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# Mechanical behavior of double-$C_{60}$-end-capped poly(ethylene oxide)

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## Abstract

Double-$C_{60}$-end-capped poly(ethylene oxide) (PEO) possesses good mechanical properties arising from a network-like structure due to the aggregation of $C_{60}$. The tensile strength is about 20 MPa, the elongation at break exceeds 640% and the fracture toughness is more than 110 MJ/$m^3$. The material also possesses shape recovery ability. In contrast, single-$C_{60}$-end-capped PEO does not possess good mechanical properties.

*Keywords:* Double-$C_{60}$-end-capped poly(ethylene oxide); Mechanical behavior; Aggregation

## 1. Introduction

[60]Fullerene, $C_{60}$, has attracted much attention in view of its unique chemical and physical properties [1]. There are many potential applications of $C_{60}$-containing polymers which combine the characteristic properties of $C_{60}$ and those of polymers such as elasticity, film formation and processability [2–5]. Recently, we reported the reinforcing effect of a functionalized $C_{60}$ in supramolecular $C_{60}$-containing polymeric materials [6,7]. Ma et al. studied the mechanical properties of blends of Novolac-type phenolic resin with fullerenol polyurethane or linear polyurethane [8]. Fullerenol polyurethane offers a better improvement on the impact strength of phenolic resin (54.3%) than linear polyurethane does (27.4%).

Poly(ethylene oxide) (PEO) is widely used in pharmacological products, cosmetics, and food [9]. The PEOs range from low-molecular-mass liquids to hard and brittle waxes at moderate molecular mass (up to about 20,000), and to thermoplastics at high molecular mass (>ca. 100,000) [10]. The grafting of biocompatible PEO chain onto $C_{60}$ is of special interest since the importance of fullerene in biomedical and biotechnological fields has been recognized [11–14]. Furthermore, PEO is well known not only for its remarkable biomedical and biocompatible properties but also for its simple linear structure, controlled mass, and narrow polydispersity. Double-$C_{60}$-end-capped PEOs can be prepared by the reaction of azido-terminated PEO with $C_{60}$ [15]. The cycloaddition proceeds primarily through monoaddition with little or no higher addition products, allowing $C_{60}$ to be attached to a single PEO chain to produce $C_{60}$-end-capped PEOs [15–18]. In this paper, we report that when the chain ends of PEO are capped with $C_{60}$, the resulting material possesses good mechanical properties arising from the aggregation of $C_{60}$.

## 2. Experimental

### 2.1. Materials and samples

$C_{60}$ (99.9% pure) was obtained from Peking University, China. Two PEOs were obtained from Aldrich; their number-average molecular weight ($M_n$)/polydispersity values are 10,000/1.06 (PEO10), and 20,000/1.08 (PEO20), respectively.

Double-$C_{60}$-end-capped FPEO10F and FPEO20F were prepared from PEO10 and PEO20, respectively, and characterized following the method as reported previously [15]. Basically, 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-teminated PEO which subsequently underwent cycloaddition reaction with $C_{60}$ to afford $C_{60}$-end-capped PEO. Thermogravimetric analysis and X-ray

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photoelectron spectroscopy confirm that both ends of PEO are capped with $C_{60}$. The end-capping of PEO by $C_{60}$ depresses the crystallinity by about 50%, but produces no apparent change on PEO crystallite structure [19].

The FPEOF samples for mechanical measurements, water uptake measurements and shape recovery study were prepared by solution casting from THF (1% w/v). FPEOF solutions were evaporated to dryness slowly at ambient temperature. The resulting films were then dried in vacuo at ambient temperature for 1 week.

### 2.2. Electron microscopy measurements

Transmission electron micrographs (TEM) were obtained with a JEOL CX100 operating at an accelerating voltage of 100 kV. For the observation of size and distribution of aggregates, a drop of dilute solution was placed onto a 200 mesh copper grid coated with carbon. The samples were dried before measurement.

Scanning electron micrographs (SEM) were obtained with a Philips XL30-FEG using an accelerating voltage of 10–20 kV. For the observation of the fracture surfaces of sample, the film was cryofractured in liquid nitrogen and the fracture surface was then sputter-coated with platinum.

### 2.3. Mechanical measurements

Tensile tests were made at ambient temperature on an Instron Micro Tester 5848 at a strain rate of $8.3 \times 10^{-2}$/s. The specimen dimension was 2.0 mm × 20 mm × 0.2 mm. Five or more specimens were tested for FPEO10F and FPEO20F, and the average values are reported.

### 2.4. Water uptake measurements

The sample film (20 mm × 20 mm × 0.2 mm) was immersed in water at room temperature. The sample was removed periodically and blotted dry with a filter paper and then weighed. The water uptake was calculated by the equation

$$\text{Water uptake (times)} = \frac{W_s - W_0}{W_0}$$

where $W_0$ is the original weight of the sample and $W_s$ the weight of the water swollen sample.

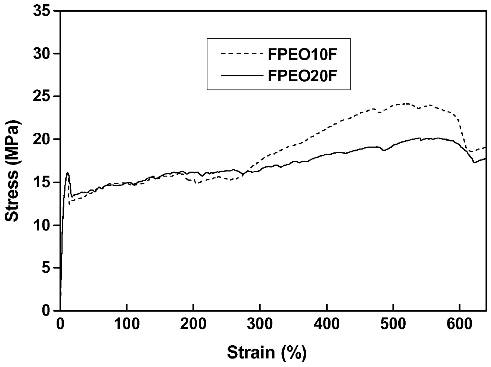


Fig. 1. Tensile stress–strain curves of FPEO10F (dash line) and FPEO20F (solid line).

## 3. Results and discussion

Typical stress–strain curves for the two FPEOFs are shown in Fig. 1. FPEO10F and FPEO20F develop a yield point at about 10% strain. Then, the stress drops as necking occurs and essentially stabilizes as a result of strain hardening. For FPEO10F, stress increases further above 270% strain. Both FPEOFs develop a very large (elongation >640%) plastic deformation. Compared to their parent brittle wax-like PEO10 and PEO20, the improvement in the mechanical performance is significant. Interestingly, ductile FPEOF specimens were not broken even at 640% strain, the limit of the testing instrument. The tensile strength, tensile modulus, yield strength, and fracture toughness of FPEOFs are summarized in Table 1. For comparison, the properties of PEO300 (weight-average molecular weight = 300, 000) are also shown [20]. Other than tensile modulus, the two FPEOFs are superior to PEO300, especially the fracture toughness. As compared to PEO300, the ultimate strain of FPEOF is at least 427 times higher and the toughness of FPEOF is at least 2700 times better. The tensile modulus of FPEOF is lower than that of PEO300, demonstrating that the $C_{60}$-containing PEOs are relatively ductile PEO materials. Fig. 2 shows the photographs of FPEOF specimens before and after deformation.

Thermoplastic elastomers based on PEO/PBT (polybutylene terephthalate) multiblock copolymers are built up of hard segments (PBT) and soft segments (PEO) [21]. The tensile strength varies from 8 to 23 MPa, elongation at break from 500 to 1300%, and water uptake from 4 to 210%. Apparently, the mechanical properties of FPEOF are as

Table 1
Tensile properties of FPEOFs

| Polymer | Tensile strength (MPa) | Tensile modulus (MPa) | Yield strength (MPa) | Fracture toughness[a] (MJ/m$^3$) |
|---|---|---|---|---|
| FPEO10F | 24.1 | 283 | 15.9 | 119 |
| FPEO20F | 20.1 | 258 | 16.0 | 110 |
| PEO300[b] | 5.5 | 650 | [c] | ~0.04 |

[a] Fracture toughness is calculated from the total area under the stress–strain curve.

[b] Source: Ref. 20.

[c] For the PEO300 ($M_w$ = 300, 000), fracture occurs at about 1.5% strain before yielding.

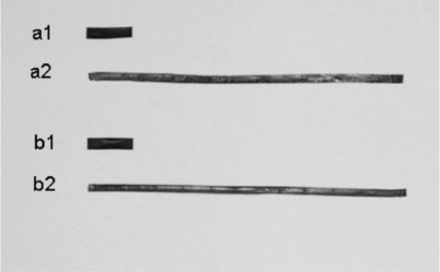


Fig. 2. FPEO10F specimen before (a1) and after (a2) deformation; FPEO20F specimen before (b1) and after (b2) deformation.

good as, if not better than, those of PEO/PBT thermoplastic elastomers.

$C_{60}$-containing polymers and $C_{60}$ derivatives form aggregates in solution or in solid state [22–26]. In principle, double-$C_{60}$-end-capped polymers can aggregate to form a network-like structure. The aggregation of FPEO10F and FPEO20F was demonstrated by TEM using dried sample obtained from the THF solutions (Fig. 3). Fig. 4 shows the SEM micrographs of fracture surfaces of FPEO10F and FPEO20F samples. Spherical $C_{60}$ aggregates in the order of tens of nanometers are observed. The aggregates serve as crosslinks, similar to those of the polystyrene domains in polystyrene-*block*-polybutadiene-*block*-polystyrene (S-B-S) thermoplastic elastomers [27] (Scheme 1). Another evidence for the aggregation of FPEOF is that the cast films of FPEOF cannot be re-dissolved in water but they only swell to a great extent and this will be discussed later. However, the films can be re-dissolved in hot chlorobenzene under sonication for several hours. This may be ascribed to the fact that water is a poor solvent for $C_{60}$ so that it cannot disrupt the aggregates but chlorobenzene is a good solvent for $C_{60}$ and PEO to facilitate the dissolution. Similarly, $C_{60}$-end-capped three-arm PEO can also be re-dissolved in chlorobenzene [28]. Therefore, the crosslinks originated from amphiphilic FPEOF aggregation are physical rather than chemical. This also affirms the ‘S-B-S’ model for the FPEOF materials. To further confirm the validity of the model, single-$C_{60}$-end-capped PEO (FPEO) was also synthesized by cycloaddition reaction of monoazido-teminated PEO with $C_{60}$ [18]. The resulting FPEO is brittle, wax-like powder just like its parent poly(ethylene glycol) monomethyl ether (MPEO) ($M_n$/polydispersity is 2200/1.07). Although FPEO also aggregates in THF solution as observed by TEM (Fig. 3), it does not show any improvement in mechanical properties over its parent MPEO. Aggregates originated from single-$C_{60}$-end-capped FPEO chains do not interconnect to form a network. This further confirms that only double-$C_{60}$-end-capped PEO (FPEOF) can form a network-like structure to achieve high performance. Similarly, only triblock S-B-S but not diblock S-B is a useful thermoplastic elastomer.

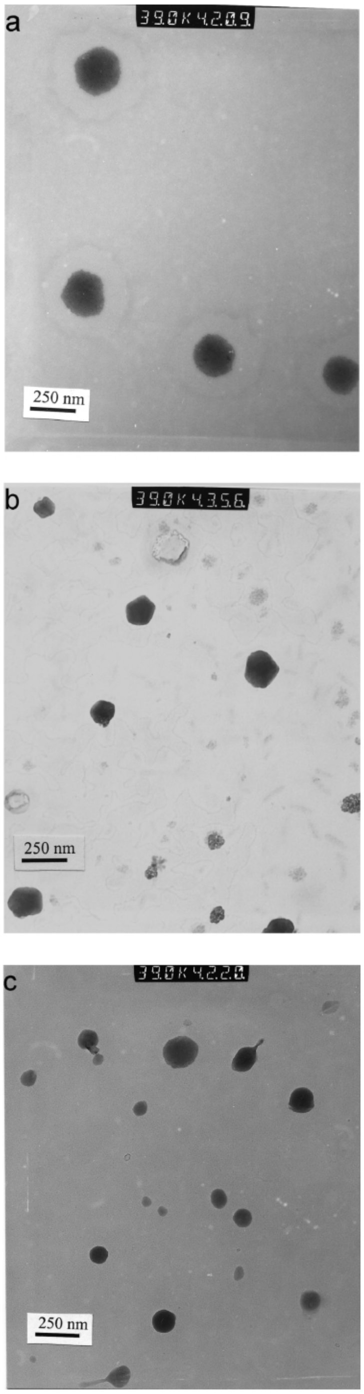
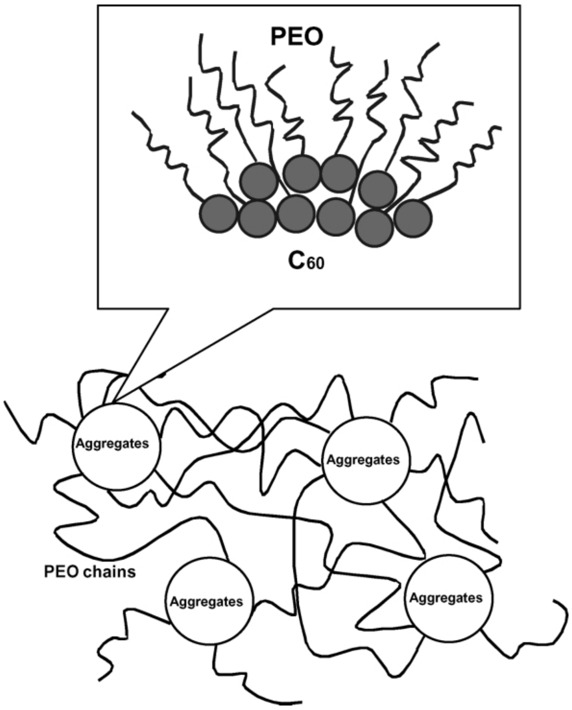


Fig. 3. TEM of aggregates prepared from the THF solutions for (a) FPEO, (b) FPEO10F, and (c) FPEO20F.

Fig. 5 shows that FPEOF films become fully swollen in water in about 1 min. The water uptake is about seven times for FPEO10F and about nine times for FPEO20F. The lower extent of swelling of FPEO10F than that of FPEO20F is consistent with the fact that a highly crosslinked material swells to a lesser extent as compared to a lightly crosslinked material. Furthermore, the swollen FPEOF films show shape recovery ability. The swollen films recover completely to their original shapes and sizes without loss in mechanical performance after being dried at 55 °C for 1 h. Fig. 6 demonstrates the swelling and recovering process of FPEO10F. Irregularly drawn FPEOF films recover



Scheme 1. Schematic diagram of FPEOF.

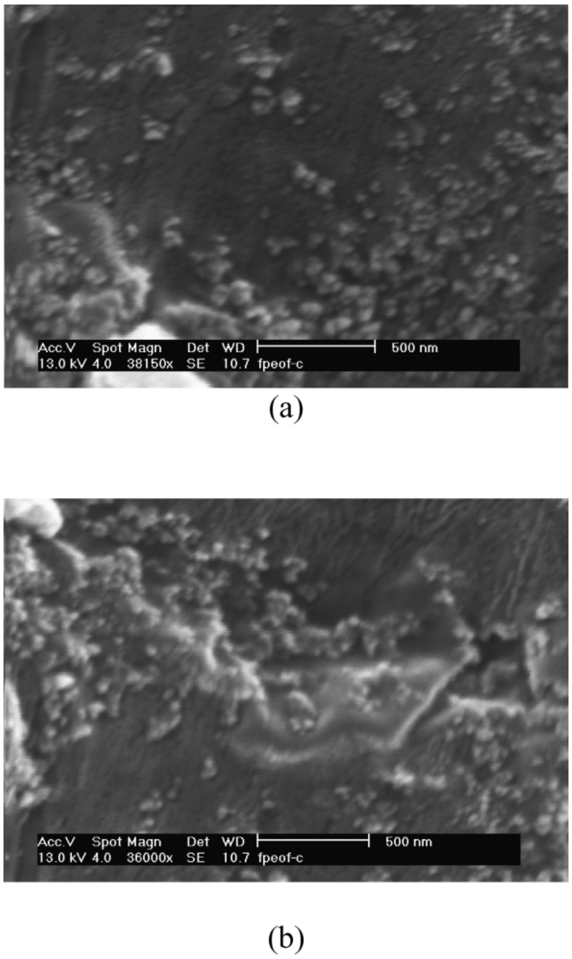


Fig. 4. SEM of fracture surfaces of (a) FPEO10F and (b) FPEO20F.

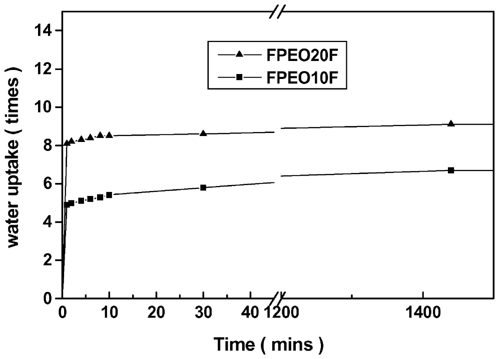


Fig. 5. Water uptake curves for FPEOFs at room temperature.

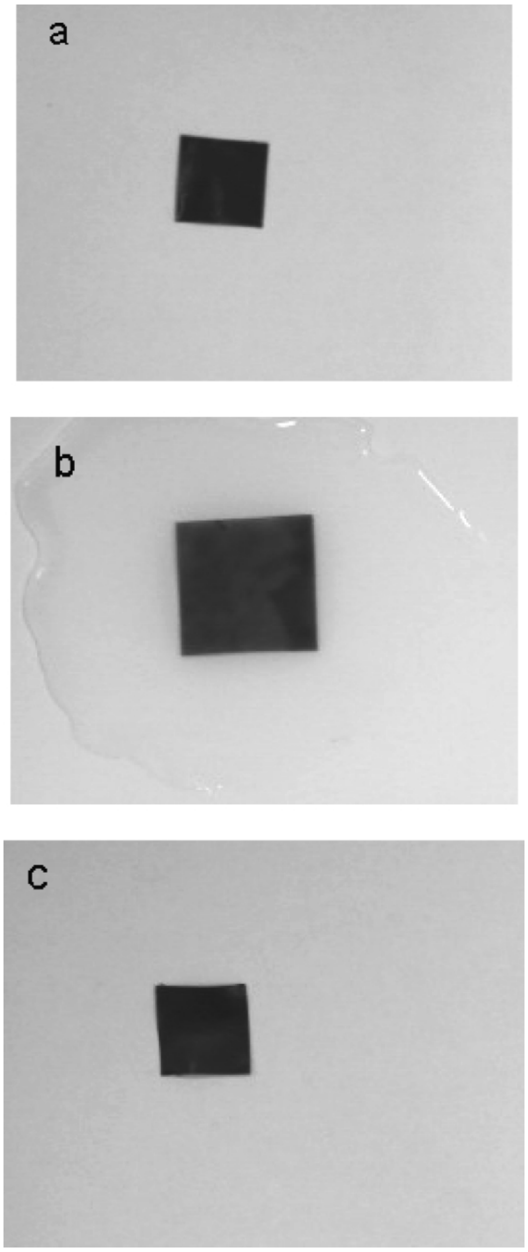


Fig. 6. Photographs for (a) the original FPEO10F film, (b) the water-swollen FPEO10F film, and (c) the recovered FPEO10F film after being dried.

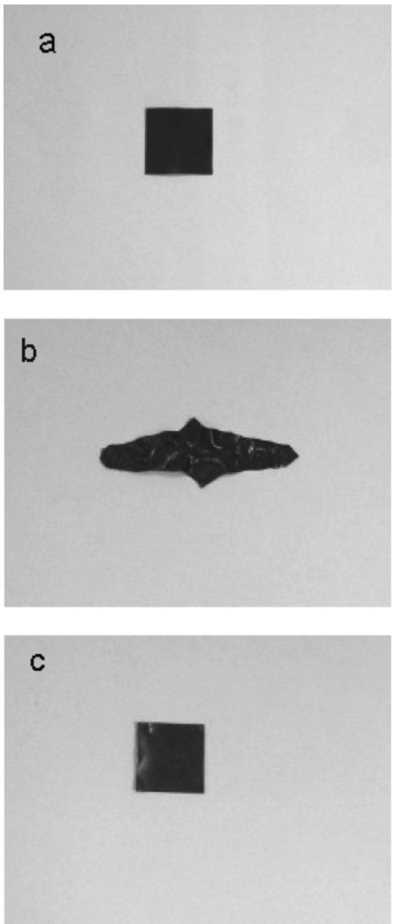


Fig. 7. Photographs for (a) the original FPEO10F film, (b) the irregularly drawn FPEO10F film, and (c) the recovered FPEO10F film after being heated.

completely to their original shapes and sizes after being heated at 55 °C for about 10 min (Fig. 7).

## 4. Conclusions

The two double-$C_{60}$-end-capped PEOs possess good mechanical properties. For example, the fracture toughness is 2700 times more than that of PEO300. FPEOFs can sustain a very large (elongation $>640\%$) plastic deformation prior to fracture. The good mechanical behavior of FPEOFs arises from the aggregation of $C_{60}$ moieties to form a network-like structure. It is envisaged that other double-$C_{60}$-end-capped polymers may also possess good mechanical properties. The mechanical properties of thermoplastic elastomers based on 'S-B-S' type or multiblock hard/soft segmental copolymers deteriorate when the hard domains soften at high temperatures. Although we were unable to conduct tensile tests at high temperatures, we envisage that the mechanical properties of the two FPEOF samples are not likely to deteriorate significantly, at least at moderately high temperatures, since $C_{60}$ molecules are not softened. Furthermore, in view of the biomedical and biotechnological properties of $C_{60}$ and PEO, such double-$C_{60}$-end-capped PEO may find possible biomedical/biotechnological applications.

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