

Mechanical Properties of Oriented Poly(Vinyl Chloride)-Poly(Caprolactone) Blends

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SYNOPSIS

Blends of poly(vinyl chloride) (PVC) with polycaprolactone (PCL) of different compositions were prepared from solutions in tetrahydrofuran (THF). The dried blends were stretched at different temperatures above the glass transition, and the birefringence and mechanical properties were studied. It is shown that the birefringence of PVC and the 75/25 PVC/PCL blend follows an affine deformation scheme with a decreasing number of segments with deformation. The 50/50 PVC/PCL blend shows a complex orientation behavior because of the presence of crystallinity in the PCL phase. The mechanical properties of the blends are shown to increase with orientation, and the aggregate model is acceptably followed by the amorphous oriented blends.

INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the most important commercial polymers with a variety of uses. It is also known that its processing presents many difficulties, essentially related to its easy degradation at relatively high temperatures even for short times. To overcome this problem, it is often mixed with plasticizers or blended with other polymers. In the last category, a wide variety of polymers are miscible with PVC. Among them, let's mention poly(caprolactone) (PCL), poly(methyl methacrylate) (PMMA), and nitrocellulose (NC). On the other hand, orientation of polymers is often used to improve the properties of polymeric materials as an emerging technology.

Molecular orientation of uniaxially stretched polymers is currently the subject of several studies. Interest is particularly focused on the evaluation and understanding of the mechanisms of orientation and deformation during stretching for plasticized and unplasticized PVC. The techniques used for these evaluations included infrared spectroscopy,¹⁻³ Raman spectroscopy,⁴ NMR,⁵ and birefringence.^{1,4,6-7} Some studies involved the evaluation of orientation

in PVC blends with PCL and NC.³ However, no studies were directed at the investigation of the mechanical properties as a function of orientation, which is the main purpose of these orientation characterizations.

The blend of interest in this study is PVC/PCL. It is well known that this blend is miscible and, depending on PCL composition, one can obtain a completely amorphous blend (no crystallization of PCL), or a semicrystalline polymer.^{8,9} We are particularly interested in molecular orientation, deformation mechanisms, and mechanical properties. The compositions of interest here are 100/0 PVC/PCL, 75/25 PVC/PCL (an amorphous blend), and 50/50 PVC/PCL (a semicrystalline blend).

Various deformation mechanism schemes have been proposed for polymers.^{1,7,10,11} One of the simplest, often called the "pseudo-affine" model, considers that there is independent orientation of individual anisotropic elements, having each a uniaxial symmetry. The unique axes of the units are considered to rotate as lines marked in the macroscopic structure of the polymer, which deforms at essentially constant volume. The pseudo-affine deformation scheme has been shown to describe the development of molecular orientation during cold drawing of polyethylene terephthalate (PET) to a

very good approximation.¹² The birefringence calculated from the pseudo-affine model¹² is given by

$$\Delta n = \frac{\Delta n_{\max}}{2} \left[\frac{3}{1 - \lambda^{-3}} - \frac{3\lambda^{-3/2} \cos^{-1}(\lambda^{-3/2})}{(1 - \lambda^{-3})^{3/2}} - 1 \right] \quad (1)$$

where Δn_{\max} is the maximum birefringence (intrinsic birefringence) and λ , the draw ratio. One of the disadvantages of this formula is that the intrinsic birefringence and its dependence as a function of temperature have to be known, which is not often the case.

A more self-consistent scheme, known as the "affine model," was proposed for rubbers, i.e., above the glass transition temperature (T_g) for polymers. In this scheme, the random anisotropic links are assumed to be connected together to form chains that interact only at well-defined junction points.¹³ According to this scheme, as deformation progresses, each chain becomes more elongated while rotating toward the draw direction. At all stages, each chain, or strictly each segment of the chain between junction points, attempts to maximize its entropy by disorienting the elements or random links, subject only to the constraints imposed by the end-to-end vectors (between junction points). These vectors are assumed to deform as would macroscopic lines drawn in the material. In a polymer such as PVC, the chains are joined only by physical entanglements, rather than by precise and permanent chemical crosslinks.

However, this model has been shown to be inappropriate for polymers because it predicts an opposite curvature to that observed experimentally.^{1,11} To overcome this shortcoming of the affine model, various modifications can be proposed. As a matter of fact, if the number of chains per unit volume is allowed to decrease with deformation, better predictions can be obtained.^{1,11,14} The modified expression proposed for birefringence becomes

$$\Delta n = CN_0(\alpha_1 - \alpha_2) \times (\lambda^2 - \lambda^{-1}) \exp[-k(\lambda - 1)] \quad (2a)$$

with

$$C = \frac{2\pi(\tilde{n}^2 + 2)^2}{45\tilde{n}} \quad (2b)$$

where \tilde{n} is the mean refractive index, $\alpha_1 - \alpha_2$ is the difference in principal polarizabilities of the random link, N_0 is the number of chains per unit volume at

zero strain, and k is the rate of breakdown of the network.

However, this equation is unsatisfactory for fitting data at large strains, since it predicts the birefringence with a decrease to zero. To avoid this anomaly, a simple extension of this equation, based on a two-network model composed of a permanent network, with N_p chains/unit volume, and a temporary network, with N_t chains/unit volume in the unstrained state, which breaks down on deformation, can be proposed.¹¹ Then, the new expression for birefringence can be written

$$\Delta n = C \{ N_p + N_t \exp[-k(\lambda - 1)] \} \times (\alpha_1 - \alpha_2)(\lambda^2 - \lambda^{-1}) \quad (3)$$

In this paper, birefringence measurements will be compared with the predictions of the different models previously mentioned. Also, an analysis of the mechanical properties of oriented and unoriented blends of PVC with PCL will be performed.

EXPERIMENTAL

The materials used in this study are PVC (#18,958-8) and PCL (#18,100-9) obtained from Aldrich Chemicals. Their molecular weight characteristics are given in Table I. Blends containing 100, 75, 50, 25, and 0 wt % of PVC were prepared from solution in tetrahydrofuran (THF). The solutions were left under an air current until the major part of the solvent is evaporated, the resulting films were then put in an oven under vacuum at 40°C for at least one month. This process ensured the total removal of the solvent from the blends and homopolymer films. This was confirmed by measurement of the T_g of PVC films and their comparison with that of the undissolved PVC powder, which was about 82°C, and by weight measurement. The thickness of the films obtained was in the range 0.08–0.2 mm.

Glass transition and melting temperature measurements for the blends were performed on a differential scanning calorimeter (Perkin-Elmer DSC-4). The results obtained are reported in Table II. It

Table I Molecular Characteristics of the Materials

Polymer	M_n	M_w
PVC	51,900	105,000
PCL	—	36,000

Table II Glass Transition and Melting Temperatures of the Blends

Blend: PVC/PCL	T_g (°C)	T_m (°C)
100/0	83	—
75/25	29	—
50/50	9	51
25/75	-30	53
0/100	-67	55

can be seen that, when the PVC content exceeds 50 wt %, no melting temperature is observed.

Drawing of standard ASTM specimen cut from the films was performed at a drawing rate of 0.5 cm/min on an Instron machine. The drawing temperatures were 70, 90, and 100°C for PVC and 30, 40, and 50°C for the 75/25 and 50/50 blends. Pure PCL and the 25/75 PVC/PCL blend were not studied because of their poor drawability.

Birefringence measurements were performed during the drawing of the samples by using a laser beam of 632.8 nm wavelength and a babinet compensator. The thickness was measured at the same

time. Measurement of the mechanical properties was made at room temperature for oriented and un-oriented blends on at least five specimens of each composition. Modulus, stress, and elongation at break were determined from the stress-strain curves with a standard deviation of about $\pm 5\%$ from the mean.

RESULTS AND DISCUSSION

Birefringence

The results obtained for the birefringence of PVC at 70°C are presented in Figure 1. Since this temperature is below the glass transition temperature of PVC, i.e., 82°C, it could be thought that the pseudo-affine model could represent the results. To do that, one needs the intrinsic birefringence of PVC. In Figure 1, results obtained using this model, i.e., eq. (1), by assuming two values for $\Delta n_{\max}^{6,7}$ are presented. It is clearly seen that the shapes of these curves are significantly different from that of the experimental results; in addition, the plateau that seems to be reached by the model is not seen ex-

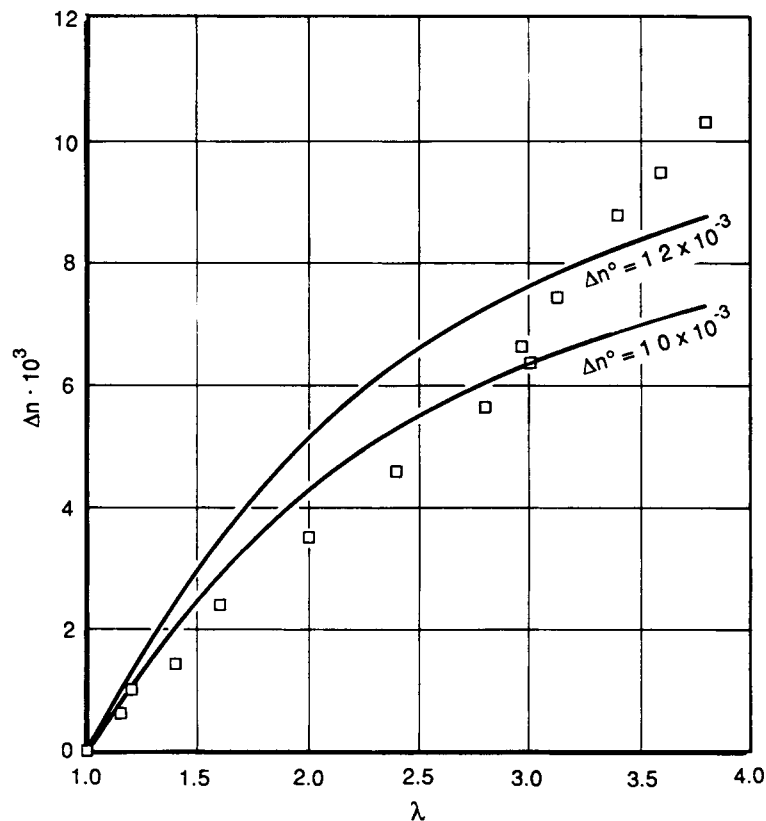


Figure 1 Birefringence as a function of draw ratio for PVC at 70°C. The lines are the predictions of Eq. (1).

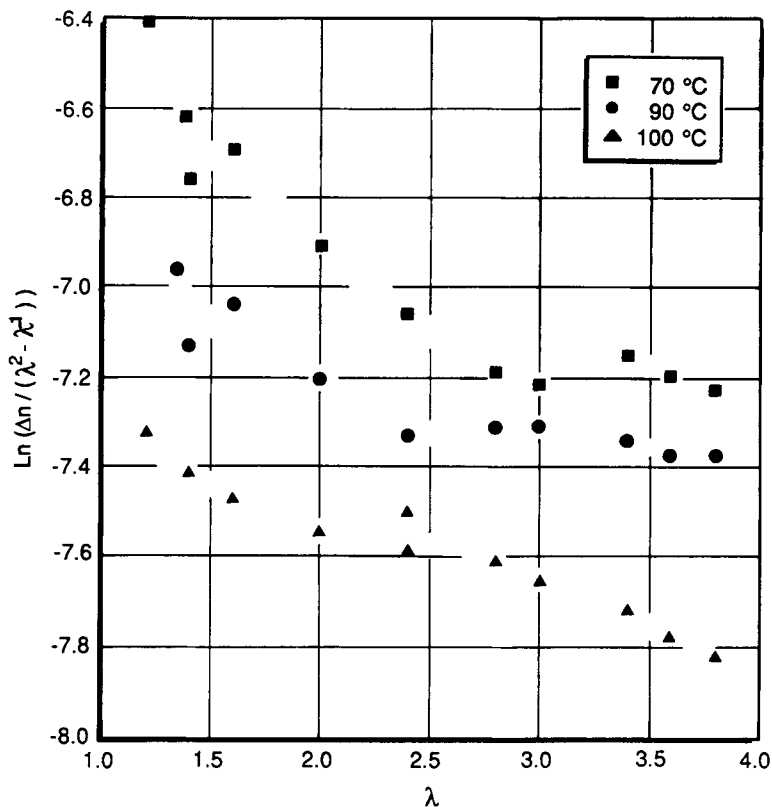


Figure 2 Plot of $\ln [\Delta n / (\lambda^2 - 1/\lambda)]$ vs. λ for PVC at different temperatures.

perimentally. It is also clear that any choice of Δn_{\max} will not provide a good fit to these data using the pseudo-affine model.

Figure 2 shows the data plotted in the form of $\ln [\Delta n / (\lambda^2 - \lambda^{-1})]$ vs. λ [log plot of eq. (2a)] for PVC at different drawing temperatures. For low draw ratios and temperatures, an acceptable straight-line fit is obtained. This fit becomes less acceptable as the temperature is raised from 70°C (below T_g) to 100°C (well above T_g). By using the extension proposed for this model at large strains, i.e., eq. (3), an excellent fit of the experimental results is obtained as shown in Figure 3. The values of N_t , N_p , and k are given in Table II.

Note that N_t decreases with temperature whereas N_p varies slightly. This result is consistent with the fact that there are two types of junction points: temporary associations, probably resulting from dipolar interactions, and permanent entanglements, probably associated with molecules in the high molecular weight tail of the molecular weight distribution. The existence of a fringe micellar-type network with physical crosslinks has also been proposed for PVC.² Upon stretching, this network is assumed to be partially destroyed.

For the 75/25 PVC/PCL, the representation of $\ln [\Delta n / (\lambda^2 - \lambda^{-1})]$ as a function of λ is shown in Figure 4. It is obvious that, for 30°C, a good linearity is obtained for a wider range of draw ratios than observed for PVC, even if this temperature is above the T_g . Acceptable lines are obtained for the other temperatures also, but for a limited range of λ . The addition of PCL in this blend acts obviously in the sense of making the blend more "rubbery" than was the PVC at the temperatures previously studied. This can explain the better fitting obtained by using the affine model. An even better fit is obtained by using the extension proposed in eq. (3) as shown in Figure 5. The parameters used for the calculations are presented also in Table III, and the same conclusion as for PVC can be drawn.

For the 50/50 blend, the results obtained for birefringence are presented in Figure 6. The shape of the curves in this figure are different from the others mentioned. The birefringence is negative for low draw ratios and becomes positive for a draw ratio of about 1.6. This behavior has already been observed for the orientation function of PCL.³ As mentioned earlier, and according to DSC results, the PCL phase crystallizes in this blend. It is known¹⁵ also that PCL

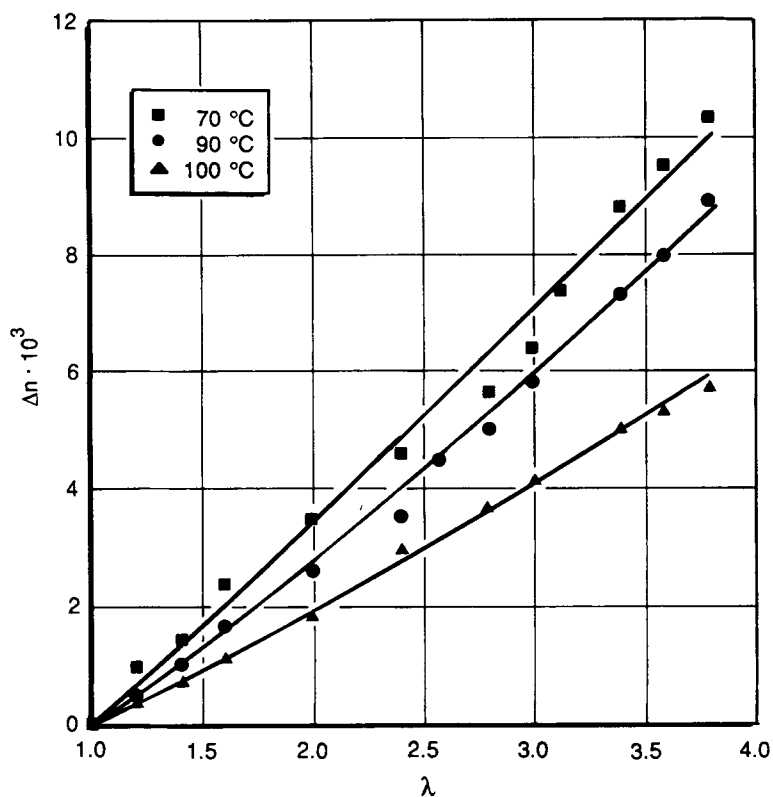


Figure 3 Birefringence as a function of draw ratio for PVC at different temperatures. The lines are the predictions of Eq. (3), with the parameters of Table III.

crystallizes into a spherulitic superstructure. At low elongations, the spherulites deform but do not break up. The overall shape becomes ellipsoidal and the lamellas tend to align in the direction of stretch. This crystallite orientation tends to orient the chain backbone perpendicular to the direction of stretch. Thus, the orientation function is initially negative.

As the sample passes through the yield point, the spherulites start to break up, and the lamellas start to orient so that chains are aligned in the stretch direction, in which case the orientation function becomes positive. The contribution of PVC to the orientation in this range of draw ratios is assumed to

be negligible as well as the amorphous part of PCL. In fact, the crystalline orientation is known to be much higher than the amorphous orientation for low draw ratios, which is seen clearly by comparing the birefringence of the 50/50 blend and the 75/25 PVC/PCL blend at 30°C. Another fact that supports the qualitative interpretation given here is the result obtained for birefringence for the 50/50 blend at 50°C. As seen in Figure 6, the birefringence observed at this temperature is no more negative, which confirms fully our interpretation since the melting temperature of this blend is about 51°C, which is the temperature of drawing. In this case, a

Table III Values of the Parameters Used for the Fittings in Equation Three

Blend: PVC/PCL	T (°C)	N_p	N_t	k
100/0	70	2.0×10^{25}	1.0×10^{26}	0.25
	90	1.5×10^{25}	8.0×10^{25}	0.20
	100	1.0×10^{25}	5.5×10^{25}	0.20
75/25	30	1.0×10^{25}	1.4×10^{26}	0.60
	40	7.0×10^{24}	7.0×10^{25}	0.40
	50	5.0×10^{24}	5.5×10^{25}	0.28

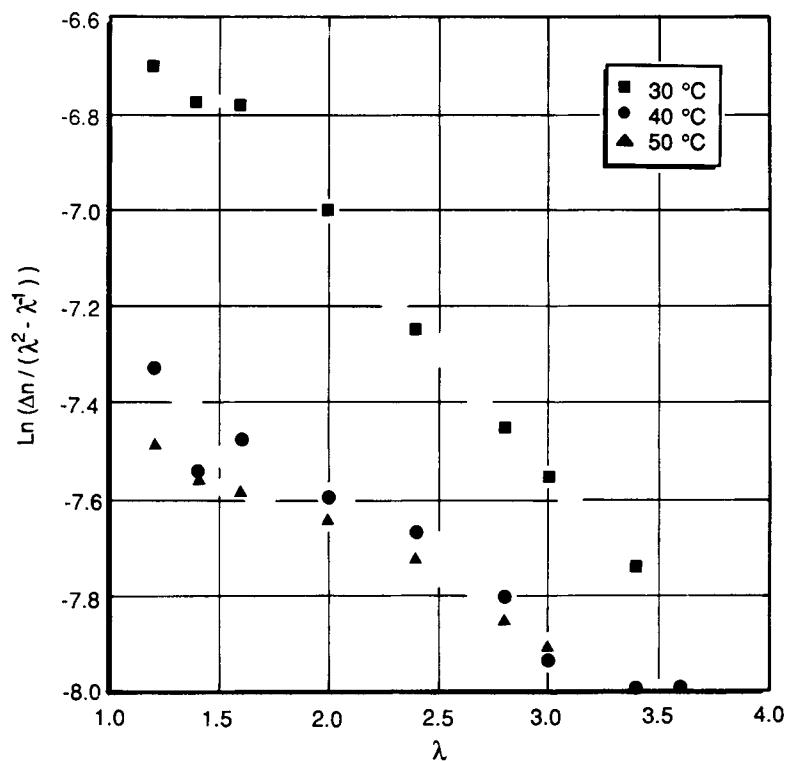


Figure 4 Plot of $\ln [\Delta n / (\lambda^2 - 1/\lambda)]$ vs. λ for the 75/25 PVC/PCL blend at different temperatures.

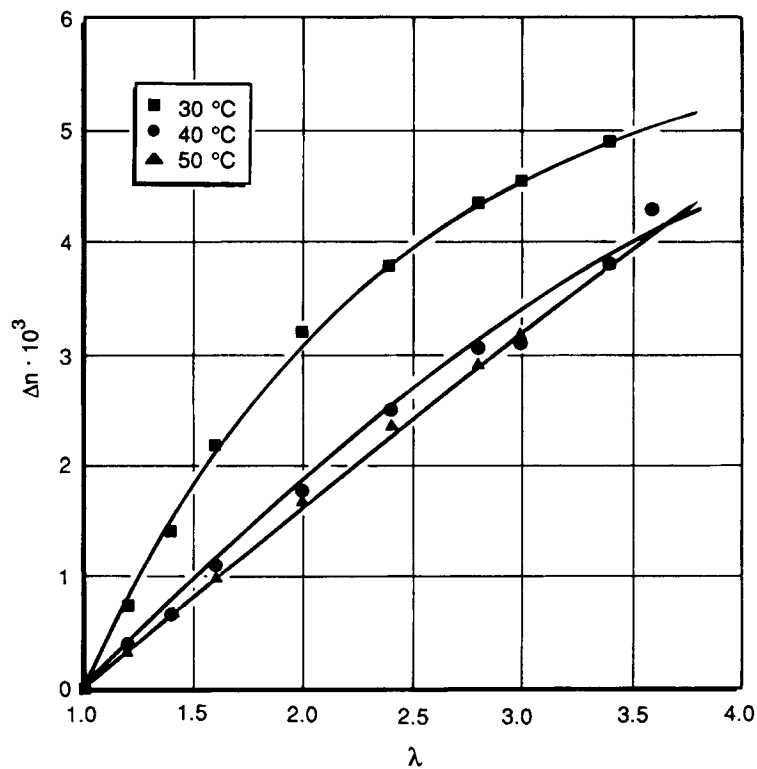


Figure 5 Birefringence as a function of draw ratio for the 75/25 PVC/PCL blend at different temperatures. The lines are the predictions of Eq. (3), with the parameters of Table III.

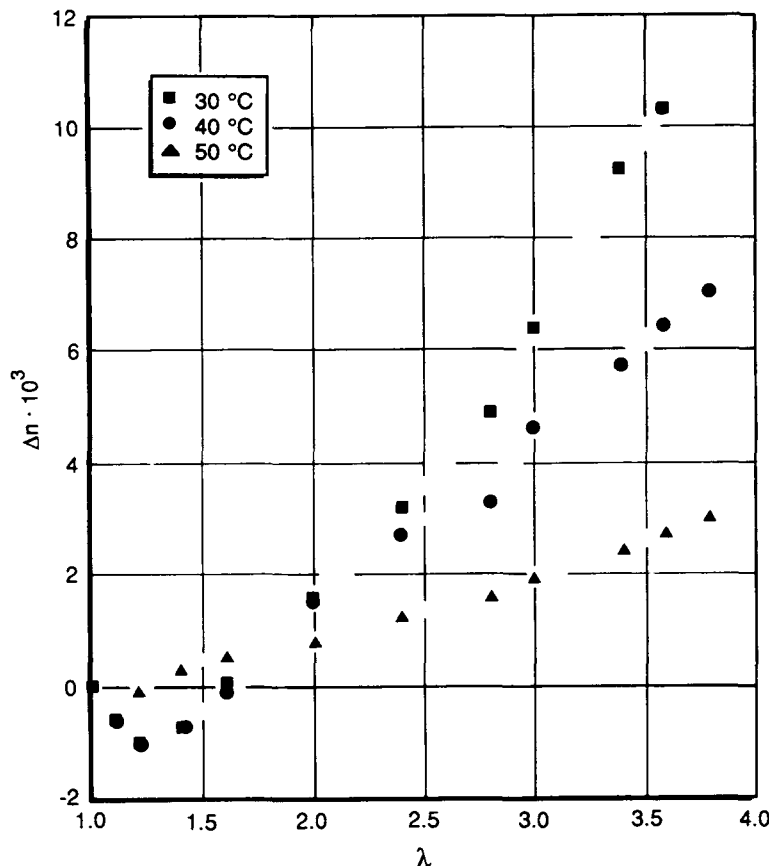


Figure 6 Birefringence as a function of draw ratio for the 50/50 PVC/PCL blend at different temperatures.

negligible, if any, crystalline region is present, and the behavior is similar to the ones observed for PVC and 75/25 PVC/PCL blend.

Due to this complex behavior of the 50/50 blend, no comparison with the models is made. Further investigation of the crystalline and amorphous contributions will be helpful in the modeling of the deformation behavior of this blend.

Mechanical Properties

First, the mechanical properties of all the unoriented blends were determined. The results in terms of the modulus and the stress and elongation at break are presented in Figures 7, 8, and 9. There is a clear competition, in the mechanical properties, between the contributions of PVC, that of the crystalline part of PCL, which both have a high modulus and strength, and that of the amorphous part of PCL, which is thought to have poor properties. This fact gives rise to more complexity for the modeling of the mechanical behavior of this multicomponent blend as a function of composition. As a matter of

fact, the shape of the modulus vs. composition is complex.

For oriented blends, the results are presented in terms of the modulus and stress at break as a function of draw ratio in Figures 10 and 11. As can be expected, a constant increase in the modulus and stress at break is observed. A slight decrease in the modulus is observed for the 50/50 blend for low draw ratios. This can be directly related to the orientation behavior of this blend at low λ , which was already discussed.

For oriented amorphous polymers, it has been shown¹⁰ that the aggregate model, with a uniform stress assumption, is satisfactorily followed. Under some conditions about the compliances of the fully oriented materials, an approximate relation between the birefringence and the axial compliance, S_{33} , related to the axial modulus by $S_{33} = 1/E$, was proposed¹⁰ and can be written

$$S_{33} = \left(\frac{2}{3}\right)S_{11} \left(1 - \frac{\Delta n}{\Delta n_{\max}}\right) \quad (4)$$

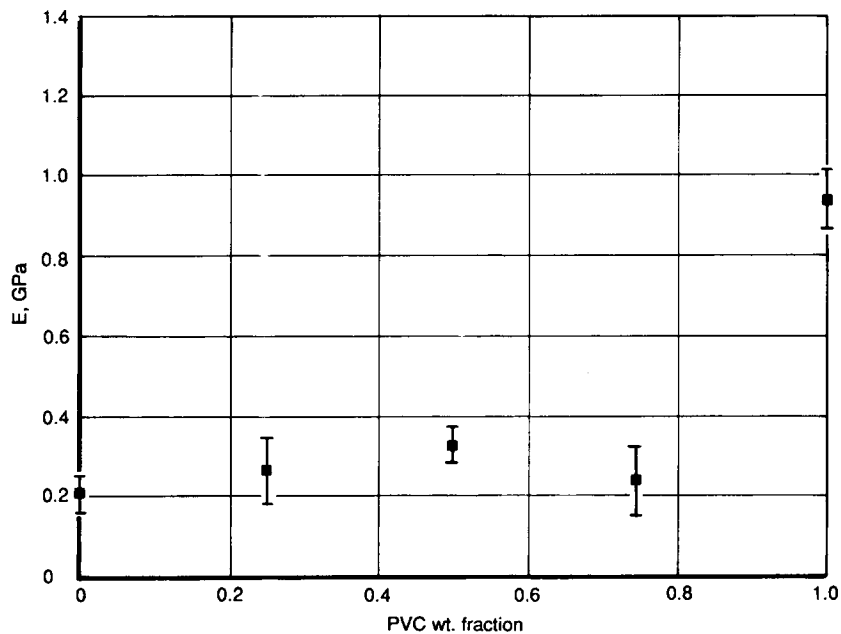


Figure 7 Modulus vs. composition for the unoriented PVC/PCL blends at room temperature.

in which Δn_{\max} is the intrinsic birefringence and S_{11} the compliance in the transverse direction. Figure 12 shows the representation of $1/E$ vs. Δn for PVC at 75°C and for the 75/25 PVC/PCL blend at 40°C , and a good linearity is obtained. The value obtained in this way for Δn_{\max} for PVC is about $10.7 \cdot 10^{-3}$,

which is close to the values reported in the literature.^{6,7} For the 50/50 blend, this representation was not used because of its complex orientation behavior and its semicrystalline character. Further investigations of the orientation and mechanical properties will be helpful for this blend.

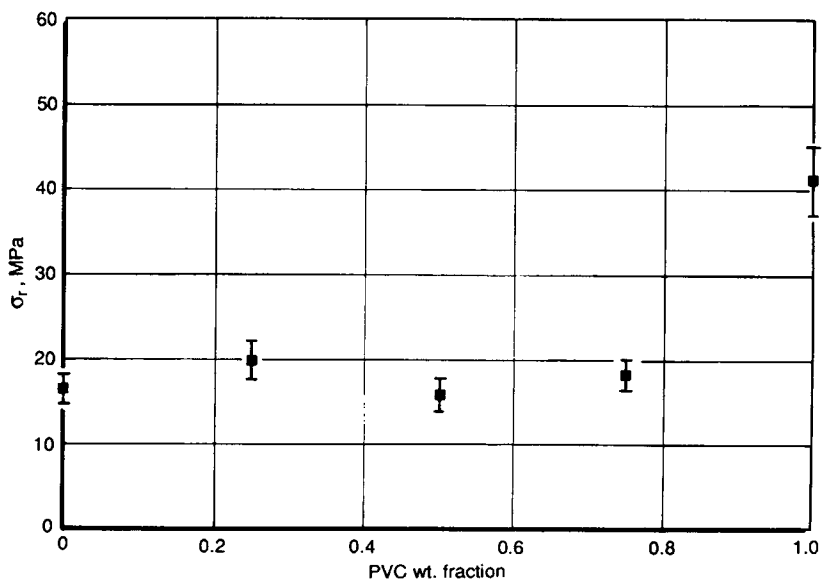


Figure 8 Stress at break vs. composition for the unoriented PVC/PCL blends at room temperature.

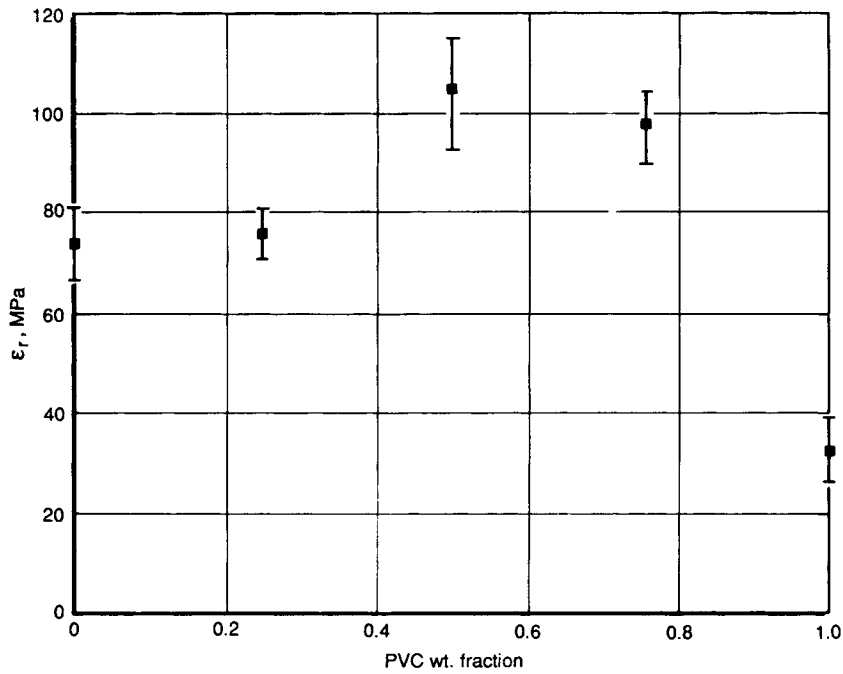


Figure 9 Elongation at break vs. composition for the unoriented PVC/PCL blends at room temperature.

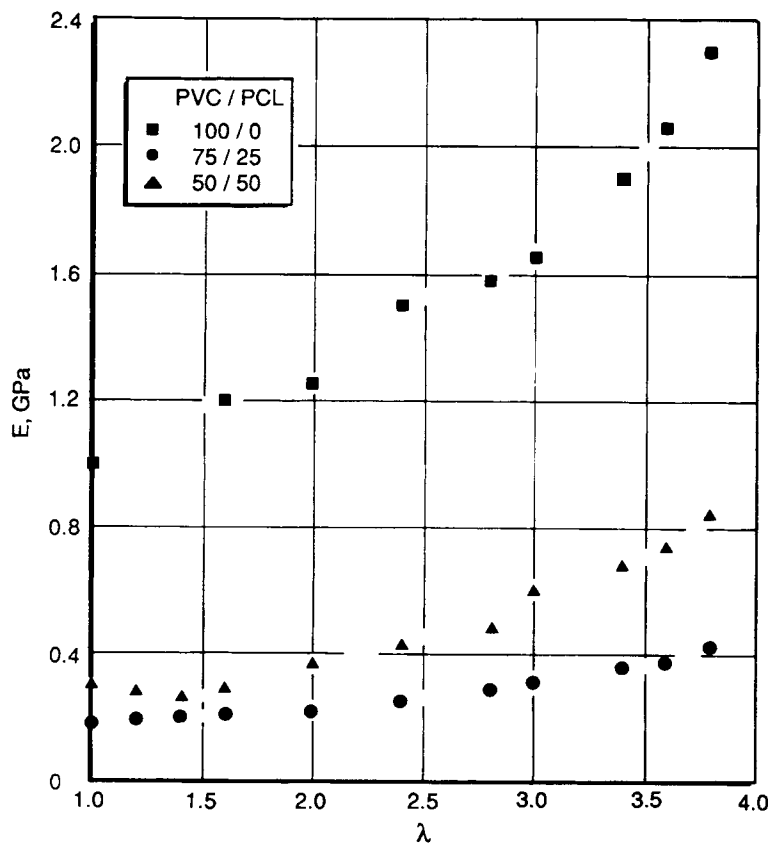


Figure 10 Modulus as a function of draw ratio for the oriented blends.

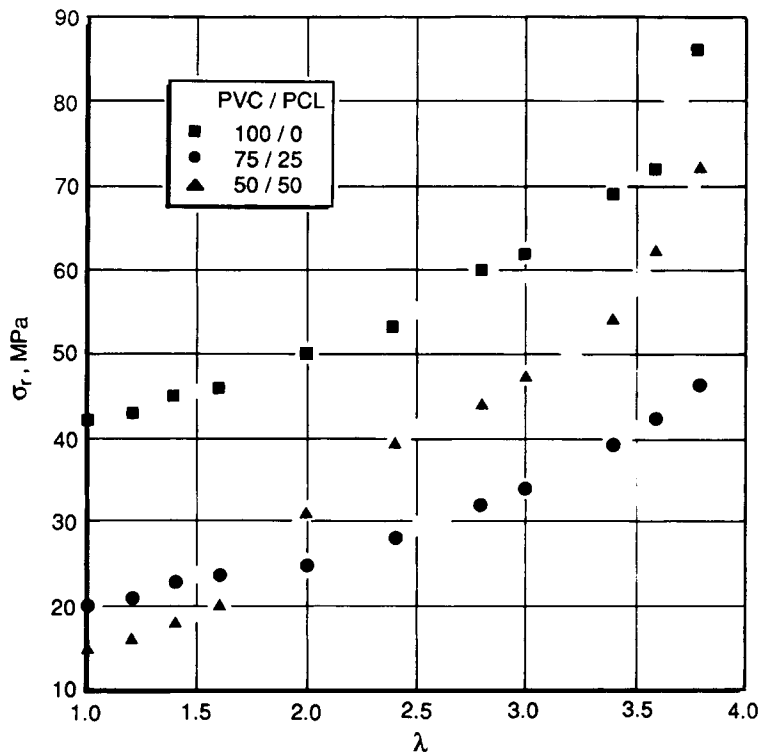


Figure 11 Stress at break as a function of draw ratio for the oriented blends.

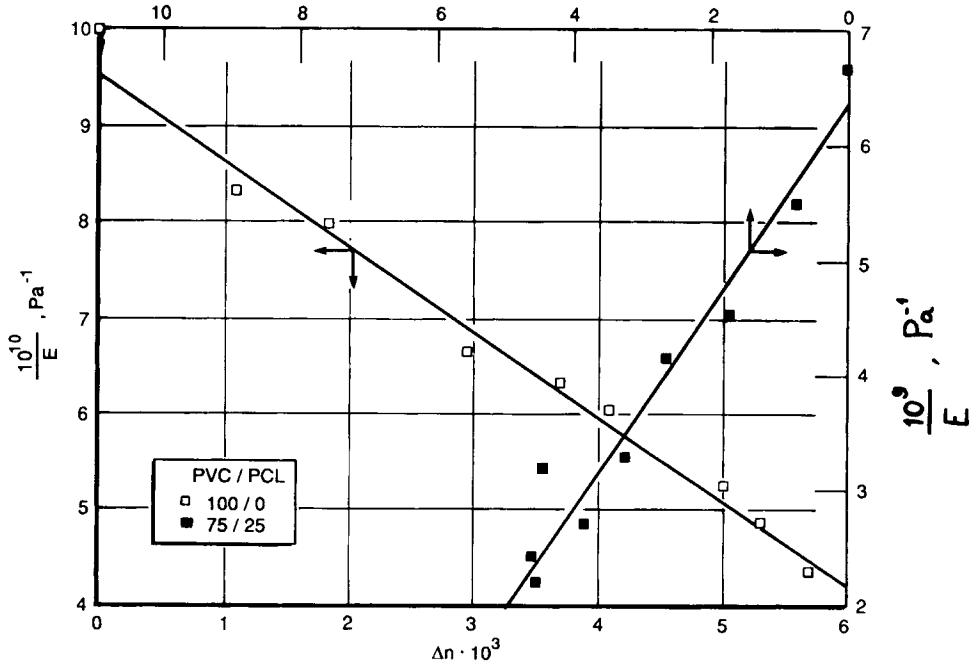


Figure 12 Axial compliance vs. birefringence for PVC and the 75/25 PVC/PCL blend.

CONCLUSIONS

Through this work, it is shown that the birefringence of PVC and its blends with PCL follows an affine deformation scheme with a decreasing number of segments with deformation. The 50/50 blend shows a complex orientation behavior because of the presence of crystallinity. The mechanical properties of the blends were shown to increase with orientation, and the aggregate model is acceptably followed by the amorphous oriented blends.

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