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# Mechanical, thermal and dielectric properties of PNBRs/BADCy composites

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Powdery nitrile butadiene rubbers (PNBRs) are introduced into the bisphenol A dicyanate ester (BADCy) matrix to fabricate the PNBRs/BADCy composites. The mass fraction of PNBRs affecting on the mechanical, heat resistance and dielectric properties of the PNBRs/BADCy composites is investigated, and the addition of PNBRs affecting on the curing reaction of the BADCy is also investigated. Results show that both flexural strength and impact strength of the PNBRs/BADCy composites are increased firstly, but decreased with excessive addition of PNBRs. Compared with that of pure BADCy, the maximum flexural strength and impact strength of the PNBRs/BADCy composites is increased by 27.8 percent and 49.6 percent, respectively. And the heat resistance and dielectric properties of the PNBRs/BADCy composites are decreased with the increasing addition of PNBRs. Additionally, the addition of PNBRs can effectively promote the curing reaction of the BADCy system.

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*Keywords:* Bisphenol A dicyanate ester (BADCy), Powdery nitrile butadiene rubbers (PNBRs), Heat resistance, Dielectric properties, Curing reaction

## 1. Introduction

Cyanate ester (CE) resins possess excellent dielectric properties, which reveal good stability in a wide range of temperature and electric field frequency, better than other thermosetting resins, such as epoxy resin, polyimide and bismaleimide, etc., Furthermore, CE resins possess high mechanical strength, excellent heat resistance properties & high dimensional stabilities, low moisture absorption rate and good processing performance, etc., and have been widely applied in aerospace, electronics, insulations, adhesives and other key areas [1-10].

However, pure cured CE resins suffer from brittleness because of their extensively high cross-linking density and rigid triazine rings. To the best knowledge of us, lots of toughing methods have proposed to increase the toughness of CE resins, such as fibres [11], thermoplastics [12], thermosets [13], rubber elastomers [14], and blending or copolymerization with other compounds containing unsaturated double bond and different CE monomers [15].

Powdery rubbers present many attractive properties, such as easy operation, low energy consumption and good dispersibility in the resin matrix. Compared with those of general liquid rubbers (CTBN, MVQ, FPM, etc.), powdery rubbers possess high specfic surface, which makes it easier for performing physical and chemical action with polymeric matrix and reinforced fillers. Researches have shown that the addition of powdery rubbers can give the special properties of polymeric matrix effectively [16].

In our present work, the powdery nitrile butadiene rubbers (PNBRs) are performed to improve the comprehensive properties of the bisphenol A dicyanate ester (BADCy). The mass fraction of PNBRs affecting on the mechanical, heat resistance and dielectric properties of the PNBRs/BADCy composites is systematically investigated. Furthermore, the addition of PNBRs affecting on the curing reaction of the BADCy system is also investigated by differential scanning calorimentry (DSC) and Fourier transform infrared spectra (FTIR).

## 2. Experimental methods

### 2.1 Main materials

Bisphenol A dicyanate ester (BADCY) is supplied by Jiangdu Wuqiao Resin Factory Co., Ltd. (Jiangsu, China); Powdery nitrile butadiene rubbers (PNBRs), mean grain diameter of 0.6mm and acrylonitrile' content of 33%, are purchased from Jingjiang Kanggaote Plastics Technology Co. Ltd. (Jiangsu, China); Epoxy resin (E-51), is supplied by Wuxi Resin Factory of Blue Star New Chemical Materials CO., Ltd (Jiangsu, China); Absolute ethanol is supplied by Tianjin Fuyu Fine Chemical Co., Ltd. (Tianjin, China); Dibutyltin dilaurate (DBTDL) is purchased from Tianjin Gang Ji Industrial and Trading Co., Ltd. (Tianjin, China).

### 2.2 Preparation of PNBRs/BADCy composites

PNBRs are firstly immerged in absolute ethanol for 24 hr, followed by filtration and washed by distilled water for several times, and finally dried at 60°C in a vacuum oven for another 24 hr. The dried BADCy and epoxy resin (E-51) are mixed and heated to 150°C in an oil bath with stirring. And appropriate PNBRs and DBTDL are then added into the BADCy/E-51 mixtures above, and then poured into the preheated die. The mixtures of PNBRs/DBTDL/BADCy/E-51 are degassed in a vacuum vessel to remove air bubbles. Finally, the mixtures are cured in an oven as the technology of 140°C/1 hr+160°C/1 hr+180°C/2 hr+200°C/2 hr, followed by post-curing at 220°C for 3 hr.

### 2.3 Analysis and characterization

The flexural strength of the samples is measured by Electron Omnipotence Experiment Machine SANS-CMT5105 (Shenzhen New Sansi Corp., China) according to standard ISO 178-1993. The impact strength of the samples is measured by ZBC-4B charpy impact testing machine (Shenzhen New Sansi Corp., China) according to standard ISO 179-1993. Scanning electric microscope (SEM) morphologies of the samples are analyzed by VEGA3-LMH (TESCAN Corporation, Czech Republic). Thermo-gravimetric (TG) analyses of the samples are performed using a thermoanalyzer (STA 449F3, Netzsch Group, Germany) in the temperature range of 40-800°C with a heating rate of 20K/min under argon atmosphere. The dielectric constant and dielectric loss of the samples are measured using high frequency Q instrument (QBG-3D) and dielectric constant detector (S914) from Aiyi Electronic Equipment Co. Ltd. (Shanghai, China), and the corresponding samples' dimension was 20mm×20mm×4mm. Fourier transformed infrared spectroscopy (FTIR, Bruker Tensor 27, Bruker Corporation, Germany) is employed using thin KBr as the sample holder. Transition mode was used and the wave-number range is set from 4000 to 400 cm$^{-1}$. Differential scanning calorimentry (DSC) analyses of the samples are carried out at 10°C/min (nitrogen atmosphere) by TA Instrument-2910 DSC.

## 3. Results and discussion

### 3.1 Mechanical properties of PNBRs/BADCy composites

Fig. 1 shows the mechanical properties of the PNBRs/BADCy composites. Both the flexural strength and impact strength of the PNBRs/BADCy composites are increased firstly, but decreased with the excessive addition of PNBRs. The flexural strength of the PNBRs/BADCy composites is optimal with 1 wt% PNBRs, and the impact strength of the PNBRs/BADCy composites is optimal with 3 wt% PNBRs. Compared with that of pure BADCy, the maximum flexural strength and impact strength of the composites is increased by 27.8 percent and 49.6 percent, respectively.

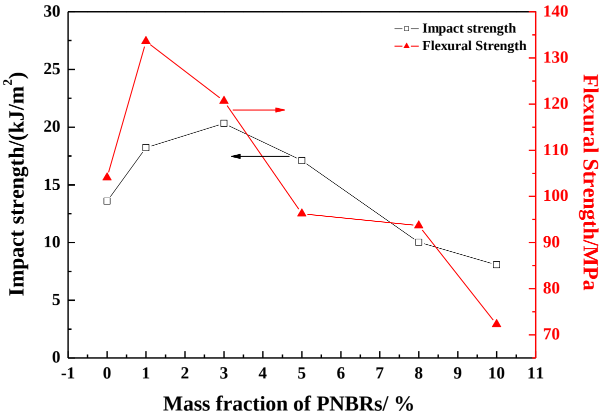

*Fig. 1. Mechanical properties of PNBRs/BADCy composites.*

Appropriate addition of PNBRs can induce shear bands, absorb energy and prevent the expanding of cracks, thus to enhance the mechanical properties of the PNBRs/BADCy composites. However, with the excessive addition of PNBRs, an incomplete dispersion and a small amount aggregate of PNBRs can occur, and more gas bubble & stress concentration points are formed easily. The corresponding mechanical properties of the PNBRs/BADCy composites are decreased.

SEM images of the impact fracture surfaces of pure BADCy and PNBRs/BADCy composites are presented in Fig. 2. It can be seen that the fracture surface of pure BADCy presents a typical brittle feature. With the addition of PNBRs, the bifurcation phenomenon is appeared on the fracture surface of the PNBRs/BADCy composites, which reveals that PNBRs is beneficial for restraining the propagation of cracks and making the cracks develop disorderly. For 3 wt% addition of PNBRs, the corresponding fracture surface appears to be dimple and ladder-like shape, to present a typical ductile fracture. With the further addition of PNBRs (5 wt%, 8 wt% and 10 wt%), some PNBRs aggregates are appeared on the fracture surface of PNBRs/BADCy composites, which are easy to form the interface stress concentration and residual stress, finally to decrease the mechanical properties of the PNBRs/BADCy composites.

### 3.2 Thermal properties of PNBRs/BADCy composites

TGA curves of pure BADCy and PNBRs/BADCy composites are presented in Fig. 3, and the corresponding thermal data are listed in Table 1. It can be seen that, with the increasing addition of PNBRs, the corresponding weight loss temperatures are all decreased at the same weight loss. When the weight loss is 50 wt%, the corresponding heat decomposing temperature of pure BADCy and PNBRs/BADCy composites is 498°C (pure BADCy), 496°C (1 wt%PNBRs), 492°C (3 wt%PNBRs), 467°C (5 wt%PNBRs) and 464°C (8 wt%PNBRs), respectively, In addition, the corresponding heat resistance index is 213°C, 209°C, 199°C, 195°C and 191°C, respectively. It reveals that the thermal resistance of the PNBRs/BADCy composites is decreased slightly with the increasing addition of PNBRs. The reason is that, compared to that of BADCy, PNBRs possesses worse thermal resistance, which can preferably decompose easier at a higher temperature. Furthermore, the addition of PNBRs can also decrease the crosslink density of BADCy system, which results in the increase of the thermal resistance of the PNBRs/BADCy composites.

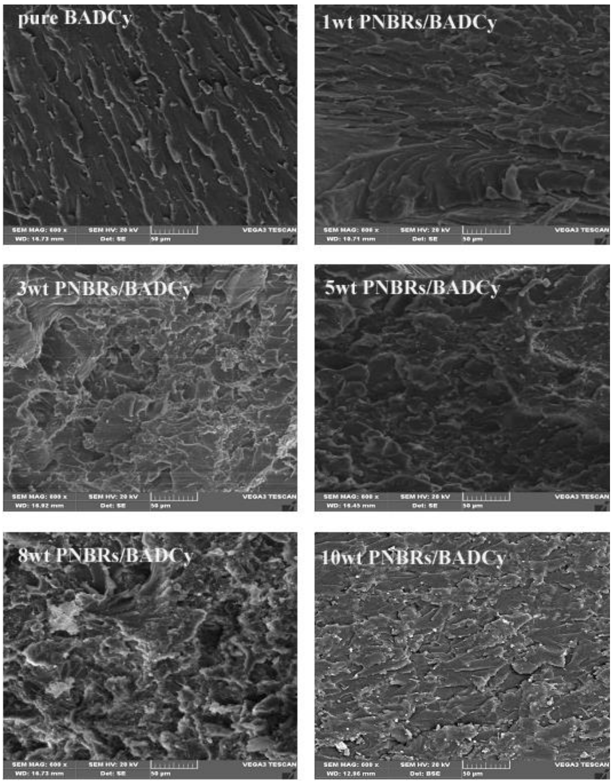

*Fig. 2. SEM images of impact fracture surfaces of PNBRs/BADCy composites.*

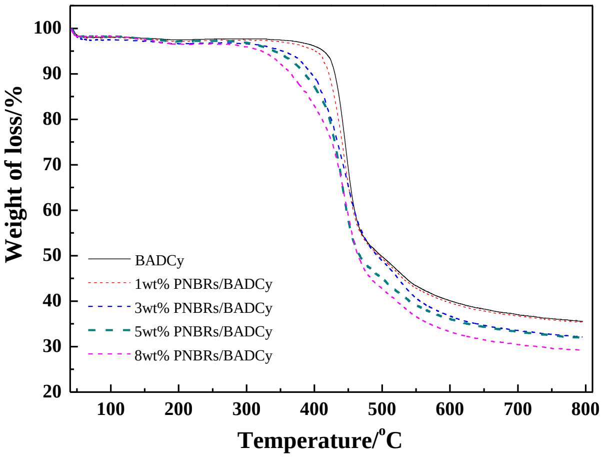

*Fig. 3. TGA curves of pure BADCy and PNBRs/BADCy composites.*

*Table 1. TGA characterization data of pure BADCy and PNBRs/BADCy composites*

| **Samples** | **$T_5$°C** | **$T_{30}$°C** | **$T_{50}$°C** | **Heat resistant index*/°C** |
|---|---|---|---|---|
| Pure BADCy | 413 | 449 | 498 | 213 |
| 1wt% PNBRs/BADCy | 401 | 445 | 496 | 209 |
| 3wt% PNBRs/BADCy | 353 | 442 | 492 | 199 |
| 5wt% PNBRs/BADCy | 341 | 436 | 467 | 195 |
| 8wt% PNBRs/BADCy | 322 | 435 | 464 | 191 |

**The sample's heat-resistance index was calculated by eq.(1)*[18]

$$T_{\text{Heat-resistance index}} = 0.49*[T_5+0.6*(T_{30}-T_5)] \quad (1)$$

*Where* $T_5$, $T_{30}$ *and* $T_{50}$ *is corresponding decomposition temperature of 5%, 30% and 50% weight loss, respectively.*

### 3.3 Dielectric properties of PNBRs/BADCy composites

The dielectric constant and dielectric loss values of pure BADCy and PNBRs/BADCy composites are presented in Table 2. It can be seen that both dielectric constant and dielectric loss values of PNBRs/BADCy composites are increased with the increasing addition of PNBRs.

*Table 2. Dielectric constant and dielectric loss values of pure BADCy and PNBRs/BADCy composites*

| **Mass fraction of PNBRs / wt%** | **Dielectric constant, ε** | **Dielectric loss, tanδ** |
|---|---|---|
| 0 | 2.76 | 0.0060 |
| 0.5 | 2.86 | 0.0069 |
| 1 | 2.91 | 0.0074 |
| 3 | 2.95 | 0.0093 |
| 5 | 2.98 | 0.0105 |
| 8 | 3.02 | 0.0129 |

PNBRs have a relatively higher dielectric constant value than that of pure BADCY. Furthermore, with the increasing addition of PNBRs, the more two-phase interfaces between PNBRs and BADCy can be formed, which can enhance the polarization performance of the PNBRs/BADCy composites, resulting in the increase of dielectric constant values. Additionally, more inner defects of the PNBRs/BADCy composites can also result in the increase of dielectric constant.

The dielectric loss values of the PNBRs/BADCy composites are resulted from intrinsic loss and interfacial polarization loss. One side, the increasing addition of

PNBRs can increase the intrinsic loss of the PNBRs/BADCy composites. On the other side, the interface gaps and defects of the PNBRs/BADCy composites are also increased with the increasing addition of PNBRs. The two aspects above result in the increase of dielectric loss of the PNBRs/BADCy composites.

### 3.4 Effects of PNBRs on the curing reaction of BADCy system

DSC curves of pure BADCy and PNBRs/BADCy composites are shown in Fig. 4. With the increasing addition of PNBRs, the corresponding maximum exothermic peak of the PNBRs/BADCy systems shifts to a relatively lower temperature. And the corresponding peak temperature of pure BADCy and PNBRs/BADCy systems is 211°C (pure BADCy), 207°C (1 wt%PNBRs), 206°C (3 wt%PNBRs), 206°C (5 wt%PNBRs) and 187°C (8 wt%PNBRs), respectively. It reveals that the reaction activity of the PNBRs/BADCy systems is gradually improved with the increasing addition of PNBRs, which can be mainly attributed that the reactive groups of PNBRs can promote the curing reaction of the BADCy system.

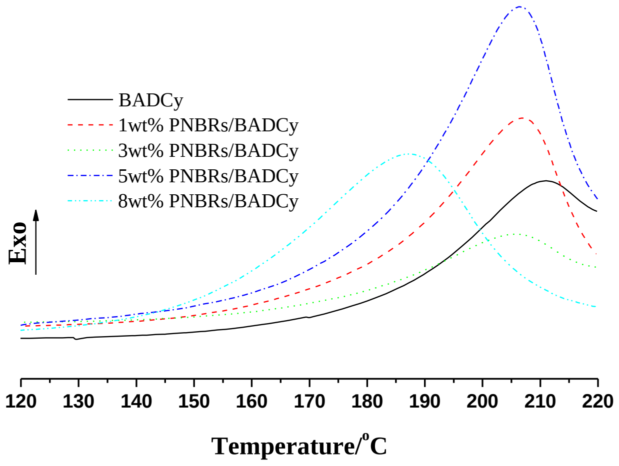

*Fig. 4. DSC curves of pure BADCy and PNBRs/BADCy composites*

The real-time tracking FTIR spectra of pure BADCy and PNBRs/BADCy system (3 wt% PNBRs) are presented in Fig. 5.

The characteristic peak of -OCN group near 2270 $cm^{-1}$ is reduced gradually with the increasing curing time, and disappeares completely via the following curing technology of 140°C/1 hr+160°C/1 hr+180°C/2 hr+200°C/2 hr, which reveals that cyanate ester monomer has reacted completely.

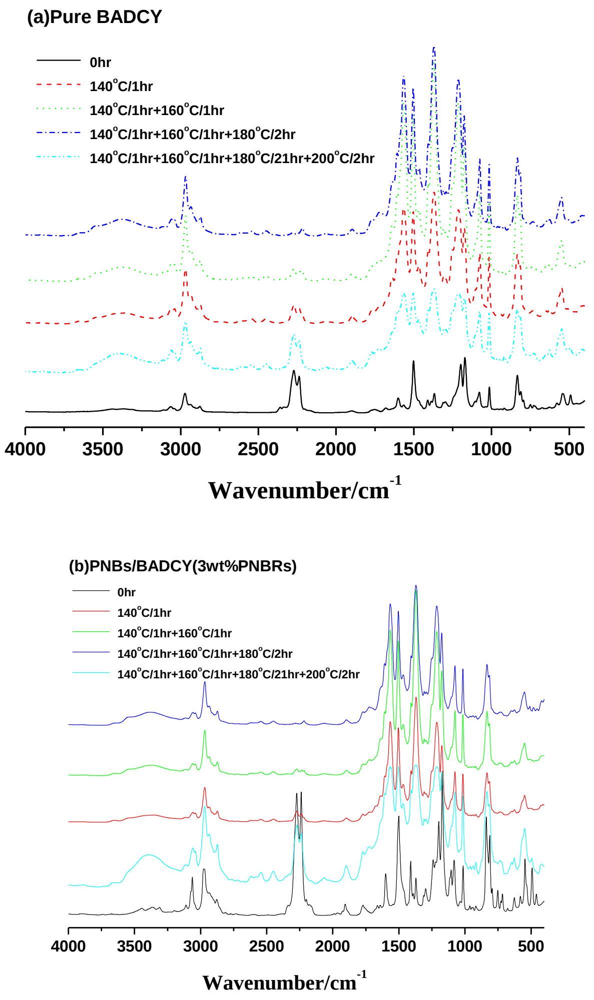

*Fig. 5. Real-time tracking FTIR spectra of the pure BADCy and PNBRs/BADCy system*

Considering the number of phenyl groups is constant during the curing course, the phenyl absorption peak at 1500 $cm^{-1}$ is used as the internal standard for quantitative comparison between different FTIR spectra. And the corresponding curing degree of pure BADCy and PNBRs/BADCy system (3 wt% PNBRs) can be calculated by Eq. (1) [17], shown in Table 3.

$$X = 1 - \frac{H_{i2270} / H_{i1500}}{H_{o2270} / H_{o1500}} \qquad (1)$$

Herein, $X$ is the curing degree; $H_{i2270}$ and $H_{i1500}$ is the peak height of 2270 $cm^{-1}$ and 1500 $cm^{-1}$ at $i$ point time, respectively; $H_{o2270}$ and $H_{o1500}$ is the peak height of 2270 $cm^{-1}$ and 1500 $cm^{-1}$ of uncured CE system, respectively.

The corresponding curing degree values of the PNBRs/BADCy systems are all greater than that of pure BADCY at the same curing technology. It reveals that the addition of PNBRs can promote the cure reaction of BADCY system, especially at a relatively low temperature stage (140°C-160°C).

*Table 3. Curing degree of pure BADCy and PNBRs/BADCy system (3wt% PNBRs) (units: %)*

| **Systems**<br>**Curing technology** | **Curing degree/%**<br>**Pure BADCy** | <br>**PNBRs/BADCy (3 wt%PBNRs)** |
|---|---|---|
| 140$^{o}$C/1h | 42.65 | 59.92 |
| 140$^{o}$C/1h+160$^{o}$C/1h | 78.52 | 91.00 |
| 140$^{o}$C/1h+160$^{o}$C/1h+180$^{o}$C/2h | 90.79 | 94.61 |
| 140$^{o}$C/1h+160$^{o}$C/1h+180$^{o}$C/2h+200$^{o}$C/2h | >99 | >99 |

## 4. Conclusions

Both the flexural and impact strength of the PNBRs/BADCy composites are increased firstly, but decreased with the excessive addition of PNBRs. Compared with that of pure BADCy, the maximum flexural strength and impact strength of the PNBRs/BADCy composites is increased by 27.8 percent and 49.6 percent, respectively. The heat resistance and dielectric properties of the PNBRs/BADCy composites are decreased with the increasing addition of PNBRs. The addition of PNBRs can promote the curing reaction of the BADCY system.

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