

Improved Properties of Aromatic Polyamide Tape-casting Films

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Improved Properties of Aromatic Polyamide Tape-casting Films

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Abstract A convenient tape-casting method was applied to prepare high performance aromatic polyamide (PA) films based on Technora®. 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

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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 terephthamide) (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] Non-

etheless, 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*-phenylenediamine (*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

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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 P_2O_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.^[27] 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, PA-t-60min, and PA-t-120min, respectively.

Preparation of PA-T Films

The semi-dried film was prepared through the same procedure as above (Scheme 2), but the immersion time was set as 10 min during water bath according to the results of PA-t films. Afterwards, the films were tightly fixed on a rectangular clamp,

followed by separately curing at 250, 275, 300, 325, 350, 375, and 400 °C, and holding at each of these temperature for 10 min to remove all solvent. Based on the processing temperature, these PA-T films were named as PA-T-250, PA-T-275, PA-T-300, PA-T-325, PA-T-350, PA-T-375, PA-T-400, respectively.

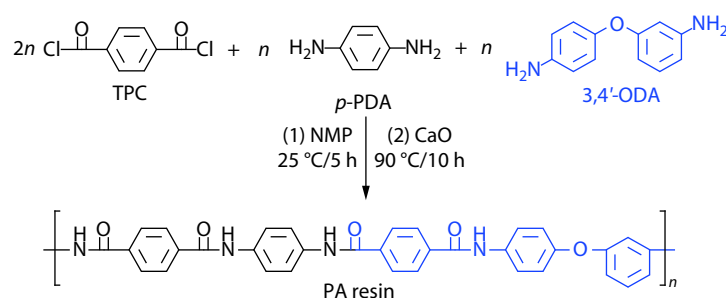
Characterization and Measurements

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 Varlo ELIII elemental (Elementar, Germany). The wide-angle X-ray diffraction (WAXD) measurements were undertaken in the range of 5°–35° at a scanning speed of 5 ($^\circ$) $\cdot\text{min}^{-1}$ on a Rigaku D/Max 2400 diffractometer with Cu K α radiation ($\lambda = 0.154 \text{ nm}$) at 40 kV.

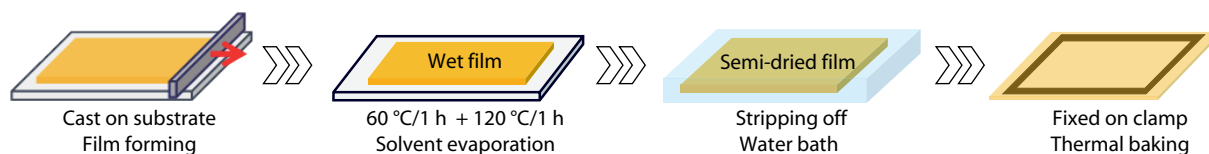
Thermogravimetric analyses (TGA) were conducted on a TA Q50 thermal analysis system with a heating rate of 20 $^\circ\text{C}\cdot\text{min}^{-1}$ under an air purge. Dynamic mechanical analyses (DMA) were performed on a TA Q800 analyzer with a heating rate of 5 $^\circ\text{C}\cdot\text{min}^{-1}$ and 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 $^\circ\text{C}\cdot\text{min}^{-1}$ and a load force of 0.05 N in a nitrogen flow. The in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices of PA films about $5 \pm 1 \mu\text{m}$ 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 $\text{mm}\cdot\text{min}^{-1}$. 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



Scheme 1 Synthesis of aromatic PA resin.



Scheme 2 Preparation of aromatic PA films.

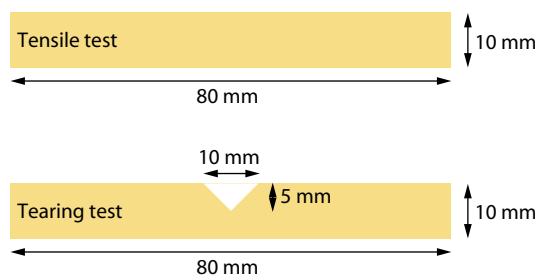


Fig. 1 Specimen sizes of tensile and tearing tests.

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.^[28] 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⁻ ion.^[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

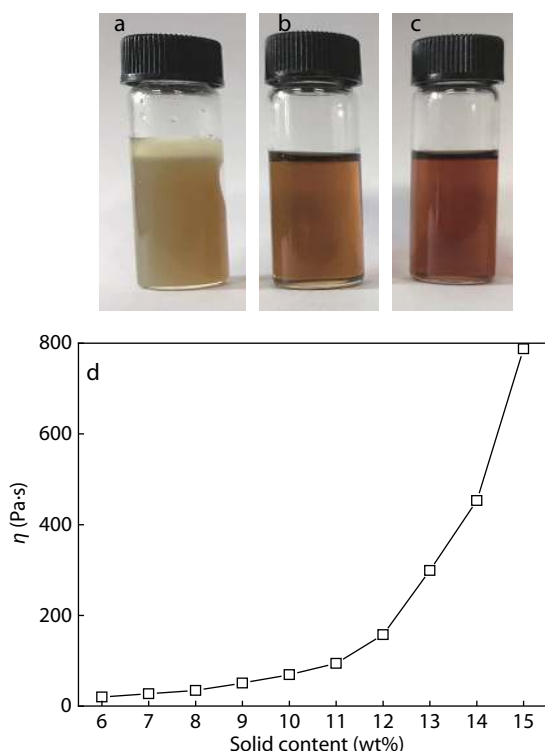


Fig. 2 PA resins in different conditions: (a) without CaO; (b) with CaO; (c) stored for a year. (d) The viscosity of PA resin solution versus solid content.

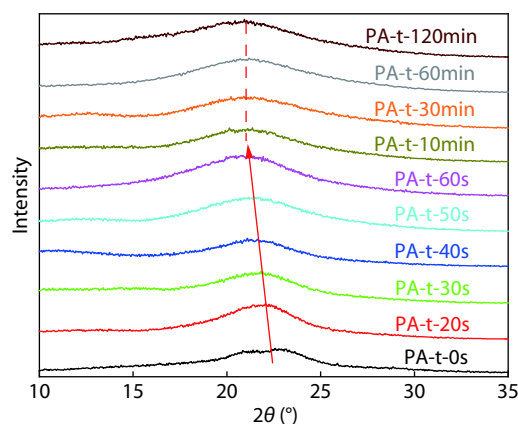


Fig. 3 XRD patterns of PA-t films.

and more water molecules penetrated into polymer matrices, enlarging the distance between molecular chains.^[32,33] 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_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_5 , T_{10} and the highest R_w simultaneously, which could be interpreted by the formation of CaCl_2 during the polycondensation. On the one hand, the generated CaCl_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_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_5 and T_{10} enhanced dramatically from 383 °C to 486 °C and 427 °C to 520 °C, while R_w dropped sharply from 38.79% to 2.38% (Fig. 4). Afterwards, T_5 and T_{10} leveled off at 490 and 520 °C, while R_w diminished slightly and stabilized nearly 0%,

Table 1 Thermal properties of PA-t films.

PA-t films	T_5^a (°C)	T_{10}^b (°C)	R_w^c (%)	T_g^d (°C)	CTE ^e (ppm·K ⁻¹)
PA-t-0s	383	427	38.79	337	17.8
PA-t-20s	486	520	2.38	329	19.6
PA-t-30s	487	519	1.97	326	18.9
PA-t-40s	489	519	1.35	324	19.5
PA-t-50s	488	520	0.94	321	19.0
PA-t-60s	490	522	0.75	314	19.3
PA-t-10min	491	520	0.87	310	18.2
PA-t-30min	489	520	0.78	311	20.4
PA-t-60min	487	517	0.58	311	19.7
PA-t-120min	485	514	0.48	312	19.8

^a T_5 : decomposition temperature at 5% weight loss; ^b T_{10} : decomposition temperature at 10% weight loss; ^c R_w : the char yield at 800 °C; ^d T_g : glass transition temperature, $\tan\delta$ peak value determined by DMA; ^e CTE: coefficient of thermal expansion from 50 °C to 250 °C.

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_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_2 . Furthermore, Fig. 5 illustrates calcium and chloride (Ca^{2+} , Cl^-) distributions in film cross-section carried out by EDS measure-

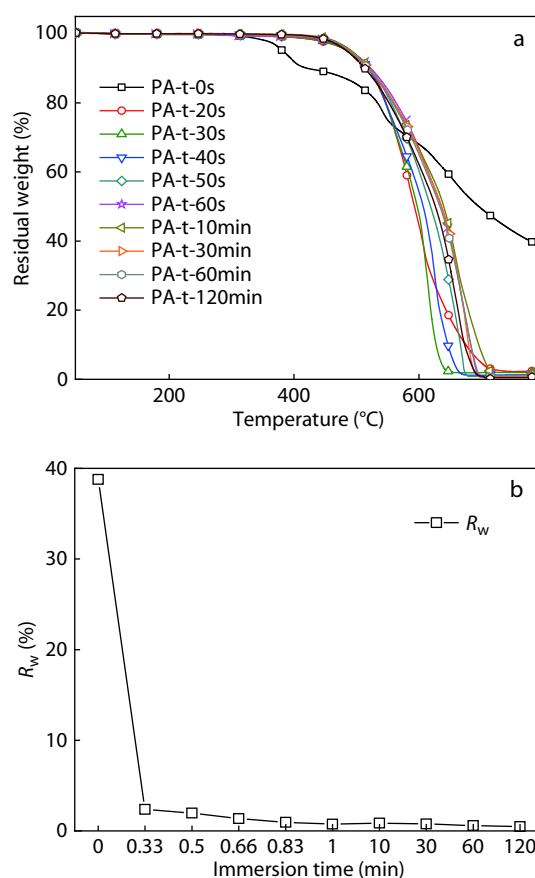


Fig. 4 (a) TGA curves in air of PA-t films; (b) R_w of PA-t films versus immersion time.

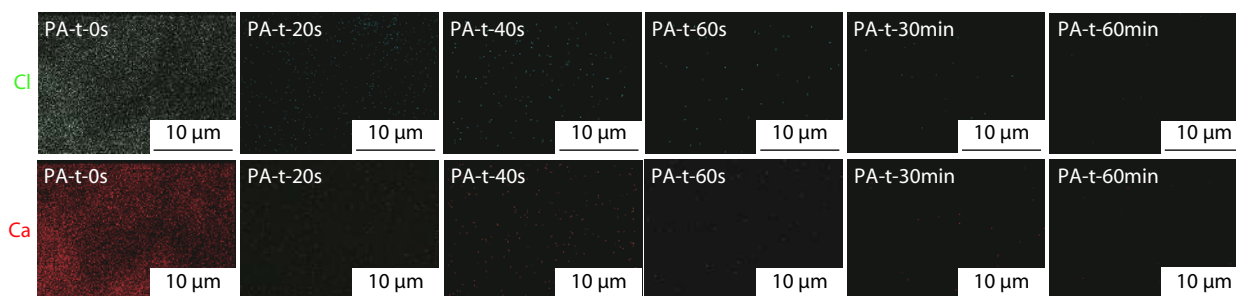


Fig. 5 Element distributions in cross sections of PA-t films.

ment, which indicates that CaCl_2 content plunged to a fairly low level in the first 1 min and then maintained at this level. Combined with TGA curves, the generated CaCl_2 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.

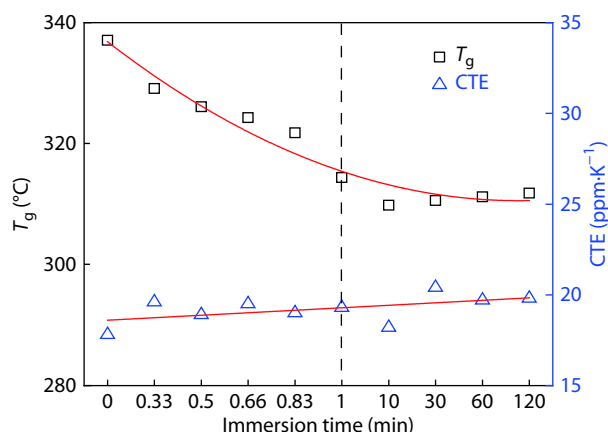


Fig. 6 T_g and CTE of PA-t films versus immersion time.

This is ascribed to the following two reasons: (a) the residual CaCl_2 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.^[33] When the immersion time exceeded 1 min, CaCl_2 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 CaCl_2 , which could be regarded as cross-linking points and restricted the mobility of polymer chains.^[34]

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 CaCl_2 . As discussed above, only 20 s of water bath could remove more than 95% CaCl_2 , so the optical properties were significantly enhanced after being exposed in water bath. During the initial 1 min, the YI and Haze values

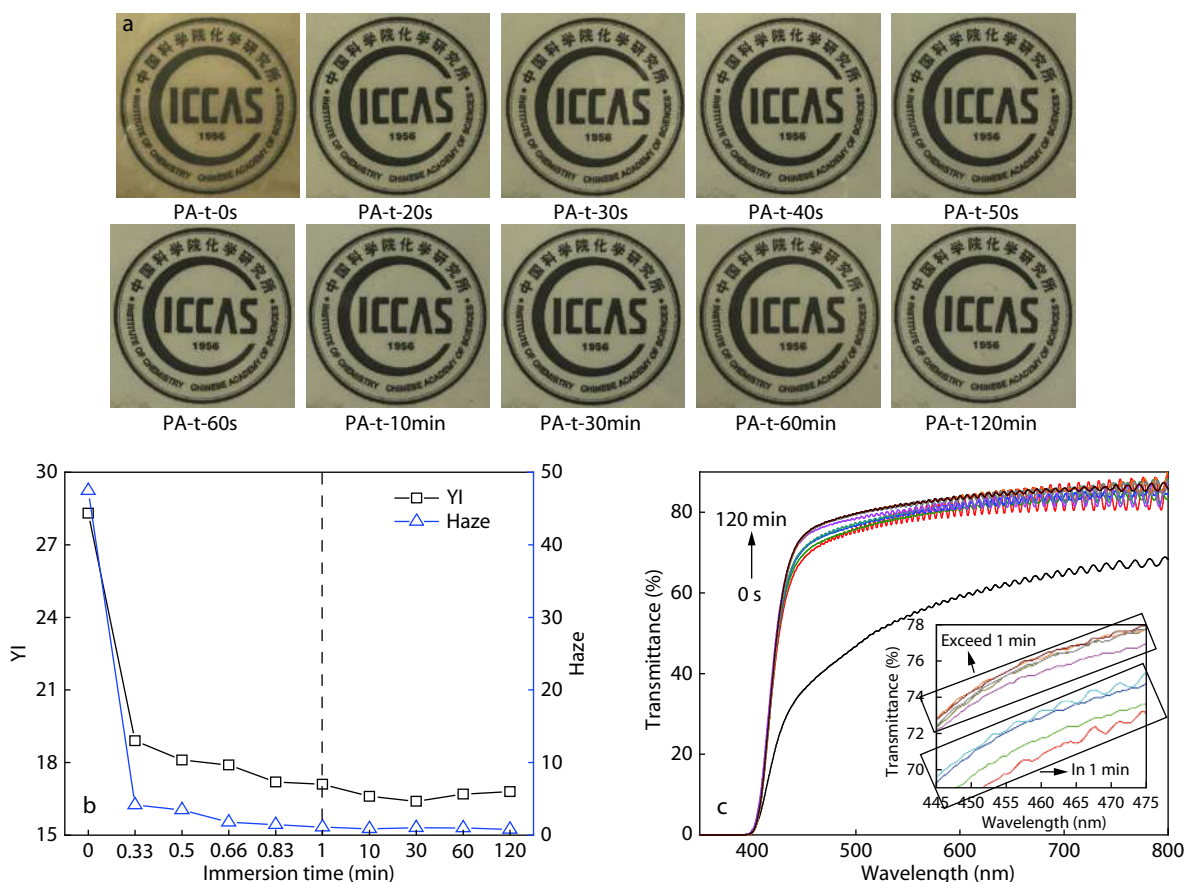


Fig. 7 (a) Images of PA-t films covered on the logo of Institute of Chemistry, Chinese Academy of Sciences; (b) YI and Haze values versus immersion time and (c) UV-Vis spectra of PA-t films.

plunged from 28.3 to 17.1 and 47.5 to 1.1, respectively, while UV-Vis transmittance increased from 58.2% 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 $\text{kN}\cdot\text{m}^{-1}$ to 504 $\text{kN}\cdot\text{m}^{-1}$, 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 $\text{kN}\cdot\text{m}^{-1}$, respectively. A typical commercial polyimide film (Kapton HN[®], Dupont) had a T_R of 288 $\text{kN}\cdot\text{m}^{-1}$,^[35] much lower than that of PA-t films, manifesting the remarkable durability of our PA films in practical applications.

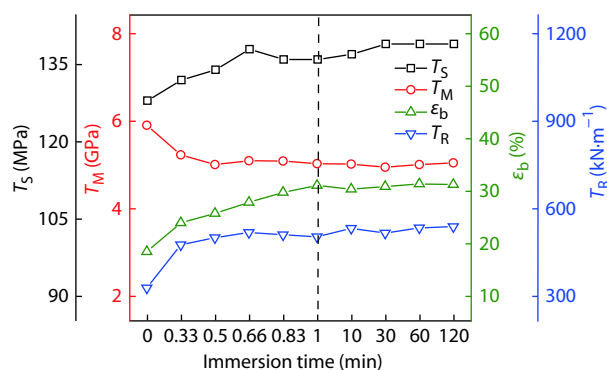


Fig. 8 Mechanical properties and tear resistance versus immersion time.

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.^[36–38] 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, suggest-

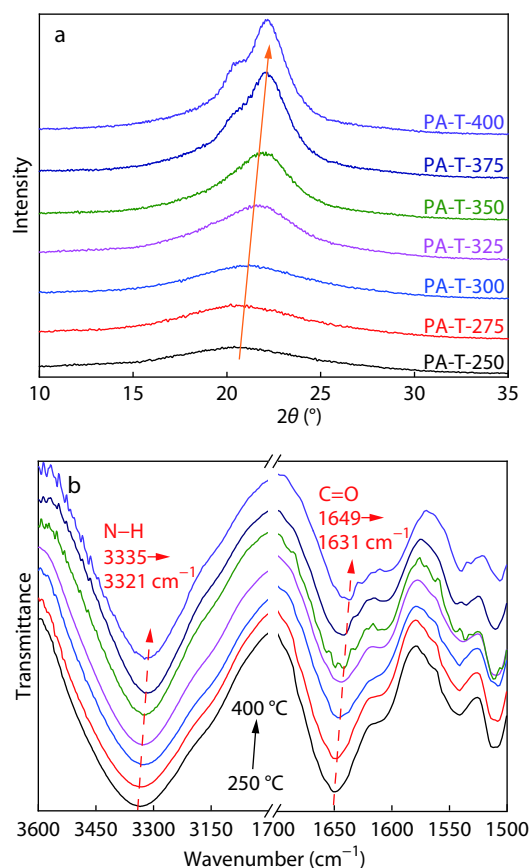


Fig. 9 (a) XRD patterns of PA-T films and (b) magnification of N—H and C=O in FTIR spectra.

ing 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.^[39] Additionally, the 2θ 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.^[40] 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.^[41] 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. These hydrogen bonds led to the decrease in wavenumbers of stretching vibrations.^[42,43] It is noteworthy that both the stretching vibrations of N—H and C=O groups gradually moved to the lower wavenumbers (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 wavenumbers 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. S3 (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_5 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 CaCl₂ was totally removed from the film via immersion in water for 10 min.

Table 2 Thermal stabilities of PA-T films.

PA-T film	T_g^a (°C)	T_5^b (°C)	T_{10}^c (°C)	R_w^d (%)	CTE ^e (ppm·K ⁻¹)
PA-T-250	304	481	511	0.79	17.8
PA-T-275	307	482	511	0.64	19.1
PA-T-300	311	492	518	0.91	19.7
PA-T-325	324	486	515	0.73	21.4
PA-T-350	368	483	512	0.67	23.6
PA-T-375	412	480	511	0.84	24.3
PA-T-400	451	487	516	0.81	25.0

^a T_g : decomposition temperature at 5% weight loss; ^b T_{10} : decomposition temperature at 10% weight loss; ^c R_w : the char yield at 800 °C; ^d T_g : glass transition temperature, $\tan\delta$ peak value determined by DMA; ^e CTE: 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 s 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 .^[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,^[44] which can be interpreted by birefrin-

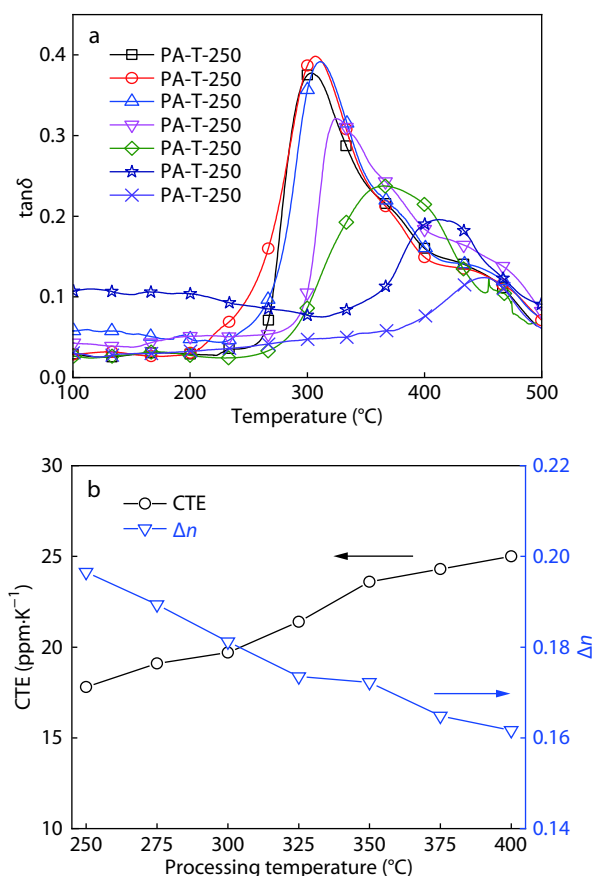


Fig. 10 (a) DMA curves and (b) CTE and Δn values of PA-T films.

gence. Fig. S4 (in ESI) depicts the in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices of PA-T films. Apparently, n_{TM} descended while n_{TE} ascended contrarily with the increase of processing temperature. Therefore, the birefringence [Δn ($= n_{TM} - n_{TE}$)] 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 polyamide chains were preferentially aligned parallel to the film plane direction.^[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,^[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.

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 (ϵ_b), and tear strength (T_R), 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

properties of PA films. Moreover, the strong intermolecular interaction also provided the PA films with outstanding tear resistance, with their T_R 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®). Since the higher processing temperature led to the more ordered regions,^[39,40] 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_M raised slightly from 4.67 GPa to 5.36 GPa while ϵ_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_S , T_M , ϵ_b , and T_R 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_S^a (MPa)	T_M^b (GPa)	ϵ_b^c (%)	T_R^d (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_S : tensile strength; ^b T_M : tensile modulus; ^c ϵ_b : elongation at break; ^d T_R : 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.^[47,48] 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	λ_{cut}^b (nm)	T_{av}^c (%)
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 λ_{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

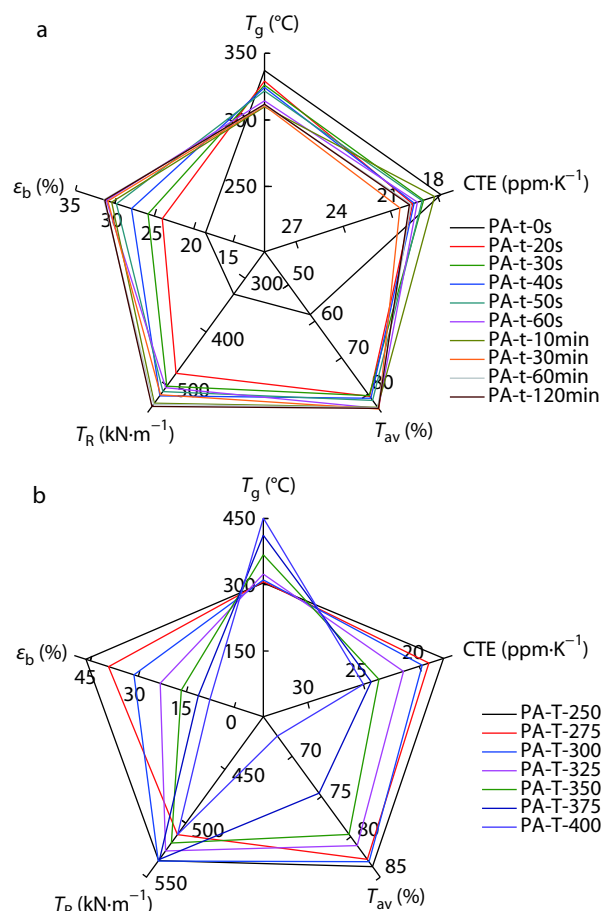


Fig. 11 The comprehensive properties of (a) PA-t films and (b) PA-T films.

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 CaCl₂ was easily removed from polymer matrices via water bath. Experimental results suggested that 1 min in water bath was a crucial point, within which CaCl₂ partially remained in PA films and deteriorated the properties of PA films. However, the comprehensive properties of PA 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_S , T_M , ϵ_b , T_R and T_{AV} more than

140 MPa, 5.0 GPa, 31%, 510 kN·m⁻¹, and 83%, respectively. Hence, this industrialized tape-casting method can be applied to aromatic polyamides to prepare high performance PA films in large scale.

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>.

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