

Preparation and modification of polyethersulfone-based hybrid materials

Burcu Oktay, Emre Baştürk, Memet Vezir Kahraman, and Nilhan Kayaman Apohan

Polyethersulfone modified by UV-induced grafting and then combined with poly(trimethoxysilyl)propyl methacrylate results in a hybrid material suitable for heat-resistant applications in homes and industries.

Because of their good mechanical properties, and high thermal and oxidative stability,¹ polyethersulfone (PES)-based membranes are useful for a variety of industrial applications (e.g., gas separation, wastewater treatment, hemodialysis, and beverage filtration). The characteristics of PES-based membranes are determined by their surface properties. For this reason, surface functionalization plays an important role during manufacturing.

The application space for PES is currently limited due to its hydrophobic nature. To overcome this limitation, and thus broaden the material's applicability, PES can be modified by UV-grafting polymerization.^{2,3} This surface modification technique, which uses green chemistry, has a number of advantages over other modification methods. For example, the method enables polymer chains to be introduced in a fast, efficient, versatile, simple, and controllable way. It also enables polymer chains to be grafted at a high density.⁴ Furthermore, when suitable monomers are employed, surface graft polymerization enables the introduction of specific functional groups. Additional functional groups are useful for introducing further reactions. For example, PES has been functionalized with tertiary amines to obtain a bis(phenyltrimethylammonium) polymer. In another study,⁵ PES was treated with UV/ozone to generate peroxide groups. In this case, activated PES was found to react with polyvinyl alcohol, chitosan, and polyethylene glycol.

In our previous studies, we have investigated the effect of grafting polyethylene glycol acrylate (PEGA) to carbon nanotube surfaces using photochemical means (i.e., UV-induced grafting).⁶ We found that the technique enabled the hydroxyl functional group (i.e., containing carbon nanotubes) to be effectively connected to the main polymer matrix.⁶ We also modified nanodiamond (by photochemical grafting of PEGA) and subsequently studied its interaction with various

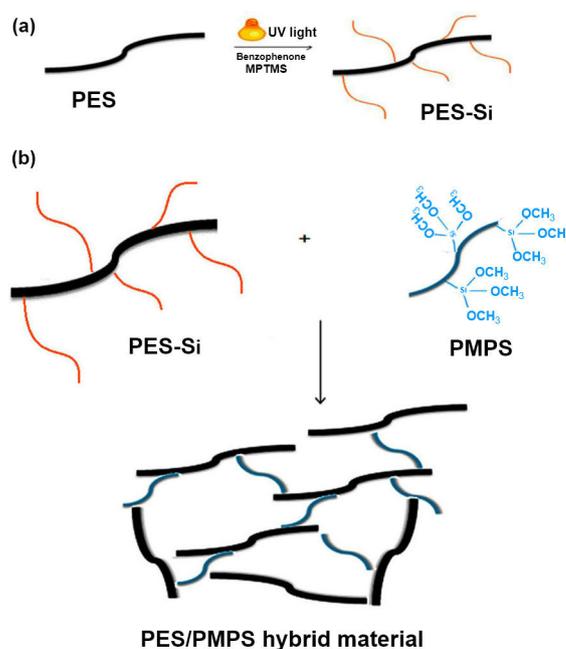


Figure 1. (a) Trimethoxysilane groups (red) are covalently grafted onto polyethersulfone (PES) by a UV-induced grafting reaction. (b) Preparation of PES/poly(trimethoxysilyl)propyl methacrylate (PES/PMPS) hybrids, fabricated via a sol-gel crosslinking process. MPTMS: (3-mercaptopropyl)trimethoxysilane. PES-Si: Trimethoxysilane functionalized PES. OCH₃: Methoxy group.

polymeric matrices. Our results from these studies showed that modifying nanoparticles and nanotubes via UV-induced grafting leads to covalent bonding.⁷

In our most recent work, we prepared surface-modified PES by UV-induced grafting to evaluate whether the approach can enable a polymer to covalently attach to PES as a copolymer.⁸ Thus modifying PES increases its compatibility with polymeric matrices—such as well-defined poly(trimethoxysilyl)propyl methacrylate (PMPS)—and

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Table 1. Thermal properties of PES and PES/PMPS samples at different ratios. $T_{5\%}$: Temperature at 5% weight loss. T_{max} : Temperature of maximum weight loss rate. Char: Percentage of solid material that remains after initial stage of combustion. T_g : Glass transition temperature.

Material	Nitrogen			Air			
	$T_{5\%}$ (°C)	T_{max} (°C)	Char at 800°C (wt%)	$T_{5\%}$ (°C)	T_{max} (°C)	Char at 800°C (wt%)	T_g (°C)
PES	175	252	0.1	181	289	0.25	147
PES/PMPS (95/5)	300	495	37.03	302	463	26.38	93
PES/PMPS (90/10)	301	514	41.28	303	493	34.06	105
PES/PMPS (70/30)	323	525	42.86	341	512	40.70	134

thereby enables the preparation of hybrid materials. First, we synthesized PES (a class of aromatic polymer) from bis(4-chlorophenyl) sulfone and 4,4'-(hexafluoroisopropylidene)diphenol, in the presence of potassium carbonate, via condensation polymerization. We then covalently grafted trimethoxysilane groups onto the PES by a UV-induced grafting reaction: see Figure 1(a). The addition of multiple trimethoxysilane functional groups enabled the further modification of PES. We then synthesized well-defined PMPS, by atom transfer radical polymerization, and covalently bonded the PMPS to the PES (via the crosslinkable trimethoxysilyl groups of PMPS): see Figure 1(b). Finally, we thermally treated (at 100°C for 1h and then at 140°C for 3h) the resultant PES/PMPS hybrids to promote the sol-gel crosslinking process via the condensation of silanol groups.

To investigate the morphological properties of our PES/PMPS hybrids, we employed scanning electron microscopy (SEM). The SEM images (see Figure 2) show that the UV-induced grafting carried out on the PES enabled high interpenetration of PMPS into the matrix. The images also show that the PMPS chains do not exhibit phase separation and are well distributed, without any significant signs of aggregation.

We also investigated the decomposition range of the PES/PMPS hybrids in inert and oxidative atmospheres (nitrogen and air, respectively) by using thermal gravimetric analysis (TGA). The decomposition temperatures for all samples are shown in Table 1. For example, the PES/PMPS sample with a ratio of 95/5 exhibited a loss of 5wt% at 300°. Furthermore, for the 95/5 PES/PMPS sample in air, the maximum weight-loss temperature (T_{max}) increases from 289 to 463° compared with neat PES. This result indicates enhanced thermo-oxidative stability (i.e., due to the crosslinked siloxane linkages in the PES/PMPS sample). Figure 3(a) and (b) show overlapped TGA curves of the PES/PMPS hybrids under the two different atmospheres. In both cases, the addition of PMPS significantly increased the thermal stability of the hybrids due to the crosslinking of polymer chains by the formation of an inorganic network. Our results therefore indicate that the presence of PMPS improves the thermal stability of the hybrids in both atmospheres. The best results were obtained with a 70/30 ratio of PES/PMPS.

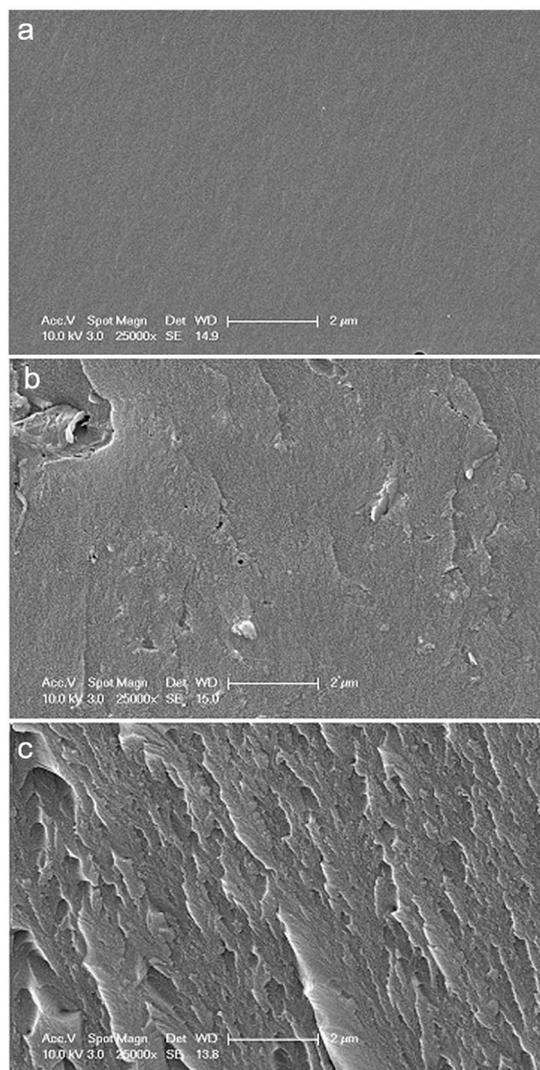


Figure 2. Scanning electron micrographs of the PES/PMPS samples at ratios of (a) 95/5, (b) 90/10, and (c) 70/30.

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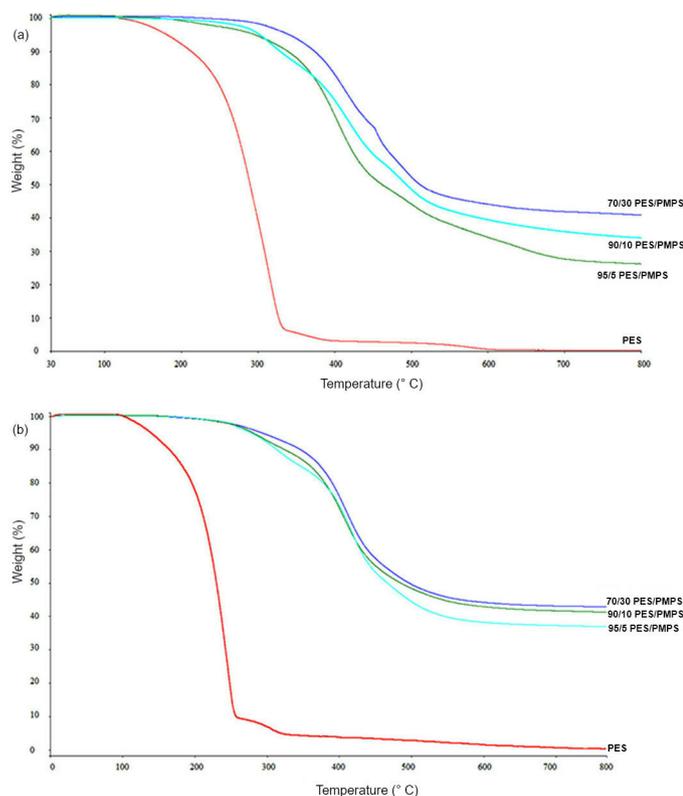


Figure 3. Thermogravimetric analysis (TGA) curves of PES and the PES/PMPS hybrids under (a) nitrogen and (b) air atmosphere.

In summary, we have investigated the modification of PES by UV-induced graft polymerization for the preparation of modified-PES-based hybrids. Our investigations into the thermal properties of the PES-based hybrid materials show that they exhibit excellent thermal stability and thermal degradation profiles. Our results therefore suggest that the PES/PMPS hybrid materials are suitable for use as heat-resistance materials. In our future work, we will investigate the mechanical properties of these hybrid materials to further determine their suitability for use as a dielectric in capacitors and for wastewater treatment applications.

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