Mechanical Behavior of Pseudo-Semi-Interpenetrating Polymer Networks Based on Double-C_{60}-End-Capped Poly(ethylene oxide) and Poly(methyl methacrylate)

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The dynamic mechanical behavior and the tensile properties of pseudo-semi-interpenetrating polymer networks (pseudo-SIPNs) based on double-C_{60}-end-capped poly(ethylene oxide) (FPEOF) and poly(methyl methacrylate) (PMMA) were studied. For pseudo-SIPNs involving FPEOF with a longer PEO chain length, the storage modulus can reach 42 GPa at 40 °C, representing an astonishing 16 times increase over PMMA. There is an optimum FPEOF content to achieve maximum enhancement in the storage modulus. With increasing FPEOF content in the network, the plasticizing effect of PEO chains begins to offset the reinforcing effect of C_{60}. The Young's moduli of the pseudo-SIPNs are about twice than that of PMMA, whereas the tensile strengths, the ultimate strains, and toughness are lower than those of PMMA. The mechanical properties of the pseudo-SIPNs are as good as those of PMMA/carbon nanotube composites.

Introduction

C_{60}-containing polymers have received much attention in recent years. The attachment of C_{60} brings along its attractive properties onto polymers.[1−10] For example, C_{60}-containing polycarbonate shows unique wavelength shielding and optical limiting properties with potential applications in optics-related industries.[4] C_{60}-containing poly(1-phenyl-1-alkyne)s show better optical limiting performance than the parent C_{60}.[5] The photoconductivity of poly(*tert*-butyl acrylate) is dramatically enhanced upon the attachment of C_{60}.[6] Cross-linked C_{60}-polyurethane films show very large, ultrafast nonresonant third-order nonlinearity in the near-IR region.[7] C_{60}-containing epoxy resin possesses better thermal stability than the parent epoxy.[8]

C_{60}-containing polymers and C_{60} derivatives form aggregates in solution and in solid state.[11−16] Similar to conventional surfactants, the C_{60}-containing polymers form micellelike core−shell aggregates with C_{60} moieties as the core and the polymer chains as the shell. C_{60} itself also aggregates in benzene to a size of ~600 nm in diameter.[17] We have recently reported that double-C_{60}-end-capped poly(ethylene oxide) (FPEOF), but not single-C_{60}-end-capped poly(ethylene oxide) (FPEO), possesses outstanding mechanical properties.[18] The aggregation of C_{60} moieties in FPEOF leads to a networklike structure. A combination of a double-C_{60}-end-capped polymer and a linear polymer is then expected to give rise to a pseudo-semi-interpenetrating polymer network (pseudo-SIPN). This paper reports the mechanical behavior of pseudo-SIPNs based on FPEOF and poly(methyl methacrylate) (PMMA). Their behavior is compared to that of PMMA/carbon nanotube composites.

Experimental Section

C_{60} (99.9%) was obtained from Peking University, China. Two poly(ethylene oxide) (PEO) samples were obtained from Aldrich; their number-average molecular

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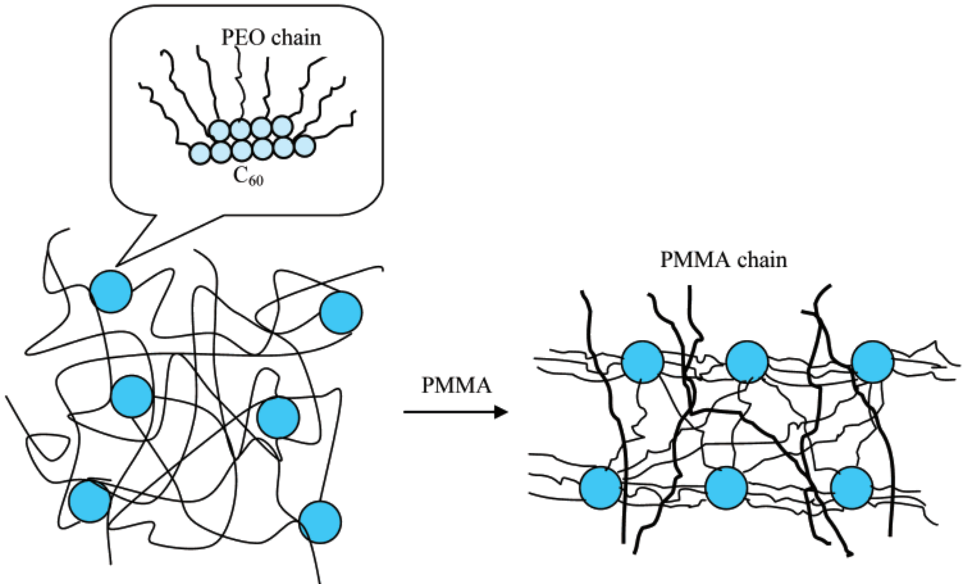
Scheme 1. Pseudo-SIPN



weight (M_n)/polydispersity index (PDI) values are 5000/1.07 (PEO5) and 12 000/1.06 (PEO12), respectively. PMMA was obtained from BDH Chemicals; its M_n/PDI values are 29 000/1.6.

Double-C_{60}-end-capped FPEO5F and FPEO12F were prepared from PEO5 and PEO12, respectively, following the methods reported previously.[19] The synthetic methodology is based on the cycloaddition reaction of azide to C_{60}.[20] The hydroxyl groups of PEO were converted to chlorine groups through reaction with thionyl chloride. The chloro-terminated PEO was then reacted with sodium azide to form azido-terminated PEO, which subsequently underwent cycloaddition with C_{60} to afford FPEOF.

Melt blending of FPEOF and PMMA was performed in a laboratory mixing molder (Atlas) at 230 °C for 20 min and then at 200 °C for 10 min. The resulting materials were then annealed at 200 °C in a hydraulic press for 30 min under atmospheric pressure and then at 200 °C for 15 min under 1 metric ton pressure. To ensure the complete removal of any trapped air bubbles in the samples, three quick press/release cycles were performed. The samples were then kept at 60 °C under vacuum before being characterized.

Thermogravimetric measurements were made using a TA Instruments SDT2960 simultaneous DTA-TGA under nitrogen using a heating rate of 20 °C/min. Dynamic mechanical measurements of materials (dimension 25 mm × 5 mm × 0.2 mm) were made using a TA Instruments DMA2980 dynamic mechanical analyzer under nitrogen using a heating rate of 3 °C/min and a frequency of 1 Hz.

The stress–strain behavior of materials (dimension 25 mm × 5 mm × 0.2 mm) was studied using an Instron model 3345 mechanical tester at room temperature. The strain rate was 2 mm/min under a load of 1 kN.

Transmission electron microscope (TEM) micrographs were obtained with a Philips CM100 (100 kV) TEM. Films (∼150 nm in thickness) were backed on 200-mesh copper grids coated with carbon.

Table 1. Compositions of Pseudo-SIPNs

sample code[a]	C_{60} content (wt %)	FPEOF content (wt %)
A	1.6	9.1
B	2.7	14.9
C	4.5	25.0
D	1.1	8.7
E	1.5	11.9
F	4.6	35.9

[a] Samples A–C are based on FPEO5F; Samples D–F are based on FPEO12F

Results and Discussion

An interpenetrating polymer network (IPN) is a combination of two network polymers, whereas a semi-interpenetrating polymer network (SIPN) consists of a linear polymer and a network polymer.[21] In most cases, the two polymers in an IPN or an SIPN are immiscible with each other. A combination of FPEOF and PMMA resembles an SIPN with aggregated C_{60} moieties functioning as physical cross-links (Scheme 1). Since PEO is miscible with PMMA,[22–24] the polymer matrix in our pseudo-SIPNs is homogeneous.

Six pseudo-SIPNs were prepared, three based on FPEO5F and the other three based on FPEO12F. The FPEOF contents in the pseudo-SIPNs are shown in Table 1. For FPEOF and various pseudo-SIPNs, the thermogravimetric curves showed that their weights remained constant at temperatures above 500 °C. The C_{60} and the corresponding FPEOF contents can then be determined by thermogravimetry.

Figure 1 shows the storage moduli of PMMA, three pseudo-SIPNs based on FPEO5F, and three PMMA/PEO5 blends. As compared to PMMA, two of the pseudo-SIPNs possess slightly higher storage moduli. However, for the pseudo-SIPN containing the highest FPEOF

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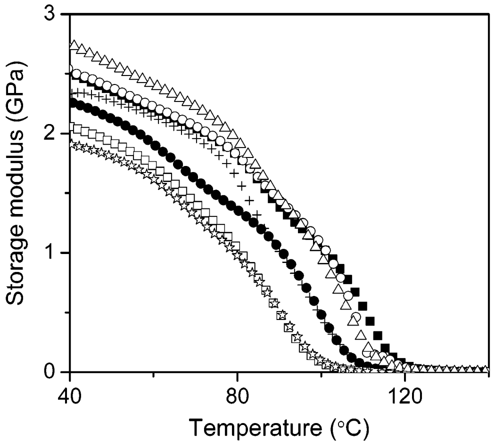

Figure 1. Storage moduli of PMMA, PEO5/PMMA blends, and FPEO5F/PMMA pseudo-SIPNs: (○) A; (△) B; (+) C; (■) PMMA; (●) PEO5/PMMA (5:95); (□) PEO5/PMMA (10:90); (□) PEO5/PMMA (20:80).

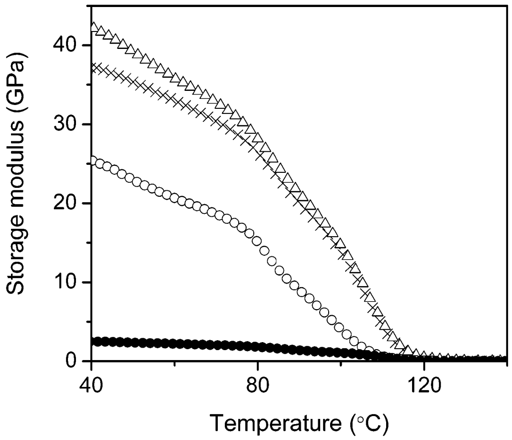

Figure 2. Storage moduli of PMMA and FPEO12F/PMMA pseudo-SIPNs: (×) D; (△) E; (○) F; (●) PMMA.

content, the storage modulus is slightly lower than that of PMMA. PEO has a low glass transition temperature of -75 °C. Since PMMA is miscible with PEO, the addition of PEO makes the polymer matrix softer as shown by the low moduli of the PMMA/PEO5 blends (Figure 1). The storage modulus of PMMA/PEO5 blend decreases progressively with increasing PEO5 content in the blend. At a higher FPEO5F content, the plasticizing effect of the PEO chains begins to offset the reinforcing effect of C_{60}.

On the other hand, the storage moduli of the three pseudo-SIPNs based on FPEO12F are substantially larger than that of PMMA (Figure 2). The storage modulus value reaches 42 GPa, representing an astonishing 16 times increase over PMMA. Similarly, there is also an optimum FPEO12F content to achieve maximum enhancement on storage modulus. The moduli of these pseudo-SIPNs are even larger than those of PMMA/carbon nanotube composites. We have found that the incorporation of 26 wt % multiwalled carbon nanotubes (MWNTs) doubles the storage modulus of PMMA at ambient temperature.[25] The mechanical performance of polymer/carbon nanotube composites depends largely on how well the nanotubes are dispersed in the polymer matrix. A better dispersion results in a better performance. Our later study showed that using poly(vinylidene fluoride) as a wetting agent, the addition of 1.5 wt % MWNT increases the storage modulus of PMMA by 200%.[26] Similarly, Velasco-Santos et al. reported that the storage modulus of PMMA is increased by 200% upon the incorporation of 1 wt % MWNT.[27,28] The C_{60} content of the pseudo-SIPN with the largest storage modulus value is 1.5 wt %. Therefore, the enhancement of storage modulus of PMMA by FPEO12F is indeed phenomenal. The storage modulus of a thermoplastic polymer such as PMMA decreases rapidly when it is heated through the glass transition region (Figure 1). The moduli of the pseudo-SIPNs also begin to decrease rapidly at 80 °C. However, even at 100 °C, the storage moduli of two of the pseudo-SIPNs are still 10 times larger than that of PMMA. Velasco-Santos et al.[28] also reported that the storage modulus of PMMA at 90 °C is raised by 11 times upon the incorporation of 1 wt % functionalized carbon nanotubes.

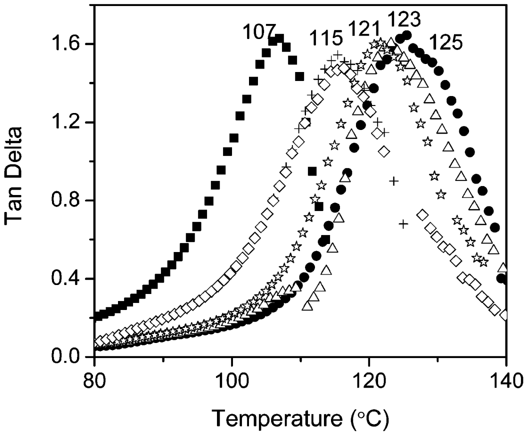

Figure 3. Tan δ peaks of various materials: (△) A; (+) C; (□) D; (□) F; (●) PMMA; (■) PEO5/PMMA (20:80).

Figure 3 shows the tan δ plots of PMMA, some pseudo-SIPNs, and PEO5/PMMA (20/80) blend. The temperature of the tan δ peak is commonly taken as the glass transition temperature (T_g) of the polymer. Our previous studies have shown that the incorporation of C_{60} or monofunctionalized C_{60} to polymers does not produce a significant effect on tan δ, but the addition of multifunctionalized C_{60} broadens the tan δ peak and moves the peak to a higher temperature.[29,30] The tan δ peak of the pseudo-SIPN moves progressively to a lower temperature with increasing FPEOF content, arising from the plasticizing effect of the PEO chains. The PEO5/PMMA blend shows the lowest T_g. In contrast, the tan δ peak moves to a higher temperature by $\sim$40 °C when carbon nanotubes are added to PMMA.[28]

The present study shows that the chain length of PEO in the FPEOF sample plays an important role in the

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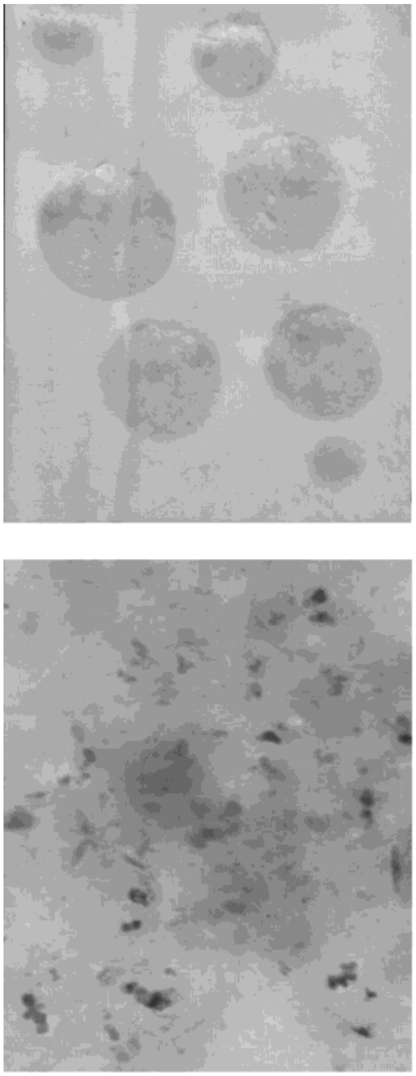

Figure 4. TEM micrographs. (Top) FPEO5F/PMMA (sample B) ×28500; (bottom) FPEO12F/PMMA (sample D) ×39000.

dynamic mechanical behavior of the pseudo-SIPN. We had found earlier that the aggregation behavior of FPEOF in water and in tetrahydrofuran is significantly affected by the polarity of solvent and the length of PEO segments.[13] Long PEO chains facilitate the formation of a network structure. Figure 4 shows the TEM micrographs of two pseudo-SIPNs, one based on FPEO5F and the other based on FPEO12F. The size of C_{60} aggregates in pseudo-SIPN based on FPEO5F ranges from 200 to 800 nm, whereas that of pseudo-SIPN based on FPEO12F is in the range of 50−150 nm. Smaller particles generally have a better strengthening effect on polymer matrixes than bigger particles.[31] For the reinforcement of rubbers by various types of carbon black, the strengthening effect increases with decreasing size of the carbon black particles.[32] Similarly, the mechanical performance of C_{60}-containing polymeric materials is improved if C_{60} or its derivatives can be dispersed more finely in the polymer matrixes.[29] Thus, the better performance of pseudo-SIPNs based on FPEO12F is partly due to the smaller size of the C_{60} aggregates. Furthermore, the longer PEO chains in FPEO12F also enable a more effective load transfer.

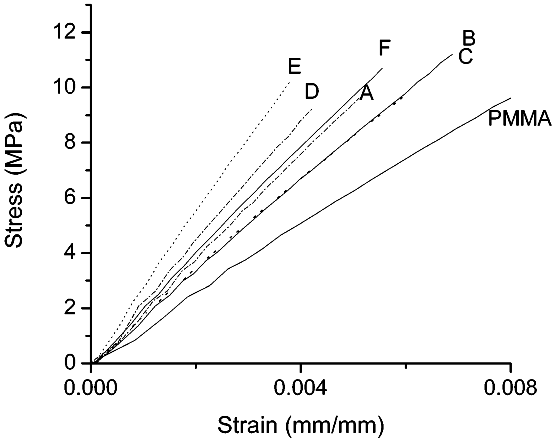

Figure 5. Initial stress−strain curves of materials.

Table 2. Strain−Stress Properties of PMMA and Pseudo-SIPNs

sample code	tensile strength $\sigma_{\max}$ (MPa)	ultimate strain $\epsilon_{\max}$ (mm/mm)	Young's modulus (MPa)	toughness (MJ/m^3)^a
PMMA	51.3	0.0627	1180	1.96
A	41.2	0.0279	1980	0.77
B	28.6	0.0216	1680	0.34
C	28.0	0.0250	1580	0.44
D	31.4	0.0220	2020	0.43
E	43.3	0.0250	2430	0.61
F	34.2	0.0238	1940	0.46

[a] Area under the stress−strain curve.

Figure 5 shows the initial stress−strain curves of various materials, and their tensile properties are summarized in Table 2. The incorporation of FPEOF to PMMA increases the Young's modulus by about 50−100%, whereas the tensile strength, the ultimate strain, and the toughness decrease slightly. Similar to the dynamic mechanical behavior discussed earlier, there also appears an optimum FPEOF content above which the tensile properties start to decrease. Interestingly, Jia et al. reported that when PMMA is reinforced with crude carbon nanotubes, the tensile strength is halved and the toughness is marginally decreased.[33] The incorporation of acid-treated carbon nanotubes increases the tensile strength of PMMA slightly and has no significant effect on toughness.[33] However, at a higher content of acid-treated carbon nanotubes, the composite possesses a lower tensile strength and toughness. On the other hand, Velasco-Santos et al. reported that the addition of crude carbon nanotubes improves the tensile strength of PMMA slightly but decreases the ultimate strain and toughness.[28]

Conclusions

Pseudo-SIPNs were prepared by melt blending of PMMA and FPEOF. For pseudo-SIPNs based on FPEO12F, the storage modulus can reach 42 GPa, 16 times larger than that of PMMA. At a higher FPEO12F content, the storage modulus starts to decrease due to

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the plasticizing effect of the PEO chains. As compared to PMMA, the pseudo-SIPNs have higher Young's moduli, but lower ultimate strains and toughness. The mechanical properties of the pseudo-SIPNs are as good as those of PMMA/carbon nanotube composites.

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