

Microstructure and Interfacial Interaction of Polyimide Based Hybrid Nanocomposites

M. A. Wahab, S. Hwang¹, S.-K.Kim¹, W. Kim¹, Il Kim, and Chang-Sik Ha*

Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea,

Fax: +82-51-514-4331; E-mail: csha@pusan.ac.kr

¹Department of Chemical Engineering, Pusan National University, Pusan 609-735, Korea

Abstract

In this work, we report the microstructure and interfacial interaction of polyimide(PI) based hybrid nanocomposites. A series of PI/silica hybrid nanocomposites were prepared via sol-gel reaction and thermal imidization. For the PI based hybrid nanocomposites, 3-aminopropyltriethoxysilane (3-APS) was used to enhance the interfacial interaction between PI and silica. The morphology and interfacial interaction of the hybrids were investigated using Scanning Electron Microscope (SEM). PI/poly(vinylsilsesquioxane) (PVSSQ) hybrid composite films were also prepared via sol-gel process and thermal imidization. The presence of the PVSSQ showed a remarkable effect on the microstructure of the PI based hybrid films. The effect of titania addition on the microstructure and interfacial interaction on the PI/silica hybrid composite films was also discussed.

Keyword; polyimide, hybrid nanocomposite, 3-aminopropyltriethoxysilane, poly(vinylsilsesquioxane), titania

Introduction

Polyimides (PIs) are high-performance polymers characterized by their high thermal stability and mechanical properties, low thermal expansion and dielectric constants, and good resistance to organic solvents and thus have been widely used in the aerospace, microelectronics devices, dielectric layers in multichip semiconductor packaging, and so on [1,2]. Recently, its application has also been extended to opto-electronic and photonic fields, nonlinear optics, optical guide, organicelectroluminescent devices, and photorefractive

materials [3,4]. On the other hand, the dispersion of inorganic nanoparticles into a polymer matrix has been proved to be effective in the improvement of the performances of the organic polymers by yielding so-called organic-inorganic hybrid nanocomposites. These nanocomposites are one of the hottest issues among the today's materials scientists since its unique combinational properties from organic and inorganic materials which could not be obtained by single component. The sol-gel reaction has been one of the

most widely used approaches to obtain hybrid nanocomposites. This reaction involves the hydrolysis of a metal alkoxide and the condensation of the hydrolysis product. In particular, an important advantage of the sol-gel synthesis route for polyimide/silica hybrid composites is that the poly(amic acid) organic matrix acts to prevent agglomeration of the silica, which can lead to nanometer scale silica clusters in the composites or, as often stated, "nanocomposites"[5]. In this paper, we wish to discuss the microstructure and interfacial interaction of the polyimide (PI) / silica(Si) hybrid nanocomposites with reviewing recent publications including our own works.

Experimental

Preparation method of PI / Si hybrid composites

Generally, polyamic acid (PAA) is prepared from a homogeneous mixture of a dianhydride (e.g., 3, 3', 4,4'-biphenyltetracarboxylic anhydride, BPDA) with a diamine (e.g., 4,4'-oxydianiline (ODA) or phenylenediamine (PDA)) in an aprotic and polar solvent such as dimethylacetamide (DMAc) or N-methyl pyrrolidinone (NMP) under nitrogen atmosphere. Then, a metal oxide precursor solution in water is added into PAA and the hydrolysis and polycondensation are carried out simultaneously. In this review, silica has been used as the main inorganic material unless otherwise noted. Sometimes, a catalyst such as HCl is used together with water to control the sol-gel reaction of the metal oxide precursor. The hybrid PAA solution are heated to different temperatures to eliminate water, solvents and finally produced inorganic network phase along with PI.

Results and Discussion

Compatibility issues in PI / Si hybrid composites

Before 1990, the incorporation of metal oxides into a polymer was often led to inhomogeneous distributions

along with agglomeration of inorganic (here i.e, silica)-particles, which degrades the properties of the resulting composites [6]. In 1990, McGrath and coworkers [7] reported the functionalized PI capable of bonding themselves into sol-gel networks and found improved properties. Then, the first successful attempt to make PI/silica hybrid was reported by Nandi et al. [8], where they suggested that the metal oxides could be chemically linked to the PAA through co-hydrolysis of carboxylic groups and phase separation can be prevented via coordination of the polyimide carbonyl groups to the metal centers. Incompatibility between polyimide and inorganic particles will not lead to composites with desired properties. Thus, it is utmost important to improve the compatibility between two phases to prepare polyimide-inorganic composites with good properties. For this goal, a recent review paper [9] led us to summarize how to make compatibilized composites: (1) By adding coupling agent which makes bond with the growing inorganic oxides and PI chains, (2) functionalizing the PI chains at their end groups, (3) choosing a polymer with appropriate groups within the repeating units, (4)using appropriate functional groups, (5) choosing judiciously the silsesquioxane, which can also make bond with the carbonyl groups of PI, (6) interestingly, introducing titania to be able to reduce particles of silica/silsesquioxane through Si-O-Ti bonding.

Microstructure and interfacial interaction in PI based hybrid composites

It was reported that the interaction between Si and PI is important and the interfacial interaction between BPDA-PDA PI and silica is stronger than that between BPDA-ODA PI and Si[10]. Highly compatibilized BPDA-ODA PI/silica films can be, however, successfully prepared if one uses 3-aminopropyltriethoxysilane (3-APS) or polyvinylsilsesquioxane

(PVSSQ) [10,11]. For instances, in Fig.1, 3-APS produced very compact structure as well as improved optical transparencies in the hybrid composites of PI with silica from tetraethoxysilane (TEOS) in comparison to the PI/Si hybrid composites without 3-APS. In this figure, the Si content is fixed at 30 wt%.

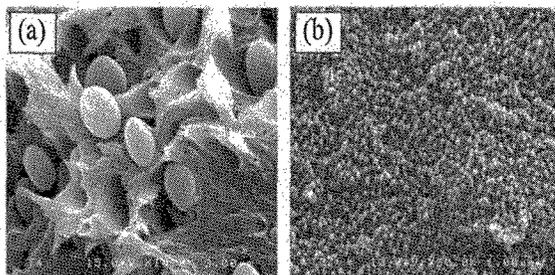


Fig.1. SEM micrographs of the PI/Si hybrid composites (30 wt% of Si) without (a) and with (b) 2 wt% of 3-APS.

It was considered that the 3-APS bonds with the growing TEOS network and the PI chain end[11]. The enhancement of phase compatibility brought via PVSSQ is also clearly seen in Fig.2. The contents of PVSSQ and TEOS are 30 wt%. The result may be associated with better interfacial interaction in the PI/PVSSQ hybrid in comparison to that of the PI/silica (from TEOS) hybrid system. The end hydrogen of PVSSQ and the hydrogen of Si-OH also provide hydrogen bonds in the carbonyl group of PI matrix, leading to compatibilized morphology.

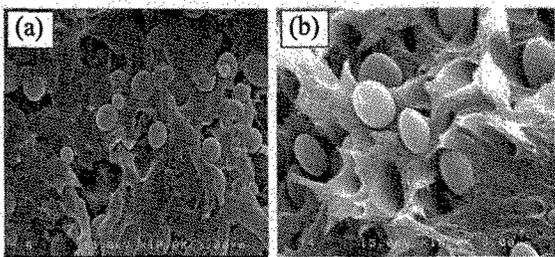


Fig.2. SEM micrographs of hybrid composite films, (a) PI/PVSSQ30, and (b) PI/TEOS30.

It was found that nanocomposites with BPDA-PDA PI

can be obtained up to 30 wt% of PVSSQ, whereas ≤ 20 wt% of PVSSQ is the maximum composition to give nanocomposites for the BPDA-ODA PI [12]. We suggested the strong interaction between BPDA-ODA PI and silica and that the motion of PI becomes restricted after incorporating of the PVSSQ. The flexible organic phase of PVSSQ played a significant role in the interfacial adhesion between PI and the PVSSQ. It was also found that addition of Si or PVSSQ affected also on the dielectric constant as well as mechanical and thermal properties of hybrid films.

On the other hand, titania(Ti) is one of promising partner of polymer in hybrid composites for photonic applications because of its high refractive index. When TiO_2 is obtained by sol-gel method, however, it is not easy to prepare hybrid composite thin films of Ti with a polymer because of very fast hydrolysis reaction and thus extremely fast gellation of titanium alkoxide. In our work, the effect of small amounts of Ti on the microstructure of the PI/Si hybrid systems was investigated using a fluorescence spectroscopy, Scanning Electron Microscopy(SEM), and an atomic force microscopy (AFM)[13].

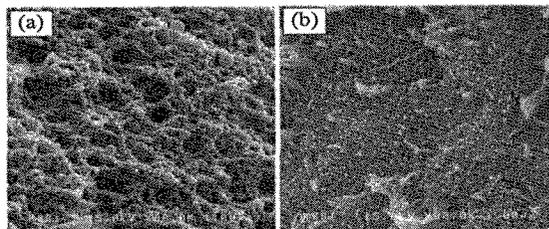


Fig.3. SEM micrographs of (a) PI / Si10 and (b) PI / Si-Ti hybrid composite films.

Fig.3 shows the SEM micrographs of the fractured surface of the PI/Si10 and PI/Si-Ti composites, where the contents of inorganic particles was fixed at 10 wt. % and the mole ratio of Si and Ti was 1/1 [13]. It is clearly seen that the particle size of the Si was significantly reduced for the ternary hybrid composites in comparison

to the PI/SiO₂ binary hybrid composite, indicating the formation of nanocomposite for the case of the ternary composite.

Ha et al. [10] introduced fluorescence spectroscopy to interpret the interfacial interaction between the inorganic particles and PI. Our previous results can be summarized as follows: (1) A large red shift is observed for BPDA-PDA PI/Si hybrid systems (up to 50-70 nm), whereas it is almost unchanged for BPDA-ODA PI/Si hybrid films.

(2) On increasing the amount of Si, wavelength of emission peak for BPDA-PDA/PI/Si hybrid films increases, whereas wavelength of emission for BPDA-ODA PI/Si hybrid films is not changed significantly.

It was also found that the addition of small amounts of Ti affected significantly on the photophysical behavior of PI/Si hybrid nanocomposites. When small amount of Ti(OPr)₄ are added to TEOS, they are transformed to Ti and Si, respectively, by sol-gel reaction. Then, small amount of TiO₂ particles exist together with SiO₂ as well as possibly covalent Si-O-Ti-O-Si network particles during molecular alignment or orientation of PAA to PI as a matrix. Thus, such a variety of local structure environment may give several different characteristic emission peaks on their fluorescent spectra of the PI/Si-Ti ternary hybrid nanocomposite in comparison to that of the PI/Si binary hybrid nanocomposite.

Conclusions

In summary, it may be concluded that PVSSQ, aminosilane, and titania can effectively play vital roles to produce better environment by reducing faster hydrolysis for the homogeneous nanoscale distribution by avoiding agglomeration of large domains, which helps the formation of hybrid nanocomposites for the PI/silica system.

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