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Preparation and Thermal Properties of Silicon-containing Polyimide Composite Films

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Aromatic polyimide is a kind of polymer material with high temperature resistance, low temperature resistance, radiation resistance, excellent chemical stability, excellent electrical properties and good mechanical strength. It has been widely used in aerospace, electrical and electronic fields. At present, the synthesis, properties and application of polyimide containing silicon is one of the hot spots in the research field of polyimide. The processing property of polyimide can be greatly improved by introducing silicon group or polysiloxane segment into the main chain structure. And it has been given a good solubility, permeability, impact resistance, UV resistance and anti-degradation in oxygen rich environment. The introduction of siloxane chain segments or silicon containing groups in polyimide framework can enhance the adhesion between polyimide and inorganic materials, including the adhesion of metal materials and other substrates. A variety of polyimide hybrid materials can be prepared by the excellent bonding properties. A series of polyimide / silicon containing polyimide / $BaTiO_3$ nanocomposite films were prepared and their structures and properties were studied in this paper. In addition, the preparation, structure and properties of polyimide / mesoporous silica composite films were studied. Silicon containing polyimide/silane mesoporous silica composite films have low infrared emissivity compared with bulk polyimide. Under the same content of mesoporous silica, the composite films prepared by copolymerization have lower infrared emissivity. Moreover, the infrared emissivity decreases with the increase of the content of silica. In short, silicon containing polyimides and their composite films with excellent performance differ from other traditional polyimides, and it has broad application prospects in the technological field of aerospace, electrical and electronic, gas separation, absorbing material preparation.

1. Introduction

Aromatic polyimide is a kind of polymer material with high temperature resistance, low temperature resistance, radiation resistance, excellent chemical stability, excellent electrical properties and good mechanical strength. It has been widely used in aerospace, electrical and electronic fields. However, the application of polyimide is limited due to the difficulty of processing and the insoluble in most organic solvents. At the same time, people have made unremitting efforts to maintain the comprehensive performance and overcome the difficulty of polyimide processing, which includes the introduction of flexible, asymmetric, and side group links in the polyimide backbone structure (Wozniak et al., 2016). Polysiloxane has the characteristics of low solubility, low water absorption, low dielectric constant and good adhesion. Therefore, the polysiloxane segment is introduced into the polyimide backbone structure, or the polyimide can be synthesized by using a silicon-containing dianhydride and an amine monomer in the presence of silicon dioxide (He et al., 2016; Yekeen et al., 2017; Aissa et al., 2015; Zhang and Chen, 2015). The processability of polyimide can be improved greatly. It has been proved to be of good solubility, hydrophobicity, air permeability, impact resistance, UV resistance and anti-degradation in oxygen rich environment (Zhang et al., 2016).

The introduction of siloxane chain segments or silicon containing groups in polyimide framework can enhance the adhesion between polyimide and inorganic materials, including the adhesion of metal materials and other substrates. A variety of polyimide hybrid materials can be prepared by the excellent bonding properties. Nano hybrid materials are the fourth generation materials after single component materials, composite materials and functionally gradient materials (Du et al., 2015). The nanoparticles belong to the transition region between the atomic group and the macroscopic object, which is composed of a small number of atoms or molecules

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composed of atoms or molecules with the scale of 1~100nm. Because of the small size of the nanoparticles and the shell structure, the nanomaterials have four kinds of effects, such as small size effect, surface and interface effect, quantum size effect and macroscopic quantum tunnelling effect (Balasubramanian, et al., 2016). Therefore, nanomaterials exhibit some extraordinary phenomena compared with the conventional materials, such as photoelectric characteristics, photoelectric catalytic properties, photoelectric conversion characteristics, electrical properties and magnetic properties. Polyimide hybrid materials has become one of the hot spots in the technological field.

The high thermal stability and high glass transition temperature (T_g) of polyimide are helpful to stabilize the dispersed particles with nanometer size, and make it impossible to together. The combination of polymers and inorganic materials at the nanoscale and molecular level will be the best embodiment of their respective advantages. There are many kinds of polyimide composites. In this chapter, the synthesis and properties of silicon containing polyimide and the preparation and application of polyimide / inorganic composites are mainly introduced.

2. Methods

The properties of composites are not only related to the properties of each component, but also closely related to the morphology and interfacial properties of the composites. A variety of common inorganic - organic complexes have been studied for many years. In recent years, inorganic - organic materials have attracted much attention in the fields of scientific research and practical application. Inorganic - organic dielectric materials composed of soft and hard materials provide many useful functional and mechanical properties of the integration. In order to effectively adjust and control the structure and properties of inorganic organic materials, it is very important to adjust and control the physical and chemical bonds between inorganic components and organic components. For the nano hole assembly system, the materials with nano space can be divided into 3 categories according to their size. The pore size less than 2 nm is called the microporous material. The pore size greater than 50 nm is called the macroporous material. Pore size between 2 nm and 50 nm is called mesoporous materials (Maclachlan et al., 2016).

In this chapter, a variety of silicon containing polyimide / mesoporous silica composite thin films were prepared by using silane treated mesoporous silica, and the structure and properties of the films were characterized.

2.1 Preparation of polyimide / mesoporous silica composite films

Polyimide / mesoporous silica composite films were prepared by two methods: Firstly, under the protection of nitrogen flow, the 10% (wt/wt) N, N-two methyl acetamide solvent was prepared by adding equimolar dianhydride and diamine. The solution was stirred at room temperature for 24 hours to obtain yellow polyamide acid viscous liquid. Then, the suspension of the mesoporous silica in the DMAc solvent was added to the solution of 5% polyamic acid, Translucent liquid can be obtained by strong mechanical stirring. Then the liquid was poured on the clean glass plate at 100 degrees C and 150 degrees C vacuum drying for 1 hours, respectively. Finally, under the forced air flow, the solution was heated at 200 °C for about 1 hours, and then heated for 1 hours at a temperature of 280 °C. It was transformed into polyimide/mesoporous silica composite membrane. Secondly, under the protection of nitrogen, solution containing a certain concentration of mesoporous silica was prepared by adding a certain amount of silane mesoporous silica and equimolar dianhydride and diamine into N, N- two methyl acetamide solvent. The solution was stirred at room temperature for 24 h to obtain yellow polyamide/mesoporous silica. Then the viscous liquid is poured on the clean glass board at 100 °C and 150 °C vacuum drying for 1 hours, respectively. Finally, under the forced air flow, the solution was heated at 200 °C for about 1 hours, and then heated for 1 hour at a temperature of 280 °C. It is transformed into polyimide / mesoporous silica composite membrane.

2.2 Characterization of polyimide / mesoporous silica composite films

The crystalline structure of mesoporous silica and silane mesoporous silica was determined by SHIMADZU XD-3A X- ray diffractometer (XRD). The infrared spectra of the mesoporous silica were determined by Nicolet Magna-IR 750 infrared spectrometer. The morphology of the mesoporous silica was observed on the surface of the particles by LEO 1530VP scanning electron microscope.

Reflection infrared spectroscopy of composite film type 670 Fourier transform infrared spectrometer was determined by Nicolet NEXUS. The crystal structure of the composite film was determined by SHIMADZU XD-3A X- ray diffractometer (XRD). The observation of the cross section of the composite film is that the thin film samples with a certain thickness are dipped in liquid nitrogen. The gold content of the section was measured by LEO 1530VP scanning electron microscope. The effect of nano barium titanate on the polyimide molecules in the composite films was measured by VG ESCALAB-MK photoelectron spectrometer under high vacuum conditions (Liu, et al., 2015). Magnesium anode X ray source with monochromator (Mg Kα) was used. All the binding energies of C peak were used as internal standard to correct the charge effect. The element distribution of the composite thin films was measured by OXFORD INSTRUMENTS INCA x-sight energy dispersive X- ray spectrometer (EDX). The glass transition temperature was measured by TA instruments Q10 differential scanning calorimeter, and the heating rate was 10 °C/min. The thermal stability was measured by TA instruments SDT Q600 thermogravimetric analyzer, and the heating rate was 20 °C/min. The dynamic viscoelastic properties of the composite films were measured by Rheometric Scientific DMTA-V dynamic mechanical thermal analyzer (Joshi et al., 2015). The heating rate was 3 °C /min, and the test frequency was 1Hz. The infrared emission spectra of the composite films were measured by Nicolet Magna-IR 750 infrared spectrometer with infrared emission accessories.

3. Results and discussion

3.1 Silicon-containing polyimide composite film

Silicon containing polyimides were prepared by two methods. The composite films containing 1% and 10% mesoporous silica prepared by the synthesis of mesoporous silica and polyamide acid were named as PI-1-m and PI-10-m respectively. The mesoporous silica composite films containing 1% and 10% mesoporous silica prepared by copolymerization of mesoporous silica with diamine and dianhydride were named as PI-1-c and PI-10-c, respectively.

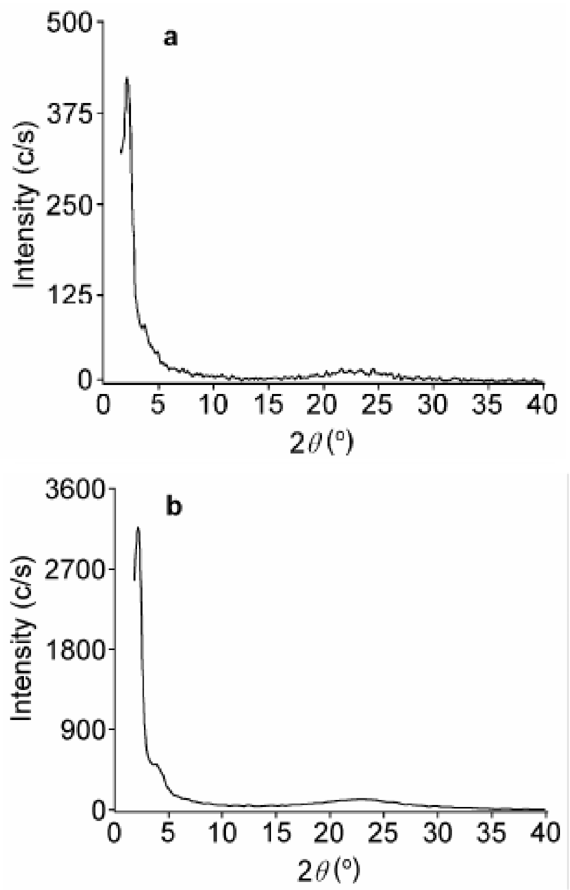

Figure 1: XRD spectra of mesoporous silica and silane mesoporous silica

3.2 Thermal properties of silicon containing polyimide composite films

The glass transition temperatures of bulk polyimide and composite films were measured by differential scanning calorimetry (DSC). Figure 3 is the DSC curve of SIDA-pBAPS polyimide composite film. It can be seen from the figure that the glass transition temperature of the composite films prepared by different methods is different from that of the silica. Specific glass transition temperatures are listed in Table 1. The glass transition temperature of the composite films prepared by direct blending increases with the raise of the silica content. For the composite films prepared by the copolymerization method, the glass transition temperature of the composite film is 6 °C higher than that of the bulk polyimide film with 1% mesoporous silica content. The glass transition temperature of the composite films decreased with the increase of the content of the mesoporous silica.

The thermal stability of bulk polyimide and composite films were measured by thermogravimetric analyzer in nitrogen or air. The heating rate is 20 °C/min. It takes the temperature of 5% weight loss as the thermal decomposition temperature of polyimide (T_{d5}). The T_{d5} of bulk polyimide and composite films are listed in table 1. For direct blend composite films, either in air or in nitrogen, compared with bulk polyimide composite films, the thermal decomposition temperature of the composite films increased with the raise of the silica content, and then it decreased. For the composite films prepared by copolymerization, the thermal decomposition temperature of the composite films is higher than that of the bulk polyimide in air and nitrogen. The change of the content of silicon dioxide in the composite film has little effect on the thermal decomposition temperature of the composite film.

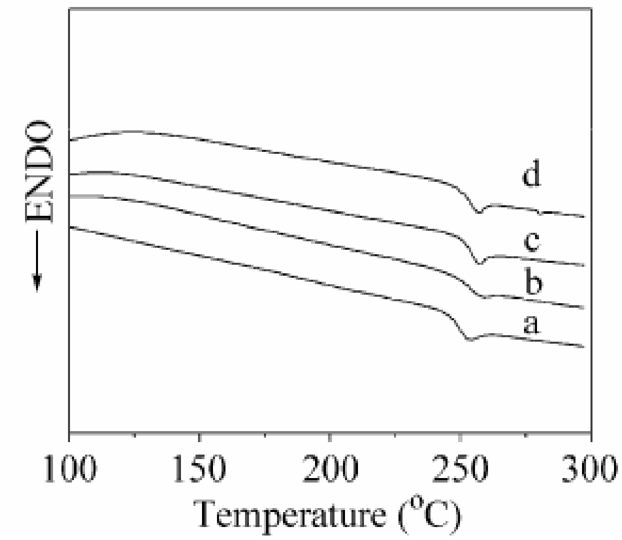

Figure 2: DSC curves of composite films

Table 1: Thermal properties of composite thin films (PI-0 is the bulk polyimide)

Sample number	T_g	T_{d5}	
	°C	In air (°C)	In nitrogen (°C)
PI-0	248	501	522
PI-1-m	250	504	525
PI-10-m	253	498	518
PI-1-c	254	510	528
PI-10-c	253	510	528

3.3 Dynamic viscoelastic properties of Polyimide

Dynamic viscoelastic properties of PI-SIDA/pBAPS and PI-SIDA/mBAPS polyimide films were measured by dynamic mechanical thermal analyzer. The determination was carried out in air, and the measured frequency and heating rate were 1 Hz and 3/min. The dynamic viscoelastic spectrum of two kinds of polyimide was shown in Figure 3. The relationship between the storage modulus and the temperature above the glass transition temperature showed the typical characteristics of the linear polyimide. Below the glass transition temperature, the storage modulus is in the same order of magnitude as that of the conventional polyimide. The glass transition temperature was determined by DMTA (a transition peak temperature as the glass transition temperature T_g).

The P transition peak temperature T and its internal friction values at T_β and T_g are listed in Table 2. It can be seen from the table that the glass transition temperature of PI-SIDA/mBAPS polyimide is basically the same as that measured under static and dynamic conditions. The glass transition temperature measured by PI-SIDA/pBAPS in the dynamic state was 10 lower than that under static condition. The significant difference of the glass transition temperature of the polyimide under dynamic and static conditions may be affected by its structure. The value of tanδ at T_g is a measure of the energy absorption properties of materials, which is related to the viscoelastic properties of materials. The tanδ value of polyimide at T_β is greater than that of PI-SIDA/pBAPS polyimide, which indicates that PI-SIDA/mBAPS has better flexibility than PI-SIDA/pBAPS. Compared with PI-SIDA/pBAPS polyimide, PI-SIDA/mBAPS polyimide exhibits higher mechanical internal friction and slightly wider P relaxation range in the whole p relaxation region of PI-SIDA/mBAPS. At the same time, the mechanical internal friction peak of PI-SIDA/mBAPS polyimide in P relaxation region is slightly higher than that of PI-SIDA/pBAPS polyimide. It is shown that there exists a high energy barrier in the PI-SIDA/pBAPS polyimide, which limits the rotation of the local bond and the motion of the molecular chain.

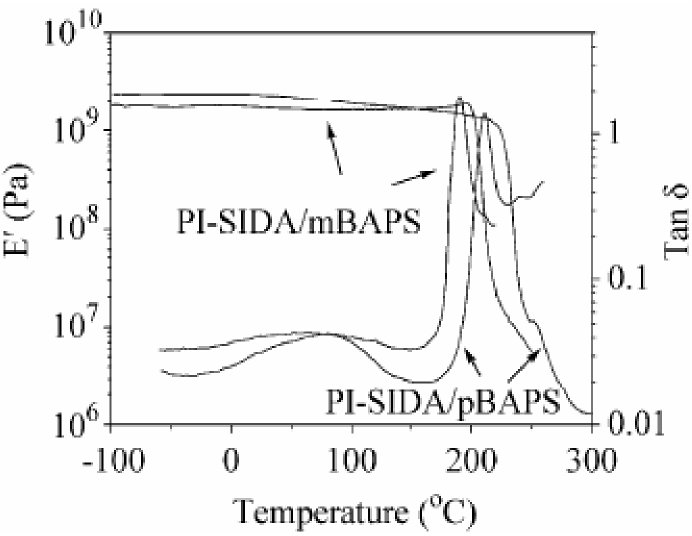

Figure 3: Dynamic viscoelastic spectra of polyimide films

Table 2: Dynamic viscoelastic properties of Polyimide (1 is determined by DSC, 2 is determined by DMTA)

Sample number	T_g^1	T_g^2 (α)		T_β^1	
	(°C)	(°C)	tanδ	(°C)	tanδ
PI-SIDA/pBAPS	248	238	1.485	69	0.042
PI-SIDA/mBAPS	212	212	1.837	56	0.043

3.4 The results

Mesoporous silica was prepared by sol-gel method using tetraethyl orthosilicate as raw material. After being treated with silica, mesoporous silica has been transformed into a silica mesoporous silica. Two groups of silicon containing polyimide composite films were prepared by direct blending and copolymerization. The following conclusions are obtained through the determination of structure and properties:

(1) The polyamide acid in the composite film was completely transformed into polyimide under the condition of thermal imidization. In the process of thin film preparation, the mesoporous silica is separated from polyimide to form a banded aggregate. The regularity of the silylation of mesoporous silica aggregates in the composite films prepared by copolymerization is lower than that of the mesoporous silica aggregates prepared by blending method.

(2) The glass transition temperature of the composite film is higher than the glass transition temperature of the bulk polyimide, but the thermal stability is different with the preparation method.

(3) The addition of silane mesoporous silica in the polyimide matrix results in a decrease of the mechanical internal friction peak at the T_g with the increase of the content of silica. Silane mesoporous silica content has a little effect on the peak temperature of P transformation and the mechanical internal friction value of T_0 composite films prepared by the copolymerization method. However, it has a large effect on P transition peak temperature and mechanical internal friction value of T_0 composite films prepared by blending method.

(4) The silicon containing polyimide composite film has low infrared emissivity compared with the bulk polyimide. Under the condition of the same content of mesoporous silica, the composite films prepared by the copolymerization method have lower infrared emissivity.

4. Conclusions

In this paper, a series of two methyl silane monomers were synthesized, and a series of polyimide films were prepared by the reaction of aromatic amines with various aromatic amines. On the basis of this, a series of silicon containing polyimide composite films with different dielectric constant and infrared emissivity were synthesized. The relationship between structure and properties was studied in detail by means of infrared spectroscopy and nuclear magnetic resonance spectrometer. The glass transition temperature (T_g) of polyimide composite film is higher than that of the corresponding bulk glass transition temperature. The internal friction values of T_β decrease with the increase of the content of barium titanate in the composite film. Therefore, the addition of barium titanate nanoparticles into the polyimide matrix will increase the rigidity of the composites and reduce the flexibility of the composites. The measurement of the dielectric properties shows that the variation of dipole orientation in polyimide composite films is not up to the electric field frequency. The relative dielectric constant of polyimide composite films decreased slowly with the increase of frequency. At 1MHz, the dielectric loss of polyimide composite films is lower than that of the corresponding bulk polyimide. The relative dielectric constant of the composite films decreased with the increase of temperature and then increased.

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