

Mechanical Properties of Silica Nanoparticle Reinforced poly(ethylene 2, 6-naphthalate)

Seon Hoon Ahn, Seong Hun Kim*, and Byoung Chul Kim

Division of Applied Chemical Engineering, College of Engineering, Hanyang University, Seoul 133-791, Korea

Kwang Bo Shim

Department of Ceramic Engineering, CPRC, College of Engineering, Hanyang University, Seoul 133-791, Korea

Bong Gyoo Cho

Industrial Waste Recycling R&D Center, Taejon 305-350, Korea

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Abstract: We added surface-modified silica nanoparticles to poly(ethylene 2,6-naphthalate) (PEN) to investigate their effect on the mechanical properties on the PEN nanocomposite material. The torque and total torque values of the composites decreased in the silica nanoparticle composites. The tensile modulus of the composites reinforced with unmodified silica nanoparticles increased upon increasing the silica content, while the tensile strength and elongation decreased accordingly. In contrast, stearic acid-modified, silica nanoparticle reinforced PEN composites exhibited an increase in elongation and a decrease in tensile modulus upon addition of the silica nanoparticles because the stearic acid that had adsorbed onto the surface of the silica nanoparticle in multilayers could act as a plasticizer during melt compounding. Stearic acid modification had a small effect on the crystallization behavior of the composites. We calculated theoretical values of the tensile modulus using the Einstein, Kerner, and Nielsen equations and compared these values with the experimental data obtained from the composites. The parameters calculated using the Nielsen equation and the Nicolais-Narkis model revealed that the interfacial adhesion between silica nanoparticles and the PEN matrix could be improved.

Keywords: poly(ethylene 2,6-naphthalate), modified silica nanoparticles, mechanical properties, processibility, melt compounding.

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.¹⁴ However, the applications of PEN are limited, because PEN exhibits a relatively high melt viscosity, which makes fiber spinning and injection molding difficult.⁵ In our previous study,⁶ unmodified silica nanoparticle reinforced PEN composites were melt-blended in an attempt to improve the mechanical properties and processibility of the polymer composite, and we confirmed the possibility of improving the processibility of PEN. When silica nanoparticles are used as the filler, they act as an internal lubricant during melt compounding, allowing slippage between the polymer matrix

and the filler, rather than decrement of molecular weight for the polymer matrix.^{7,8}

However, the mechanical properties of the unmodified silica nanoparticle reinforced composites tended to be worse than pristine PEN. The major problem of the above approach is the non-uniformity of the resulting properties due to the poor dispersion of the silica nano-filler in the polymer matrix, and the adhesion occurring at the polymer and filler interface.⁸⁻¹⁰ These problems have been solved by surface modification of the dispersed silica nano-fillers by incorporating a suitable surface modifier.¹¹

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.⁹ 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

*e-mail: kimsh@hanyang.ac.kr

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strengthen the adhesion. Two reagents are mainly used in chemical surface modification to obtain a hydrophobic surface. One example of such a reagent is an alkyl silane coupling agent,⁸ and another is an alcohol.^{7,8}

(2) Surface modification by non-reactive modifier. A non-reactive modifier reduces the interaction between the filler particles within agglomerates by reducing the physical attraction rather than by any chemical reaction.^{12,13}

Stearic acid has been widely used as a non-interacting surface modifier. Modified nanofiller can easily be incorporated into a polymer matrix, resulting in a decrease in the melt viscosity and, in most cases, an improved dispersion of the nanofiller in the composite.^{12,13} In our other study, the wettability of silica nanoparticles and the adhesion between the filler and the polymer matrix were improved by modifying the silica nanoparticles with stearic acid.¹⁴ The non-reactive stearic acid reduces the interaction between the filler particles within agglomerates by reducing the physical attraction, rather than by any chemical reaction. However there has been little research related to the mechanical properties of silica nanoparticle reinforced PEN composites with the modification of stearic acid.

In this research, surface modified silica nanoparticle reinforced PEN composites were melt-blended to investigate the effect of stearic acid modification on the mechanical properties, crystallization behavior, and the processibility of the silica nanoparticle reinforced PEN composites. The interfacial properties of the composites with stearic acid modification were quantitatively analyzed from tensile test results with various theoretical models.

Experimental

Materials and surface modification. The PEN used (IV = 0.93 dL/g) was supplied by the Hyosung Co., Korea, and the hydrophilic fumed silica used (primary particle size = 7 nm, surface area = 390 m²/g, purity = 99.8%, hydroxyl group content = 2.5 nm²) was purchased from the Aldrich Co., USA. The granular-type stearic acid used as a surface modifier ($M_w = 284.48$, m.p. = 6871 °C, b.p. = 361 °C) was purchased from the Junsei Chemical Co. Ltd., Japan. The isopropyl alcohol used as a solvent (b.p. = 82.5 °C) was purchased from Carlo Erba Reagenti, Italy, and used without further purification. Surface modification of the 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 eq.¹⁵

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

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 m²/g), and w is the wetting surface of the stearic acid (445 m²/g)¹⁶. In this study, four stearic acid concentrations in the total mixture (1, 2, 4.25, and 5wt%) were used to investigate the effect of surface modification, with the silica nanoparticle content remaining at 5wt% 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.

Sample preparation. PEN and silica nanoparticles 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., Germany) at various silica contents (0, 0.5, 1, 2wt%). 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 measurement of the torque and total torque values were recorded using the Haake rheometer during melt compounding.

Characterization. The crystallization behavior of the silica nanoparticle-filled composites was studied using a Perkin-Elmer DSC7 differential scanning calorimeter, and the weight of all the samples was approximately 6 mg. The DSC was calibrated using a 10 mg sample of indium metal ($T_m^0 = 156.4$ °C, $\Delta H_f^0 = 28.5$ J/g) before performing the measurements. The samples were heated to 300 °C using a heating rate of 10 °C/min under a nitrogen atmosphere, and held at that temperature for 5 min to remove any previous thermal history. The samples were then cooled from $T = 300$ °C to $T = 30$ °C at a constant cooling rate of 10 °C/min. The average particle size and size distribution of the silica nanoparticle were performed using a laser particle size analyzer (LS 230, Beckman Coulter Inc., USA). The surface wettability of the modified silica nanoparticles was calculated using the Washburn sorption method. The mechanical properties of the silica nanoparticle reinforced PEN composites were investigated using an Instron 4465 UTM tensile testing machine employing 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 Inc., Japan) to investigate

Table I. Composition of the Surface Modified Fumed Silica Samples

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

the dispersed state of the silica nanoparticles in the PEN matrix. A thin layer of platinum was sputtered on the surface of the samples to achieve an electrically conducting coating before measurements were carried out.

Results and Discussion

Processibility. The torque values of silica nanoparticle reinforced PEN composites and pristine PEN were measured during melt compounding, and the results are shown in Figure 1. The torque values of the silica nanoparticle reinforced PEN composites decreased when compared to pristine PEN. Although the torque values of all the samples in the initial stages were nearly the same, the silica nanoparticle reinforced PEN composites exhibited a more rapid decrease in their torque values than pristine PEN did with increasing mixing time. As shown in Figure 2, the total torque values

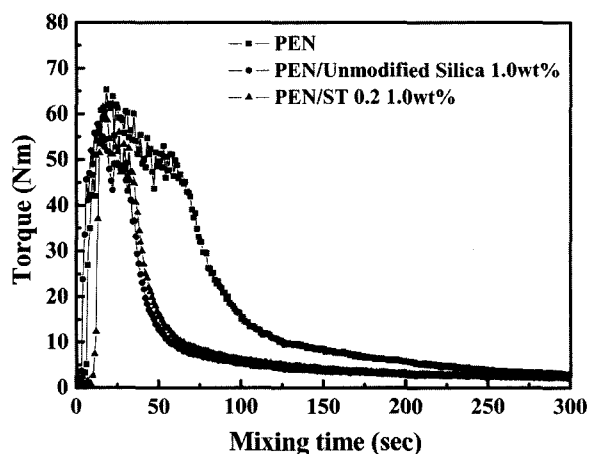


Figure 1. Online measurement of the torque values during melt compounding.

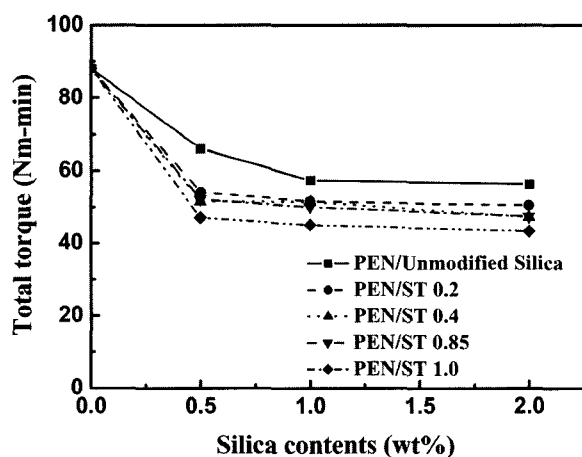


Figure 2. Total torque values of the silica nanoparticle reinforced PEN composites with different silica content and concentration of stearic acid.

of the modified silica nanoparticle filled PEN composites also decreased with increasing silica content and stearic acid concentration. These torque and total torque values were measured using the Haake rheometer directly, and represent the melt viscosity of the molten polymer. The variation in viscosity in conventional processing can be evaluated from the total torque values.^{6,17} In our previous studies, we found that the depression of the melt viscosity was caused mainly by the silica nanoparticles.⁶ *Im et al.*⁸ have 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 forces and heat experienced during melt compounding. This is because the silica particles are spherical and have a smooth, non-porous surface, which lowers the coefficient of friction. The above properties allow for the possibility of improving the processibility, and promise additional applications for nanoparticle filled polymer composites. In particular, the fabrication of PEN is 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 concentration of silica nanoparticles to a PEN matrix could enhance the processibility of PEN.

Crystallization behavior. The non-isothermal crystallization behavior of pristine PEN and silica nanoparticle reinforced PEN composites with different concentrations of stearic acid are shown in Table II. The glass transition temperature (T_g) of reinforced PEN composite samples ST 0.85 and ST 1.0 were shifted to lower temperatures with increasing concentration of modifier. According to Eq. (1), for samples ST 0.85 and ST 1.0 the nanoparticles had adsorbed stearic acid in multilayers. Stearic acid adsorbed on the surface of the silica nanoparticles as a multilayer can act as a plasticizer.^{12,13} Therefore, the T_g of nanoparticle reinforced PEN composites ST 0.85 and ST 1.0 decreased with increasing silica content. The melting temperature (T_m) of all the samples during the second heating was almost the same as pristine PEN. However, the degree of supercooling (T) was decreased by incorporating silica nanoparticles in the PEN matrix. This indicates that the fumed silica nanoparticle acted as nucleation agents in the polymer matrix, and accelerated the crystallization rate,⁶ regardless of any modification by the silica nanoparticles. In general, homogeneous nucleation began spontaneously by chain aggregation below the melting point, and required a long time, whereas heterogeneous nuclei were formed as soon as the samples reached the crystallization temperature. Therefore, the crystallization of the silica nanoparticle reinforced PEN composites proceeded mainly *via* heterogeneous nucleation on the silica nanoparticles.

As listed in Table II, the degree of crystallinity (X_c) of the composites was increased by incorporating silica particles compared to pristine PEN, and these results can be explained by the supercooling temperature. When the polymer crystal-

Table II. Thermal Transitions of PEN and Silica Nanoparticle Reinforced PEN Composites Measured Using the DSC on the Second Heating and Cooling Stages at a Rate of 10°C/min

Specimen	Silica content (wt%)	T_g (°C)	T_{cc}^a (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	ΔT^b (°C)	T_{mc}^c (°C)	X_c^d (%)
PEN	-	119.8	197.1	25.3	266.9	40.1	53.8	213.1	34.4
PEN/unmodified silica	0.5	119.9	193.1	33.1	266.6	41.8	47.9	218.7	39.4
	1	120.1	193.3	35.6	266.9	41.3	48.6	218.3	40.5
	2	120.9	190.8	35.5	266.8	42.8	46.4	220.4	41.2
PEN/ST0.2	0.5	120.9	196.5	32.5	266.6	40.4	50.9	215.7	38.4
	1	120.3	194.4	34.2	267.1	41.3	48.0	219.1	39.7
	2	120.7	191.2	35.1	267.4	44.2	45.9	221.5	41.7
PEN/ST0.4	0.5	120.3	195.7	33.1	267.2	40.6	51.3	215.9	38.8
	1	119.8	192.1	35.2	266.8	44.3	46.0	220.8	41.8
	2	118.9	190.1	35.8	267.3	44.7	45.2	222.1	42.4
PEN/ST0.85	0.5	119.9	194.2	34.3	267.1	40.5	49.6	217.5	39.4
	1	118.3	194.7	34.4	266.9	43.0	48.6	218.3	40.7
	2	117.0	193.0	33.3	267.1	44.7	45.0	222.1	41.0
PEN/ST1.0	0.5	119.0	196.1	31.2	266.9	42.5	49.6	217.3	38.7
	1	117.5	193.1	32.8	267.3	44.7	48.4	218.9	40.7
	2	116.3	193.3	32.8	267.2	44.3	45.9	221.3	40.6

^aThe cold crystallization temperature using a heating rate of 10°C/min.

^bThe degree of supercooling (ΔT) = $T_m - T_{mc}$.

^cThe melt crystallization temperature using a cooling rate of 10°C/min.

^dApparent crystallinity, X_c (%) = $(\Delta H_m - \Delta H_c) / \Delta H_m^0$, where ΔH_m^0 is the heat of fusion of an infinitely thick crystal [ca. 190 J/g].¹⁷

lized with less supercooling, it crystallized more perfectly than that with more supercooling. In this research, fumed silica nanoparticles acted as nucleation agents in the PEN matrix under non-isothermal crystallization conditions, and the supercooling of the composites at a given cooling rate was reduced by the silica contents; hence, the degree of crystallinity of silica nanoparticle-filled PEN composites was increased by the silica content.

However, the concentration of stearic acid did not provide a significant effect on the crystallization rate and the degree of crystallinity of the silica nanoparticle reinforced PEN composites.

FE-SEM observations and average particle size distribution. In general, unmodified fumed silica easily forms aggregates due to particle-particle interactions. While the primary particle size of the fumed silica was around 7 nm, the average particle size distribution of the unmodified silica nanoparticles was approximately 108 nm as shown in Figure 3. However the stearic acid modified silica nanoparticles had a mean particle size of 80-90 nm. In our previous study,⁶ we found that loosely aggregated particles could not be broken down by the shear forces experienced during melt compounding, and hence, 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 was imposed on the composites. As shown in Figure 4, the stearic acid modified silica nanoparticles were well distributed, with small particle sizes (< 100 nm). There-

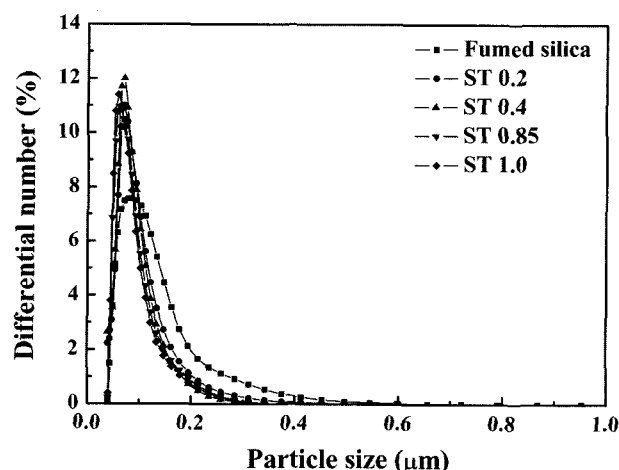


Figure 3. Average particle size distribution of the silica nanoparticles with concentration of stearic acid.

fore, stearic acid can successfully work as a surface modifier for silica nanoparticles.

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 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 eq.,¹⁸ which

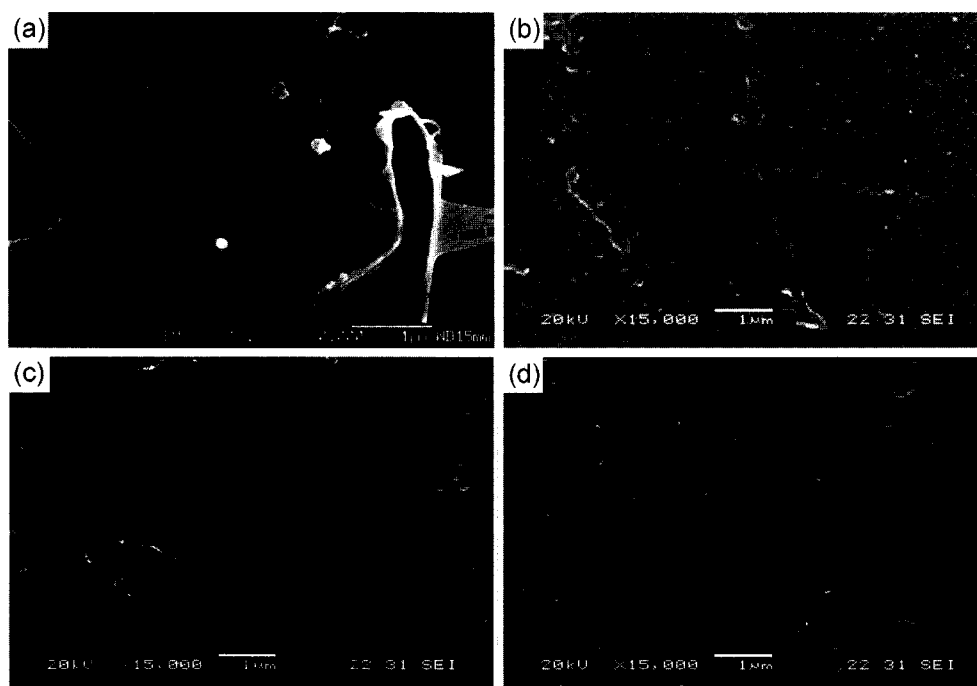


Figure 4. FE-SEM microphotographs of stearic acid modified silica nanoparticle reinforced PEN composites using a magnification of 15,000X. Key: (a) PEN/Unmodified silica 0.5wt%, (b) PEN/ST 0.2 (0.5wt%), (c) PEN/ST 0.2 (1wt%), and (d) PEN/ST 0.2 (2wt%).

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:

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

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 mPas), 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 eq.: 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 ($\theta \sim 0^\circ$) 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 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, while 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 measure-

Table III. Characteristics of the Test Liquids (N-hexane, Methanol, and Water)

	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

Table IV. The 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°
	Water	48.0°	74.0°	80.4°	83.0°

ments, 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.

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 5, the Young's

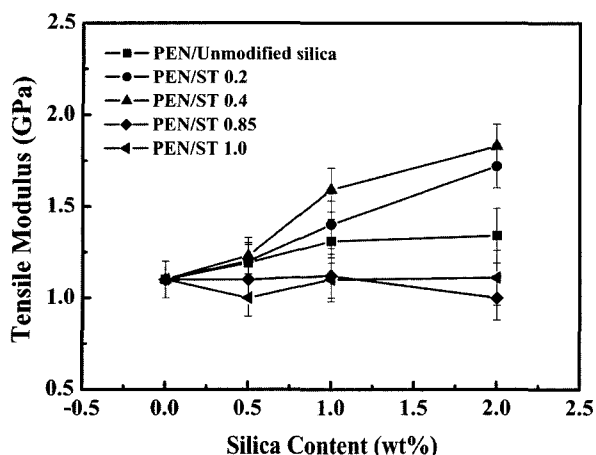


Figure 5. Variation of the Young's modulus of the silica nanoparticle reinforced PEN composites with silica content and stearic acid modification.

modulus of the composites increased with increasing silica content. The increase in Young's modulus of the silica nanoparticle reinforced composites indicates an increase in rigidity of the PEN, which is related to the restriction of mobility of the PEN matrix due to the presence of the filler.^{19,20} Surface modification of the silica nanoparticles also leads to an increase in Young's modulus of the samples, due to the improvement in adhesion between the silica nanoparticles and the PEN matrix. However, the Young's modulus of nanoparticle reinforced composites ST 0.85 and ST 1.0 decreased when compared to pristine PEN. The decrease in the Young's modulus of nanoparticle reinforced composites ST 0.85 and ST 1.0 can be explained by the plasticizing effect of the surface modifier, which was adsorbed on the surface of the silica nanoparticles as a multilayer.

A simple model that has been used to predict the modulus of spherical filler reinforced composite uses Einstein's eq.²¹ In its original form, Einstein's eq. was proposed to predict the viscosity of rigid spherical particles (Brownian particles) in a dilute solution. Einstein's eq. is valid when the rigid spherical particles are mono-dispersed in the solution, and when the particles do not interact with each other. Guth²² justified the theoretical relationship between the modulus of particle-reinforced composites and the viscosity of a solution containing suspended particles. In composite materials therefore, Einstein's eq. can be used to predict the modulus of particle-reinforced composites.

$$\frac{E_c}{E_m} = 1 + 2.5 \times V_f \quad (3)$$

where E_c is the tensile modulus of the composite material; E_m is the tensile modulus of the polymer matrix, and V_f is the volume fraction of filler. As shown in Figure 6, the modulus calculated using Einstein's eq. has a lower value than the

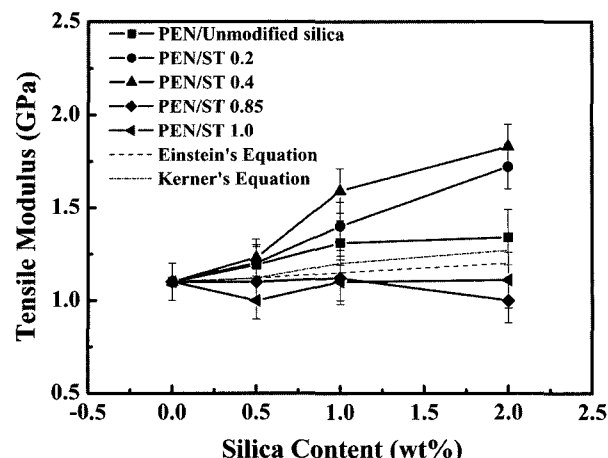


Figure 6. Calculated tensile modulus curves using the Einstein and Kerner eqs.

experimental data. In particular, for nanoparticle reinforced PEN composites ST 0.2 and ST 0.4, a much higher modulus was observed than the modulus calculated using Einstein's eq. Einstein's eq. is valid for non-interacting particles and mono-dispersed particles. However, the silica nanoparticles had a strong particle-particle interaction, even though surface modification was performed, and they easily formed agglomerates. Agglomeration of the particles tends to increase the modulus of the composites,¹⁹ and the surface modification of the silica nanoparticles can lead to an improvement in the adhesion between the silica nanoparticles and the PEN matrix. Therefore, predicting the modulus using Einstein's eq. is not appropriate.

Another approach used to calculate the modulus of composites is to use Kerner's eq. For composites containing nearly spherical particles, Kerner's eq. can be used to calculate the modulus of composite if there is some adhesion between the two phases and if the particles are much more rigid than the polymer matrix^{19,23}

$$\frac{E_c}{E_m} = 1 + \frac{15(1-\gamma_p)}{8-10\gamma_p} \times \frac{V_f}{1-V_f} \quad (4)$$

where γ_p is the Poisson ratio of the matrix. The modulus values calculated using Kerner's eq. are shown in Figure 6. Using Kerner's eq. also resulted in lower modulus values than the experimental data, because most of the nanoparticle filled composites had a better reinforcing efficiency due to the large surface area of the silica nanoparticles,¹⁰ even though the volume fraction of the nanofiller was very small. Therefore, prediction of the modulus of the nanoparticle reinforced composites was not possible using either Einstein's or Kerner's eqs.

Nielsen proposed the following eq., which is one of the most generalized theoretical eqs. used to calculate the mod-

ulus of two-phase composites. Nielsen modified eq. (3) by assuming that the filler occupies voids without having any influence on the mechanical properties of the composite^{19,24}

$$\frac{E_c}{E_m} = \frac{1 + ABV_f}{1 - B\phi V_f} \quad (5)$$

where A is a constant that depends on the geometry of the filler and the Poisson ratio of the matrix (*i.e.*, $A = K_E - 1$); K_E is Einstein's coefficient, and B is a constant related to the ratio of the filler/matrix moduli (E_f/E_m). For very large filler/matrix moduli, $B = 1.0$.

$$B = \frac{(E_f/E_m) - 1}{(E_f/E_m) + A} \quad (6)$$

The factor ϕ , is a reduced concentration term, which depends on the maximum packing fraction (ϕ_m) of the particles. In Eq. (4), Nielsen defined the reduced concentration term ϕ , as in Eq. (6), and McGee *et al.*¹⁹ proposed a different eq. for ϕ , shown as Eq. (7), which is used when the modulus of the filler is much higher than that of the matrix (*i.e.*, $B = 1.0$), and agglomerates exist in the system.

$$\phi = 1 + \left(\frac{1 - \phi_m}{\phi_m^2} \right) V_f \quad (7)$$

$$\phi = 1 + \frac{V_m}{\phi_m} [\phi_m V_f + (1 - \phi_m) V_m] \quad (8)$$

Lewis and Nielsen²⁵ reported that the theoretical maximum packing fraction (ϕ_m) and the Einstein coefficient (K_E) were 0.37 and 6.76, respectively, for large agglomerates containing spherical particles in a random packing arrangement, and that the parameters vary with the shape of particles and the degree of agglomeration.

The modulus values of the silica nanoparticle reinforced PEN composites calculated using Nielsen's eq. are shown in Figure 7. The modulus of the unmodified silica nanoparticle reinforced PEN composites are in good agreement with Nielsen's eq. over the entire range of filler loadings. However, the tensile modulus of nanoparticle reinforced PEN composites ST 0.2 and ST 0.4 have much higher values than the theoretical modulus values. There are several possible reasons for this discrepancy between theory and experiment. The first reason is the size of the particles and their distribution in the polymer matrix.²⁵ From particle size analysis results on the modified silica nanoparticles, the size of the silica nanoparticles had decreased by the modification of stearic acid, and their distribution had narrowed with increasing concentration of stearic acid. In general, the surface area of a particle increases as the particles size decreases, and smaller particles have more interfacial adhesion in a polymer matrix. The distribution of the particle size also has an effect on the

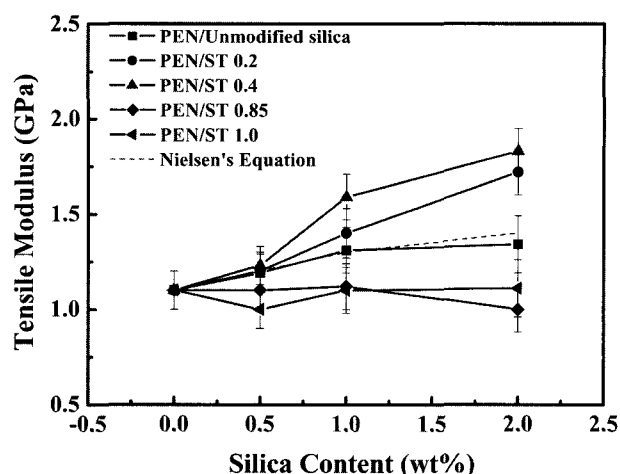


Figure 7. Calculated tensile modulus of silica nanoparticle reinforced PEN composites using Nielsen's eq.

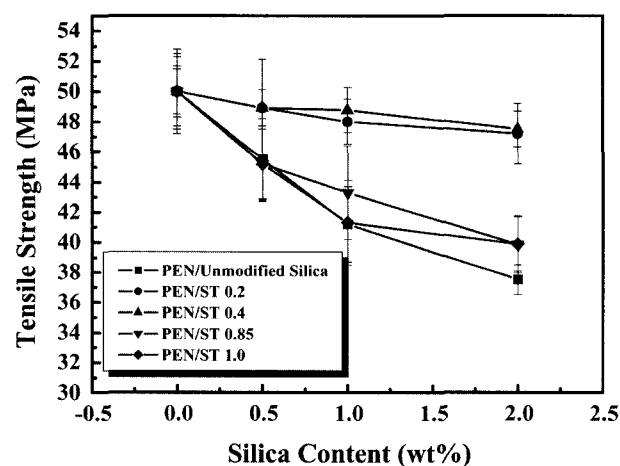


Figure 8. Variation of the tensile strength of the silica nanoparticle reinforced PEN composites with silica content and stearic acid modification.

modulus of the composites. If the particles exhibit a broad size distribution peak, then they can be packed in the polymer matrix more densely than mono-dispersed particles. Thus, the distribution of particle size enables a larger value of ϕ_m , and therefore, it lowers the modulus for a given filler loading.²⁶ Another reason to explain the discrepancy is the improvement in surface adhesion between the surface modified silica nanoparticles and the polymer matrix, resulting from surface modification. Therefore, nanoparticle reinforced PEN composites ST 0.2 and ST 0.4 had a higher modulus than pristine PEN and unmodified silica nanoparticle reinforced PEN samples.

The variation in tensile strength of the composites with silica content and concentration of surface modifier is shown in Figure 8. The tensile strength of the composites

decreased with increasing silica content. Theoretically, a smaller-sized 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 takes place due to strong interactions between the nanoparticles. The agglomeration of these particles leads to premature failure when an external force is imposed on the composite, and hence, the strength of the composite decreases with increasing filler content.^{21,22}

As shown in Figure 8, unmodified silica nanoparticle reinforced PEN composites exhibited the lowest tensile strength, because unmodified silica nanoparticles easily form agglomerates due to the strong interfacial attraction between the nanoparticles. In contrast, the tensile strength of modified nanoparticle reinforced composites exhibited higher tensile strengths than the unmodified silica nanoparticle reinforced PEN composites.

Analysis of the tensile strength data as a function of blend composition based on existing theoretical models permits information to be gained on the interfacial interactions between the fillers and the matrix. The tensile strengths of the composites can be predicted using Nielsen's²⁷ and Nicolais-Narkis²⁸ models, which are derived from the relationship between the volume fraction and the projected area fraction of the particulate inclusions.

For the case of a rigid, spherical particle, Nielsen proposed Eq. (8), which explains the compositional dependence of the mechanical properties of a two-phase composite

$$\sigma_c = \sigma_m(1 - V_f)S \quad (8)$$

where σ_c and σ_m are the tensile strength of the composite and polymer matrix, respectively, and V_f is the volume fraction of filler in the composite. The parameter, S describes the weakness of the structure due to stress concentration at the filler-matrix interface. From the experimental data, S was calculated with different silica contents and increasing concentration of surface modifier. The results are listed in Table V. S was found to vary from 0.77-0.91, and had much higher values for lower concentrations of particles in the reinforced composites. According to Nielsen's definition,

Table V. S Values Calculated from Nielsen's Eq.

Silica content (wt%)	Unmodified silica	Stearic acid modified silica			
		ST 0.2	ST 0.4	ST 0.85	ST 1.0
0.5	0.91	0.99	0.98	0.93	0.94
1.0	0.83	0.98	0.98	0.90	0.91
2.0	0.77	0.97	0.97	0.82	0.82

the maximum value of $S = 1$ for the case where there is "no stress concentration effect" (*i.e.*, where there is perfect adhesion), whereas lower values of S denote a greater concentration of stress (or poorer adhesion).^{21,29} Therefore, the interfacial adhesion between the silica nanoparticles and the PEN matrix was more ideal when a lower portion of filler was contained within the matrix. As listed in Table V, the stearic acid modified silica nanoparticles imparted a higher S value than unmodified silica nanoparticles, because stearic acid that had been adsorbed on the surface of the silica nanoparticles improves the interfacial adhesion between the silica nanoparticle and the PEN matrix.

Nicolais and Narkis²⁸ proposed that the area fraction depended on the volume fraction to the power of two-thirds, if enough micro-cavitations occurred before a critical flaw size develops which then results in premature fracture

$$\sigma_c = \sigma_m(1 - KV_f^{2/3}) \quad (9)$$

where σ_c and σ_m are the tensile strength of the composite and polymer matrix, respectively. The parameter, K , in the Nicolais-Narkis model accounts for the adhesion between the filler particles and the matrix. In the Nicolais and Narkis model, the theoretical value of K for an extreme case of poor adhesion is $K = 1.21$, whereas a value of $K < 1.21$ represents the case where a spherical filler has good adhesion with the composite. As shown in Figure 9, the variation in tensile strength of the composites containing silica can be explained using the Nicolais and Narkis model. By modeling the tensile strength of unmodified silica nanoparticle reinforced PEN composites using the Nicolais-Narkis eq., we found $K = 1.2$, while the nanoparticle reinforced PEN composites ST 0.2 and ST 0.4 showed $K = 0.55$, and nanoparticle reinforced PEN composites ST 0.85 and ST 1.0 showed $K = 1.1$. All of the modified composites exhibited K values

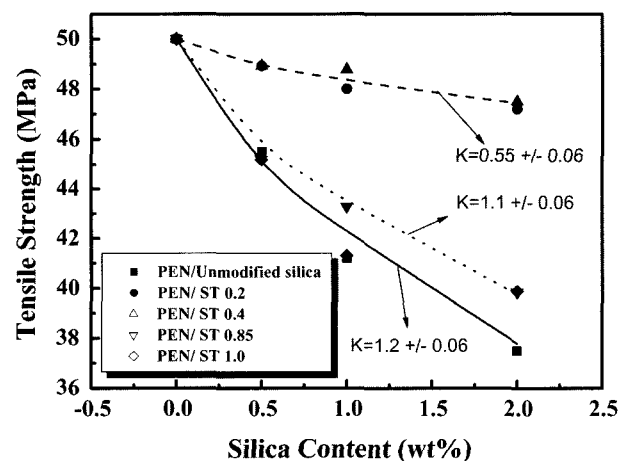


Figure 9. Values of the adhesion parameter, K , fitted with the Nicolais-Narkis model.

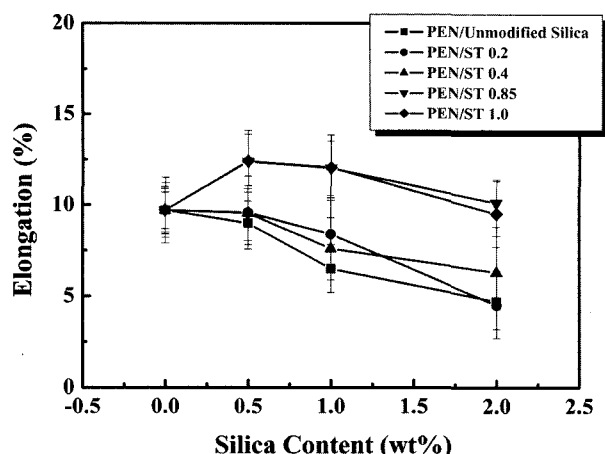


Figure 10. Elongation of the silica nanoparticle reinforced PEN composites with silica content and concentration of surface modifier.

lower than 1.21, which is a good indicator of adhesion between the filler and the polymer matrix. These results suggest that there was little difference in the interfacial adhesion between the unmodified and the modified fillers and the polymer matrix.

The tensile strength of the composites can be changed by surface modification, which changes the adhesion and the nature of the filler-polymer matrix interface.³⁰ Unmodified silica nanoparticles easily form agglomerates due to the strong interaction between particles. This agglomeration tends to reduce the strength of the composites. These agglomerates can act as weak points in the material, and easily break down when stress is applied to the composite.³¹ Therefore, the tensile strength of the unmodified silica nanoparticle reinforced PEN composites decreased with increasing silica content.

As shown in Figure 10, the elongation of the modified silica nanoparticle reinforced composites increased with increasing stearic acid concentration compared to unmodified silica nanoparticle reinforced PEN samples. In particular, reinforced PEN composites ST 0.85 and ST 1.0 exhibited increase in elongation at break, while the elongation of 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 had nanoparticles coated with multilayers of stearic acid, and the residual stearic acid that had adsorbed on the surface of the silica nanoparticles could act as a plasticizer. Therefore, the elongation of nanoparticle reinforced PEN composites ST 0.85 and ST 1.0 increased.

Conclusions

The effects of modification by stearic acid on the mechanical and thermal properties of silica nanoparticle reinforced

PEN composites have been investigated. The torque and total torque values, which were measured using a Haake rheometer during melt compounding decreased with increasing silica content. This allows for the possibility of improving the processibility of PEN.

The non-isothermal crystallization behavior of silica nanoparticle reinforced PEN composites with different silica content and concentration of modifier were determined to investigate the effect of stearic acid modification. The degree of supercooling was decreased by incorporating silica nanoparticles in the PEN matrix. This indicates that the fumed silica nanoparticles acted as nucleating agents in the polymer matrix, regardless of any modification of silica nanoparticles. However, there was no significant change in the crystallization behavior of PEN by modification of the silica nanoparticles.

The dispersion of the silica nanoparticle in the PEN matrix was investigated using FE-SEM for different concentrations of stearic acid. The stearic acid modified silica nanoparticles were well distributed, showing small sizes (< 100 nm), and the SEM data was in good agreement with particle-size distribution results.

The stearic acid modified silica nanoparticle reinforced PEN composites exhibited an increasing tensile modulus up to Sample PEN/ST 0.4, while the tensile modulus of Samples PEN/ST 0.85 and PEN/ST 1.0 was decreased.

Prediction of Young's modulus using Einstein's, Kerner's, and Nielsen's eqs. was performed to investigate any adhesion between the spherical filler and the polymer matrix. Nielsen's eq. was in good agreement with the data from unmodified silica filled composites. However, modified silica nanoparticle filled composite samples ST 0.2 and ST 0.4 exhibited much higher values compared to the theoretical modulus. The parameters calculated from Nielsen's eq. and the Nicolais-Narkis model, revealed that the interfacial adhesion between the silica nanoparticles and the PEN matrix could be improved that.

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