PEN/BADCy Interlayer Dielectric Films with Tunable Microstructures via an Assist of Temperature for Enhanced Frequency Stability

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Abstract Low dielectric interlayer films have become an important element to ensure the development of the microelectronics industry. A kind of flexible interlayer dielectric, polyarylene ether nitrile/bisphenol A cyanate ester (PEN/BADCy) film, with good thermal stability and low frequency dependence, has been developed by solution casting method. Herein, materials were designed to incorporate bisphenol A cyanate ester as a part of blend, contributing to the frequency stability and structural integrity. The morphological study combined with electron microscopy revealed the uniform and flexible microstructure information with controllable morphology through self-polymerization of cyanate esters with different prepolymerization time and curing temperatures. The dielectric films could present high thermal stability with $T_g > 180 \, ^\circ{C}$. Significant improvement in the dielectric properties was achieved for the dielectric constant and loss was much stabler than neat PEN over the frequency range from 100 Hz to 5 MHz. When the prepolymerization time was 3 h and final curing temperature reached 230 °C, the dielectric constant and dielectric loss of the films were 3.36 and 0.013 at 100 kHz, respectively. The dimensional stability (CTE = 53.67 × 10$^{-6}$ K$^{-1}$) was confirmed and considered beneficial to use as an interlayer dielectrics.

Keywords Polyarylene ether nitrile; Bisphenol A cyanate ester; Interlayer dielectrics; Tunable microstructures

INTRODUCTION

Semiconductor manufacturers have been working to reduce the transistors size in integrated circuits (ICs) to improve the performance of electronic chips. However, the continued miniaturization in the size of electronic chips used in ultralarge scale integration (ULSI) circuits will lead to interconnection delays, which will become a bottle neck for the development of ULSI circuits.[11] The use of low dielectric constant (low $k$) insulating materials that have a small effect on the transmitted signal can significantly reduce the crosstalk, resistance-capacitance time delay, and power dissipation.[2–5] So far, various candidates of low dielectric materials have been developed based on two parameters, the molecular polarizability and free volume of the material.[6] However, commercially available low $k$ materials are rare due to numerous reliability issues caused by the deteriorated thermomechanical properties, which may cause damage in ICs for accumulated stress.[7,8] Low $k$ materials have different coefficients of thermal expansion compared with coated metals, which can generate serious thermal problems and local tensile stresses. Additionally, repeated thermal cycling can change the molecule and structure of the low $k$ material so that the interlayer dielectric film which is exposed to more thermal cycles may not be able to meet the application needs.

To solve these problems, the improvement of the thermal-resistant low dielectric polymer becomes a common approach. The design of new polymer material involves balancing the competition of cost of production, time consuming, and source of raw materials.[11–14] Mixing polymers is a suitably suggested method for obtaining new polymer materials. It can endow materials with properties better than those of the individual component.[15] Polymer blends are generally easy to process and mold, and have excellent flexibility. Thus, researchers have focused their investigation on the polymer blends, for the extensive application outlooks in the modern electronics industry.[11–14]

It has been revealed from the previous study that polyarylene ether nitrile (PEN) as a kind of high-performance thermoplastic polymer has attracted plenty of attention in dielectric materials.[15–20] It is well-known for possessing superior characteristics, such as excellent mechanical property, thermal stability, radiation resistance, and chemical inertia. However, the dimensional stability and frequency stability of PEN tend to be unstable, which affect the safety and application range of the dielectric interlayer. Cyanate ester resins are the most important high-performance thermosetting poly-
mer in the microelectronics industry for its low moisture absorption, excellent thermal properties, and ultra-low dielectric constant (\(k = 2.6–3.2\)) and dielectric loss (\(\tan \delta = 0.005–0.010\)) values, which is relatively stable over a wide temperature and electric field frequency range compared with bismaleimide (BMI), polyimide (PI), or epoxy resin (EP).\(^{[21–25]}\) Low \(k\) materials consisting of molecules with low polarizability are always subjected to degrade adhesion to the surface, because they are inert, and do not form interfacial films on the target substrate.\(^{[26]}\) Due to the strong polar \(–CN\) groups that can be adjusted by the crosslink degree in PEN and cyanate esters, both of them have good adhesion to many substances. The curing mechanism of neat cyanate resin belongs to autocatalytic reaction process and includes two stages, as shown in Fig. 1. Firstly, the intermediate iminocarbonate is formed by the reaction of cyanate groups with the impurity phenol \(–OH\) group produced by the synthesis of monomer. Secondly, the iminocarbonate can react with two \(–OCN\) groups to form stable triazine ring and regenerate phenol group. In fact, no reaction will occur if absolutely neat cyanate ester is heated without catalyst. The starting reaction is caused by the scheme catalyzed by impurities (ArOH/metal ions).\(^{[26–29]}\)

\[
\begin{align*}
\text{Ar}–\text{OH} + \text{Ar}–\text{OCN} &\rightarrow \text{Ar}–\text{O}–\text{C}–\text{OAr} \\
\text{ArO}–\text{C}–\text{Ar} + 2\text{Ar}–\text{OCN} &\rightarrow \text{ArO}–\text{C}–\text{Ar} + \text{Ar}–\text{OH}
\end{align*}
\]

**Fig. 1** The curing mechanism of neat cyanate.

Trifluoromethyl-containing PEN was used because it can easily be dissolved in not only high-boiling dipole solvents but also low-boiling organic solvents at room temperature.\(^{[30]}\) In this work, we have described our attempt for preparing low-\(k\) interlayer dielectrics composites with a controllable morphology and frequency stability of dielectric properties based on trifluoromethyl-containing PEN and cyanate ester (CE) resin blends by means of solution blending. The effects of the prepolymerization time and final curing temperature on the morphology, thermal stabilities, dielectric properties, and mechanical properties of the blends were studied and are discussed here in detail.

**EXPERIMENTAL**

**Materials**

4,4′-Hexafluoroisopropylidenediphenol (bisphenol AF, 99%) and \(N\)-methylpyrrolidone (NMP, 99%) were purchased from Tianjin Bodi Chemical Holding Co., Ltd., Tianjin, China. 2,6-Dichlorobenzonitrile (DCBN, 99%) was offered from Yangzhou Tianchen Fine Chem Co., Ltd., Yangzhou, China. Potassium carbonate anhydrous (\(\text{K}_2\text{CO}_3\), AR) and toluene (AR) were supplied by Chengdu Kelong chemicals Co., Ltd., Chengdu, China. Bisphenol-A cyanate ester (BADCy, > 99%) with the melting point at 80 °C was offered by Wuxiao Resin Factory, Yangzhou, China.

**Synthesis of PEN**

Polyarylene ether nitrile (PEN) was synthesized through a nucleophilic substitution reaction. Specific experimental steps and descriptions can be found in the reference.\(^{[18]}\) Gel permeation chromatography (GPC): \(M_n = 7.14 \times 10^4, M_w = 4.05 \times 10^4\), polydispersity index (PDI) \((M_w/M_n) = 1.76.\) \(^1\)H-NMR (400 MHz, deuterated chloroform, \(\delta, \text{ppm}\)): 7.451–7.401 (t, 5H), 7.137–7.115 (d, 4H), 6.701–6.680 (d, 2H) (Fig. S1 in the electronic supplementary information, ESI).

**Preparation of PEN/BADCy blends**

Polyarylene ether nitrile (PEN, 1.6 g) and bisphenol-A cyanate ester (BADCy, 0.4 g) were dissolved in \(N\)-methylpyrrolidone (NMP, 16 mL). Different prepolymers were obtained after the continuously stirred at 180 °C for 1, 2, and 3 h, respectively. After prepolymerization, the mixed solution was cast on a piece of clean glass. On the basis of the previous study, the blends were obtained under a preset program for 80 °C/1 h, 100 °C/1 h, 140 °C/1 h, 160 °C/2 h, and 200 °C/2 h.\(^{[19]}\) Then, the curing process was studied in detail shown in Figs. S2 and S3 (in ESI). Thus, the film shaping and curing temperature procedure was executive as shown in Fig. 2. According to the prepolymerization time and heating temperature, samples were marked as 0-200, 1-200, 2-200, and 3-200 with the final curing temperature of 200 °C for 2 h, marked as 0-220, 1-220, 2-220, and 3-220 with the final curing temperature of 220 °C for 3 h, marked as 0-230, 1-230, 2-230, and 3-230 with the final curing temperature of 230 °C for 1 h.

**Characterization**

Gel permeation chromatography (GPC) measurement was carried out on Breeze 2 HPLC system (Waters, USA). The proton nuclear magnetic resonance (\(^1\)H-NMR) spectroscopy was conducted on a JNM-ECA300 spectrometer (JEOL, Japan) in CDCl\(_3\), at a proton frequency of 400 MHz. TA Instrument DSC Q100 equipment (New Castle, USA) was used for the tests of differential scanning calorimetry (DSC) under nitrogen at a flow rate of 50 mL·min\(^{-1}\) with a heating rate of 10 °C·min\(^{-1}\) from room temperature to 300 °C. Scanning electron microscopy (SEM) was performed on the JSM-5900LV (JEOL, Japan) electron microscope. SEM samples were fractured in liquid nitrogen and then sputtered with gold on the fractured surface. Attenuated total internal reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was conducted on Nicolet iS10 (Thermo Fisher,
USA) from 4000 cm⁻¹ to 400 cm⁻¹. Thermogravimetric analysis (TGA) was carried out on a TA Instruments TGA Q50 (New Castle, USA) with a heating rate of 20 °C min⁻¹ from room temperature to 800 °C under nitrogen at a flow rate of 40 mL min⁻¹. Dielectric properties were analyzed with a TH2826/A LCR meter (Tonghui Electronic Co., Ltd., China) from 100 Hz to 5 MHz. The thermal expansion coefficient of the samples was measured by TMA-Q400 (TA instrument, USA) with a 5 °C·min⁻¹ heating rate under nitrogen atmosphere over the range of 25–200 °C. Mechanical properties were recorded on SANS CMT6104 (Shenzhen, China) series desktop electromechanical universal testing machine at room temperature. Tensile strength, tensile modulus, and elongation at break were obtained according to the GB/T 1040.3-2006 standard test method.

RESULTS AND DISCUSSION

DSC of the PEN/BADCy Films Controlled by Synthesis Procedure

Cyanate esters resins are usually cured by a transition metal carboxylate or chelate catalyst in the presence of an active hydrogen cocatalyst, such as nonylphenol. In the present study, there is no catalyst to accelerate the polymerization of the nitrile groups. DSC measurement was carried out to investigate the curing behavior of the PEN/BADCy system. After heat treatment at 200 °C, Tg of the system is 138–150 °C (Fig. 3a). Since the cyanate ester molecule still exits at 200 °C and plays the role of plastication, Tg of the system is much lower than that of neat PEN at this programming temperature. Composite 0-200 shows a higher glass transition temperature compared to 3-200. In the system without prepolymerization, the cyanate monomer gradually evaporates above 150 °C in the programmed temperature process, and the system shows more PEN characteristics. When the final curing temperature is 220 °C (Fig. 3b), all materials show Tg s about 170 °C. As the final curing temperature increases to 230 °C, Tg of the system also rises to 178–180 °C (Fig. 3c). The observed increase of Tg is in consistent with the increase in curing degree of cyanate esters. The higher curing temperature contributes to the formation of triazine ring. Besides, the effect of prepolymerization time on the system can be clearly distinguished. When the final curing temperature is 230 °C, Tg of the prepolymerized blend for 3 h is significantly higher than that of the un-prepolymerized blend.

**Morphology of the PEN/BADCy Films Controlled by Synthesis Procedure**

The morphology of a thermoplastic/thermosetting blend depends on the amount of thermosetting plastic and the curing temperature. When the thermosetting plastic accounts for 90 wt%, the final morphology is the dispersion of thermoplastic particles in the thermosetting matrix. When the thermosetting plastic accounts for less than 80 wt%, a phase inversion structure can be obtained. When the thermosetting plastic content is 80 wt%–85 wt%, various morphologies, including bicontinuous phase structure, double-phase morphology, and ribbon structure, may be formed. Although the morphology is mainly determined by the content of the thermosetting plastic, the curing temperature of the thermosetting plastic will also affect the morphology of the blend. Various elements of thermodynamics and kinetics affect the phase separation in the curing process, so the solubility of the blend is constantly changed to achieve the best heterogeneous structure.

The image contrast of SEM shows the structure information of matters. As shown in Fig. 4, the morphology of the PEN/BADCy films varies greatly, highlighting the effect of the prepolymerization time and final curing temperature. Figs. 4a, 4b, 4e, and 4c depict the SEM images of composite films finally cured at 220 °C with different prepolymerization time. When the films are prepolymerized for 0 and 1 h, BADCy forms a large number of isolated domains (Figs. 4a and 4b), where some air voids exist in the gaps on the interfaces between the spherical BADCy and the PEN matrix. When
the blends are pre-polymerized for 2 h, isolated domains partly connect with each other. Note here that the partly interconnected structure is a kind of co-continuous structure (Fig. 4e). When the time of prepolymerization reaches 3 h, the PEN/BADCy blend forms a full fusion system, as shown in Figs. 4(c). Figs. 4(a), 4(b), 4(e), and 4(c) show a tendency to shift from isolated dual micro-domains to a quasi-continuous phase morphology.

The composition and prepolymerization time of the film affect the morphology and the phase separation mechanism of the film. The phase separation mechanism depends on the viscosity of the medium in the initial phase of phase separation, which is determined by the amount of thermoplastic and curing temperature, and is closely related to the final morphology. Because of the high viscosity in the system for the 80 wt% content of PEN, the PEN/BADCy blends display no phase separation through the nucleation and growth to form PEN particle structure. Phase separation occurs through spinodal decomposition (SD) to form the combined morphology having the BADCy particle structure disperse in PEN matrix. At the early stage of prepolymerization, the non-reactive PEN/BADCy mixture is homogeneous at the prepolymerization temperature. As the prepolymerization reaction proceeds, the system thrusts into the two-phase regime, and the phase separation takes place according to SD. The prepolymerization material has the two-phase morphology fixed at the late stage of SD. Phase separation also depends on the cross-linking chemical reaction. The crosslink degree of cyanate increases along with the extension of prepolymerization time. Meanwhile, at the prepolymerization temperature of 180 °C, the molecular chain of PEN (T_g is 173 °C) starts to move, and the diffusion and migration ability becomes stronger. In this case, the PEN chains have better interfacial interaction with cross-linked cyanate to form a partially fused morphology or even a quasi-continuous morphology. Fig. 5 shows the schematic representation of the morphology changes from phase separation to phase fusion.

Moreover, to elucidate the effect of the final curing temperature on the morphology of the films, Figs. 4(d)−4(f) illustrate the changes observed for the PEN/BADCy films at different temperatures. As can be appreciated from the SEM images, small spherical BADCy microstructures are seen inside the PEN rich matrix at 200 °C and some co-continuous phase structures are observed at 220 °C. However, it is found that, at a higher final curing temperature, 230 °C, BADCy isolated domains appear again. On the one hand, the curing process is accelerated by the increasing temperature, and then the duration time of phase separation process will be reduced at the higher temperature (from Fig. 4d to Fig. 4e). On the other hand, the PEN/BADCy films belong to a lower critical solution temperature system, and the Flory-Huggins interaction parameter is proportional to curing temperature; the
driving force of phase separation increases with temperature in terms of thermodynamics, making the phase separation process being expedited at the higher temperature (from Fig. 4e to Fig. 4f).\cite{16} As a result, proper curing temperature and prepolymerization time assist to form homogeneous PEN/BADCy films.

**ATR-FTIR Spectra of PEN/BADCy Films**

Chemical structures of PEN/BADCy films at different curing stages were monitored by attenuated total internal reflectance fourier transform infrared spectroscopy (ATR-FTIR), as shown in Fig. 6. The bands at 1600, 1577, 1507, and 1460 cm\(^{-1}\) belong to the skeleton vibration of benzene rings.\cite{15} Those at 831 and 731 cm\(^{-1}\) are the out-of-plane flexural vibration absorption bands of C–H on benzene ring.\cite{19} The absorption band emerging at 1239 cm\(^{-1}\) is attributed to skeleton vibration of the ether.\cite{16} These results indicate the formation of aryl ether (Ar–O–Ar). The absorption band at 2232 cm\(^{-1}\) corresponds to the stretching vibration of cyano groups (–CN). On the one hand, at the curing temperature of this experiment, the –CN group on the side chain of PEN scarcely undergoes crosslinking, for in the case of phenol hydroxyl as catalyst, the polymerization of –CN on the PEN side chains occurs about 300 °C.\cite{19} On the other hand, even if the cross-linking reaction will reduce the cyano group of the cyanate part, observation in the spectrum is inconspicuous for the small amount of cyanate ester (20 wt%). Therefore, the intensity of the bands corresponding to the vibration of –CN groups has no significant change going from (a) to (d). Most importantly, weak band at 1380 cm\(^{-1}\) belongs to the stretching vibration of –C=–N= originated from the self-polymerization of cyanate esters to form triazine ring.\cite{19} The relevant reaction process is shown in Fig. S4 (in ESI).

![Fig. 6 ATR-FTIR spectra of PEN/BADCy films at different curing stages: (a) 3-140, (b) 3-200, (c) 3-220, (d) 3-230.](image)

**Thermal Stability of the PEN/BADCy Films**

The thermal degradation properties of the PEN/BADCy films cured at different temperatures were investigated by TGA under nitrogen atmosphere at the heating rate of 20 °C·min\(^{-1}\) from room temperature to 800 °C, as shown in Fig. 7. The main results, including the decomposition temperatures at the weight loss of 5% (\(T_{5\%}\)), the decomposition temperatures at the weight loss of 10% (\(T_{10\%}\)), the maximum decomposition temperatures (\(T_m\)), and the char yield at 800 °C, are listed in Table 1.

![Fig. 7 (a) TGA curves and (b) DTG curves of PEN/BADCy films cured at different temperatures, (c) schematic representation of \(S_1\), \(S_2\), and \(S_3\).](image)

| Sample | \(T_{5\%}\) (°C) | \(T_{10\%}\) (°C) | \(T_m\) (°C) | \(T_{m2}\) (°C) | Char yield (%) | IPDT (°C) |
|--------|-----------------|-----------------|-------------|-----------------|-----------------|-------------|
| 2-200  | 297.70          | 325.63          | 319.46      | 547.84          | 45.24           | 1432        |
| 2-220  | 364.60          | 445.57          | 348.20      | 549.36          | 51.03           | 1649        |
| 2-230  | 374.71          | 460.76          | 350.11      | 550.11          | 51.58           | 1672        |

Table 1. According to the results, the decomposition temperatures at the weight loss of 5% vary from 297 °C to 374 °C and the decomposition temperatures at the weight loss of 10% vary from 325 °C to 460 °C, indicating that the higher the curing
treatment is, the greater the degree of crosslinking of the films will be. Moreover, by controlling the time of prepolymerization, the char yield at 800 °C (Fig. S5 in ESI) was varied. Blends without prepolymerization have the lowest char yield because of the low polymerization reaction rate and conversion.

Therefore, proper prepolymerization time and final curing temperature are critical in the preparation of materials containing thermosetting resins. The differentiation curves, shown in Fig. 7(b), clearly reveal the changes of weight loss rate of each treating temperature on the composite films. The double maximum decomposition appears at about 350 and 550 °C, corresponding to the decomposition processes of BADCy and PEN. The second maximum decomposition temperatures ($T_{m2}$) does not change with increasing final curing temperatures, which stems from the decomposition of PEN dominated by initial structure. However, the first maximum decomposition temperatures ($T_{m1}$) exhibit an uptrend with the increasing final curing temperatures because of the greater crosslinking degree of BADCy.

To estimate the inherent thermal stability of the polymer composites, the integral procedure decomposition temperature (IPDT) was employed.\(^{39}\) IPDT was calculated from:

$$\text{IPDT (°C)} = A^*K^*(T_{\text{final}} - T_{\text{initial}}) + T_{\text{initial}} \quad (1)$$

$$A^* = \frac{S_1 + S_2}{S_1 + S_2 + S_3} \quad (2)$$

where $A^*$ is the area ratio of total experimental curve defined by the total TGA thermogram. $T_{\text{initial}}$ is the initial experimental temperature, and $T_{\text{final}}$ is the final experimental temperature. In our study, $T_{\text{initial}}$ and $T_{\text{final}}$ were 50 and 790 °C, respectively. $A^*$ and $K^*$ can be calculate by Eqs. (2) and (3). Fig. 7(c) shows a representation of $S_1$, $S_2$, and $S_3$. The IPDT values cured at different temperatures are 1432, 1649, and 1672 °C, respectively, as listed in Table 1. As can be seen, IPDT values rise as the final curing temperatures increase, which is because of the cure degree of BADCy in the composite films, including the intermolecular polymerization of cyanate monomers to form triazine rings.

**Dielectric Properties of the PEN/BADCy Films Controlled by Synthesis Procedure**

The dielectric properties of films prepared by different prepolymerization time and different cure temperatures versus the operating frequency from 100 Hz to 5 MHz are shown in Fig. 8. It is observed that over the whole frequency range, the dielectric constant of all films decreases as the frequency increases. The reason is that the electronic, interfacial, and orientation polarization lag behind the change of the electric field.\(^{17}\) Alternatively, the dielectric properties vary greatly in terms of the processing condition: (1) the value of dielectric constant decreases from 3.56 to 3.36 (Fig. 8a) and the dielectric loss

![Fig. 8 Dielectric properties of PEN/BADCy films (a, b) pre-polymerized for different time and (c, d) cured at different temperatures.](https://doi.org/10.1007/s10118-020-2417-7)
decreases from 0.016 to 0.013 (Fig. 8b) at 100 kHz as prepolymerization time increases from 0 h to 3 h; (2) the value of dielectric constant decreases from 3.65 to 3.36 (Fig. 8c) and the dielectric loss decreases from 0.031 to 0.014 (Fig. 8d) at 100 kHz as the final curing temperature increases from 200 °C to 230 °C. When the prepolymerization time reaches 2 h and the final curing temperature is 230 °C, the dielectric constant of the film is equivalent to that of neat PEN. The decrease of the dielectric constant is mainly due to the longer prepolymerization time and higher final curing temperature, which is beneficial to the self-polymerization of cyanate esters to form triazine ring, resulting in the decrease of the amount of cyano groups in the films. When the frequency is higher than 10^4 Hz, the dielectric constant of 2-230 is a little bit lower than that of 3-230, for air voids exist in the gaps on the interfaces between spherical cyanate esters and the PEN matrix, shown in Fig. 4(e).

At the same time, it is notable from Fig. 8(b) that the dielectric loss of neat PEN in the low frequency region (<10^3 Hz) is much higher than that of the blend films, which is influenced by the interfacial polarization (also known as Maxwell-Wagner-Sillars effect). Cyanate ester particles hinder the thermal movement of PEN chains, reducing the thermal expansion of the blend. It should be noted that prepolymerization time and final curing temperature play an important role in determining the interfacial properties between PEN and BADCy, as discussed above.

### Coefficient of Thermal Expansion of Neat PEN and PEN/BADCy Film

Coefficient of thermal expansion (CTE) is an important index parameter to materials that defines the dimensional stability of engineering structures affected by temperature variations. The linear coefficient of thermal expansion was calculated from the slope of the dimension change versus temperature curve using Eq. (4):

\[
\alpha = \frac{dL}{dT} \frac{1}{L_0} \tag{4}
\]

where \(dL\) is the change in dimension, \(dT\) is the change in temperature, and \(L_0\) is the initial length of the specimen. The reversing curves of neat PEN and PEN/BADCy marked as 3-220 were characterized by TMA, as shown in Fig. 9. The CTE of PEN/BADCy is 53.67 × 10^-6 K^-1, which is 18% lower than that of neat PEN, whose CTE is 65.47 × 10^-6 K^-1. A detailed comparison of CTE of PEN/BADCy blends and other high performance polymers are listed in Table 2. Clearly, CTE of the PEN/BADCy blends is almost the same with those of the polyimide and polyphenylene sulfide.

However, CTE of the cyanate ester is higher than that of the PEN/BADCy blend. In fact, the parameter of CTE is strongly influenced by the degree of conversion and cross-link density of cyanate. It has been demonstrated that thermophysical properties, including CTE and \(T_g\), are significantly affected by the interfacial properties of composites. Strong interactions between blends will promote better ther-

### Mechanical Properties of the PEN/BADCy Films Controlled by Synthesis Procedure

The mechanical properties of PEN/BADCy films with different prepolymerization time and final curing temperatures are presented in Fig. 10. They are the average values of five measurements performed on each samples. The tensile modulus of the films tends to increase as the prepolymerization and final curing temperatures increase (Fig. 10b). For instance, the tensile modulus of 0-200 is 0.79 GPa lower than that of the 3-230 sample. Simultaneously, the tensile strength and elongation at break of the films show a decreasing trend following the increase of prepolymerization and final curing temperature. This occurrence is also noticeable visually by a decrease in tensile strength shown in Fig. 10(a). These observations echo with the observed increase in cyanate esters self-polymerization with the increasing prepolymerization and final curing temperature, resulting in a stronger interfacial force between the PEN polymer matrix and cyanate that weakens the movement ability of the PEN chains. A decrease in elongation at break in this system accounts for low elastic deformation, which further results in decrease in tensile strength. However, PEN/BADCy films still maintain good mechanical properties.

### CONCLUSIONS

In summary, PEN/BADCy blends with different morphologies ranging from isolated dual micro-domains to quasi-continuous phase morphology were fabricated by solution casting met-
which is 18\% lower than that of the neat PEN. The results from this work extend the application scope of our thermoplastic resin, PEN, for dealing the reliability issues associated with emerging microminiaturized electronic devices.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://dx.doi.org/10.1007/s10118-020-2417-7.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (Nos. 51603029 and 51773028), China Postdoctoral Science Foundation (No. 2017M623001), and National Postdoctoral Program for Innovative Talents (No. BX201700044).

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Fig. 10  Mechanical properties of PEN/BADCy films: (a) tensile strength; (b) tensile modulus; (c) elongation at break.
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