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Structure and mechanical properties of UHMWPE/EPT blends and their vulcanizates

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In order to improve the mechanical properties of EPT rubber with ultra-high molecular weight polyethylene (UHMWPE), a new method of two-step mixing has been developed. First, the blend films of UHMWPE and EPT were prepared by casting the mixture of both polymer solutions. Second, the thermal and mechanical mixing of the EPT rubber with the blend film was carried out on a roll mill so that the rubber should contain 10 phr (parts per hundred resin) of UHMWPE. Then, it was vulcanized. Some structure and properties of these blend films and the vulcanized rubber have been studied. The blend films did not give spherulitic morphology, but gave a lot of small crystallites of UHMWPE. The partial miscible phase was suggested to be formed in the blend film. This phase seemed to play an important role in the second step of mixing, in which UHMWPE fibres were formed to result in the reinforcement of the EPT rubber. Copyright © 1996 Elsevier Science Ltd.

INTRODUCTION

Polymer blends and alloys have been widely studied, especially the preparation method, statistical thermodynamic approach on compatibility, mechanical properties, and the formation of structures in various blend or alloy systems, and summarized in several books[1–4]. Nowadays it is one of the most important subjects from the viewpoint of material design for polymers, which is directly related to an actual application in the polymer industry. Polymer blends in elastomer systems are of interest and much attention has been paid recently to the high performance of elastomers, including the reinforcement of rubber-based ones on blending materials such as inorganic and organic compounds, other rubbers and short fibres of semicrystalline polymers[5]. Among these, the short-fibre reinforced rubber has been considered to be one of the most important methods to improve the mechanical property of elastomers[6,7].

The car industry requires reduction in the weight of cars' tyres by a few 10% without reduction of performance by the end of this century. This will be achieved by the reinforcement of rubber which requires material design such as the control of phase structures and superstructures, and the improvement of affinity of interfaces.

Recently, the mechanical properties, morphology and crystallization behaviour have been investigated in ethylene–propylene–diene terpolymer (EPT) and ethylene–propylene copolymer (EPR) blended with

crystalline polyolefins, such as high-density polyethylene (HDPE), low-density polyethylene (LDPE) and isotactic polypropylene (iPP)[8–14].

Ultra-high molecular weight polyethylene (UHMWPE) is known to have a special characteristic of ultra-high drawability by gel-spinning due to the existence of many molecular chain entanglements, resulting in a limited extended structure. This gives properties such as ultra-high strength and modulus[15,16]. Therefore, EPT rubber could be expected to experience improved mechanical properties if the miscibility of EPT and UHMWPE could be attained to some extent in a specific way.

In this work, we first focus on films of UHMWPE/EPT blends prepared from a mixture of polymer solutions. The effect of the composition on the morphology, and the thermal and mechanical properties has been studied. Second, the mechanical properties of EPT rubbers vulcanized after blending with the UHMWPE/EPT films prepared here are examined.

EXPERIMENTAL

Material

Ultra-high molecular weight polyethylene (UHMWPE: Hizex Million 240M, $M_v = 2 \times 10^6$) was kindly supplied by Mitsui Petroleum Chemical Co., Tokyo. Ethylene–propylene–diene terpolymer (EPT: Esprene 505, 52 wt% ethylene, 48 wt% propylene component, a small amount of ethylidene norbornene) was purchased from Sumitomo Kagaku Kogyo Ltd, Tokyo.

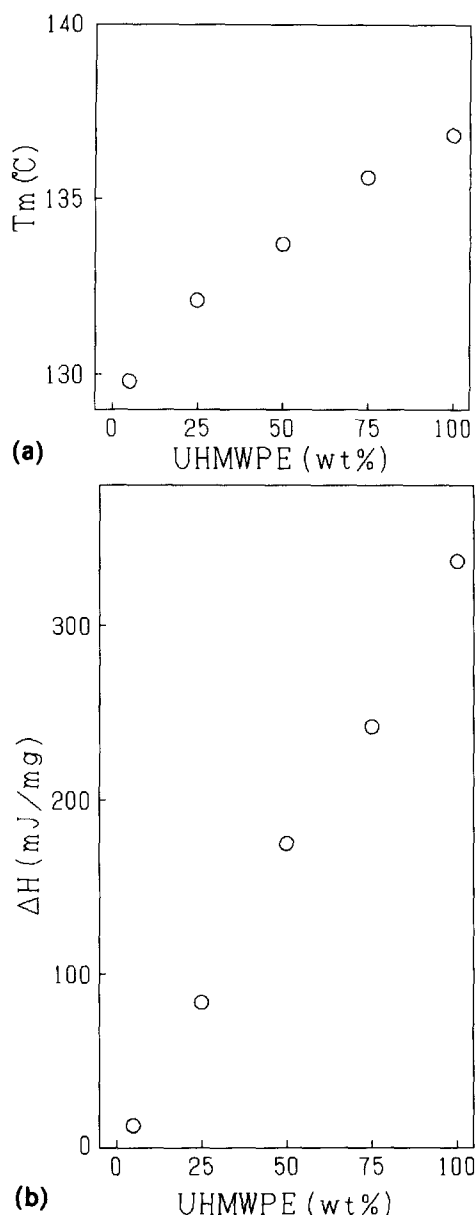---
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Figure 1 Variation of (a) melting temperature and (b) heat of fusion of UHMWPE/EPT blends prepared from the solutions as a function of UHMWPE content

Figure 2 Stress–strain curves of UHMWPE/EPT blend films prepared from the solution, with the weight ratio of (a) (100:0), (b) (75:25), (c) (50:50) and (d) (25:75), measured at 25°C

Blend film preparation

The blend films of UHMWPE and EPT with various weight ratios were prepared through gelation from 1 wt% solution in hot decalin according to the method of Mitsuhashi and Iguchi[17]. First both polymers were swollen in a small amount of decalin including a little anti-oxidizing agent (di-*t*-butyl-*p*-cresol) in a flask at room temperature for about 12 h. The rest of the decalin was warmed at 170°C and then poured into the flask in an oil bath at 150°C so that the polymers were dissolved, and then stirred for 10 min. The solution was moved to a glass dish at 100°C, cast for 90 min, immersed in methanol at room temperature for 12 h and then dried at atmospheric pressure overnight to obtain a blend film with a thickness of about 0.1 mm.

Vulcanized EPT rubber preparation
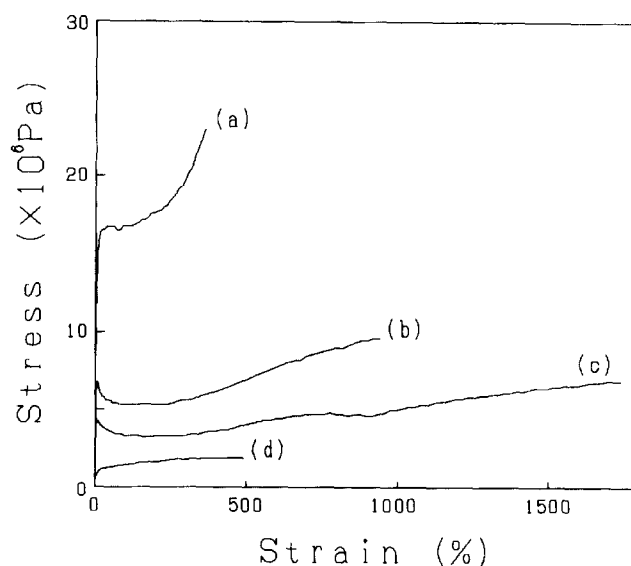
The EPT rubber was mixed with the UHMWPE/EPT

(50:50) blend film or the UHMWPE powder so as to contain 10 phr (parts per hundred resin) of UHMWPE on a roll mill at 40 rpm at 140°C for 10 min. Then the vulcanizer, consisting of 3 phr of zinc oxide, 2 phr each of stearic acid and sulfur, and 1.6 phr of facilitating agent of TBBS, was added and were mixed at 40 rpm at 110°C for 4 min to produce a sheet about 1 mm thick. The sheet was vulcanized at 160°C for 20 min.

Measurements

D.s.c. measurement was performed on a Seiko Denshi Kogyo DSC 200 differential scanning calorimeter at a constant heating rate of 10 K min^{-1}.

Tensile testing was carried out on a Shimadzu IM 100 at 10 mm min^{-1} at 25°C for UHMWPE/EPT blend films 0.3 cm wide and 2 cm long.

Wide-angle X-ray diffraction photographs were obtained with a Toshiba Model XC100H, utilizing nickel-filtered CuK$_\alpha$ radiation.

RESULTS AND DISCUSSION

Figure 1 shows the variations of melting temperature and heat of fusion of the blend films. The pure UHMWPE film (100:0) gives a melting temperature lower than that of the original UHMWPE powder around 143°C. It implies that the solution crystallization should produce smaller crystallites than the melt crystallization. In fact, spherulites were not observed in the pure UHMWPE film (100:0) or other blend films unless they were melted and recrystallized.

A relatively large and monotonous decrease in the melting temperature of UHMWPE can be seen with decreasing UHMWPE content. It seems that the amorphous EPT molecules may prevent the crystal lamellae of UHMWPE from growing, as observed in other blend systems[18,19], although there is also a small possibility of compatibility of both polymers[20,21]. The heat of fusion changes linearly with the UHMWPE content, which means that the EPT component does not affect the crystallinity of UHMWPE. Accordingly, a lot

of small crystallites should be formed in the blend films, which was realized in a polarized optical microscopic observation where many scattered retardations with brightness (or optical anisotropy) appeared under cross-polarizing conditions.

The glass transition temperature of the blend films, judging from the baseline gap of d.s.c. curves, may shift slightly to higher temperatures with a small deviation as the EPT content decreases. This may support partial miscibility between EPT and UHMWPE molecules in the amorphous phase.

Stress–strain curves of blend films are shown in *Figure 2*. The yield stress and the breaking strength decrease as the EPT content increases. The Young's modulus, estimated from the initial slope in the stress–strain curve, is plotted against the UHMWPE content in *Figure 3*. It changes monotonously with content. The variation of breaking strain with increase of the EPT content should be noted; it varied from 353% for the
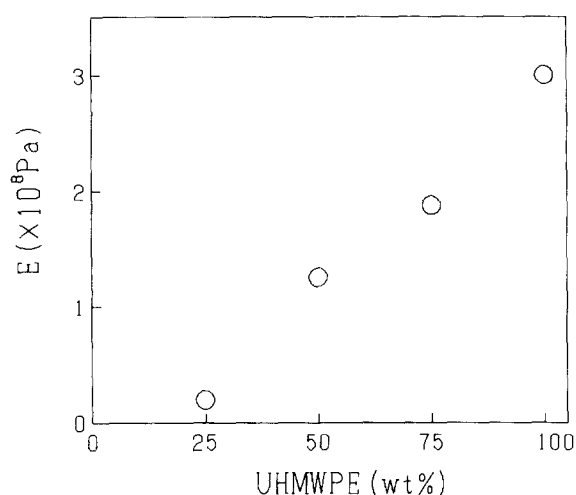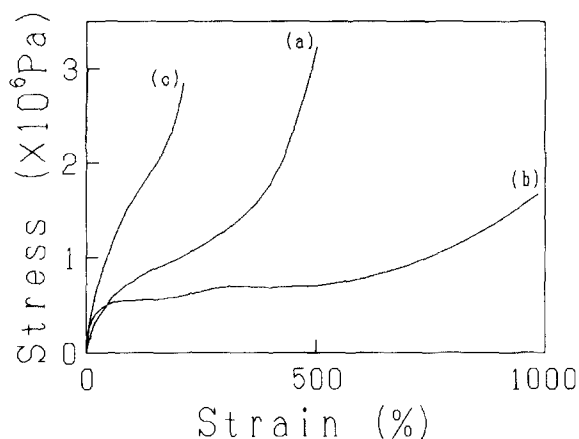
(100:0) pure UHMWPE film to 490% for the (25:75) blend film through a maximum of more than 1750% for the (50:50) blend film. The (5:95) blend film broke too readily to measure the stress–strain curve. The breaking strain of the (50:50) blend film was very large and several times as much as that of the pure UHMWPE film, though the pure EPT film (0:100) behaved like a clay, tearing readily. This implies that there exists an intermolecular interaction between the components, while the modulus simply varies with the UHMWPE content. In other words, the molecules of two components should be partially in a miscible state in the amorphous phase. The large breaking strain of the (50:50) blend film must be due to the adequately loose chain entanglements between UHMWPE and EPT molecules.

Figure 4 shows WAXD photographs of the drawn samples. The pure UHMWPE film (100:0), drawn four times, gives a well oriented c-axis pattern. UHMWPE molecules are directly subjected to the tensile stress effective to the orientation of crystallites in this film. On the other hand, the UHMWPE/EPT (50:50) blend film, drawn 14 times, indicates a low orientation of UHMWPE crystallites and, besides, it seems that most of the crystallites remain in a random orientation despite the extremely large draw ratio. It suggests that EPT molecules should act like a plasticizer in the blend film to make a well miscible state of the two components in the amorphous phase which does not contribute to the orientation of UHMWPE crystallites on drawing.
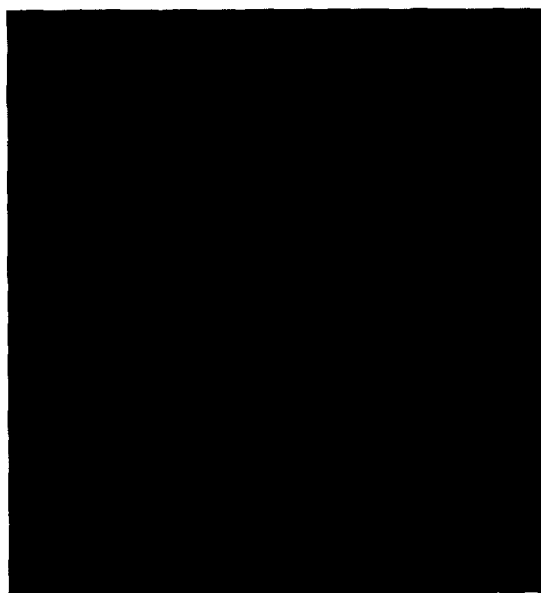
The effect of the (50:50) blend film on the strength of the EPT rubber is discussed when the EPT rubber is mixed and rolled with the UHMWPE/EPT (50:50) blend film before vulcanization. *Figure 5* shows the stress–strain curves of vulcanized EPT rubbers, in which remarkable effects are seen. It gives higher strength at low strains as well as higher Young's modulus, i.e. improvement of mechanical properties in EPT rubber. This must be caused by the 10 phr UHMWPE molecules in the EPT rubber. However, the UHMWPE powder (or the original UHMWPE sample) indicated the opposite

Figure 3 Variation of Young's modulus of UHMWPE/EPT blend films, estimated from the initial slope in the stress–strain curve, as a function of UHMWPE content

Figure 4 WAXD photographs of (a) four times drawn UHMWPE (100:0) film and (b) 14 times drawn UHMWPE/EPT (50:50) blend film

Figure 5 Stress–strain curves of vulcanized EPT rubbers: (a) pure EPT, (b) and (c) EPT mixed with UHMWPE powder or UHMWPE/EPT (50:50) blend film so as to contain 10 phr of UHMWPE before vulcanization

Figure 6 WAXD photograph of UHMWPE fibres taken out of the EPT rubber mixed with UHMWPE/EPT (50:50) blend film before vulcanization

the UHMWPE molecules were sufficiently subjected to the shear force and extended enough to form fibres during mixing, resulting in the reinforcing effect.

The fibre, long enough, and $10-20\,\mu$m thick without a fine circular cross-section, could be taken out of the mixed rubber before vulcanization by dissolving the EPT rubber component with decalin at room temperature. A WAXD photograph of the UHMWPE fibres is shown in *Figure 6*. The equatorial reflections give slight broadening of the arcs but they indicate the much higher orientation compared with the (50:50) blend film drawn 14 times, shown in *Figure 4b*. It may be due to the shear deformation during roll-mixing at 140°C.

On the contrary, simple mixing of the UHMWPE powder does not have a miscible phase to cause adhesion and as a result the UHMWPE molecules or the powdery particles might slip, not forming a fibre during mixing and the powdery particles remained to act like a lubricant on stretching.

CONCLUSION

In order to improve the mechanical properties of EPT rubber, a new method using the UHMWPE/EPT blend film which is prepared from the polymer solution, has been developed instead of directly using the UHMWPE powder when mixing UHMWPE into the EPT rubber. The UHMWPE/EPT blend film has the following structure and properties. Spherulitic morphology of UHMWPE crystal was not observed but minute crystallites appeared. The melting temperature decreased relatively rapidly with increasing EPT content. The formation of partially miscible phase of both UHMWPE and EPT components was suggested by several observations such as the variation of glass transition temperatures, the breaking strain on the stress–strain behaviour and low orientation of UHMWPE crystallites in the highly drawn blend film. Furthermore, it was supported by the fact that fibres of UHMWPE appeared when the blend film was mixed and rolled with the EPT rubber, while use of the original UHMWPE powder did not produce them. Finally, the remarkable improvement of strength of the EPT rubber was achieved by mixing the UHMWPE/EPT blend film before vulcanization.

effect on mixing; decrease of strength and increase of elongation, which are also seen from *Figure 5*, implying an effect like an internal lubricant. It is, thus, important to utilize not the UHMWPE powder but the blend film for improvement. At the same time, the UHMWPE fibres were found to be formed only when the blend film was used for mixing, but not in the case of using the original UHMWPE powder.

Thus, there must be quite a difference in the behaviour of the UHMWPE molecules when EPT rubber is mixed with either the UHMWPE/EPT blend film or the original UHMWPE powder on the roll mill at 140°C. On mixing the blend film, which may have the three phases: UHMWPE, EPT and the partially miscible phase of the two components, the miscible phase plays an important role in making the UHMWPE molecules adhesive to the EPT molecules of the matrix like a compatibilizer, since the EPT phase is apparently compatible with the EPT matrix rubber. Consequently,

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