Structural effects of the monomer type on the properties of copolyimides and copolyimide–silica hybrid materials

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Abstract: In this work, the effects of two different diamine monomers containing phosphine oxide on the thermal, mechanical and morphological properties of copolyimides and their hybrid materials were investigated. The gas separation properties of the synthesized copolyimides were also analyzed. The two different diamine monomers containing phosphine oxide were bis(3-aminophenyl]phenylphosphine oxide (BAPPO) and bis[4-(3-aminophenoxy)phenyl)phenylphosphine oxide (*m*-BAPPO). In the synthesis of the copolyimides, 3,3′-diaminodiphenyl sulfone (3,3′-DDS) was also used as the diamine, as well as 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA). Copolyimide films were prepared by thermal imidization. Furthermore, hybrid materials containing 5 % SiO_2 were synthesized by the sol–gel technique. Fourier-transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (NMR) confirmed the expected structures. Dynamic mechanical analysis (DMA) demonstrated that the *m*-BAPPO-based copolyimides had lower glass transition temperatures (T_g) than the BAPPO-based ones. The thermal decomposition temperature of the *m*-BAPPO-containing copolyimide without silica was shifted to a higher value. The moduli and strength values of the BAPPO diamine-containing copolyimide and its hybrid were higher than those of the *m*-BAPPO-containing materials. Contact angle measurements showed their hydrophobicity. Scanning electron microscope (SEM) analysis showed the dispersion of the silica particles in the copolyimides. These copolyimides may be used in the coating industry. The CO_2 permeability and the permselectivity were the highest, among the other values found in this study, when the *m*-BAPPO-containing copolyimide in the absence of silica was used. The gas permeabilities obtained from this work were in the decreasing order: $P_{CO_2} > P_{O_2} > P_{N_2}$.

Keywords: copolyamic acid; inorganic compound; sol–gel; imidization; hydrophobic nature; permeation.

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INTRODUCTION

Polyimides (PIs) exhibit outstanding characteristics such as high tensile modulus, high thermal stability and solvent resistance. They find applications ranging from aerospace,[1] microelectronic devices, and the coating industry to separation membrane technologies.[2]

The thermal and mechanical properties of PIs can be further improved by the introduction of silica into the PI matrix, forming hybrid organic–inorganic materials. These materials can be prepared utilizing the sol–gel process to form silica in a polyamic acid solution. Films are formed from the solution by solvent casting.[3] The silica nanoparticles are formed in the PI matrix *via* hydrolysis and polycondensation of organic silanes.[4]

The unique characteristics of fluorine, such as high electronegativity, low polarity, low cohesive and surface free energy, gave rise to attempts to fluorinate PIs in 1972. Since then, fluorine-containing diamines and dianhydrides have been introduced to prepare fluorinated PIs. However, fluorinated PIs have drawbacks, such as poor adhesion and low mechanical strength. Phosphine oxide-containing polyimides, which show excellent adhesive properties with excellent thermal stability, enabled fluorinated PIs to exhibit improved properties.[5] Much research has been performed on PIs to investigate the relationship between chemical structure and gas transport properties. 2,2-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA)-based PIs show high gas permeability. The presence of the bulky $-C(CF_3)_2-$ group provides restricted intrasegmental mobility and stiffened backbones. Moreover, some of 6FDA-based PIs were employed to fabricate high performance membranes.[6]

In the present work, the effects of two different diamine monomers containing phosphine oxide on the thermal, mechanical and morphological properties of copolyimides and their hybrid materials were investigated. The gas separation properties of the synthesized copolyimides were also analyzed. The two diamine monomers with phosphine oxide were bis(3-aminophenyl)phenylphosphine oxide (BAPPO) and bis[4-(3-aminophenoxy)phenyl]phenylphosphine oxide (*m*--BAPPO). In the synthesis of the copolyimides, 3,3′-diaminodiphenyl sulfone (3,3′-DDS) was also used as the diamine, as well as 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA). Copolyimide films were prepared by thermal imidization. Furthermore, hybrid materials containing 5 % SiO_2 were synthesized by the sol–gel technique.

EXPERIMENTAL

Materials

The dianhydride monomer, 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA, >99 %) was purchased from Aldrich and used as received. 3,3′-Diaminodiphenyl sulfone (3,3′-DDS), phenylphosphonic dichloride (98 %), *N*-methyl-2-pyrrolidone (NMP) and dimethylacetamide (DMAc) were obtained from Merck. NMP and DMAc were dried over

phosphorus pentoxide (P_2O_5) and freshly distilled under vacuum before use. 1-Bromo-4-
-fluorobenzene (99 %), Mg powder (99.9 %), anhydrous potassium carbonate (K_2CO_3, 99.9 %) and 3-aminophenol were provided by Aldrich and used as received. Tetrahydrofuran (THF) was freshly distilled under nitrogen over sodium. Tetraethyl orthosilicate (TEOS) and 3-(glycidyloxy)propyltrimethoxysilane (GPTMS) were purchased from Merck. Some common solvents, such as chloroform, ethanol, methanol and dichloroethane, were used as received.

Synthesis of diamine monomers

In this study, two different diamine monomers (BAPPO and *m*-BAPPO) were synthesized. Bis(3-aminophenyl)phenylphosphine oxide (BAPPO) was synthesized by a three-step reaction as mentioned in the previous work.[7] First, triphenylphosphine (TPP) was oxidized to triphenylphosphine oxide (TPPO) by treating with H_2O_2. Then, bis(3-nitrophenyl)phenyl-phosphine oxide (BNPPO) was prepared by the nitration of TPPO using concentrated nitric acid in the presence of sulfuric acid. Finally, BNPPO was subjected to hydrogenation in a high-pressure reactor (Parr Instrument Co.) to produce BAPPO.

Bis[4-(3-aminophenoxy)phenyl]phenylphosphine oxide (*m*-BAPPO) was synthesized as described in the literature.[8] First, bis(4-fluorophenyl)phenylphosphine oxide (BFPPO) was synthesized by treating 1-bromo-4-fluorobenzene with phenylphosphonic dichloride in the presence of Mg turnings *via* the Grignard technique. Then, *m*-BAPPO (Scheme S-1 of the Supplementary material to this paper) was prepared by treating 37.23 g (0.118 mol) BFPPO with 26.56 g (0.243 mol) 3-aminophenol in a DMAc/toluene mixture using 40.20 g (0.292 mol) K_2CO_3 as a weak base to form the required aminophenolate nucleophile.

Preparation of copolyamic acid solution

The copolyamic acid solution (PAA) used as a copolyimide precursor was prepared in NMP as follows: the diamine monomers and dried NMP were charged into a three-necked flask equipped with a nitrogen inlet and a condenser. Then, equimolar amount of the dianhydride monomers were incrementally added into the content of the flask. The concentration afforded was 20 %. The reaction mixture was stirred overnight at room temperature to obtain a viscous PAA solution.

In this study, 6FDA-based copolyimides were synthesized from the aromatic diamines 3,3′-DDS, BAPPO and *m*-BAPPO.

Silica sol preparation

Silica sol was prepared by the hydrolysis and condensation of TEOS as follows: TEOS (8.7 g, 0.042 mol), GOTMS (2.25 g, 0.010 mol) and EtOH (2.21 g, 0.048 mol) were charged into a glass vial and then distilled water (1.77 g, 0.098 mol) that had been acidified by adding HCl was slowly dropped into the vial. The mixture was magnetically stirred at room temperature until a clear solution was obtained. Then, the silica sol was kept at room temperature for about 1 h.

Preparation of copolyimide–silica hybrid materials

To obtain the hybrid solution, 5 % silica sol was added dropwise into a PAA solution and stirred continuously at room temperature for 4 h. This preparation procedure is illustrated in Scheme S-2 of the Supplementary material. After thorough stirring, the clear and viscous hybrid solutions were cast onto glass plates using a 30-μm wire gaged applicator and then thermal imidization was performed stepwise at 80, 100, 150, 200 and 300 °C for 1 h at each temperature. After the imidization was completed, the glass plates were immersed in hot water (90 °C) for 1 h to remove easily the hybrid films from the glass surfaces.

Characterization

The FTIR spectra were recorded on a PerkinElmer Spectrum 100 ATR FTIR spectro-photometer. The NMR spectra were recorded on a Varian 600 MHz spectrometer operating for ^{1}H-NMR and ^{31}P-NMR using $CDCl_3$ as the solvent. Thermogravimetric analyses (TGA) of the hybrid free films were performed using a Perkin Elmer thermogravimetric analyzer Pyris 1 TGA model. Samples were run from 30 °C to 750 °C at a heating rate of 10 °C min^{-1} under an air atmosphere. The glass transition temperatures of free films prepared as 10 mm×20 mm samples were obtained from an SII Nanotechnology ExStar 6000 model dynamic mechanical analyzer (DMA). The scans were obtained at a heating rate of 5 °C min^{-1}, from 30 to 450 °C. The limiting oxygen index (*LOI*) values of the free hybrid films were measured using a fire testing technology (FTT) type instrument according to ASTM D2863-08. The mechanical properties of the free films were determined by standard tensile stress–strain tests in order to measure the moduli, tensile strength, and elongation at break. Standard tensile stress–strain experiments were performed at room temperature on a Material Testing Machine Z010/TN2S, using a crosshead speed of 5 mm min^{-1}. In order to determine the hydrophobic properties of the materials, contact angle measurements were performed with a Kruss (Easy Drop DSA-2) tensiometer, equipped with a camera. Analyses were made at room temperature by means of the sessile drop technique. For each sample, at least four measurements were made, and the average was taken. The measuring liquid was distilled water. To determine the morphological behavior, secondary electron images (SEI) were applied in SEMs. SEM imaging of the films were performed on a Philips XL30 ESEM-FEG/EDAX. The specimens were prepared for SEM by freeze fracturing in liquid nitrogen and applying a gold coating of approximately 300 Å. An SEM–energy-dispersive X-ray spectroscopy (SEM-EDS) spectrum was recorded to verify the presence of silica in the copolyimide–silica hybrid. In addition, a gas permeation analyzer (Brugger GDP-C 2000) was used to measure the pure gas permeability coefficients of the polymeric membranes to O_2, N_2, and CO_2. The pure gas permeability coefficients were measured using the constant volume and variable pressure method. The experiments were performed at 35 °C with atmospheric feed-side pressure. The samples were masked for gas permeation measurement following the technique of the Koros group[9] with a permeation area of 3.94 cm^2.

RESULTS AND DISCUSSION

The aim of this study was to investigate the effect of diamine monomers containing phosphine oxide on the thermal, mechanical and morphological properties of copolyimides and their hybrid materials, as well as the gas separation properties. Two different diamine monomers were synthesized (BAPPO and *m*-BAPPO). The BAPPO monomer was synthesized according to a previous study.[7] The synthesis route for the other monomer (*m*-BAPPO) is illustrated in Scheme S-1 of the Supplementary material. The chemical structure of *m*-BAPPO was identified by FTIR, ^{1}H-NMR and ^{31}P-NMR spectroscopy.

The FTIR results for *m*-BAPPO (shown in Fig. S-1 of the Supplementary material) displayed aromatic C–H stretching at 3058 cm^{-1}, C–H out-of-plane bending at 830 cm^{-1}, C–H in-plane bending at 1143 and 1115 cm^{-1}, aromatic C–C stretching at 1577 and 1486 cm^{-1}, asymmetric C–O–C stretching at 1232

cm^{-1}, P=O stretching at 1170 cm^{-1}, P–aryl stretching at 1436 and 996 cm^{-1}, N–H stretching at 3445,3324 and 1594 cm^{-1}, and C–N stretching at 1283 cm^{-1}.

In the ^{1}H-NMR spectrum (Fig. S-2 of the Supplementary material) of m-BAPPO, proton peaks arising from the ether and amino groups were observed up-field because of the shielding effects of the electron-donating ether and amino moieties. As could be seen in Fig. S-2, the protons in the amino groups appeared at 3.4–3.8 ppm as a broad peak. In addition, the other proton peaks of m-BAPPO were: 7.71–7.40 ppm (5H, m, O=P–C_6H_5,), 6.80–7.20 ppm (4H, m, O=P–C_6H_4–O–), 6.60–6.37 ppm (4H, m, –O–C_6H_4–NH_2). As shown in Fig. S-3 of the Supplementary material, the ^{31}P-NMR analysis provided a sharp single peak at 29 ppm for m-BAPPO.

In this study, BAPPO–3,3′-DDS/6FDA, m-BAPPO–3,3′-DDS/6FDA copolyimides and their hybrids were prepared. The hybrid materials containing the polyamic acid (PAA) solution and silica sol, which was obtained in a sol–gel reaction, were synthesized. TEOS and GPTMS acted as an inorganic networker and a coupling agent, respectively. In addition, HCl acid acted as the acid catalyst for the partial hydrolysis. The compositions of the PI–SiO_2 hybrids are presented in Table I. Hybrid formulations applied on glass plates were cured by stepwise heating at elevated temperatures. The chemical structures of the copolyimides and copolyimide–silica hybrids were shown in Scheme S-3a–d of the Supplementary material. The FTIR spectra of the copolyimides and their hybrid copolyimides containing 5 % silica are shown in Fig. S-4a–d of the Supplementary material. As seen in Fig. S-4, characteristic imide absorptions at 1783 and 1720 cm^{-1} (typical of imide carbonyl asymmetrical and symmetrical stretching, respectively) were present. The peaks at 1363 and 718 cm^{-1} indicated C–N–C stretching and imide ring deformation. Moreover, the peaks at 1203, 1300 and 1100 cm^{-1} were ascribed to C–F multiple stretching bands. As shown in Figs. S-4b and d, when the inorganic components were introduced into the polyimide matrix, strong absorption bands were observed in the range 1000 to 1100 cm^{-1} and at 423 cm^{-1}. These bands were ascribed to the characteristic Si–O–Si stretching vibration and bending vibration, respectively.[10,11] The spectra given in Fig.

TABLE I. The composition (mass, g) of copolyimide–silica hybrid films; the PAA solution was 20 wt. %. The PAA solution used in the experiment was 3 g PAA/15 mL solvent. This means that the PAA in solid form was 3 g after removal of the solvent; silica mass: 0.15 g of silica sol was added. Therefore, the silica solution used in the experiment was 0.15 g silica/3 mL solution (5 wt. %); 6FDA mass: 1.777 g; 3,3′-DDS mass: 0.4966 g

Sample	BAPPO	m-BAPPO	Silica sol used
BAPPO–3,3′-DDS/6FDA	0.6160	0	0
m-BAPPO–3,3′-DDS/6FDA	0	0.9850	0
BAPPO–3,3′-DDS/6FDA/SiO_2	0.6160	0	0.15
m-BAPPO–3,3′-DDS/6FDA/SiO_2	0	0.9850	0.15

S-4 of the Supplementary material confirmed the formation of the expected structures.

As seen in Tables II and III, thermal properties of the copolyimides and hybrid copolyimides were evaluated by dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA). The storage modulus (E', Fig. S-5a–d of the Supplementary material) and tan δ (Figs. S-6–S-9 of the Supplementary material) were plotted. The values of the glass transition temperatures of copolyimides and hybrid copolyimides are very important for the determination of the optimum processing and service temperatures at which the polymer preserves its desirable properties.[12,13] The T_g of the copolyimides increased when silica was introduced into the PI matrix. This result indicated that the coupling agent improved the interaction between the polymer matrix and the inorganic segment, which caused an increased restricting strength of silica on PI and hence an increased T_g of the material. The data were collected by DMA. Due to the flexible etheric linkage of *m*-BAPPO, the obtained T_g values were lower than those of the BAPPO-containing copolyimides and their hybrids. However, BAPPO based copolyimides exhibited higher elongation at break values than those of the *m*-BAPPO-based copolyimides. This result is likely due to the three dimensional geometry of the monomers (BAPPO and *m*-BAPPO). The monomer BAPPO alone is a tetrahedral structure so that the aminophenyl groups are in approximately 110° tetrahedral geometry. Therefore, the amino groups can be in different directions when reacted with the dianhydride. The obtained copolyimide might be an asymmetric structure. On the other hand, the obtained copolyimide might be a symmetric structure (more symmetric than the BAPPO-based one) when the *m*-BAPPO moiety reacted with the dianhydride. The aminophenyl groups of the monomer *m*-BAPPO are in trigonal (approximately 120°) geometry, due to the etheric linkages. Trigonal structures are more symmetric than tetrahedral systems. When the asymmetry exits throughout the molecular structure, the asymmetric structure shows greater elasticity (greater elongation at break). Easier molecular packing properties can be observed in the presence of symmetric structures. Two or three T_g values were obtained due to small amounts of phase separation. This might have been possible, since the reactivities of the diamines (BAPPO, *m*-BAPPO and 3,3′-DDS) are different when they react with the dianhydride (6FDA). The introduction of the inorganic material can also cause phase separation due to differences in the reactivity.

TABLE II. Glass transition temperatures of the copolyimides and hybrid copolyimides

Sample	T_1 / °C	T_2 / °C	T_3 / °C
BAPPO–3,3′-DDS/6FDA	218	272	301
m-BAPPO–3,3′-DDS/6FDA	209	245	–
BAPPO–3,3′-DDS/6FDA/SiO$_2$	217	274	323
m-BAPPO–3,3′-DDS/6FDA/SiO$_2$	220	257	–

TABLE III. Thermal properties of the copolyimides and hybrid copolyimides

Sample	1st decomposition temperature, T_1 / °C	2nd decomposition temperature, T_2 / °C	Char wt. %	LOI wt. %
BAPPO–3,3′-DDS/6FDA	319	523	20	46.0
m-BAPPO–3,3′-DDS/6FDA	310	537	28	48.0
BAPPO–3,3′-DDS/6FDA/SiO$_2$	350	525	15	46.7
m-BAPPO–3,3′-DDS/6FDA/SiO$_2$	330	509	7	47.4

The thermal degradation behaviors of the copolyimides and hybrid copoly-imides are summarized in Table III. The polymers exhibited first weight loss at temperatures between 310 and 350 °C, which could probably be attributed to incomplete imidization. The second weight loss started between 509 and 537 °C, which corresponded to the degradation of the polymer. The incorporation of silica into the polyimide matrix may cause the production of $SiF_{4(g)}$ in the presence of $-CF_3-$ present in the 6FDA moiety.[14] The char yields of the copolyimide silica hybrid materials between 7–28 % were found. The thermal decomposition temperature of the hybrids shifted to lower values because of the removal of silica as $SiF_{4(g)}$. It was found that the thermal decomposition temperature of the m-BAPPO-containing copolyimide without silica was shifted to a higher value, increasing the char yield.

Moreover, the flame retardant properties of the copolyimide and hybrid copolyimide films were evaluated by measuring their limiting oxygen index (LOI) values. From Table III, it can be seen that the LOI values for the copolyimides were changed only slightly on addition of the silica particles into the PI matrix.

The tensile properties of copolyimide films were examined by stress–strain measurements and the results were summarized in Table IV. The moduli and the strength values of BAPPO diamine-containing copolyimide and its hybrids were higher than those of the m-BAPPO-containing materials. This situation was explained by higher free volume of m-BAPPO because of the extra phenyl group that resulted in a lowering of the moduli. In other words, the more space the bulky groups take, the lower are the observed moduli. Compared to the neat copolyimides, a decrease in mechanical properties was observed when silica was introduced into the copolyimide matrix. This result may be due to the increased crosslinking density by the formation of an organic–inorganic network structure.

TABLE IV. Physical and mechanical properties of the copolyimides and hybrid copolyimides

Samples	Modulus, GPa, at 40 °C	Tensile strength, MPa	Elongation at break, %	Contact angle θ / °
BAPPO–3,3′-DDS/6FDA	3.54	518	3.92	93
m-BAPPO–3,3′-DDS/6FDA	3.12	226	1.62	102
BAPPO–3,3′-DDS/6FDA/SiO$_2$	3.36	267	3.32	97
m-BAPPO–3,3′-DDS/6FDA/SiO$_2$	2.95	189	1.98	107

Contact angle measurements provide information about the hydrophobicity and hydrophilicity of a material surface. These measurements were performed with drops of distilled water at four different areas on the sample. The averages of these four measurements were calculated. The obtained contact angle values, for each material were given in Table IV. The contact angles had a tendency to increase on addition of silica, demonstrating a more hydrophobic coating surface. The presence of $-C(CF_3)_2-$ also provided for a more hydrophobic surface.

SEM analysis (Fig. S-10a–d of the Supplementary material) exhibited that the silica particles were dispersed in the copolyimide matrix. A microphase separation was observed in the *m*-BAPPO-containing copolyimide–silica hybrid. SEM–energy-dispersive X-ray spectroscopy (SEM–EDS, Fig. S-10e of the Supplementary material) verified the presence of silica in the copolyimide–silica hybrids.

In addition to the thermal, mechanical and morphological studies, the gas permeability coefficients and permselectivity data measured at 35 °C are reported in Table V. The gas permeabilities and permselectivities can be calculated as follows:

$$P = DS \tag{1}$$

$$\alpha_{A/B} = P_A/P_B \tag{2}$$

where P is the permeability coefficient, D is the diffusion coefficient and S is solubility coefficient. α represents the permselectivities of gases A and B.[6] The order of the kinetic (Å) diameters of the studied gases is CO_2, 3.3; O_2, 3.46 and N_2, 3.64. The gas permeabilities from this study were in the decreasing order: $P_{CO_2} > P_{O_2} > P_{N_2}$. Thus, the larger is the kinetic diameter of a gas, the lower is its permeability. As seen in Table V, the *m*-BAPPO-containing copolyimide without silica was better than the others in terms of the permeabilities of O_2 and CO_2, whereas the BAPPO-containing copolyimide in the presence of silica was better than others for the permeability of N_2. The introduction of silica increased the volume of the copolymer due to the effect of crosslinking so that the N_2 gas, possessing the largest kinetic diameter, could easily diffuse throughout the

TABLE V. Permeability coefficients and permselectivity of the copolyimides and hybrid copolyimides at 35 °C

Sample	Permeability coefficients			Permselectivities	
	P_{O_2} /barrier	P_{N_2} /barrier	P_{CO_2} /barrier	a_{O_2/N_2}	a_{CO_2/N_2}
BAPPO–3,3′-DDS/6FDA	0.310	0.046	0.365	6.74	7.93
m-BAPPO–3,3′-DDS/6FDA	0.405	0.084	1.137	4.82	13.54
BAPPO–3,3′-DDS/6FDA/ /SiO₂	0.229	0.104	0.232	2.20	2.23
m-BAPPO–3,3′-DDS/ /6FDA/SiO₂	0.165	0.093	0.366	1.78	3.94

BAPPO-containing hybrid matrix. Due to the increased volumes, the selectivities were adversely affected. The reason is that all gases can pass through without determining their diffusion rates in the presence of large volumes. Since CO_2 is a condensable gas, it should have a higher permeability value than those of the other two gases. It is too difficult to obtain the highest permeability as well as the highest selectivity. As seen in Table V, the permeability and permselectivity of CO_2 were the highest among the values for the copolyimides and copolyimide–silica hybrids in this study, when the *m*-BAPPO containing copolyimide in the absence of silica was used.

CONCLUSIONS

In this study, copolyamic acid solutions (PAAs) were obtained by the reaction between *m*-BAPPO or BAPPO, DDS and 6FDA. Copolyimide films were prepared by thermal (bulk) imidization. Hybrid materials containing 5 % SiO_2 were synthesized by the sol–gel technique. The FTIR, ^{31}P-NMR and ^{1}H-NMR spectra confirmed the expected structures. DMA analysis showed that the *m*-BAPPO-based copolyimides had lower T_g values than those of the BAPPO-based copolyimides. T_g of copolyimides increased when silica was introduced into the copolyimide matrix. Thermal analysis showed that in the presence of silica, the weight loss was shifted to lower temperatures because of the removal of silica as $SiF_{4(g)}$, compared to the neat copolyimide. However, the thermal stability was sufficiently high compared to that of branched-silica hybrid membranes.[15] The *LOI* results did not change significantly on addition of silica particles into the matrix. Mechanical tests showed a decrease in mechanical properties on introduction of silica into the copolyimide matrix, compared to the neat copolyimides. This result may be due to the increased crosslinking density caused by the formation of organic–inorganic network structures. However, the moduli of the hybrids could be considered good.[16] Contact angle measurements confirmed the hydrophobic nature of the surface of the coating. SEM analyses confirmed that silica particles are able to disperse in the polyimide matrix. These copolyimides with various properties may be used in the coating industry. In addition to the thermal, mechanical and morphological studies, gas permeability coefficients and permselectivity measurements were also performed. The condensable gas (*i.e.*, CO_2) was observed to have higher permeability value than those of other two examined gases (*i.e.*, N_2 and O_2). This could be explained by the plasticization effect. More soluble penetrants induce significant plasticization. The CO_2 permeability and the selectivity were the highest among the values of copolyimides and copolyimide–silica hybrids in this study when the *m*-BAPPO--containing copolyimide in the absence of silica was used. The gas permeabilities obtained from this work were in the decreasing order: $P_{CO_2} > P_{O_2} > P_{N_2}$.

SUPPLEMENTARY MATERIAL

FTIR, ^{1}H-NMR and ^{31}P-NMR spectra, SEM images, storage moduli and tan δ values, as well as the synthesis routes and structures of the samples, are available electronically from http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

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УТИЦАЈ СТРУКТУРЕ МОНОМЕРА НА СВОЈСТВА КОПОЛИИМИДА И КОПОЛИИМИД/СИЛИЦИЈУМ-ДИОКСИД ХИБРИДНИХ МАТЕРИЈАЛА

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У овом раду је приказан утицај структуре мономера, тј. два различита диамина на бази фосфорин-оксида, на термичка, механичка и морфолошка својства синтетисаних кополиимида и њихових хибридних материјала. Поред тога, анализирана је способност синтетисаних кополиимида за раздвајање гасова. Два различита мономера односно диамина на бази фосфор-оксида су коришћена: бис(3-аминофенил)фенилфосфин-оксид (BAPPO) и бис[4-(3-аминофенокси)фенил]фенилфосфорин-оксид (*m*-BAPPO). У синтезама кополиимида 3,3′-диаминодифенил-сулфон (3,3′-DDS) је коришћен као диамин, а такође и 2,2-бис(3,4-дикарбоксифенил)хексафлуорпропан-дианхидрид (6FDA). Кополиимидни филмови су добијени термичком имидизацијом у другом ступњу реакције поликондензације. Хибридни материјали са 5 % SiO$_2$ су синтетисани користећи сол–гел поступак. Стуктура синтетисаних кополиимида је потврђена FTIR и NMR спектроскопијом. Динамичка механичка анализа (DMA) је показала да кополиимиди на бази *m*-BAPPO имају ниже температуре остакљивања (T_g) у односу на BAPPO кополиимиде. *m*-BAPPO кополиимиди без SiO$_2$ испољавају бољу термичку стабилност. Модули и затезна чврстоћа кополиимида на бази BAPPO диамина као и њихових хибридних материјала била је већа у односу на *m*-BAPPO аналогне материјале. Мерења контактних углова су потврдила хидрофобност њихове површине. Скенирајућа електронска микроскопија (SEM) је показала диспергованост силицијум-диоксидних честица у кополиимидној матрици. Синтетисани кополиимидни материјали могу се потенцијално користити у индустрији премаза. Највећу пропустљивост према CO$_2$ и највећу селективну пропустљивост према гасовима је показао кополиимид на бази *m*-BAPPO без присуства честица SiO$_2$. Пропустљивост према гасовима материјала, приказаних у овом раду, следила је опадајући тренд: $P_{CO_2} > P_{O_2} > P_{N_2}$.

REFERENCES

1. . Y. K. Yang, W. J. Koros, H. B. Hopfenberg, V. T. Stannet, *J. Appl. Polym. Sci.* **31** (1986) 1619
2. D. Hofman, J. Ulbrich, D. Fritsch, D. Paul, *Polymer* **37** (1996) 4773
3. C. Joly, S. Goizet, J. C. Schrotter, J. Sanchez, M. Escoubes, *J. Membr. Sci.* **130** (1997) 63
4. Y. W. Wang, C. T. Yen, W. C. Chen, *Polymer* **46** (2005) 6959
5. K. U. Jeong, J. J. Kim, T. H. Yoon, *Polymer* **42** (2001) 6019
6. L. Wang, Y. Cao, M. Zhou, S. J. Zhou, Q. Yuan, *J. Membr. Sci.* **305** (2007) 338
7. C. Kızılkaya, S. Karataş, N. K. Apohan, A. Güngör, *J. Appl. Polym. Sci.* **115** (2009) 3256
8. A. Gungor, C. Smith, J. M. Wescott, S. Srinivasan, J. E. McGrath, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **32** (1991) 172
9. T. T. Moore, S. Damle, P. Williams, W. J. Koros, *J. Membr. Sci.* **245** (2004) 227

10. X. Fang, Z. Wang, Z. Yang, L. Gao, Q. Li, M. Ding, *Polymer* **44** (2003) 2641
11. S. Xiao, X. Feng, Y. Robert, M. Huang, *Macromol. Chem. Phys.* **208** (2007) 2665
12. A. Y. Ardashnikov, I. Y. Kardash, A. N. Pravednikov, *Polym. Sci. USSR* **13** (1971) 2092
13. W. Volksen, P. M. Cotts, in *Polyimides: Synthesis, Characterization and Applications*, Vol. 1, K. L. Mittal, Ed., Plenum, New York, 1984, p. 163
14. C. Hibshman, C. J. Cornelius, E. Marand, *J. Membr. Sci.* **211** (2003) 25
15. M. Miki, T. Suzuki, Y. Yamada, *J. Appl. Polym. Sci.* **130** (2013) 54
16. A. C. Lua, Y. Shen, *Chem. Eng. J.* **20** (2013) 441.