

Influence of Two-Stage Drawing Conditions on Ultradrawing Behavior of Gel Films of Ultrahigh-Molecular-Weight Polyethylene and Low-Molecular-Weight Polyethylene Blends

JEN-TAUT YEH, SHENG-SHAN CHANG

Graduate School of Textile and Polymer Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan

Received 5 October 1999; accepted 14 March 2000

ABSTRACT: The influence of two-stage drawing conditions on the ultradrawing behavior of the gel films of ultrahigh-molecular-weight polyethylene/low-molecular-weight polyethylene blends is reported in this article. The critical draw ratios (λ_c) of the gel films prepared near their critical concentrations were found to depend significantly on the draw ratio attained in the first drawing stage (D_{1r}) and on the temperature utilized in the second drawing stage (T_{sec}). After drawing the gel films to a fixed draw ratio in the first drawing stage, each two-stage drawn gel film was made to exhibit a maximum λ_c (λ_{cmax}) by drawing the drawn gel film at its corresponding optimum T_{sec} . In addition, the optimum T_{sec} was found to increase significantly with the D_{1r} value of the drawn gel films. It is worth noting, on the other hand, that the λ_{cmax} of two-stage drawn gel films increased consistently with an increasing D_{1r} , until its value reached an optimum value of 160. These results clearly suggest that, as T_{sec} and D_{1r} are increased to their optimum values, the λ_{cmax} of the two-stage drawn gel films can be improved further so as to be higher than those of the corresponding one-stage drawn gel films. These interesting phenomena were investigated in terms of reduced viscosities of the solutions and by an analysis of the thermal, birefringence, and tensile properties of the drawn gel films. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1890–1901, 2001

Key words: ultradrawing; gel; temperature utilized in second drawing stage (T_{sec}); achievable draw ratios (D_{ra}); draw ratio attained in first drawing stage (D_{1r}); maximum critical draw ratio (λ_{cmax})

INTRODUCTION

Competition among high-performance fibers has prompted new processing methods for obtaining high-performance fibers of ultrahigh-molecular-

weight polyethylene (UHMWPE).^{1–11} Among these processing methods, the gel spinning/casting method^{2,3} has attracted much attention since its invention in the 1970s because of its availability in the production of commercial high-strength/modulus fibers. This method of ultradrawing the gel specimens spun or cast from gel solutions of UHMWPE is referred to as the gel-deformation method. As reported by several authors,^{12–20} the tensile strengths and moduli of the drawn gel specimens were found to improve consistently with their draw ratios, although their orientation

Correspondence to: J.-T. Yeh (jyeh@http730.tx.ntust.edu.tw).

Contract grant sponsor: National Science Council; contract grant numbers: NSC 83-0405-E011-076, 84-2216-E011-006, 85-2216-E011-011, 88-2216-E011-028.

Journal of Applied Polymer Science, Vol. 79, 1890–1901 (2001)
© 2001 John Wiley & Sons, Inc.

and crystallinity values increased slowly at draw ratios above about 30.^{16,20} The drawability of the gel specimens was found to depend principally on the compositions of the solutions from which the gels were made.^{12–15} The achievable drawability was reduced significantly, as the gel films were prepared from solutions whose concentrations deviated from their critical values, in which the numbers of entanglements in the coherent network structure of the gel films were too many or too few to yield the maximum extension of the UHMWPE during the gel-deformation processes.^{12–17}

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,^{14–17,21–24} 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. 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 UHMWPEs, which not only can increase the production rate of these high-performance specimens but can also reduce the amounts of solvent required for recycling. However, the literature shows very few investigations have ever been reported on the preparation and drawing of gel specimens of UHMWPE–LMWPE blends.^{14–17,21–24}

Our recent studies^{14–17} focused on the achievable draw ratios (D_{ra}) of the gel films of each weight ratio of LMWPE to UHMWPE as it approached a maximum value, when prepared at concentrations close to their critical concentrations (C_c). These critical draw ratios (λ_c) of gel films prepared near their C_c were found to decrease significantly with an increasing amount of LMWPE added to the gel films. However, the addition of a small but optimum amount of LMWPE to the films of UHMWPE–LMWPE blends can significantly improve their λ_c compared to that of gel film prepared from pure UHMWPE gel solution, and this improvement in λ_c is enhanced further with decreasing lengths of short-chain branches of LMWPEs.¹⁵ The drawability of these gel films was found to depend significantly on the temperatures used in the one- and two-stage

Table I Compositions of Solutions of UHMWPE–LMWPE Blends

Sample	Weight Ratio UHMWPE/LMWPE	Concentration (g/dL)
UL _{-0.6}	98/2	0.6
UL _{-0.7}		0.7
UL _{-0.8}		0.8
UL _{-0.9}		0.9
UL _{-1.0}		1.0

drawing processes. The λ_c of each gel film was found to approach a maximum value when the gel film was drawn at an “optimum” temperature, ranging from 95°C to 105°C. In addition, it was discovered that the maximum λ_c of two-stage drawn gel films could be improved even more, to be higher than those of corresponding single-stage drawn gel films. This was accomplished by having the drawn gel films drawn at an additional, “optimum,” temperature of 115°C, in a second drawing stage following a first draw at 95°C to a draw ratio of 40.¹⁶

In this study the ultradrawing behavior of gel films of plain UHMWPE and UHMWPE–LMWPE blends was investigated using the two-stage drawing process, during which varying temperatures were used in the second drawing stage on drawn gel films after a first draw at 95°C to different fixed draw ratios. The influence of the two-stage drawing conditions on the drawability, birefringence, and thermal behaviors of the UHMWPE–LMWPE gel films was also investigated.

EXPERIMENTAL

Materials and Sample Preparation

The UHMWPE resin used in this study, with a weight-average molecular weight (\bar{M}_w) of 4.5×10^6 , will be called resin U in the following discussion. The linear LMWPE used in this study will be called resin L, which is a linear high-density polyethylene and has a \bar{M}_w of 8.9×10^4 . Resins U and L were supplied by Bruce Lu of Yung Chia Chemical Industrial Corporation, Kaohsiung, Taiwan. UHMWPE and LMWPE were mixed at a weight ratio of 98:2 and then dissolved in decalin at 135°C for 90 min, to which 0.1 wt % of di-*t*-butyl-*p*-cresol was added as an antioxidant. The compositions of the gel solutions prepared in this study are summarized in Table I.

Table II C_c , Solution Compositions and D_{ra} of One- and Two-Stage Drawn Gel Films

Sample	C_c	D_{ra} of One-Stage Drawn Gel Film Drawn at					
		95°C	105°C	115°C			
UL _{-0.6}	0.76	277	242	222			
UL _{-0.7}		360	301	295			
UL _{-0.8}		288	286	268			
UL _{-0.9}		268	254	250			
UL _{-1.0}		238	229	221			
Sample	C_c	D_{ir} at 95°C	D_{ra} of Two-Stage Drawn Gel Film Drawn at a T_{sec} of				
			105°C	115°C	125°C	135°C	140°C
UL _{-0.6}	0.76	15	289	281	258		
UL _{-0.7}			372	291	274		
UL _{-0.8}			294	283	251		
UL _{-0.9}			280	272	235		
UL _{-1.0}			267	261	228		
UL _{-0.6}	0.76	30	344	329	325		
UL _{-0.7}			389	377	369		
UL _{-0.8}			367	350	280		
UL _{-0.9}			361	324	279		
UL _{-1.0}			304	289	264		
UL _{-0.6}	0.76	40	356	363	342		
UL _{-0.7}			391	425	384		
UL _{-0.8}			375	407	358		
UL _{-0.9}			345	385	321		
UL _{-1.0}			315	374	304		
UL _{-0.6}	0.76	60	383	405	396	341	
UL _{-0.7}			417	453	434	368	
UL _{-0.8}			402	421	405	314	
UL _{-0.9}			375	410	384	309	
UL _{-1.0}			344	392	356	272	
UL _{-0.6}	0.76	80	401	420	413	365	
UL _{-0.7}			428	462	452	392	
UL _{-0.8}			417	433	427	377	
UL _{-0.9}			393	422	411	359	
UL _{-1.0}			367	406	392	346	
UL _{-0.6}	0.76	120	409	427	451	449	360
UL _{-0.7}			429	471	508	488	391
UL _{-0.8}			421	439	463	457	383
UL _{-0.9}			401	432	442	437	363
UL _{-1.0}			372	407	421	406	349
UL _{-0.6}	0.76	160	419	438	472	489	439
UL _{-0.7}			430	488	525	540	476
UL _{-0.8}			428	443	479	501	451
UL _{-0.9}			402	438	453	471	423
UL _{-1.0}			393	412	432	457	401

Table II Continued

Sample	C_c	D_{1r} at 95°C	D_{ra} of Two-Stage Drawn Gel Film Drawn at a T_{sec} of				
			105°C	115°C	125°C	135°C	140°C
UL _{-0.6}	0.76	200	373	392	421	466	400
UL _{-0.7}			397	431	480	500	445
UL _{-0.8}			378	411	452	481	423
UL _{-0.9}			337	381	421	445	400
UL _{-1.0}			306	353	389	414	371

The hot homogenized solutions were poured into an aluminum tray and cooled in an oven to form the gel films at 35°C. The decalin was then evaporated from the gel in an oven. The dried gel was immersed in ethanol to remove antioxidants and residual traces of Decalin. The prepared gel film was about 250 μm thick.

Determination of Viscosity and Critical Concentration of the Solution

The viscosities of the polymer solutions were determined at 135°C using a Brookfield viscometer model LVDV-II⁺. As explained in our previous articles,^{14,15} two distinct regions were found on the plots of the reduced viscosities against the concentrations of the polymer solutions. The re-

duced viscosities increase slightly with concentration in region 1, which is 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 the C_c was determined by the intersection of the two straight lines drawn parallel to the two distinct regions shown in these plots. The values of the C_c of the solutions prepared in this study were determined in our previous studies^{14,15} and will be described in the Results and Discussion section.

One- and Two-Stage Drawing Experiments

The strip specimens used in one- and two-stage drawing experiments were cut from the dried gel

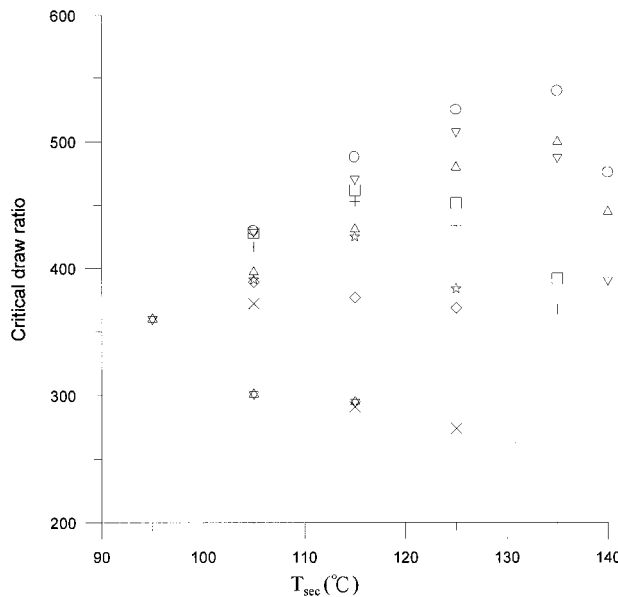


Figure 1 The critical draw ratio (λ_c) of one-stage drawn (\star) and two-stage drawn UL_{-0.7} gel films drawn at varying T_{sec} and with a D_{1r} of (\times)15, (\diamond)30, (\star)40, ($+$)60, (\square)80, (∇)120, (\circ)160, and (\triangle)200.

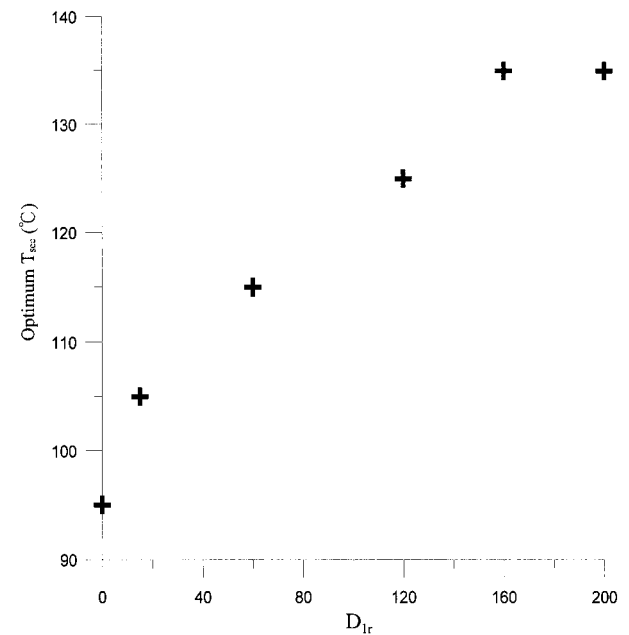


Figure 2 The plot of optimum T_{sec} as a function of D_{1r} of two-stage drawn UL_{-0.7} gel films.

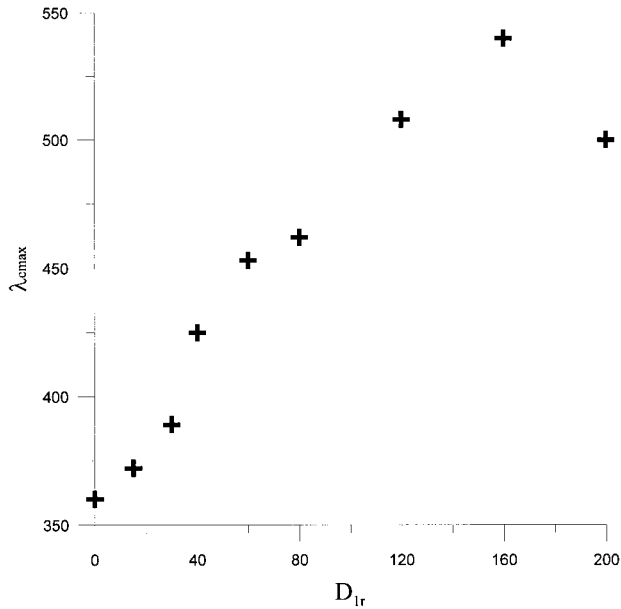


Figure 3 The maximum critical draw ratio (λ_{cmax}) of two-stage drawn $UL_{-0.7}$ gel films with varying D_{1r} .

films and then stretched on a Tensilon testing machine model RTA-1T equipped with a temperature-controlled oven at a crosshead speed of 20

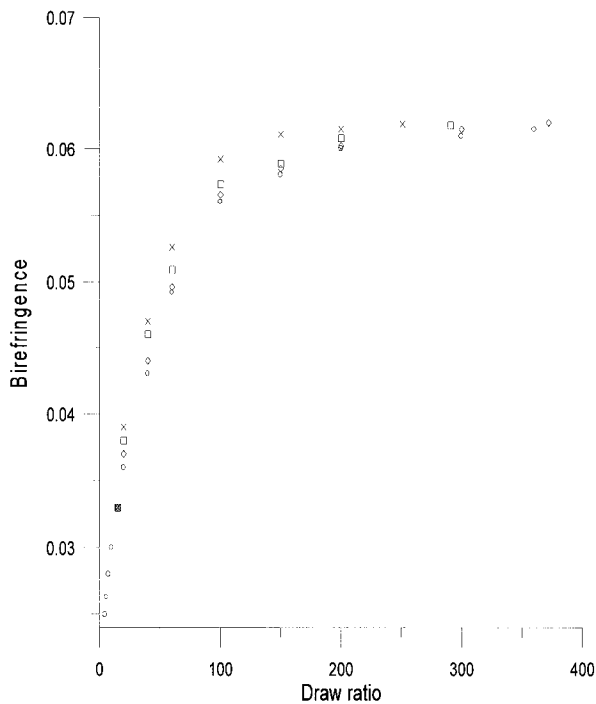


Figure 4 Birefringence of one-stage drawn (\circ) and varying draw ratios of two-stage drawn $UL_{-0.7}$ gel films with D_{1r} of 15 at (\diamond) 105°C, (\square) 115°C, and (\times) 125°C.

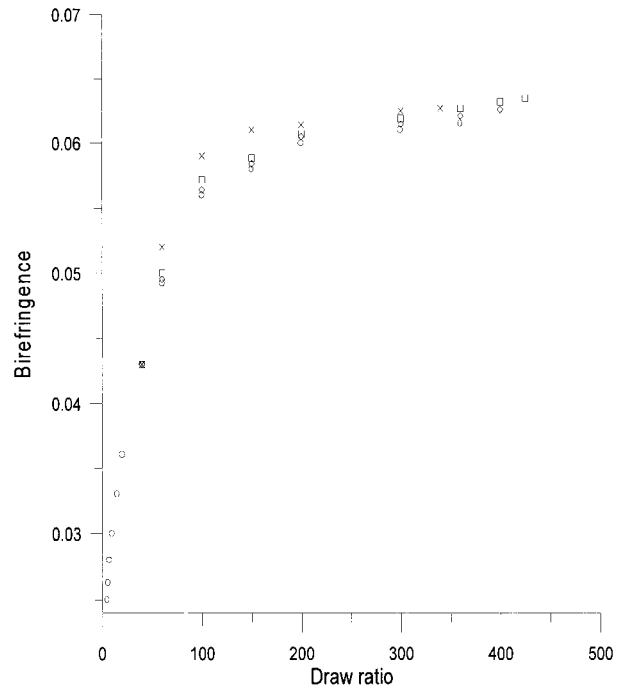


Figure 5 Birefringence of one-stage drawn (\circ) and varying draw ratios of two-stage drawn $UL_{-0.7}$ gel films with D_{1r} of 40 at (\diamond) 105°C, (\square) 115°C, and (\times) 125°C.

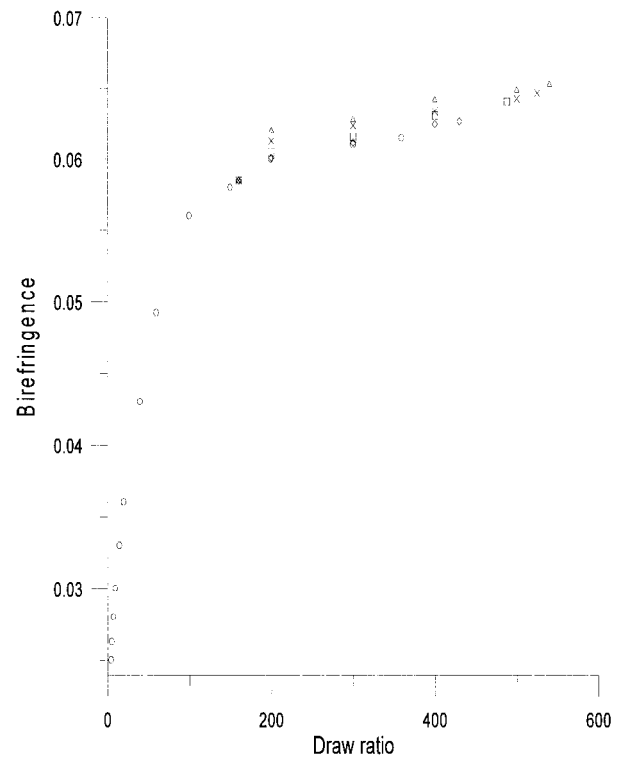


Figure 6 Birefringence of one-stage drawn (\circ) and varying draw ratios of two-stage drawn $UL_{-0.7}$ gel films with D_{1r} of 160 at (\diamond) 105°C, (\square) 115°C, (\times) 125°C, and (\triangle) 135°C.

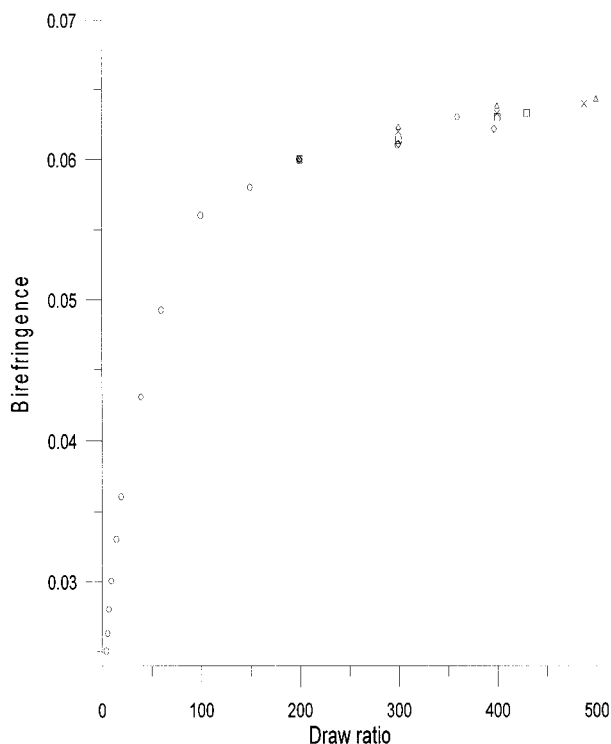


Figure 7 Birefringence of one-stage drawn (\circ) and varying draw ratios of two-stage drawn $UL_{-0.7}$ gel films with D_{1r} of 200 at (\diamond) 105°C, (\square) 115°C, (\times) 125°C, and (\triangle) 135°C.

mm/min. The specimens were 30 mm long and 10 mm wide. They were first drawn at 95°C to draw ratios of 15, 30, 40, 80, 120, 160, and 200. These drawn specimens were then further drawn at 105, 115, 125, 135, and 140°C, respectively. This type of drawing experiment is called the two-stage drawing process in the following discussion. The draw ratio of each specimen was determined as the ratio of the marked displacement after drawing to the marked displacement before drawing. For purposes of comparison, the strip specimens were also drawn at 95°C up to varying draw ratios at a crosshead speed of 20 mm/min. This type of drawing experiment will be called the one-stage drawing process. The marked displacement before drawing was 5 mm. The tensile properties of the one- and two-stage drawn gel films were also determined using a Tensilon testing machine model RTA-1T at 28°C and at a crosshead speed of 20 mm/min.

Birefringence and Thermal Analysis

Birefringence of the drawn gel films was measured by using a polarizing microspectrumeter

model TFM-120 AFT. The thermal behavior of all samples was performed on a Du Pont 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 mL/min. Samples weighing 0.5 mg were placed in standard aluminum sample pans for a determination of their thermal behavior.

RESULTS AND DISCUSSION

Drawing Properties of One- and Two-Stage Drawn Gel Films of UHMWPE–LMWPE Blends

The influence of drawing conditions on the achievable draw ratios (D_{ra}) of two-stage drawn gel films of plain UHMWPE and of UHMWPE–LMWPE blends is summarized in Table II and Figure 1. After drawing the gel specimens to any fixed draw ratio (D_r) at 95°C, the draw ratios of the two-stage drawn gel films prepared at concentrations close to their critical concentration (C_c) are always higher than those of other gel films prepared at concentrations deviating from their C_c (Table II).

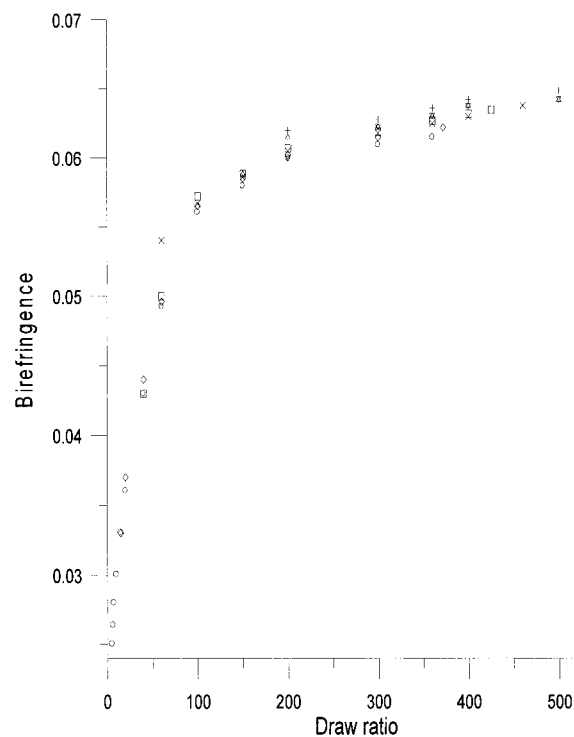


Figure 8 Birefringence of one-stage drawn (\circ) and varying draw ratios of two-stage drawn $UL_{-0.7}$ gel films with D_{1r} of (\diamond) 15, (\square) 40, (\times) 80, (\triangle) 120, ($+$) 160, and (∇) 200, all drawn at their optimum T_{sec} .

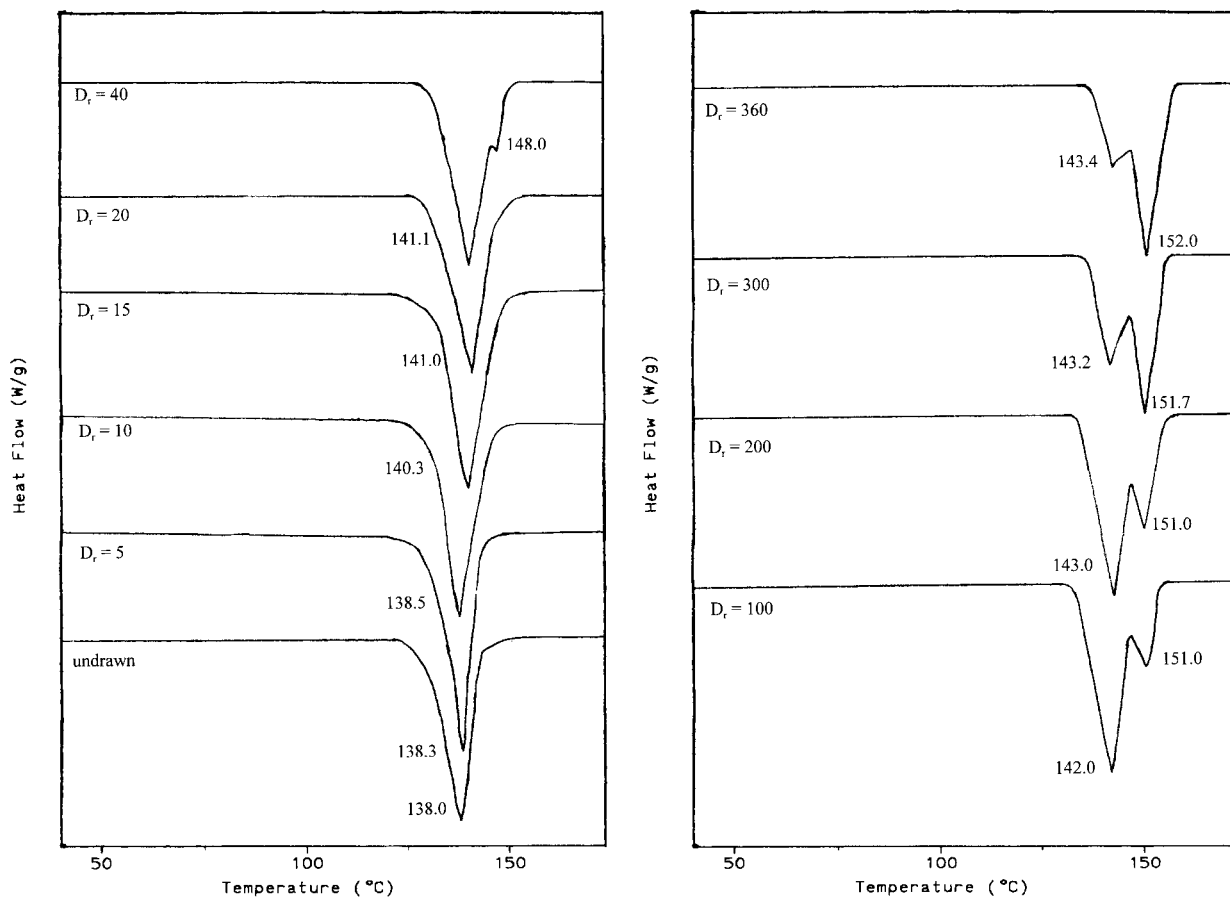


Figure 9 DSC thermograms of varying draw ratios of one-stage drawn $UL_{-0.7}$ gel films drawn at 95°C .

The achievable D_{ra} obtained for a sample prepared near its C_c will be referred to as the critical draw ratio (λ_c) in the following discussion. It is interesting to note that, after drawing the gel specimens up to a fixed draw ratio ranging from 40 to 80, the λ_c of two-stage drawn gel films can be further improved by drawing the gel specimens in the second stage at an optimum temperature of about 115°C (Table II and Fig. 1). The λ_c of the two-stage drawn gel specimens then decreases significantly as the temperatures used in the second drawing stage (T_{sec}) increases to 125°C and 135°C , respectively. For instance, after drawing the $UL_{-0.7}$ gel specimens up to a draw ratio of 60 at 95°C , the maximum λ_c (λ_{cmax}) of the gel film drawn at a T_{sec} of 115°C was about 20% higher than that of gel films drawn at a T_{sec} of 135°C (Fig. 1). A similar optimum T_{sec} was found for other two-stage drawn $UL_{-0.7}$ gel films with different first-stage draw ratios (D_{1r}). In fact, the optimum T_{sec} associated with λ_{cmax} of two-stage

drawn gel films increases significantly with an increasing D_{1r} . As shown in Table II and Figure 2, the optimum T_{sec} increased from 105°C to 135°C as the D_{1r} of $UL_{-0.7}$ gel films increased from 15 to 200, respectively. On the other hand, it is worth noting that the λ_{cmax} of the two-stage drawn gel films increased consistently with an increasing D_{1r} value until its value reached about 160 (Fig. 3).

In contrast, the value of λ_{cmax} became significantly lower, to 500, after $UL_{-0.7}$ gel film was first drawn up to a draw ratio of 200 at 95°C . Finally, it is important to note that the λ_{cmax} value of the two-stage drawn gel films can be another 50% higher (540 vs. 360) than the maximum λ_c obtained by drawing $UL_{-0.7}$ gel film using the optimum one-stage drawing temperature of 95°C . These results clearly suggest that the λ_{cmax} of the two-stage drawn gel films can be further improved to be even higher than those of the corresponding one-stage drawn gel films, as T_{sec} and D_{1r} are increased to their optimum values.

Birefringence of One- and Two-Stage Drawn Gel Films of UHMWPE and UHMWPE/LMWPE Blends

Typical birefringence values of one- and two-stage drawn gel films are shown in Figures 4–7. The birefringence values of one- and two-stage drawn UL_{-0.7} gel films initially increase dramatically with the draw ratio. The increasing rate of birefringence (IRB) becomes slower when the draw ratios of the drawn gel films are greater than about 15. In fact, the IRB reduces consistently with the increasing draw ratio until its value reaches about 200. After this value, the IRB remains approximately constant with an increasing draw ratio. On the other hand, it is interesting to note that at a fixed draw ratio, the two-stage drawn UL_{-0.7} gel films drawn at a higher T_{sec} always exhibit higher values of birefringence than those of gel films with the same D_{1r} but drawn at a lower T_{sec} . This is presumed to be because of the higher mobility of these UHMWPE molecules at higher temperatures, such that the UHMWPE molecules can be more easily oriented along the drawing direction during the second drawing stage. However, it is not completely clear why the IRB reduces consistently as the draw ratio increases from about 15 to 200 and remains approximately constant if the draw ratios of the drawn gel films are higher than 200 or lower than 15. Figure 8 summarizes the birefringence values of two-stage drawn UL_{-0.7} gel films drawn at their optimum T_{sec} .

It is of some interest that at a fixed draw ratio, the birefringence values of gel films drawn at a fixed optimum T_{sec} increase consistently with an increasing D_{1r} until its value reaches 160. The birefringence values then go down significantly as D_{1r} reaches 200. For example, after drawing UL_{-0.7} gel film up to a draw ratio of 160 at 95°C, the birefringence value of the two-stage drawn UL_{-0.7} gel film with a draw ratio of 200 or 300 is about 5–10% higher than those of the one- and two-stage drawn gel specimens with D_{1r} values other than 160.

Thermal Analysis of One- and Two-Stage Drawn Gel Films

Figures 9–12 summarize the DSC thermograms of one- and two-stage drawn UL_{-0.7} gel films of varying draw ratios. A main melting endotherm with a peak temperature of about 138°C was found for the undrawn UL_{-0.7} gel film. No significant change in the shape and peak temperature

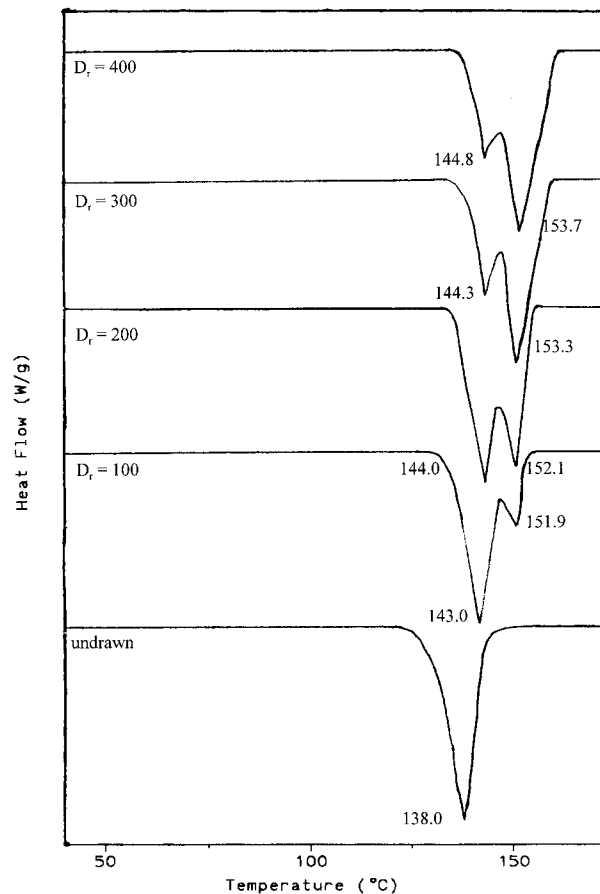


Figure 10 DSC thermograms of varying draw ratios of two-stage drawn UL_{-0.7} gel films with a D_{1r} of 40 and a T_{sec} of 115°C.

was found on the main melting endotherm of the one-stage drawn UL_{-0.7} gel films until they were drawn up to a D_r of 10 at 95°C. In contrast, as described previously, the birefringence values of one- and two-stage drawn UL_{-0.7} gel films increase dramatically with D_r until reaching about 15. After this value, the increasing rate of birefringence reduces consistently with D_r until its value reaches about 200. These results suggest that the initial rise in birefringence values of the drawn gel films is mostly due to the increase in UHMWPE orientation in the amorphous regions but is not due to the change in orientation and/or crystal perfection in the crystalline regions of the drawn UL_{-0.7} gel films. However, at higher draw ratios, the beneficial birefringence effect from the increasing molecular orientation of the amorphous regions may become less prominent and even negligible compared to that from the increasing molecular orientation of the crystalline regions of the drawn gel films. It is, therefore, the

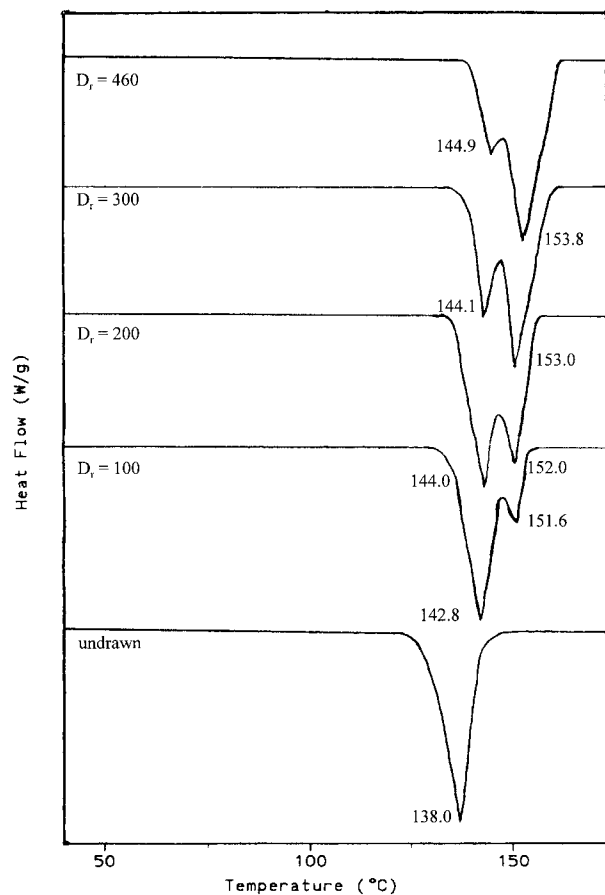


Figure 11 DSC thermograms of varying draw ratios of two-stage drawn $UL_{-0.7}$ gel films with a D_{1r} of 80 and a T_{sec} of 115°C.

increasing rate of birefringence that reduces consistently as the draw ratios increase from about 15 to 200 and remain approximately constant as long as the values of D_r are above 200.

A slight rise on the right of the main melting endotherm was found when the $UL_{-0.7}$ gel film was stretched to a D_r of about 20 at 95°C (Fig. 9). In fact, a small shoulder at a temperature around 148°C could be clearly observed on the right of the main melting endotherm when the one- or two-stage drawn $UL_{-0.7}$ gel films were stretched to a D_r of 40 (Fig. 9). This small shoulder continued to grow into another melting endotherm at the expense of the magnitude of the original main melting endotherm. The melting temperatures of the main and newly developed melting endotherms then increased significantly as the draw ratios of $UL_{-0.7}$ gel films increased (Figs. 9–12).

However, it is not completely clear what accounts for the interesting double-melting behav-

ior found above. It is generally recognized that the orientation of the polymer chain and reduction of crystal defects during drawing can enhance the perfection and melting temperature of the crystals. Presumably, the double-melting endotherms found above reflect the melting of two different groups of crystals with different degrees of crystal perfection. The fold-chain UHMWPE crystals not only reform into thicker and more perfect lamellae during drawing but also gradually transform into extended-form crystals at higher draw ratios. However, even up to a draw ratio of 540, the fully extended chain crystals are unlikely to be present as the main portion of the drawn $UL_{-0.7}$ gel films because their corresponding tensile strengths are still far below the theoretical tensile strengths of the fully extended chain crystals.²⁵

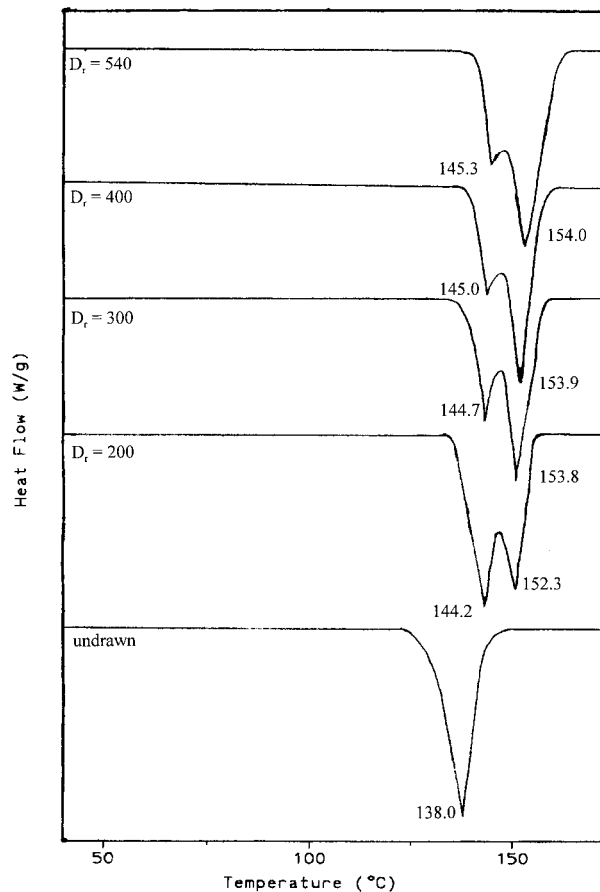


Figure 12 DSC thermograms of varying draw ratios of two-stage drawn $UL_{-0.7}$ gel films with a D_{1r} of 160 and a T_{sec} of 135°C.

Tensile Properties of One- and Two-Stage Drawn Gel Films of UHMWPE-LMWPE Blends

In a way similar to the improvement in the birefringence properties of drawn $UL_{-0.7}$ gel films, the tensile strengths and moduli of one- and two-stage drawn $UL_{-0.7}$ gel films drawn at their optimum T_{sec} were found initially to improve dramatically with the draw ratios (Figs. 13 and 14). The increasing rates of tensile strengths and moduli then reduced significantly with further increases in the draw ratios. At even higher draw ratios (say 200), the increasing rates of tensile strengths and moduli then remained relatively constant with the increasing draw ratios. After drawing $UL_{-0.7}$ gel films up to a fixed draw ratio at 95°C , the tensile strengths and moduli of the two-stage drawn $UL_{-0.7}$ gel films of the same draw ratios were found to improve substantially because they were drawn at a higher T_{sec} (Figs. 15 and 16).

Most interestingly, at a fixed draw ratio, the tensile strengths and moduli of the two-stage drawn gel films drawn at their optimum T_{sec} were also found to improve substantially as D_{1r}

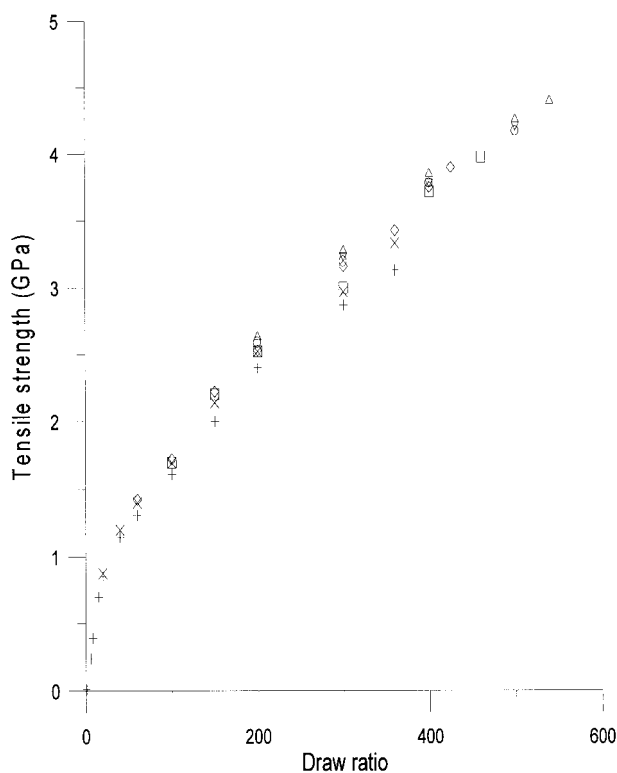


Figure 13 Tensile strengths of one- (+) and two-stage drawn $UL_{-0.7}$ gel films drawn at their optimum T_{sec} and with a D_{1r} of (x) 15, (◇) 40, (□) 80, (○) 120, (△) 160, and (▽) 200.

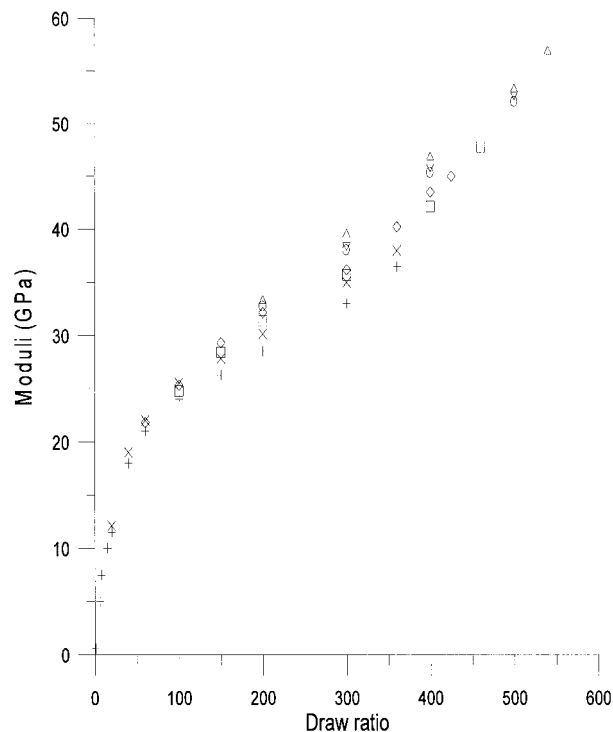


Figure 14 Moduli of one- (+) and two-stage drawn $UL_{-0.7}$ gel films drawn at their optimum T_{sec} and with D_{1r} of (x) 15, (◇) 40, (□) 80, (○) 120, (△) 160, and (▽) 200.

was increased to its optimum value of 160 (Figs. 13 and 14). It is generally believed that the mechanical properties of the drawn gel films depend mainly on the degree of orientation of the drawn gel films, as long as their molecular weights are constant.²⁶⁻²⁷ As mentioned previously, the degree of orientation and/or birefringence, tensile strength, and moduli of the two-stage drawn $UL_{-0.7}$ gel films all exhibited similar draw-ratio dependence. Moreover, at a fixed draw ratio, the degree of orientation and/or birefringence improved consistently with the increasing T_{sec} and D_{1r} until T_{sec} and D_{1r} were increased to their optimum values. These results suggest that a good orientation of UHMWPE molecules along the drawing direction has a beneficial influence on the tensile strengths and moduli of the gel films, which can be obtained by drawing the gel films using their corresponding optimum T_{sec} and D_{1r} .

CONCLUSIONS

The achievable draw ratios of the two-stage drawn $UL_{-0.7}$ gel films prepared at concentra-

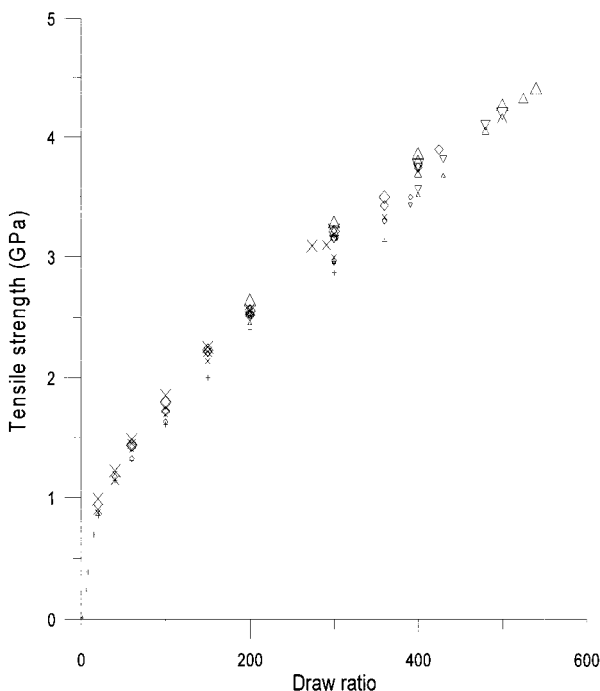


Figure 15 Tensile strengths of one- (+) and two-stage drawn $UL_{-0.7}$ gel films with D_{1r}/T_{sec} of (\times) 15/105°C, (\times) 15/115°C, (\times) 15/125°C, (\odot) 40/105°C, (\odot) 40/115°C, (\odot) 40/125°C, (Δ) 160/105°C, (Δ) 160/115°C, (Δ) 160/125°C, (Δ) 160/135°C, (∇) 200/105°C, (∇) 200/115°C, (∇) 200/125°C, and (∇) 200/135°C.

tions near their critical concentrations (C_c) are always higher than those of other gel films prepared at concentrations deviating from their C_c . The critical draw ratios (λ_c) of the gel films prepared near their C_c were found to depend significantly on the draw ratio obtained in the first drawing stage (D_{1r}) and on the temperature utilized in the second drawing stage (T_{sec}). After drawing the gel films up to a fixed draw ratio in the first drawing stage, the maximum λ_c (λ_{cmax}) was always obtained by drawing the drawn gel film at its corresponding optimum T_{sec} . It was found that the optimum T_{sec} further increased significantly with the increasing D_{1r} of the drawn gel films. On the other hand, the λ_{cmax} of two-stage drawn gel films increased consistently with an increasing D_{1r} until its value reached an optimum value of 160. In fact, by using an optimum D_{1r} and T_{sec} , a 50% improvement of the λ_{cmax} of the two-stage drawn gel films can be achieved, making it higher than the maximum λ_c obtained by drawing the gel films using the optimum one-stage drawing temperature at 95°C. The birefringence, tensile strengths, and moduli of the two-

stage drawn gel films were initially found to improve dramatically with the draw ratio. With further increase in the draw ratio, a significant reduction in the increasing rates of these properties then ensued until the draw ratio reached a value of about 200. In addition, at a fixed draw ratio, the degree of orientation and/or birefringence improved consistently with the increasing T_{sec} and D_{1r} until they reached their optimum values. These results suggest that good molecular orientation of UHMWPE molecules along the drawing direction has a beneficial influence on the tensile and moduli of the gel films, which can be obtained by drawing the gel films using their corresponding optimum T_{sec} and D_{1r} . Thermal and birefringence results suggest that the initial rise in birefringence values is due mostly to the increase in UHMWPE orientation in the amorphous regions but is not the result of the change in orientation and/or crystal perfection in the crystalline regions of the drawn $UL_{-0.7}$ gel films. However, at higher draw ratios, the beneficial birefringence effect from the increasing molecular

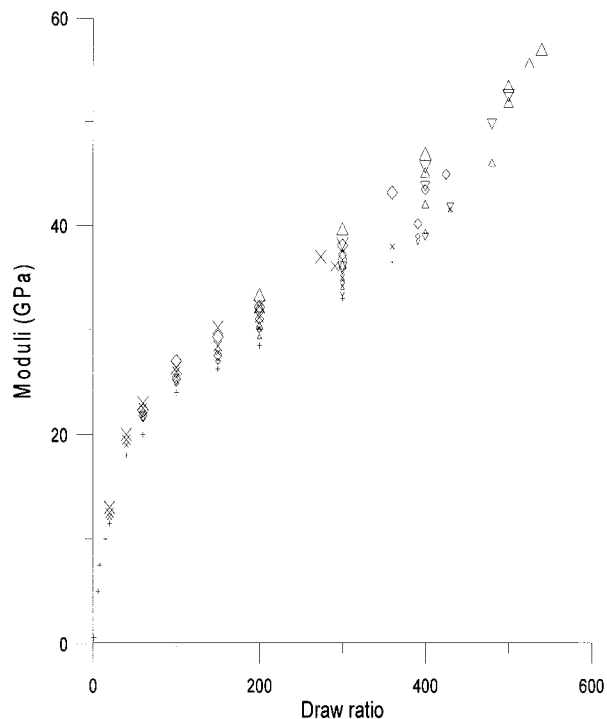


Figure 16 Moduli of one- (+) and two-stage drawn $UL_{-0.7}$ gel films with D_{1r}/T_{sec} of (\times) 15/105°C, (\times) 15/115°C, (\times) 15/125°C, (\odot) 40/105°C, (\odot) 40/115°C, (\odot) 40/125°C, (Δ) 160/105°C, (Δ) 160/115°C, (Δ) 160/125°C, (Δ) 160/135°C, (∇) 200/105°C, (∇) 200/115°C, (∇) 200/125°C, and (∇) 200/135°C.

orientation of amorphous regions may become less prominent and even negligible compared to that from the increasing molecular orientation of the crystalline regions of the drawn gel films.

The authors would like to express their thanks to Mr. Bruce Lu of Yung Chia Chemical Industrial Corporation for supplying the UHMWPE and L resins.

REFERENCES

- Zwijnenburg, A.; Pennings, A. *Colloid Polym Sci* 1975, 253, 452.
- Smith, P.; Lemstra, P. J. *Macromol Chem* 1979, 180, 2983.
- Smith, P.; Lemstra, P. J.; Pijpers, J. P. L.; Kiel, A. M. *Colloid Polym Sci* 1981, 259, 1070.
- Ohta, T.; Okada, F. U.S. Pat. 4,643,865 (1987).
- Ohta, T.; Okada, F.; Hayashi, M.; Mihoichi, M. *Polymer* 1989, 30, 2170.
- Furuhata, K.; Yokokawa, T.; Ohsawa, K.; Miyasaka, K. *Polym Prepr Jpn* 1983, 32, 874.
- Kanamoto, T.; Ooki, T.; Tanaka, K.; Takeda, M. *Polym Prepr Jpn* 1983, 32, 741.
- Smith, P.; Chanzy, H. D.; Rotzinger, B. P. *Polym Commun* 1985, 26, 258.
- Chanzy, H. D.; Rotzinger, B. P.; Smith, P. Patent WO-8703288 (1987).
- Smith, P.; Chanzy, H. D.; Rotzinger, B. P. *J Mater Sci* 1987, 22, 523.
- Kanamoto, T.; Ohama, T.; Tanaka, K.; Takeda, M.; Porter, R. S. *Polymer* 1987, 28, 1517.
- Sawatari, C.; Okumura, T.; Matsuo, M. *Polymer J* 1986, 18, 741.
- Darras, D.; Sequela, R.; Rietsch, F. *J Polym Sci, Polym Phys Ed* 1992, 30, 349.
- Yeh, J. T.; Lin, Y. L.; Fan-Chiang, C. C. *Macromol Chem Phys* 1996, 197, 3531.
- Yeh, J. T.; Wu, H. C. *Polym J* 1998, 30, 1.
- Yeh, J. T.; Chang, S. S.; Yen, M. S. *J Appl Polym Sci* 1998, 70, 149.
- Yeh, J. T.; Chang, S. S. *J Mater Sci*, to appear.
- Ohta, T. *Polym Eng Sci* 1983, 23, 697.
- Hoogsteen, W.; ten Brinke, G.; Pennings, A. J. *Colloid Polym Sci* 1988, 266, 1003.
- Xiao, C.; Zhang, Y.; An, S.; Ji, G. *J Appl Polym Sci* 1996, 59, 531.
- Nakajima, N.; Ibata, J. *Jpn. Pat.* 57,177,035, 57,177,036, 57,177,037 (1983).
- Sawatari, C.; Matsuo, M. *Polymer* 1989, 30, 1603.
- Simeonov, I.; Nikolova, Z.; Komitov, P.; Naidenova, K. *Bul. Pat.* 31,868 (1982).
- Mihailov, M.; Minkova, L. *Colloid Polym Sci* 1987, 265, 681.
- Ohta, T.; Sen, I. *Gakkaishi* 1984, 40, 407.
- Ohta, T. *Polym Eng Sci* 1983, 23, 697.
- Hoogsteen, W.; ten Brinke, G.; Penning, A. J. *Colloid Polym Sci* 1988, 266, 1003.