

Thermal Behaviors of Heat Shrinkable Poly(vinyl chloride) Film

Chang Kook Hong,¹ Hakmyun Maeng,¹ Kigook Song,² Shinyoung Kaang¹

¹School of Applied Chemical Engineering, Chonnam National University, Gwangju 500-757, Korea

²Department of Chemical Engineering, Kyung Hee University, Yongin-si, Kyunggi-do 446-701, Korea

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ABSTRACT: The thermal behaviors of heat shrinkable poly(vinyl chloride) (PVC) film, used as a packaging material in electronic applications, were investigated. The entropic shrinkage and the thermal shrinkage force were monitored as functions of time and temperature. The shrinkage of the drawn film started in the vicinity of the glass transition temperature, and the percentage shrinkage increased with increasing temperature. The degree of shrinkage depended primarily on the draw ratio. The shrinkage force of the drawn film became dominant at around T_g . At a lower temperature, the shrinkage force did not fully develop, whereas at a higher temperature,

the relaxation process was very fast and partially inhibited the build-up of the force. The peak shrinkage force reached a maximum and decreased as the temperature increased. The orientation in the drawn film decreased and the dichroic ratio increased at elevated temperatures. No significant change in the degree of crystallization was observed during the shrinkage of the drawn PVC films. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 886–895, 2009

Key words: thermal behavior; poly(vinyl chloride); entropic shrinkage; thermal force; molecular orientation

INTRODUCTION

Poly(vinyl chloride) (PVC) is a thermoplastic polymer that exhibits good mechanical and thermal properties and fair chemical resistance.¹ PVC is widely used for cable insulation and heat shrinkable tubes. Shrinkable tubes or films are used as packaging materials in electronic applications. When heated up to certain temperatures they shrink, thus providing better product conditioning and protection. In most packaging applications, a high shrink force is desirable, combined with good mechanical performance. In addition, PVC actually retards fires both from starting and from spreading because of the inherent flame-retardant nature of its chlorine content.¹

Thermal shrinkage behaviors have been investigated for poly(ethylene terephthalate),^{2–7} polyethylene,^{8,9} polystyrene,¹⁰ poly(methyl methacrylate),¹¹ and other semicrystalline polymers.^{12,13} Drawn polymeric films shrink at elevated temperatures, since the extended molecules tend toward a coiled conformation because of entropic considerations. In drawn polymeric films, the molecules are oriented. These molecules are in a low entropy state because of their high order. If heat is applied to an unconstrained

film, the polymer chains will rapidly collapse through a coordinated set of molecular motions and return to a state of high entropy.¹¹ This shrinkage results in a change of the shapes of the film as its length shortens. It has been reported that the shrinkage behavior of semicrystalline polymers could be satisfactorily explained in terms of a two-phase system: an amorphous phase and a crystalline phase.¹⁴ The macromolecules in the amorphous region are linked to one another to form a network structure similar to that of a crosslinked rubber, and the macroscopic shrinkage results from the disorientation of the oriented amorphous region.^{5,14} On the other hand, there is negligible disorientation in the crystalline region during shrinkage.⁵

If the drawn polymer film is held at constant length to prevent shrinkage, shrinkage force develops. This force reflects the mobility of the segments in the noncrystalline region.⁵ Because of their entropic nature, these forces increase in magnitude with increasing temperature and are therefore greatest at high temperatures.⁹ The thermal shrinkage force develops rapidly and reaches a maximum. After that, the force is observed to relax with time, depending on the temperature and draw ratio. This stress relaxation is mainly due to the disorientation of the molecules in the amorphous regions.⁶ As the entropic force is developed, it can be measured as functions of time and temperature because of the molecular-relaxation processes.

Correspondence to: S. Kaang (kaang@chonnam.ac.kr).

TABLE I
Formulation of PVC Film Compound^a

Ingredients	Composition (part) ^b
PVC	100
Plasticizer DOP ^c	8
Heat stabilizer Zinc stabilizer	2
Impact modifier MBS ^d	1.5
Lubricant Calcium stearate	0.4
Process aid Acrylic process aid	0.1

^a Supplied by Moodeung Co. Ltd.

^b Ratio per hundred of PVC.

^c Di-2-ethylhexyl phthalate.

^d Methacrylate-butadiene-styrene.

In this study, the thermal shrinkage and shrinkage force of amorphous PVC film were investigated under various drawing conditions, such as the draw ratios, drawing speeds, and temperatures. The thermal shrinkage behaviors of shrinkable PVC films are not well understood. The characterization of the mechanical shrinkage stress is one of the primary methods of examining the orientation in amorphous materials. The orientation measurements of the drawn films were made using Fourier transform infrared spectrometer (FTIR), and the geometric analysis of the oriented polymer film was conducted by the infrared dichroism method. The changes of the glass transition temperature and degree of crystallinity in the drawn films were also estimated.

EXPERIMENTAL

Sample preparation

PVC film, supplied by Moodeung, was used for the measurement of the shrinkage behaviors in this study. The formulation of the film compound is given in Table I. The sample used was a suspension-polymerized PVC and its number-average molecular weight was 62,500 g/mol. The films were uniaxially drawn on a Universal Tensile Tester (Shimadzu Autograph AGS-500D) equipped with a temperature-controlled chamber. The drawing conditions for the

TABLE II
Drawing Conditions of PVC Films

Draw temperature (°C)	Draw speed (mm/min)	Draw ratio (DR)
50	10	1.50, 2.00, 2.75
	500	1.50, 2.00, 2.75
	1000	1.50, 2.00, 2.75
70	10	1.50, 2.00, 2.75
	100	2.00

TABLE III
The Dimensions of Tensile Test Samples

Sample	Thickness (mm)	Width (mm)	Length (mm)
Draw ratio = 1.00	16.0	0.19	20
Draw ratio = 1.50	12.0	0.16	20
Draw ratio = 2.00	9.9	0.13	20
Draw ratio = 2.75	9.0	0.12	20

samples are summarized in Table II. The films were drawn above their glass transition temperature.

Tensile property measurement

A universal tensile tester was used for the tensile property measurements of the drawn films. All tests were performed in a temperature-controlled chamber with a crosshead speed of 10 mm/min. The test temperature was varied to examine the effect of temperature on the tensile properties. The PVC films used for the tensile test were drawn at a temperature of 50°C and a draw speed of 10 mm/min. The dimensions of the films with various draw ratios are given in Table III.

Shrinkage measurements

The percentage of shrinkage was measured in a silicone oil bath maintained at a selected temperature. The films with a length of 10 mm were kept in the silicon oil bath for 15 min and then removed and allowed to cool to room temperature. No external constraint was imposed on the drawn films. The percentage shrinkage was obtained using the following expression:

$$\text{Shrinkage (\%)} = \frac{(l_o - l_s)}{l_o} \times 100 \quad (1)$$

where l_o is the initial length and l_s is the length after shrinkage.

The apparatus used for the shrinkage of stress measurements was previously described by Capaccio and Ward.⁸ The apparatus used is shown schematically in Figure 1. The shrinkage stresses of undrawn (draw ratio of 1.0) and drawn films were measured using the same procedures. The test involved clamping a sample with a length of 6 cm between two grips to keep its length constant. It was then lowered quickly into a silicon oil bath maintained at a constant temperature. The shrinkage force that developed was transmitted to a strain gauge transducer and the output was recorded as a function of time. The peak shrinkage force was determined from the maximum shrinkage force upon heating in a shrinkage force–time plot.

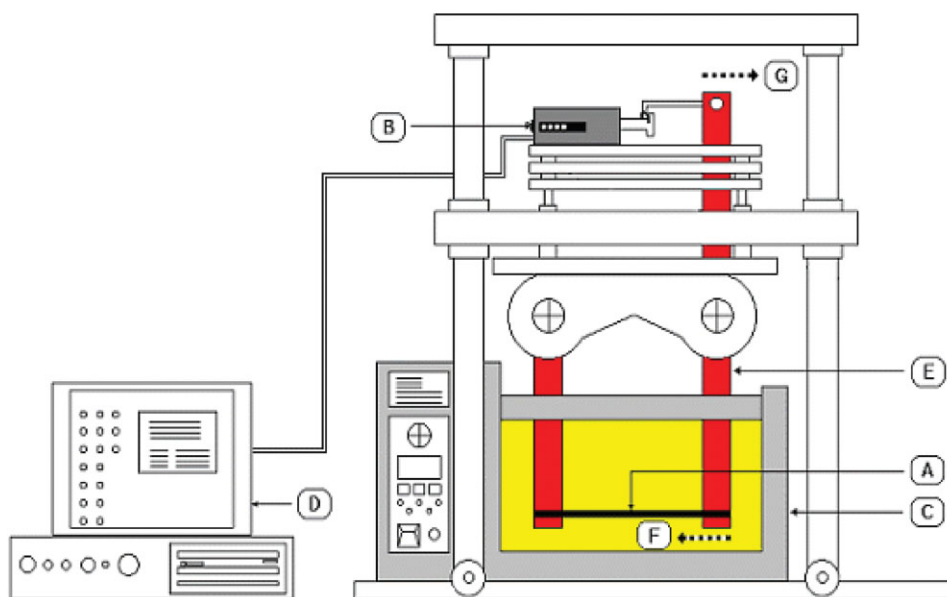


Figure 1 Schematic diagram of the apparatus used for the measurement of the shrinkage force: A: specimen; B: load cell; C: silicon oil bath; D: detector and personal computer; E: arm; F: shrinkage direction of specimen; G: direction of shrinkage force. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Orientation analysis by FTIR-ATR

The surface molecular orientation of the drawn film was analyzed by an attenuated total reflection FTIR-ATR dichroism method. Also, polarized FTIR was used to directly quantify the degree of molecular orientation in the polymer films.¹⁵⁻¹⁷ The FTIR spectrometer (Perkin-Elmer system 2000) equipped with a KRS-5 wire grid polarizer (Harrick Scientific) and a variable angle specular reflectance accessory (Perkin-Elmer) was used to record the reflection spectra with the polarized direction parallel and perpendicular to the draw direction. All of the IR spectra were obtained at an incident angle of 45°, a resolution of 4 cm⁻¹ and at room temperature. The dichroic ratio (D) of the analyzed bands was calculated from the ratio of the absorption intensities measured with the IR radiation polarized parallel (A_{\parallel}) and perpendicular (A_{\perp}) to the draw direction, as given by the following equation:

$$D = \frac{A_{\parallel}}{A_{\perp}} \quad (2)$$

The dichroic ratio provides useful information on the geometrical structure of the polymer chains. The dichroic ratio of a uniaxially oriented polymer is a function of two characteristic orientation angles, θ and α .¹⁵ θ is the angle the polymer chain axis makes with the draw direction, and α is the angle the transition moment makes with the polymer chain axis. If all of the molecular chain axes of an oriented film were perfectly aligned parallel to the reference direction, the dichroic ratio would be a function of the transition moment angle, α :

$$D_o = 2 \cot^2 \alpha \quad (3)$$

where D_o is the dichroic ratio for perfectly aligned chains. For a uniaxially drawn film, the molecular orientation is sufficiently described by the Hermans orientation function. Under normal conditions, when the molecular chain axis is oriented at an average angle of θ to the draw direction, the equation takes the form:¹⁵

$$f = \frac{(D-1)(D_o+2)}{(D+2)(D_o-1)} = \frac{3(\cos^2 \theta) - 1}{2} \quad (4)$$

A value of 1 for f represents perfect orientation of the chain axes parallel to the draw direction, a value of zero is obtained when the chains are randomly oriented, and a value of $-1/2$ represents perfect orientation of the chains perpendicular to the draw direction.¹⁷

Thermal property measurements

A differential scanning calorimeter (Perkin-Elmer DSC 7) was used to determine the thermal properties of the drawn films. A heating rate of 10°C/min was used under a nitrogen atmosphere. The degree of crystallinity is defined as follows:

$$X_c (\%) = \frac{\Delta H_f}{\Delta H_f^0} \times 100 \quad (5)$$

where X_c is the degree of crystallinity, ΔH_f is the enthalpy of fusion measured at the melting point, and ΔH_f^0 is the enthalpy of fusion of the totally

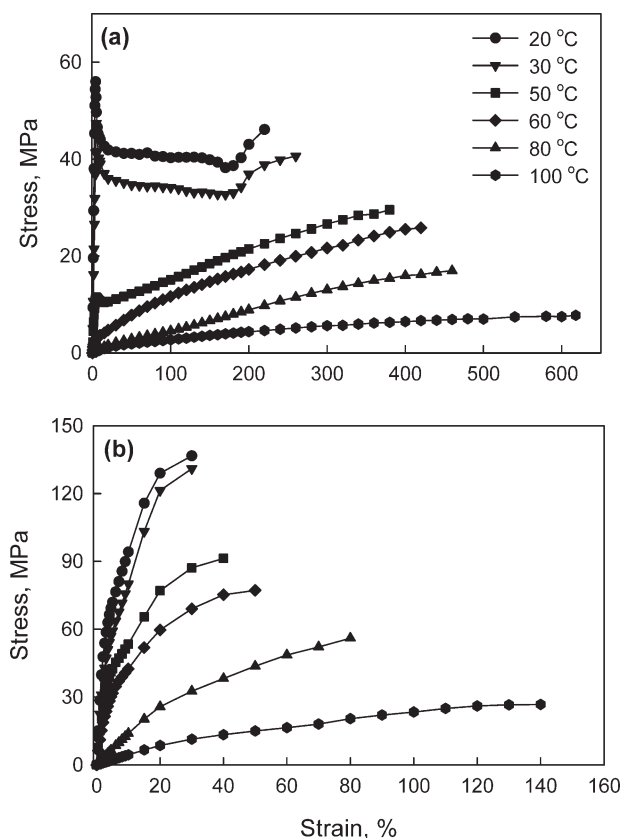


Figure 2 The effect of temperature on the stress–strain curves of the PVC films: (a) undrawn and (b) drawn at 50°C, 10 mm/min and draw ratio (DR) = 2.75.

crystalline polymer measured at the equilibrium melting point. The ΔH_f^0 value of PVC is 43.932 J/g.¹⁸

RESULTS AND DISCUSSION

Tensile properties of the films

Figure 2 shows the effects of temperature on the stress–strain curves of the undrawn and drawn PVC films. The undrawn sample at ambient temperature was yielded through the formation of a neck, followed by a region of cold drawing at almost constant stress. A neck is the narrowing of a portion of the stressed material to a smaller cross section.¹⁹ In the region of the neck, an extensive reorganization of the polymer chain took place. This was reflected in the sharp drop in the measured stress–strain curve corresponding to the yield point. The necked region then grew until the whole gauge length of the film had undergone necking. The yield strength decreased with increasing test temperature. However, as the test temperature approached the glass transition temperature (T_g), the yield behavior and subsequent deformation was significantly modified. PVC deforms in a rubber-like manner at temperatures above T_g because of its long-range coordinated

molecular motion, as shown in Figure 2(a). The T_g of the PVC film measured by DSC in this study is decreased to about 50°C because of the added ingredients shown in Table I. The T_g of PVC was lowered by adding a plasticizer. When the material was drawn at temperatures above the T_g , the polymer chains were progressively straightened and became loosely aligned in the direction of the applied draw.²⁰ The mechanical properties of PVC can be improved substantially by stretching at temperatures above the T_g value. When the film is fully stretched at temperatures above T_g , the molecules of the film are highly oriented parallel to the draw direction. The highly oriented film has a high tensile strength and turns brittle. When a sufficiently high strain was imposed on the rigid PVC film formed by inducing its orientation above the T_g value, no necking was observed during the subsequent testing of the tensile samples at ambient temperature, because the molecules had become highly oriented, and the yield point was seen as an inflection point in the stress–strain curve, as shown in Figure 2(b).

The effect of temperature on the Young's modulus of the PVC films drawn at various draw ratios is shown in Figure 3. Increasing the temperature led to a drastic decrease in the Young's modulus. The film was softened by the increased molecular motion at elevated temperature. An inflection point was also observed near the T_g of the PVC film. The Young's modulus increased with increasing draw ratio because of the orientation of the chains. It is thought that the draw ratio is an important factor determining the Young's modulus of oriented PVC films.

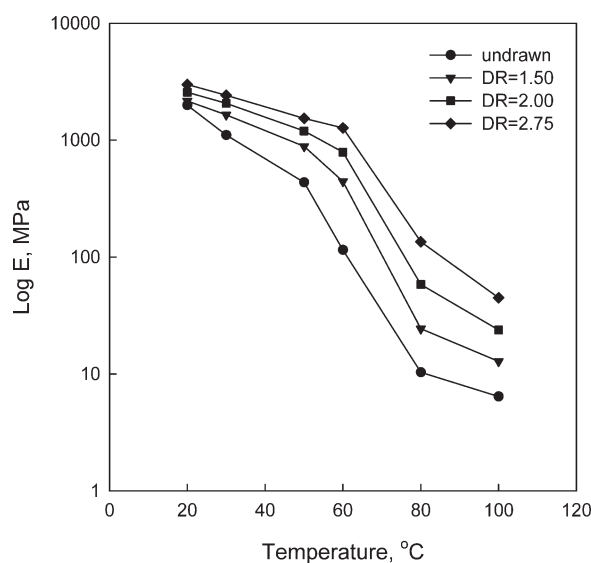


Figure 3 Effect of temperature on the Young's modulus of the drawn PVC films at various draw ratios (drawing condition: draw speed of 10 mm/min and draw temperature of 50°C).

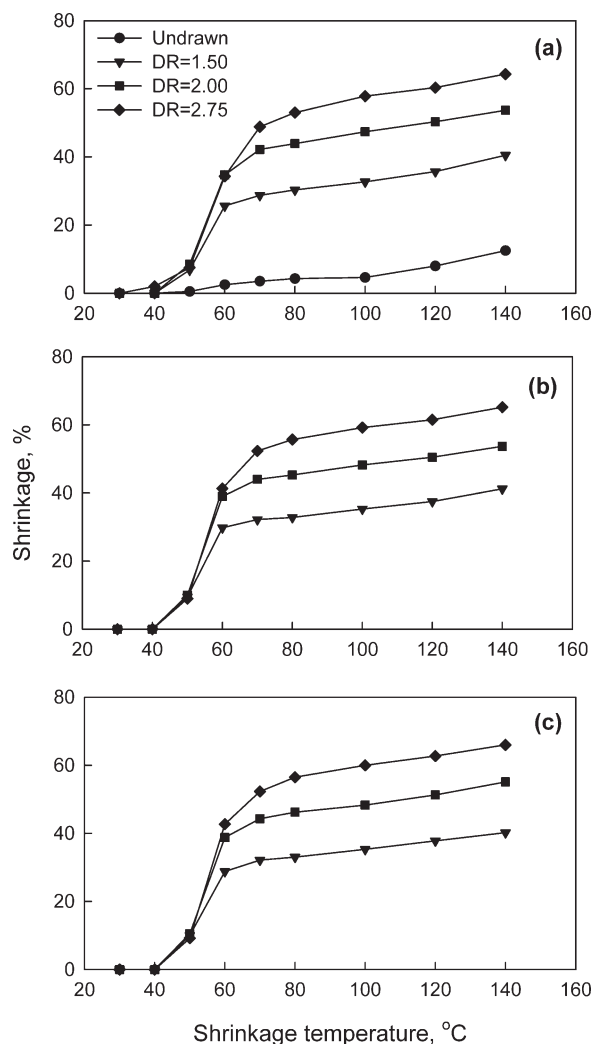


Figure 4 Shrinkage versus shrinkage temperature for the PVC films drawn at 50°C and at various draw ratios: at draw speeds of (a) 10, (b) 500, and (c) 1000 mm/min.

Thermal shrinkage

Figure 4 shows the percent shrinkage of the films as a function of the shrinkage temperature at various draw ratios. The drawn PVC films shrunk at elevated temperatures. The shrinkage started in the vicinity of the glass transition temperature of the films and increased with increasing temperature. Once the film is stretched, the elastic potential energy and the molecular orientation can be frozen-in. This film is in a low entropy state. The frozen-in elastic potential energy will, however, be dissipated as soon as the film is heated above the glass transition temperature, as a result of the resultant enhanced molecular mobility. In the absence of external constraints, the dissipation of energy will manifest itself as shrinkage and a return to a state of high entropy. The shrinkage was found to depend primarily on the draw ratio. The draw speed had little effect on the shrinkage of the oriented PVC films. The effects observed in

the results can be largely understood in terms of the structure of PVC, which effectively consists of a three-dimensional amorphous network of chains linked together by small crystallites that typically account for 5–10% of the structure.²¹ The molecular structure of PVC is similar to that of a crosslinked rubber, and the shrinkage is primarily associated with the oriented amorphous parts. The PVC films shrunk in a rubber-like elasticity, and the shrinkage percent increased with increasing the molecular orientation.^{20,22}

Figure 5 shows the shrinkage of the films drawn at various draw temperatures, as a function of the shrinkage temperature. As the draw temperature increased, the shrinkage started at a higher temperature and the onset temperature was increased. The effect of increasing the draw temperature was to improve the dimensional stability of the oriented PVC. Increasing the draw temperature decreases the molecular orientation because of the resultant greater relaxation of the chains at a higher draw temperature.²⁰ It is also 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.²²

Shrinkage force

Figure 6(a) shows the shrinkage forces of the undrawn PVC films as a function of time at various temperatures. The shrinkage force was measured in a silicon oil bath maintained at a constant

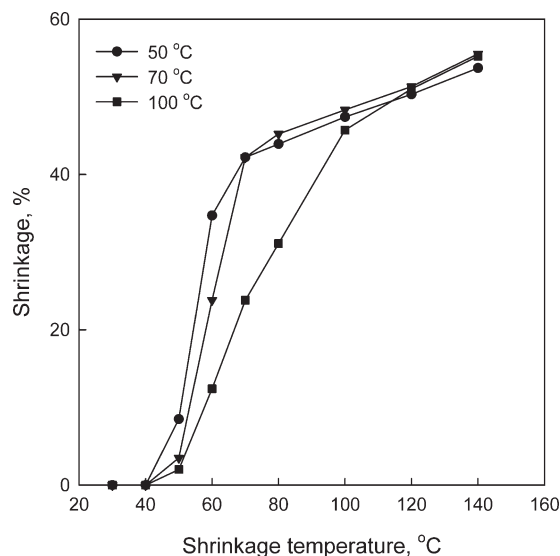


Figure 5 Shrinkage versus shrinkage temperature for the drawn PVC films at various draw temperatures (drawing condition: DR = 2.0 and draw speed of 10 mm/min).

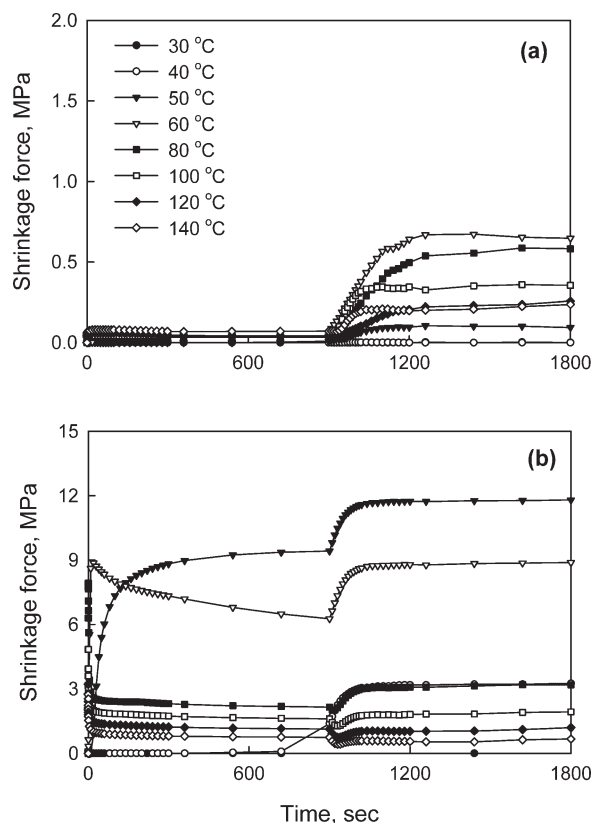


Figure 6 Thermal shrinkage force measurements of the PVC films at various temperatures: (a) undrawn and (b) drawn at 50°C, 10 mm/min, and draw ratio (DR) = 2.75.

temperature for 900 s and afterward the shrinkage force during cooling was measured in the outside at room temperature. In the oil bath, the shrinkage force of the undrawn film at elevated temperatures was very low. During cooling in the outside, the force increased slightly because of its contraction or crystallization of the molecules. The force started to develop near the T_g , reached a maximum at 60°C, and thereafter the shrinkage force showed a decreasing trend with increasing test temperature, within experimental error ranges. The shrinkage force of the drawn PVC films as a function of time at various test temperatures is given in Figure 6(b). The shrinkage forces of the drawn PVC films became dominant near the T_g . The force was generated at temperatures near the T_g as the oriented molecules in the amorphous regions of the film tended to assume a more coiled conformation. When the film is restrained from shrinking and is not cooled down immediately, it will inevitably relax to maximize the entropy and, as a result, the force decays.¹⁰ As soon as the sample was dropped in the oil bath, the temperature of the sample increased and the entropic force developed rapidly and reached a maximum. It relaxed more or less rapidly toward maximum entropy depending on the temperature. At lower temperatures, below

T_g , the shrinkage force did not fully develop because of the low mobility of the chains, whereas at higher temperatures, the relaxation processes were so fast that they were active even during the time required for the force to reach its maximum and thus partially inhibited the build-up of the force. Therefore, at temperatures above T_g , the shrinkage force decreased with increasing temperature, but the percent shrinkage increased with increasing temperature. These behaviors have been explained by two competing mechanisms,⁶ namely (a) stress generation, which arises largely from entropic forces exerted by contracting segments in the amorphous phase and, to a lesser extent, from the melting of the ordered regions at appropriate temperatures, and (b) stress relaxation, which results primarily from molecular disorientation, at least some viscoelastic flow, which may be preceded by network rupture leading to disentanglement and intermolecular slippage. It is also seen in Figure 6(b) that the force was increased during cooling (after 900 s) in air because of the competition between the disappearance of the entropic force and the development of the thermal contraction force.

Figure 7 represents the peak shrinkage forces of the PVC films drawn at various draw ratios as a function of the shrinkage temperatures. As expected, the peak shrinkage force was low at low temperature, especially at temperatures below the T_g values of the films. As the temperature increased beyond T_g , the entropic mechanism would be expected to start contributing to the shrinkage stress. With further increase in temperature, the shrinkage force decayed because of the fast relaxation. The shrinkage force relaxed depending on the temperature, and the peak shrinkage stress reached a maximum and subsequently decreased. Also, the peak shrinkage force increased with increasing draw ratio. This is an expected result and highlights the importance of molecular orientation. The higher the orientation, the higher is the shrinkage percent and shrinkage stress. The peak shrinkage force decreased with increasing draw speed at draw ratios of 1.5 and 2.0, possibly because of a viscous flow from slippage of molecules or the reorganization of the crystal phase. However, at higher draw speed of 1000 mm/min with higher draw ratio of 2.75, the contribution of the viscous flow decreases in favor of the elastic deformation, resulting in increased concentration of the oriented molecules and then higher peak shrinkage forces [see Fig. 7(c)]. At lower draw speeds and at around T_g , the molecules were oriented with partial relaxation (or viscous flow), and the amount of oriented molecules decreased with increasing draw speed at the same draw ratio. However, at higher draw speed of 1000 mm/min with a draw ratio of 2.75, the molecules in the amorphous region of PVC

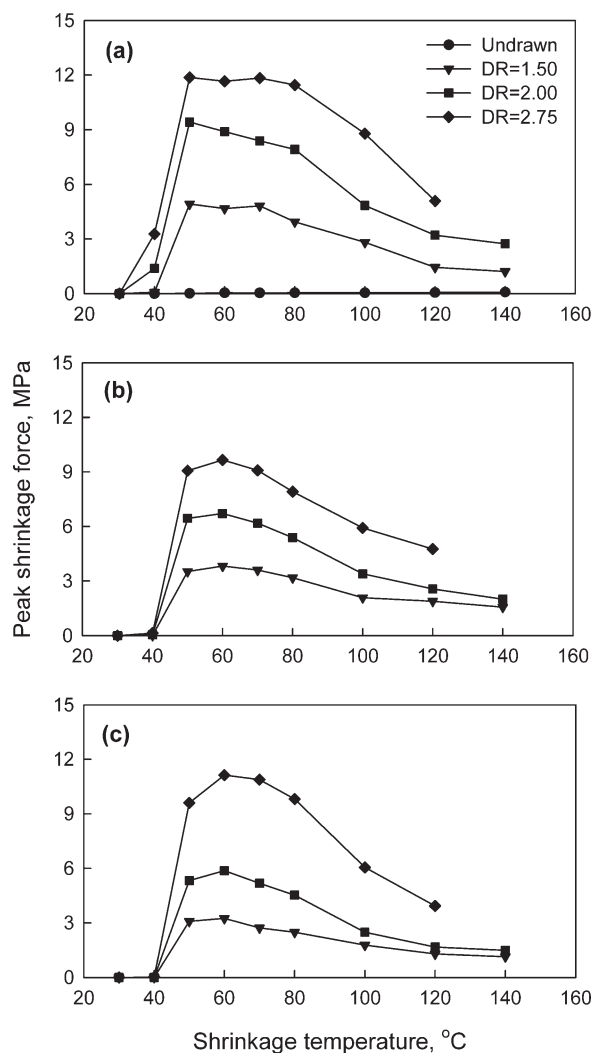


Figure 7 Peak shrinkage force of the drawn PVC films (at 50°C) at various draw ratios as a function of the shrinkage temperature: at draw speeds of (a) 10, (b) 500, and (c) 1000 mm/min.

were oriented with elastic deformation, thus the amount of oriented molecules increased. It is thought that the peak shrinkage force depends on the amount of oriented molecules at the same draw ratio (or orientation), and the shrinkage percent depends mainly on the molecular orientation. These can also explain why the draw speed had little effect on the shrinkage percent, as shown in Figure 4.

Figure 8 shows the effect of the draw temperature on the peak shrinkage forces of the films as a function of the shrinkage temperature. As the draw temperature increased, the peak shrinkage force decreased, suggesting that there was a decrease in the degree of orientation because of the increase in mobility of the polymer chains and relaxation at a higher draw temperature. Also, increasing the draw temperature increases the rearrangement of the crystallites, resulting in more stable structure.

Orientation measurements

Polarized FTIR-ATR was utilized to evaluate the molecular orientation of the drawn and shrunken PVC films. The polarized ATR spectra of the PVC films drawn at various draw ratios are shown in Figure 9 for representative values of the draw ratio: DR = 1.0, 1.5, 2.0, and 2.75 at 50°C and a draw speed of 500 mm/min. The stronger peaks at 610 and 630 cm^{-1} are assigned to the C—Cl stretching vibration of the chain segments.²³ The polarized spectra obtained for the undrawn film are almost identical. However, increasing the draw ratio resulted in pronounced differences between the spectra measured with the polarization perpendicular and parallel to the stretching direction.

Figure 10 shows the representative polarized ATR spectra of the shrunken PVC films at various temperatures. The orientation is generally assumed to disappear when the temperature is raised above T_g , because this allows the polymer chains to be released from the constraints induced by their orientation and, consequently, to recover the high entropy state because of their increased molecular mobility.

The dependence of the dichroic ratio on the draw ratio is shown in Figure 11 for the 610 and 630 cm^{-1} bands. For both bands, the dichroic ratio decreased with increasing draw ratio. Since the dipole moment for the C—Cl stretching vibration is directed perpendicular to the polymer chain backbone,²⁴ the decrease of the dichroic ratio is indicative of the degree of molecular orientation of the polymer chains along the stretching direction. Figure 12 shows the dichroic ratios of the shrunken PVC films

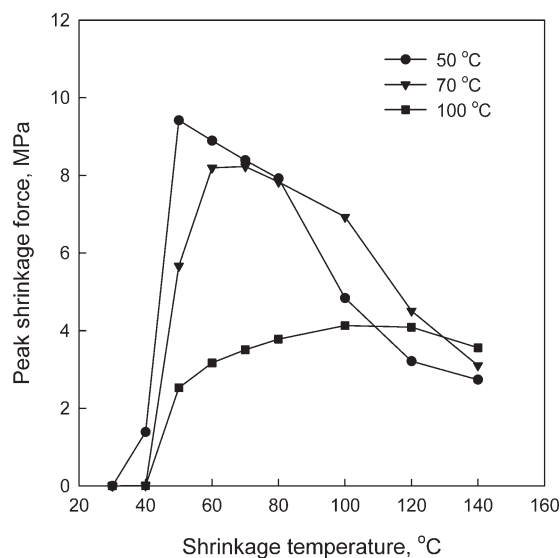


Figure 8 Peak shrinkage forces of the drawn PVC films at various draw temperatures as a function of the shrinkage temperature (drawing condition: DR = 2.0 and draw speed of 10 mm/min).

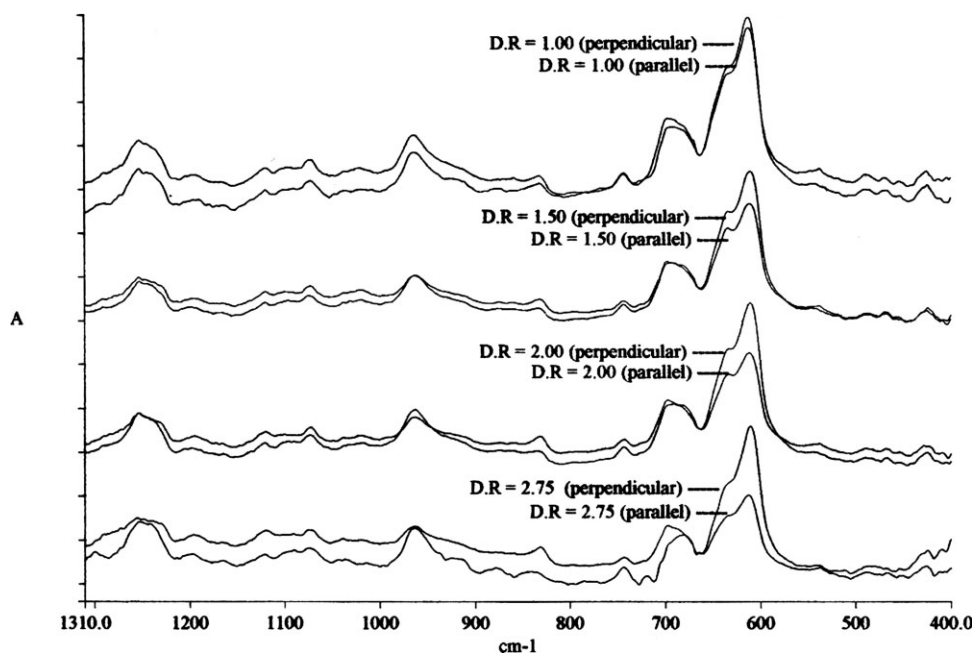


Figure 9 Representative polarized ATR spectra of the drawn PVC films at various draw ratios (drawing condition: draw speed of 500 mm/min and draw temperature of 50°C).

as a function of the shrinkage temperature. The dichroic ratio increased as the temperature increased. The oriented molecules that are in a low entropy state tend to shift toward a high entropy state at elevated temperature. The dichroic ratio of the films with a higher draw ratio increased more rapidly because of the entropic considerations associated with their higher orientation. However, the films did not totally recover their initial state, possi-

bly because of some viscoelastic flow during the draw process.

Assuming that α is 90°, eq. (4) can be used to calculate the Hermans orientation function of the orientation distribution of the PVC chains. A value of 1 for the orientation function represents perfect orientation of the chain axes parallel to the draw direction, and a value of zero is obtained when the chains are randomly oriented. Figure 13 gives the

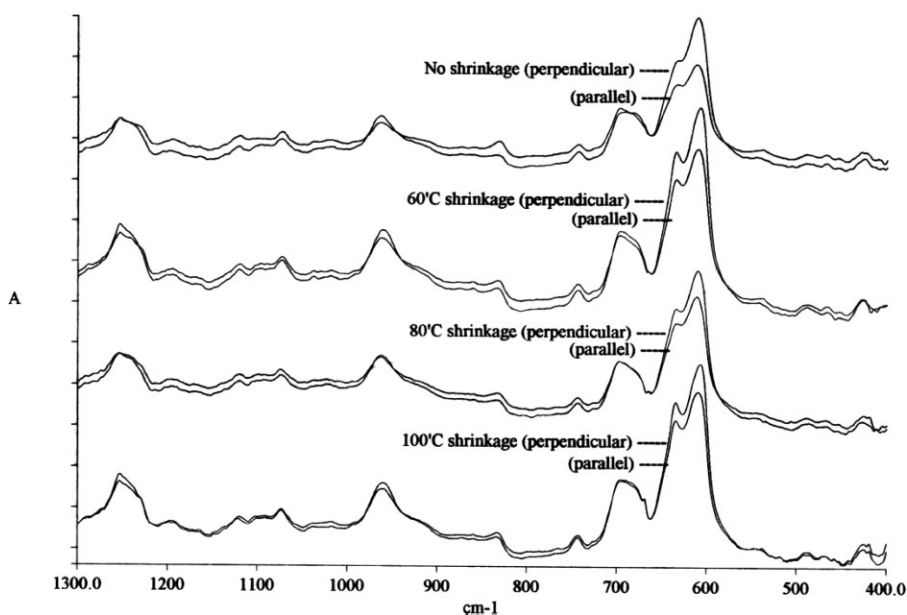


Figure 10 Representative polarized ATR spectra of the shrunken PVC films at various temperatures (drawing condition: DR = 2.0 and draw speed of 500 mm/min).

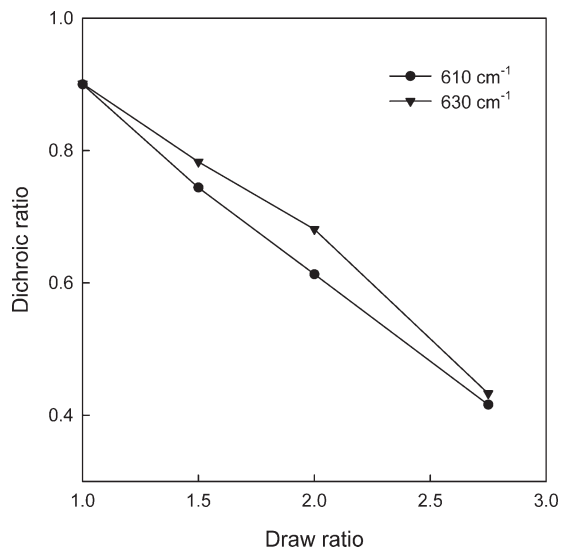


Figure 11 Dichroic ratio for the 610 and 630 cm⁻¹ peaks of the drawn PVC films as a function of the draw ratios (drawing condition: draw speed of 500 mm/min and draw temperature of 50°C).

dependence of the orientation function on the shrinkage temperature for the 610 and 630 cm⁻¹ bands of the drawn PVC films at various draw ratios. The orientation function increased as the

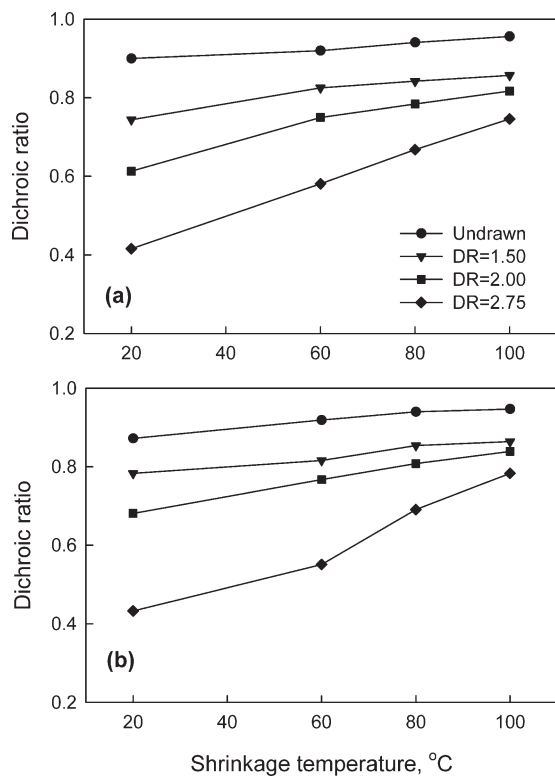


Figure 12 Dichroic ratio of the shrunken PVC films at various draw ratios as a function of the shrinkage temperature: (a) 610 cm⁻¹ and (b) 630 cm⁻¹ (drawing condition: draw speed of 500 mm/min and draw temperature of 50°C).

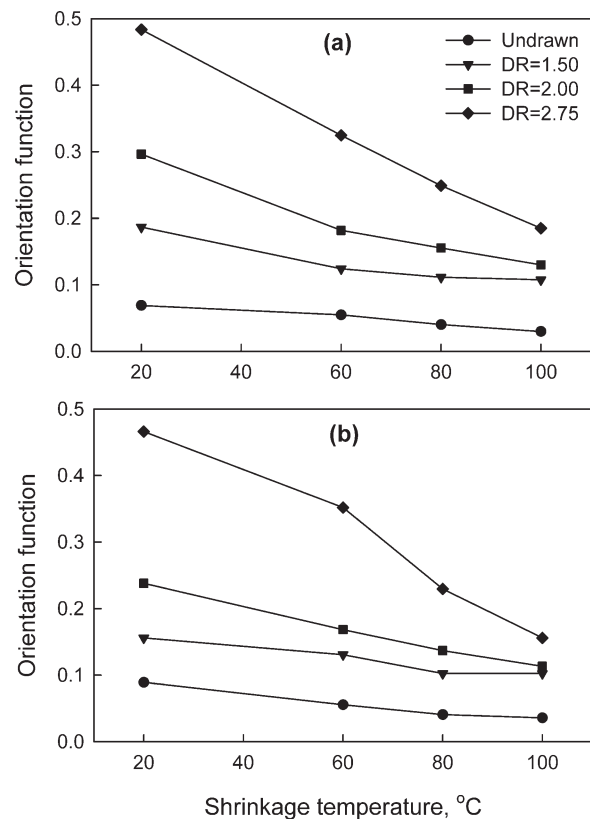


Figure 13 Orientation function of the shrunken PVC films as a function of the shrinkage temperature: (a) 610 cm⁻¹ and (b) 630 cm⁻¹ (drawing condition: draw speed of 500 mm/min and draw temperature of 50°C).

draw ratio increased and decreased with increasing temperature. The orientation function of the PVC films at a higher draw ratio decreased more rapidly.

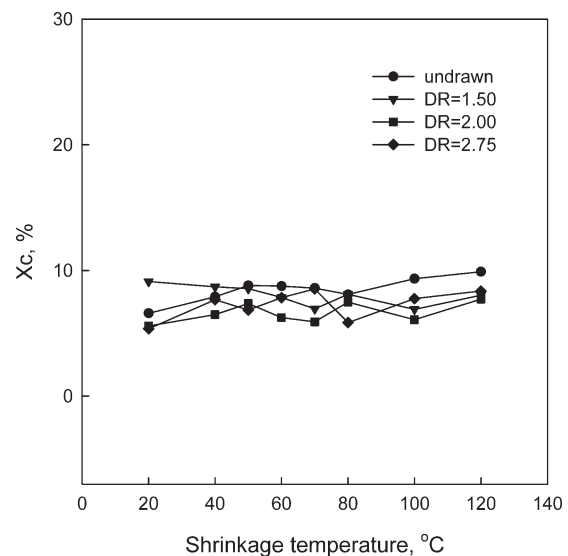


Figure 14 The degree of crystallinity of the shrunken PVC films at various draw ratios as a function of the shrinkage temperature (drawing condition: draw speed of 10 mm/min and draw temperature of 50°C).

Degree of crystallinity

The degree of crystallinity of the shrunken PVC films was characterized by DSC and it is given as a function of the shrinkage temperature in Figure 14. PVC consists of small crystallites that typically account for 5–10% of the structure.²¹ No significant change in the degree of crystallization occurred during the shrinkage of the drawn PVC films. It has also been reported that negligible disorientation of the crystallites occurs during shrinkage.⁵

CONCLUSION

In this study, the thermal shrinkage and shrinkage force of uniaxially drawn PVC films were investigated under various conditions. The shrinkage of the drawn films started in the vicinity of the glass transition temperature of the film and increased with increasing temperature. The degree of shrinkage depended primarily on the draw ratio because of its effect on the molecular orientation. The shrinkage forces of the drawn PVC films also became dominant at temperatures near the T_g . At lower temperatures, the shrinkage force did not fully develop because of the low mobility of the chains, whereas at higher temperatures, the relaxation processes were so fast that they partially inhibited the build-up of the stress. The peak shrinkage stress reached a maximum and then decreased as the temperature increased. At elevated temperature, the orientation in the drawn film decreased and the dichroic ratio increased because of the recovery of the high entropy state because of the increased molecular mobility of the chains. No significant change in the degree of crystallization occurred during the shrinkage of the drawn PVC films.

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