Materials Research Express

PAPER

Preparation and properties of MDA-BAPP-BTDA copolyimide/18-crown ether-6 supramolecular films with inclusion structure and ultralow dielectric constants

Chunguang Xiao¹, Duxin Li¹, Feng Lang¹, Yu Xiang¹, Yi Lin¹ and Baoli Ou²

¹ State Key Laboratory of Powder Metallurgy, Central South University, Changsha, People’s Republic of China
² School of Materials Science and Engineering, Hunan University of Science and Technology, Xiangtan, People’s Republic of China

E-mail: liduxin6404@csu.edu.cn

Keywords: copolyimide, supramolecular films, crown ether, inclusion structure, dielectric constant, mechanical properties

Abstract

In order to obtain polyimide composites with ultra-low dielectric constant, a series of MDA-BAPP-BTDA copolyimides/18-crown ether-6 (CPI/18-CE) supramolecular films with inclusion structure were prepared. The effects of 18-CE on CPI’s thermal, mechanical, dielectric and water absorption properties were investigated. The inclusion rate of 18-CE to CPI backbone was ~50%. The introduction of 18-CE slightly reduced the thermal properties of CPI/18-CE supramolecular films, but greatly improved their mechanical, dielectric and hydrophobic properties. The tensile strength, young’s modulus and elongation at break of CPI/18-CE supramolecular films were maximally increased by 21.8%, 34.1% and 92.9% respectively. Meanwhile their dielectric constant, dielectric loss and water absorption were as low as 2.10, 0.007 and 0.63%, respectively. In summary, CPI/18-CE supramolecular films possess excellent dielectric properties and broad application prospect in the field of microelectronics.

1. Introduction

With the rapid development of microelectronics technology, the requirements for integrated circuits of electronic components were getting higher and higher. The reduction of the size and interconnection spacing of advanced integrated components makes it easy to cause the delay of signal transmission and power loss, which shortened the life of integrated components. Therefore, it was urgent to develop a new type of insulating material with low dielectric constant ($\varepsilon < 3.0$) and dielectric loss ($\tan \delta < 0.01$) to replace the traditional SiO$_2$ material [1, 2]. In recent years, aromatic polyimide (PI) was considered as candidate material, which had been widely concerned by researchers due to its outstanding dimensional stability, thermal and mechanical properties [3–7]. However, the rigidity of molecular chains and strong intermolecular interactions made PI matrix insoluble in ordinary solvents or difficult to melt, which was difficult to process. especially, the dielectric constant of PI composites was still too high to meet the requirements of microelectronic application.

In order to obtain PI insulating materials with excellent processing performance and low dielectric constants and dielectric loss, recently, researchers had done a lot of works, which mainly focused on the modification of PI molecular structure, the doping of inorganic fillers in PI matrix and the preparation of porous PI films [8–13]. For example, PI materials with low dielectric constant could be obtained by introducing an appropriate number of flexible groups, asymmetric structural units, asymmetric spiral structural units or the large volume substituent into PI main chain [14–16]. The methyl and methylene belong to typical flexible groups, they could not only prevent the electron transition and the charge dispersion of intramolecule, but also reduce the rigidity and tight accumulation degree of PI main chain, reduce the interaction between molecular chains, reduce the density of PI composites. At present, the main challenge for researchers was how to prepare PI insulating materials with low dielectric constants but without affecting other key characteristics, such as mechanical, thermal properties and hydrophobicity. Although the introduction of C–F bond with low polarization rate or
microporous structure in the PI matrix can greatly reduce dielectric constant of PI composites [17–19], which imposed a negative effect on their thermal and mechanical properties. Moreover, it could also be difficult to balance the relationship between mechanical properties and dielectric constants of PI composites by introducing large-volume rigid non-planar group on the PI molecular chain [20], the complexity and high cost of this preparation method limited their application. While in the aspect of compound modification, the dielectric constant could also be greatly reduced by doping nanoparticles with porous structure in PI matrix [21], but the dispersion of nanoparticles in PI matrix and the compatibility between nanoparticles and PI matrix would seriously affect its comprehensive performance.

Additionally, PI composites with low dielectric constant could also be obtained by nesting crown ether (CE) ring with low polarizability onto the PI main chain, which form supramolecular inclusion structure like necklace [22], even the comprehensive properties of PI composites could be regulated by introducing different CE. Yang Li et al prepared a series of PMDA-ODA PI/CE supramolecular films, and investigated the effect of CE molecules on PI main chains, as well as the structure, thermal properties, mechanical properties, dielectric properties and hydrophobic properties of PI supramolecular films [23]. The results indicated that the introduction of CE slightly reduced the thermal properties of PI, improved the tensile strength and young’s modulus, meanwhile reduced the dielectric constants and hydrophobicity of composites. But their minimum dielectric constants were still above 3.0 at 1.0 MHz, which was caused by strong molecular chain rigidity of homopolyimide (HPI) prepared. Nowadays, The design and preparation of PI composites using copolyimide (CPI) as matrix was the development trend of future research and industrial application. CPI was superior in structure design and performance control compared to HPI. The structure and performance of the CPI composites could be adjusted by selecting different diamines and dianhydrides, changing the feeding molar ratio and feeding sequence of monomers respectively [24–28]. Additionally, CPI molecular chains was difficult to accumulate tightly because of the different molecular thermal motion and orientation polarization ability of different chain units, thus having lower density and lower dielectric constants compared to HPI, therefore, CPI had lower density and dielectric constant compared to HPI [29]. For this reason, CPI as the high performance gas separation membrane materials had also attracted the great interest of many researchers [30–36].

To sum up, we designed and synthesized a series of MDA-BAPP-BTDA CPI/18-crown ether-6 supramolecular films containing the flexible groups such as −O−, −CH3, −CH2− and −C(=O)− in hope of
obtaining CPI composites with ultralow dielectric constant. The preparation process and mechanism was shown in scheme 1. Meanwhile, the effects of 18-CE on the thermal, mechanical, dielectric and hydrophobic properties of CPI supramolecular films were investigated.

2. Experimental section

2.1. Materials

1-Methyl-2-pyrrolidinone (NMP, China National Medicine Group, Shanghai, China) was purified by vacuum distillation over CaSO₄. Prior to use; 4, 4′-methylenebisphenol; 4-aminophenoxyphenyl-Propane (BAPP, Suzhou Yinsheng Chemical Co., Ltd, China) were recrystallized from ethanol and then dried in a vacuum at 80 °C for 5 h. 3, 3′, 4, 4′-Benzophenonetetraacryloxylic dianhydride (BTDA, Alfa Aesar, Tianjin, China) was recrystallized from acetic anhydride/acetic acid and then dried at 140 °C for 10 h in vacuum; 18-CE (Shanghai Macklin Biochemical Co., Ltd, China) were individually purified by distillation. Other reagents and solvents were commercially available and used without further purification.

2.2. Preparation of CPI/18-CE supramolecular films

The preparation procedure for CPI/18-CE supramolecular films is illustrated in scheme 1. CPI/18-CE supramolecular films from MDA, BAPP, BTDA and 18-CE was prepared as follows: Briefly, MDA (2.5 mmol), BAPP (5.0 mmol) and NMP (15 ml) were added into a three-neck flask and continuously stirred for 1 h under N₂ protect, a certain amount of 18-CE was subsequently added into the flask and stirred for 1.5 h at room temperature, then BTDA (7.5 mmol) was added in three portions with a time interval of 0.5 h between batches, after finished, the mixture was continued to stir for 12 h at room temperature and a viscous homogeneous co-polyamic acid (CPAA)/18-CE solution with a solid content of ~20.0 wt% was obtained. The solution was then casted onto a precleaned glass plate and thermally dried in vacuum at 80 °C for 3 h to remove most of the solvent, and then subsequently cured at 80 °C for 2 h, 120 °C for 1 h, 180 °C for 1 h, 250 °C for 1 h, and 300 °C for 2 h in furnace to achieve full imidization. After that, the plate was soaked into boiling water and CPI/18-CE supramolecular films peeled off from the glass surface. In this way, a series of CPI/18-CE supramolecular films (80 ~ 120 µm thickness) were obtained. For comparison, the control experiment was represented by adding 18-CE of 0.4 or 0.5 times the molar amount of BTDA with different addition order. In other words, pure CPAA solution was synthesized prior to the addition of 18-CE.

2.3. Measurements

A nuclear magnetic resonance (1H NMR, Bruker AVANCEIII 500 MHz) and a fourier transform infrared spectroscopy (FTIR, Nicolet 6700) over the range of 4000 to 400 cm⁻¹ with a KBr disk or thin film were used to identify the chemical structures of CPI supramolecular films. X-ray diffraction (XRD) studies were performed on a Rigaku D/Max 2550 instrument with CuKa radiation at 40 kV and 250 mA. The wide-angle diffraction patterns in the 2θ range from 5° to 60° were collected with a step size of 0.02°, at a scanning rate of 8° min⁻¹. Thermogravimetric analysis (TGA) was measured by a NETZSCH STA 449C thermal analyzer instrument at a rate of 10 °C min⁻¹ from 50 to 800 °C under argon gas protection. Tensile tests were performed by a UTM5504 microcomputer control machine (SUNS Co., Ltd, Shenzhen, China) at room temperature with a drawing rate of...
5.0 mm min$^{-1}$ in accordance with ISO 527-2:2012. More than six specimens were tested for each supramolecular film and the mean value was adopted for each batch. Sample’s water absorption (wt%) was obtained by comparing dry samples and those soaked in distilled water for 24 h at 23 °C according to ASTM D570-98 (2010) standard. Sample’s capacitance ($C$) and dielectric loss ($\tan \delta$) of CPI supramolecular films was tested at room temperature using a precision impedance analyzer (WAYNE KERR 6500B) with dielectric test fixture in the frequency range of $10^2$–$10^7$ Hz, in the process, the samples were cut to dimensions of 80 mm × 80 mm. The dielectric constant ($\varepsilon_r$) was calculated with the following equation:

$$\varepsilon_r = \frac{C \times d}{\varepsilon_0 \times S}$$

Where $C$ is the sample’s capacitance, $d$ is the sample’s thickness, $S$ is the electrode area, and $\varepsilon_0$ is $8.854 \times 10^{-12}$ F m$^{-1}$.

### 3. Results and discussion

#### 3.1. Structural characterization of CPI supramolecular films

As illustrated in scheme 1, initially, MDA/BAPP/18-CE inclusion complex was formed via molecular self-assembly and hydrogen bonding interaction between amino groups of diamine monomers (MDA and BAPP) and oxygen atoms of 18-CE. The chemical shifts of hydrogen atoms were shown in figure 1. In the dimethyl sulfoxide mixed solution of MDA and BAPP, the chemical shift of amino groups hydrogen from MDA and BAPP located at 4.8057 ppm, 4.9560 ppm respectively. After the addition of 18-CE, the two chemical shift peaks disappeared, and a new chemical shift peak was observed at 4.8986 ppm (Inset N in figure 1). However, other hydrogen atoms’ chemical shift of MDA, BAPP and 18-CE did not changed, which indicated that the two kinds of diamines and 18-CE constituted a new whole by hydrogen bonds. In other words, the diamine reacted with 18-CE to form the inclusion complex. Theoretically, three kinds of complexing fragments were formed (as shown in scheme 1, such as Complex 1, Complex 2 and Complex 3). It can be inferred that the surrounding environment of amino groups in the three kinds of inclusions was the same, so which showed a single peak in $^1$H-NMR spectra.

CPI/18-CE supramolecular films were not suitable for running the $^1$H-NMR analysis due to the insolubility of supramolecular films in ordinary organic solvents, so we tested their precursor co-polyamic acid (CPAA). A small amount of pure CPAA and CPAA-18-4 solution were dried for 5 h at 80 °C in vacuum, and light yellow colloidal solids were obtained. In the control experiment, pure CPAA solution was synthesized prior to the addition of 18-CE, The molar amount of 18-CE added was 0.4 times that of BTDA, the $^1$H NMR spectra of pure CPAA and CPAA-18-4 were shown in figure 1. The chemical shift of CPAA’s carboxyl group hydrogen was above 10.0000 ppm, and the isomerism phenomenon carboxyl groups on CPAA main chain caused the chemical shift of carboxyl hydrogen to show multiple peaks. When the 18-CE was nested on the CPAA main chain, the chemical shift peaks of carboxyl group hydrogen were moved to low field from the initial quintet peaks.

![Figure 1](image-url)

Figure 1. $^1$H-NMR spectra (Bruker-500MHz, DMSO-$d_6$): (a) the mixture of BAPP (6.00 g.L$^{-1}$) and MDA (1.46 g.L$^{-1}$), (b) the mixture of BAPP (6.00 g.L$^{-1}$), MDA (1.46 g.L$^{-1}$) and 18-CE (2.90 g.L$^{-1}$), (c) CPAA (14.54 g.L$^{-1}$), (d) CPAA-18-4 (the precursor of CPI-18-4, 17.44 g.L$^{-1}$), (e) the mixture of CPAA (14.54 g.L$^{-1}$) and 18-CE (2.90 g.L$^{-1}$) (control experiment).
for CPAA to heptet (10.4134 ~ 10.5741 ppm) for CPAA/18-CE (Inset M in Figure 1), while for control experiment, the chemical shift only was consistent with pure CPAA, which implied that CPAA and 18-CE formed an inclusion structure similar to necklace.

Figure 2 showed the FT-IR spectra of Pure CPI, representative CPI-18-4 and its control experiment. As can be seen from Figure 2, the characteristic absorption bands at near 1721 and 1778 cm$^{-1}$ are assigned to symmetrical and asymmetrical C=O stretching of the imide ring on pure CPI backbone, and the bands at near 722 cm$^{-1}$, 1380 cm$^{-1}$, 3070 cm$^{-1}$, 3489 cm$^{-1}$ are assigned to C=O bending, C–N stretching, –CH$_3$ stretching and the hydrogen bond interaction between 18-CE and CPI backbone, respectively. The corresponding characteristic absorption bands of –CO–NH– on CPAA backbone at near 1660 cm$^{-1}$ and 2500 ~ 3000 cm$^{-1}$ were not appear in Figure 2(a) [24], which indicated that the thermal imidization reaction of CPAA was complete. After the 18-CE was nested on the CPI backbone, the FT-IR spectrum of CPI-18-4 showed a new characteristic absorption band at near 2900 cm$^{-1}$ corresponding to the –CH$_2$– stretching of 18-CE. Meanwhile, the characteristic absorption bands of C=O at near 722 and 1721 cm$^{-1}$ for CPI demonstrated a blue shift to 717 and 1717 cm$^{-1}$ for CPI-18-4, which further confirmed the inclusion structure between 18-CE and CPI backbone. In control experiment, after the mixture of pure CPAA and 18-CE was totally thermol-cured, the CPI film obtained exhibited same characteristics as pure CPI. The characteristic absorption bands corresponding to –CH$_2$– of 18-CE were not appeared in Figure 2(c), and there was no blue shift phenomenon in the C=O.
characteristic absorption band of the imide ring on the CPI backbone, which indicated that 18-CE might completely evaporate during the thermal imidization process.

To sum up, CPI/18-CE supramolecular films with inclusion structure were successfully prepared, the inclusion rate of 18-CE on CPI main chain would be calculated and discussed in detail in the later thermogravimetric analysis section.

XRD patterns were employed to investigate the crystalline structures of supramolecular films. Figure 3 showed the XRD contrast of CPI supramolecular films with different 18-CE content. As can be seen from figure 3, they all presented very large diffraction dispersion peaks at $2\theta = 5 \sim 50^\circ$, which meant that these CPI supramolecular films had typical amorphous structure. It could also be seen that the content of 18-CE did not affect the peak strength of these supramolecular films, which meant that the introduction of 18-CE did not affect the original amorphous structure of CPI supramolecular films, and 18-CE was evenly distributed in supramolecular films without accumulation. All CPI supramolecular films had the same homogeneous amorphous structure [37]. Nevertheless, the 18-CE content affected the peak width, the XRD Diffraction peak width of CPI supramolecular films increased slightly with the increasing of 18-CE content, which meant that the introduction of 18-CE decreased the crystallization ability of CPI supramolecular films and played a similar role of ordinary plasticizers to some extent.

3.2. Thermal properties of CPI/18-CE supramolecular films

18-CE belong to organic small molecular compounds with low boiling point, volatile evaporation and poor thermal stability, and their boiling points are below 220 °C [23]. Therefore, 18-CE in the free state would escape from the solution in the form of evaporation or decomposition during the thermal imidization process of precursor CPAA. Figure 4 showed the TGA curves of CPI/18-CE supramolecular films with different 18-CE contents. For pure CPI film, no obvious weight loss was found on its TGA curve below 500 °C; for CPI/18-CE supramolecular films, a new thermal decomposition stage at between 280 °C and 500 °C was appeared, which was mainly from the thermal decomposition of 18-CE, and thermal weight loss above 500 °C was mainly from the thermal decomposition CPI matrix. Therefore, the introduction of 18-CE did not affect the intrinsic structure and thermal properties of CPI backbone.

The thermal properties of polymer composites were the research hotspot of high-tech applications, especially when they were employed as heat-resistant materials for microelectronic devices or aerospace applications. Thermal stability of CPI composites was usually reflected by 5% or 10% thermal weight loss temperature. The related data of $T_{5\%}$ (the temperature for 5% weight loss), $T_{10\%}$ (the temperature for 10% weight loss) and $RM\%$ (the percentage of residual mass at 800 °C) for CPI/18-CE supramolecular films with different 18-CE content was shown in table 2. Their thermal stability slightly decreased with the increase of 18-CE content. When the molar amount of 18-CE added is 0.4 times that of BTDA, the $T_{5\%}$, $T_{10\%}$ and $RM\%$ of CPI-18-4 obtained are 468.4 °C, 509.2 °C and 43.3% respectively, which decreased by 38.7 °C, 16.2 °C and 16.2% compared with the $T_{5\%}$ (507.1 °C), $T_{10\%}$ (525.4 °C) and $RM\%$ (39.5%) of pure CPI respectively, but these CPI/18-CE supramolecular films still possess excellent thermal stability.

As mentioned earlier, the thermogravimetry stage of CPI/18-CE supramolecular films at about 280 ~ 500 °C is generated by the decomposition of 18-CE. Therefore, the content of 18-CE in CPI supramolecular films can be
calculated according to the thermal weight loss curve. In this study, inclusion rate of 18-CE (IRCE) is defined as 18-CE’s content in CPI supramolecular films divided by its original dosage [38–40], and calculated with the following equation (1):

$$\text{IRCE} = \left( \frac{W_{\text{MDA}} + W_{\text{BAPP}} + W_{\text{BTDA}} - \frac{2W_{\text{BTDA}} \times M_{\text{H}_2\text{O}}}{M_{\text{BTDA}}}}{W_{\text{CE}} \times (1 - X)} \right) \times 100\%$$

Here, X stands for the weight loss rate of 18-CE in the CPI supramolecular films obtained from thermal weight loss curve; $W_{\text{MDA}}, W_{\text{BAPP}}, W_{\text{BTDA}}$ and $W_{\text{CE}}$ stand for the initial addition amount of MDA, BAPP, BTDA and 18-CE respectively; $M_{\text{H}_2\text{O}}$ and $M_{\text{BTDA}}$ stand for the relative molecular weight of H$_2$O (thermal imidization dehydration reaction) and BTDA respectively. The sample preparation experiment with different 18-CE content was repeated three times in NMP solvent, and the average value was obtained. The related resulting data was shown in figure 5.

Table 2. Thermal decomposition datasheet of CPI/18-CE supramolecular films.

| Samples | T$_{5\%}$,°C$^{-1}$ | T$_{10\%}$,°C$^{-1}$ | RM,% |
|---------|-------------------|-------------------|------|
| CPI     | 507.1             | 525.4             | 59.5 |
| CPI-18-1| 487.8             | 517.1             | 54.3 |
| CPI-18-2| 476.3             | 515.3             | 51.2 |
| CPI-18-3| 475.0             | 514.2             | 48.8 |
| CPI-18-4| 468.4             | 509.2             | 43.3 |

T$_{5\%}$ stand for the temperatures for 5% weight loss, T$_{10\%}$ stand for the temperatures for 10% weight loss, and RM/ stand for the percentage of residual mass at 800 °C.

As you could see from figure 5, the content of 18-CE in CPI supramolecular films increased linearly with the increase of its addition amount, and the IRCE value stabilized at about 50%. During the reaction process, two diamine monomers MDA, BAPP are mixed and added into the reaction solution. After reacted with 18-CE, three kinds of inclusion complexes (Complex 1, Complex 2 and Complex 3) generated, whose structures are shown in scheme 1. We marked the amino group N atom of MDA and BAPP in complex 1 as ‘a’ and ‘b’ respectively, in complex 2 as ‘a’ and ‘a’ respectively, and in complex 3 as ‘b’ and ‘b’ respectively. When BTDA reacted with three kinds of inclusion complexes above respectively, the successful nesting on the CPAA backbone of 18-CE depended on the direction of BTDA’s attack. Take the reaction of BTDA and complex 1 as an example, when BTDA is on the same side as MDA in complex 1 molecular structure, there are two situations for the reaction (as shown in scheme 1). If BTDA attacks the amino group atom ‘b’ of BAPP preferentially, the CPAA backbone will pass through 18-CE ring like a necklace. Consequently, 18-CE ring will be stuck on CPI molecular backbone and construct a very stable inclusion structure after thermal imidization; If BTDA attacks the amino group atom ‘a’ of MDA on the same side preferentially, there is no chance for CPAA backbone to pass through 18-CE ring, thereby forming separate CPAA molecular and free 18-CE in reaction solution. Subsequently, the
free 18-CE will volatilize or decompose during the subsequent thermal imidization process. As an asymmetric structure complex 1, theoretically, BTDA is on the same side of MDA due to the larger molecular volume of BAPP compared to MDA in complex 1. So the reaction probability of BTDA-BAPP segment on CPAA molecular chain passing through 18-CE ring is greater than that of BTDA-MDA segment, and the total molar amount of BAPP/BTDA/18-CE fragment should be bigger than that of MDA/BTDA/18-CE fragment in CPAA/18-CE molecular chain. Nevertheless, BTDA could react with amino group from another side to pass through 18-CE ring, or reacts with the ipsilateral amino group, in which situation is more priority and does not affect the reaction system. In fact, the single chemical shift peak in $^1$H NMR spectra (Inset N in figure 1) of complex 1 indicates that two diamines have identical chemical environment, thus the reaction probability between BTDA and amino group ‘a’ or ‘b’ is equal, and ~50% inclusion rate of 18-CE in CPI supramolecular films verifies this. For the complex 2 and complex 3 with symmetrical structures, theoretically, the reaction probability between BTDA and amino group ‘a’ or ‘b’ is equal. The relevant $^1$H NMR data well explained the reaction mechanism of scheme 1.

### 3.3. Mechanical properties of CPI/18-CE supramolecular films
The mechanical properties are an important parameter in the practical application of polymer composites, which includes tensile strength, Young’s modulus and elongation at break. Figure 6 present the effects of different 18-CE content on the mechanical properties of CPI supramolecular films, and the relevant data is shown in table 3. As can be seen from figure 6, CPI/18-CE supramolecular films exhibited more excellent mechanical properties than pure CPI. Their tensile strength, Young’s modulus and elongation break increase gradually with the content of 18-CE, and exhibits a gradual upward trend of Yang’s modulus with the increase content of 18-CE, while the tensile strength and break at elongation reach a relatively stable extreme value after a slow increase. As shown in table 3, the tensile strength, Young’s modulus and elongation break of CPI/18-CE supramolecular films increase from 94.5 MPa, 4.1 Gpa and 8.5% (pure CPI) to 115.1 MPa, 5.5 Gpa and 16.4% (CPI-18-4), which increased by 21.8%, 34.1% and 92.9%, respectively. The introduction of 18-CE enlarges the distance of adjacent CPI molecular chains, and an internal interlocking structure is formed between the 18-CE rings on adjacent CPI molecular chains [41]. The external force needs to overcome the block effect caused by this
The interlocking structure at the initial tensile stage, so the CPI/18-CE supramolecular films have more excellent mechanical properties than pure CPI.

When the molar amount of crown ether added was 0.5 times that of BTDA, the viscosity of the reaction solution after reaction rapidly decreases, which is possibly because the formation of MDA/BAPP/18-CE inclusion complex limits the movement of diamine monomers molecule under the matching action of 18-CE, and the prepared CPI-18-5 is fragile so that their mechanical properties could not be tested (as shown in table 1).
3.4. Dielectric properties of CPI/18-CE supramolecular films
The dielectric properties of materials are an extremely important parameter in the application field of microelectronics technology. Figures 7 and 8 showed the correlation between the dielectric constant and dielectric loss of CPI/18-CE supramolecular films with different 18-CE contents in the frequency range of $10^5 \sim 10^7$ Hz, and the relevant data was shown as in table 4.

As you can see from figure 7, the dielectric constant of CPI/18-CE supramolecular films is relatively high in the low frequency region, and their dielectric constants are virtually unaffected by changes in frequency, which may be caused by the lower response of polar groups in CPI matrix to varying electric field; In the high frequency region, their dielectric constants decreases as the frequency increases, which may be due to the fact that the response of polar groups in CPI matrix could not catch up with the change of electric field caused by the internal viscosity of the medium, and the orientation polarization is reduced. The above similar phenomena had been reported in the literature [42].

As figure 7 present, the dielectric constant of CPI/18-CE supramolecular films decreased obviously in the frequency range of $10^5 \sim 10^7$ Hz with the increase of 18-CE content, and the maximal decreases were reduced from 3.01 of pure CPI to 2.10 of CPI-18-4 at 1.0 MHz (as shown in table 4). The reason is that 18-CE is nested on the CPI main chain to form a necklace structure, which makes the original molecular skeleton structure develop from lateral to vertical direction. Therefore, the introduction of 18-CE increases the free volume and intermolecular distance of the CPI matrix. This inclusion structure of 18-CE to CPI backbone can shield the electron cloud of imide group on CPI matrix, thereby reduced the molecular polarizability, which together with the above contribute to the decrease of dielectric constant of CPI supramolecular films [23]. Additionally, the dielectric constant of CPI supramolecular films is closely related to their density. The lower density means that they possess larger molecules free volume and lower dielectric constant. The relevant density data for CPI/18-CE supramolecular films is shown in table 4. As can be seen from table 4, their density gradually decreases with the increase of 18-CE content, which means that their dielectric constant gradually decreases, the result was consistent with the previous conclusion.

Dielectric loss is also an important parameter of dielectric materials. It can be seen from figure 8 and table 4 that the dielectric loss of CPI/18-CE supramolecular films is lower than pure CPI at 1.0 MHz. The maximal decrease of the dielectric loss was from 0.017 of pure CPI to 0.007 of CPI-18-4 at 1.0 MHz. The introduction of crown ether reduces the dielectric loss of CPI composites, which may be because the introduction of 18-CE enlarges CPI’s intermolecular distance and limits the movement of CPI backbone due to the interlocking structure of 18-CE, which reduces the friction of the space-charge and dipole polarization under the electric fields. Figure 8 also shows the decrease of the dielectric loss of CPI/18-CE supramolecular films increases with frequency in the low frequency region, which is due to obstruction of CPI backbone movement caused by interlock structure of 18-CE. When the frequency reaches a certain value, the dielectric loss also reaches the corresponding maximum value. Their dielectric loss decreases as the frequency continues to increase, which is because the orientation polarization of CPI supramolecular films does not keep up with the change of the electric field in the high frequency region.

3.5. Water absorption of CPI/18-CE supramolecular films
The water absorption of polymer also greatly affects its dielectric property, the main reason for CPI matrix adsorbing water is its abundant imide groups with strong polarity, which can increase dielectric constant and loss or result in unstable dielectric properties. In scientific research, the hydrophilic or hydrophobic property of polymer is usually characterized by water absorption [43, 44]. The related data of the water absorption of CPI/18-CE supramolecular films with different crown ether contents were showed in table 4. It can be seen from table 4, the water absorption of CPI supramolecular films declines with the increase of 18-CE content, the reason is that 18-CE shields some imide groups of CPI molecule backbone, and accordingly reduces their polarity to some extent. The water absorption obviously dropped gradually from 1.52 wt % of pure CPI to 0.63 wt % of CPI-18-4. Therefore, the results proved that 18-CE is beneficial to improve the surface wettability and dimensional stability of CPI supramolecular films.

4. Conclusions
In this study, CPI/18-CE supramolecular films with inclusion structure were successfully prepared via in situ polymerization of MDA/BAPP/18-CE inclusion complex and BTDA. Their structures were characterized by $^1$H NMR, FT-IR spectra, XRD, TGA, and their synthesis mechanism was analyzed. The results indicated that the inclusion rate of 18-CE to CPI matrix was about 50%. 18-CE had a toughening effect on the CPI matrix, the introduction of 18-CE slightly reduced the thermal properties of CPI/18-CE supramolecular films, increased the tensile strength, Young’s modulus and elongation at break of CPI composites, the individual largest
increasing rate was 21.8%, 34.1% and 92.9% respectively, and simultaneously reduced their dielectric constant, dielectric loss and water absorption. Among them, the dielectric constant of CPI-18-4 has lowest value of 2.10, 0.007 and 0.63%, respectively. In summary, 18-CE had great research value and application prospect in modifying CPI composites, which might be able to open up another world in the field of microelectronics and aerospace.

Acknowledgments

This work was financially supported by the Key Research and Development Project of Hunan Province ‘Research on Key Technologies of Advanced Functional Polyimide Materials’ (Grant No. 2018GK2063); National Natural Science Foundation of China (Grant No. 51775183), and the Hunan Provincial Natural Science Fund of China (Grant No. 2018JJ2125).

Data availability statement

No new data were created or analysed in this study.

ORCID iDs

Duxin Li https://orcid.org/0000-0002-9548-9181

References

[1] Tsuchiya K, Ishii H, Shibasaki Y, Ando S and Ueda M 2004 Synthesis of a novel poly(binaphthylene ether) with a low dielectric constant Macromolecules 37 4794–7
[2] Fukukawa K, Shibasaki Y and Ueda M 2004 A Photosensitive semi-alicyclic poly(benzoxazole) with high transparency and low dielectric constant Macromolecules 37 8256–61
[3] Hu J, Huang Y, Yao Y, Pan G, Sun J, Zeng X, Sun R, Xu J, Song B and Wong C P 2017 Polymer composite with improved thermal conductivity by constructing a hierarchically ordered three-dimensional interconnected network of BN ACS Appl. Mater. Interfaces 9 13544–53
[4] Yuan H, Wang Y, Li T, Ma P, Zhang S, Du M, Chen M, Dong W and Ming W 2018 Highly thermal conductive and electrically insulating polymer composites based on polydopamine-coated copper nanowire Compos. Sci. Technol. 153 153–9
[5] Terraza C A et al 2018 Synthesis and properties of new aromatic polyimides containing spirocyclic structures Polymer 137 283–92
[6] Yang C, Xu W, Nan Y, Wang Y, Gao C, Hu Y and Chen X 2019 Preparation and characterization of acid and solvent resistant polyimide ultrafiltration membrane Appl. Surf. Sci. 483 278–84
[7] Wang S, Ma S, He H, Ai W, Wang D, Zhao X and Chen C 2019 Aromatic polyimides containing pyridine and spirocyclic units: preparation, thermal and gas separation properties Polymer 168 199–208
[8] Mi Z, Liu Z, Yao J, Wang C, Zhou C, Wang D, Zhao X, Zhou H, Zhang Y and Chen C 2018 Transparent and soluble polyimide films from 1,4:3,6-dianhydro-D-mannitol based dihydride and diamines containing aromatic and semi-aromatic units: preparation, characterization, thermal and mechanical properties Polym. Degrad. Stabil. 151 80–9
[9] Lei X, Chen Y, Qiao M, Tian L and Zhang Q 2016 Hyperbranched polysiloxane (HBPSi)-based polyimide films with ultralow dielectric permittivity, desirable mechanical and thermal properties J. Mater. Chem. C 4 2134–40
[10] Cui X, Zhu G and Liu W 2017 Synthesis, characterisation and enhanced properties of polyimide/mica hybrid films Plast. Rubber Compos. 46 35–41
[11] Huang Z and Zhao Z 2016 Low-κ and superior comprehensive property hybrid materials of fluorinated polyimide and pure silica zeolite RSC Adv. 6 34825–32
[12] Li Q, Liao G, Zhang S and Pang L 2018 Effect of adjustable molecular chain structure and pure silica zeolite nanoparticles on thermal, mechanical, dielectric, UV-shielding and hydrophobic properties of fluorinated copolyimide composites Appl. Surf. Sci. 427 437–50
[13] Shi C, Liu S, Li Y, Yuan Y, Zhao J and Fu Y 2017 Imparting low dielectric constant and high modulus to polyimides via synergy between coupled silsesquioxanes and crown ethers Compos. Sci. and Technol. 142 117–23
[14] Chern Y T, Two J T and Chen C J 2009 High Tg and high organosolubility of novel polyimides containing twisted structures derived from 4-(4-amino-2-chlorophenyl)-1-(4-aminophenoxy)-2,6-di-tert-butylbenzene Eur. Polym. J. 45 1127–38
[15] Chern Y T and Tsai J Y 2008 Low dielectric constant and high organosolubility of novel polyimide derived from unsymmetric 1,4-bis(4-aminophenoxy)-2,6-di-tert-butylbenzene Macromolecules 41 9556–64
[16] Tang I C, Wang M W, Wu C H, Dai S A, Jeng R J and Lin C H 2017 A strategy for preparing spirobithromian dihydride from bisphenol A and its resulting polyimide with low dielectric characteristic RSC Adv. 7 11011–9
[17] Qu W L and Ko T M 2001 Studies of dielectric characteristics and surface energies of spin-coated polyimide films J. Appl. Polym. Sci. 82 5462–52
[18] Jiang L, Liu J, Wu D and Jin R 2006 A methodology for the preparation of nanoporoporous polyimide films with low dielectric constants Thin Solid Films 510 241–6
[19] Chu H J, Zhu B K and Xu Y Y 2006 Polyimide foams with ultralow dielectric constants J. Appl. Polym. Sci. 102 1734–40
[20] Chen W, Zhou Z, Yang T, Bei R, Zhang Y, Liu S, Chi Z, Chen X and Xu J 2016 Synthesis and properties of highly organosoluble and low dielectric constant polyimides containing non-polar bulky triphenyl methane moiety React. Funct. Polym. 108 71–7
[21] Lou C M, Chang Y T and Wei K H 2003 Synthesis and dielectric properties of polyimide-tethered polyhedral oligomeric silsesquioxane (POSS) nanocomposites via POSS-diamine Macromolecules 36 9122–7
[22] Yang J Y, Jung B T and Suh D H 2001 A simple attempt to change the solubility of polyimide by physical inclusion with beta-cyclodextrin and its derivatives Polymer 42 8349–54
[23] Li Y, Zhao J, Yuan Y, Shi C, Liu S, Yan S, Zhao Y and Zhang M 2015 Polyimide/crown ether composite films with necklace-like supramolecular structure and improved mechanical, dielectric, and hydrophobic properties Macromolecules 48 2173–83
[24] Li D, Yang Y, Yang C and Lai D 2015 Synthesis and characterization of a novel high-temperature structural adhesive based on MDABAPP-BTDA co-polyimide J. Macromol. Sci. A. 52 540–7
[25] Piroux F, Espuche E, Mercier R, Pinier M and Gebel G 2002 Gas transport mechanism in sulfonated polyimides: consequences on gas selectivity J. Membr. Sci. 209 241–53
[26] Chen X Y and Kaliaquique S 2013 Mixed gas and pure gas transport properties of copolyimide membranes J. Appl. Polym. Sci. 128 380–9
[27] Huertas R M, Maya E M, Abajo I and Campa I G 2011 Effect of 3,5-diaminobenzoic acid content, casting solvent, and physical aging on gas permeation properties of copolyimides containing pendant acid groups Macromol. Res. 19 797–808
[28] Wang L and Cao Y 2010 Gas permeation properties of 6FDA-2,4-DAT/mPDA copolyimides Int. J. Global. Warming. 2 57–64
[29] Yuan Y, Lin B, Zhang X, Wu L and Zhan Y 2008 Nonfluorinated copolymerized polyimide thin films with ultralow dielectric constants J. Appl. Polym. Sci. 110 1515–9
[30] Wang L, Cao Y, Zhou M, Liu Q, Ding X and Yuan Q 2008 Gas transport properties of 6FDA-TMPDA/MOCA copolyimides Eur. Polym. J. 44 225–32
[31] Xiao S, Feng X and Huang R Y M 2010 Synthetic 6FDA-ODA copolyimide membranes for gas separation and pervaporation: correlation of separation properties with diamine monomers Polymer Eng. Sci. 48 795–805
[32] Lu Y, Hao J, Li L, Song J, Xiao G, Zhao H, Hu Z and Wang T 2017 Preparation and gas transport properties of thermally induced rigid membranes of copolyimide containing cardo moieties React. Funct. Polym. 119 134–44
[33] Heck R et al 2017 Block copolyimide membranes for pure- and mixed-gas separation Sep. Purif. Technol. 173 183–92
[34] Qian K, Fang J, Liu R, Jiang J, Tong J, Guo X and Feng J 2018 Six-membered ring copolyimides as novel high performance membrane materials for gas separations Mater. Today. Commun. 14 254–62
[35] Wu D, Yi C, Wang Y, Qi S and Yang B 2018 Preparation and gas permeation of crown ether-containing co-polyimide with enhanced CO2 selectivity J. Membrane. Sci. 551 191–203
[36] Ahmad M Z, Martin-Gil V, Perfilov V, Sysel P and Filip V 2018 Investigation of a new co-polyimide, 6FDA-bisP and its ZIF-8 mixed matrix membranes for CO2/CH4 separation Sep. Purif. Technol. 207 523–34
[37] Lin C T, Kuo S W, Huang C F and Chang F C 2010 Glass transition temperature enhancement of PMMA through copolymerization with PMAAM and PTCM mediated by hydrogen bonding Polymer 51 883–9
[38] Hsiao S H and Chang Y H 2004 Synthesis and properties of soluble trifluoromethyl-substituted polyimides containing laterally attached p-terphenyls J. Polym. Sci. Pol. Chem. 42 1255–71
[39] Liu D J and Chang F C 2004 Highly organosoluble and flexible polyimides with color lightness and transparency based on 2,2-bis-[4-(2-trifluoromethyl-4-aminophenoxy)-3,5-dimethylphenyl] propane J. Polym. Sci. Pol. Chem. 42 5766–74
[40] Wang K, Fan L, Liu J, Zhan M S and Yang S Y 2008 Preparation and properties of melt-processable polyimides based on fluorinated aromatic diamines and aromatic dihydrides J. Appl. Polym. Sci. 107 2126–35
[41] Lin C T, Kuo S W, Lo J C and Chang F C 2010 Resonance effect on self- and inter-association hydrogen bonding interaction of polymer blend J. Phy. Chem. B. 114 1603–10
[42] Zhang Y H et al 2005 Dielectric properties of polyimide–mica hybrid films Macromol. Rapid. Comm. 26 1473–7
[43] Yim J H, Seon J B, Jeong H D-D, Pu L S, Baklanov M R and Gidley D W 2004 Morphological control of nanoporous films by the use of functionalized cyclodextrins as porogens Adv. Funct. Mater. 14 277–82
[44] Wenz G, Steinbrunn M B and Landfester K 1997 Solid state polycondensation within cyclodextrin channels leading to water soluble polyamide rotaxanes Tetrahedron. 53 15575–92