Preparation and Properties of Poly(imide-siloxane) Copolymer Composite Films with Micro-Al$_2$O$_3$ Particles

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Abstract: In the current study, poly(imide-siloxane) copolymers (PIs) with different siloxane contents were synthesized and used as a matrix material for PI/Al$_2$O$_3$ composites. The PIs were characterized via their molecular weight, film quality, and thermal stability. Among the PI films, free-standing and flexible PI films were selected and used to prepare PI/Al$_2$O$_3$ composite films, with different Al$_2$O$_3$ loadings. The thermal conductivity, thermal stability, mechanical property, film flexibility, and morphology of the PI/Al$_2$O$_3$ composite films were investigated for their application as heat-dissipating material.

Keywords: poly(imide-siloxane) copolymer; Al$_2$O$_3$; thermal conductivity; heat-dissipating

1. Introduction

Recent electronic devices such as smart applications and laptops are becoming smaller and lighter with developments in the electronics industry [1–3]. To ensure the proper operation of smaller devices, unwanted heat that is generated in electronic devices must be removed. The dissipation of heat has attracted increasing attention, and is an important issue that reqiures resolution [4,5]. Currently, polymer composite materials containing ceramic powder are widely used as heat dissipation materials in electronic devices [6,7].

Among the polymer materials, polysiloxane has some advantages and is used as a heat-dissipating polymer matrix [8–10]. It is composed of a linear Si-O-Si moiety with a bond-angle between 104° and 180°, which introduces flexibility to the polymer [11,12]. In addition, polysiloxane can be used permanently without any change at 150 °C, it is able to withstand 200 °C for 1000 h, and 350 °C for shorter periods of time [13,14]. However, some studies on the long-term reliability of silicone rubber suggest that commercial high-temperature silicones, which are being aged at 250 °C could suffer from severe thermal decomposition [15–17].

Polyimides have widely been used in display, vehicle, aerospace, and microelectronic industries as high-performance material owing to their good mechanical properties, excellent thermal stability, flexibility, low dielectric permittivity, and good chemical resistance [4,18–21]. Polyimides are also good candidates for use as thermal conductive composite materials that can be operated at high temperatures, due to their high thermal stability [22–27]. By introducing siloxane chain segments to the polyimide backbone structure, adhesion between the polyimide and inorganic materials can be improved, including the adhesion of the metal materials and other substrates [28–31]. Previously,

poly(imide-siloxane) copolymers (PIs) have been studied for applications in aerospace, separation, and microelectronics [32–35]. On the other hand, alumina (Al_2O_3) fillers are used as thermally conductive material embedded in the polymer matrix [36–40]. Alumina is commercially very inexpensive and often employed to improve the dissipation of polymer materials' heat properties due to its better insulating qualities and higher thermal conductivity [40].

In this paper, we first report the preparation method and properties of PI composite films containing Al_2O_3 particles, for their application as heat dissipating material. We report the preparation and properties of PIs with varyingmolar ratio of two diamines (an aromatic diamine and bis(3-aminopropyl)-terminated polydimethylsiloxane). Furthermore, PI/Al_2O_3composite films were prepared by adding various Al_2O_3contents into the PI matrix. Then the thermal conductivity, thermal stability, mechanical properties, film flexibility, and morphology of the composite films were investigated according to the change in Al_2O_3loadings.

2. Materials and Methods

2.1. Materials

4,4′-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA), 4,4′-methylenedianiline (MDA), and bis(3-aminopropyl)-terminated polydimethylsiloxane (PDMS) ($\overline{M}_n$~2500) were purchased from Sigma-Aldrich Korea (Seoul, Korea), and were used as received. Tetrahydrofuran (THF) was purchased from Samchun Chemicals (Seoul, Korea), distilled from N_2/benzophenone, and stored under nitrogen until use. 1-Methyl-2-pyrrolidinone (NMP) was purchased from Duksan Pure Chemical (Seoul, Korea), distilled in reduced pressure, and kept under nitrogen until use. Polygonal alumina (Al_2O_3; average particle size = 4 μm) was purchased from Denka Co. Ltd. (Seoul, Korea) and was dried at 120 °C in an oven for 24 h to remove the adsorbed water before use. Tetrahydrofuran-d_8 (THF-d_8) was purchased from Acros Organics BVBA (Geel, Belgium).

2.2. Characterization

Proton nuclear magnetic resonance (^{1}H NMR) spectra of samples dissolved in THF-d_8 were acquired using a Bruker Avance II 400 MHz spectrometer (Bruker Corporation, Billerica, MA, USA). Gel permeation chromatography (GPC; Waters Corporation, Milford, MA, USA) analysis was carried out in refractive index mode using a doubly connected Showa Denko Shodex KF-806L column at 100 °C and an eluent of 0.05 mol/L LiBr in NMP at a flow rate of 1.0 mL/min; the results were calibrated with respect to polystyrene standards. Fourier Transform Infrared (FT-IR) spectroscopy was carried out using a Spectrum One B FT-IR spectrometer (PerkinElmer, Inc., Waltham, MA, USA) using the KBr pellet technique with the following scan parameters: scan range 500–4000 cm^{-1}; number of scan 1; resolution 4 cm^{-1}. Thermal analyses were carried out under a nitrogen atmosphere with a balance flow rate of 40 mL/min and a furnace flow rate of 60 mL/min using a Discovery TGA 55 (TA instrument, Inc., New Castle, DE, USA) at a heating rate of 10 °C/min. The thickness of the polyimide films was measured using a 293–348 IP65 digimatic outside micrometer (Mitutoyo Corporation, Kawasaki, Japan). Thermal conductivities (in-plane) of the composite films were measured using a LFA 467 Nanoflash (NETZSCH Korea Co., Ltd., Koyang, Korea). A universal testing machine (UTM) (QC-505M1, Daeha Trading Co., Seoul, Korea) was used to determine tensile properties. A 3-cm gauge and a strain rate of 2 cm/min were used. Film specimen measurements were performed at room temperature using 0.5 cm wide, 6 cm long, and ca. 0.3 mm thick films. An average of five individual determinations were used for each sample. Field emission scanning electron microscopy (FE-SEM) was carried out using a SU-70 (Hitachi, Ltd., Tokyo, Japan), with an acceleration voltage of 30 kV and a working distance in the range of 10 to 11.6 mm. The samples were sputter-coated with platinum.

2.3. Preparation of Poly(amic acid-siloxane)s (PAAs)

Scheme 1 shows the general method of copolyimide synthesis. A representative example for the synthesis of poly(amic acid-siloxane)-4 (PAA-4) (molar feed ratio of 6FDA:MDA:PDMS was 1:0.5:0.5) is described below. A dried 50-mL flask was charged with MDA (0.002 mol, 0.198 g) and PDMS (0.002 mol, 2.500 g) in THF (14.3 mL) under a nitrogen atmosphere. After 6FDA (0.004 mol, 0.888 g) was added, the resulting solution was stirred at 0 °C for 1 h, and then further stirred at room temperature for 23 h to yield a clear viscous PAA-4 solution. The other PAA solutions were prepared in a similar fashion by varying the molar feed ratio of the diamines. As an exception, NMP was used in the synthesis of PAA-1 with a molar feed ratio of 6FDA:MDA:PDMS of 1:1:0. The PAA solutions was used to prepare PI films, powders, and composite films (see below).
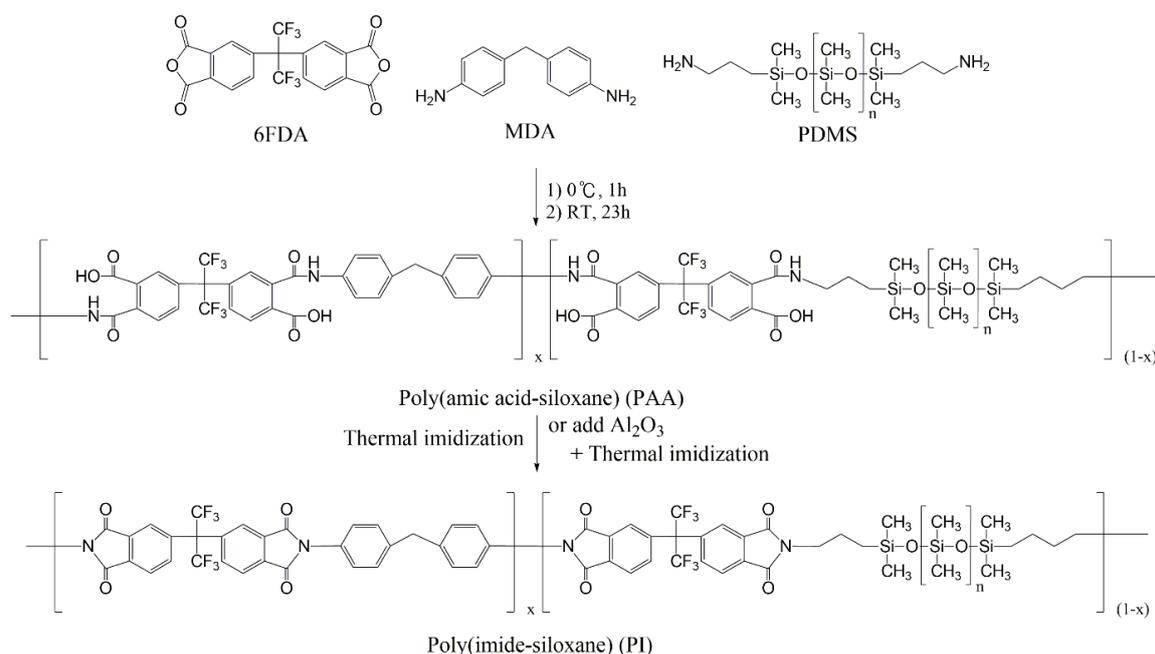
Scheme 1. Synthesis of PIs and their composites.

2.4. Preparation of PI Films

The PAA-4 solution obtained above was drop-cast onto slide glasses and the solution was stepwisely heated (at 50, 100, and 150 °C). The solution was allowed to stand at each temperature for 1 h. The resulting films were finally heated at 250 °C for 2 h, and PI-4 films were obtained. The PI-4 films were cooled to room temperature and put in a water bath for 1 h to allow easy peel off. The resultant films were dried in a vacuum oven at 100 °C for 1 h. The other PI films were prepared in a similar manner by varying the molar feed ratio of the diamines.

2.5. Preparation of PI Powders

The PAA-4 solution obtained above was poured into distilled water, forming a precipitate that was collected via filtration. The precipitate was washed with distilled water and then dried in a vacuum oven, yielding a PAA-4 powder. The PAA-4 was thermally imidized by stepwise heating in a furnace (50, 100, and 150 °C). The powder was kept for 1 h at each temperature and finally heated at 250 °C for 2 h to obtain PI-4 powder. The other PAA and PI powders were prepared in a similar manner by varying the molar feed ratio of the diamines. The prepared PAA and PI powders were used in FT-IR spectroscopy and GPC.

2.6. Preparation of PI Composite Films

Al$_2$O$_3$ powder (30, 60, 75, or 80 wt%) was added to the PAA-4 solution obtained above. The mixture was ultrasonicated using an ultrasonic device (VCX750, Sonics & Materials, Newtown, CT, USA), with an output power of 150 W and a frequency of 20 kHz for 1 h to yield a milky suspension. The suspension was drop-cast onto slide glasses, and then heated in a stepwise manner (at 50, 100, and 150 °C). The suspension was allowed to stand at each temperature for 1 h and finally heated at 250 °C for 2 h to obtain PI/Al$_2$O$_3$ composite films (PI-4-30, PI-4-60, PI-4-75, and PI-4-80). The obtained films were cooled to room temperature and put in a water bath for 1 h to facilitate peeling it off. The resultant composite films were dried in a vacuum oven at 100 °C for 1 h.

3. Results and Discussion

3.1. Preparation of PIs and Their Composite Films

The preparation of poly(imide-siloxane) copolymers (PIs) is illustrated in Scheme 1. The PIs were synthesized according to a conventional two-step procedure. During typical conventional polyimide synthesis, aprotic polar solvents such as NMP, dimethylacetamide (DMAc), or dimethylformamide (DMF) are usually used. However, the siloxane group underwent microphase separation when aprotic solvents were used during the copolymerization. To overcome this problem, the preparation of PIs required the use of a co-solvent system or THF [41,42].

In this work, 6FDA, MDA, and PDMS were copolymerized using THF as a solvent (Table 1), except for PAA-1 which was prepared without the PDMS moiety and used NMP as a solvent. 6FDA and mixed diamines (MDA and PDMS) were first polymerized to prepare poly(amic acid-siloxane)s (PAA-1–PAA-7). The diamine molar feed ratio was controlled as summarized in Table 1. The PDMS content of PAA copolymers was determined by ^{1}H NMR (Table 1 and Figure S1). The mole percent of PDMS was calculated from the ratio of the integration values of the methyl groups in PDMS and the methylene groups of MDA. It was found that the determined values agreed well with those corresponding to PDMS contents in the feeds. The PAA solutions were drop-cast onto slide glasses and then PAAs were converted to PI-1–PI-7 films by thermal imidization. The PAA and PI powders were also prepared for characterization via FT-IR spectroscopy and GPC. Table 1 lists the molecular weights and polydispersity indexes (PDIs) of the PAAs measured by GPC. In addition, PI/Al$_2$O$_3$ composites were prepared by adding various amount of Al$_2$O$_3$ powder to PAA solutions. The resulting suspensions were drop-cast onto galss slides and subsequent thermal imidization was carried out to obtain PI/Al$_2$O$_3$ composite films.

Table 1. Molar feed ratios and molecular weights of PAAs.

PAA Code [a]	Molar Feed Ratio (6FDA:MDA:PDMS)	PDMS Content (mol%) [b]	$\overline{M}_n$ ($\times 10^4$ g/mol)	$\overline{M}_w$ ($\times 10^4$ g/mol)	PDI [c]
PAA-1	1:1:0	-	1.03	2.32	2.2
PAA-2	1:0.9:0.1	13	10.8	37.8	3.5
PAA-3	1:0.7:0.3	32	10.8	18.1	1.6
PAA-4	1:0.5:0.5	49	3.73	13.2	3.5
PAA-5	1:0.3:0.7	70	21.1	48.8	2.3
PAA-6	1:0.1:0.9	89	16.3	50.9	3.1
PAA-7	1:0:1	-	7.92	25.1	3.2

[a] PAA: poly(amic acid-siloxane); [b] Calculated from ^{1}H NMR integrations of PAA copolymers; [c] Polydispersity index ($\overline{M}_w / \overline{M}_n$).

3.2. Characterization of PAAs and PIs

The structures of PAAs and PIs were confirmed by FT-IR spectroscopy (Figure 1). FT-IR spectra of PAA-4 and PI-4 showed absorption bands at 1021 and 1095 cm^{-1}, respectively, due to Si-O-Si stretching in the structure of PDMS. The absorption band at 1259 cm^{-1} was also attributed to the symmetric

deformation of the –CH$_3$ group in –Si(CH$_3$)$_2$-, and the absorption band at 803 cm^{-1} was assigned to the Si-C vibration [11,41,43–45]. The FT-IR spectrum of PAA-4 showed bands at 1721 cm^{-1} (carboxyl) and 1660 cm^{-1} (amide) owing to C=O stretching, and at 1545 cm^{-1} owing to C-N stretching (amide), suggesting the formation of PAA (Figure 1a) [11,34,46]. PI-4 exhibited absorption bands at 1785 cm^{-1} owing to imide C=O asymmetric stretching, 1726 cm^{-1} owing to imide C=O symmetric stretching, and 1375 cm^{-1} owing to imide C–N stretching (Figure 1b) [11,34,46–48]. FT-IR spectra of the other PAAs and PIs are shown in Figures S2–S7.
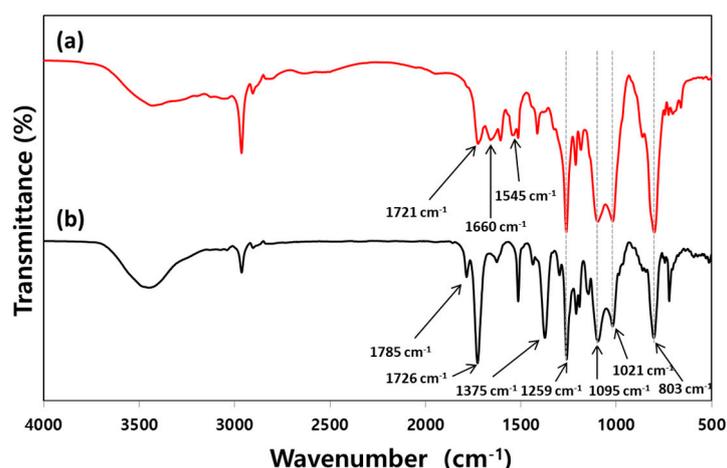
Figure 1. FT-IR spectra of (**a**) PAA-4, and (**b**) PI-4.

3.3. Properties of PI Films

Thermal stability of PIs was investigated by thermogravimetric analysis (TGA) (Table 2 and Figure 2). TGA was conducted to study the effects of the molar ratio of diamines on decomposition temperature (T_5 and T_{10}) and char yield of PIs. T_5 and T_{10} values of the PIs ranged from 373 to 505 and 419 to 528°C, respectively, and the decomposition temperature decreased with increasing PDMS molar ratio. Nevertheless, PIs' decomposition temperatures were much higher than those of silicone [17]. The char yield at 800 °C of PI-1 without siloxane moiety was the highest (62.4%) and the other char yields were much lower.

Table 2. Film quality and thermal properties of PIs.

PI Code [a]	Film Quality	T_5 (°C) [b]	T_{10} (°C) [c]	Char Yield (%) [d]
PI-1	Brittle	505	528	62.4
PI-2	Brittle	446	473	28.2
PI-3	Flexible	438	454	16.7
PI-4	Flexible	428	443	0.7
PI-5	Flexible	423	441	2.1
PI-6	Sticky	403	426	4.3
PI-7	Sticky	373	419	3.2

[a] PI-1–PI-7 were prepared from PAA-1–PAA-7, respectively; [b] The temperature at which a sample exhibits 5 wt% decomposition in a nitrogen atmosphere; [c] The temperature at which a sample exhibits 10 wt% decomposition in a nitrogen atmosphere; [d] Char yield at 800 °C in a nitrogen atmosphere.
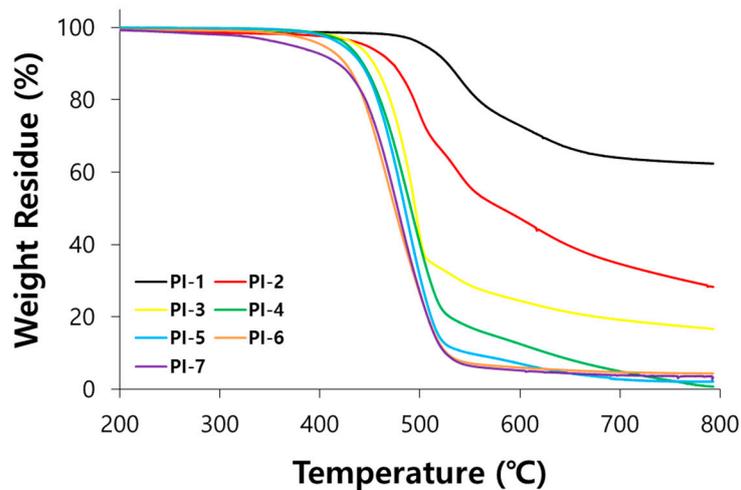
Figure 2. TGA curves of PIs.

Flexible and free-standing PI films (PI-3, PI-4, and PI-5) could be prepared from PAA-3, PAA-4, and PAA-5, respectively (Table 2 and Figure 3). When the films were bent, twisted, rolled-up, or wrapped on the 3-mm diameter bar numerous times, their appearance was almost unchanged (no damage occurred). However, PI-1 and PI-2 films were brittle due to their rigid chemical structures. On the other hand, PI-6 and PI-7 films were sticky due to the very high PDMS group contents.
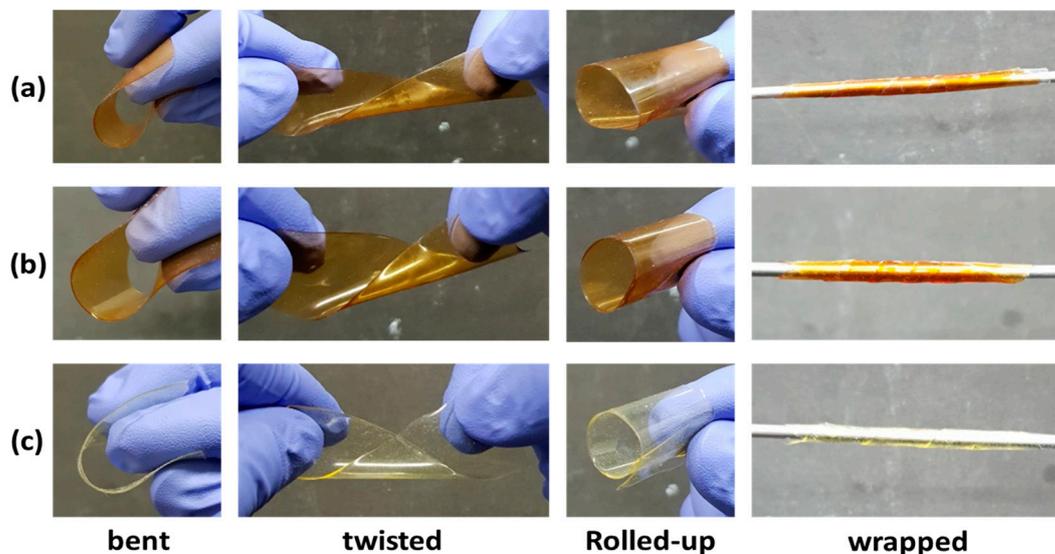
Figure 3. Photographs of (**a**) PI-3; (**b**) PI-4; (**c**) PI-5 films.

3.4. Properties of PI/Al$_2$O$_3$ Composite Films

Because the PI-3, PI-4, and PI-5 films were free-standing and flexible, they were used to prepare PI/Al$_2$O$_3$ composite films. Figure 4 shows the thermal conducting properties of neat PI films and PI/Al$_2$O$_3$ composite films, with different Al$_2$O$_3$ loadings along an in-plane direction ($D_\perp$) at room temperature (see Tables S1–S3). The films' thermal diffusivity (α) was determined at room temperature and under ambient pressure. From the equation K = $\alpha \times \varrho \times$ C$_p$, the thermal conductivity (K) value can be calculated. In the equation, ϱ is the measured film density, and C$_p$ is the specific heat capacity of the film [5,49]. The thermal conductivities of neat PI-3, PI-4, and PI-5 were 0.11, 0.13, and 0.14 W/m·K, respectively. It is known that thermal conductivities of polyimide and polydimethylsiloxane are 0.11 and 0.25 W/m·K at room temperature, respectively [22]. The incorporation of Al$_2$O$_3$ fillers increased thermal diffusivity and thermal conductivity of PI/Al$_2$O$_3$ composite films (Figure 4a,b). When the

Al_2O_3 loading was 80 wt%, PI-3 and PI-4 composites showed high thermal conductivity values, greater than 1.3 W/m·K. The thermal diffusivity and conductivity data are quite reproducible as presented in Tables S1–S3.
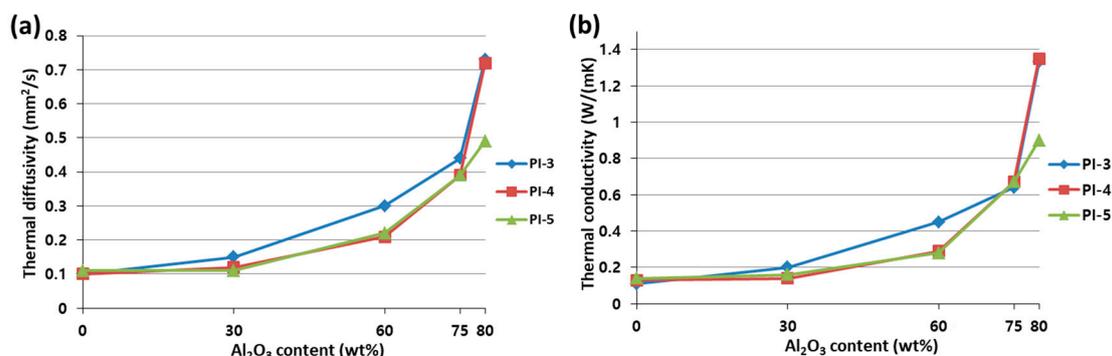
**Figure 4.** (**a**) Thermal diffusivity ($D_\perp$), and (**b**) thermal conductivity ($D_\perp$) of the PI and PI/Al_2O_3 composite films with different Al_2O_3 loadings.

In addition, thermal and mechanical properties of the PI/Al_2O_3 composite films were studied (Table 3 and Figures S8 and S9). Among the flexible PI films, PI-3 was selected because it exhibited the best thermal conducting properties. The T_5 and T_{10} values of the neat PI-3 and PI-3/Al_2O_3 composite films ranged from 437 to 454 °C and 456 to 474 °C, respectively. Generally the decomposition temperatures of the PI/Al_2O_3 composite films were higher than those of the neat PI film. The improvement in thermal stability can be attributed to restrained polymer chain mobility by Al_2O_3 particles [17]. Furthermore, it should be noted that the PI/Al_2O_3 composites showed much higher thermal stability compared to polysiloxane/Al_2O_3 composites [17,50]. From the char yield data, each mass value retained around 800 °C and was almost identical to the corresponding Al_2O_3 content in each composite.

Table 3. Thermal and mechanical properties of the PI-3/Al_2O_3 composite films.

PI/Al_2O_3 Composite Code [a]	T_5 (°C) [b]	T_{10} (°C) [c]	Char Yield (%) [d]	Tensile Strength (MPa)	Elongation at Break (%)
PI-3	438	461	16.7	14.6 ± 2.7	210.4 ± 38.4
PI-3-30	440	456	30.7	7.3 ± 0.2	41.7 ± 2.8
PI-3-60	454	469	61.3	6.5 ± 0.4	10.4 ± 0.6
PI-3-75	450	474	75.2	5.7 ± 0.5	4.8 ± 0.6
PI-3-80	437	471	79.1	5.2 ± 0.5	3.7 ± 0.6

[a] PI-3, PI-3-30, PI-3-60, PI-3-75, and PI-3-80 films have Al_2O_3 loadings of 0, 30, 60, 75, and 80 wt%, respectively; [b] The temperature at which a sample exhibits 5 wt% decomposition in a nitrogen atmosphere; [c] The temperature at which a sample exhibits 10 wt% decomposition in a nitrogen atmosphere; [d] Char yield at 800 °C in a nitrogen atmosphere.

The neat PI-3 film showed a tensile strength of 14.6 ± 2.7 MPa, and a high elongation at a break of 210.4 ± 38.4%. However, the PI/Al_2O_3 composite films exhibited decreased tensile strength and elongation at break, and the mechanical properties decreased with increasing Al_2O_3 loadings. It is well known that the incorporation of an inorganic filler to the polymer matrix reduces the polymer's flexibility. Furthermore, the polymer's strength is reduced if there are no binding sites between the polymer phase and inorganic material phase [51]. Nevertheless, the composite films with up to 75 wt% Al_2O_3 are sufficiently flexible, as shown in Figure 5. They may be useful as a flexible heat-radiating film in flexible electronic devices requiring a high operating temperature. Even though the composite films with 80 wt% Al_2O_3 loading are not flexible, they could also be used in high-temperature electronic devices.
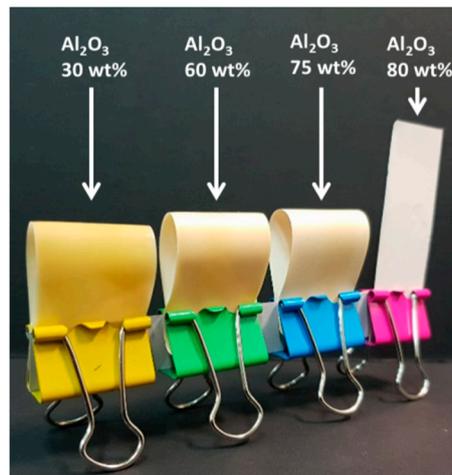
Figure 5. Photographs of PI composite films containing different Al_2O_3 contents.

Scanning electron microscopy (SEM) was carried out to investigate the morphology of the PI/Al_2O_3 composite films. Figure 6a shows the SEM image of micro-Al_2O_3 particles. The particles are irregularly shaped with 4 μm average size. The neat PI-3 film before Al_2O_3 addition showed a very smooth surface (Figure 6b). As shown in Figure 6c, Al_2O_3 particles were well dispersed in the PI/Al_2O_3 composite film and no significant fractures were observed across the film's surface.
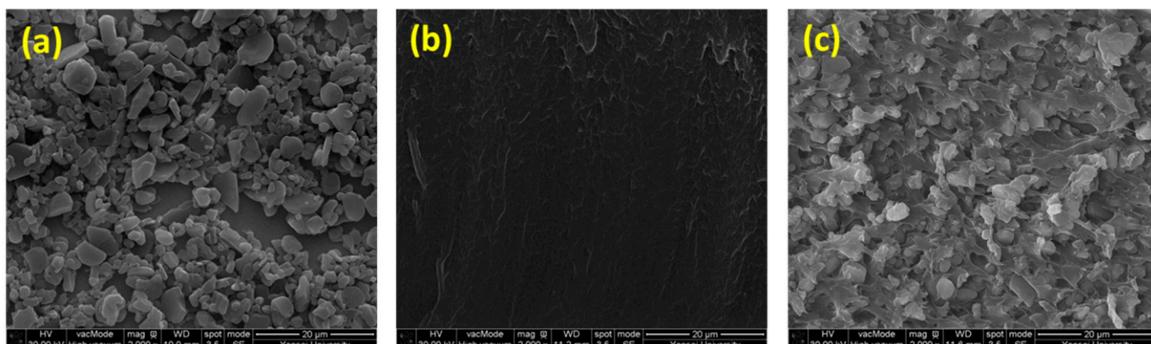
Figure 6. SEM images of (**a**) Al_2O_3 particles; (**b**) PI-3 film; (**c**) PI-3-75 film.

4. Conclusions

The PIs with different siloxane contents were prepared using 6FDA, MDA, and PDMS.Free-standing, flexible films of PI-3, PI-4, and PI-5 were obtained, and the PIs were used to prepare PI/Al_2O_3composite films. The thermal conductivities of the composite films increased with increasing Al_2O_3 content. It was demonstrated that the composite films with up to 75 wt% Al_2O_3 were both free-standing and flexible. The composite films with 80 wt% Al_2O_3 loading showed a relatively good thermal conductivity, higher than 1.3 W/m·K. Besides, PI/Al_2O_3 composite films exhibited higher thermal stability compared to conventional polysiloxane/Al_2O_3 composites. The PI/Al_2O_3 composite films could be used as a heat-radiating film in electronic devices requiring high operating temperatures.

Author Contributions: Conceptualization, J.-Y.C., S.P., and C.-M.C.; methodology, J.-Y.C.; formal analysis, J.-Y.C., K.-N.N., and S.-W.J.; investigation, D.-M.K., I.-H.S., and H.-J.P.; writing—original draft preparation, J.-Y.C. and C.-M.C.; writing—review and editing, C.-M.C.; supervision, C.-M.C.

Conflicts of Interest: The authors declare no conflict of interest.

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