Anisotropic creep behaviour of oriented polycarbonate

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The anisotropic character of the creep behaviour of polycarbonate, oriented at a temperature 12°C above the glass transition to different draw ratios, has been studied using the model of Boyd and Jansson. This model is based on molecular assumptions and results in a second-order relation, $\varepsilon = D_1\sigma + D_2\sigma^2$, where D_1 is the linear and D_2 the non-linear compliance component. The segmental orientation was determined by infra-red dichroism and the chain extension by shrinkage. It was found that both the linear and non-linear compliance components decreased with increasing orientation, although the non-linear component is affected much more by the orientation. The same result was found both in tension and contraction.

(Keywords: bisphenol A polycarbonate; orientation; creep)

INTRODUCTION

It is well known that most non-crystalline, glassy polymers[1] show a marked non-linear viscoelastic behaviour at strains larger than 0.5–1%. The transition from linear to non-linear viscoelasticity is, however, gradual and the definition of the stress and strain level of the transition is arbitrary and depends, for instance, on the accuracy of the measurements. The strain level above which the non-linearity becomes substantial corresponds approximately to the strain at which the first 'visible' cracks appear[2] and at which long-term fracture occurs. The theory of linear viscoelasticity can be used to calculate stress–strain distributions in linear or approximately linear viscoelastic materials, but similar calculations cannot yet be made for non-linear viscoelastic materials. Fracture is also dominated by non-linear viscoelasticity and plasticity[3], and both the transition from linear to non-linear behaviour and the degree of non-linearity are therefore important in polymer engineering and design.

Many studies have been reported concerning the dependence of the 'linear limit' on time and temperature[4–6], heterogeneity[7] and antiplasticization[8,9]. It is also known that physical ageing affects the non-linear viscoelasticity[3]. Little attention has been paid, however, to how orientation influences the non-linearity, although most plastic products are oriented to some extent.

From studies on the change in volume[10–12] and segmental orientation measured by infra-red (i.r.) dichroism[13] during tensile deformation, it is known that the transition from linear to non-linear viscoelasticity is accompanied by a pronounced increase in the volume change, corresponding to a decrease in the contraction ratio, and by the onset of large-scale molecular motions and an orientation of the chains in the stress direction.

Accurate measurements[14] on PMMA and PVC have shown that the isochronous stress–strain diagrams for glassy polymers are non-linear even at very small stress–strains and that the curves can be very accurately fitted to a second-order relation[14,15]:

$$\varepsilon = D_1\sigma + D_2\sigma^2 \qquad (1)$$

where D_1 is the linear compliance component and D_2 the non-linear compliance component. The degree of non-linearity, i.e. the relation between D_1 and D_2, varies from polymer to polymer and with time and temperature. This model, proposed by Boyd *et al.*[15], is based on a molecular approach and shows that the non-linear behaviour is related to stress-induced changes in the deformation mechanisms connected to the β-process[10,16,17]. The phenomenon is assumed to be associated with the local conformational transitions which take place within a glassy polymer in which general segmental motion is quiescent, i.e. motions associated with side-group reorientation, local motions in the main chain, etc. The reorienting groups are treated as defects in an elastic medium in which the influence of the stress is described by 'flip-flop', two-site motions. Thus it has been proposed[15] that the stress-induced changes in the β-mechanism emanate from an acceleration of the relaxation process, changes in the nature of the mechanisms and activation of new mechanisms, resulting in a saturation of the relaxed (equilibrium) compliance associated with the secondary relaxation mechanism, a broadening of the relaxation spectrum and a shift of the average relaxation time towards shorter times.

Thus, although the behaviour is considerably more complex, creep studies on oriented materials give the engineer important information about application conditions of the material, and they also provide the materials scientist with a deeper basic understanding of the deformation mechanisms than do creep studies on isotropic materials.

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This paper presents the results from a study on the non-linear viscoelastic creep behaviour and stress dilatational behaviour of oriented polycarbonate.

EXPERIMENTAL

Materials

The polycarbonate (PC) used in this study is the commercially available Makrolon 1143 from Bayer, delivered in extruded bars with a diameter of 6 mm. The structural formula for PC is shown in *Figure 1*. The material has a weight-average molecular weight (M_w) of 35000–37000 and a glass transition temperature (T_g) of 148°C, according to the manufacturer's product information. Bars were chosen instead of sheets because of their better orientation homogeneity and more clearly defined stress–strain distribution under a uniaxial tensile load.

Orientation

To avoid the risk of gas inclusions being formed on heating, the samples were dried for about 12 h at 120°C and kept at 75°C until the moment of orientation. The bars were fixed in the orientation device and placed in an oven at 160°C (12°C above T_g). After 20 min, when it had reached temperature equilibrium, the sample was stretched, under a constant load at an average deformation rate of about 4% s^{-1} to the desired draw ratio and then quenched in a water bath. The rate of cooling of the sample through the glass transition obtained in this way was 50–80°C s^{-1}.

The draw ratio was defined by the relation between the sample cross-section area before, A_0, and after, A_{orient}, stretching:

$$\lambda_{\mathrm{draw}} = A_0/A_{\mathrm{orient}}$$

This value is identical to the draw ratio defined as l_{orient}/l_0 if the volume is constant during the deformation. This is a reasonable assumption at the chosen temperature and deformation rate. Unoriented samples were also prepared with the same thermal heat treatment.

Heat treatment

To reduce the effect of enthalpy relaxation (physical ageing), the samples were annealed at 120°C for 24 h. This temperature and time were chosen in accordance with the work of Struik[18] and of Golden *et al.*[19]. The temperature used is high enough to allow the enthalpy relaxation to reach an approximate equilibrium within a reasonable time without any relaxation of the molecular orientation. In the case of PC, Golden *et al.*[19] found that at temperatures above 130°C the ordering effect appears to enter into competition with a disordering effect which increases markedly between 135 and 140°C. This disordering is due to the onset of the glass transition. During the heat treatment the residual thermal stresses, if any, also relax[20]. The treatment does not cause crystallization[21].

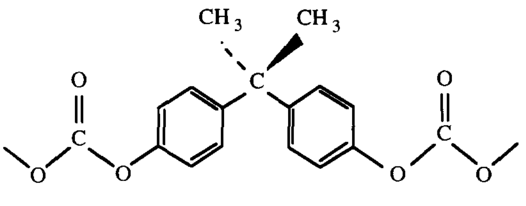

Figure 1 Structure of bisphenol A polycarbonate

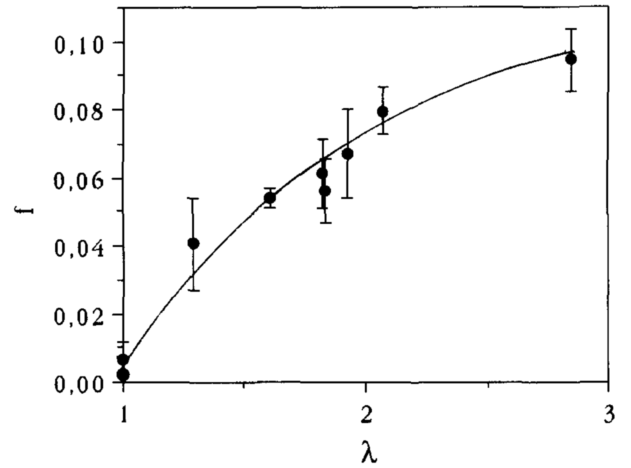

Figure 2 Dependence of the orientation function, *f*, on the draw ratio, λ

Measurement of segmental orientation

The segmental orientation was measured by i.r. dichroism on a Perkin–Elmer FTIR Spectrometer 1725X. Parts about 15 mm in length were taken from the oriented bars and were then microtomed into thin sections suitable for the i.r. dichroism measurements.

The dichroism, *R*, of the 1364 cm^{-1} band, assigned to the in-phase symmetrical bending vibration of the two methyl groups in the chain (*Figure 1*), was calculated according to the baseline procedure presented by Lunn and Yannas[22]. The segmental orientation is then given by the Hermans orientation function, *f*:

$$f = \frac{3\langle\cos^2\theta\rangle - 1}{2} = \frac{(R_0+2)(R-1)}{(R_0-1)(R+2)} \qquad (2)$$

where R_0 is the dichroic ratio for the perfect oriented material. R_0 can be calculated if the transition moment vector α is known, since $R_0 = 2\cot^2\alpha$. For the 1364 cm^{-1} band, this vector is perpendicular to the chain axis ($\alpha = 90°$).

Figure 2 shows the orientation calculated in this way plotted against the draw ratio, λ. The data represent the average orientation of the samples. Owing to relaxation, the molecular orientation will be slightly lower in the interior regions of the samples where the cooling is slower. This mainly explains the scatter in the data. The relation between *f* and λ is progressively less steep. The data for *f* and λ were compared with the data reported by Wu[23], von Falkai *et al.*[24], and Ito and Hatakeyama[25]. Although no exact comparison could be made since none of those studies used the same molecular weight or the same orientation procedure as that used in the present study, it is evident that the results are similar.

Measurement of chain extension

If an oriented amorphous polymer is heated to above T_g the orientation relaxes, producing a sample with changed shape and an isotropic state. Thus, shrinkage can represent a method for assessing the prior average chain deformation. The method is simple and rapid. The molecular draw ratio (*MDR*) can be calculated from the changes in dimensions on shrinkage and is defined[26] as:

$$MDR = (l_d - l_s + l_0)/l_0 \qquad (3)$$

where l_d is the length after drawing, l_s the length after shrinkage and l_0 the original length. It is important that the shrinkage experiment is designed properly so that the shrinkage is fully elastic with no viscous dissipation through network slip[26]. Therefore, for example, the samples for a shrinkage test must be thin to minimize self-constraint during shrinkage due to the generally poor heat transfer through polymers.

If the drawing involves no chain slippage, the samples shrink back to the original length, i.e. $l_s = l_0$ and $MDR = l_d/l_0 = \lambda_{draw} = \lambda_{shrink} = l_d/l_s$.

Shrinkage measurements were made here on the thin microtomed slices used for the i.r. dichroism measurements, the samples being heated in a silicone oil bath at 170°C for 30 min. *Figure 3* shows λ_{shrink} plotted against λ_{draw}, these parameters being defined by $\lambda_{shrink} = l_d/l_s$ and $\lambda_{draw} = A_0/A_d$.

The draw ratio measured by shrinkage, λ_{shrink}, is less accurate than the draw ratio measured by the extension, λ_{draw}, since the samples with highest extension are small and crumpled after shrinkage. Therefore shrinkage measurements were made on only a few samples from each draw ratio to check whether or not they shrank back to the original length. As all samples except one, $\lambda_{draw} \approx 3$, show nearly the same λ_{shrink} as λ_{draw}, it is obvious that no chain slippage occurred during the drawing and it is therefore correct to use λ_{draw} as a measure of the chain extension. The deviation between λ_{shrink} and λ_{draw} for the samples at $\lambda_{draw} \approx 3$, can be explained through the theoretical elongation ratio at which chains between entanglement points are fully stretched, λ_e. Dettenmaier[27] calculated this value to be 2 for PC without considering the relaxation of orientation. Of course, temperature and deformation rate will influence λ_e. It is reasonable to believe that for the temperatures and deformation rates used in this study some chains between entanglement points are fully stretched before $\lambda = 3$ and possibly break. This leads to unevenly oriented molecular structure.

Tensile creep apparatus

The tensile creep apparatus consisted of a 4.9:1 lever-loading arm, supported on knife-edge bearings with a manual loading system. The load was transferred to the specimen via small clamps, the lower being fixed with a universal joint to the main frame whilst the upper was fixed to the chain from the lever and was free to move.

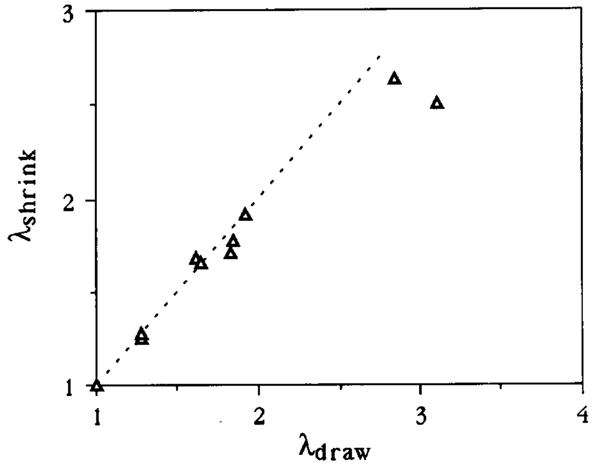

Figure 3 Relationship between λ_{shrink} and λ_{draw}

The loading assembly was carefully balanced. Since only small extensions were involved in the measurements, the movement of the lever was small enough not to cause any trouble with angular distortion etc.

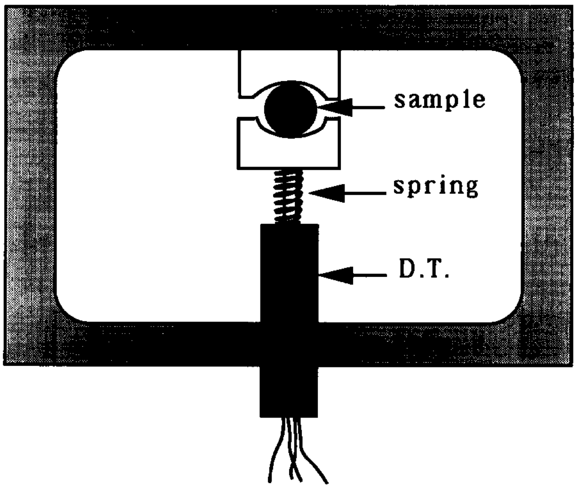

Figure 4 Contraction measurement device. D.T., differential transformer

The longitudinal extension measurements were made with an Instron extensiometer, G-51-11-M-A. To compensate for its weight, the extensiometer was suspended on two springs. The extensiometer was connected to the computer via a HBM KWS 3082 AC-bridge and an AD-card. The total accuracy, including equipment, reproducibility and sample deviation, was about ±3%. To minimize scattering, three to seven creep curves were measured on different samples at each orientation level.

A special device was designed to measure the contraction of the samples using a differential transformer to record the displacement. The differential transformer was applied to the sample by a prestressed spring device, *Figure 4*. The contraction sensor was also suspended on two springs. To achieve greater amplification, another bridge with higher resolution was used, HBM KWS 3082A. To increase both reproducibility and overall accuracy, all measurements were made in the same displacement region of the differential transformer for which the linearity was carefully checked. The greatest source of error was internal friction in the differential transformer. Three to five creep curves were used for each draw ratio giving a total accuracy better than ±5%.

Tensile creep measurements

Samples were subjected to a series of successively increasing loads and the uniaxial tensile creep and lateral contraction were measured over 110 s. After each measurement, the samples were allowed to relax for a period of time equal to three times the creep time. Although all irregularities in the material were reduced to a minimum, the effects of inevitable play, friction and bending in the fastening were compensated for by a small 'zero load', producing a strain of approximately 0.1%. The 'zero load' was maintained constant during all measurements and was considered not to cause any disturbances in the measurement.

When the longitudinal creep strain exceeded 0.8% a control measurement corresponding to a strain of approximately 0.1% was added between the successive loads to check whether the sample had been damaged by the previous loading.

The merits of this simplified technique for producing isochronous stress–strain curves for non-linear isotropic materials by successive loading and unloading of a single sample have been amply demonstrated over many years[28,29]. The technique becomes even more valuable in studies of anisotropy[30] where samples may be difficult to obtain in large numbers.

RESULTS

Longitudinal and transverse compliance

The creep behaviour at different orientation levels was analysed based on isochronous stress–strain diagrams at 100 s. Although its validity has not been proved for oriented structures, the data were fitted to a second-order equation in accordance with the model developed by Boyd and Jansson[15] (equation (1)). The correlation was equally good for all orientation levels. An example of the correlation of one isochronous stress–strain experiment is shown in *Figure 5* for $\lambda = 1.5$.

To obtain the parameters D_1 and D_2 for the longitudinal data and D_{t1} and D_{t2} for the contraction data, shown in *Figures 6* and *7*, several creep curves from different samples for each orientation level were put together and the second-order equation was fitted to the data using a least-squares method. The calculation was done with the program MATLAB from The Math Works Inc. which is based on matrices. The calculations also gave the standard deviations for the parameters. The total accuracy in D_1 and D_{t1} is better than ±3 and ±5%, respectively. The total accuracy of the D_2 and D_{t2} measurements is about 13% and 11%, respectively, and is not as good as that of the linear parameters, mainly due to the fact that these terms are very small. The standard deviation of D_{t2} for $\lambda = 2$ increases markedly and may be due to the lowered accuracy in the measurement of the contraction as the diameter of these samples decreases with λ. This is also the reason why no contraction data were taken from $\lambda = 3$.

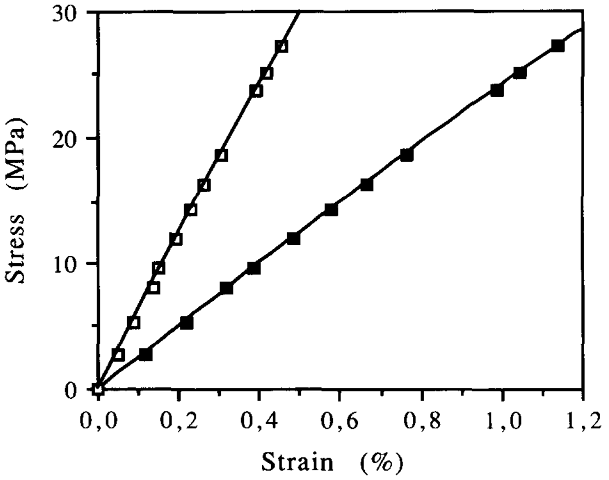

Figure 5 Isochronous stress–strain diagram for longitudinal (■) and transverse data (□) at a draw ratio of 1.5

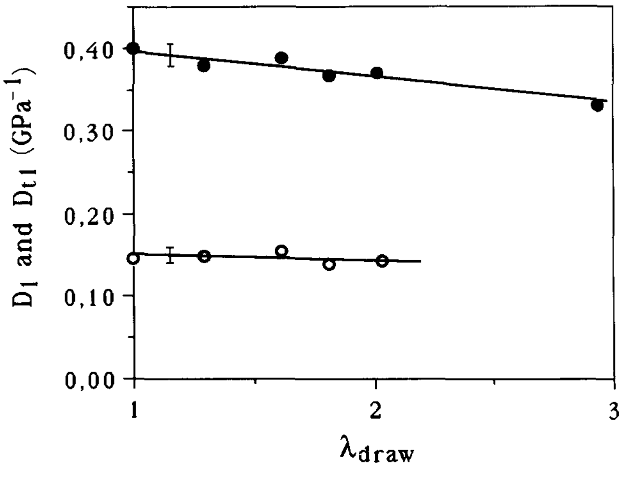

Figure 6 Variation in D_1 (●) and D_{t1} (○) with draw ratio

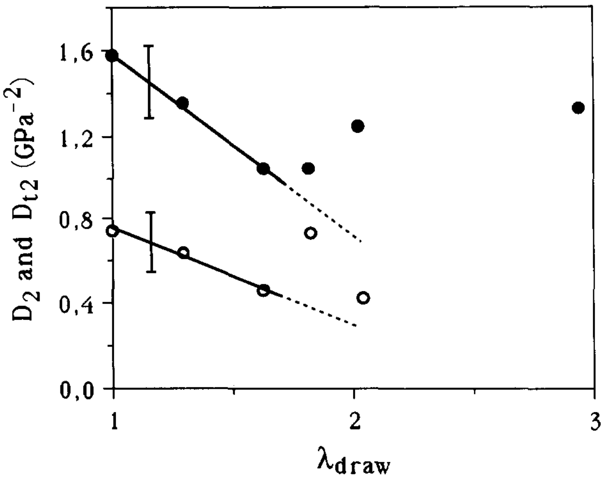

Figure 7 Variation in D_2 (●) and D_{t2} (○) with draw ratio

The ratio of D_2 to D_1 is less than 1/100 and the non-linearity is thus very small. In accordance with other studies[31–36], the dependence on the molecular orientation of the overall stiffness of PC is small. The linear longitudinal compliance, D_1, has decreased by less than 15% at $\lambda = 3$ and the linear contraction compliance, D_{t1}, decreased by 6% at $\lambda = 2$. The contraction ratio is about 0.39 and varies very little with orientation.

The influence of the orientation on the non-linear longitudinal and contraction compliances, D_2 and D_{t2}, is stronger and complex. The non-linearity decreases with increasing orientation up to a level corresponding to $\lambda \approx 1.75$, D_2 decreases by 37% and D_{t2} by 50%. For $\lambda > 1.75$, D_2 increases in a complex way, whereas the scattering of D_{t2} data increases, making a detailed analysis more difficult.

Stress dilatation, volume strain

The stress dilatation was calculated from:

$$\frac{dV}{V} = \varepsilon_1 - 2\varepsilon_2 \qquad (4)$$

where V is the volume and ε_1 and ε_2 are the longitudinal and transverse strains, respectively.

The isochronous dilatation was plotted for 100 s at the different orientation levels and fitted to the second-order relation of the Boyd–Jansson theory. *Figure 8* shows the expected linear decrease in the linear stress dilatation compliance, but the relatively large scatter in the non-linear data makes it difficult to conduct a similar analysis in this case.

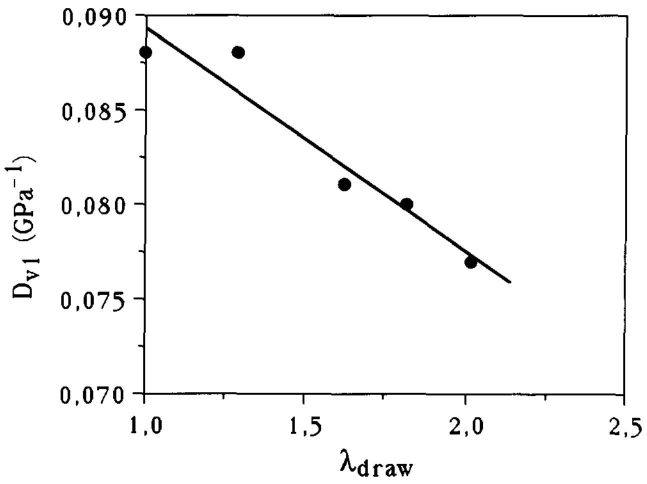

Figure 8 Variation in D_{v1} with draw ratio

DISCUSSION

PC is unique in the sense that the temperature (time) interval between its main and secondary transitions is very wide, resulting in a broad region within which the secondary relaxation mechanisms are fully relaxed long before the main transition appears. The mechanical secondary relaxation mechanism for PC is believed to be combined phenyl and carbonyl motion, involving several segments[37]. At room temperature, changes in the average molecular distance and covalent bond geometry are the dominating mechanisms together with the fast secondary relaxation mechanism. The behaviour is elastic and the creep rate very low. Because of the large distance to both the α- and β-transition in this region, the stress-dependent non-linearity of the viscoelastic behaviour of PC at room temperature and moderate times appears mainly as a stress-induced increase in the relaxed compliance and/or inducement of 'α-similar' mechanically induced molecular mechanisms.

By altering the temperature, the influence of either the main or the secondary transitions can be uniquely studied. PC, therefore, offers unique possibilities for studies of the influence of molecular orientation on the creep behaviour and its stress dependence.

In accordance with theory and in agreement with the results of previous studies[31–36] showing that the overall stiffness of PC increases with molecular orientation, our measurements show that the linear creep compliance decreases linearly in the orientation region studied. The reduction is less than 15% at an orientation level corresponding to a draw ratio of $\lambda=3$ and a Hermans orientation function of $f=0.1$. Also the linear contraction compliance decreases linearly with orientation showing a reduction of about 6% at $\lambda=2$ and $f\approx 0.07$. As can be expected from general ideas of the influence of molecular orientation, the stress dilatation also decreases with orientation.

The non-linear creep compliance components for both elongation and contraction are also found to decrease at a molecular orientation less than $\lambda=1.75$. This seems reasonable as a consequence of the reduced chain mobility due to the orientation in the studied area, above $\lambda=1.25$, where the orientation between entanglement points gives deformation hardening. Above $\lambda=1.75$, D_2 increases in a complex way, most plausibly due to the inhomogeneously oriented molecular structure induced above this draw ratio as mentioned earlier. For D_{t2} the scatter in the data reduces the possibility of detailed analyses of the transverse behaviour.

CONCLUSIONS

The stress-induced non-linear creep behaviour of PC, oriented by stretching at temperatures above its glass transition and quenched to low temperatures, has been studied at room temperature using the Boyd–Jansson model.

It has been found that both the linear and the non-linear creep compliance components in the Boyd–Jansson model decrease with orientation, both in tension and contraction. Also the stress dilatation decreases. This is in accordance with the general ideas of the influence of molecular orientation on the local molecular mobility at draw ratios for which a pronounced deformation of the molecules between entanglement points is obtained. The appearance of new phenomena in addition to molecular orientation is noticed at high draw ratios.

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