Influence of crosslinking on thermal shrinkage behaviour of poly(vinyl chloride) fibres

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Measurements of poly(vinyl chloride) thermal shrinkage and shrinkage force permit the measurement of a yield flow temperature between elastoplastic behaviour and viscoplastic behaviour. Then, an analogy with mechanical modulus allowed an intrinsic shrinkage modulus to be defined. This concept illustrates the influence of crosslink density on thermal shrinkage.

(Keywords: poly(vinyl chloride) fibres; thermal shrinkage; crosslink density)

INTRODUCTION

Poly(vinyl chloride) (PVC) fibres are widely used in textile applications because of the specific properties of PVC homopolymers and copolymers. However, their processing and consequently their applications are restricted by some deficiencies such as poor thermal and dimensional stability under heat treatment above the glass transition temperature. Generally, when PVC fibres are subjected to finishing treatments at temperatures higher than 100–110°C, they lose their toughness. In a previous paper, Cousin *et al.*[1] have shown that annealing treatments carried out between 110 and 150°C lead to the formation of ordered entities[2] and consequently to the formation of a temporary physical network, which hinders the relaxation of PVC chains. Nevertheless, annealing treatments are not efficient enough to prevent shrinkage above 120°C. Additionally, it is known that thermal degradation of PVC is always accompanied by crosslinking. Hence, this is a way to improve the thermomechanical behaviour of PVC fibres when PVC degradation is carried out under controlled conditions. But these treatments always lead to the appearance of unwanted colouring, and articles made under these conditions lose their toughness, to a greater or lesser extent. Furthermore, such a process does not allow good control of the crosslink density. That is why it is more attractive to build up a three-dimensional network through a chemical reaction involving the whole bulk of the fibre to prevent flowing of PVC chains under heat treatment. Thus, it is the purpose of this study to take into account the influence of crosslinking upon the shrinkage behaviour in comparison with uncrosslinked PVC fibres.

In consequence, this paper is focused on the influence of the physical network, chemical network, or both (when they are superimposed), on the thermal shrinkage of PVC fibres. In order to reveal these influences, we have defined some new thermomechanical concepts such as intrinsic shrinkage and shrinkage modulus.

EXPERIMENTAL

Materials

Spinning of uncrosslinked and crosslinked PVC fibres was performed through a spinneret according to a dry spinning process from polymer in solution in a mixture of acetone and carbon disulfide. Solvents are removed from the fibres by evaporation. PVC fibres are 300% stretched in boiling water, then annealed at 110°C under applied stress to avoid any shrinkage, and finally shrunk in boiling water for 20 min. The commercial LX PVC fibre has been considered as a control sample.

We have obtained chemically crosslinked fibres by carrying out the reaction of hydroxyethyl acrylate/vinyl chloride copolymers with blocked diisocyanates at 140°C[3] under stress, after drawing and stretching according to the continuous spinning process of PVC fibres, and before shrinkage in boiling water. Thus, crosslinking takes place instead of the annealing step (for the control sample).

Various comonomer contents have been used (*Table 1*). These copolymers were either industrial products (Vinika P100 from Vinyl Kasei Co.) or development products (from Atochem). Their microstructure has been checked by ^{13}C n.m.r. In all cases, they are statistical copolymers.

Molecular-weight values, calculated relative to polystyrene standards, have been determined by gel permeation chromatography (g.p.c.) and glass transition temperatures (T_g) by differential scanning calorimetry (d.s.c.) at a heating rate of 10°C min^{-1}. T_g values were defined as the inflection point on the d.s.c. thermogram. These data are summarized in *Table 1*.

Crosslinking is characterized by the relatively poor solubility of the fibres and their swelling rate (G) in tetrahydrofuran (THF). Indeed, a relationship exists

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between this value and the chemical network density. Swelling rate, after crosslinking, is assessed according to the following relation (*Table 2*):

$$G=\left(\frac{M_s}{M_i}-1\right)\frac{\rho_{\mathrm{PVC}}}{\rho_{\mathrm{THF}}}+1$$

where M_s is the weight of swollen polymer, M_i is the weight of insoluble fraction, and ρ_{PVC} and ρ_{THF} are the densities of PVC (1.38 g cm^{-3} at 25°C) and of THF (0.9478 g cm^{-3} at 25°C).

We have checked by sonic modulus measurements[4] that all samples have the same degree of molecular orientation as a result of total drawing and finishing treatments.

Apparatus

Shrinkage measurement. Continuous measurement of shrinkage has been performed during a heating run (heating rate 2°C min^{-1}). A sample, of about 30 cm length (l_0), is placed into a tubular heating chamber. One of its ends is maintained fixed, and the other is allowed to move. The stress applied to fibres was negligible, about 0.1 mg/dtex. So, the recorded translation (Δl) could be directly converted into shrinkage per cent (R):

$$R=(\Delta l/l_0)\times 100$$

Shrinkage force measurement. Shrinkage force measurements have been carried out with a Rheometrics RMS800 mechanical spectrometer. A sample, composed of a defined number of fibres, is placed between two stationary clamps that were specially designed for these experiments. The whole device is placed into an oven. Then, temperature is increased at a linear heating rate (2°C min^{-1}). Measurements of the shrinkage force are obtained by means of a transducer (2000 g, sensitivity 0.1%), which can measure the normal force. The normal force, due to shrinkage, is registered continuously during heating.

RESULTS AND DISCUSSION

Shrinkage

Variations of shrinkage *versus* temperature are plotted in *Figure 1*. Shrinkage of PVC fibre exhibits a straight-line evolution from 100°C up to 125°C. In this range of temperatures, PVC shows an elastoplastic behaviour due to the existence of ordered structures responsible for the physical network[2,5]. Between 125 and 160°C, shrinkage increases less rapidly until it reaches a plateau value. A viscous flow process is then superimposed onto the elastic behaviour. Thus, the observed effect is the result of competition between shrinkage and the tendency of fibres to lengthen under their own weight. This can be explained by the appearance of molecular motions that concern either longer and longer segments of chains or chains in the whole. Finally, this last process becomes predominant beyond 170°C and leads quickly to the breaking of the fibre at about 180°C.

Crosslinked fibres show a different behaviour. The whole curve is shifted to higher temperatures than for uncrosslinked PVC fibres. Moreover, shrinkage values are obviously lower than for uncrosslinked PVC fibres. The elastoplastic behaviour exists up to temperatures of about 160°C. This effect is more pronounced as the crosslink density is high. Even at these temperatures, breaking of the fibres is fully suppressed. Then, the existence of a covalent network supplies the deficiency of the physical network at temperatures higher than 125°C.

Variations of shrinkage *versus* temperature can be expressed with a sigmoidal law of the general form:

$$\text{shrinkage }(\%)=A+\frac{B-A}{1+(10^{C}/10^{X})^{D}}$$

where X is the logarithm of temperature, A is the bottom plateau (number 0 in this case), B is the top plateau, C is the X value in the middle of the curve and D is the slope factor. All the curves have been adjusted on this model by a non-linear least-squares procedure. In *Figure 1*, full curves represent the adjusted curves.

Table 1 Characteristics of PVC homopolymer and copolymers

Ref. code	Comonomer (mol%)	M_w ($\mathrm{g\,mol^{-1}}$)	M_w/M_n	T_g (°C)
PVC	0	87000	2.35	85
A	3	87500	2.25	81
B	3.4	90200	2.70	81
C	6.9	87700	2	81

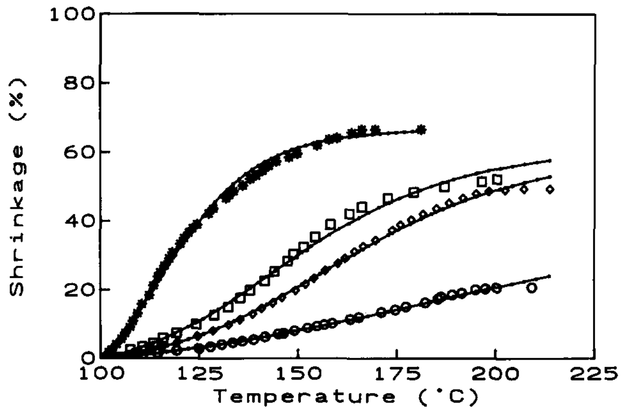

Figure 1 Variation of shrinkage *versus* temperature: (✱) PVC, (□) sample A, (◇) sample B, (○) sample C

Table 2 Swelling rate, maximum specific shrinkage and yield flow temperature for fibres before and after crosslinking

Ref. code	G	Maximum specific shrinkage (% $°\mathrm{C}^{-1}$)	Yield flow temperature (°C)		
			Shrinkage	Shrinkage force	Shrinkage modulus
PVC	∞	1.97	120	118	117
A	22	0.72	145	136	139
B	10	0.70	160	155	152
C	7.5	0.25	170	185	175

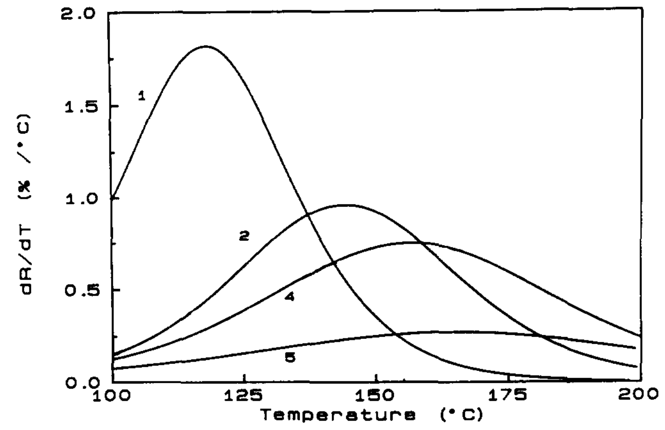

Figure 2 Variation of specific shrinkage *versus* temperature: (1) PVC, (2) sample A, (4) sample B, (5) sample C

The sigmoidal law is just convenient to fit the curves and is very useful to provide a mathematical expression of the registered phenomenon.

The time necessary for shrinkage to reach its equilibrium value is very much lower than the time of measurement. Thus, shrinkage appears as a quasi-instantaneous phenomenon and is then mainly governed by temperature. We propose to study shrinkage variations that correspond to a unit step of temperature (1°C). In mathematical terms, it is the derivative of the shrinkage curve *versus* temperature and we shall call this 'specific shrinkage':

$$\text{specific shrinkage} = \frac{dR}{dT}\ (\%\ ^{\circ}C^{-1})$$

Figure 2 shows the evolution of specific shrinkage *versus* temperature. Here, the curves are the analytical derivatives of the sigmoidal laws obtained for each sample. Specific shrinkage increases with temperature until a maximum value. This maximum corresponds to the temperature at which a molecular flow appears due to motions of longer and longer segments of chains because of decrease of chain interactions and disappearance of ordered structures such as mesophases associated with isotactic sequences[5]. Moreover, we can point out that an e.s.r. study of the molecular dynamic of a spin probe in PVC matrix has also revealed the same yield flow temperature[6].

We can then define a yield flow temperature T_s as the temperature at which the flowing process appears, i.e. the temperature at which specific shrinkage is maximum. For PVC homopolymer, T_s is about 120°C.

For temperatures lower than or equal to T_s, the phenomenon recorded is pure shrinkage. In this domain, it is possible to counterbalance the shrinkage with an external stress and to restore the initial state of internal stress of the material. This behaviour is then called an elastoplastic behaviour.

For temperatures higher than T_s, shrinkage and flow occur simultaneously. It is not possible to counterbalance shrinkage with an external stress. This behaviour is then called a viscoplastic behaviour.

Values of maximum specific shrinkage and yield flow temperatures are reported in *Table 2*. First, crosslinking tends to decrease the maximum value of specific shrinkage and all the more so as the crosslink density is high. Secondly, it shifts the yield flow temperature T_s to high temperatures. These effects can be explained by the existence of a covalent network, which restricts molecular motions. Increasing the crosslink density very much would result in the complete suppression of the flow process. In fact, the shape of the curve tends to be linear when the average length between two chemical crosslinks is about 200 monomer units. Then, the average molecular weight between chemical bridges reaches the same order of magnitude as the critical molecular weight between entanglements.

Shrinkage force

At any temperature, the shrinkage force is an intrinsic property of the material, fully independent of heating rate.

Figure 3 shows the variations of shrinkage force with temperature. They have the same shape as the variations of shrinkage with temperature (*Figure 1*). For PVC homopolymer, the shrinkage force increases up to a maximum value at about 140°C. Above this temperature, shrinkage force decreases because of flowing, which precedes breaking. For crosslinked fibres, the behaviour is strongly modified. First, the maximum is shifted to about 200°C for low crosslink density ($G = 22$) and to temperatures higher than 200°C when the crosslink density increases ($G \leqslant 10$). This behaviour is well explained by the existence of the covalent network, which restricts molecular motions and shrinkage.

After that, if we look at the behaviour of crosslinked fibres, it must be pointed out that, for any temperature, shrinkage force is always lower than for uncrosslinked PVC fibre. This is more pronounced when the crosslink density is high.

Finally, the inflection point of the curves also characterizes the yield flow temperatures. These temperatures are reported in *Table 2*, and it can be seen that they are very close to those obtained from shrinkage measurements.

Shrinkage stress–intrinsic shrinkage strain relationship, and definition of a shrinkage modulus

As the variations of shrinkage and shrinkage force (homogeneous to a stress) *versus* temperature have been obtained, the stress–strain curves can be plotted.

Intrinsic shrinkage strain $\varepsilon(T)$ can be calculated according to:

$$\varepsilon(T) = \ln\left(\frac{l}{l_0}\right) = \ln\left(1 - \frac{R(T)}{100}\right) < 0$$

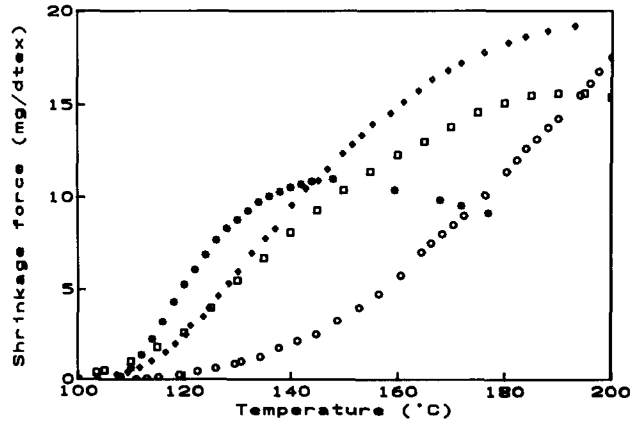

Figure 3 Variation of shrinkage force *versus* temperature: (✱) PVC, (□) sample A, (◇) sample B, (○) sample C

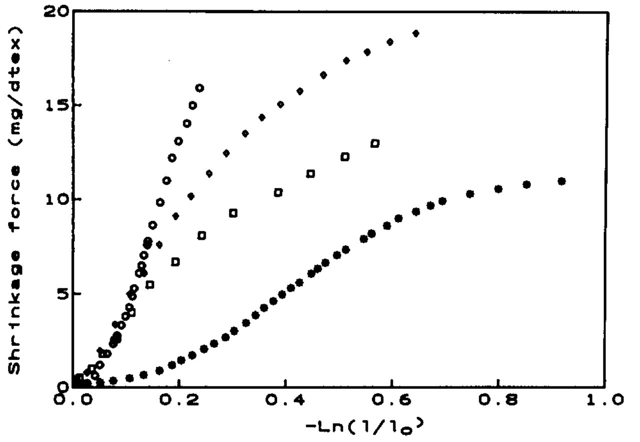

Figure 4 Variation of shrinkage force *versus* intrinsic strain: (✱) PVC, (□) sample A, (◇) sample B, (○) sample C

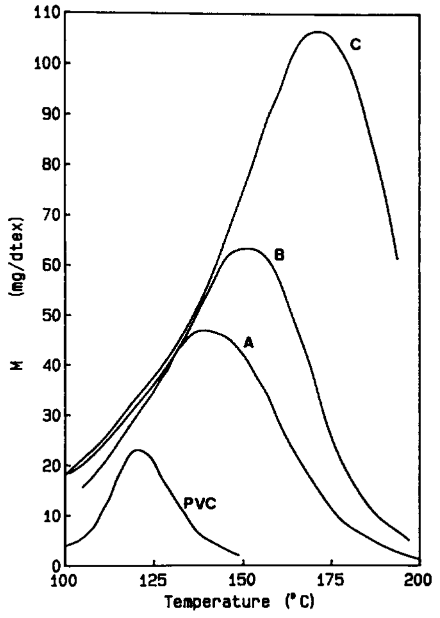

Figure 5 Variation of shrinkage modulus *versus* temperature

Shrinkage stress–intrinsic shrinkage strain curves are plotted in *Figure 4*. These curves have been obtained from shrinkage and shrinkage force variations *versus* temperature. It must be pointed out that the same intrinsic strain does not correspond to the same temperature for each sample because of differences in shrinkage thermal behaviour. In this figure, it can be seen that, for a given strain, the shrinkage force increases with the crosslink density.

Now, an arbitrary ratio can be calculated for any temperature. We have defined it as the ratio of the stress over the intrinsic strain, and obviously it presents an analogy with the definition of a modulus. Thus, we shall name it later 'shrinkage modulus':

$$M\ (\text{mg/dtex}) = \frac{\mathrm{d}F_R}{\mathrm{d}\varepsilon} = f(T/^\circ\text{C})$$

However, modulus measurements are generally carried out in the case of an applied strain, which is not the case here. But shrinkage strain can only be generated by means of heating. Thus, this ratio is temperature-dependent.

Figure 5 exemplifies the variations of shrinkage modulus *versus* temperature. At each temperature, higher than or equal to 100°C, crosslinking greatly increases the shrinkage modulus, and this is in close relation with the covalent network density. Moreover, the curves go through a maximum value. This maximum value falls in with the yield flow temperature, as can be seen in *Table 2*.

Finally, it must be pointed out that the applied stress is intrinsic to the material. After stretching in the solid state the material is in an unstable thermodynamic state. The system can only change if it possesses sufficient energy to go back to a more stable thermodynamic state[7] and then the consequence is the shrinkage phenomenon. The activation energy of this process is dependent on the surrounding chain segments and in particular it depends mainly on the existence of defects, of ordered zones such as crystallites and especially crosslinks. Thus, stress (shrinkage force), strain (shrinkage) and temperature are in very close relation, but the stress (or the strain) appears to be a function of both strain (or stress) and temperature.

CONCLUSION

The formation of a covalent chemical network increases very much the resistance of PVC fibres to shrinkage at temperatures higher than 100°C. By hindering molecular motions, it prevents the flow of the chains until temperatures of 200°C and even higher when the crosslink density is of the same magnitude as the entanglement density. Hence, at any temperature, shrinkage is lowered by the existence of a covalent network, which supplies the deficiency of the physical network. Then, covalent crosslinking permits one to widen the elastoplastic temperature range by limiting the flow phenomenon.

The concepts of intrinsic shrinkage and shrinkage modulus allow one to define accurately the range of temperatures of elastoplastic or viscoplastic behaviour for PVC fibres.

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