Preparation of Polyimide-Silica Nanocomposites from Nanoscale Colloidal Silica

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ABSTRACT: The polyamic acid (PAA) solutions were blended directly with a commercial nanoscale colloidal silica sol, and converted to polyimides (PIs)/silica nanocomposite films. Polyamic acid was prepared from the reaction of Pyromellitic anhydride (PMDA), 4,4-oxydianiline (ODA). The nanoscale silica particles were dispersed well in PI from scanning electron microscopy (SEM) and the nanocomposite films showed a moderated optical transparency for up to 30 wt % of silica content. These PI/silica nanocomposite films exhibited better mechanical properties, higher glass transition temperature (T_g), better thermal stability and lower coefficient of thermal expansion (CTE) with increasing silica content from tensile tests, dynamic mechanic analysis (DMA) and thermogravimetric analysis (TGA).
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Many properties of polymers can be improved by the addition of inorganic additives. Nanocomposites are a class of composites in which the reinforcing phase dimensions are in the order of nanometers,[1–3] since Nanocomposites combine the desirable properties of a inorganic phase (rigidity, high stability, mechanical properties and low thermal expansion) and organic polymers (toughness, flexibility, dielectric, ductility and processibility). However, the dispersion process and the interfacial adhesion between the organic matrix and inorganic reinforcing material are important factors in determining properties of a polymer composite.[3]

Polyimides (PIs) have been widely used in microelectronic industries because of their outstanding tensile strength, modulus, low coefficient of thermal expansion and low dielectric constant.[4–10] Properties of PIs can be further improved by adding inorganic particles. Angelo added organometallic complexes to PIs.[11] Taylor studied PI films which contained metaly-metal oxide particles.[12–14] Recent researches have discovered that PI/inorganic particles hybrid films are prepared to improve the properties of PIs, such as PI/titanium,[15,16] PI/silica,[17–23] PI/clay[10] and other fillers.[24,25]

Most organica-inorganic hybrid films are prepared by applying sol-gel process which provides a chemical route to ceramics of high purity, controlled microstructure; the sol-gel technique also allows coupling with organic polymeric materials.[26–28] However, some efforts are necessary to improve the interfacial problems between two phases to reduce the phase separation.[19,23]

The sol-gel process consists of two stages, hydrolysis of a metal alkoxide and polycondensation of the hydrolysis products. There are many factors may influence the kinetics of hydrolysis and condensation reaction in the sol-gel process and the final structure of the hybrid material, such as temperature, pH, nature of the solvent, and the type of alkoxide precursors.[28] Moreover, the released volatiles from the gelation of alkoxysilane sol may bring undesirable effects to the resin and the residual of the silanoxy groups may cause dehydration reaction under high temperatures and reduce thermal stability.[20,23,29]

Nanoscale colloidal silica sol has been used in poly-(methyl methacrylate)[29] and epoxy[30] to overcome the above problems of a sol-gel process. In this article, the polyamic acid (PAA) solutions (the precursor of PI) were blended with a commercial nanoscale colloidal silica sol then cured to form PI/silica nanocomposite films. Thus, this research investigated in dispersion of silica particles in PI, tensile properties, thermal mechanical properties and thermal stability.

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EXPERIMENTAL

Materials

Pyromellitic anhydride (PMDA), 4,4-oxydianiline (ODA) and *N,N*-Dimethy-acetamide (DMAc) were purchased from MERCK(Darmstadt, Germany). PMDA was recrystallized from acetic anhydride and dried at 150 °C in vacuum. ODA was purified by sublimation under reduced pressure. DMAc was dried over P$_2$O$_5$ and distilled before use. Silica sol was purchased from Nissan Chemical Co., Tokyo, Japan. The commercial product of DMAC-ST, in which 20–21 wt % of silica (particle size: 10–15 nm) was dispersed in DMAc.

Preparation of Polyamic Acid (PAA)

PAA from PMDA and ODA was prepared as follows: ODA was added into a flask and dissolved in DMAc with nitrogen inlet and mechanical stirrer, followed by the addition of an equivalent amount of PMDA in several portions. The reaction was carried out at room temperature for 24 h. The solid content of the solution was about 20 wt %. The inherent viscosity of the PAA was 1.89 dL/g in DMAc.

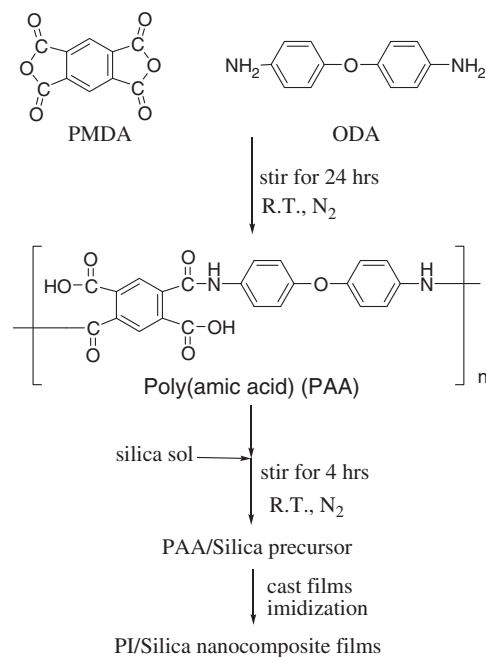### Preparation of PI/Silica Nanocomposites

The PAA solution was blended with the required ratios of silica sol and stirred for 4 h. The blends were cast on glass plates, and cured at 50 °C, 100 °C, 150 °C, 200 °C, 250 °C, 300 °C and 350 °C for 1 h. each, in nitrogen. The silica content in PI was 10 wt % (PI/10SiO$_2$), 20 wt % (PI/20SiO$_2$) and 30 wt % (PI/30SiO$_2$). As a reference, neat PI film was obtained by the same process without addition of silica sol. The thickness is *ca.* 43 μm. The process was shown in Scheme 1.

Characterizations

The morphologies of silica particles dispersed in PI/silica nanocomposite films were photographed by Hitachi S-3500H scanning electron microscopy (SEM). The fracture surfaces were coated with a gold–palladium layer by vacuum sputtering.

Tensile properties were tested by an Instron Instrument 4505 with a dumb-bell specimen with waist dimensions of 20 mm × 3.5 mm and at a cross-head speed of 5 mm/min. The Tensile properties of each sample were determined from an average of ten specimens.

The dynamic mechanical properties were performed by Perkin Elmer TMA-7 at a heating rate of 5 °C/min. and a frequency 1 Hz. The linear coefficient of thermal expansion (CTE) was also measured by Perkin Elmer TMA-7 over the temperature range of

Scheme 1. Flow chart to prepare PI/silica nanocomposite films.

50 °C to 250 °C a heating rate of 5 °C/min. and under a force of 0.1 N. Each CTE value was the average of five pieces with the size 2 mm × 20 mm.

The thermal stability of the PI and PI/silica nanocomposite films were characterized with a Perkin Elmer TGA 6 at a heating rate of 10 °C/min. from 100–800 °C under nitrogen.

RESULTS AND DISCUSSION

Morphology

Figure 1a, b and c show SEM micrographs of the cross-section of PI/10SiO$_2$, PI/20SiO$_2$ and PI/30SiO$_2$, respectively. The SEM micrograph of polyimide blended directly with nano-size silica powders (trade name: P25, purchased from Degussa) is also shown in Figure 1d for comparison. The high loading of silica in the resulting PI composite films is noteworthy, especially without employing any coupling agents and surfactants. It can be seen that the silica particles are homogeneously dispersed in the composites films from the SEM micrographs. Figure 1d shows obvious phase separation with poorer interfacial adhesion between the two phases. Figure 1a and b show no obvious phase separation and reveal a uniform dispersion of silica particles throughout the PI matrix. Figure 1c indicates that silica particles had formed aggregates of various sizes for PI/30SiO$_2$. Figure 1a, b, and c also do not exhibit debonding or holes, which indicating there are good interaction at the interfaces of PI and silica.
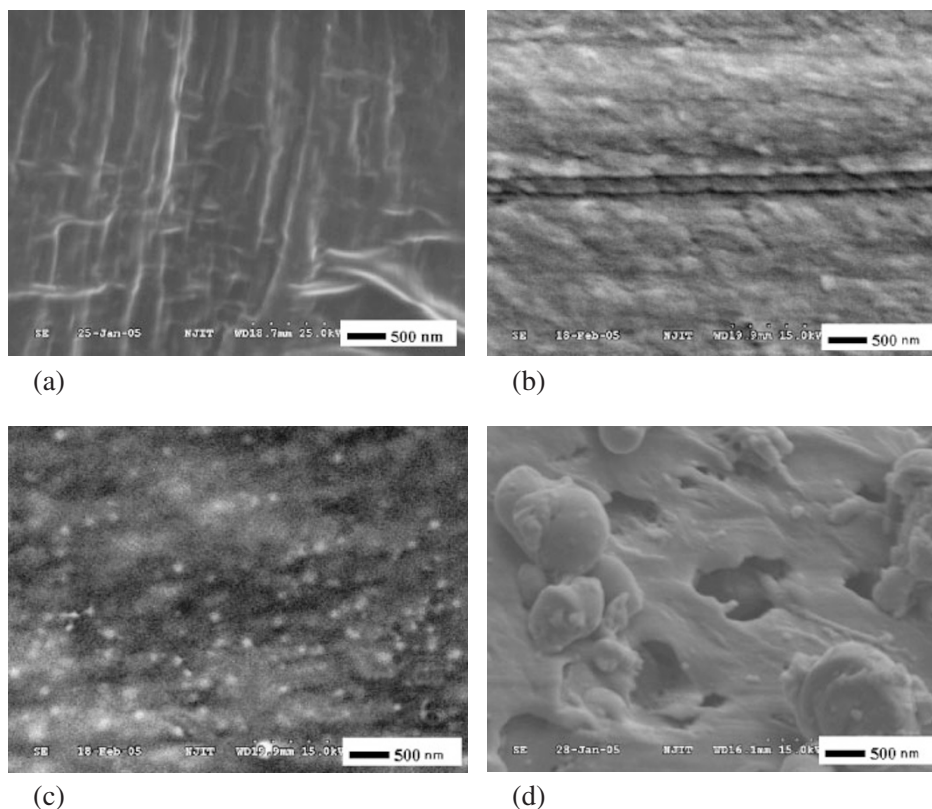
All three nanocomposite films obtained without

Figure 1. SEM photographs of the PI/silica nanocomposite films: (a) PI/10SiO$_2$, (b) PI/20SiO$_2$, (c) PI/30SiO$_2$, (d) blend of PI and silica particle (Degussa P25).
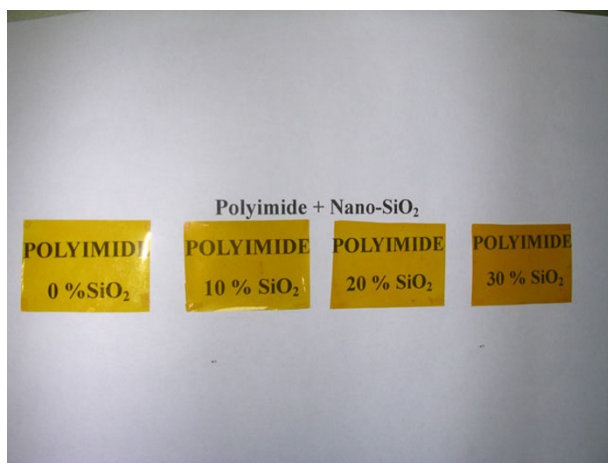

Figure 2. Translucency of PI/silica nanocomposite films as a function of silica content.

moisture contamination in the fabrication appeared optically transparent as shown in Figure 2. The nano-composite films are light brown in color, but highly translucent, and levels of translucency are not affected significantly by increasing the silica content. The dispersed phase should be smaller than the wavelengths of visible light to prevent light scattering[31] and a clear film indicates that the size of silica phase was no greater than the wavelengths of the visible lights. It also indicates that the nano-size silica particles are

well dispersed in the PI matrix. The translucency was decreased with increases of the content of silica because of agglomeration of the silica particles. PI/30SiO$_2$ containing 30 wt % silica became slightly darker brown because the silica particles might have aggregated to a larger silica domain.

Tensile Properties

Introducing silica into the PI by colloidal silica gives well-dispersed particles in the PI matrix. This would give the advantage of achieving reinforcement of the hybrid materials. Morikawa reported that T_g of PI/silica hybrids is decreased by a small content of silica with low molecular weight because of the plasticizing effect,[32] the plasticizing effect, however, was not observed in three PI/Silica nanocomposite films. The tensile properties of the PI/silica nanocomposite films are summarized in Table I; there is a significant tendency that the tensile modulus increases and elongation decreases with an increase in the silica content. With the incorporation of 10% silica, the tensile modulus increases from 2.96 GPa to 3.62 GPa, which is 22% higher than that of the original polyimide. Addition of 30% of silica further increases the modulus to 4.35 GPa, which is *ca.* 47% higher than the neat polyimide. This means that the increase of tensile modulus is mainly based on the reinforcement effect of the dispersed silica particles. The better interfacial interac-

**Table I.** Mechanical properties of PI/silica nanocomposites

PI/silica nanocomposites	Modulus at initial (GPa)	Tensile Strength (MPa)	Elongation at break (%)	CTE ppm/°C
Neat PI	2.96	98	28	38.1
PI/10SiO$_2$	3.62	112	19	22.4
PI/20SiO$_2$	4.08	116	16	12.5
PI/30SiO$_2$	4.35	105	9	9.2
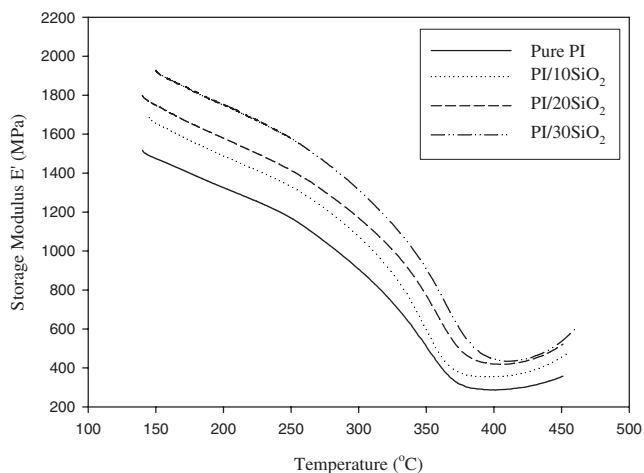
Figure 3. Dynamic mechanical properties of PI/silica nano-composite films as a function of silica content.

Figure 4. tan δ of PI/silica nanocomposite films as a function of silica content.

tion between PI matrix and silica particles as well as the development of fine morphology (SEM images in Figure 1) in the composite films has a positive effect on the improvement of the mechanical properties of the composite films. In fact that modulus does not increase linearly with increasing silica content suggested that silica particles might have aggregated to various degree.

Dynamic Mechanical Properties

The effects of nano-size silica on the thermo-mechanical properties of PI/silica nanocomposites were tested by dynamic mechanical analysis and the results were shown in Figures 3 and 4. From Figure 3, the storage modulus (E') of the films increases with increasing the amount of silica. However, the tan δ of the films decreases with increasing the amount of silica as shown in Figure 4. The decrease of loss modulus could be due to the particles in the films, which make lower the interaction force between molecular chains and a decrease of the viscous response of the visco-elastic material.[22,33] The maximum tan δ is defined as glass transition temperature (T_g) and the values are shown in Figure 4 as 359.5, 378.3, 389.6 and 397.2 °C at the silica content of 0, 10, 20, and 30 wt%, respectively. All PI/silica nanocpoposites show higher T_g than the neat PI. Since the glass transition process is related to the molecular motion, the nano-size particles restrict segmental motion near
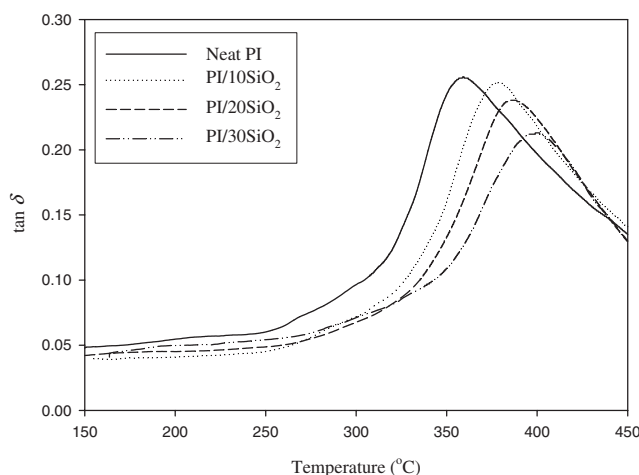
the organic-inorganic interface and result in a higher T_g.[34] The similar results were also observed in PI and layered silicate composites.[10]

Coefficient of Thermal Expansion (CTE)

The coefficient of thermal expansion (CTE) of the neat PI and PI/silica nanocomposite films and the values are listed in Table I. The results indicate that the CTE decreased from 38.1 ppm/°C (neat PI) to 9.2 ppm/°C (PI/30SiO$_2$) with the addition of silica up to 30 wt% loading. The well-dispersed fine particles greatly increase the interfacial area at given silica content and lead to a decrease in the segmental mobility of the PI chain, denser molecular packing, and less free volume. Furthermore, good adhesion between silica and PI matrix, and that inorganic silica has inherently lower CTE value are also factors contributing to decreasing the CTE of PI/silica nanocomposites.

Thermal Stability

TGA were used to monitor the effect of the silica on the thermal stability of the composites. Figure 5 shows the results of TGA analysis of PI/silica nanocomposites. It is shown that the thermal stability increased with silica loading. As shown in Figure 5 the decomposition temperature increases from 562 °C (5% weight loss), 579 °C (10% weight loss) for pure PI to 584 °C, 605 °C for PI/30SiO$_2$. This increase might be due to the filler effect of the silica
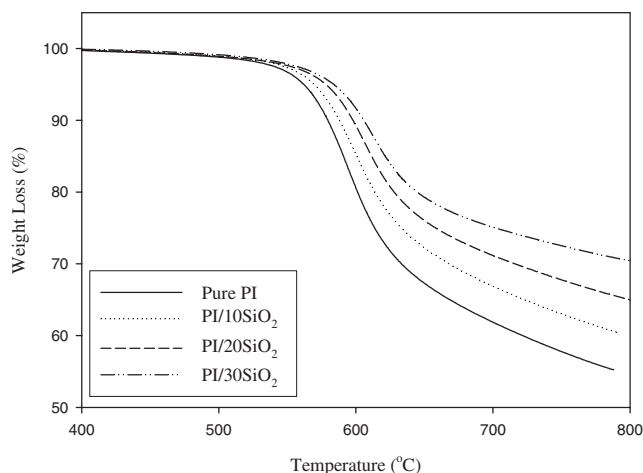
Figure 5. TGA analysis of PI/silica nanocomposite films.

which limited the mobility of molecular chains and hindered the permeability of volatile degradation products out from the material.[9,35] Boggess and Taylor[36] have reported that metallic compounds can oxidatively degrade polyimide and reduce the thermal stability of hybrid films by metal-catalyzed oxidative decomposition. However, the phenomenon is not observed in PI/Silica composites. Silica did not show significant improvement in increasing the thermal stability of the polyimide as clay which only 1% content in the polyimide, the 5% decomposition temperature became higher for *ca.* 208 °C than the corresponding pristine polyimide.[9]

CONCLUSIONS

The PI/silica nanocomposite films were prepared by blending the PAA solutions and commercial colloid silica sol, followed heating to imidazation. The nanoscale silica particles are dispersed well in PI matrix and demonstrated no obvious phase separation. The tensile modulus, T_g and thermal stability of the nanocomposites increase with silica content; this demonstrated that the well-dispersed particles of silica in the hybrid indeed reinforce these nanocomposite films. When CTE decrease with silica content, it implys that the silica particles lead to a decrease in the segmental mobility of the PI chain.

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