Yielding Processes in Glassy Polymers*

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Synopsis

Our contribution deals with a description of yield in glassy polymers, being treated as an activated process. For description the Eyring equation in simplified form has been selected:

$$\sigma_y = A - BT + CT. \log \dot\varepsilon \tag{1}$$

where σ_y = yield stress, T = absolute temperature, $\dot\varepsilon$ = deformation (strain) rate, and A, B, C = equation parameters. In the first part the applicability of this equation has been verified by applying data of our own as well as those published elsewhere. For a more comprehensive representation of the results the data were processed in the form of generalized master curves by using the appropriate shift factors derived from eq. (1).

EXPERIMENTAL

All data material of the yield properties were measured on an Instron tensile testing machine. The standardized specimens were prepared in our laboratories. Data from reference literature were applied without any readjustment. As basic polymers the following were used: PVC, Halvic 239 (Halvic Kunststoffwerke G.m.b.H., Austria); polycarbonate, Makrolon S-1039 (BASF AG., West Germany); and PMMA, solely those of reference literature. With PVC, moreover, a number of compounds with plasticizer and rubber polymers were used.

The yield data were measured at every temperature for four orders of deformation rates. The obtained values were then plotted in a graph of yield stress versus log of deformation rate, and in this way a graph of the type demonstrated in Figure 1 was gained for each material. The points for each temperature were plotted by a straight line and from the graph the parameters of the equation describing this straight line were determined:

$$\sigma_y = U + CT \log \dot\varepsilon \tag{2}$$

From these straight lines the mean value of the parameter C was determined. Provided the values of the C parameter consisted of two or more separate value groups, then the mean values were determined for these

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groups and designated in the direction from high temperatures as $C\alpha$-, $C\beta$-, or $C\gamma$-process, respectively. The B parameter values of eq. (1) were ascertained in a similar way. The mean values of the parameters B and C thus gained were then plotted for expressions (3) and (4) for temperature shift and rate yield factors respectively:

$$\log a_T = [1 - (T/T_r)] \cdot [\log (B/C) - \log \dot{\epsilon}] \qquad (3)$$

where $T, \dot{\epsilon}$ = temperature and deformation rate of measurement, T_r = reference temperature at which the generalization is being carried out, and
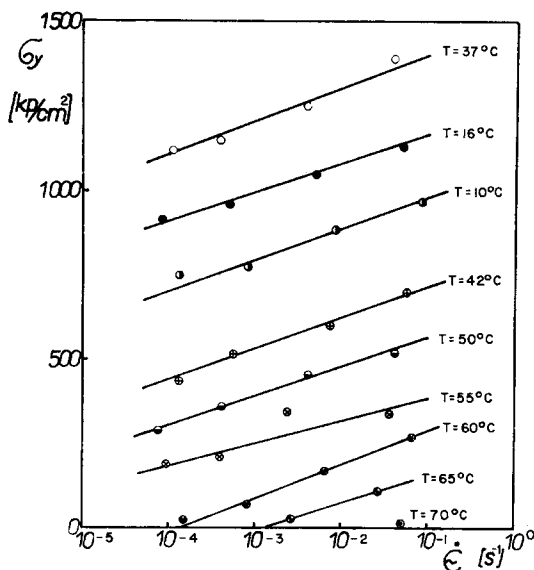

Fig. 1. Yield stress dependence σy on log of deformation rate, log $\dot{\epsilon}$ at various temperatures for hard PVC.

a_T = temperature shift factor representing that section on the axis of the deformation rate which the point gained at another than reference temperature has to be shifted.

$$a_{\dot{\epsilon}} = T \cdot \log (\dot{\epsilon}/\dot{\epsilon}_r)/[\log \dot{\epsilon}_r - \log (B/C)] \qquad (4)$$

where $\dot{\epsilon}_r$ = reference deformation rate at which generalization is being carried out, and $a_{\dot{\epsilon}}$ = rate shift factor representing the section on the temperature axis by which the point having been gained at another deformation rate than at the reference rate has to be shifted. In the generalized graph σ_y — log $\dot{\epsilon}$ the values of the yield stress σ_y were plotted versus log $\dot{\epsilon} \cdot a_T$ at the reference temperature. Similarly, in the generalized graph of the temperature dependence of the yield stress the values of σ_y were plotted versus $T + a_{\dot{\epsilon}}$ at the reference strain rate.

RESULTS AND DISCUSSION

Figure 2 shows a generalized temperature dependence of the yield stress of pure PVC at two reference strain rates.   It is apparent from the picture that the parameters of eq (1) are constant over a large temperature range but tend to change at certain temperatures abruptly.   The temperature regions with parameters remaining constant were designated in a similar manner as the well-known dynamic dispersions in the glassy state.
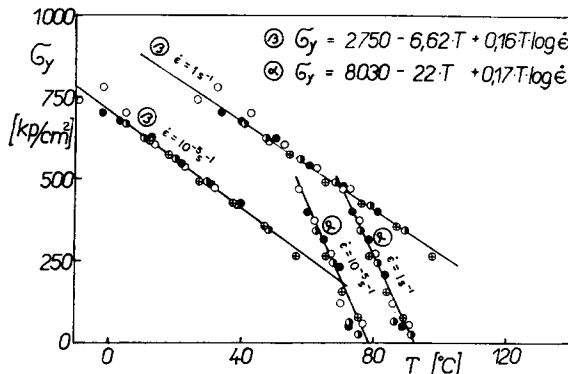

Fig. 2. Generalized yield stress dependence σy on temperature T for hard PVC (Halvic 239): (O) $4.17 \times 10^{-1} s^{-1}$; (●) $4.17 \times 10^{-2} s^{-1}$; (◑) $4.17 \times 10^{-3} s^{-1}$; (⊕) $4.17 \times 10^{-4} s^{-1}$.

The experimental data (obtained on the commercial PVC compound*) processed in this way are shown in Figure 3.   In the low-temperature region there appears a third linear portion corresponding to the yield behavior of PVC under conditions equivalent to the conditions under the dynamic β-dispersion.   Parameters of the β-portion of the curve differ slightly from these obtained on pure PVC.

In Figures 4 and 5 the data on PMMA[1,2] and polycarbonate[3] are treated in the same way.   On the curve for higher referential deformation speed (Fig. 4) we can see the disappearing of the β-process of PMMA due to its lower activation energy, as is well known from dynamic measurements. From graphs 2, 3, 4, and 5 it is apparent that the shape of the dependence is of a general character.   This is shown in Figure 6.

The individual regions bear a close relationship to the analogous dynamic dispersions which are denoted in the same way.   If the parameters of eq. (1) are given a structural interpretation consistent with the Eyring equation, the following conclusions may be formulated:

α-**Process.** (a) It begins to manifest itself in the vicinity of the glass temperature.   (b) The magnitude of the kinetic unit, being inversely

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* The experimental data were measured by Dr. A. Gonze of Solvay & Cie, Bruxelles, within the collaboration program of the Working Party on "The Relationship of Performance Characteristics to Basic Parameters of Polymers," Macromolecular Division of IUPAC.   The complete results will be published by Dr. A. Gonze.
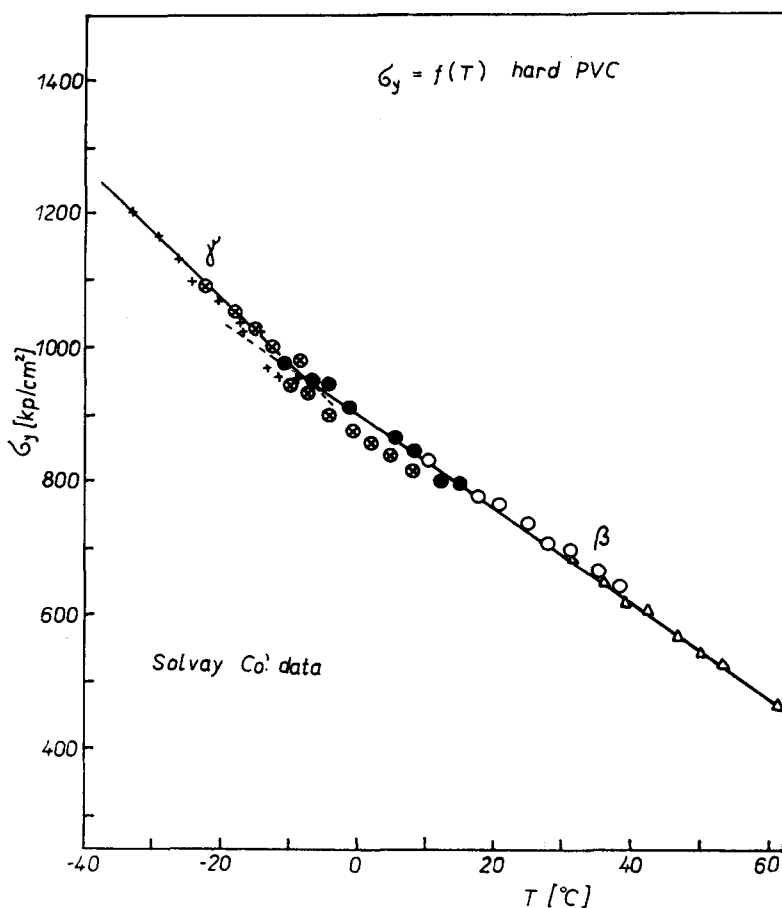
Fig. 3. Generalized yield stress dependence σy on temperature T for hard commercial PVC blend.   Data supplied by Solvay Company: $(+)$ $-42°C$; $(\otimes)$ $-31°C$; $(\bullet)$ $-19.5°C$;   (O) $+1°C$; $(\triangle)$ $+21°C$.

proportional to the parameter C, does not change during the transition from the β- to the α-process.   (c) The temperature of transition from the β- to the α-process is rate-independent within the limits of experimental error.   (d) This transition occurs below the glass temperature of the material.   For technical (commercial) PVC the temperature difference is 10°C, for pure PVC, 4.5°C, for PMMA, 5°C, and for polycarbonate, 4°C.

β-**Process.**   (a) It begins to manifest itself in the region of β-transition of glassy polymers.   (b) The volume of the kinetic unit is the same as in the α-process.   (c) The temperature dependence of the γ-β-transitions is strongly rate dependent.

γ-**Process.**   (a) It describes the yield behavior under the conditions where neither α- nor β-process can operate.   (b) The kinetic unit in this process is substantially smaller than in the α- and β-processes.

In the second part of this paper we have attempted to find the same relations between the parameters of eq. (1) and the polymer structure.   All the experimental work was conducted on PVC–rubber blends.   Rapid cooling of PVC from the temperature above T_g leads to an increase in free volume and to high internal stresses.   The course of the temperature dependence of
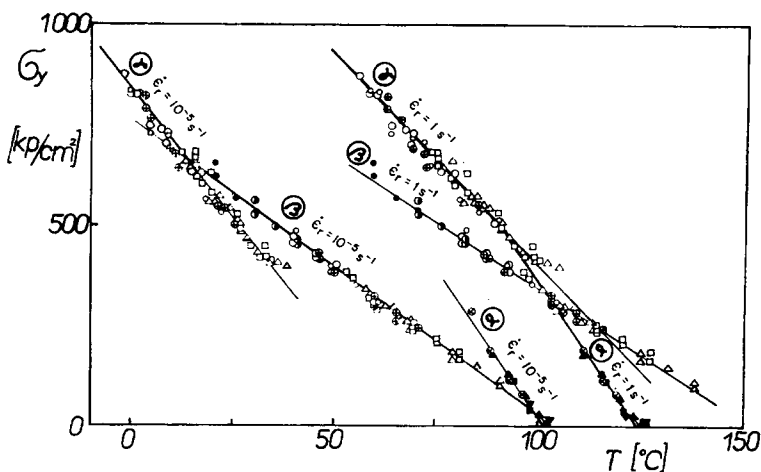

Fig. 4. Generalized yield stress dependence σy on temperature T for PMMA.   Data of Roetling:[1] (●) 30°C; (◑) 40°C; (⊕) 50°C; (○) 60°C; (◎) 70°C.   Data of Lohr[2]: (□) 80°C; (△) 90°C; (▲) 105°C; (■) 110°C; (▼) 115°C.
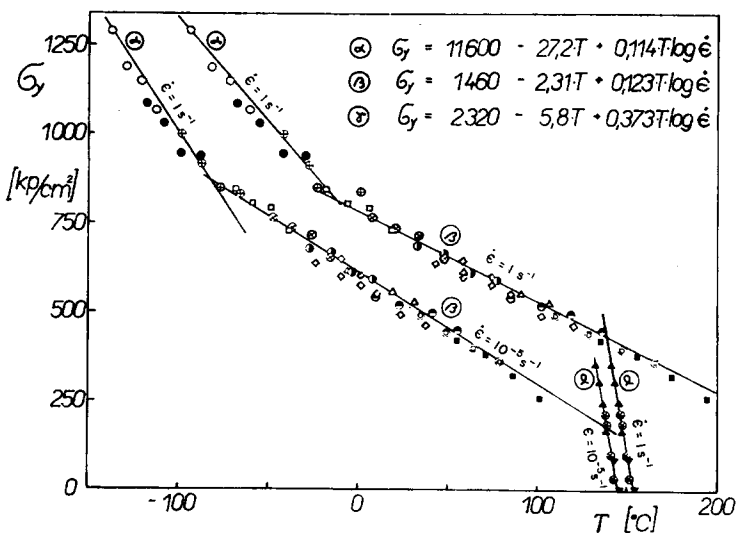

Fig. 5. Generalized yield stress dependence σy on temperature T for polycarbonate[3]: (○) −100°C; (●) −75°C; (⊕) −50°C; (□) −25°C; (⊗) 0°C; (◑) 25°C; (△) 50°C; (◓) 75°C; (◔) 100°C; (■) 125°C; (▲) 140°C; (⊛) 145°C; (▼) 150°C; (◇) our own measurement.
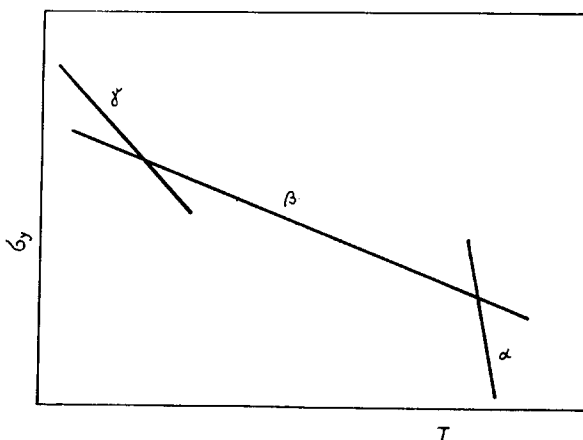
Fig. 6. Schematic illustration showing the common shape of the yield stress dependence σy on temperature T for glassy polymers.
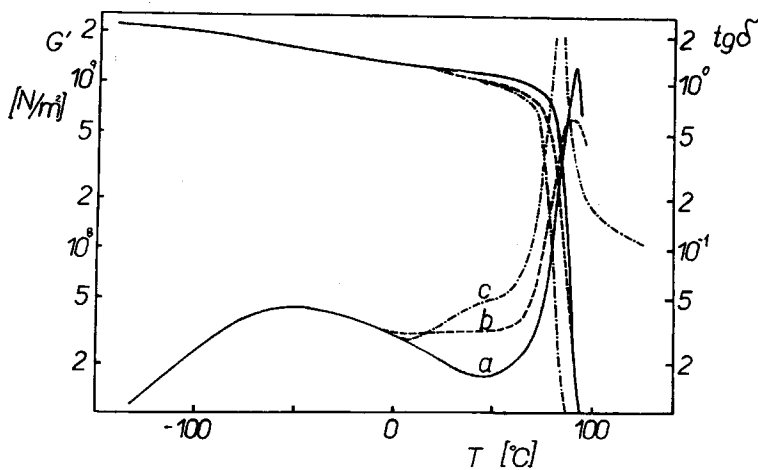

Fig. 7. Course of dependence $G'(T)$ and tg $\delta(T)$ for hard PVC (Halvic 239) with different temperature history: (a) cooled from 100°C to normal temperature at a rate of 10°C/hr; (b) quenched from 100°C to −60°C; (c) quenched from 200°C to −60°C.

dynamic shear modulus G' and of tg δ (Fig. 7) shows that probably a new damping process takes place or the α-dispersion is broadened in the direction of low temperatures. The generalized dependence of yield stress on temperature and on deformation rate, respectively, is shown in Figure 8. By comparison with the behavior of normal PVC we can see that the major change is in the value of parameter A containing the flow activation energy (it dropped). The quenched polymer behaves (at first approximation) like the normal polymer at a temperature higher by 17°C. From this value and from the expansion coefficient we can estimate the corresponding theoretical volume change. The value thus obtained is roughly twice the ex-
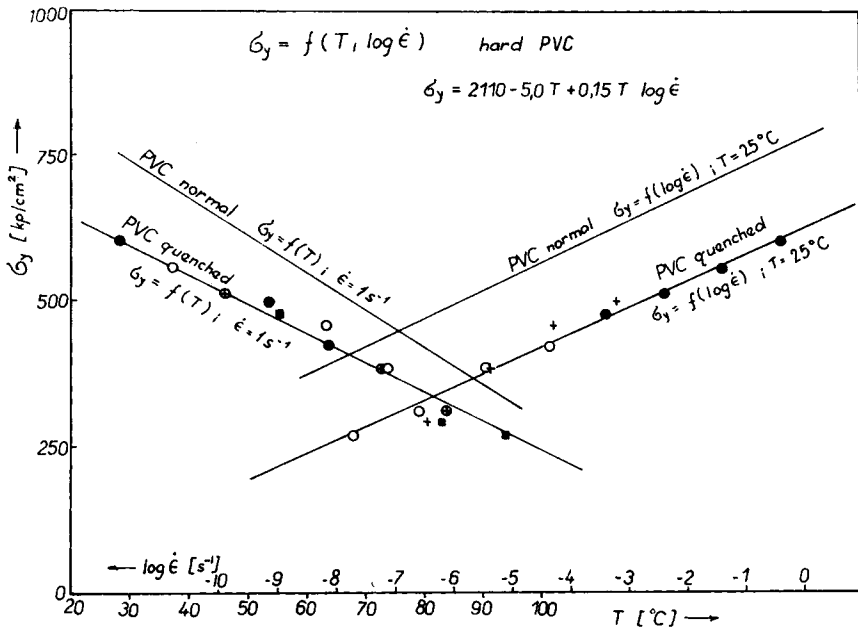
Fig. 8. Generalized yield stress dependence σy on temperature T and on log of deformation rate, log $\dot\epsilon$, for hard PVC (Halvic 239) and for the same PVC quenched from 100°C to −60°C: (●) 25°C; (+) 50°C; (○) 60°C; (●) 4.17 × 10^{-1} s^{-1}; (○) 4.17 × 10^{-2} s^{-1}; ⊕ 4.17 × 10^{-3} s^{-1}; ■ 4.17 × 10^{-4} s^{-1}.
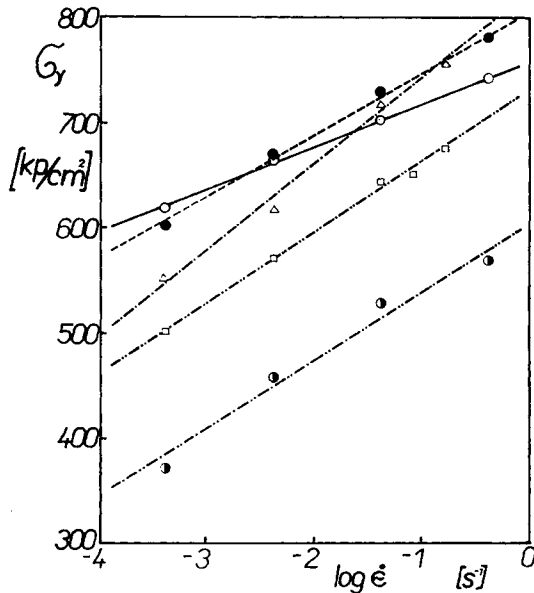

Fig. 9. Yield stress dependence σy on log deformation rate, log $\dot\epsilon$, for PVC blends (Halvic 239) + TCP: (○) PVC/TCP = 100/0; (●) PVC/TCP = 95/5; (△) PVC/TCP = 90/10; (□) PVC/TCP = 85/15; (◑) PVC/TCP = 80/20.
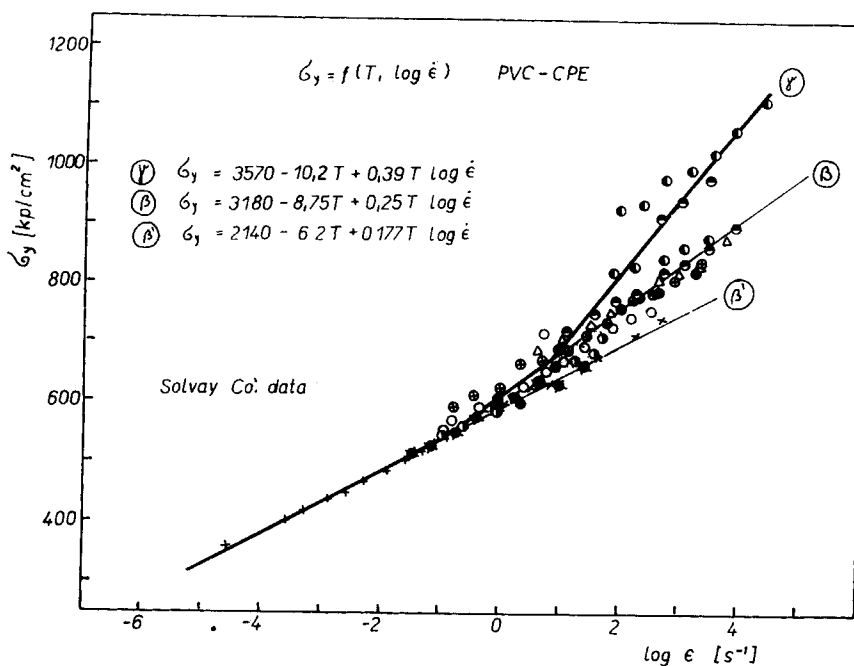
Fig. 10. Generalized yield stress dependence σy on log deformation rate, log ė, for PVC with chlorinated polyethylene. Data material supplied by Solvay Company: (●) −22°C, −19°C, −16°C, −13°C; (◑) −10°C, −7°C, −3°C; (◐) −42°C; (◓) − 31°C; (△) − 19.5°C; (⊕) −16°C; (○) − 12.5°C; (×) 10.5°C; (◉) + 1°C; (+) +21°C.

perimental value. The property change is probably due to the free volume change and the internal stress, not excluding the impact of other factors.

The dependence of the yield stress on the strain rate is shown in Figure 9 for increasing concentrations of the plasticizer TCP. A similar characteristic was obtained when a number of other plasticizers were applied. In all cases the slope of yield stress–strain rate dependence was increased by adding plasticizers. This slope is proportional to the parameter C defined by eq. (1) and is thus inversely proportional to the volume of the kinetic unit. All these measurements were performed in the region of the β-process. By the addition of plasticizer the volume of the kinetic unit is decreased, and for plasticizers with a high solvation power it reaches the value found for the γ-process. Thus we get a similar depression of the yield β-process (by the action of plasticizers) as observed in dynamic measurements. From the mechanical point of view these results can be used to explain most of the anomalies found in this region.

It follows from the evaluation of the yield behavior of PVC–rubber compounds that compatible rubbers (NBR 40) and incompatible rubbers (NR) affect only the absolute values without substantially changing the type of the dependence. On the other hand, the semicompatible rubbers (NBR
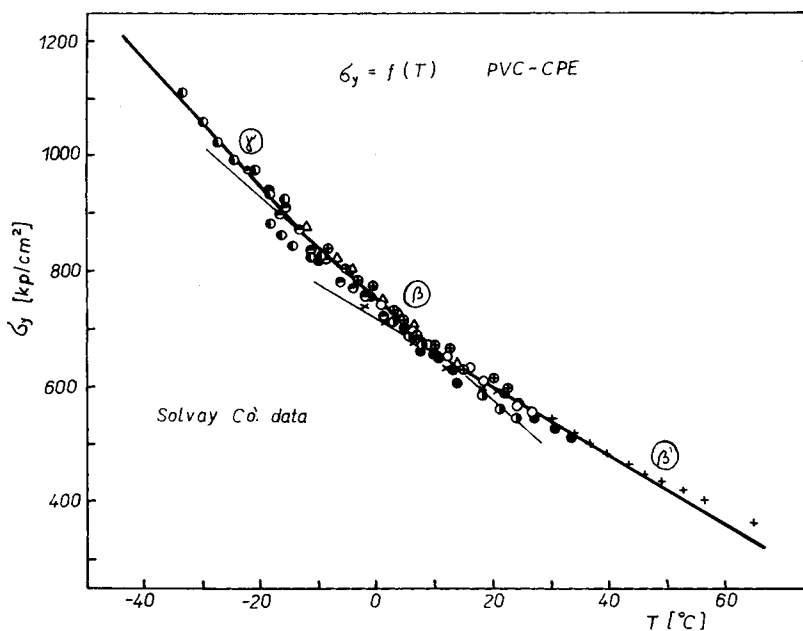
Fig. 11. Generalized yield stress dependence σ_y on temperature T for PVC blend with chlorinated polyethylene. Data material supplied by Solvay Company. Symbols are same as in Figure 10.

18, chlorinated polyethylene, rubbers grafted by VC) decrease the rate and temperature dependence of yield stress in the region of the β-process. In Figure 10 we can see the rate dependence of yield stress of the PVC–CPE compound. It was obtained by the evaluation of the data applied by the Solvay Co. The β-portion of the curve may be separated into two linear parts which are denoted as β and β'.

Figure 11 illustrates the same in temperature dependence. The break between β- and β'-processes is located in the vicinity of T_g of rubber. Below this temperature the parameters are the same as that found with pure PVC; above this temperature the parameters B and C are significantly lower. That means that the kinetic unit is larger. A similar phenomenon was observed in the study of ABS polymers in connection with the increasing degree of grafting of the rubber phase.

SUMMARY

This contribution deals with a description of the yield process in glassy polymers by means of a simple Eyring-type equation. The wide applicability of such an equation has been tested while using our own and other literature data. The parameters of the equation are practically constant in certain temperature and deformation rate regions, while in some points they tend to change abruptly. The different regions with constant values of

parameters were designed according to the mechanical dispersions observed in the glassy state and may be given a molecular interpretation.

Relationships between the parameters and polymer structure were also studied. Higher content of free volume (obtained by fast cooling from temperatures well above T_g) lowers the flow activation energy. Plasticizers first change the volume of flowing units and then suppress the intermediate yielding process. Rubbery polymers lower the flow activation energy and in some special cases give rise to a new process.

References

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