Improved Properties of Aromatic Polyamide Tape-casting Films

Fu-Lin Liu\(^a,b\), Jian-Jun He\(^a,b\), Hai-Xia Yang\(^a\), and Shi-Yong Yang\(^a\)

\(^a\) Laboratory of Advanced Polymer Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
\(^b\) School of Chemical Sciences, University of Chinese Academy of Sciences, Beijing 100049, China

Electronic Supplementary Information

Abstract A convenient tape-casting method was applied to prepare high performance aromatic polyamide (PA) films based on Technora\(^a\). During the polycondensation, CaO was introduced to improve the solubility of the PA resin, and the generated halides were totally removed from the film via a simple water bath, without leaving any defects in PA films. The factors of processing temperature and immersion time had been systematically investigated, and the experimental results demonstrated that both of them had impressive impacts on aggregation state and comprehensive properties of the PA film. It was suggested that immersion in water for more than 1 min and baking below 300 °C for 10 min were the optimal conditions for the thermal, tensile, tear, and optical properties to be in the best equilibrium. The resultant PA films integrated outstanding film-forming ability and excellent general performance, especially the tensile property and tear resistance.

Keywords Tape-casting; Aromatic polyamide film; Solubility; Aggregation state; Tensile property; Tear resistance

INTRODUCTION

Aromatic polyamides (PAs) exhibit remarkable mechanical properties, excellent chemical resistance, and superior thermal stabilities owing to their regular and rigid backbones as well as multiple intermolecular hydrogen bonds.\(^{[1−6]}\) Meanwhile, these two characters contrarily reduce the solubility and fusibility of PAs, restricting their commercial products mainly in fibers, such as Kevlar, Twaron, and Nomex.\(^{[7−10]}\) Particularly, poly(p-phenylene terephthalamide) (PPTA) with planar sheet-like structure has the poorest solubility—merely dissolved in concentrated sulfuric acid, and as a result, it can only be processed in concentrated sulfuric acid via spinning. Although poly(m-phenylene isophthalamide) (PMIA) shows promoted solubility through the adoption of meta-structure, it is still difficult to prepare PA film products.\(^{[11−13]}\)

A tremendous number of researches on PAs reveal two ways to obtain PA films: one is the fiber spinning film and another is the interfacial polymerized film,\(^{[14−17]}\) but neither of these two methods can produce high performance films, or large-scale films. Consequently, it is indispensable to develop tape-casting PA films via the synthesis of soluble aromatic polyamide resins. The main strategy to improve the solubility and processability is the introduction of non-coplanar structures, flexible segments, and bulky side groups.\(^{[18−22]}\) Nonetheless, films originated from these soluble PA resin exhibit unsatisfactory mechanical properties due to the loose chain packing and the weakened intermolecular hydrogen bonding interactions.\(^{[23−25]}\) In our research group, we developed two series of soluble polyamides based on two novel fluorinated monomers, but all these PA films showed tensile modulus, tensile strength, and elongation at break lower than 3.0 GPa, 100 MPa, and 7%, respectively.\(^{[26]}\)

In the present study, we focused on improving the solubility of PA resin and the mechanical properties of the resultant PA films. Therefore, CaO was utilized to ameliorate the solubility of PA resin and was eliminated easily through a water bath, providing us with a simple tape-casting method for preparing films derived from aromatic PA. The effects of processing temperature and immersion time on films' structures and comprehensive properties were systematically investigated. All these films demonstrated excellent tensile properties, tear resistances, thermal properties, and transparencies. This research has laid a solid foundation for the industrialized preparation and application of high performance aromatic PA films.

EXPERIMENTAL

Materials

3,4′-Diaminodiphenyl ether (3,4′-ODA, 98%) and p-phenyleneedianine (p-PDA, 99%) were obtained from J&K Scientific Co., Ltd. (China) and dried under vacuum at 80 °C for 12 h prior to use. Terephthaloyl chloride (TPC, 99%) and calcium oxide (CaO, 99.99%) were purchased from Shanghai Aladdin

*Corresponding authors, E-mail: yanghx@iccas.ac.cn (H.X.Y.)
E-mail: shiyang@iccas.ac.cn (S.Y.Y.)

Received March 10, 2020; Accepted April 17, 2020; Published online June 22, 2020
Bio-Chem Technology Co, Ltd. (China) and used as received. Commercially available N-methyl-2-pyrrolidinone (NMP, 99%, J&K Scientific Co., Ltd. China) was distilled under reduced pressure with \( \text{P}_2\text{O}_5 \) and dehydrated with 4Å molecular sieves before utilization. Other solvents and reagents were directly used as received.

**Synthesis of PA Resins**

In a 150 mL three-necked flask equipped with an electric agitation and nitrogen gas inlet and outlet, p-PDA (1.0814 g, 10 mmol), 3,4′-ODA (2.0024 g, 10 mmol), and 30.0 g of anhydrous NMP were added, and the reaction mixture was stirred at room temperature until diamines were completely dissolved. Then, equimolar amount of TPC (4.0604 g, 20 mmol) and another 18.6 g of anhydrous NMP were added into the solution with stirring for 5 h to get a brown slurry. After the addition of CaO (1.1216 g, 20 mmol) and another 10 h reaction at 90 °C, the brown slurry turned into a viscous and homogeneous resin (Scheme 1).

**Preparation of PA-t Films**

As illustrated in Scheme 2, the viscous PA solution was filtrated by G1 sand cored funnel, deaerated and coated onto a pre-cleaned glass plate. The resultant wet film was heated at 60 °C for 1 h and 120 °C for another 1 h in a blast oven to evaporate most free solvent. In order to investigate the impact of immersion time on structures and performances of PA films, the semi-dried films were stripped off the glass plate in a water bath for various time (0 s, 20 s, 30 s, 40 s, 50 s, 60 s, 10 min, 30 min, 60 min, and 120 min), followed by thermal baking at 300 °C for 10 min on a rectangular clamp to eliminate the residual solvent. Corresponding to the immersion time, these PA-t films were named as PA-t-0s, PA-t-20s, PA-t-30s, PA-t-40s, PA-t-50s, PA-t-60s, PA-t-10min, PA-t-30min, and PA-t-120min, respectively.

**Characterization and Measurements**

FTIR spectra were measured in the range of 400–4000 cm\(^{-1}\) on a Tensor-27 Fourier transform spectrophotometer (Bruker, Germany). The elemental analysis of PA precipitate was carried out with a Vario EL III elementar (Elementar, Germany). The wide-angle X-ray diffraction (WAXD) measurements were undertaken in the range of 5°–35° at a scanning speed of 5 °(°)·min\(^{-1}\) on a Rigaku D/MAX 2400 diffractometer with Cu Kα radiation (λ = 0.154 nm) at 40 kV.

Thermogravimetric analyses (TGA) were conducted on a TA Q50 thermal analysis system with a heating rate of 20 °C·min\(^{-1}\) under an air purge. Dynamic mechanical analyses (DMA) were performed on a TA Q800 analyzer with a heating rate of 5 °C·min\(^{-1}\) and a load frequency of 1 Hz under nitrogen atmosphere. Thermomechanical analyses (TMA) were carried out on a TA Q400 analyzer with a heating rate of 5 °C·min\(^{-1}\) and a load force of 0.05 N in a nitrogen flow. The in-plane (\( n_{||} \)) and out-of-plane (\( n_{\perp} \)) refractive indices of PA films about 5 ± 1 μm thickness were obtained by a prism coupler (Metric model PC-2000, Korea) at a wavelength of 633 nm.

Tensile property and tear resistance were measured on an Instron 5567 universal testing machine (Instron, USA) at a drawing rate of 2.0 mm·min\(^{-1}\). The specimen sizes are shown in Fig. 1, and for each film, 7 specimens were investigated to get an average value. Cross section morphologies of the PA films were imaged by scanning electron microscopy (SEM, Hitachi S-4800, Japan) at 15 kV voltage. Analyses of element distributions in cross sections were performed by energy dispersive spectroscopy (EDS, Hitachi S-4800, Japan) with 15 kV.

Ultraviolet-visible (UV-Vis) spectra of PA films were recorded on a Hitachi U3900 spectrophotometer at room temperature. The color intensity and haze of PA films were evaluated by X-rite Color i7 spectrophotometer, using an observational
angle of 8° and a CIE (Commission International de l’Eclairage) standard D65 illuminant.

RESULTS AND DISCUSSION

Preparation and Characterization of PA Resin

Based on Technora®, the molar ratio of p-PDA and 3,4′-ODA was kept at 50/50 for solubility of PA resins and physical properties of PA fibers to be in the best equilibrium.[30] Although 3,4′-ODA was introduced into polymer main chain up to 50 mol%, the PA resin was still insoluble and easy to get gelation, as shown in Fig. 2(a). This can be interpreted by the fact that during the polycondensation of PA, the by-product HCl lacked the capability of releasing Cl⁻ ions.[29] However, Cl⁻ ions are of great significance in improving the solubility of PA, because they can interact with protons of secondary amide moieties and disrupt the intermolecular hydrogen bonds of PA itself simultaneously.[30] Generally, chloride salts such as LiCl or CaCl₂ are dissolved in NMP beforehand to provide Cl⁻ ions for the promotion of solubility. In this study, chloride salts were replaced by CaO, which can react with the by-product HCl and offer Cl⁻ ion, making the slurry turned into homogenous resin (Fig. 2b). Meanwhile, the consumption of HCl changed the reaction environment from acid to neutral, which was beneficial to industrial manufacture. Besides, the storage stability of PA resin was also greatly improved, since the resultant resin solution can be stored for a year without any gelation or precipitation (Fig. 2c). Additionally, the solid content of PA solution was adjusted from 15 wt% to 6 wt%, and the corresponding viscosity dropped from 788 Pa·s to 20 Pa·s (Fig. 2d). Conspicuously, the best solid content for film casting was controlled around 8 wt% to 10 wt%, at which the viscosity of PA solution spanned a regime of 35 Pa·s to 69 Pa·s.

The PA solution was trickled into excess ethanol to form a white precipitate, whose chemical compositions and structures were characterized by elemental analysis and FTIR spectroscopic measurements, respectively, and the results are shown in Fig. S1 (in the electronic supplementary information, ESI). Conspicuously, the most intensive absorption around 3330 cm⁻¹ was ascribed to the stretching vibrations of N−H bonds, and the other two strong absorption bands observed near 1650 and 1550 cm⁻¹ were assigned to the stretching vibrations of C=O groups (amide I) and the bending vibration of N−H groups (amide II).[31] Furthermore, the experimental values of element contents were in good accordance with the calculated values, suggesting the PA based on TPC, p-PDA, and 3,4′-ODA had been successfully synthesized.

Aggregation Structures in PA-t Films

Fig. 3 compares the XRD patterns of PA-t films soaked in water bath for 0 min to 120 min, and the specific data of 2θ and d-spacing are displayed in Table S1 (in ESI). It is conspicuous that the 2θ values reduced impressively from 22.1° to 20.8°, and then appeared to level off at 20.9°, inferring to the augment in d-spacing from 4.02 Å to 4.26 Å and stabilization at around 4.25 Å. When the semi-dried film was immersed in water, the residual NMP and water could be soluble mutually, accompanied by the dissolution of generated CaCl₂ and the formation of hydrogen bonds between water molecules and amide groups in polymer main chain. Subsequently, the bonded water molecules formed extra hydrogen bonds with other free water molecules, so more
and more water molecules penetrated into polymer matrices, enlarging the distance between molecular chains.\cite{5,33} Obviously, the intermolecular space got increasingly larger with the accumulation of immersion time in the first one minute. However, the d-spacing was stabilized at 0.422 nm after being soaked in water for 1 min, which was assumed to be caused by the saturation of both bonded and absorbed water molecules. Thus, it was rational to hypothesize that the procedure of bonding and absorbing water molecules by amide groups was surprisingly rapid, which could be finished in a minute. After 1 min in water bath, the water molecules did not affect the aggregation structures of PA chains anymore because of their saturation.

### Thermal Stabilities of PA-t Films

The thermal degradation, glass transition temperature (T\text{g}), and coefficient of thermal expansion (CTE) of PA-t films were systematically examined by TGA (in air), DMA, and TMA, and the data are summarized in Table 1. Compared with others, PA-t-0s film without water bath demonstrated the lowest T\text{g}, T\text{d}, and the highest Rw \text{w} simultaneously, which could be interpreted by the formation of CaCl\text{2} during the polycondensation. On the one hand, the generated CaCl\text{2} hindered the formation of hydrogen bonds between polymer chains, thus deteriorating the thermal stabilities of PA-t films. On the other hand, the generated CaCl\text{2} was thermally stable under 800 °C, resulting in the highest residue weight. When the semi-dried film was immersed for only 20 s, T\text{g} and T\text{d} enhanced dramatically from 383 °C to 486 °C and 427 °C to 520 °C, while Rw \text{w} dropped sharply from 38.79% to 2.38% (Fig. 4). Afterwards, T\text{g} and T\text{d} leveled off at 490 and 520 °C, while Rw \text{w} diminished slightly and stabilized nearly 0%, suggesting that the immersion time had no effect on thermal degradation performance of PA-t films after 1 min in water bath (Table 1).

It was presumed that during the water bath, CaCl\text{2} dissolved in water rapidly, as only 1 min was sufficient for its complete elimination from the film. To confirm the assumption, the cross-sections of PA-t films were imaged by SEM with a magnification of 5000 times and the results are shown in Fig. S2 (in ESI). It is remarkable that no porous structure was observed in PA-t films after water bath, implying the dense stacking of polymer chains after the removal of CaCl\text{2}. Furthermore, Fig. 5 illustrates calcium and chloride (Ca\text{2}\text{+}, Cl\text{2}+) distributions in film cross-section carried out by EDS measure-
ment, which indicates that CaCl₂ content plunged to a fairly low level in the first 1 min and then maintained at this level. Combined with TGA curves, the generated CaCl₂ was easily eliminated from semi-dried films via a water bath without leaving any defects in PA-t films.

Fig. 6 presents the plots of \( T_g \) and CTE (from 50 °C to 250 °C) versus immersion time. Obviously, PA-t-0s exhibited the highest \( T_g \) of 337 °C, which reduced slightly with the increase of immersion time, and ultimately stabilized at around 310 °C. This is ascribed to the following two reasons: (a) the residual CaCl₂ particles dispersed evenly in polymer matrices, restricting the mobility of polymer chains; (b) both the bonded and absorbed water molecules enlarged the inter-chain space. When the immersion time exceeded 1 min, CaCl₂ was completely eliminated and the water molecules were saturated, resulting in the stabilization of \( T_g \). On the other hand, the immersion time had little impact on CTE values, since all PA-t films exhibited CTE values ranging from 17.8 ppm·K⁻¹ to 20.4 ppm·K⁻¹, much lower than that of most amorphous polymers, e.g., polyethersulfone (~50 ppm·K⁻¹), polycarbonate (~70 ppm·K⁻¹), polyimide (~60 ppm·K⁻¹), and polyarylate (~50 ppm·K⁻¹). It is noteworthy that PA-t-0s film displayed the lowest CTE of 17.8 ppm·K⁻¹, probably attributed to the by-product CaCl₂, which could be regarded as cross-linking points and restricted the mobility of polymer chains.

**Optical and Mechanical Properties of PA-t Films**

It can be seen in Fig. 7 and Table S2 (in ESI) that PA-t-0s film without being exposed in water bath exhibited the poorest optical properties, with its yellow index (YI) and Haze exceedingly larger than those of other samples and its UV-Vis transmittance unfavorably lower than that of others, which was caused by the residual CaCl₂. As discussed above, only 20 s of water bath could remove more than 95% CaCl₂, so the optical properties were significantly enhanced after being exposed in water bath. During the initial 1 min, the YI and Haze values
plunged from 28.3 to 17.1 and 47.5 to 1.1, respectively, while UV-Vis transmittance increased from 82.8% to 83.9% (average transmittance from 450 nm to 800 nm). After being soaked in water for 1 min, PA-T films exhibited relatively low YI and Haze as well as excellent transmittance.

The mechanical properties of PA-T films including tensile strength ($T_s$), tensile modulus ($T_m$), elongation at break ($ε_b$), and tear strength ($T_R$) were also taken into investigation, and the results are illustrated in Fig. 8 and Table S3 (in ESI). Considering the high rigidity of CaCl$_2$ itself and the prohibited hydrogen bond in polymer chain to chain, CaCl$_2$ enhanced film rigidity while weakened intermolecular interaction. As for PA-T-0s film, all the generated CaCl$_2$ remained in polymer matrices, leading to its highest $T_m$ and lowest $T_s$, $ε_b$, and $T_R$. As the immersion time prolonged to 1 min, the resultant CaCl$_2$ was gradually swept out from the film, accompanied by the formation of hydrogen bonds between polymer chains. Meanwhile, $T_m$ was decreased from 5.91 GPa to 5.03 GPa, whereas $T_s$, $ε_b$, and $T_R$ were increased from 128 MPa to 136 MPa, 18.5% to 31.1%, 311 kN·m$^{-1}$ to 504 kN·m$^{-1}$, respectively. Afterwards, $T_m$, $T_s$, $ε_b$, and $T_R$ values began to level off at approximately 5.00 GPa, 140 MPa, 31%, and 530 kN·m$^{-1}$, respectively. A typical commercial polyimide film (Kapton HN, Dupont) had a $T_m$ of 288 kN·m$^{-1}$, much lower than that of PA-T films, manifesting the remarkable durability of our PA films in practical applications.

From the perspective of aggregation structures and physical properties of PA-T films, at least 1 min in water bath is essential for the by-product CaCl$_2$ to be eliminated from PA films without deteriorating the comprehensive properties of PA films.

**Aggregation Structures in PA-T Films**

Apart from water bath, the processing temperature played another crucial role in governing film's structure and comprehensive properties. Since the impact of immersion time has been detailedly analyzed above, 10 min of water bath was applied to the research on processing temperature. PA-T films with various processing temperature ranging from 250 °C to 400 °C were prepared as depicted in Experimental section.

The aggregation structure of polymer chains in PA films was evaluated by XRD and the results are shown in Fig. 9(a). Instead of sharp peaks of crystalline polymers, broad amorphous halos were detected in those PA films, suggesting that the PA films we synthesized were amorphous. However, with the augment in final processing temperature, the broad halo gradually converted into a sharper peak, accompanied by the increase of peak’s relative intensity and the decrease of peak’s half-width. It is supposed that there was a rearrangement of polymer chains in PA film at high processing temperature, which enhanced the regularity of intermolecular stacking and induced more ordered phase. Additionally, the $θ_0$ values shifted from 20.4° to 22.2° as the ultimate processing temperature rose from 250 °C to 400 °C. According to Bragg’s law, the $d$-spacing reduced from 0.435 nm to 0.4 nm, which means the smaller average intermolecular space at higher curing temperature. It is reasonable to assume that during the elevated thermal treatment, the semi-dried film shrank drastically on the clamp and generated a biaxially oriented extentional force on itself in turn; then a closer stacking of polymer chains occurred, leading to stronger intermolecular hydrogen bonds and more ordered regions.

To confirm our assumption, FTIR measurement was applied to PA-T films (Fig. S2 in ESI), and the signals of N–H and C=O are magnified in Fig. 9(b). Generally, the stretching vibrations of “free” N–H and “free” C=O groups (without hydrogen bonds) are detected around 3450 and 1680 cm$^{-1}$, respectively. Nevertheless, in our study, the wavenumbers of N–H and C=O groups were all smaller than that of “free” groups, indicating the existence of hydrogen bonds in PA films.
films. These hydrogen bonds led to the decrease in wave-numbers of stretching vibrations.\textsuperscript{[42,43]} It is noteworthy that both the stretching vibrations of N–H and C=O groups gradually moved to the lower wave-numbers (3335–3321 cm\(^{-1}\) for N–H and 1649–1631 cm\(^{-1}\) for C=O) as the processing temperature rose from 250 °C to 400 °C. This could be interpreted by the fact that the higher processing temperature contributed to the closer stacking of polymer chains, thus making it easier for N–H and C=O groups to form hydrogen bonds. In our PA structures, N–H groups can only form hydrogen bonds with C=O groups, so their decrease in wave-numbers was synchronous as the treatment temperature rose.

**Thermal Stabilities of PA-T Films**

The thermal performances of PA-T films were evaluated by TGA, DMA, and TMA, with the specific data summarized in Table 2. Fig. 3 (in ESI) shows the weight loss curves in air of PA-T films from 50 °C to 800 °C. Clearly, all these PA films exhibited extraordinary thermal stabilities, without any weight loss in air below 450 °C. Furthermore, the \( T_g \) and \( T_{10} \) values of PA-T films in air spanned a regime of 480 °C to 492 °C and 511 °C to 518 °C, respectively. Obviously, all these PA films displayed similar thermal degradation behaviors, demonstrating that the variation of processing temperature had little impact on thermal stability. It should be mentioned that \( R_w \) values of PA-T films were all found at approximately 0%, which confirmed that CaCl\(_2\) was totally removed from the film via immersion in water for 10 min.

![Fig. 10](https://doi.org/10.1007/s10118-020-2445-3)

**Table 2** Thermal stabilities of PA-T films.

| PA-T film | \( T_g \) a (°C) | \( T_{10} \) b (°C) | \( R_w \) d (%) | CTE\(^e\) (ppm·K\(^{-1}\)) |
|-----------|----------------|----------------|---------------|---------------------|
| PA-T-250  | 304            | 481            | 0.79          | 17.8\textsuperscript{a} |
| PA-T-275  | 307            | 482            | 0.64          | 19.1\textsuperscript{a} |
| PA-T-300  | 311            | 492            | 0.91          | 19.7\textsuperscript{b} |
| PA-T-325  | 324            | 486            | 0.73          | 21.4\textsuperscript{b} |
| PA-T-350  | 368            | 483            | 0.67          | 23.6\textsuperscript{b} |
| PA-T-375  | 412            | 480            | 0.84          | 24.3\textsuperscript{b} |
| PA-T-400  | 451            | 487            | 0.81          | 25.0\textsuperscript{b} |

\( a \): decomposition temperature at 5% weight loss; \( b \): decomposition temperature at 10% weight loss; \( c \): \( T_g \) (°C); \( d \): char yield at 800 °C; \( e \): glass transition temperature, tan\( \delta \) peak value determined by DMA; \( T \): coefficient of thermal expansion from 50 °C to 250 °C.

Fig. 10(a) depicts the DMA curves of PA-T films. Regarding the peak temperature in tan\( \delta \) curve as \( T_g \), these films’ \( T_g \) rose along with the increase of processing temperature from 304 °C (PA-T-250) to 451 °C (PA-T-400). As discussed above, higher temperature resulted in closer stacking of polymer chains and stronger hydrogen bonds, which restricted the mobility of polymer chains, thus enhancing the \( T_g \).\textsuperscript{[38]} It is noteworthy that \( T_g \) rose steadily at relatively low processing temperature (< 300 °C) but increased significantly after 325 °C. This trend might be explained by the more intensive contraction of semi-dried film on clamp at higher temperature.

As expressed in Table 2, the in-plane coefficient of thermal expansion (CTE) between 50 and 200 °C for these PA-T films grew monotonously from 17.8 ppm·K\(^{-1}\) to 25.0 ppm·K\(^{-1}\). It has been revealed that CTE is closely related to the extent of in-plane orientation,\textsuperscript{[44]} which can be interpreted by birefrin-

![Fig. 10](https://doi.org/10.1007/s10118-020-2445-3)

**Mechanical and Optical Properties of PA-T Films**

The tensile properties and tear resistance of PA-T films, including tensile strength (\( T_s \)), tensile modulus (\( T_M \)), elongation at break (\( \varepsilon_b \)), and tear strength (\( T_p \)), were systematically investigated and the results are illustrated in Table 3. The rigid backbone composed of \( p \)-PDA and TPC enhanced stiffness of molecular chains, contributing to the great tensile
gence. Fig. 54 (in ESI) depicts the in-plane \( n_{11} \) and out-of-plane \( n_{13} \) refractive indices of PA-T films. Apparently, \( n_{11} \) descended while \( n_{13} \) ascended contrarily with the increase of processing temperature. Therefore, the birefringence \( \Delta n \) was diminished (Fig. 10b), which declared the decline in anisotropy of the corresponding PA film. All PA-T films exhibited the birefringence values greater than 0.162, although it dropped slightly from PA-T-250 to PA-T-400 film, implying the polymer chains were preferentially aligned parallel to the film plane direction.\textsuperscript{[45]} This is because at the elevated temperature, the rectangular clamp had an intense stretching effect on the semi-dried film, on account of its severe contraction. However, the in-plane orientation induced by the stretching effect was thermodynamically reversible,\textsuperscript{[46]} and the disorientation originated from molecular random thermal motions was easier to occur at higher temperature. Hence, the segmental relaxation at higher processing temperature lowered the in-plane orientation degree, leading to the decrease in birefringence and the increase in CTE values.
properties of PA films. Moreover, the strong intermolecular interaction also provided the PA films with outstanding tear resistance, with their $T_g$ ranging from 510 kN·m$^{-1}$ to 535 kN·m$^{-1}$, much higher than that of the high performance commercial polyimide film (288 kN·m$^{-1}$ of Kapton HN$^\text{®}$). Since the higher processing temperature led to the more ordered regions, it improved the regularity of polymer chains and simultaneously reduced the flexibility of molecular chains. Thus, with the ultimate processing temperature moved onto 400 °C, $T_g$ raised slightly from 4.67 GPa to 5.36 GPa while $\varepsilon_b$ reduced drastically from 46.4% to 7.7%. Distinctly, 300 °C was a critical processing temperature, below which PA-T films exhibited excellent mechanical properties with $T_g$, $T_M$, $\varepsilon_b$, and $T_b$ greater than 140 MPa, 4.7 GPa, 31%, and 510 kN·m$^{-1}$, respectively.

### Table 3 Tensile properties and tear resistance of PA-T films.

| PA-T film | $T_g$ (MPa) | $T_M$ (GPa) | $\varepsilon_b$ (%) | $T_b$ (kN·m$^{-1}$) |
|-----------|-------------|-------------|---------------------|---------------------|
| PA-T-250  | 141         | 4.67        | 46.4                | 534.6               |
| PA-T-275  | 148         | 4.74        | 39.3                | 510.5               |
| PA-T-300  | 139         | 5.01        | 31.4                | 535.0               |
| PA-T-325  | 139         | 5.06        | 23.2                | 525.8               |
| PA-T-350  | 143         | 5.13        | 16.6                | 518.4               |
| PA-T-375  | 156         | 5.21        | 11.3                | 533.5               |
| PA-T-400  | 145         | 5.36        | 7.7                 | 510.3               |

$a$ $T_g$: tensile strength; $b$ $T_M$: tensile modulus; $c$ $\varepsilon_b$: elongation at break; $d$ $T_b$: tear strength.

The representative data of optical properties are expressed in Table 4 and Fig. S5 (in ESI). All those PA films exhibited low haze values at approximately 1.5, demonstrating their excellent clarity. Additionally, the average transmittance from 450 nm to 800 nm of PA-T films was maintained above 83% as long as the final temperature was lower than 300 °C. When the processing temperature exceeded 300 °C, the YI values ascended drastically from 16.7 to 74.5, while the UV-Vis transmittance descended sharply from 83.1% to 67.5%. This trend was associated with the following reason that the denser structure increased the degree of charge transfer complexes (CTC) between neighboring chains at higher temperature, especially higher than 350 °C. This suggested a critical thermal treatment at around 300 °C, below which the processing temperature hardly deteriorated the optical performance of PA films.

### Table 4 Optical properties of PA-T films.

| PA-T film | YI $^a$ | Haze | $\lambda_{\text{cut}}$ (nm) | $T_{av}$ (%) |
|-----------|---------|------|---------------------------|--------------|
| PA-T-250  | 16.7    | 1.03 | 394.5                    | 83.7         |
| PA-T-275  | 16.3    | 1.05 | 394.5                    | 82.8         |
| PA-T-300  | 16.7    | 1.13 | 395.0                    | 83.1         |
| PA-T-325  | 19.7    | 1.51 | 394.5                    | 81.1         |
| PA-T-350  | 24.3    | 1.59 | 394.5                    | 79.7         |
| PA-T-375  | 40.3    | 1.69 | 394.0                    | 74.6         |
| PA-T-400  | 74.5    | 1.87 | 397.0                    | 67.5         |

$a$ YI: yellow index; $b$ $\lambda_{\text{cut}}$: cutoff wavelength; $c$ $T_{av}$: average transmittance from 450 nm to 800 nm.

### Overall Properties of Aromatic PA films

Taking thermal stability, tensile flexibility, tear resistance, and transparency into consideration, Fig. 11 summarizes the comprehensive properties of PA-t and PA-T films. Although PA-t-0s film had a little higher thermal stability, it suffered the lowest mechanical and optical properties. It is obvious in Fig. 11(a) that the overall properties of PA-t films maintain at relatively high levels when the immersion time exceeds 1 min. On the other hand, Fig. 11(b) suggests that the processing temperature under 300 °C would provide PA films with better comprehensive properties, which has been discussed above.

### CONCLUSIONS

A series of high performance aramid films were prepared through a simple tape-casting method, in which CaO was employed for the dissolution of aromatic polyamide and the generated CaCl$_2$ was easily removed from polymer matrices via water bath. Experimental results suggested that 1 min in water bath was a crucial point, within which CaO partially remained in PA films and deteriorated the properties of PA films. However, the comprehensive properties of PA-T films all maintained at a relatively high level after immersion for 1 min, demonstrating the water bath was an indispensable process during film formation. Additionally, processing temperature also played a significant role in dictating structures and properties of PA films. It was found that 300 °C was a critical processing temperature, below which films exhibited excellent optical and mechanical properties, with $T_g$, $T_M$, $\varepsilon_b$, $T_b$, and $T_{av}$ more than

https://doi.org/10.1007/s10118-020-2445-3
nanofibrous \textit{meta-}aramid separators for lithium batteries. J. Nanosci. Nanotechnol. \textbf{2016}, \textit{16}, 10720–10729.

16. Jeong, B.H.; Hoek, E. M. V.; Yan, Y.; Subramani, A.; Huang, X.; Hurwitz, G.; Ghosh, A. K.; Jawor, A. Interfacial polymerization of thin film nanocomposites: a new concept for reverse osmosis membranes. \textit{J. Membr. Sci.} \textbf{2007}, \textit{294}, 1–7.

17. Lind, M. L.; Suk, D. E.; Nguyen, T. V.; Hoek, E. M. V. Tailoring the structure of thin film nanocomposite membranes to achieve seawater RD membrane performance. \textit{Environ. Sci. Technol.} \textbf{2015}, \textit{49}, 8320–8325.

18. Yagoub, M.; Behzad, K. Z.; Hemayat, S.; Reza, Z. M.; Gholam, H. Polyamides with pendant 1,3,4-oxadiazole and pyridine moieties. \textit{Chinese J. Polym. Sci.} \textbf{2012}, \textit{30}, 112–121.

19. Lee, H. S.; Kim, S. Y. Synthesis of poly(arylene ether amides containing CF$_3$ groups by nitro disbursement reaction of AB-type monomers. \textit{Macromol. Rapid Commun.} \textbf{2002}, \textit{265}–671.

20. In, I.; Kim, S. Y. Soluble wholly aromatic polyamides containing unsymmetrical pyridyl ether linkages. \textit{Polymer} \textbf{2006}, \textit{47}, 547–552.

21. Na, L.; Yu, J. R.; Yan, W.; Jing, Z.; Hu, Z. M. Synthesis and characterization of easily colored \textit{meta-}aramid copolymer containing ether bonds. \textit{Chinese J. Polym. Sci.} \textbf{2018}, \textit{37}, 227–234.

22. Wang, C. Y.; Li, P. H.; Li, G.; Jiang, J. M. High optical transparency and low dielectric constant of novel organosoluble poly(ether ketone amides derived from an unsymmetrical diamine containing trifluoromethyl and methyl pendant groups. \textit{Colloid Polym. Sci.} \textbf{2009}, \textit{287}, 495–500.

23. Cheng, L.; Jian, X. G.; Mao, S. Z. Aromatic polyamides derived from unsymmetrical diamines containing the phthalazine moiety. \textit{J. Polym. Sci., Part A: Polym. Chem.} \textbf{2010}, \textit{40}, 3489–3496.

24. Mohsen, H.; Khaill, F.; Majid, K. T.; Zeinab, M. Thermally stable and organo-soluble polyamides containing triazine rings and ether linkages in the main chain: synthesis and characterization. \textit{Chinese J. Polym. Sci.} \textbf{2015}, \textit{33}, 109–117.

25. Tec-Sánchez, J. A.; Arias, A. I. O.; Aguilar-Vega, M.; Cauch-Rodriguez, J. V.; Santiago-Garcia, J. L. Preparation and characterization of flexible, transparent and thermally stable aromatic co-polyamides. \textit{Chinese J. Polym. Sci.} \textbf{2018}, \textit{36}, 136–141.

26. Ge, Z.; Yang, S.; Tao, Z.; Liu, J.; Fan, L. Synthesis and characterization of novel soluble fluorinated aromatic polyamides derived from fluorinated isophthalamid dichlorides and aromatic diamines. \textit{Polymer} \textbf{2004}, \textit{45}, 3627–3635.

27. Chen, W.; Chen, W.; Zhang, B.; Yang, S.; Liu, C. Y. Thermal imidization process of polyimide film: interplay between solvent evaporation and imidization. \textit{Polymer} \textbf{2017}, \textit{109}, 205–215.

28. Matsuoka, S.; Asakura, T.; Nakagawa, Y. Sequence analysis of technora (copolyamide of terephthaloyl chloride, \textit{p}-phenylenediamine, and \textit{3,4'}-diaminodiphenyl ether) using \textit{13}C NMR. \textit{Macromolecules} \textbf{2003}, \textit{36}, 6160–6165.

29. Dai, Y.; Cheng, Z.; Yuan, Y.; Meng, C.; Qin, J.; Liu, X. In situ complex with by-product HCl and release chloride ions to dissolve aramid. \textit{ChemPhysChem} \textbf{2018}, \textit{19}, 2468–2471.

30. Yan, H.; Li, J.; Tian, W.; He, L.; Xiao, T.; Qiu, T. A new approach to the preparation of poly(\textit{p}-phenylene terephthalamide) nanofibers. \textit{RSC Adv.} \textbf{2016}, \textit{6}, 26599–26605.

31. Skrovanek, D. J.; Painter, P. C.; Coleman, M. M. Hydrogen bonding in polymers. 2. Infrared temperature studies of nylon 11. \textit{Macromolecules} \textbf{1986}, \textit{19}, 699–705.

32. Zhang, K.; Yu, Q.; Zhu, L.; Liu, S.; Chi, Z.; Chen, Z.; Zhang, Y.; Xu, J. The preparations and water vapor barrier properties of polyimide films containing amide moieties. \textit{Polymers (Basel)} \textbf{2017}, \textit{9}.

33. Yu, S.; Chen, F.; Wu, Q.; Roth, S. V.; Brüning, K.; Schneider, K.; Kuktaite, R.; Hedenqvist, M. S. Structural changes of gluten/glycerol plastics under dry and moist conditions and during tensile tests. \textit{ACS Sustain. Chem. Eng.} \textbf{2016}, \textit{4}, 3388–3397.

34. Wu, J.; Yang, S.; Gao, S.; Hu, A.; Liu, J.; Fan, L. Preparation, 

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at https://doi.org/10.1007/s10118-020-2445-3.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (No. 51973225).
morphology and properties of nano-sized Al₂O₃/polyimide hybrid films. *Eur. Polym. J.* 2005, 41, 73−81.

35 https://www.dupont.com/content/dam/dupont/amer/us/en/products/ei-transformation/documents/DEC-Kapton-HN-datasheet.pdf

36 Bullions, T. A.; Stoykovich, M. P.; McGrath, J. E.; Loos, A. C. Monitoring the reaction progress of a high-performance phenylethynyl-terminated poly(etherimide). Part II: advancement of glass transition temperature. *Polym. Compos.* 2002, 23, 479−494.

37 Ishii, J.; Takata, A.; Oami, Y.; Yokota, R.; Vladimirov, L.; Hasegawa, M. Spontaneous molecular orientation of polyimides induced by thermal imidization (6). Mechanism of negative in-plane CTE generation in non-stretched polyimide films. *Eur. Polym. J.* 2010, 46, 681−693.

38 Song, G.; Zhang, X.; Wang, D.; Zhao, X.; Zhou, H.; Chen, C.; Dang, G. Negative in-plane CTE of benzimidazole-based polyimide film and its thermal expansion behavior. *Polymer* 2014, 55, 3242−3246.

39 Jung, Y.; Yang, Y.; Lee, S.; Byun, S.; Jeon, H.; Cho, M. D. Characterization of fluorinated polyimide morphology by transition mechanical analysis. *Polymer* 2015, 59, 200−206.

40 Shao, L.; Chung, T. S.; Wensley, G.; Goh, S. H.; Pramoda, K. P. Casting solvent effects on morphologies, gas transport properties of a novel 6FDA/PMDA-TMMDA copolyimide membrane and its derived carbon membranes. *J. Membr. Sci.* 2004, 244, 77−87.

41 Rusu, G.; Ueda, K.; Rusu, E.; Rusu, M. Polyamides from lactams by centrifugal molding via anionic ring-opening polymerization. *Polymer* 2001, 42, 5669−5678.

42 Song, Y.; Yamamoto, H.; Nemoto, N. Segmental orientations and deformation mechanism of poly(ether-block-amide) films. *Macromolecules* 2004, 37, 6219−6226.

43 Wen, L.; Zhang, J.; Zhou, T.; Zhang, A. Hydrogen bonding in micro-phase separation of poly(polyamide 12-block-polytetrahydrofuran) alternating block copolymer: enthalpies and molecular movements. *Vib. Spectrosc.* 2016, 86, 160−172.

44 Hasegawa, M.; Sakamoto, Y.; Tanaka, Y.; Kobayashi, Y. Polyimide imide/s possessing low coefficients of thermal expansion (CTE) and low water absorption (III). Use of bis(4-aminophenyl)terephthalate and effect of substituents. *Eur. Polym. J.* 2010, 46, 1510−1524.

45 Hasegawa, M.; Ishigami, T.; Ishii, J.; Sugiura, K.; Fujii, M. Solution-processable transparent polyimides with low coefficients of thermal expansion and self-orientation behavior induced by solution casting. *Eur. Polym. J.* 2013, 49, 3657−3672.

46 Ma, S. P.; Sasaki, T.; Sakurai, K.; Takahashi, T. Morphology of solution-cast thin films of wholly aromatic thermoplastic polyimides with various molecular weights. *Polymer* 1994, 35, 5618−5625.

47 Kovalev, M. K.; Kalinina, F.; Androstov, D. A.; Cho, C. Synthesis of transparent and thermally stable polyimide-aramid nanocomposites-prospective materials for high-temperature electronic manufacture applications. *Polymer* 2013, 54, 127−133.

48 Kim, S. K.; Wang, X.; Ando, S.; Wang, X. Highly transparent triethoxysilane-terminated copolyimide and its SiO₂ composite with enhanced thermal stability and reduced thermal expansion. *Eur. Polym. J.* 2015, 64, 206−214.

https://doi.org/10.1007/s10118-020-2445-3