

Effect of Silanes on the Morphology, Hydrophobicity, and Dynamical Mechanical Properties of Polyimide/Silica Hybrid Membranes

Chiou-Juy Chen, Hsu-Tung Lu, Wen-Yen Tseng, I-Hsiang Tseng, Shih-Liang Huang, Mei-Hui Tsai

Department of Chemical and Materials Engineering, National Chin-Yi University of Technology, Taichung 411, Taiwan, Republic of China

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ABSTRACT: Polyimide (PI)/silica hybrid membranes with high contact angles were prepared through the *in situ* sol-gel process. The precursor, poly(amic acid) with controlled block chain length, was synthesized using 4,4'-diaminodiphenyl ether (ODA), 3,3',4,4'-benzophenone-tetracarboxylic dianhydride (BTDA) and 3-aminopropyl-trimethoxysilane (APrTMOS) or 3-aminopropyl-dimethylethoxysilane (APDiMOS). And then, phenyltrimethoxysilane (PTS) or tetramethoxysilane (TMOS) or methyltrimethoxysilane (MTrMOS) was respectively, added to the above polyamic acid and mixed thoroughly. Following curing reaction, the PI/silica hybrid membranes with different cross-linkages, silica content, and hydrophobic properties were prepared. The effect on the formation of PI imide ring during imidization reaction is

increased as the increase of silanes content and characterized by frequency shiftment and absorbance ratio of Fourier transform infrared (FTIR) measurements. All the hybrid membranes show high transparency though with high silica contents. The storage modulus, $\tan \delta$, and damping intensity by DMA measurements are all correlated with silane content or block chain length. And all these membranes with silane content possess high contact angle as compared to pure PI without any silanes added and the contact angles increase with increasing the silane content. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 648–656, 2011

Key words: polyimide; hybrids; silanes; morphology; hydrophobicity; dynamical mechanical properties

INTRODUCTION

Polyimide (PI) is a polymer material with many superior properties^{1–4} and widely used in engineering plastics and electronic industries. It requires high hydrophobicity and thermal stability for electronic usages.⁵ In general, the addition of inorganics into PI can largely increase the thermal properties and hydrophobicity of PI hybrids. But the incompatibility between silica and rigid PI segment may induce serious phase separation and the results are the increase of the heat durability but sacrifice other properties. So that how to homogeneously disperse the inorganics into polymer is an important studying topic.

At present, sol-gel method is widely used to prepare the polymer/inorganics hybrid materials.^{6–13} No phase separation formed between polymer and silica and intermolecular cross-linkage are formed most in the bulk of film, which then induce high hydrophobicity and heat durability property can be

expected.^{14–18} In this manuscript, intermolecular covalent bonding will be formed between PI chain and silica by adding silane compound of 3-aminopropyl-trimethoxysilane (APrTMOS), 3-aminopropyl-dimethylethoxysilane (APDiMOS), phenyltrimethoxysilane (PTS), tetramethoxysilane (TMOS), or methyltrimethoxysilane (MTrMOS). The effect of composition and content of silane on PI block chain length, imide ring formation, hydrophobicity and thermal (DMA) properties are investigated.

EXPERIMENTAL

Materials

Dianhydride (BTDA, Acros organics) was purified by recrystallization of using acetic anhydride (99.8%, Tedia) to obtain recrystallized dianhydride. Diamine (ODA, 98%, Lancaster) was heated in vacuum oven at 120°C for 24 h. Water was removed from NMP (*N*-methyl-2-pyrrolidinone) solvent by treating with 4Å molecular sieve. Silanes of APrTMOS, APDiMOS, PTS, TMOS, and MTrMOS were used as received. APrTMOS and APDiMOS act as blocking/coupling agent and TMOS acts as pure silica precursor and PTS, MTrMOS are used as precursors of organo-

Correspondence to: M.-H. Tsai (tsaimh@ncut.edu.tw).

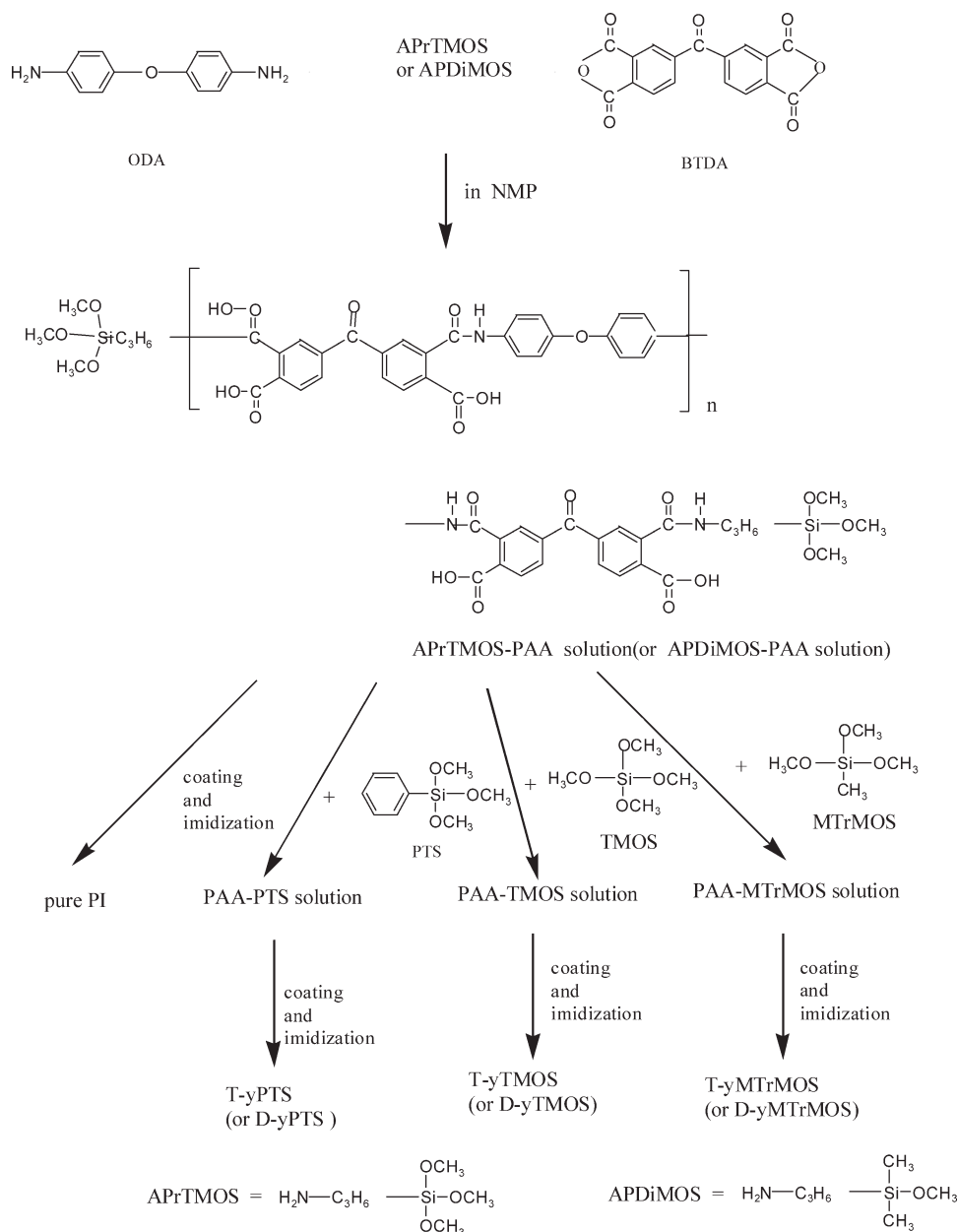


Figure 1 Synthesis procedures of PI hybrids.

silicates. The element's structures and the preparation flow chart are shown in Figure 1.

Preparation of membranes

Suitable stoichiometric ratio of diamine (ODA) and NMP were added to the reactor and stirred at room temperature. After thoroughly stirred and dissolved, APrTMOS (or APDiMOS) was added. And then stoichiometric quantity of BTDA was added in three portions and each addition of BTDA must be thoroughly dissolved. Continue stirring reaction for 2 h and then put in the refrigerator before usage and named as APrTMOS-Polyamic acid (APrTMOS-PAA) (or APDiMOS-PAA)

solution. Addition of APrTMOS or APDiMOS was for controlling the PI block chain length with 5000 or 10,000 g/mol and the polyamic acid was with 18 wt % solid content¹¹⁻¹³ and named as T-*x* (or D-*x*). Where T (or D) means that APrTMOS (or APDiMOS) is added and *x* represents as the PI block chain length with 5000 or 10,000 g/mol. Then the above solutions were poured on the glass plate, which had been put on the PET film and then 250 μm thick film obtained by knife coating. And then imidization condensation (or curing) reaction were carried on putting in the oven from 60, 100, 150, 200 to 300°C for each 1 h, respectively, and membranes of T-*x* (or D-*x*) were then prepared.

While the 2nd stage was that suitable different amount of PTS or TMOS or MTrMOS were, respectively, added to the above APrTMOS-PAA (or APDiMOS-PAA) solution, which were only with 10,000 g/mol block chain length and then obtain 25, 80, 120 wt % solution, respectively. And the following film preparation procedures and imidization conditions were the same as above. Sample abbreviations in this stage are named as T-*y*PTS (or D-*y*PTS), D-*y*TMOS, D-*y*MTrMOS. And *y* acts as wt % of PTS (or TMOS or MTrMOS)/APrTMOS-PAA (or APDiMOS-PAA). While T (or D) means that only 10,000 g/mol block chain length of APrTMOS-PAA (or APDiMOS-PAA) solution is used and the preparation flow chart is shown in Figure 1. And pure PI is only with ODA and BTDA content without any silane added.

Characterization and measurements

Infrared spectra were obtained by using a Nicolet Protégé-460 Fourier transform infrared (FTIR) spectrophotometer. Transparency of the membranes was obtained from the transmittance, which was measured at 550 nm by using a UV-vis spectroscopy (Shimadzu-UV1800) and taken air as reference with 99.9% transmittance. Contact angles were measured using a contact angle meter, shapes of droplets on PI membranes were photographed and used to characterize the hydrophobicity of hybrid's surface. The glass transition temperature (T_g), peak intensity, and storage modulus were measured by a TA Instrument DMA 2980 at a heating rate of 3°C/min and 1 Hz.

RESULTS AND DISCUSSION

Imide ring formation and characterizations by FTIR

Imidization condensation (or curing) reactions were performed by step heating of polyamic acid at 60, 100, 150, 200, and 300°C for every 1 h, respectively. Transparent and cross-linked structure of PI hybrid films were then obtained. Their transparencies are all larger than 88%, which are detected through UV-vis spectroscopy and membrane's thickness is 38 μm . Figure 2 shows the infrared spectra of T-10,000, T-25PTS, T-80PTS, and T-120PTS. The characteristic peaks of symmetric C=O stretching and asymmetric C=O stretching are clearly visible at about 1708 and 1763 cm^{-1} , respectively. The assignment of the stretching of the imide ring is at about 1363 cm^{-1} . Besides, the characteristic absorption peak at about 1110 cm^{-1} indicates that the formation of linear or networked Si-O-Si chain. And the absorption peak at 820–900 cm^{-1} indicates the Si-OH formed from the hydrolysis of methylol silane or unreacted

Si-OCH₃ group of silane agent. The above-mentioned characteristic absorption peaks were measured in the FTIR spectra of the pure PI film and all PI/silica hybrid films. Moreover, the above three absorption peaks, at about 1363, 1708, 1763 cm^{-1} , are shifted to higher frequency as the increase of silane or coupling agent content and will be discussed in the following section.

The formation of imide ring of PI chain during the imidization reaction stage may be hindered by the addition of silane to prepare PI hybrids.¹⁹ And the interruption of PI imide ring formation is investigated by two measurements: R_I values of absorbance ratio of C=O (carbonyl group) with =N- (imide ring) and absorption frequency shiftment. The larger R_I values and frequency shiftment indicate that the interruption of PI imide ring formation, which is that part of -Si-OCH₃ group of silane may react with H₂O to -Si-OH group, is more obvious. Furthermore, dipole-dipole interactions may exhibit between -Si-OH group and carboxylic acid groups of imide segment and the condensation reaction may be performed to form -Si-O-C(O)- segment during imidization reaction stage and then the imide ring formation is interrupted, which means that the absorbance of =N- (imide ring) decreased. Therefore, the R_I values of absorbance ratio of C=O (carbonyl group) with =N- (imide ring) will be increased and consequently the absorption peak shifts to higher frequency.

In the 1st stage of silane addition (APrTMOS or APDiMOS), the R_I values are of pure PI, T-5000, T-10,000, D-5000, and D-10,000 hybrids are nearly the same and at 1.18. And the absorption peak frequency of symmetric C=O stretching, asymmetric C=O stretching and imide ring stretching are all the same at 1708, 1763, and 1363 cm^{-1} , respectively. The above results may be used to explain that the imide ring formation of PI chain may be unaffected in the 1st stage of silane (APrTMOS or APDiMOS) added.

As the 2nd step of silane addition (PTS or TMOS or MTrMOS), more -Si-OCH₃ (or -Si-OH) groups will be participated into the condensation reaction with carboxylic acid groups of the above APrTMOS-PAA (or APDiMOS-PAA) solution at elevated temperature and with the liberation of H₂O during imidization reaction. Therefore, the imide ring structure formation of PI chain may be hindered and consequently the R_I values will be changed as different type or amount of silanes added. The R_I values are changed from 1.18, 1.27, 1.29–1.33 of T-10,000, T-25PTS, T-80PTS to T-120PTS. The increase of R_I values is owing to the decrease of imide ring peak absorption as the increase of PTS content, which may react with carboxylic acid groups and then hinder the formation of imide ring of PI chain during the imidization reaction stage. Furthermore, the

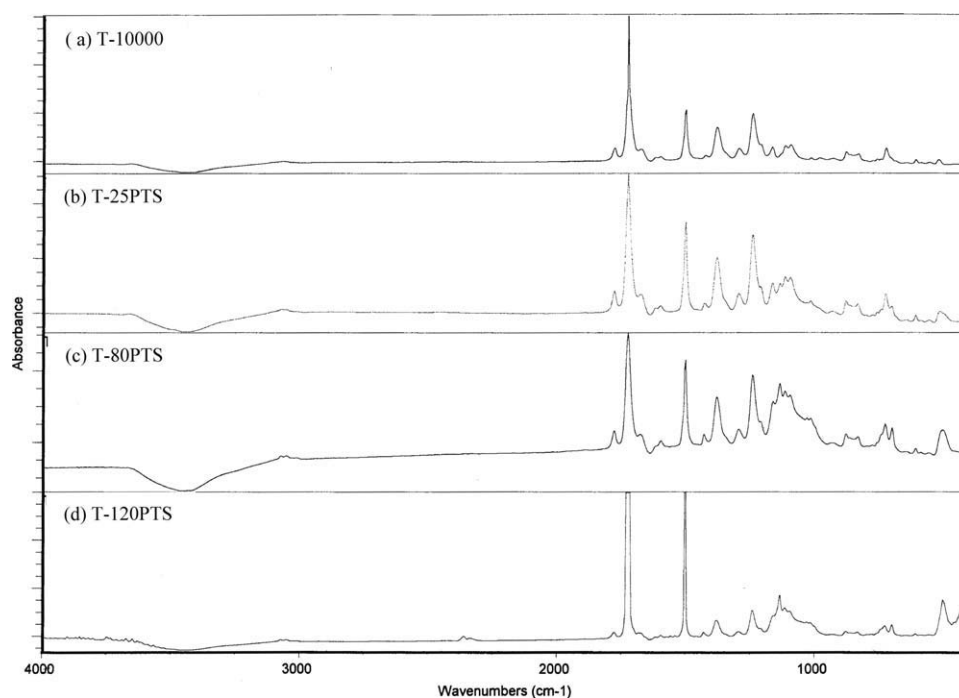


Figure 2 FTIR spectrum of (a) T-10, (b) T-25PTS, (c) T-80PTS, (d) T-120PTS hybrids.

changes of R_f values of the other two silanes-containing PI hybrids (TMOS or MTrMOS) possess the same trend as the above PTS-containing hybrids.

As discussed in the previous reports,^{20,21} infrared absorption frequency shiftment has been used as a measure of the average strength of intermolecular interactions. In this work, frequency shiftment was utilized to discuss the effect of silanes content on PI imide ring formation. It is due to that upon the decrease of imide ring formation, the absorption band of imide and C=O groups will be shifted to a lower frequency by the addition of silanes agent. And the frequency of three absorption peak, imide ring stretching, symmetric C=O stretching and asymmetric C=O stretching of T-10,000, T-25PTS, T-80PTS to T-120PTS, are increased from 1363 to 1372, 1708 to 1723, and 1763 to 1778 cm^{-1} , respectively. In addition, the changes of frequency shiftment of the other two silanes-containing PI hybrids (TMOS or MTrMOS) possess the same trend as the above PTS-containing hybrids. The explanation for the above R_f values changing sequence and frequency shiftments due to the added content and different structure of these three silanes (PTS or TMOS or MTrMOS) will be discussed in the following section of T_g value measurements also.

Contact angle measurements

Effect of APrTMOS or APDiMOS content

Contact angle analysis can provide information on the surface of hydrophobicity or hydrophilicity and

molecular mobility at the air–water–solid interface.²² High contact angle values, included between 70° to 90° , indicate very hydrophobic surfaces such as silicone or fluorocarbon polymers, while low contact angle values (0 – 30°) indicate highly hydrophilic surfaces such as glass or mica.²³ Hence, the hydrophobicity of PI and hybrid membrane's surface are characterized by contact angle measurements in this study.

The following discussions of the hydrophobicity of PI and hybrid membrane's surface are based on two factors: intermolecular cross-linkage density (or intermolecular attraction) and nonpolar content in membrane surface composition. In general, the increase of the above two factors will increase the contact angle or hydrophobicity of membrane's surface.

Table I indicates that the contact angles of PI hybrids are all larger than that of pure PI and increase as the increase of APrTMOS or APDiMOS content and are shown in Figure 3 also. The explanation is that the addition of APrTMOS (or APDiMOS) 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 cross-linkage will occur between $-\text{SiOCH}_3$ groups by sol–gel reaction. The intermolecular cross-linkage, $-\text{Si}-\text{O}-\text{Si}-$, will be occurred between $-\text{Si}-\text{OCH}_3$ and $-\text{Si}-\text{OH}$ groups, the latter is formed by the hydrolysis of $-\text{Si}-\text{OCH}_3$ group of APrTMOS (or APDiMOS), by sol–gel reaction to take off CH_3OH or H_2O . Furthermore, the intermolecular cross-linkage will increase

TABLE I
Contact Angles of Pure PI and Hybrids

	Contact angle (deg)
Pure PI	65.72
T-10000	68.95
T-5000	71.25
D-10000	76.64
D-5000	82.28
T-25PTS ^a	72.79
T-80PTS ^a	85.71
T-120PTS ^a	87.08
D-25PTS ^b	89.95
D-80PTS ^b	91.56
D-120PTS ^b	92.73
D-25MTrMOS ^b	86.37
D-80MTrMOS ^b	88.29
D-120MTrMOS ^b	90.16
D-25TMOS ^b	93.45
D-80TMOS ^b	93.68
D-120TMOS ^b	94.58

^a Coupling agent of PTS is added to the APrTMOS-PAA solution, which are only with 10,000 g/mole block chain length used to obtain 25, 80, 120 wt % solution, respectively.

^b Coupling agents of PTS or TMOS or MTrMOS are added to the APDiMOS-PAA solution, which are only with 10000 g/mole block chain length used to obtain 25, 80, 120 wt % solution, respectively.

the intermolecular attraction and toughness (or rigidity) of polymer chain. This phenomenon will induce the polymer chain packed more closely in the bulk of membrane and then push more hydrophobic segment to the membrane's surface and therefore the contact angle of membrane increased. The result is that contact angle of APrTMOS or APDiMOS-containing hybrids are all larger than that of pure PI.

Meanwhile, T-5000(or D-5000) is synthesized with higher APrTMOS (or APDiMOS) content than T-10,000 (or D-10,000) does. The increase of APrTMOS (or APDiMOS) content will decrease the BTDA-ODA block chain length and increase the intermolecular cross-linked density and contact angle. Then T-5000 (or D-5000) possesses shorter block chain length and higher cross-linked density comparing with that of T-10,000 (or D-10,000) polymer. On the other hand, polymer with shorter rigid segment and higher cross-linked density will induce the ODA-BTDA segments clustering more closely and dispersed in the bulk of membrane. Therefore, this will induce the nonpolar hydrophobic PI segment migrating to the membrane's surface and increase the contact angle of membranes. The above explanations may be the reason for the hydrophobicity changes in the following sequence: T-5000 > T-10,000 > pure PI or D-5000 > D-10,000 > pure PI.

By the way, contact angles of APDiMOS-containing hybrids are all larger than those of correspond-

ing APrTMOS-containing hybrids and shown in Figure 3. APDiMOS contains more nonpolar segment, $-\text{CH}_3$ group, than that of APrTMOS and two functional groups, $-\text{NH}_2$ and $-\text{OCH}_3$, which will induce linear structure segment and is more soft or flexible than the other PI segment. This linear, soft and nonpolar APDiMOS-containing segment will be easier migrated to membrane's surface than that of APrTMOS does. Therefore, the APDiMOS-containing hybrids possess higher contact angles than those of corresponding APrTMOS-containing hybrids: D-10,000 > T-10,000; D-5000 > T-5000.

Effect of APrTMOS or APDiMOS coupling with PTS

T-10,000 (or D-10,000) hybrid prepared from APrTMOS-PAA (or APDiMOS-PAA) solution with 10,000 g/mol block chain length are used in this and the following sections due to these two series hybrids are more flexible than T-5000 (or D-5000) hybrid, respectively.

The contact angle of PTS-containing hybrids are changed in the following sequence: T-10,000 < T-25PTS < T-80PTS < T-120PTS; D-10,000 < D-25PTS < D-80PTS < D-120PTS, which are depicted in Table I and shown in Figure 4. The addition of PTS agent to the APrTMOS-PAA (or APDiMOS-PAA) solution will increase the $-\text{Si}-\text{OCH}_3$ or $-\text{Si}-\text{OH}$ functional groups, which will increase the intermolecular cross-linkage or bonding and induce more nonpolar segment migrating to membrane's surface and then increase the contact angle of membrane. Therefore, the contact angles of hybrids are increased as the increase of PTS content.

On the other hand, contact angles of D series hybrids are all larger than that of the corresponding T series hybrids. For example, the contact angle of D-80PTS is larger than that of T-80PTS. The explanations are the same as above paragraph and due to two contrary effects: one is APDiMOS contains only

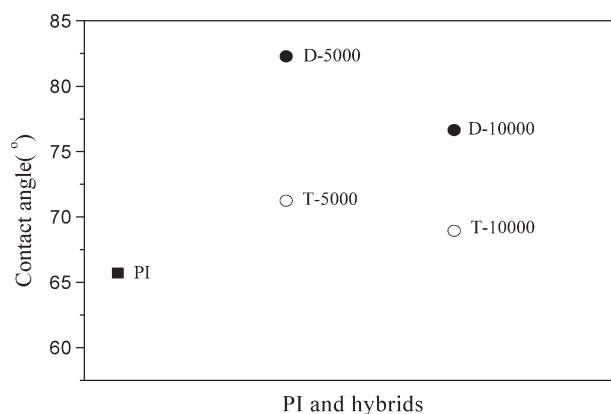


Figure 3 Effect of blocking agent content (or block chain length) on contact angle.

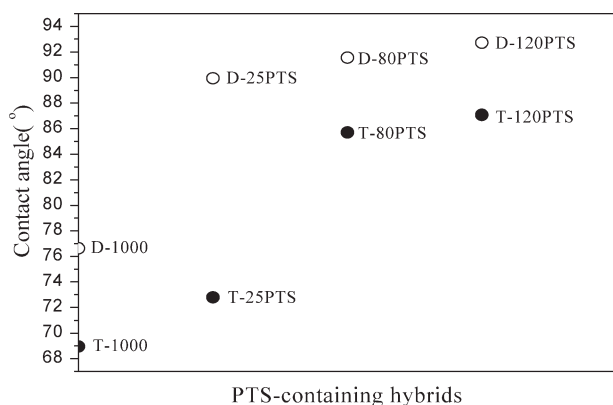


Figure 4 Effect of coupling agent (PTS) content on contact angle.

one $-\text{Si}-\text{OCH}_3$ functional group and form lesser intermolecular cross-linkage and decreases membrane's contact angle. The other is that APDiMOS contains more nonpolar groups, $-\text{CH}_3$, and forms linear, flexible segments comparing with APrTMOS does and will increase membrane's contact angle. The competition of the above two contrary effects shows that the latter effect possesses superiority and induces that the contact angle of APDiMOS-containing hybrids are all larger than that of corresponding APrTMOS-containing hybrids.

Effect of APDiMOS coupling with PTS, TMOS or MTrMOS

APDiMOS-containing hybrids with 10,000 g/mol of block chain length are used owing to it is more soft than APrTMOS-containing hybrids and the effect on the change of contact angle will be more obvious. The hybrid's contact angles of D-10,000 with different PTS, TMOS, or MTrMOS content are depicted in Table I and shown in Figure 5. The contact angle of the above three agent-containing hybrids are changed in the following sequence: $\text{D-10,000} < \text{D-25PTS} < \text{D-80PTS} < \text{D-120PTS}$; $\text{D-10,000} < \text{D-25TMOS} < \text{D-80TMOS} < \text{D-120TMOS}$; $\text{D-10,000} < \text{D-25MTrMOS} < \text{D-80MTrMOS} < \text{D-120MTrMOS}$. The addition of three silanes to the APDiMOS-PAA solution will increase the $-\text{Si}-\text{OCH}_3$ or $-\text{Si}-\text{OH}$ functional groups, which will increase the intermolecular cross-linkage or bonding and induces more nonpolar segment migrating to membrane's surface and hence increase the contact angle of membrane. This may be the reason for the increase of contact angle of hybrids as the increase of three agent content.

Furthermore, the contact angles are changed in the following sequence: TMOS-containing hybrids > corresponding PTS-containing hybrids > corresponding MTrMOS-containing hybrids; $\text{D-25TMOS} > \text{D-25PTS} > \text{D-25MTrMOS}$; $\text{D-80TMOS} > \text{D-80PTS} >$

D-80MTrMOS ; $\text{D-120TMOS} > \text{D-120PTS} > \text{D-120MTrMOS}$. As the addition of TMOS to the APDiMOS-PAA solution, a longer, cross-linked segment extended from APDiMOS segment is formed due to the methoxy groups ($-\text{OCH}_3$) of TMOS can be easily reacted with other methoxy groups without any steric hindrance. Then strongly cross-linked structure will be formed and largely dispersed in the bulk of membrane. The result is nonpolar segment will be more easily migrating to membrane's surface and then possesses the largest contact angle of TMOS-containing hybrids comparing with the other two types of hybrids. On the other hand, MTrMOS coupling agent containing three methoxy groups can't react completely with other methoxy groups to form $-\text{Si}-\text{O}-\text{Si}-$ segment due to two methyl groups' steric hindrance. And then the hybrid's chain can't aggregate closely and remain some unreacted $-\text{Si}-\text{OH}$ groups, which is a polar group and part of $-\text{Si}-\text{OH}$ groups may be dispersed on membrane's surface and hence decrease the membrane's contact angle. This is the reason for the MTrMOS-containing hybrids possess the lowest contact angle values among these three types of hybrid. By the way, PTS agent possesses three methoxy groups and one nonpolar benzene group. The steric hindrance of benzene ring will hinder the neighboring two methoxy groups to react with other methoxy group to form $-\text{Si}-\text{O}-\text{Si}-$ cross-linkage and remain some unreacted $-\text{Si}-\text{OH}$ groups. Furthermore, some polar $-\text{Si}-\text{OH}$ group will be dispersed on membrane's surface and then decrease the contact angle value of hybrids. For the same time, some nonpolar benzene ring will be dispersed on membrane's surface and then increase the contact angle value of hybrids. The competition of these two contrary effects may induce the PTS-containing hybrids possess the medium contact angle value among these three types of hybrids.

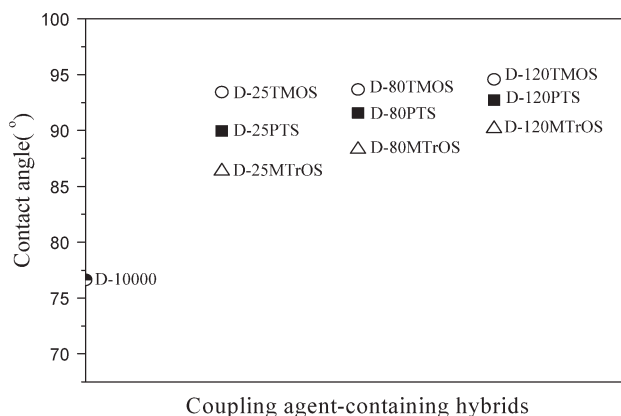


Figure 5 Effect of three coupling agent content with APDiMOS on contact angle.

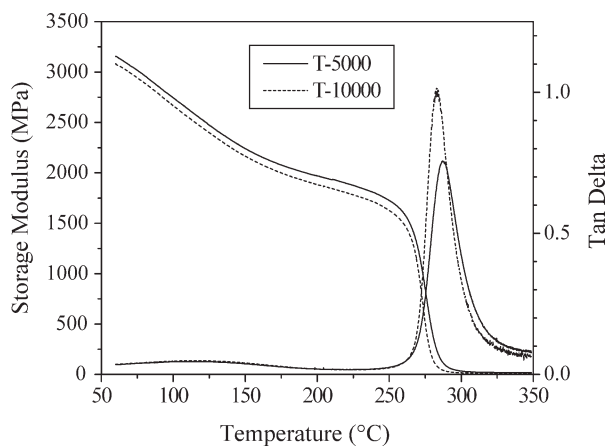


Figure 6 Storage modulus and $\tan \delta$ curves of APrT-MOS-containing hybrids.

Dynamical mechanical analysis (DMA)

In this paragraph, T_g values are measured from the peak temperature of loss modulus curves. The following discussions are based on three factors that affect PI and hybrid's T_g values. The 1st factor is intermolecular attraction (or cross-linkage) of polymer chain. The larger it is the lesser of polymer chain's rotation freedom and hence increases the T_g value of polymer chain. And the 2nd factor is the stiffness of polymer chain. The increase of cross-linkage or containing benzene or cyclic ring of polymer chain will decrease polymer chain's rotation freedom and hence increase the T_g value of polymer chain. As the 3rd factor is polymer's free volume. If polymer contains more, soft segment, e.g., aliphatic segment, the polymer chain will be more entangled and then the free volume of polymer chain increased and the T_g value decreased.

Effect of APrT-MOS or APDiMOS content

Figure 6 shows the storage modulus and $\tan \delta$ value curves of membrane with 5000 and 10,000 g/mol block chain length, T-5000 and T-10,000, and the T_g values of all membranes are summarized in Table II. Figure 6 shows that the storage modulus of membrane with 5000 g/mol block chain length (T-5000) is larger than membrane with 10,000 g/mol chain length (T-10,000) and the damping intensities of T-10,000 is higher than that of T-5000. Factors that affect polymer's storage modulus curves and damping intensity in this section are polymer chain's length and stiffness. The longer chain length of polymer will induce the lower storage modulus, T_g value and higher damping intensity. The increase of APrT-MOS content will decrease the PI block chain length and increase the intermolecular cross-linked density. T-5000 is synthesized with higher APrT-MOS content than T-10,000 does. Therefore, T-5000 possesses

lower block chain length and higher cross-linked density comparing to that of T-10,000 polymer. On the other hand, polymer with shorter rigid segment and more cross-linkage will induce the decrease of damping intensity and the increase of storage modulus. This is the reason why T-5000 possesses higher storage modulus and lower damping intensity than T-10,000 hybrid. Meanwhile, the same change trend of D-5000 with higher storage modulus and lower damping intensity compared to D-10,000 hybrid.

Whereas the T_g values of these hybrids are slightly shifting to higher temperature as APrT-MOS content increased. Table II indicates that the T_g values increase from pure PI, T-10,000, to T-5000. In other words, the T_g values of these films are increased as the increase of blocking/coupling agent content (i.e., cross-link density). Factors that affect polymer's $\tan \delta$ value in this section are polymer chain's length and stiffness. The reason is that BTDA-ODA is a rigid segment. And T-5000, which possesses more rigid segment and cross-link density than those of T-10,000 polymer, will possess the highest T_g value. On the other hand, the APrT-MOS component possesses soft aliphatic $-C_3H_6-$ structures, which is the soft segment. While T-5000, which contains more soft $-C_3H_6-$ content, will decrease the T_g value. As a result of the competition of the above two contrary effects, T_g values of T-5000 hybrid will be slightly higher than that of T-10,000 hybrid.

TABLE II
Glass Transition Temperatures of Pure PI and Hybrids

	T_g values (°C)
Pure PI	268.6
T-10000	281.9
T-5000	287.5
D-10000	273.6
D-5000	278.5
T-25PTS ^a	277.8
T-80PTS ^a	280.6
T-120PTS ^a	281.3
D-25PTS ^b	278.3
D-80PTS ^b	280.1
D-120PTS ^b	280.8
D-25MTrMOS ^b	276.7
D-80MTrMOS ^b	277.9
D-120MTrMOS ^b	279.6
D-25TMOS ^b	280.2
D-80TMOS ^b	281.5
D-120TMOS ^b	283.3

^a Coupling agent of PTS is added to the APrT-MOS-PAA solution, which are only with 10,000 g/mole block chain length used to obtain 25, 80, 120 wt % solution, respectively.

^b Coupling agents of PTS or TMOS or MTrMOS are added to the APDiMOS-PAA solution, which are only with 10000 g/mole block chain length used to obtain 25, 80, 120 wt % solution, respectively.

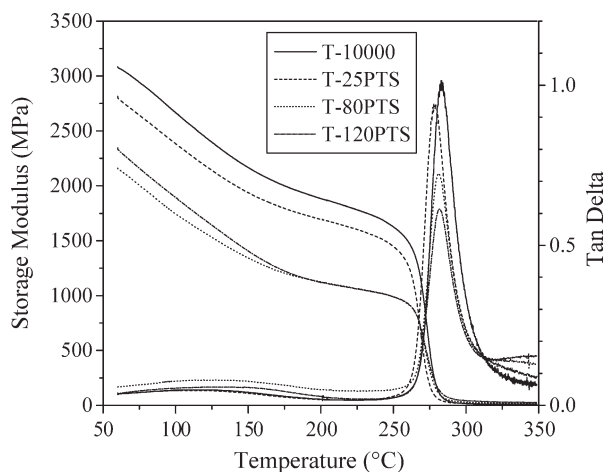


Figure 7 Storage modulus and $\tan \delta$ curves of PTS coupling agent with APrTMOS-containing hybrids.

As the blocking/coupling agent, APDiMOS, replaces APrTMOS added to the PAA solution. The T_g value increases from pure PI, D-10,000 to D-5000. The reason is the same as above discussion owing to D-5000 is synthesized with higher APDiMOS content than D-10,000 does. By the way, the T_g values of D-10,000, D-5000 and are lower than that of T-10,000, T-5000, respectively. The explanation is that APDiMOS possesses only one $-\text{SiOCH}_3$ functional group and two $-\text{CH}_3$ groups compared with that of APrTMOS containing three $-\text{SiOCH}_3$ functional groups. As APDiMOS added to the PAA solution and through imidization reaction, it will form a linear segment in hybrid's structure comparing with that of APrTMOS forming a three dimensional cross-linked structure. Furthermore, APDiMOS possesses two methyl groups, which is aliphatic and steric hindrance for polymer chain's packing. The result is that APDiMOS-containing hybrids will be softer and possess lower T_g value than that of corresponding APrTMOS-containing hybrids.

Effect of APrTMOS coupling with PTS

Figure 7 shows that the T_g values of these hybrids are slightly shifting to lower temperature as PTS content increased and are changed in the following sequence: T-10,000 > T-120PTS > T-80PTS > T-25PTS and depicted on Table II. The reason is that APrTMOS and PTS both possess three methoxy functional groups and PTS also possesses one benzene ring. Hence, the condensation reaction between these two agents can not completely accomplished, especially PTS with steric hindrance of benzene ring. Then part of methoxy functional groups are reacted with H_2O to $-\text{Si}-\text{OH}$ groups, which is polar and may react with carboxylic acid ($-\text{C}(\text{O})-\text{OH}$) group of PI ring to hinder the imide ring formation. This hindrance

of imide ring formation may be increased as the increase of PTS content. Intuitively, the stiffness of PI segment will be decreased and polymer chain's free volume increased and therefore the T_g values will be decreased as the increase of PTS content. Furthermore, the intermolecular attraction (or cross-linkage) will be increased as the PTS content increased and therefore the T_g value increased. The competition of the above two contrary effects indicates that the stiffness and free volume effects possess superiority and then the T_g value of T-25PTS is lower than that T-10,000 hybrid. Meanwhile, as the PTS content increased, the intermolecular cross-linkage densities of PTS-containing with APrTMOS hybrids are increased as the increase of PTS content. The result is that T_g values are slightly increased from T-25PTS, T-80PTS to T-120PTS as the increase of PTS content. In addition, those of PTS-containing with APDiMOS hybrids possess the same trend: D-10,000 > D-120PTS > D-80PTS > D-25PTS and the explanations are the same as above.

Effect of APDiMOS coupling with PTS, TMOS, or MTrMOS

APDiMOS-containing hybrids with 10,000 g/mol of block chain length are used due to it is more soft than APrTMOS-containing hybrids and the effect on the change of T_g values is more obvious. Table II indicates that the T_g values are all increased with the increase of respective PTS, TMOS, or MTrMOS content. And the T_g values are changed in the following sequence for the corresponding hybrids: TMOS-containing hybrids > PTS-containing hybrids > MTrMOS-containing hybrids. From the 1st affecting factor of cross-linkage density: the intermolecular attraction (or cross-linkage formation) and T_g values are changed in the following sequence for the corresponding hybrids: TMOS-containing hybrids > MTrMOS-containing hybrids > PTS-containing hybrids. The above phenomena are explained as following: APDiMOS possessing only one $-\text{SiOCH}_3$ group will be easily reacted with other $-\text{SiOCH}_3$ functional group to form $-\text{Si}-\text{O}-\text{Si}-$ cross-link segment and taken off CH_3OH or H_2O . And TMOS possesses four $-\text{SiOCH}_3$ functional groups and can be easily reacted with APDiMOS and form intermolecular cross-linkage. On the other hand, MTrMOS contains three $-\text{SiOCH}_3$ functional groups and one $-\text{CH}_3$ groups with slight steric hindrance and can be easily reacted with APDiMOS and form linear, soft segment. On the other hand, PTS contains three $-\text{SiOCH}_3$ functional groups and one benzene ring and can't completely react between methoxy groups owing to the steric hindrance of benzene ring.

While from the 2nd factor is polymer chain's stiffness: rigid segment-containing or cross-linkage

density of polymer chain. And the stiffness and T_g values of polymer chain is changed in the following sequence for the corresponding hybrids: TMOS-containing hybrids > PTS-containing hybrids > MTrMOS-containing hybrids. The explanation is that TMOS-containing hybrids contain the highest cross-linkage density and PTS-containing hybrids contain benzene rigid segment. Therefore, the above two types of hybrids possess nearly the same chain's stiffness. While MTrMOS-containing hybrids contain lesser cross-linkage and soft, $-\text{CH}_3$, segment and hence possess lowest chain's stiffness.

Finally, from the 3rd factor is polymer's free volume. And the free volume of polymer chain is changed in the following sequence for the corresponding hybrids: PTS-containing hybrids > MTrMOS-containing hybrids > TMOS-containing hybrids. And then the T_g value will be changed in the reverse trend: PTS-containing hybrids < MTrMOS-containing hybrids < TMOS-containing hybrids. The explanation is that PTS-containing hybrids contain benzene ring side chain with higher volume and lower cross-linkage density. While MTrMOS-containing hybrids contain lower cross-linkage density also. And then PTS-containing hybrids possess higher free volume of polymer chain than MTrMOS-containing hybrids. On the other hand, TMOS-containing hybrids possess higher cross-linkage density and lower free volume. Combination of the above three affecting factors and the results, which may be the explanations for the T_g values changed in the following sequence for the corresponding hybrids: D-25TMOS > D-25PTS > D-25MTrMOS; D-80TMOS > D-80PTS > D-80MTrMOS; D-120TMOS > D-120PTS > D-25MTrMOS.

CONCLUSIONS

The PI/Silica hybrid membranes possess high purity, transparency, hydrophobicity, and thermal properties. The imide ring formation is affected by silane addition and characterized by the absorption band ratio (R_I) of C=O (carbonyl group) with =N- (imide ring) and absorption frequency shiftment. The R_I values and absorption frequencies of only APrTMOS or APDiMOS-containing PI hybrids are nearly the same. While those of hybrids with PTS, TMOS, or MTrMOS content are changed with different type of silane and increased as the increase of three silanes content, respectively. The contact angles

of PI hybrids are all larger than that of pure PI and increase as the increase of silanes content. The storage modulus and T_g values of hybrids are all increased as the increase of blocking agent/coupling content, while the damping intensity decreased. The T_g values of hybrids increased with increasing PTS, TMOS, or MTrMOS content also. And the T_g values are changed in the following sequence for the corresponding hybrids: TMOS-containing hybrids > PTS-containing hybrids > MTrMOS-containing hybrids.

References

1. Ghosh, M. K.; Mittal, K. L.; Eds., *Polyimides: Fundamentals and Applications*; Marcel Dekker: New York, 1996.
2. Mittal, K. L. *Polyimides: Synthesis, Characterization and Applications*; Plenum Press: New York, 1984.
3. Abadie, J. M.; Sillion, B., Eds. *Polyimides and other High-Temperature Polymers*; Elsevier: New York, 1991.
4. Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M., Eds. *Polyimides*; Blackie: New York, 1990.
5. Policastro, P. P.; Lupinski, J. H.; Hernandez, P. K. In *Polymeric Materials for Electronics Packaging and Interconnection*; Lupinski, J. H.; Moore, R. S., Eds.; American Chemical Society: Washington, DC, 1989, p 140.
6. Wang, S.; Ahmad, Z.; Mark, J. E. *Polym Bull* 1993, 31, 323.
7. Morikawa, A.; Iyoku, Y.; Kakimoto, M. A.; Imai, Y. *Polym J* 1992, 24, 689.
8. Morikawa, A.; Iyoku, Y.; Kakimoto, M. A.; Imai, Y. *Polym J* 1992, 24, 107.
9. Ahmad, Z.; Sarwar, M. I.; Mark, J. E. *J Mater Chem* 1997, 7, 259.
10. Sysel, P.; Pulec, R.; Maryska, M. *Polym J* 1997, 7, 607.
11. Tsai, M. H.; Whang, W. T. *Polymer* 2001, 42, 4197.
12. Tsai, M. H.; Huang, S. L.; Chen, P. J.; Chiang, P. C.; Chen, D. S.; Lu, H. H.; Chiu, W. M.; Chen, J. C.; Lu, H. T. *Desalination* 2008, 233, 232.
13. Tsai, M. H.; Lin, Y. K.; Chang, C. J.; Huang, S. L.; Yen, C. H. *Thin Solid Films* 2009, 517, 5333.
14. Mo, T. C.; Wang, H. W.; Chen, S. Y.; Dong, R. X.; Kuo, C. H.; Yeh, Y. C. *J Appl Polym Sci* 2007, 104, 882.
15. Jiang, L.; Wang, W.; Wei, X.; Wu, D.; Jin, R. *J Appl Polym Sci* 2007, 104, 1579.
16. Qin, J.; Zhao, H.; Liu, X.; Zhang, X.; Gu, Y. *Polymer* 2007, 48, 3379.
17. Liaw, W. C.; Chen, K. P. *J Appl Polym Sci* 2007, 105, 809.
18. Matienzo, L. J.; Egitto, F. D. *J Mater Sci* 2007, 42, 239.
19. Qin, J.; Liu, X.; Zhang, X.; Gu, Y. *Polymer* 2007, 48, 3379.
20. Tanaka, T.; Yokoyama, T.; Yamaguchi, Y. *J Polym Sci Polym Chem Ed* 1968, 6, 2137.
21. Moskala, E. J.; Varnell, D. F.; Coleman, M. M. *Polymer* 1985, 26, 228.
22. Wasserman, S. R.; Tao, Y. T.; Whitesides, G. M. *Langmuir* 1989, 5, 1074.
23. Gilliland, J. W.; Yokoyama, K.; Yip, W. T. *J Phys Chem B* 2005, 109, 4816.