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Modification of dicyanate ester resin by liquid carboxyl-terminated butadiene acrylonitrile copolymer

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ABSTRACT

Bisphenol A dicyanate ester (BADCy) was modified with liquid carboxyl-terminated butadiene acrylonitrile (LCTBN). The cured BADCy resin was formed through the cyclotrimerization of cyanate functional groups into triazine rings, and there was the chemical reaction between BADCy and LCTBN. Mechanical performance indicated that the introduction of LCTBN into BADCy resin improved the impact strength with maintenance in flexural strength. Scanning electron microscopy (SEM) showed that the pure resin had a smooth glassy fracture surface, whereas cured blends containing LCTBN showed rougher fracture surfaces, and exhibited enhanced impact resistance. The TEM observation showed that the two phases in the cured resins exhibit a good interaction adhesion. Thermograms of BADCy modified with LCTBN showed the little reduction of heat deflection temperature, and a reduction in thermal stability temperature by 30 K. Dynamic mechanical analysis (DMA) showed that the pure BADCy had higher storage modulus (E') values than that of the BADCy modified with LCTBN, whereas the loss modulus (E'') was lower, and that the glass transition temperature (Tg) of modified BADCy was 229 °C and lower than that (249 °C) of pure BADCy resin.

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1. Introduction

Cyanate esters (CE) resins are readily converted into thermosetting polymers, which possess good dielectric, thermal and mechanical characteristics and low water absorption, excellent heat resistance, low volume shrinkage, rendering them the materials of choice in high performance applications [1,2]. They have extensive applications, including printed circuit boards, radomes, and the matrix resin in structural composites for aircraft and in high temperature encapsulation. After heating, the ester monomer undergoes self-cyclotrimerization to form a three-dimensional network structure of polycyanurate. However, like any other highly cross-linked thermosetting resins, CE formed polymer also tend to be brittle and need to be modified suitably to be able to serve mechanical or structural functions. Several methods [3–9] have been proposed to increase the toughness of polycyanurate. The most widely researched toughening approach in order to attain an enhancement in fracture toughness has been the incorporation of a high modulus and high glass transition temperature thermoplastic [4,9,10–16], and the modification mechanism and improved properties have been clearly understood now. Another attempt to address the toughness of the CE resin upon conversion to the network system, a synthetic method to incorporate variable length spacer groups between the reactive ends of the CE resin was envisioned, and satisfactory result was achieved, but this kind of approach was complicated and difficult to get widespread application [17]. The most novel approach is the addition of a suitable rubber to the uncured CE resin and then controlling the polymerization reactions in order to induce phase separation. Until now the related researches of polycyanurate modified with rubbers have not been widely carried out, so it is interesting to do some research in the field. The cured rubber-modified polycyanurate will exhibit a two-phase microstructure consisting of relatively small rubbery particles dispersed and bonded in a CE matrix. This microstructure results in a material that has a considerable higher toughness compared to the unmodified system and, since the matrix contains relatively little rubber, there is only a minimal modification to thermal properties.

The main objective of the present work was the development of hybrid composites of bisphenol A dicyanate ester (BADCy) modified with carboxyl-terminated butadiene acrylonitrile copolymer (LCTBN). A series of different composites were prepared: BADCy modified with LCTBN in proportions ranging of 0–16 parts per hundred parts of resin (phr). In a first step, the BADCy/LCTBN was investigated by in situ FTIR and DSC to illuminate the cur-

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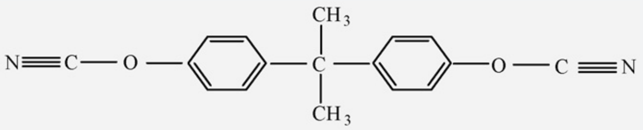
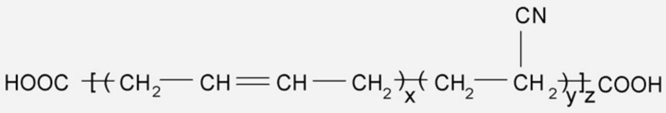
Table 1
The chemical structure of materials.

Materials	Chemical structure
BADCy	
LCTBN	 $\mathrm{HOOC}\,[(\mathrm{CH_2-CH=CH-CH_2})_x(\mathrm{CH_2-\overset{\overset{CN}{\vert}}{CH}_2})_y]_z\mathrm{COOH}$

ing reaction procedure. Then the properties of cured BADCy/LCTBN system were investigated using SEM, TEM, HDT, TGA and DMA, etc.

2. Experimental

2.1. Materials

A bisphenol A-based cyanate resin (BADCy) monomer was kindly supplied by Prof. Liang Guozheng of Northwestern Polytechnical University and used as received. Carboxyl-terminated butadiene acrylonitrile (LCTBN) with a molecular weight of 3000–4000 is used as the modifier, and was kindly supplied by LAN-Zhou Chemical medicine Co. The materials are listed in Table 1.

2.2. Preparation of samples

Appropriate quantities of BADCy and LCTBN were placed in a flask equipped with a mechanical stirrer and thermometer. The mixtures were heated to 80–90 °C and maintained at that temperature range with stirring till a clear brown homogeneous liquid was obtained. Each mixture was thoroughly degassed at 80 °C and poured into preheated (80 °C) metal mold, then cured using appropriate curing procedure.

2.3. Instruments

Gel time was measured on a temperature-controlled hot plate by standard knife method [6].

FTIR measurements were used to investigate the interaction between BADCy and LCTBN, and were performed with a WQF-310 spectrophotometer made in Beijing, China, using 64 scans with a 2 cm^{-1} resolution step. After the mixture of BADCy and LCTBN was cast on the surface of KBr slice, the KBr slice was then placed in an oven at a given temperature. In order to monitoring the cyanate ester curing, the vibration band of the –OCN chemical group, that appears as a double band (2270–2240 cm^{-1}), has been chosen.

Differential scanning calorimeter (DSC) thermograms were recorded with a USATAMDSC-2901 (USA), ranging from 20 to 300 °C, at a heating rate of 10 K min^{-1} under a nitrogen atmosphere. DSC analysis was used to confirm the curing procedure of BADCy/LCTBN systems.

A XCL-40 pendulum impact test machine was used to test the impact strength of cured resins according to GB2570-81Standard of China. A ZMF1250 equipment was used to test the flexural properties of cured resins according to GB2571-81 Standard of China. The data was the average of ten samples. The heat deflection temperature (HDT) was carried out as per ASTM D648-72 method.

Scanning electron microscopy (SEM), used to investigate the fracture surface of samples, was performed in AMRAYModel1000B (JAP) equipment with an accelerating voltage of 20 kV and a distance between 12 and 14 mm. Samples were sputter coated with a thin gold layer under vacuum situation. Transmission electron microscopy (TEM), used to analyses the phase separation, was performed in a HITACHI-600 equipment (JAP). The ultrathin sections of thickness about 70 nm were obtained with ultramicrotome (Ultracut N, Reichert-Nissei). The sections were stained by OsO_4 vapour for 10 min at room temperature.

Thermogravimetry (Tg) thermograms were recorded with SDT2960DTA-TGA, ranging from 25 to 800 °C, at a heating rate of 10 K min^{-1} under nitrogen atmosphere.

Dynamic mechanical analysis (DMA) was performed at a heating rate of 3 K min^{-1} using a DMAQ800 (USA). Rectangular samples with size of 350 mm × 100 mm × 4 mm were tested at a fixed frequency of 1 Hz between −100 and 300 °C.

3. Results and discussion

3.1. Curing process of BADCy resins

It is reported that polycyclotrimerization is the exclusive reaction in the neat aromatic dicyanate system and only one type of linkage (i.e., the sys-triazine ring) is formed during the whole course of the reaction with or without external catalysts [18,19]. Polycyclotrimerization of aromatic dicyanates proceeds via a combination of three functional groups to form a triazine ring, as illustrated in path of Scheme 1. After the addition of LCTBN into BADCy resins, the curing process must be greatly affected.

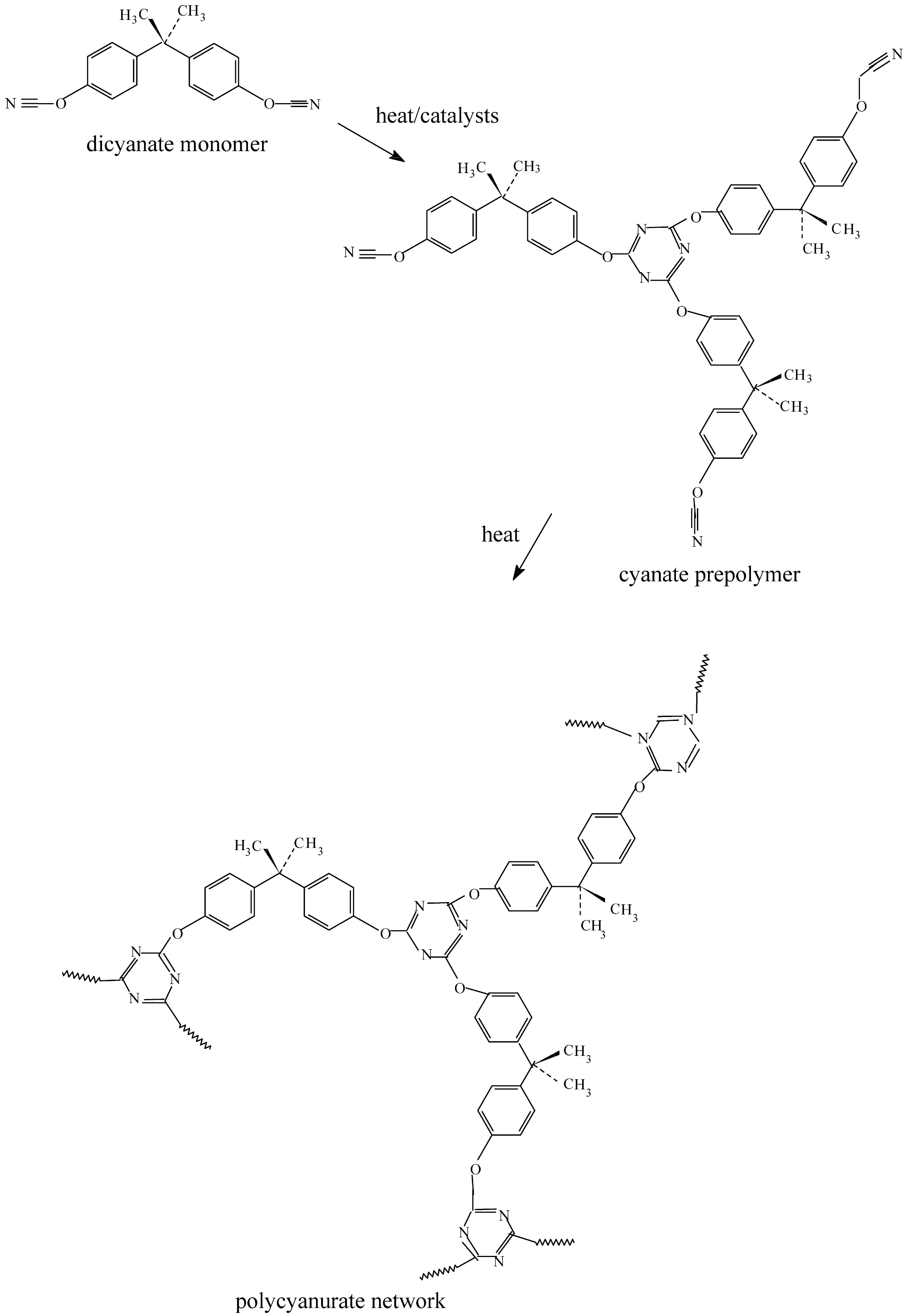
The effect of different content LCTBN on the gel time of BADCy resin was studied as shown in Fig. 1. LCTBN decreased the reactivity of BADCy resin, so at a given temperature, the gel time increased with the content of LCTBN increasing. But with the temperature increasing, the difference of gel time of BADCy resin systems decreased. When the temperature was fixed at 120 °C, the gel times of BADCY system of pure BADCy, BADCy/6 phrLCTBN, BADCy/10 phrLCTBN and BADCy/16 phrLCTBN were 38, 67, 87 and 106 min, respectively, but at 150 °C, the difference of gel time of BADCy/LCTBN system was less than 15 min. The reason of gel time with LCTBN content is that there is a simple dilution effect. Rates of chemical reactions increase with the concentration of reactants. Therefore if the –OCN content is reduced by adding a rubber, the rate of trimerization will fall and the gel time will increase.

The sketch of chemical reaction between the group of –NCO in BADCy resin and the group of –OH in LCTBN is shown in Scheme 2.

Series of FTIR spectra (Fig. 2) have been obtained to evidence the occurrence of any chemical interaction between BADCy resin and LCTBN. The comparative study of such spectra will be used to draw conclusions relating to the chemical linkages formed during the modification reaction. The main conclusion drawn is that a chemical linkage reaction between the BADCy and LCTBN led to the weak appearance of absorption carbamate peaks at 1540, 1250 and 769 cm^{-1}. It is not the dominant reaction shown in Scheme 1, but the reaction can bring out better consistency of interface and result in excellent mechanical performances.

To confirm the curing procedure and test the physical and chemical process of curing procedure, DSC analysis of pure BADCy and BADCy/10 phrLCTBN was studied, respectively, as shown in Fig. 3. The peaks in lower temperature about 70 °C were related to the endothermic process of melting of resin monomer; the exothermal peaks in high temperature about 170 °C should be a consequence of formation of triazine rings.

The detailed temperature data of formation of triazine rings were listed in Table 2, from which it is obvious that the peak temperature of BADCy modified by LCTBN was very little affected. So the introduction of LCTBN into BADCy has very little effect on the curing procedure.



Scheme 1. Pathway for the reaction of dicyanate ester.

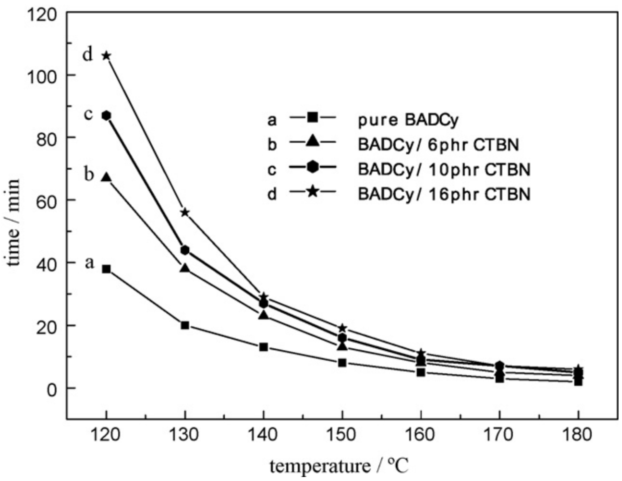


Fig. 1. The dependency of gel time on temperature.

Based on the above researches, the curing procedure of $120\,^{\circ}\mathrm{C}\,(2\,\mathrm{h})^{-1} + 150\,^{\circ}\mathrm{C}\,(2\,\mathrm{h})^{-1} + 180\,^{\circ}\mathrm{C}\,(2\,\mathrm{h})^{-1} + 200\,^{\circ}\mathrm{C}\,(2\,\mathrm{h})^{-1}$ was determined. After the curing procedure, the cured sample was demolded and post-cured in an air oven at 250 °C for 5 h. FTIR can be used to monitor the curing procedure of BADCy/LCTBN as follows.

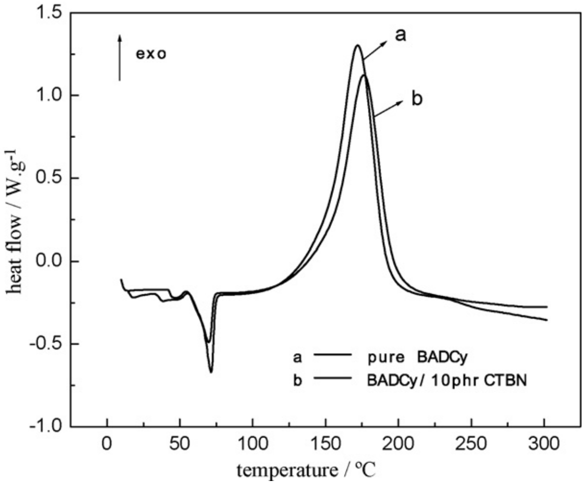
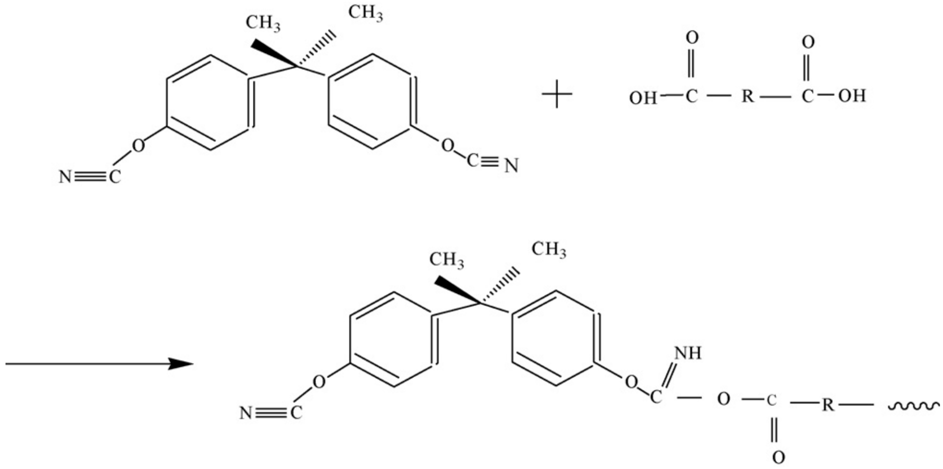


Fig. 3. DSC thermogram of (a) BCE and (b) BCE/10 phrLCTBN.

Fig. 4 shows the FTIR spectrum evolution at different curing temperature for the system of BADCy/10 phrLCTBN. It is observed a decrease in the area of the –OCN band at 2270–2240 cm^{-1} with curing time.



Scheme 2. Pathway of the reaction of dicyanate ester with LCTBN.

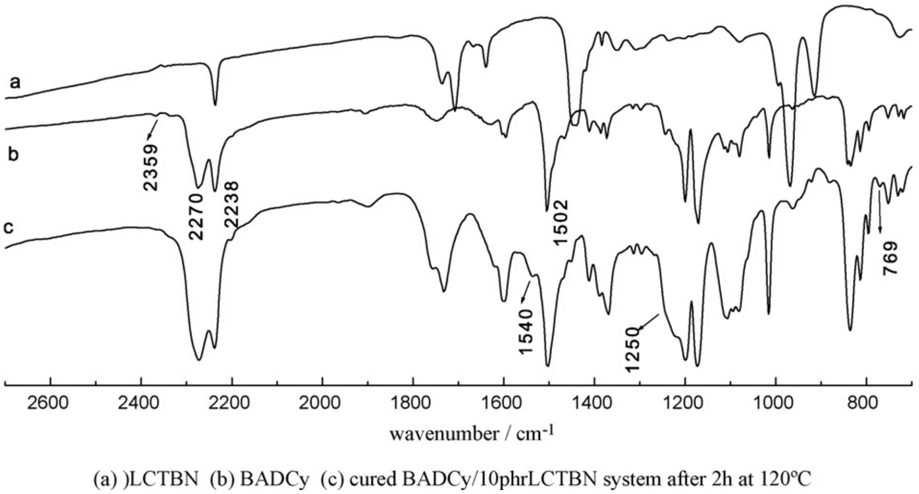


Fig. 2. FTIR spectra analysis of chemical reaction between BADCY and LCTBN: (a) LCTBN, (b) BADCy, (c) cured BADCy/10 phrLCTBN system after 2 h at 120 °C.

Table 2
Dynamic DSC data for pure BADCy and BADCy/10 phrLCTBN.

	Peak value of curing procedure		
	Onset temperature $T_i/^\circ$C	Peak temperature $T_p/^\circ$C	Offset temperature $T_f/^\circ$C
Pure BADCy	103.6	172.1	242.2
BADCy/10 phrLCTBN	94.0	176.5	259.2

When at 200 °C after 2 h, the –OCN band diminishes up to minimum (but does not disappear completely) denoting the existence of terminal cyanate groups in the cured material. The degree of OCN groups that have reacted, at a fixed temperature in a certain time, has been calculated from the peak areas, *A*, after testing their direct proportionality with the concentration. Then, the conversion of cyanate group, *a*, has been calculated according to

$$\alpha = 1 - \left[\frac{A(T,t)}{A(T,0)}\right] \quad (1)$$

where *A*(*T*,*t*) and *A*(*T*,0) are the areas of the cyanate peak at temperature *T* and times *t* = *t* and *t* = 0, respectively. In both cases, –OCN peak area was determined by subtracting the absorption of a reference sample without –OCN groups from the total absorption in the range 2270–2240 cm^{-1}. According to Eq. (1), the evolution of conversion versus curing time for different curing temperature was calculated. The conversion of cyanate group for four stage of curing procedure was 40.7%, 73.2%, 88.4% and 99.5%, respectively. So the used curing procedure for BADCy/LCTBN is completely appropriate and satisfying.

3.2. Properties of cured BADCy/LCTBN systems

After the modification with LCTBN, many properties of BADCy should be changed, so the investigation for modified BADCy systems is necessary. Firstly, the mechanical property was researched.

The observed values for impact and flexural properties of pure BADCy and BADCy systems modified with LCTBN are presented in Fig. 5. The introduction of 6, 10 and 16 phr of LCTBN into BADCy greatly increased the impact strength by 117%, 150% and 171%, respectively, when compared with the unmodified BADCy system. But for the flexural property, the values appeared little changed with LCTBN adding amount. In a word, LCTBN can significantly improve the mechanical properties of BADCy resin, and does not influence the static strength too much.

Correspondingly, the enhancement of toughness also can be reflected on the fracture surface morphology of samples and can be tested using Scanning electron microscope (SEM).

Scanning electron microscope (SEM) was used to investigate the fracture morphology of pure BADCy, BADCy/6 phrLCTBN and BADCy/10 phrLCTBN systems. SEM micrograph (Fig. 6(a)) of fracture surface of the unmodified BADCy system showed the smooth glassy fracture surface, which indicated the cured pure BADCy resin was fractured in an extreme fragile way. The morphology in Fig. 6(b) and (c) showed a steady increase in the surface roughness and the presence of conical marks, which absorbed much energy during the occurrence of impact fracture. So the phenomena explained reason of enhancement of impact strength for BADCy/LCTBN systems.

The larger magnification of SEM of the materials modified with LCTBN (Fig. 6(d) and (e)) can give us the morphology of fracture surface of modified systems. It is clear that these materials presented phase separation between BADCy and elastomer, while the CTBN particles are well dispersed in the BADCy matrix, which is benefit to improve impact resistance.

In order to understand the morphology of dispersion phase in the matrix, we use the transmission electron microscopy (TEM) to observe the detail of modified systems (in Fig. 7). The dark areas are the LCTBN phase whereas the white ones are cured BADCy phase. The particles of LCTBN elastomer of size between 0.8 and 0.9 μm are observed within the white BADCy continuous phase. In some particles, the BADCy resin is the dispersed phase whereas the LCTBN works as the local continuous matrix, and the interfacial layers between BADCy and LCTBN are not uniform. It can be seen that staining is most intense at the interface between rubber particles and matrix, and gradually becomes paler towards the centre of the LCTBN particles. The TEM observation presented here clearly reveals that a good interfacial adhesion exists between the BADCy and LCTBN phases because of the chemical reaction mentioned above. Such kind of particles can greatly increase the mechanical properties of cured BADCy resin system, as shown in Fig. 5. Morphology studies through TEM showed that the spherical LCTBN particles presented good interaction with the BADCy matrix. The dispersion of the particles of LCTBN in the BADCy matrix was satisfactory, since agglomerates of these particles were not observed in the micrographs.

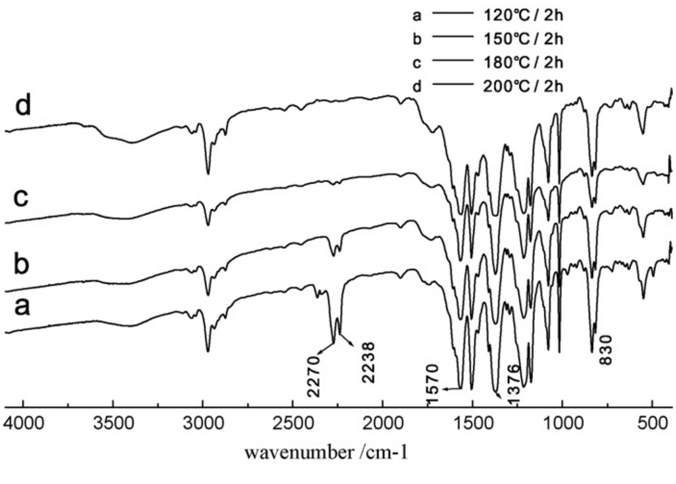


Fig. 4. FTIR analysis of different cured BADCY resin systems: (a) 120 °C (2 h)$^{-1}$; (b) 150 °C (2 h)$^{-1}$;(c) 180 °C (2 h)$^{-1}$; (d) 200 °C (2 h)$^{-1}$.

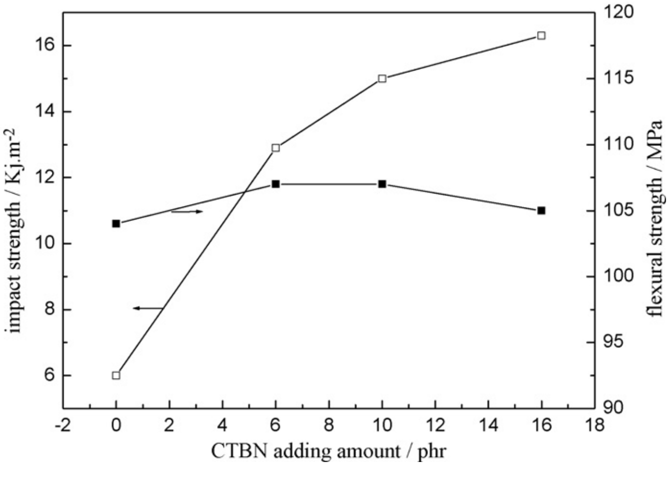
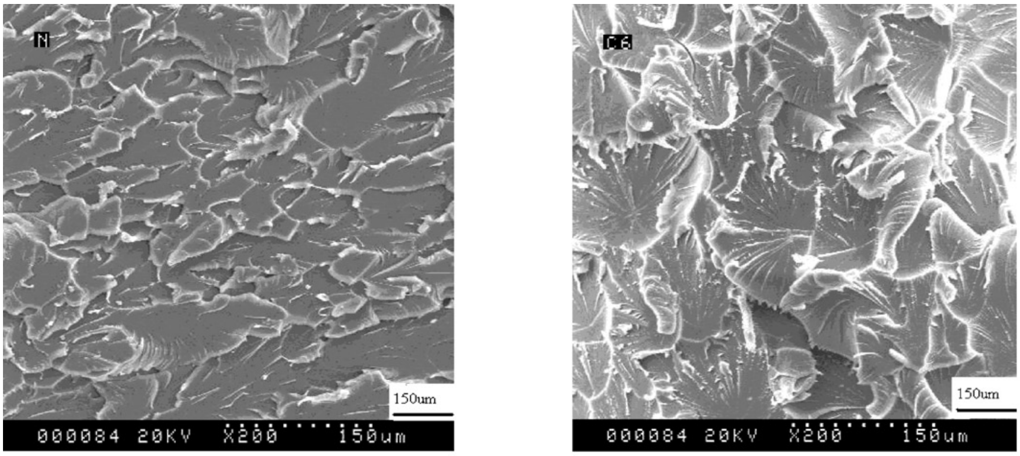
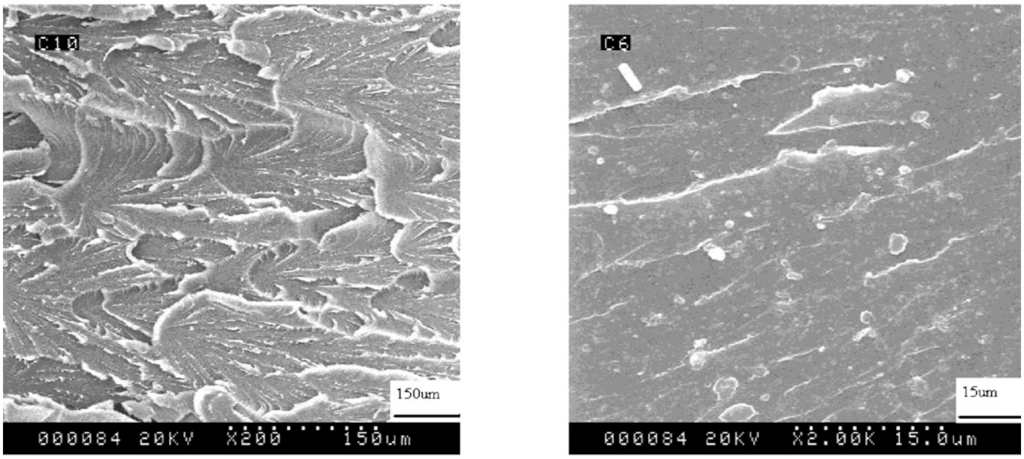


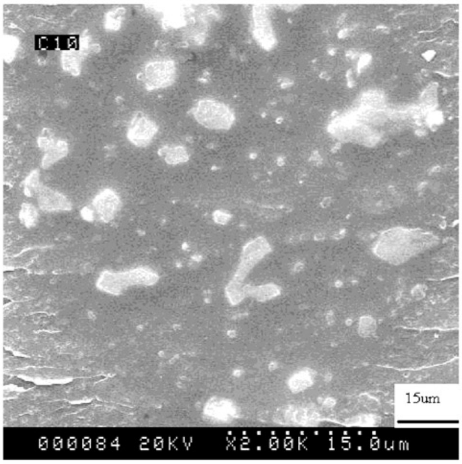
Fig. 5. The mechanical properties of cured BADCy.



(a) pure BADCY (b) BADCY/6phrLCTBN



(c) BADCY/10phrLCTBN (d) BADCY/6phrLCTBN



(e) BADCY/10phrLCTBN

Fig. 6. The SEM micrograph of fracture surface of cured BADCY resin: (a) pure BADCY, (b) BADCY/6 phrLCTBN, (c) BADCY/10 phrLCTBN, (d) BADCY/6 phrLCTBN and (e) BADCY/10 phrLCTBN.

HDT measurements are carried out to determine the thermomechanical behavior of matrix systems. HDT values for pure BADCy and BADCy systems modified with various content LCTBN are presented in Fig. 8. It is evident that HDT decreases with increasing LCTBN content, this must be attributed to the presence of liquid elastomer, but in the range of systems studied in paper, the decrease in HDT is within 10 °C.

Thermal stability of BADCy and its modified systems with various LCTBN contents can be evaluated by thermogravimetric analysis (TGA), as shown in Fig. 9. The decomposition temperature at 5% weight loss is decreased to 357 °C from 386 °C and is still higher than 350 °C, so in the range of LCTBN adding content studied in the research, the effect of LCTBN on the thermal stability is not serious.

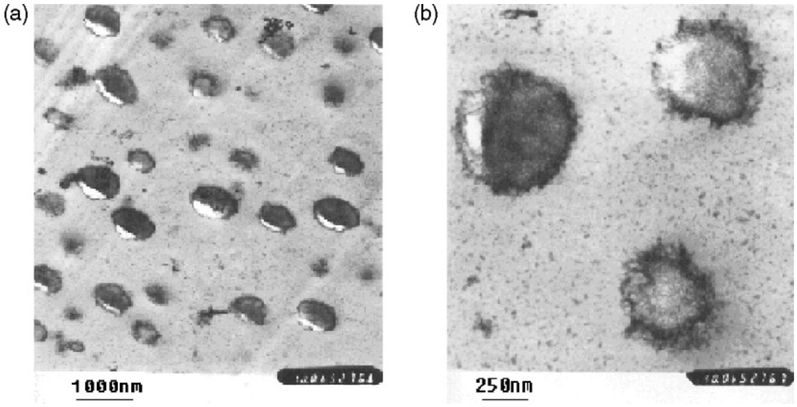


Fig. 7. The TEM micrograph of cured BADCY/10 phrLCTBN: (a) (×10k), (b) (×40k).

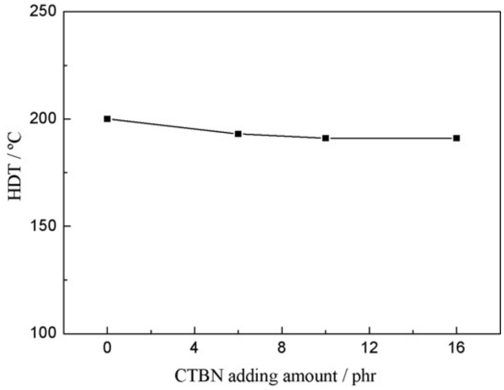


Fig. 8. The effect of LCTBN content on HDT.

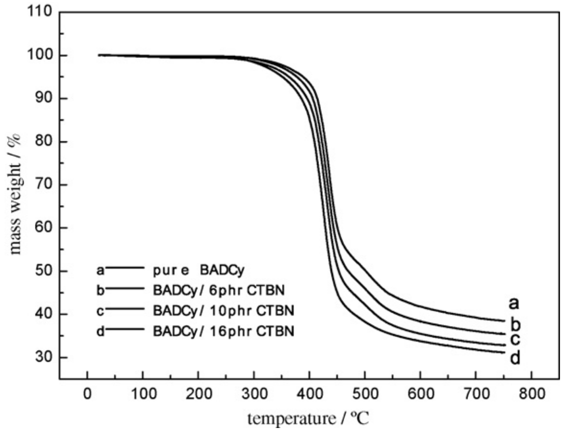


Fig. 9. TGA analysis of cured BADCY resin systems.

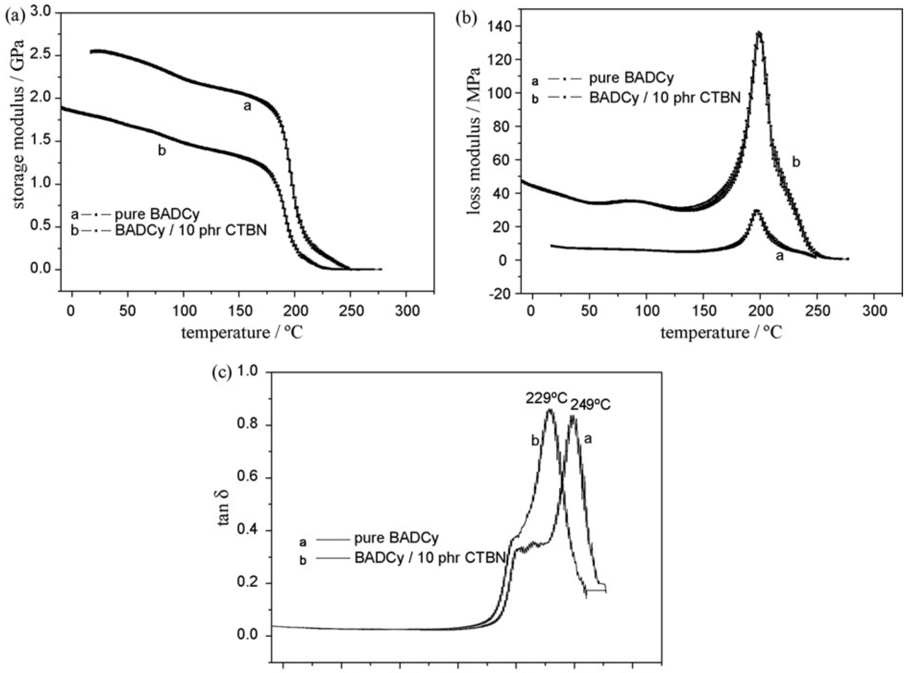


Fig. 10. DMA analysis of cured resin systems. (a) Storage modulus curves of BADCy and BADCy/10 phrLCTBN. (b) Loss modulus curves of BADCy and BADCy/10 phrLCTBN. (c) tan δ curves of BADCy and BADCy/10 phrLCTBN.

DMA was carried out to monitor the effect of LCTBN on the thermodynamic property of BADCy systems. The storage modulus (E′), loss modulus (E″), and loss factor (tan δ) are plotted in Fig. 10. It can be seen that the pure BADCy has higher *E*′ values than that of the BADCy modified with LCTBN (Fig. 10 (a)). This can be explained as that the incorporation of LCTBN into the BADCy matrix remarkably reduce its rigidity and has bad reinforcing effects, especially for lower temperature such as below 175 °C. Fig. 10 (b) shows the loss modulus evolution with the temperature. In the test temperature range, the loss modulus of modified BADCy sample is always higher than that of pure BADCy resin, which indicates that the modified system can consume more energy during the dynamic processes because of more inter-friction between molecule chains in the modified systems.

In polymer blending process, the dynamic mechanical behavior has relation with the compatibility of different polymers. The favorable compatibility of different polymers which forms one phase, results in one peak in loss factor (tan δ) profile, but if the compatibility is not well, and at least two phases are appeared, so there should be at least two peaks. In the loss factor Fig. 10(c), the glass transition temperature of modified BADCy is 229 °C and lower than that (249 °C) of pure BADCy resin. The tan δ plot demonstrates good separation of elastomer of LCTBN in BADCy matrix, which results from the chemical reaction of them, so the modified BADCy system is copolymer and blend system.

4. Conclusions

The BADCy systems modified with different adding amount LCTBN were developed. Through FTIR and DSC, it was found that the introduction of LCTBN had little effect on the curing procedure of BADCy resin. The cured BADCy resin was formed through the cyclotrimerization of cyanate functional groups into triazine rings and that there was the chemical reaction between BADCy and LCTBN. The good interfacial adhesion exists between the BADCy and LCTBN phases because of the chemical reaction of them result in the enhancement of toughness of BADCy resin, so the mechanical studies reveal that the incorporation of LCTBN into BADCy resin greatly improves the impact strength. The thermal properties such as glass transition temperature, heat distortion temperature and thermal stability of modified BADCy showed little decrease trend, compared with those of unmodified systems. MDA shows that the pure BADCy has higher storage modulus (*E*′) values than that of the BADCy modified with LCTBN, whereas the loss modulus (*E*″) of pure BADCy is lower than that of modified BADCy, corresponding to the enhancement of toughness of BADCy resin modified with LCTBN.

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