Effects of *meta* and *para* Diamines on the Properties of Polyetherimide Nanocomposite Films Prepared by the Sol-Gel Process

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ABSTRACT: The effects of chemical structure of diamines on the properties of polyetherimide (PEI) nanocomposite films prepared by the sol-gel process were investigated. For *meta* diamine, nanocomposites with improved thermal, mechanical, and dielectric properties can be prepared by a sol-gel process from soluble PEI via chemical imidization, with silica content up to 10%. However, for the PEI with *p*PDA as diamine and bisphenol A dianhydride, a two-stage sol-gel process via thermal imidization was necessary to prepare the nanocomposites. The thermal stability and mechanical properties were improved with the addition of up to 5 wt % of silica content. The variation could be attributed to the fact that differences in the compatibility between PEI and SiO_2 for two kinds of PEI with the different *meta* and *para* structure of the diamine monomer. The morphology of the fracture surfaces investigated by SEM showed a finely interconnected or cocontinuous phase for PEI nanocomposites with the silica content of up to 10% and 5 wt % for *m*PDA and *p*PDA as diamine, respectively. At higher silica contents, thermal and mechanical properties were reduced due to the aggregation of SiO_2. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 1093–1100, 2007

Key words: polyimides; polyetherimide; sol-gel; nanocomposites; incompatibility

INTRODUCTION

In many advanced microelectronic applications, aromatic polyimides (PIs) are the widely used engineering polymers. However, PIs are difficult to fabricate due to their high softening temperature and insolubility. One of the successful approaches to increase the solubility of polyimides is the introduction of flexible linkages into the polymer backbone.[1] An important commercialized product, which contains flexible ether and isopropylidene groups, is Ultem 1000. An amorphous polyetherimide (PEI) introduced by General Electric Co. (Pittsfield, MA), which is synthesized via the polycondensation of a dianhydride, 4,4′-(4,4′-isopropylidene diphenoxy)bis(phthalic anhydride) [BPADA], with *m*-phenylene diamine (*m*PDA),[2] exhibits good solvent solubility, thermal stability, and mechanical properties. Ether units supply chain flexibility and good melt flow characteristics to PEI, while the aromatic imide units provide thermal resistance and mechanical properties. Although Ultem 1000 has good melt processability and solubility in some solvents, its relatively poor thermal stability limits its

application in advanced materials. To improve the thermal properties of Ultem 1000, General Electric further introduced Ultem 5000 by substituting *m*PDA with *p*-phenylene diamine (*p*PDA) as one of the monomers.[3] Though the thermal stability was improved, it is insoluble in most solvents. This difference in the chemical structure of diamines has resulted in PEIs with different properties.

In an attempt to improve the thermal and mechanical properties of these two important PEIs with different diamines, we studied the preparation of hybrid nanocomposites of PEI. Hybrid materials combine the properties of organic and inorganic materials, and offer specific advantages with improved thermal and mechanical properties.[4–6] Thus, organic–inorganic hybrid materials have attracted much attention. The sol-gel process is one of the most extensively applied methods for preparation of organic–norganic nanomaterials, which allows the formation of inorganic frameworks under mild conditions and the incorporation of minerals into polymers, resulting in increased thermal stability, mechanical, and dielectric properties without decreasing the properties of the polymers.[7–10] In this article, we utilized sol-gel process to prepare hybrid nanocomposites for these two important PEIs. The nanocomposites were characterized by FT-IR to identify the chemical structures. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)

were used to measure the thermal properties. X-ray diffractometer (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were utilized to study the morphology of the nanocomposites. Their preparation method, morphological, thermal, and mechanical properties are compared and discussed.

EXPERIMENTAL

Materials

Reagent grade chemicals were purchased from various commercial sources, including 4,4'-(4,4'-isopropylidene diphenoxy)bis(phthalic anhydride) [BPADA] (Aldrich), *m*-phenylene diamine (*m*PDA) (Acros), *p*-phenylene diamine (Acros), tetraethoxysilane [TEOS] (Acros), 3-glycidyloxypropyl trimethoxysilane [GPTMOS] (Acros), 3-aminopropyl-triethoxysilane [APrTEOS] (Acros), *N*-methyl-2-pyrrolidone [NMP] (Tedia), and toluene (Tedia). BPADA was dehydrated by drying under a vacuum at 100°C for 24 h. Diamines were further purified by sublimation before use. NMP was purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves prior to use. Common reagents, such as TEOS, GPTMOS, and toluene were used as received without further purification.
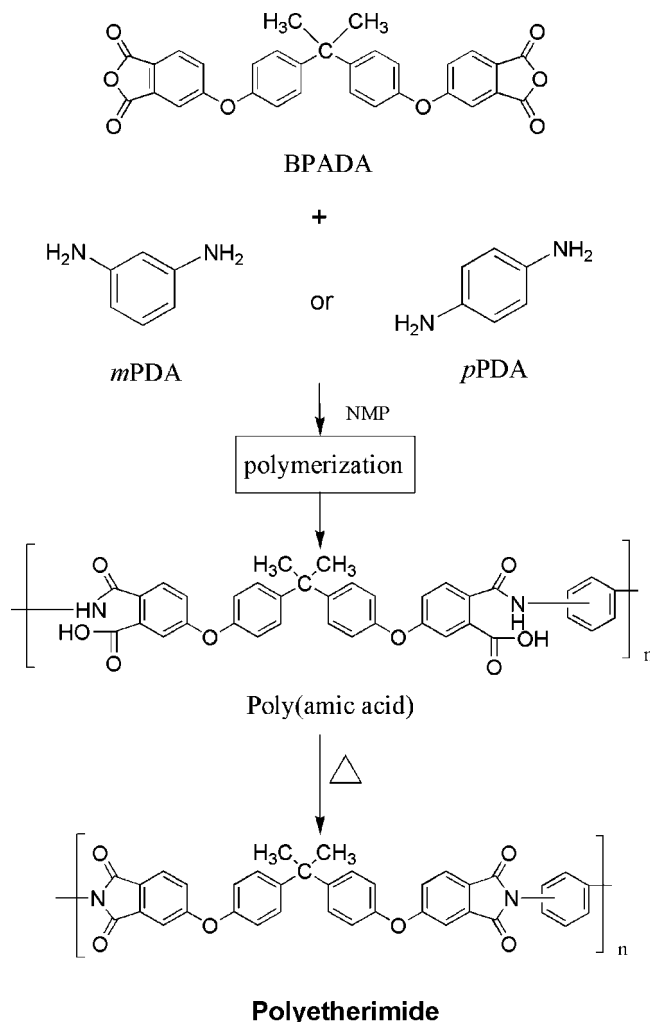
Synthesis of polyamic acid

Polyetherimide (PEI) was synthesized by reacting a diamine, *m*PDA or *p*PDA, with BPADA as illustrated in Scheme 1. Diamine 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 diamine solution to make a solution with a solid content of 20%. The reaction mixture was stirred for 2 h at 60°C and resulted in a transparent yellow viscous solution of polyamic acid (PAA).

Preparation of the PEI/silica nanocomposite films from PAA

PEI or polyimide nanocomposites have been prepared by two-stage sol-gel process via polyamic acid (PAA), the precursor.[5,6] For PEI with *p*PDA as the diamine, the procedure to prepare PEI/silica nanocomposite films as follows.

In a flask, different contents of the coupling agent APrTEOS was charged into the above-mentioned PAA solution and stirred for 1 h. Then, hydrolyzed TEOS solution was added and stirred at 70°C for 4 h to produce a hybrid solution (Scheme 2). The

**Scheme 1** Synthesis of polyetherimide.

amount of APrTEOS and TEOS used are tabulated in Table I.

The hybrid PAA solution was spread on a glass plate using a spin-coater to obtain a PAA hybrid film. The films were thermally dried at 60°C for 4 h to remove most of the solvent in a forced air oven and were imidized to PEI hybrid with a heating program of 100, 150, 200°C for 1 h each, and at 250°C for another hour. The films were cooled, soaked in water, and stripped from the plates. After drying the aforementioned films at 110°C for 24 h in vacuum, the PEI/silica hybrid films were obtained.

Preparation of the PEI/silica nanocomposite films from soluble PEI

For a soluble PEI, the nanocomposite can also be prepared utilizing a novel sol-gel process.[11,12]

Twenty-milliliter of toluene was added to PAA (with *m*PDA as the diamine) and the mixture was heated to ~ 160°C at reflux for ~ 8 h until the water was azeotropically distilled off via a Dean-Stark
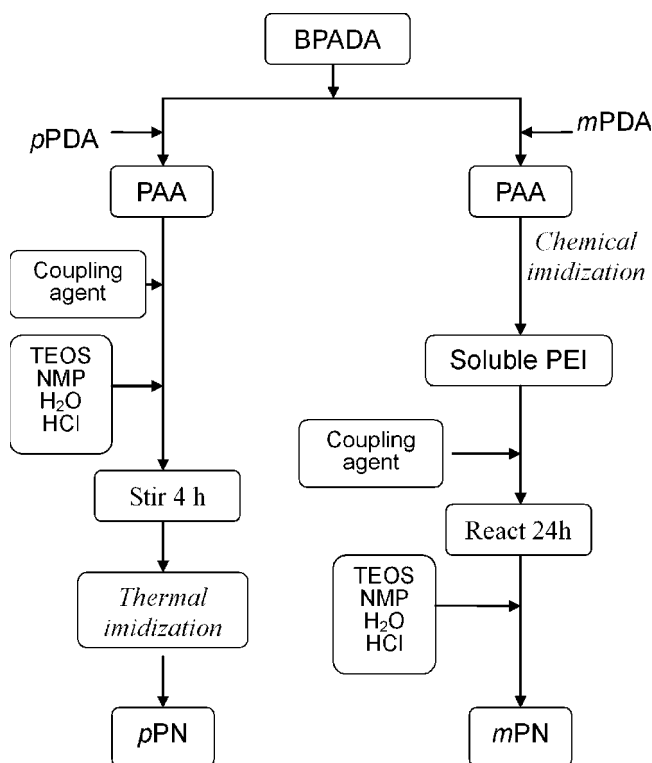
Scheme 2 Synthesis of PEI nanocomposites via the sol-gel process.

trap. Heating was continued to distill off the residual toluene. After the completion of polymerization, the viscous PEI solution was cooled; coupling agent GPTMOS was charged into the PEI solution and stirred at 70°C for 24 h. Then, pH adjusted hydrolyzed TEOS solution was added and stirred for 6 h to produce a hybrid solution (Scheme 2). The amount of GPTMOS and hydrolyzed TEOS solution used for various hybrid nanocomposites are shown in Table I. 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 an oven gradually up to 250°C and hold for another hour to remove all solvents. The rest of the steps for preparing the PEI/silica hybrid films are the same as the procedure described above.

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. 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). The morphologies of the fracture surfaces of hybrid materials were observed with a JEOL JSM-6700 scanning electron microscope. The samples for TEM study were prepared by placing PEI films in an epoxy resin and curing the resin at 60°C for 48 h. The cured epoxies containing PEI-silica were microtomed with a diamond knife into ~ 70 nm thick slices and placed on a 200-mesh copper grid and examined with a Hitachi TEM H-7500 using an acceleration voltage of 100 KV. 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).

RESULTS AND DISCUSSION

The difference in the chemical structure affected the sol-gel process

Polyimide nanocomposites have been prepared by two-stage sol-gel process through polyamic acid (PAA) and imidized via thermal imidization.[5,6] For a soluble PEI with mPDA as the diamine, the nanocomposite can also be prepared utilizing a novel sol-gel process via chemical imidization.[12] However, due to its insolubility in organic solvents, the PEI with pPDA as diamine the nanocomposite films can only be prepared by a two-stage sol-gel process.

TABLE I
The Codes of Polymers and Experimental Conditions for Preparing PEI/Silica Hybrids

Diamine	$SiO_2{}^a$ (wt %)	Code	Coupling agent^c (g)	TEOS (g)	$H_2O{}^d$ (g)
mPDA	0	mPEI^b	–	–	–
mPDA	5	mPN05	0.125	0.99	0.34
mPDA	10	mPN10	0.263	2.08	0.72
mPDA	15	mPN15	0.417	3.31	1.14
mPDA	20	mPN20	0.591	4.69	1.62
pPDA	0	pPEI^b	–	–	–
pPDA	3	pPN03	0.069	0.58	0.20
pPDA	5	pPN5	0.117	0.99	0.34
pPDA	7	pPN7	0.167	1.41	0.49
pPDA	10	pPN10	0.246	2.08	0.72

^{a} Weight percent of total silica in the hybrid, 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.
^{b} Basis, BPADA and diamine 0.01 mole.
^{c} GPTMOS for mPN, APrTEOS for pPN.
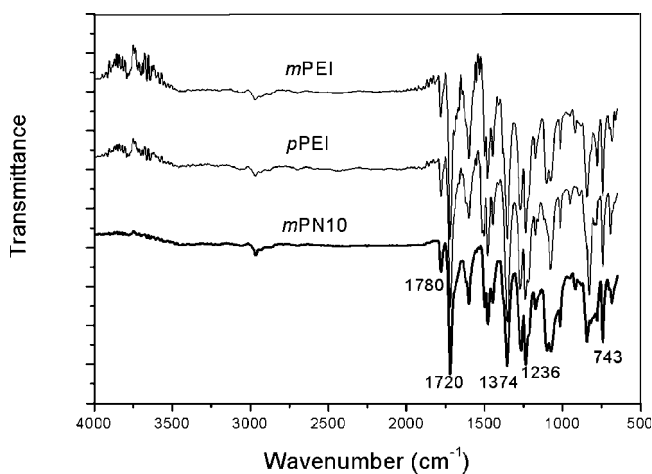^{d} Add water to make molar ratio TEOS : H_2O = 1 : 4.

Figure 1 FTIR spectra of *m*PEI, *p*PEI, and *m*PN10.

FTIR

Synthesis of PEI

The FTIR spectra of the PEI with mPDA or pPDA as the diamines are 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 1374 and 743 cm^{-1} (C—N stretching and bending), and at 1236 cm^{-1} (aromatic ether C—O—C). However, the difference in diamines did not show much variation in the IR spectra.

PEI/silica nanocomposites by sol-gel process

The FTIR spectrum of *m*PN10 is also shown in Figure 1. It exhibits all the characteristic absorptions of PEI as discussed above. Figure 2 illustrates the expanded FTIR spectra of PEI/silica hybrids with various amount of silica. The PEI was synthesized from mPDA. 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. The PEI/silica hybrids synthesized from pPDA have similar spectra.

Coupling agents

For the preparation of PEI/silica nanocomposites *p*PN, coupling agent GPTMOS was used first and the experimental results showed that hybrids could not be prepared successfully. This can be attributed to the reaction scheme as shown in Figure 3(a); the PAA reacted with GPTMOS and could not be cyclized to become an imide. When APrTEOS was

employed as coupling agent instead, the intermediate could be cyclized to become the imide structure as illustrated in Figure 3(b). This demonstrated that the difference in the chemical structure of the diamine would affect not only the sol-gel process used in the preparation of PEI/silica nanocomposites, but also the coupling agent chosen.

Morphological properties

The XRD curves of PEI and PEI/silica hybrids for the diamine is *m*PDA and *p*PDA are shown in Figure 4 (a,b), respectively. For PEI/silica hybrids synthesized from *m*PDA, the curves show no peak even with a SiO$_2$ content as high as 20%. However, for PEI hybrids with *p*PDA as the diamine, silica content above 5% demonstrated a small peak in 2θ = 5.0, and the peak intensity increased with the addition of silica content. This indicated that there was a small amount of silica that could not be effectively dispersed and existed as aggregates. A full-scale XRD spectrum (2θ = 3–60°) did not show other peaks. This could be attributed to the difference of compatibility between PEI and silica for two kinds of diamines.

The morphology of the fractured surfaces was elucidated by SEM to investigate the distribution of silica in the hybrid matrix. The SEM in Figure 5(a–d) compared the fractured surface of hybrid films made by various methods. For pristine PEI, the morphology was smooth.[12] As the coupling agent was added to prepare hybrid films from soluble PEI when diamine was *m*PDA, the morphology of fracture surfaces with 10% silica content showed a finely interconnected or cocontinuous phase [Fig. 5(a)], demonstrating good miscibility between polymer and silica phases. This elucidated the contribution of the coupling agent to the improved compatibility and physi-
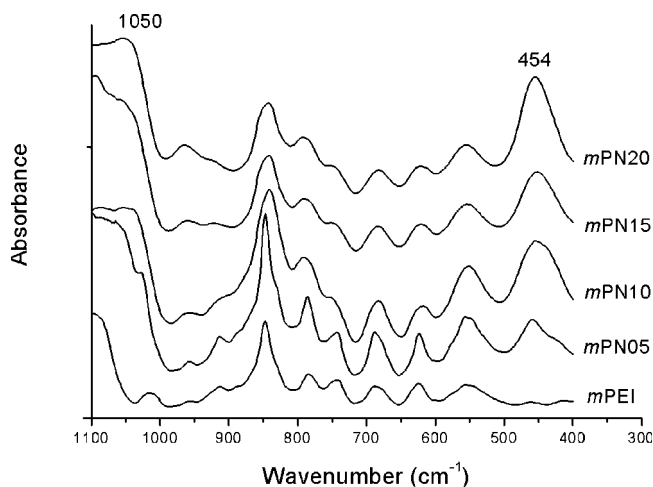

Figure 2 Expanded FTIR spectra of PEI and nanocomposites to show the existence of Si—O—Si absorption.

Poly(amic acid)
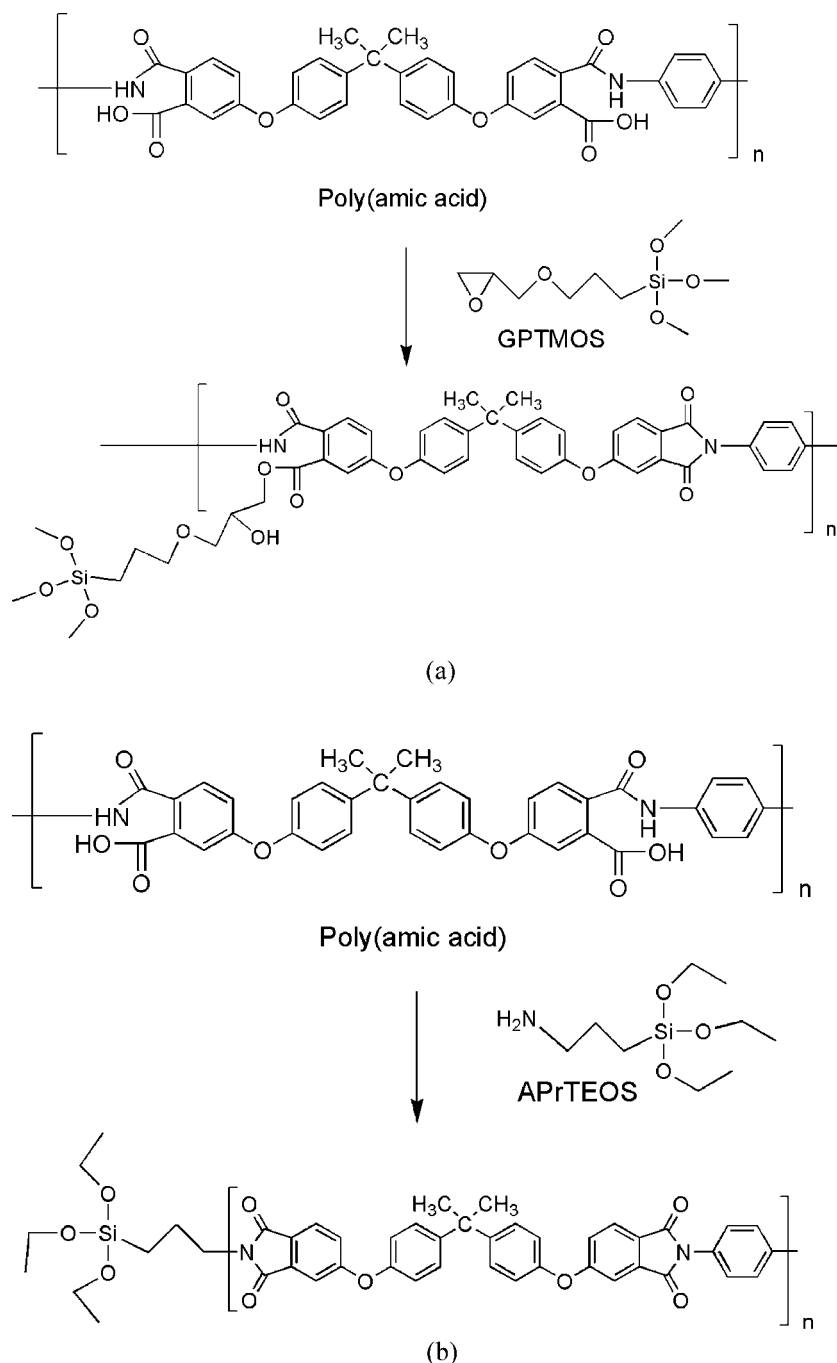
(a)

Poly(amic acid)

(b)

Figure 3 Reaction scheme of PAA with coupling agents, (a) GPTMOS, (b) APrTEOS.

cal properties of hybrid nanocomposites. From the TEM of mPN10, one can see the shape of the included silica particles is round and the particle sizes within the hybrid films is $\sim$ 100 nm as shown in Figure 6(a). This demonstrated that nanocomposites can be made by the sol-gel process. When pPDA was used as the diamine, only at up to 5% silica content the morphology of the fractured surfaces of hybrid film (pPN05) showed a continuous phase [Fig. 5(b)]. When the silica content was 10%, the morphology [Fig. 5(c)] was worse than that of

mPN15 (mPDA as diamine with 15% silica content) as illustrated in Figure 5(d). The differences in the morphology of nanocomposites could be attributed to the fact that differences in the compatibility between PEI and SiO_2 for two kinds of PEI. From the TEM of pPN05 as shown in Figure 6(b), one can see the aggregation of SiO_2, such aggregation was probably caused by the interaction between the Si—OH groups. These Si—OH groups were formed through hydrolysis of TEOS and APrTEOS.[8] The aggregation phenomenon was also observed by XRD.
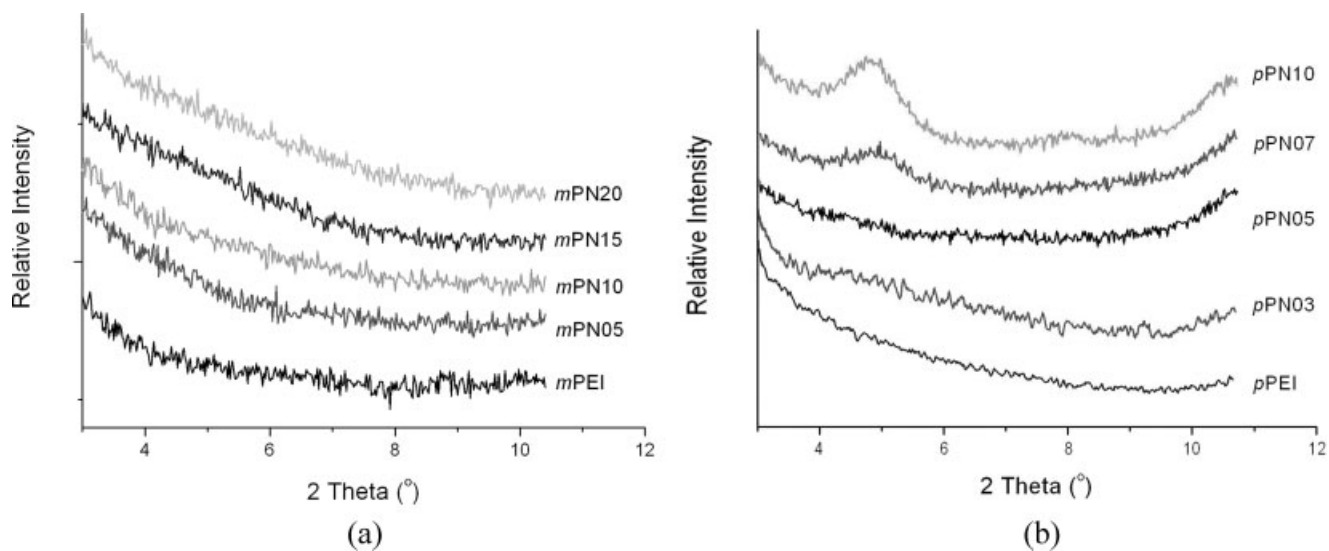
Figure 4   X-ray diffractograms of PEI/silica nanocomposites, (a) *m*PN and (b) *p*PN.
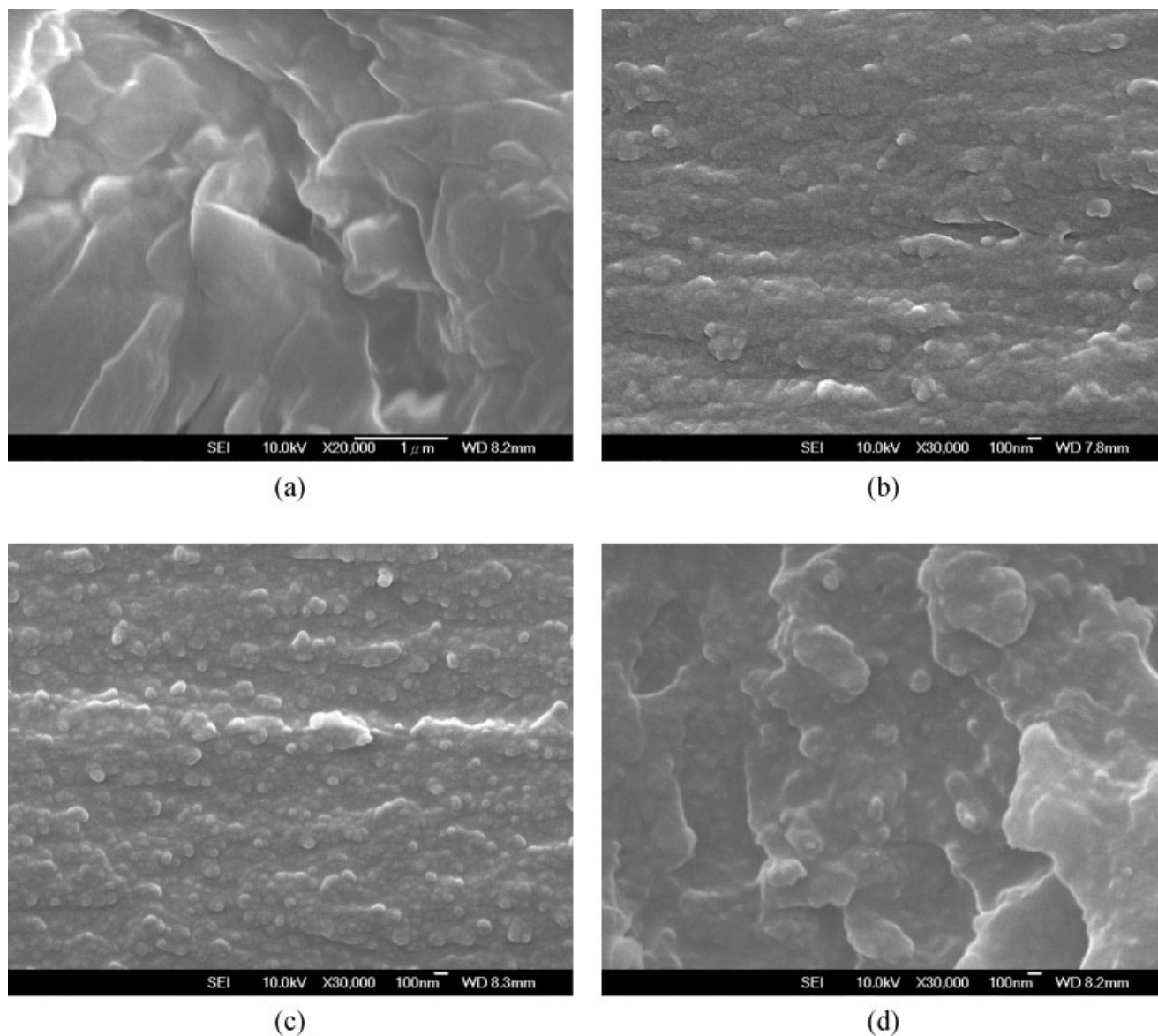

Figure 5   SEM micrographs of the fracture surface of PEI nanocomposites. (a) PEI hybrid *m*PN10, (b) *p*PN05, (c) *p*PN10, and (d) *m*PN15.
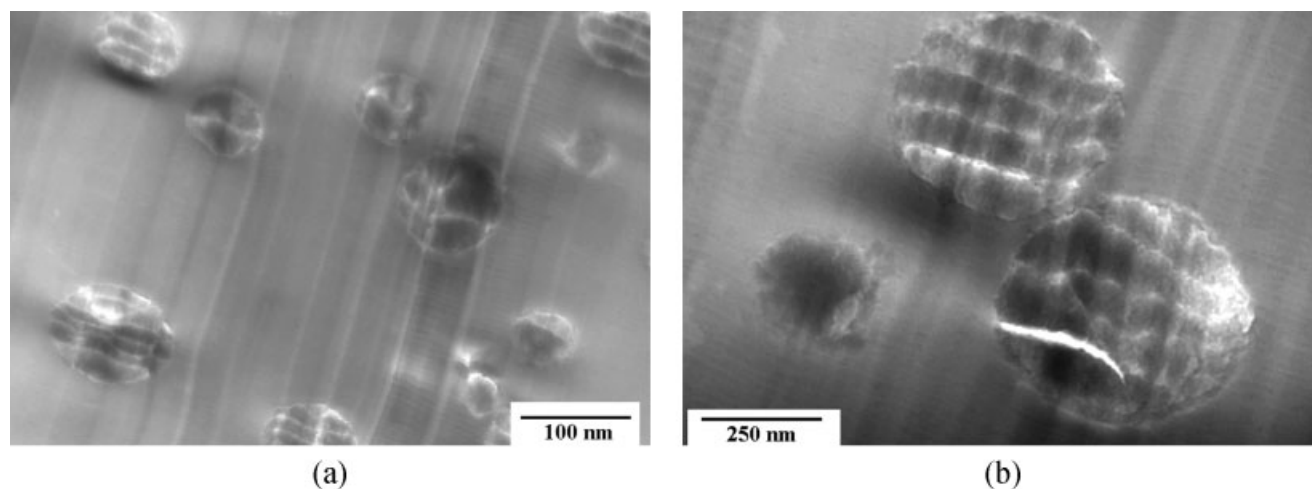
Figure 6 TEM micrographs of (a) *m*PN10 and (b) *p*PN05 nanocomposites.

Thermal properties

The chemical structure affects the thermal properties of polymers.[13] The glass transition temperature (T_g) of polymers is closely related to the flexibility of the chains.[14] The measured glass transition temperatures are listed in Table II. It can be seen that the T_g of PEI synthesized with *p*PDA is higher than that made with *m*PDA. This can be explained by the difference in chemical structure of PEIs, since *m*PEI is less ordered and more flexible in 3D structure than *p*PEI. The T_g of hybrids increased gradually with increasing silica content in both cases. The increase in the T_gs can be attributed to the strong interaction between the organic polymer matrix and the inorganic silica, which caused an increased restricting strength of silica on PEI molecules and hence increased the T_g of the composite.[15] However, at higher SiO$_2$ content, T_g started to decrease slightly due to the aggregation of SiO$_2$ in the hybrids. TGA curves of some representative nanocomposites and pure PEI had been presented in Figure 7. The thermal decomposition temperatures at 10% weight loss ($T_{d,10\%}$) in nitrogen (listed in Table II) had similar trends as the T_g. $T_{d,10\%}$ increased gradually with increasing silica content, but at higher SiO$_2$ content it again decreased and was slightly lower than that of pristine PEI. This may result from the Si—OH residual groups in hybrid thin films, which increases with the inorganic content because of the incomplete condensation reaction.[16] The trend of these thermal properties is consistent with the data observed by other researchers.[17] However, $T_{d,10\%}$ values are above 550°C, which indicates that the PEI/silica nanocomposites have a high thermal stability. The char yields of the hybrid materials increased with greater amounts of silica. These results indicate that the coupling agent strengthens the interaction between the organic polymer matrix and the inorganic particles.

TABLE II
Thermal and Mechanical Properties of PEI/Silica Nanocomposites

Code	$T_g{}^a$ (°C)	$T_{d,10\%}$ (°C)	Char yield[b] (%)	Tensile strength (MPa)	Modulus (GPa)
*m*PEI	214	568	48.0	90	2.14
*m*PN05	217	572	51.5	95	2.23
*m*PN10	221	582	56.9	106	2.32
*m*PN15	223	570	60.0	84	2.04
*m*PN20	220	566	60.8	72	1.84
*p*PEI	225	571	50.4	90	3.08
*p*PN03	233	575	54.3	94	3.25
*p*PN05	235	577	54.9	96	3.57
*p*PN07	230	569	55.8	74	2.82
*p*PN10	226	564	60.2	50	2.44

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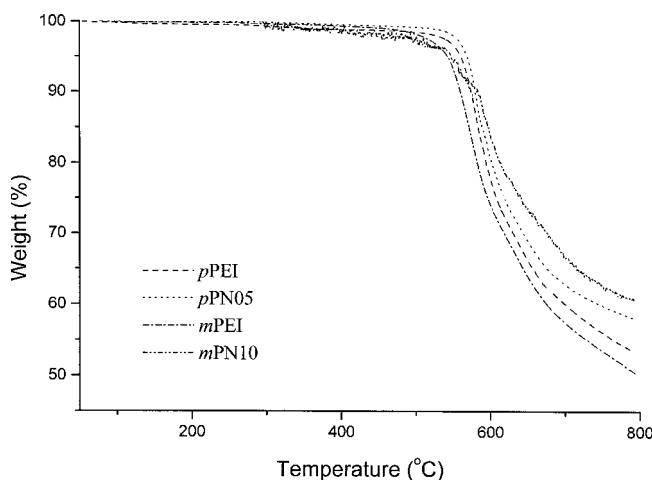[b] Residual wt % in nitrogen at 800°C.

Figure 7 TGA curves of some representative nanocomposites and pure PEIs.

Mechanical properties of the hybrid films

The effects of *meta* and *para* diamines on the mechanical properties of PEI are similar to that of the thermal properties, which is mainly caused by the orderly structure of PEI with *para* diamine. The compatibility between PEI and silica strongly affects the thermal and mechanical properties of PEI hybrids. The influence of silica content on the mechanical properties is tabulated in Table II. For PEI hybrids synthesized with *m*PDA, both the tensile strength and the modulus increased with the addition of silica up to 10 wt %. 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 coupling agent, and the development of a cocontinuous phase morphology that resulted in a more efficient stress transfer mechanism between the two components.[5] In comparison, for PEI hybrids synthesized with *p*PDA, both the tensile strength and the modulus only increased with the addition of silica up to 5 wt %. These results are consistent with the findings in morphological study. The addition of silica greater than 10 wt % in *m*PN hybrids or 5% in *p*PN produced a fast reduction of tensile strength and modulus that was related to the aggregation of SiO_2 in the hybrids.

CONCLUSIONS

The difference in the chemical structure of diamines in PEI affected the properties of nanocomposites and preparation method of the sol-gel process. For the PEI synthesized with *meta* diamine, nanocomposites with improved thermal and mechanical properties can be prepared from soluble PEI via the chemical imidization. Whereas, only a two-stage sol-gel process via thermal imidization can be utilized to prepare the nanocomposites for PEI synthesized with *p*PDA as the diamine.

The thermal stability and mechanical properties were improved with the addition of silica content up to 10% and 5 wt % for *m*PEI and *p*PEI, respectively.

The variation could be attributed to the difference of the compatibility between PEI and silica for two kinds of diamines. At higher silica contents, thermal and mechanical properties were reduced due to the aggregation of SiO_2 in the hybrids. The synthesized PEI nanocomposites have high thermal stability (the thermal decomposition temperatures were above 550°C) and good mechanical properties. Thus, these polymers may be the candidates for high-performance microelectronic applications.

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