Microstructure and Stability of Polymer Nanocomposite

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ABSTRACT

The SiO_2 and Al_2O_3 nanoparticles hybrid Polyimide (PI) films were prepared by Sol-Gel. The microstructure, nanoparticle distribution and stability in the hybrid films were studied by SEM and TEM. The results shown that there were SiO_2 and Al_2O_3 nanoparticles dispersing homogeneously in the inorganic hybrid PI films and they were stable usually, even if they were irradiated by electron beam at 20 keV. The particle sizes were about 5 ~ 40 nm, while SiO_2 was smaller than Al_2O_3. The results of TEM observation shown that the clusters of SiO_2 with amorphous structure in hybrid PI film irradiated by high energy electron beam of 200 keV for 2s can be easily broken up. However, some grains of Al_2O_3 with the crystalline structure were rather stable and PI structure did not any change under the condition of high energy irradiation.

Keywords: sol-gel, SiO_2 and Al_2O_3 nanoparticle, hybrid PI films, microstructure, stability

1 INTRODUCTION

Recently preliminary work has been already done to investigate the capability of nanocomposite polymeric materials for electrical insulation to show improved electrical performances with respect to the corresponding conventional materials, possibly filled by nanoparticles [1-4]. Small particle nanocomposites are more important as functional materials than structural materials. The development of nanocomposites represents a very attractive route to upgrade and diversify properties of polymers without changing polymer compositions and processing.

Polyimide (PI), at temperature of less than 300^{o}C, possesses excellent mechanical, dielectric, thermal and radiation-resistant properties, it has been widely applied in electrical equipments, integrated circuits and semiconductor devices. But polyimide is not corona - resistance and it can not be applied to inverter - fed motor insulation suffered strong corona corrosion. By mixing inorganic materials, especially, nanopaticles having huge specific surface in PI, its corona - resistance can be greatly raised [5-6]. The nanocomposite technology would improve the characteristics of dielectrics and electrical insulation. Shape and sizes of nano-fillers, inter-filler distances, stability and interfacial morphology are all important parameters to characterize polymer nanocomposites [7].

In this paper, we study the microstructure and stability of two kind nanoparticles (SiO_2 and Al_2O_3) in nanocomposite which are irradiated by electron beam of different energy and observe the changes of nanoparticle and PI matrix in nanocomposite by SEM and TEM.

2 EXPERIMENTAL PROCEDURE

The sol-gel methods is characterized by the fact that inorganic or organic-inorganic materials are made at relatively low temperatures, and in principle, consists of hydrolysis of the constituent molecular precursors and subsequent polycondensation to glass-like form. It allows incorporation of organic and inorganic additives during the process of formation of the glassy network at room temperature.

The preparation of hybrid PI films is as follows. First, polyimide acid PAA was used as a precursor in an N, N-dimethylacetamide (DMAc) solution. Second, PAA, SiO_2 and Al_2O_3 were mixed in the same solution by sol-gel method. Finally, the sol was coated on glass plates and heated up to 300 ℃ to form imidized inorganic nanoparticles hybrided PI films which were yellowish and transparent. The thicknesses of the films were about 20~50 μm.

The stability of the nanoparticles in the PI- inorganic films after high energy electron beam irradiation was studied by TEM (JEM-2000 FX) and the microstructure of films were analyzed by SEM (Fei Sirion, examined at 20 keV) and XRD (Philips X' Pert). The samples were cut into strips measured approximately 3×3 mm2 and the films were thinned by JIT-100 ion-milled machine with an ion beam of 4 kV and 30 μA. The samples were examined by means of TEM at 200 keV. The resolution power was 0.19 nm. The distribution of Si and Al in the films was measured by energy dispersive spectroscopy EDX. XRD spectra were obtained with a Cu target under the following operation conditions: λ: 0.1542 nm; voltage: 4kV; current: 35mA; step: 0.02°; scanning: 2θ.

3 RESULTS and DISCUSSION

Fig.1 is the surface morphology of the films (examined at 20 keV), which is flatter and homogeneous and some clusters are in the PI matrixes. The composition of clusters (Fig.2) shows that the inorganic hybrid PI films contain Si and Al elements which could combine with O forming SiO2 and Al2O3 and they are stable under the condition of 20 keV electron beam. The size of clusters is about of magnitude μm and some smaller clusters exist in them. At the same time, the clusters morphology of nanocomposites do not any change when the sample is irradiated by electron beam for long time.

Fig.3 shows that the TEM image and transmission electron diffraction pattern of the SiO_2-Al_2O_3 hybrid PI film irradiated by high energy electron beam of 200 keV at the beginning. A large number of nanoparticles are embedded in the film (Fig. 3 (a)). The sizes of the particles are from several nm to 30 nm. The most of them are small particles and the sizes are smaller than 10 nm. The shape of nanoparticles is regular, with most of them being spherical. The PI matrix is made up domain-like matter, which is about 200 ×300 nm^2. The larger particles located in the edge of domains generally. The electron diffraction pattern consists of spots and rings (Fig. 3 (b)) which demonstrates that the film is composed of polycrystalline and amorphous matter.

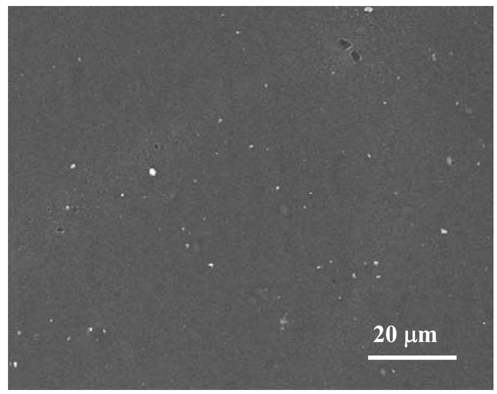

Figure 1: The surface morphology of the films.

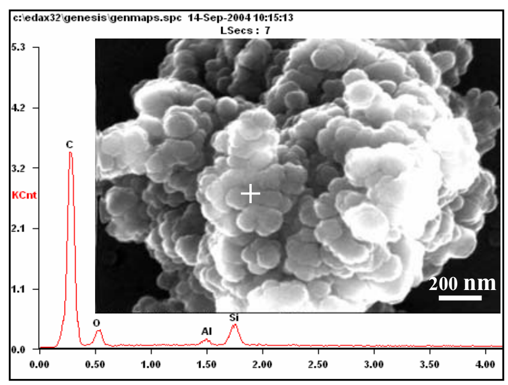

Figure 2: The composition of clusters and morphology.

After 2 second, the microstructure and electron diffraction pattern of the films take place changing, as shown in Fig.4. Fig.4 compared with Fig.3, the significant differences are found that a large number of nanoparticles are embedded in the film for Fig.3 (a), but for Fig.4 (a), the number of nanoparticles decrease obviously after irradiating (from about one hundred in Fig.3(a) to eight in Fig.4 (a)). And at the same time, the size of nanoparticles

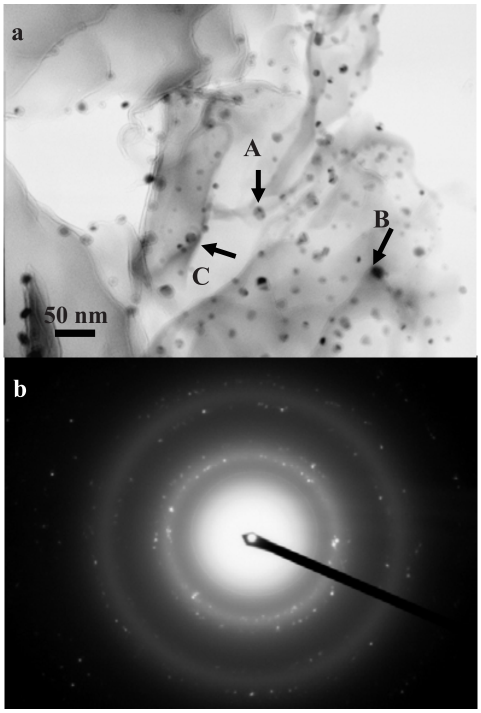

Figure 3: TEM image and transmission electron diffraction pattern of the hybrid PI film irradiated by high energy electron beam of 200 keV at the beginning.
(a) the morphology of the hybrid PI film
(b) transmission electron diffraction pattern of the hybrid PI film

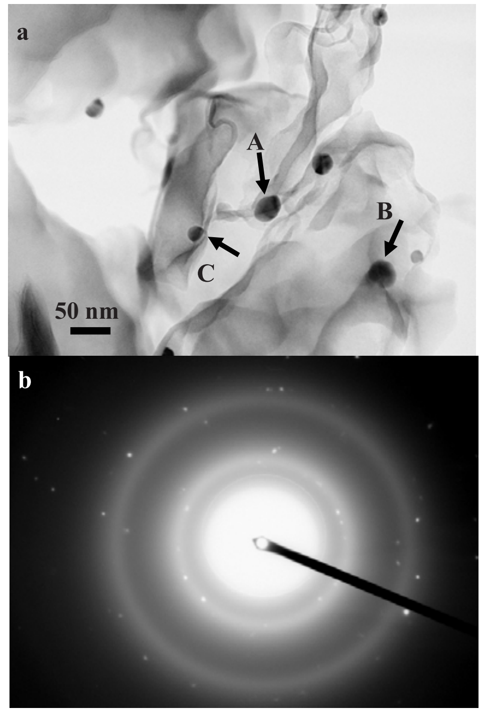

Figure 4: TEM image and transmission electron diffraction pattern of the hybrid PI film irradiated by high energy electron beam of 200 keV after 2 second.
(a) the morphology of the hybrid PI film
(b) transmission electron diffraction pattern of the hybrid PI film

left in the PI matixes becomes larger, seen the position A and B in Fig. 4 (a), about 30 ~ 40 nm. But there is an exception, for example, the nanoparticle in the position C for Fig. 4(a) has not changed, and the number of diffraction spots also reduce correspondingly. With the help of XRD analysis, the diffraction spots are proved from crystallizing Al_2O_3.

The results of SEM, TEM and XRD show that there are two kinds of nanoparticles in the hybrid PI films, i.e., SiO_2 and Al_2O_3. Under 20 keV electron beam illuminating, both kinds of nanoparticles and PI matrix are stable and not any changing. When the irradiation energy reaches 200 keV, the larger crystalline nanoparticle Al_2O_3 and PI matrix are still stable while smaller amorphous SiO_2 or crystalline Al_2O_3 nanoparticles are unstable. Ref. [8] reported that small nanoparticles may disappear under high energy electron beam irradiation. Here the instability of the smaller nanoparticles particle is also this case.

Table 1 lists some properties of PI, SiO_2 and Al_2O_3. The melting point and thermal conductivity of SiO_2 are much lower than that ones of Al_2O_3. These parameters are the important facts effecting on some materials stability. Although the melting point PI is lower than that of SiO_2, but the shape of PI domain did not any change, which indicate that the positions of the smaller particles aggregate a lot of defects to cause the nanoparticles state decomposing. The simulation results by MS (Material Studo) software also show that the total energy of PI/α-Al_2O_3 is much lower than that of PI/SiO_2. Thus, by the action of high energy electron beam of 200 keV, some chemical bonds of SiO_2 clusters are destructed, so the clusters or amorphous particles are broken up, thus finally disappear in the PI matrix. Otherwise, some Al_2O_3 reserve and the other vanish and the orientation of diffraction spots left is much stronger, which might show that when the orientation of nanoparticles Al_2O_3 match that of PI domain the nanoparticles grow easily, and the phenomenon would be discussed further.

Materials	Melting point ℃	Dielectric constant	Thermal conductivity
SiO_2	1700	3.9	0.02
α- Al_2O_3	2030	9.4	0.46
PI	800	3.4	0.19

Table 1: The materials properties of PI, SiO_2 and α- Al_2O_3.

Above all, the main reasons for effecting on the stability of nanoparticles hybrid Polyimide Nanocomposite are as follows. First, there are more Si –OH bonds on the surfaces of SiO_2 grains which make them aggregate into theclusters easily. Second, because the sizes of SiO_2 grains are smaller, there are many dangling bonds on the grain surfaces, which make the free energy per unit area on the surfaces increase, then the structure stability and the fusion point drop. The above reasons could explain why the SiO_2 grains decompose rapidly and then diffuse into the PI matrix to form stronger chemical bonds, as well as they may volatilize after they have been exposed to a high energy electron beam. The crystalline structure of the Al_2O_3 particles is rather stronger, as some small Al_2O_3 grains have grown together to form larger grains.

4 CONCLUSIONS

The most significant conclusion can be drawn as following: 1) PI is made up a large number of domains about 200 ×300 nm^2 which is not changed by high energy electron beam; 2) the nanoparticles of SiO_2 and Al_2O_3 are homogeneously dispersed in continuous PI matrices, which are stable usually, but while they are irradiated by high energy electron beam of 200 keV, the smaller particles disappear whose melting point are lower, and the bigger grow up; 3) the crystalline of Al_2O_3 is better than that of SiO_2.

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REFERENCES

[1] E. Müh, H. Frey, J. E. Klee, R. Mülhaupt, Macromol. Mater. Eng., 280/281, 41, 2000.

[2] J. K. Nelson, J. C. Fothergill, L. A. Dissado and W. Peasgood, IEEE Conf. Electr. Insul. Dielectr. Phenomena (CEIDP), Caucun, Mexico, 295, 2002.

[3] S. S. Ray and M .Okamoto, Progress in Polymer Science, 28, 1539, 2003

[4] T. Tanaka, G. C. Montanari and R. Mülhaupt, IEEE Transactions on Dielectrics and Electrical Insulation. 11, 763, 2004

[5] M. Hashizume, S. Kawanami, S. Iwamoto, T. Isomoto, J. Kikuchi, Thin Solid Films 438, 20, 2003.

[6] U. Schubert, N. Husing, A. Lorenz, Chem. Mater. 7, 2010, 1995.

[7] T. Tanaka, M. Kzako, N. Fuse, Y. Ohki. IEEE Transactions on Dielectrics and Electrical Insulation. 12, 669, 2005

[8] Feng Duan, Shi Changxu, Liu Zhiguo. Introduction to Materials Science – An Integrated Approach, Chemical Industry Publisher, Beijing, China, 143,