

Synthesis and Characterization of Nanohybrids from Polyimide and Organosilica Having Different Chain Length

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In this work, polyimide-silica hybrid composites were prepared from organosilicas having three different chain lengths. Polyimide was prepared from pyromellitic dianhydride (PMDA) and 4,4'-oxydianiline (ODA). Organosilicas used were triethoxyvinylsilane, 4-(triethoxysilyl)-butyronitrile, and tetraethylorthosilicate. Nanohybrids of polyimide and organosilicas having different chain length were prepared using an in situ sol-gel reaction and multistep curing. The characteristics of these polyimide-silica hybrids have been studied by universal testing machine (UTM), thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), infra-red (IR) spectra and UV-VIS transmission spectra. It was found that the properties of the polyimide-silica hybrids are strongly dependent on the kinds of organosilica precursors of different chain length.

Introduction

In recent years, increasing attention has been paid to preparing organic/inorganic hybrid composite materials that comprise desirable organic and inorganic characteristics.[1] Molecular design of the organic and inorganic segments has produced new hybrid composite materials with distinguished physical and chemical properties via the sol-gel process. The sol-gel processes are affected by many controllable synthetic parameters such as structure and concentration of reactants, solvent, and catalysis, as well as reaction temperature and the rate of removal of byproducts and solvents. For these hybrids, polyimides (PIs) have been used as the high performance polymer matrix materials due to their outstanding thermal stability, mechanical properties, and electrical properties. [2] In this paper, we investigated the microstructure, interfacial interaction, thermal and mechanical properties and optical behavior of the PI-silica hybrids films. For this work, we prepared polyimide-silica hybrid composites containing 5,10, 20, 30 wt. % of organosilica precursors.

Experimental

Materials

4,4'-oxidianiline (ODA), pyromellitic dianhydride (PMDA), triethoxyvinylsilane(97%), tetraethylorthosilicate (98%) , 4-(triethoxysilyl)-butyronitrile (98%) and anhydrous dimethylacetamide (DMAc) were purchased from Aldrich.

Preparation of Polyimide-Silica Hybrid Films

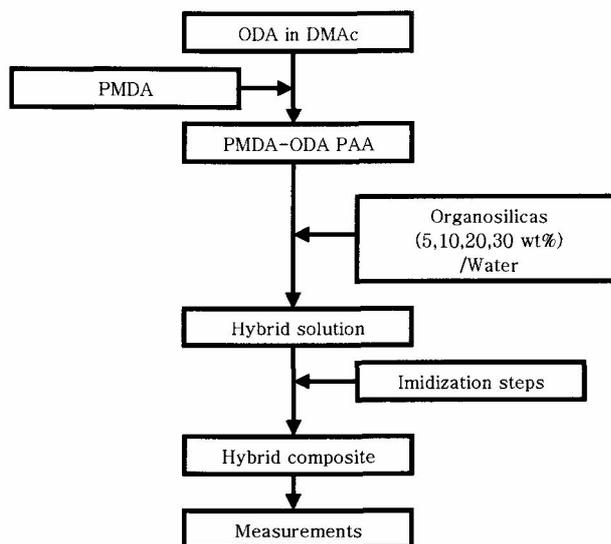


Figure 1. Preparation scheme of PAA, hybrid solution and hybrid films

Figure 1 illustrates the procedures for preparing polyimide hybrid films containing either of three different organosilica precursors. The PMDA-ODA poly(amic acid) (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. This solution was added to different weight percentage of various organosilica precursors with stoichiometric amount of water, and then stirring for 12 h to form homogeneous solution. 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. For the sample notations, Tx, Vx or Bx means that the organosilica used is triethoxyvinylsilane, tetraethylorthosilicate, and 4-(triethoxysilyl)-butyronitrile, respectively, with the organosilica content of x wt.%.

Results and discussion

We confirmed by IR spectra that polyimide-silica hybrid films were successfully prepared. Absorption peaks of PI-silica hybrid films were confirmed near at 1780, 1711, 1368 and 730 cm^{-1} . [1] The hybrid films with organosilica precursors < 20 wt % showed high transparencies, but the transparency significantly decreased when the content was 30 wt % of organosilica precursors. This phenomenon can be explained in terms of the increase of the organosilica domain sizes with increasing organosilica content, resulting in high scattering. [2,3] When the organosilica contents were higher than 20 wt. %, the tensile strength of the composites was decreased, meaning that there are no bonding sites between the organic polymer phase and the inorganic phase. The mechanical properties of the composites are generally dependent on the bonding between the two phases, the inorganic surface area of the filler, and the arrangement between the fillers. [4] The tan delta peak shifts to higher temperatures with increasing organosilica precursor contents, regardless of the kinds of organosilica, reflect the reduced segmental mobility of the PI chains, due to the incorporation of interaction introduced by the fairly dispersed organosilica domains with the matrix PI as well as the increasing degree of crosslinking with increasing the amount of the organosilica precursors. [5] The Tg of PI in the hybrid prepared from 4-(triethoxysilyl)-butyronitrile precursor was lowest due to high flexibility of the long CH_2 chains, as expected (Figure 2(left)). The thermal stability of the hybrid films were comparable, however, to the pristine PI, as shown in Figure 2 (right).

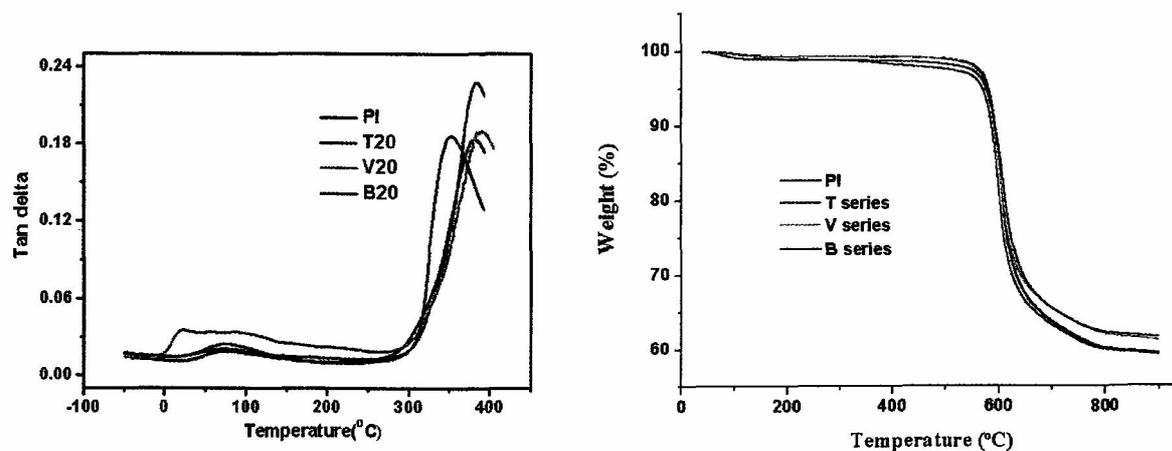


Figure 2. DMA data (left) and TGA data (right) of PI-silica hybrid films.

Conclusions

In this work, PI-organosilica hybrids have been prepared using organosilica precursors which

can provide good interaction between the organic and the inorganic phase. When the organosilica contents are less than 20wt%, the hybrid films showed good optical transparency. Mechanical properties of the hybrids were, however, decreased by using organosilicas. Thermal stability of the PI-organosilica hybrids was also comparable to the pristine PI.

Acknowledgements

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