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Synthesis and Properties of a Novel Isomeric Polyimide/SiO_2 Hybrid Material

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***Abstract*--A novel isomeric polyimide/SiO_2 hybrid material was successfully prepared through sol–gel technique, and its structure, thermal properties and nano-indenter properties were investigated. First, 3-[(4-phenylethynyl) phthalimide]propyl triethoxysilane (PEIPTES) was successfully synthesized, its structure was characterized by elemental analysis, FT-IR and ^{13}C NMR. The researches on solubility and thermal properties of PEIPTES show that it can be used for modifying nano-SiO_2 precursor. Nano-SiO_2 precursor was synthesized by tetraethoxysilane (TEOS) through sol–gel technique. Then the PEIPTES solution and the nano-SiO_2 precursor were mixed for 6 h to let the PEIPTES molecules react with the nano-SiO_2 precursor, and modified nano-SiO_2 precursor was obtained. The modified reaction was confirmed by the analyses of FT-IR. At last, isomeric polyimide/SiO_2 hybrid material was produced by using isomeric polyimide resin solution and the modified nano-SiO_2 precursor after heat treatment process. The structure analysis by SEM indicated that SiO_2 particles dispersed in isomeric polyimide matrix homogeneously with nanoscale. Thermogravimetric analyzer, dynamic mechanical thermal analyzer and nano-indenter XP was employed to detect the properties of the materials, the results demonstrated that isomeric polyimide/SiO_2 hybrid material has much better thermal properties and nano-indenter properties than those of isomeric polyimide. It is confirmed that PEIPTES acts as a bridge between the SiO_2 particles and the isomeric polyimide matrix in the hybrid material, because the ethoxyl of PEIPTES could participate in the hydrolyzation and condensation to form chemical bond with SiO_2 particles and its phenylethynyl group could take part in the cross-curing reaction of isomeric polyimide.**

***Keywords*-- polymides, peiptes, hybrid material, phenylethynyl groub, NMR**

I. INTRODUCTION

Polyimides (PIs) are a class of high performance polymers because of their high-temperature stability, excellent electrical and mechanical properties, and good chemical resistance [1]. However, most polyimides are often insoluble and intractable in their fully imidized form so that they show poor processability.

In order to improve the processability of polyimides and extend their utility, many attempts have been made to modify their melt processing properties and/or solubility in organic solvents.

The common ways to improve the processability are to introduce flexible bridging linkage groups and/or bulky units into the rigid PIs backbones, or to attach bulky side groups [2]. Unfortunately, these structure modifications have also resulted in a decrease in the rigidity of the polymer backbones so that their thermal properties may be reduced. Recently, an effective method for improving polyimides' processability, which has been attracting much interest of researchers, is to introduce geometrically asymmetric unit by altering catenation patterns of dianhydrides in polyimide chain structure. It has been demonstrated that the isomeric polyimides produced by isomeric dianhydrides and diamines exhibited broad processing windows and good solubilities without loss of thermal properties [3],.

In recent years, organic/inorganic hybrid materials, which combine the advantages of organic polymers with the benefits of inorganic components, have received a great deal of attention [4]. And polyimide/SiO_2 hybrid materials have been under extensive study in order to improve the thermal stability and mechanical properties of polyimides [5], [5]. The sol–gel process is a unique and versatile approach among the various methods used to produce polyimide/SiO_2 hybrid materials [6]. The nature of the interfaces between SiO_2 particles and polyimides matrix, the content and size of SiO_2 particles, greatly affect the properties of the hybrid materials. Strong interfaces in which covalent bond should be formed between SiO_2 particles and polyimides matrix, are needed for obtaining excellent properties [7],.

In the present study, 3-[(4-phenylethynyl) phthalimide]propyl triethoxysilane (PEIPTES) was synthesized to prepare modified nano-SiO_2 precursor, using which the isomeric polyimide/SiO_2 hybrid material was made. PEIPTES was characterized by elemental analysis, FT-IR and ^{13}C NMR.

The modification reaction was confirmed by FT-IR spectrums. SEM was used to investigate microstructures of the materials. A nano-indenter, a thermogravimetric analyzer and a dynamic mechanical thermal analyzer were used to detect the properties of the materials.

II. MATERIALS AND METHODS

Materials

Dimethyl sulfoxide (DMSO) was dried over 4-Å molecular sieves and purified by vacuum distillation prior to use. 4-(Phenylethynyl) phthalic anhydride (PEPA) and isomeric polyimide were prepared in Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, and the structural formula of the novel isomeric polyimide is shown as Fig. 1 (*n* = 3).

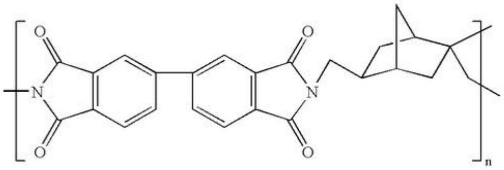

Fig. 1: The structural formula of the novel isomeric polyimide

γ-Aminopropyltriethoxysilane (APTES), tetraethoxysilane (TEOS) and other chemicals were obtained commercially and used as received.

Synthesis of 3-[(4-phenylethynyl) phthalimide]propyl triethoxysilane (PEIPTES)

133.059 g DMSO and 11.069 g (0.05 mol) APTES were added to a 250 ml three-necked round bottom flask equipped with a mechanical stirrer and a condenser, and then 12.412 g (0.05 mol) PEPA were added gradually to make them dissolve. The solution was stirred at 30 °C for 48 h after the complete addition of the PEPA to make 3-[(4-phenylethynyl) phthalic amide acid propyltriethoxysilane (PEAPTES). Imidization was carried by adding the mixture of 10.209 g acetic anhydride (Ac_2O) and 2.53 g triethylamine (Et_3N) into the PEAPTES solution and stirring at 30 °C for 72 h, and PEIPTES solution with a solids content of approximately 15 wt% was obtained. The PEIPTES solution was poured into methanol, and the light yellow precipitate was collected by filtration, washed thoroughly with ethanol (EtOH), and then dried at 100 °C under vacuum. The yellow powder of PEIPTES was obtained. The yield of the product was 16.212 g (71.8%). The reaction scheme is shown as Fig. 2.

PEIPTES was designed and synthesized to play an important role in isomeric polyimide/SiO_2 hybrid material. The ethoxyl of PEIPTES could participate in the hydrolyzation and condensation of nano-SiO_2 precursor, thus the size growth of SiO_2 particles was held down. PEIPTES has excellent miscibility with isomeric polyimide because of its structure characteristic, so that PEIPTES which reacted with nano-SiO_2 precursor enhanced miscibility between the SiO_2 and isomeric polyimide, and improved the homogeneity of the isomeric polyimide/SiO_2 hybrid materials. Furthermore, the phenylethynyl imide group of PEIPTES took part in cross-linking reaction during curing period, therefore strong interphase between isomeric polyimide and SiO_2 was formed.

Preparation of isomeric polyimide/SiO_2 hybrid material

TEOS, H_2O and EtOH were mixed in the approximate molar ratio 1:4:15. This amount of water is needed to form anhydrous silica, according to the net reaction. The catalyst, HCOOH was added. The molar ratio of HCOOH and Si is 4:1. The mixture was stirred at 50 °C for 4 h, then aged at room temperature to obtain the nano-SiO_2 precursor. Then 10.84 g nano-SiO_2 precursor was mixed with 1 g 15 wt% PEIPTES solution, and the mixture was stirred at 50 °C for 6 h to form covalent bond between the nano-SiO_2 precursor and PEIPTES, so modified nano-SiO_2 precursor solution was synthesized. The mass ratio of SiO_2 and PEIPTES through chemistry calculation is about 100:25.

Isomeric polyimide/SiO_2 hybrid material was produced through homogeneously mixing 10 g 30 wt% isomeric polyimide in DMF solution and 2.65 g modified nano-SiO_2 precursor solution, coating on the clean slide glasses and heat treatment. The mass ratio of isomeric polyimide and SiO_2 through chemistry calculation is about 100:5. Heat treatment process included 100 °C for 1 h, 150 °C for 1 h, 200 °C for 1 h, 230 °C for 2 h, 370 °C for 2 h.

Measurements and instruments

A Nicolet Nexus 670 FT-IR spectrometer was used to investigate PEIPTES. SiO_2 gel and modified SiO_2 gel were also investigated by FT-IR. The samples for FT-IR analyses were mixed with KBr powder and pressed into pellets. SiO_2 gel was prepared by drying to remove the solvents of the nano-SiO_2 precursor. Modified SiO_2 gel was prepared as follows: first, the solvents of the modified SiO_2 precursor were removed, then before the heat treatment, DMSO was employed to extract the modified SiO_2 to make sure that PEIPTES which had not reacted was cleaned up, then the modified SiO_2 gel which was light yellow powder was obtained.

The ^{13}C NMR spectra were obtained at 100 MHz on a Bruker AV400 spectrometer, dimethyl sulfoxide-d_6 (DMSO-d_6) and tetramethylsilane (TMS) were used as solvent and internal reference, respectively.

Elemental analysis for C, H, N was detected on a Element-Varioel elemental analysis instrument made in German, and elemental analysis for Si was performed on a POEMS analysis instrument made by TJA Corp., USA.

The fracture surface morphologies of the isomeric polyimide and its hybrid material were observed by SEM photographs. The apparatus used was HITACHI S-4700 and the specimens were pre-coated with a thin layer of gold to eliminate electron charging effect.

Thermogravimetric analysis (TGA) was conducted with a ZRY-2P thermogravimetric analyzer. Experiments were performed at a heating rate of 20 °C/min in air or in N_2. The temperature range for TGA measurements were from 0 to 1000 °C. The isothermal thermal properties were investigated with a differential scanning calorimeter (DSC). The apparatus used was NEJSCH-SET449C and the temperature was maintained at 370 °C for 2 h after temperature rise period at a heating rate of 10 °C/min in Ar.

Dynamic mechanical thermal analysis (DMTA) was carried out with a GDP-4 DMTA at a heating rate of 2 °C/min from room temperature to 400 °C. The specimens used for DMTA were prepared by applying isomeric polyimide solution and isomeric polyimide/SiO_2 hybrid solution to a glass braid, respectively, and drying at 100 °C for 1 h, 150 °C for 1 h, 200 °C for 1 h, and then heating at 230 °C for 2 h, 370 °C for 2 h.

A nano-indenter XP made by MTS Corp. (USA) was employed to measure the nano-indentation hardness and nano-indentation modulus of isomeric polyimide and its hybrid material. The specimens were the films prepared on the clean slide glasses. The size of the specimens was 2 mm × 2 mm.

III. RESULTS AND DISCUSSION

Characterization of PEIPTES

Elemental analysis of PEIPTES

The chemical structure of PEIPTES was confirmed by means of elemental analysis, FT-IR and NMR. The result of elemental analysis is shown in Table 1. As shown in Table 1, the values detected were in good agreement with the calculational values.

Table 1:
Elemental analysis of PEIPTES

	Molecular		Elemental analysis (%)			
			C	H	N	Si
$C_{25}H_{29}O_5NSi$	451.64	Calculational values	66.49	6.47	3.1	6.22
		Experimental values	65.73	6.55	3.42	6.86

Analysis by FT-IR

Fig. 4 shows the FT-IR spectra of PEIPTES. The characteristic bands of >C═O asymmetric stretching and >C═O symmetric stretching of the imides group are clearly visible at 1775 cm^{-1} and 1720 cm^{-1}, respectively. It also includes some peaks located at 1393 cm^{-1} (the stretching of the imide ring), and 744 cm^{-1} (the deformation of the imide ring). The double bands at 1075 cm^{-1} and 1095 cm^{-1} are the characteristics of –Si–O–CH_2CH_3, and the peak at 1220 cm^{-1} is the characteristics of –Si–C–.

Other functional groups, such as –C≡C– (stretching vibration at 2215 cm^{-1}), –CH_2CH_3 (stretching vibration at 2982–2816 cm^{-1}, bending vibration at 1442 cm^{-1}, bending wagging vibration at 1316 cm^{-1}) and aromatic ring (stretching vibration of Ar–H at 3062 cm^{-1}, bending vibration at 1600–1450 cm^{-1}) are also shown in Fig. 4.

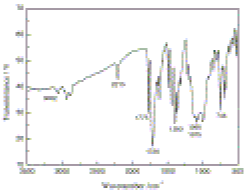

Fig. 4: FT-IR spectrum of PEIPTES

Analysis by NMR

The ^{13}C NMR spectrum is a useful tool to determine compound structure. Fig. 5 is the chemical structure of PEIPTES. Fig. 6 shows the ^{13}C NMR spectrum of PEIPTES. Contrast Fig. 5 and Fig. 6, it is confirmed that PEIPTES is successfully synthesized. The region between 38.8–40.2 ppm, which is signed peak 20 in Fig. 6, is the characteristic of the methyl carbons of the solvent. Because there was no characteristic of COOH group in the spectrum, it can be concluded that great the efficiency of the transformation of the amic acid into an imide was obtained.

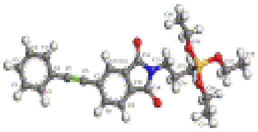

Fig. 5: Chemical structure of PEIPTES

Solubility of PEIPTES

The solubility of PEIPTES was investigated qualitatively, and the results indicated that although PEIPTES is insoluble in THF, acetone, $CHCl_3$ or EtOH, it is soluble in DMF, NMP, DMAC or DMSO. Thus, it may be dissolved in DMF, NMP, DMAc or DMSO to modify the nano-SiO_2 precursor.

Though PEIPTES is not soluble in ethanol, its solubility in DMSO is very excellent. Because the mutual solubility of ethanol and DMSO is good, DMSO is used as a cosolvent of PEIPTES and ethanol. It is because of the presence of proper quantity of DMSO that makes the precipitation of PEIPTES not occur in the final solution.

Thermal properties of PEIPTES

The thermal stability of PEIPTES was evaluated by TGA. The two curves detected in air and in N_2 are shown in Fig. 7. As shown in Fig. 7, the temperature of 5% weight loss ($T_{5\%}$) detected in air and in N_2 is 483 °C and 490 °C, respectively. The temperature of 10% weight loss ($T_{5\%}$) detected in air and in N_2 is 520 °C and 532 °C, respectively. Therefore, it is confirmed that PEIPTES exhibited excellent thermal stability, and it can be used for the modification of isomeric polyimide.

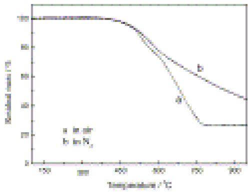

Fig. 7: TGA curves of PEIPTES in air and in N_2

Characterization of isomeric polyimide/SiO_2 hybrid material

Analysis by FT-IR

The two curves (a and b) in Fig. 8 show the FT-IR spectrums of SiO_2 gel and modified SiO_2 gel, respectively. The characteristic bands of SiO_2 are shown in Fig. 8(a), the wide bands that appear at 1030–1230 cm^{-1} are attributed to Si–O–Si bond, the bands at 3427 cm^{-1}, 962 cm^{-1} and 809 cm^{-1} are owing to Si–OH group. The characteristic bands of PEIPTES are clearly visible besides the bands of SiO_2 in Fig. 8(b), 1775 cm^{-1} (>C═O asymmetric stretching of the imide group), 1720 cm^{-1} (>C═O symmetric stretching of the imide group), 1378 cm^{-1} (the stretching of the imide ring), and 744 cm^{-1} (the deformation of the imide ring). Other functional groups, such as –C≡C– (stretching vibration at 2215 cm^{-1}) and aromatic ring (stretching vibration of Ar–H at 3062 cm^{-1}, bending vibration at 1600–1450 cm^{-1}) are also shown in Fig. 8(b). In the experiments, the modified SiO_2 gel was extracted by DMSO thoroughly before the test of FT-IR so that PEIPTES which did not participate in the sol–gel reaction was removed. Therefore the appearance of the characteristic bands of PEIPTES in FT-IR spectrum of modified SiO_2 gel confirms that molecules of PEIPTES were introduced to the modified SiO_2 gel through chemical bond.

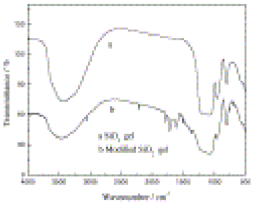

Fig. 8: FT-IR spectrum for SiO_2 gel and modified SiO_2 gel

Analysis by SEM

The SEM fracture surface images of isomeric polyimide and isomeric polyimide/SiO_2 hybrid material are shown in Fig. 9(a) and (b), respectively. The fracture surface morphology of isomeric polyimide is obviously single-phase structure, while isomeric polyimide/SiO_2 hybrid material exhibits good double-phases structure. Fig. 9(b) indicates that the second phase particles appear in isomeric polyimide/SiO_2 hybrid material, and they are dispersed in isomeric polyimide matrix homogeneously, the size of the particles is about 50–100 nm.

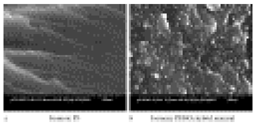

Fig. 9 SEM fracture surface micrographs of the two materials.

Thermal properties of isomeric polyimide/SiO_2 hybrid material

The curing process of the hybrid material was investigated by the analysis of DSC, and the isothermal thermal properties at 370 °C for 2 h (in Ar) are shown in Fig. 10. The temperature–time curve is shown in Fig. 10(a), which exhibits the temperature was maintained at 370 °C for 2 h after temperature rise period. The DSC–time curve is shown in Fig. 10(b), the peak appeared at the 30th minute, the corresponding temperature of which was 370 °C. As temperature is increased during cure, the material undergoes vitrification and consolidation in the glassy state. The TGA–time curve is shown in Fig. 10(c), the weight loss occurred from 14.5 to 17.5 min at 200–230 °C, which is ascribed to the evolution of water arising from the condensation of SiOH groups present in the reaction product of PEIPTES with pre-condensed TEOS. Then the mass percent was almost constant, though the temperature was raised to 370 °C and maintained at 370 °C for 2 h. This means that there is no decomposition in the isomeric polyimide during the thermal treatment.

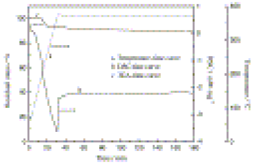

Fig. 10: The curing process analysis of the hybrid material by DSC (in Ar)

The TGA curves detected in air for polyimide and hybrid material are shown in Fig. 11. It shows that $T_{5\%}$ of isomeric polyimide occurred at 463 °C, while that of isomeric polyimide/SiO_2 hybrid material increased to 494 °C. $T_{5\%}$ of isomeric polyimide increased by 31 °C. It can be assumed that the thermal stability of organic materials can be improved by introducing inorganic components such as SiO_2, TiO_2 and so on, because these materials have inherently good thermal stability. The residual weight of isomeric polyimide after thermal decomposition was about 17 wt% above 600 °C, while that of isomeric polyimide/SiO_2 hybrid material was about 50 wt% under the same conditions. The increase in the weight of residues above 600 °C suggests successful incorporation of silica into the hybrid film.

It means that the thermal stability of isomeric polyimide/SiO_2 hybrid material is better than that of isomeric polyimide.

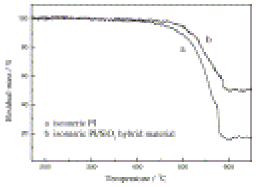

Fig. 11: TGA curves of the two materials (in air)

The relationship between energy dissipation (Tan Delta) and temperature is shown in Fig. 12, the maximum peak on the energy dissipation–temperature curve is the glass transition temperature (T_g). As shown in Fig. 12, T_g for isomeric polyimide and isomeric polyimide/SiO_2 hybrid material are 347.7 °C and 351.9 °C, respectively. The increase T_g of the hybrid material may imply that strong interphase (chemical bond) between organic phase (isomeric polyimide) and inorganic phase (SiO_2 particles) was formed so that the mobility of polymer chains decreased.

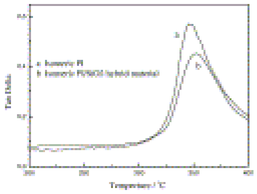

Fig. 12: Energy dissipation–temperature curves of the two materials

According to the analyses of FT-IR and SEM, it is confirmed the ethoxyl of PEIPTES was hydrolyzed and then condensed with the hydroxyl of the SiO_2 precursor during the modification process of nano-SiO_2 precursor. This means that the ethoxyl of PEIPTES could participate in the hydrolyzation and condensation of SiO_2 precursor solution to make chemical bond between macromolecules of phenylethynyl imide group and nano-SiO_2 precursor, so that the size of SiO_2 particles was controlled. When the isomeric polyimide cured, SiO_2 particles were formed in situ at the same time, and the phenylethynyl group could take part in the cross-linking reaction of isomeric polyimide. Because of the chemical bonds between the isomeric polyimide and SiO_2 particles, the interphase between them was increased.

Nano-indentation properties of isomeric PI/SiO_2 hybrid material

In this study, nano-indentation hardness and nano-indentation modulus were used to analyze the mechanical properties of the two materials.

The results are shown in Table 2, which indicates that the mechanical properties of the isomeric polyimide/SiO_2 hybrid material were much better than those of isomeric polyimide.

Nano-indentation hardness and nano-indentation modulus were increased by 138% and 141%, respectively. The hybrid material had better mechanical properties because of the introduction of nano-SiO_2 particles, especially because the chemical bonds between the isomeric polyimide and SiO_2 particles were formed.

Table 2:
Nano-indenter properties of the two materials

	Isomeric PI	**Novel isomeric PI/SiO_2 hybrid material**
Nano-indentation modulus (GPa)	6.290	15.188
Nano-indentation hardness (GPa)	0.510	1.215

IV. CONCLUSION

1) A compound, 3-[(4-phenylethynyl) phthalimide]propyl triethoxysilane (PEIPTES) was designed and successfully synthesized.
2) PEIPTES has suitable properties for modifying nano-SiO_2 precursor solution.
3) Isomeric polyimide/SiO_2 hybrid material was made by using isomeric polyimide and modified nano-SiO_2 precursor. Chemical bond was formed between isomeric polyimide and SiO_2 particles.
4) The isomeric polyimide/SiO_2 hybrid material has better thermal properties and nano-indenter properties, $T_{5\%}$ of isomeric polyimide increased by 31 °C, and nano-indentation hardness and modulus were increased by 138% and 141%, respectively.
5) The isomeric polyimide/SiO_2 hybrid material exhibits good double-phases structure, nanoscale SiO_2 particles dispersed in isomeric polyimide matrix homogeneously.

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