Dimensional Stability of Oriented, Rigid Poly(vinyl chloride)

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ABSTRACT: Oriented PVC has enhanced properties, but on heating it begins to shrink and eventually reverts to its original dimensions. Thermomechanical analysis was used to study the effects of orientation variables and subsequent annealing or aging on the shrinkage of rigid PVC. The thermal history of the oriented PVC affected its crystallinity and the free volume in the oriented structure. These changes modified the temperature at which the oriented samples began to shrink (i.e., their dimensional stability.) Higher draw and annealing temperatures can be used to improve dimensional stability; however, their effective use is limited because PVC has a peak elongation at 90°C. Increased annealing time also increases dimensional stability. Aging greatly improves the dimensional stability of the material; this process can be accelerated at temperatures up to 60°C. The shrinkage onset temperature can be increased without compromising the enhancement of mechanical properties achieved by orientation. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 3859–3867, 2003

Key words: aging; drawing; orientation; PVC; shrinkage

INTRODUCTION

The enhancement of the mechanical properties of PVC by orientation is well known and has been reported widely in the literature.[1–7] The process continues to attract attention as a means of developing the performance of PVC products; see, for example, the recent number of articles on biaxially oriented PVC pipes.[8–11] However, the structure developed in oriented PVC products is not permanent. When an oriented PVC product is reheated, the material will at some temperature begin to shrink and under certain conditions can revert to its original dimensions. Thus, it is very important to understand how the dimensional stability of oriented PVC relates to the stretching process. This will determine whether the temperature at which oriented PVC products begin to shrink can be manipulated to increase the service temperature range of such products without compromising the enhancement of the mechanical properties.

Previous studies on thermomechanical analysis (TMA) of oriented polymers generally have fallen into two categories: measurement of retractive force[12–14] and measurement of dimensional change.[15–17] Both methods have been applied to rigid PVC,[12,15] showing that significant changes in the oriented samples only occurred as the glass-transition temperature (T_g) of the material under test was approached. For example, a biaxially oriented sheet of rigid PVC with a T_g of 74°C began to shrink at 64°C.[12]

Research in our laboratories on the orientation of PVC has made a significant contribution to the subject.[18–23] The main objective throughout has been to develop an understanding of the structure–property relationships in oriented PVC. A detailed study was done of all the parameters that affect biaxial orientation, namely, the draw conditions of temperature, rate and ratio and the subsequent annealing conditions of temperature and time. The tensile and impact properties of the oriented sheets were measured and techniques such as X-ray diffraction, TMA, and birefringence were used to characterize the structure. The draw ratio was found to be the most significant factor controlling the enhancement of mechanical properties. This improvement in properties could be optimized by drawing PVC at its peak elongation temperature, 90°C. Annealing of the oriented PVC under restraint for longer times or at increased temperature improved the dimensional stability of the material on subsequent reheating.

The shrinkage of oriented rigid and plasticized PVC was considered in a recent article.[23] The objective of the current article is to provide an understanding of how the shrinkage of oriented rigid PVC relates to the process of orientation. To do this, examples are presented to show how each of the draw parameters and the annealing variables affects the shrinkage of oriented PVC. To complement the TMA data, tensile properties for the oriented materials are also included

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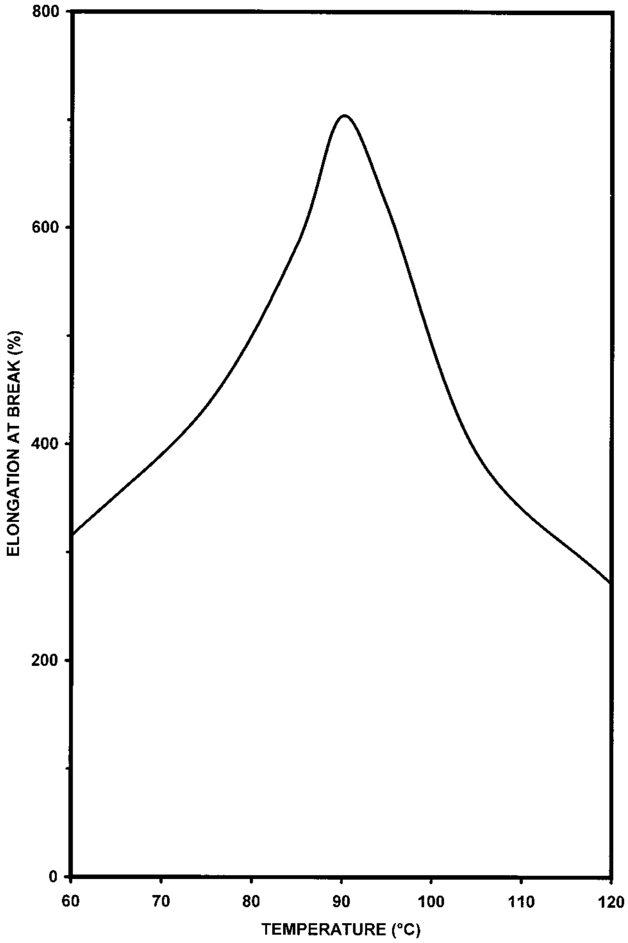

Figure 1 Characteristic curve of elongation at break for PVC: uniaxial tensile data for the SH70 formulation.

where considered appropriate. Finally, some more recent data on the effects of aging on shrinkage are presented.

EXPERIMENTAL

Materials

Two rigid PVC formulations were used. For the first, referred to as WS, pressed sheets of a formulation using a K61 PVC resin were supplied by Wardle Storeys (Brantham, UK) (Cobex 0680). These were initially produced by calendering and then pressed under hot platens to relieve any residual stresses. This material had a T_g of 77°C, a yield strength of 60 MPa and a strength at break of 54 MPa. The other formulation, which will be called SH70, contained 100 phr of PVC (Evipol SH7020), 2 phr of a liquid Ba/Zn stabilizer (Interstab M722), and 0.5 phr of stearic acid. Sheets of this latter formulation were prepared in our own polymer-processing area, initially by dry blending the compound in a high speed Fielder mixer, followed by milling at 160°C. Compression moldings were then produced from the milled product by pressing at 190°C. Finally, the moldings were cooled under pressure to ambient temperature in 7 min. The SH70 formulation had a T_g of 80°C, a yield strength of 61 MPa and a strength at break of 59 MPa. Figure 1 illustrates the previously mentioned characteristic property of rigid PVC formulations: its peak elongation temperature of 90°C.[24,25]

Sample preparation

Sheets of both formulations were cut into squares 116 mm × 116 mm and marked with a precise grid of 100 squares of 10 mm × 10 mm before stretching. The sheets were then stretched under a range of controlled drawing and annealing conditions using biaxial stretching equipment (the BASE) that was designed and built in our laboratories. (The specifications of the BASE and its operating procedures have been described previously.[26,27]) Draw conditions of 90°C and 50 mm/min were normally used except when the draw temperature and draw rate were the parameters under examination. Annealing of drawn samples was carried out under restraint in the environmental cabinet of the BASE, and, still under restraint, all oriented

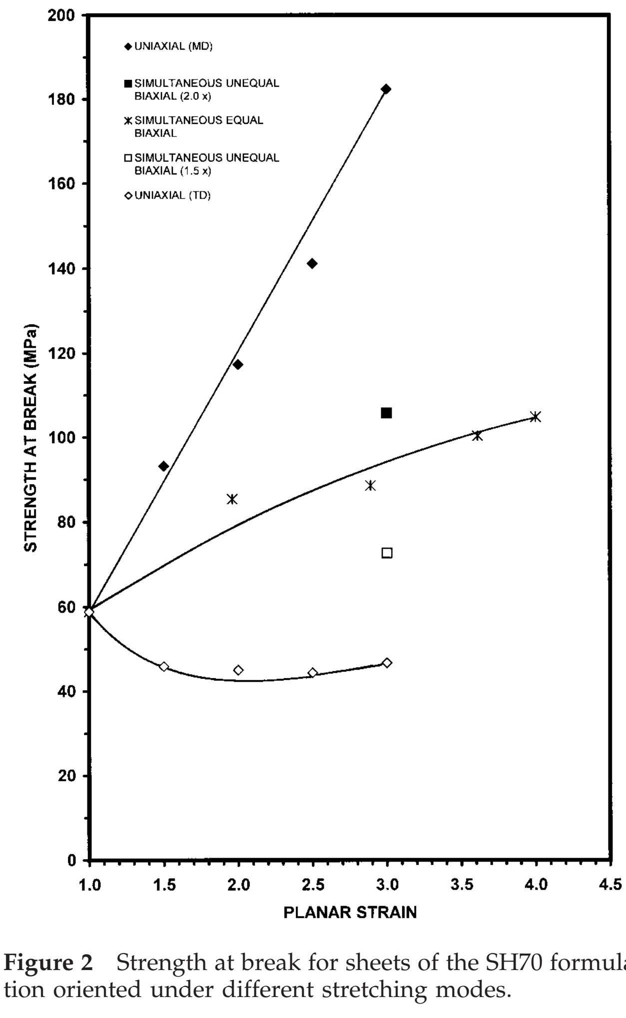

Figure 2 Strength at break for sheets of the SH70 formulation oriented under different stretching modes.

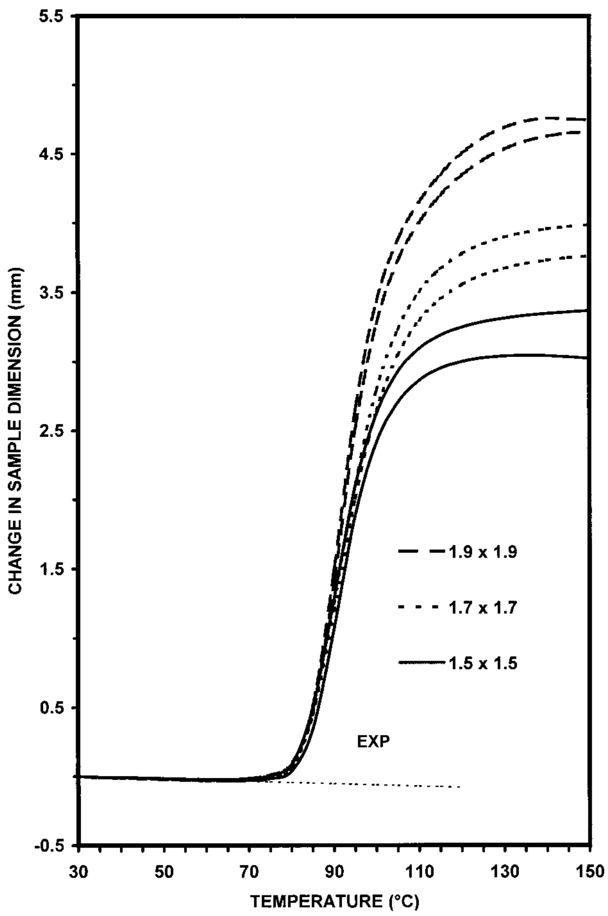

Figure 3 TMA curves for simultaneously equally biaxially oriented samples of the SH70 formulation (drawn at 10 mm/min and 90°C followed by 10 min of annealing at 90°C). Note: the pair of curves at each draw ratio represents measurements along the two perpendicular draw directions.

samples, whether annealed or not, were cooled to ambient temperature under the same regime. It took 15 min to cool the environmental cabinet and its contents to 25°C, the temperature at which oriented samples were removed from the cabinet. (Note: initial cooling was rapid, with the air temperature in the cabinet falling to 50°C in under 1 min.) The dimensions of the grid on the oriented product enabled the draw ratios achieved to be determined accurately.

The BASE offers a range of stretching modes: constant width uniaxial, unequal biaxial, and equal biaxial. In the constant width uniaxial mode the sheet dimension in the transverse direction is held constant while the sheet is drawn in the machine direction. Both biaxial modes can be carried out either simultaneously or sequentially. When the tensile properties were measured for sheets of both formulations oriented under various stretching modes, a well-defined pattern of behavior was established.[21,22] This can be seen in Figure 2 for the SH70 formulation where the properties for the uniaxially oriented sheet in the machine (MD) and transverse (TD) directions define the boundaries within which the properties for biaxially oriented sheets will lie. The dependence on stretching is well illustrated at a planar strain of 3, at which the tensile strength increases as the mode changes in the following order: uniaxial (TD), simultaneous unequal biaxial (minor draw), simultaneous equal biaxial, simultaneous unequal biaxial (major draw), uniaxial (MD). (Planar strain is defined as the final sample area divided by the initial sample area. It is also the product of the draw ratios of the oriented sheet.)

Thermomechanical analysis

In this work a Mettler TMA40 thermomechanical analyzer fitted with a film-and-fiber attachment was used to thermomechanical analysis (TMA) to measure dimensional change in the oriented samples. The attachment holds a narrow strip of material in its grips, leaving a precise sample length of 10 mm exposed to heating. In this study a sample width of 2 mm was used. A controlled heating rate of 10°C/min was employed, and a weight of 1 g (~ 0.01*N*) was applied to the probe attached to the free-moving grip. The oriented samples varied in thickness from 0.2 to 0.4 mm,

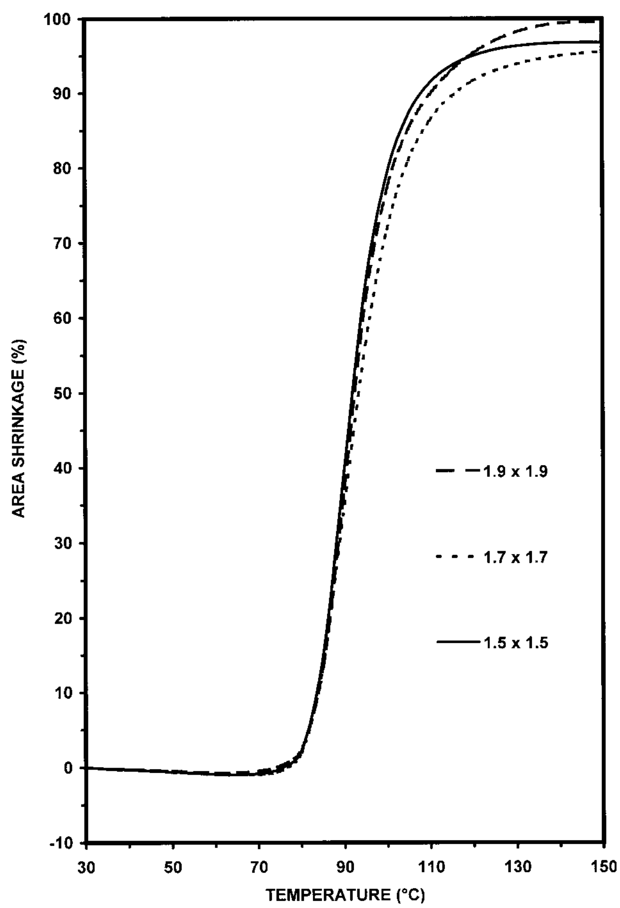

Figure 4 Calculated area shrinkage curves for the pairs of TMA curves of Figure 3.

TABLE I
Properties of Uniaxially Oriented Sheets of the WS Formulation (Drawn to 2.0 × and Annealed for 1 min at the Draw Temperature)

Draw temperature (°C)	Yield strength (MPa)	Strength at break (MPa)	Elongation at break (%)	Shrinkage temperatures O		
				Onset (°C)	5% As (°C)	50% As (°C)
80	89.8	116.5	70.3	59.5	78.3	85.8
90	82.3	114.9	82.7	61.6	78.8	89.4
100	79.1	109.7	91.2	64.7	80.2	94.8

so that applied stresses were initially low, ranging from 0.0125 to 0.025 MPa. (Note: as oriented samples start to shrink in the film-and-fiber attachment, sample thickness increases and the applied stress is reduced.)

Unoriented samples of both WS and SH70 were tested under a stress of 0.04 MPa up to a temperature of 150°C. In both cases only sample expansion was detected. Thus, it can be assumed that no contribution to the measured shrinkage from oriented samples can arise from the release of any strains imposed on the materials during processing.

For uniaxial sheets TMA samples were only cut parallel to the draw direction, whereas for biaxial sheets two TMA samples were examined: one cut parallel to the vertical draw direction of the BASE[26] and one cut perpendicular to it. Figure 3 shows typical TMA curves of change in sample dimension against temperature for pairs of rigid PVC samples cut from simultaneously drawn equal biaxial sheets of the SH70 formulation. The sheets were stretched at 10 mm/min and 90°C to different draw ratios and then annealed at 90°C for 10 min. Two important findings can be seen in Figure 3: first that samples with higher draw ratios will ultimately shrink more, which was the expected result; and second, the TMA curves initially showed a steady slope because of expansion until approaching the T_g (80°C) of the material, at which point the onset of shrinkage caused the curves to deviate from the expansion slope. In this study the shrinkage onset temperature was taken as the temperature at which the shrinkage curve began to deviate from the initial expansion slope (the line labeled EXP in Fig. 3).

RESULTS

To analyze the data for biaxial sheets, a method was adopted of combining the pairs of TMA curves to generate a single area shrinkage curve.[23] In this the changes in sample dimensions were used to calculate the change in area of the sheet as a function of temperature. Changes in area were then expressed as a percentage of the maximum recoverable area as determined by the draw ratios applied to the sheet. For convenience three temperatures were derived from the area shrinkage (As) curve: the shrinkage onset temperature and the temperatures at which 5% and 50% shrinkage had occurred. The 5% value is a measure of when shrinkage was established, and the temperature difference between the two percentage values is a good indicator of the slope of the curve once shrinkage has become established. The calculation of the area shrinkage curve for uniaxially drawn samples used a simplified form of the method for biaxial samples.

Draw parameters

Draw ratio

Figure 4 shows that the result of converting the pairs of TMA curves in Figure 3 into area shrinkage curves is to produce practically identical curves with similar shrinkage onset temperatures (Tobias and Taylor[15] also showed the onset of shrinkage to be unaffected by draw ratio). Thus, although draw ratio is the most important factor in determining the mechanical properties of oriented PVC, it has no effect on shrinkage

TABLE II
Properties of Equally Biaxially Oriented Sheets of the WS formulation (Simultaneously drawn to 1.8 × 1.8 and Annealed for 4 min at the Draw Temperature)

Draw temperature (°C)	Yield strength (MPa)	Strength at break (MPa)	Elongation at break (%)	Shrinkage temperatures		
				Onset (°C)	5% As (°C)	50% As (°C)
85	72.4	95.3	107.8	62.0	78.0	86.4
90	73.0	92.7	110.0	61.4	78.3	88.9
95	72.3	91.4	111.8	62.6	79.2	92.1
100	71.9	88.1	118.6	63.3	79.5	94.4

TABLE III
Shrinkage Temperatures for the SH70 Formulation under Different Stretching Modes (Drawn at 90°C and Annealed for 5 min at 90°C)

Stretching mode	Draw ratios	Planar strain	Shrinkage temperatures Onset (°C)	5% As (°C)	50% As (°C)
Uniaxial	3.0 × 1.0	3.0	61.0	80.8	93.0
Simultaneous unequal biaxial	2.0 × 1.5	3.0	64.5	83.7	94.6
Simultaneous equal biaxial	1.7 × 1.7	2.9	66.5	85.0	95.4

when the dimensional changes are expressed in terms of recoverable area, as the normalized curves are seen to overlap. It also can be observed that as final area shrinkage values approached 100%, the samples almost fully recovered their original dimensions. This also confirms that the low stress applied in the TMA did not affect the measurement of shrinkage.

Draw temperature

Oriented samples of the WS formulation were prepared by simultaneous uniaxial stretching and equal biaxial stretching. Tensile properties and shrinkage temperatures are presented in Tables I and II, respectively. In both cases, as the draw temperature was increased, there was a slight reduction in both the yield strength and strength at break, accompanied by increases in shrinkage temperatures, especially the onset temperature for the uniaxially stretched samples.

Draw rate

The BASE is capable of drawing sheets at a minimum rate of 1.3 mm/min and a maximum rate of 500 mm/min. When sheets of the SH70 formulation were oriented at these extremes to equal biaxial draw ratios of 1.8 × 1.8 (simultaneous mode), it was found that a similar enhancement of mechanical properties and similar temperatures were achieved (see the section of this article on aging).

Stretching mode

In Figure 2 tensile properties are given for sheets of the SH70 formulation oriented under different stretching modes and annealed for 5 min at 90°C. The shrinkage temperatures for these sheets are given in Table III. The results show that as the mode moved from uniaxial to simultaneous equal biaxial, the shrinkage temperatures increased.

Annealing parameters

Annealing temperature

Table IV gives the properties of the equally biaxially oriented sheets of the SH70 formulation that were annealed for 10 min at different temperatures after simultaneous stretching to 1.4 × 1.4. A low draw was necessary for this comparison because of the peak elongation behavior of PVC. This ensured that the sheet annealed at 110°C did not fail when heated to that temperature. The annealing time of 10 min included the time taken for the temperature to increase from the draw temperature to the chosen annealing temperature. Table IV shows that increasing the annealing temperature improved the dimensional stability of the oriented sheet, especially the onset and the 50% As temperatures. The yield strength of the material was largely unaffected by the annealing temperature, whereas the strength at break was reduced slightly.

Annealing time

Figure 5 illustrates the effect of annealing time on the shrinkage of equally biaxially oriented sheets of the WS formulation that were drawn simultaneously to 1.6 × 1.6. The sheets were annealed at a draw temperature of 90°C for various lengths of time. Table V

TABLE IV
Properties of Equally Biaxially Oriented Sheets of the SH70 Formulation Annealed at Various Temperatures (Simultaneously Drawn at 90°C to 1.4 × 1.4 and Annealed for 10 mins)

Anneal temperature (°C)	Yield strength (MPa)	Strength at break (MPa)	Elongation at break (%)	Shrinkage temperatures Onset (°C)	5% As (°C)	50% As (°C)
90	66.0	85.4	143.0	64.0	84.8	95.2
100	67.6	77.6	107.0	65.5	85.4	100.3
110	64.9	75.0	126.3	68.0	85.8	103.0

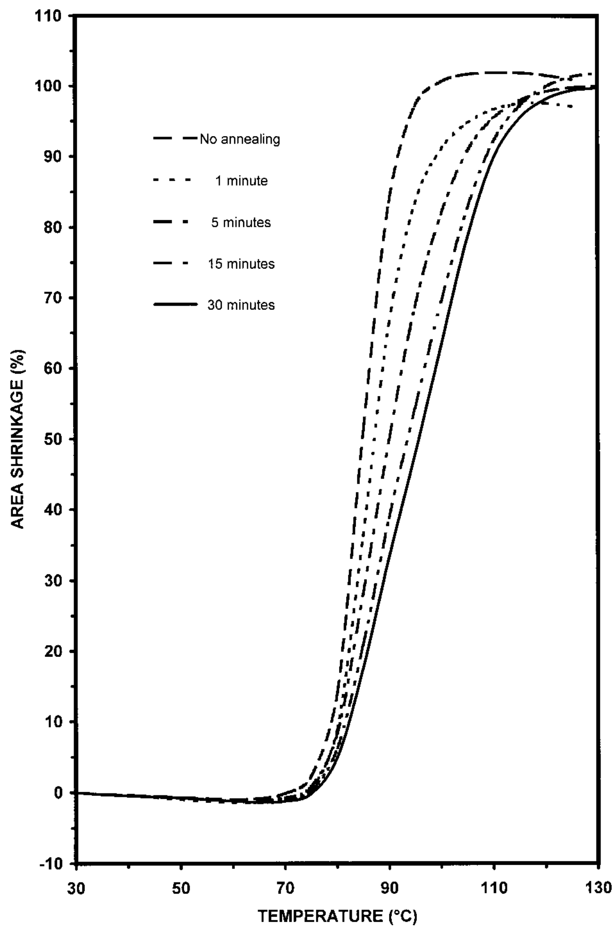

Figure 5 Effect of annealing time on simultaneously equally biaxially drawn sheets of WS (stretched at 90°C to draw ratios of 1.6 × 1.6).

shows that the annealing time had the same effect as the annealing temperature—although the tensile strength of the material was practically unaffected, the shrinkage onset temperature could be improved by several degrees.

In sequential stretching the option is available of having different drawing and annealing conditions for each step of the process. Given this situation, for practical reasons only two of the stretching parameters were considered worth investigating: draw ratio and annealing time. (It had been found that for sheets of rigid PVC biaxially oriented to the same draw ratios by the different modes of sequential and simultaneous stretching, the same enhancement in mechanical strength was achieved.[7,21])

To assess different annealing times, a series of equally biaxially oriented sheets of the WS formulation were prepared by sequential stretching at 90°C. In the first stage of drawing the sheet was uniaxially stretched (constant width) to produce draw ratios of 1.0 × 1.8, and in the second stage the sheet was drawn perpendicularly to the first draw direction to achieve final equal biaxial draw ratios of 1.8 × 1.8. Annealing times were varied from 1 to 10 min after the first draw and from 0 to 5 min after the second draw. For every combination of annealing times a slower shrinkage response was found in the first draw direction, as illustrated in Figure 6. Also, as with simultaneous equal biaxial orientation, variations in annealing time had little effect on the tensile properties of sequentially drawn equal biaxial sheets.

Aging

Aging over time

Table VI shows the shrinkage temperatures for sheets prepared at the extreme rates available using the BASE. Both sheets were simultaneously stretched to equal biaxial draw ratios of 1.85 × 1.85 and annealed for 2 min at 90°C. The sheets were first analyzed by TMA in April 1994 and then tested again more recently, in June 2000. It is clear that time had a substantial effect on the shrinkage temperatures. The reason for this can be seen in Figure 7, where typical DSC traces are shown for a pair of samples before and after aging. The aged sample shows an additional peak at around 75°C that arose because of a reduction in free volume in the PVC structure over time.[28] Clearly, the presence of this modified structure greatly delays the onset of shrinkage.

Oven aging

An oriented sheet of the WS formulation was prepared by uniaxial stretching to a draw ratio of 2.1 × and then annealed for 40 min at 90°C. The results shown in Table V suggest that such an oriented sheet should be dimensionally stable at 60°C. A strip measuring 125 mm by 20 mm was cut from the sheet and placed in an oven at 60°C for 10 days. On removal the length of the strip had been reduced by only 1.3%. Figure 8 shows that oven aging greatly modifies the shrinkage behavior with the onset temperature rising from 61°C without aging to 76.5°C after 10 days of aging.

TABLE V
Effect of Annealing Time on Properties of Equally Biaxially Oriented Sheets of WS (Simultaneously Drawn at 90°C to 1.6 × 1.6 and Annealed at 90°C)

Annealing time (mins)	Shrinkage onset (°C)	Yield strength (MPa)	Strength at break (MPa)
0	55.9	71.9	85.0
1	*	71.9	87.2
5	56.9	72.0	86.8
15	61.2	71.8	87.9
30	62.6	70.8	83.4

* Onset point could not be defined

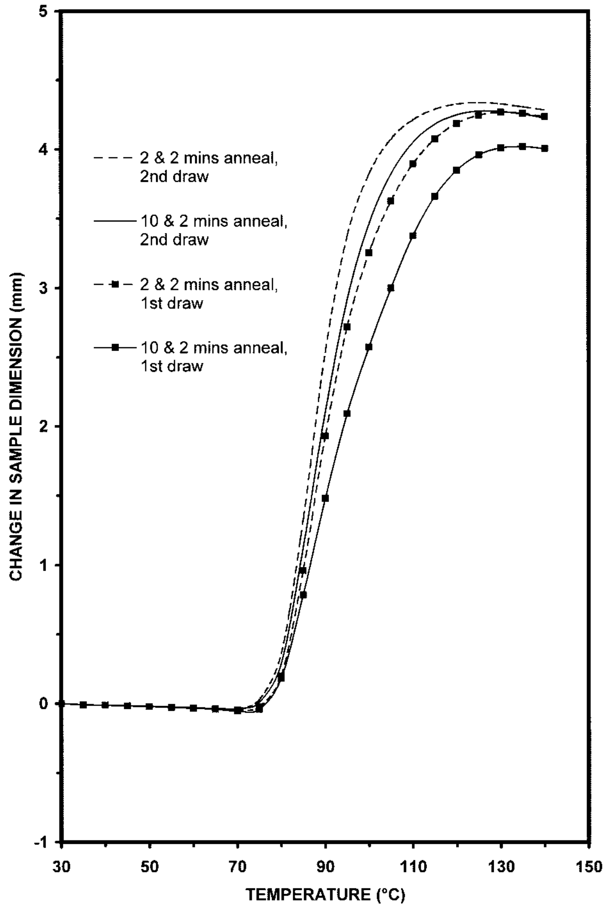

Figure 6 Pairs of TMA curves for sequentially oriented sheets of WS stretched at 90°C to draw ratios of 1.8 × 1.8 (the annealing times for the two draws in the sequence are given along with the draw direction for each sample).

The unaged and aged samples were also examined by DSC. The traces are shown in Figure 9. As with aging over time, an additional peak appeared in the trace for the aged sample. However, this time the peak was far bigger and sharper relative to the aging peak shown in Figure 7.

The same aging process of oven heating at 60°C for up to 10 days was applied to a series of equally biaxially oriented sheets of the WS formulation. These were drawn sequentially to 1.8 × 1.8 and annealed for 2 min at 90°C after each stage of drawing. The tensile properties in line with the second draw direction are listed

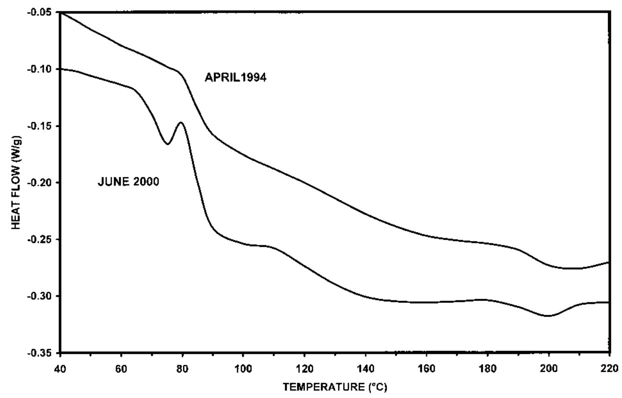

Figure 7 DSC traces for biaxially oriented sheets of SH70 before and after aging (stretching conditions as in Table VI: draw rate of 1.3 mm/min).

in Table VII, showing that properties at break were relatively unaffected by aging whereas yield strength improved.

DISCUSSION

The effects presented in the results can be largely understood in terms of the structure of PVC.[29] This effectively consists of a three-dimensional amorphous network of chains linked together by small crystallites that typically account for 5%–10% of the structure.

The improvement in dimensional stability of the oriented PVC as the mode was changed from uniaxial to equal biaxial is related to the nature of the oriented structure. When PVC sheets are oriented, it can be shown by X-ray diffraction that chains are aligned in the plane of the sheet. New mesomorphous structures are also produced.[22] In uniaxial stretching the alignment of crystallites effectively only occurred in the draw direction, whereas in the equal biaxial case the alignment was the same in all directions in the plane of the sheet. Thus, when the uniaxial sheet was reheated, its preferred orientation enabled shrinkage to occur more readily.

Chain alignment can also explain the effect of the draw ratio. Figure 3 shows that samples of increasing equal biaxial draw ratio will shrink more. However, when these dimensional changes are expressed in terms of recoverable area (Fig. 4), draw ratio was seen

TABLE VI
Effect of time on Shrinkage temperatures of oriented sheets of SH70 (Simultaneously Drawn at 90°C to 1.85 × 1.85 and Annealed for 2 mins at 90°C)

	April 1994			June 2000		
Draw rate (mm/min)	Onset (°C)	5% As (°C)	50% As (°C)	Onset (°C)	5% As (°C)	50% As (°C)
1.3	61.5	82.8	91.7	69.5	84.1	92.8
500	63.0	82.7	90.8	73.0	83.6	91.4

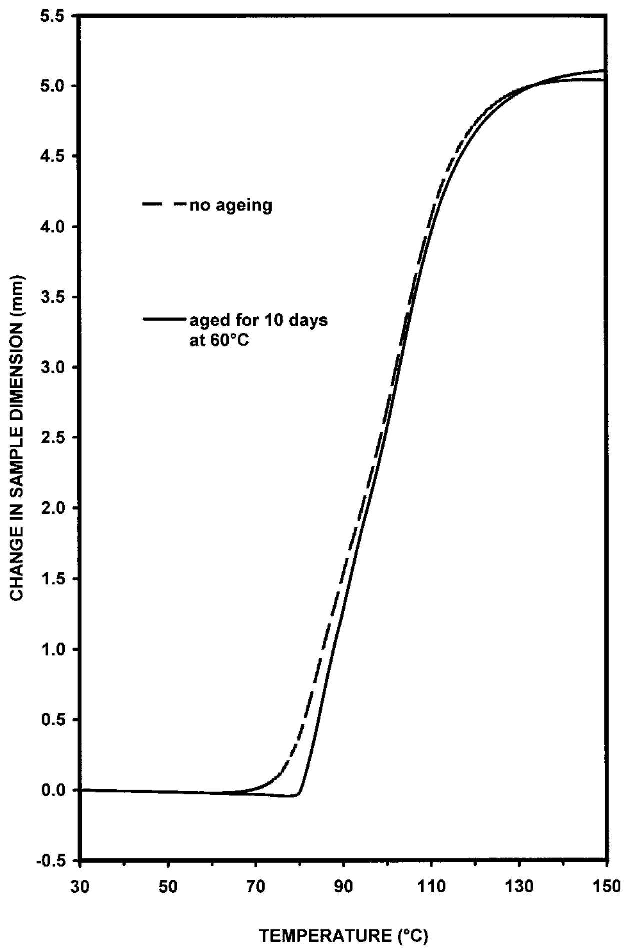

Figure 8 Effect of oven aging on the shrinkage of uniaxially oriented sheets of WS (drawn at 90°C to 2.1 × and annealed for 40 min at 90°C).

to have no real effect. It also was shown by X-ray diffraction[22] that increasing the draw ratio simply created more structural order of the same nature in the plane of the sheet. Thus, the temperatures required to

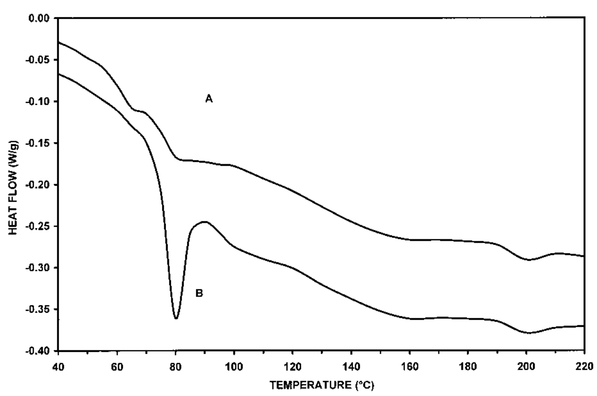

Figure 9 DSC traces for uniaxially oriented sheets of WS: (A) unaged and (B)oven aged for 10 days at 60°C (drawn at 90°C to 2.1 × and annealed for 40 min at 90°C).

TABLE VII
Tensile Properties of Oven-Aged Equally Biaxially Oriented Sheets of WS (Sequentially Drawn at 90°C to 1.8 × 1.8 and Annealed for 2 mins at 90°C After Each Stage of Drawing)

Days at 60°C	Yield strength (MPa)	Strength at break (MPa)	Elongation at break (%)
0	73.9	94.1	104.1
0.03	77.3	96.3	106.2
0.1	76.2	92.2	102.6
0.3	79.4	93.5	91.0
1	80.1	85.7	98.7
3	81.9	90.8	106.2
10	82.5	95.0	109.5

initiate shrinkage and to effectively promote full recovery were unaffected by draw ratio.

The effect of increasing the draw temperature was to improve the dimensional stability of oriented PVC (Tables I and II). At the same time, yield strength and tensile strength decreased, and elongation at break increased, suggesting a decrease in orientation because of more relaxation at the higher draw temperature. However, decreased orientation did not change shrinkage temperatures, as shown in Figure 4. It is known that heating PVC above its T_g results in the formation of 1%–4% crystallinity (by development of new crystallites and/or rearrangement of existing ones) that melts just above the annealing temperature, and increases in amount as annealing temperature increases.[28,30] It is suggested that an increase in draw temperature increases the amount and perfection of the crystallites in the structure, which "locks" the amorphous chain alignment in place, and as a result the whole structure becomes more dimensionally stable. However, this advantage of drawing at higher temperatures is offset by the limitation this places on the achievable draw ratio, as dictated by characteristic peak elongation curve (Fig. 1).

Increasing the annealing temperature after stretching (Table IV) had the same effect as draw temperature, that is, dimensional stability was improved. However, the effective use of this parameter was also restricted by the peak elongation curve. The initial draw ratio must be less than the extensibility of the PVC at the chosen annealing temperature to avoid failure of the drawn sheet during annealing. Tobias and Taylor[15] also found that dimensional stability of biaxially oriented PVC improved by increasing the draw temperature and by heat-setting of the material at temperatures above the draw temperature.

Increasing the annealing time also improved the stability of oriented PVC (Table V), and again it is suggested that the crystallites were perfected during this process. In sequential stretching shrinkage the response is always slower in the first draw direction

(Fig. 6). This is simply because the first draw direction is effectively annealed for longer than the second.

Physical aging is a widespread phenomenon that can be explained by the free-volume concept.[31] It is well known that rigid PVC, having a T_g above room temperature, undergoes property changes during room temperature storage.[32] The results here showed that it also occurs in oriented PVC samples and affects shrinkage behavior. In fact, aging of PVC produces far larger improvements in the dimensional stability of oriented PVC than any of the parameters discussed so far. Whether oriented PVC is aged over time or aged in an oven, significant changes in free volume occur, causing tighter packing of the PVC chains (this accounts for the increase in yield strength with aging shown in Table VII). The reduction in available free volume will prevent movement of the oriented chains on reheating until some free volume is generated.[28] The additional peaks in the DSC traces of the aged samples (Figs. 7 and 9) show that temperatures of 75°C and higher were needed to enable the free volume to increase sufficiently for chain relaxation to occur. This explains why aged samples had such high shrinkage onset temperatures.

CONCLUSIONS

The dimensional stability of the oriented structure was dependent on the thermal history of the sample and on how this changed the crystallinity and free volume in the oriented structure.

Higher draw and annealing temperatures can be used to improve dimensional stability; however, their effective use for highly oriented samples is limited because PVC has a peak elongation temperature of 90°C. Increased annealing time also increases dimensional stability.

Aging is the easiest way to manipulate the shrinkage of oriented PVC and to significantly improve the dimensional stability of the material. This can be achieved in a practical way by oven aging.

The mechanical properties of oriented PVC were determined by the draw ratios achieved during the stretching process. None of the means by which the shrinkage onset temperature can be increased appeared to significantly affect the enhancement of the mechanical properties.

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