)	\overline{D}_v (μm)	\overline{D}_w (μm)	\overline{D}_n (μm)	\overline{D}_v (μm)	\overline{D}_w (μm)
5	0.81	1.28	0.87	0.85	1.31	0.91
10	0.82	1.39	0.92	0.87	1.47	0.96
15	0.86	1.46	0.94	0.90	1.54	1.06
20	0.88	1.65	0.97	0.94	1.67	1.11
25	0.92	1.60	1.00	—	—	—
30	0.95	1.71	1.20	—	—	—

TABLE IV
Percentage of Extracted Elastomer Phase

Weight percentage of rubber in the sample/sample code	Percentage of rubber phase extracted
5 CTBN	36
10 CTBN	41
15 CTBN	45
20 CTBN	50
25 CTBN	56
30 CTBN	63
5 HTPB	50
10 HTPB	63
15 HTPB	72
20 HTPB	78

To establish the tendency of attaining the co-continuous morphology in higher rubber-modified epoxies, extraction of the rubber phase has been done from the blends. The SEM photographs, due to some artifacts, will not always show clearly the morphological shift from particulate to continuous nature and hence the extraction results are more significant. Therefore complementary techniques like selective quantitative extraction of one of the phases and diffusion studies are often used to probe the cocontinuity. In this study, we rely upon the extraction results to determine the cocontinuity behavior. The result of the extraction in toluene for 24 h is provided in Table IV. The percentage of extracted CTBN and HTPB phases in high rubber-modified epoxies is around 60 and 75, respectively. Also, the percentage of extracted elastomer phase was found to be increased with rubber content. This is a signature of co-continuous tendency. Extraction of HTPB has been found to be higher than CTBN from samples containing the same weight percentage of elastomer, this shall be attributed to the lower polar character of HTPB and hence lesser interaction with the resin.

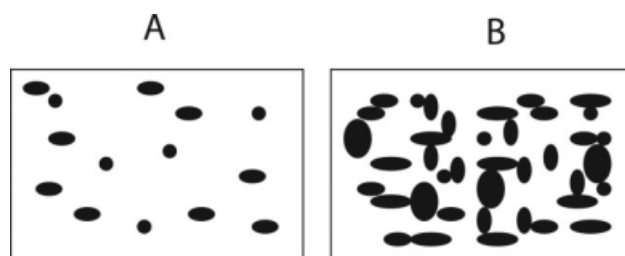
A schematic representation of the tendency towards co-continuous morphology is depicted in the Scheme 1. In a cured blend of epoxy/liquid rubber, having a lower concentration of elastomeric particles, the phase separated domains are dispersed in the matrix, and this state of cure is represented in the Scheme 1(A). However, the phase separated domain behavior in a cured blend with the incorporation of higher weight percentage of elastomer is different. At higher concentration of rubber, generally, there will be an increase in particle size and number. The phase separated particles come closer during cure and shows a tendency to form co-continuous morphology.

Unlike CTBN, HTPB is initially immiscible in the resin and hence the distribution of rubber domains,

even at lower concentrations (say, 5 and 10 phr) results in a slightly higher size of dispersed domains in comparison to that of CTBN. This is mostly due to the nonpolar character of HTPB, which makes it different from CTBN. In CTBN the acrylonitrile content induce polar characteristics, which helps it soluble in epoxy resin. Figure 3(a,b) represent SEM micrographs of 5 and 10 phr HTPB-modified epoxies, where the dispersed domains are smaller than the ones of 15 and 20 wt % of rubber samples, depicted in Figure 3(c,d). The inclusions of higher weight percentage of elastomer, surely leads to the agglomeration of smaller particles. As HTPB is almost insoluble in the epoxy resin co-continuous nature of morphology will be evolved by a lesser amount of rubber inclusion as compared to CTBN elastomer. When the rubber content is 20 phr the rubber particles are close to another and one can notice a tendency to form a continuous phase. As the elastomer is insoluble in epoxy, it seems difficult to get good samples of modified epoxies having HTPB greater than 20 wt %.

Thermal conductivity

All the following results are presented as a function of volume fraction because conventionally the models of prediction of the effective thermal conductivity for two-phase systems are depending on both component volume fractions. The thermal conductivity was measured for both neat and modified epoxies (blends) with various volume contents of CTBN and HTPB. The values of thermal conductivity and corresponding uncertainties are shown in Figure 4. We notice a small increase of thermal conductivity as a function of the volume fraction of CTBN and HTPB. The results show that the modification of rubbers with epoxy improves slightly the heat transport of the blend. These results are foreseeable; in fact for the Epoxy/HTPB case, the ratio between the thermal



Scheme 1 Schematic representation of the development of co-continuous morphology. (A) represents the phase separated rubber domains dispersed in the epoxy matrix at lower weight percentage of the rubber. The particles are well separated. (B) represents the morphological development at higher concentration of the elastomer. Particles are closer and tend to form a co-continuous behavior.

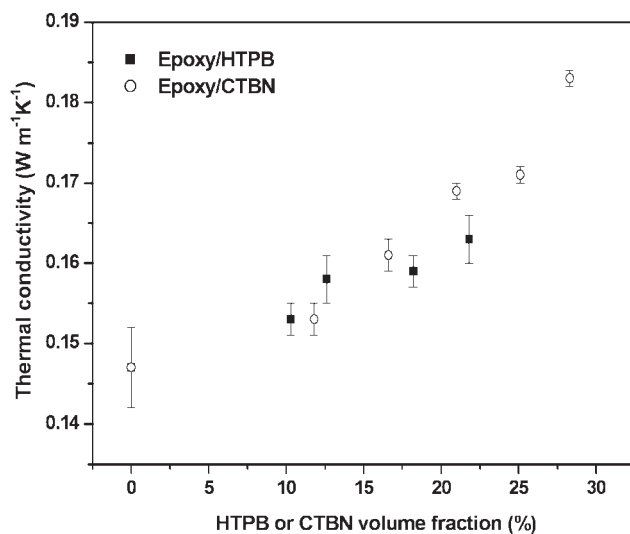


Figure 4 Thermal conductivity of blends as a function of CTBN and HTPB volume fraction.

conductivity of the HTPB rubber ($k = 0.22 \text{ Wm}^{-1}\text{K}^{-1}$)³² and pure matrix ($k = 0.147 \text{ Wm}^{-1}\text{K}^{-1}$) is lower than 1.5. The increase in thermal conductivity of blends as a function of the volume fraction of rubber can be attributed to the partial replacement of the matrix resin by the more conductive (polar) liquid rubbers that favor the energy (heat) dissipation mechanism.

In the case of CTBN-modified epoxy blends, the thermal conductivity values show significant increase from 25 vol % of rubber inclusion where the rubber phase has a tendency towards forming a continuous phase. This is quite understandable because of the polar character of the liquid rubber, which enable to enhance the conductivity nature. We have observed a 28% increase in thermal conductivity for 30 wt % of CTBN inclusion as compared to neat epoxy sample. This is a reasonable increase at the region of cocontinuity when compared to the value at low liquid rubber content. HTPB-modified blends also show a noticeable increase of almost 20% in thermal conductivity values, at the junction where the rubber phase has a tendency to become a continuous phase. Studies on transport behaviors of the polymer blends and composites and its dependence on the nature of morphological evolution are widely discussed and studied. Previous studies of various research groups have already reported that morphological structures are crucial for enhancing charge carrier mobility in organic materials.³³ An overview of these studies are worth mentioning here. Stephen et al.³⁶ have established transport properties of nano-structured layered silicates reinforced natural fiber and carboxylated styrene butadiene rubber and their blends, and were able to explain the behavior based on morphol-

ogy. Transport properties of polymers are strongly dependent on crosslinking nature of the morphology. In Mathai et al.³⁷ study, transport behavior of an organic solvent in a 50/50 blend of nitrile rubber/natural rubber has been analyzed. The developed co-continuous morphology was proved to be responsible for the diffusion process. A study based on the ionic conductivity in a polymer blend composed of poly(vinyl chloride)/poly(methylmethacrylate) (PMMA), plasticized with ethylene carbonate and propylene carbonate is reported.³⁸ The analyses establish that the specific phase separated morphology of the plasticizer rich phase provides a pathway for the ionic conduction. In an interesting study³⁹ on solid polymer electrolyte films consisting of poly(vinyl chloride) (PVC) and poly(vinylidene fluoride) (PVdF), LiBF_4 have been prepared and showed that the phase separated morphology and increase in porosity account for increase in conductivity. Morphology and transport properties are correlated in a particular study⁴⁰ on hollow fiber (HF) membranes prepared from a modified poly(ether etherketone) (PEEKWC). The transport properties are explained as due to the generated macro porous as a result of local phase separation phenomenon.

Thermal diffusivity

The variation of thermal diffusivity transport coefficient (α) as a function of HTPB or CTBN volume fraction is presented in Figure 5. We also noted a raise of the composite thermal diffusivity by increasing the HTPB and CTBN content. This is attributed to the occupancy of more polar elastomeric phase in the epoxy phase. The isolated increase in thermal diffusivity for 20 phr CTBN-epoxy blend may be considered as due to experimental error. Besides, we

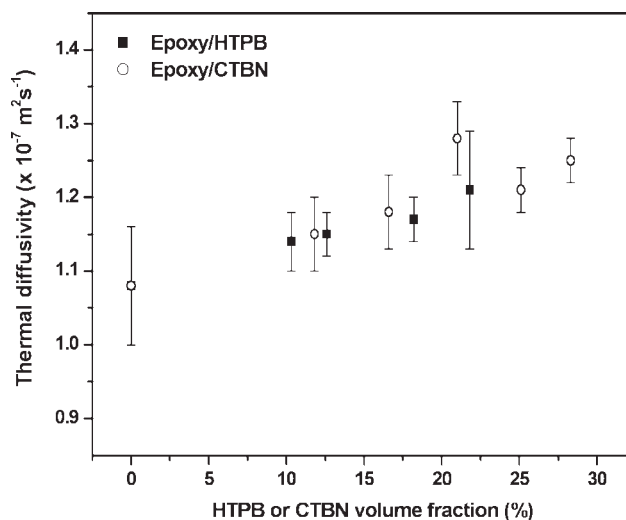


Figure 5 Thermal diffusivity of blends as a function of CTBN and HTPB volume fraction.

TABLE V
Specific Heat and Density Values of Modified Epoxies

Sample	phr of liquid rubber in composite	ρ (g cm ⁻³)	$\Delta \rho$ (g cm ⁻³)	C_p (J kg ⁻¹ K ⁻¹)	ΔC_p (J kg ⁻¹ K ⁻¹)
Epoxy	0	1.21	0.002	1128	150
HTPB5	5	1.26	0.002	1096	80
HTPB10	10	1.25	0.001	1130	73
HTPB15	15	1.26	0.001	1117	64
HTPB20	20	1.16	0.002	1141	157
CTBN10	10	1.20	0.002	1056	96
CTBN15	15	1.22	0.001	1090	96
CTBN20	20	1.21	0.001	1051	83
CTBN25	25	1.22	0.001	1216	62
CTBN30	30	1.18	0.002	1224	60

noticed that the relative thermal diffusivity uncertainties are more significant than the ones noted for the thermal conductivity. Unlike thermal conductivity, thermal diffusivity results did not show a direct relationship with morphology.

Specific heat and density

As described previously, the computation of C_p values requires the knowledge of samples densities. We noticed that the density of the blends remained almost the same. An insignificantly slight decrease is noted for 25 phr CTBN-modified epoxy and for 20 phr HTPB-modified epoxy. This decrease can be probably attributed to a less controlled preparation of this sample and more precisely to the presence of air in the blend. The specific heat values obtained from thermal conductivity and diffusivity measurement values and the density calculated from eq. (2) are reported in Table V. To check the validity of the

measurements; the specific heat was also measured using DSC. Figures 6 and 7 compare the specific heat values estimated from thermal property and DSC measurements for both the liquid rubbers (CTBN & HTPB) modified epoxies with the corresponding uncertainties in the measurement. A good agreement is noted at lower concentration of both liquid rubbers while a slight deviation is observed at higher concentration.

Thermal conductivity models

A deeper understanding of thermal transport in polymer blends and polymer composite materials requires modeling approach by considering the influence of various parameters (interaction between the components, filler orientation, and geometry). In fact, several theoretical and experimental models have been proposed to predict the effective thermal conductivity of composite materials.^{30,41,42} The

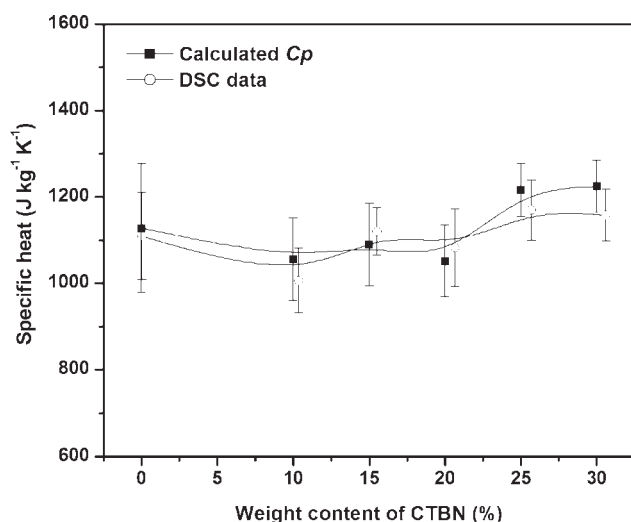


Figure 6 Specific heat capacity of blends as a function of weight content of CTBN.

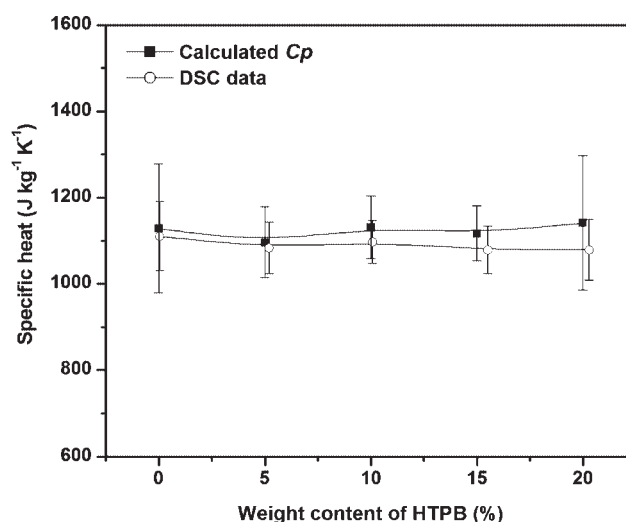


Figure 7 Specific heat capacity versus weight content of HTPB.

simplest alternative would be the use of upper or lower bounds of effective thermal conductivity, which are defined when materials are arranged in either parallel or series with respect to the heat flow. The lower bounds are often useful for the estimation of composite thermal conductivity, especially for low filler concentrations and when the ratio between the thermal conductivity of filler and matrix is lower than 10.⁴¹

The parallel conduction model is described by:

$$k_c = k_f \phi_f + k_m \phi_m \quad (7)$$

and series conduction model by:

$$\frac{1}{k_c} = \frac{\phi_f}{k_f} + \frac{\phi_m}{k_m} \quad (8)$$

where k_c , k_m , and k_f are thermal conductivities of composite, matrix, and filler, respectively and ϕ_f and ϕ_m are the volume fractions of filler and matrix.

The Hatta and Taya model takes into account the filler geometry, as well as the perturbation between the matrix and the filler.³⁰ This thermal conductivity model was developed with the analogy of the short fiber modulus at different orientation. The solution of the Hatta and Taya model^{30,42} for the spherical inclusion was given by:

$$\frac{k_c}{k_m} = 1 + \frac{\phi_f}{\frac{(1-\phi_f)}{3} + \left(\frac{k_m}{k_f - k_m} \right)} \quad (9)$$

Models were plotted (Fig. 8) using the thermal conductivity of HTPB and the measured value of the epoxy thermal conductivity. The series conduction model provides the lowest values of thermal con-

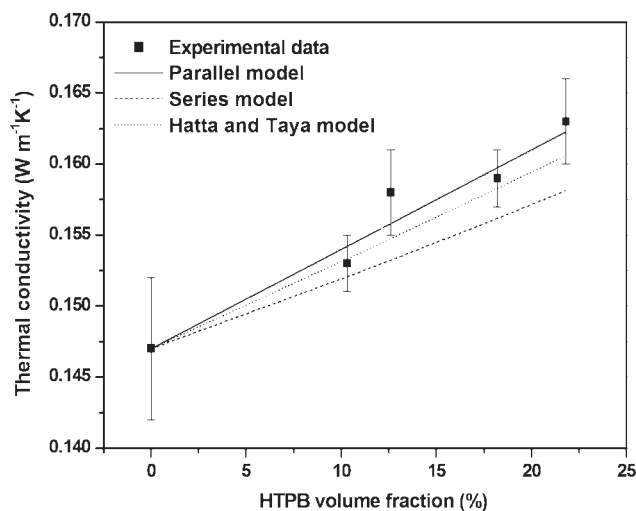


Figure 8 Theoretical and experimental thermal conductivity of epoxy/HTPB blends as a function of volume fraction.

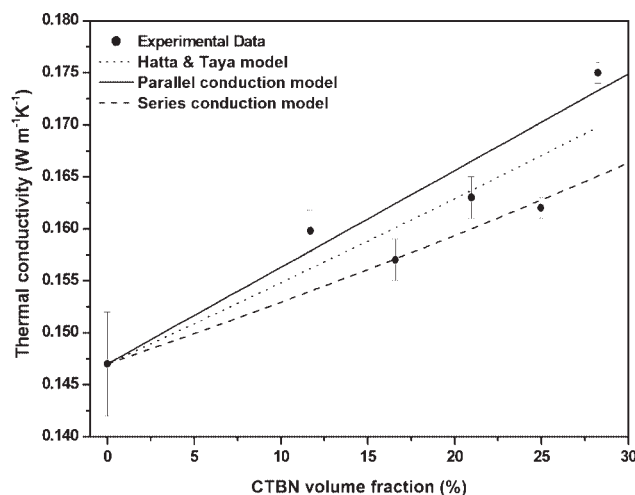


Figure 9 Theoretical and experimental thermal conductivity of epoxy/CTBN blends as a function of volume fraction.

ductivity, and a discrepancy with respect to experimental values is observed for the highest HTPB volume fractions. On the contrary, the computed values obtained from parallel conduction and Hatta and Taya models agree with experimental results. Thus, these models can be used to predict the thermal conductivity of HTPB/epoxy blends in this range of HTPB volume fraction.

To our knowledge, there is no value of thermal conductivity of CTBN available in literature. So, this value can be estimated using experimental data obtained for CTBN/epoxy blends and a thermal conductivity prediction model. Results presented in Figure 4 show that the increase of CTBN/epoxy thermal conductivity versus CTBN volume fraction is non linear. Thus, the Hatta and Taya model seems to be more suitable for the prediction of the thermal conductivity of CTBN/epoxy blends, as the parallel conduction model assumes a linear variation of the thermal conductivity upon volume fraction. So, the estimation of CTBN thermal conductivity was carried out using the Hatta and Taya model. The CTBN thermal conductivity value obtained using a least-square minimization procedure is: $k_{\text{CTBN}} = 0.240 \pm 0.022 \text{ W m}^{-1} \text{ K}^{-1}$. The comparison of experimental values of CTBN/epoxy blends to the Hatta and Taya model using the identified value of k_{CTBN} is presented in Figure 9. Moreover, we have plotted on the same figure, the predictions given by the parallel and series conduction models using the identified value of k_{CTBN} . A quite good agreement between experimental and theoretical data was obtained.

CONCLUSION

Epoxy resin blend systems with the incorporation of two liquid rubbers (CTBN/HTPB), were prepared

by varying the composition of liquid rubbers. The prime aim of this study was to estimate the thermophysical properties, such as thermal conductivity and diffusivity of these liquid rubbers toughened epoxies using a periodical method. The SEM observation was used to quantify the size and volume fraction of the dispersed liquid rubber domains in the epoxy matrix. A significant increase in thermal conductivity values were observed for CTBN systems from the region of cocontinuity. The same was observed for HTPB systems too, but not as prominent as the other case. This effect is relating to the greater polar character of CTBN, which favors the energy dissipation mechanism. The thermal diffusivity transport coefficient was also increased with the volume content of rubber. However, a direct relationship with morphology was not observed in both systems. The specific heat of the samples were estimated from density and thermophysical measurements and compared with the same obtained from dynamic DSC measurements. A good agreement was observed between the values obtained by both methods. Finally, thermal conductivity of CTBN was estimated ($k_{\text{CTBN}} = 0.24 \text{ Wm}^{-1} \text{ K}^{-1}$) with a relative uncertainty of lower than 10% using Hatta and Taya model by a least-square minimization procedure.

References

- May, C. A.; Tanka, G. Y. *Epoxy resin chemistry and technology*; Marcel Decker: New York, 1973.
- Francis, B.; Poel, G. V.; Posada, F.; Groeninckx, G.; Rao, V. L.; Ramaswamy, R.; Thomas, S. *Polymer* 2003, 44, 3687.
- Varley, R. J.; Hodgkin, J. H.; Simon, G. P. *Polymer* 2001, 42, 3847.
- Bonnet, A.; Lestriez, B.; Pascault, J. P.; Sautereau, H. *J Polym Sci Part B: Polym Phys* 2001, 39, 363.
- Iijima, T.; Fujimoto, K.; Tomoi, M. *J Appl Polym Sci* 2002, 84, 388.
- Shih, W. C.; Ma, C. C. M.; Yang, J. C.; Chen, H. D. *J Appl Polym Sci* 1999, 73, 2739.
- Riew, C. K. *Rubber Chem Technol* 1985, 58, 622.
- Lin, K.-F.; Shieh, Y.-D. *J Appl Polym Sci* 1998, 70, 2313.
- Kim, J. K.; Robertson, R. E. *J Mater Sci* 1992, 27, 161.
- Bascom, W. D.; Hunston, D. C. *Rubber Toughened Plastics*, *Advances in Chemistry Series*; American Chemical Society: Washington, DC, 1989; Vol. 222, p 193.
- Shaw, S. J. In *Chemistry and Technology of Epoxy Resins*; Ellis, B., Ed.; Blackie: Glasgow, 1993.
- Ohashi, K.; Hasegawa, K.; Fukuda, A.; Uede, K. *J Appl Polym Sci* 1992, 44, 419.
- Barcia, F. L.; Soares, B. G.; Gorelova, M.; Cid, J. A. *J Appl Polym Sci* 1999, 74, 1424.
- Bussi, P.; Ishida, H. *J Appl Polym Sci* 1994, 53, 441.
- Bussian, P.; Ishida, H. *Polymer* 1994, 35, 956.
- Latha, P. B.; Adhinarayanan, K.; Ramaswamy, R. *Int J Adhes Adhesives* 1994, 14, 57.
- Nigam, V.; Setua, D. K.; Mathur, G. N. *J Appl Polym Sci* 1998, 70, 537.
- Chen, D.; Pascault, J. P.; Sautereau, H. *Polym Int* 1993, 32, 361.
- Achary, P. S.; Gouri, C.; Ramaswamy, R. *J Appl Polym Sci* 1991, 42, 743.
- Achary, P. S.; Latha, P. B.; Ramaswamy, R. *J Appl Polym Sci* 1990, 41, 151.
- Thomas, R.; Abraham, J.; Thomas, S. P.; Thomas, S. *J Polym Sci Part B: Polym Phys* 2004, 42, 2531.
- Thomas, R.; Durix, S.; Sinturel, C.; Omonov, T.; Goossens, S.; Groeninckx, G.; Moldenaers, P.; Thomas, S. *Polymer* 2007, 48, 1695.
- Thomas, R.; Yumei, D.; Le, Y.; Moldenaers, P.; Weimin, Y.; Thomas, S. *Polymer* 2008, 49, 278.
- Sabzi, F.; Boushehi, A. *Eur Polym J* 2004, 40, 2689.
- Lazaridou, A.; Biliaderis, C. G. *Carbohydr Polym* 2002, 48, 179.
- Roussel, F.; Maschke, U.; Coqueret, X.; Buisine, J. M. *CR Acad Sci Paris 326, Serie* 1998, 11, 449.
- Idicula, M.; Boudenne, A.; Umadevi, L.; Ibos, L.; Candau, Y.; Thomas, S. *Compos Sci Technol* 2006, 66, 2719.
- Wills, J. R. *J Mech Phys Solids* 1977, 25, 185.
- Normura, S.; Chou, T. W. *J Compos Mater* 1980, 14, 120.
- Hatta, H.; Taya, M. *J Appl Phys* 1985, 58, 2478.
- Chen, C. H.; Wang, Y. C. *Mech Mater* 1966, 23, 217.
- Timnat, Y. M.; Korting, P. A. O. G. *Hybrid rocket motor experiments, LR-452*, TU-Delft: The Netherlands, February 1985.
- Bav, Z.; Dodabalapur, A.; Lovinger, A. *J Appl Phys Lett* 1996, 69, 4108.
- Boudenne, A.; Ibos, L.; Candau, Y. *Meas Sci Technol* 2006, 17, 1870.
- Moré, J. J. In *The Levenberg-Marquardt Algorithm: Implementation and Theory Numerical Analysis*; Watson, G. A., Ed.; *Lecture Notes in Mathematics*; Springer Verlag: Berlin, Germany, 1977; Vol. 630.
- Stephen, R.; Varghese, S.; Joseph, K.; Oommen, Z.; Thomas, S. *J Membr Sci* 2006, 282, 162.
- Mathai, A. E.; Singh, R. P.; Thomas, S. *J Membr Sci* 2002, 202, 35.
- Rhoo, H. J.; Kim, H. T.; Park, J. K.; Hwang, T. S. *Electrochim Acta* 1997, 42, 1571.
- Vickraman, P.; Ramamurthy, S. *Mater Lett* 2006, 60, 3431.
- Tasselli, F.; Jansen, J. C.; Sidari, F.; Drioli, E. *J Membr Sci* 2005, 255, 13.
- Godovsky, Y. K.; Privalko, V. P. *Advances in Polymer Science 119: Thermal and Electrical Conductivity of Polymer Materials*; Springer-Verlag: Heidelberg, 1995.
- Mottram, J. T.; Taylor, R. *Thermal Transport Properties, International Encyclopedia of Composites*; Lee, S. M., Ed.; VCH Publishers: New York, 1991; Vol. 5.