A Comparison of Some Rheological Properties of Concentrated Solutions of Chlorinated Polyethylene and Polyvinyl Chloride in Dioctyl Phthalate

M. E. MUÑOZ, J. J. PEÑA, and A. SANTAMARÍA, *Laboratorio de Reología, Fac. Ciencias Químicas de San Sebastian, Universidad del País Vasco, Apartado 1072, San Sebastian, Spain*

Synopsis

Steady-state and transient shear flow properties of poly(vinyl chloride) and chlorinated polyethylene dissolved in dioctyl phthalate were studied at different temperatures and polymer concentrations. In the case of poly(vinyl chloride)/dioctyl phthalate systems the presence of a sol–gel transition temperature was observed, whereas for chlorinated polyethylene/dioctyl phthalate systems the mechanism of flow was the same in the whole range of temperatures and concentrations. On the basis of the data obtained for both polymer/solution systems, we conclude that the presence of crystallites, rather than hydrogen bonds, determines the rheological behavior of poly(vinyl chloride)/dioctyl phthalate systems.

INTRODUCTION

The rheology of melts and concentrated solutions of poly(vinyl chloride), PVC, presents some unusual aspects, differing from other thermoplastics such as polystyrene or polyethylene in liquid elastic behavior and in its potential to form gels in different solvents.

Recent measurements[1] of sol–gel transition temperatures for PVC/solvent gels indicate that intermolecular hydrogen bonding Cl– – –H, rather than crystal formation, is responsible for PVC/solvent gel formation.

In this paper we analyze some steady-state and transient shear flow properties of PVC/dioctyl phthalate systems and chlorinated polyethylene/dioctyl phthalate systems in order to compare the mechanism of flow for both systems at different temperatures and interpret the results in terms of H bonds and crystallites.

EXPERIMENTAL

Materials

We used commercial samples of chlorinated polyethylene (CPE) and polyvinyl chloride (PVC) provided, respectively, by E. I. Du Pont de Nemours and Industrias Químicas Asúa, Bilbao, Spain. The chlorinated polyethylene (Hypalon 40) had a 35% chlorine content and was dissolved in dioctyl phthalate (DOP) at the following concentrations: 8%, 10%, 12%, 14%, and 16%.

The solution samples, after 24 h of gentle warming and stirring, were immediately introduced into the viscometer.

In the case of the PVC/DOP system, the solution ranged in concentration from 10% to 30%. Details of the preparation of the solutions are given elsewhere.[2]

Rheological Measurements

For CPE/DOP systems, the viscosity measurements, as well as the overshoot effect experiments, were carried out in a rotational viscometer (Haake Rotovisco RV 3) over a temperature range of 16°–100°C. Working at a constant velocity of the rotating cylinder (constant shear rate), the shear stress σ_{21} was recorded in a V-t Kipp and Zonen BD8 recording system. The stress overshoot phenomenon was registered and steady-state flow was confirmed by the fact that σ_{21} remained constant with time.

For the viscosity measurements at the concentrations and temperatures considered in this work, we could utilize only two values of the shear rate (γ); 2 s^{-1} and 6 s^{-1}, corresponding to 0.4 rpm and 1.1 rpm, respectively. Non-Newtonian behavior was observed for these shear-rate values.

The stress overshoot effect was analyzed by means of a special flag-type (a cylindrical shaft with six blades) rotor Haake SVII at 90.5, 128, 181, and 256 rpm. We did not carry out an analysis of the influence of the load-cell compliance which may not be negligible. Nevertheless, because the main aim of this work was to study the rheological properties of CPE as compared with those of PVC, this source of error can be neglected.

The experimental aspects relating to PVC/DOP systems has been developed in earlier work.[2]

RESULTS

Figure 1 shows the dependence of the viscosity, η; at $\gamma = 6$ s^{-1}, upon the temperature at various concentrations. In all cases, the data can be fitted to an Arrhenius type of equation [$\eta = B \exp (E_a/RT)$] with an activation energy of flow (E_a) of 11 Kcal/mol. The stress-overshoot effect is analyzed in terms of the maximum stress after an "infinite" rest time, σ_∞, and an entanglement reestablishment time, τ_e, obtained, following the work of Stratton and Butcher,[3] in a plot of the maximum stress from "stop–start" experiments versus logarithmic rest time.

In Figure 2, we present a plot of maximum stress versus rest time (the time during which the drive is disengaged) in the case of 10% CPE/DOP at different temperatures. τ_e is defined as the rest time required for the stress maximum to reach $(1-e^{-1})$ of σ_∞. Figures 3 and 4 show the effect of temperature on σ_∞ and τ_e, respectively, for various concentrations. As in the case of the viscosity, the data can be fitted to an Arrhenius type of equation. In Figure 5, we present the viscosity, η, determined at 0.09 s^{-1} versus the inverse of the temperature for the PVC/DOP system at different concentrations. Taking into account that in this case a structural transition—which leads to the appearance of a new mechanism of flow—occurs, the data can be adjusted to two straight lines within the range of experimental error.
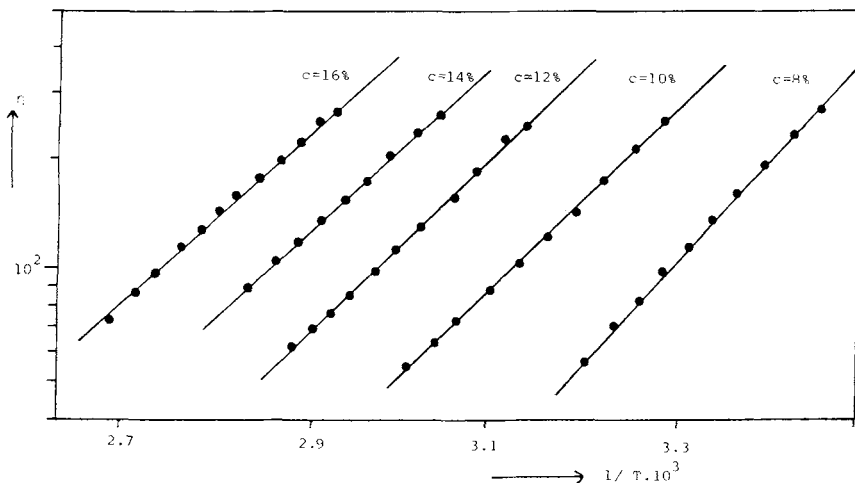
Fig. 1. Dependence of the viscosity, η, at $\gamma = 6 \text{ s}^{-1}$, upon the temperature at various concentrations for the CPE/DOP systems.

DISCUSSION

From the obtained results, we can see that at least in the range of concentrations we are considering in this work, CPE/DOP systems present rheological characteristics that are in agreement with the general behavior of concentrated polymer solutions, which are dominated by entanglement effects. Maxwell and Nguyen[4] pointed out that polystyrene melts exhibit abrupt "transitions" as a function of temperature which are detected by stress overshoot measurements. This is not the case with CPE/DOP systems.
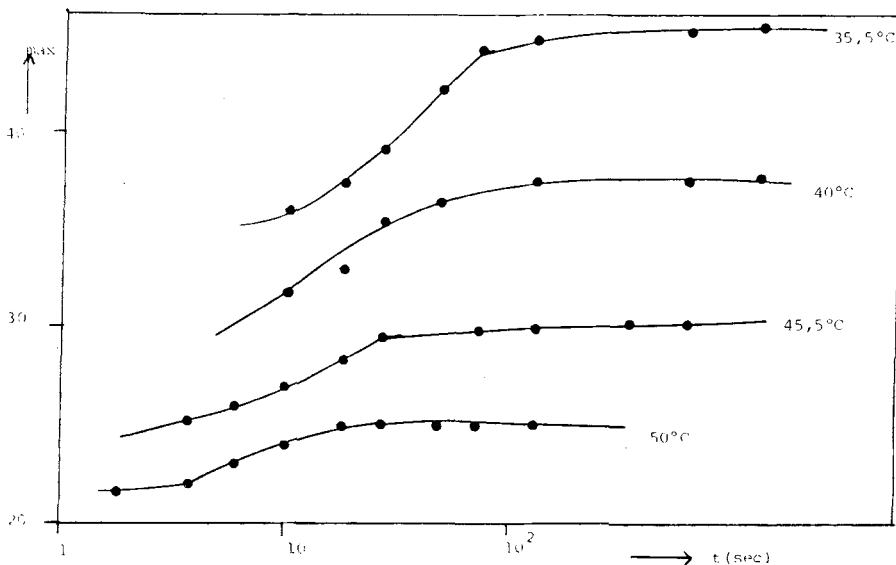

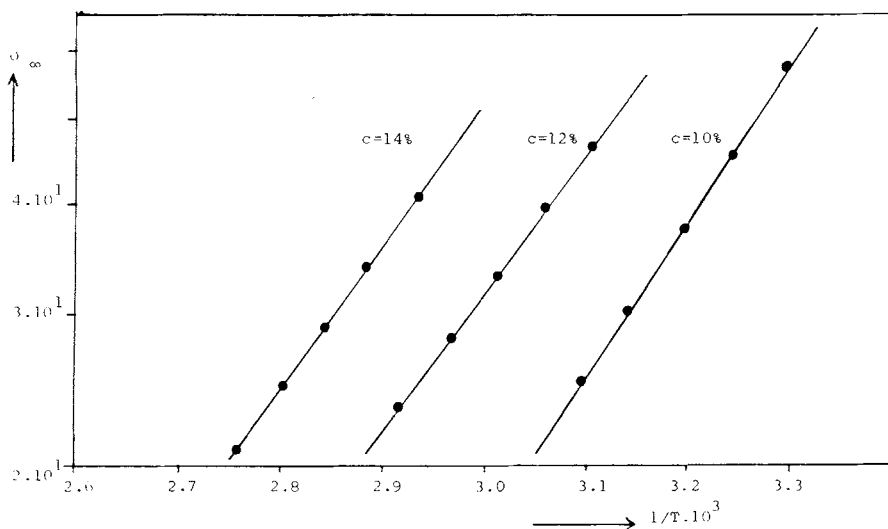Fig. 2. Maximum stress, σ_∞, versus rest time (σ_∞ is in arbitrary units).

Fig. 3.   Effect of temperature on maximum stress, σ_∞, at "infinite" rest time.

As is seen in Figures 1, 3, and 4, the mechanism of flow is the same throughout the range of temperatures considered.

These results differ from those obtained for PVC/DOP systems, where we observe the existence of a critical temperature (see Fig. 5 and Ref. 2), T_c, which separates two different flow regions. According to Pezzin and Giglo,[5] when PVC is dissolved at a high temperature in a plasticizer and is then cooled, the polymer forms a three-dimensional network consisting partly of a polycrystalline structure. On the other hand, the existence of a critical temperature in PVC melts has been considered,[6] because the crys-
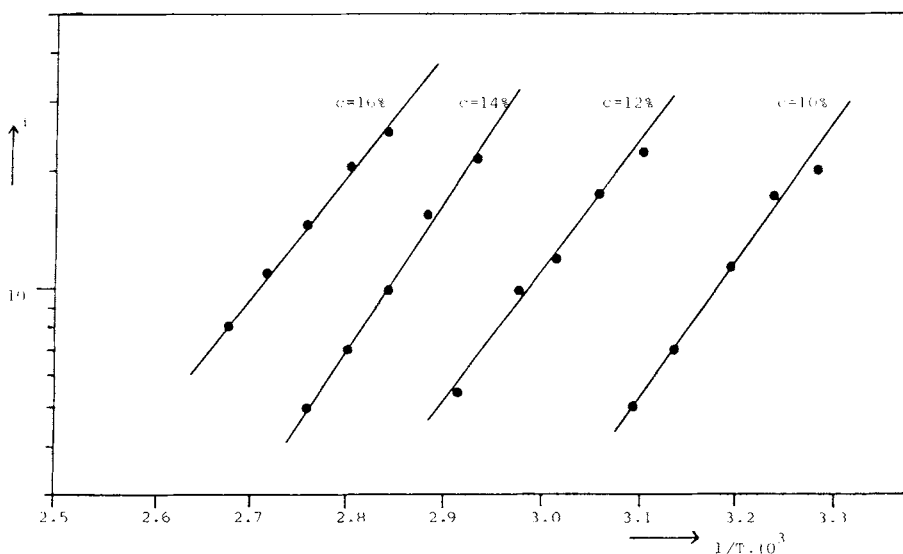

Fig. 4.   Effect of temperature on entanglement reestablishment time, τ_e.
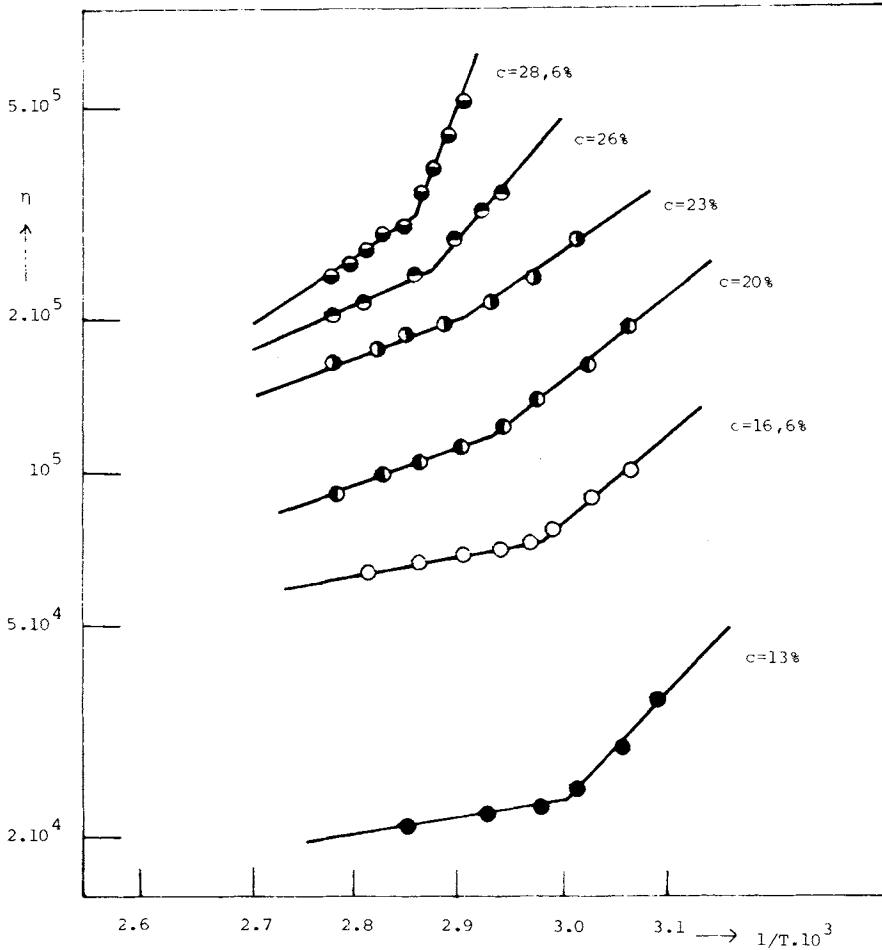
Fig. 5. Viscosity, η, determined at 0.09 s^{-1} versus the inverse of the temperature for PVC/DOP systems.

tallites act as cross-links and the corresponding network does not dissipate until a certain temperature is reached.

A relationship between the value of the Flory–Huggings interaction parameter, χ, for a solvent, and the temperature at which the last trace of polymer disperses into the solvent has been proposed:[7,8]

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{\phi - \chi\phi^2}{V} \frac{R}{\Delta H_v} \tag{1}$$

where T_m and T_m^0 are, respectively, the melting point in the polymer that contains diluent at volume fraction ϕ and the melting point of the pure polymer; V is the molar volume of the solvent; and ΔH_v is the enthalpy change that occurs with the formation of a unit volume of pure amorphous polymer from crystalline polymer. If, as pointed out above, we assume that the critical temperature (T_c) results from the dissipation of all crystallinity,

then we can identify T_m with T_c and use eq. (1) to obtain the enthalpy of fusion (ΔH_v). Literature values of χ are 0.05 and -0.03 (Refs. 9 and 10, respectively). In this work, we have considered $\chi = 0$. Therefore, eq. (1) becomes:

$$\frac{1}{T_c} = \frac{1}{T_c^0} + \frac{\phi}{V}\frac{R}{\Delta H_v} \qquad (2)$$

In Table I, we present the values of $1/T_c$ at different values of ϕ. Least-squares regresion analysis gives a correlation of 0.9996 and the corresponding values of $\Delta H_v = 2.25$ kJ/mol and $T_c^0 = 207°C$. These values are in reasonable agreement with the values found in the literature for the enthalpy of melt[8] and for the values of the critical temperature for PVC undiluted polymers,[6] respectively.

On the other hand, from differencial scanning calorimetry (see Fig. 6), at a heating rate of 40°C/min, we have obtained a value of $\Delta H_v = 2.6$ KJ/mol, which can be considered in agreement with the value obtained from eq. (2). An alternative explanation of the origin of the critical temperature, T_c, is the presence of intermolecular hydrogen bonding Cl- - -H below this temperature. It has been shown[11,12] that for some polymers the flow behavior is dominated by entanglement effects above a critical temperature and by a combination of H bonds and entanglements at lower temperatures.

Following a recent paper by Yang and Geil,[1] we evaluated the melting enthalpy of the network existing below T_c. This was carried out using the differential form of the Ferry and Elridge equation:[13]

$$\frac{\delta \ln c}{\delta\, 1/T_c}\,\ddot{e}\,\frac{\Delta H_c}{R}\,(\text{M}_w = \text{constant})$$

where c is the polymer concentration and the T_c is the critical temperature at which the network dissolves.

In our case we have obtained a value of $\Delta H_c = 10.7$ Kcal/mol, which is in agreement with the melting enthalpy obtained by Yang and Geil for PVC/dimethyl phthalate gel. As pointed out by these authors, this value of ΔH_c corresponds approximately to twice the hydrogen bonding energy. Taking into account that DOP (like DMP) is a solvent having two polar groups in one molecule, it could be suggested that intramolecular bonding of Cl- - -H is responsible for the thermolabile network.

TABLE I
The Inverse of the Critical Temperature T_c at Different Values of Dilution Volume
Fraction Φ

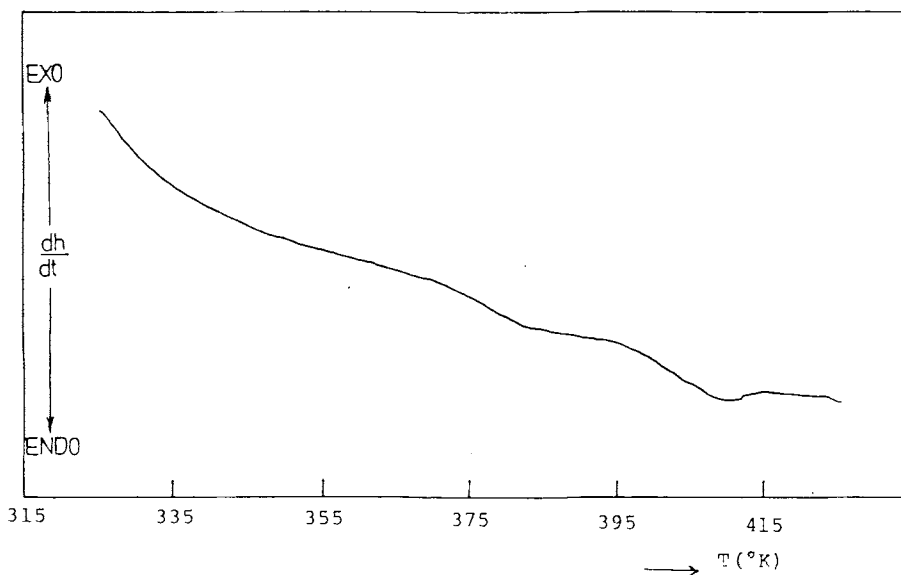| Φ (%)	$1/T_c$
87.16	2.895×10^{-3}
83.59	2.865×10^{-3}
80.22	2.833×10^{-3}
77.25	2.803×10^{-3}
74.37	2.776×10^{-3}
71.69	2.750×10^{-3}

Fig. 6. DSC scan at a heating rate of 20°C/min, for the PVC/DOP system (30% concentration of PVC).

As pointed out above, the fact that the CPE/DOP system does not demonstrate critical temperatures separating two different mechanisms of flow, leads us to consider that the mechanism of flow for PVC/DOP systems at a temperature below the apparent critical temperature is dominated by the presence of crystallites rather than by H bonds. Actually, as can be seen from the DSC spectra, CPE/DOP systems do not show crystals, whereas PVC/DOP systems do, and the probability of hydrogen bond formation (Cl - - -H) is the same, at the degree of chorination considered in this work, for both CPE/DOP and PVC/DOP systems.

References

1. Y. C. Yang and P. H. Geil, *J. Macromol. Sci. Phys., B*, **22**(3), 463 (1983).
2. A. Santamaria, M. E. Muñoz, and J. J. Peña, *J. Vinyl Tech.*, **7**, 22 (1985).
3. R. A. Stratton and A. F. Butcher, *J. Polym. Sci., Polym. Phys. Educ.* **11**, 1747 (1973).
4. B. Maxwell and M. Nguyen, *Polym. Eng. Sci.*, **19**, 1140 (1979).
5. G. Pezzin and N. Giglo, *J. Appl. Polym. Sci.*, **10**, 1 (1966).
6. H. Münstedt, *J. Macromol. Sci. Phys., B*, **14**, 195 (1977).
7. A. Nakajima, H. Hamada, and S. Hayashi, *Makromol. Chem.*, **95**, 40 (1966).
8. M. A. Harrison, P. H. Morgan, and G. S. Park, *Eur. Polym. J.*, **8**, 1361 (1972).
9. D. C. H. Bigg, *J. Appl. Polym. Sci.*, **19**, 3119 (1975).
10. C. E. Anagnostopoulos, A. Y. Coran, and H. R. Gamrath, *J. Appl. Polym. Sci.*, **4**, 181 (1960).
11. L. L. Blyler, Jr., and T. W. Haas, *J. Appl. Polym. Sci.*, **13**, 2721 (1969).
12. H. P. Schreiber, G. Thibault, and C. Prairie, *J. Rheol.* **24**(1), 99 (1980).
13. J. E. Eldridge and J. D. Ferry, *J. Phys. Chem.* **58**, 992 (1954).