Preparation and characterization of polyimide/mesoporous silica hybrid nanocomposites based on water-soluble poly(amic acid) ammonium salt

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Abstract
Recently, mesoporous silica was blended with polyimide to develop low dielectric constant (k) materials with improving mechanical and thermal properties of polyimide by utilizing both the nanoporous structure and silica framework. However, even the use of mesoporous silica did not show a significant decrease of k due to the phase segregation in between polyimide and the mesoporous silica materials. In this work, we attempted to prepare polyimide/mesoporous silica hybrid nanocomposites having relatively good phase mixing behavior by utilizing polyimide synthesized from a water soluble poly(amic acid) ammonium salt, which lead to low k up to 2.45. The thermal properties of polyimide were improved by adding mesoporous silicas. For this work, we have fabricated mesoporous silicas through surfactant-templated condensation of tetraethyl orthosilicate (TEOS). Pyromellitic dianhydride (PMDA)-4,4'-oxydianiline (ODA) polyimide was prepared from poly(amic acid) ammonium salt, which had been obtained by incorporating triethylamine (TEA) into PMDA-ODA poly(amic acid) in dimethylacetamide (DMAc), followed by thermal imidization.

1. Introduction
Organic–inorganic hybrids have attracted much interest, since they usually combine desirable organic and inorganic characteristics [1]. These hybrid materials are usually produced by sol–gel reaction which consists of two step reaction: hydrolysis of metal alkoxides to produce hydroxyl groups, followed by the polycondensation of the hydroxyl groups and residual alkoxy groups to form a three dimensional network. Among organic materials, polyimides (PIs) have been widely applied as matrix polymers for the advanced applications such as in the aerospace and the microelectronics industries due to their outstanding characteristics such as good chemical and mechanical properties as well as low dielectric constant (k) [2–5].

Conventionally PIs were prepared in two steps: First, aromatic dianhydride is added to a solution of aromatic diamine in a highly polar aprotic solvent such as dimethylformamide (DMF), dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), or N-methyl-2-pyrrolidone (NMP), until a highly viscous poly(amic acid) (PAA) solution was obtained. Second, poly(amic acid) is converted to polyimide by either thermal or chemical imidization. Since poly(amic acid)s are soluble only in strongly polar solvents as mentioned above, which are toxic, careful handling is necessary to avoid environmental problems. Moreover, due to the hydrolytic instability for PAA over storage, there have been efforts to prepare other precursors of polyimides, such as poly(amic acid) esters, [6,7] and poly(amic acid) ammonium salts (PAS), [8–11] which have no storage problem in solution. Especially, compared to poly(amic acid) and poly(amic acid) ester, PAS is attractive because it is easy to synthesize and is soluble in water, which are beneficial for both the environmental and practical issues.

Silica has been widely used as an inorganic component in hybrid composites to achieve various properties to meet the requirements of different applications [12–25]. Recently,
mesoporous silica (MS) has attracted considerable interests in applications of molecular sieves, catalysts, adsorbents, optical devices, and sensor devices due to their highly ordered and uniform mesoporosity [26]. Most importantly, mesoporous silica films synthesized via a surfactant templating process could provide large pore sizes (5–30 nm), high porosities (45–75%) and controlled pore structures [27]. This makes it possible to introduce voids into the bulk so that the low-\( k \) air (\( k = 1 \)) can be utilized to reduce the dielectric constant of the materials. Many studies showed that the mesoporous silica films have low-dielectric constants in the range of 1.42–2.1 [28–30], which is lower than most of other low dielectric materials, such as silsesquioxane based dielectric, fluorine doped silica film, carbon doped silica film, and organic polymer dielectrics [31]. The low-\( k \) mesoporous silica films can meet the requirements of the new dielectric films with low dielectric constant (\( k < 2.5 \)) for the applications in the microelectronics and the insulations. However, owing to the poor processability of the mesoporous silica films, it is difficult to endue them with toxic solvents or surface modification of mesoporous silica [33–35]. Through using a water-soluble polymeric ammonium salt, these problems could be solved.

This work reports the homogeneous dispersion of mesoporous silica into polyimide matrix. We have fabricated mesoporous silicas through surfactant-templated condensation of tetraethyl orthosilicate (TEOS). PIs using pyromellitic dianhydride (PMDA) and 4,4’-oxydianiline (ODA) were prepared from a water-soluble precursor, poly(amic acid) ammonium salt (PAS), expecting that it might have great advantages from the economical and ecological points as well as dispersibility of mesoporous silicas.

This paper suggests a method which we can prepare low-\( k \) PI hybrid films without significant decreases of properties using nanosheres of MCM-41-like mesoporous silicas.

2. Experimental part

2.1. Materials

Pyromellitic dianhydride (PMDA), 4,4’-oxydianiline (ODA), dimethylacetamide (DMAc), triethylamine (TEA), hexadecyltrimethylammonium bromide (CTAB), and tetraethyl orthosilicate (TEOS) were purchased Aldrich and used as received.

2.2. Preparation of mesoporous silicas

Mesoporous silicas, nanospherical MCM-41 silicas, have been hydrothermally synthesized in sodium hydroxide medium with low surfactant concentration. In the hydrothermal preparation, CTAB was used as cationic surfactants [36], while TEOS served as the silica source. During preparation strong stirring was used to inhibit agglomeration of the formed beads. Aqueous sodium hydroxide was used as base. The mole ratio of starting reactants is 1 TEOS: 0.125 CTAB: 1197 H2O: 0.31 NaOH. The synthesis procedure was as follows: (1) 3.5 cm³ of NaOH (2 mol dm⁻³) solution was mixed with 480 cm³ distilled water; (2) 1.0 g of surfactant was added into the solution with stirring and heating; (3) when the solution became homogeneous, 5 cm³ of TEOS were dropped, giving rise to a white slurry, then keeping the slurry at temperature of about 350 K (This slurry is called as “NC”); (4) after 2 h, the resulting product was filtered, washed with distilled water, dried at ambient temperature, followed by calcination in air at about 820 K for 4 h [37].

2.3. Preparation of poly(amic acid) ammonium salt (PAS) as a water-soluble precursor

As shown in Fig. 1, PAS was prepared from poly(amic acid) in DMAc, by incorporating triethylamine(TEA), followed by mixing to a homogeneous state. The PMDA-ODA PAS solution was prepared with equimolar ratio of PMDA(0.002 mol) and ODA(0.002 mol) in DMAc under nitrogen atmosphere. The reaction was continued for 16 h to make a homogeneous mixture. The solid content of the solution was 10 wt%. After making PAS solution, a given amount of TEA (0.004 mol) was added into PAS solution at room temperature and the mixture was stirred for 45 min under nitrogen atmosphere. Upon the addition of TEA, large increase of viscosity was observed with a local white precipitation of polymer as reported by Kreuz et. al. [38]. The solution was poured into acetone, and the precipitated solid was filtered, dried in vacuum and pulverized in a mortar. Subsequent drying in vacuum at 40 °C for 24 h gave light yellow PAS powder [39].

2.4. Preparation of polyimide/mesoporous silica hybrid films

As shown in Fig. 2, hybrid films were prepared using mesoporous silicas (Nanospherical MCM-41 silicas) and PAS powder. In order to increase solubility of PAS powder in H2O, TEA was added in deionized water (\( \nu/\nu = 2: 98 \text{ TEA}/\text{H}_2\text{O} \)). The MCM-41 were dispersed in TEA/H2O mixture using sonication for 30 min, then adding PAS powder and mixing for 16 h to a homogeneous state. The mixture solutions were spin-coated onto a glass slide, and softbaked at 60 °C for overnight. The solid concentration of hybrid solution was 5 wt% for all solutions due to high viscosity of PAS solutions. These softbaked films were thermally imidized and the process was carried out at 80 °C for 2 h, 140 °C for 1 h, 200 °C for 1 h, 250 °C 0.5 h and 300 °C 0.5 h under nitrogen atmosphere to get hybrid films. The heating rate was 1 °C/min. The sample names (\( M_x \)) were designated according to increasing contents of MS (\( x = 0, 1, 3, 5, 7, 10 \)). For comparison, PMDA-ODA PI was prepared also from their corresponding PAA in DMAc by similar methods as mentioned above (in the absence of TEA). This PI was designated as “conventional PI.”
2.5. Measurements

The wide-angle X-ray diffraction (XRD) data were collected on a Rigaku Miniflex X-ray diffractometer, operated at 40 kV and 30 mA, using Cu Kα (λ = 1.5401 Å) radiation. Nitrogen adsorption and desorption isotherms were measured at 77 K on a Micromeritics ASAP2010 with an accelerated surface area and porometry system. Surface area was
determined by the BET method. The pore size distributions were calculated from the analysis of the adsorption branch of the isotherm by the Barret-Joyner-Halenda (BJH) method coupled with the apparatus software. Transmission electron microscopy (TEM) images were obtained using a JEOL-JEM 2010 electron microscope operated at 200 kV. A drop of diluted suspension of each NC aliquot was placed on a copper TEM grid, covered completely with carbon, and then the solvent was left to evaporate. The functional groups of composite films were examined using a FT-IR spectrometer (React IR\(^\text{TM}\) 1000, Applied System. Materials were characterized by \(^1\text{H}\) NMR (300 MHz, DMSO, 293 K, Varian Unity Plus-300) spectrometer. Small-angle X-ray scattering (SAXS) patterns were measured using synchrotron X-ray source of Pohang Accelerator Laboratory (PAL, South Korea): Co K\(\alpha\) radiations with an energy range of 4–16 keV (energy resolution (\(AE/E\)) = \(5 \times 10^{-4}\), photon flux = \(10^{10}\)–\(10^{11}\) ph/s, beam size = 1 mm\(^2\)). The SAXS scan range was fixed as 0.0012 < \(q\) < 0.3316 Å\(^{-1}\).

The morphology of the fractured surfaces of the hybrid films was measured using a field emission-scanning electron microscopy (FE-SEM, JSM-6700 F, Korea Basic Research Institute) with an acceleration voltage of 20 kV. The thermal decomposition of composite films was measured using thermogravimetric analysis (TGA, Q50, TA Instrument). The heating rate was 20 °C/min in the temperature range between 30 and 900°C. The thermal analysis (thermogravimetric analyser (TGA, Q50, TA Instrument). The heating rate was 20 °C/min in the temperature range between 30 and 900°C. The mechanical (tensile) properties of composite films were measured using a universal testing machine (UTM, Korea Apparel Testing & Research Institute) by employing a strain rate of 10 mm/min at room temperature. The glass transition temperature \(T_g\) was taken from differential scanning calorimeter (DSC, Q100, TA Instrument). The measured dielectric constant was taken by LCR meter (4284A, Agilent) with dielectric kit (16451B, Agilent) at 1 kHz. Before the measurement of dielectric constants, the hybrid films were dried for 1 h at 200°C in order to remove water. Measurements were done in an ambient atmosphere with a constant relative humidity of <20%. Special care was taken in order not to expose the hybrid films to additional artificial moisture when sampling and measuring.

3. Results and discussion

3.1. Characterization of synthesized mesoporous silica

The XRD pattern of the mesoporous silica sample exhibits four sharp Bragg peaks, which can be indexed as (100), (110), (200) and (210) of MCM-41 (Fig. 3). It means that a regular and hexagonal array of uniform channels for conventional MCM-41 materials was successfully synthesized. The repeat distance \(a_0\) between two pore centers in MCM-41 can be calculated from

\[ a_0 = \frac{2}{\sqrt{3}}d_{100} \]  

The pore diameter can therefore be calculated from \(a_0\) by subtraction of the pore wall thickness (~1.0 nm from TEM measurements). Using the obtained \(d_{100}\) value in the XRD pattern, the pore diameter is determined as 3.0 nm [40,41]. We have also investigated the nitrogen adsorption and desorption behavior for the MCM-41 particles with sizes of around 100 nm. The nitrogen sorption isotherm of the sample is shown in Fig. 4, where the isotherm can be classified as the type IV isotherm according to the IUPAC nomenclature [42,43]. In Fig. 4, a linear increase of absorbed volume at low pressures is followed by a steep increase in nitrogen uptake at relative pressure of 0.24 < \(p/p_0\) < 0.34, which is due to capillary condensation inside the mesopores. The long plateau at higher relative pressures indicates that pore-filling is restricted to the inflection point at \(p/p_0 = 0.30\). It is interesting to note in this figure that second steep increase occurs in nitrogen uptake and an adsorbed hysteresis loop appears at the relative pressure of 0.9 < \(p/p_0 < 1.0\). The inset figure gives the pore size distribution evaluated by the BJH method. One sharp peak due to the pore size is at 3 nm and another broad peak due to the bulk particle size is around 100 nm. The surface area is 1921 m\(^2\)/g and pore volume is 2.1 cm\(^3\)/g. The morphologies and microstructure of the obtained MCM-41 samples are clearly revealed by TEM. Fig. 5 shows a typical TEM image of the samples, where nano-sized particles with round sphere or elongated sphere can be seen. The sizes of the particles range from 80 to 140 nm. Careful observation of the high-resolution TEM image of the samples (Fig. 5c, scale bar, 20 nm) shows the existence of highly ordered hexagonal array (of around 3 nm of pore) and streak structural features, which revealed the mesoporous structure of the samples [37]. The results are in agreement with the nitrogen sorption data.

3.2. NMR/FT-IR spectroscopy

The \(^1\text{H}\) NMR spectra of TEA, PAA and PAS can show the chemical structure of these materials obtained by adding TEA into PAA as shown in Fig. 6. The peaks at 1 and 3.5 ppm in Fig. 6 (1) are related to two kinds of protons for –CH\(_3\) and –CH\(_2\) groups. The \(^1\text{H}\) NMR spectra of PAA in Fig. 6 (2) displays different four peaks at 6–9 ppm, which is associated with chemical structure of benzene. We can
confirm the same peaks in Fig. 6 (3). The new two peaks at 1 and 3 ppm are related to protons for attachment of TEA into PAA. The proton of $-\text{CH}_2-$ of TEA was shielded by proton of COOH group of PAA and that peak was shifted to the right. Another peak in Fig. 6 (3)-e indicates proton of COOH, which was shifted to the left due to deshielding of N atom in TEA (see inset).

Fig. 7 shows FT-IR spectra of the conventional polyimide and hybrid composite films. Upon curing, the characteristic adsorption 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, respectively. The bands at 1502 and 830 cm$^{-1}$ correspond to C$_6$H$_4$ and Si–O–Si, respectively. The band at 1173 cm$^{-1}$ is attributed to the C$_6$H$_4$ or C$_6$H$_2$. The peak at 677 cm$^{-1}$ is assumed due to C–C@O in plane swing vibration. FT-IR spectra were used to verify imidization of the PAA by observing the disappearance of the band at 1650 cm$^{-1}$ and the growth of the imide group at 1711 cm$^{-1}$. This observation showed a good agreement with the earlier studies [17,44–48]. The broad band near 1080 cm$^{-1}$, caused by the presence of the Si–O–Si bond, is indicative of the incorporation of mesoporous
silica (MS) in the hybrid composites. It became much stronger and increased with increasing contents of the mesoporous silicas, as can be seen in the selected wavelength ranges in the inset.

3.3. Periodicity of PI in hybrid nanocomposite films

Fig. 8 shows the XRD patterns of the conventional PI and hybrid composite films. The conventional PMDA-ODA
PI is characterized with a major diffraction peak at $2\theta = 10\text{–}40^\circ$. There were no significant differences in between PI and M0. This result indicates that the M0 sample using the PAS has almost same crystallinity comparing with the conventional PI’s amorphous structure. The XRD pattern of the M10 sample shows that there is another structure, which has an original framework as well as pristine PI in the composite film. It is revealed more evidently in the inset. The XRD pattern of M10 ($2\theta = 0\text{–}10^\circ$ in the inset) is consistent with the XRD pattern of the original MS (Fig. 3). The sharp peak at $2\theta = 0\text{–}6^\circ$ was increased with increasing contents of MS. From this result, we can conclude that the structure of MS was not destroyed or changed in hybrid composite films with maintaining the order and/or packing of PI molecular chains. In addition to the ordering characteristics (Fig. 8), the nanostructure of hybrid nanocomposite films can be analyzed from the Lorentz-corrected SAXS patterns (Fig. 9) [49–51]. All films show a broad SAXS peak at $0.01 < q < 0.14 \text{ Å}^{-1}$ which is attributed to the mean long period of PMDA-ODA PI.

**Fig. 8.** XRD patterns of composite film Mx (scan speed 2°/min; inset: 0.2°/min for PI/M0/M10).

**Fig. 9.** Lorentz-corrected SAXS patterns of conventional PMDA-ODA PI and hybrid films (a): PI, (b): M0, (c): M1, (d): M3, (e): M5, (f): M7, and (g): M10 (inset: magnified $iq^2$ of PI in the range of $0.01 < q < 0.14 \text{ Å}^{-1}$).
(~66 Å for pristine film; see also inset). Basically the increased long period can be attributed to the grown size of crystal or phase domains. The long period of the hybrid nanocomposite films was increased with increasing contents of mesoporous silica in the hybrid films. The peaks around $0.15 \leq q \leq 0.20 \text{ Å}^{-1}$ became stronger when adding MS, which was consistent with previous XRD patterns.

### 3.4. Morphology of hybrid nanocomposite films

Fig. 10 displays the effective dispersion of MS, as revealed by the FE-SEM images of cross section of hybrid nanocomposites. Even for the sample with 10 wt% mesoporous silicas, MS, are well dispersed in the film as shown in Fig. 10f. It displays that the MS's particle sizes range from 80 to 140 nm in the hybrid nanocomposite films. This result is following the characterizations of original MS by BET/TEM/XRD measurements. Though some researchers experienced difficulties in dispersion of mesoporous silica in nanocomposite films [33–35], we can see that there were no significant aggregations of MS in the hybrid films. As discussed previously, we prepared the hybrid nanocomposite precursor in water and thus it is much easier to disperse MS that is synthesized in water.

### 3.5. Mechanical, thermal, and electrical properties of hybrid nanocomposite films

Table 1 shows mechanical properties of hybrid nanocomposite films and indicates that the contents of mesoporous silica have significant effects on the mechanical properties of PI. The tensile modulus for M3 and M5 hybrid

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**Fig. 10.** Fractured surface morphology of composite films (a) M0, (b) M1, (c) M3, (d) M5, (e) M7, and (f) M10 in high magnification (40,000×).
nanocomposites was slightly higher than that of the pristine PI, though the tensile strength of hybrid films shows gradual decrease with increasing mesoporous silica contents. The elongation at break of hybrid films also presents decrease with the addition of MS.

Thermogravimetric curves of the conventional PMDA-ODA PI and hybrid nanocomposites are shown in Fig. 11. It is shown that the thermal stability of the PMDA-ODA PI is increased by increasing contents of MS in terms of the initial loss of weights around 550 °C (see a dotted line). The increase in the weight residues above 750 °C suggests successful formation of hybrid nanocomposites possessing higher amount of silica. The thermal stability of PI is increased by addition of the mesoporous silica materials in terms of the weight residues above 750 °C. The increase in weight residues above 750 °C suggests successful incorporation of higher amount of silica into the composite films and ultimately increases the thermal stability [34,35,52]. It should be noted, however, that dynamic thermogravimetry registers only decomposition products which evaporate at a given temperature. A polymer may suffer quite a bit of chemical degradation before it loses the first gaseous products. In a hybrid film, often only the polymer can contribute to the formation of volatile decomposition products. This appears as a reduced weight loss at a given temperature as compared to the parent polymer, but it may do not tell about the actual chemistry of the decomposition reaction and hence the actual thermal stability. Thus, further detailed kinetic analysis of the TGA curves should be done to draw a definite conclusion on the thermal stability of hybrid films [53].

The glass transition temperature ($T_g$) of the hybrid nanocomposite films are presented also in Table 1. The polyimide with 10 wt% MS has higher $T_g$ by up to 16.4 °C than that of the pristine polyimide. The rigidity of MS effectively constrains the polyimide main chain motion, thus increasing the $T_g$ of the hybrid nanocomposites. As shown in Table 1, the dielectric constant was decreased with increasing contents of MS up to 5 wt% from 3.34 of the neat PI to 2.45 by addition of 5% MS. The reduction of the dielectric constant is attributed to the addition of the air volumes ($k = 1$) stored within mesoporous silica and the air voids existing in the gaps on the interfaces between the PI matrix and MS (as shown in Figs. 5 and 10). In case of over 7 wt%, however, the dielectric constants were gradually increased with increasing contents of MS. The incorporation of too much mesoporous silica results in its aggregation and poor dispersion. In this case, parts of both the air volumes and the air voids may be closed up due to aggregated MS particles, leading to a decrease of the total air volumes, and thus an increase of the dielectric constant. [35].

<table>
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<tr>
<th>Sample</th>
<th>Tensile modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
<th>$T_g$ (°C)</th>
<th>Dielectric constant</th>
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<tr>
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</table>

**Table 1**
Mechanical, thermal, and electrical properties of PI/MS nanocomposites films

Fig. 11. TGA curves of the conventional PMDA-ODA PI and polyimide hybrid nanocomposites with various MS contents.
4. Conclusions

We have discussed preparation and characterization of PMDA-ODA polyimide/mesoporous silica hybrid nanocomposite films using a water soluble poly(amic acid) ammonium salt. The mesoporous silica materials were hydrothermally synthesized and their size ranged from 80 to 140 nm in diameter. The $^1$H NMR and FT-IR spectra show that PAS as a water soluble precursor of PI and PI/MS hybrid nanocomposite films were successfully prepared. The XRD patterns and FE-SEM images confirmed that there were mesoporous silicas in hybrid films without aggregation or deformation. The thermal stabilities were increased though mechanical properties were generally decreased with increasing mesoporous silica contents. The dielectric constant of these materials can be reduced decreasing air voids between PI matrix and MS. The hybrid nanocomposite materials based on nanosphere of MCM-41 and PI prepared from a water-soluble precursor may attract much interest because of their potential applications in the electronic and environment-friendly industries.

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