Notes

Reinforcing and Toughening of Poly(vinyl chloride) with Double-C_{60}-End-Capped Poly(*n*-butyl methacrylate)

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Received March 5, 2006
Revised Manuscript Received April 28, 2006

Introduction

Additives are used to improve the properties of polymers. Plasticizers are often added to make a rigid and hard polymer flexible by lowering the modulus, tensile strength, and glass transition temperature (T_g) of the polymer and increasing the ultimate strain. For example, plasticizers such as dioctyl phthalate or low-T_g polymers such as polycarprolactone are commonly added to poly(vinyl chloride) (PVC) to make it flexible. On the other hand, the addition of reinforcing fillers increases the modulus and strength but reduces the ultimate strain and toughness (energy to break the polymer) of polymers. For example, the incorporation of carbon nanotubes to a polymer enhances stiffness and strength but often reduces ultimate strain and toughness.[1−5] It is therefore a challenging task to find an additive that can strengthen and also toughen a polymer.

[60]Fullerene (C_{60}) forms aggregates in benzene to a size of about 600 nm in diameter.[6] C_{60} derivatives and C_{60}-containing polymers also form aggregates in solution and in solid state.[7−15] Similar to conventional surfactants, C_{60}-containing polymers form micelle-like core−shell aggregates with C_{60} moieties as the core and the polymer chains as the shell. We have found that double-C_{60}-end-capped poly(ethylene oxide) (FPEOF), but not single-C_{60}-end-capped poly(ethylene oxide), possesses outstanding mechanical properties.[16] The aggregation of the C_{60} moieties in FPEOF leads to a network-like structure. While the parent poly(ethylene oxide) is a waxy material, FPEOF can be stretched to 6 times its original length and possesses shape recovery ability. A combination of a double-C_{60}-end-capped polymer and a linear polymer forms a pseudo-semi-interpenetrating polymer network (pseudo-SIPN). We have studied the mechanical properties of pseudo-SIPNs based on FPEOF and poly(methyl methacrylate) (PMMA).[17] The incorporation of FPEOF increases the storage modulus and the Young's modulus of PMMA significantly. However, the tensile strength, the ultimate strain, and the toughness of PMMA are slightly reduced. A recent study by Inoue and co-workers showed that the toughness of poly(L-lactic acid) (PLLA) was dramatically improved by the incorporation of FPEOF.[18] However, the yield stress and the tensile strength of PLLA were lowered. In this Note, we report the reinforcing and toughening of PVC by double-C_{60}-end-capped poly(*n*-butyl methacrylate) (FPBMAF). Poly(*n*-butyl methacrylate) (PBMA) has a lower T_g (20 °C) than PVC (82 °C) and is miscible with PVC.[19−21] It is envisaged that while the softer PBMA chains may render ductility, the C_{60} aggregates offer stiffness and strength. As a result, PVC can be strengthened and toughened by FPBMAF.

Experimental Section

Materials. C_{60} (purity 99.9%) was obtained from Peking University, China. PVC (inherent viscosity 1.02) and PBMA ($M_w = 288\,000$) were obtained from Aldrich. *n*-Butyl methacrylate from Aldrich was passed through a column of aluminum oxide and then distilled under vacuum before polymerization. CuBr (98%) obtained from Aldrich was purified by stirring in acetic acid, washing with methanol, and then drying in a vacuum. α,α'-Dibromo-*p*-xylene (DBX) was recrystallized from *n*-hexane. Tetrahydrofuran (THF) was distilled from sodium. Chlorobenzene was distilled before use. 2.2′-Bipyridyl (BPY), trimethysilyl azide, tetrabutylammonium fluoride (TBAF) solution (1.0 M THF solution), and methanol were used as received.

Polymerization of *n*-Butyl Methacrylate. Double-bromine-terminated PBMA was prepared by atom transfer radical polymerization. A dry round-bottom flask containing BPY (139 mg, 0.894 mmol) was evacuated and refilled with nitrogen, followed by the addition of a mixture of dry THF (10 mL) and *n*-butyl methacrylate (5 mL, 31 mmol) which had been bubbled with nitrogen for 20 min before use. After degassing by three freeze−pump−thaw cycles, the reaction mixture was stirred for 1 h at room temperature. CuBr (42.7 mg, 0.298 mmol) and DBX (51.6 mg, 0.149 mmol) were then added. After another degassing procedure, the flask was placed in an oil bath at 60 °C. After 24 h of reaction, the mixture was cooled and diluted with dry THF, followed by precipitation in a large amount of methanol. To remove residual catalyst, the precipitated polymer was further purified by filtration through an aluminum column eluted with THF, followed by reprecipitation into methanol to afford double-bromine-terminated PBMA. The molecular weight and the polydispersity of the polymer determined by GPC are 60 000, and 1.2, respectively.

Synthesis of FPBMAF. FPBMAF (1.5 g, 0.0244 mmol) was converted to double-azide-terminated PBMA by reacting with trimethysilyl azide (9.73×10^{-3} mL, 0.0732 mmol) in THF solution in the presence of TBAF (7.32×10^{-2} mL, 0.0732 mmol) at room temperature for 24 h.[22] Then the reaction mixture was precipitated into methanol to afford double-azide-terminated PBMA which underwent cycloaddition with C_{60} in chlorobenzene for 24 h under reflux to afford FPBMAF.

Fabrication of PVC/FPBMAF Pseudo-SIPNs. PVC/FPBMAF pseudo-SIPNs were prepared by solution casting from THF. Appropriate amounts of PVC and FPBMAF were dissolved in THF (5 wt %) and stirred overnight at room temperature to obtain homogeneous solutions. The solutions were then poured into Petri dishes, and the solvent was allowed to evaporate slowly. The resulting films were then dried in a vacuum oven at 40 °C for 2 weeks before characterization. Two pseudo-SIPNs were prepared. Their effective C_{60} contents are 0.06 and 0.1 wt %, and they are designated as samples A and B, respectively.

Characterization. The dynamic mechanical measurements of materials (dimension 25 mm × 5 mm with varying thickness) were

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10.1021/ma0604901 CCC: $33.50

Scheme 1. Synthesis Procedure of Double-C_{60}-End-Capped PBMA

$$\mathrm{BMA} \xrightarrow[\mathrm{DBX/THF}]{\mathrm{CuBr/bpy}} \mathrm{Br{-}PBMA{-}Br} \xrightarrow[\mathrm{TBAF\ /THF}]{\mathrm{N_3{-}SiMe_3}} \mathrm{N_3\text{-}PBMA\text{-}N_3} \xrightarrow{\mathrm{C_{60}}} \mathrm{C_{60}\text{-}PBMA\text{-}C_{60}}$$

made using a TA Instruments DMA2980 dynamic mechanical analyzer under nitrogen using a heating rate of 3 °C $\mathrm{min^{-1}}$ and a frequency of 1 Hz.

The tensile properties of materials (the same dimension as those used in DMA measurements) were measured using an Instron model 3345 mechanical tester at room temperature. The strain rate was 2 mm $\mathrm{min^{-1}}$ under a load of 1 kN. At least three measurements were made for each sample.

High-resolution TEM (JEOL JEM 3010F, 300 kV) was used to obtain transmission electron micrographs. Microfilms (100 nm in thickness) were backed on 200 mesh copper grid coated with carbon.

Results and Discussion

The synthesis procedure of double-C_{60}-end-capped PBMA is shown in Scheme 1. The molecular weight and polydispersity of Br−PBMA−Br measured by GPC are 60 000, and 1.2, respectively. The C_{60} content of FPBMAF is 2.12 wt % determined by thermogravimetry, and this is in good agreement with the theoretical value of 2.34 wt %.

Figures 1 and 2 compare the storage moduli and tan δ curves of FPBMAF and PBMA. The storage modulus of PBMA is increased upon end-capping with C_{60}. The network-like structure of FPBMAF also enables the polymer to retain its modulus at higher temperatures. For example, the storage modulus of FPBMAF at 20 °C is more than double that of PBMA. As compared to PBMA, the T_g of FPBMAF, as indicated by the maximum of tan δ peak, is about 5 °C higher. The C_{60} aggregates serve as cross-links to restrict the segmental motions of the polymer chains, and hence T_g increases.

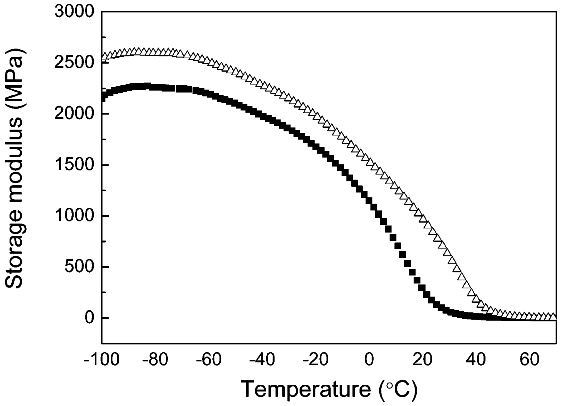

Figure 1. Storage moduli of PBMA (■) and FPBMAF (△).

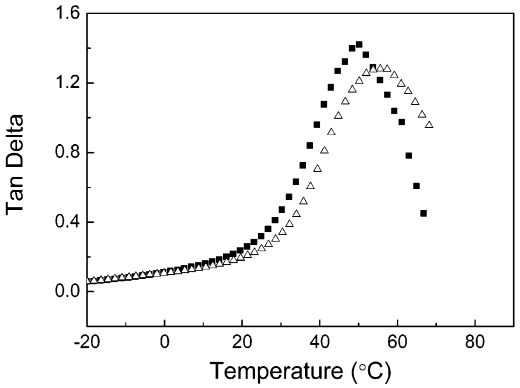

Figure 2. Tan δ of PBMA (■) and FPBMAF (△).

The tensile strength of FPBMAF is 240% higher than that of PBMA. The ultimate strain of PBMA is slightly decreased upon the end-capping with C_{60}. The toughness of PBMA (the area under the stress−strain curve) increases dramatically by 190%. Therefore, the end-capping of PBMA with C_{60} produces a stiffer, stronger, and tougher material. The stress−strain curves of FPBMAF and PBMA are available in the Supporting Information.

The dynamic mechanical properties of PVC and PVC/FPBMAF pseudo-SIPNs are shown in Figures 3 and 4. The incorporation of FPBMAF (C_{60} content of 0.06 wt %) increases the storage modulus of PVC by nearly 30%. Furthermore, FPBMAF has a larger effect in raising the modulus at high temperatures. For example, the storage modulus of FPBMAF (C_{60} content of 0.1 wt %) is about twice as that of PVC at 65 °C. This dramatic increase in modulus is ascribed to the pseudo-network structure formed by C_{60} aggregates in the PVC matrix. It has been found that FPEOF can form core−shell aggregates in solutions with C_{60} in the core and PEO in the shell.[9] Furthermore, FPEOF forms a pseudo-semi-interpenetrating network with PMMA.[17] This network structure is responsible for the dramatic increases in strength and modulus of PMMA. For PVC/FPBMAF pseudo-SIPNs fabricated from THF, the C_{60} aggregates can be observed with high-resolution TEM as shown in Figure 5. The size of C_{60} aggregates is about

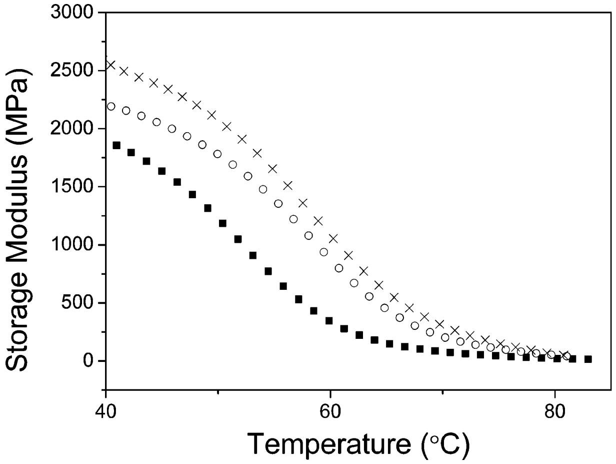

Figure 3. Storage moduli of PVC (■) and PVC/FPBMAF pseudo-SIPNs: sample A (○); sample B (×).

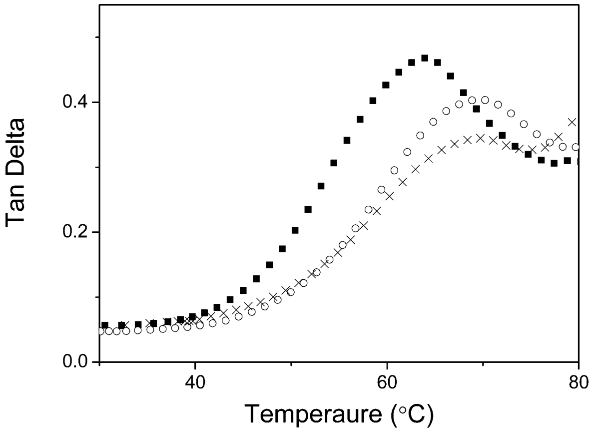

Figure 4. Tan δ of PVC (■) and PVC/FPBMAF pseudo-SIPNs: sample A (○); sample B (×).

Table 1. Mechanical Properties of PVC and Pseudo-SIPNs

sample	effective C_{60} content (wt %)	tensile strength (MPa)	yield stress (MPa)	ultimate strain (mm/mm)	Young's modulus (MPa)	toughness (MJ/m^3)[a]
PVC	0	36.3	49.2	1.08	1470	39.7
A	0.06	42.4	57.5	0.903	1570	38.1
B	0.1	47.9	61.0	1.34	1680	61.8

[a] Area under the stress−strain curve.

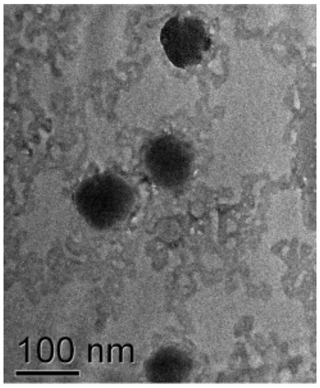

Figure 5. TEM micrograph of PVC/FPBMAF pseudo-SIPN sample A.

80−90 nm in diameter. For pseudo-SIPN based on FPEOF (M_w of PEO = 12 000) and PMMA, the size of C_{60} aggregates is in the range 50−150 nm.[17]

The tensile properties of PVC and the two pseudo-SIPNs are summarized in Table 1. For the PVC/FPBMAF pseudo-SIPN containing 0.1% C_{60}, the tensile strength, the Young's modulus, the yield stress, the ultimate strain, and the toughness are increased simultaneously as compared to those of pure PVC. It is of interest to compare the reinforcing and toughening effect of FPBMAF on PVC with those of nano-$CaCO_3$ and carbon black reported in recent literature.[23−25] For PVC reinforced with 3 wt % of carbon black (average diameter 30 nm), the yield stress, the tensile strength, and the Young's modulus were improved from about 4.02, 4.02, and 97 kg mm^{-2}, respectively, to 4.07, 4.08, and 103 kg mm^{-2}, respectively.[25] The improvement is marginal. For PVC/nano-$CaCO_3$ composites, the ultimate strain and the tensile strength decreased with increasing $CaCO_3$ content, but the notched Izod impact strength was improved.[23,24] These studies illustrate the difficulty in improving the strength and toughness of PVC simultaneously. Therefore, the reinforcing and toughening effect of FPBMAF on PVC is noteworthy. For polymer composites, the interfacial adhesion between filler particles and polymer chains plays an important role in the mechanical behavior of the composites. A weak filler−polymer interaction results in a poor stress transfer between filler and polymer, leading to premature failure and hence low values of tensile strength, ultimate strain, and toughness. An improvement in filler−polymer interaction improves the mechanical performance. For PVC/nano-$CaCO_3$ composites, the interfacial adhesion between $CaCO_3$ particles and PVC is improved by the use of $CaCO_3$ treated with a titanate coupling agent.[23,24] As compared to untreated $CaCO_3$, surface-treated $CaCO_3$ imparts a higher Izod impact strength to PVC, and the decreases in tensile strength and the ultimate strain are smaller. For PVC/FPMBAF pseudo-SIPNs, the C_{60} aggregates serve as reinforcing fillers. The miscibility between PVC and PBMA allows intimate mixing between the two polymers, enabling an effective stress transfer between filler and PVC matrix through the PBMA chains. Moreover, the low-T_g nature of PBMA also imparts ductility. In view of our present and previous studies and that of Inoue and co-workers, double-C_{60}-end-capped polymers are useful additives to modify the mechanical properties of other polymers.

In conclusion, the end-capping of PBMA with C_{60} has resulted in a significant improvement in dynamic mechanical and tensile properties. Pseudo-SIPN based on FPBMAF and PVC with a low C_{60} content of 0.1 wt % is stronger and tougher than PVC. FPBMAF is a more effective filler for PVC than carbon black and nano-$CaCO_3$.

Acknowledgment. We thank the National University of Singapore for financial support of this research.

Supporting Information Available: TGA curve of FPBMAF, stress−strain curves of PBMA and FPBMAF, and stress−strain curves of PVC and PVC/FPBMA pseudo-SIPNs. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA0604901