RHEOLOGY AND PLASTICIZATION OF POLYVINYL CHLORIDE

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ABSTRACT

The behaviour of polyvinyl chloride in the range of temperatures from 77°C to 230°C is characterized by the persistence of a slight amount of crystallinity, which gives rise to very peculiar rheological properties. In particular, flow takes place partially through particle slippage, which predominates, with respect to molecular deformation, the lower the temperature and the higher the molecular weight and the crystallinity. The flow behaviour may change appreciably with shearing time and with thermal history. Viscous heat generation must be taken into account, even at relatively low shears. The molecular weight dependence of viscosity and relaxation time is anomalous for both rigid and plasticized samples. For the latter, the composition dependence of the glass transition temperature appears to be in line with predictions based on free volume concepts.

INTRODUCTION

In this paper I shall first discuss the information available in the literature on the rheological properties of PVC. Then I shall consider the influence of

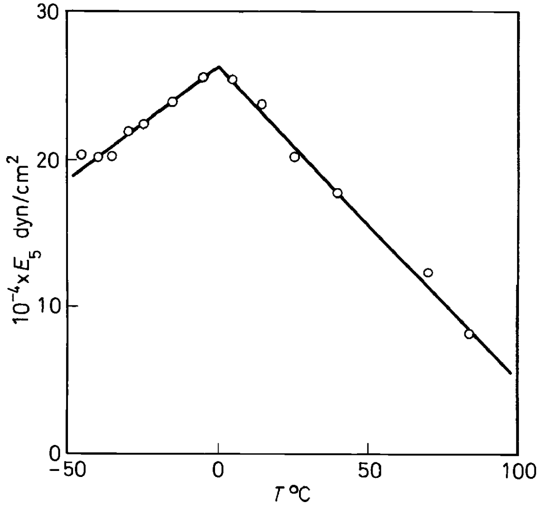

Figure 1. Young's modulus of a PVC-cyclohexanone gel, measured at 5 seconds, as a function of temperature. Melting takes place between 0°C and 120°C.

the addition of low molecular weight plasticizers on the rheological and thermal properties of this polymer. Some reference will be made to the properties of PVC of high crystallinity (syndiotactic PVC). The rheology of PVC pastes will not be dealt with here.

Commercial PVC is a slightly crystalline polymer, whose degree of crystallinity is estimated to be between 3 and 10 per cent. It is generally accepted that the crystallinity is related to the presence of short syndiotactic sequences, which give rise to small ordered regions (crystallites) whose dimensions range from about 20 Å[1, 2] up to approximately 100 Å or more[3, 4]. Melting takes place over a rather large range of temperature, not only for the unplasticized polymer[5], but also for PVC gels, as shown by the modulus-temperature curve, obtained in the author's laboratory, and reported in *Figure 1*. There is some evidence that in the unplasticized polymer the crystallites do not all melt below 230°C. In this context it is worthwhile remembering that the empirical rule $T_g/T_m = 0.65$ gives, for the maximum temperature of melting of PVC, $T_m = 250°\mathrm{C}$[6]. In addition, Guyot and coworkers report, in this Symposium, experimental x-ray evidence for $T_m = 250\text{–}260°\mathrm{C}$.

The presence in PVC of ordered regions of the nematic type has been described by Mammi and Nardi[7, 8], and supermolecular structures, in the form of globules and fibrils, have been revealed by Kargin[9].

RHEOLOGY OF POLYVINYL CHLORIDE

When talking of 'rheology of PVC' we usually refer to the processes of deformation and flow above the glass transition temperature ($T_g = 77°\mathrm{C}$). Accordingly, we shall discuss the viscous and elastic properties of this polymer in the range of temperatures from 77°C to about 230°C, the upper temperature limit depending on the degradation velocity of the polymer.

From the above review, it appears that the study of PVC rheological properties is commonly made below the melting point of some of the crystallites, and thus in conditions under which supermolecular structures of various types can possibly be present in the polymer. Given the presence of these heterogeneities it is not unreasonable to expect some peculiar rheological behaviour. In the case in which commercial PVC compounds are concerned, additional heterogeneities are introduced by other compounding additives, such as stabilizers, lubricants, fillers, pigments and impact modifiers. As a consequence of the above mentioned structure and of the high viscosity of the polymer in the processing range of temperature and shear, a number of anomalous effects appear when rheological measurements are carried out on unplasticized PVC. A partial list comprises:

(1) Particle flow.
(2) Change of flow properties with time and thermal history.
(3) Slip flow.
(4) Viscous heat generation.

A review of the information available on these topics will therefore be useful before discussing the influence of molecular parameters on the rheological behaviour.

(1) Particle flow

Recently Berens and Folt[10–12] have extensively investigated the flow of pure resins and have studied the fracture surfaces of the extrudates. They showed that the flow of an original PVC resin obtained by emulsion polymerization in a piston driven capillary rheometer can take place partially through slippage of the unmelted original particles (whose diameter is of the order of 10^3–10^4 Å) past one another, even at temperatures as high as 210°C. The most interesting features revealed are the following:

(a) a substantial decrease of the 'apparent viscosity' of the system with increasing particle size. This effect can be accounted for, in a qualitative way, by the Mooney theory of flow of supermolecular units.

(b) the flow curves are extremely non-Newtonian, which was interpreted as evidence for the existence of a yield stress for particle slippage at a value of $PR/2L$ (nominal shear stress at the wall of a capillary of radius R and length L) of about 100–150 psi (7–10×10^6 dyn/cm^2).

(c) the molecular deformation may predominate at low shear rates, whereas particle flow prevails at high shear rates.

(d) the die swell, i.e. the elasticity of the melt, increases with increasing temperature, which is contrary to the behaviour of normal polymer melts. This was interpreted, of course, as evidence for progressive fusion of particles and consequently for increasing contribution of molecular flow mechanism[13] with increasing temperature.

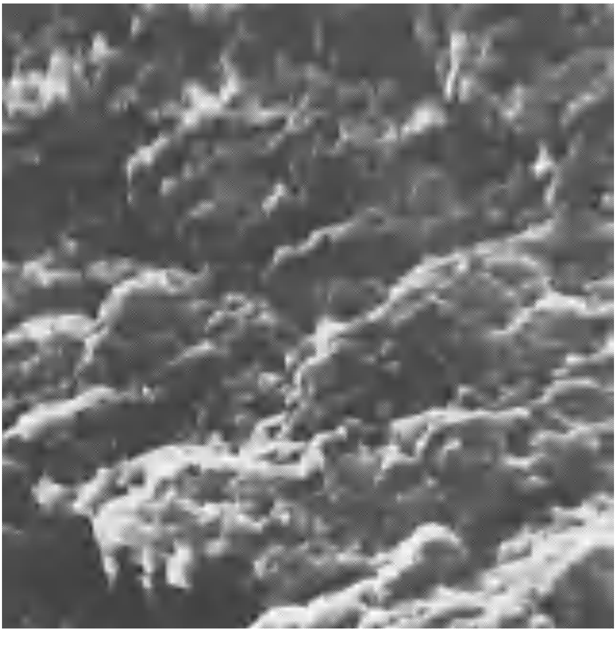

Figure 2. Stereoscanning electron microscopic picture of the fracture surface of a sample of suspension PVC extruded at high shears, at 190°C. Sample fractured at liquid N_2 temperature.

(e) the melt elasticity decreases with increasing molecular weight, which is in contrast with the viscoelastic theories.

Investigations were also extended, by the same authors, to suspension PVC resins, whose particles have a complex porous structure and a diameter of the order of 10^6 Å. They are composed of elementary or 'primary' particles of diameter about 10^3–10^4 Å. Berens and Folt found that in the extrusion of suspension resins a contribution of particle flow is also present because the primary particles structure is usually maintained. An example is given in *Figure 2*, where a stereoscanning electron microscopic picture of the fracture surface of a PVC sample sheared at 190°C is shown. The primary particles are clearly still present.

Summing up, in the flow of PVC a major role is played by particle flow, which is favoured, with respect to the molecular deformation mechanism, by high molecular weight, by low temperature, by large particle size, and, I can add, by high crystallinity of the sample. Further evidence for the presence of two distinct mechanisms of flow has been reported by Collins and Krier[14]. They studied thoroughly the flow of a typical stabilized PVC dry-blend and found two different flow activation energies, in the range of temperatures from 160°C to 230°C, both at constant shear rate and at constant shear stress. A schematic representation is drawn in *Figure 3*. In the low temperature region, characterized by the predominance of particle flow, the activation energy at constant $\dot{\gamma}$ is low (of the order of 10 Kcal/mole), whereas

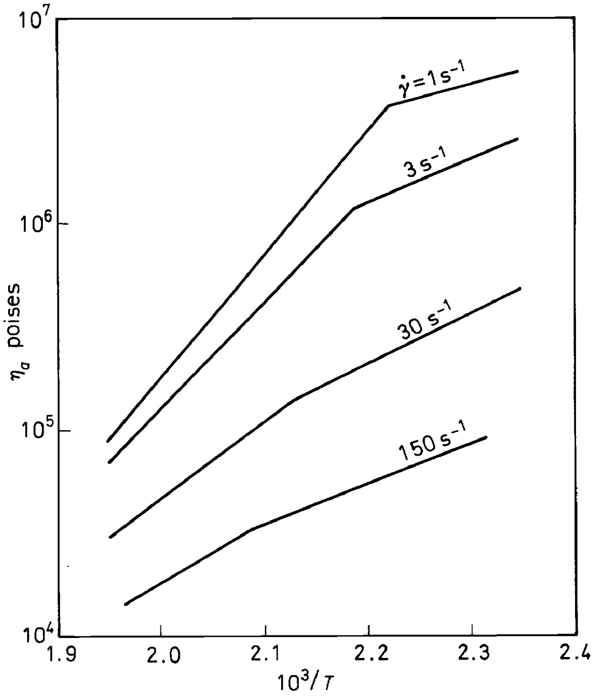

Figure 3. Schematic example of Arrhenius plots showing dual activation energy for PVC flow[14].

in the high temperature region, where molecular flow becomes important, its values are of the order of 20 Kcal/mole. The transition from one flow region to the other was attributed to the melting of crystallites.

Similar 'rheological phase changes' are known for other polymers: a multiple activation energy has been reported for polyethylene[15], with a transition temperature of 105°C (corresponding to the melting point of the sample), and for polypropylene[16].

Is the dual valued activation energy for PVC flow to be interpreted as a real phase change? In a very recent paper of Collins and Metzger[17] it is concluded that for some specific samples of emulsion resin the temperature, at which the value of the activation energy shifts, is close to the temperature at which the PVC particles lose their identity. However it is also shown that the critical transition temperature (at a shear rate of 10 $\sec^{-1}$) increases markedly with molecular weight for suspension resins, going for example from 165°C to 217°C as M_w increases from 60000 to 450000.

Molecular weight also markedly influences the value of the activation energy itself[17] whereas the addition of solvating agents of different types does not affect the critical temperature at which the viscous and elastic responses of the melt abruptly change their temperature dependence[18, 19].

All these results do not appear to be completely interpreted on the basis of simple phase changes, and possibly require additional investigations by rheological and optical methods to be satisfactorily clarified. There appears to be little doubt, however, about the strict connection existing between crystallinity of PVC and particle flow, as shown by very recent investigations[20, 21] on PVC samples of high crystallinity (obtained by polymerization at −30°C). Stereoscanning electron microscopic pictures of fracture surfaces of milled samples showed that the elementary particles of crystalline PVC begin to melt at a temperature about 40°C higher than that at which conventional PVC melts. Similar conclusions were drawn from Brabender Plastograph data[21]. Furthermore, the elasticity of the melt, evaluated from the swelling ratio D/D_0 of extruded compounds, was found to be very low and almost independent of temperature and shear stress for crystalline PVC, whereas for conventional PVC D/D_0 is larger and increases with temperature and shear stress. Thus the contribution of molecular processes to the flow of crystalline PVC, in the range of temperatures investigated (180–220°C), appears to be much lower than that present in conventional PVC.

(2) Change of flow properties with time and thermal history

Although properly carried out rheological measurements on this subject are rather scarce, there are several papers dealing with the changes accompanying the compounding of PVC, i.e. the fusion of the resin (previously mixed with various additives) under the combined effects of temperature and shear[22, 23]. Measurements are carried out usually on the screw extruder or the roll-mill, i.e. on apparatus directly used for compounding PVC, and on the Brabender torque rheometer. The latter, which is a miniature Banbury mixer, can be treated as a coaxial cylinder viscometer[24] and used to follow the viscosity changes of PVC mixtures with shearing time, at constant temperature. The curves, thus obtained, often show a maximum (interpreted as the 'gelation', or melting, of the PVC dry-blend) followed by a plateau (or equilibrium torque value) and finally by an upward inflection which marks the beginning of degradation induced cross-linking. The influence of additives on the flow properties of PVC as well as on the thermal stability of the sheared polymer are studied usually with this rheometer[25–27].

In general, the thermal history strongly influences the flow properties of PVC. It has been reported previously that by increasing the mutual fusion of the PVC particles *before* measurements, both the viscosity and the elasticity of the polymer are increased[11, 14, 28]. These rheological changes are, of course, attributable to melting, but often chemical degradation and cross-linking have to be also taken into account[29], even at relatively low temperatures. Burke and Portingell[30] showed that repeated extrusion of a PVC compound resulted in increased power consumption and reduced output rate, which can be attributed either to the progressive fusion of crystallites or to formation of cross-linking due to polymer degradation.

According to Russian authors[31] the main structural change taking place during rolling of PVC resins at low temperatures is the conversion of globular particles into fibrillar ones, orientated in the rolling direction. The orientation is larger on the surface of the system, i.e. where the shear rate is larger.

Naturally, as a consequence of structural changes, it is not unreasonable to expect the flow curves of PVC from different sources (or tested on different apparatus) to be very rarely reproducible. These difficulties could possibly be eliminated if real PVC melts were investigated. In this context it is worthwhile mentioning that recently De Vries[32] has claimed to have obtained PVC melts of high fluidity by rapidly melting the polymer at rather high temperatures by shearing forces. On the other hand, the reports on the influence of heat history on the mechanical properties above T_g are also very scarce. The effect of processing on the tensile properties has been reported by Pinner[33], and Horsma[34] has shown that the relaxation spectrum, obtained in the temperature range 150–220°C from measurements of the shear relaxation modulus, is substantially changed by an increase in the milling temperature of the sample, the terminal zone being displaced toward higher relaxation times. Of course if there is a progressive change of the PVC structure with increasing temperature, the principle of reduced variables should be applied with great caution, and the calculation of activation energies from the shift-factors or from the flow curves could give discordant results[34, 35].

(3) Slip flow

It is well known that addition of lubricants plays a major role in the processing and end-use performance of PVC[36], which is undoubtedly related mainly to their influence on the particle flow. However lubrication also prevents the adhesion of the polymer to the walls of the processing equipment, thus minimizing the occurrence of thermal degradation. Slip at the rheometer walls can sometimes be revealed very simply because the application of a low tensile stress to the polymer extruded from a constant speed, piston-driven capillary rheometer, strongly decreases the extrusion pressure. A good lubricant must form a coherent film between the flowing polymer and the extruder wall, which means that lubricants must favour plug flow, i.e. slip. A consequence of plug flow is an increase of flow rate, as shown by the influence of lubricant addition on the output rate in the extrusion of PVC[30]. In the presence of slip, the rheometer dimensions and geometry, as well as the nature of the walls, will in general affect the flow curves, unless appropriate corrections are applied[37]. Some careful studies of wall slippage in the extrusion of polyethylene have appeared recently[38–40], and it would be highly desirable if similar measurements were also carried out for PVC.

(4) Viscous heat generation

It is well known that almost all the rheological data on molten polymers are described in the literature by equations applicable only to isothermal systems, although the mechanical energy dissipation involved is often so high that the fluid temperature may be markedly increased. For instance Gerrard and coworkers[41] have shown that for nearly adiabatic flow in a capillary at high shears (shear stress from 10^5 to 10^6 dyn/cm^2 and shear rate from 10^4 to 10^5 sec^{-1}) the maximum wall temperature rise for a Newtonian oil, having a viscosity of only 10 poise, can be as high as 20–200°C. Given the high viscosity and the marked non-Newtonian behaviour of PVC, the influence of viscous heat generation should be taken into account even at relatively low shear rates (or shear stresses), whereas very often, from uncorrected rheological data obtained at high shear conditions (typically $PR/2L$ about 10^6–10^7 dyn/cm^2 and $4Q/\pi R^3$ about 10^2–10^4 sec^{-1}), conclusions regarding the mechanism of flow are drawn and values of the activation energy are derived[12, 14, 42]. Unfortunately, to correct the rheological data for the viscous heat generation is a very difficult task, unless the axial and radial distribution of temperatures in the flowing melt are determined[43]. Kim and Darby[44] have recently measured the radial temperature profile of PVC in the extruder head and have shown that it is a complex function of polymer properties and flow conditions. Maximum temperature rises of the order of 10°C were obtained even at relatively low shears (shear stress about 3×10^6 dyn/cm^2, shear rate about 30 sec^{-1}).

A different approach to the solution of the problem has been presented by Morrette and Gogos[45], who solved, analytically, the problem of viscous heat generation in the capillary flow of PVC for both the adiabatic and the isothermal wall cases. From their solution for the flow at the maximum volumetric flow rate investigated ($4Q/\pi R^3 = 400$ sec^{-1}, $PR/2L = 2 \times 10^6$ dyn/cm^2, $T = 202$°C $R = 3.2$ mm, $L/R = 40$) several interesting conclusions can be drawn. These are listed below:

(a) the maximum temperature rise of the melt is about 30°C for the isothermal wall and about 70°C for the adiabatic wall.

(b) the pressure gradient along the capillary is not linear (as experimental evidence from other sources indicates[46]).

(c) the maximum shear rate does not appear at the wall, but where the temperature rise is maximum, i.e. 'close' to the wall.

(d) a flattening of the flow curve $PR/2L$ against $4Q/\pi R^3$ appears at high shears, where apparently the 'experimental' flow index n reaches zero and even negative values.

These results indicate clearly that, even at moderate flow rates, considerable viscous heating can be achieved in the extrusion of PVC. The last conclusion,

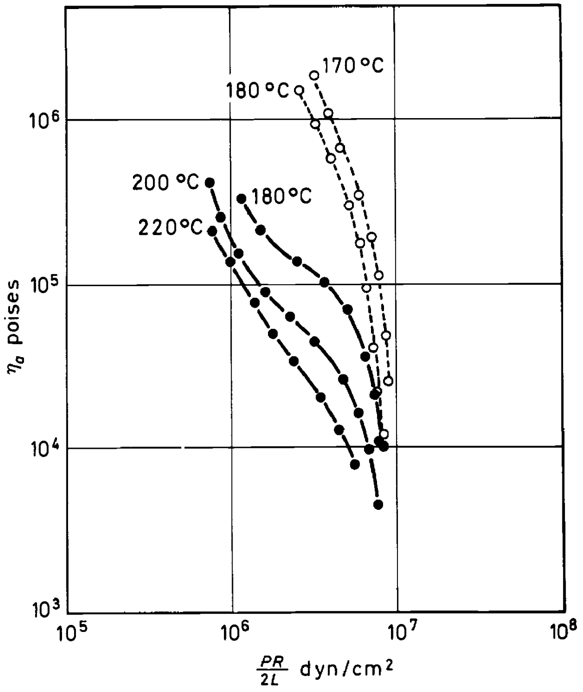

Figure 4. Apparent uncorrected viscosity ($\eta_a = PR^4/8QL$) against wall shear stress for two different PVC compounds at various temperatures.

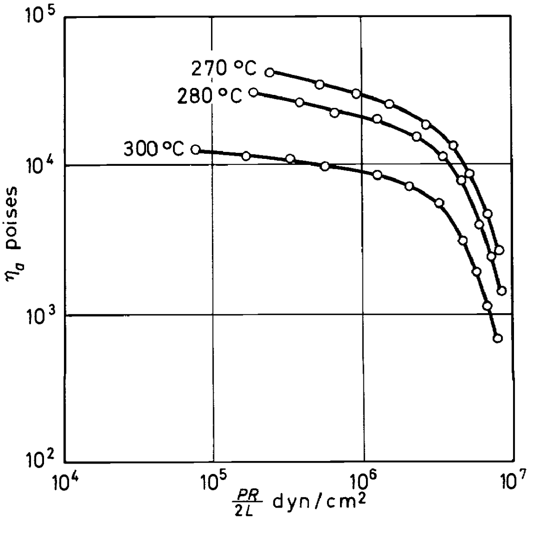

Figure 5. Apparent uncorrected viscosity against wall shear stress for a polycaprolactam sample at various temperatures.

namely the maximum predicted for the experimental shear stress–shear rate curve, appears to be a general feature of the flow of highly viscous fluids. In fact, theoretical evidence for different rheometer geometries[47, 48], as well as experimental data, supports the conclusion that a limiting value of the shear stress which can be sustained in the fluid may exist. This is due to the fact that the heat generation is so high that flow rates can increase at 'lower' shear stress, i.e. flow rate is a double function of shear stress. As a consequence, the apparent melt viscosity tends rapidly to zero when plotted against shear stress.

For the capillary geometries usually encountered in laboratory tests, this limiting shear stress appears to be very close to 10^7 dyn/cm^2, as shown in *Figure 4* for rigid PVC compounds (capillary diameter 1.5 mm) and in *Figure 5* for nylon-6 (capillary diameter 0.75 mm) and as can be argued from published data on PVC[12, 17], plasticized PVC[49], butadiene and ethylene-propylene rubbers[50] and polyisoprene[51]. The limiting shear stress value is rather close to the 'yield shear stress' for particle slippage postulated for PVC resin flow[12].

Influence of molecular parameters on PVC flow

From the above review, it is clear that PVC does not usually obey the rules of flow of simple amorphous polymeric melts. In particular, the expected molecular weight dependence of flow properties can be changed or masked by supermolecular flow effects, complicated by degradation, slip and viscous heat generation.

The viscosity of PVC does indeed 'increase' with increasing molecular weight, as shown for emulsion PVC resins of the same particle size[12], for suspension resins[17], for previously milled or extruded compounds[30, 42, 52], and for crystalline PVC compounds[21]. The approximate dependence of η on weight-average molecular weight M_w can be calculated, for suspension resins, from the paper of Collins and Metzger[17]. At a shear rate of 3 sec^{-1} (apparent Newtonian shear rate, no Rabinowitsch correction applied) and at 200°C one finds that η varies approximately with the third power of M_w. A similar dependence has been reported by Sieglaff[42], at a wall shear rate of 1 sec^{-1}, for compounded samples (viscosity data extrapolated). Since the flow curves are strongly non-Newtonian under these conditions, the high value of the exponent can be taken as a further indication that PVC has a cross-linked paracrystalline structure[52]. This appears to be confirmed by the fifth power dependence of both Newtonian viscosity and maximum relaxation time on molecular weight that can be derived from Horsma data[34] on rigid PVC, and from the still higher power dependence of viscosity and relaxation time on M_w reported by Pezzin and coworkers[49] for plasticized PVC.

Thus, molecular weight may have opposite effects on the rheological properties of PVC, depending on the polymer history and the range of temperatures. When particle flow predominates, an increase of M_w decreases the elasticity of the melt, apparently because the fusion of the particles becomes more difficult. On the contrary, when well-melted compounds are investigated at high temperatures, the presence of crystallites, which bond together the PVC macromolecules to form a permanent network, causes the viscosity and elasticity dependence on molecular weight to be higher than expected.

PLASTICIZATION OF PVC

I will not spend much time attempting to review the theories on plasticization[53, 54] or discussing the processes of blending and fusion of PVC and plasticizer, but I will confine this part of the paper to a picture of some recent rheological and thermal findings on plasticized PVC.

There is ample evidence that crystallinity is still present in plasticized PVC, as confirmed by x-ray diffraction studies[55–57] and by the temperature dependence of mechanical properties. Paracrystalline lamellar structures have been postulated also. According to Bonart[58], Hendus has shown that with increasing plasticizer concentration their dimensions increase from 150 Å to about 300 Å, as revealed by low-angle x-ray diffraction measurements. It is also well known that low plasticizer concentrations increase markedly the degree of ordering of the polymer structure[57]. In the useful range of plasticizer concentration, some crystallinity is maintained up to temperatures of the order of 180–190°C, as demonstrated by the anomalous dependence of viscosity on molecular weight reported by Pezzin, Ajroldi and Garbuglio[49]. Additional evidence was given by the same authors, who showed that thermal history markedly influences the flow curves at 150°C–170°C (see also Rudin[59]). Previously the influence of continuous shearing in a cone- and plate rheometer has been investigated by Khanna and Pollett[60], who had found a reversible decrease of both tangential and normal stresses upon shearing, between 150°C and 200°C. Since the glass transition of plasticized PVC is usually below room temperature, storage of the polymer is expected to cause changes of crystallinity and consequently of physical properties. As a matter of fact, density and Young's modulus increase linearly with the logarithm of storing time[61].

It seems clear from the works cited, as well as from other evidence, that the viscoelastic behaviour of plasticized PVC is strictly related to the history of the compound. For instance, the tensile properties of injection moulded samples change markedly with injection temperature[62], and those of milled samples with mill temperature[63]. As a consequence a specific optimum processing temperature is required by a given compound in order to develop its best physical properties.

Influence of composition and molecular parameters

The flow properties of plasticized PVC will be conveniently studied when a true fusion of the system has taken place. In this context, it is worth mentioning that different fusion temperatures are obtained by using different methods of measurement. For instance, microscopic determination of the disappearance of the PVC particles' boundary give melting temperatures much lower[64] than those obtained from the maxima of the Brabender Plastograph, used as a temperature scanning rheometer[65]. The influences of composition and plasticizer nature on flow behaviour have been recently investigated by Schreiber[64, 65] in the temperature range from 150°C to 190°C. The flow curves have been reduced to single master curves by a complex procedure, which requires extrapolation of logarithmic viscosity (at constant shear rate) to the undiluted polymer, and shifting of the flow curves, on the log-log plot, along a line of slope = −1. The viscosity shift factor a_ϕ has been found to correlate well with the appropriate Flory–Huggins interaction parameter χ (determined from the Brabender fusion peaks by using the Flory equation describing the melting point of polymer-diluent systems) and with the polymer fraction ϕ_2, according to the equation:

$$a_\phi = \phi_2^{3.4} \exp(6.12\chi - 3.06)$$

This result indicates that the flow behaviour of highly plasticized PVC can possibly be predicted from a knowledge of the χ value only. This appears to be a rather peculiar result, because the melt viscosity is expected to depend not only on polymer-solvent interactions, but also on the free volume of the system, i.e. on a complex function of concentration and thermal properties of the diluent.

The molecular weight dependence of loss tangent, stress relaxation modulus and flow curves has been investigated by Pezzin *et al*[49]. From the minimum of the loss tangent above T_g they calculated, on the basis of the Marvin theory, the molecular weight between cross-links M_c. Its value was 3000, in excellent agreement with other reports. From the stress relaxation curves, the maximum relaxation time τ_m was found to vary linearly with the eighth power of M_w, instead of the usual 3.4 power found for other polymers. As previously mentioned, the Newtonian viscosity η_0 also varies with an excessively high power of M_w, up to temperatures of the order of 180°C[49]. Finally, the shear dependence of viscosity could not be described by theoretical equations, such as those given by Bueche and Graessley, probably due to the great stability of some macromolecular network junctions (crystallites).

The constancy of the rubbery modulus above T_g has been interpreted by Shen and Tobolsky[66] by assuming that plasticizer interacts only with the amorphous regions of PVC, so that the crystallites remain intact. This point of view appears to be supported by the broadening of the main transition region often found in plasticized PVC samples[66–69], which is broadened still more when the crystallinity of the sample is high[21].

Thermal properties

Plasticizers are added to PVC primarily in order to lower the polymer glass transition temperature T_g below room temperature, and in practice the 'efficiency' of a plasticizer is often evaluated by its capacity of lowering T_g and related parameters (such as the brittle temperature, or the dielectric or mechanical loss tangent maximum). Several empirical relations have been used to express the variation of T_g with solvent weight fraction w_1, or volume fraction ϕ_1. For instance Boyer and Spencer[69] suggested:

$$T_{g2} - T_g = kw_1$$

where T_{g2} is the T_g of the undiluted polymer.

Jenckel and Heusch[70] added a quadratic term to a similar equation, obtaining:

$$T_g = w_2T_{g2} + w_1T_{g1} + k'w_1w_2$$

where T_{g1} is the solvent glass transition temperature. A very simple treatment, based on free volume concepts, has been suggested by Kelley and Bueche[71]. Let the fractional free volume of polymer and solvent at the temperature T be called f_2 and f_1. If they are additive, the plasticized polymer free volume will be:

$$F = \phi_2f_2 + \phi_1f_1$$

where of course:

$$f_2 = f_{g2} + \alpha_2(T - T_{g2})$$
$$f_1 = f_{g1} + \alpha_1(T - T_{g1})$$

If T_g is considered to be an iso-free volume temperature, one obtains:

$$T_g = \frac{\phi_2\alpha_2T_{g2} + \phi_1\alpha_1T_{g1}}{\phi_2\alpha_2 + \phi_1\alpha_1}$$

which Kelley and Bueche applied successfully to a polymethyl-methacrylate-solvent system. According to Kovacs[72], however, this equation cannot be applied below $T_c = T_{g2} - f_{g2}/\alpha_2$, because f_2 would be negative; he derives

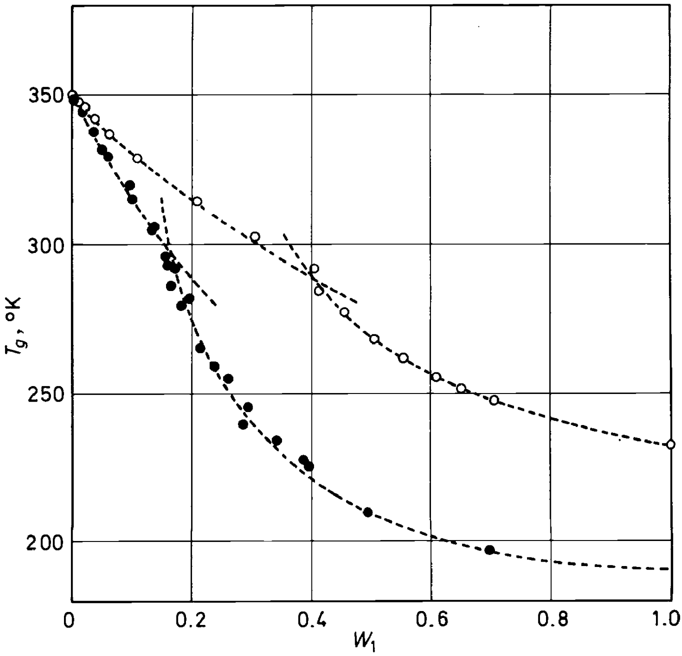

Figure 6. Plot of experimental T_g/composition curves for PVC-dibutylphthalate (●) and for PVC-dicyclohexylphthalate (○). The dotted curves are calculated according to the Kelley–Bueche and Kovacs equations.

for $T_g < T_c$ the equation:

$$T_g = T_{g1} + \frac{f_{g2}}{\alpha_1}\left(\frac{\phi_2}{\phi_1}\right)$$

We have recently applied the Kelley–Bueche and Kovacs equations to an extensive series of data relative to the systems PVC-dibutylphthalate and PVC-dicyclohexylphthalate, and have found[73] that for both systems a singular point T_c is present in the T_g/composition curves, as predicted by Kovacs (*Figure* 6), T_c is found to be about 55°C below the glass transition temperature of PVC, i.e. at 295°K (22°C), in close agreement with the T_2 transition temperature obtained by Adam and Gibbs[74] in their statistical thermodynamic treatment.

By assuming that the above equations can apply successfully to other systems, the plasticizer efficiency should of course be easily predicted from a knowledge of T_{g1} and α_1, the glass transition and expansion coefficient of the diluent.

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