

Mechanical Properties of an Ultrahigh-Molecular-Weight Polyethylene/Polypropylene Blend Containing Poly(ethylene glycol) Additives

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ABSTRACT: It was recently reported that poly(ethylene glycol) (PEG) additives (PEG and its hybrids with inorganic fillers) could significantly improve the processability of ultrahigh-molecular-weight polyethylene (UPE)/polypropylene (PP) blends. The influence of PEG additives on the mechanical properties of UPE/PP blends was investigated in this study. With the addition of small amounts of PEG additives, the tensile properties of UPE/PP blends were little affected, whereas the loss in impact strength

was relatively noticeable; however, the toughness was maintained at a high level. Stress–relaxation and stress–strain tests showed that the PEG additives acted mainly in the amorphous phase, reducing the entanglement density of the blends. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3148–3153, 2008

Key words: blends; mechanical properties; polyethylene (PE)

INTRODUCTION

Ultrahigh-molecular-weight polyethylene (UPE) can be used in many fields because of properties such as excellent toughness, high abrasion resistance, low friction, good chemical resistance, and biocompatibility. Among these, the mechanical properties are crucial for its application as a load-bearing material. For instance, the stiffness, toughness, and strength of UPE composites should reach the corresponding levels of natural bone when they are used as bone substitutes.¹ Some correlations between the tensile properties and the wear rate have also been observed.² The mechanical properties have been found to depend on several factors, including the molecular weight and its distribution^{3,4} and the composition and morphology of the blend or composite.^{5,6} The processing methods^{7,8} and parameters^{9–11} are also important for the mechanical properties of UPE products.

It is well known that the processability of UPE is very poor because of its extremely high viscosity. The melting fluidity of UPE must be enhanced to mold it with conventional thermoplastic processing equipment. There are several methods for improving the flowability of UPE, which include blending with conventional polyolefins^{12–15} such as high-density polyethylene, low-density polyethylene, and polypropylene (PP) at ratios of the same order of magnitude and incorporating small quantities of processing aids^{16,17} such as polyethylene wax, stearate, fluoroelastomers, and liquid-crystal polymers. A problem often arises simultaneously: small quantities of conventional polyolefins do not improve the flowability of UPE sufficiently to make it amenable to conventional melt processing, whereas the mechanical and tribological properties of UPE decrease sharply if it is blended with effective amounts. In the case of processing aids, there is usually a small saturation level for them, although they do behave effectively in reducing the melt viscosity. Therefore, proper amounts of conventional polyolefins together with small amounts of processing aids for lubrication have been adopted in some investigations, and this seems to be a promising way to improve the processability of UPE.

In previous studies of our group,^{15,18,19} the processability of UPE was effectively improved through blending with 10–20 wt % PP, and the mechanical and tribological properties of the blends were as

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TABLE I
Mechanical Properties of the UPE/PP (80/20) Blends with PEG-Containing Additives

	Young's modulus (MPa)	Yield strength (MPa)	Tensile strength (MPa)	Elongation at break (%)	Izod notched impact strength (kJ/m ²)
UPE	490.5	19.94	38.77	386.0	Unbroken
UPE/PP (80/20)	662.07	23.43	25.92	329.80	103.9
UPE/PP/PEG (80/20/1)	703.48	23.66	26.17	304.27	99.9
UPE/PP/PEG (80/20/2)	681.97	23.68	26.92	332.84	91.7
UPE/PP/PPA1 (80/20/3)	665.19	23.50	25.05	338.53	90.0
UPE/PP/PPA1 (80/20/6)	624.75	22.52	24.74	308.5	77.3
UPE/PP/PPA2-2500 (80/20/3)	705.08	23.19	27.40	351.27	83.4
UPE/PP/PPA2-2500 (80/20/6)	622.66	22.22	26.53	336.97	67.8

good as or better than those of pure UPE. With the addition of a small amount of poly(ethylene glycol) (PEG),²⁰ the melt viscosity of the blends was further reduced significantly. The investigation of the mechanism showed that the viscosity reduction caused by the addition of PEG additives was related to the disentanglement and internal lubrication in the interior of the melt.^{20,21} The objective of this article is to study the effects of PEG additives on the mechanical properties of UPE/PP blends.

EXPERIMENTAL

Materials and blend preparation

UPE (molecular weight = 2.5×10^6 ; M-II, Beijing No. 2 Auxiliary Agent Factory, Beijing, China), PP melt flow rate (MFR) = 2.0 g/10 min; F401, Lanzhou Chemical Industry Factory, Lanzhou, China), and PEG (molecular weight = 6000; Aoke Chemical Limited Co., Liaoyang, China) were used in this study. The inorganic fillers were diatomite (particle size $\approx 5 \mu\text{m}$; Nahui Desiccating Agent Co., Shanghai, China) and three glass beads (5000, 2500, and 800 mesh; Shanghai Zhengmei Sub-Nanoscale Material Co., Ltd., Shanghai, China). PEG/diatomite and PEG/glass bead hybrids were first blended for 10 min in a two-roll mill and then pulverized. UPE/PP and UPE/PP/PEG blends were prepared with a single-screw extruder (diameter = 25 mm, length/diameter = 25) through a circular die (diameter = 3 mm, length/diameter = 8). The barrel temperatures were 100, 190, and 230°C for the back, middle, and front sections, respectively, and the die temperature was 210°C. The screw rotation speed was 30 rpm.

To prepare the specimens for mechanical tests, UPE powder and the extrudates of UPE/PP blends were first compression-molded at 195°C and 10 MPa for 10 min to get 1- and 4-mm-thick plates. Then, samples for tests were cut from the plates.

Evaluation of the mechanical properties

Stress–relaxation and stress–strain tests were conducted on an Instron (Instron Corp., Canton, MA)

4302 tensile tester. For the stress–relaxation measurements, samples were preconditioned for 2 h at 25°C and then loaded to a 8% strain at a rate of 100 mm/min. Decaying of the stress was monitored over a period of 20 min. Stress–strain curves and the tensile strength were measured according to GB 1040-79 with a crosshead speed of 100 mm/min.

The Izod notched impact strength was measured on an XJ-40A impact tester (Chengde Precision Testing Machine Co., Ltd., Chengde, China) according to GB 1843-80.

RESULTS AND DISCUSSION

Mechanical properties of the UPE/PP blends containing PEG and its hybrids

Table I shows the mechanical properties of UPE/PP blends containing PEG and its hybrids. Blending with 20 phr PP improved the Young's modulus and yield strength of UPE. This is explainable because the Young's modulus and yield strength of PP are much higher than those of UPE. The tensile properties of the UPE/PP blends at large deformation, namely, the break strength and elongation at break, decreased to some extent. This probably resulted from the remarked disentanglement effect of PP on the amorphous phase of UPE.^{21,22} With decreasing entanglement density, the elastomeric characteristics of the blends were reduced, and less strain hardening could be attained; this resulted in a lower break strength and elongation at break.

With the addition of a small amount of PEG (1–2 phr), there were few changes in the tensile properties of the blends. However, a relatively noticeable reduction in the Izod notched impact strength occurred in the blends. It seems that PEG/diatomite (PPA1) and PEG/glass bead (PPA2) hybrids had effects on the mechanical properties of the blends similar to the effects of PEG, except that more serious deterioration of the impact strength of the blends was caused by the hybrids than pure PEG. This was more evident when 2 phr PEG was involved; the Izod notched impact strength of the blend containing 2 phr PEG was still as high as

TABLE II
Effect of the Size of the Glass Bead on the Mechanical Properties of the UPE/PP (80/20) Blends with PPA2

	Young's modulus (MPa)	Yield strength (MPa)	Tensile strength (MPa)	Elongation at break (%)	Izod notched impact strength (kJ/m ²)
UPE/PP/PPA2-800 (80/20/3)	709.86	23.97	25.96	307.00	58.7
UPE/PP/PPA2-800 (80/20/6)	650.31	22.91	25.16	285.20	31.3
UPE/PP/PPA2-2500 (80/20/3)	705.08	23.19	27.40	351.27	83.4
UPE/PP/PPA2-2500 (80/20/6)	622.66	22.22	26.53	336.97	67.8
UPE/PP/PPA2-5000 (80/20/3)	784.12	24.30	28.03	358.78	95.8
UPE/PP/PPA2-5000 (80/20/6)	690.45	23.17	26.97	340.15	80.2

90 kJ/m², and the values for blends containing 6 phr PPA1 or 6 phr PPA2 (they consisted of 2 phr PEG and 4 phr inorganic filler) were sharply reduced to 77.3 and 67.8 kJ/m², respectively, yet the toughness was maintained at a good level with these values from a practical point of view. The difference between the hybrids and PEG may come from the inorganic filler. A weaker interface was produced in the blends containing hybrids, and this led to a lower impact strength. The impact strength of the blends containing hybrids was influenced by the size of the filler. For blends containing PPA2, the impact strength increased with the decreasing size of the glass beads, as shown in Table II.

The phenomenon in which the addition of small amounts of PEG and its hybrids made a more pronounced impact on the impact strength of the material may be interpreted as follows: these additives acted mainly in the amorphous phase, and the impact strength was controlled not only by the crystalline structure but also by the amorphous structure. Further study on the action of PEG is presented in the following section. Considering that the influence of PP on the mechanical properties of UPE had been studied in the previous work of our group¹⁸ and that the UPE matrix was most crucial to the mechanical properties of UPE/PP (80/20) blends, we

emphasized the effect of PEG on the mechanical behavior of UPE in this investigation.

Effects of PEG on the stress relaxation of UPE

Stress–relaxation curves of UPE and UPE/PEG blends are shown in Figure 1. For all samples, the stress decayed with time, showing two trends. In the beginning, the decay was very fast, but it gradually slowed with time. The data for the initial and residual stresses are listed in Table III. With the addition of PEG, both the initial stress and the residual stress at 1200 s decreased. When more PEG was added, the reduction in the initial stress and residual stress was greater. These results indicated that the mechanical properties of UPE were impaired to some extent by the incorporation of PEG.

According to Djokovic and coworkers,^{23,24} a two-process model, obtained in terms of two Maxwell elements (a dashpot and a spring in a line) connected in parallel, can be used to describe the stress–relaxation in semicrystalline polymers. By solving a differential equation of the system, they found the following equation for stress relaxation:

$$\sigma(t) = \varepsilon E_1(1 + t)^{-E_1/\eta_1} + \varepsilon E_2(1 + t)^{-E_2/\eta_2} \quad (1)$$

where σ is the stress, ε is the strain, t is the time, E_1 and E_2 are the Young's moduli, and η_1 and η_2 are the viscosity coefficients. In the expression, it is assumed that the stress relaxation can be well explained by two thermally activated processes acting in parallel, each represented by one Maxwell element. The first process is associated with the crystal

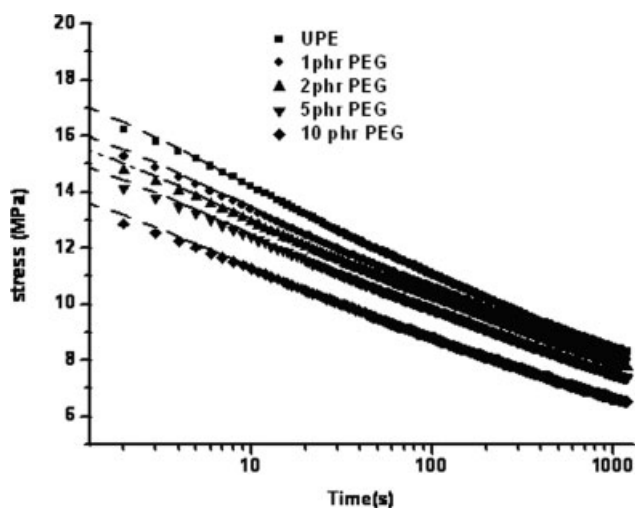


Figure 1 Stress–relaxation curves for UPE/PEG blends.

TABLE III
Stress–Relaxation Data of the UPE/PEG Blends

Sample	Initial stress at 0 s (MPa)	Residual stress at 20 min (MPa)
UPE	17.74	8.27
1 phr PEG	16.72	7.99
2 phr PEG	16.18	7.60
5 phr PEG	15.52	7.35
10 phr PEG	14.13	6.52

Strain = 8%; temperature = 25°C.

TABLE IV
Results of the Nonlinear Fit of Stress–Relaxation Curves for the UPE/PEG Blends

	UPE	1 phr PEG	2 phr PEG	5 phr PEG	10 phr PEG
E_1 (MPa)	212.42	205.34	199.21	193.35	178.58
η_1 (MPa s)	1845.55	1872.21	1816.31	1733.14	1525.42
E_2 (MPa)	21.62	13.65	12.71	10.66	8.78
η_2 (MPa s)	187.84	124.41	115.88	95.59	74.98

fraction of the polyethylene sample, and the second is associated with the amorphous fraction of the polyethylene sample.

The influence of PEG on the viscoelastic properties of each fraction can be found when the experimental data in Figure 1 are fitted to eq. (1). Fits are shown by a dashed line in Figure 1. From the fitting procedure, viscosities η_1 and η_2 and moduli E_1 and E_2 of the crystal and amorphous fractions were obtained, and they are summarized in Table IV. η_1 and E_1 were at least 1 order of magnitude larger than η_2 and E_2 for all samples. That was why process 1 was associated with the crystal fraction and process 2 was associated with the amorphous fraction.

Figure 2 shows the percentage reduction in η_1 and E_1 and in η_2 and E_2 for the blends. The addition of PEG reduced all four parameters (except for the blend containing 1 phr PEG). The reduction amplitude increased with an increasing amount of PEG. Although all four parameters varied with the PEG content in a similar decreasing trend, the percentage reduction in η_2 and E_2 was much higher than that in η_1 and E_1 . In the case of 1 phr PEG, the percentage reduction in E_1 was only about 3%, whereas those values for η_2 and E_2 reached 37 and 34%, respectively. When the PEG content was increased to 5 phr, the percentage reduction in η_1 and E_1 and in η_2 and E_2 rose up to 6 and 9% and 49 and 51%, respectively. There was still much reduction in η_2 and E_2 . These results suggested that PEG was mainly located in the amorphous fraction of the UPE matrix.

To clarify the nature of the stress–relaxation process and to eliminate the confusion caused by the changes in the initial stress for different blends, the data have been replotted in Figure 3 in a reported normalized manner.^{25,26} The normalized stress was defined as S_t/S_0 , where S_0 is the stress at time zero when the desired strain is reached and S_t is the stress after time t . Figure 3 shows that the major effect of PEG was on the slow relaxation region in a long time range, especially more than 100 s. The curves for UPE and the blends almost overlapped one another in the fast relaxation region. With the addition of a small amount of PEG, the stress–relaxation rate in a long time range slowed down. It was assumed that in an early stage stress relaxed through

the crystal fraction, and the relaxation in the long time range was controlled by the viscoelastic network in the amorphous fraction.²⁵ The relaxation behavior of the UPE/PEG blends also supported the idea that PEG had a minor effect on the crystalline fraction and its effect on the amorphous fraction was major. It has been found in our work²¹ that PEG in UPE/PEG and UPE/PP/PEG blends can lead to the disentanglement of UPE. The reduction of the entanglement density in a UPE/PEG blend will retard the stress distribution in the material, leading to a decrease in the relaxation rate.

Effects of PEG on the stress–strain behavior of UPE

The stress–strain curves of UPE and UPE/PEG blends are shown in Figure 4, and the tensile properties are summarized in Table V. Unlike other polyethylenes, UPE showed early onset of strain harden-

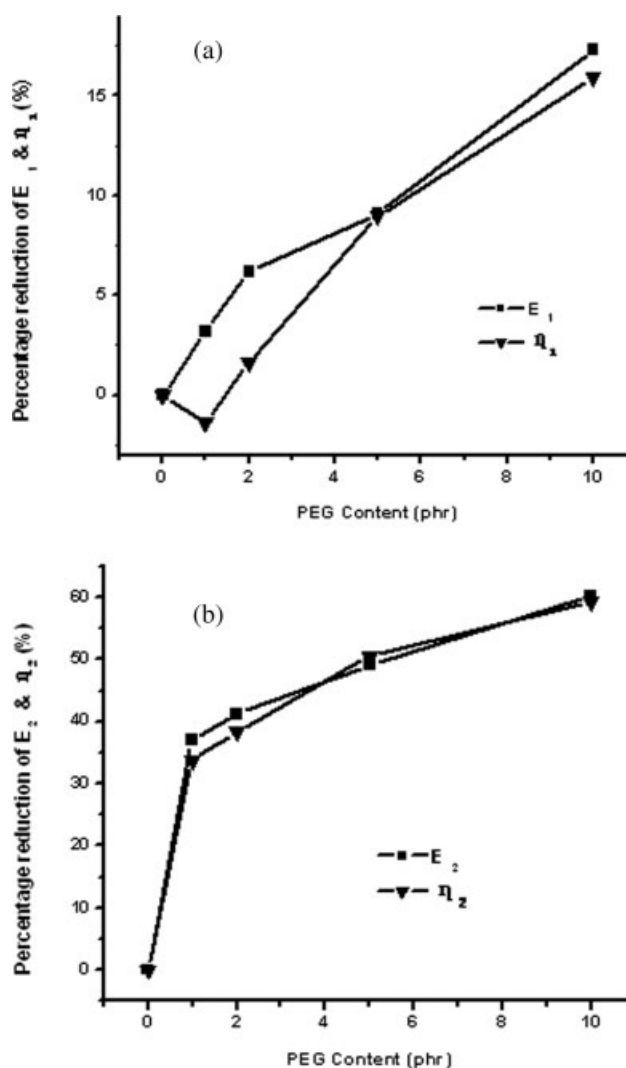


Figure 2 Percentage reduction of (a) E_1 and η_1 and (b) E_2 and η_2 .

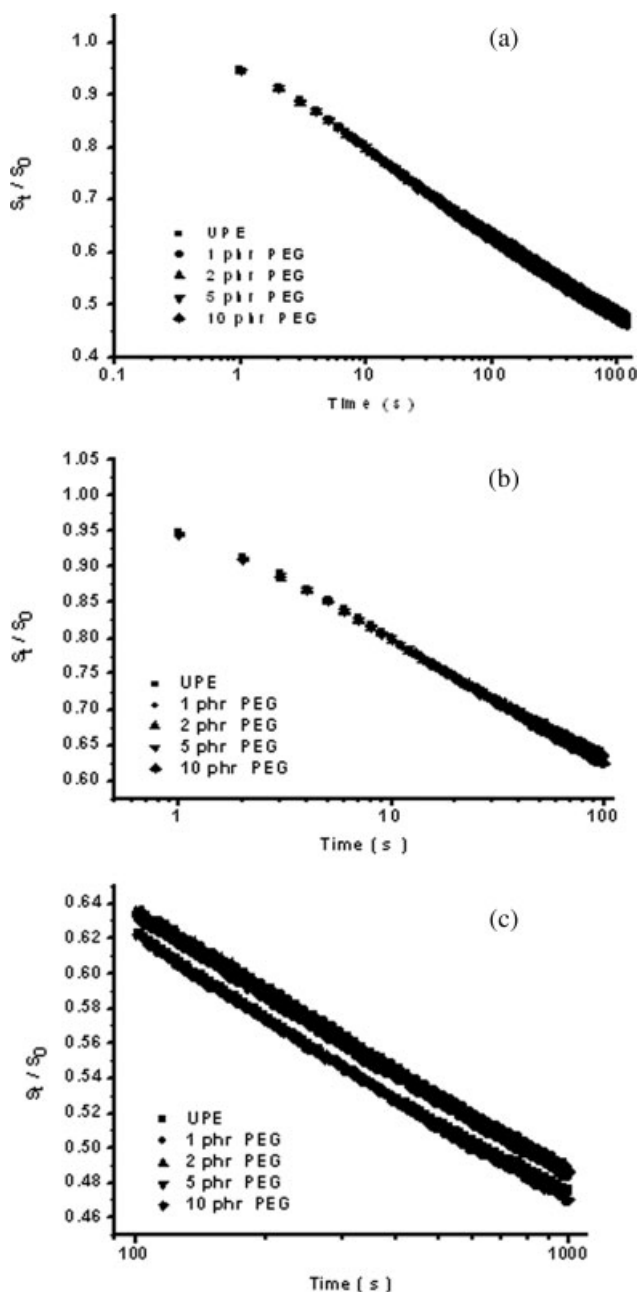


Figure 3 (a) Stress–relaxation curves for UPE/PEG blends in terms of S_t/S_0 versus time, (b) magnification of panel a from 1 to 100 s, and (c) magnification of panel a from 100 to 1000 s.

ing after the yield without an apparent yield drop, which is a characteristic found in elastomeric materials.²⁷

The UPE/PEG blends containing small amounts of PEG (≤ 5 phr) almost followed the same path in stress–strain behavior as UPE. The decreases of the Young's modulus and yield strength caused by blending with a small amount of PEG were very small, whereas those for the ultimate strength and elongation were more pronounced. This also meant that PEG mainly acted in the amorphous fraction. It

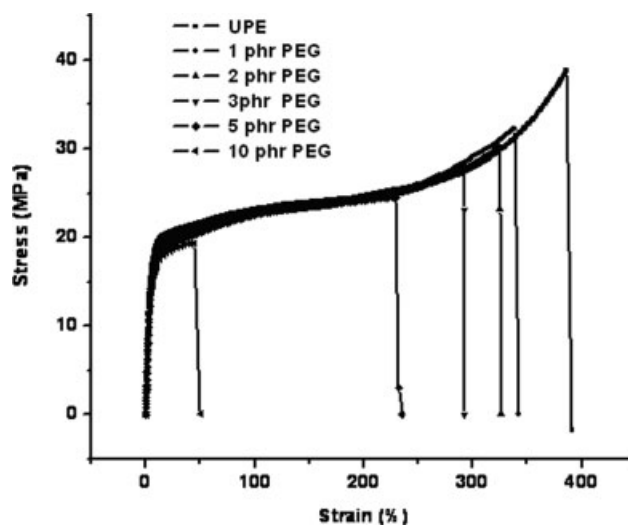


Figure 4 Stress–strain curves of UPE/PEG blends.

is usually thought that the small-strain tensile properties of a polymer are controlled by the structure of the crystalline fraction, such as the crystallinity and lamellar thickness, and the tensile properties at large deformations are related to the structure in the amorphous and crystalline regions.^{28,29} With the incorporation of PEG, the entanglement density of UPE would be reduced. Correspondingly, the break strength would be weakened, and the elongation at break would be reduced.

On the basis of these results, it can be reasonably deduced that PEG additives are mainly located and play an important role in the amorphous fraction of the UPE matrix, and their influence on the mechanical properties of the blends can be expected. However, other direct proofs from a morphological study would make this more convincing. That is the aim of our future work. In addition, the action of PP in UPE/PEG blends will be considered.

CONCLUSIONS

The effects of PEG and its hybrids, which were used as processing additives, on the mechanical properties of UPE/PP blends were investigated. With the addi-

TABLE V
Tensile Properties of the UPE/PEG Blends

	Young's modulus (MPa)	Yield strength (MPa)	Tensile strength (MPa)	Elongation at break (%)
UPE	490.5	19.9	38.8	386.0
1 phr PEG	411.0	19.7	32.3	338.9
2 phr PEG	436.6	19.5	30.2	324.7
3 phr PEG	535.8	19.7	28.0	292.3
5 phr PEG	456.2	19.2	24.5	229.8
10 phr PEG	431.1	16.6	19.3	45.3

tion of small amounts of PEG and its hybrids, the tensile properties of UPE/PP blends were little affected, whereas the loss in impact strength was relatively noticeable, yet the toughness was maintained at a high level.

The stress–relaxation data of UPE containing PEG additives were analyzed through a two-process model and normalization treatment separately. The results suggested that PEG mainly acted in the amorphous fraction of the UPE matrix, reducing the entanglement density of the blend. A similar conclusion was also drawn from stress–strain tests of UPE/PEG blends.

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