Preparation and Properties of Nano-sized Al_2O_3/Polyimide Hybrid Films

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Abstract

Nano-sized Al_2O_3/polyimide (PI) hybrid films based on 4,4'-oxydianiline (ODA) and pyromellitic dianhydride (PMDA) were prepared by incorporation with different content of nano-sized Al_2O_3 via in situ polymerization. The TEM and SEM micrographs indicated that the Al_2O_3 particles were homogenously dispersed in the polyimide matrix by means of the ultrasonic treatment and the addition of coupling agent. The mechanical properties and thermal stability of the pure PI film can be improved by adequate addition of Al_2O_3. The PI hybrid film was strengthened and toughened simultaneously by the introduction of the well-dispersed Al_2O_3 particles. The PI hybrid films showed improved electrical aging performance as compared with pure PI film. Especially, the PI hybrid films with 10 wt.% of Al_2O_3 content exhibited obviously enhanced electrical aging performance with the time to failure of 3.4 times longer than that of pure PI film. The improved electrical aging performance of the hybrid film was attributed to the nano-sized Al_2O_3 particles highly dispersed in the hybrid film, which confirmed by the investigation of the morphology and the surface composition of PI hybrid film before and after electrical aging.

1. Introduction

Polyimides have been extensively applied in microelectronics and electric industries as a material for electronic packaging and electrical insulating, especially in high electric field and high temperature application, owing to their outstanding combination of thermal, mechanical and electrical insulating properties. With the rapid development of advanced industry, polyimide materials with unique functions are usually required [1-2].

In recent years, polyimide hybrid materials have received considerable attention due to the dramatic improvements over their pristine state in thermal stabilities, mechanical properties and other special features by introducing only small fraction inorganic additives. PI hybrid materials generally can be formed utilizing intercalation approach, sol-gel route or blending process [3-13]. Yano et al. [3-4] reported that the clay/PI hybrids based on ODA and PMDA possess better gas barrier property and lower thermal expansion coefficient than that of pristine polyimides. Mascia et al. [8] studied the silica/polyimide hybrids and found that the thermal and mechanical properties of polyimide could be improved by the dispersed silica particles in matrix. Many other researches have been made on the polyimides reinforced with other inorganic additives, such as titania and aluminum nitride [10-13].

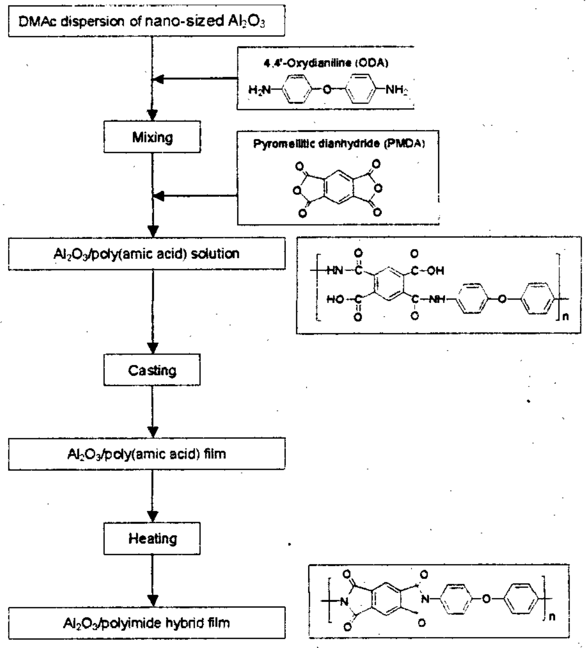
In our previous work [14], layered silicate/polyimide hybrids based on 4,4'-oxydianiline (ODA) and 4,4'-oxydiphthalic anhydride (ODPA) were prepared. We found that the layered silicate/polyimide hybrid films not only exhibited enhanced mechanical and thermal properties, but also showed the improved electrical aging property, which attributed to the highly dispersion and adequate addition of layered silicate in the polyimide matrix.

As a series work aimed at improvement the electrical insulating properties of polyimide films to prolong the life of the film in a voltage stressed environment, the Al_2O_3/polyimide hybrid films were investigated in the present work. The Al_2O_3/polyimide hybrids based on ODA and PMDA were prepared by incorporation with different content of nano-sized Al_2O_3 via in situ polymerization. The alumina was chosen to improve the electrical insulating properties of polyimide films because of its superior insulating qualities and high thermal conductivity. The preparation of PI hybrid films with homogenous dispersed Al_2O_3 was investigated. The mechanical and thermal properties of the PI hybrid films with different Al_2O_3 content were characterized. The effect of addition of nano-sized Al_2O_3 on the electrical aging properties of the PI hybrid films was discussed combination with the surface morphology observation and XPS analysis.

2. Experimental

2.1. Preparation of Al_2O_3/polyimide hybrid films

The Al_2O_3/poly(amic acid) was prepared via in situ polymerization with the procedure as shown in Scheme 1. In a typical experiment, 2.05 g of Al_2O_3 powder and 0.10 g of 3-aminopropyltriethoxysilane was added into 160 ml of DMAc and dispersed by ultrasonic treatment to yield a milky suspension. Then, 17.62 g of ODA (88 mmol) was added to the suspension under a nitrogen atmosphere. After the ODA completely dissolved (ca. 0.5 h), 19.20 g of PMDA (88 mmol) and additional 20 ml of DMAc were added. The mixture was stirred at room temperature for 6 h under nitrogen to give a homogeneous and viscous Al_2O_3/poly(amic acid) solution.



Scheme 1. Preparation of Al_2O_3/polyimide hybrid films.

The Al_2O_3/poly(amic acid) solution was casting on a glass substrate and followed by successively heated at 80, 120, 180, 250, and 300 °C each for 1 h. The polyimide hybrid film with 10 wt.% of Al_2O_3 was obtained after the film peeled off from the glass substrate.

A series of polyimide hybrid films with the Al_2O_3 content of 0, 2, 5, 10, 15 and 20 wt.%, respectively, was prepared in the similar procedure. The films were 25±2 μm in thickness.

2.2. Characterization

Transmission electron microscope (TEM) photographs were obtained with a JEM-2010 electron microscope. Scanning electron micrographs (SEM) were performed on a Hitachi S-4300 scanning electron microscope using film samples coated with platinum. Dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA) were recorded on a Perkin-Elmer 7 series thermal analysis system at a heating rate of 20 °C/min. The in-plane coefficients of thermal expansion (CTE) measurement of samples were carried out on a Perkin-Elmer 7 series thermal analysis system at a heating rate of 10 °C/min. Mechanical properties were measured on Instron 1122 Tensile Apparatus with 120 ×10 mm specimens in accordance with GB1040-79 at a drawing rate of 50 mm/min. Ultraviolet-visible (UV-vis) spectra were recorded on a Hitachi U3210 spectrophotometer. The dielectric strength and electrical aging were tested on the electric assembly consisted of cylinder electrode and plane electrode in accordance with IEC-343 standard. In electrical aging test, the voltage applied on the sample was 1 kV. Absolute viscosity was measured using a Brookfield HADV-II+CP viscometer with a 12 wt.% of poly(amic acid) in DMAc solution at 25±0.5 °C. X-ray photoelectron spectroscopy (XPS) measurements were carried out using an ESCALab 220I-XL instrument with Al Kα source. Spectra were recorded at a takeoff angle of 90° with respect to the sample surface. All XPS-peaks were referenced to the C 1s hydrocarbon signal at a binding energy of 284.6 eV.

3. Results and discussion

3.1. Preparation of Al_2O_3/PI hybrid films

The Al_2O_3/PI hybrid films with different Al_2O_3 content were prepared via in situ polymerization. At first, the alumina powder with the mean particle size of 20 nm was added to the solvent to get the dispersion. However, we found that the Al_2O_3 particles are difficult to be dispersed uniformly in DMAc under conventional mechanical stirring. The nano-sized Al_2O_3 particles are easily aggregated in solvent because of the high surface energy [15]. The TEM micrograph shown in Figure 1(a) revealed that the Al_2O_3 particles are poorly dispersed under mechanical stirring and the aggregates are formed with the size in submicrometer range. For getting the highly dispersed Al_2O_3 suspension, we applied the ultrasonic device instead of the conventional mechanical stirring in this process. We expect that the aggregates of Al_2O_3 can be broken down by ultrasonic treatment, in which immense shock wave and microstream are produced by ultrasonic cavitation as an ultrasonic wave passes through a liquid medium [15]. From Figure 1(b), it is observed that the Al_2O_3 particles are highly dispersed in the DMAc at the nano scale under ultrasonic treatment.

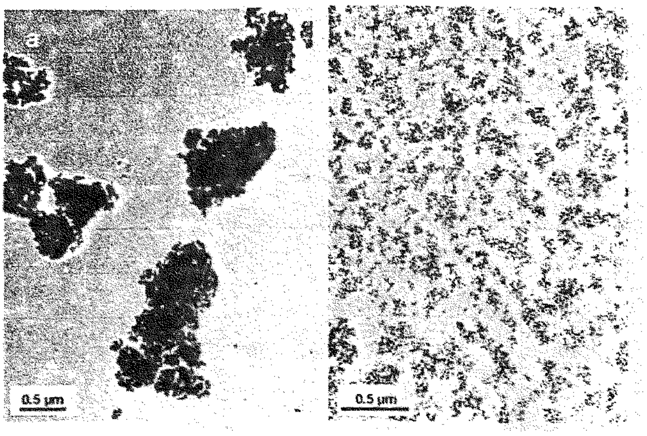


Figure 1. TEM micrographs of nano-sized Al_2O_3 dispersed in DMAc by mechanical stirring (a) and ultrasonic treatment (b).

The white suspension of Al_2O_3 nanoparticles in DMAc was gained after ultrasonic treatment. However, sediments were observed after the suspension was placed over 12 h. Therefore, the coupling agent 3-aminopropyltriethoxysilane was added to stabilize the Al_2O_3 dispersion and to increase the interaction between polyimide and Al_2O_3. There are no sediments observed over 12 h after the coupling agent was applied.

After the nano-sized Al_2O_3 particles were homogenously dispersed in DMAc, the aromatic diamine ODA was added and dissolved in DMAc. Then, the aromatic dianhydride PMDA was added stepwise to polycondense with the aromatic diamine to produce a homogeneous and viscous Al_2O_3/poly(amic acid) resin. The absolute viscosity of the Al_2O_3/poly(amic acid) solution was in the range of 500-600 poise at 25 °C. The Al_2O_3 particles were well dispersed in the solution, and no particle clustering or aggregation was observed. Finally, the Al_2O_3/poly(amic acid) solution was casting on a glass plate and followed by heated to remove the solvent and thermal imidization. The Al_2O_3/polyimide hybrid films with different Al_2O_3 content were obtained.

The morphology of the Al_2O_3 in the PI hybrid films was investigated by TEM and SEM micrographs. Figure 2 shows the TEM micrographs of Al_2O_3/PI hybrid films with different Al_2O_3 content. It can be observed that the Al_2O_3 particles (black spots) are homogeneously dispersed in the polyimide matrix with the particle size in nano scale. There is no large particle cluster or aggregate detected even when the Al_2O_3 content increased to 10 wt.%.

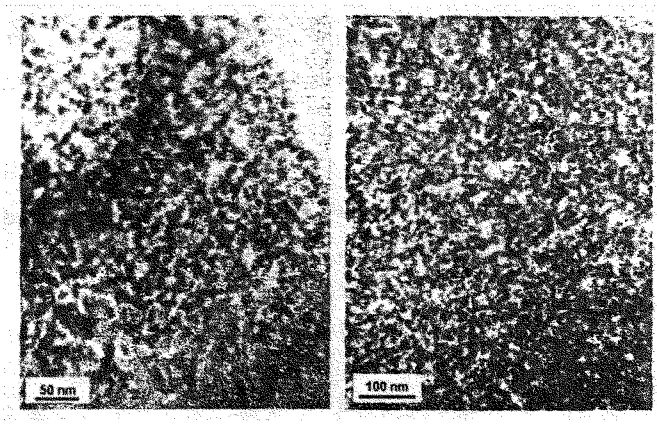


Figure 2. TEM micrographs of Al_2O_3/PI hybrid films with different Al_2O_3 content. (a) 2 wt.%; (b) 10 wt.%.

3.2. Mechanical properties

The mechanical properties of the Al_2O_3/PI hybrid films were examined and the results are listed in Table 1. We found that the Young's moduli of the hybrid films increase with the increasing of the Al_2O_3 content. For pure PI film, the Young's modulus is 1.6 GPa. As the film incorporated with 2 wt.% of Al_2O_3, the Young's modulus slightly increased to 1.9 GPa. When the Al_2O_3 content further increased to 10 wt.%, the Young's modulus markedly increased to 2.6 GPa, which is 62% higher than the pure PI film. The increase in the Young's modulus reflects the reinforcement effect that attributed to the dispersion of nano-sized Al_2O_3 into the polyimide film. The tensile strength and the elongation at break for the pure PI film are 123.5 MPa and 25.9%, respectively. As the film added with 2 wt.% of Al_2O_3, the tensile strength and the elongation at break are increased to 128.8 MPa and 28.2%, respectively. The PI hybrid film is strengthened and toughened simultaneously by the introduction of the well-dispersed Al_2O_3 particles, which may be attributed to the strong interfacial interaction between the polyimide matrix and the Al_2O_3 particles. Further increase in the Al_2O_3 content leads to a gradual decrease in the tensile strength and the elongation at break, which is probably caused by the partial aggregation of the Al_2O_3 particles. However, for the PI hybrid films with the Al_2O_3 content less than 10 wt.%, their tensile strength values are still higher than the pure PI film and the elongation at break exceeds 18.7%. The results indicated that the PI hybrid films with good mechanical properties could be achieved by in situ polymerization. However, as the Al_2O_3 content increased to 20 wt.%, the tensile strength and elongation at break of the film decreased abruptly, which give the tensile strength of 112.2 MPa and the elongation at break of 8.1%. This may be caused by the aggregation of the Al_2O_3 particles.

Table 1. Mechanical properties of Al_2O_3/PI hybrid films.

Al_2O_3 Content (wt.%)	Young's Modulus (GPa)	Tensile Strength (MPa)	Elongation (%)
0	1.6	123.5	25.9
2	1.9	128.8	28.2
5	2.2	124.0	21.5
10	2.6	124.2	18.7
15	3.0	123.3	14.6
20	3.6	112.2	8.1

3.3. Thermal properties

The TGA curves were examined to evaluate the thermal stability of the PI hybrid films (Figure 3 and Table 2). It is found that the Al_2O_3/PI hybrid films have improved thermal stability than the pure PI film. The pure PI film gives the onset decomposition temperature (T_d) of 601 °C and the decomposition temperature at 5% weight loss (T_5) of 574 °C. However, as 2 wt.% of Al_2O_3 was added to the film, the T_d and T_5 are enhanced to 618 and 611 °C, respectively. As the Al_2O_3 content increased to 10 wt.%, the hybrid film shows the best thermal stability with the T_d of 624 °C and T_5 of 616 °C, which are 21 and 42 °C higher than those of the pure PI film, respectively. With the further increase of Al_2O_3 content, a slight decrease in decomposition temperatures of the hybrid film was detected. The results indicated that the thermal stability of pure PI film could be improved by addition of nano-sized Al_2O_3.

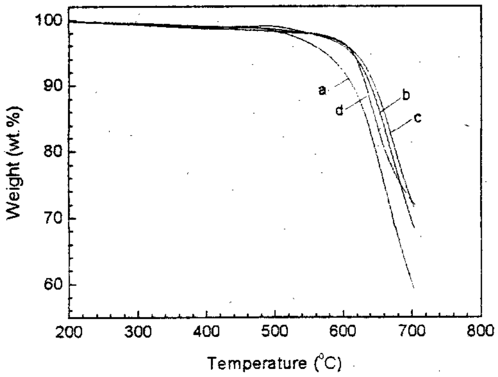


Figure 3. TGA curves of Al_2O_3/PI hybrid films; (a) 0 wt.%; (b) 2 wt.%; (c) 10 wt.%; (d) 20 wt.%.

Table 2. Thermal properties of Al_2O_3/PI hybrid films.

Al_2O_3 Content (wt.%)	Decomposition Temperature (°C) T_d	T_5	T_{10}	CTE (ppm/°C)
0	601	574	614	37.3
2	618	611	639	35.7
10	624	616	645	32.9
20	610	611	631	31.6

The effect of nano-sized Al_2O_3 on the coefficient of thermal expansion (CTE) of the PI hybrid films was also investigated. It is found that the CTE of the PI hybrid films decreases gradually with the increasing of the Al_2O_3 content as shown in Table 2. The hybrid film with 10 wt.% of Al_2O_3 has a CTE of 32.9 ppm/°C in the range of 50-300 °C, 12% lower than that of the pure PI film. As the Al_2O_3 content increased to 20%, CTE of the hybrid film further decreased to 31.6 ppm/°C. It is revealed that the CTE of the PI film could be reduced by incorporation of nano-sized Al_2O_3.

3.4. Dielectric strength and electrical aging

Both dielectric strength and electrical aging performance are the important factors for the polyimide film used as electrical insulation material, especially for high electric field and high temperature application. A phenomenon generally known as "corona" that could cause ionization in the insulating layer is recognized as the major reason for electric breakdown of an insulation material when the voltage stress reached a critical level. It was reported that the polyimide films with addition of some ultrafine inorganic additives showed good corona-resistance property [16].

Figure 4 shows the dielectric strength of the PI hybrid films with different Al_2O_3 content. It can be seen that the dielectric strength were slightly increased with the Al_2O_3 content increasing and then decreased gradually. The hybrid film with 2 wt.% of Al_2O_3 shows the dielectric strength of 199 MV/m, which is about 6% higher than that of pure PI film (188 MV/m). As the Al_2O_3 content increased to 20 wt.%, the dielectric strength of the hybrid film reduced to 159 MV/m, which is 20% lower than the hybrid film with 2 wt.% of Al_2O_3. It is suspected that the Al_2O_3 aggregates, which found at the polyimide films with a relative high Al_2O_3 content, might act as an impurity that cause some defects to deteriorate the dielectric strength.

Figure 5 shows the time to failure of PI hybrid films in electrical aging test, which determined by detecting the breakdown time of the films as a voltage of constant electric field applied. The PI hybrid films show improved electrical aging performance as compared with pure PI film. Especially, the hybrid PI film with 10 wt.% of Al_2O_3 exhibited a significant enhancement, the time to failure of the hybrid film with 10 wt.% of Al_2O_3 in electrical aging at 1 kV is 208 h, which is 3.4 times longer than that of pure PI film (61 h). We suppose that the improved electrical aging performance of PI hybrid film is related to the highly dispersion and adequate addition of Al_2O_3 particles in the matrix resin, which exhibited excellent effect to prevent the corona damage.

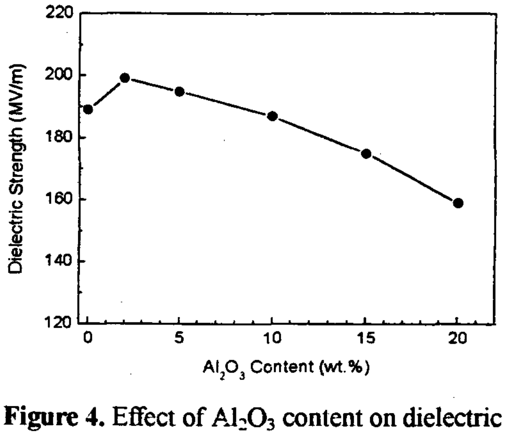


Figure 4. Effect of Al_2O_3 content on dielectric strength of Al_2O_3/PI hybrid films.

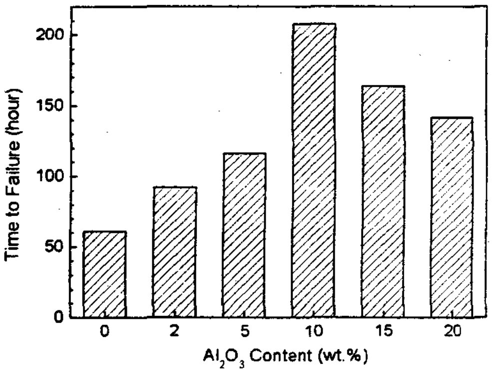


Figure 5. Time to failure of Al_2O_3/PI hybrid films in the electrical aging.

3.5. Morphology and surface composition

The surface morphology of pure PI film and PI hybrid film with 10 wt.% of Al_2O_3 content before and after electrical aging was investigated by SEM micrographs, which are shown in Figure 6. The pure PI film shows a very smooth surface before electrical aging (Figure 6a). However, after electrical aging, the crater-like structure on the surface of the pure PI film is clearly observed in the SEM micrograph (Figure 6b), suggesting the occurrence of electric breakdown. On the other hand, the hybrid film before electrical aging exhibits the surface with some of the filler grains covered by the matrix resin (Figure 6c). However, the hybrid film shows an interesting surface change after electrical aging. The fine grain-like structure with a broad size distribution is detected spreading on the surface of the hybrid film (Figure 6d), which is very different from the phenomenon observed for pure PI film. There is no crater-like structure observed on the surface of the hybrid film.

We suppose that the crater-like structure on the surface of pure PI film after electrical aging is derived from the partial discharge at the defective point of PI film, leading to melting followed by decomposition and final damage of the film [17]. In contrast, the fine grain-like structure on the surface of PI hybrid film after electrical aging might be related to Al_2O_3 particles in the hybrid film which exposed on the surface of the film in the course of electrical aging.

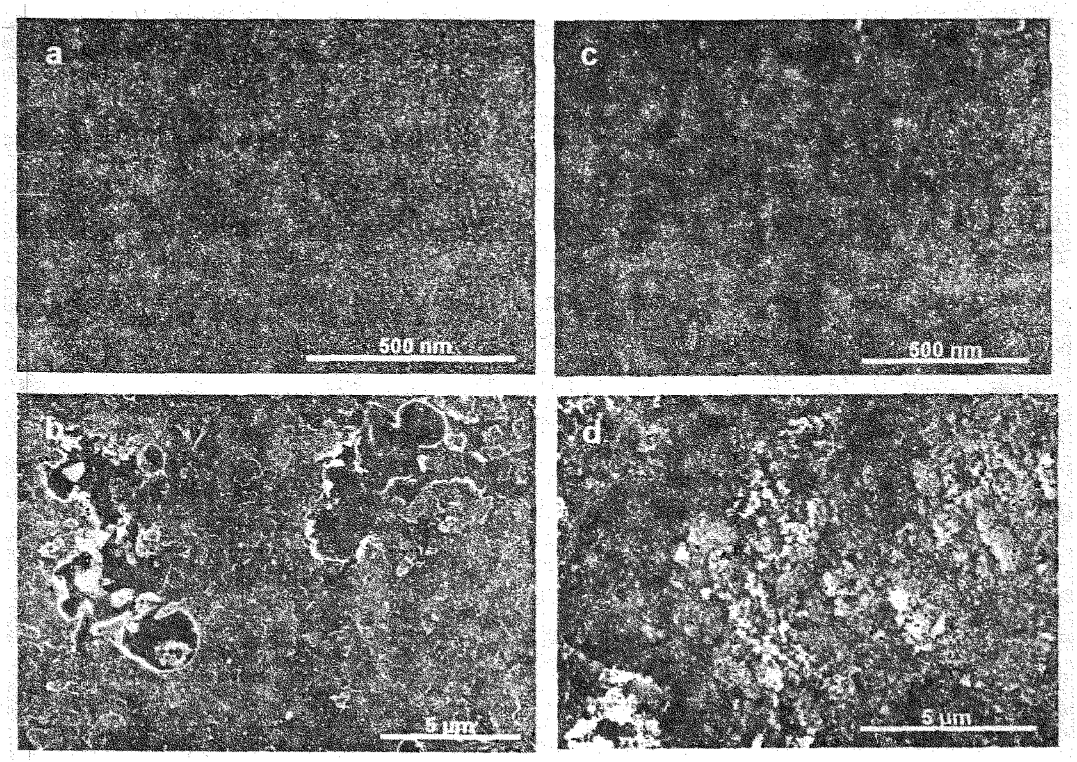


Figure 6. SEM micrographs of pure polyimide film before (a) and after (b) electrical aging as well as the Al_2O_3/PI hybrid film with 10 wt.% of Al_2O_3 before (c) and after (d) electrical aging.

The XPS analysis was carried out to obtain more information about the surface of PI film. The elemental surface composition of pure PI film and the hybrid film with 10 wt.% of Al_2O_3 determined by XPS is summarized in Table 3. For the pure PI film, only expected components of C, O and N was found, the concentration of them is 77.5, 15.9, and 6.6 at.% for the untreated film. The electrical aging caused an increase of O to 24.2% accompanied by an decrease of C and N to 70.8 and 5.0 at.%, respectively, revealing that some surface oxidation happened. In the case of PI hybrid film with 10 wt.% of Al_2O_3, Al was detected besides the components of C, O and N. The Al signal obviously stems from the alumina used as filler. As comparing the surface concentration of elements on the hybrid film before and after electrical aging, we found that the surface concentration of C and N obviously decreased after the hybrid film treated by electrical aging, meanwhile, the concentration of Al and O dramatically increased. It is proposed that the observed drastic increase of Al and O is essentially accounted for the laying bare of the filler in the course of electrical aging [18]. The XPS results confirmed the assumption derived from the SEM observation.

From the above SEM observation and XPS analysis we suggest that the enhanced electrical aging performance of PI hybrid films is attributed to the highly dispersion of Al_2O_3 particles in PI matrix. The nano-sized alumina additives with superior insulating qualities and high thermal conductivity cause the diffusion of partial discharge and dissipation of local dielectric heating as a constant voltage applied on the hybrid film, which result in the decomposition of PI matrix in a relative slow rate under the action of a homogeneous electric field and the final exposition of the Al_2O_3 particles on the film surface. Therefore, the corona damage could be prevented in some extent.

Table 3. Elemental surface composition of PI films before and after electrical aging determined by XPS.

Al_2O_3 Content (wt.%)	Electrical Aging	Surface Concentration of Elements (at.%)			
		C	O	N	Al
0	before	77.5	15.9	6.6	—
	after	70.8	24.2	5.0	—
10	before	72.7	21.8	4.2	1.3
	after	29.2	44.8	2.1	23.9

4. Conclusions

Nano-sized Al_2O_3/polyimide hybrid films with different Al_2O_3 content were prepared via in situ polymerization. The Al_2O_3 particles were successfully dispersed in the polyimide matrix by means of the ultrasonic treatment and the addition of coupling agent. The mechanical properties and thermal stability of the pure PI film can be improved by adequate addition of Al_2O_3. The PI hybrid films with 10 wt.% of Al_2O_3 content exhibited obviously enhanced electrical aging performance with the time to failure of 3.4 times longer than that of pure PI film, which is attributed to the nano-sized Al_2O_3 particles highly dispersed in the hybrid film.

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Al_2O_3/聚酰亚胺纳米杂化薄膜的制备性能研究

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摘 要 本研究以均苯四甲酸二酐（PMDA）和 4,4'-二胺基二苯醚(ODA)为单体，以 Al_2O_3 为添加材料，通过原位聚合法制备了一系列 Al_2O_3/聚酰亚胺纳米杂化薄膜。我们通过透射电镜（TEM）对 Al_2O_3 在薄膜中的分散状态进行了观察，结果发现 Al_2O_3 粒子均匀地分散在基体树脂中，甚至当 Al_2O_3 的添加量增加至 10%时，也没有发生粒子团聚。此外研究结果表明，在聚酰亚胺中添加适量的 Al_2O_3 粒子可以改善薄膜的力学性能和热性能，并降低基体的热膨胀系数。将 Al_2O_3 均匀分散于聚酰亚胺基体中，还可以明显改善薄膜的电老化性能。当 Al_2O_3 含量为 10%时，其电老化时间达 208 小时，为纯聚酰亚胺薄膜电老化时间的 3.4 倍。通过扫描电镜（SEM）对电老化前后纯膜及 Al_2O_3/聚酰亚胺纳米杂化薄膜（Al_2O_3 添加量为 10%）的表面状态进行观察，并结合从 X 射线光电能谱（XPS）得到的表面元素组成的结果，我们认为，在强电场的作用下，聚酰亚胺杂化薄膜中均匀分散的 Al_2O_3 粒子起到了扩散局部放电并分散介电热量的作用，在电老化过程中，基体树脂在均匀的电场作用下以相对缓慢的速度分解，并最终将 Al_2O_3 粒子暴露在表面，从而使薄膜的电老化性能得到改善。