

Carboxyl-Terminated Butadiene–Acrylonitrile Rubber Modified Cyanate Ester Resin

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ABSTRACT: The carboxyl-terminated butadiene-*a*-acrylonitrile rubber (CTBN) has been proved to be the most effective toughener for cyanate ester (CE) resin. This work mainly focuses on the different modification effects caused by the addition of CTBN with different acrylonitrile content. The phase separation, morphology of fracture surface, and physical properties of the blends are studied by scanning electron microscopy (SEM), transmission electron microscopy (TEM),

dynamic mechanic analysis (DMA), and thermogravimetric analysis (TGA). It is testified that the compatibility and toughness between CE and CTBN had a positive correlation with the acrylonitrile content of CTBN. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3098–3104, 2007

Key words: blends; compatibility; CTBN; CE resins; toughness

INTRODUCTION

Cyanate ester (CE) resin is currently an important material for the encapsulation of electronic devices, high-temperature adhesive, and structural aerospace composites. CE monomers undergo polycyclotrimerization to form trifunctional triazine rings, which exhibit excellent dielectrical, thermal, and adhesive properties.¹ Unfortunately, like other highly cross-linked thermosets, CE has low toughness that restricts its further application. Appreciative modification is required to improve its toughness.

Various studies have been carried out on the toughening of CE resin such as copolymerization with flexible monocyanates, utilization of rubber or organo-clay, and preparation of semiinterpenetration networks (SIPNs) have been proven useful.^{2–5} Among the methods mentioned earlier, using the reactive elastomers such as liquid nitrile rubber was proven to be one of the most effective techniques.^{6–13} Researches have proved that the butadiene–acrylonitrile rubber with carboxylic acid terminated group is the most effective in toughening. It is well known that toughening thermoset with rubber depends on the content, molecular weight of the rubber, and the compatibility between them. Nowadays, there are many studies on how the CTBN content in CE/CTBN blend and the molecular weight of CTBN affect the toughness of CE/CTBN

system.^{7–12} But, there is still a blank in the studies on how the acrylonitrile content of CTBN affects the toughening effect on CE resin.

Because the various contents of acrylonitrile in CTBN will induce different compatibility between CTBN and CE matrix, the morphology and interfacial behavior in CE/CTBN blends could be tailored by changing the acrylonitrile content of CTBN. Consequently, the toughness of CE/CTBN blends could be adjusted. This work mainly focuses on the different modification effects caused by the addition of different acrylonitrile content of CTBN with close molecular weight. The purpose of this study is to offer a better and deeper understanding of CE's toughening by reactive liquid butadiene–acrylonitrile rubber.

EXPERIMENTAL

A diphenolic-based cyanate ester (CE) monomer (melt point: 79°C) was supplied by Jinan Special Structure Institute of China Aero-Industry (Jinan, China). The liquid butadiene–acrylonitrile rubbers were provided by Noveon Asia Pacific and were used as received. The molecular weight, acrylonitrile content, and solubility parameter were listed in Table I. The solubility parameter was calculated based on the molar attraction constants.¹⁴ The carboxyl terminated butadiene rubber (CTB) can be considered as carboxyl terminated butadiene-*a*-acrylonitrile rubber (CTBN) with 0% acrylonitrile content.

In this study, the blends were coded by the weight ratio of their components in this order: CE, type of

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TABLE I
Designations of the Liquid Rubbers Used in This Work

Liquid rubber	CTB200X162	CTBN1300X31	CTBN1300X8	CTBN1300X13
Acrylonitrile content (wt %)	0	10	18	26
Molecular weight (M_n)	4200	3800	3550	3150
Solubility parameter ($\text{cal}/\text{cm}^3)^{1/2}$	8.14	8.46	8.82	9.15

reactive liquid butadiene–acrylonitrile rubber and its product code. For example, a blend containing 100 phr CE and 10 phr CTBN1300X31 was abbreviated as CE/CTBNX31 = 100/10.

To compare the different toughening effects of various acrylonitrile content of CTBN conveniently and clearly, the molecular weights of CTBN and CTB are nearly the same and the weight ratio of CE and the liquid butadiene–acrylonitrile rubber of the blends were fixed at 100 : 10.

CE monomer was placed in a beaker maintained at 90°C by water bath. CTBN was mixed into CE monomer with thorough stirring for 15 min at 90°C. After completely mixing, the mixture was degassed under vacuum at 140–150°C over 30 min and the cure schedule was: 160°C/1 h + 180°C/1 h + 200°C/1 h + 220°C/1 h + 240°C/1 h. After curing, the composites were exposed to air and let the temperature of composites decreased from 240°C to room temperature.

In this work, five types of specimens were made: pure CE resin; CE/CTBX162 = 100/10; CE/CTBNX8 = 100 : 10; CE/CTBNX13 = 100/10; CE/CTBNX31 = 100 : 10. We name them as pure CE; CE/CTBX162; CE/CTBNX8; CE/CTBNX13; CE/CTBNX31 for convenience.

The impact test was performed according to GB/T2571-1995 (similar to ISO179-1993) on an XCF-4 Charpy impact instrument at $(23 \pm 2)^\circ\text{C}$. The results of the impact test were obtained by averaging the results of five measurements. Scanning electron microscopy (SEM) photographs were taken on a Hitachi S-570 SEM, Japan. Fractured specimens after impact test were gold-coated before observation. Transmission electron microscopy (TEM) was done using a JEM-1200EX electron microscope, Japan. Dynamic mechanical analysis (DMA) was performed using a DMA Q800 V3.13 Build 74 by TA Instruments. The testing was carried out under air atmosphere in dual cantilever bending mode at a vibration frequency of 1 Hz in a temperature range from 40 to 320°C, and the heating rate was 10°C/min. The dimension of the sample is 60 mm \times 12.5 mm \times 2 mm. Thermogravimetric analysis (TGA) was performed under N₂ atmosphere, using a PerkinElmer Pyris1 Thermal Analyzer.

RESULTS AND DISCUSSION

Phase structure and morphology

Figure 1 consists of a series of SEM micrographs obtained from the fracture surfaces of the specimens after impact test. Figure 1(a) shows a few cracks in the pure CE matrix and the cracks go straight. The smooth fracture surface illustrates a brittle fracture behavior. The SEM pictures of CE/CTBN blends [Fig. 1(b–d)] show rough surfaces consist of more and shorter cracks spreading in all the directions. These significant changes in the SEM images imply the dominant fracture mode in these systems is likely crack branching/bifurcation. It also infers that there will be a great improvement in the toughness of these blends. In Figures 1(b–d), no phase-separated domain was observed. It suggests that the phase-separated domains are too small to be detected by SEM. But, in Figure 1(e), obvious phase separation is seen easily, revealing that the compatibility between CE and CTB is worse than CE and CTBN. There is an interesting phenomenon in Figure 1(c): many cavities are found in the fracture surface. For observing these cavities clearly, Figure 1(f), a higher magnification ($\times 5000$) SEM image, was provided. In Figure 1(f), the cavities have a well-proportioned separation and some cracks are terminated by the cavities. The dispersed CTBN phase is generally accepted as the toughening mechanism of CE/CTBN blend. Our previous work¹² has proved that for CTBN-modified system, rubber particles and cavities toughening mechanism worked together. The cavities are thought to result from the low molecular weight part of CTBN engendered by the curing process. This suggestion is confirmed by the results of TGA, as shown in Figure 2. It shows the results of TGA (under air) of CTBNX8 and CTBNX31. The weight loss of CTBNX8 is about 3% before 240°C, while that of CTBNX31 is nearly zero. The gaseous low molecular weight CTBN was trapped by the crosslinking network of CE and formed the cavities after the curing process. The detail mechanism of the forming of the cavities needs further studies.

Referring to the literature,¹⁵ the solubility parameter of CE is $9.41 (\text{cal}/\text{cm}^3)^{1/2}$. Comparing the solu-

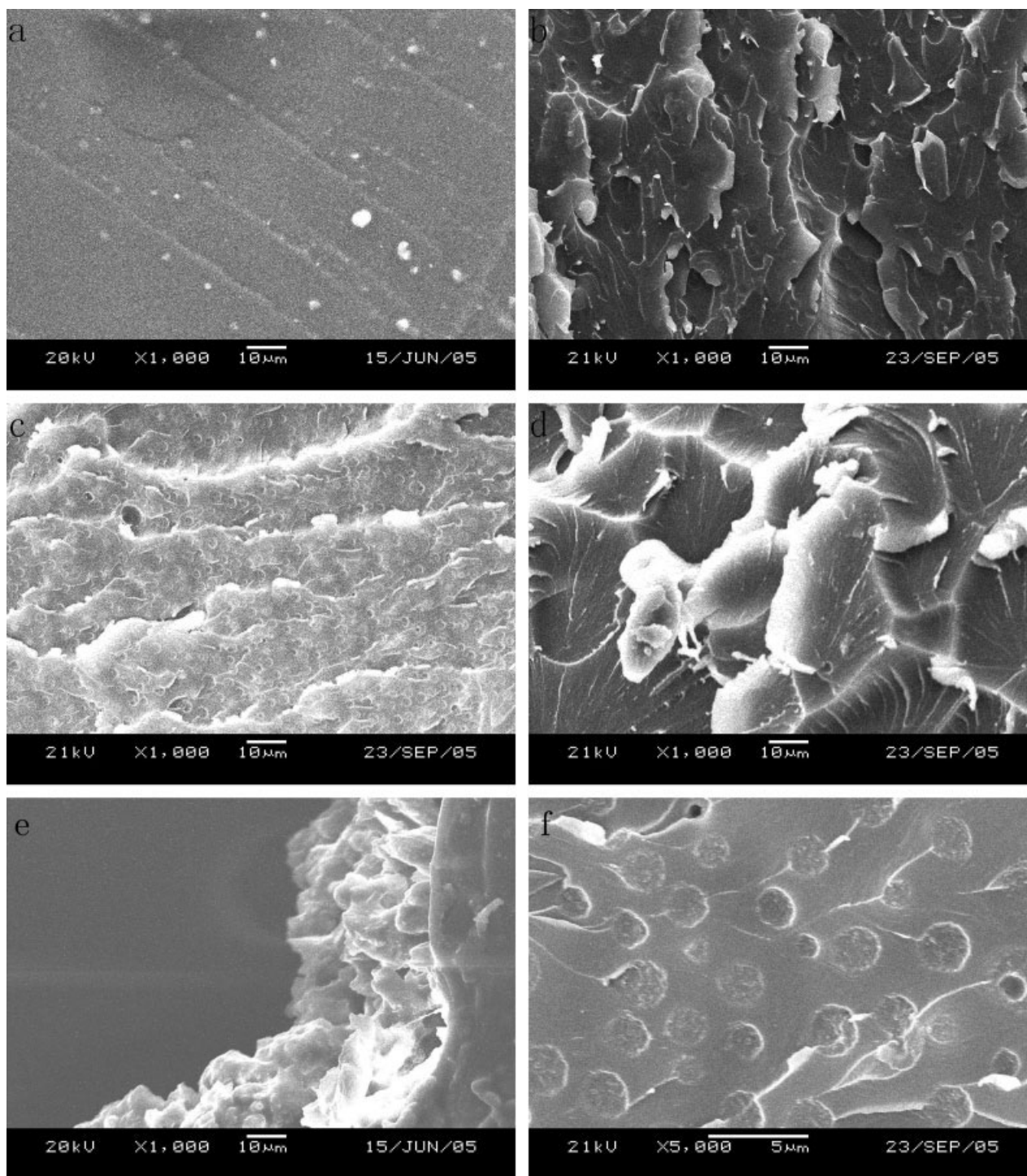


Figure 1 SEM images of the fractured surfaces of pure CE and CE/CTBN blends: (a) pure CE, (b) CE/CTBNX31, (c) CE/CTBNX8, (d) CE/CTBNX13, (e) CE/CTBNX162, and (f) CE/CTBNX8.

bility parameters of CTB and CTBN from Table I, it is proposed that the compatibility between CE and CTBN will be better as the increase of acrylonitrile content in liquid butadiene–acrylonitrile rubber. Figure 3 is the TEM photos of rubber-modified CE systems that show more details and evidences of the compatibilities of blends. The black globular

particles, which are considered as CTBN-rich phase existing in the CE matrix can be seen clearly in Figure 3. According to Figures 3(a–c), it is found that when the acrylonitrile content in CTBN increased from 10%, 18 to 26%, the diameter of the rubber particles decreased from $\sim 2 \mu\text{m}$, 1 to $0.2 \mu\text{m}$, and the number of the particles increased correspondingly.

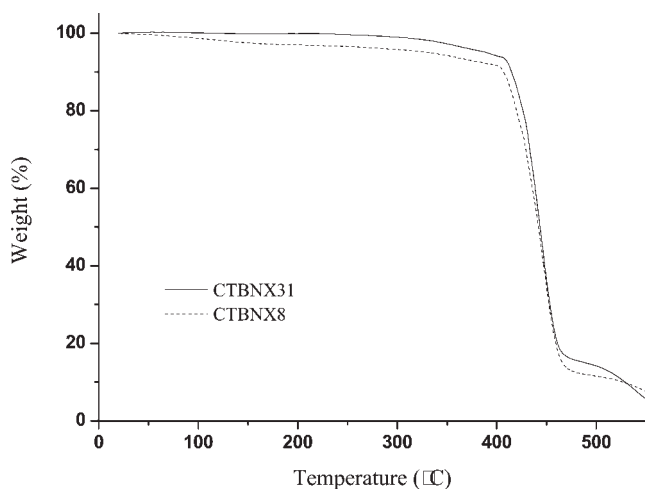


Figure 2 Thermogravimetric curves of CTBNX8 and CTBNX31.

By higher magnification ($\times 30,000$) as shown in Figure 3(d), the diameter of rubber particles is minimal and the concentration of rubber particles is maximal. Figure 3(e) is the TEM image of CE resin phase in CE/CTBX162 blend. Unlike other TEM images of CE/CTBN blends, there are no rubber particles in the CE matrix. It is a pity we were not able to take a TEM picture of the overall morphology of CE/CTB blend because of the restriction of magnification. But the truth is that no CTB particles existing in the CE matrix implies a macro phase-separation formed in their blend and the poor compatibility between CE and CTB. The result of TEM images analysis is in accordance with the analysis by solubility parameters. It is concluded that the compatibility between CE and CTBN improved when the acrylonitrile content in CTBN increased. These TEM photos also verify that CE/CTBN blend is a multiphase material. It is the existence of rubber particle that improves the toughness of CTBN-modified resin.

Physical properties

The data of impact strength tests are shown in Figure 4. The horizontal line represented pure CE's impact strength. The impact strength of the blends was improved significantly with the addition of CTBN except CTB. The impact strength of CE/CTBX162 blend was the lowest, even lower than that of pure CE. As shown in Figures 1(e) and 3(e), a macro phase-separation was formed in CE/CTB blend. So the rubber particle toughening mechanism did not work in this blend. When the acrylonitrile content in liquid butadiene-acrylonitrile rubber increased, the impact strength of blends also increased. In other words, there is a positive correlation

between the acrylonitrile content and the impact strength. In the view of rubber particle toughening mechanism, the better compatibility between CE and CTBN leads to more rubber particles in the CE matrix that can improve the toughness.

The results of dynamic mechanical analysis can be seen in Figure 5. The figures show the dependence of storage modulus (E') and loss tangent ($\tan \delta$) on temperature of pure CE and CE/CTBN blends. According to Figure 5(a), the storage modulus (E') of CE/CTBN blends decreased when CTBN was added, especially when the addition was CTB. This is a reasonable result for adding low modulus rubber and it is consistent with literatures. An interesting phenomenon was found in Figure 5(a): the initial storage modulus of the blends increased when the acrylonitrile content of CTBN increased. In our point of view, it is resulted from the high polarity of nitrile group in rubber. It is well known that high modulus of a glassy material results from the fact that the chain conformations are frozen into an amorphous rigid network. The high polarity of nitrile group restricted the changes of chain conformations in the blends. When the acrylonitrile content in liquid CTB rubbers increased, the number of nitrile groups increased and the restrictive effects became stronger.

The systems are basically two-phase systems consisting of the CE matrix and the rubbery CTBN domains. The corresponding temperature of the peak in Figure 5(b) is considered as the glass transition temperature (T_g) of CE phase. It could be imagined that the T_g of the CE matrix would not change significantly as acrylonitrile content of CTBN was changed. However, it is seen from Figure 5(b) that the T_g of the matrix decreased with increasing a-acrylonitrile content of CTBN. The T_g of pure CE, CE/CTBX162, CE/CTBNX31, CE/CTBNX8, and CE/CTBNX13 are 262.3, 244.4, 243.1, 240.1, and 236.5, respectively. This could be because of the plasticizing effect of CTBN. Some CTBN may actually "dissolve" in the CE matrix, and thus lowers the T_g of the matrix. The increase in acrylonitrile content enabled a higher solubility in the matrix and thus T_g continuously decreased. It is again confirmed that the compatibility between CE and CTBN tends to be better with the acrylonitrile content in CTBN enhanced.

Figure 6 shows the TG curves and corresponding derivative curves (DTG curves) for CE and CE/CTBN blends. According to Figure 6(a), the initial thermal decomposition temperatures (onset temperature) of pure CE, CE/CTBX162, CE/CTBNX31, CE/CTBNX8, and CE/CTBNX13 are 428.3, 421.2, 419.8, 414.7, and 406.0°C, respectively. The onset degradation temperatures of the CE/CTB and CE/CTBN blends are lower than pure CE. The same tendency is found in Figure 6(b). The maximum degradation rate temperatures of pure CE, CE/CTBX162, CE/CTBNX31,

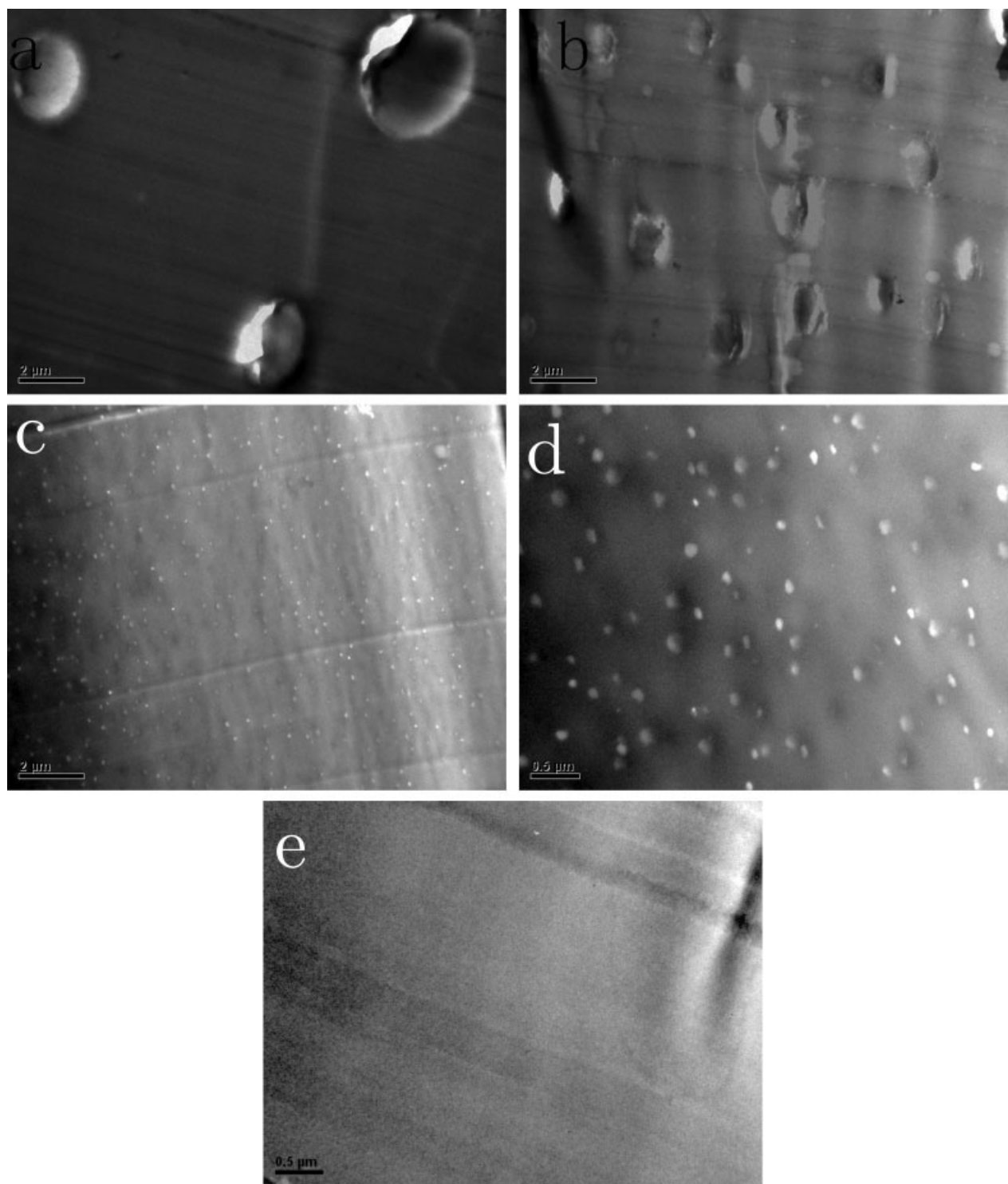


Figure 3 TEM micrographs of CE/CTBN and CE/CTB blends: (a) CE/CTBNX31, (b) CE/CTBNX8, (c) CE/CTBNX13, (d) CE/CTBNX13, and (e) CE/CTBNX162 (CE resin phase).

CE/CTBNX8, and CE/CTBNX13 are 455.2, 452.9, 449.3, 445.4, and 444.7°C, respectively. The more the content of acrylonitrile, the lower the onset and maximum degradation temperature of the blend are. It is easy to conclude that the addition of liquid rubbers deteriorates the thermal stability of CE resin. Fur-

thermore, the analysis of Figure 6 indicates that the thermal stability of CE/CTBN blend is related to the acrylonitrile content in CTBN of the blend. With the increase of acrylonitrile content in CTBN, the thermal stability of blend deteriorates. Because more acrylonitrile content in CTBN will induce better

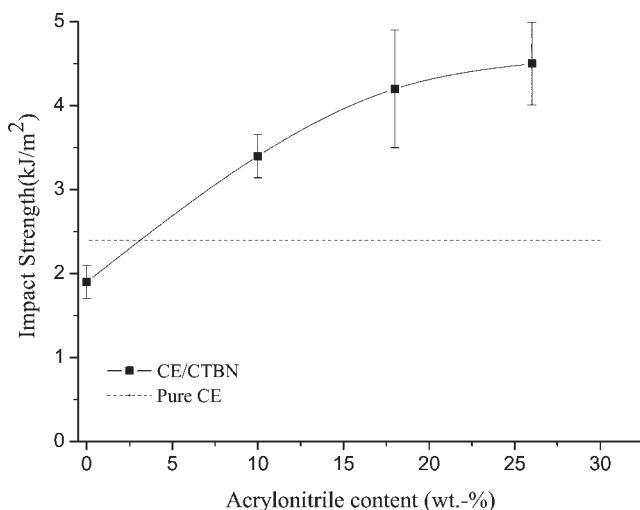


Figure 4 Impact strength of pure CE and CE/CTBN blends.

compatibility between CE and CTBN, as seen in TEM photos, it will induce smaller rubber particles and more homogeneous distribution. These changes

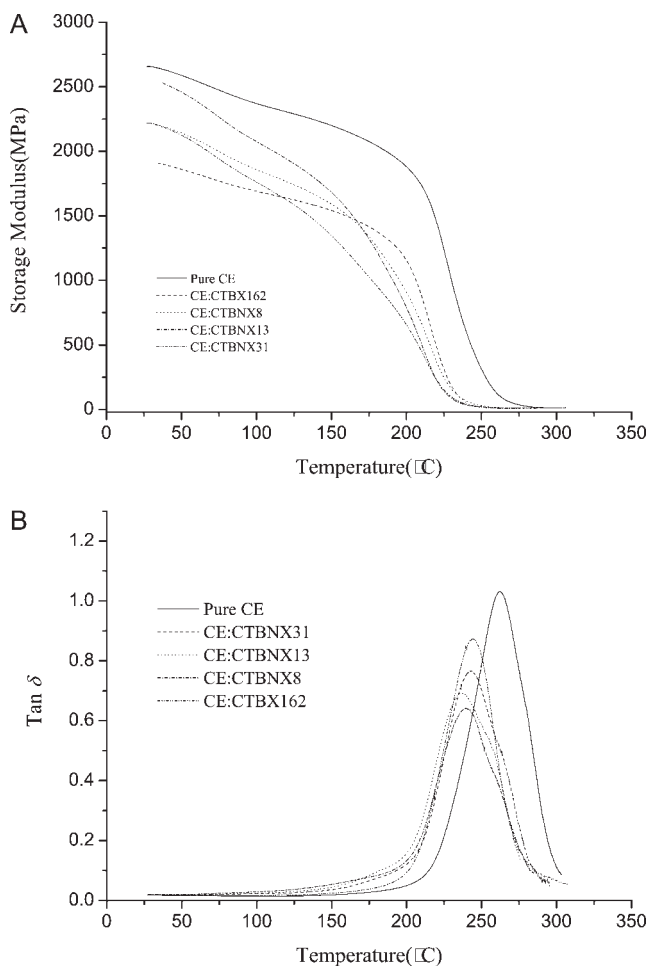


Figure 5 Temperature dependences of storage modulus (a) and loss tangent (b) for CE and CE/CTBN blends.

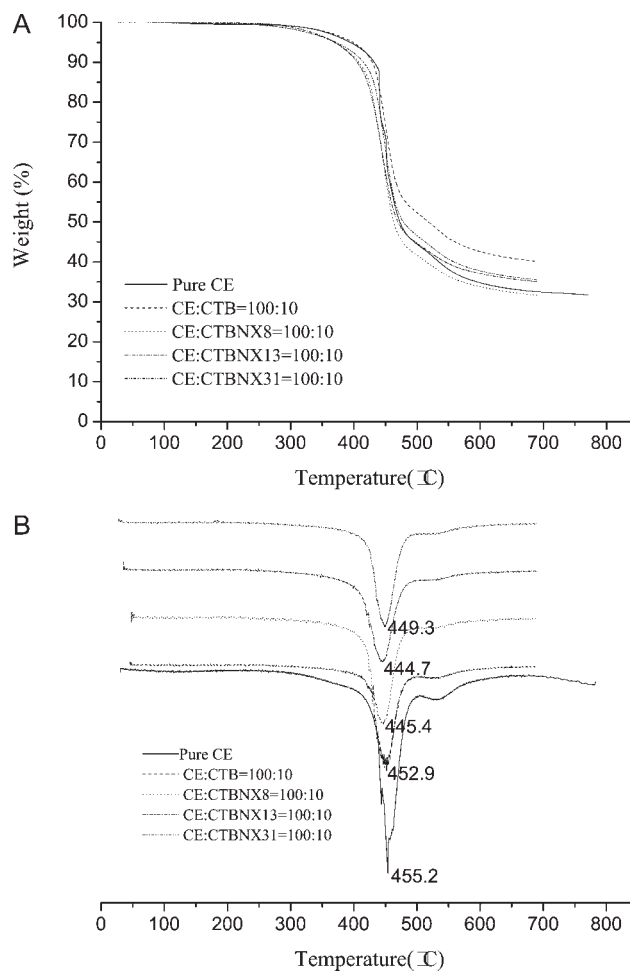


Figure 6 TG (a) and DTG (b) curves of CE and CE/CTBN blends under nitrogen.

in rubber particles are the advantages to absorb the heat homogeneously and effectively. That is the reason why the more the acrylonitrile content, the lower thermal stability of the blend is.

CONCLUSIONS

There is a positive correlation between acrylonitrile content in CTBN and its compatibility with CE. In other words, the compatibility between CE and CTBN improves when the acrylonitrile content increases. The impact strength of the blends was improved significantly with the addition of CTBN except CTB. The different compatibility between CE and CTBN caused by various acrylonitrile content in liquid carboxyl-terminated rubber also affect the dynamic mechanical and thermal properties of the blends. The initial storage modulus of the blends increases but the thermal stability of the blend deteriorates when the acrylonitrile content increases in CTBN.

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