

Synthesis and Properties of Hydrogen-Bonded Poly(amide-imide) Hybrid Films

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ABSTRACT: Poly(amide-imide), PI, hybrid films are prepared by using sol-gel techniques. First, the poly(amide amic acid) with controlled block chain length of 5000 and 10,000 g/mol and uncontrolled chain length are synthesized by condensation reaction with 4,4'-diaminodiphenyl ether (ODA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), trimellitic anhydride chloride (TMAC) and terminated with *p*-aminopropyltrimethoxysilane (APrTMOS). And then the imidization reactions of poly(amide amic acid) are proceeded to obtain the poly(amide-imide) hybrid film. Hybrid films with 5000 g/mol block chain length possess higher storage modulus, lower glass transition temperature and damping intensity comparing to films with 10,000 g/mol block chain length. The addition of TMAC to the poly(amide-imide) hybrids is due

to the increase of toughness and intermolecular hydrogen bonding, which is the average strength of intermolecular bonding and studied by the hydrogen-bonded fraction (f_{bonded}), frequency difference ($\Delta\nu$) and shiftment. Meanwhile, PI hybrid films containing more APrTMOS and TMAC content possess higher thermal and mechanical properties. On the other hand, hybrid films with 10,000 g/mol block chain length and more TMAC content have higher gas permeabilities than other films. The degradation temperatures of 5 wt % loss of all hybrid films are all higher than 540°C and increased as the increase of TMAC content. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3689–3697, 2007

Key words: poly(amide-imide); sol-gel; hydrogen bonding; gas permeability; dynamic mechanical properties

INTRODUCTION

Poly(amide-imide) (PI) possesses excellent mechanical properties, outstanding thermal stability, ultrathin films forming ability, and almost for the needs of the separation requirements.^{1–8} Spinu et al.⁹ used the precursors for the chemical bonding of PI/inorganics (tetramethoxysilane, TMOS). Morikawa et al.^{10,11} prepared PMDA-ODA/silica hybrid material by sol-gel method. While as the content of TMOS exceed 70 wt %, serious phase separation are happened and the particle size of silica dispersing in polyimide matrix are larger than 5 μm . While Hedrick and coworkers¹² used *p*-aminophenyltrimethoxysilane (APTS) for the bonding chemicals between silica chains. Small amount of APTS addition can increase the tensile strength and transparency of hybrid materials, while

phase separation is decreased. Recently, sol-gel reaction method has been widely used in polymer/inorganics hybrid materials. Generally, these polymer/inorganics hybrid materials can effectively increase the mechanical and thermal properties by the microstructure of inorganics dispersing in polymer matrices and the phase separation phenomenon is reduced owing to the interpenetrating network formed by hybrid structures.

In this manuscript, the poly(amide-imide) by trimellitic anhydride chloride (TMAC) and dianhydride (BTDA) with diamine(ODA) and monoamine (APrTMOS) is solution polymerized in polar aprotic NMP solvent. TMAC is added to the synthesis of poly(amide-imide) films for the formation of intermolecular hydrogen bonding and the increase of toughness due to the linear structure of amide groups formed by TMAC and ODA. These two changes of structures will influence the mechanical properties and gas transport phenomena of hybrids. While, the higher mechanical strength and heat resistance will be increased by the induction of APrTMOS, which can control the PI block chain length and crosslink density. Glass transition temperature, dynamical mechanical properties, functional groups, heat resistance, and O₂/N₂ separation per-

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formance were analyzed by DMA, FTIR, TGA, and gas permeability analyzer, respectively.

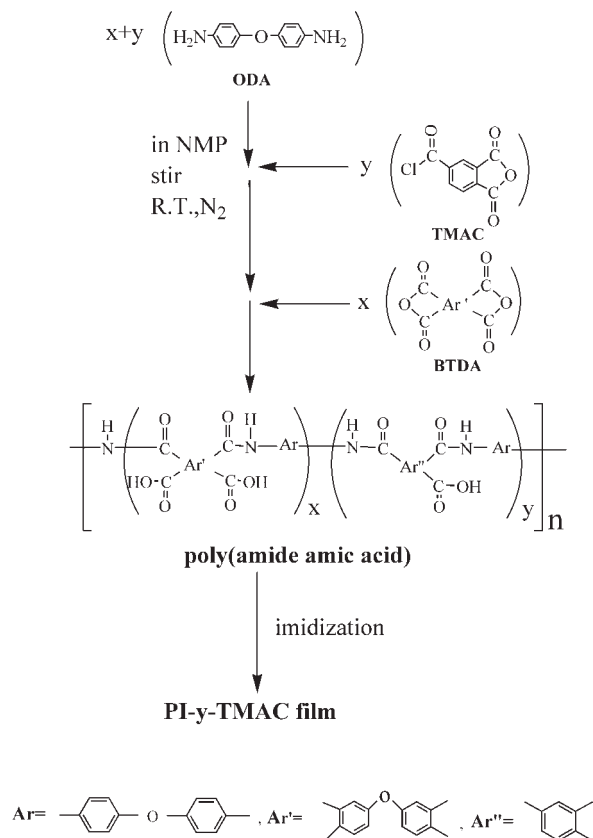
EXPERIMENTAL

Materials

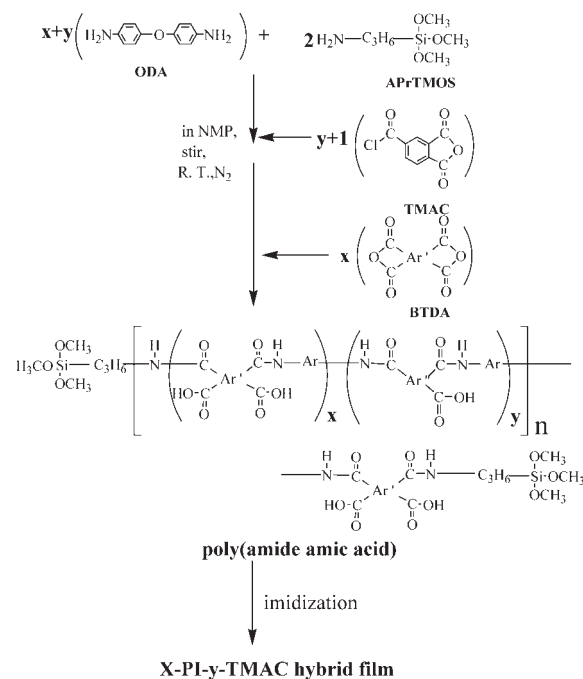
4,4'-diaminodiphenyl ether (ODA, 98%) from Lancaster is subjected to a thermal treatment in a vacuum oven at 120°C for 3 h prior to use. 3,3', 4,4'-benzophenonetetracarboxylic dianhydride (BTDA) from Tokyo Chemical Industry is purified by recrystallization from acetic anhydride and then dried in a vacuum oven at 125°C over night. *P*-aminopropyltrimethoxysilane (APrTMOS) and trimellitic anhydride chloride (TMAC) from Tokyo Chemical Industry are used as supplied. *N*-methyl-2-pyrrolidone (NMP) from Tedia Company is dried over molecular sieves.

Preparation of films

Suitable stoichiometric ratio of diamine (ODA) and NMP are added to the reactor and stirred at room temperature. After thoroughly stirred and dissolved, APrTMOS and TMAC are added in sequence. And then BTDA is added by three times and each addition of BTDA must be thoroughly dissolved. Continue



Scheme 1 Preparation of chemical structure of PI-*y*-TMAC films.



Scheme 2 Preparation of chemical structure of X-PI-*y*-TMAC hybrid films.

stirring and reaction for 2 h and then poly(amide amic acid) with 18 wt % solid content are obtained and put in the refrigerator before usage. Add TMAC and APrTMOS to the reaction owing to the hydrogen bonding formation and controlling block chain length of 5000 or 10,000 g/mol, respectively. While the block chain length are calculated as presented in the previous manuscript.^{13–16} Pour the poly(amide amic acid) solution on the glass plate, which has been put on the PET film beforehand and then 250 μm thick film obtained by knife coating and preparing for the imidization in the oven. Imidization condensation reaction from 60 to 100, 150, 200 and 300°C for each 1 h, respectively, are carried. Imidization reactions between amide group and carboxyl acid group are then proceeded to form the imide ring structure. Sample abbreviations are named as *x*-PI-*y*-TMAC. Where *x* represents as the block chain length of BTDA-ODA and *y* acts as mole ratio of TMAC/TMAC + BTDA. If no *x* or *y* expressed, which means that film prepared under uncontrolled chain length or no TMAC added. Schemes 1 and 2 show the preparation and chemical structure of PI-*y*-TMAC and *x*-PI-*y*-TMAC hybrid films, respectively. For example, 5000-PI-10-TMAC means that PI with block chain length of 5000 g/mol and 0.1 mol ratio (or 10 mol %) of TMAC with respect to total mole of BTDA and TMAC. As in the preparation of the APrTMOS-terminated polyamic acid with

TABLE I
Mole Ratio of All Samples^a

Sample Code ^a	ODA	BTDA	APrTMOS	TMAC
Pure PI	1	1	0	0
PI-05-TMAC	1	0.95	0	0.05
PI-10-TMAC	1	0.90	0	0.10
PI-15-TMAC	1	0.85	0	0.15
5000-PI ^b	1	1.121	0.242	0
10000-PI	1	1.056	0.112	0
5000-PI-05-TMAC	1	1.065	0.242	0.056
5000-PI-10-TMAC	1	1.009	0.242	0.112
5000-PI-15-TMAC	1	0.953	0.242	0.168

^a Mole of ODA + mole of AprTMOS \times 1/2 = mole of BTDA + mole of TMAC.

^b Block chain length is calculated by Carother's equation,

$$n = \frac{1+r'}{1-r'} r = \frac{n_{ODA} - n_{APrTMOS}}{n_{BTDA} + n_{TMAC}}$$

a polyamic acid block molecular weight of 5000, 0.00667 mol of BTDA(or BTDA + TMAC) is added into the solution containing 0.00595 mol of ODA and 0.00144 mol of APrTMOS in 16.4 g of NMP(for the solution with 18% solid content(w/w)). Meanwhile, the block chain lengths are calculated by theoretical equation of Carother's and presented on Table I. The mole ratio corresponding to all samples are worked out (see Table I).

Characterization and measurements

Infrared spectra and hydrogen-bonded carbonyl are obtained using a Nicolet Protégé-460 fourier transform infrared spectrophotometer (FTIR) with a heating stage and at high temperature. The samples are spin coating on the KBr plate and then the FTIR spectra are in situ measured through different temperatures. Hydrogen-bonded fraction (f_{bonded}), frequency difference ($\Delta\nu$) and shiftment of absorption frequency are used to study the average strength of intermolecular hydrogen bonding for the TMAC containing PI hybrids. The peak due to hydrogen-bonded C=O stretching is centered at about 1680 cm^{-1} and that due to free-bonded C=O stretching is centered at about 1725 cm^{-1} . The extent of the carbonyl group participating in hydrogen-bonded is represented by f_{bonded} , which is the relative absorbances of the hydrogen-bonded carbonyl peak ($A_{\text{C=O, bonded}}$) to that of the total absorbances of the C=O groups. While the frequency difference is defined as $\Delta\nu = \nu_f - \nu_b$, where ν_f and ν_b are the frequencies of maximum absorption for the free and hydrogen bonded C=O group, respectively. The frequency difference in the stretching frequency is considered as a measure of the strength of the hydrogen bond between molecules.¹⁷⁻¹⁹ On the other hand, frequency shiftment of hydrogen-bonded C=O stretching to lower frequency as the degree of hydrogen bonding between molecules increased and

can be used as a measure of the strength of hydrogen bonding also.^{20,21}

Thermogravimetric analysis (TGA) is carried out with a TA Instrument 2950 at a heating rate of 10°C/min and under air environment. The glass transition temperature, $\tan \delta$ peak and dynamic mechanical properties are measured by a TA Instruments DMA 2980 dynamic mechanical analyzer with a heating rate of 3°C/min and 1 Hz. Oxygen and nitrogen permeability of hybrid films are measured by using the Yanaco GTR-10 gas permeability analyzer and tested at 35°C. The data of gas permeabilities are the average of at least three times of measurements. Experiments are obtained by measuring flows through the film under constant 38 cmHg pressure difference (ΔP), which is the gauge pressure and must be added with 76 cmHg for the calculation of gas permeability. The gas permeation area is 15.6 cm^2 and the gas permeability is evaluated by the following equation:

$$P = \frac{ql}{(P1 - P2)A}$$

where P is the gas permeability [cm^3 (STP) $\text{cm}/(\text{cmHg cm}^2 \text{ s})$], q is the volumetric flow rate of gas permeation [cm^3 (STP)/s], l is the film thickness (cm), $P1$ and $P2$ are the upstream and downstream pressures (cmHg) and A is the effective film area (cm^2).

RESULTS AND DISCUSSION

FTIR characterization

Imidization condensation reaction are performed by step heating of poly (amide amic acid) at 60, 100, 150, 200 300°C for every 1 h, respectively. Transparent, linear, and crosslinked structure of poly (amide-imide) hybrid films are then obtained. Because of the same imidization procedures for all pure PI and PI hybrids, only four examples of pure PAA, pure PI, PI-15-TMAC, and 5000-PI-15-TMAC are investigated in Figure 1. Characterized absorption peaks of polyimide are all obviously presented.

Absorption peaks at 1600 ~ 1750 cm^{-1} for carboxylic acid of pure polyamic acid and peaks at 3250 ~ 3450 cm^{-1} for amine groups are all disappeared, which means that the imidization reaction of these materials have completely attained as shown in Figure 1. The absorption intensity at 3200 ~ 3500 cm^{-1} of amide and polyamic acid decreases as the increase of imidization temperature and then disappeared for PI-15-TMAC as shown in Figure 2. While the characterized absorption peaks, which are (1780 cm^{-1}) of C=O asymmetrical stretching of aromatic imide, (1720 cm^{-1}) of C=O symmetrical stretching of aromatic imide and (1379 cm^{-1}) of C—N stretching, are more obviously presented for pure PI and all PI hybrids.

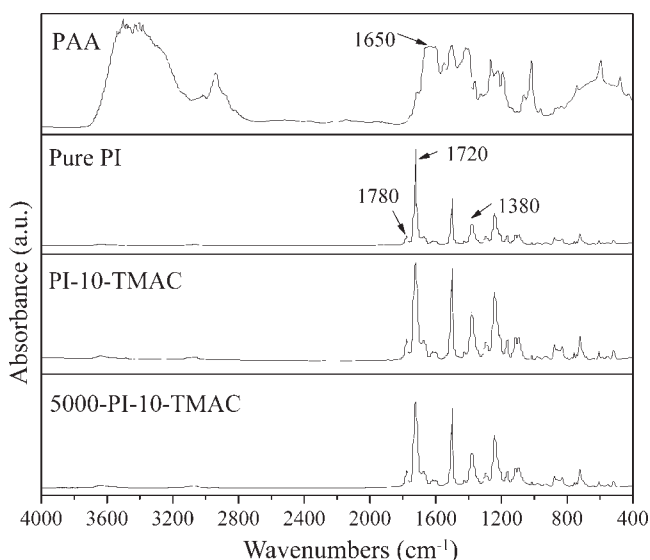


Figure 1 Infrared spectra of Pure PI, PI-10-TMAC and 5000-PI-15-TMAC films.

Effect of TMAC content: Analysis of PI-*y*-TMAC

Hydrogen bonding fraction (f_{bonded})

Hydrogen-bonded fraction (f_{bonded}), frequency difference ($\Delta\nu$) and shiftment of absorption frequency are used to study the average strength of intermolecular hydrogen bonding for the TMAC containing PI hybrids. There are two characteristic absorption peaks of carbonyl group of poly(amide-imide). One is hydrogen-bonded absorption peak, which is at about 1670 cm^{-1} . The other is free-bonded at about 1720 cm^{-1} . Hydrogen bonded carbonyl bands correspond to those groups that are mainly in the TMAC components, while the free C=O bands mainly correspond to those groups in the BTDA component. The reason is that amide groups formed through TMAC and ODA is linear structure. While amide groups formed through BTDA and ODA is at polyamic acid stage and then most amide group will react with the nearby carboxyl group to form imide ring structure, which is rigid and the C=O group on the imide ring can not be hydrogen bonded with N—H group. The extent of the carbonyl absorption group detected by FTIR participating in hydrogen bonding is expressed by the hydrogen bonding fraction (f_{bonded}). While the fraction of hydrogen-bonded of C=O group can be expressed by the following equation²²:

$$f_{\text{bonded}} = \frac{A_{\text{bonded}}}{A_{\text{bonded}} + A_{\text{free}}}$$

The A_{bonded} is the absorption peak area, which is Gaussian absorption peak using suitable base line, of hydrogen-bonded C=O group. While the A_{free} is

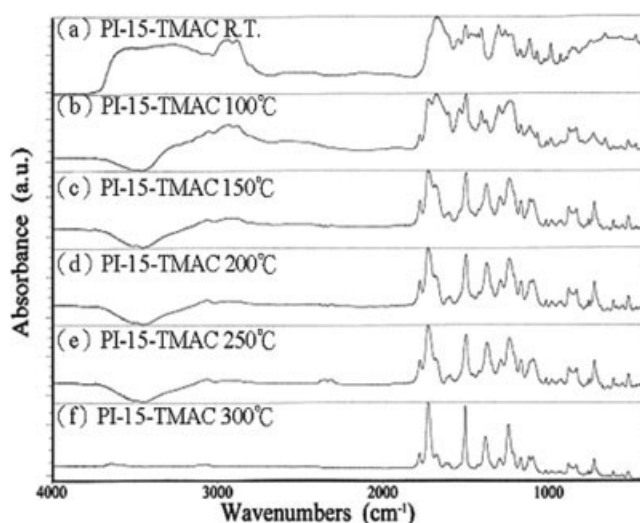


Figure 2 PI-15-TMAC by FTIR spectrophotometer (a) room temperature (b) 100°C (c) 150°C (d) 200°C (e) 250°C (f) 300°C .

absorption peak area of free-bonded C=O group. Then the values of f_{bonded} are without any unit.

Figure 3 shows the FTIR spectra of PI-5-TMAC, PI-10-TMAC and PI-15-TMAC hybrid film. It shows that the hydrogen bonded C=O absorption peak (1674 cm^{-1}) of PI-15-TMAC film has larger absorption intensity and shifts to lower frequency. And the hydrogen-bonded fraction (f_{bonded}) of PI-*y*-TMAC hybrid films increase from 7.8 to 8.2, 14.5 and 19.4 as the TMAC content increases from 0 to 5, 10 and 15 mol %. The values of f_{bonded} decrease in the following sequence: PI-15-TMAC > PI-10-TMAC > PI-5-TMAC > pure PI. The result can then be evidenced that the intermolecular hydrogen bonding of PI films are increased as the increase of TMAC content.

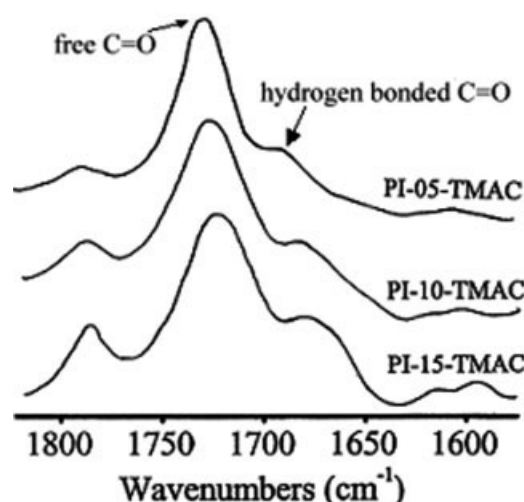


Figure 3 Analysis of carbonyl groups hydrogen bonding of PI-*y*-TMAC by FTIR spectrophotometer at imidization temperature 300°C .

TABLE II
Thermal and Dynamic Mechanical Properties of Pure PI, PI-*y*-TMAC, X-PI,
and X-PI-*y*-TMAC Hybrid Films

Sample code	Decomposition temperature $T_d(^{\circ}\text{C})^a$	Storage modulus (MPa) ^b	Glass transition temperatures $T_g(^{\circ}\text{C})^c$
Pure PI	545	2006	287.0
PI-05-TMAC	545	2253	288.2
PI-10-TMAC	546	2010	290.8
PI-15-TMAC	548	2427	292.1
5000-PI	546	2408	286.6
10000-PI	546	2257	286.3
5000-PI-05-TMAC	549	2225	292.1
5000-PI-10-TMAC	553	2250	293.5
5000-PI-15-TMAC	557	2583	294.0

^a Temperature at 5% weight loss.

^b Storage modulus of hybrid films are measured at 60°C.

^c The maximum in $\tan \delta$ curve is designated as glass transition temperature.

Frequency difference and wavenumber shiftment

Frequency difference ($\Delta\nu$) and shiftment are utilized to study the average strength of intermolecular interaction by hydrogen bonding. Coleman and coworkers²² used the frequency difference ($\Delta\nu$) between hydroxyl groups as a measure of the average strength of the hydrogen bonding between molecules and the values of $\Delta\nu$ is increased as the increase of hydrogen bonding. The frequency differences of these PI-*y*-TMAC increase from 41 to 44, 47 and 49 cm^{-1} as the TMAC content changes from 0 to 5, 10 and 15 mol % as shown in Figure 3. Then, the increase of frequency difference ($\Delta\nu$) can be used as an indication that the intermolecular average strength of these PI hybrids is increased as the TMAC content increased.

On the other hand, the infrared data of the bonded C=O group frequency of these PI-*y*-TMAC hybrids shift to the lower frequency, which changes from 1688 to 1684, 1678 and 1674 cm^{-1} as the TMAC content increases from 0 to 5, 10 and 15 mol % as shown in Figure 3. The explanation is that upon hydrogen bonding between the C=O groups of TMAC groups with —N—H group of ODA, the energy and force constant of the bonded C=O group absorption decreased and the absorption band shifts to a lower frequency.

From the above two discussions, we can confirm that the increase of TMAC content will enhance the intermolecular attraction of these PI hybrids.

TGA

TGA data as shown in Table II, which is operated by purging with air, of pure-PI, PI-*y*-TMAC and X-PI-*y*-TMAC films, can be used to manifest the formation of hydrogen bonding between molecules. Table II also shows that the decomposition temperature (T_d) of pure PI film is at about 545°C. While those of hybrid films are all above 545°C and slightly increases as the

increase of TMAC content. All the films are showing only one-step thermal weight loss. And 5 wt % loss temperatures are increased in the following sequence: PI-15-TMAC (548°C) > PI-10-TMAC (546°C) > PI-05-TMAC (545°C) > pure PI (545°C). This indicates that TMAC containing PI hybrid films possess a little better thermal property than pure PI film. Meanwhile, the 5 wt % loss temperatures are increased in the following sequence: 5000-PI-15-TMAC (557°C) > 5000-PI-10-TMAC (553°C) > 5000-PI-05-TMAC (549°C) > PI-*y*-TMAC (545 ~ 548°C) > pure PI (545°C). This indicates that block chain length (by APrTMOs) and hydrogen bonding (by TMAC) show synergistic effects on the decomposition temperatures. So that TGA data of T_d values can be used as a collateral evidence for the intermolecular hydrogen bonding due to the addition of TMAC.

Dynamical mechanical analysis

The storage modulus, $\tan \delta$ peak and damping intensity are investigated by dynamical mechanical analysis (DMA) measurements. The storage modulus of films containing TMAC components are all higher than that of pure-PI possesses and increase as the TMAC content increased and shown in Figure 4(a). While Figure 4(b) shows that damping peak position, which is T_g , shifts to higher temperature and increases as the increase of TMAC content and the damping peak height decreases as the increase of TMAC content. From the $\tan \delta$ values, the film of PI-15-TMAC possesses the highest T_g values at 292.1°C and lowest damping peak height. Table II indicates that the T_g values are increased from 287 to 288.2, 290.8 and 292.1°C as the TMAC content increases from 0 to 5, 10 and 15 mol %. The explanation for the above results is due to the addition of TMAC to the PI polymer. There are two contradictory effects of

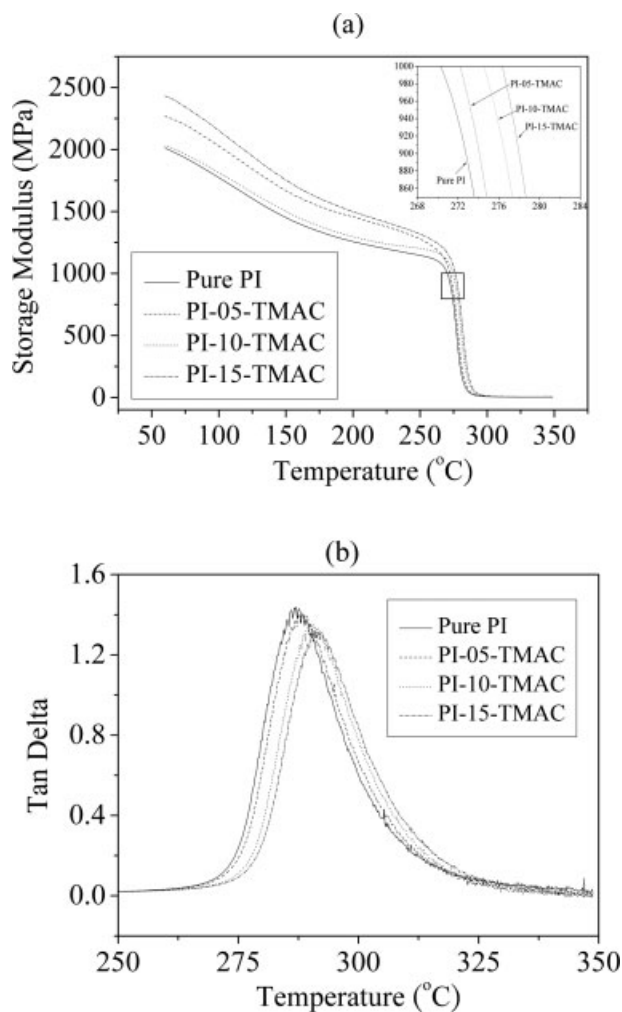


Figure 4 (a) Storage modulus and (b) Tan δ of pure-PI and PI-y-TMAC films.

adding TMAC for dealing with the mechanical properties of PI hybrids. One is that TMAC is a soft segment and linear structure comparing to the rigid BTDA component, which is with ring structure after imidization reaction. This will induce the decrease of storage modulus with respect to the increase of TMAC content. In spite of this drawback, the other is that the intermolecular hydrogen bonding of PI films are increased as the increase of TMAC content. The increase of hydrogen bonding, due to the increase of TMAC component, will restrict the molecular chain mobility and then increase the storage modulus and T_g value of PI hybrids. Furthermore, the number of hydrogen bonding point of polymer chain will be increased as the increase of TMAC content and then the rotation and stretching of polymer chain become difficultly, which is the reason for the decrease of damping intensity. While PI-15-TMAC polymer has the largest TMAC content and hence possesses the highest intermolecular hydrogen bonding that will result in that PI-15-TMAC polymer has the largest

storage modulus, T_g value and lowest damping intensity comparing than those of PI-05-TMAC and pure PI.

Effect of block chain length on X-PI films: DMA measurements

Figure 5(a) shows that PI film with block chain length of 5000 g/mol possesses higher storage modulus than 10,000 g/mol and pure-PI. The storage modulus decreases in the following sequence as 5000-PI > 10,000-PI > pure-PI. While Figure 5(b) shows the damping intensities of tan δ decrease in the following sequence as pure-PI > 10,000-PI > 5000-PI. The purpose of the addition of AP_rTMOS for the PI synthesis is to control the block chain length of BTDA-ODA, which is a rigid segment in PI chain, and then intermolecular crosslink will occur between $-\text{Si}(\text{OCH}_3)_3$

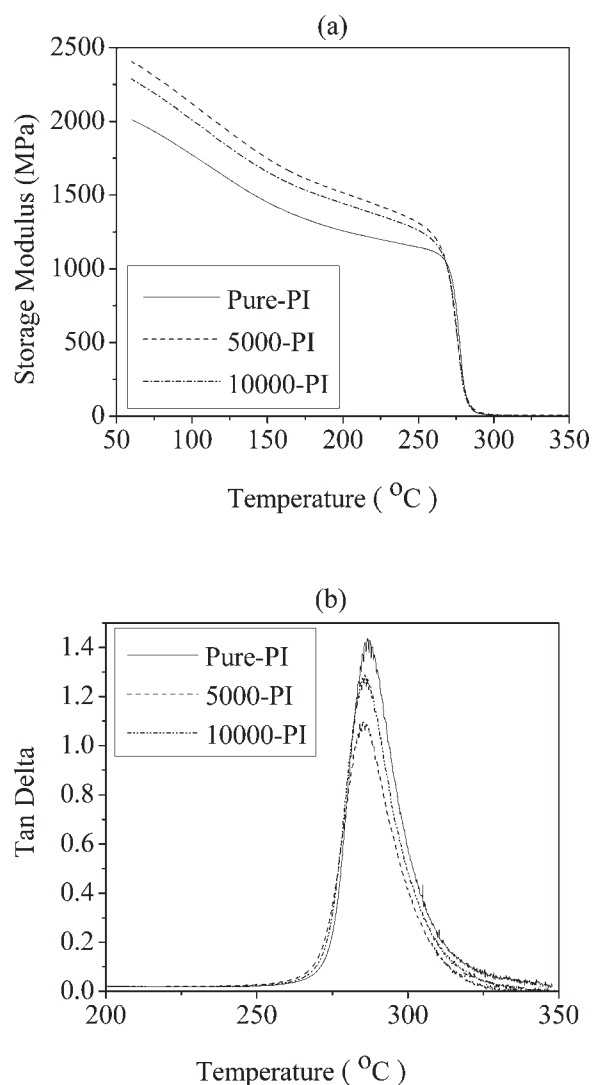


Figure 5 (a) Storage modulus and (b) Tan δ of pure-PI and X-PI hybrid films.

groups of APrTMOS by sol-gel reaction. Because $-\text{Si}(\text{OH})_3$ groups are formed through the sol reaction between $-\text{Si}(\text{OCH}_3)_3$ groups. And then $-\text{Si}-\text{O}-\text{Si}-$ crosslink structures are formed through the gel reaction to take off water. The increase of APrTMOS content will decrease the BTDA-ODA block chain length and increase the intermolecular crosslinked density. 5000-PI is synthesized with higher APrTMOS component than 10,000-PI does. Then 5000-PI possesses lower block chain length and higher crosslinked density comparing to that of 10,000-PI polymer. On the other hand, polymer with rigid segment and more crosslinkage will induce the decrease of damping intensity. This is the reason why 5000-PI possesses the highest storage modulus and lowest damping intensity among these three polymers.

Table II presents that the T_g and T_d value of these films are nearly the same. In other words, the T_g and T_d value of these films do not increase as the increase of crosslink density. Intuitively, this is not in agreement with the traditional comment. The reason may be that BTDA-ODA is a rigid segment. And 5000-PI, which possesses more rigid segment and crosslink density, will possess the highest T_g value. On the other hand, the APrTMOS component possesses aliphatic $-\text{CH}_2\text{CH}_2\text{CH}_2-$ structures, which is the soft segment. Then 5000-PI, which contains more APrTMOS content, will have lowest T_g and T_d value. These two contradictory effects have the reverse same effect on the T_g and T_d value. As a result of the competition of these two effects, T_g and T_d values of 5000-PI polymer are nearly the same as 10,000-PI polymer.

Effect of TMAC content: DMA and TGA measurements of 5000-PI- y -TMAC

Different contents of TMAC are added to the 5000-PI polymer for the study of TMAC content effect on the dynamic mechanical properties and thermal decomposition temperature. Figure 6(a,b) show the storage modulus and $\tan \delta$ curves of same PI block chain length with 5000 g/mol but with different TMAC content from 0 to 10 and 15 mol ratios with respect to BTDA, which named as 5000-PI, 5000-PI-10-TMAC and 5000-PI-15-TMAC. The 5000-PI-15-TMAC hybrid possesses the highest storage modulus, T_g value, and lowest damping intensity than the other two polymers. The T_g values are increased from 286.6 to 292.1, 293.5 and 294°C. While the decomposition temperatures of these 5000-PI- y -TMAC hybrids are increased from 545 to 549, 553 and 557°C as the TMAC content increased from 0 to 5, 10 and 15 mol % as presented in Table II. The explanation is that 5000-PI-15-TMAC possesses the highest number of hydrogen bonding point among three polymers and hence the intermolecular attraction increased and as shown in Figure 3. Then the increase of hydrogen bonding due to TMAC

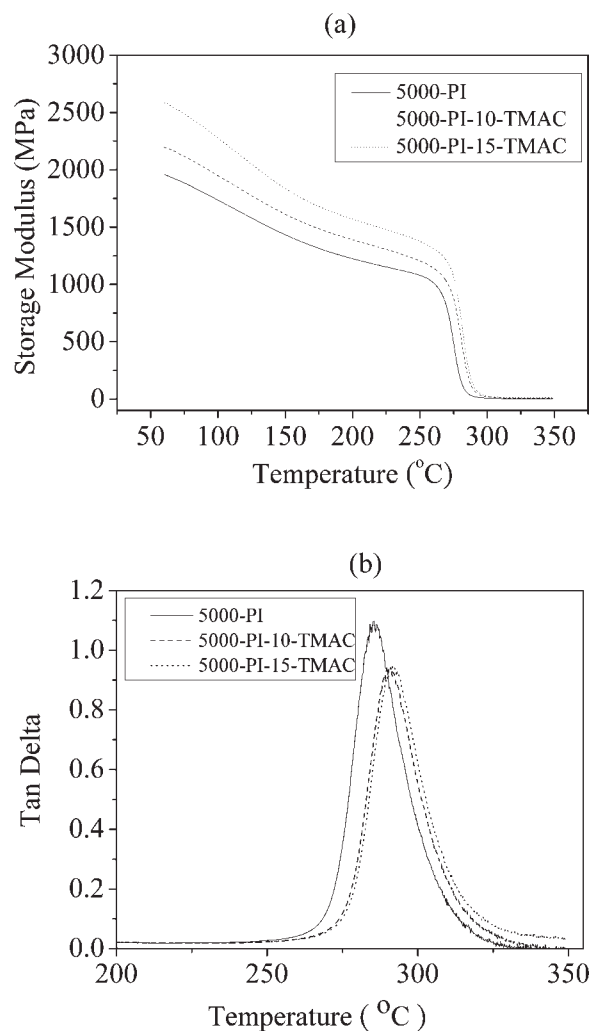


Figure 6 (a) Storage modulus (b) $\tan \delta$ of 5000-PI and 5000-PI- y -TMAC hybrid films.

component will restrict the molecular chain mobility and the rotation and stretching of polymer chain become more difficultly. The above explanations are the reason for the increase of storage modulus, T_g and T_d value as the increase of TMAC content.

Gas separation performances

Effect of block chain length

Figure 7 shows that the oxygen permeabilities are decreased in the following sequence: 10,000-PI > 5000-PI > Pure-PI. While the nitrogen permeability of these films has the same trend as oxygen permeability does. The reason for the gases permeabilities of 10,000-PI and 5000-PI are higher than Pure-PI is that the permeation of O_2 and N_2 gases is mainly through the soft segment of PI hybrids. That is there are rarely low gases permeate through hard segment of PI hybrids. Membranes of 10,000-PI or 5000-PI are prepared by adding different amount of APrTMOS,

which contains $-\text{C}_3\text{H}_6-$ of soft aliphatic composition, to the PI synthesis. Meanwhile the ether soft segment of $-\text{Si}-\text{O}-\text{Si}-$ chains will be formed by sol-gel reaction $-\text{Si}-\text{OCH}_3$ groups between intermolecular polyamic acid chains. And the pure PI is without APrTMOS content and only rarely ether group of ODA composition possesses. These explanations may be the reason for the gas permeabilities of pure PI is lower than those of 10,000-PI or 5000-PI possess.

While the gas permeability of 10,000-PI is larger than that of 5000-PI. The reason is that that the permeation rate of O_2 and N_2 gases through polymer through soft segment of polymer are depending on the free volume between molecules. There are two factors affecting the free volume of polymer film. One is block chain length of PI, the other is the crosslink density.^{23,24} The increase of these two effects will increase the free volume between polymer chains and hence increase the gas permeability. PI polymer with 10,000 g/mol possesses the highest block chain length and lowest crosslink density. The combination of above two parallel effects indicates that the former possesses superior influence on the gas permeability. This may result in the largest gas permeability for the 10,000-PI film compared with 5000-PI polymer.

Effect of TMAC content on PI-y-TMAC films

Figure 8 shows that the gas permeabilities of hybrid films increase as the increase of TMAC content, while the O_2/N_2 selectivity has the reverse trend and the values are all above 8.3. The explanation is the same as above section described and due to the free volume of polymer. In this section, there is only one factor, which is TMAC content in the PI hybrids, affects the free volume between molecules. After imidization reaction, the only soft segment of PI chain is TMAC chain with carboxyl chloride group, which is linear structure compared with other ring structure. In general,

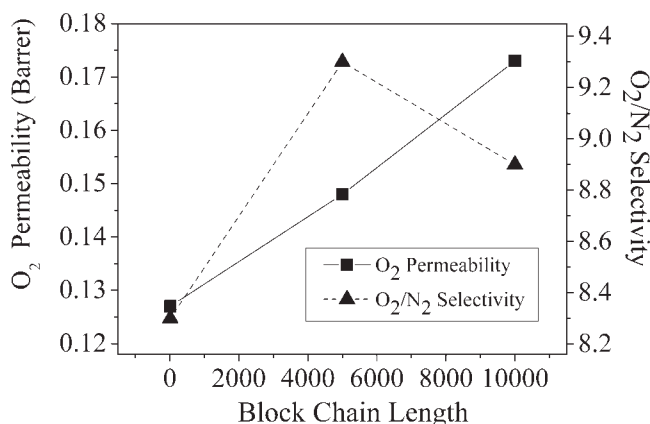


Figure 7 O_2 permeability and O_2/N_2 selectivity of pure-PI, block chain length 5000-PI and 10,000-PI hybrid films.

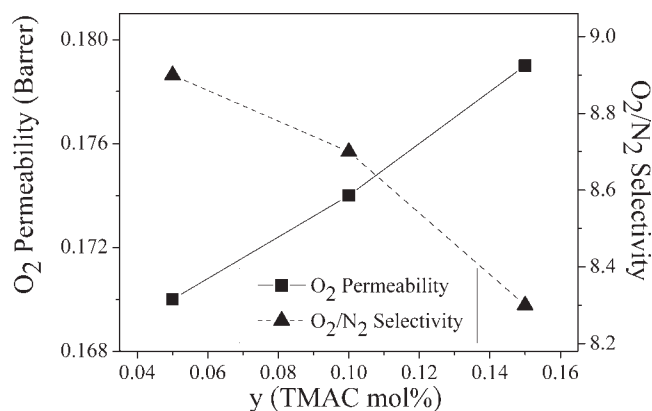


Figure 8 O_2 permeability and O_2/N_2 selectivity of PI-y-TMAC films.

gas are mainly permeating through soft segment of polymer and that diffuses through hard portion of polymer can be neglected. While as the increase of TMAC content in the PI hybrids, the soft portion (or segment) of poly (amide-imide) chain will be increased. In other words, O_2 and N_2 gases are mainly permeating through the TMAC component of these PI hybrids. Therefore, the increase of O_2 or N_2 gas permeabilities of hybrid films increase as the increase of TMAC content.

Figure 8 also shows that the O_2/N_2 selectivities are decreased as the TMAC content increased. The O_2 and N_2 gas are largely permeating through soft segment of TMAC component as in the above description. While there are three explanations for the O_2/N_2 selectivity dealing with TMAC component. One is TMAC only contain $\text{C}=\text{O}$ and $-\text{NH}$ groups and has not available usage to the selectivity of O_2 gas. The second is that the increase of intermolecular attraction by TMAC component has slight increase to the O_2/N_2 selectivity. The third is that TMAC is a soft segment will induce the decrease of O_2/N_2 selectivity. Competition with the above three effects indicate that the third effect has superior influence on the selectivity and hence the O_2/N_2 selectivities are decreased as the increase of TMAC content.

CONCLUSIONS

High thermal durability and mechanical properties of poly(amide-imide) hybrid films are prepared by sol-gel method. The characteristic absorption peak of $\text{C}=\text{O}$ groups are obviously increased as the imidization reaction temperature increased. All types of films show one-step thermal weight loss and 5 wt % loss temperature of hybrid films are all above 540°C and increase as the increase of TMAC content. It means that hybrid films maintain superior heat properties at atmosphere. The storage modulus, damping intensity and T_g of PI hybrids are all increased as the PI chain

block length decreased. While the storage modulus increases and the $\tan \delta$ peak shifts to higher temperature and damping intensity decreases as the increase of TMAC content. Film with 5000 g/mol block chain length and 15 mol % TMAC content possess the highest storage modulus and T_g values, while the damping intensity has the lowest value. Films with longer block chain length (10,000 g/mol) or more TMAC content possesses larger gas permeabilities, while the O_2/N_2 selectivities are only slightly decreased and the values are all above 8.3. And the studies on the gas permeability through X-PI- y -TMAC hybrid films are the further research aspects of our laboratory.

References

1. Stern, S. A. *J Membr Sci* 1994, 94, 1.
2. Ghosh, M. K.; Mittal, K. L. Eds. *Polyimides: Fundamentals and Applications*; Marcel Dekker: New York, 1996.
3. Huang, M. S.; Yang, M. C.; Chou, S. *Polym Polym Comp* 2006, 14, 89.
4. Ranade, A.; D'Souza, N. A.; Gnade, B. *Polymer* 2002, 43, 3759.
5. Hsiao, S. H.; Yang, C. P.; Chen, C.W.; Liou, G. S. *Eur Polym J* 2005, 77, 226.
6. Ha, S. Y.; Park, H. H.; Lee, Y. M. *Macromolecules* 1999, 32, 2398.
7. Lee, Y. B.; Park, H. B.; Shim, J. K.; Lee, Y. M. *J Appl Polym Sci* 1999, 74, 965.
8. Hu, Q.; Marand, E. *Polymer* 1999, 40, 4833.
9. Spinu, M.; Brennan, A. B.; Rancourt, K.; Wilkes, G. L.; McGrath, K. E. *Mater Res Soc Symp Proc* 1990, 175, 179.
10. Morikawa, A.; Yamaguchi, H.; Kakimoto, M.; Imai, Y. *Chem Mater* 1994, 6, 913.
11. Morikawa, A.; Iyoku, Y.; Kakimoto, M.; Imai, Y. *Polym J* 1992, 24, 107.
12. Srinivasan, S. A.; Hedrick, L. J.; Miller, R. D.; Pietro, R. D. *Polymer* 1997, 38, 3129.
13. Tsai, M. H.; Whang, W. T. *J Appl Polym Sci* 2001, 81, 2500.
14. Tsai, M. H.; Whang, W. T. *Polymer* 2001, 42, 4197.
15. Tsai, M. H.; Liu, S. J.; Chiang, P. C. *Thin Solid Film* 2006, 515, 1126.
16. Tsai, M. H.; Chiang, P. C.; Whang, W. T.; Ko, C. J.; Huang, S. L. *Surf Coating Technol* 2006, 200, 3297.
17. Chao, M. S.; Huang, S. L. *J Chinese Chem Soc* 2005, 52, 287.
18. Huang, S. L.; Chao, M. S.; Ruaan, R. C.; Lai, J. Y. *Eur Polym J* 2000, 36, 285.
19. Huang, S. L.; Chao, M. S.; Lai, J. Y. *J Appl Polym Sci* 1998, 67, 865.
20. Chen, S. H.; Huang, S. L.; Yu, K. C.; Lai, J. Y.; Liang, M. T. *J Membr Sci* 2000, 172, 105.
21. Chen, S. H.; Yu, K. C.; Huang, S. L.; Lai, J. Y. *J Membr Sci* 2000, 173, 99.
22. Skrovanek, D. J.; Howe, S. E.; Painter, P. C.; Coleman, M. M. *Macromolecules* 1985, 18, 1676.
23. Chung, T. S.; Cheng, M. L.; Pramoda, K. P.; Xiao, Y. C. *J Membr Sci* 2004, 20, 2966.
24. Liu, Y.; Wang, R.; Chung, T. S. *J Membr Sci* 2001, 189, 231.