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Morphology and mechanical properties of ultrahigh-molecular-weight polyethylene films prepared from solutions in mixtures of diphenyl and diphenylether as co-solvent

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Abstract: In an attempt to check solvent dependence of drawability of ultrahigh-molecular-weight polyethylene films, gels were prepared from diphenyl/diphenylether solution, which is well known as Θ-solvent. The content of diphenyl in the mixed solvent was chosen to be 25 wt%. Rapid gelation occurred when the solution had been cooled down to temperature lower than 147 °C. The gel shrunk drastically with the further decrease of temperature and formed a bulk specimen. The maximum draw ratio was 20 and the corresponding Young's modulus reached 27 GPa. The value of Young's modulus was higher than the maximum value of melt film stretched up to 30 times, but it was much lower than the value of film which was prepared by gelation from decalin solution and was elongated up to 300. Thus, it turned out that the drastic shrinkage in the process of rapid gelation hampers a suitable level of the entanglement mesh that effectively transmits the drawing force.

Key words: Ultrahigh-molecular-weight polyethylene – diphenyl/diphenylether solution – mixed solvent – rapid gelation – Young's modulus

Introduction

The effective drawability of ultrahigh-molecular-weight polyethylene (UHMWPE) is drastically enhanced by using specimens spun or cast from macroscopic gels [1–6]. This method has been developed by Smith and Lemstra [2–4]. According to their concept [4], the maximum achievable draw ratio depended principally on the concentration of the solution from which the gel was made for a sufficient high molecular weight. This phenomenon was attributed to a reduced number of entanglement mesh per molecule in solution-cast/spun polymers in comparison with those obtained from the melt. This concept is based on the assumption that the reduced number of entanglement per molecule in solution remains within the resultant gel films through the quenching and drying processes [4–6].

A question arises as to why only decalin and *p*-xylene have been used as solvents to prepare UHMWPE gels with high drawability. To facilitate understanding this phenomenon, this paper deals with the drawability of UHMWPE films prepared by gelation using diphenyl(DP)/diphenylether(DPE), the content of diphenyl in the mixed solvent being 25 wt% as co-solvent, since the mixed solvent is known as Θ-solvent of polyethylene [7, 8]. It was found that the drawability of films prepared from the DP/DPE solution is much lower than that of the gel films prepared from decalin and *p*-xylene solutions. In this paper, this phenomenon is discussed in terms of morphological aspects.

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Experimental section

The sample used in this experiment was linear polyethylene, Hizex Million 240 M, with viscosity-average molecular weight of 3×10^6 and negligible degree of branching. The linear polyethylene was furnished as a powder by Mitsui Petrochemicals Co. Ltd. Mixtures of diphenyl and diphenylether were used as co-solvent. The content of diphenyl in the mixed solvent is chosen to be 25 wt% as described before. This composition was determined to decrease the melting point of co-solvent as much as possible, since diphenyl and diphenylether exist as solid state at temperatures lower than 69.2 and 28 °C, respectively [8].

A solution containing 0.5 g/100 ml of polyethylene and 0.1 wt% of antioxidant, di-*t*-butyl-*p*-cresol, was prepared by heating the well-blended polymer-solvent mixture at 170 °C for 40 min under nitrogen. Through pre-experiments, 170 °C was found to be the most suitable temperature to prepare the well-blended polymer-solvent mixture. The hot homogenized solution was poured into an aluminum tray at 170 °C and was then cooled slowly to desired temperature. In this process, the solution began to form a gel when the temperature reached 147 °C. A drastic shrinkage occurred with the further decrease of temperature. The gel was picked up from the tray when temperature reached 120 °C. As one method to prepare gel films, the solvent-content within the gel was almost 300%. The gel was pressed at 120 °C under a pressure of 20 MPa to prepare a film and subsequently vacuum-dried to remove residual traces of the co-solvent. This film is designated as DP/DPE I film.

For the other method, the gel was cooled down to room temperature. The gel was immersed in ethanol and subsequently vacuum-dried to remove residual traces of the co-solvent. The gel whitened. The resultant gel was pressed at 120 °C for 30 min under a pressure of 20 MPa. This film is designated as DP/DPE II film. The two kinds of films were elongated manually as 135 °C under nitrogen.

The specimens were characterized by differential scanning calorimetry (DSC), density, x-ray, small-angle light scanning under Hv condition (SALS), scanning electron microscopy (SEM), and load-elongation measurements. These methods have already been described elsewhere [5, 9].

The melt films were prepared by sandwiching polyethylene powder between Teflon sheets at 220 °C for 30 min under a pressure of 5 MPa. The molten sample was cooled down to room temperature slowly. The specimens were cut into strips of length 30 mm and width 5 mm. The strips were elongated manually at 125 or 140 °C under nitrogen.

Results and discussion

For samples with sufficiently high molecular weights, the maximum achievable draw ratio depends principally on the concentration of the solution from which the gel is made. Quantitative theoretical consideration led to the expectation that an optimum level of entanglements can be realized by a proper choice of solution concentration. The viscosity-concentration data for UHMWPE in decalin and *p*-xylene solutions at 135 °C indicated that there exists a critical concentration range where there is an abrupt change. This critical concentration corresponds to the onset of coil overlapping in the solution. This concept was demonstrated for the films prepared from decalin and *p*-xylene solutions [5, 6].

Based on the above concept, the relationship between the reduced-viscosity. η_{sp}/c, and the concentration, c, was obtained. Figure 1 shows the result of a solution of diphenyl/diphenylether (DP/DPE). In spite of small degradation of polymerization at 170 °C, 170 °C was the most suitable temperature for measuring the viscosity in the given concentration range. To pursue the detailed analysis, the measurements were also done for decalin solution at the same temperature, which is shown in the same figure.

In the given concentration, the η_{sp}/c for the solution of mixture was lower than that for decalin, indicating the Θ-solvent of polyethylene. It is seen that the plots of reduced-viscosity against concentration for the DP/DPE solution can be classified approximately into two linear straight regions which intersect around 0.69 g/100 ml. This profile is similar to that observed for decalin solution. As discussed in previous works [5, 6, 9], dry films prepared by gelation from the decalin solution with the critical concentration corresponding to the intersection at 135 °C could be

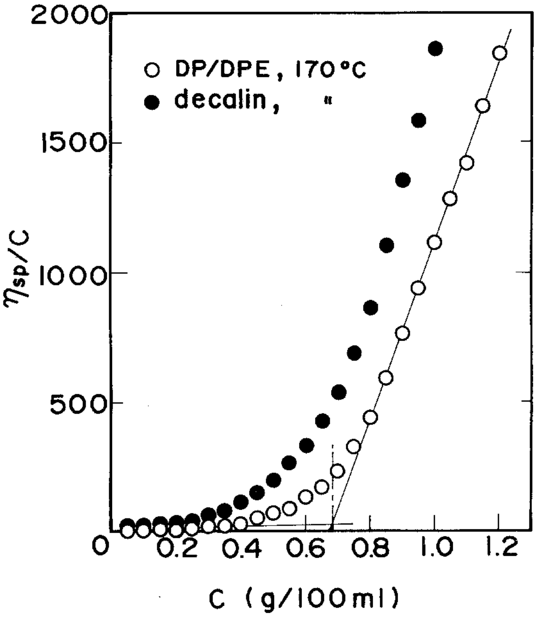

Fig. 1. Relationships between reduced-viscosity η_{sp}/c and concentration c for diphenyl/diphenylether and decalin solutions, respectively

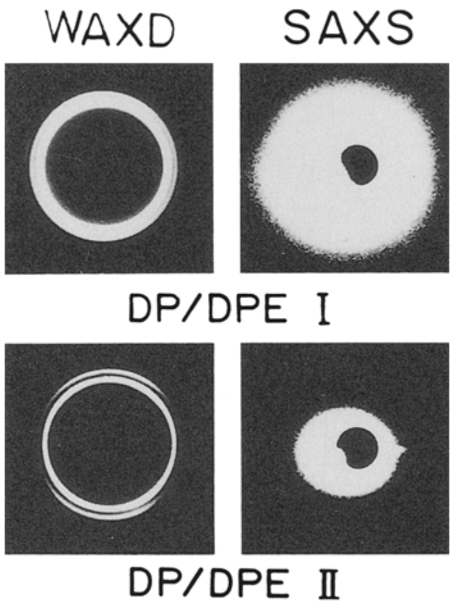

Fig. 2. WAXD and SAXS patterns of DP/DPE I and DP/DPE II films (end view)

elongated to a remarkably high draw ratio ($\lambda = 300$) [5, 6]. The possibility of successful drawing up to $\lambda = 300$ decreases as the concentrations are away from the critical one.

In contrast, for a solution of DP/DPE mixture, the mechanical properties and morphology of the resultant films were independent of the concentration of solution, which was confirmed by preliminary experiments. This independence thought to be probably due to drastic shrinkage of gels at temperature < 147 °C. This phenomenon hampers to assure a suitable level of entanglement mesh per molecule. To confirm this concept, the morphology and mechanical properties were measured.

Figure 2 shows WAXD and SAXS patterns (end view) of DP/DPE I and DP/DPE II films. The WAXD pattern indicates the preferential orientation of the *a*-axes perpendicular to the film surface and SAXS pattern shows a random orientation of crystal lamellae. This is probably attributed to drastic isotropic shrinkage of gel at < 147 °C. Actually, such a orientational mode is quite different from that of the gel films prepared from decalin and *p*-xylene solutions. According to previous works, the latter gel film was composed of crystal lamellae oriented highly with their large flat faces and within the lamellar crystals constituting the gel; the c-axes are oriented perpendicular to the large flat faces [3, 5, 10].

Figures 3 and 4 show photographs of SEM and SALS patterns under Hv polarization condition as a function of draw ratio. λ, observed for DP/DPE I and DP/DPE II films, respectively. The SEM photographs of the both specimens at $\lambda = 1$ show a number of voids. In spite of a number of voids, the specimens could be stretched up to $\lambda = 20$. In this process, the cracks appeared in the stretching direction. The SALS patterns for DP/DPE I and DP/DPE II films at $\lambda = 1$ show the lobes at odd multiples of 45°, indicating a random orientation of rods, the optical axes being oriented at 0° or 90° with respect to the rod axis [11]. As for the DP/DPE I film, the pattern shows indistinct streaks extended in the horizontal direction with increasing λ. This suggests the disruptive process of fibrillar textures. In contrast, the pattern of DP/DPE II film shows clear scattering lobes extended in the horizontal direction, indicating the preferential orientation of rods with respect to the stretching direction. Incidentally, the orientation mechanism of rods could not be observed by the corresponding photographs of SEM because of flat surfaces of pressed films.

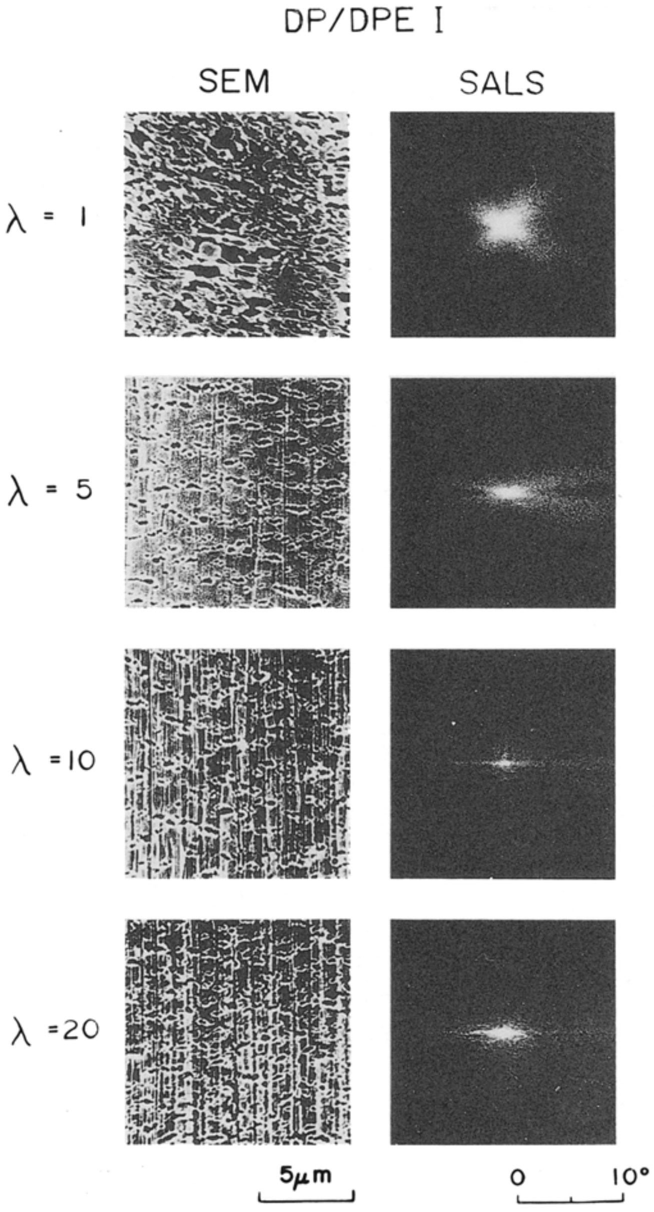

Fig. 3. Scanning electron micrographs and Hv light scattering patterns for DP/DPE I films as a function of draw ratio λ

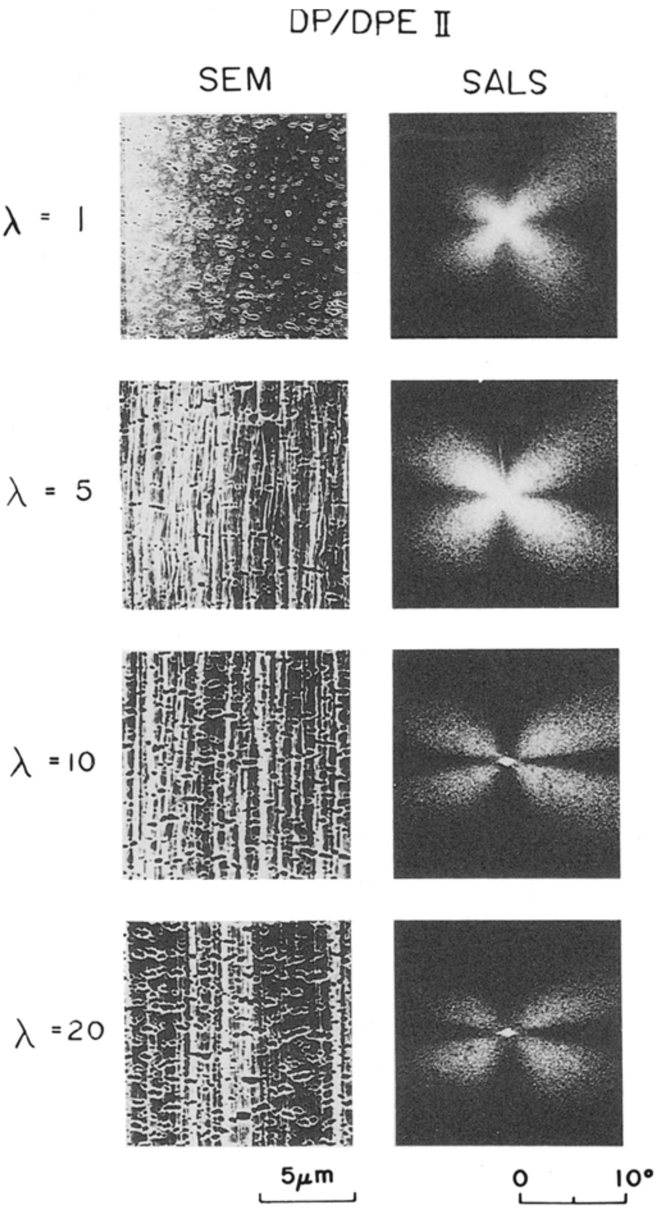

Fig. 4. Scanning electron micrographs and Hv light scattering patterns for DP/DPE II films as a function of draw ratio λ

Figure 5 shows the change in crystallinity with increasing λ. The crystallinity was calculated by assuming that the intrinsic densities of crystal and amorphous phases are constant to be 1.000 and 0.852 g·cm^{-3}, respectively [12]. The repeated measurements provided the values within experimental error less than 3%. The crystallinity of the undrawn gel film ($\lambda = 1$) depends on the sample preparation method. Interestingly, the crystallinity decreases at initial draw ratio up to $\lambda = 5$ and tends to increase. This suggests the significant crystal transformation from a folded to fibrous type. In contrast, the draw ratio of the melt films reached 30 times. Although the crystallinity increases gradually with draw ratio, the maximum value is lower than that of gel film,

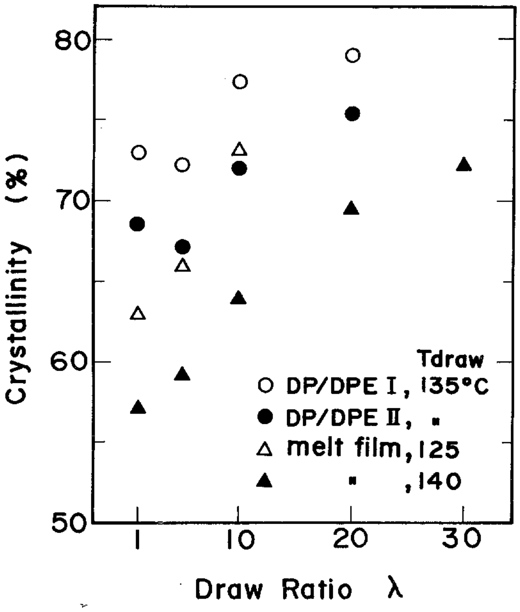

Fig. 5. Crystallinity as a function of draw ratio λ for DP/DPE I, DP/DPE II, and melt films

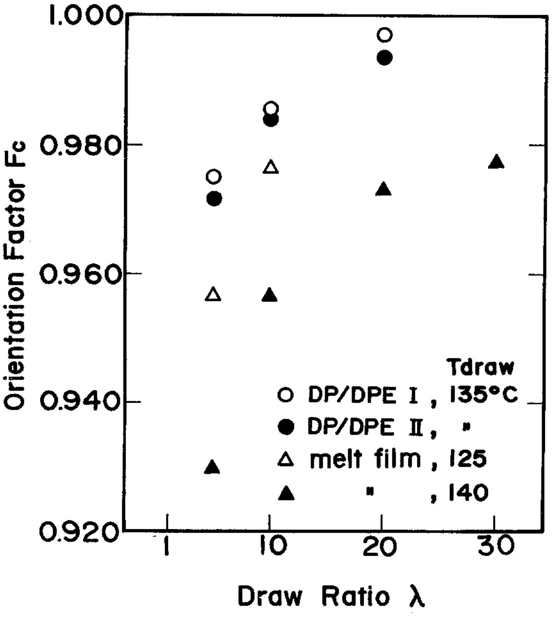

Fig. 6. The second-order orientation factor of the c-axis as a function of draw ratio λ for DP/DPE I, DP/DPE II, and melt films drawn at 125° and 140 °C

because of lower value of the original (undrawn) films.

Figure 6 shows the second-order orientation factor, F_c, of the c-axis with draw ratio. The orientation factor was estimated directly from the orientation distribution function of the (0 0 2) plane. F_c characterizes the orientation distribution of c-axes with variation between $-1/2$ and 1. For random orientation, F_c is 0, while for complete orientation parallel and perpendicular to the stretching direction, F_c is unity and $-1/2$, respectively. A considerable increase in the orientation factor can be observed for the DP/DPE I and DP/DPE II films with increasing λ. At draw ratio < 10, the orientation factors are higher than those of the melt films drawn at 125° and 140 °C. This is attributed to two factors. One is due to a reduced number of entanglement mesh per molecule in solution-cast/spun polymers in comparison with that obtained from the melt films. The other is due to molecular slippage during elongation up to 30 times at 140 °C. The maximum values of F_c for DP/DPE I and DP/DPE II films are much lower as shown in this figure in comparison with the value of the specimens with $\lambda = 300$, prepared from decalin and p-xylene solutions [5, 6]. This is due to poor drawability because of an excess level of entanglement mesh to hamper smooth crystal transformation from a folded to a fibrous type.

Figure 7 shows the change in the DSC curve with increasing λ for the DP/DPE I and DP/DPE II films. The DSC curves at $\lambda = 1$ show a single main peak around 136° and 137 °C for the DP/DPE I and DP/DPE II films, respectively. With increasing λ, the main peak shifts to higher temperature and at $\lambda = 20$ a new very small peak appeared at higher temperature than the main peak. Returning to Fig. 5, the crystallinity decreased at $\lambda = 5$ indicating the significant crystal transformation from a folded to a fibrous type. The DSC profiles, however, are not sensitive enough to detect the transformation.

Figure 8 shows the Young's moduli of the DP/DPE I, DP/DPE II, and melt films, respectively. The value increases with λ. Among three kinds of specimens, the value of DP/DPE I takes the maximum value at each draw ratio and reached 27 Gpa. This is a reasonable result, since the crystallinity and the second-order orientation factor of the DP/DPE I are higher than those of DP/DPE II and melt films.

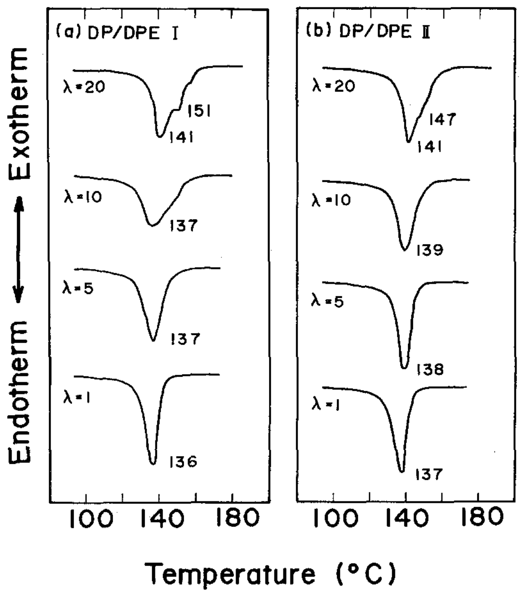

Fig. 7. Change in DSC curves with increasing λ for DP/DPE I and DP/DPE II films

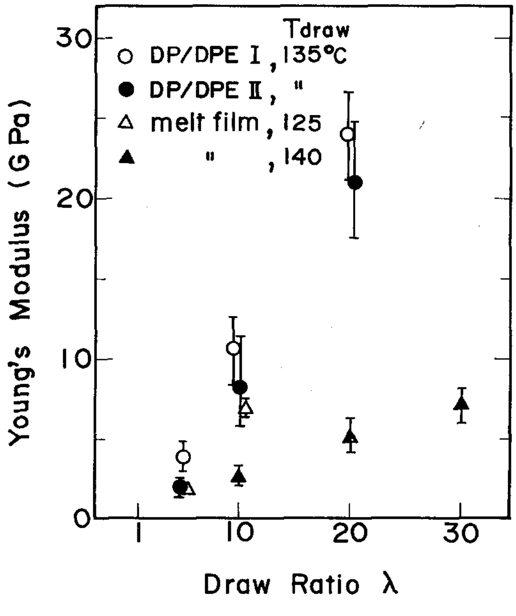

Fig. 8. Young's modulus as a function of draw ratio λ for DP/DPE I, DP/DPE II, and melt films drawn at 125° and 140 °C

Conclusion

The co-solvent of DP/DPE causes a drastic rapid gelation at temperature $< 147\,^{\circ}\mathrm{C}$ associated with a drastic shrinkage of gels. The Young's modulus of the drawn film ($\lambda = 20$) reached $20 \sim 27$ GPa, which is higher than the maximum value of melt films. The above values, however, are much lower than that of UHMWPE at $\lambda = 300$ because of poor drawability [3, 5, 9]. This is probably due to an excess level of entanglement mesh per molecule. Thus, it may be concluded that the rapid gelation associated with drastic shrinkage of gels disturbs maintaining a suitable level of the entanglement mesh that acts as intermolecular crosslinks and effectively transmits the drawing force. To realize this condition, good solvents such as decalin and *p*-xylene are found to be much more favorable than a poor solvent like co-solvent of DP/DPE mixture, since large expansion of chains in good solvents play an important role for assuring a suitable level of entanglement which connects large crystal lamellae and causes significant crystal transformation from a folded to a fibrous type.

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