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Dispersion of nanofillers in high performance polymers using reactive solvents as processing aids

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Abstract

Melt mixing of nanoparticles with high performance polymers is not feasible due to severe shear heating and formation of particle aggregates. An alternative scheme was investigated in the present study involving the use of low molecular weight reactive solvents as processing aid and dispersing agent. Dispersion of nanosize fumed silica particles in polyethersulphone (PES) matrix was studied with the aid of small amounts of low molecular weight epoxy. Viscosity and processing temperatures of PES were significantly reduced and fumed silica particles were successfully dispersed to nanoscales. Epoxy component was polymerized after dispersion of fumed silica to recover the mechanical properties. Significant improvement in barrier resistance and heat deflection temperature over neat PES was observed.

Keywords: Dispersing agent; Reactive solvents; Nanoparticles

1. Introduction

Thermoplastic and thermosetting polymers are filled with particulate reinforcements to augment various mechanical, thermal, and chemical properties, such as tensile strength and fracture toughness, barrier to diffusion of solvents and chemicals, and dimensional stability against thermal fluctuations at high temperatures. Nanosize particulate reinforcements are particularly attractive as the properties of filled polymers can be taken much beyond their intrinsic values [1–5]. Recent studies have shown improvement in flammability in nylon 6 due to incorporation of layered silicate nanofillers [6] and 10-fold increase in tensile strength and 3-fold increase in fracture toughness in PP due to Sn–Pb nanofillers [7]. Also, graphite nanoparticles have rendered semiconductor nature in *in situ* polymerized nylon 6 [8] and smectite clay particles have been successfully incorporated into polypropylene to augment the properties [9].

High performance thermoplastic polymers (HPP), such as polyethersulphone (PES), polyphenylene ether (PPE), polyetheretherketone (PEEK), polyimide, polyetherimide, etc. exhibit superior thermal stability and strong mechanical properties. However, many of these polymers lack proper resistance to attacks by solvents or chemicals and do not provide adequate dimensional stability at high application temperatures. Nanosize filler particles, if well dispersed, may significantly augment these properties, although the issues of shear heating and poor polymer-particle interactions, arising respectively due to high viscosity and non-polar nature of the polymeric chains, must be addressed.

Fumed silica is a very useful reinforcement of thermoplastic and thermosetting polymers and finds usage as component material for dental filling [10], electronic packaging [11], thickeners of paints and coatings [12], reinforcement of silicones, PVC, and acrylics for various sealing and structural applications [13–17], and reinforcement of vulcanized rubbers [18]. Fumed silica is available as individual particles ranging from 10–20 nm and, if dispersed well to the scale of 10–50 nm in matrix polymers, it has the potential to improve heat deflection temperature (HDT) and barrier to diffusion of solvents apart from increasing the modulus. However, achieving good dispersion of fumed silica to the size of primary particles is a challenge, primarily due to formation of aggregates originating from the incompatibility of chemistry of the surfaces of the silica particles and many matrix polymers. Surfaces of fumed silica particles usually contain a significant concentration of –OH groups due to the formation of silanol functionalities at the time of manufacturing [19,20]. The silanol groups residing on adjacent particles, in turn, form hydrogen bonds and lead to formation of aggregates, as shown in Fig. 1(a). These bonds, though weak, hold individual fumed silica particles together and the aggregates remain

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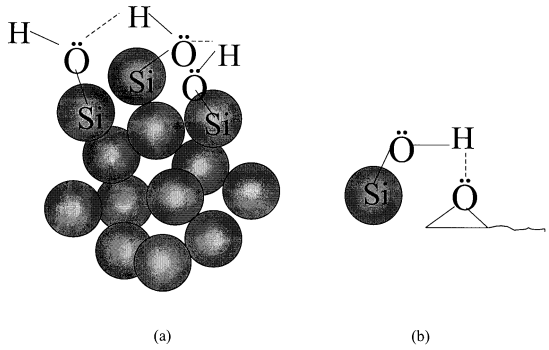

Fig. 1. (a) Schematic of aggregate formation between adjacent fumed silica particles through hydrogen bonding among the silanol groups. (b) Possible interaction between unreacted epoxy and fumed silica particles through hydrogen bonding.

intact even under the best mixing conditions, if stronger filler-polymer interactions are not present.

Dispersion of fumed silica particles into the matrix polymers can be carried out either in the molten state — called melt-mixing — or in polymer solutions in selective solvents. Melt-mixing methods, although practical from the point of view of direct manufacturing of composite articles, suffer from such problems as degradation and aggregate formation. The matrix polymers may potentially degrade due to shear heating, especially if the mixing time is long and the mixing temperature is high; the nanofiller particles may form aggregates if not chemically treated beforehand to augment filler-polymer interactions. The issues with shear heating and aggregate formation can be somewhat alleviated if nanoparticles are mixed in polymer solutions, but solvent recovery adds extra costs and poses environmental concerns.

A more attractive method of incorporation of nanosize filler particles into polymers in conjunction with melt-mixing may be to use reactive solvents. The reactive solvents can be low molecular weight thermosetting resins, which form miscible blends with matrix polymers and, consequently, cause reduction of processing temperatures and blend viscosity. It was reported that polar groups in certain thermosetting resins, such as epoxy, strongly interact with active functional groups of fillers [21,22], such as oxidized carbon fibers, treated fiber glass etc. and form coating layers around the filler particles upon curing [23–25]. In view of this, the polar reactive solvents are expected to aid dispersion and prevent aggregate formation by the nanoparticles. Also, the reactive solvents can be polymerized at the end of mixing process — usually during the fabrication step — to recover or even significantly improve the mechanical properties. Fig. 1(b) presents a sketch of possible interactions between epoxide groups of epoxy and the interfacial silanol groups of fumed silica. As it will be seen later, epoxy formed coating layers around fumed silica particles upon curing.

The aim of the present study was to investigate the use of low molecular weight reactive solvents as processing aid and dispersing agent of fumed silica nanoparticles in high performance polymers. Polyethersulphone (PES) was considered a model high performance thermoplastic polymer for the study. Fumed silica nanoparticles were dispersed in PES with the aid of reactive solvent — a low molecular weight epoxy — as processing aid and dispersing agent. The blends of PES-epoxy-fumed silica were studied with special emphasis on barrier to solvent diffusion and thermal properties, such as heat deflection temperature (HDT). PES is a highly viscous polymer with typical processing temperatures of 340–380°C and forms miscible blends with low molecular weight epoxy with reduction in both processing temperatures and melt viscosity [26–29]; 20% by wt of epoxy can reduce the processing temperature of the blend by almost 100°C.

2. Experimental section

2.1. Materials

Typical properties of the materials used in the study are presented in Table 1. PES was obtained from BASF in natural form and a general purpose, low molecular weight epoxy resin, Epon® 828, was used as reactive solvent for PES. Samples of fumed silica were obtained from Degussa and were used as received. 4,4′-diaminodiphenyl sulfone (DDS) was used as a curing agent of epoxy.

Table 1
Properties of the materials used in the study (T_p = typical processing temperature; T_g = glass transition temperature)

Component	Supplier and grade	Typical properties (Source: supplier)
PES	BASF Ultrason E 1010 Natural	T_g: 218°C; T_p: 340–380°C. Notched Izod at 73°F (ASTM D256): 59.9 J/m.
Epoxy (diglycidyl ether of bisphenol A, DGEBA)	Shell chemical; EPON 828	T_g: −18°C. Specific gravity: 1.17. Epoxy equivalent weight (EEW): 180–190. Viscosity, room temp.: 110–150 Poise.
4,4′-diaminodiphenyl sulfone (DDS)	Ciba; HT 976	Powder; melting point: 174–178°C. Typical curing temperature: 4 h at 175°C. Hydrogen equivalent weight: 63.
Fumed silica	Degussa; Aerosil 90	Powder; primary particle size: 12–20 nm; silanol groups: 2–3 nm^{-2}; bulk density: 0.08; specific gravity: 2.2; BET surface area ($m^2\ g^{-1}$): 75–105.

2.2. Sample preparation

Blends of PES, epoxy, and fumed silica were prepared by melt-mixing using an internal mixer — Brabender Plasticorder. Fumed silica and epoxy were first mixed at room temperature by stirring with a glass rod in a beaker to form a semi-solid paste, which was mixed with PES for 30 min in the internal mixer at about 200–220°C and at 35–100 rpm, depending upon the compositions of PES and epoxy in the blends. The mixing temperature was reduced to about 140–180°C near the end of the mixing experiments before the curing agent was added to the mixture. The materials were further mixed for about 5 min and the mixed materials were withdrawn from the batch mixer. The glass transition temperatures (T_g) of sample specimens collected from different parts of the mixed materials were measured and we found very small variation (2–3°C). The homogeneity of mixture was therefore assumed and longer mixing times were not used. The weight ratio of the amount of curing agent and epoxy was maintained at 0.8 to obtain the maximum degree of crosslinking. The mixed materials were molded into test specimens using a Morgan Press mini-injection molder with barrel and nozzle temperatures in the range of 220–250°C with a clamping force of 6–8 tons and injection pressure of 100 psi. The test specimens were cured at prescribed cure temperatures in a specially designed compression mold that retained the shape of the test specimens during curing. The cured specimens were used for evaluation of barrier, mechanical, and thermal properties.

Some mixtures were also prepared by solution blending to determine suitable curing temperatures and to assess the effects of epoxy curing on the state of dispersion of fumed silica particles. A mixed solvent, containing 90% by volume of methylene chloride and 10% by volume of methanol was used. PES and epoxy were first dissolved in the solvent at room temperature. DDS was then added to the mixture and the mixture was continuously stirred till clear solutions were obtained. The solutions were kept first in a hood at room temperature for 24 h to remove a majority of the solvent and then in a vacuum oven at room temperature for approximately 48 h to eliminate traces of the solvents.

The epoxy component of the solution-blended samples was cured at 200°C for 2–5 h and in some cases post-curing was carried out at 250°C for 2 h.

2.3. Solvent uptake

Methylene chloride is known to be a good solvent for PES and was, therefore, chosen to investigate the barrier properties of blends containing PES, epoxy, and fumed silica. The sample specimens of 25 mm diameter and 0.375 mm thickness, prepared by compression molding as specified in ASTM D543-95, were exposed to solvent vapor in a closed chamber at room temperature. The percentage gain in weight per unit weight of non-silica component, i.e. polymeric part of blends over a period of time was measured and compared with that of PES. Fig 2 shows a schematic of the experimental set-up. Molded specimens were clamped to a hanger, which in turn, was kept above the liquid solvent in a closed chamber. Samples were removed at regular intervals, put into a covered glass container, and weighed instantaneously to avoid evaporation of absorbed solvent. Solvent uptake was measured using three samples at each condition to check of reproducibility and reliability of the data.

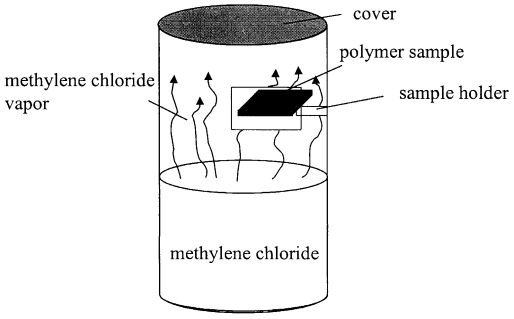

Fig. 2. Schematic of the apparatus used for testing of methylene chloride uptake by polymer samples. Polymer samples were hanged above the liquid and exposed to the vapor.

2.4. Mechanical and thermal properties

Tensile strength and tensile modulus were evaluated at room temperature following ASTM D638 method using an Instron tensile testing machine, Model 4204, Instron Corp. An Izod impact tester, TMI No 43-I was used to evaluate notched Izod impact strengths following ASTM D256 method. Heat deflection temperatures of sample specimens, molded using Morgan Mini-injector Press, were evaluated using ASTM D5945.

3. Results and discussion

3.1. Epoxy as processing aid

The addition of epoxy in blends with PES and PES/DDS reduced the glass transition temperatures of the systems significantly as shown in Fig. 3. The solid lines in Fig. 3 presents a fit obtained with Fox equation [30]. As observed in Fig. 3, a 20% by weight of epoxy in the blend caused a reduction in T_g of about 100°C over pure PES and that the addition of DDS did not significantly change the glass transition temperature of the mixtures. This indicates that PES-epoxy blends containing 20% by weight of epoxy can be processed at around 230–240°C, compared to 340–380°C for PES. The addition of epoxy also reduced the viscosity of the blends as reflected from the values of torque, registered by Brabender Plasticorder during melt mixing. A blend containing 20 parts of epoxy, 80 parts of PES, and 4 parts of fumed silica produced the same torque at 200°C as

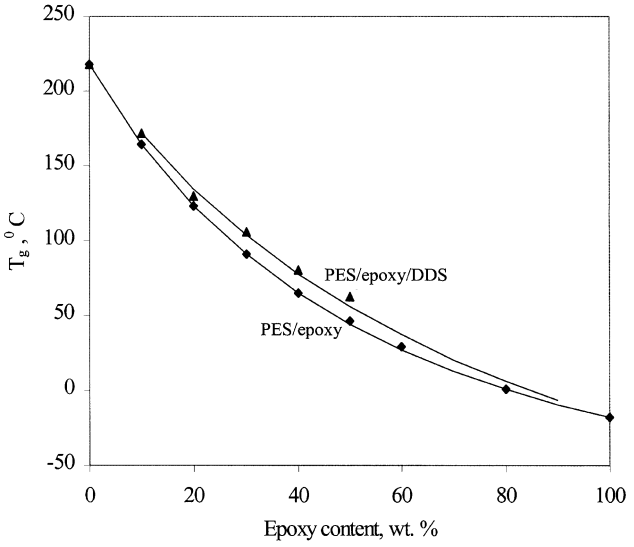

Fig. 3. Glass transition temperature (T_g) of the blends of PES and epoxy (uncured) as function of epoxy content. Solution blended samples were used. The solid lines are fits obtained using Fox equation.

that produced by a mixture of 80 parts of PES and 4 parts of fumed silica at 300°C. In the latter case, the mixed materials showed signs of degradation, e.g. the blends turned black, due to high mixing temperatures.

It was observed using DSC thermograms that the speed of curing of the PES/epoxy/DDS blends was slower than the speed of curing of neat epoxy due to lowering of epoxy and DDS concentrations by the presence of PES. As epoxy was present as minor component — 10 to 30 parts by weight — its glass transition temperatures could not be captured and only one value of glass transition temperature i.e. of PES-rich phase was obtained in cured, phase separated PES/epoxy blends. The glass transition temperatures of the blends approached that of neat PES with continuation of curing. For example, a blend containing 80 parts by weight of PES and 20 parts by weight of epoxy showed glass transition temperatures of 192°C, 204°C, and 212°C when cured respectively at 200°C for 2 h, 200°C for 5 h, and 200°C for 5 h, followed by postcuring at 250°C for 2 h.

The presence of fumed silica did not have much effect on glass transition temperatures — neat epoxy, when cured at 200°C for 2 h showed T_g of 164°C, while epoxy/fumed silica blend containing 10% by weight of silica exhibited a T_g of 167°C. In separate experiments, epoxy and fumed silica mixtures, of the same compositions as in PES/epoxy/silica blends, were allowed to 'react' at 200°C in an oven under nitrogen sweep for 2–3 h. A small change in T_g, from −18°C to about −14°C, was observed. This small change can be thought of due to the presence of fumed silica particles. The possibility of reactions between silanol groups and epoxy was therefore ignored.

3.2. Epoxy as dispersing agent

As alluded to earlier, the polar epoxide and ether groups of epoxy molecules may potentially interact with the silanol groups of fumed silica through hydrogen bonding and help dispersion of the particles. Since the dimensions of the individual particles were in the range of 12–20 nm, the state of dispersion of fumed silica particles was evaluated primarily using TEM. All blends were cured at 200°C for 2 h and at 250°C for 1 h. Fig. 4 shows a comparison of the effect of epoxy on the state of dispersion using TEM of unstained specimens. The state of dispersion was found to be poor in the absence of epoxy in melt-mixed PES/fumed silica blends, containing only 5 parts by weight of particles, Fig. 4(a). The particles formed poorly dispersed aggregates of 500–1000 nm in size. Higher loadings of silica were not attempted to avoid degradation of materials during melt-mixing. The state of dispersion improved dramatically in presence of epoxy even in systems containing higher loadings of fumed silica particles, Fig. 4(b),(c). The particles appeared well dispersed in a window of 2μ with typical dispersed aggregate sizes of 60–100 nm, Fig. 4(b),(c), with an order of magnitude reduction in aggregate sizes compared to PES/fumed silica blends. Fig. 4(c) shows that curing of epoxy has almost no effect on the state of dispersion of fumed silica particles — the aggregate sizes remained more or less the same before and after curing of epoxy.

The dispersion of fumed silica particles, although improved dramatically in the presence of epoxy, was not complete to the scale of individual particles (12–20 nm). The particle aggregates of 60–100 nm seen in Fig. 4(b),(c) were due to poor pre-dispersion process of stirring by glass rods. Other pre-dispersion techniques, such as dispersion in solvents or dispersion using a sonicator in hot epoxy at 50–70°C may potentially improve the quality of dispersion. These will be explored in a separate study.

The locations of crosslinked epoxy phase relative to fumed silica aggregates were not detected in TEM of unstained samples, Fig. 4(b),(c). For this purpose, the sample specimens, after curing, were stained in RuO_4 vapor (Fig. 4d). The darker regions in Fig. 4(d) represent the epoxy phase as it was stained more than the PES phase. Comparing Fig. 4(c), (d), it is evident that 'free' fumed silica particles were not present in RuO_4-stained specimens, as the particle aggregates appeared whiter in the unstained samples. It is, therefore, strongly believed that, in Fig 4(d), epoxy molecules formed coating layers around fumed silica aggregates during curing. In view of this, it is interesting to find the minimum amount of epoxy needed to form coating layers around the particle aggregates or primary particles of fumed silica. In a simple calculation, the thickness of epoxy coating layer was assumed to be of the order of half the size of a particle aggregate/individual particle and it was found that approximately 1.26 parts by weight of epoxy would be needed per unit part by weight of fumed silica to coat all the particles. A comparison of Fig. 4(c) and (d), however, revealed much smaller thickness of epoxy coating layers around the particles, of the order of 10 nm compared to

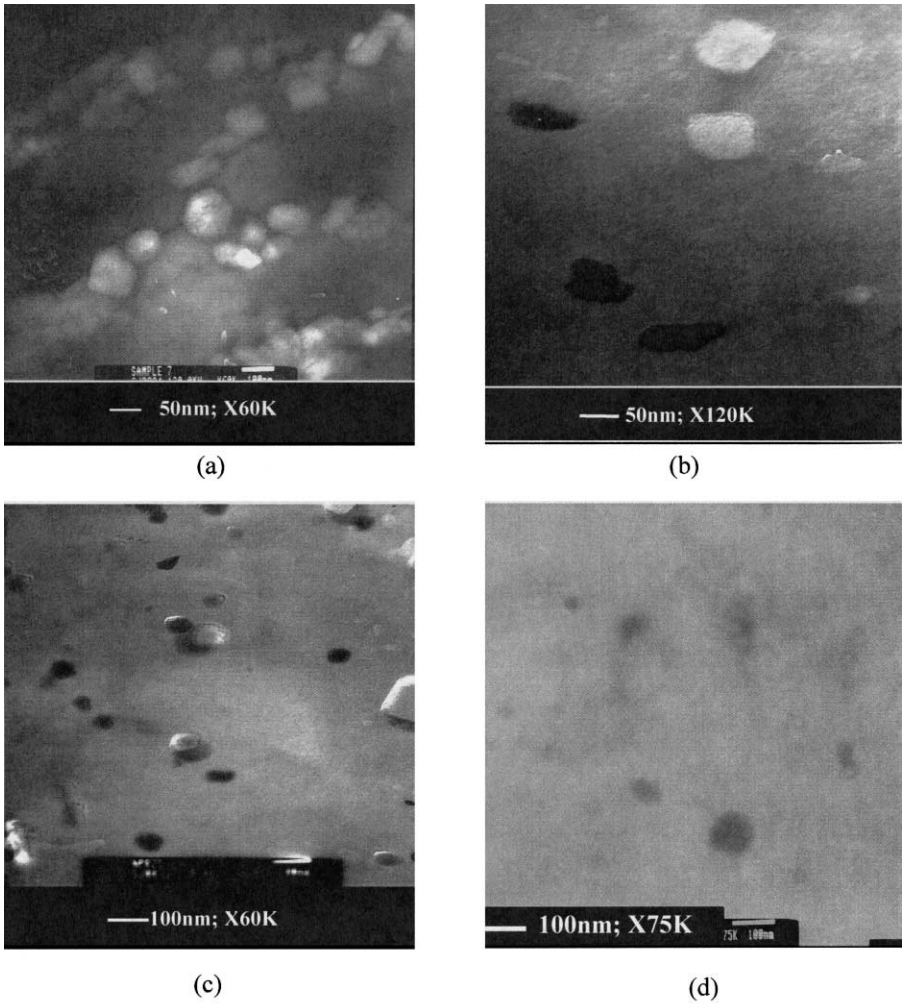

Fig. 4. Transmission electron micrographs of polymeric specimens containing PES, fumed silica, and epoxy. (a) PES:fumed silica = 100:5 (No epoxy). (b) PES:epoxy:silica = 100:25:12.5, before curing of epoxy. (c) Same as (b), after curing of epoxy at 200°C for 2 h. (d) PES:epoxy:fumed silica = 100:25:2.5. After staining cured samples (cured at 200°C for 2 h) in RuO_4 vapor. Dark regions represent epoxy coated fumed silica particles. All compositions are in parts by weight.

100 nm size of an aggregate, requiring about 0.2 parts by weight of epoxy per unit weight of fumed silica, i.e. a coating layer of approximately $1/10^{th}$ the size of an aggregate. Nevertheless, a large excess of epoxy compared to these amounts was used in this study and it is believed that some dispersed epoxy domains may not contain any fumed silica particles in them. This, however, was not confirmed. The mode of reaction-induced phase separation and the role of dispersed nanofillers such as fumed silica on the size of cross-linked epoxy domains will be reported in a separate study.

An excess of epoxy than is required to form coating layers around the particles was used to facilitate reduction of processing temperatures of PES and to help premix fumed silica particles before melt-mixing with PES. Larger quantities of epoxy than were used in this study would negatively impact the tensile and fracture modulus of the resultant materials. Also, the speed of mixing of fumed silica particles would be hindered due to excessive lowering of the viscosity of the mixtures.

3.3. Barrier, mechanical, and thermal properties

The effect of fumed silica on barrier to diffusion of methylene chloride was studied at room temperature. As there are three components in the blends, a continuous PES phase and two dispersed phases, cross-linked epoxy and fumed silica, methylene chloride uptake by each of the components was first evaluated and compared with that of the blends. It was found that fumed silica particles did not absorb any methylene chloride vapor due to non-polar nature of the latter and the presence of fumed silica particles in cured epoxy significantly reduced methylene chloride uptake, as shown in Fig. 5. This reduction in solvent uptake from 3.5% to 0.75% over a period of 22 h with 10% by weight of fumed silica is attributed to the fine state of dispersion of fumed silica particles. In both cases, epoxy was cured for 2 h at 200°C. Epoxy, if completely cured, however, absorbs very small quantities of methylene chloride and, therefore, its presence may also add to diffusion barrier along with fumed silica particles.

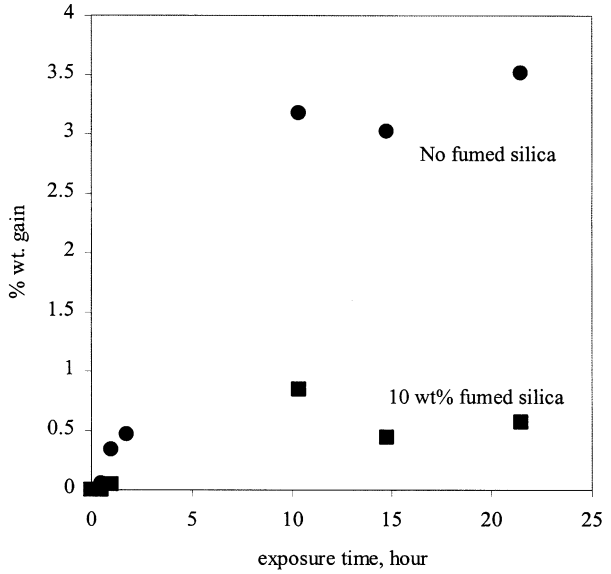

Fig. 5. Methylene chloride uptake by cured epoxy samples. Epoxy was cured using DDS at 200°C for 2 h.

PES and its blends with fumed silica, in absence of epoxy, showed between 5–16% gain in weight due to solvent uptake over a period of 6 h (Fig. 6). The lowest uptake of methylene chloride was obtained with 2phr of fumed silica and increasing the weight % of fumed silica increased the solvent uptake even above that of neat PES, probably due to trapped air bubbles around the large particle agglomerates, which was a direct consequence of poor dispersion.

Methylene chloride uptake by the blends of PES/epoxy depended strongly on the degree of curing of epoxy. The

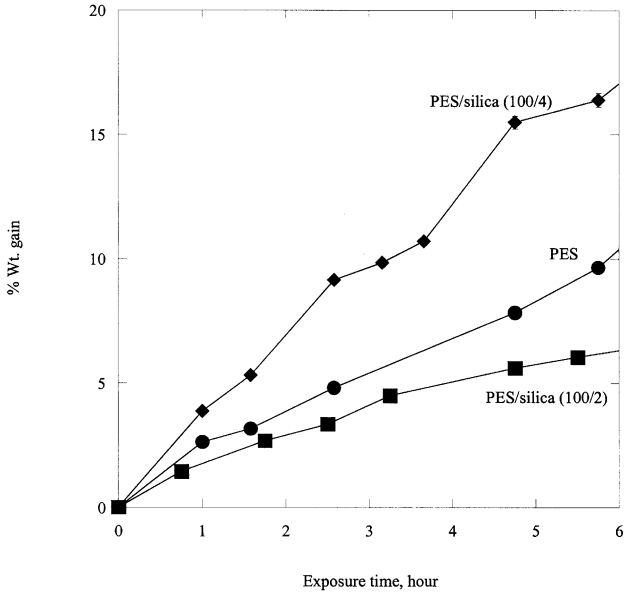

Fig. 6. Effect of fumed silica content on methylene chloride uptake by PES/fumed silica blends (no epoxy). Fumed silica content in parts per hundred parts of PES, all by weight.

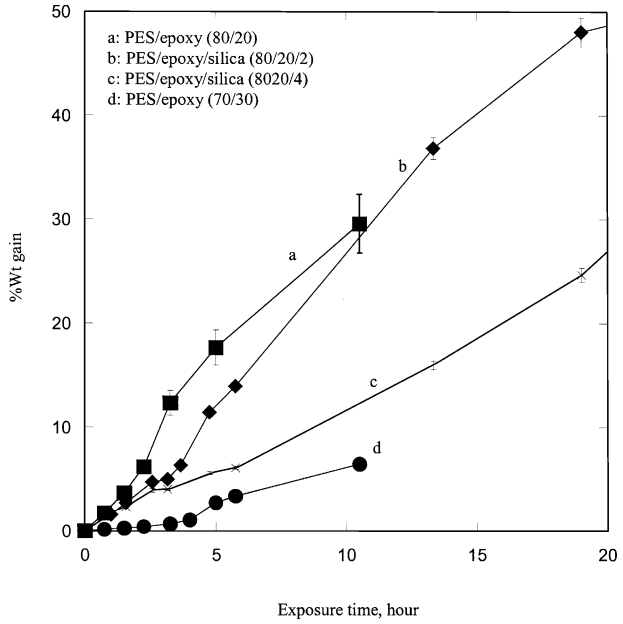

Fig. 7. Effect of fumed silica and epoxy content on methylene chloride uptake. Epoxy was cured at 200°C for 2 h. Blend compositions in parts by weight.

blend with 30% by weight of epoxy provided better barrier to solvent diffusion compared to blends with 20% by weight of epoxy (Fig. 7, curves a and d). Using a separate curing study in DSC, it was observed that the blends with 10 and 20% by weight of epoxy did not go to complete curing in 2 h. Complete curing, however, was achieved with blends containing 30% epoxy; T_g did not change after subsequent curing of 5 h at 250°C. The lower degree of curing in blends with 10 and 20% epoxy can be attributed to the dilution effect; the presence of PES decreased the effective concentration of epoxy and epoxy curing agents. This was further confirmed from much less solvent uptake by the blends containing 10 and 20% by weight of epoxy after curing for 5 h at 200°C.

The presence of uniformly dispersed fumed silica particles at nanoscales increased barrier resistance further in PES/epoxy/silica blends, as supported by the experimental results presented in Fig. 7 (curves b and c). Even though epoxy in such blends was not completely cured, the presence of nanodispersed fumed silica particles helped reduce methylene chloride uptake; compare curves a, b, and c in Fig. 7. The solvent uptake also reduced with an increase in fumed silica content, unlike in the case of PES/fumed silica blend, where epoxy was not used as dispersing agent (Fig. 6).

3.4. Tensile and impact properties

Melt-mixed PES/fumed silica blends showed poor tensile and impact strengths compared to their epoxy-dispersed

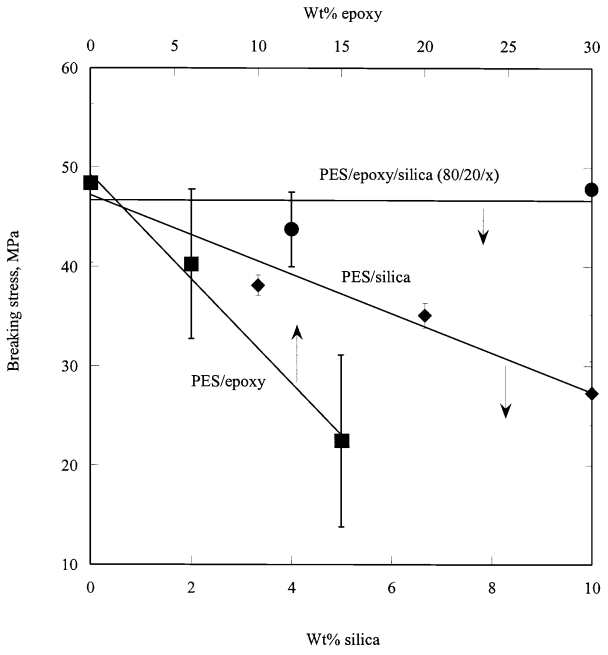

Fig. 8. Effect of fumed silica and epoxy content on tensile strengths of PES/epoxy/fumed silica blends. Epoxy was cured at 200°C for 2 h. PES and epoxy contents are given in parts by weight in PES/epoxy/fumed silica blends.

counterparts, as presented in Figs. 8 and 9. In absence of epoxy as dispersing agent, both tensile and impact strengths reduced with increased fumed silica content, in corroboration with the formation of larger particle aggregates at higher

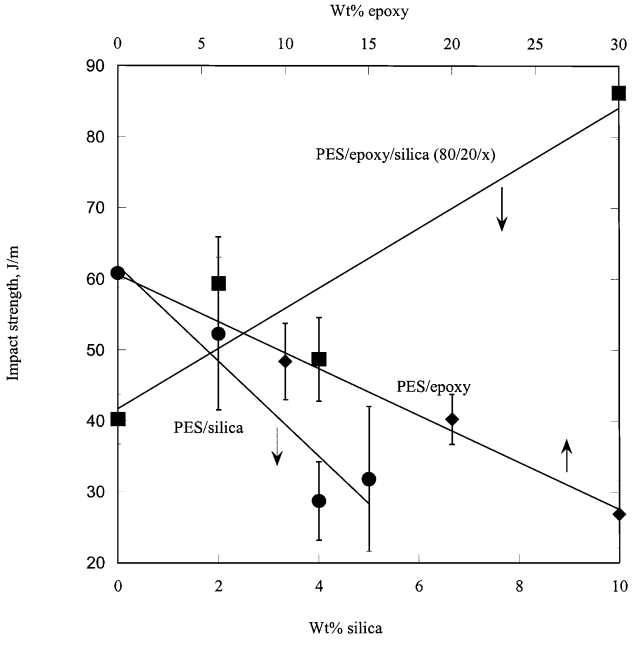

Fig. 9. Effect of fumed silica and epoxy content on impact strengths of PES/epoxy/fumed silica blends. Epoxy was cured at 200°C for 2 h. PES and epoxy contents are given in parts by weight in PES/epoxy/fumed silica blends.

Table 2
Heat deflection temperature data

Sample	Heat deflection temperature (°C)
PES	182
PES/fumed silica	187
PES/epoxy/fumed silica (80/20/10). Cured at 200°C for 3 h. Compositions are in parts by weight.	206.2
PES/epoxy/fumed silica (90/10/2). Cured at 200°C for 4 h. Compositions are in parts by weight.	206
PES/epoxy (80/20) cured at 200°C for 4 h. Compositions are in parts by weight.	176.5

silica content, as seen in Fig. 4(a). These big aggregates substantially weakened the local integrity and therefore prompted rapid breakage of the blend specimens. As cross-linked epoxy component itself has weak tensile and impact properties and the epoxy phase was present as nearly spherical domains (Fig. 4(d)), the blends of PES/cured epoxy and PES/cured epoxy/fumed silica were not expected to show much improvement in tensile and impact strengths over that of PES. Fig. 8 shows that the tensile strength is almost insensitive to fumed silica content when epoxy was used as dispersing agent, although the tensile strength of PES/cured epoxy blends decreased with an increase in epoxy content.

The notched Izod impact strength, however, increased 25–100% as function of fumed silica content (Fig. 9). It is believed that epoxy coating somewhat improved the filler-matrix interactions between fumed silica particles and PES matrix to yield higher impact strength than PES or PES/cured epoxy blends.

3.5. Heat deflection temperature

Table 2 presents the HDT data for virgin PES and its blends with fumed silica and epoxy. As expected, the presence of epoxy-aided nanodispersed fumed silica particles substantially improved the HDT of the blends, although epoxy separately caused reduction of HDT in PES/epoxy blends. The marginal improvement in HDT in melt-mixed PES/fumed silica system can be attributed to larger size particles aggregates.

4. Conclusions

It was shown that epoxy-aided dispersion of nanosize fumed silica particles played important role in modifying the barrier, thermal, and impact properties of PES. Epoxy was successfully used in the present study as a processing aid and as a dispersing agent of fumed silica particles in producing melt-mixed nanoblends of a high performance polymer. Reduction in Brabender torque and processing temperature of PES established the

usefulness of epoxy as a processing aid. Strong interaction between the polar groups of epoxy and silanol groups on the surface of fumed silica particles helped dispersion of fumed silica particles into PES. TEM of stained samples confirmed coating of epoxy layers around fumed silica particles. It was also found that curing of epoxy did not affect the state of dispersion of fumed silica particles.

Fumed silica particles, dispersed to nanoscale with the aid of epoxy, helped increase barrier to diffusion of solvents such as methylene chloride. The tensile strength of PES/epoxy/fumed silica composites was found to be almost as good as pure PES, while the impact strength increased due to strong interaction between filler and polymer matrix. The presence of nanosize dispersed fumed silica improved HDT by 25°C over PES and PES/fumed silica blends.

Although PES-epoxy-fumed silica system was chosen as a model system in this study, other thermoplastic polymers, such as PPO, PEEK, and polyimide can also be investigated using the same methodology [23,31–33]. Some classes of cyanate esters can also serve as reactive solvent of thermoplastic polymers [34,35] and layered silicate nanoparticles can be used without any loss of generality.

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