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Research Article

The Effects of Coupling Agents on the Properties of Polyimide/Nano-Al_2O_3 Three-Layer Hybrid Films

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PI/nano-Al_2O_3 hybrid films were prepared by ultrasonic-mechanical method. Before addition, nano-Al_2O_3 particles were firstly modified with different coupling agents. The micromorphology, thermal stability, mechanical properties, and electric breakdown strength of hybrid films were characterized and investigated. Results indicated that nano-Al_2O_3 particles were homogeneously dispersed in the PI matrix by the addition of coupling agents. The thermal stability and mechanical properties of PI/nano-Al_2O_3 composite films with KH550 were the best. The tensile strength and elongation at break of PI composite film were 119.1 MPa and 19.1%, which were 14.2% and 78.5% higher than unmodified PI composite film, respectively.

1. Introduction

As an engineering material, polyimide had been extensively applied in many areas such as microelectronics, electric industries, and aerospace and so forth [1]. During the past decade, increasing attention has been paid to the polyimide organic-inorganic hybrid materials, and it has been proved that the mechanical, thermal, and electrical properties of PI hybrid films can be improved by incorporation of fillers such as carbon nanotube [2], aluminum nitride [3], silica [4–7], and titania [8] into the pristine polyimide matrix.

Among these inorganic particles, nanoalumina (Al_2O_3) is often chosen as fillers to improve insulation properties of the polymer materials due to its extremely high insulating qualities and thermal conductivity [9–13]. These polyimide/Al_2O_3 composites could widely be applied in electrical insulating fields. However, due to its huge surface areas and large surface free energy, nano-Al_2O_3 particles will aggregate with each other easily. So the combination of nano-Al_2O_3 particles with PI in nano scale is very difficult. One of the most important key points of PI/Al_2O_3 hybrid films is to control the dispersion of alumina in the polymer matrix.

The coupling agents can make organic and inorganic materials connect together and improve the compatibility between the two phases effectively. However, little information has been focused on the effects of different coupling agents on structure and properties of polyimide/Al_2O_3 hybrid films.

In our present work, a series of PI/inorganic hybrid films with different kinds of coupling agents and different contents of each coupling agent was prepared. The microstructure and properties of these PI/nano-Al_2O_3 hybrid films were studied. Especially, the effects of different coupling agents on the microstructure and properties of hybrid films were investigated.

[a]T_0: the initial decomposition temperature.

[b]T_{10}: the decomposition temperature at 10wt% weight loss.

[c]T_{30}: the decomposition temperature at 30wt% weight loss.

2. Experiment

2.1. Materials. Pyromellitic diananocomposite(PMDA) and 4,4′-Oxydianiline(ODA) were chemic grade and purchased from Shandong Wanda Chemical Co. N,N-dimethylacetamide (DMAc) was analytical grade and purchased from Tianjin Basifu Chemical Co. α-Al_2O_3(30 nm) was obtained from Shanghai Wanjing New Materials Co. γ- aminopropyl triethoxysilane (KH550, $NH_2(CH_2)_3Si(OCH_2CH_3)_3$), γ -glycidoxypropyl trimethoxysilane (KH560, $C_6H_{11}O_2Si(OCH_3)_3$) were purchased from Nanjing Shuguang Chemical Plant. 3-(N-Styrylmethyl-2-aminoethylamino)-propyltrimethoxysilane hydrochloride (AE3012, $C_{14}H_{21}N_2HClSi(OCH_3)_3$) was purchased from Dalian Aolikai Chemical Co. Ethanol absolute was analytical grade and purchased from Tianjin Shentai Chemical Reagent Co.

2.2. Preparation of PI/Al_2O_3 Hybrid Films. Nanometer alumina particles were firstly dissolved in ethanol absolute, then heated up in a water bath of 70–75°C, and 4% content of coupling agent was added with the treatment of ultrasonic wave. The mixture was stirred mechanically again for 4 h, followed by heating at 100 °C for 16 h, and then abraded to use.

Poly(amic acid) (PAA) was synthesized by appropriate PMDA and ODA in DMAc. The solid content of PAA solution was 10 wt%. A typical synthesis of the precursors to alumina containing polymer is as follows ODA was added into a 250 mL three-necked bottle, and an appropriate amount of DMAc was added into it. After the ODA was completely dissolved, PMDA was added to this solution with a certain time sequence, and the mixture was stirred to get a yellow PAA solution. A calculated quantity of modified nano-Al_2O_3 particles with KH550 content 2 wt% was added to PAA solution with the aid of ultrasonic wave, and the mixture was stirred mechanically again for 10 h to form a homogeneous Al_2O_3/poly(amic acid) solution.

The Al_2O_3/PAA solution was casted on a clean glass substrate and followed by heating successively at 80°C, 100°C and 140°C for 1 h, 220°C for 2 h, and 300°C for 3 h, respectively. The PI/Al_2O_3 hybrid films were obtained after the film peeled off the glass substrate.

2.3. Characterization. The fracture surfaces of film samples with aurum were examined on the FEI. Sirion Scanning Electron Micrographs (SEMs) at the voltage of 20.0 kV. FT-IR spectra of the nano-Al_2O_3 before and after treatment with the coupling agent were recorded on a BRUKER EQUINOX55 FT-IR spectrophotometer. The acquisition time was one minute at a resolution of four wave numbers. UV-Vis spectra were measured on a UV757CRT UV-Vis Spectrometer using the wavelength from 190 to 800 nm. Thermogravimetric analysis (TGA) was performed on a Pyris 6 series thermal analysis system at a heating rate of 20°C/min under nitrogen atmosphere. TGA curves were recorded. The tensile-strength and elongation at break were measured on XLD-series Liquid Screen Electronic Tensile Apparatus 100×10 mm with specimens in accordance with GB/T13541-92 at a drawing rate of 50 mm/min. Averages of five individual determinations were used, the values took three significant digits, and the unit was MPa, the elongation ratio computation to the integer position, by percentage expression. The electric breakdown strength was tested on the regulating assembly at boosting manually in the polymethylphenyl siloxane fluid.

3. Results and Discussion

3.1. Microstructures of PI/Al_2O_3 Hybrid Films. Figure 1 shows the fractural surface microstructures of PI/Al_2O_3 hybrid films with or without coupling agents. It can be seen that all of the samples show the three-layer structure characteristics. However, there are also some obvious differenes between these four samples. Sample of PI/unmodified-Al_2O_3 hybrid film (Figure 1(a)) shows an obvious stripping between three layers, indicating a bad structure integrity. While samples of PI/modified-Al_2O_3 hybrid films by KH560 and AE3012, respectively, as Figures 1(c) and 1(d) reflect a slight stripping phenomenon. A best combinational characteristics among these four samples can be found in Figure 1(b), which has a flattest fracture surface with smallest stripping among these four figures. This fairly good in microstructure of Figure 1(b) indicates a better combinational condition than others when KH560 addition.

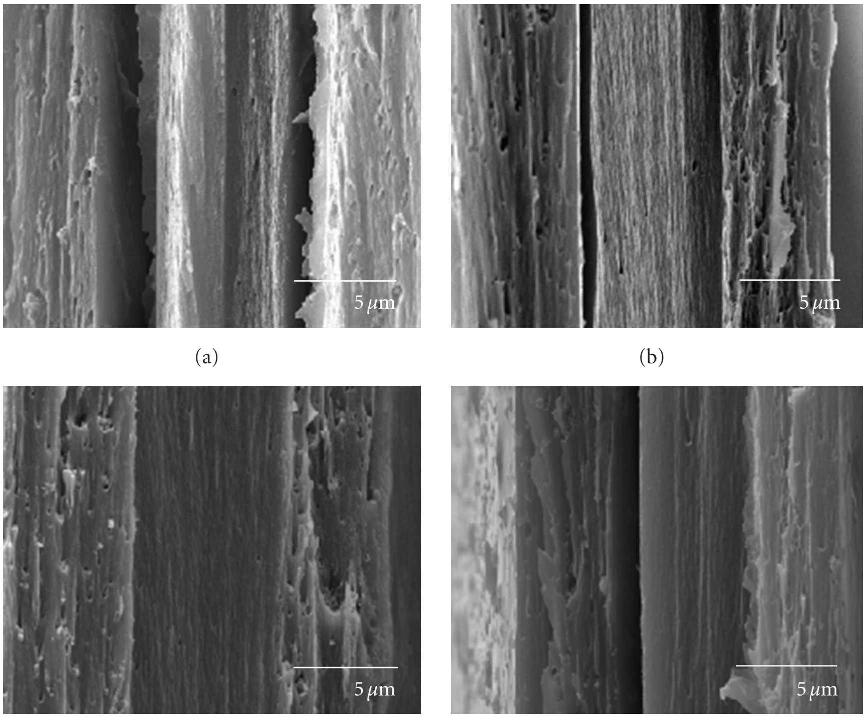
3.2. FTIR Analysis of PI/Al_2O_3 Hybrid Films. Figure 2 illustrated the FT-IR spectra of the nano-Al_2O_3 particles before and after treatment with the coupling agent KH560, which was donated as a) and b)), respectively. The characteristic peaks in these two FT-IR spectra present near at 3407.1 cm^{-1} , 1628.5 cm^{-1} indicate the stretching vibration and bending vibration of hydroxyl group peaks on the Al_2O_3 particles' surface. Comparing a) and b) spectra, it can be clearly found that the strength of O-H peaks after treatment by coupling agent was greatly weaker than that of raw Al_2O_3 particles, indicating the decrease of absorbed water and the surface hydroxyl group after treatment by coupling agent. Moreover, the band at 2931 cm^{-1} is the C-H band stretching vibration, it also indicated the effective linkage between KH560 and Al_2O_3 particles.

3.3. UV-Vis Transmittance of PI/Al_2O_3 Hybrid Films. UV-vis absorption spectra of PI hybrid films with unmodified and modified Al_2O_3 by coupling agents are shown in Figure 3. The cutoff wavelengths of the films are observed at about 440–460 nm. Comparing to the PI/unmodified-Al_2O_3 hybrid films, the transmittances of the PI/modified-Al_2O_3 hybrid films by coupling agents are slightly increase, which is attributed to the effective dispersion of Al_2O_3 inorganic phases. The addition of coupling agent can connect the Al_2O_3 inorganic particles and PAA organic phase through its reactive group then improve the interfacial compatibility between inorganic/organic phases. Further investigation indicates that the transmittances of the PI/modified-Al_2O_3 by coupling agent KH560 has a highest value among these four samples when the wavelength of UV is in the range of 500~600 nm. It can possibly attribute to the better interface combination of PI/Al_2O_3 hybrid films modified by coupling agent KH560 than the other three composites.

3.4. Thermal Stability of PI/Al_2O_3 Hybrid Films. The TGA analysis was examined to evaluate the thermal stability of the PI/Al_2O_3 hybrid films without and with coupling agents. Results are shown in Figure 4 and Table 2. It can be found

Table 1: Mechanical properties of PI composite films.

Samples	PI/unmodified Al_2O_3	PI/unmodified with KH550	PI/unmodified with KH560	PI/unmodified with AE3012
Tensile strength (MPa)	104.3	119.1	108.5	107.5
Elongation (%)	10.7	19.1	10.9	11.6



(a) (b) (c) (d)

Figure 1: SEM images of the cross-section of PI/Al_2O_3 hybrid films: (a) PI/unmodified Al_2O_3 film; (b) PI/modified Al_2O_3 film with KH550; (c) PI/modified Al_2O_3 film with KH560; (d) PI/modified Al_2O_3 film with AE3012.

that the thermal stability of PI films with modified-Al_2O_3 addition is better than that of PI/unmodified-Al_2O_3 hybrid film. This superior in thermal stability of PI/modified-Al_2O_3 also indicates a rather good compatibility between the inorganic particles and the organic matrix by using the coupling agents to modify the inorganic particles, resulting in the occurrence of hydrogen bonds or other coordination bonds between PI and Al_2O_3 inorganic particles. These coordination bonds prevent the thermal motion of PI molecular and the breakdown of the polymer molecular chains, resulting in the increase of the breaking energy during the heating process and the improvement on thermal stability of the PI/Al_2O_3 hybrid films. Table 2 also indicates that the PI/Al_2O_3 composite film modified by KH550 has the highest value in decomposition temperature, about 624.7°C, among these four kinds of composites when 10wt.% mass lose is reached. This also can be attributed to the formation of some coordination bonds between the group of $-NH_2$ in the KH550 and the acid anhydride groups or the carboxyl group in PAA molecular chain, which cause the improvement in thermal decomposition temperature of the composite.

3.5. Mechanical Properties of PI/Al_2O_3 Hybrid Films. The mechanical properties of PI/Al_2O_3 hybrid films with different coupling agent (KH550, KH560, and AE3012) are examined and the results are listed in Table 1. It can be found that all of the tensile strength and the elongation at break of PI/modified-Al_2O_3 hybrid films are higher than that of the PI/unmodified-Al_2O_3 films. Table 1 also indicates that the tensile strength and the elongation at break of PI/Al_2O_3 hybrid films modified by KH550 are 119MPa and 19.1%, respectively, both of which are the best among these four samples. This can be attributed to the formation of some coordination bonds between the $-NH_2$ structure of coupling agent KH550 and the PAA or the nano-Al_2O_3 surface, such as Al-O-Si bonds and the hydrogen bond. The formation of these two linkages leads to form the strong single molecular interfacial layers between PI matrix and Al_2O_3 particles [14, 15]. The formation of these strong single molecular interfacial layers effectively improve the interactions between PI molecular and Al_2O_3 particles then increase the bonding strength between matrix and fillers, resulting in the increase in stiffness of PI composites.

Table 2: Thermal decomposition temperature of samples under nitrogen atmosphere.

Samples	T_0 (°C)	T_{10} (°C)	T_{30} (°C)
PI/unmodified Al_2O_3	597.8	617.4	679.9
PI/modified Al_2O_3 with KH550	604.3	624.7	687.0
PI/modified Al_2O_3 with KH560	601.6	622.3	698.9
PI/modified Al_2O_3 with AE3012	599.3	623.5	682.2

[a]T_0: the initial decomposition temperature. [b]T_{10}: the decomposition temperature at 10wt% weight loss. [c]T_{30}: the decomposition temperature at 30wt% weight loss.

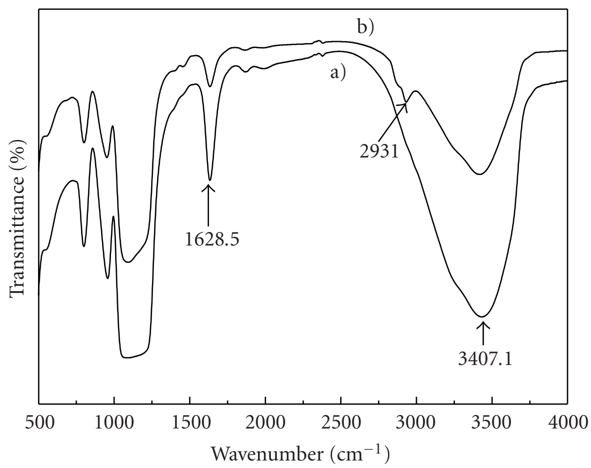


Figure 2: FT-IR spectra of nano-Al_2O_3 particles before and after treatment by coupling agent KH560.

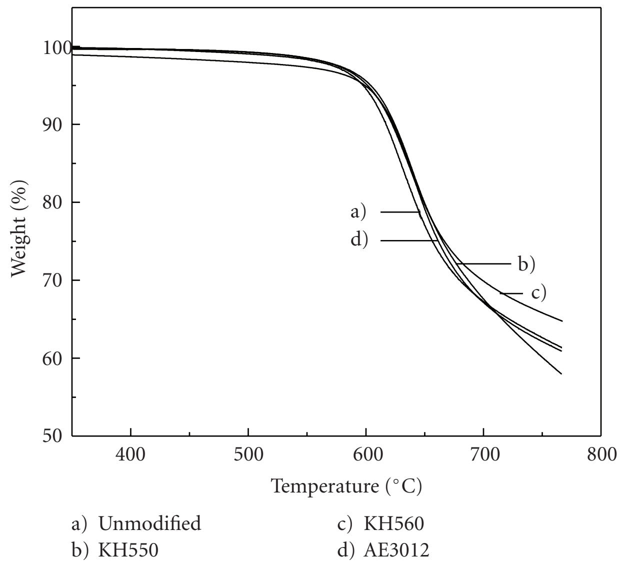


Figure 4: TGA cures of PI/Al_2O_3 hybrid films with different coupling agents.

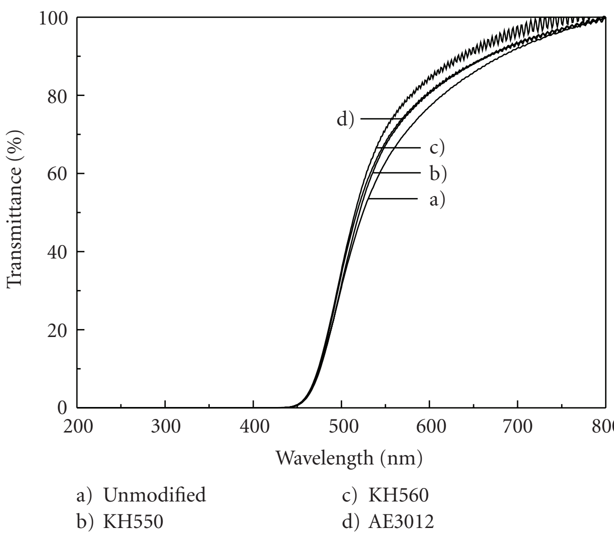


Figure 3: UV-Vis spectra of PI/Al_2O_3 hybrid films with different coupling agents.

3.6. Electric Breakdown Strength of PI/Al_2O_3 Hybrid Films. Being a key parameter, the electrical breakdown strength is widely used to measure the insulating capability of the dielectrics, because breakdown would cause short circuit which could be a fatal malfunction for the power equipment [9, 16]. Figure 5 shows the average electric breakdown strength of the PI/Al_2O_3 hybrid films with different coupling agent varieties. It can be found that all of the average electric breakdown strengths of the PI/Al_2O_3 hybrid films are over 260 kV/mm. Moreover, Figure 5 also indicates that the average electric breakdown strengths of PI-modified Al_2O_3 hybrid films are higher than that of PI-modified Al_2O_3 hybrid film. Combining with the SEM microstructural analysis, we could attribute this better antielectric breakdown properties of PI/modified Al_2O_3 hybrid films to a better homogenous microstructures and a fewer structure defects than PI/unmodified Al_2O_3 film.

Further study indicates that among the PI hybrid films added with three kinds of Al_2O_3 particles modified by KH550, KH560, and AE3012, respectively, the average electric breakdown strength of PI/modified Al_2O_3 with AE3012 is the highest, which is as high as 290 kV/mm. This can be attributed to the homogeneously dispersion of nano-Al_2O_3, particles in the PI matrix.

4. Conclusions

In this work, a series of PI/Al_2O_3 hybrid films is prepared by ultrasonic-mechanical method. The nano-Al_2O_3

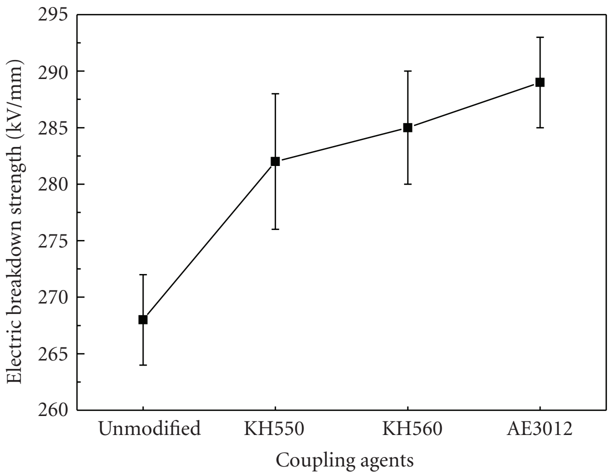


Figure 5: Average electric breakdown strength of the PI/Al_2O_3 hybrid films with different coupling agents.

particles are firstly modified by different coupling agents then dispersed homogenously in polyamic(acid) by some modes under the assistant of ultrasonic wave. Results of microstructure and performance analysis indicate that the coupling agents have a great effect on the microstructure of the PI/Al_2O_3 hybrid films. The usage of coupling agent can effectively improve the compatibility and the homogenous dispersion of nano-Al_2O_3 particles in PI matrix. Results also indicate that the PI/Al_2O_3 hybrid film modified by KH550 has the best of thermal stability and mechanical properties, while the PI/Al_2O_3 hybrid film modified by AE3012 has the highest of average electric breakdown strength.

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