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Preparation of Polyetherimide Nanocomposites with Improved Thermal, Mechanical and Dielectric Properties

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Summary

Thermoplastic polyetherimide (PEI)-SiO_2 nanocomposites were prepared from a soluble PEI, which was synthesized from *m*-phenylenediamine and bisphenol A dianhydride, in combination with tetraethoxysilane solution via a novel sol-gel process. A coupling agent was used to enhance the compatibility between PEI and silica. This approach was compared with PEI-clay nanocomposite in which montmorillonite was modified with ammonium salts of 12-aminododecanoic acid using an intercalation polymerization. The size and dispersion of the silica or clay in the PEI nanocomposites were analyzed by x-ray diffractometer and scanning electron microscopy. It was found that the sol-gel process offered a fine interconnected or co-continuous phase, whereas the clay remained dispersed in nanocomposites. Though the thermal properties of PEI-clay nanocomposites were improved over pristine PEI, physical testing showed that the films become brittle as the organoclay content increased to over 2%. The thermal stability and mechanical properties of the PEI/silica nanocomposites prepared by sol-gel process were improved with silica content up to 10%. The onset decomposition temperatures were 550-600°C. The dielectric constant decreased with increasing amounts of silica. At higher silica contents, the mechanical properties were reduced as a result of the phase separation.

Introduction

Aromatic polyimides (PIs) are versatile engineering polymers that have been widely used in many advanced technology applications due to their outstanding thermal stability, mechanical properties, and low dielectric constants. However, PIs are difficult to process and the research in the last few years has been directed toward novel linear polymers that are soluble in organic solvents or melt-processable when fully imidized [1]. The most important of them, based on the production figures, are polyetherimides (PEIs). PEI resins are advanced polymers developed by General Electric Co.[2] These polymers are amorphous thermoplastic materials that result from the combination of ether units and aromatic imides. Ether units supply the chain flexibility and good melt flow characteristics to PEI, while the aromatic imide units provide thermal resistance and mechanical properties. One commercialized PEIs is

Ultem® 1000, which is synthesized via the polycondensation of a dianhydride, 4,4'-(4,4'-isopropylidene diphenoxy) bis(phthalic anhydride), with *m*-phenylene diamine (*m*PDA). Although Ultem 1000 has good melt processability and solubility in some solvents, its relatively poor thermal stability limits its application in the aerospace and automotive fields.

It is difficult to adjust PI's thermo-physical properties by changing their chemical structure alone. The incorporation of inorganic materials like clay or SiO_2 is a promising approach to enhance the thermal and mechanical properties of PI. Many synthesis and processing methods have been developed for preparing organic/inorganic hybrid materials [3-9]. Intercalation of polymers with clay, such as montmorillonite (MMT), has proven to be an effective method to prepare nanocomposites [8]. The sol-gel process is another commonly used method to prepare PI/silica nanocomposites [9]. Though Huang et al.[10] claimed that PEI-MMT nanocomposites can be prepared by melt intercalation, Morgan et al. found that PEI nanocomposites cannot be processed at typical conditions, however [11]. In this study, we first mixed organophilic clay with polyamic acid (PAA), a PEI precursor, to prepare a PEI-clay hybrid nanocomposite, but this approach only had limited success (only $< 3\%$ clay could be added). This can be ascribed to the thermal decomposition of alkyl ammonium MMT, as recent studies [12-13] found that thermal decomposition starts at temperatures as low as 180°C. Consequently, clay-polymer mixing or curing can subject alkyl ammonium ions to thermal decomposition, which in turn can exert potential detrimental effects on product properties and performance. Note that many thermoplastic polymers are processed at temperatures in the range of 200-250°C.

Although many papers on the synthesis of inorganic-organic hybrids have been published, the preparation of hybrid of the well-known PEI, Ultem 1000, has seldom been reported. In this paper, we utilized a novel sol-gel process [14] to prepare hybrid nanocomposites directly from the soluble PEI in an attempt to reduce the cost and improve the thermal, mechanical and dielectric properties. The nanocomposites were characterized by FT-IR to identify the chemical structures. TGA, DSC, and DMA were used to measure the thermal properties. X-ray diffractometer (XRD) and scanning electron microscopy (SEM) were utilized to study the morphology of the nanocomposites. Their thermal, mechanical and dielectric properties are presented and discussed.

Experimental

Materials

Chemicals of high purity were purchased from various commercial sources, which include 4,4'-(4,4'-isopropylidene diphenoxy) bis(phthalic anhydride) [BPADA] (Aldrich), *m*-phenylene diamine (Acros), 12-aminododecanoic acid [C12-Acid] (TCI), tetraethoxysilane [TEOS] (Acros), 3-glycidyloxypropyl trimethoxysilane [GPTMOS] (Acros), N-methyl-2-pyrrolidone [NMP] (Tedia), toluene (Tedia), and Kunipia F (Na-Montmorillonite) clay with cation exchange capacity of 119 meq /100 g (Kunimine Industries Co., Japan). NMP was purified by distillation under reduced pressure over calcium hydride and stored over 4Å molecular sieves prior to use. BPADA was dehydrated by drying under a vacuum at 100°C for 24 h. The other reagents were used as received.

Intercalative polymerization

Preparation of organophilic clay

The organophilic clay was prepared by a cationic exchange reaction between the sodium cations on the MMT surface and the organic cations of an intercalating agent. We have followed the modified Yano's procedure [8] in this investigation (as described in our earlier report [15]) to prepare organophilic MMT treated with 12-aminododecanoic acid ammonium salt (C12A-MMT).

Preparation of PEI-clay nanocomposite films

Poly(amic acid) (PAA) was first synthesized from dianhydride and diamine (as shown in Scheme 1), then organophilic clay was added to prepare the composite. *m*PDA 1.10 g (0.01 mol, 99%) and NMP 29.4 g were placed into a 250-mL three-neck flask under nitrogen purge. The mixture was stirred until the solution was clear. Equal molar amounts of solid BPADA were added to the *m*PDA solution to make a solution with a solid content of 18%. The reaction mixture was stirred for 2 h at 60°C and resulted in a transparent yellow viscous solution of PAA. To prepare different concentrations (1%, 2%, 3% and 5% in weight) organoclay, various quantities of C12A-MMT clay were each added to NMP and mixed for 4 h. The organoclay suspensions were mixed with PAA to yield PAA-organoclay mixture. The resulting PAA-clay mixture was allowed to stir at room temperature overnight (~ 12 h). Upon completion of the reaction, it was spread on a glass plate using a spin-coater to control the film thickness. The films were thermally dried at 60°C for 8 h to remove most of the solvent in a forced air oven and subsequently heated at 100°C, 150°C for 1 h each, and at 205°C for 3 h in a nitrogen atmosphere to achieve fully imidization. The films were then cooled to room temperature and peeled off from the glass plate to obtain the PEI-clay hybrid films. Table 1 listed the codes of various hybrids with different formulations.

Table 1. Code of PEI-clay nanocomposites and their thermal properties

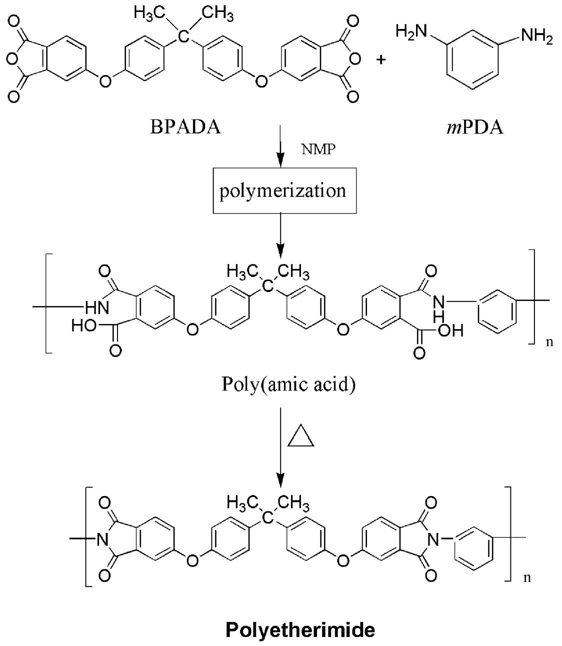
Code	% Organoclay	T_g (°C)	$T_{d,\ onset}$ (°C)
PEI	0	214	542
PM1	1	218	554
PM2	2	219	568
PM3	3	220	570
PM5	5	-- [a]	-- [a]

[a] The film was too brittle to test.

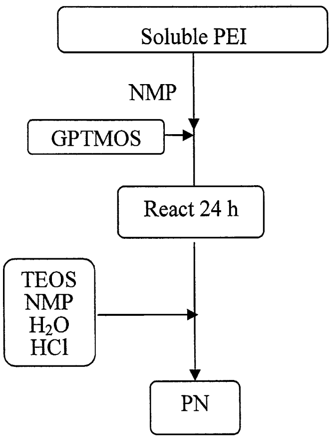
Sol-gel process directly from soluble PEI

Synthesis of polyetherimide

Polyetherimide was synthesized by reacting *m*PDA with BPADA as illustrated in Scheme 1. PAA was first synthesized as described above. 20 mL of toluene was then added and the mixture was heated to ~160°C at reflux for ~12 h until the water was azeotropically distilled off via a Dean-Stark trap. Heating was continued to distill off the residual toluene. After the completion of polymerization, the viscous PEI solution was cooled, and the polymer solution was ready for the preparation of PEI/silica nanocomposites.



Scheme 1. Synthesis of polyetherimide.



Scheme 2. Synthesis of PEI nanocomposites via the sol-gel process.

Preparation of the PEI/silica nanocomposite films

GPTMOS was charged into the PEI solution and stirred at 70°C for 24 h to complete the reaction. Then, hydrolyzed TEOS solution was added and stirred for 6 h to produce a hybrid solution (see Scheme 2). The amount of GPTMOS and hydrolyzed TEOS solution used for various hybrid nanocomposites are shown in the Table 2. The hybrid polymer solutions were spread on a glass plate using a spin-coater to control the film thickness. The films were thermally dried at 60°C to remove most of solvent and were stripped from the glass. Then, the films were fixed in a film casting apparatus and heated in a vacuum oven at 205°C for 4 h to remove all solvents.

Table 2. Experimental conditions for preparing PEI/silica hybrids.

Code	PEI solution [a] (g)	SiO_2 [b] (wt %)	GPTMOS (g)	TEOS (g)	H_2O [c] (g)
PN05	30	5	0.125	0.99	0.34
PN10	30	10	0.263	2.08	0.72
PN15	30	15	0.417	3.31	1.14
PN20	30	20	0.591	4.69	1.62
PN30	30	30	1.013	8.04	2.78

[a] Solid content 20%. [b] Weight percent of total silica in the hybrid material, as calculated from the initial amounts of TEOS and GPTMOS, assuming complete reaction. The weight ratio of silica obtained from GPTMOS to that obtained from TEOS is 10/90. [c] Add water to make molar ratio TEOS: H_2O =1:4.

Characterization

Fourier transfer infrared (FTIR) spectra were recorded on a Bio-Rad Digilab FTS-40 spectrometer. Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer Pyris 1 TGA at a heating rate of 20°C /min in N_2. Differential scanning calorimetry (DSC) data were obtained from a Perkin-Elmer Pyris Diamond DSC. Samples were scanned at a heating rate of 10°C /min under N_2. The T_g values were measured as the change of the specific heat in the heat flow curves. Dynamic mechanical analysis (DMA) was performed on a model 2980 DMA (TA Instruments) in the tensile mode at a frequency of 1 Hz from 50°C to 300°C at a heating rate of 5°C/min. A sample 15 mm in length, 5 mm in width and approximately 1.5 mm in thickness was used. X-ray diffractograms (XRD) were obtained at room temperature on a Rigaku RINT 2000 instrument, using Ni-filtered CuK_α radiation (40 kV, 100 mA). Molecular weight was determined by gel permeation chromatography (GPC) with polystyrene calibration using a Perkin-Elmer series 200 HPLC system equipped with a Jordi Gel DVB column at 40°C in THF. The morphologies of the fracture surfaces of hybrid materials were observed with a JEOL JSM-6700 scanning electron microscope (SEM). An Instron universal tester model 4467 was used to study the stress-strain behavior. The load cell used was 5 Kg and the crosshead rate was 5 mm/min. Measurements were performed with film specimens (1.35 cm wide, 6 cm long and 50~60 μm thick). The dielectric property of the polymer films was tested by the Agilent 4284A LCR meter with 16451B dielectric test fixture at a frequency of 1 MHz.

Results and discussion

Synthesis of Polyetherimide

The FT-IR spectrum of the PEI is shown in Figure 1. It exhibits characteristic imide group absorptions at 1780 and 1720 cm^{-1} (typical of imide carbonyl asymmetrical and symmetrical stretch), at 1355 and 743cm^{-1} (C-N stretching and bending), and at 1234 cm^{-1} (aromatic ether C-O-C). Molecular weight (*Mw*) of the soluble PEI was measured by GPC and the chromatogram indicated that the *Mw* was 34,000.

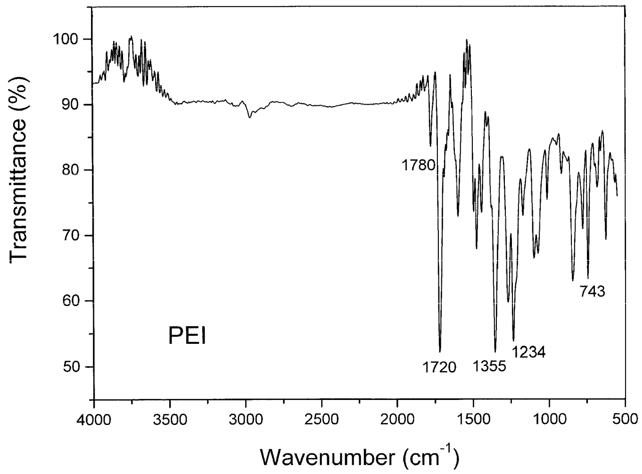


Figure 1. FT-IR spectrum of PEI.

PEI-clay nanocomposites

MMT was treated with the ammonium salt of 12-aminododecanoic acid because it was reported to give a well-dispersed intercalated nanocomposite [11]. Figure 2 shows the x-ray diffraction patterns for the dried MMT and organoclay C12A-MMT. The interlayer spacing of MMT (2θ=7.08, d=12.5Å) increased after surface treatment (with C12-Acid) to 17.8 Å (2θ=4.96). This result confirms the expansion of silicate layers in the organoclay.

Using XRD, we investigated how well the clay was dispersed in PEI. The XRD curves of PEI, PM1~PM5 are shown in Figure 2. For PM1 and PM2, the curves show no peak as pristine PEI, indicating that the peak corresponding to the basal spacing disappeared. This suggests that the organoclay in the nanocomposite dispersed homogeneously into the PEI matrix. When the amount of organoclay was increased to above 3%, there was a small peak at 2θ=6.4°, indicating there was a small amount of organoclay existing in the form of an aggregate structure. The shift of the peak might be attributed to the thermal decomposition of alkyl ammonium ions during imidization [13]. Since ammonium salt is not stable at an elevated temperature, it can decompose to form an amine. The amine is capable of reacting with PAA during imidization and the decomposed organophilic tactoids can form into aggregates [16].

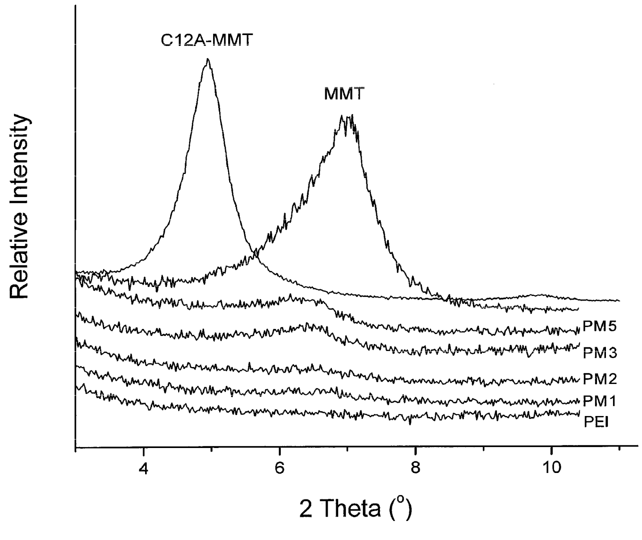


Figure 2. X-ray diffractograms of MMT, organoclay, and PEI-clay nanocomposites.

The onset thermal decomposition temperature increases with increasing clay content (see Table 1); this increase in the thermal stability may be caused by the "barrier effect" of the organoclay layer structure, which hinders mobility of the small molecules produced during the thermal decomposition of the PEI [17]. Though the thermal properties of PEI-clay nanocomposites improved over pristine PEI, the physical test results showed that the films become brittle as the organoclay content increased over 2%. This indicated that the C12A-MMT organoclay is not suitable for the preparation of the PEI nanocomposites.

PEI/silica nanocomposites by sol-gel process

To prepare PEI nanocomposites, we then turned to the sol-gel process. As depicted in Scheme 2, soluble PEI was reacted with a coupling reagent and then TEOS to successfully prepare PEI-silica nanocomposites. Figure 3 illustrates the FTIR spectra of PEI/silica hybrids with various amount of silica. All the films have the characteristic absorption peaks of Si-O-Si. The band of Si-O-Si bending vibration at 454 cm^{-1} increased with greater silica content. However, the characteristic peak of Si-O-Si stretching vibration (near 1050 cm^{-1}) was not obvious and was caused by the presence of a strong absorption at 1090 cm^{-1} from C-O.

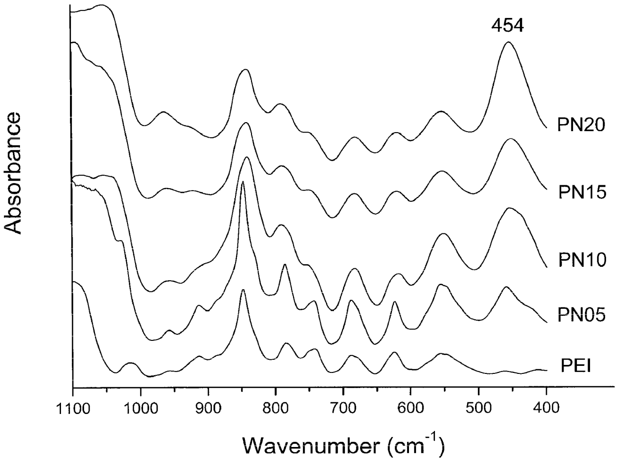


Figure 3. Expanded FTIR spectra of PEI and nanocomposites to show the existence of Si-O-Si absorption.

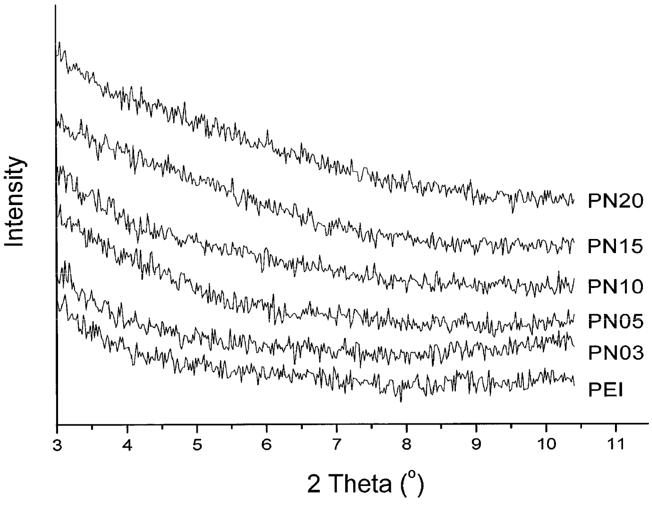
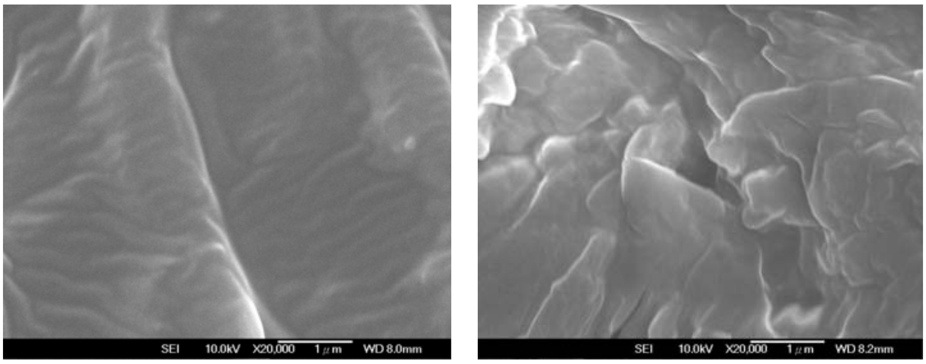


Figure 4. X-ray diffractograms of PEI/silica nanocomposites prepared by the sol-gel process.

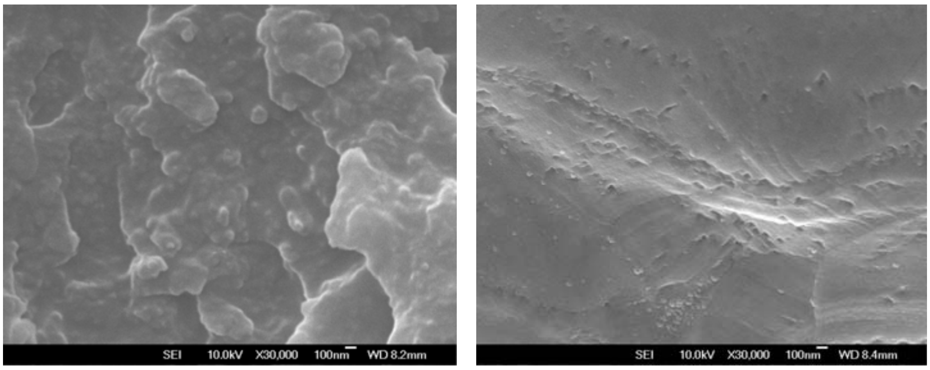
Morphological properties

The XRD curves (Figure 4) show no peak even with a SiO_2 content as high as 20%, indicating an amorphous polymer structure for these PEI nanocomposites. The morphology of the fractured surfaces was elucidated by SEM to investigate the distribution of silica and microphase separation in the hybrid matrix. The SEM in Figure 5a-d compared the fractured surface of hybrid films made by various methods with pristine PEI. In Figure 5a, it showed a smooth morphology for pristine PEI. As the coupling agent was added to prepare hybrid films by sol-gel process, the morphology of fracture surfaces showed a finely interconnected or co-continuous phase (Figure 5b), demonstrating good miscibility between polymer and silica phases. This elucidates the contribution of the coupling agent to the improved compatibility and physical properties of hybrid nanocomposites. Even at 15% silica content, the phase separation situation (see Figure 5c) improved over PEI-clay film made by intercalation (Figure 5d). From the scale, one can see the particle sizes within the hybrid films made by sol-gel process is 50~100 nm. This demonstrates that nanocomposites can be made with current process.



(a) PEI

(b) PEI hybrid with 10% SiO_2.



(c) PEI hybrid with 15% SiO_2.

(d) PEI nanocomposite with 2% MMT organoclay.

Figure 5. SEM micrographs of the fracture surface of PEI and nanocomposites.

Thermal Properties

The glass transition temperature (T_g) of polymers is closely related to the flexibility of the chains. The glass transition temperatures measured by DSC are listed in Table 1 and 3 for PEI-clay and PEI/silica nanocomposites, respectively. It can be seen that the T_g of hybrids increases gradually with increasing silica content. The increase in the T_gs can be attributed to the strong interaction between the organic polymer and the inorganic silica, which causes an increased restricting strength of silica on PEI molecules and hence increases the T_g of composite. These data are consistent with the results by DMA as also shown in Table 3. The onset thermal decomposition temperature increases with increasing silica content as listed in Table 3. They are all above 500°C. This indicates that the synthesized PEIs have high thermal stability. The char yields of the hybrid materials increase with greater amounts of silica. These results indicate that the coupling agent strengthens the interaction between the organic polymer matrix and the inorganic particles. A potential cause of the low char yield of PEI is that *m*-phenylene diamine, one of the necessary monomers for the synthesis, is very susceptible to oxidation. This can result in lower molecular weight PEIs and incomplete imidization, thus creating defects in the polymer chain.

Mechanical properties of the hybrid films

The compatibility between PEI and silica strongly affects the thermal and mechanical properties of PEI. The influence of silica content on the mechanical properties is tabulated in Table 3. Both the tensile strength and the modulus increased with the addition of silica up to 10% wt, with a peak tensile strength and modulus of 106 MPa and 2.32 GPa, respectively. This increase in tensile strength and modulus can be attributed to the improved interaction between the PEI matrix and the silica resulting from the chemical bonds introduced by the GPTMOS coupling agent, and the development of a co-continuous phase morphology (Figure 5b) resulted in a more efficient stress transfer mechanism between the two components [4]. In contrast, addition of greater than 10% wt of silica produced a fast reduction of tensile strength and modulus was related to the phase separation. The elongation at break decreased with the increasing silica content due to the formation of the physical cross-linking between silica and polymer matrix.

Table 3. Thermal and mechanical properties of PEI nanocomposites.

Code	T_g [a] (°C)	T_g [b] (°C)	$T_{d,\ onset}$ (°C)	Char yield [c] (%)	Tensile strength (MPa)	Modulus (GPa)	Elongation at break (%)
PEI	214	220	542	48.0	90.4	2.14	51
PN05	217	223	559	51.5	95.3	2.23	43
PN10	221	226	589	56.9	105.9	2.32	36
PN15	223	227	600	60.0	83.5	2.04	23
PN20	224	228	608	60.8	71.6	1.84	14

[a] Measured by DSC. [b] Measured by DMA. [c] Residual wt % in nitrogen at 800°C.

Dielectric properties

The dielectric strength is an important parameter for selecting an appropriate electrical insulation material [18]. Dielectric constants of polyimides, in general, are known to decrease gradually with increasing frequency [19]. The measurement results of the dielectric constants of PEI/silica nanocomposite films at 1 MHz are shown in Figure 6. The dielectric constant decreased with increasing amounts of silica. The decreased dielectric constants might be attributed to the reduction in the freedom of orientation of the silica and main-chain flexibility of the PEI matrix [20].

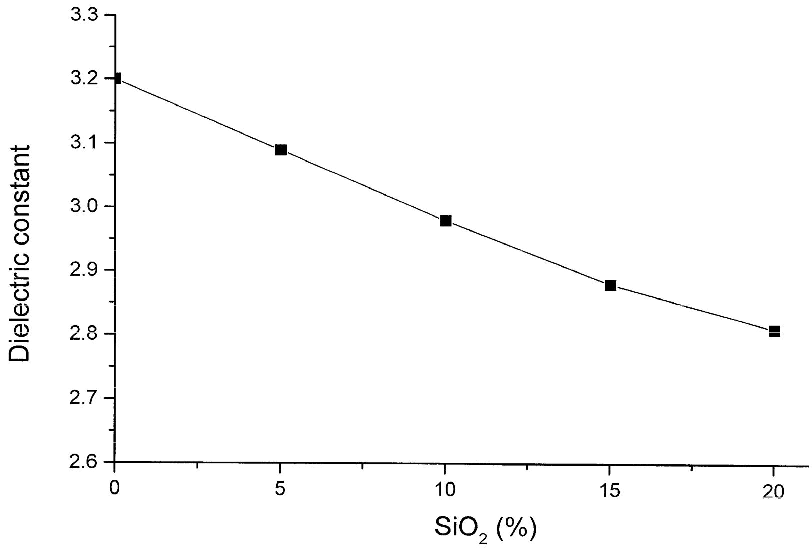


Figure 6. Dielectric constants of PEI nanocomposites measured at 1 MHz.

Conclusions

The thermal properties of PEI-clay nanocomposites improved over pristine PEI, but the physical test results showed that the films become brittle as the organoclay content increased over 2%. This indicated that the organoclay is not suitable for the preparation of the PEI nanocomposites.

The PEI/silica nanocomposites with improved thermal, mechanical and dielectric properties can be prepared via a sol-gel process from soluble PEI. The thermal stability and mechanical properties of the PEI were improved with the addition of silica content up to 10%. The onset thermal decomposition temperatures were 550-600°C. The morphology of the fracture surfaces investigated by SEM showed a finely interconnected or co-continuous phase. This demonstrated the coupling agent contribution to the improved miscibility between polymer and silica phases in hybrid nanocomposite. The dielectric constants were decreased with the incorporation of silica. At higher silica contents (15~20%), mechanical properties were reduced due to the phase separation resulting from the aggregation of silicates.

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