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Polymer glasses : defects and plasticity on a molecular scale

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1. INTRODUCTION

Polymeric materials are systems build up as an intricate assembly of long covalent molecular chains. Because of entropy, chains are highly folded and neutron experiments, probing a few deuterated chains in the bulk, picture them rather as coils of radius $R \sim N^{1/2}$, with N the number of units in the chain. In order to build up a bulk density independent on molecular weight ($M = Nm$), such coils have to be strongly interpenetrated, at least in three dimensions ; for, their spacing g goes as $M^{1/3}$ (since $g^3 = Md^{-1}$, with d the density), which leads to an interpenetration parameter $q = R/g \sim M^{1/6}$ increasing with M . Finally, long chains loop back on themselves forming "physical nodes" or entanglements, a configuration where two different segments (belonging either to the same or to different chains as well) can only slip onto each other but cannot cross over each other. As density is independent on molecular weight, so is the entanglement spacing ; every N_e units, an entanglement is found along a chain. N_e is a characteristic number of the polymer and is most of the time as high as a few hundred.

The deformation of such materials occurs by uncoiling covalent links rather than breaking them ; therefore only van der Waals interactions are involved, much as the deformation of general organic solids. However, the chain structure imposes geometrical constraints on these uncoilings. Keeping unchanged the valence lengths and angles, lets bonds still free to move on their valence cones. In this way, uncoiling a bond requires moving a number of neighbouring bonds - at least, ten in a real chain. These collective movements can take place under stress in fluid phase, like polymer melts above their glass tran-

sition temperature T_g , i.e. when thermal energy is larger than the weak intermolecular (van der Waals) potential. Thus, rubber elasticity account for deformation from essentially a perfect gas theory taking into account only gauche-trans transitions in a single chain.

Deformation processes in the solid state are quite different. Intermolecular barriers are now dominant over kinetic energy and preclude any of those collective movements to occur, given the small mechanical energy input available at yield conditions, about $\sigma_o \epsilon_o b^3 \approx 10^{-3}$ eV per unit link with (σ_o, ϵ_o) the stress and strain value at yield, and b^3 , the monomer volume in the solid. As a result, perfect covalent parameters cannot be preserved everywhere along deforming chains ; instead, distortions in bonding have to be strictly confined within cores of defects in the molecular arrangement, the propagation of which produces a local shear strain. By this means, molecular rods are left kinked in the wake of the moving front of micro-shear bands which proceeds by distorting just a few more chains at a time while some others relax out behind, into the kinked (trans-) shape. Of course, this picture is nothing else than the mere dislocation picture of plastic shear propagation, and it helps to understand here how links can be unfolded without entailing the unrealistic motion of numerous successive units.

A part from the early model of Robertson [1], which deals with a fluid-like model of deformation and is only relevant near to T_g [2], the proposed models of non elastic deformation in glassy polymers introduce all this central idea of local defects in the chain arrangement ; they describe their yielding as a process basically heterogeneous at the molecular scale, like the repeated expansion of such defects. Therefore, we give first in the following a brief survey of the physics about these defects, with predictions about flow parameters which can be expected. As a matter of fact a great deal can be learned about defects from the flow kinetics of materials, and specially from the stress sensitivity of strain-rate, or the activation volume. We show in particular, that this type of data give a strong support to a localized dislocation loop mechanism as a realistic model to account for experimental mechanical behaviours of thermoplastics and thermo-set resins as well. Inversely, the knowledge of defect physics in polymers can stimulate further understanding and control of such behaviours. Finally, we report on recent accurate mechanical data, with a special attention to temperature effects. Thus two different deformation modes are found in current glassy polymers depending on

temperature. At lower temperatures, the mode is quite reminiscent of usual dislocation glide in crystals, while it is the thermal movement of a few in-chain units above some temperature (near to T_g in the internal friction notations) which gives rise to another mode, quite akin to the diffusive plasticity well-known in crystals, and characterized here by an almost complete relaxation of chain unit orientations.

2. THE DEFECT PHYSICS

According to the basically heterogeneous nature of deformation processes in solids, plastic shear strains are confined to a small ratio of total volume. In glassy polymers, they take place either within more or less diffuse shear bands, visible as surface markings left by the deformation [3,4], or as localized crazes [5,6]. Crazes are crack-like defects with numerous polymer fibrils which bridge the gap between crack interfaces, giving an overall density about half the one of the bulk. Typical of the low surface energy in polymers, they form from a mechanical instability of the crack front under a hydrostatic tensile component of the stress field. They have been much studied in the last ten years, and numerous reviews are now available [7]. Shear banding is more poorly known, and is at present the interest of a number of works. We restrict our review to it in the following.

2.1 The Frenkel picture of an elementary shear band

The simplest way to confine strains to a shear band is to allow the same shear shift everywhere at each monomer site, within a deformation band reduced simply to two successive layers of chain segments. In this configuration, featuring one part of the solid shifted relative to the other, strains are delocalized over the slip interface, while they are localized along its normal; accordingly, it can be viewed as a one dimensional confinement. Let us assume that segments have slipped a distance x one above each other at any segment site, and let b be an average species between units, Frenkel produced a simple argument for estimating the corresponding stress, which has to be zero at $x \approx 0.5 b$ and $x \approx b$, and linear in shear, $\sigma = \mu x/b$ at $x \rightarrow 0$ (μ is the elastic shear modulus); the simplest function fitting these conditions is a sine curve, $\sigma = (\mu/2\pi) \sin(2\pi x/b)$, giving a flow stress $\sigma = \sigma_M = \mu/2\pi$. As pointed out by Bowden and Raha [8], this argument, first developed for crystals, still holds for any amorphous solid as well since periodicity is not essential to it;

actually, extrapolating experiments down to zero Kelvin shows that flow stresses of order $\mu/2\pi$ are reached in polymeric glasses [2,9,10]. This value represents the theoretical (or maximum) shear resistance of solid polymers.

2.2 Dislocations in glasses : a simple model

At temperatures different from zero Kelvin, yield stresses are much lower (from $\mu/10$ at 150 K down to $\mu/40$ at 300 K for polymethylmethacrylate - PMMA - for example), so that strains have to be more strongly confined. The next step is to localize molecular misfits only along a line - or a narrow ribbon - of the slip interface, much like a fold in a carpet, so that a two dimensional confinement is obtained. Clearly, the line defect introduced here is the boundary between the part of slip interface which has undergone slip and the part which has not ; given a constant shift vector equal to the average unit spacing b , the line is a Volterra dislocation of Burgers vector b , the simplest model of a micro-shear band front.

Due to the random distribution of molecular sites over the slip interface, the relative shift of one of its lips relative to the other by a constant vector b creates unavoidably a number of molecular misfits, i.e. a stacking fault interface of energy per unit area γ is trailed behind the moving dislocation. Friedel [11] has developed this model in order to account for flow stresses at lower temperatures in metallic glasses. The energy γ is modelled as the strain energy build up in shifting one lip of a corrugated surface relative to the other by b ; there, corrugations are assumed to have a height $h \approx 0.1 b$ and a repeat period b , featuring the ensued atomic misfits in a volume b per unit area of the interface. Therefore $\gamma \approx 0.5 \mu \epsilon^2 b$ with a shear strain $\epsilon \approx h/b$, i.e. $\gamma \approx \mu b/200$. The stress σ for trailing the fault, $\sigma \approx \gamma/b \approx \mu/200$, is the flow stress in this model. It shows that σ/μ is temperature independent and of the order 10^{-2} , which is actually observed for metallic glasses at lower temperatures ; also, it is at the origin of a back stress which accounts for the recoverable part of the strain.

2.3 The case of polymeric glasses : dislocations with fluctuating Burgers vector

Glassy polymers show flow stresses higher than the above figures almost by a factor ten. In addition the flow stress is clearly temperature dependent and can be written [13] :

$$\sigma = \sigma^* (T, \dot{\epsilon}) + \sigma_i$$

where σ_i/μ is taken as independent on temperature, in contrast to σ^*/μ , which is termed the thermal component of flow stress. Recent experiments show σ_i is of order $10^{-2}\mu$ ($1.3 \cdot 10^{-2}\mu$ in P.M.M.A. and 0.8 in polystyrene [12]), so that it might well result from the above stacking fault mechanism. However, the appreciable thermal component σ^* , varying for ex. from $\mu/12$ at 150 K down to $\mu/86$ at 300 K in P.M.M.A., is a characteristic feature of polymeric glasses and must have another origin; it is typical of the existence of specific localized obstacles.

Turning back to the above picture of a dislocation in a metallic glass, the model is visibly oversimplified. The computation of stacking fault energy does not take into account severe atomic misfits which have yet to be produced at some places by a constant shift of the random atomic layer, like one atom sitting just at the top of the atom below. In fact, the computed energy γ corresponds to some subsidiary minima in configuration energy, or maxima in compactness, in which very bad misfits have already been relaxed out by local atomic rearrangements. The latter are equivalent to allow for some fluctuations of Burgers vector along the dislocation line, in order to fit it to the local atomic structure swept out. In terms of Volterra dislocations - which must keep a constant Burgers vector along their lines - it means that at point M where the local structure fits some Burgers vector $b(M)$, a small dislocation loop of vector $b(M) - b = \beta$ merges into the main dislocation line of vector b ; β is much smaller than b , and should be close to the width of the distribution of atomic spacings. Such loops describe above atomic rearrangements, making the shift vector varied from place to place through the swept area. In other words dislocations in glasses have to be of the Somigliana type, as Li pointed out [14]; these can be represented by a continuous distribution of Volterra dislocations of infinitesimal Burgers vectors which we sketch here by a stacking fault, there where atomic misfits are weaker, plus a collection of localized loops of vectors β , there where they are stronger.

In metallic glasses, where units are simply atoms and bonds are not strongly oriented, these accommodation loops should be a few b in size, with a vector β very small as judged from the glass density, for example, which achieves about 99 % of the crystal density. Therefore, they should form easily with the aid of the only thermal energy at all temperatures accessible by

experiments ; as a result they do not contribute sensibly to the flow stress, i.e. $\sigma^* \ll \sigma_i$ and $\sigma \approx \sigma_i \approx \gamma/b$. In such materials, flow stresses at lower temperatures (i.e. in the so-called heterogeneous flow mode) are probably due essentially to stacking faults, as proposed by Friedel.

In polymeric glasses, covalent chains restrict local molecular movements to some extent owing to two major structural features : (i) the chain stiffness, as represented by the statistical chain element b_{st} ; and (ii) the chain entanglements, characterized by their spacing λ in the slip interface. Both factors result into a glass structure more open than for metallic glasses with a density ratio to crystalline phase of only 0.85 to 0.95 [15]. The statistical chain element is the step length of the freely jointed chain (i.e. with all valence angle requirements removed) "equivalent" to the real chain as for its contour length and its end-to-end distance. Physically, b_{st} means the distance beyond which only, two links of the same chain are completely random in direction due to successive rotations on valence cones. It ranges around a few C-C lengths ($\ell_o = 1.5 \text{ \AA}$), being about 22 \AA for polystyrene (P.S.) and only 11 \AA for P.M.M.A., as obtained from small angle neutron or X-ray experiments [16]. This parameter allows us to model chain entanglements as spherical regions of radius b_{st} within which relative movements of units are strongly restricted to some directions by local steric hindrances. The spacing of such regions in the slip interface, λ , is related to their three dimension spacing $x = N_e^{1/2} a$ (where a is an elementary length defined for the purpose) by :

$$2b_{st} \lambda^2 = x^3 = a^3 N_e^{3/2}$$

a can be evaluated experimentally from the ratio $\alpha = R^2/M$ (R is the end-to-end distance and M is the molecular weight of the chain) and the molecular weight m of monomer unit, $a^2 = m\alpha$, so that :

$$\lambda = (N_e \alpha m)^{3/4} (2b_{st})^{-1/2}$$

In spite of some experimental scatter in different parameters, this leads to figures as $\lambda = 140 \text{ \AA}$ for P.S., and $\lambda \approx 110 \text{ \AA}$ for P.M.M.A. at room temperature.

Finally, a reasonable estimation of the Burgers vector length b is the distance of closest approach of two chains. Electronic radial distribution functions from X-ray data [17] give $b \approx 5 \text{ \AA}$ and $\beta \approx 1 \text{ \AA} \approx 0.2 b$ (taken from the width of corresponding peaks on the r.d.f.) for vinyl chains like P.S. or P.M.M.A. Note this value for b is consistent with the monomer volume v

allowed by density data, which we can write for cylindrical units $v = \pi b^2 c$, with c as the unit length along the chain : $c \approx 2 \text{ \AA}$, hence $b \approx 4.8 \text{ \AA}$ and 4.6 \AA in the case of P.S. and P.M.M.A. respectively.

Above numerical estimates show entanglements might be efficient obstacles to dislocation motion in glassy polymers ($\lambda \approx 28 b$ in P.S. and $22 b$ in P.M.M.A.), responsible for the thermal component σ^* specific to their flow stresses. In order to move forward, dislocations have to cut through such entangled zones in changing locally their Burgers vector from b into ca , $b \pm \beta$; this can be done readily in nucleating small loops of vector β right at contact with zones. As a result dislocations can only move when nucleating ahead small adjacent β -loops of approximated diameter $2b_{st}$ ($9b$ for P.S., and $4.5 b$ for P.M.M.A.) and leaving behind in their wake a series of similar small loops [18]. Given some moving dislocation length, fluctuations in its Burgers vector entail fluctuations in its (core) energy. From the point of view of dislocation mechanics, the situation looks quite the same as in those crystals where intrinsic lattice friction (Peierls forces) is dominant; β -loop nucleation finds its analogue there in the well-known double kink mechanism. Accordingly, flow stresses (or σ^*) should depend strongly on temperature, which is reflected in a small activation volume V_a , proportional to $(\partial T / \partial \sigma^*)_{\epsilon}$ [13].

The latter writes here $V_a = \beta A$, where A is the area swept out by the dislocation from its equilibrium to its critical activated configuration. For polymers in which $\lambda \gg b_{st}$, A should be some fraction of loop area πb_{st}^2 :

$$V_a \approx f \beta b_{st}^2$$

with f being in principal stress dependent and in practice in between 1 and 3. Experiments give $V_a \approx 900 \text{ \AA}^3$ and 220 \AA^3 for P.S. and P.M.M.A. respectively at lower temperatures [9,10,12,13]. With previous estimates of β and b_{st} , it gives a reasonable value for f , $f \approx 2$.

For strongly cross-linked resins or stiff thermoplastics, it may occur that $\lambda \lesssim b_{st}$, that is to say that steric hindrances exist everywhere so that sensible Burgers vector fluctuations are needed all along the dislocation line. This case is still more akin to the Peierls forces picture; the area A should then have a width b and a length $\ell_c(\sigma)$ which by analogy decreases with σ rather strongly from about $100 b$ down to a few b in the activation range. Typically in the middle of the range, one might expect $\ell \approx 10 b$, so that:

$$V_a \approx 10 b^2 \beta \approx b^3$$

that is to say activation volume of the order of one monomer volume or less should be anticipated. Such values have been observed on polyimide resins, together with a stress dependent activation volume of this type [19], in agreement with these predictions.

2.4 Other specific models

The above description of dislocation motion in polymeric glasses has stressed the need to consider local dislocation loops as the type of defect merely responsible for σ^* , i.e. for the largest part of flow stress. Loop defects have been also invoked about ten years ago in two prominent models we would briefly review now.

Bowden and Raha [8] have proposed to describe the yield behaviour of glassy polymers by the repeated nucleation of platelet-shaped sheared zones which can be modelled readily by standard dislocation loops of constant Burgers vector b . Once a nucleus is formed by thermal activation over some small critical size (which is stress dependent and in practice not larger than a few b), the loop expands to some extent under applied stresses. For the essential, this kind of model already worked out in dislocation physics is known to give relatively large activation volumes - i.e. critical sizes - as soon as (σ/μ) is of order of the low values observed in experiments, that is to say, is hardly thermally activated. Although (σ/μ) for polymers is relatively large ca. a few 10^{-2} , the model still suffers from this limitation ; in order to account for the steep experimental σ vs. T plots, authors fit these plots with T dependent b values and with a one Herz elastic modulus $\mu(T)$ - which varies sensibly with T at this frequency - without justifications. Eventhough, activation volumes which can be calculated from the fits are about ten times larger than experimental ones (e.g. $b = 3.5 \text{ \AA}$, critical loop radius $R_c = 5b$, hence $V_a \approx \pi R_c^2 b \approx 75 b^3$ for P.M.M.A. instead of a few b^3 in experiments).

Argon has given a theory of yielding of glassy polymers by modelling deformation as a kinking of a micro-bundle of a few parallel molecular rods (1 to 3 or 4) [20] . Elastic counteraction of neighboring chains against kinking is evaluated in an elegant way, by describing the kinking of molecular rods as resulting from the stress fields of two equal and opposite, closely

spaced wedge disclination loops extending over the bundle cross-section at points of kinking. Parameters of the model are the kink angle, the rod radius and the bulk site density. Although parameter fitting can reproduce σ vs T plots (with μ taken apparently once again at 1 Hz), activation volumes are only weakly stress dependent (as $\sigma^{-1/6}$) and still too large : in P.S., around 1750 \AA^3 (experiment gives 900) and in P.M.M.A., around 1500 \AA^3 (experiment gives 220).

To sum up, all the models are based on some very local defects, nucleated repeatedly. In comparing with experiments, crucial points are (i) the choice of the measurement frequency of the used shear modulus and (ii) the agreement with experimental activation volumes [13]. Although being still developed in a semi-quantitative form, the model of dislocations with fluctuating Burgers vector seems to be the one which is able both to cope with experimental values of V_a and to describe analogies and differences with metallic glasses on a structural basis.

3. THE EFFECT OF TEMPERATURE ON DEFORMATION MODES OF GLASSY POLYMERS

A precise thermodynamical analysis of activated deformation (yielding) can be performed in glassy polymers, following recent techniques of physical metallurgy [13]. The aim is to achieve defect parameters of concern in flow processes, the kinetics of which is of Arrhenius type :

$$\dot{\epsilon} = \dot{\epsilon}_0(\sigma, \sigma_i, T) \exp - \Delta G_a(\sigma, \sigma_i, T)/kT$$

where $\dot{\epsilon}$ is the strain rate and ΔG_a the Gibbs activation energy. From this analysis, a number of defect features can be learned like their mobile density (from $\dot{\epsilon}_0$), their nucleation rate per unit stress $(\partial N/\partial \sigma)_{\dot{\epsilon}}$ [see in ref 13], and characteristics of the obstacles which impede their motion. In particular two parameters are relevant for theoretical defect dynamics, the (Gibbs) activation energy ΔG_a for flow processes and the activation volume V_a which we identified above as βA , with A the critical area swept out, and which can be shown to be the stress derivative of ΔG_a , $V_a = -(\partial \Delta G_a / \partial \sigma)_T$.

However direct experimental quantities are not the wanted ones. Experiment yields only the stress or temperature sensitivity of strain rate, i.e.

$kT(\partial \ln \dot{\epsilon} / \partial \sigma)_T = V^*$ and $kT^2(\partial \ln \dot{\epsilon} / \partial T)_\sigma = \Delta H_a$, the latter being the activation enthalpy. Like metallurgical studies in the fifties or sixties, most of the polymer work in the last ten years fails to take these differences into

account. Thus V^* may stem merely from the stress dependence of $\dot{\epsilon}_0$, and in this case has nothing to do with A , or $\Delta H_a = \Delta G_a + T\Delta S_a$ may be quite larger than ΔG_a due to noticeable entropy contributions, i.e. temperature dependence of ΔG_a : $\Delta S_a = -(\partial\Delta G_a/\partial T)_\sigma$. The latter is of special interest in polymers since ΔG_a is likely to be proportional to shear modulus μ , which turns to be here appreciably temperature dependent because of several possible molecular relaxations. Thus, it has been shown that room temperature ΔH_a values may be more than three times ΔG_a for P.S. or P.M.M.A. [9,10,12].

Accurate analysis of this type has been done so far only for a few cases in constant strain rate compression tests, e.g. P.S. or P.M.M.A. [9,10,12], P.V.C. [21], polyimide resins [19]. At least for the studied thermoplastics, it shows conclusively the existence of two different deformation modes on both sides of a "critical" temperature T_c . Below T_c , it has been demonstrated that $V^* \approx V_a = \beta A$ is small and moderately variable - of order of a few monomer volume in the solid : 5.5 v for P.S. and only 1.5 v for P.M.M.A. -; furthermore ΔG_a is proportional to T , as Arrhenius equation predicts when $\dot{\epsilon}$ is a constant, and $\dot{\epsilon}_0$ not a sensible function of stress. Hence the strain rate is exponential with stress for the essential, and corresponds to a barrier energy $\Delta G_0 = \Delta G_a + (\sigma - \sigma_i)V_a \approx 0.65$ eV both for P.S. and P.M.M.A. Above T_c in contrast, a lower energy process takes place. ΔG_a vs T levels up to a plateau at 0.4 eV in P.M.M.A. and 0.5 eV in P.S., while $\dot{\epsilon}_0$ becomes very sensitive to stress. Correspondingly the experimental volume V^* does not reflect anymore the activated area A , but only the stress dependence of $\dot{\epsilon}_0$; it rises steeply as yield stress decreases and is consistent with a law of the type $\dot{\epsilon}_0 \sim (\sigma - \sigma_i)^2$. All these findings are reminiscent of a "diffusional" plasticity by opposition to the low temperature mode, rather akin to a "glide" plasticity as referred to crystal terminology. Note that such values of energies allow us to rule out any breaking reforming of covalent bonds as deformation process.

T_c values increase roughly logarithmically with $\ln \dot{\epsilon}$ and at usual laboratory rates (10^{-4} to 10^{-5} s $^{-1}$) fall generally below room temperature : 160 K for P.V.C., 230 K for P.M.M.A., 280 K for P.S. so that room temperature deformation belongs to the high temperature diffusional mode. In particular the relatively large values of V^* quoted in the literature as "Eyring volumes" are not true activation volumes as often concluded misleadingly.

This two mode scheme has been successfully confirmed recently by neutron structural investigations [22]. The shape of polymer coils in a shear band has been observed by small angle neutron scattering, in atactic polystyrene deformed by compression at a constant strain rate. When straining below that temperature T_c , coils are seen deformed into an oblate spheroidal shape which can be deduced from the initial sphere by simple shear ; the shear strain observed at coil scale is then equal to the one carried by the macroscopic shear band itself, as measured from the offset of a surface groove - i.e. about unity at yield. This observation demonstrates clearly that as micro-shear bands extend through the bulk, they leave in their wake chain segments oriented along the shear band direction, which is confirmed by the rising of a strong and homogeneous birefringence in the whole band. For the essentials, this process is akin to dislocation glide in solids.

On the contrary, it is quite surprising to find polymer coils in their unperturbed shape, and still as unchanged spheres, after deformation above T_c . This is found to hold not only at the overall coil scale (i.e. in the Guinier range) but also at a scale ten times smaller (i.e. in the intermediate range); only at the scale of two or three links some change is observed as compared with a blank specimen. This means that a large part of chain orientations in the band has relaxed out, probably as β -loops can now climb in addition to glide resulting in a more extensive molecular rearrangement. Yet some remanent shear-strain, of order 0.6 to 0.7, is retained in the band - now much more diffuse in character and with a birefringence oscillating from place to place. While internal stresses of order $10^{-2}\mu$ are still present, being likely produced by the created stacking fault as explained above, the thermal component of flow stress decreases exponentially with temperature like in crystalline climb deformation. Although it is clear that T_c and the constant value obtained for ΔG_a are related to the so-called β -secondary relaxation (i.e. the motion of a small number of monomer units about the chain backbone) [13], and that this relaxation in turn is involved in free volume transport at short to moderate range in solid polymers, it has to be said that no detailed model is at present available for the defect behaviour and the origin of thermal component σ^* above T_c . This should be, with the unresolved important problem of defect nucleation, one of the main challenge left for future work in this field.

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