Preparation and properties of polyimide/graphene oxide nanocomposite films with Mg ion crosslinker

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A B S T R A C T
Polyimide(PI)/graphene oxide(GO) nanocomposite films were prepared by chemical cross-linking using small amounts of divalent Mg ions. The PI/GO nanocomposites showed enhanced tensile properties compared to pristine PI due to the presence of exfoliated GO in the PI matrix as well as crosslinking between poly(amic acid) (PAA), which is a precursor of PI, and GO by Mg ions. The hydrogen bonds between PAA and GO suppressed the phase separation between PI and GO, and small amounts of Mg ions can bond between the oxygen functional groups and carboxylate groups of GO and PAA.

1. Introduction
Polymer-based composites were reported in the 1960s as a new paradigm for materials. High-performance lightweight composites could be developed and tailored to individual applications by dispersing strong and highly stiff fibres in a polymer matrix [1]. Polymer composites, particularly those containing conducting fillers, have been studied extensively over the past few decades because they can be utilized in electromagnetic shielding, antistatic coatings, batteries, light emitting devices and other applications [2]. Among these conducting fillers, nanostructured carbon materials with graphene structures, such as carbon nanotubes (CNTs), carbon nanofibres (CNFs) and fullerenes, have been studied widely owing to their unique electric and micro- and macro-structural characteristics [3]. Graphene has attracted recent attention in material sciences owing to its unique structure of a two-dimensional sheet composed of sp²-bonded carbon atoms with a one-atomic thickness. Graphene has a high aspect ratio (the ratio of lateral size to thickness), excellent electrical conductivity, and good tensile properties, which makes it an attractive candidate for use as an electronic and tensile filler. Furthermore, the presence of a paper-like structure may render graphene superior to CNTs for dispersion in a polymer matrix [4]. Among the known methods for creating graphene-based materials, graphene oxide (GO) by the oxidation of graphite is a versatile and easy processing method. GO has a wide range of oxygen functional groups on both the basal planes and edges [5–8]. In addition, it can be simply exfoliated and well-dispersed as graphene paper in both water and organic solvents for a range of applications in materials science including nanocomposites. Therefore, these materials have attracted attention as prominent hosts for hybrid materials, particularly with a polymer matrix [4,9–18].

Aromatic polyimides (PIs) are well known high-performance polymeric materials owing to their good tensile properties, high-temperature durability, excellent chemical and thermal stabilities, low thermal expansion coefficient and low-dielectric constant [18–20]. Recently,
the development of new technologies, such as large-scale integrated circuits and superconducting cables, etc., has highlighted the need for high performance polyimide hybrid films with a lower dielectric constant. For this application, a polyimide composite is one of the best candidates because it can maintain these excellent properties with a lower dielectric constant for superconducting cables and large-scale integrated circuits as well as further enhance the specific properties. In this regard, polyimide/GO nanocomposites were synthesized in our previous work by dispersing graphene sheets in a PI matrix, where the GO was found to be aligned two-dimensionally (2-D) in the polymer matrix with no covalent interactions between the PI chains and graphene sheets. In the work, graphene carboxylic acid (GCA) was synthesized by modifying COG with excess carboxylic acid groups (−COOH) [21].

The present paper introduces graphene in polyimide to control the dielectric constant (k) from low k to high k by chemical cross-linking using small amounts of divalent metal, i.e. Mg2+ ions. The PI composites with GO nano-sheets exhibited enhanced tensile properties compared to those of pristine PI. These properties were attributed to the presence of exfoliated graphene oxide in PI composite films. The hydrogen bonds between poly(amic acid) (PAA) and GO suppressed the phase separation between PI and GO and showed enhanced tensile properties. In addition, the introduction of small amounts of Mg ions also enhanced the tensile properties of the composites due to chemical cross-linking between GO and PAA. Recently, Park et al. reported cross-linked graphene paper with metal ions [22]. The material showed enhanced tensile properties (tensile stiffness = 100–200%) and fracture strength (~50%) of graphene oxide with small amounts of Mg2+ and Ca2+, where Mg2+ was found to be more effective than Ca2+. They also suggested bridging the edges of GO paper through carboxylate chelates to the metal. In this sense, PI–GO nanocomposites were prepared and characterized with Mg2+ ion as a crosslinker in this work.

2. Experimental part

2.1. Materials

Natural graphite powder of conducting grade (−325 mesh) was purchased from Alfa Aesar and used as received. Pyromellitic dianhydride (PMDA) and 4,4’-oxydianiline (ODA) were used to prepare the precursor poly(amic acid). PMDA was purified by heating in a vacuum oven at 150 °C for 12 h. Mg(OH)2 was used as the crosslinker. The other chemicals used, including N,N-dimethylacetamide (DMAc), NaNO3, H2SO4, KMnO4 and H2O2, were of reagent grade. These materials were purchased from Aldrich and used as received.

2.2. Preparation of graphene oxide

Graphene oxide was prepared using the Hummers method [23–25]. Ten grams of natural graphite and 7.5 g of NaNO3 were placed in a flask. Subsequently, 621 g of H2SO4 was added to the flask, and the mixture was stirred vigorously for 12 h in an ice water bath. 45 g of KMnO4 was added gradually and the solution was stirred for 5 days at 20 °C to obtain a viscous liquid. The solution was added to 1 L of an aqueous 5 wt.% H2SO4 solution with stirring for 1 h. H2O2 (as 30% aqueous solution, 30 g) was then added to the above liquid with stirring for 2 h.

The mixture was purified by repeating the following procedure cycle 15 times to remove any ions of oxidant origin: 1 (centrifugation) →2 (elimination of the supernatant liquid) →3 (re-dispersion in 3 wt.% H2SO4/0.5 wt.% H2O2). These purification procedures were repeated a further 3 times except that the liquid added was replaced with water. The supernatant liquid was removed and the residue was freeze dried over a 2 day period to obtain a homogeneous graphene oxide powder.

2.3. Preparation of polyimide-graphene oxide nanocomposite films

To obtain a homogeneous GO suspension for the preparation of poly(amic acid) (PAA)–GO nanocomposites with different concentrations of GO were dispersed in DMAc (5 ml) under sonication for 6 h. ODA (0.48 g, 2.4 mmol) was placed into a flask containing different concentrations of the GO suspension under a nitrogen purge in a ultrasound bath. After ODA was dissolved in solution, PMDA (0.52 g, 2.4 mmol) was added and the mixtures were stirred at room temperature with a nitrogen purge for 12 h. Mg(OH)2 (0.012 g, 0.2 mmol) was then added to the above.

Table 1
Preparation of the PI–GO nanocomposite films.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>PAA + DMACa</th>
<th>Graphene oxideb (Wt.%)</th>
<th>Mg(OH)2 (g)</th>
<th>Film statec</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI</td>
<td>6</td>
<td>–</td>
<td>0</td>
<td>T</td>
</tr>
<tr>
<td>PI 0.5</td>
<td>6</td>
<td>0.5</td>
<td>0</td>
<td>T</td>
</tr>
<tr>
<td>PI 1</td>
<td>6</td>
<td>1</td>
<td>0</td>
<td>O</td>
</tr>
<tr>
<td>PI 2</td>
<td>6</td>
<td>2</td>
<td>0</td>
<td>O</td>
</tr>
<tr>
<td>PI 5</td>
<td>6</td>
<td>5</td>
<td>0</td>
<td>O</td>
</tr>
<tr>
<td>XLPIa</td>
<td>6</td>
<td>–</td>
<td>0.012</td>
<td>T</td>
</tr>
<tr>
<td>XLPI 0.5a</td>
<td>6</td>
<td>0.5</td>
<td>0.012</td>
<td>T</td>
</tr>
<tr>
<td>XLPI 1a</td>
<td>6</td>
<td>1</td>
<td>0.012</td>
<td>O</td>
</tr>
<tr>
<td>XLPI 2a</td>
<td>6</td>
<td>2</td>
<td>0.012</td>
<td>O</td>
</tr>
<tr>
<td>XLPI 5a</td>
<td>6</td>
<td>5</td>
<td>0.012</td>
<td>O</td>
</tr>
</tbody>
</table>

a Weight of PAA + DMAC (=1:5) solution.
b Graphene oxide content (wt.%) in PAA.
c Film state of PI and PI–GO nanocomposite films: T;Transparent. O;Opaque.
d API-GO nanocomposite films crosslinked with Mg ions.
solution to cross-link PAA with GO with constant stirring. The amount of Mg(OH)$_2$ was adjusted to be almost the same quantity as that of 1 wt.% GO powder. (It was difficult to measure the number of moles of GO). After 1 day, viscous PAA–GO solutions were obtained. The precursor mixture solutions were cast onto a clean and dry glass substrate, and soft-baked at 80 °C for 6 h. These soft-baked films were imidized thermally by a stepwise imidization

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**Fig. 1.** XRD patterns of graphite (black) and graphene oxide (red) powder (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

**Fig. 2.** TGA curves of graphite (black) and graphene oxide (red) powder (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).
process under a nitrogen atmosphere for 30 min at 140, 220 and 250 °C. The heating rate was ~2 °C/min, which resulted in the poly (4,4’-oxydianiline pyromellitimide) (PMDA–ODA PI)–GO nanocomposite films. Table 1 lists the detailed specifications for the preparation of hybrid precursor films and corresponding name of the samples, where XLPI stands for the PI/GO nanocomposite films crosslinked with Mg ions.

2.4. Characterization

Wide-angle X-ray diffraction (WAXD) measurements were performed using a conventional X-ray diffractometer [Rigaku Miniflex, CuKα (λ = 1.5418 Å)] at a scan speed of 1 °C/min. Thermogravimetric analysis (TGA) was performed using a TGA (Q500 Series, TA Instrument). The heating rate was 10 °C/min over the temperature range, 30 and 800 °C, under a nitrogen atmosphere. The glass transition temperature (Tg) was determined using a dynamic mechanical analyzer (DMA) (N535-0001, Perkin-Elmer) by employing a sample (guage) length of 5 cm, sample width of 1 cm, heating from room temperature to 500 °C at a rate of 5 °C/min, and a head oscillation frequency of 1 Hz. The morphology of graphite and graphene oxide powder was measured by field emission–scanning electron microscopy (FE–SEM, JSM-6700F) with an acceleration voltage of 15 kV. Mg mapping of the fractured SEM images with energy dispersive X-ray (EDX) spectra of the PI–GO and XLPI–GO nanocomposite films were also measured. The UV–Vis spectra were obtained on a Hitachi U-2010 spectrometer. The scan wavelength ranged from 400–800 nm. The tensile properties of the composite films were measured using a universal testing machine (UTM, Korea Apparel Testing & Research Institute) at a strain rate of 10 mm/min at room temperature (sample length = 2.5 cm; sample width = 0.5 cm). The mean of five specimens per sample was taken as the final values. The dielectric constant was measured by Broadband Dielectric Spectroscopy (Novocontrol-Concept 80, Novocontrol) from 1 to 1 MHz. Energy dispersive X-ray (EDX) fluorescent mapping of a cross-section of the PI-GO nanocomposite was carried out by Hitachi scanning electron microscopy (SEM, 955288(A), Hitachi, Japan). The morphology of the composite films were measured by Field Emission Transmission Electron Microscope (FE-TEM, EM-912). The surface resistance of the PI–GO nanocomposite films were measured using a surface resistance tester (ST-3, SIMCO).

Fig. 3. SEM images of (a),(b) graphite powder and (c),(d) graphene oxide powder (scale bars-low magnification (a),(c) 10 μm and high magnification (b),(d): 300 nm).

Fig. 4. Photographs of PMDA–ODA PI–GO nanocomposite films with various graphene oxide contents.
3. Results and discussion

3.1. Characterization of graphene oxide

Fig. 1 shows the X-ray diffraction (XRD) patterns of natural graphite and graphene oxide. The diffraction peak at approximately 10.4° 2θ (d spacing = 8.5 Å) corresponding to the (001) plane reflection of GO was lower than that of natural graphite at approximately 26° 2θ (d spacing = 3.4 Å), which confirms the successful oxidation of graphite [26] and Fig. 2 shows the thermogravimetric analysis (TGA) curves for graphite and graphene oxide. GO powder underwent a two step thermal degradation process, which was distinctly different from the graphite curve. The 1st step was attributed to the loss of H2O at ~100 °C, and the 2nd step appeared at ~200 °C for the loss of acidic functional groups and residues. In contrast, natural graphite showed no weight loss until 800 °C [27].

Fig. 3 shows a low-magnification (a and c scale bars are 10 μm) and high-magnification (b and d scale bars are 300 nm) image of the graphite and graphene oxide powder. The graphite papers (Fig. 3a) had a 50 μm diameter and a regular square-layered structure. On the other hand, graphene oxide powder had a small build by ultrasonication. Individual graphene has a wrinkled paper-like structure with a size up to 10 μm.

3.2. Characterization of PI–GO nanocomposite films

The prepared PI–GO nanocomposites were high-quality flexible films, as shown in Fig. 4. Fig. 5 shows XRD patterns of the PMDA–ODA PI–GO nanocomposite films as well as

![XRD patterns](image-url)
graphite powder (Fig. 5a) and PMDA–ODA XLPI–GO nanocomposite films (Fig. 5b) with various graphene oxide contents. In Fig. 5, none of the PI and XLPI composite films showed a diffraction peak at $10.4^\circ 2\theta$ ($d$ spacing = 8.5 Å) corresponding to the (001) plane reflection of GO. Normally, there are two types of nanocomposites depending on the dispersion of particles. The first type is an intercalated polymer-inorganic material nanocomposite that consists of well-ordered multilayers of inorganic fillers. In the nanocomposite samples, the extent of polymer penetration was not sufficient to delaminate the ordered structures. The second type is an exfoliated polymer-inorganic filler nanocomposite, in which there is a loss of ordered structures due to the extensive penetration of polymer into the inorganic filler layers [28]. With the PI–XLPI composite films, XRD indicated the possibility of having exfoliated graphene layers dispersed in PI. On the other hand, a broad but more intensive peak was observed at approximately $20^\circ 2\theta$ with increasing GO content. This may not be related to graphene oxide but to graphite, meaning that the graphene oxide paper had been converted to a layer-by-layered structure similar to graphite, as confirmed by SEM, which will be shown later.

The optical properties of the nanocomposite films were characterized by UV–visible transmittance spectroscopy (Fig. 6). PI and XLPI exhibited 70–80% optical transmittance.

![Image](image.png)

Fig. 6. UV–visible transmittance spectra of the PMDA–ODA PI–GO nanocomposite films (a) and cross-linked PI–GO nanocomposite films (XLPI, b) with various graphene oxide contents.

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On the other hand, the transmittances of the composite films decreased with increasing graphene oxide content. The cut off wavelength in the visible region (400–800 nm) was observed in the 5 wt.% graphene oxide composite films. The visible opacity of GO increased in proportion to the number of few-layered graphene layers, which is a consequence of the special electronic structure of graphene oxide. Recently, Geim et al. also reported that a single graphene paper, only one atom thick, absorbed a significant fraction (optical transparency = 2.3%) [29]. In this point of view, a cross-linker (Mg(OH)₂) in the XLPI series contributed to the layer-by-layer structure of the GO and the increase in visible opacity, even for the composites with a low weight concentration of GO.

The tensile properties of the PI–GO composite films were measured at room temperature. In general, for a particular polymer, the tensile properties are dependent on many factors, such as viscosity (molecular weight), processing conditions, thermal history of the polymer specimens, etc. [30]. Table 2 summarizes the tensile properties of the PMDA–ODA PI–GO nanocomposite films. Both the tensile strength and Young’s modulus increased with increasing graphene oxide content up to a certain composition (~1 wt.% for both the PI and XLPI composite series. The enhanced tensile properties were attributed to the dispersion of graphene oxide via chemical cross-linking, which results in enhanced interactions between graphene oxide and polyimide. Both 1 wt.% composite films in PI and XLPI showed the highest tensile properties. The tensile strength and Young’s modulus of the 1 wt.% composite films were increased by 4% and 24%, respectively. In the case of XLPI, these properties also increased at 1 wt.% (tensile strength; 10%, Young’s modulus; 21%). This was caused by the presence of exfoliated graphene oxide as a tensile filler in the PI composite films. On the other hand, the tensile strength and Young’s modulus were reduced significantly over 2 wt.% graphene oxide by a heterogeneous dispersion and aggregation in a polyimide matrix (see also the TEM images, which will be shown later). For comparison, we prepared PI–GO composite films with another condition for checking the improvement of tensile properties. We just changed the imidization temperature step to 30 min at 140 °C, 30 min at 220 °C and 2 h at 300 °C, respectively. In this case, tensile properties were improved compared to the present imidization conditions used in this paper. Especially Young’s modulus of PI was increased about 1.7 times compared to the present PI (see Supplementary Table S1). Careful inspection of Table 2 and Supplementary Table S1 indicates the enhancement of Young’s modulus and tensile strength by the incorporation of GO nanoparticles into PI matrix for both PI and XLPI nanocomposite films, when the GO content was 1 wt.%. It should be noteworthy, however, that the effect of the incorporation of Mg²⁺ ions is higher than the effect of introduction of GO nanoparticles into the PI, though both GO nanoparticles and Mg²⁺ crosslinker synergistically enhanced the mechanical properties of PI. This result might be possibly due to the role of Mg²⁺ ions that can bond between the PI’s with electrostatic attractions. Fig. 7 presents theoretical predictions using the Halpin-Tsai theory for nanocomposite films. The Halpin-Tsai model is used widely for predicting the modulus of unidirectional or randomly distributed filler-reinforced composites [31–34]. For randomly oriented or unidirectional graphene sheets in a polymer matrix, the composite modulus \( E_c \) and \( E_l \) can be expressed as follows:

\[
E_c = E_m \left( \frac{3 + \nu_g + \nu_t}{1 - \nu_t} \right) \left( \frac{1}{1 - \nu_t} \right)^{\frac{1}{1 - \nu_t}}
\]

\[
E_l = E_m \left( \frac{1 + \nu_g + \nu_t}{1 - \nu_t} \right) \left( \frac{1}{1 - \nu_t} \right)^{\frac{1}{1 - \nu_t}}
\]

\[
\eta_l = \frac{(E_g/E_m) - 1}{(E_g/E_m) + \zeta}
\]

\[
\eta_t = \frac{(E_g/E_m) - 1}{(E_g/E_m) + 2}
\]

\[
\zeta = 22/3 = 2l_g/\ell_g
\]

where \( E_c \) and \( E_l \) represent the Young’s modulus of the randomly distributed GO and GO aligned parallel to the surface of the composite films, respectively. \( E_g \) and \( E_m \) are the Young’s modulus of the GO and polymer matrix. \( l_g \) and \( \ell_g \) refer to the aspect ratio, length and thickness of the modified graphene oxide sheet, respectively, and \( V_c \) is the volume fraction of GO in the hybrid composites. The Young’s modulus of approximately 0.25 TPa was taken from the literature for a chemically reduced graphene oxide sheet [35]. The Young’s modulus of pure polyimide was 1.34 GPa (PI series) and 2.22 GPa (XLPI series) from the experimental data. The density of the polyimide matrix and GO was 1.43 and 2.25 g cm⁻³, respectively. The statistical average, \( l_g \) and \( \ell_g \), of the graphene oxide sheet were approximately 350 and 2.3 nm. Substituting these parameters into Eqs. (1)-(5), the Young’s modulus of the nanocomposite was calculated according to Liang, et al. [36] under two hypotheses: (i) GO aligned parallel to the surface of the sample film and (ii) GO dispersed randomly as 3D network throughout the polymer matrix. The experimental results for the PI–GO nanocomposites (Fig. 7a) shows that GO is distributed randomly in the polymer matrix, rather than aligned parallel to the surface in the polyimide matrix. In the case of XLPI (Fig. 7b), it also has a similar 3D random behavior except for the 2D aligned pattern in the 0.32 vol.% GO composite. Cross-linking by

### Table 2
Tensile properties of the PI–GO nanocomposite films.

<table>
<thead>
<tr>
<th>Sample (wt%)</th>
<th>Tensile strength (MPa)</th>
<th>Young’s modulus (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI</td>
<td>87.5 (±5)</td>
<td>1347.3 (±70)</td>
<td>22.2 (±7)</td>
</tr>
<tr>
<td>PI 0.5</td>
<td>82.1 (±2)</td>
<td>1352.3 (±100)</td>
<td>18.6 (±2)</td>
</tr>
<tr>
<td>PI 1</td>
<td>90.6 (±1)</td>
<td>1680.6 (±10)</td>
<td>11.2 (±3)</td>
</tr>
<tr>
<td>PI 2</td>
<td>88.3 (±3)</td>
<td>15.1 (±100)</td>
<td>11.7 (±3)</td>
</tr>
<tr>
<td>PI 5</td>
<td>74.3 (±6)</td>
<td>1331.5 (±90)</td>
<td>7.3 (±4)</td>
</tr>
<tr>
<td>XLPI 0.5</td>
<td>73.5 (±5)</td>
<td>2215.9 (±60)</td>
<td>6.5 (±1)</td>
</tr>
<tr>
<td>XLPI 1</td>
<td>80.0 (±5)</td>
<td>2668.7 (±90)</td>
<td>4.7 (±1)</td>
</tr>
<tr>
<td>XLPI 2</td>
<td>59.5 (±6)</td>
<td>2535.6 (±120)</td>
<td>4.2 (±1)</td>
</tr>
<tr>
<td>XLPI 5</td>
<td>51.3 (±6)</td>
<td>2597.1 (±100)</td>
<td>3.9 (±1)</td>
</tr>
</tbody>
</table>

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Mg$^{2+}$ ions between poly(amic acid)(PAA) and GO suppressed the phase separation between PI and GO, enhanced the tensile properties and exhibited a 2D aligned behavior at low GO contents. On the other hand, this cross-linking trend decreased above these contents. This 2D aligned tendency was reported in the literature [37,38] with the explanation that external tensile loads are transmitted to a GO filler across the graphene–polyimide interface through strong interfacial interactions, and the graphene oxide sheets prefer to align parallel to the surface of the sample film within the nanocomposites at low GO concentrations [38]. Both PI–GO and XLPI–GO nanocomposite films rather fit the 3D random distribution model of the Halpin-Tsai theory. Nevertheless, the elongation at break of the composite films decreased with increasing graphene oxide content. These tensile results are similar to those reported elsewhere [39,40]. Although traditional composites require a significant quantity (≈60 vol.%) of filler for property enhancements, a dramatic change in properties is possible even at a very low GO loading (<2 vol.%) for the GO containing nanocomposites, and such performance modulation is generally related to optimizing the dispersion, interface chemistry and nanoscale morphology of the composite matrix. [41]

Fig. 7. Young’s modulus of PMDA–ODA PI–GO nanocomposite films (a) and cross-linked PI–GO nanocomposite films (b) with various GO contents. Theoretical predictions using the Halpin-Tsai theory for the nanocomposite films are also shown in the figure.
Fig. 8 shows the FE–TEM images of the PI–GO nanocomposite film(a) and XLPI–GO nanocomposite film(b) with 1 wt.% of graphene oxide contents. In the PI–GO nanocomposite, graphene oxide sheets are aggregated and not dispersed well in the polymer matrix. In contrast, graphene oxide films are homogeneously dispersed in the XLPI–GO nanocomposite. In XLPI–GO films, we may expect the improvement of mechanical and dielectric properties due to the well dispersed graphene oxides in PI films. Fig. 9 shows the Mg mapping of the fractured SEM images and EDX spectra of the PI–GO 5 wt.% nanocomposite film and XLPI–GO 5 wt.% nanocomposite film. The maintenance of well-dispersed Mg ions as a cross-linker was clearly observed in the XLPI–GO 5 wt.% film but was not found in PI–GO 5 wt.%.

The glass transition temperature ($T_g$) of the hybrid films was measured using a dynamic mechanical analyzer (DMA), as shown in Fig. 10. The tan $\delta_{\text{max}}$ was identified as the glass transition temperature ($T_g$). The $T_g$ of pure PI could not be determined by differential scanning calorimetry (DSC).

Fig. 8. FE–TEM images of the PI–GO nanocomposite films(A) and XLPI–GO nanocomposite films(B) with 1 wt.% of GO contents.

Fig. 9. Mg mapping of the fractured SEM (A,B) images and EDX spectra of the PI–GO 5 wt.% nanocomposite film and XLPI–GO 5 wt.% nanocomposite film (C, D, respectively).
The Tg of PMDA–ODA polyimide was observed at approximately 390 °C. With increasing content of graphene sheets, the Tg of the composite films was similar to that of neat polyimide, but was lower at 5 wt.% GO due to the aggregation and heterogeneous dispersion of GO in the PI matrix. Similar results were reported for polyurethane–GO nanocomposites with the suggestion that crystallization of the hard segment in polyurethane was inhibited by GO [42].

Fig. 11 shows the dielectric constant ($k$) of the composite films as a function of frequency. In the case of low concentrations (0.5 and 1 wt.%), the dielectric constant was almost fixed at approximately three over all frequency ranges. On the other hand, the dielectric constant of the composite containing >2 wt.% graphene oxide was slightly higher at 1 Hz. There was a noticeable increase in the 5 wt.% GO composite films. In particular, the 5 wt.% GO non-cross linked PI film was approximately 20000 at 1 Hz. With increasing frequency, the high dielectric constant of the 5 wt.% GO composite films decreased and finally showed similar behavior to

![Fig. 10. DMA thermograms of the pristine PI and PI–GO nanocomposite films with various graphene oxide contents.](image)

![Fig. 11. Dielectric constants as a function of the frequency of pristine PI, PI–GO nanocomposite films and cross-linked PI–GO nanocomposite films.](image)
near PI at approximately 1 MHz. From this point of view, the dielectric constant can be controlled from low \(k\) to high \(k\) by changing the frequency.

We also checked the surface resistance values for PI–GO films. When increasing the GO contents in PI–GO films, the surface resistance was decreased, regardless of the presence or absence of Mg\(^{2+}\) crosslinker. In the case of XLPI5, the surface resistance reached to \(10^{10}\ \Omega/cm^2\). It means that we can apply these composite films for dielectric materials (see Supplementary Table S2). Note that the XLPI showed lower surface resistivity (i.e., higher current conductivity) over all the GO content ranges than the PI nanocomposite films.

4. Conclusions

PMDA–ODA polyimide–graphene oxide nanocomposite films were prepared by chemical cross-linking using a small amount of Mg\(^{2+}\) ions. The graphene sheets of the paper-like scroling structure were well dispersed in the polyimide matrix up to a 1 wt.% content. In the case of a high concentration of graphene sheets, the graphene sheets aggregated during thermal imidization and had a layer-by-layer structure in the polyimide matrix. This morphological effect in polyimide contributed to the increase in tensile and thermal properties at low graphene contents. In particular, the tensile properties of the cross-linked PI–GO composite films (XLPI) showed more enhancement than the non-cross-linked PI–GO composite films due to the presence of Mg\(^{2+}\) ions as a cross-linker. The dielectric constant was also controlled from low \(k\) \((\sim 3)\) to high \(k\) \((\sim 20000)\) by changing the frequency, which has potential use as dielectric materials.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.eurpolymj.2012.05.015.

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