Fabrication and Properties of Polyimide/Aluminum Oxide Composite Films via Different Alkali Etching and Ion Exchange Technique

Mingyu Zhang 1,2,3, *, Lizhu Liu 1, Chunqi Zhang 2
1Suzhou Vocational Institute of Industrial Technology, Suzhou, China
2Suzhou Taihu Electric Advanced Material Co.Ltd, Suzhou, China
3Harbin University of Science and Technology, Harbin, China

*Corresponding author e-mail: zmy_hlg@163.com

Abstract. The polyimide (PI)/aluminum oxide (Al₂O₃) composite films were prepared via alkali surface modification and ion exchange technique on flexible PI films. Firstly, the polyamide acid layers were formed on both surfaces of PI film through chemical surface modification in aqueous KOH and NaOH solution, respectively. Subsequently the ion exchange process was processed in AlCl₃ aqueous solution. After final thermal annealing in air, the aluminum ions which exchanged on both surfaces of PI film became continuous Al₂O₃ composite layers. The surface morphology, microstructures, thermal and electrical properties of the PI/Al₂O₃ composite films were tested by the scanning electron microscopy (SEM), fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), electric breakdown voltage and corona-resistant measurement. Results from SEM measuring revealed that the surfaces of composite films became much rougher with the increasing alkali treatment time. FT-IR spectrums showed that the treatments of alkali surface modification and ion exchange had no effect on molecular structure of polyimide. TGA results showed that the excellent thermal properties of the film are maintained. Electric breakdown voltage of composite films showed monotonically decreased with the increasing alkali treatment time. Corona-resistant test results showed that the best corona-resistant times of composite films which using NaOH and KOH modification were up to 22.6 minutes and 15.4 minutes, respectively.

1. Introduction
Polyimide, as an excellent engineering polymer material, has widely used in many fields, such as mechanical and chemical industry, household appliances, electronic and electrical industry, microelectronics, information industry, military industry, atomic energy industry, and aerospace industry, etc. With the progress of society and the further development of science and technology, polyimide shows more and more disadvantages in the field of special performance requirements. For example, it does not always provide reliable and long-lasting protection against high-voltage corona attacks. Polyimide composite materials have received much attention because of the dramatic improvements than their pristine state in mechanical properties, thermal stabilities and electric breakdown strength by introducing small fraction inorganic compounds [1-6]. Among these inorganic
particles, nano-alumina (Al₂O₃) is often chosen as filler to improve the insulation properties in polymer materials. Some researchers have studied the nano-sized polyimide/Al₂O₃ composite films and found that the thermal properties and electric breakdown strength of polyimide could be improved by the dispersed alumina particles in matrix. The polymer/Al₂O₃ oxide composites have been traditionally prepared by mixing metal oxide nanoparticles with polymer solution and followed curing of the material or sputtering metal oxide on polymer substrate. However, these processes often lead to inhomogeneous dispersion and uncontrollable size distribution of the metal oxide particles. Kim and co-workers [7-9] developed a new method to fabricate Al₂O₃ films in the surface layers of PI film by dip-coating technology. However, the thickness and distribution of the Al₂O₃ and the composite film thickness are difficult to control.

Recently, several groups reported that the surface metallized PI films could be prepared through the ion exchange self-metallization technique. This method mainly relies on a simple alkali treatment-based surface modification of PI films to form carboxylic acid groups (i.e., carboxyl groups) in the modified layer through imide ring-cleavage reactions and subsequent incorporation of metal ions via ion-exchange reaction. Final thermal reaction of metal ions leads to the formation of metal oxide embedded in PI film surface layers. This method allows control of the morphologies and properties of the composite films by adjusting the initial alkali treatment (time, concentration, and temperature), subsequent ion-exchange conditions (time, concentration, and temperature). In this article, we reported on preparing PI/Al₂O₃ composite films via ion exchange method. The effect of two different alkanes (KOH, NaOH) and treatment time on the morphologies and properties of the PI/Al₂O₃ composite films were investigated.

2. Experiment

2.1. Materials
Pyromellitic dianhydrides oxidianiline (PMDA/ODA) PI films with thickness of 25μm from a factory were cleaned in distilled water at room temperature for 10 min under ultrasonication prior to use. Aluminium chloride hexahydrate (AlCl₃•6H₂O) (>98.5%) with analytical quality was obtained from Tianjin Tianli Chemical Reagent Co., Ltd. Sodium hydroxide (NaOH) and potassium hydroxide (KOH) with analytical quality were purchased from Tianjin Chemicals Factory and Tianjin Yaohua Chemicals Reagent Company, respectively.

2.2. Preparation of Al₂O₃/ PI composite films
PI films were hydrolyzed in 5M/L⁻¹ aqueous NaOH and KOH solution respectively for 1, 2, 3, 4 and 5 hours, respectively, at room temperature, and followed by washing with copious amount of distilled water. The aluminum ions were incorporated by immersing the surface modified PI films into 0.1M/L⁻¹ aqueous AlCl₃ solution for 24 h at room temperature. After being rinsed with distilled water and dried in ambient air, the films were thermally cured under tension in a forced oven. Then the films place on a glass substrate and dried at 80° C for 1 h, 100° C for 1h, 140° C for 1 h, 220° C for 2 h, 300° C for 1 h, 350° C for 2 h, respectively. The possible and ideal chemistry for the formation of Al₂O₃/PI composite films have been shown in Scheme 1. According to references report[8-10], sodium-polycarboxylate salt (sodium polyamate) and potassium-polycarboxylate salt would be formed in situ when PI films were immersed into the aqueous NaOH and KOH solution because of the hydrolytic cleavage of the imide groups contained in the repeating unit. To fabricate continuous Al₂O₃ layers, it is important to ensure enough aluminum ions loading, which mainly depends on the modified time of PI films and thus we have chosen enough time (24 h) to ensure the full implementation of ion exchange. Subsequent process made Aluminum ions convert to Al₂O₃ during final thermal treatment in ambient air, resulting in a thin PI layer containing Al₂O₃ nanoparticles. Besides, the nanocomposite film could maintain the excellent mechanical properties of original PI film for its inside is intact during the whole procedure [11].
2.3. Characterization of composite films

Transmission FTIR spectra were obtained using a System 2000 spectrometer from Perkin-Elmer. The surface morphologies of the composite films were characterized with a scanning electron microscopy (SEM) (FEI Philips Quanta 200) at an accelerating voltage of 20 kV after samples were coated with gold alloy. Thermogravimetric analyses (TGA) (Perkin-Elmer Pyris 6) were performed at a heating rate of 20 °C/min under a nitrogen atmosphere. The electrical breakdown strength of the composite films were measured with a 1kV/s loading rate of voltage, and the area of the copper electrode used was about 28.26mm². The corona-resistance of composite films was tested by corona-resistance equipment. The test parameters are chosen as below: the waveform is bipolar square, wave pulse voltage is 2 kV peak to peak, and frequency is 20 kHz, and duty cycle is 50%.

3. Results and Discussions

3.1. FTIR spectra of composite film

In order to study the influence of the alkali modification and ion exchange on the molecular structure of polyimide, we used IR spectroscopy as the principal tool to characterize the composite film. In fact, this technique is well suited for studying thin films and the functional group involved in the reaction. IR spectra of PI films were show in Fig. 1. Curve (a) was the original pure PI films, the wavenumbers of 1780 and 1720cm⁻¹ were assigned to C=O antisymmetric and symmetric swing vibrations of polyimide, 1370cm⁻¹ to imide rings C-N-C stretching vibration. Curve (b) was the PI film after using KOH solution etching treatment for 30 minutes. In curve (b), the wavenumbers of 1780, 1720 and 1370cm⁻¹ became weaker even disappear compared with curve(a) that indicated imide rings were cleavage to –COOK and -NH in alkali solution. Curve (c) was the IR of composite film, which using KOH solution etching treatment for 30 minutes and then through Al³⁺ ion exchange for 24 h and thermal treatment at 350°C for 2 h. We can saw from the curve (c) that the wavenumbers of 1780, 1720, 1370cm⁻¹ are all strong.
again when compared with curve (b) and curve (a). Those results indicated that imide rings were closed again and alkali surface modification and ion exchange have no effect on molecular structure of polyimide.

![IR spectra of films: (a) original pure PI film; (b) KOH treatment; (c) composite film.](image)

**Figure 1.** IR spectra of films: (a) original pure PI film; (b) KOH treatment; (c) composite film.

3.2. **SEM Characterization**

In order to investigate the surfaces of composite films, the morphology of the composite films was studied using scanning electron microscopy (SEM). Fig. 2 showed the morphologies of the surface of original PI film and composite films (using KOH treatment for 1, 3, and 5 h). As can be observed from the SEM photos, after being treated in 5M aqueous KOH solution for 1 h, 3 h, and 5 h, the roughness of the surface of composite films were more and more serious with increasing the alkali treatment time. The SEM photos of the composite films which using NaOH treatment has similar change, so we don’t list it at here. However, further prolonging the alkali treatment time is not recommended because of the alkali etching effect that will destroy the mechanical property [12, 13]. According to our observation, visible fissure has appeared on the surface of PI films after 5h alkali treatment. Moreover, the surfaces of composite films obtained at different KOH treatment time are rougher than that of the composite film after NaOH treatment at same etching times that indicated the surface etching effect of the PI film in aqueous KOH solution are much serious than that in aqueous NaOH solution. According to other research, it was hard to distinguish nanoparticles from the surfaces of composite films because most of the inorganic particles with very small size are homogeneously dispersed in the bulk of the alkali treated layers.

![SEM images of original PI(a) and composite PI films( KOH treatment time b.1 h, c.3 h,d.5 h).](image)

**Figure 2.** SEM images of original PI(a) and composite PI films( KOH treatment time b.1 h, c.3 h,d.5 h).
3.3. TGA Analysis

Fig. 3 illustrated the TGA profiles of the original PI and composite films from 300°C to 800°C in nitrogen atmosphere. Fig 3a) is using KOH at different treatment times and b) is using NaOH at different treatment times, respectively. The original PI and composite films all exhibit one-step decomposition. The thermal decomposition temperatures of the films are listed in Table 1. Compare with original PI film, results of the TGA indicated that all the thermal stability of the composite films as good as the original PI film. The TGA curves from 450°C to 650°C of the composite films decreased a little with the increase of time compare with original PI film may be due to etching effect of alkali solutions. The etching effect of KOH was more obvious than NaOH from Fig 3a) with Fig 3b). The possible reason was PI molecular chain was cut off more easily at KOH etching processes than NaOH.

**Table 1.** The thermal decomposition temperature of films.

| Sample          | \( T_{5\%}/^\circ\text{C} \) | \( T_{10\%}/^\circ\text{C} \) | \( T_{30\%}/^\circ\text{C} \) |
|-----------------|-------------------------------|-------------------------------|-------------------------------|
| Original PI     | 590                           | 606                           | 663                           |
| KOH treat 1h    | 570                           | 594                           | 656                           |
| KOH treat 3h    | 527                           | 573                           | 655                           |
| KOH treat 5h    | 523                           | 568                           | 657                           |
| NaOH treat 1h   | 589                           | 605                           | 663                           |
| NaOH treat 3h   | 590                           | 607                           | 670                           |
| NaOH treat 5h   | 569                           | 594                           | 655                           |

**Figure 3.** Thermogravimetric curves of original PI and composite films (a, using KOH treatment; b, using NaOH treatment).
3.4. Electrical breakdown strength of composite films
Being a key parameter, the electrical breakdown voltage 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. When a small amount of Al$_2$O$_3$ particles was introduced to the PI film, the inorganic particles could be dispersed uniformly in the PI matrix, and form an ordered organic–inorganic–organic three phase structure. This structure can make the polymer molecules connect more closely so that the space charge can move between molecules, reducing the possibility of capturing charge by trapping. In addition, the agglomeration of interior space free charge can be avoided, resulting in a uniform internal electric field. Furthermore, the interface can also help capture some of the free space charge. Therefore, Al$_2$O$_3$ particles can enhance effectively the PI electric breakdown performance of the PI film. Fig.4 showed the average electric breakdown voltage of the composite films with different alkali treatment time. The average electric breakdown voltage monotonically decreased with increasing treatment time. The main reason is quite likely alkali solutions cut off the chain of polyimide and lead to the decrease of polymerization degree and destroyed the surface of polyimide. Because KOH solutions have more strong destructive effect than NaOH at same etching times, the electric breakdown voltage of composite films using KOH treatment were reduce faster than NaOH.

![Figure 4. Electrical breakdown strength of composite films.](image)

3.5. Corona-resistance of composite films
The corona-resistance time is an important parameter for selecting appropriate electrical insulation materials to avoid short circuit. Fig.5 displayed the corona-resistance times of composite films using alkali etching for different time at room temperature. It could be observed that the corona-resistance of composite films after KOH treatment was decrease from 22.6 minutes down to 9.5 minutes with increase KOH treatment time. The corona-resistance times of composite films that using NaOH treatment exhibited first increased then decreased. The optimum corona-resistance time was 15.4 minutes which using NaOH treatment for 4 h. The corona-resistance time of original PI was 4.4min, which was shorter than all of the composite films. The best corona-resistance times of composite film which using KOH treated 1 h improved five times compare with original PI.
Fig. 5. Effect of treatment time on the corona-resistance of composite films.

Fig. 6 showed the corona degradation mechanism of pure film (Fig. 6a) and composite film (Fig. 6b). The alumina would not be destroyed because of its stronger bond energy and higher melting point and the Al₂O₃ particles concentrating in the surface layers has higher heat conductivity, which can dissipate the heat produced by corona, and thus reduces the danger of thermal breakdown. Meanwhile, corona will concentrate on the Al₂O₃ on the surface of nanocomposite specimen due to the different in permittivity, but the Al₂O₃ are more resistant against corona than the PI matrix and has good ability to tolerate the corrosion of the corona products. The original film was continuously damaged by corona discharge, which cause the early breakdown of film by corona aging as showed in Fig. 6a. While composite film which included alumina on the surface layers that can protect the internal matrix reduced the damage of corona on polyimide greatly and improved corona resistance time as showed in Fig. 6b.

Fig. 6. Diagram of corona damage process (a. original film b. composite film).

4. Conclusion

PI/Al₂O₃ composite films were successfully prepared by alkali surface modification and ion exchange method. SEM showed the roughness of the surface of composite films was more and more serious with increasing the alkali treatment time. TGA results showed the thermal stability of composite films was excellent as original film. Electric breakdown voltage of composite monotonically decreased with the increasing alkali treatment time. The best corona-resistance times of composite film which using KOH treated 1 hour improved five times compare with original PI from 4.4 minutes up to 22.6 minutes. The method of obtaining composite films in this paper is worth consideration, but additional research will be needed in order for obtaining composite films with tailored properties.
Acknowledgments
This work was financially supported by the Jiangsu Planned Projects for Postdoctoral Research Funds (2019K006), the Project of Philosophy and Social Science Research in Colleges and Universities in Jiangsu Province (2019SJA1375), the National Natural Science Foundation of China(50137010, 51177030), the Natural Science Major Foundation of Heilongjiang Province of China(ZD201004), the Natural Science Foundation of Heilongjiang Province (E200907), the key Science and Technology project of Heilongjiang Provincal Education Department (12511z007) and the Science and Technology project of Heilongjiang Provincial Education Department (12511074).

References
[1] Yi-He Zhang, Yan Li, Shao-Yun Fu, John H. Xin, Walid A. Daoud, et al. Synthesis and cryogenic properties of polyimide-silica hybrid films by sol-gel process [J]. Polymer, 46, 2005, 8373-8378.
[2] Cheol Park, Joseph G. Smith Jr., John W. Connell, Sharon E. Lowther, Dennis C. Working, et al. Polyimide/silica hybrid-clay nanocomposites [J]. Polymer, 46, 2005, 9694-9701.
[3] Shun-He Zhong, Chuan-Feng Li, and Xiu-Fen Xiao. Preparation and characterization of polyimide-silica hybrid membranes on kieselguhr-mullite supports [J]. Journal of Membrane Science, 199, 2002, 53-58.
[4] Xiu-yong Shang, Zi-kang Zhu, Jie Yin, and Xiao-dong Ma. Compatibility of soluble polyimide/silica hybrids induced by a coupling agent [J]. Chemistry of Materials, 2002, 14, 71-77.
[5] Zheng-dao Wang, Jian-Jun Lu, Y. Li, S.Y. Fu, Shao-qing Jiang et al. Studies on thermal and mechanical properties of PI/SiO2 nanocomposite films at low temperature [J]. Composites Part A- Applied Science and Manufacturing, 2005, 1-6.
[6] Mei-Hui Tsai, Wha-Tzong Whang. Low dielectric polyimide/poly (silsesquioxane)-like nanocomposite material [J]. Polymer, 42, 2001, 4197-4207.
[7] Shuxiang Mu, Dezhen Wu, Yue Wang, Zhanpeng Wu, Xiaoping Yang, and Wantai Yang. Fabrication of Nickel Oxide Nanocomposite Layer on a Flexible Polyimide Substrate via Ion Exchange Technique [J]. Applied Materials and Interfaces, 2010, 2, 111-118.
[8] Zhanpeng Wu, Dezhen Wu, Shengli Qi, Teng Zhang, and Riguang Jin. Preparation of surface conductive and highly reflective silvered polyimide films by surface modification and in situ self-metallization technique [J]. Thin Solid Films, 2005, 493: 179-184.
[9] Zhanpeng Wu, Dezhen Wu, WantaiYang, and Riguang Jin. Preparation of highly reflective and conductive metalized polyimide films through surface modification: processing, morphology and properties [J]. Journal of Materials Chemistry, 2006, 16(3): 310-316.
[10] Mingyu Z., Lizhu L., Ling W., et al. Fabrication and Properties of Polyimide Film with Aluminum Oxide Thin Films via Sol-Gel Method [J]. Proceedings of the Csee, 2014, 34(12):1965-1971.
[11] Yanqing Wang, Jun Ding, Ning Li, et al. Conductive silver coatings with ultra-low silver consumption on polyimide film via a mild surface ion exchange self-metallization method [J]. Journal of Materials Chemistry C, 2017, 5(40).
[12] Shuxiang Mu, Dezhen Wu, Yue Wang, et al. Fabrication of Nickel Oxide Nanocomposite Layer on a Flexible Polyimide Substrate via Ion Exchange Technique [J]. Applied Materials and Interfaces, 2010, 2(1):111-118.
[13] Shuxiang Mu, Zhanpeng Wu, Yue Wang, et al. Formation and characterization of cobalt oxide layers on polyimide films via surface modification and ion-exchange technique [J]. Thin Solid Films, 2010, 518(15):4175-4182.