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Ultradrawing gel films of blends of ultrahigh molecular weight polyethylene and low molecular weight polyethylenes with different molecular weights

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The ultradrawing behavior of five series of gel films prepared from the blends of one ultrahigh molecular weight polyethylene (UHMWPE) and five other low molecular weight polyethylene (LMWPE) resins with varying molecular weight is reported. The critical draw ratio (λ_c) of each of the five UHMWPE/LMWPE gel film series were found to depend significantly upon the amount of LMWPE present in each of the gel film series. The presence of optimum amounts of LMWPE in each of the five gel film series can significantly improve their λ_c values, and this improvement in λ_c can further be enhanced with the addition of an optimum molecular weight of LMWPE. These interesting phenomena were investigated in terms of reduced viscosities of the solutions, thermal analysis, birefringence and tensile properties of these undrawn and drawn gel films.

1. Introduction

In ultrahigh molecular weight polyethylene (UHMWPE), there has been good progress in new processing methods for obtaining high performance fibers [1–11]. The strength of UHMWPE fibers exceed those of carbon and aramid fibers, because of the successful invention of fibrillar-crystal-growing [1] and gel-spinning/casting methods [2, 3] in the 1970s. However, the production rate of longitudinal crystals of fibrillar-crystal-growing method is far below the commercially interesting speed. On the other hand, the gel spinning/casting method [2, 3] has attracted much attention because of its availability in production of high strength/modulus fibers commercially. By far, the strongest fibers available in the industry are UHMWPE fibers. The highest tenacity of commercially available UHMWPE fibers can reach as high as 3.87 GPa, which is about 10 times higher than those of steel fibers.

The method by ultradrawing the gel specimens prepared by quenching solutions of UHMWPE is referred to as the gel deformation method. It is often found that the strength and modulus of UHMWPE improve relatively consistently with increasing draw ratio of the corresponding gel specimens [12–16]. Therefore, a significant proportion of researches reported in this field has concentrated on the investigation of drawing behavior of UHMWPE gel specimens. Several authors [12–16] found that the drawability of the gel specimens with a sufficiently high molecular weight depends principally on the concentration of the solution from which the gel was made. The drawability improved considerably with increasing dilution as a result of gradual disentanglement of the coils before crystallization of the polymer chains in solution. However, the drawability then drops sharply as the concentration reduces to a “critical concentration”, at which the intermolecular cohesion of the polymer chains began to be lost and the chains disengaged from the network of the gel.

Although very few, ultradrawing gel films of UHMWPE and low molecular weight polyethylene (LMWPE) blends have been used to prepare high strength and high modulus gel specimens [14–20]. In fact, it has been reported [17] that the modulus of the fiber prepared from ultradrawn gel film of 50/50 UHMWPE/LMWPE blend can reach as high as 80 GPa. Such fibers and ultradrawn gel films of UHMWPE/LMWPE blends are very important commercially, because the production rate of high modulus fibers prepared from UHMWPE gels is far below that commercially required. In fact, the drawability of gel films prepared from pure UHMWPE solution can be lower than that of gel films prepared from UHMWPE/LMWPE blends because the enormous entanglements of UHMWPE gel films may inhibit drawability. Moreover, the solid content of the solutions used for preparation of gel specimens can increase significantly by the addition of LMWPE in gel solutions of

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UHMWPEs, that can not only increase the production rate of these high performance specimens, but can also reduce the amounts of solvent required to be recycled. However, even up to the present time, very few investigations have ever been reported with regard to the preparation and drawing of gel specimens of UHMWPE/LMWPE blends [14–20].

Most recently, the drawability of the gel specimens were found to depend significantly on the compositions of solutions from which gels were made [14–16]. The achievable draw ratios of the gel films prepared from each weight ratio of LMWPE to UHMWPE approached a maximum value, when they were prepared at concentrations close to their critical concentration. These critical draw ratios (λ_c) of gel films prepared near their critical concentrations were found to decrease significantly with increasing amount of LMWPE added in the gel films. However, addition of a small but optimum amount of LMWPE in the films of UHMWPE/LMWPE blends can significantly improve their λ_c compared to that of the gel film prepared from pure UHMWPE gel solution. In fact, this improvement in λ_c is further enhanced with decreasing lengths of short chain branches of LMWPEs [15]. Presumably, this improvement in λ_c of these gel films is attributed to a suitable reduction of number of entanglements within gel films caused by addition of an optimum amount of a suitable branched length of LMWPE in UHMWPE/LMWPE blends. On the other hand, in our most recent study [16]. λ_c of each gel specimen was found to reach a maximum value as it was drawn at an "optimum" temperature ranging from 95 to 105°C. Somewhat interestingly, the birefringence and thermal properties of these one-stage drawn gel specimens drawn at each temperature exhibited an abrupt change as their draw ratios reached about 40. Based on this transition draw ratio, the critical draw ratios of the two-stage drawn gel specimens can be further improved as the temperatures used in the second drawing stage increased to an other optimum temperature of 115°C. However, it is still not clear what is the optimum amount, molecular length and/or branch length of LMWPE that one can add in gel films of UHMWPE/LMWPE blends to yield the maximum and the most improved tensile properties of the UHMWPE/LMWPE gel specimens.

In this study, a series of low molecular weight polyethylenes (LMWPEs) were added in ultrahigh molecular weight polyethylene (UHMWPE) solutions to prepare and investigate the drawing behavior of the gel specimens of UHMWPE/LMWPE blends. The main purpose of this study is to investigate the influence of molecular weight of LMWPE on the drawing behavior of UHMWPE/LMWPE gel specimens, and further to enhance the mechanical performance of UHMWPE/LMWPE specimens.

TABLE I Compositions and C_c of U and U/L_5 solutions and the achievable D_r of the corresponding gel films

Sample	Weight ratio U/L_5	Concentration (kg/m^3)	C_c	D_r of gel films drawn at 95°C	Standard deviation
U_6	100/0	6	7.0	216	2.6
U_7		7		240	3.0
U_8		8		224	3.0
U_9		9		221	1.9
U_{10}		10		200	2.5
UL_{5A-6}	99/1	6	7.3	230	2.9
UL_{5A-7}		7		329	2.4
UL_{5A-8}		8		244	2.3
UL_{5A-9}		9		227	2.2
UL_{5A-10}		10		212	1.4
UL_{5B-6}	98/2	6	7.6	273	3.2
UL_{5B-7}		7		362	2.3
UL_{5B-8}		8		313	1.4
UL_{5B-9}		9		254	4.2
UL_{5B-10}		10		230	2.1
UL_{5C-6}	95/5	6	8.4	208	1.8
UL_{5C-7}		7		229	0.8
UL_{5C-8}		8		294	2.9
UL_{5C-9}		9		282	1.7
UL_{5C-10}		10		238	1.8
UL_{5D-7}	90/10	7	8.7	197	2.3
UL_{5D-8}		8		200	2.4
UL_{5D-9}		9		223	1.8
UL_{5D-10}		10		200	2.3
UL_{5D-11}		11		193	3.5
UL_{5E-9}	80/20	9	11.5	183	2.6
UL_{5E-10}		10		188	2.2
UL_{5E-11}		11		196	2.4
UL_{5E-12}		12		169	3.4
UL_{5E-13}		13		153	2.3

2. Experimental

2.1. Materials and sample preparation

One UHMWPE resin and five other polyethylenes with weight average molecular weights ($\bar{M}_w$) lower than that of UHMWPE were selected for this study. UHMWPE is associated with an $\bar{M}_w$ of 4.5×10^6, which will be referred to as resin U in the following discussion. Five other linear high density polyethylenes with $\bar{M}_w$ of 5×10^4, 8.9×10^4, 2.2×10^5, 5.0×10^5 and 1.0×10^6 will be referred to as resins L_5, $L_{8.9}$, L_{22}, L_{50} and L_{100}, respectively, in the following discussion. These resins were kindly supplied by Mr. Bruce Lu of Yung Chia Chemical Industrial Corporation. For purposes of convenience, L_5, $L_{8.9}$, L_{22}, L_{50} and L_{100} will be referred to as low molecular weight polyethylenes (LMWPEs) in the following discussion, although resin L_{50} and L_{100} are associated with relatively high $\bar{M}_w$. Mixtures of varying weight ratios of UHMWPE to LMWPE were dissolved in decalin at 135°C for 90 minutes, in which 0.1 weight percentage of di-*t*-butyl-*p*-cresol was added as an antioxidant. The compositions of the gel solutions prepared in this study were summarized in Tables I to V. The hot homogenized solutions were poured into an alumina tray and cooled in an oven to form the gel films at 35°C. The decalin was then evaporated from the gel in the oven. The dried gel was immersed in ethanol to remove antioxidant and residual traces of decalin. The prepared gel film had a thickness of about 250 μm.

2.2. Viscosity measurements, birefringence and thermal analysis

The viscosities of polymer solutions were determined at 135°C by a Brookfield viscometer model LVDV-II$^+$.

TABLE II Compositions and C_c of U and U/$L_{8.9}$ solutions and the achievable D_r of the corresponding gel films

Sample	Weight ratio U/L_{22}	Concentration (kg/m^3)	C_c	D_r of gel films drawn at 95°C	Standard deviation
U_6		6		216	2.6
U_7		7	7.0	240	3.0
U_8	100/0	8		224	3.0
U_9		9		221	1.9
U_{10}		10		200	2.5
$UL_{8.9A-6}$		6		234	4.0
$UL_{8.9A-7}$		7	7.3	330	2.7
$UL_{8.9A-8}$	99/1	8		245	2.4
$UL_{8.9A-9}$		9		229	5.0
$UL_{8.9A-10}$		10		216	4.9
$UL_{8.9B-6}$		6		277	5.0
$UL_{8.9B-7}$		7	7.6	360	1.2
$UL_{8.9B-8}$	98/2	8		288	1.3
$UL_{8.9B-9}$		9		268	2.3
$UL_{8.9B-10}$		10		238	1.1
$UL_{8.9C-6}$		6		210	2.6
$UL_{8.9C-7}$		7		236	4.1
$UL_{8.9C-8}$	95/5	8	8.4	295	2.9
$UL_{8.9C-9}$		9		285	2.8
$UL_{8.9C-10}$		10		240	2.8
$UL_{8.9D-7}$		7		195	2.3
$UL_{8.9D-8}$		8		204	3.5
$UL_{8.9D-9}$	90/10	9	8.5	229	3.2
$UL_{8.9D-10}$		10		213	1.4
$UL_{8.9D-11}$		11		209	3.2
$UL_{8.9E-09}$		8		185	5.5
$UL_{8.9E-10}$		9		194	3.0
$UL_{8.9E-11}$	80/20	10	11.3	200	4.9
$UL_{8.9E-12}$		11		175	1.5
$UL_{8.9E-13}$		12		160	2.1

TABLE III Compositions and C_c of U and U/L_{22} solutions and the achievable D_r of the corresponding gel films

Sample	Weight ratio U/$L_{8.9}$	Concentration (kg/m^3)	C_c	D_r of gel films drawn at 95°C	Standard deviation
U_6		6		216	2.6
U_7		7	7.0	240	3.0
U_8	100/0	8		224	3.0
U_9		9		221	1.9
U_{10}		10		200	2.5
UL_{22A-6}		6		350	2.7
UL_{22A-7}		7	7.3	363	3.6
UL_{22A-8}	99/1	8		331	3.1
UL_{22A-9}		9		322	3.6
UL_{22A-10}		10		302	3.6
UL_{22B-6}		6		361	3.9
UL_{22B-7}		7	7.5	400	2.9
UL_{22B-8}	98/2	8		380	4.5
UL_{22B-9}		9		342	1.9
UL_{22B-10}		10		324	2.3
UL_{22C-6}		6		313	4.1
UL_{22C-7}		7	8.0	352	1.6
UL_{22C-8}	95/5	8		331	2.6
UL_{22C-9}		9		286	5.7
UL_{22C-10}		10		256	2.5
UL_{22D-7}		7		303	1.9
UL_{22D-8}		8	8.4	314	1.8
UL_{22D-9}	90/10	9		309	4.5
UL_{22D-10}		10		271	2.4
UL_{22D-11}		11		265	1.9
UL_{22E-8}		9		233	1.3
UL_{22E-9}		10		253	1.9
UL_{22E-10}	80/20	11	10.5	265	3.3
UL_{22E-11}		12		260	4.4
UL_{22E-12}		13		249	4.0

Birefringence of the drawn and undrawn gel films was measured by using a polarizing micro-spectrometer model TFM-120 AFT. The thermal behavior of all samples was performed on a Dupont differential scanning calorimeter (DSC) model 2000. All scans were carried out at a heating rate of 10°C/min under flowing nitrogen at a flow rate of 25×10^{-6} m^3/min. Samples weighing 0.5 mg were placed in the standard aluminum sample pans for determination of the melting temperature.

2.3. Drawing and tensile properties of the gel films

The strip specimens used in drawing experiments were cut from the dry gel films and then stretched on a Tensilon testing machine model RTA-1T equipped with a temperature controlled oven at a crosshead speed of 20 mm/min. The dimensions of the specimens are 30 mm in length and 10 mm in width. The specimens were drawn at varying temperatures to find out the temperature dependence of the drawability of the UHMWPE/LMWPE gel films in our previous investigation [16], and it was found that 95°C is the optimum drawing temperature to yield the highest drawability of most of the UHMWPE/LMWPE gel specimens. Based on this premise, all the strip specimens were clamped in a stretching device and then stretched at a temperature of 95°C. The draw ratio of each specimen was determined as the ratio of the marked displacement after and before drawing. The marked displacement before drawing was 5 mm. The tensile properties of the undrawn and drawn gel films were also determined using a Tensilon testing machine model RTA-1T at 28°C and a crosshead speed of 20 mm/min. The achievable draw ratio was obtained based on the drawing of a minimum of three sample samples of each specimen.

3. Results and discussion

3.1. Reduced viscosities of the gel solutions

Figs 1–5 summarize the reduced viscosity (η_{sp}/C) against the concentration of the UHMWPE/LMWPE and UHMWPE solutions prepared in this study. Similar to those reported in our previous studies [14–16], two distinct regions were found on these plots. The reduced viscosities increase slightly with concentration in region 1, which are associated with low concentrations. However, the reduced viscosities increase dramatically as the concentrations of solutions reach their critical values. The region associated with concentrations higher than the critical concentration (C_c) is referred to as region 2. The value of C_c was determined by the intersection of the two straight lines drawn parallel to the two distinct regions shown in these plots and were summarized in Tables I–V. This critical value of concentration shifted to a higher value with decreasing weight ratio of UHMWPE to LMWPE associated with

TABLE IV Compositions and C_c of U and U/L$_{50}$ solutions and the achievable D_r of the corresponding gel films

Sample	Weight ratio U/L$_{50}$	Concentration (kg/m^3)	C_c	D_r of gel films drawn at 95°C	Standard deviation
U$_6$		6		216	2.6
U$_7$		7	7.0	240	3.0
U$_8$	100/0	8		224	3.0
U$_9$		9		221	1.9
U$_{10}$		10		200	2.5
UL$_{50A-6}$		6		391	4.4
UL$_{50A-7}$		7	7.2	400	4.2
UL$_{50A-8}$	99/1	8		386	3.4
UL$_{50A-9}$		9		341	2.1
UL$_{50A-10}$		10		332	2.0
UL$_{50B-6}$		6		403	3.7
UL$_{50B-7}$		7	7.4	429	1.6
UL$_{50B-8}$	98/2	8		410	5.4
UL$_{50B-9}$		9		365	0.5
UL$_{50B-10}$		10		354	4.2
UL$_{50C-6}$		6		341	4.9
UL$_{50C-7}$		7		363	1.9
UL$_{50C-8}$	95/5	8	7.7	371	2.1
UL$_{50C-9}$		9		352	4.2
UL$_{50C-10}$		10		324	0.9
UL$_{50D-7}$		7		319	3.7
UL$_{50D-8}$		8	8.3	361	2.2
UL$_{50D-9}$	90/10	9		345	1.6
UL$_{50D-10}$		10		330	5.1
UL$_{50D-11}$		11		304	2.7
UL$_{50E-8}$		8		281	4.8
UL$_{50E-9}$		9		294	3.2
UL$_{50E-10}$	80/20	10	9.7	321	2.3
UL$_{50E-11}$		11		297	1.6
UL$_{50E-12}$		12		288	4.4

TABLE V Compositions and C_c of U and U/L$_{100}$ solutions and the achievable D_r of the corresponding gel films

Sample	Weight ratio U/L$_{100}$	Concentration (kg/m^3)	C_c	D_r of gel films drawn at 95°C	Standard deviation
U$_6$		6		216	2.6
U$_7$		7	7.0	240	3.0
U$_8$	100/0	8		224	3.0
U$_9$		9		221	1.9
U$_{10}$		10		200	2.5
UL$_{100A-6}$		6		282	1.6
UL$_{100A-7}$		7	7.0	301	2.4
UL$_{100A-8}$	99/1	8		271	4.3
UL$_{100A-9}$		9		245	2.7
UL$_{100A-10}$		10		200	1.8
UL$_{100B-6}$		6		340	2.7
UL$_{100B-7}$		7	7.1	388	3.5
UL$_{100B-8}$	98/2	8		356	2.2
UL$_{100B-9}$		9		322	1.6
UL$_{100B-10}$		10		301	2.3
UL$_{100C-6}$		6		273	1.1
UL$_{100C-7}$		7	7.3	321	2.7
UL$_{100C-8}$	95/5	8		300	2.3
UL$_{100C-9}$		9		269	0.9
UL$_{100C-10}$		10		253	1.1
UL$_{100D-7}$		7		260	5.5
UL$_{100D-8}$		8	8.0	288	3.1
UL$_{100D-9}$	90/10	9		300	5.2
UL$_{100D-10}$		10		259	3.2
UL$_{100D-11}$		11		224	3.6
UL$_{100E-7}$		7		232	1.6
UL$_{100E-8}$		8		243	1.1
UL$_{100E-9}$	80/20	9	8.7	261	2.3
UL$_{100E-10}$		10		234	0.6
UL$_{100E-11}$		11		201	1.8

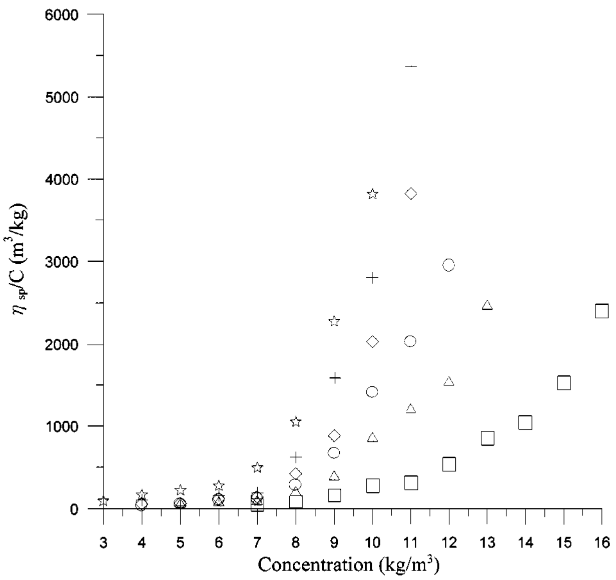

Figure 1 Reduced viscosity (η_{SP}/C) of the solution of samples (☆) U, (+) UL$_{5A}$, (◇) UL$_{5B}$, (○) UL$_{5C}$, (△) UL$_{5D}$, and (□) UL$_{5E}$.

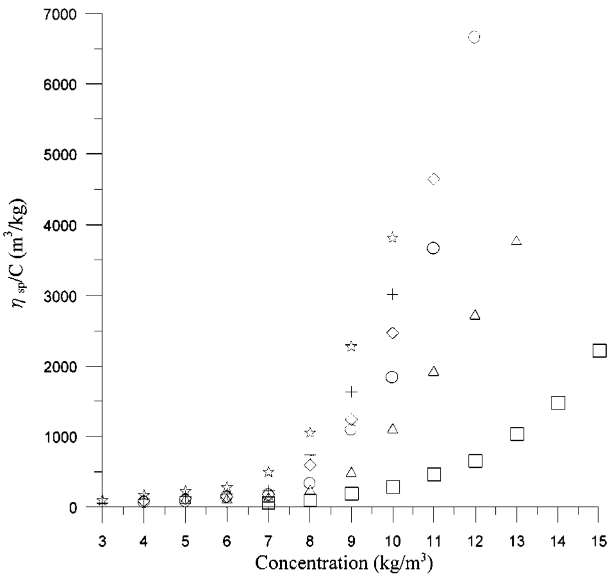

Figure 2 Reduced viscosity (η_{SP}/C) of the solution of samples (☆) U, (+) UL$_{8.9A}$, (◇) UL$_{8.9B}$, (○) UL$_{8.9C}$, (△) UL$_{8.9D}$, and (□) UL$_{8.9E}$.

each UHMWPE/LMWPE (i.e. UL$_5$, UL$_{8.9}$, UL$_{22}$, UL$_{50}$ and UL$_{100}$) solution series.

Somewhat interestingly, the critical concentrations decreased significantly with increasing molecular weight of LMWPE for UL$_5$, UL$_{8.9}$, UL$_{22}$, UL$_{50}$ and UL$_{100}$ solution series associated with a fixed weight ratio of UHMWPE to LMWPE. The critical concentration is generally interpreted [12] as a concentration at which the coherent network of UHMWPE molecules was formed. The numbers of entanglements within UHMWPE and/or between LMWPE and UHMWPE molecules are also believed to reduce as the contents

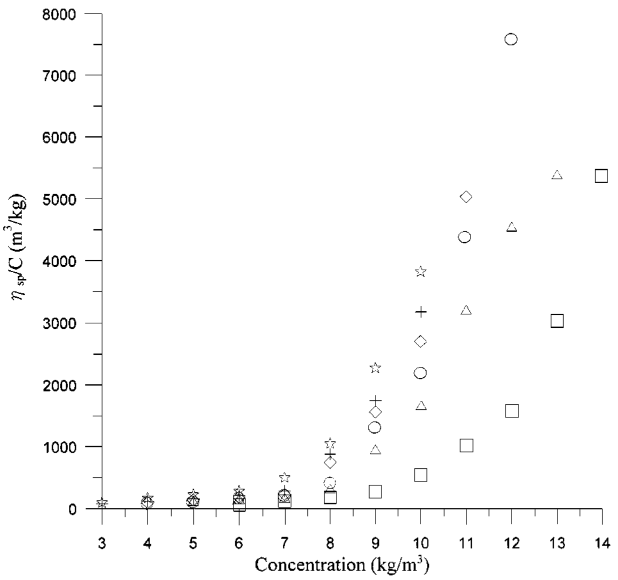

Figure 3 Reduced viscosity (η_{SP}/C) of the solution of samples (☆) U, (+) UL_{22A}, (◇) UL_{22B}, (○) UL_{22C}, (△) UL_{22D}, and (□) UL_{22E}.

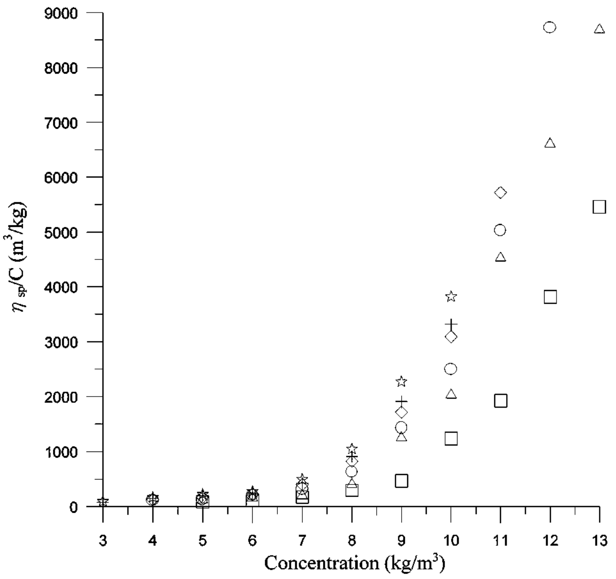

Figure 4 Reduced viscosity (η_{SP}/C) of the solution of samples (☆) U, (+) UL_{50A}, (◇) UL_{50B}, (○) UL_{50C}, (△) UL_{50D}, and (□) UL_{50E}.

of LMWPE present in gel solutions increase, because the average lengths of the main chains of LMWPE are significantly shorter than those in UHMWPE. This idea is supported by the evidence found in our previous investigation [15] that tie molecule density reduced significantly with increasing LMWPE content present in UHMWPE/LMWPE gel films. By the same analogy, the decrease in molecular weight of LMWPE can further reduce the number of entanglements within LMWPE and/or between LMWPE and UHMWPE molecules in gel solutions of UHMWPE/LMWPE. As a consequence, in order to maintain the coherent network of UHMWPE molecules in UHMWPE/LMWPE solution, the amount of UHMWPE present in solution must increase to an appropriate value, as the weight ratio of UHMWPE to LMWPE or the molecular weight of LMWPE present in the solutions decrease.

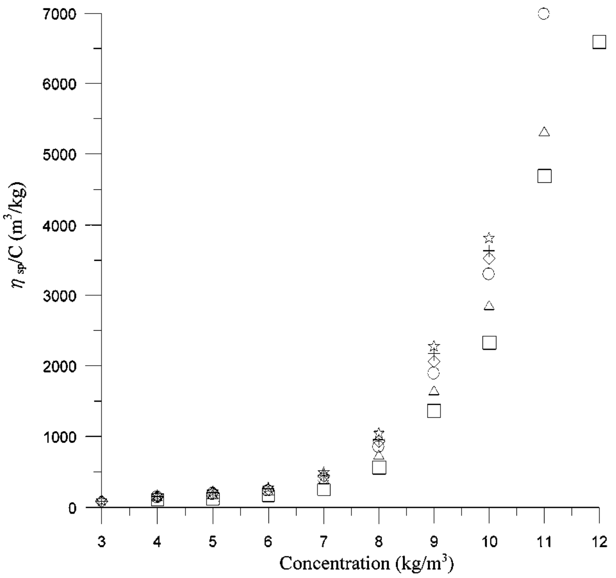

Figure 5 Reduced viscosity (η_{SP}/C) of the solution of samples (☆) U, (+) UL_{100A}, (◇) UL_{100B}, (○) UL_{100C}, (△) UL_{100D}, and (□) UL_{100E}.

3.2. Achievable draw ratios of UHMWPE/LMWPE gel films

The achievable draw ratios (D_r) of U, UL_5, $UL_{8.9}$, UL_{22}, UL_{50} and UL_{100} gel film series are shown in Tables I to V. Similar to those found in our previous investigations [14–16], the achievable draw ratios of each of the above gel film series with a fixed weight ratio of UHMWPE to LMWPE approached a maximum value, when they were prepared at concentrations close to their critical concentrations. These achievable draw ratios obtained for samples prepared near their critical concentrations will be referred to as the critical draw ratio (λ_c) in the following discussion. Fig. 6 shows the critical draw ratios as a function of weight percentage of LMWPE present in U, UL_5, $UL_{8.9}$, UL_{22}, UL_{50} and UL_{100} gel film series. The critical draw ratios of each of the above gel film series reached a maximum, when

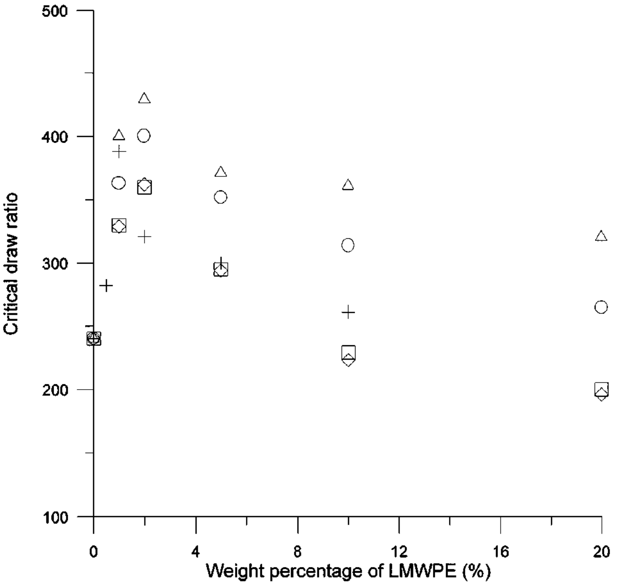

Figure 6 Plots of critical draw ratios versus the weight percentage of LMWPE in (◇) UL_5, (□) $UL_{8.9}$, (○) UL_{22}, (△) UL_{50} and (+) UL_{100} gel film series.

a small but optimum amount of LMWPE was added in these gel films. For instance, the critical draw ratios of UL$_5$, UL$_{8.9}$, UL$_{22}$, UL$_{50}$ and UL$_{100}$ gel film series with less than about 2% LMWPE are at least 40% higher than that of pure UHMWPE gel film. For instance, λ_c of UL$_5$ series (i.e., sample UL$_{5B\text{-}7}$) is about 50% higher than that of the gel film prepared from pure UHMWPE solution. It is further interesting to note that the maximum λ_c of the five gel film series approaches the highest value as the gel film series were prepared by addition of an optimum amount and molecular weight of LMWPE in these gel films. For example, the maximum critical draw ratio (λ_{cmax}) of UL$_{50}$ gel film series (i.e., sample UL$_{50B\text{-}7}$) is about 75% higher than that of the gel film prepared from pure UHMWPE solution, that is about another 10 to 25% higher than those of other gel film series. These results suggest that the presence of optimum amounts of LMWPE in gel films of UHMWPE/LMWPE blends can significantly improve their critical draw ratios, and this improvement in λ_c can further be enhanced with the addition of an optimum molecular weight of LMWPE. It is not completely clear what accounts for these interesting behaviors. Presumably, the presence of LMWPEs in UHMWPE gel films may cause some defects in the lamellar crystals, crystal boundaries, or amorphous regions of UHMWPE. On the other hand, the presence of LMWPEs in gel films of UHMWPE/LMWPE can also significantly reduce the number of inter and intramolecular entanglements of UHMWPE in UHMWPE/LMWPE gel films. These crystal defects and reduced number of inter and intramolecular entanglements of UHMWPE increase with increasing LMWPE contents present in UHMWPE/LMWPE gel films, which can cause stress concentration on the significantly reduced tie molecules, and early breakage of UHMWPE molecules in crystal boundaries or the amorphous regions of UHMWPE during the drawing process of these gel films. A significant reduction of λ_c with increasing amounts of LMWPEs added was then observed. However, it is also well recognized that a slight decrease in the enormous number of inter and intramolecular entanglements of UHMWPE can help disentangling UHMWPE molecules and pulling them out of lamellar crystals during the drawing process if the amounts of LMWPEs present in gel films of UHMWPE/LMWPE are less than a critical value, at which the "stress concentration" effect caused by the "crystal defects" and significantly reduced tie molecules is overcome by the "beneficial drawing" effect mentioned above. Adding LMWPE with slightly longer but optimum chain lengths is believed to further enhance pulling UHMWPE molecules out of lamellar crystals during the drawing process of gel films. Therefore, addition of a small but optimum amount of LMWPE in gel films

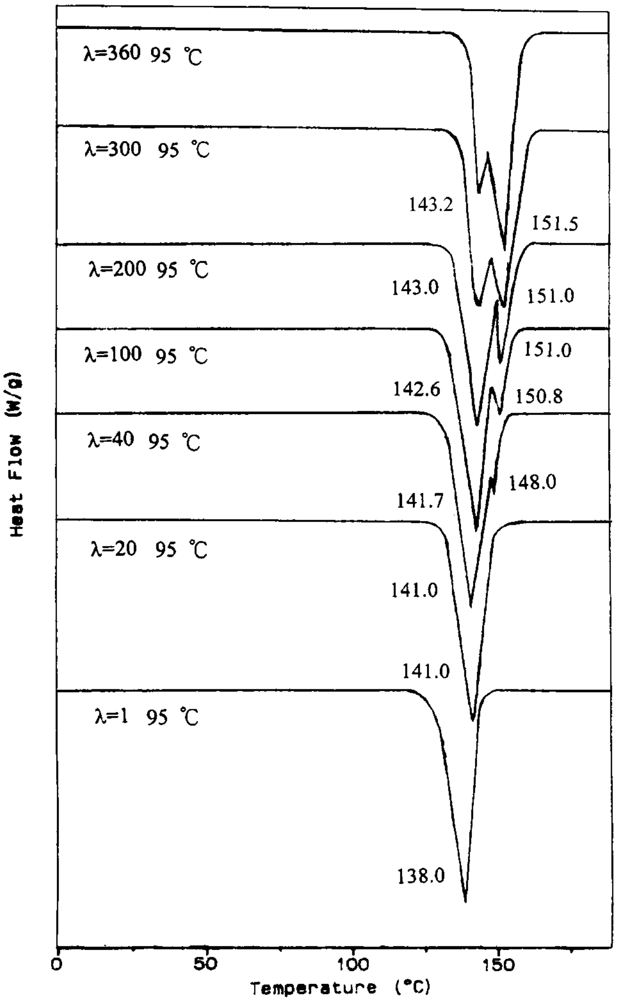

Figure 7 DSC thermograms of varying draw ratios of sample UL$_{5B-7}$ drawn at 95°C.

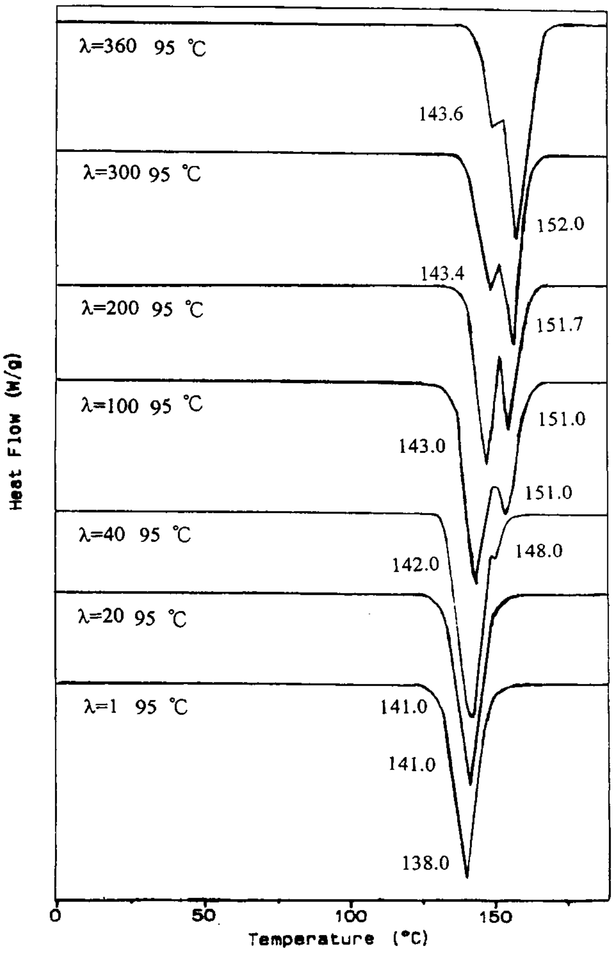

Figure 8 DSC thermograms of varying draw ratios of sample UL$_{8.9B-7}$ drawn at 95°C.

of UHMWPE/LMWPE blends can significantly improve their λ_c better than that of gel film prepared from pure UHMWPE gel solution, and this improvement in λ_c is further enhanced by using an optimum molecular weight of LMWPE in the UHMWPE/LMWPE gel films.

3.3. Thermal analysis

Typical DSC thermograms of each of pure UHMWPE gel films and the above five UHMWPE/LMWPE gel film series drawn at various D_r values are shown in Figs 7–12. A main melting endotherm with a peak temperature of about 138°C was found for the undrawn UHMWPE and UHMWPE/LMWPE gel films. This main melting temperature of the gel films then increases significantly as the draw ratio increases. Similar to those found in our previous investigations [15–16], a small shoulder at a temperature around 148°C was found on the right of the main melting endotherm when these gel films were stretched to a draw ratio of about 40 at 95°C. In fact, this small shoulder continues to grow into another melting endotherm, and the temperature associated with this new melting peak increased up to about 152°C as the gel film was drawn up to a draw ratio of 300. Moreover, it is interesting to note that the magnitude of the new developed melting endotherm continues to grow at the expense of the magnitude of the original main melting endotherm. On the other hand, it is also worth noting that, at a fixed draw ratio more than 40, the peak temperatures of the main and new developed melting endotherms of the UHMWPE/LMWPE gel films are significantly lower than those of the pure UHMWPE gel film, and decrease consistently as the molecular weight of LMWPE present in the gel films dereases. As shown in Figs 7–12, at a draw ratio of 200, the peak temperatures of the main and new developed melting endotherms increase from 142.6 and 151.0°C to 143.8 and 152.2°C, respectively, as the molecular weight of LMWPE present in UL_{xB-7} gel films increases from 50000 to 1000000. In fact, at a draw ratio of 200, the peak temperatures of the main and new developed melting endotherms of pure UHMWPE gel film (i.e. sample U_7) are higher than those of UHMWPE/LMWPE gel films and reach 143.9 and 152.9°C, respectively (see Fig. 12). It is not completely clear what accounts for these interesting thermal properties. However, even at a draw ratio of 400, the UHMWPE molecules are highly unlikely to be present as an extended form in the crystalline regions of these gel films. Presumably, the main and new developed endotherms are associated with the melting of two different groups of crystals with different degrees of crystal perfection, such as different crystal thicknesses.

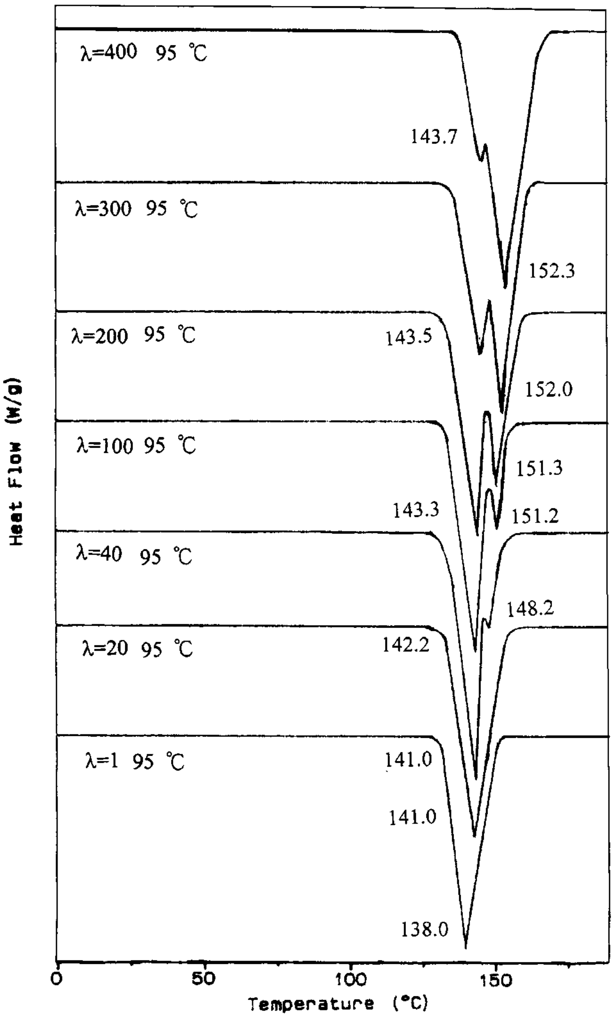

Figure 9 DSC thermograms of varying draw ratios of UL_{22B-7} gel film drawn at 95°C.

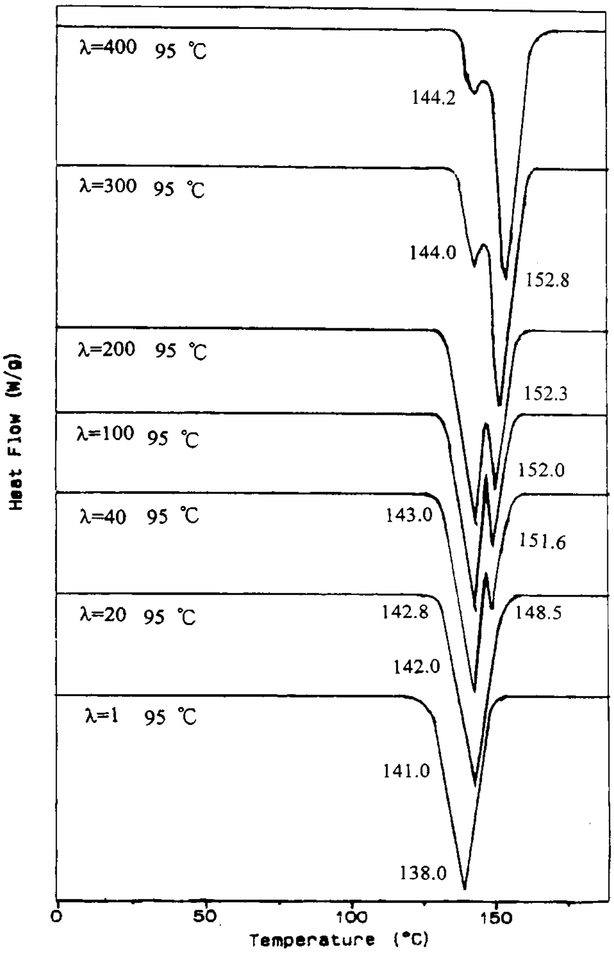

Figure 10 DSC thermograms of varying draw ratios of UL_{50B-7} gel film drawn at 95°C.

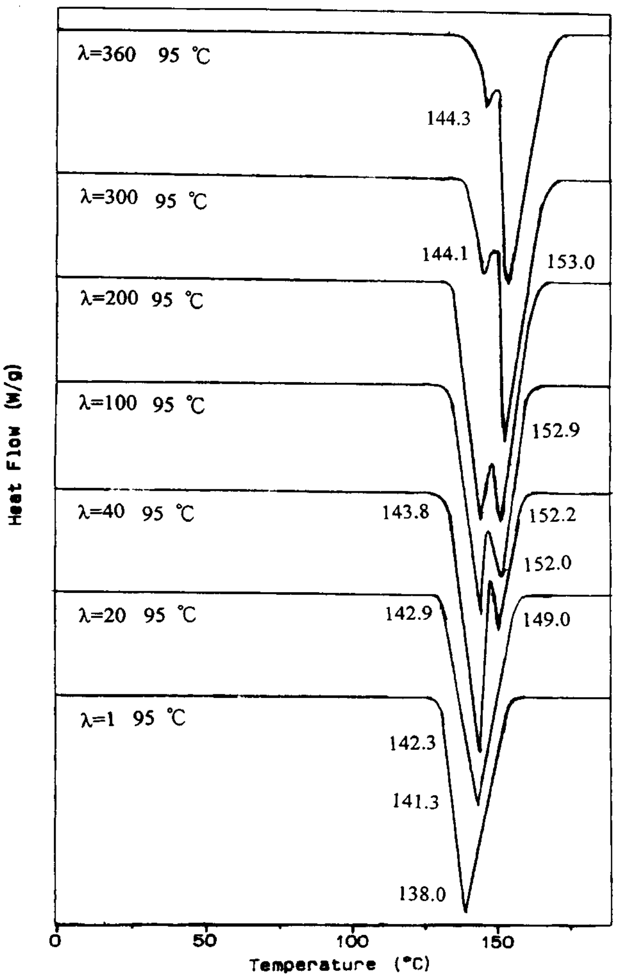

Figure 11 DSC thermograms of varying draw ratios of UL$_{100B-7}$ gel film drawn at 95°C.

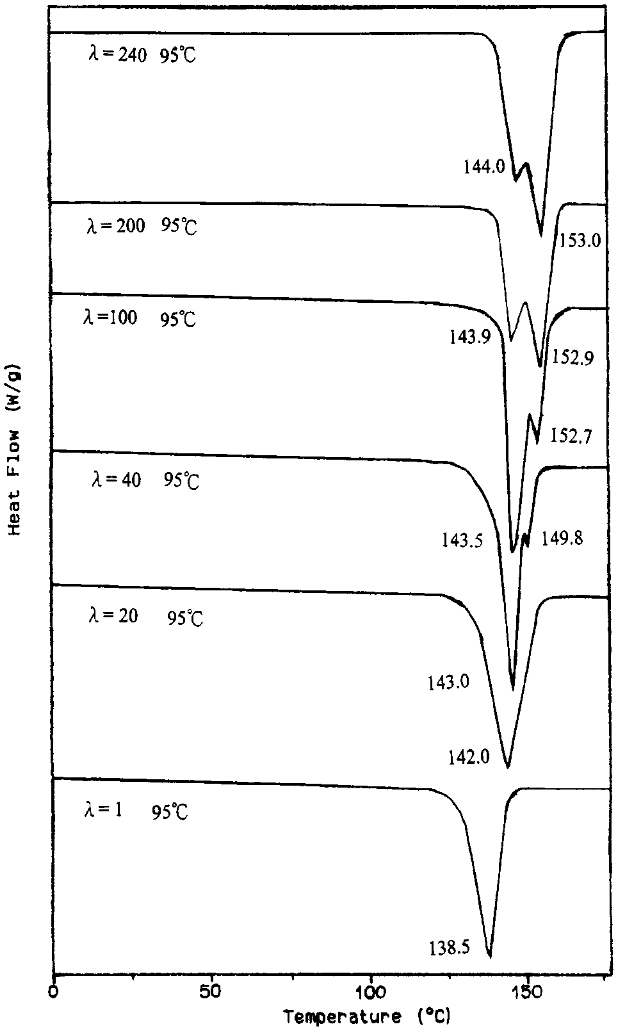

Figure 12 DSC thermograms of varying draw ratios of U$_7$ gel film drawn at 95°C.

3.4. Birefringence

Typical birefringence measurement for the drawn and undrawn gel films of U, UL$_5$, UL$_{8.9}$, UL$_{22}$, UL$_{50}$ and UL$_{100}$ gel film series are summarized in Fig. 13. The value of birefringence increases consistently with D_r, wherein the increasing rate of birefringence becomes slower as the draw ratio of the gel film is greater than about 40. As mentioned in previous section, a "small shoulder" was found on the right of the main melting endotherm when these gel film were stretched to a draw ratio of about 40. The melting temperatures associated with the main and new grown melting endotherm of the drawn gel films also increase consistently with the draw ratios of the gel films. On the other hand, it is interesting to note that, at a fixed draw ratio, the birefringence values of the UHMWPE/LMWPE gel films are lower than that of pure UHMWPE gel film. Moreover, these birefringence values reduce consistently as the molecular weight of LMWPE present in UHMWPE/LMWPE gel films decreases. For instance, at a draw ratio of 200, the birefringence value of pure UHMWPE gel film U$_7$ is about 10 and 15% higher than that of gel films UL$_{8.9B-7}$ and UL$_{5B-7}$, respectively. The improved birefringence properties apparently correlate with the increased peak temperatures of the main and new developed melting endotherms observed previously as the molecular

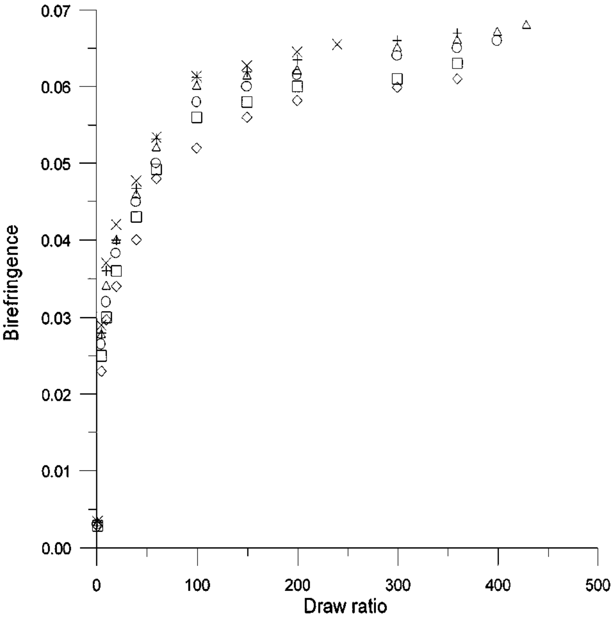

Figure 13 Birefringence of (◇) UL$_{5B-7}$, (□) UL$_{8.9B-7}$, (○) UL$_{22B-7}$, (△) UL$_{50B-7}$, (+) UL$_{100B-7}$, and (×) U$_7$ gel films drawn at different draw ratios.

weight of LMWPE in UHMWPE/LMWPE gel films increases. However, it is not completely clear what accounts for these interesting melting and birefringence properties of gel films. As mentioned previously, the enormous numbers of inter and intramolecular entanglements of UHMWPE molecules in pure UHMWPE gel films can be reduced significantly by addition of LMWPE in these UHMWPE/LMWPE gel films. Moreover, the numbers of inter and intramolecular entanglements of UHMWPE molecules can be further reduced by decreasing the molecular weight and increasing the amounts of LMWPE added in the UHMWPE/LMWPE gel films. Presumably, at a fixed achievable draw ratio, the more entangled UHMWPE network can more effectively pull UHMWPE molecules out of lamellar crystals, reform into thicker crystals and higher degrees of molecular orientation than those of drawn UHMWPE/LMWPE gel films with lower content or molecular weight of LMWPE. However, at high draw ratios, the more entangled UHMWPE network can prohibit the disentanglement of the UHMWPE molecules, and inhibit further drawing of the pure UHMWPE and/or UHMWPE/LMWPE gel films with higher contents and/or molecular weight of LMWPE. As a consequence, addition of an optimum content and molecular weight of LMWPE in gel films of UHMWPE/LMWPE blends can help disentangling UHMWPE molecules, effectively pulling them out of lamellar crystals during the drawing process and significantly improve their λ_c compared to that of gel film prepared from pure UHMWPE gel solution.

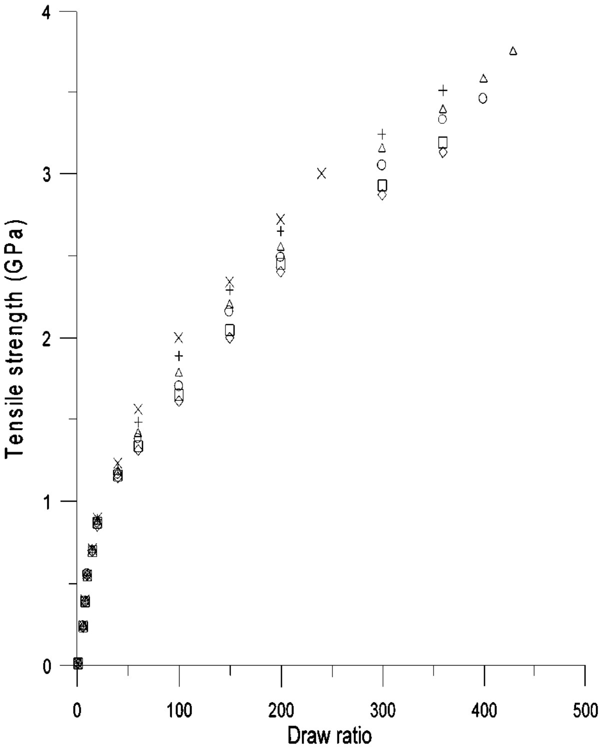

Figure 14 Tensile strengths of (◇) UL$_{5B-7}$, (□) UL$_{8.9B-7}$, (○) UL$_{22B-7}$, (△) UL$_{50B-7}$, (+) UL$_{100B-7}$ and (×) U$_7$ gel films drawn at varying draw ratios.

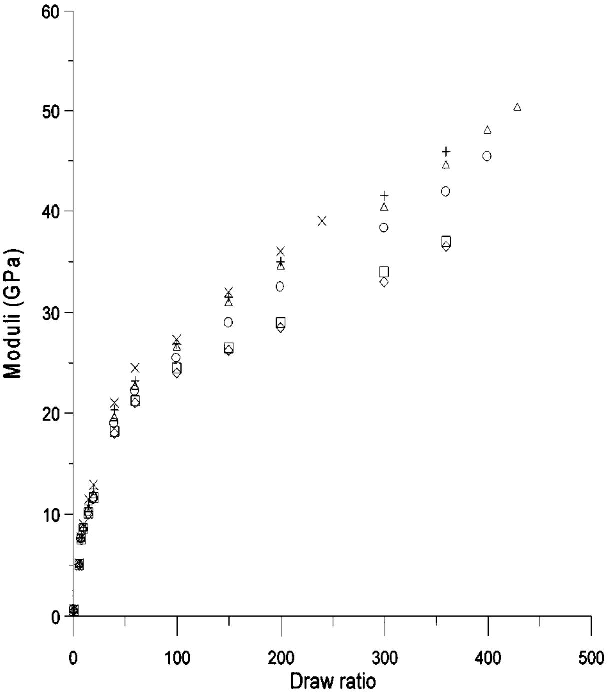

Figure 15 Moduli of (◇) UL$_{5B-7}$, (□) UL$_{8.9B-7}$, (○) UL$_{22B-7}$, (△) UL$_{50B-7}$, (+) UL$_{100B-7}$ and (×) U$_7$ gel films drawn at varying draw ratios.

3.5. Tensile properties of undrawn and drawn gel films of UHMWPE and UHMWPE/LMWPE

As shown in Figs 14 and 15, the tensile strengths and moduli of the UHMWPE and UHMWPE/LMWPE gel films were found to improve consistently as the D_r increased. At a fixed achievable draw ratio, the tensile strengths and moduli of the gel films were also found to improve substantially as the UHMWPE/LMWPE gel films are associated with a higher molecular weight of LMWPE. In fact, at a fixed achievable draw ratio, the tensile strengths and moduli of the pure UHMWPE gel film U$_7$ are significantly higher than those of UHMWPE/LMWPE gel films. As mentioned previously, the degree of orientation of the UHMWPE molecules and the crystal thickness associated with the double-melting endotherms increased significantly with D_r, and improved substantially with the molecular weight of LMWPE present in UHMWPE/LMWPE gel films. These results suggest that the orientation of the UHMWPE molecules along the drawing direction have a beneficial influence on the tensile strengths and moduli of these gel films.

4. Conclusions

At a fixed achievable draw ratio, the birefringence values, tensile strengths, moduli and peak temperatures associated the double-melting endotherms of the UHMWPE/LMWPE gel films are lower than those of pure UHMWPE gel film. Moreover, the values of these properties reduce significantly with addition of a lower molecular weight of LMWPE in the UHMWPE/LMWPE gel films. However, at high draw ratios, the more entangled UHMWPE network prohibits the disentanglement of the UHMWPE molecules, and inhibits further drawing of the pure UHMWPE and UHMWPE/LMWPE gel films with higher contents and/or molecular weight of LMWPE. As a consequence, the maximum critical draw ratios of the five gel film series approaches the highest value as the gel film series were prepared by addition of an optimum amount and molecular weight of LMWPE in these UHMWPE/LMWPE gel films. For instance, the critical draw ratios of the five UHMWPE/LMWPE gel film series with less than about 2% LMWPE are at least 40% higher than that of pure UHMWPE gel films. The maximum critical draw ratio of UL_{50} gel film series is about 75% higher than that of the pure UHMWPE gel film, and about 10 to 25% higher than those of other UHMWPE/LMWPE gel film series.

Acknowledgements

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References

1. A. ZWIJNENBURG and A. PENNINGS, *Colloid Polym. Sci.* **253** (1975) 452.
2. P. SMITH and P. J. LEMSTRA, *Macromol. Chem.* **180** (1979) 2983.
3. P. SMITH, P. J. LEMSTRA, J. P. L. PIJPERS and A. M. KIEL, *Colloid Polym. Sci.* **259** (1981) 1070.
4. T. OHTA and F. OKADA, US Patent no. 4,643,865 (1987).
5. T. OHTA, F. OKADA, M. HAYASHI and M. MIHOICHI, *Polymer* **30** (1989) 2170.
6. K. FURUHATA, T. YOKOKAWA, K. OHSAWA and K. MIYASAKA, *Polym. Prepr. Jpn.* **32** (1983) 874.
7. T. KANAMOTO, T. OOKI, K. TANAKA and M. TAKEDA, *ibid.* **32** (1983) 741.
8. P. SMITH, H. D. CHANZY and B. P. ROTZINGER, *Polym. Commun.* **26** (1985) 258.
9. H. D. CHANZY, B. P. ROTZINGER and P. SMITH, Patent no. WO-8703288.
10. P. SMITH, H. D. CHANZY and B. P. ROTZINGER, *J. Mater. Sci.* **22** (1987) 523.
11. T. KANAMOTO, T. OHAMA, K. TANAKA, M. TAKEDA and R. S. PORTER, *Polymer* **28** (1987) 1517.
12. C. SAWATARI, T. OKUMURA and M. MATSUO, *Polymer J.* **18** (1986) 741.
13. D. DARRAS, R. SEQUELA and F. RIETSCH, *J. Polym. Sci., Polym. Phys. Ed.* **30** (1992) 349.
14. J. T. YEH, Y. L. LIN and C. C. FAN-CHIANG, *Macromol. Chem. Phys.* **197** (1996) 3531.
15. J. T. YEH and H. C. WU, *Polym. J.* **30** (1998) 1.
16. J. T. YEH and S. S. CHANG, *J. Appl. Polym. Sci.* **70** (1998) 149.
17. C. SAWATARI and M. MATSUO, *Polymer* **30** (1989) 1603.
18. N. NAKAJIMA and J. IBATA, Japan Patent no. 57177035, 57177036 and 57177037 (1983).
19. I. SIMEONOV, Z. NIKOLOVA, P. KOMITOV and K. NAIDENOVA, Bulgarian Patent no. 31868 (1982).
20. M. MIHAILOV and L. MINKOVA, *Coll. & Polym. Sci.* **265** (1987) 681.

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