POLYIMIDE BASED HYBRID NANOCOMPOSITES

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Polyimides (PIs) have been used as attractive matrix polymers for hybrid composites due to their good thermo-mechanical properties. Properties of the polyimide based hybrid nanocomposites can be obtained in a wide range by dispersing inorganic nanoparticles via sol-gel process during thermal imidization. This review concerns a brief summary of microstructure, interfacial interaction, and properties of the polyimide based hybrid nanocomposites.

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 photonics fields, nonlinear optics, optical guide, optical interconnection, and photorefractive materials [3,4]. Some applications such as circuit-printing films and semiconductor coatings need enhancement of certain properties. More specifically, thermal expansion coefficient, mechanical properties and thermal deflection temperature have to be improved for specific applications.

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

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issues among the today’s materials scientists since its unique combinational properties from organic and inorganic materials 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 products. The structure and properties of the resulting hybrids is dependent on the hydrolysis and condensation, which are controlled by pH, nature of solvent, and types of alkoxide, and so on. [5].

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, “nano-composites.” In this paper, we wish to discuss the microstructure, interfacial interaction and some properties of the polyimide/silica hybrid nanocomposites with reviewing recent publications including our own works.

**EXPERIMENTAL**

**Preparation Method of Polyimide/Silica Hybrid Composites**

Polyamic acid (PAA) is prepared from a homogeneous mixture of a dianhydride (e.g., 3, 3', 4,4'- biphenyltetra carboxylic 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. Sometimes, a catalyst such as HCl is used together with water to control the sol-gel reaction of the precursor. Typical synthetic route for preparing organic-inorganic hybrids is shown in Figure 1.

In this review, tetraethyl orthosilicate (TEOS) has been used as a precursor of silica unless otherwise specified. As depicted in Figure 1, the hybrid PAA solution are heated to different temperatures (usually sequentially from 80°C for soft-baking up to 350°C for thermal imidization) to eliminate water, solvent and finally produced inorganic network phase along with PI. In most of the cases, the conversion of PAA to polyimide are confirmed by FTIR studies by observing the decrease in carboxylic acid peak and increase in imide peak and NMR spectroscopy has also been used for characterization of the chemical reaction in the polyimide/silica hybrids.
RESULTS AND DISCUSSION

Compatibility Issues in Polyimide/Silica 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 do 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. Various methods employed for preparing compatibilized hybrid composites have also been discussed [9]. Kakimoto et al., [10] described flexible polyimide/silica hybrid composite films with small silica loading (as small as 8%). The hybrid composites showed lower Tg compared to pure polyimide because of uncrosslinked and incomplete hydrolysis of TEOS. The thermal expansion coefficients were found to be $1.3 \times 10^{-5} \text{K}^{-1}$ by extrapolation. Thermo-mechanical behaviors showed that the motion of PI becomes restricted as the number of bonding sites increased. The compatibilized PI/silica composites gave improved moduli, and strengths of these composites. This is consistent with the well-known fact that tensile strength is reduced if there are no bonding sites [10].

**Microstructure and Interfacial Interaction in PI Based Hybrid Composites**

Ha et al. [11] introduced fluorescence spectroscopy to interpret the interfacial interaction between the inorganic particles and PI as shown in Figure 2. In this figure, the emission peaks of the PI hybrid films based on BPDA and PDA or ODA were compared. The peaks were obtained with the excitation wavelength of 350 nm. The results in Figure 2 can be summarized as follows: On increasing the amount of silica, the wavelength of emission peak for the BPDA-PDA/PI/silica composite films increases, whereas the wavelength of emission for BPDA-ODA/silica films is not changed significantly. A large red shift was observed for the BPDA-PDA PI/silica hybrid system (up to 50–70 nm) at high silica loadings (22 wt.%). The result suggests that the interaction between silica and polyimide is important and the interfacial interaction between BPDA-PDA PI and silica is stronger than that between BPDA-ODA PI and silica. It was reported that in the BPDA-ODA PI/silica composite there is no specific interaction or chemical bonding holding the silica to the polyimide matrix.

Highly compatibilized BPDA-ODA PI/silica films can be, however, successfully prepared if one use 3-aminopropyltriethoxysilane (3-APS) or polyvinylsilsesquioxane (PVSSQ) [12–13]. For instance, in Figure 3, 3-APS produced very compact and fine microstructure as well as improved optical transparencies in the hybrid composites of PI with silica from TEOS in comparison to the PI/silica hybrid composite without 3-APS, which exhibits gross phase separation. In this figure, the silica content is fixed at 30 wt.%. The enhancement of phase compatibility brought via PVSSQ is also clearly seen in Figure 4. The contents of PVSSQ and TEOS are 30 wt.%. The result may be associated with better interfacial interaction in the PI/PVSSQ hybrids in comparison to that of the PI/silica (from TEOS)
FIGURE 2 Emission wavelength change of BPDA-PDA and ODA PI/Si hybrid composites.

FIGURE 3 SEM images of the PI/silica hybrid composites containing 30 wt% of silica without (a) and with (b) 3APS.
hybrid system. The end hydrogen of PVSSQ and the hydrogen of Si-OH also provide hydrogen bonds in the carbonyl of PI matrix, leading to compatibilized morphology. Interestingly enough, the enhancement of compatibility is much larger for the hybrid system based on TEOS than for that based on tetramethoxysilane (TMOS) [12]. 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 [13]. The interfacial interaction can be also evaluated by atomic force microscope (AFM) [13]. We suggested the weak interaction between BPDA-ODA PI and silica is enhanced by incorporating the PVSSQ [13]. Figure 5 indicates the compositional effect of TEOS and vinylsilsesquioxane (VSSQ) on mechanical properties of the PI/silica-PVSSQ hybrid composites. The improvement of mechanical properties has already been explained, that is, the introduction of fine silica particles into a polymer matrix and better adhesion as well as strong interaction between PI and PVSSQ. It is noteworthy that the flexible organic phase of PVSSQ played a significant role in the interfacial adhesion between polyimide and the PVSSQ. It was also found that the addition of silica or PVSSQ affected on the dielectric constant of hybrid films, which was explained in terms of increasing free volume as well as domains sizes of PVSSQ [13] and inherently higher dielectric value of silica [14]. It is known that titania has very fast hydrolysis rate and ultimately produces inhomogeneous and large agglomeration of domains, which can significantly impact on the polymer matrix. The introduction of titania into the PI/silica hybrid composites, however, improves the interfacial interaction between silica and PI [15], as shown in Figure 6. In this figure, the silica or silica-titania contents

**FIGURE 4** Fractured surface morphology of hybrid composite films, (a): PI/PVSSQ30, and (b)PI/TEOS30.
are fixed at 10 wt.%. In the silica-titania mixture, the ratio of silica and titania is 1/1 by mole ratio.

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

![FIGURE 5](image-url) Variation of mechanical properties of the hybrid composite films of PI and silica(from TEOS) and PVSSQ as function of different weight fraction of TEOS in the TEOS/VSSQ mixture, (a) Tensile strength, and (b) Elongation at break.

![FIGURE 6](image-url) SEM micrographs of PI/Si10 and PI/silica-titania hybrid composite films.
REFERENCES
