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Temperature Dependence of Melt Viscosity of Polymers

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Summary

The temperature dependence of steady-state melt viscosity of several polymers - semicrystalline and amorphous - in a broad temperature range has been studied. In many cases this dependence can not be expressed by an Arrhenius type equation. Breaks and slope changes have been observed. The influence of polymer morphology and molecular weight and the influence of pressure are presented.

Introduction

There are fairly numerous proofs about liquid-liquid transitions in n-alkanes and polymers (KRÜGER, 1979; PIETRALLA and KRÜGER, 1980; BOYER, 1981). For polyethylenes of molecular weight ($\overline{M}_w$) 2475 and 6600 such transitions were evidenced at 163°C and 230°C respectively; in polymethylpentene the transition was observed at 316°C (KRÜGER et al., 1980; 1981). In polystyrene transition temperatures were reported between 160°C and 190°C (SPENCER and DILLON, 1949; FOX and FLORY, 1950; MAXWELL and NGUYEN, 1979; LACABANNE at al., 1980). The nature of these transitions has not been elucidated yet. However, one of the interpretations assignes it to a transition from rubbery region or from coiling-uncoiling deformation mechanism to slippage between molecules in the viscous flow region (HEDVAT, 1981). This change of the flow mechanism was explained by the diminishing or disappearance of interactions between molecules. An alternative interpretation of this transition assignes it to a transition from a locally mesomorphic structure to an isotropic one, i.e. from partly helix-like conformations to random coils (PIETRALLA and KRÜGER, 1980; KRÜGER et al., 1980; 1981). In a previous paper dealing with the temperature dependence of the viscosity of carbon black filled linear and branched polyethylenes (DOBRESCU et al., 1981), anomalies have been observed in the temperature range 210-230°C. In order to find the origin of these anomalies the temperature dependence of viscosity was studied for pure polyethylenes as well as for other polymers, different as chemical nature, molecular weight and morphology:polypropylene, polystyrene, styrene-acrylonitril copolymers, high impact polystyrene and polymer blends. This contribution reports some data on temperature dependence of steady-state viscosity in a broad temperature range.

Experimental

The flow curves were determined, depending on polymer stability, their molecular weight and melting temperature, in the temperature range 150–290°C, using an INSTRON capillary rheometer. If not otherwise specified the capillary was of 0,06 inch in diameter and 4 inch in length. The melt flow index and melt densities have been determined in the same temperature range.

Results and discussion

In Figs. 1 and 2 the temperature dependence of viscosity at the same shear rate is presented for samples of linear and branched polyethylene of different molecular weight.

The shape of the dependence is generally the same if the viscosity at constant shear stress is considered. However, a very important difference exists.

Indeed, if a reference temperature is taken, for example 250°C and the temperature dependence of the ratio of the viscosity at a given temperature over that at reference temperature is ploted, one gets completely different images. Thus, the curves obtained on the basis of constant shear stress viscosities for polymers of the same type but of various molecular weights practically superimpose – Fig. 3.

It is worth to note that the data obtained with the same capillary represent in this case the viscosities at the same pressure.

The curves for viscosities at constant shear rate – Fig. 4 – do not superimpose.

In this case the activation energy decreases with the increase of viscosity. It should be recalled that the lower activation energies correspond, at constant shear rate, to higher pressures due to the higher viscosities of high molecular weight polymers.

As a matter of fact it is already known that at higher shear stresses, that is at higher pressures, the activation energy is low. This may be ascribed to the decrease of the free volume due to pressure and to its weaker temperature dependence as well as to the influence pressure exerts upon the flow mechanism and especially upon the flow units.

It is possible therefore to obtain master curves for each type of polymer plotting the ratio of viscosities at constant shear stress at a given temperature over those at the reference temperatures as a function of temperature. In Fig. 5 such curves for several polymers are presented. The temperature of 250°C was choosen as reference temperature since it lies outside the range in which viscosity-temperature curves exhibit transitions.

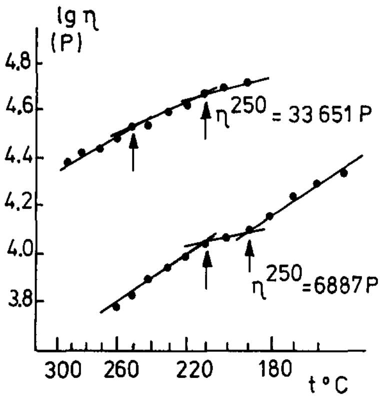


Fig. 1. Temperature dependence of viscosity for linear polyethylenes at constant shear rate (10 sec^{-1}).

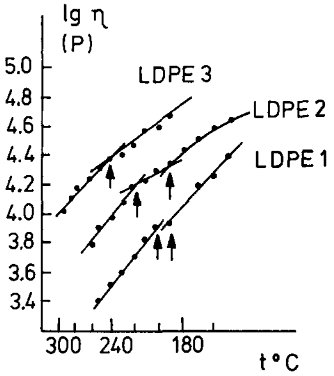


Fig. 2. Temperature dependence of viscosity for branched polyethylenes at constant shear rate (10 sec^{-1}).

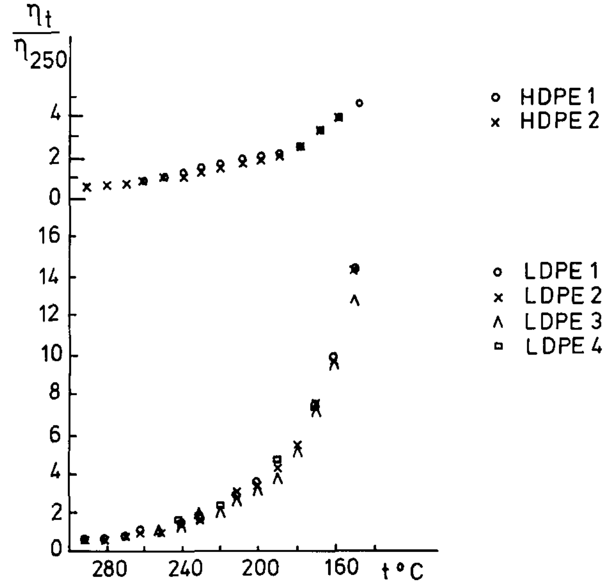
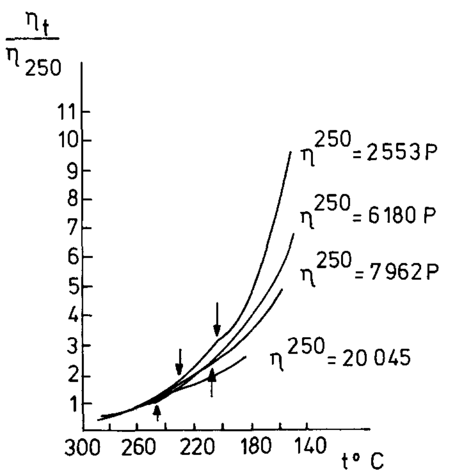


Fig. 3. Temperature dependence of the ratio of viscosity at different temperatures over that at 250°C, at constant shear stress (5.10^5 dyne/cm^2) for linear and branched PE.



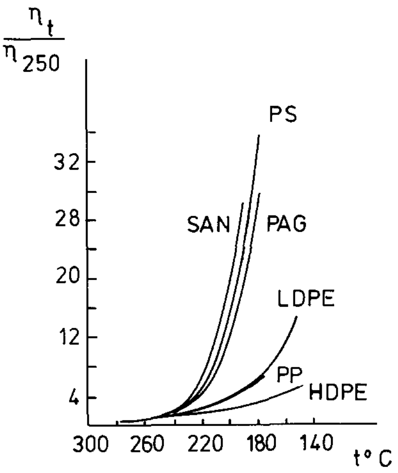
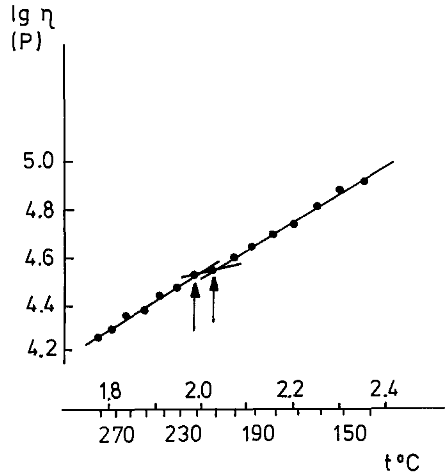


Fig. 4. Temperature dependence of the ratio of viscosity at different temperatures over that at 250^{0}C, at constant shear rate (10 sec^{-1}), for branched PE.

Fig. 5. Temperature dependence of the ratio of viscosity at different temperatures over that at 250^{0}C at constant shear stress (5.10^5 dyne/cm^2). Master curves for different polymers.



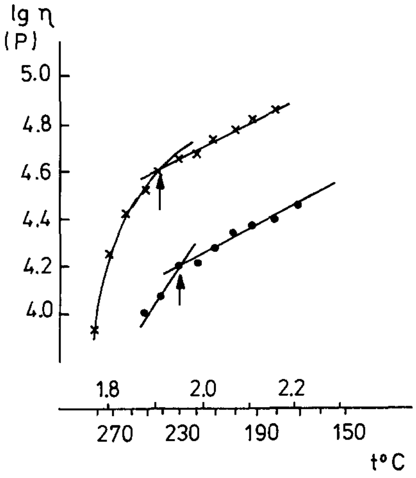


Fig. 6. Arrhenius plot for linear low density polyethylene ($\dot{\gamma}$ = 10 sec^{-1}).

Fig. 7. Arrhenius plot for polypropylene ($\dot{\gamma}$ = 10 sec^{-1}).

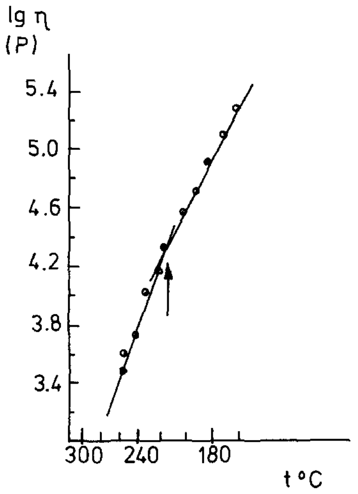


Fig. 8. Arrhenius plot for styrene-acrylonitrile copolymer ($\dot{\gamma}$ = 10 sec^{-1}).

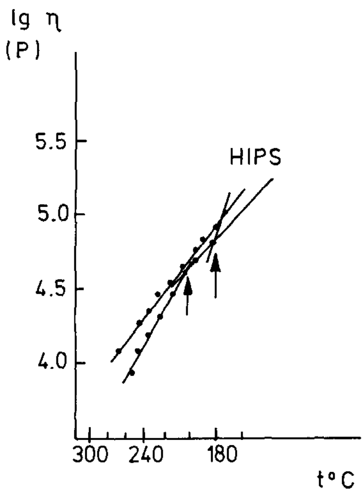


Fig. 9. Arrhenius plot for polystyren and high-impact polystyrene ($\dot{\gamma}$ = 10 sec^{-1}).

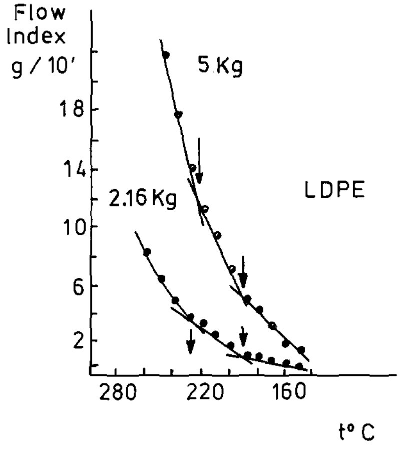


Fig. 10. Temperature dependence of the melt flow index for a branched polyethylene.

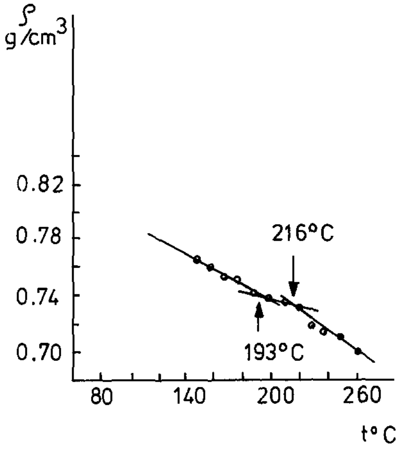


Fig. 11. Temperature dependence of the melt density for a linear polyethylene.

Indeed, Figs. 1, 2, 6–9 show that for some polymers the dependence of melt viscosity on temperature records discontinuities and slope changes. In all polymers studied the transition temperature rises with the increase of the molecular weight and hence of the melt viscosity, according to the examples in Figs. 1, 2 and 7. The temperature dependence of the flow index, that is of the viscosity at very low shear streasses also exhibits slope changes – Fig. 10.

Examination of density versus temperature curves – Fig. 11 – shows that there are slope changes on them in the same temperature region, suggesting that the processes occurring in the transition range entail modification of the packing density and therefore of the free volume.

Therefore one should expect that the modification of pressure should cause the shift of the transition. Experiments with cappilaries of various sizes have yielded plots of viscosity at constant shear stress versus temperature with different transition temperatures. In Fig. 12 an example is presented for linear polyethylene.

Conclusions

From our studies, the following observations must be considered

- discontinuities and slope changes have been observed on the viscosity–temperature curves for semicrystalline as well as for amorphous homo- and copolymers, pointing out to the existence of T_{ll} transitions;
- it is not always a transition temperature but a temperature range where the transition occurs;
- in multiphase materials, as HIPS, no such transitions are found;
- the transition is accompanied by a free volume change;
- the transition is pressure - dependent and shifts to lower temperatures with increasing pressure;
- the melt retains its viscoelastic behaviour at temperatures higher than transition temperature;
- the activation energy is higher at temperatures higher than transition temperature.

On the basis of these observations one can suggest the following conclusion : in a certain temperature range, above the melting temperature, the molten polymer retains elements of the order existing in solid state. With the rising of temperature (which increases the chain mobility) and the increasing of pressure (which may determine the change of conformation even at lower chain mobilities) these elements gradually dissapear, new conformations show up and, in the end, the macromolecular chains are stretched and oriented along the flow direction.

Studies wich must support this point of view are underway.

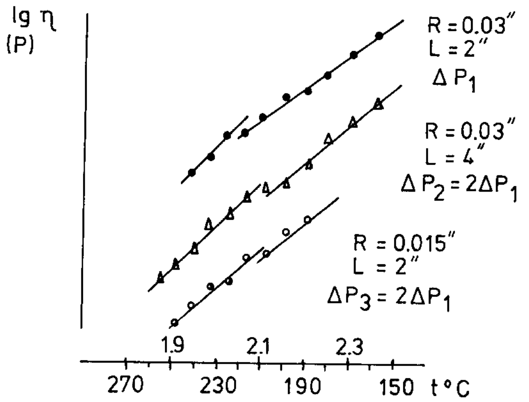


Fig. 12. Temperature dependence of the viscosity of a HDPE sample determined using different capillaries ($\tau = 5.10^5$ dyne/cm^2).

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