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Electrical and thermal properties of polyamideimide-colloid silica nanohybrid for magnetic enameled wire

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Polyamidimide (PAI)-colloidal silica (CS) nanohybrid films were synthesized by an advanced sol-gel process. The synthesized PAI-CS hybrid films have a uniform and stable chemical bonding and there is no interfacial defects observed by TEM. The thermal degradation ratio of PAI-CS (10 wt%) hybrid films is delayed by 100 °C compared with pure PAI sample determined by on set temperature range in TGA. The dielectric constant of PAI-CS (10 wt%) hybrid films decreases with increasing CS content up to about 5 wt% but increases at higher CS content, which is not explained simply by effective medium therories (EMT). The duration time of PAI-CS (10 wt%) hybrid coil is 38 sec, which is very longer than that of pure PAI coil sample. The PAI-CS (10 wt%) hybrid film has a higher breakdown voltage resistance than the pure PAI film at surge environment and exhibits superior heat resistance. The PAI-CS (10 wt%) sample shows the advanced and stable thermal emission properties in transformer module compared with the pure PAI sample. This result illustrates that the advanced thermal conductivity and expansion properties of PAI-CS sample in the case of appropriate sol-gel processes brings the stable thermal emission in transformer system. Therefore, new PAI-CS hybrid samples with such stable thermal emission properties are expected to be used as a high functional coating application in ET, IT and electric power products.

Key words: PAI (polyamidimide)-CS (colloidal silica), Nanoybrid, Sol-gel.

Introduction

In recent years, the attention of organic-inorganic hybrid has been increased because of the inherent limitations in physical properties of organics materials. Organic-inorganic hybrid materials usually have unique properties that traditional composites and conventional materials do not have. In these hybrid materials, aromatic polyimide have been considered to be a suitable matrix materials for advanced technological applications in the electric and microelectronic industries because they have excellent chemical, physical, thermal and mechanical properties owing to the phenyl and imide moieties of the backbone. In addition, silica has been most extensively investigated as an inorganic component due to its catalytic and electronic applications [1, 2, 17].

Since thin films are required in microelectronic, electric motor wires and photonic applications, a special process must be applied instead of the conventional composite preparation technique used for carbon or glass fiber reinforced plastics [3, 4]. One reasonably good approach is the sol-gel process, which can produce small particles which are finely dispersed through in situ polymerization of monomeric precursors. In particular, an important advantage of the sol-gel synthesis for polyimide-silica composites is that the polyamic acid organic matrix acts to prevent agglomeration of the silica, which can lead to nano silica clusters in the composites [5]. In order to make high efficient electric motors, the enameled magnet wire with high winding condensation has to be coated with such insulation film with high thermal resistance and stable dielectric properties [6, 7].

CS is known as its excellent property for preventing thermal and electric stress [6]. Therefore, in sol-gel process, minimizing the degree of phase segregation is most important. In this study, PAI (polyamidimide)-CS (colloidal silica) nanohybrid films were synthesized by an advanced sol-gel process. CS surface was modified by silane treatment for the uniform dispersion and improved interfacial stability of silica nanoparticles in the PAI resin, consequently high performance of PAI-CS nanohybrids. The resulting hybrid samples were evaluated many material characteristics such as microstructure, thermal properties and electrical properties [8]. Especially, the dielectric and thermal properties of these samples were studied in the point of view of stable chemical bonding of nano silica to base resin. The resistance properties of PAI-CS nanohybrid samples were studied by V-t (voltage-time) life test and arc and tracking test. In addition, it was attempted to test the effect of thermal stability on a transformer magnet coil fabricated by PAI-CS nanohybrid enamel, the miniature transformer modules were manufactured, and thermal emission properties were examined [6, 8].

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Experimental

PAI-CS hybridization

Colloidal silica with different size (12 nm and 24 nm) were used as nano filler and methyletrimethoxysilane (MTMS) was used for surface modification of the CS. After silanization of the CS sol MTMS, the CS sol was prepared with the condensation of ethylene monothic-carbonate ethoxy ethanol (EMTC-EC) solution. Commercial polyamideimide (PAI) was used as a varnish resin. The hybridization of PAI and CS sol was via in situ curing condition as show in Fig. 1. Then, the CS composition to PAI was controlled from 0 to 30 wt%. The test films were prepared under the curing condition of 200 °C for 2 hrs, and the resulting film thickness was 30 ± 2 μm. For comparison of electrical and thermal properties, pure PAI and PAI-CS nanohybrid resins were coated on glass or magnetic copper wire as 30 ± 2 μm in film thickness. The compositions and type of test samples are listed in Table 1.

Measurements

FT-IR (Fourier transform infrared) spectra were recorded on a Nicolet Nexus FT-IR spectrophotometer. UV (ultraviolet) visible spectroscopy were measured on a Perkin-Elmer Lambda UV-Vis Spectrometer with the wavelength from 200 nm to 800 nm. The cross-sectional morphologies of PAI-CS nanohybrid samples were observed using a TEM (transmission electron microscopy). TGA (thermal gravimetric analyses) were performed on a Perkin-Elmer Pyris of thermo-gravimetric analyzer at a heating rate of 10 °C/min under air with the temperature range from 30 °C to 800 °C. Dielectric properties were measured on an impedance analyzer (ASTM D 3359), and surge voltage properties were measured on a high voltage test system. The surface-resistance characteristics of samples against thermal arcing were measured on an arc resistance test system (ASTD D495) and tracking test system (ASTM D3638). The thermal stability of magnetic wire was tested according to a temperature rising method on a miniature transformer module as shown in Fig. 2.

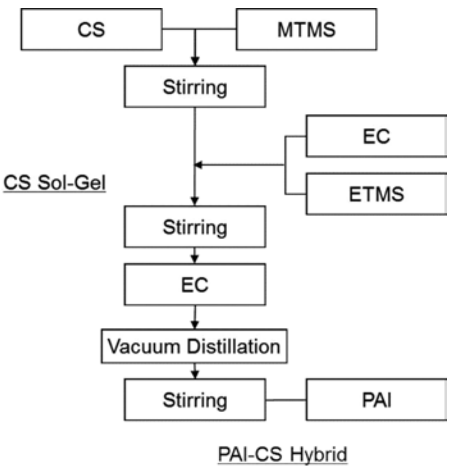

Fig. 1. The preparation of PAI-CS hybrid.

Table 1. Recipe for the PAI and PAI-CS hybrid film.

Samples	Silica Content wt%	Remarks
PAI	0	Commercial
MB06	10	12 nm of Silica
EB06	10	24 nm of Silica

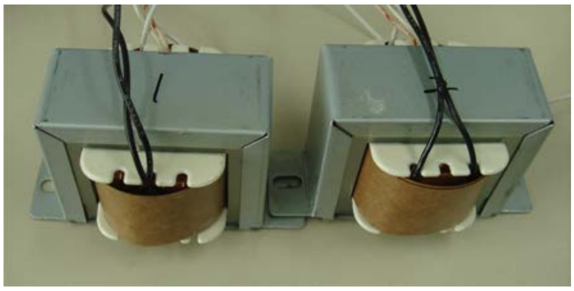

Fig. 2. TR modules for temperature rising test.

Results and Discussion

Hybridization

The IR spectra of PAI resin and PAI-CS (10 wt%) hybrid samples are shown in Fig. 3. The IR peaks of the imide groups near 1650 cm^{-1} and 1720 cm^{-1} were observed. The typical absorption bands from Si-O-Si network vibrations were observed at 1100 cm^{-1}, and which increased with the amount of CS, indicating the formation of a more integrated silica network within the hybrids [9-11]. As shown in Fig. 4, UV optical characteristics of PAI-CS hybrid samples are similar to that of pure PAI in the visible range of 400 nm to 1,000 nm, which indicates the good and stable hybridization. There was no significant difference on FTIR and UV spectra properties with respect to silica particle size between MB06 (12 nm) and EB06 (24 nm).

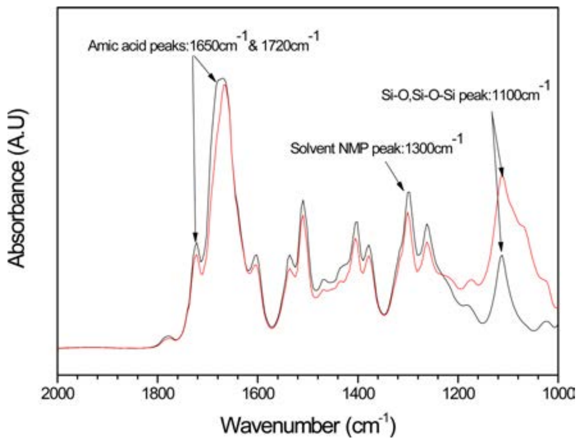

Fig. 3. FT-IR spectra of the PAI-CS hybrids with and without silica.

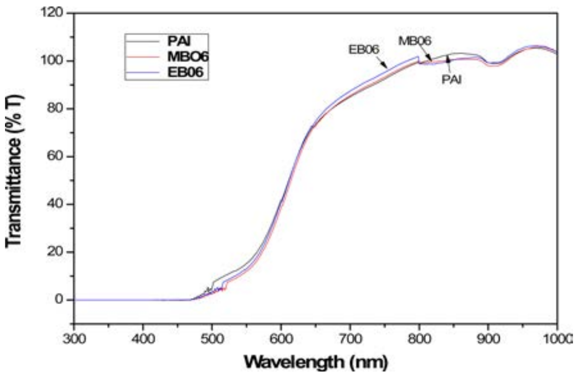

Fig. 4. The effect of silica on the UV-Vis spectra of PAI-CS hybrid films.

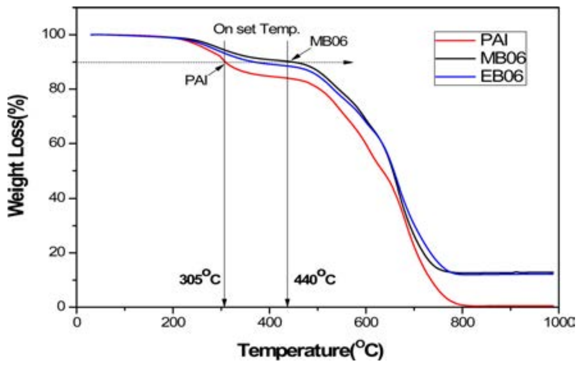

Fig. 6. The TGA curves of PAI-CS hybrid films.

Microstructure

TEM images were used to study the particle dispersion in PAI-CS nanohybrid films. The TEM microstructure of PAI-CS (MB06) hybrid film is shown in Fig. 5. The dispersed silica particles have a diameter of about 12-24 nm, are well distributed without serious aggregation at high silica content. If serious agglomerated clusters were formed, this could create voids in and around the particle clusters due to limited polymer flow in that region or poor wettability. Poor processing can weaken the interaction between the particles and the polymer matrix with creating interfacial defects. Generally, lighter or white boundaries in the TEM image indicate the interfacial defects [12, 13]. In our TEM microstructure photograph, there were no such defects. This shows that PAI-CS hybrid films prepared by CS sol-gel process are uniform with stable chemical bonding. Moreover, there is no particle size increases with the CS content due to the increasing aggregation of silica particles at high silica content. As a result, the nano silica distribution in PAI resin can be effectively controlled by CS sol-gel method according to the suggested processing condition in this study.

Thermal properties

Fig. 6 shows the TGA curves of PAI and PAI-CS (10 wt%) samples. Both the pure PAI and PAI-CS nanohybrid samples are stable up to 500 °C, above which they undergo rapid degradation. But the degradation ratio of MB06 (CS 10 wt%) is delayed by 100 °C compared with the pure PAI sample determined by onset temperature range. Thus, this result shows that the thermal stability of the PAI-CS hybrid films improved compared to the pure PAI film. There was no significant difference in TGA properties respect to the silica particle size between MB06 (12 nm) and EB06 (24 nm).

Electrical properties

The properties of dielectric constant at 100 kHz as a function of CS content in PAI-CS hybrid films are shown in Fig. 7. Generally, the dielectric constant of untreated organic-inorganic composite insulators at kHz-MHz frequency range and room temperature are affected by the content ratio of filler in the base resin when calculated using the effective medium theories (EMT) [9]. The dielectric constant slightly decreases with increasing CS content up to about 5 wt%, however increases at higher content (> 10 wt%), which is contradictory to EMT. The dielectric values calculated using EMT has to decrease with silica contents due to lower dielectric constant value of silica (4.0) than it of the pure PAI (4.5). Here the decrease of dielectric constant of PAI-CS hybrid samples up to CS 5 wt% is because the nano particles appear to reduce the chain movement of polymer through chemical bonging or

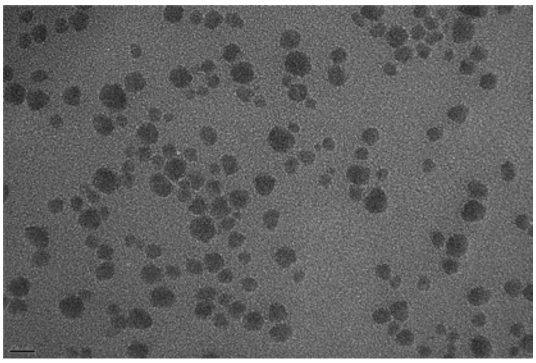

Fig. 5. The TEM photograph of PAI-CS hybrid (MB06).

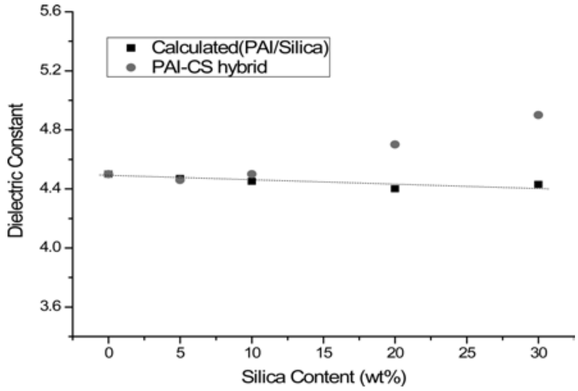

Fig. 7. The dielectric constant with silica content in PAI-Si hybrid film.

confinement. This reduction in chain mobility might contribute to the reduction in polymer chain relaxation due to the physical and chemical bonding of the polymer chain with silica particles. Therefore the increase of interfacial region in polymer networks creates a zone of altered polymer properties which reduces the dielectric constant of nanohybrid sample [14-17]. However, when CS content exceed 10 wt%, the dielectric constant value gradually increases, and reach to 5.0 at 30 wt%. This result may be due to unstable interfacial adhesion with increasing CS content. Thus, appropriate range of CS content in nanohybrid films is found to be under 10 wt% to achieve high performance in thermal and electric properties in this study.

V-t (voltage-time) characteristic test was assessed as an index of resistance against electrical surge aging [6]. We measured the resistance capacity near breakdown voltage (4.6 kV) at 1 kHz on enameled coating samples. As shown in Fig. 8, the duration time of MB06 is 38 sec, which is very longer than that of the pure PAI sample. The PAI-CS hybrid film had a higher breakdown voltage resistance than that of the pure PAI film at surge environment and exhibited superior heat resistance. Since this similar to results from thermal properties, both of the thermal and electrical results may be attributed to the strong interfacial interaction between the PAI resin and nano silica particles.

Fig. 9 shows the arc resistance properties according to ASTM (American Society for Testing and Materials). It is seen that PAI-CS hybrid sample shows the higher

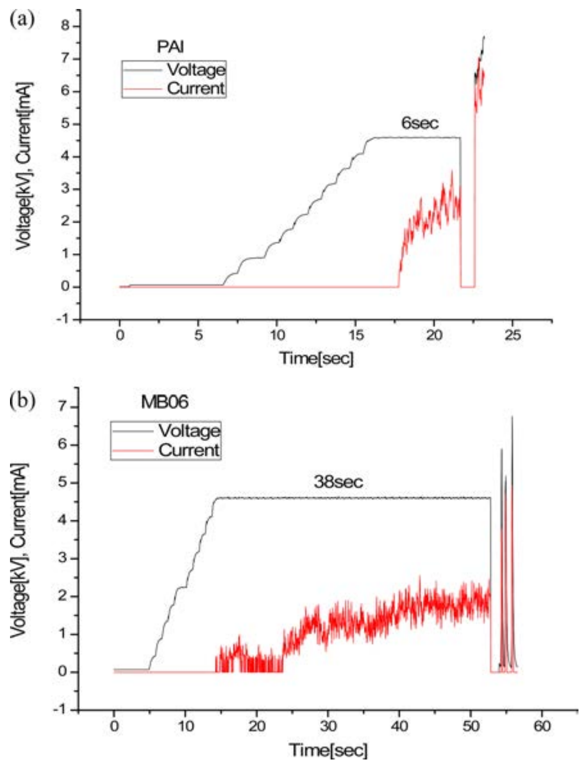

Fig. 8. The V-t properties of PAI-CS hybrid films. (a) PAI and (b) MB06.

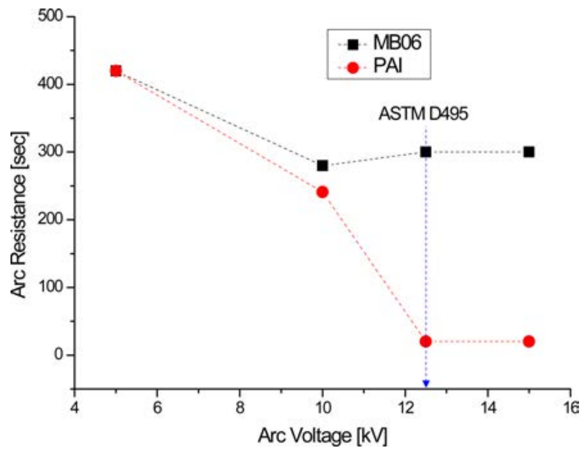

Fig. 9. The duration properties against arc aging of PAI and PAI-CS hybrid films.

resistance ability to arc aging than the pure PAI sample with increasing arc voltage. Especially, the difference of arc resistance ability was increased rapidly above 10 kV. This advanced phenomenon is also reflected in the tracking test. Since the PAI-CS hybrid sample has very uniform and well distributed nano silica in base resin, this can make narrow tracking path and long life against thermal and high voltage erosion as can be seen in Fig. 10.

Thermal stability of magnet wire in TR (transformer) module was investigated through temperature rising test as seen in Fig. 11. In this test condition, the PAI-

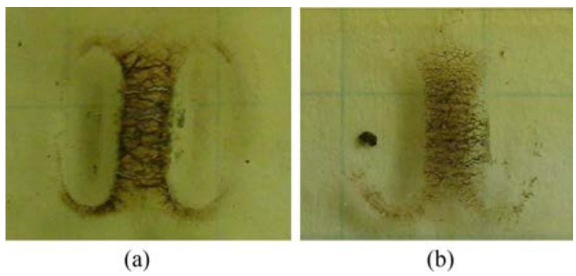

Fig. 10. The surface photography after tracking erosion. (a) PAI and (b) MB06.

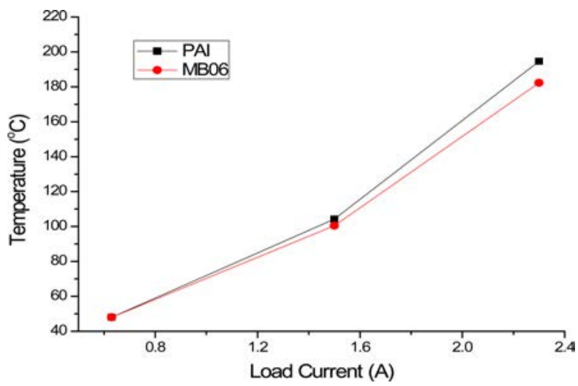

Fig. 11. The thermal emission properties on TR modules.

CS (10 wt%) sample shows the advanced and stable thermal emission properties in TR module compared with the pure PAI sample.

Conclusions

PAI-CS nanohybrid films were synthesized by an advanced sol-gel process. The UV property of PAI-CS (10 wt%) hybrid samples were similar to that of pure PAI in the visible range of 400 nm to 1000 nm, which shows the good and stable hybridization. The dispersed silica particles had a diameter of about 12-24 nm, were well distributed without serious aggregated clusters at high silica content as shown by TEM micrograph. In thermal properties measured by TGA, the degradation ratio of PAI-CS (10 wt%) hybrid sample was delayed by 100 ^{o}C compared with the pure PAI sample determined by on-set temperature range, which shows that the improved thermal stability of the PAI-CS hybrid films. In electrical properties, The dielectric constant slightly decreases with increasing CS content until about 5 wt%, however increases at higher content (>10 wt%), which is contradictory to EMT. This result showed that the appropriate range of CS content in nanohybrid films is found to be under 10 wt% to achieve high performance in thermal and electric properties. From V-t test the duration time of PAI-CS (10 wt%) hybrid coil is 38 sec, which is very longer than that of pure PAI coil sample. The PAI-CS (10 wt%) hybrid film has a higher breakdown voltage resistance than the pure PAI film at surge environment and exhibits superior heat resistance. Especially, from arc and tracking resistance test, the difference of arc resistance was increased rapidly above 10 kV. These advanced properties are suggested to be due to the uniform distribution of nano silica in the base PAI resin, which can make narrow tracking path and long life against thermal and high voltage erosion. The PAI-CS (10 wt%) hybrid sample showed the advanced and stable thermal emission properties in TR module compared with the pure PAI sample. This result illustrates that the thermal conductivity and expansion properties of PAI-CS sample in the case of appropriate sol-gel processes brings the stable thermal emission in TR system. Therefore new PAI-CS hybrid samples with such stable thermal emission properties are expected to be used as high functional materials in ET, IT and electric power products.

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