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# Thermal, mechanical and structural investigation of copolyimide–silica hybrids containing phosphine oxide

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ABSTRACT

In this study, a novel hybrid copolyimide was synthesized from copolyamic acid solutions (PAAs) obtained by the reaction between bis(3-aminophenoxy-4-phenyl)phenylphosphine oxide (*m*-BAPPO), 3,3′-diaminodiphenyl sulfone (DDS) and 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA), followed by thermal imidization. Hybrid materials containing 5% $SiO_2$ were synthesized by sol–gel technique. The polyimide–silica hybrids were characterized by Fourier Transform Infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). Thermogravimetric analysis showed that the weight loss of hybrids is shifted to the higher temperature compared to the neat copolyimide. The contact angle measurements confirmed the hydrophobic surface of hybrids. Moreover, the gas permeability measurements were also done to take a step for forthcoming gas separation studies. The tensile modulus and strength of the copolyimides are good.

## 1. Introduction

Polyimides (PI) are one of the most studied polymers, since many of them present good mechanical properties as well as high chemical and thermal stability [1]. They have found applications as high performance materials in electrical, microelectronics and aircraft industries. To achieve the outstanding properties, inorganic particles have been introduced into PI matrix to form polyimide–silica (PI–$SiO_2$) hybrids [2–4]. These materials are useful for a number of applications such as packaging materials, abrasion resistant coating, optically active films, sensors, contact lenses, absorbents and semi permeable membranes [5,6].

Sol–gel method is a convenient way to produce hybrid materials, where silica particles are dispersed in a polyimide matrix. The sol–gel technique involves two step reactions such as hydrolysis of metal alkoxide to produce hydroxyl groups and the formation of a three dimensional (3-D) network by the polycondensation of the hydroxyl groups and residual alkoxy groups. In order to achieve homogeneous hybrid materials, one approach is to control the chain length of polymer segment (i.e. polyimides), and the second one is the selection of suitable coupling agents and/or the use of effective compatibilizer (TEOS: tetraethyl orthosilicate, GOTMS: 3-glycidyloxypropyltrimethoxysilane) [7]. Polyimide–silica materials offer favorable properties in high performance/high temperature applications. The degree of interaction between the filler and polymer controls the phase separation. The imide linkage in the silica network produces hybrids with better optical, mechanical and thermal properties [8,9].

The polymers containing phosphine oxide groups are of great interest when compared with other polymers. The phosphine oxide moieties show excellent flame retarding, very good mechanical characteristics. Since the change in the molecular symmetry caused by phosphonyl group takes place, many of these polymers are amorphous and they can be soluble in organic solvents [10]. The phosphine oxide containing polymers yield high char. The formation of char is too important for flame resistance, because the polymer is isolated through char. In this way, the entrance of oxygen and the flame growth are prevented [11].

PI–$SiO_2$ hybrid materials have received much attention not only in packaging, coating, electronic industry but also in gas separation applications. Over the traditional separation technologies such as cryogenic, absorption and pressure swing adsorption technology, gas separation membranes have significant advantages by presenting lower energy, lower cost and simplicity of the equipment. Although polymer membranes for gas separation exhibit good mechanical property, they still suffer from a “trade-off” relationship between permeability and selectivity [12,13]. The development of these membranes is important in order to improve the permeation characteristics. The effect of the addition of some additives on polymeric membranes was reported [14]. Nanoscale inorganic particles synthesized by sol–gel reaction in a polymer matrix can enhance the permeability coefficient [15].

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The present study aims to improve not only thermal and mechanical properties of polyimides but also gas separation performance (i.e. permeability), where applicable. The purpose in this study is also to investigate intrinsic properties of the phosphine oxide based copolyimides taking into consideration of the predicted, possible reactivity differences of the diamines, monomer (BAPPO or *m*-BAPPO) structural effects and estimated mechanisms between silica and copolyimide due to the feasible interactions (covalent bonding, hydrogen bonding) occurred in the different phases. In this regard, a novel hybrid copolyimide containing phosphine oxide component was synthesized. Copolyamic acid solutions (PAAs) were obtained by the reaction between bis(3-aminophenoxy-4-phenyl)phenylphosphine oxide (*m*-BAPPO), 3,3′-diaminodiphenyl sulfone (DDS) and 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA). Copolyimide films were prepared by thermal (bulk) imidization. Hybrid materials containing 5% $SiO_2$ were synthesized by sol–gel technique. The molecular structure and morphology of the PI–$SiO_2$ hybrids were characterized by Fourier Transform Infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). Thermal, mechanical properties as well as contact angle and limiting oxygen index (LOI) were studied. Moreover, the permeability for $O_2$, $N_2$ and $CO_2$ gases was determined so as to take an initial step for gas separation studies. The research based on gas separation using inorganic particles filled polyimides is still in progress. Copolyimide–silica hybrids showed good mechanical properties. The contact angle measurements confirmed the hydrophobic nature.

## 2. Experimental

### 2.1. Materials

The dianhydride monomer, 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA, >99%) was purchased from Aldrich and used as received. 3,3′-Diaminodiphenyl sulfone (DDS), phenylphosphonic dichloride (98%), N-methyl-2-pyrrolidone (NMP) and dimethylacetamide (DMAc) were obtained from Merck. NMP and DMAc were dried over phosphorous pentoxide ($P_2O_5$) and freshly distilled under vacuum before used. 1-Bromo-4-fluorobenzene (99%), Mg powder (99.9%), anhydrous potassium carbonate ($K_2CO_3$, 99.9%), 3-aminophenol were provided by Aldrich and used as received. Tetrahydrofuran (THF) was freshly distilled under nitrogen over sodium. Tetraethyl orthosilicate (TEOS), 3-glycidyloxypropyltrimethoxysilane (GOTMS) were purchased from Merck. Some common solvents such as chloroform, ethanol, methanol, dichloroethane were used as received.

### 2.2. Synthesis of diamine monomers containing phenylphosphine oxide group

In this study, two diamine monomers (BAPPO and *m*-BAPPO) were synthesized.

#### 2.2.1. Synthesis of bis(3-aminophenyl)phenylphosphine oxide (BAPPO)

Bis(3-aminophenyl)phenylphosphine oxide (BAPPO) was synthesized by a three step reaction as mentioned on previous work [16]. First, triphenyl phosphine (TPP) was oxidized to triphenyl phosphine oxide (TPPO) by treating with $H_2O_2$. Then, bis(3-nitrophenyl)phenylphosphine 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. Hydrogenation was carried out at 50 °C under hydrogen pressure of 100 psi for 48 h. Yield: 70%.

FTIR (KBr): 3460 and 3358 $cm^{-1}$ (N—H str.), 3059 $cm^{-1}$ (aromatic C—H str.), 1595 $cm^{-1}$ (N—H bend.), 1437 $cm^{-1}$ (aromatic C—P str.), 1199 $cm^{-1}$ (P=O str.), 1281 $cm^{-1}$ (C—N str.).

$^1H$ NMR ($CDCl_3$, ppm): $\delta$ 7.75–6.80 ppm (aromatic ring, 13H, multiple); 3.2–3.4 ppm (amino group 4H).

$^{31}P$ NMR ($CDCl_3$, ppm): $\delta$ 29.3 ppm.

#### 2.2.2. Synthesis of bis(3-aminophenoxy-4-phenyl)phenylphosphine oxide (m-BAPPO)

Bis(3-aminophenoxy-4-phenyl)phenylphosphine oxide (*m*-BAPPO) was synthesized as described in the literature [17]. First, 4,4′-bis(fluorophenyl)phenylphosphine oxide (BFPPO) was synthesized by treating 1-bromo-4-fluorobenzene with phenylphosphonic dichloride in the presence of Mg turnings via Grignard technique. Then, *m*-BAPPO was prepared by treating 37.23 g (0.118 mol) BFPPO with 26.56 g (0.243 mol) 3-aminophenol in DMAc/toluene mixture using 40.20 g (0.292 mol) $K_2CO_3$ as a weak base to form the required aminophenolate nucleophile. Yield: 85%.

FTIR (KBr): 3445 and 3324 $cm^{-1}$ (N—H str.), 1594 $cm^{-1}$ (N—H bend.), 1436 $cm^{-1}$ (aromatic C—P str.), 1170 $cm^{-1}$ (P=O str.), 1232 $cm^{-1}$ (C—O str.).

$^1H$ NMR ($CDCl_3$): 7.71 (*o*-, *m*-, *m*-, *p*-coupling, d, H-7), 7.54 (*o*-, *m*-, *p*-coupling, d, H-6), 7.52 (*o*-, *o*-, *m*-, *m*-coupling, d, H-9), 7.45 (*o*-, *o*-, *m*-, *p*-coupling, d, H-8), 7.12 (*o*-, *m*-, *p*-coupling, d, H-5), 7.07 (*o*-, *o*-, *p*-coupling, d, H-3), 6.46 (*o*-, *m*-, *m*-coupling, d, H-4), 6.42 (*o*-, *m*-, *m*-coupling, d, H-2), 6.37 (*m*-, *m*-, *p*-coupling, d, H-1), 3.4–3.8 ppm (amino protons).

$^{31}P$ NMR ($CDCl_3$, ppm): $\delta$ 29 ppm.

### 2.3. Preparation of copolyamic acid solution

Copolyamic acid solution (PAA) used as a copolyimide precursor was prepared in NMP as follows: The diamine monomers and the 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 solid concentration was afforded as 20% (wt/v). The reaction mixture was stirred overnight at room temperature to obtain a viscous PAA solution.

In this study, BTDA based copolyimides were synthesized from the aromatic diamines (DDS, BAPPO and *m*-BAPPO).

### 2.4. Preparation of sol–gel precursor

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.

### 2.5. Preparation of copolyimide–silica hybrid materials

The compositions of the hybrid materials are shown in Table I. To obtain the hybrid solution, 5% silica sol was added dropwise into the PAA solution and stirred continuously at room temperature for 4 h. After through stirring, the clear and viscous hybrid solutions were cast onto glass plates and then thermal imidization was carried out stepwise at 80 °C, 100 °C, 150 °C, 200 °C and 300 °C for 1 h at each temperature. After imidization was completed, glass plates were immersed in hot water (80–90 °C) for 1 h to remove the hybrid films from glass surfaces, easily.