

Heat Setting of Stretched and Microvoided PE/CaCO₃ Films

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ABSTRACT: Calcium-carbonate-filled linear low-density polyethylene (LLDPE) films play an important role in the hygienics market because these materials allow for the diffusion of water vapor (breathability) and retain a liquid barrier while providing a barrier to liquids. This is achieved when properly formulated composites are stretched to create pores. There are many important issues surrounding this technology; this report focuses on the effects of poststretching heat-set treatment on moisture vapor transmission rate (MVTR), dynamical mechanical thermal analysis (DMTA), tensile heat distortion temperature (THDT), and differential scanning calorimetry (DSC) thermal transitions of the porous film properties. Eastman personnel provided the LLDPE/CaCO₃ breathable films for this study. In general, the film properties were insensitive to heat-setting time beyond that of 1 min. This result suggests that the molecular reorientation and recrystallization associated with the changes in film properties occur rapidly. Properties were, however, strongly sensitive to the heat-set temperature when MVTR decreased and DMTA properties [specifically storage modulus (E') and the α -transition temperature] increased as the heat-set temperature increased. This is believed to have been mainly caused by pore closure and the annealing of crystalline regions. The heat-set temperature was easily detectable by DSC techniques when a thermal transition was apparent at the applied temperature, and changes in the heat of fusion for the sample could be observed. Ultimately, the changes in the properties of these porous films were related to changes in the molecular orientation and crystallinity of the matrix in combination with changes in the void structure of the composite. In particular, changes in E' could be related to these separate effects. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2454–2471, 2001

Key words: polyethylene; calcium carbonate; porous; breathable; heat setting

INTRODUCTION

Mineral-filled polyolefin films play an important role in the hygienics market. When properly formulated, these materials can be stretched under appropriate conditions to create a porous structure that allows for the diffusion of water vapor while providing a liquid water barrier.^{1–7} A series

of articles have described studies of CaCO₃-filled polypropylene (PP) microporous films where the effects of filler size and biaxial stretch ratio on pore structure were examined.^{8–11} The CaCO₃ loading was fixed at 60 wt % because the literature shows that at least 30 vol % is required to create an interconnecting series of pores, thus allowing for vapor diffusion.² For the PP/CaCO₃ system, it was shown that a higher average CaCO₃ particle size and/or higher stretch ratios result in the creation of higher degrees of porosity; however, larger stretch ratios were shown to create an imbalance in certain mechanical prop-

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Table I Average Data for Non-Heat-Set Films

	Material						
	–	A	B	C	D	E	F
MD × TD							
stretch ratio	1 × 1	1 × 1.5	1.375 × 1	1.19 × 1	1.375 × 1.5	1.125 × 1.125	1 × 1.375
Total area							
strain	0	0.5	0.375	0.19	1.063	0.266	0.375
MVTR (g mL m ⁻² day ⁻¹)	40	3117	2799	1941	3723	2083	2417
Film thickness	2.5	2.41	2.47	2.49	2.64	2.45	2.41
MVTR (g m ⁻² day ⁻¹)	16	1293	1134	780	1410	850	1003
THDT, MD (°C)	74.3	60.9	62.9	67.3	115.4	103.7	75
THDT, TD (°C)	67.8	93.5	64	61.8	46	79.3	114.4
T _{tan δ} ^m , MD (°C)	78	61	73	83	20	83	66
T _{tan δ} ^m , TD (°C)	82	27	79	77	61	86	29
E' at 25°C, MD (10 ⁸ Pa)	5.2	3.5	1.8	2.2	0.7	2.4	3.8
E' at 25°C, TD (10 ⁸ Pa)	4.8	1.1	3.8	4.2	0.34	0.93	1.5

erties without the benefit of increased moisture vapor transmission rates (MVTRs). Recent work in this lab for CaCO₃-filled linear low-density polyethylene (LLDPE) films has shown that a Fickian diffusion model accurately describes water vapor transmission when the MVTR was related to pore characteristics.¹² It was demonstrated that the critical factor affecting MVTR for a fixed CaCO₃ type and loading was the specific pore number (number of pores per gram), where more pores increased the vapor transmission rates. The number of pores was shown to increase with the stretch ratio, whereas the pore radius remained relatively constant.

There are many important issues surrounding this application, such as the quantity and type of filler, polyolefin choice, stretching method, and poststretching film treatment.^{2,13,14} This study focused on the latter with regard to heat setting, which as seen, has a significant effect on film properties. In industry, these films are heat-set under restrained conditions and allowed to shrink slightly to reduce residual stresses present in stretched films, which is believed to be important during the manufacture of the hygienic products that contain the porous film and during consumer use.^{4,15} Mechanically, any residual stresses present in stretched film are allowed to relax, thus making the film stronger and more uniform. Aesthetically, the surface of the film becomes

smoother and more clothlike, which is particularly important when the stretching method of interdigitation is applied.¹⁶ *Interdigitation* is a stretching process whereby the filled film, while under tension, is passed between intermeshing, grooved cylinders or intermeshing disks. Each point of contact with the grooves or disks applies localized stress to the film. It is at these points that the film stretches. The resulting stretched film consists of narrow, parallel bands where stretching has occurred separated by bands of unstretched film. Pores in films stretched by this process are found in the stretched bands. When films are stretched biaxially by the interdigitation process, a cross-hatched pattern of stretched bands is produced. Ideally, a microporous structure that allows for water vapor diffusion will remain intact throughout any poststretching film treatments. The time, temperature, and amount of restraint applied to films during heat setting must be controlled carefully to maintain such a structure. Excessively high heat-setting temperatures or unrestrained conditions may allow pores to collapse and close off interconnecting pathways traversing the film thickness, thereby reducing the MVTR.

EXPERIMENTAL

The polyethylene (PE) resin used in these experiments was Tenite L2029-C supplied by Eastman

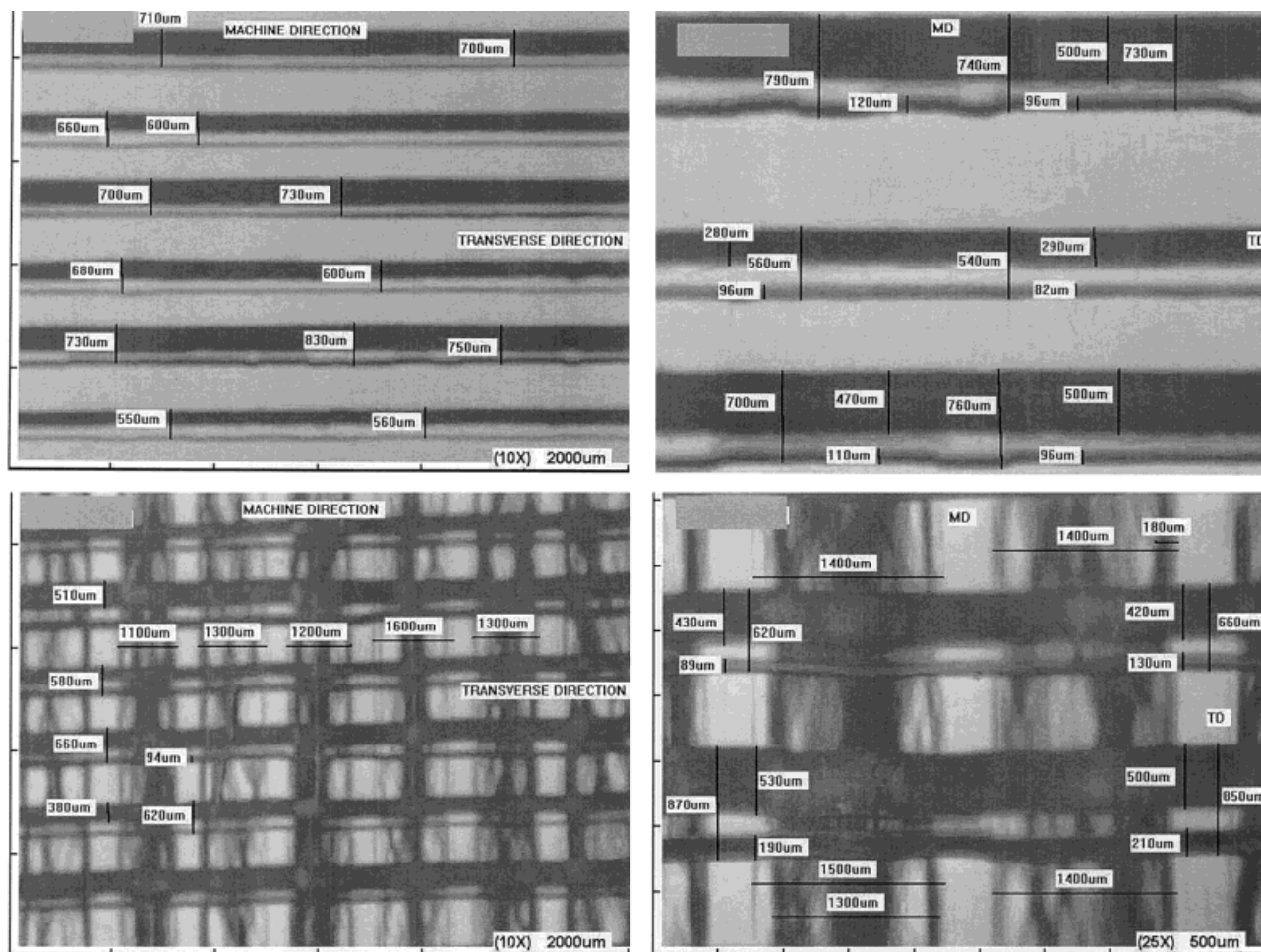


Figure 1 Optical micrographs of films with MD \times TD stretch ratios of (a) 1.375×1 and (b) 1.375×1.5 .

Chemical Co. (Kingsport, TN). Tenite L2029-C had a density of 0.917 g/cm^3 , a melt index of 2.3 g/10 min, and a Vicat softening point of 104°C . Calcium carbonate was supplied by English China Clay under the trade name SupercoatTM calcium carbonate. SupercoatTM calcium carbonate is reported to be 97.6% CaCO_3 with a mean particle size of $1 \mu\text{m}$. These components of the formulation were compounded with 1000 ppm of a fluoropolymer processing aid in a continuous mixer at 400°F so that the final formulation was 55 wt % CaCO_3 . The formulation was then extrusion-cast into film at 550°F . These materials were then stretched at room temperature with the interdigation method at Biax FiberFilm Corp. (Appleton, WI) with a different machine and transverse direction stretch ratios.⁷ For films that were stretched biaxially, stretching was performed sequentially with the machine direction

(MD) as the first stretching direction. Films were cut into 9×9 in. squares and sealed in the heat-set frame by a restraining shim and C-clamps for an overall effective area of 25 in.^2 Care was taken to ensure the films were neither strained while being placed in the frames nor excessively taut in the frames. Prior to heat setting, the centers of the films in the frames could be displaced by about 0.5 cm normal to the film with only slight pressure. These films were heat-set under restrained conditions at 65, 85, and 115°C for 1, 3, and 5 min each. Replicate samples were tested at each condition. All of the films changed in appearance under all the heat-setting conditions. These changes were markedly less under the heat-setting conditions at 65°C than under the conditions at 115°C . Several of the films became smoother on heat setting. All films were tested for MVTR and differential scanning calorimetry (DSC); films

Table II Average MVTR Data for Heat-Set Films

Material	Heat-Set Temperature (°C)	Heat-Set Time (min)	Observations	MVTR (g mL m ⁻² day ⁻¹)	Film Thickness (mL)	MVTR (g m ⁻² day ⁻¹)
A	65	1	T	2733	2.36	1158
A	65	3	T	2911	2.42	1203
A	65	5	T	2886	2.39	1208
B	65	1	T	2686	2.45	1096
B	65	3	T	2343	2.37	989
B	65	5	T	2694	2.44	1104
C	65	1	T	1942	2.4	809
C	65	3	T	1838	2.44	753
C	65	5	T	1699	2.41	705
D	65	1	T, Sm	3075	2.45	1255
D	65	3	T, Sm	3347	2.41	1389
D	65	5	T, Sm	3198	2.44	1311
E	65	1	T	2235	2.57	870
E	65	3	T	1943	2.52	771
E	65	5	T, Sm	1882	2.44	771
F	65	1	T	2654	2.49	1066
F	65	3	T	2335	2.44	957
F	65	5	T	2331	2.47	944
A	85	1	T, Sm	2868	2.44	1174
A	85	3	T	2929	2.48	1183
A	85	5	T	2830	2.43	1166
B	85	1	T	2032	2.41	845
B	85	3	T	2360	2.41	980
B	85	5	T	2191	2.45	896
C	85	1	T	1741	2.50	697
C	85	3	T	1632	2.48	658
C	85	5	T	1582	2.44	648
D	85	1	T	2897	2.42	1196
D	85	3	T, Sm, S	2587	2.34	1103
D	85	5	T, Sm, S	2787	2.39	1168
E	85	1	T, Sm	1600	2.48	645
E	85	3	T, Sm	1365	2.45	557
E	85	5	T, Sm	1431	2.50	572
F	85	1	T	2259	2.48	911
F	85	3	T	2302	2.49	923
F	85	5	T, Sm	2197	2.52	873
A	115	1	T, Sm	2214	2.37	934
A	115	3	T, Sm	1927	2.38	810
A	115	5	T, Sm, S	1862	2.43	766
C	115	1	T, Sm	843	2.43	347
C	115	3	L, T, Sm	705	2.57	274
C	115	5	T, Sm	538	2.49	216
D	115	1	T, Sm, S	2726	2.37	1150
D	115	3	T, Sm, S	1971	2.22	888
D	115	5	T, Sm, S	1712	2.7	634
E	115	1	T, Sm, S	440	2.37	186
E	115	3	T, Sm, S	591	2.53	234
E	115	5	T, Sm, S	415	2.47	168
F	115	1	T, Sm	1080	2.45	441
F	115	3	T, Sm, S	1408	2.51	561
F	115	5	T, Sm, S	1296	2.48	523

T = Film inside frame was very taut after heat setting; Sm = heat setting produced a smoother film; S = film in heat-set area appeared stretched.

Table III Average THDT Data for Heat-Set Films

Material	Heat-Set Temperature (°C)	Heat-Set Time (min)	Observations	THDT, MD (°C)	THDT, TD (°C)
A	65	3	T	60.6	116.2
B	65	3	T	88	67.3
C	65	3	T	116.2	66.6
D	65	3	T, Sm	116.3	50.2
E	65	3	T	78	96.5
F	65	3	T	68.9	113.5
A	85	1	T, Sm	63.8	111.6
C	85	1	T	109.3	70.3
D	85	1	T	84.7	65.1
D	85	3	T, Sm, S	73.7	72.9
D	85	5	T, Sm, S	87.2	55.0
E	85	1	T, Sm	79.0	70.0
E	85	3	T, Sm	75.8	74.4
E	85	5	T, Sm	81.4	71.2
A	115	3	T, Sm	60.2	84.6
C	115	3	T, Sm	83.8	65.2
D	115	3	T, Sm, S	79.8	61.6
E	115	3	T, Sm, S	72.8	82.7
F	115	3	T, Sm, S	70	68.4

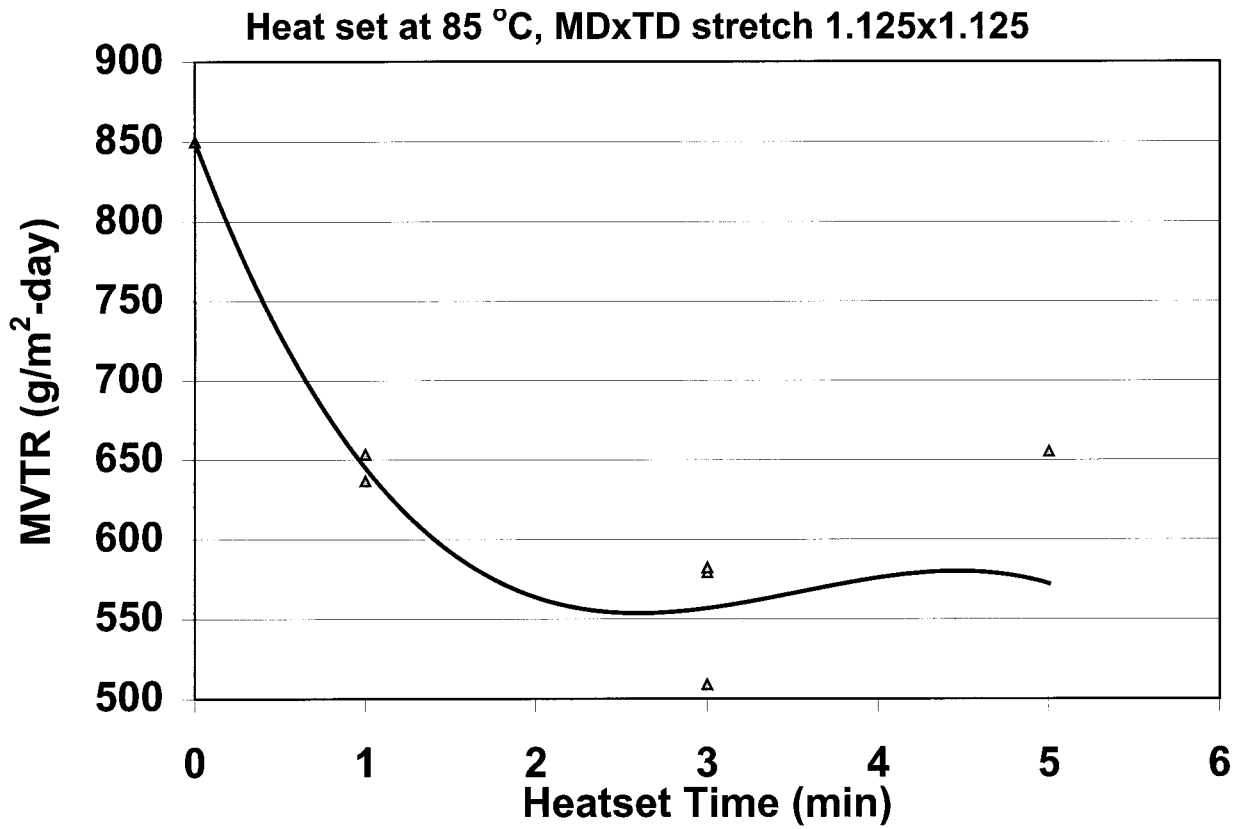
T = Film inside frame was very taut after heat setting; Sm = heat setting produced a smoother film; S = film in heat-set area appeared stretched.

Table IV Average DMTA Data for Heat-Set Films

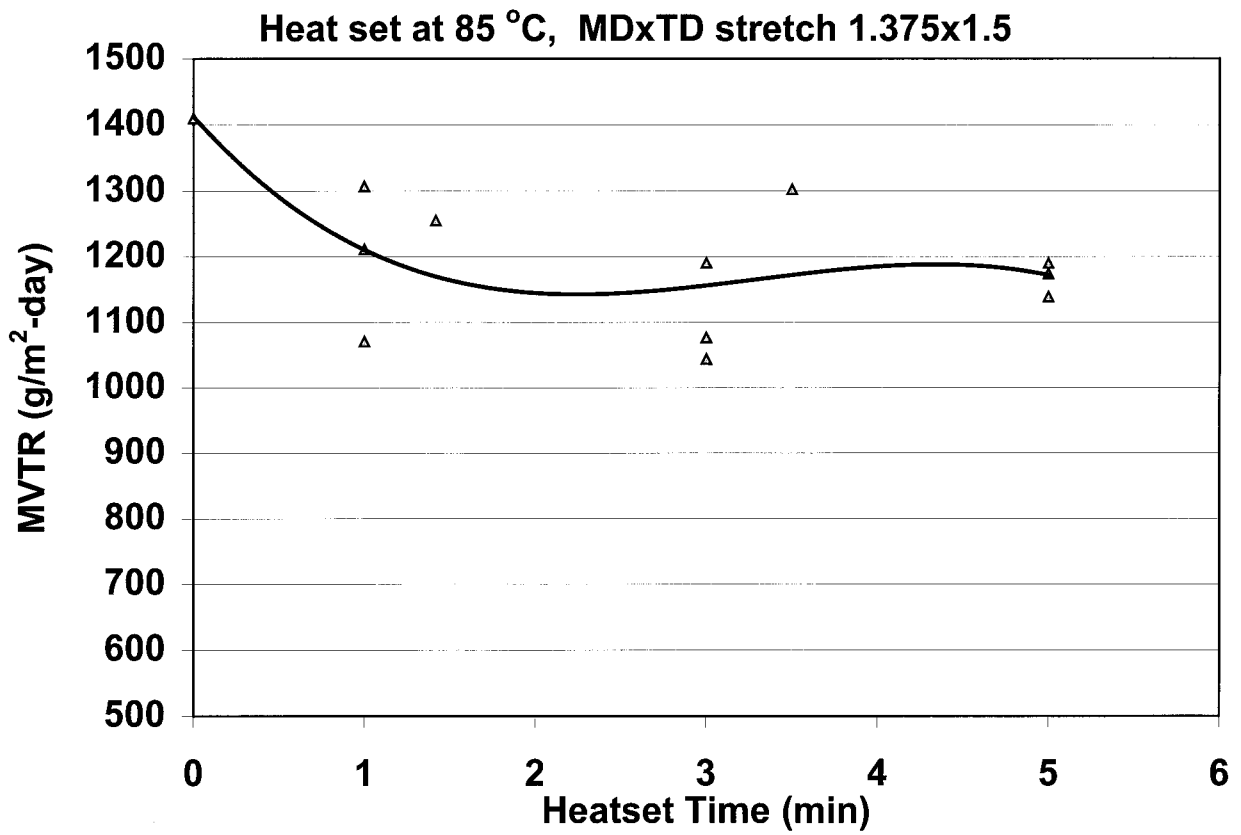
Material	Heat-Set Temperature (°C)	Heat-Set Time (min)	Observations	$T_{\tan \delta}^m$ MD (°C) ^a	$T_{\tan \delta}^m$ TD (°C) ^a	E' (10 ⁸ Pa) MD	E'_{25} (10 ⁸ Pa) TD
A	65	3	T	79	41,88	3.2	1.2
B	65	3	T	46	76	2.1	3.6
C	65	3	T	82	78	2.3	3.9
D	65	3	T, Sm	37	35	1.1	0.4
E	65	3	T	85	75	2.5	1.2
F	65	3	T	83	37	4.4	1.6
A	85	1	T, Sm	79	53	3.7	1.5
A	85	3	T	80	53	3.4	1.6
C	85	1	T	56	82	2.7	4.4
C	85	3	T	64	80	3.3	4.1
D	85	1	T	53	51	1.5	1.1
D	85	3	T, Sm, S	53	56	1.6	1.2
D	85	5	T, Sm, S	54	57	1.5	1.1
E	85	1	T, Sm	57	62	3.1	2.1
E	85	3	T, Sm	63	65	3.3	2.4
E	85	5	T, Sm	66	61	3.4	2.4
A	115	3	T, Sm	97	88	4.3	2.1
C	115	3	T, Sm	83	83	3.9	4.5
D	115	3	T, Sm, S	92	93	2.3	1.9
E	115	3	T, Sm, S	89	84	4.5	3.2
F	115	3	T, Sm, S	95	89	4.2	2.3

T = Film inside frame was very taut after heat setting; Sm = heat setting produced a smoother film; S = film in heat-set area appeared stretched.

^a For most of these materials, this temperature was the α transition temperature.



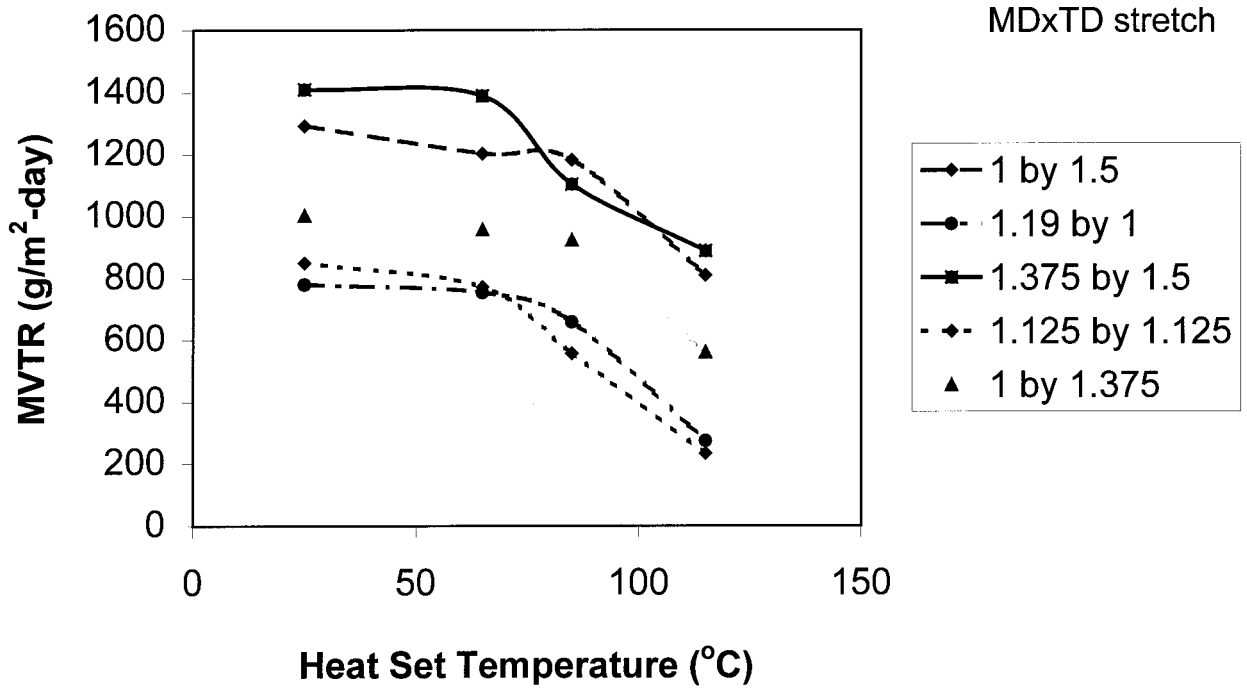
(a)



(b)

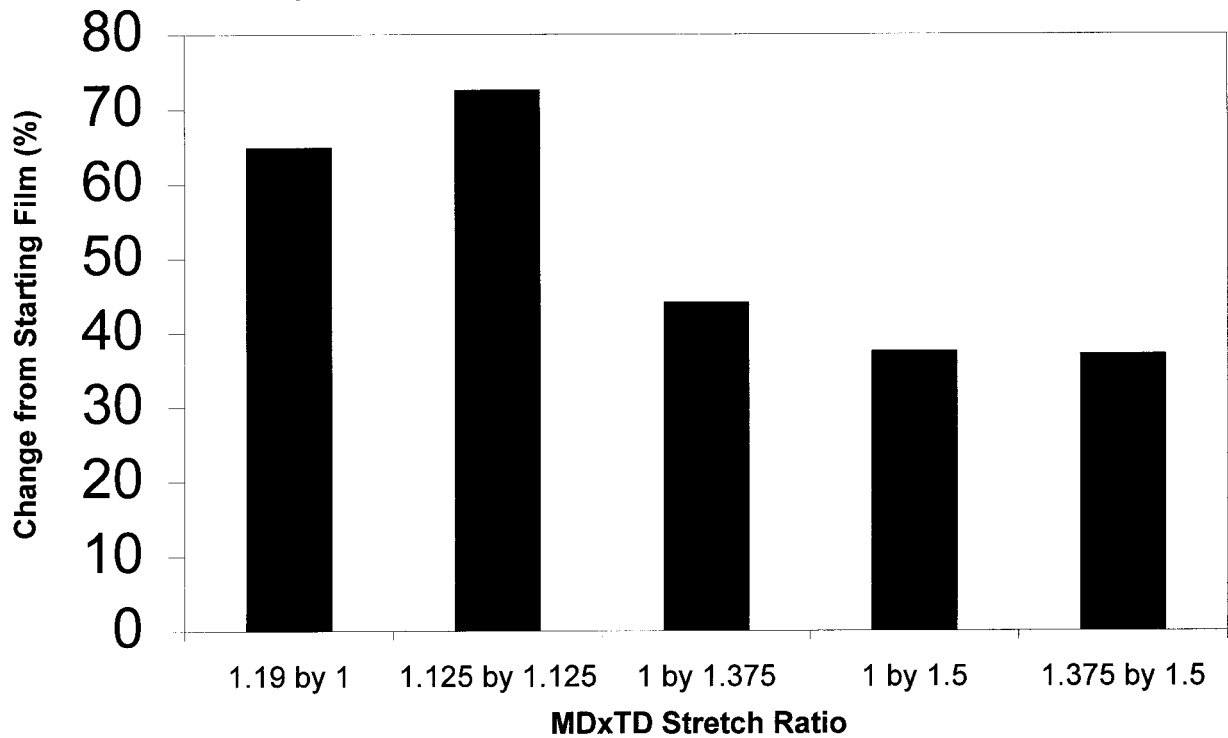
Figure 2 Effect of heat-set time at 85°C on MVTR of restrained Biax films with MD × TD stretch ratios of (a) 1.125 × 1.125 and (b) 1.375 × 1.5.

Effect of Heat-set Temperature on MVTR



(a)

Change in MVTR upon Heat Setting at 115 °C



(b)

Figure 3 Effect of stretch ratio and heat-set time at 3 min on MVTR of Biax films.

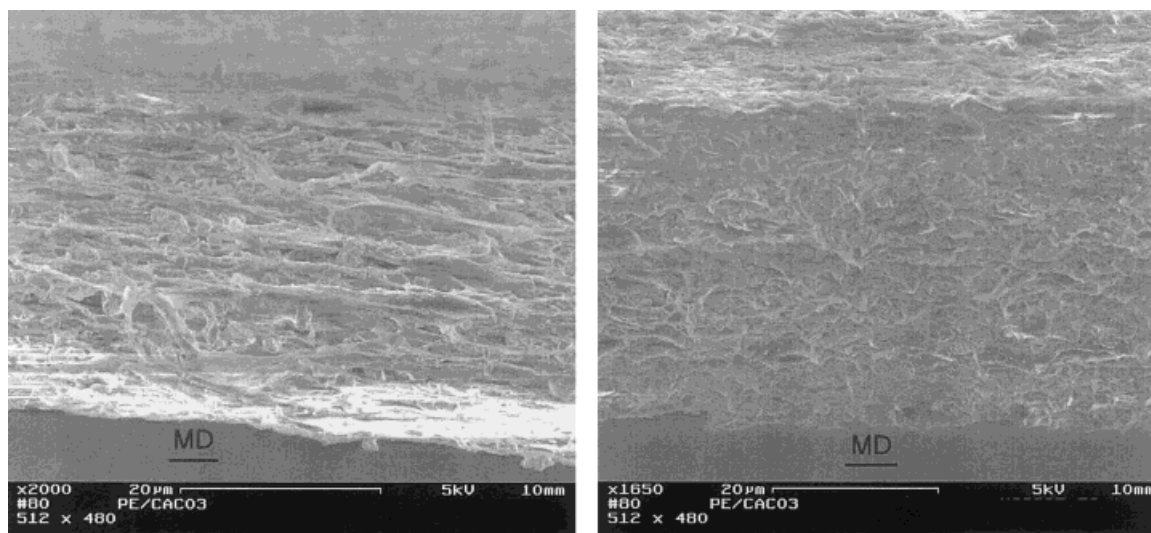


Figure 4 Scanning electron micrograph of heat-set (right; 115°C for 5 min) and non-heat-set (left) films stretched $1.375 \times 1.5 \text{ MD} \times \text{TD}$.

were also tested for tensile heat distortion temperature (THDT) and dynamic mechanical thermal analysis (DMTA) in the MD and transverse direction (TD). MVTR was measured at 32°C and 50% relative humidity according to ASTM E-96. Film THDT was measured according to ASTM D1637. Thermal properties were analyzed by a TA Instruments 2920 (dual sample cell) machine with a liquid nitrogen cooling unit, model II DCS, at 20°C/min ramp. Storage modulus (E') and thermal transitions [α -transition temperature (T_α)] were determined from DMTA measurements on a Rheometrics RSA II and environmental controller from -145–105°C at 16 Hz and 20°C/min ramp. From DMTA a peak temperature in $\tan \delta$ was measured, $T_{\tan \delta}^m$. The α -transition is normally associated with this temperature (typically >40°C for LLDPE); however, some measurements were much lower than 40°C and were not to be considered α -transitions. This may have resulted from the large amount of noise present for some samples. The morphology was examined both by an SEM LEO Gemini 982 (2 kV) and by optical microscopy with a Wild Makroskop M400.

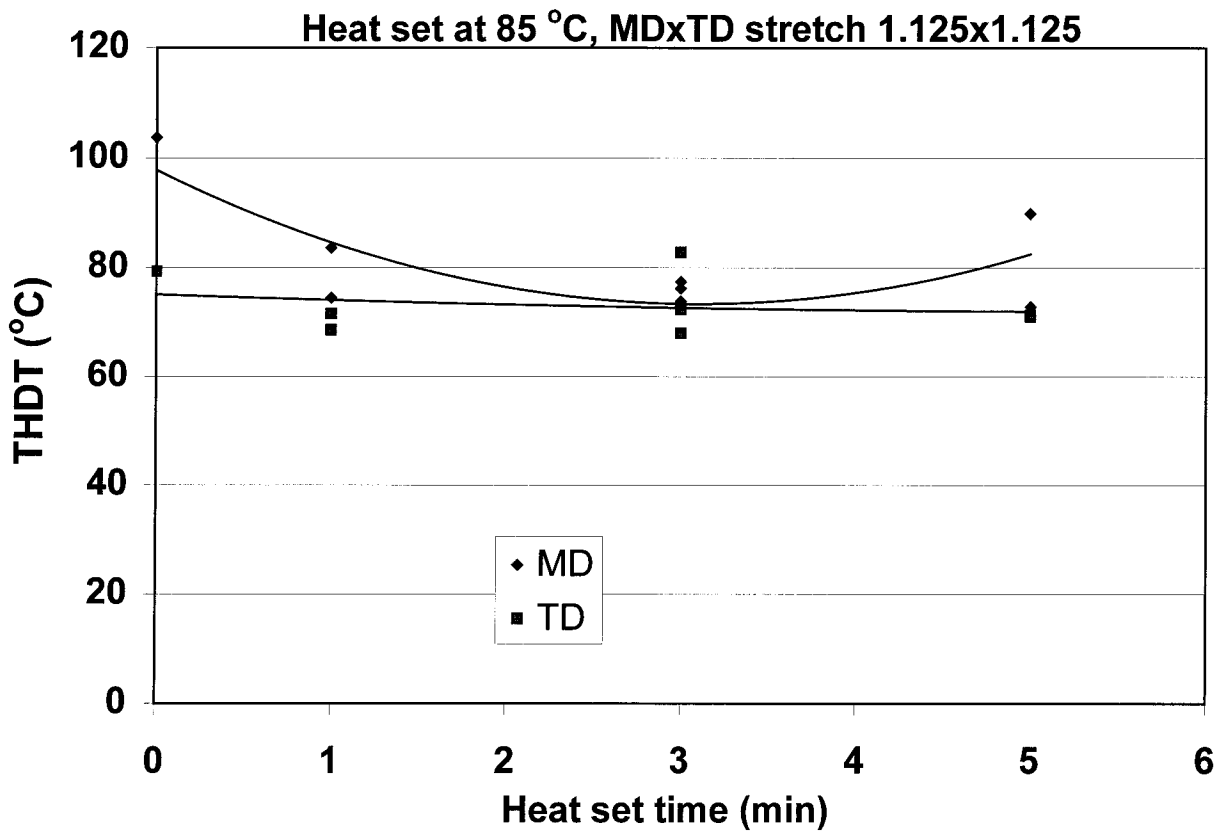
RESULTS AND DISCUSSION

Non-Heat-Set Films

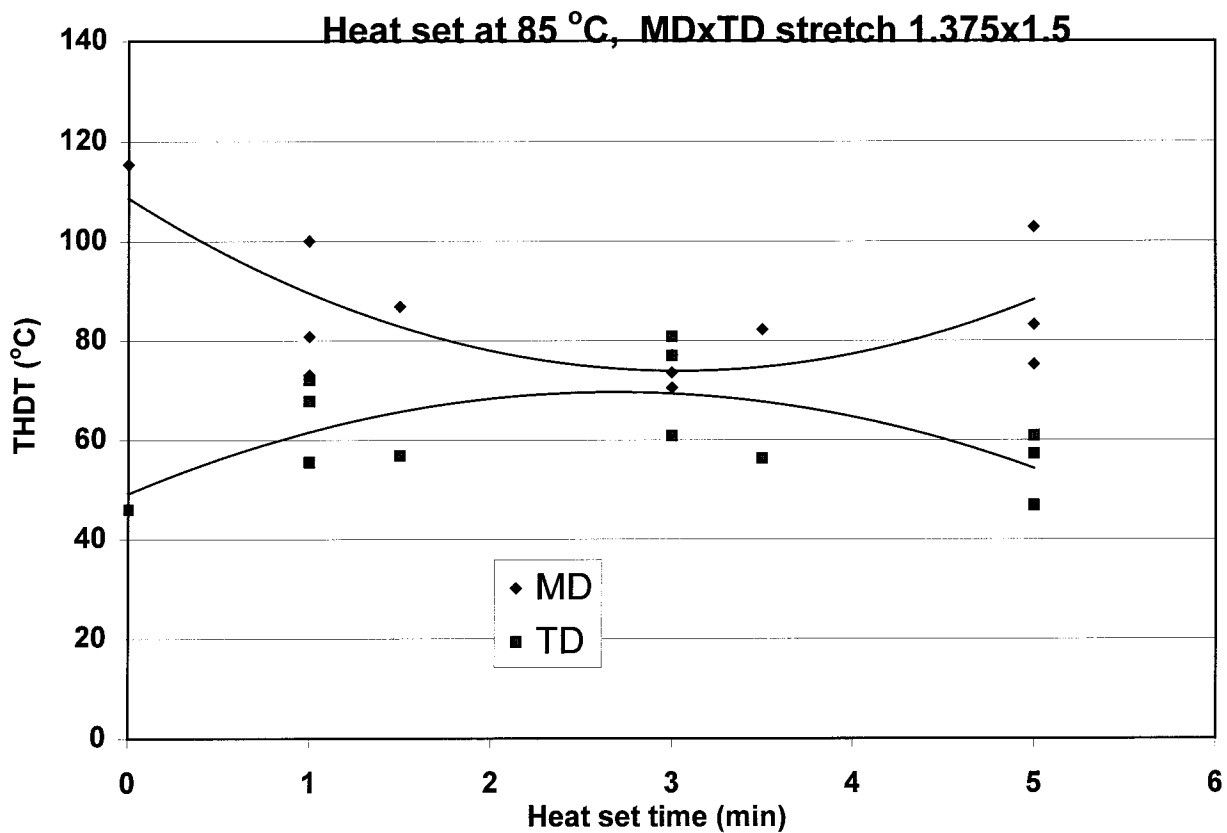
Table I contains data for filled films stretched by interdigitation to several MD and TD ratios without further poststretching thermal treatment.

See Figure 1 for an example of the effect of uniaxial and biaxial stretching on these films. A progressive increase in MVTR of these films was observed as the total area strains increased. Greater area strain produced more breathability that was interpreted to arise from increased porosity. There was no clear relationship between total strain and THDT; however, as the degree of MD stretch increased, the TD THDT decreased. There were two effects of stretching on the film. The first effect was the matrix orientation during MD stretching, thereby decreasing the amount of thermal energy required to induce sufficient yielding in the cross-direction of the oriented film. The second effect was increased voiding as the degree of MD stretching was increased. Voiding effectively reduced the cross-sectional area being tested, thereby leading to lower TD THDT. The reason this relationship was not observed between the degree of TD stretch and MD THDT was likely because the biaxial samples were oriented in the MD first. The orientation that took place during the MD stretch reduced the possible amount of orientation that could occur on TD stretching.

Uniaxially stretching an unfilled PE film under conditions that give rise to orientation typically increases the modulus in the direction of stretch and, for restrained films, increases the modulus perpendicular to the direction of stretch. However, in this filled system, the amount of load-bearing matrix per unit area was reduced from



(a)



(b)

Figure 5 Effect of heat-set time at 85°C on THDT of restrained Biax films with MD × TD stretch ratios of (a) 1.125 × 1.125 and (b) 1.375 × 1.5.

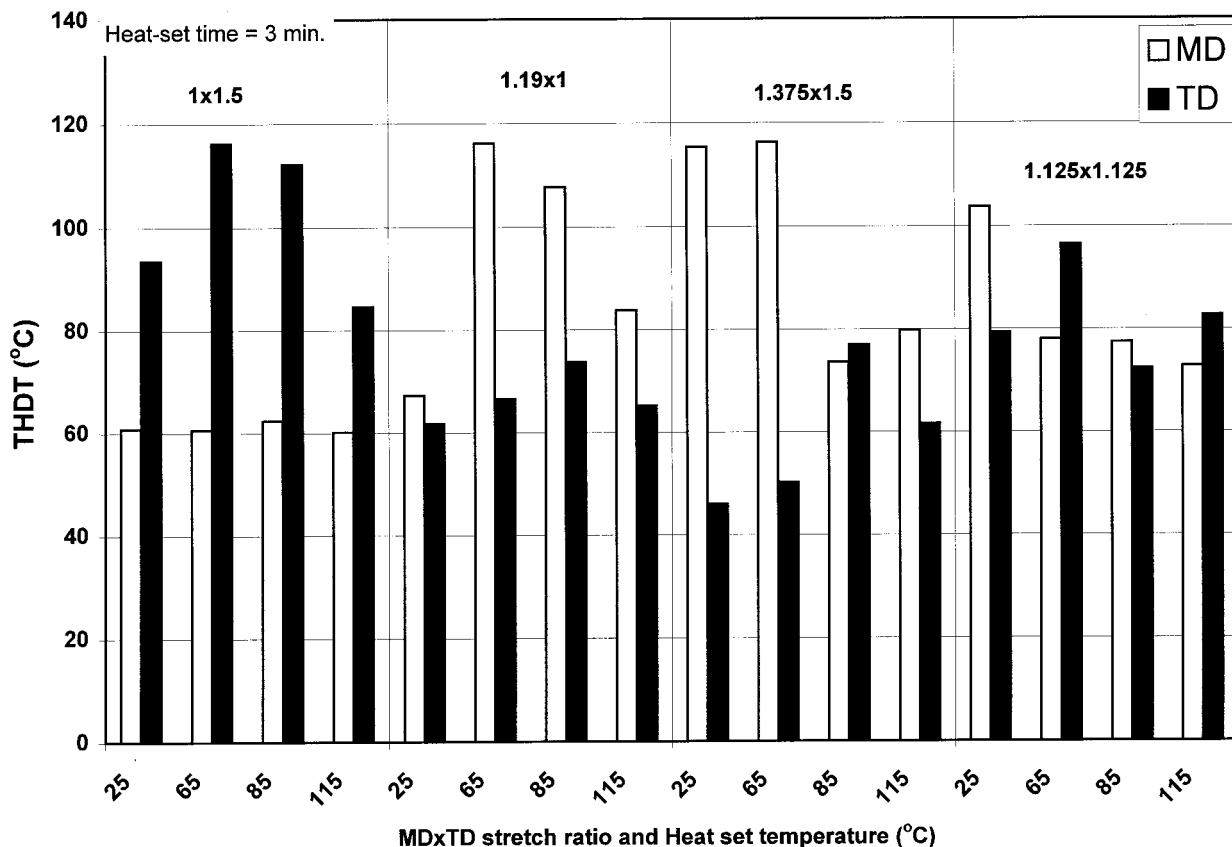


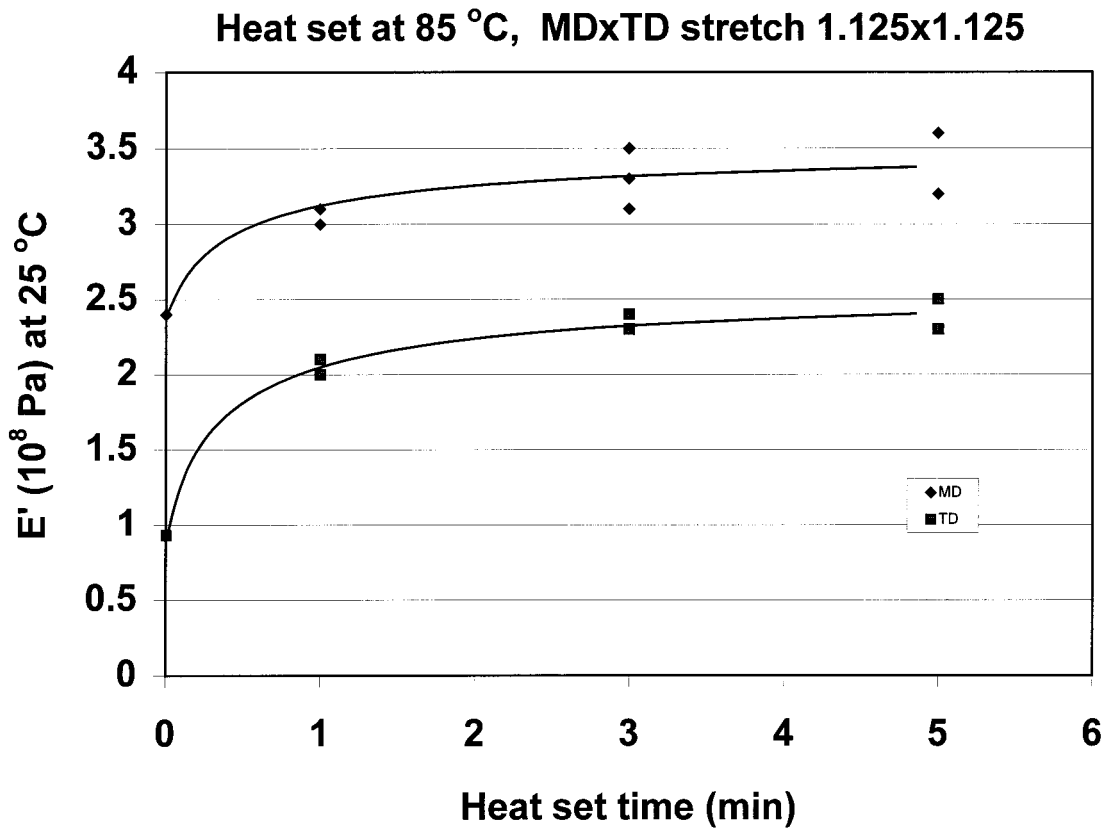
Figure 6 Effect of stretch ratio and heat-set time at 3 min on THDT of Biax films.

the creation of voids. This reduced the amount of load-bearing matrix material in both the MD and TD, thereby reducing E' relative to the unstretched film. Samples stretched uniaxially had a much lower E' , corresponding to the direction of stretch compared to the E' in the cross-direction. One likely explanation for this observation comes from series versus parallel contributions to modulus. For example, when a film was stretched in the MD by the interdigitation method, there were porous bands perpendicular to the MD and parallel to the TD. When this film was pulled in the MD during DMTA testing, the modulus contribution of the voided regions was in series with that of the unvoided areas. Furthermore, when the film was pulled in the TD, these voided regions were in parallel with the unvoided material, resulting in a lesser contribution of the voided area to the modulus. This type of behavior was not clearly observed for biaxially stretched materials.

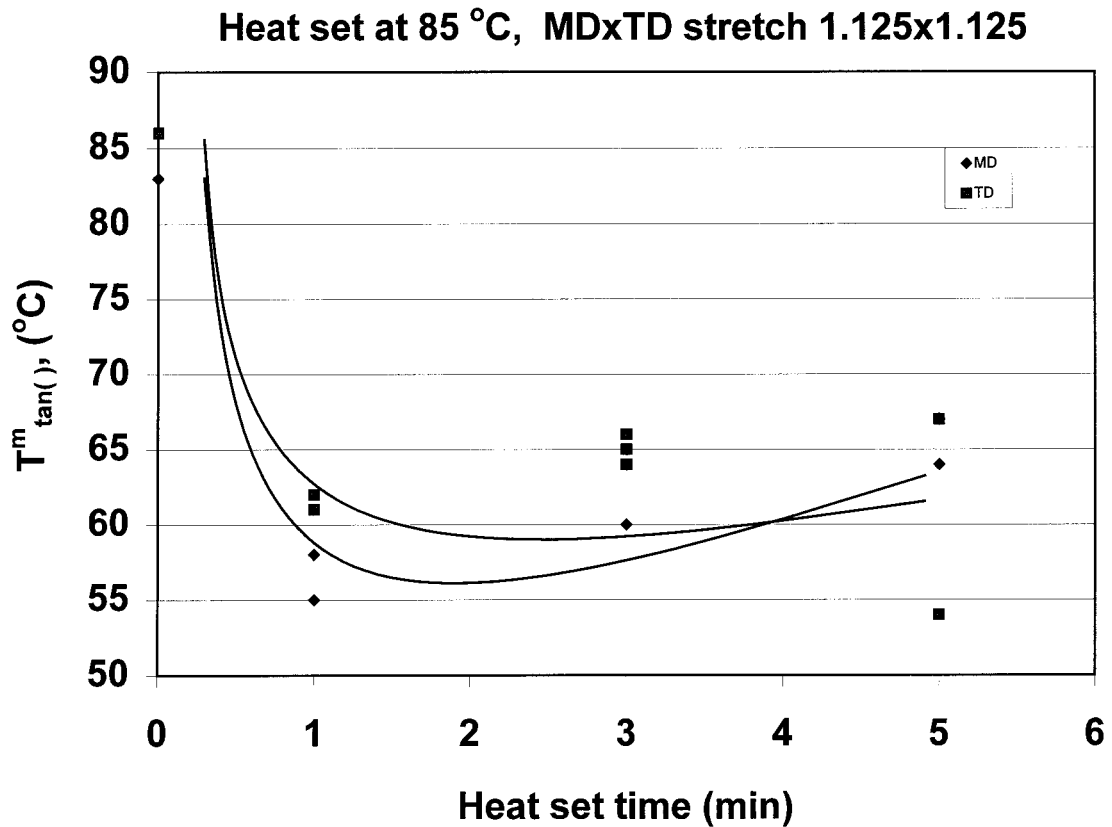
Heat-Set Films

Tables II–IV contain MVTR, THDT, and DMTA data, respectively, for heat-set films. Figures 2(a)

and 2(b) show the effect of heat-set time at 85°C on MVTR for biaxially stretched films. There was a drop in MVTR once the films were heat-set for 1 min; longer heat-set times resulted in few additional breathability changes. This suggests that the molecular rearrangement or recrystallization that affects this property was occurring in less than 1 min. The effect of heat-set temperature and stretch ratio on MVTR is shown in Figure 3(a). All materials, regardless of stretch ratio, exhibited similar behavior when higher heat-set temperatures produced a decrease in MVTR. The reduction in MVTR appeared to begin at lower temperatures for biaxially stretched films than for uniaxially stretched films. The patent literature suggests that it is preferable to heat-set 10°C below the Vicat softening point.² All films showed significant drops in MVTR when heat-set at 115°C. The Vicat softening point of these composites was around 94°C, some 10°C lower than that of the neat resin; hence, heat setting above this temperature allowed the microvoids to collapse, reducing breathability. Furthermore, the relative decrease in MVTR was dependent on the degree



(a)



(b)

Figure 7 Effect of heat-set time at 85°C of restrained Biax films on E' at 25°C with MD × TD stretch ratios of (a) 1.125 × 1.125 and (c) 1.375 × 1.5 and T_{α} with MD × TD stretch ratios of (b) 1.125 × 1.125 and (d) 1.375 × 1.5.

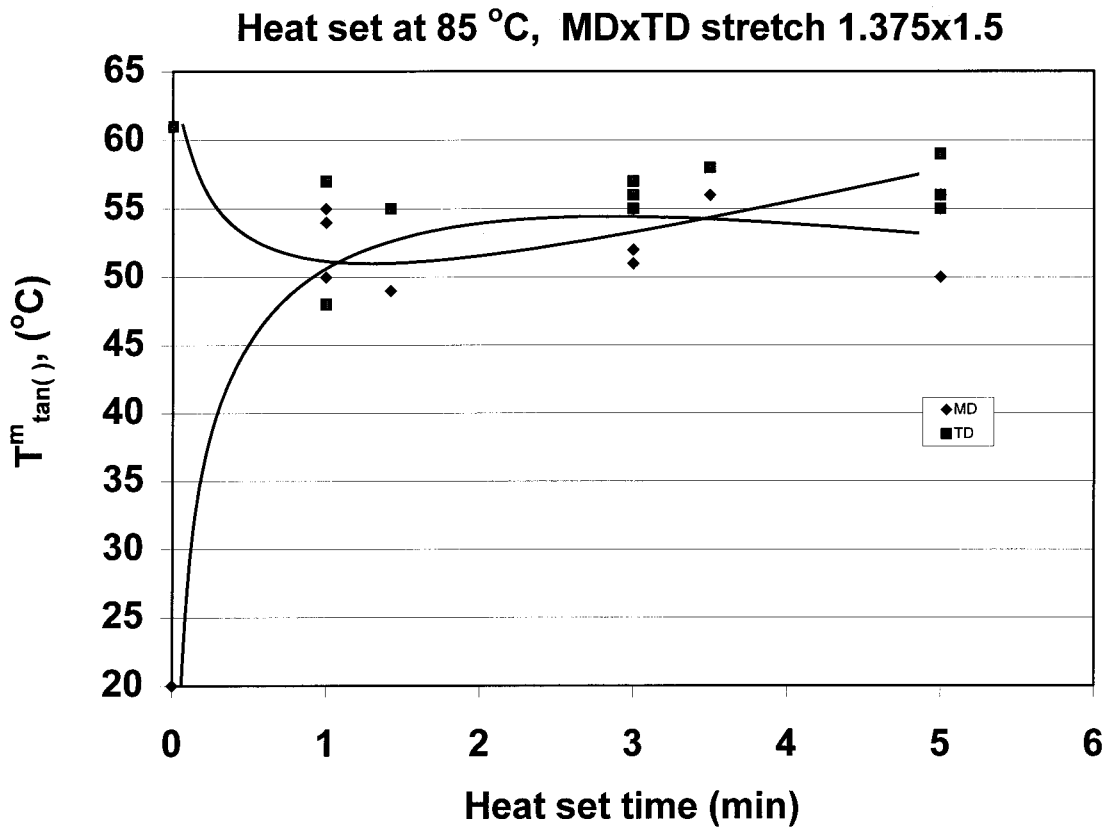
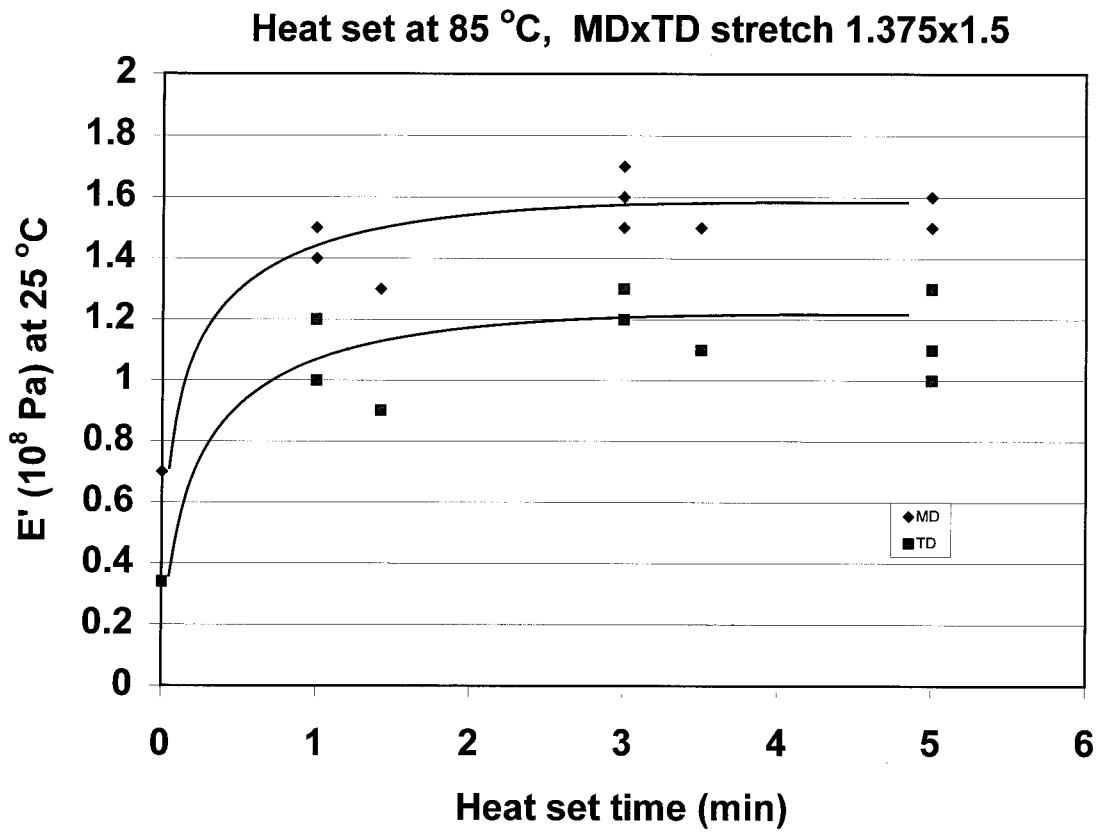
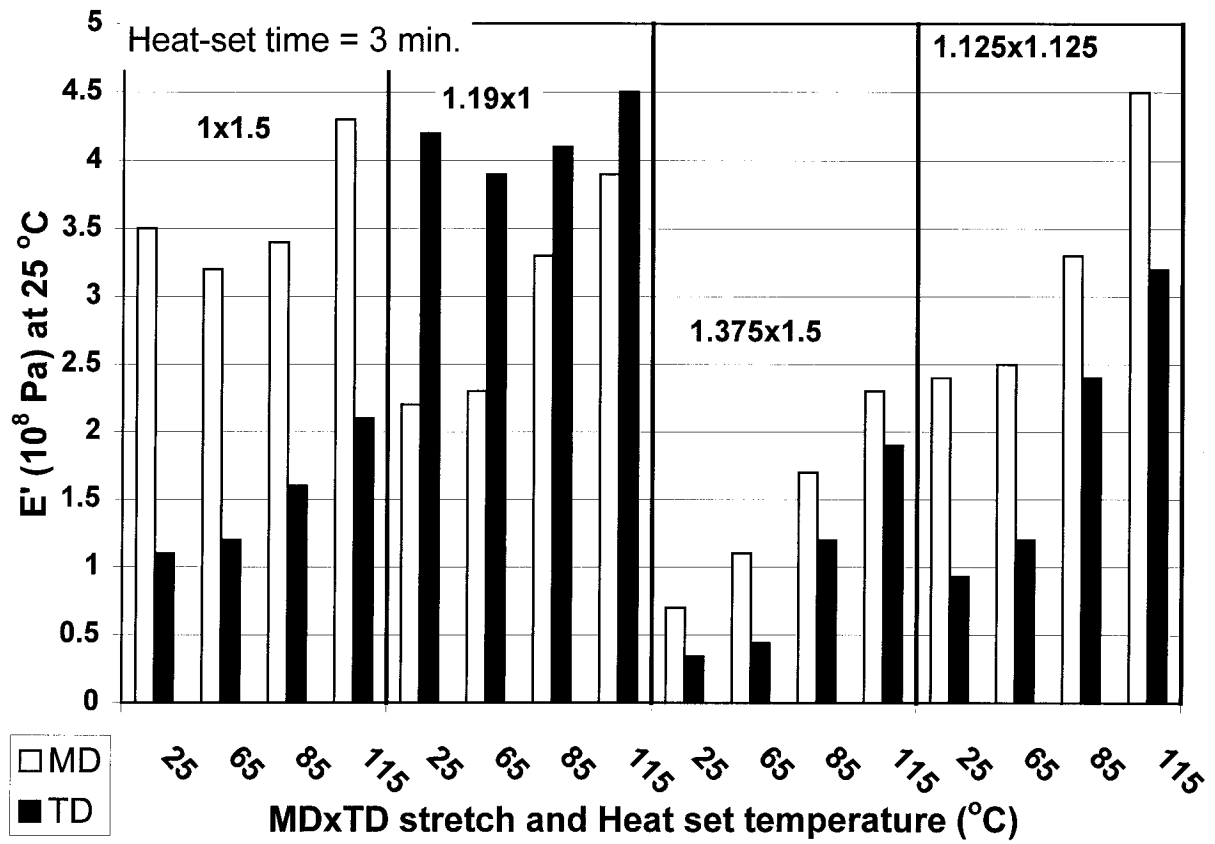
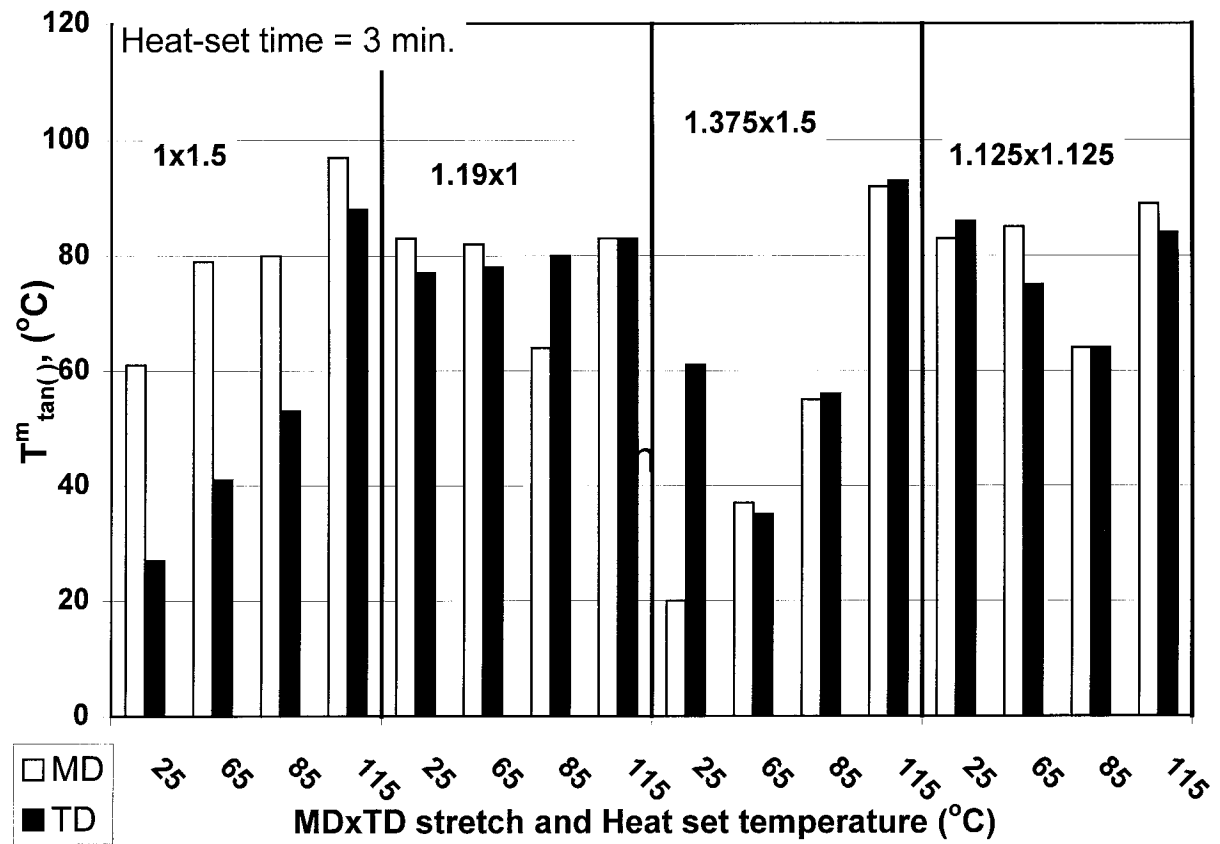


Figure 7 (Continued from the previous page)



(a)



(b)

Figure 8 Effect of stretch ratio and heat-set time at 3 min of Biax films on (a) E' at 25°C and (b) T_{α}^m .

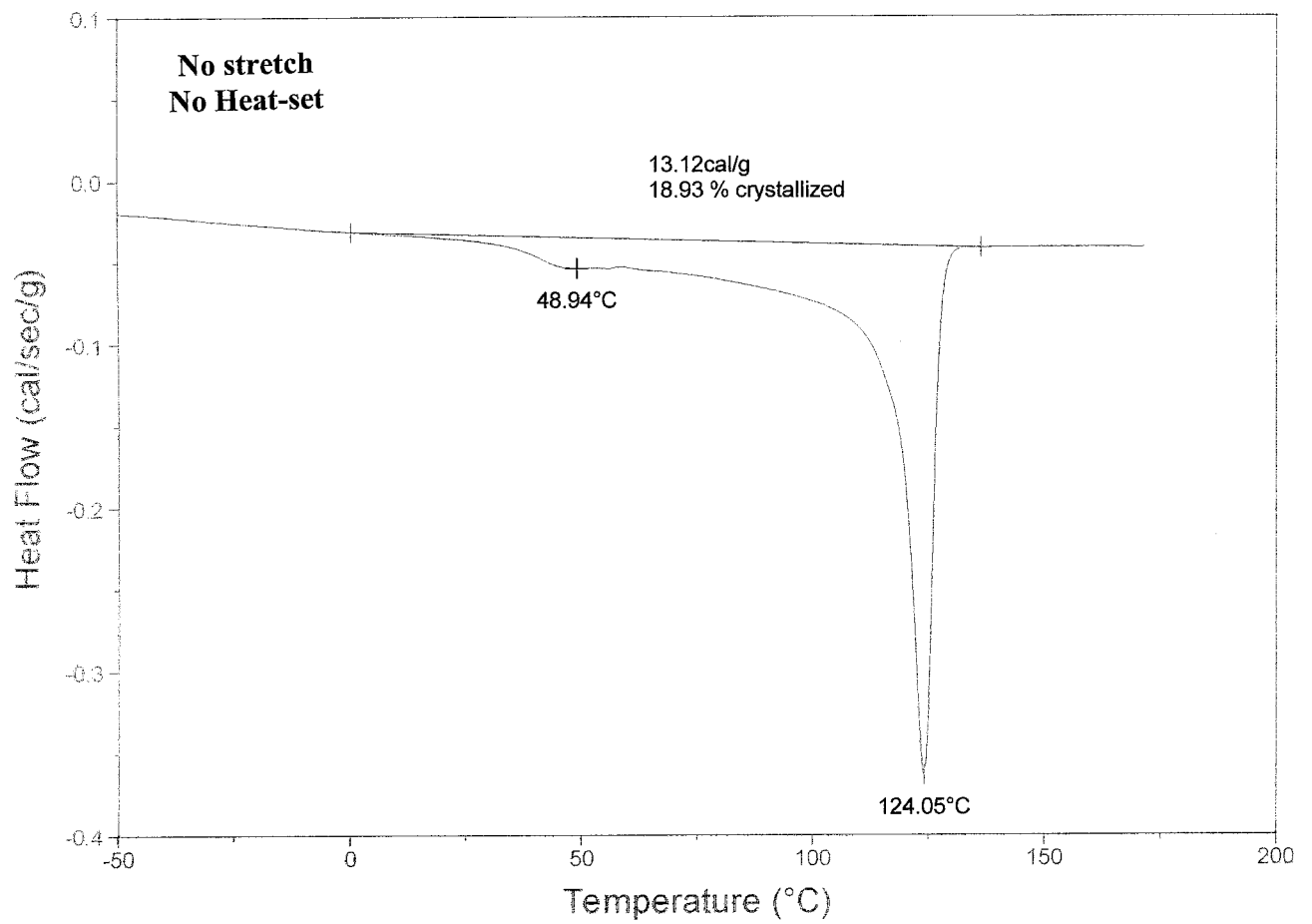
of stretching the film had undergone. Figure 3(b) compares the relative change in MVTR for films heat-set at 115°C; the films fell into two clear categories that were independent of whether the films were stretched uniaxially or biaxially. Those films stretched less than 1.2× in any direction defined the first category, and those films stretched more than 1.2× in any direction defined the second category. Films in the first category lost relatively more of the MVTR present prior to heat setting than the films in the second category. This distinction was likely to be dependent on the yield strain for these filled films. It was to be expected that in the voided regions, there would be a transition from unstrained composite to composite strained beyond its yield point. This transition region would be capable of recovering on heating so that any pores present in the region could close, hence reducing MVTR. Films that underwent a higher degree of stretch had a greater proportion of material stretched beyond the yield strain so that proportionally less MVTR was lost on heating and recovery. Thus, these more highly stretched films also retained more of their porosity following heat setting at temperatures near or above the Vicat softening point. An example of pore closure is shown in Figure 4, where when heat-setting a sample stretched at 1.375 × 1.4 (MD × TD) at 115, the porous quantity clearly decreased.

The THDT response to heat-set time at 85°C for biaxially stretched films is shown in Figure 5. In general, when heat-set time increased, the MD and TD THDT became more equal and then approached that of the non-heat-set material. This behavior was more prominent for the films stretched biaxially at 1.375 × 1.5 [Fig. 5(b)]. The effect of heat-set temperature and stretch ratio is shown in Figure 6. Samples that were stretched uniaxially showed the same THDT trend in the direction of stretch when there was a sharp increase in THDT when heat setting at 65°C was followed by a progressive decrease at higher temperatures. The THDT in the cross-direction for these uniaxially stretched samples seemed to be largely unaffected by heat setting. There was no apparent THDT versus heat-set temperature relationship for biaxially stretched samples; however, heat setting at 85°C (~ 10°C below the softening point) produced a film with balanced MD and TD distortion temperatures. This result may also relate to a desirable balance of properties in commercially produced films.

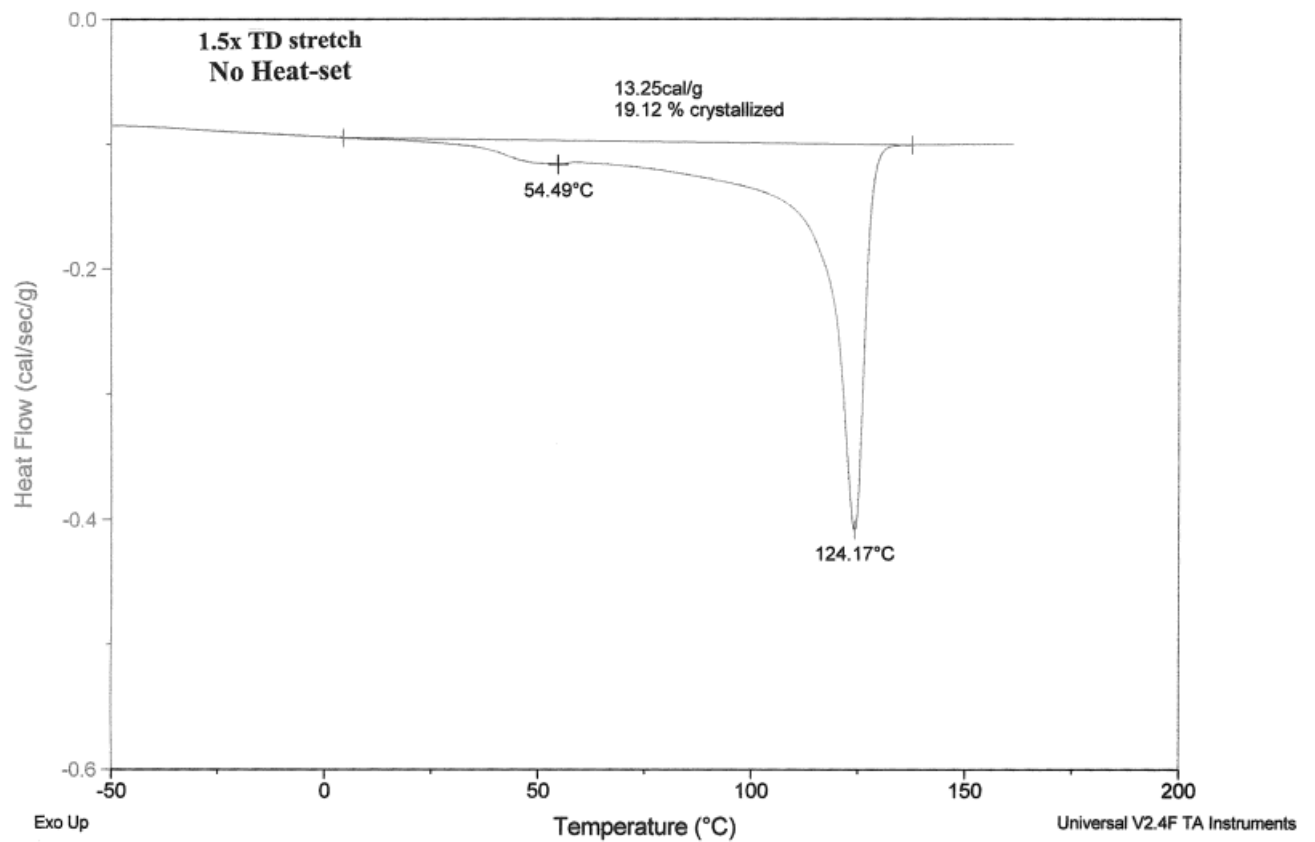
The heat-set time response at 85°C of the room-temperature E' and T_{α} determined from DMTA is shown in Figure 7. For samples heat-set for 1 min or more, both E' and $T_{\tan \delta}^m$ remained relatively constant. However, as shown in Figure 7(d) there was a large difference in the MD and TD $T_{\tan \delta}^m$ of non-heat-set films ($t = 0$) with a 1.375 × 1.5 stretch ratio. This behavior was different from that shown in Figure 7(b) for non-heat-set samples stretched at 1.125 × 1.125, where the MD and TD $T_{\tan \delta}^m$ was similar. This can most likely be explained by the subjective interpretation of $T_{\tan \delta}^m$ mentioned previously.

Figure 8 shows room-temperature E' and $T_{\tan \delta}^m$ at various heat-set temperatures and stretch ratios. All samples showed the same response to heat-set temperature, regardless of stretch method. As the heat-set temperature increased, the modulus also increased [Figure 8(a)]; there were two possible contributing mechanisms: annealing (crystallization) and void closure (increase of load-bearing material). As evident from the MVTR data shown in Figure 3, an increase in heat-set temperature resulted in a decrease in open pore space that allowed for diffusion; however, as shown later, evidence for crystallization also existed. Changes in $T_{\tan \delta}^m$ from heat setting at various temperatures are shown in Figure 6(b) for various stretch ratios. As heat-set temperature increased, $T_{\tan \delta}^m$ typically increased for samples with large total strains (1 × 1.5 and 1.375 × 1.5), whereas there was no obvious trend for samples with low total strains (1 × 1.19 and 1.125 × 1.125). Again, the $T_{\tan \delta}^m$ is subject to some scrutiny because of its method of determination.

Figure 9 shows the DSC traces for films stretched at 1 × 1.5 and heat-set at 65, 85, and 115°C. Data for a non-heat-set unstretched and stretched film are also shown for comparison. Stretching did not significantly alter the DSC traces relative to unstretched film; however, it is clear from this figure that heat setting produced a peak in the curve that corresponded to the heat-set temperature, indicating that a certain amount of crystallization occurred at the heat-set temperature.^{17–19} As mentioned previously, the total crystallinity of the films increased with increasing heat-set temperature; this can be seen from the heats of fusion in Table V. These results suggest that changes in E' resulting from heat setting could be directly related to voiding and crystallization. For the 1 × 1.5 sample, changes in E' in the TD, the stretching direction, were more

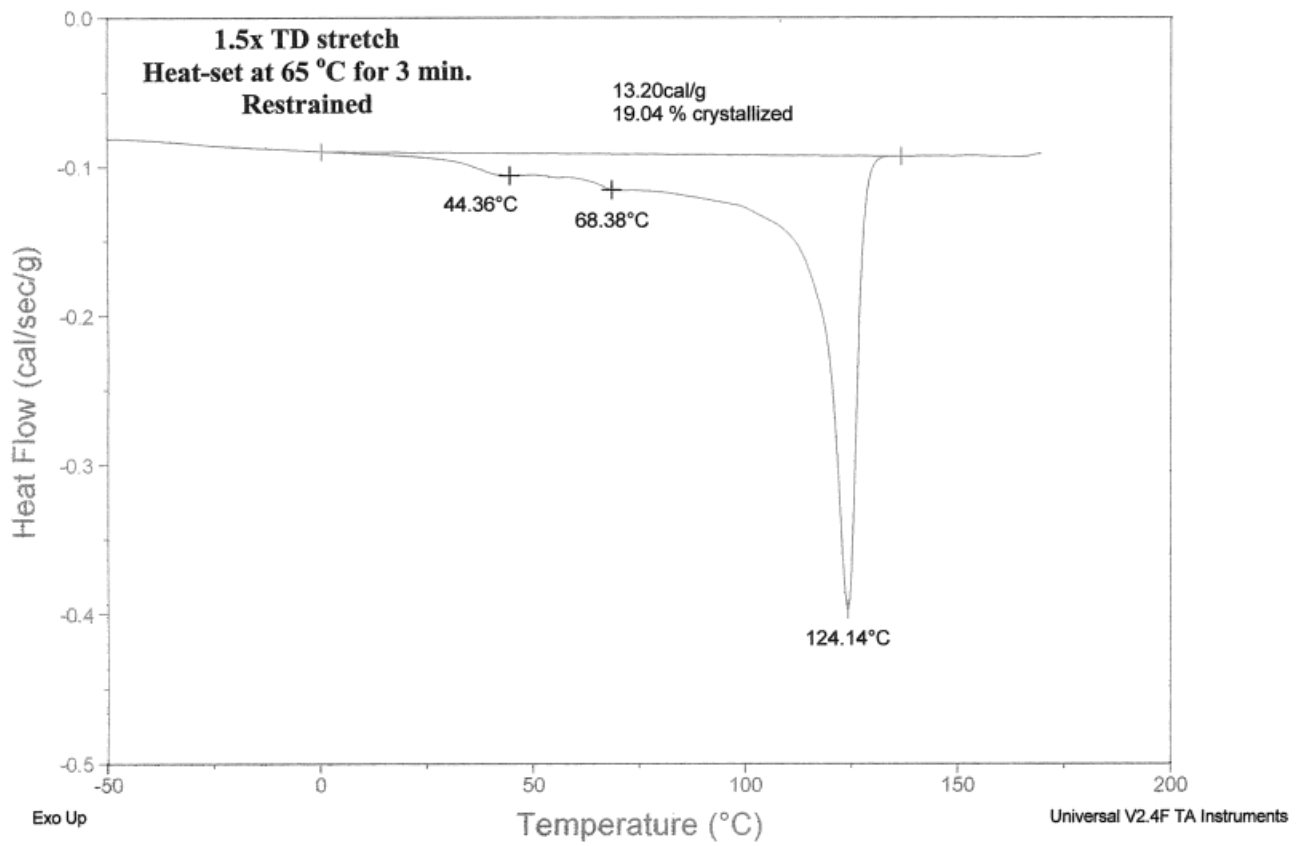


(a)

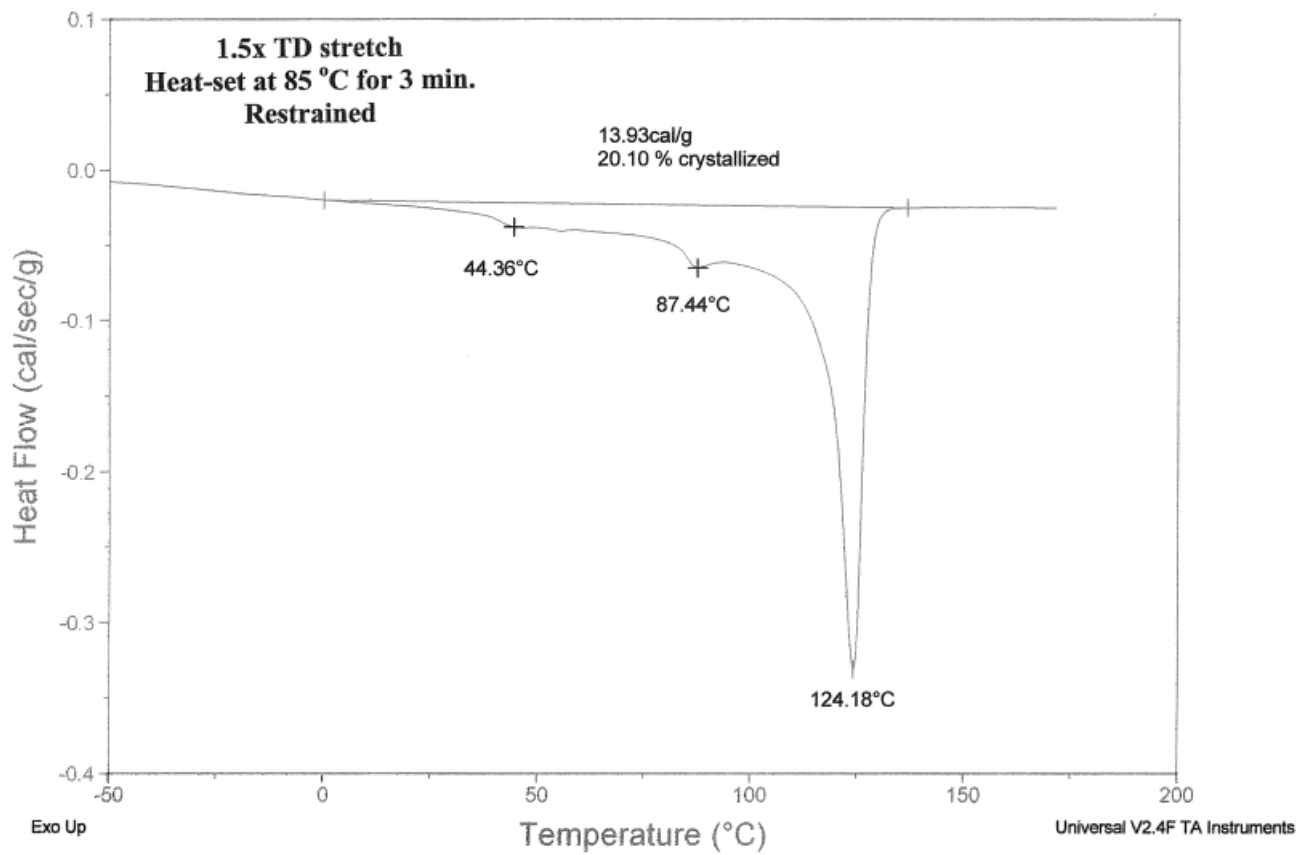


(b)

Figure 9 DSC response to heat-set temperature at 3 min of Biax films treated at (a) 25°C with no stretch or heat-set, (b) 25°C with no heat-set, (c) 65°C, (d) 85°C, and (e) 115°C.



(c)



(d)

Figure 9 (Continued from the previous page)

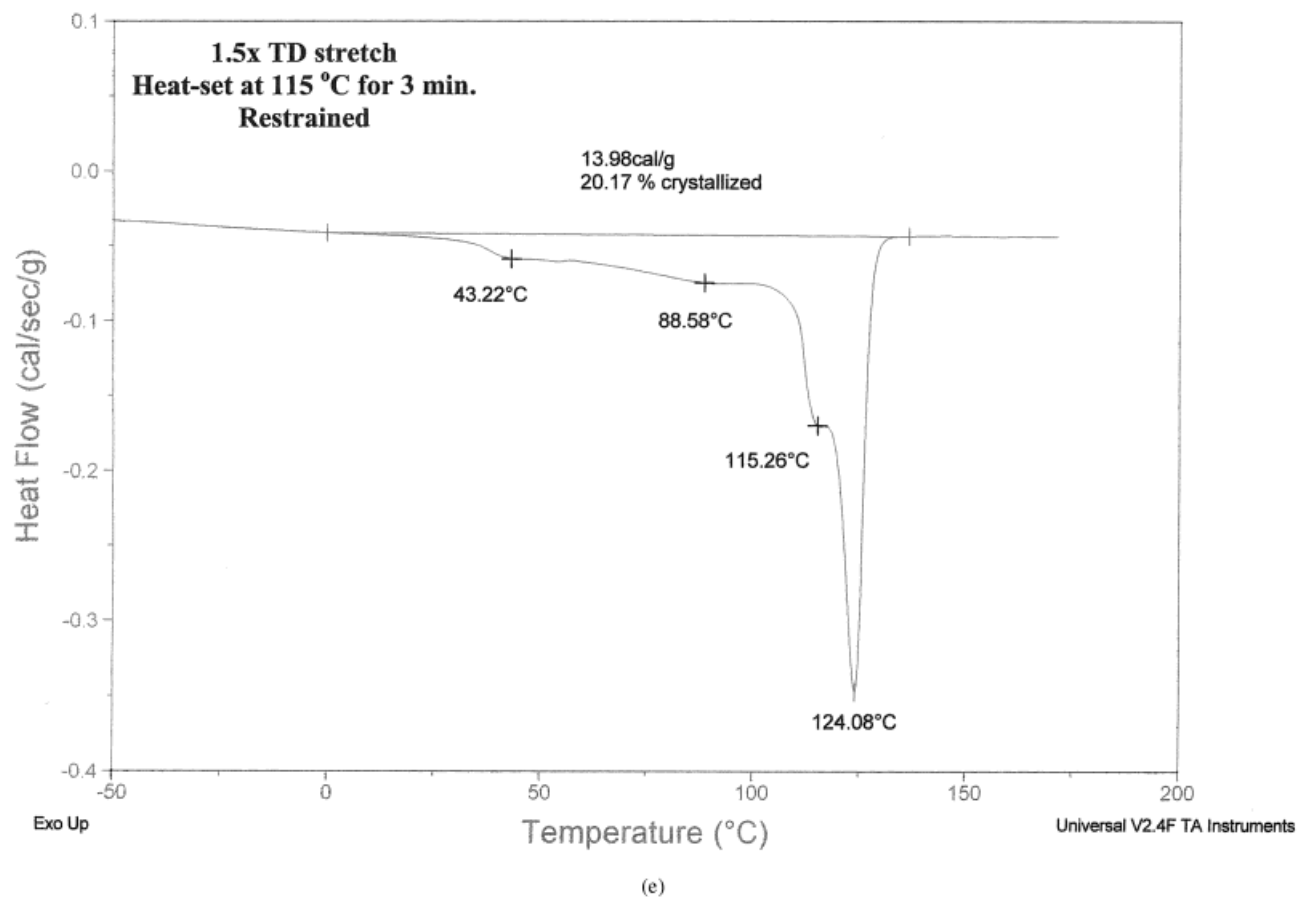


Figure 9 (Continued from the previous page)

clearly associated with increasing crystallinity. This was reasonable if we consider the fact that the activation energy for crystallization would be expected to decrease in the oriented film, thereby affecting E' more in the orientation direction. Alternatively, changes in E' in the MD were more clearly associated with closure of the pores because no significant change in the MD E' or MVTR occurred until the heat-set temperature was 115°C. The pores had the general shape of a prolate ellipsoid, with the major axis parallel to

the stretching direction. When such a pore is closed, then a greater change in E' would be expected parallel to the minor axis because that is the direction of the greatest change in the cross-sectional area of the void.

CONCLUSIONS

Calcium-carbonate-filled LLDPE films were successfully stretched by the interdigitation method to create a porous material that allowed for the diffusion of water. Higher degrees of stretch resulted in increased MVTRs and reduced E' because of the creation of more pores. These films were heat-set to remove residual stresses and to create a smooth, more clothlike, aesthetically pleasing material, while retaining necessary MVTRs. Heat-set times greater than 1 min did not have significant effects on the film properties. Heat setting at temperatures equal to or below 85°C reduced MVTR to a small degree and in-

Table V Heat of Fusion at 1 × 1.5 Stretched Heat-Set Film

Heat-Set Temperature (°C)	Heat of Fusion (cal/g)
No stretch	13.12
25	13.25
65	13.2
85	13.93
115	13.98

creased E' . The former effect was attributed to pore closure, and the latter effect was attributed to a combination of pore closure and annealing of the matrix material. Heat setting also created a better balance of properties between the MD and TD. Heat-set temperatures above the Vicat softening point of the filled film resulted in large shifts in all properties because of pore closure when THDT and DMTA increased and MVTR decreased toward that of the unstretched film. Crystallization occurred because of heat setting as thermal transitions corresponding to the heat-set temperature were detectable by DSC.

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