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A COLLABORATIVE STUDY ON TENSILE PROPERTIES OF RIGID PVC. LONG-TIME TRANSITION

A Report of the IUPAC Working Party on
"Structure and Properties of Commercial Polymers"

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A COLLABORATIVE STUDY ON TENSILE PROPERTIES OF RIGID PVC. LONG TIME TRANSITION

Abstract—Previous work on rigid PVC has shown that two transition zones occur in tensile tests when the speed of elongation is raised.

—brittle–tough transition at high strain rates or low temperatures. This transition is doubtless due to the secondary relaxation processes in PVC.

—a tough–tough transition at low strain rates (long times).

This report presents the results of a study of the tough–tough transition made by BASF and Solvay and Co., as members of the IUPAC Macromolecular Division's Working Party on "Structure and Properties of Commercial Polymers".

At the two laboratories, tensile tests were performed at low strain rates on PVC sheets of different thicknesses extruded from the same compound. The temperature rise in the striction zone of the specimens was measured.

The results show that the transition can be directly correlated with the heating that accompanies the deformation of the specimen.

1. INTRODUCTION

A previous study of the tensile properties of rigid PVC showed[1] that in a plot of rupture strain versus strain rate, two transition regions can be observed:

—at high strain rates or low temperatures, the elongation at break increases from a few % to about 30% with decreasing drawing speed. The transition is due to a change in the rupture mode of PVC. At drawing speeds lower than that of the transition zone the rupture is tough; it is brittle, however, when the drawing speed exceeds that of the transition zone.

—at low strain rates (10^{-2}–10^{-3} s^{-1}) the elongation at break increases from 30 to more than 150% with decreasing strain rate. Temperature does not greatly influence the position of the transition zone.

The work done by Retting and Oberst[2] on the one hand, and by Solvay on the other, shows that the second transition zone (tough–tough) is caused or influenced by relaxation mechanisms in the main molecular chain, and by the heat generated by the deformation.

The aim of this new study of the tensile properties of rigid PVC was to give a clear and complete picture of the tensile properties of the polymer, in particular of the tough–tough zone.

At the laboratories of BASF and Solvay and Cie, tensile measurements have been carried out on four grades of rigid PVC sheet.

During the tests, the temperature rise in the striction zone of test pieces cut from sheets was measured at both laboratories by means of infra-red thermographs.

2. PREPARATION AND CHARACTERIZATION OF THE SHEETS AND TEST PIECES

Four grades of rigid PVC sheet were extruded with a four-screw extruder Anger A4 80–84 provided with a 300 mm Johnson flat die. The extruded sheets were polished with an Olier Calander. All sheets were made from Solvic 227 (suspension PVC—viscosity index 105†) containing lead stabilizers and lubricants. The powder compound was mixed in a two-speed Henschel 150 mixer. The four grades of sheets only differed in thickness, the mean values of which were 0.66, 1.1, 2.02 and 4.06 mm.

The extruded sheets were annealed at 100°C for 2 h and cooled at a rate of 8°C per hour.

ISO R 527 type I test pieces were prepared by means of a Tensilkut machine running at 20,000 rev/min. All test pieces were cut parallel to the extrusion direction. This prevents slight transverse irregularities in thickness from affecting the geometry of the deformation zone.

3. EXPERIMENTAL RESULTS

The specimens for the tensile experiments were milled by Solvay & Cie, and they were tested with an Instron tensile testing machine (type TT-BM at BASF, TT-CM at Solvay & Cie).

3.1. *Mechanical data at room temperature*

At both laboratories yield stresses, rupture strains and rupture stresses were measured between $1.9\,10^{-2}$ and $4.4\,10^{-4}$ s^{-1}. The results are given in Figs. 1–3.

There is good agreement between the results obtained at the two laboratories. For rupture stresses and strains, slight differences in testing temperatures can be neglected.

Figure 1 shows that the thickness of the test piece has no influence on the yield stress. Figures 2 and 3, on the other hand, show that the rupture stress of the specimens is higher, and their elongation greater, at the lowest strain rates. At the highest strain rates, rupture occurs before stretching can start. At intermediate speeds, only the two thinner specimens were able to stretch. The two thicker specimens broke before they could stretch appreciably. When the thickness of the specimen increases from 0.6 to 4.1 mm, the transition zone is shifted from about $6\,10^{-2}$ s^{-1} to $2.3\,10^{-2}$ s^{-1}.

The thicker the test piece the lower the drawing speed at which the initial necking zone is propagated.

3.2. *Maximum temperature generated in the stretching zone*

The maximum temperature generated in the specimen by stretching at room temperature was recorded at BASF with a Heimann IR thermometer (Germany) type PBT, and at Solvay & Cie with an AGA IR thermovision system (type 680).

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†Test method: ISO R 174-61.

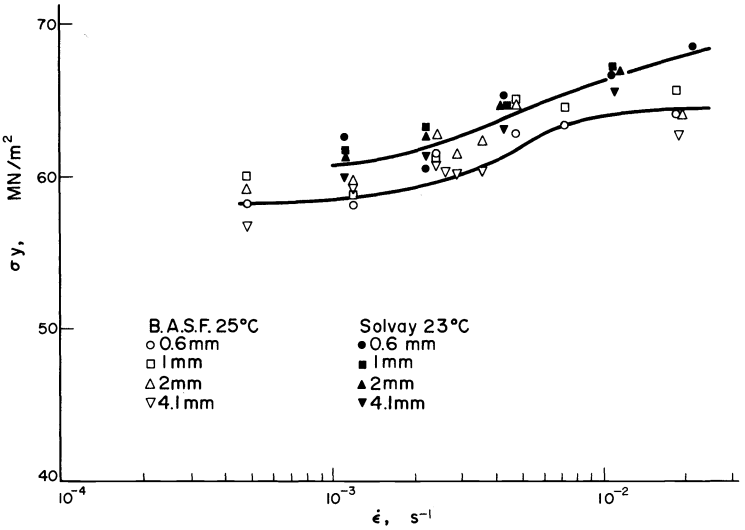

Fig. 1. Tensile properties of rigid PVC. Influence of thickness on yield stress.

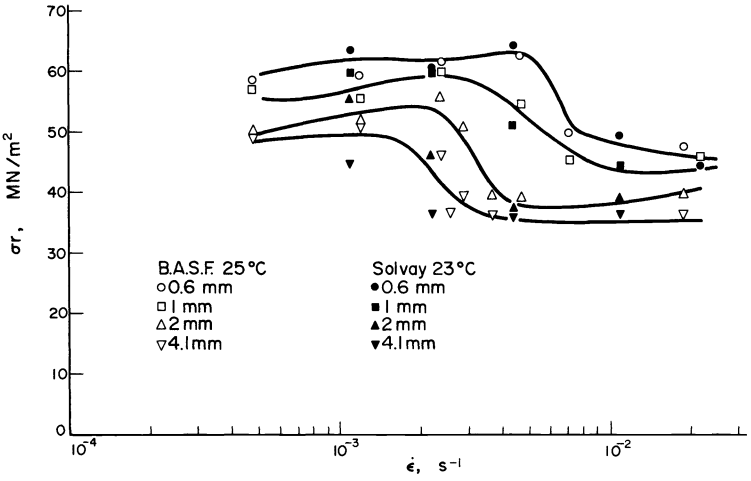

Fig. 2. Tensile properties of rigid PVC. Influence of thickness on rupture stress.

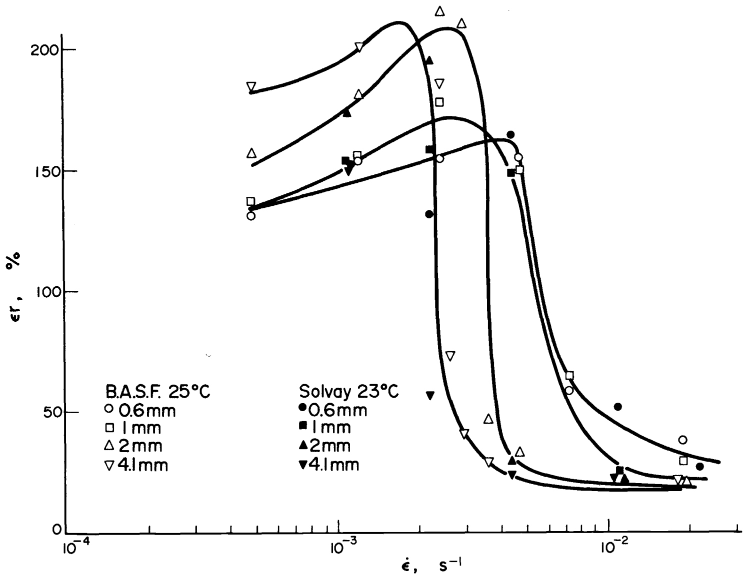

Fig. 3. Tensile properties of rigid PVC. Influence of thickness on rupture strain.

The temperature of the test piece remains roughly constant until the deformation exceeds the yield strain. The temperature in the necking zone then increases.

The extent to which the deformation zone in the test piece is propagated is a function of the temperature rise. If this is small, the higher temperature in the striction zone becomes stable, and the test piece can be stretched to a high strain level (150%).

This situation is shown in Fig. 4, part 4, which depicts stress and temperature as functions of time for 4.1 mm sheet stretched at a strain rate of $1.1\ 10^{-3}\ s^{-1}$.

On the other hand, if the amount of heat generated by the plastic deformation is too large to be quickly dissipated, the temperature rises, and the deformation is limited to the initial zone of striction. As a result the test piece soon breaks.

This situation is shown in Fig. 4, part 3, for 4.1 mm sheet stretched at a tensile strain of $4.4\ 10^{-3}\ s^{-1}$. In transitional situations, the rate of temperature rise is lower, and the initial striction can propagate before rupture occurs (Fig. 4, parts 1 and 2).

Table 1 shows that there is good agreement between the maximum temperatures found at BASF and Solvay & Cie.

3.3. *Effect of air cooling on the tough–tough transition*

Complementary tensile tests were made on test pieces cooled in an air current at 23°C.

Table 2 shows that air cooling always shifts the tough–tough transition to higher strain rates.

3.4. *Appearance of the stretched specimens and fractures*

The appearance of the fracture surfaces (see Fig. 5) indicates that in this range of strain rates rupture is caused by local melting if the short duration of the test (at high strain rates) or the thickness of the specimen or both prevent adequate dissipation of the heat generated in the neck by stretching.

Consequently the long time (resp. the low strain rate)

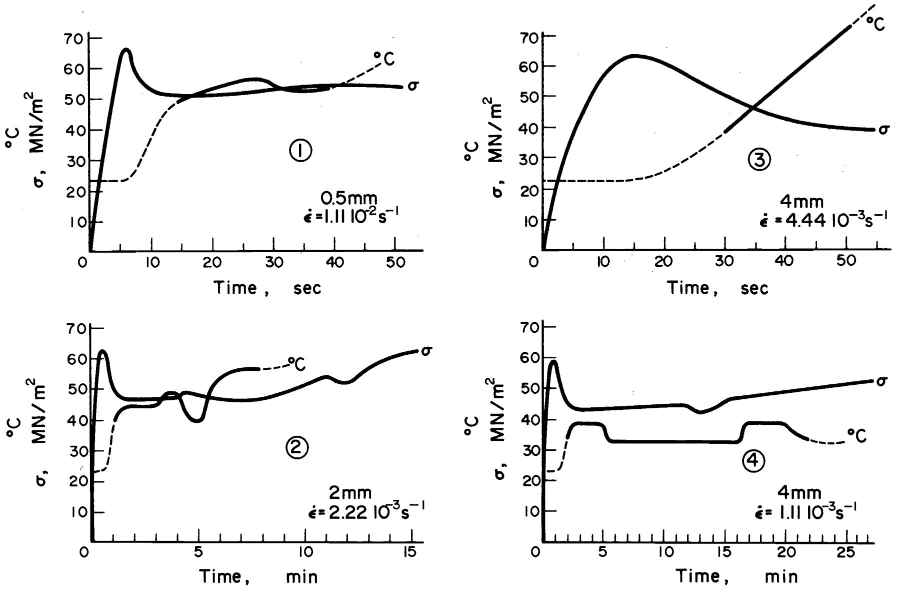

Fig. 4. Tough–tough transition comparison of stress–strain relations and thermal effects.

Table 1. Maximum temperature generated by stretching at the surface of the test piece

Thickness (mm)	Strain rate (s^{-1})	Rupture strain (%)	T max (°C)	Thickness (mm)	Strain rate (s^{-1})	Rupture strain (%)	T max (°C)
0.6	$1.19\ 10^{-3}$	154	28(1)	2.0	$2.2\ 10^{-3}$	194	50(2)
	$2.2\ 10^{-3}$	131	22(2)		$2.38\ 10^{-3}$	216	47(1)
	$7.14\ 10^{-3}$	58	52(1)		$4.71\ 10^{-3}$	32	60(1)
	$1.11\ 10^{-2}$	52	54(2)				
1.1	$2.38\ 10^{-3}$	180	34(1)	4.1	$1.1\ 10^{-3}$	149	34(2)
	$2.22\ 10^{-3}$	158	33(2)		$1.19\ 10^{-3}$	200	42(1)
	$7.14\ 10^{-3}$	64	50(1)		$4.4\ 10^{-3}$	23	68(2)
	$1.11\ 10^{-2}$	25	52(2)		$1.9\ 10^{-2}$	24	65(1)

(1) BASF.
(2) Solvay & Cie.

Table 2. Shift of the tough–tough transition

Sheet grade	Tough–tough transition without air cooling	Tough–tough transition with forced air cooling
1	$5.6\ 10^{-3}\ s^{-1}$	$8.8\ 10^{-3}\ s^{-1}$
2	$5.4\ 10^{-3}\ s^{-1}$	$8.0\ 10^{-3}\ s^{-1}$
3	$3.6\ 10^{-3}\ s^{-1}$	$3.8\ 10^{-3}\ s^{-1}$
4	$2.3\ 10^{-3}\ s^{-1}$	$3.0\ 10^{-3}\ s^{-1}$

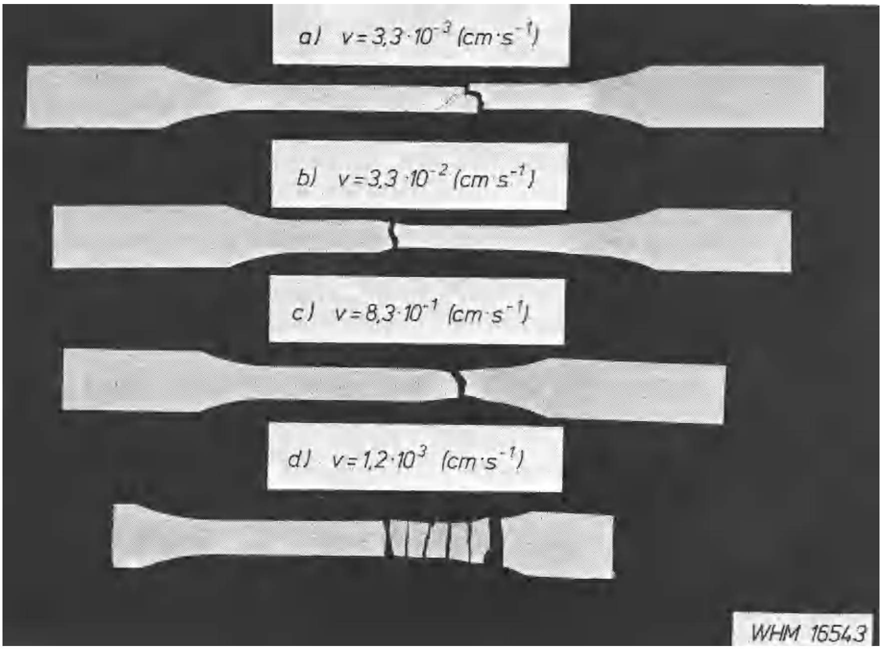

Fig. 5. Dependence of the rupture of rigid PVC (thickness of specimens 0.6 mm) on the elongation rate (T = 25°C).

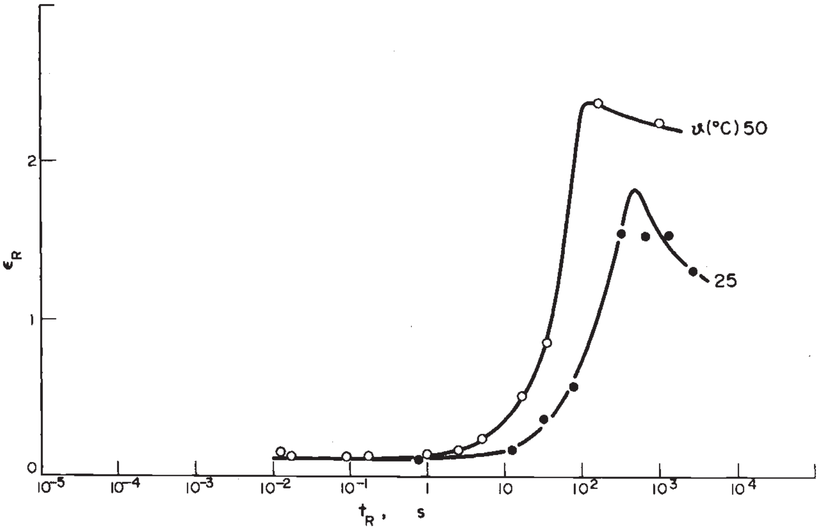

Fig. 6. Rupture strain as a function of rupture time. Dependence on temperature.

transition of PVC is shifted more towards longer times (resp. lower strain rates) the thicker the tested specimen (see Fig. 5).

3.5. *Effect of temperature on the long time transition*

This effect has been measured earlier.[1] Above room temperature an increase in ambient temperature shifts the transition towards shorter times. Recent measurements made by BASF (Fig. 6) on the 0.6 mm sheets corroborate this fact.

On the other hand, below room temperature, the position of the transition seems to be nearly independent of temperature. A decrease in temperature merely reduces the height of the transition.

The results, like the previous ones, can be explained as follows:

The tough–tough transition that occurs at low strain rates (long times) is determined by the transition from an adiabatic to a more nearly isothermal deformation in the stretched region of the specimen. When the ambient temperature approaches the glass temperature, the influence of the main relaxation processes becomes important, and the tough–tough transition is shifted to high strain rates. In other words, the higher the temperature, the earlier the transition occurs.

4. CONCLUSIONS

The results presented here confirm earlier assumptions.

The tough–tough transition is caused by the heat generated in the PVC by stretching. When the rate of dissipation of heat is comparable to its rate of generation, orientation can occur in the initial deformation area of the test piece.

This necking zone may become more rigid than other parts of the test piece, and the deformation may now extend to the whole test piece.

Rupture will occur only when the test piece is completely deformed and oriented.

When the rate of dissipation of heat is lower than its rate of generation, the deformation is limited to a small part of the test piece. The elongation at break is directly correlated with the temperature rise. The higher this is, the smaller the elongation at break.

Some experimental results obtained by Cross and Haward[3] are relevant to the present study. These authors found that the longer the PVC specimen, the more easily rupture occurs as a result of melting in the neck zone. This is promoted by the elasticity energy stored in the longer test pieces. Under the conditions of neck formation, energy is converted into heat and a rise in temperature of about 25°C results.

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