Surface-Modified Silica Nanoparticle–Reinforced Poly(ethylene 2,6-naphthalate)

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ABSTRACT: The effect of stearic acid modification on the dispersity of silica nanoparticles and the adhesion between the filler and polymer matrix with stearic acid concentration were investigated. The wettability of silica nanoparticles was improved by the addition of stearic acid. The presence of adsorbed stearic acid on the surface of the silica nanoparticles reduced the interaction between silica nanoparticles, and reduced the size of agglomerates with increasing concentration. Silica nanoparticle–reinforced poly(ethylene 2,6-naphthalate) (PEN) composites were melt-blended to investigate their mechanical properties and the processability of the composites. The torque and total torque values of the composites decreased with increasing silica nanoparticle content. The tensile moduli of the composites reinforced with unmodified silica nanoparticles increased with increasing silica content, whereas the tensile strength and elongation decreased. However, the stearic acid–modified silica nanoparticle–reinforced PEN composites exhibited increased elongation and decreased tensile moduli with increasing content because stearic acid, which adsorbs onto the surface of the silica nanoparticles in layers thicker than a monolayer, acts as a plasticizer during the melt-compounding stage. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 812–818, 2004

Key words: poly(ethylene 2,6-naphthalate) (PEN); nanoparticles; mechanical properties; composites; silicas

INTRODUCTION

High-performance poly(ethylene 2,6-naphthalate) (PEN), with its superior physical and mechanical properties, has been used in specialty films, fibers, and in blow moldings.[1–3] However, the applications of PEN are limited because PEN exhibits a relatively high melt viscosity, which makes fiber spinning and injection molding difficult.[4] In our previous study,[5] unmodified silica nanoparticle–reinforced PEN composites were melt-blended in an attempt to improve the mechanical properties and processability of the polymer composite, and we confirmed the possibility of improving the processability of PEN. When silica nanoparticles are used as the filler, they act as a lubricant during melt compounding, because they allow for slippage between the polymer matrix and filler, rather than relying on the decrease in molecular weight of the polymer matrix.[6,7]

However, the mechanical properties of the unmodified silica nanoparticle–reinforced composites tended to be worse than those of pristine PEN. A major problem of such materials is the nonuniformity of the resulting properties attributed to the poor dispersion of the filler in the polymer matrix, and to adhesion occurring at the polymer–filler interface.[7–9] These problems have been solved by the surface modification of the dispersed phase by incorporating a suitable modifier.[10]

Chemical surface modification is widely used to obtain a high wettability for a solid surface, a good dispersion of particles, and adhesion of fillers in composite materials.[8] Chemical surface modification can be categorized as follows:

1. *Surface modification by chemical reaction*. This type of surface modification promotes a chemical reaction between the polymer matrix and an inorganic filler to strengthen the adhesion. Two reagents are mainly used in chemical surface modification to obtain a hydrophobic surface: an alkyl silane coupling agent[7,11–14] and an alcohol.[8,9]

2. *Surface modification by a nonreactive modifier*. A nonreactive modifier reduces the interaction between the filler particles within agglomerates by reducing the physical attraction rather than by any chemical reaction.[15,16] Stearic acid has been widely used as a noninteracting surface modifier. A modified nanofiller can easily be incor-

porated into a polymer matrix, resulting in a reduction in the melt viscosity and, in most cases, an improved dispersion of the nanofiller in the composite.[15,16]

In this study, silica nanoparticles were modified with stearic acid to improve their dispersion and the adhesion between the filler and polymer matrix. The wettability, surface density of the modifier, and the average particle size of the silica nanoparticles were investigated. Surface-modified silica nanoparticle–reinforced PEN composites were prepared by melt compounding, which is expected to be more economical and simpler to use than *in situ* polymerization. The effects of silica nanoparticles modified with stearic acid on the mechanical properties and the processability of PEN were also investigated.

EXPERIMENTAL

Materials and surface modification

The PEN used [intrinsic viscosity (IV) = 0.93 dL/g] was supplied by the Hyosung Co. (Seoul, Korea) and the hydrophilic fumed silica used (primary particle size = 7 nm, surface area = 390 m^2/g, purity = 99.8%, hydroxyl group content = 2.5 nm^{-2}) was purchased from the Aldrich Co. (Milwaukee, WI). The granular-type stearic acid, used as a surface modifier (M_w = 284.48, mp = 68–71°C, bp = 361°C), was purchased from the Junsei Chemical Co. (Tokyo, Japan). The isopropyl alcohol, used as a solvent (bp = 82.5°C), was purchased from Carlo Erba Reagenti (Milan, Italy) and used without further purification.

Surface modification of fumed silica nanoparticles by stearic acid was achieved as follows. Stearic acid was initially added to isopropyl alcohol and the mixture stirred for 1 h. Fumed silica nanoparticles were then added to the mixture, with the ratio of silica nanoparticles and stearic acid being defined using the following equation[11]:

$$X = (A/w)B \qquad (1)$$

where X is the mass of stearic acid needed to obtain a minimum uniform coverage of the filler particles (in g), B is the mass of filler (in g), A is the surface area of the filler (380 m^2/g), and w is the wetting surface of the stearic acid (445 m^2/g).[17] In this study, four stearic acid concentrations in the total mixture (1, 2, 4.25, and 5 wt %) were used to investigate the effect of surface modification, with the silica nanoparticle content remaining at 5 wt % for the total mixture. The sample codes used are listed in Table I. Ball milling of the mixture was performed for 6 h at 200 rpm. The homogeneous mixture was placed in a rotary evaporator to remove the solvent, and then dried *in vacuo* at 90°C for 24 h.

TABLE I
Compositions of the Surface-Modified Fumed Silica

Sample code	Stearic acid (wt %)	Fumed silica (wt %)	Ratio of stearic acid to fumed silica
Unmodified silica	—	5.0	—
ST 0.2	1.0	5.0	0.2:1
ST 0.4	2.0	5.0	0.4:1
ST 0.85	4.25	5.0	0.85:1
ST 1.0	5.0	5.0	1:1

Sample preparation

All the samples were dried for 24 h at 100°C *in vacuo* to ensure low moisture levels. Silica nanoparticle–reinforced composites were prepared using a Haake Rheomix 600 internal mixer (Haake Co., Bersdorff, Germany) at various silica contents (0, 0.5, 1, 2 wt %). The melt compounding was performed at 275°C for 5 min, using a rotor speed of 60 rpm, with the total mixing weight per batch being 50 g. Online measurements of the torque and total torque values were performed using the Haake rheometer during melt compounding.

Characterization

The number of stearic acid molecules existing on the surface of the silica nanoparticles was determined using a thermogravimetric analyzer (TGA Model 2960; TA Instruments, New Castle, DE). The TGA was used to calculate the difference in sample weights before and after burning off the hydrocarbons of the modifier. The surface wettability of the modified silica nanoparticles was calculated using the Washburn sorption method, and the average particle size was determined using a laser particle size analyzer (LS 230, Beckman Coulter Inc., Fullerton, CA). The mechanical properties of the silica nanoparticle–reinforced PEN composites were investigated using a UTM Instron 4465 tensile-testing machine (Canton, OH) using a crosshead speed of 1 mm/min and a gauge length of 7 cm. The morphology of the prepared samples was observed using a field-emission scanning electron microscope (FE-SEM, Model JSM-6330F; JEOL, Tokyo, Japan) to investigate the dispersed state of the silica nanoparticles in the PEN matrix. A thin layer of platinum was sputtered onto the surface of the samples to achieve an electrically conducting coating before measurements were carried out.

RESULTS AND DISCUSSION

Characterization of the surface modification

Surface density of the modifier

The results of the TGA measurements for silica nanoparticles with different concentrations of stearic acid
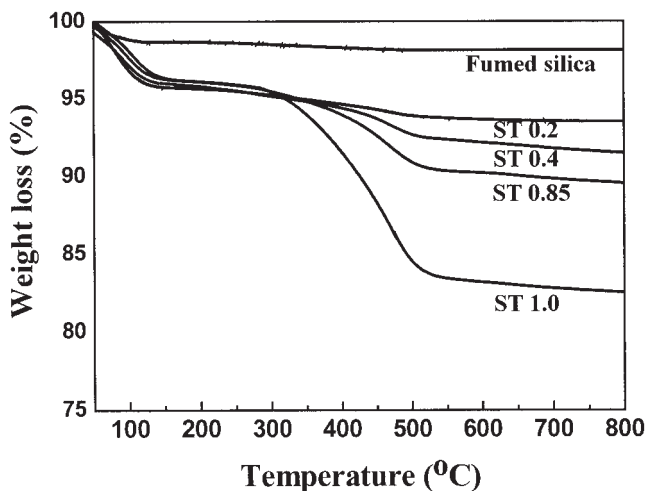
Figure 1 Variation in the TGA curves on modification of nanoparticles with stearic acid.

are shown in Figure 1. The mass of modifier was estimated from the weight loss from the TGA curves in the combustion region. However, the weight loss obtained from the TGA curves involves the combined weight loss of desorbed water molecules and of the surface silanols in the sample. Therefore, it was necessary to determine the weight loss of the desorbed water molecules from the weight loss of the unmodified sample. The mass of modifier was determined using the combined weight loss of the modifier,[8] as follows:

$$OR = \frac{(\delta W_m - \delta W_h) \times N_A}{M \times W_s \times S_{BET}} \qquad (2)$$

where OR is the surface density of the modifier (in nm^{-2}), δW_m is the weight loss attributed to pyrolysis of the modifier (in μg), δW_h is the weight loss attributed to dehydration of the silanols (in μg), N_A is Avogadro's number (6.022×10^{23} mol^{-1}), M is the molecular weight of the modifier (in g/mol), W_s is the weight of the sample (in μg), and S_{BET} is the BET surface area (in m^2/g). The surface coverage ratio was calculated from the ratio of the surface density of the modifier and the concentration of hydroxyl groups in the unmodified silica (2.8 nm^{-2}),[8] and the experimental values are listed in Table II.

TABLE II
Surface Characterization of Silica Nanoparticles with Stearic Acid

Sample	ST 0.2	ST 0.4	ST 0.85	ST 1.0
Surface density of modifier, nm^{-2}	0.08	0.15	0.27	0.88
Coverage ratio, %	2.8	5.3	9.6	31.4

TABLE III
Characteristics of the Test Liquids (*N*-Hexane, Methanol, and Water)

Property	*N*-Hexane	Methanol	Water
Density, g/cm^3	0.66	0.79	1.00
Viscosity, cP	0.32	0.59	0.89
Surface tension, mN/m	18.43	22.70	72.80

The coverage ratio was calculated by considering the surface density of the modifier and the concentration of surface silanol groups alone. The unmodified fumed silica nanoparticles had a specific surface area of 390 m^2/g and, therefore, 1 g of stearic acid could cover around 445 m^2 of the inorganic filler surface.[18] Hence, this mass of stearic acid is sufficient to cover the surface silanol groups of the silica nanoparticles.[18,19]

Wettability of the modified silica nanoparticles

The wettability was estimated from contact angle measurements, which indicates the degree of wetting when a solid interacts with a liquid. The lower the value of the contact angle, the higher the degree of wetting. Although various methods have been used to characterize wettability,[20] the contact angle method is still the primary method for characterizing wettability. The wetting of powders also involves a contact angle. However, in this case it is complicated by the presence of a porous structure. In this study, the wettability of modified silica nanoparticles, with various concentrations of modifier, was investigated using the Washburn equation,[21] which has been widely used to analyze the contact angles of powders. When a powder is brought into contact with a liquid, then the adherence of the liquid onto the powder's surface will obey the following relationship:

$$\cos\theta = \frac{m^2}{t} \frac{\eta}{\rho^2 \sigma_L c} \qquad (3)$$

where m is the sample weight (in g), t is the time (in s), θ is the contact angle between the liquid and the powder, ρ is the liquid density (in g/cm^3), σ_L is the liquid surface tension (in mN/m), η is the liquid viscosity (in mPa s^{-1}), and c is a factor that depends on the powder and sample holder geometry. The viscosity, density, and surface tension of the test liquids are known parameters, and are listed in Table III. Hence, there are two unknown parameters in the above equation: the contact angle and the material constant. The material constant can be calculated using the values for *N*-hexane, which has a very low surface tension ($\theta \approx 0°$) for each nanoparticle, and these are listed in Table IV. Therefore, the contact angle of the silica nanoparticles was calculated from the gradient of a plot of time (t) versus the square of the weight of

TABLE IV
Material Constant (c) Calculated from N-Hexane and Variation of the Contact Angle with Concentration of Modifier

Sample	Fumed silica	ST 0.2	ST 0.4	ST 0.85	ST 1.0
Material constant (c)	1.0×10^{-2}	8.0×10^{-3}	7.0×10^{-3}	6.0×10^{-3}	6.0×10^{-3}
Contact angle, θ					
Methanol	88.8°	71.3°	60.0°	37.0°	23.5°
Water	48.0°	74.0°	80.4°	83.0°	87.3°

adsorbed liquid (m^2). These values are also listed in Table IV.

The contact angle of unmodified fumed silica was found to be 88.8 and 48.0° for methanol and water, respectively, whereas the stearic acid–modified silica nanoparticles showed contact angles of 23.5 and 87.3° for methanol and water, respectively. From the results of the contact angle measurements, it was found that the stearic acid modification caused the filler's surface to become hydrophobic. Therefore, the stearic acid–modified filler was more easily wetted by the polymeric matrix melt.
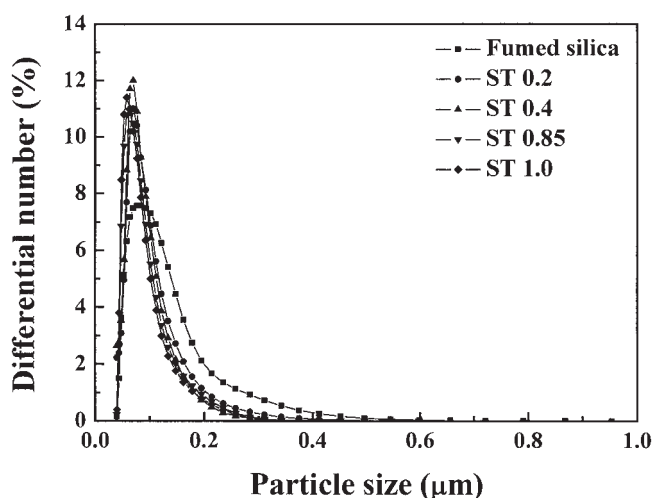
Average particle size distribution

The average particle size distributions of unmodified silica nanoparticles and stearic acid–modified silica nanoparticles are shown in Figure 2. The unmodified silica nanoparticles had a mean particle size of 109.8 nm, whereas the stearic acid–modified fumed silica nanoparticles had a mean particle size of 80–90 nm. Although the primary particle size of the fumed silica nanoparticles was 7 nm, it easily formed aggregates that agglomerated. It is difficult to break down these aggregates by surface modification of the nanoparticles because the aggregates are the product of strong siloxane bonds formed during the chemical reaction of neighboring hydroxyl groups at the particle–particle

interface.[22,23] These aggregates had a mean particle size distribution of 50 nm. The aggregates and primary silica nanoparticles form loosely bonded agglomerates from physical interactions between the aggregates and the primary particles, such as the formation of hydrogen bonds and other nonspecific forces between the aggregates and the primary particles.[22,23] The presence of adsorbed stearic acid on the surface of the silica nanoparticles reduces the interactions between the silica nanoparticles within the agglomerates, and therefore the agglomerates can be broken down more easily.[16] This reduces the observed particle size with increasing concentration of stearic acid.

Processability

The torque values of silica nanoparticle–reinforced PEN composites and pristine PEN were investigated during melt compounding, and the results are shown in Figure 3. The torque values of the silica nanoparticle–reinforced PEN composites decreased with increasing silica content compared to those of pristine PEN. Although the torque values of all the samples in the initial stages were nearly identical, the silica nanoparticle–reinforced PEN composites exhibited a more rapid decrease in torque values than did pristine PEN with increasing mixing time. As shown in Figure 4, the total torque values of the modified silica nanoparticle–

Figure 2 Average particle size distribution of silica nanoparticles with concentration of stearic acid.
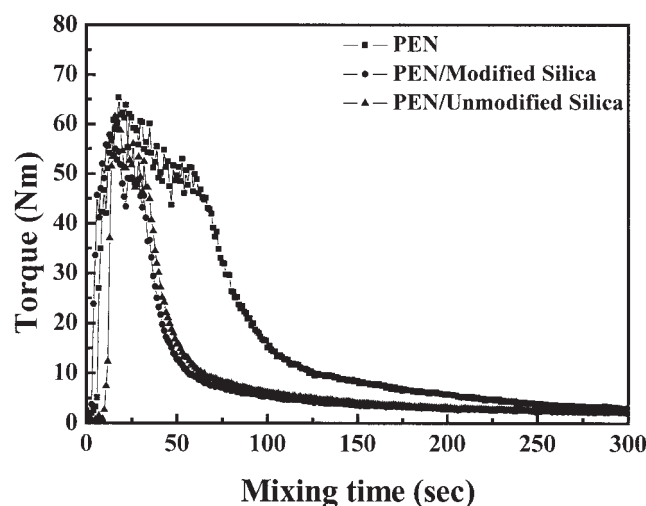
**Figure 3** Online measurements of the torque values during melt compounding.
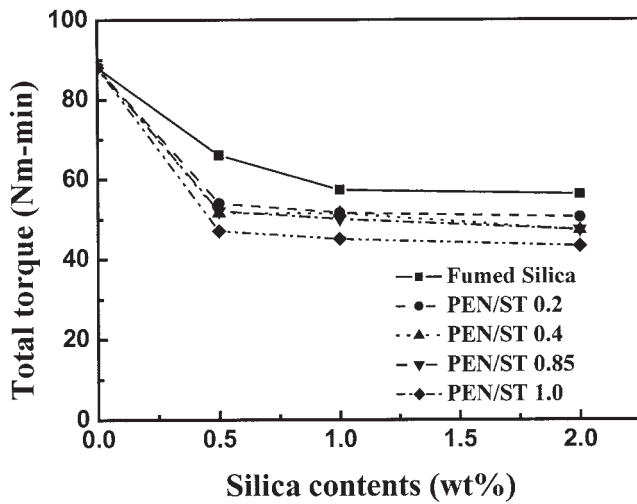
Figure 4 Total torque values of the silica nanoparticle–reinforced PEN composites with silica content and concentration of stearic acid.

filled PEN composites also decreased with increasing silica content and stearic acid concentration. These torque and total torque values measured using the Haake rheometer indirectly represent the melt viscosity of the molten polymer, and the variation in viscosity in conventional processing can be evaluated from the total torque values.[5,24]

In our previous studies, we found that the depression of the melt viscosity was caused mainly by the silica nanoparticles.[5] Im et al.[7] reported that when silica nanoparticles were used as a filler, they acted as a lubricant rather than degrading the polymer matrix when exposed to the high shear force and heat experienced during melt compounding. This is because the silica particles have a spherical shape and smooth, nonporous surfaces, which lower the coefficient of friction.
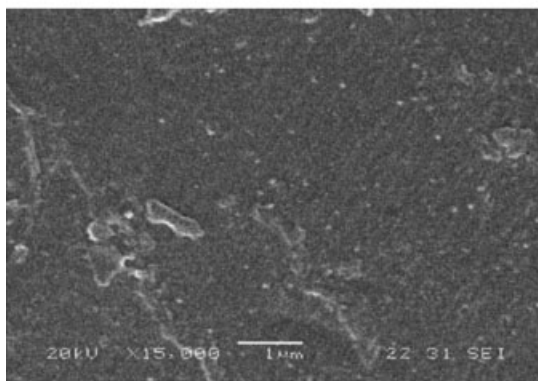
The above properties not only allow for the possibility of improving the processability but also promise additional applications for nanoparticle-filled polymer composites. In particular, the application of PEN is
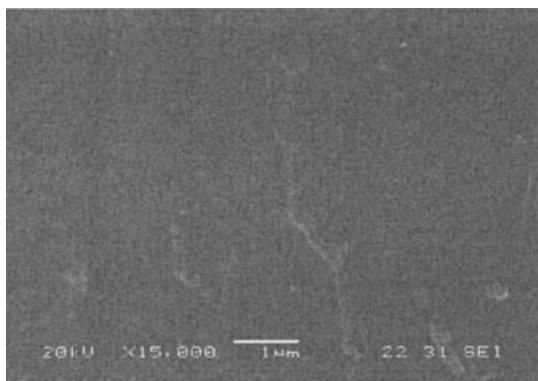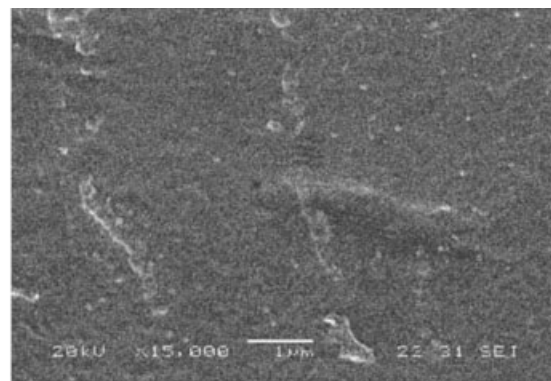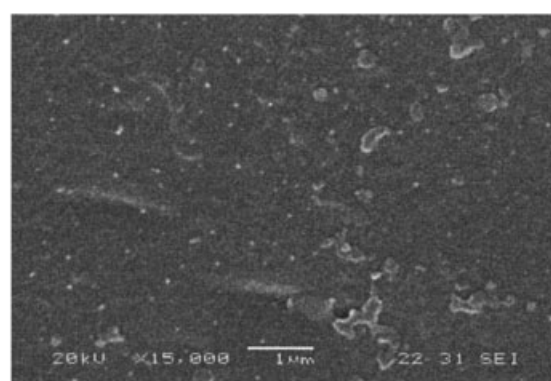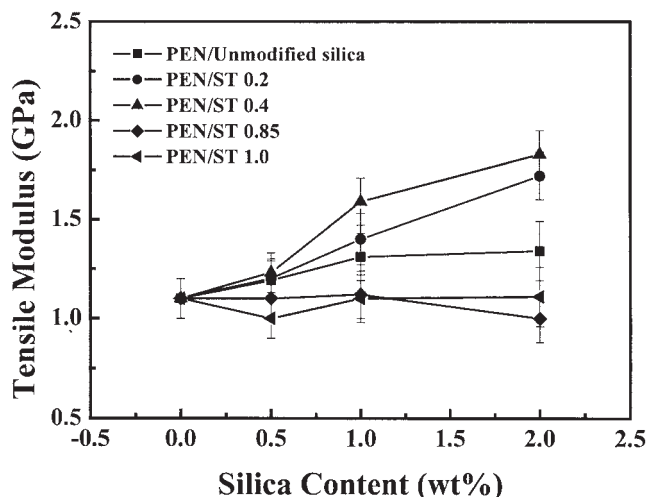

Figure 5 FE-SEM microphotographs of stearic acid–modified silica nanoparticle–reinforced PEN composites using a magnification of ×15,000: (a) PEN, (b) PEN/ST 0.2 (0.5 wt %), (c) PEN/ST 0.2 (1 wt %), and (d) PEN/ST 0.2 (2 wt %).

Figure 6 Variation of the Young's modulus of silica nanoparticle–reinforced PEN composites with silica content and stearic acid modification.

presently limited to melt spinning and injection molding because PEN has a relatively high melt viscosity, which is attributed to the rigid naphthalene ring in the main chain. Therefore, adding a small amount of silica nanoparticles to a PEN matrix could enhance the processability of PEN.

Dispersion of the nanoparticles

In general, unmodified fumed silica easily forms aggregates as the result of particle–particle interactions.[22] Whereas the primary particle size of the fumed silica was 7 nm, the average particle size distribution of the unmodified silica nanoparticles was 108 nm. In our previous study,[5] it was found that loosely aggregated particles could not be broken down by the shear forces experienced during melt compounding; thus, when the filler loading increased, the unmodified silica nanoparticles formed agglomerates that were dispersed with a particle size in the range 300–400 nm. These agglomerates cause premature failure when deformation is imposed on the composites.

As shown in Figure 5, the stearic acid–modified silica nanoparticles were well distributed, with small particle sizes (<100 nm). The SEM images are in good agreement with the particle size distribution results. Therefore, stearic acid can successfully be used as a surface modifier for silica nanoparticles. In addition, the adhesion between the filler and the PEN matrix was improved by stearic acid modification.

Mechanical properties

Tensile tests on silica nanoparticle–reinforced PEN composites were performed to study the effect of surface modification on the mechanical properties of the composites. As shown in Figure 6, the Young's moduli
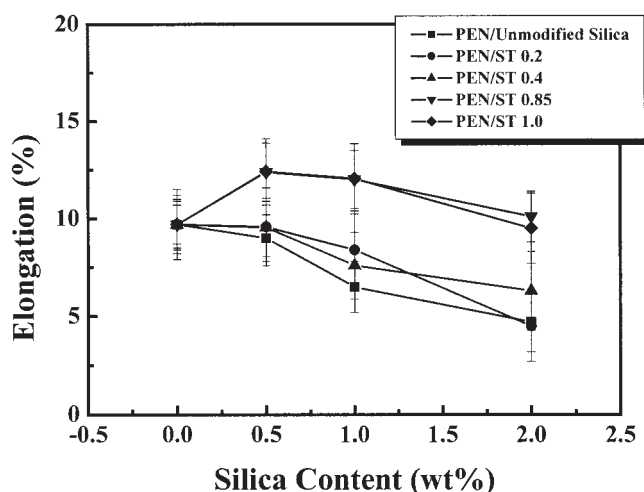
of the composites increased with increasing silica content. The increase in the Young's modulus of the silica nanoparticle–reinforced composites indicates an increase in the rigidity of PEN, which is related to the restriction in the mobility of the PEN matrix attributed to the presence of the filler.[25,26] Surface modification of the silica nanoparticles also leads to an increase in the Young's modulus of the samples because of the improvement in adhesion between the silica nanoparticles and the PEN matrix. However, the Young's moduli of samples ST 0.85 and ST 1.0 nanoparticle–reinforced composites decreased compared to that of pristine PEN. The decrease in the Young's moduli of samples ST 0.85 and ST 1.0 nanoparticle–reinforced composites can be explained by the plasticizing effect of the surface modifier, which is adsorbed on the surface of the silica nanoparticle as a multilayer.

The variation in tensile strength of the composites with silica content and concentration of surface modifier is shown in Figure 7. The tensile strength of the composites decreased with increasing silica content. Theoretically, a small-size particle incorporated in a polymer matrix has many opportunities to physically and chemically bond with the polymer chains. Therefore, the adhesive force between the filler and the matrix increases, and the strength of the matrix is improved if the particles are dispersed homogeneously in the composite. However, as the filler loading increases, agglomeration of the particles occurs because of the strong interaction between the nanoparticles. The agglomeration of the particles leads to premature failure when an external force is imposed on the composite, and thus the strength of the composite decreases with increasing filler content.[27,28]

As shown in Figure 7, unmodified silica nanoparticle–reinforced PEN composites have the lowest tensile strength because unmodified silica nanoparticles easily form agglomerates as a result of the strong inter-
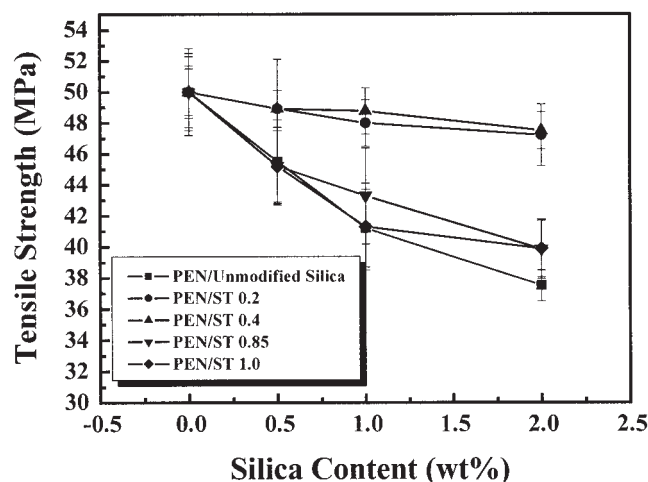
Figure 7 Variation of the tensile strength of silica nanoparticle–reinforced PEN composites with silica content.

Figure 8 Elongation of silica nanoparticle–reinforced PEN composites with silica content and concentration of surface modifier.

facial attraction between the nanoparticles. In contrast, the tensile strength of modified nanoparticle–reinforced composites exhibited higher tensile strengths than those of the unmodified silica nanoparticle–reinforced PEN composites.

Elongation of the modified silica nanoparticle–reinforced composites increased with increasing stearic acid concentration compared to that of unmodified silica nanoparticle–reinforced PEN samples, as shown in Figure 8. In particular, Samples ST 0.85- and ST 1.0-reinforced PEN composites exhibited an increase in their elongation at breakage, whereas the elongation of the other samples decreased significantly with increasing silica content. Although the wettability of the silica nanoparticles increased with increasing concentration of stearic acid, Samples ST 0.85 and ST 1.0 contained nanoparticles coated with stearic acid as a multilayer, and the residual stearic acid adsorbed on the surface of the silica nanoparticles could act as a plasticizer. Therefore, the elongation of Samples ST 0.85 and ST 1.0 nanoparticle-reinforced PEN composites increased.

CONCLUSIONS

The wettability of silica nanoparticles can be improved by modification with stearic acid. From contact angle measurements, it was found that the stearic acid modification enabled the filler's surface to become hydrophobic, and thus the stearic acid–modified filler was more easily wetted by the polymeric matrix melt. The presence of adsorbed stearic acid on the surface of the silica nanoparticles reduces the interactions between the silica nanoparticles within any agglomerates, and these agglomerates can be broken down more easily. Torque and total torque values measured using a Haake rheometer during melt compounding were found to decrease with increasing silica content. These properties allow for the possibility of improving the processability of PEN. The dispersion of silica nanoparticles in the PEN matrix with different concentrations of stearic acid was studied using FE-SEM micrographs. Stearic acid–modified silica nanoparticles were well distributed, with small particle sizes (<100 nm). The SEM images were in good agreement with the particle size distribution results. Stearic acid–modified silica nanoparticle–reinforced PEN composites exhibited higher tensile moduli. The tensile strength of the composites decreased, and the elongation at breakage of the composites decreased with increasing silica content.

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