Nanohybrids of Polyimide and Organosilicas Containing Different Functional Groups

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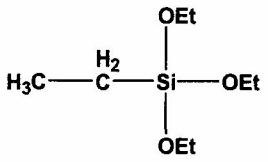
Recently organic/inorganic hybrid materials have been widely studied because novel material's properties can be produced through systematic design of the organic and inorganic segments. In this study, nanohybrids of polyimide (PI) and organosilicas containing two different contents of ethoxy groups were prepared using an in situ sol-gel reaction and multistep curing. PI was prepared from pyromellitic dianhydride (PMDA) and 4, 4'-oxydianiline (ODA) poly(amic acid) (PAA). The PI/organosilica nanocomposite films were characterized by IR spectra, UV-VIS transmission spectra, dynamic mechanical analysis (DMA), small angle X-ray scattering (SAXS), and universal testing machine (UTM).

Introduction

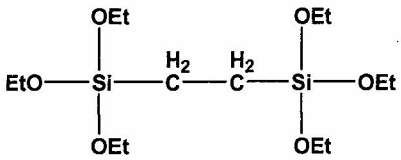
Organic–inorganic hybrid composites have been recognized as a new class of advanced materials because they combine the advantages of an inorganic material (rigidity, high thermal stability) and an organic polymer (flexibility, dielectric, ductility, and processability) [1]. Among polymers as matrix materials for high-performance composites, aromatic polyimides (PIs) have attracted much interest because of their potential applications in the electronic and aerospace industries due to their outstanding dielectric and mechanical properties even at high temperatures. Additionally, the incorporation of silica (SiO_2) has been proved very effective in enhancing the mechanical and thermal properties of PI. Several studies have been carried out on the preparation of polyimide/silica (PI/SiO_2) hybrids, mostly by the sol–gel method [2]. However, the main concern here is to obtain significant improvements in the interfacial adhesion between polymer matrix and inorganic filler phases by suppressing the phase separation involved. In this work, nanohybrids of polyimide and organosilicas from two different organosilica precursors of different amounts of ethoxy groups were prepared and characterized.

Experimental

In this study, nanohybrids of PI and organosilica containing different functional groups were prepared using an in situ sol-gel reaction and multistep curing. PI was prepared from pyromellitic dianhydride (PMDA) and 4, 4'-oxydianiline (ODA) poly(amic acid) (PAA). We used triethoxy(ethyl)silane (96%) and 1,2-bis(triethoxysilyl)ethane (96%), purchased from Aldrich, as organosilicas. Chemical structures of the two different organosilicas are shown in Figure 1.



Triethoxy(ethyl)silane(96%)
M.W=192.33
d=0.895



1, 2-bis(triethoxysilyl)ethane(96%)
M.W=354.60
d=0.958

Figure 1. Organosilica precursors to prepare hybrid materials.

Preparation of Hybrid Films. The hybrid films were prepared from PMDA-ODA PAA precursor solution in DMAc, then incorporating organosilica precursor and mixing to a homogeneous state, followed by adding deionized water; the sol–gel reaction then took place, followed by spin-coating the resulting silica sol/PAA precursor solution onto a glass substrate, soft-baking the films, and finally imidizing the films thermally. The PMDA–ODA PAA solution was prepared with equimolar ratio of PMDA and ODA in DMAc under nitrogen atmosphere. The reaction was continued for 12 h to make a homogeneous mixture. Different weight percentage of organosilica precursors with stoichiometric amount of water was added into the reaction mixture with stirring for 12 h to form homogeneous solution. The solid content of the solution was 10 wt%. The imidization process was carried out at 80 °C for 4 h, 130 °C for 1 h, 180 °C for 1 h and 240 °C for 1 h, 300 °C for 1 h in a vacuum under nitrogen atmosphere to get hybrid films. The heating rate was 2 °C /min. We designated the hybrid samples as Sx and Ex, where S or E means that triethoxy(ethyl)silane or 1,2-bis(triethoxysilyl)ethane, respectively, was used as an organosilica precursor, and x means the weight % of the organosilica.

Results and discussion

IR Spectra. Upon curing, the characteristic absorption peaks of imide groups are present near at 1780, 1711, 1368, and 730 cm^{-1} in the hybrid samples as well as PI. Among them, the peaks at 1711 cm^{-1}, representing an imide group, and 1780 cm^{-1}, indicating a cyclic five membered ring,

confirmed imide formation. The bands at 1368 and 730 cm^{-1} are attributed to the C–N–C bond and the imide ring deformation. It was confirmed by IR spectra that polyimide/orgnosilica nanocomposite film was successfully prepared [3].

UV-Vis Spectra. Generally, we can see that the transmittances of hybrid films were decreased with increasing wt % of organosilica precursors. Polyimide–silica hybrids having lower contents of organosilicas are transparent, because the nanoparticle diameter is less than the wavelength of visible light. When hybrids are produced with higher silica contents (>10%), however, phase separation becomes evident, which leads to an opaque appearance.

Tensile Strength. Tensile strength of hybrid films was lower for the organosilicas prepared from lower contents of ethoxy groups. And the elongation at break of hybrid films was also lower when the content of the ethoxy group of the organosilica was smaller.

DMA. Tg of hybrid films was higher when the contents of the ethoxy groups are higher for the precursors. Storage modulus was increased according to the increasing weight percent of silica particles at below 300 °C, regardless of the kinds of organosilica precursors.

Small Angle X-ray Scattering. SAXS data of hybrid films with various organosilica contents are shown in Figure 2. For $q > 0.1 Å^{-1}$, the scattered beam intensity gradually increased with q. This might be due to the formation of silica particles of less than 100 Å [4, 5]. The peak at $q < 0.02 Å^{-1}$ indicates that some samples contain large nanoparticles of 350 Å. The SAXS results indicate that several sizes of silica particles were made during the sol-gel process, regardless of the contents of the ethoxy group in the organosilica used in this work.

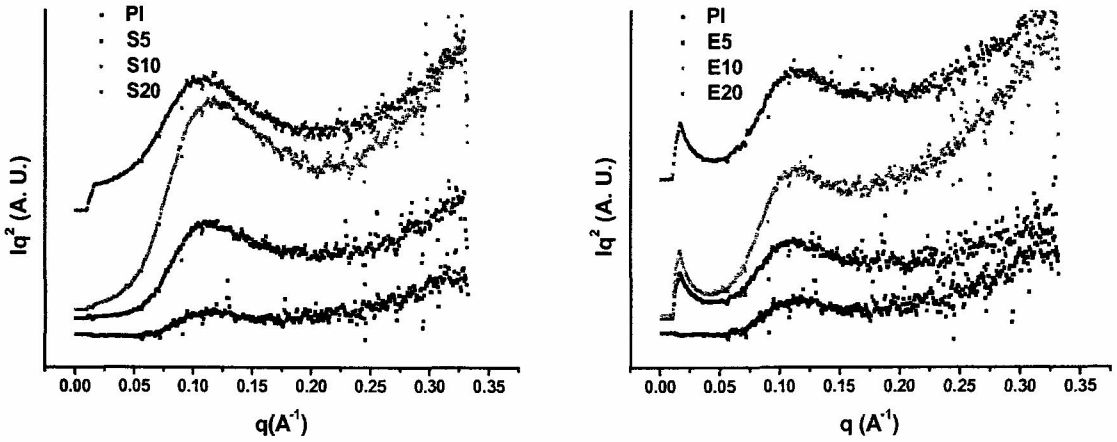


Figure 2. The Lorentz-corrected small angle X-ray scattering data of the PI/organosilica nanohybrids.

Conclusions

In this work, new hybrid composite films of polyimide and organosilicas with two different contents of ethoxy groups were prepared. We confirmed by IR spectra that organosilica precursor was successfully incorporated to prepare hybrid films. In general, polyimide based hybrids prepared from organosilica precursors having more ethoxy groups showed better properties. And nanohybrids of polyimide and organosilica exhibited good properties when the content of organosilica is 10 wt. %, regardless of the kind of the organosilica.

Acknowledgement

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