

Dislocations in glassy polymers do they exist? Are they useful?

Christian G'Sell

Laboratoire de Physique des Matériaux, UMR CNRS 7556, Ecole des Mines de Nancy, INPL, Parc de Saurupt, 54042 Nancy, France

Abstract

This paper reviews a series of models which apply the concept of dislocation to the interpretation of yield phenomena in glassy polymers. The point is made on three different scales. At the macroscopic scale (≈ 1 mm) shear fronts are observed at the tips of deformation bands, their elastic singularity being modeled by the theory of spread dislocations. At the mesoscopic scale ($\approx 1 \mu\text{m}$) the development of localized sheared domains is readily predicted by micromechanical simulations. At the microscopic scale (≈ 1 nm), the existence of dislocations among chain distributions is more problematic, but is supported by the large Baushinger effect observed during plastic cycling. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Baushinger effect; Mesoscopic dislocations; Macroscopic dislocations; Glassy polymers

1. Introduction

Since experimental evidence of plasticity was presented in amorphous materials below glass-transition temperature in the 1960s (previously reviewed for metals [1] and for polymers [2,3]), many authors were tempted to apply to disordered materials the concept of dislocation which was so successful for crystallized metals and ceramics. Not only glassy materials yield abruptly within localized shear bands, but also their disordered microstructure exhibit remarkable regularity when analyzed at the scale of the first atomic neighbors (Voronoi polyhedron). The aim of this work is to make a point on some experimental facts and theoretical arguments concerning dislocations in glassy polymers and to figure out their usefulness in the search for predictive modeling of yield behavior and microstructural transformations.

2. Macroscopic dislocations

Among the specific features of glassy polymers, their plastic behavior during a deformation cycle under simple shear is of particular interest [4,5]. As shown in Fig. 1 in the case of polycarbonate at room temperature (that is well below glass transition temperature, $T_g = 145^\circ\text{C}$), the upper yield point is followed by an abrupt decrease of the shear stress (B to C). As stress decreases, plastic deformation concentrates in a single shear band which elongates until it reaches the extremities of the sample at point C (Fig. 1). Consequently, during this softening stage, the band is confined within the specimen, each tip of the band constituting a 'shear front'. As shown in Fig. 2, the local shear inside the band is as

large as $\gamma_b \approx 0.75$, while the applied shear is only $\gamma \approx 0.1$ [6]. Subsequently, during the long stress plateau (C to D) the band gradually widens at the expense of the undeformed material, until it covers the whole sample at point D. Taking into account the true shear behavior of polycarbonate, $\tau(\gamma_b, \dot{\gamma}_b)$, obtained from local measurements inside the band, it was shown that this plastic instability phenomenon could be reproduced quite accurately by means of the theory of spread dislocations [7] otherwise applied with much success in seismology [8].

In the test of Fig. 1, shear strain rate is reversed at point D. In the return stage (D to G), it is observed that shear returns homogeneously to zero, not by formation of negative shear bands. Although the macroscopic state at point G is identical to the initial state, it is remarkable that the cycled sample behaves quite differently to the first run if direct shear strain is applied a second time (G to I): (1) yield stress is reduced by a factor of nearly 1/2 (point H); (2) no stress drop is observed at yield; (3) deformation is still homogeneous in the whole sample without further banding. This large Baushinger effect indicates that cycling introduces some 'defects' in the microstructure. Since scanning electron microscopy of fine markers shows no microstructural inhomogeneities down to a scale of 20 nm within the shear band, such defects should be expected at an a smaller scale [9].

3. Mesoscopic dislocations

Investigation of polymer plasticity at the mesoscopic scale was recently performed by Argon et al. [10] by means of a stochastic simulation for a pseudo-3D aggregate whose

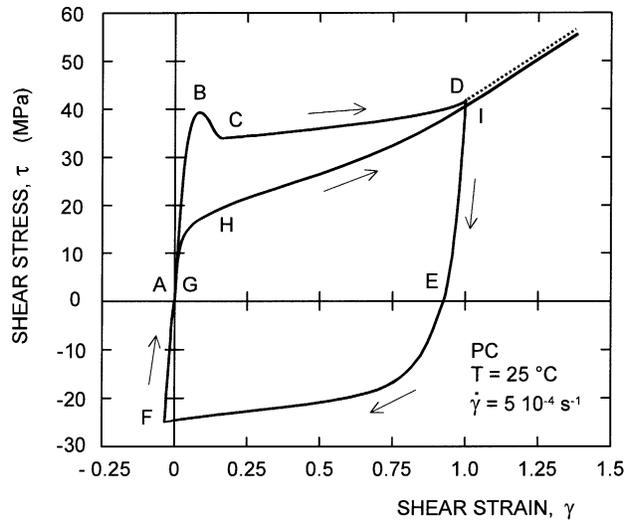


Fig. 1. Stress-strain behavior of polycarbonate under simple shear in the case of a plastic cycle (after G'Sell and Gopez [4]).

size is about 0.2 μm. This structure combines about 60,000 cells, each of them containing 500-1000 individual atoms and measuring 2-3.5 nm.

Within the cells, the simulation is based on molecular mechanics. It takes into account the rotation potential of the covalent bonds and the predominant van der Waals interactions between the molecules. It correctly reproduces the transition jumps from the trans conformations to gauche conformations predicted by previous theories [11] and FTIR experiments [12]. However, only the plastic behavior at zero

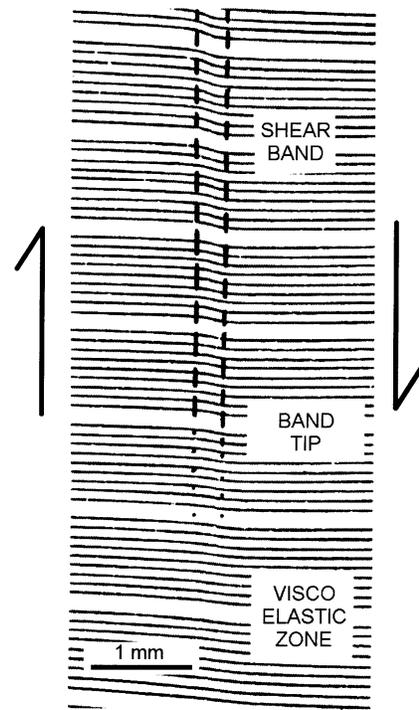


Fig. 2. Aspect of the lower tip of the shear band in polycarbonate during the strain softening stage (after Grenet and G'Sell [6]).

Kelvin is predicted, since no thermal activation is taken into account at the level of the cells. Under such conditions, it is found that the elementary molecular jumps correspond to local increments of shear not larger than about 2%. How-

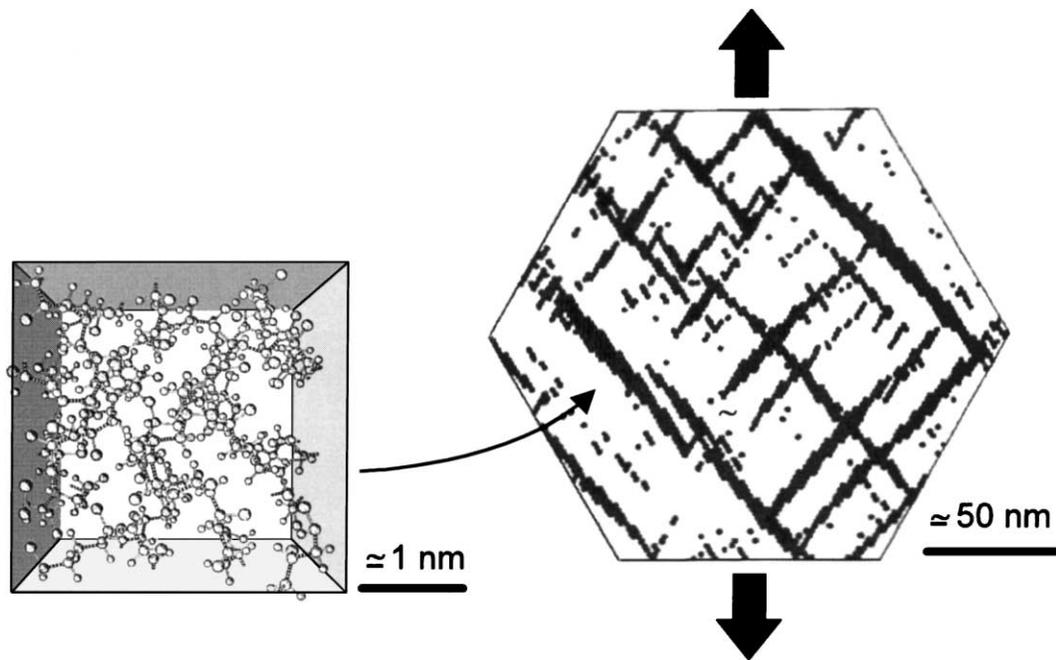


Fig. 3. Mesoscopic shear bands in the stochastic modeling of Bulatov and Argon [10]. The small drawing apart shown an constitutive microscopic cell in the case of amorphous polypropylene [11].

ever, similar modeling by Fan [13] shows that yield stress and softening amplitude differ considerably from a cell to another. The weakest cells are thus likely to behave as initial 'defects'.

At the level of the mesoscopic aggregate, Bulatov computes the internal stresses generated by the yield inhomogeneities, each cell being considered as an Eshelby inclusion among their neighbors. The viscoplastic behavior of the assembly is obtained by a thermally activated Eyring analysis.

For a polymeric glass well below T_g , the model of Bulatov generates shear bands, about 5–10 nm in width, which multiply and grow at about 45° with the tensile axis (Fig. 3). Therefore, the band tips can be considered as mesoscopic dislocations. However, the model seems unable to reproduce the Baushinger effect observed experimentally when cycling under shear. This is probably due to the absence of thermal activation at the microscopic scale in the individual cells.

4. Microscopic dislocations

After the pioneer works of Li and Gilman [14] and Argon [15] who analyzed the interaction of chain kinks with the surrounding elastic medium, several authors have modeled the cooperative distortion of macromolecules in a microscopic shear domain. Their approach was inspired from the work of Gilman [16] who imagined that mobile dislocations (screw or edge) could be nucleated in glasses as well as in crystalline metals and ceramics, with a Burgers vector equal to the short range interaction distance of the microstructure.

From this idea, Bowden and Raha [17] developed a yield model in which the nucleation of a dislocation loop is the critical step in the formation of a microscopic shear band. Polymer segments are brought to high-energy conformations as they are swept by the dislocation line, in such a

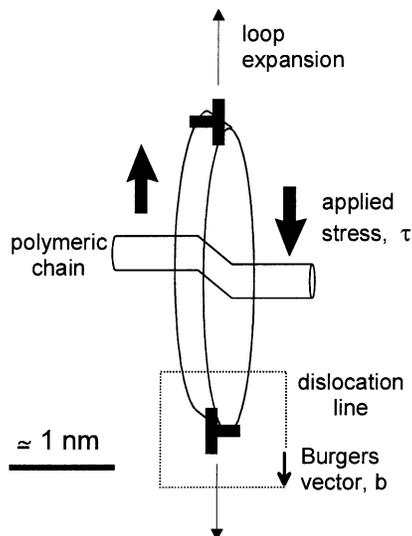


Fig. 4. Dislocation loop after Bowden and Raha [17].

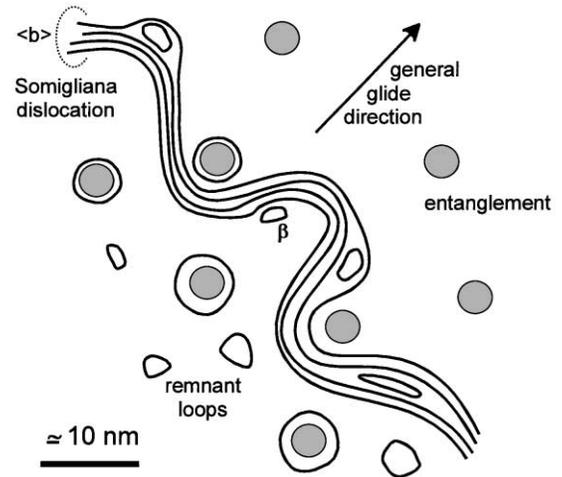


Fig. 5. Somigliana dislocation after Escaig [20].

way that the shear strain jumps from nearly zero up to about unity from outside to inside the loop (Fig. 4). Burgers vectors ranging from 0.27 to 0.49 are thus obtained for various polymers such as PMMA, PVC, PS, PC and PET. Although the oversimplifying assumptions of the model lead to some discrepancies with experimental yield stress at low temperature, it should be considered as an important step toward the correct description of yield.

More elaborated dislocation models were published by Li [18,19] and Escaig and coworker [20–22] from the topological scheme of Somigliana [23]. While overall compatibility requires that deformation should proceed by a uniform shear displacement $\langle b \rangle$ along the strain direction, the fluctuations oblige the Burgers vector, \mathbf{b} , to vary along the line and generates topological resistance to the dislocation propagation (Fig. 5). A Somigliana dislocation can be represented as a distribution of Volterra dislocations of resulting misfit $\langle b \rangle$, plus a collection of localized dislocation loops of individual burgers vector β . Consequently, its propagation is controlled by the formation of new loops ahead of the shear front and the trailing of remnant loops behind the front. Because of that, after Escaig, dislocation propagation is more difficult than in simple van der Waals monoatomic structures, particularly at chain entanglements where topological constraints impose large deviations to \mathbf{b} . Highly energetic loops must

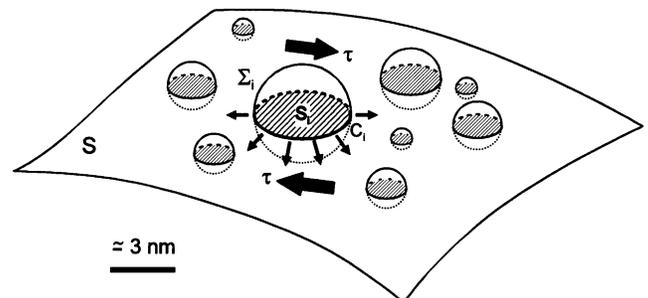


Fig. 6. Dislocation loops after Perez [24].

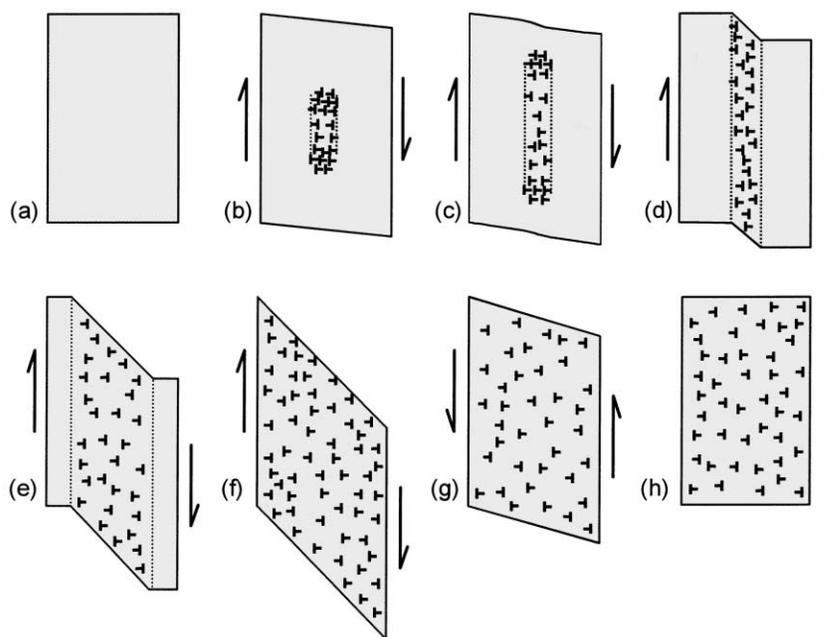


Fig. 7. Microscopic interpretation of the cyclic shear test of Fig. 1, after G'Sell and coworker [9,27].

be formed around the entanglement, whose radius is of the order of the length of the statistical chain element. Another source of glide hindrance is imposed by the component of \mathbf{b} normal to the glide plane, which is mainly responsible for the pressure effects in the plasticity of glassy polymers [22].

Furthermore, Perez and coworkers [24,25] has related the mechanisms of plastic deformation to molecular dynamics. He ascribes the mobility of chains in the glassy state to the β -transition movements, with an increasing cooperativity at large stress and/or large temperature. At yield, collective chain motion occurs in shear microdomains surrounded by Somigliana dislocations which multiply and coalesce as plastic strain increases (Fig. 6). In this model, temperature, strain rate and hydrostatic pressure play important roles on the deformation kinetics, since they affect the degree of cooperativity on the β processes and the relaxation of the defects [26].

In previous papers [9,27], we have also applied the concept of microscopic dislocations for interpreting the different features of transient yield effects. The classical Orowan equation, $\dot{\gamma}_{pl} = N(\tau, \gamma_b)\mathbf{b}v(\tau)$, is thus valid for expressing the influence of dislocation density, N , and velocity v , on plastic strain rate, $\dot{\gamma}_{pl}$. Following Johnston [28] we interpret strain softening after the yield point as a period of intense dislocation multiplication as dislocation loops get more numerous and/or enlarge. In polycarbonate under shear (Fig. 7a and b), this process is concentrated in a single shear band initiated from any geometrical or microstructural defect. By the virtue of its own internal stress field, the band propagates quickly up the ends of the specimen (Fig. 7c and d), before widening and eventually occupying the whole volume of the sample, at $\gamma \approx 1$ (Fig. 7e and f). When plastic

cycling is imposed by reverting the strain rate, dislocation density is high enough to ensure homogeneous deformation (Fig. 7g). At the end of the cycle, the specimen retrieves its original shape, but keeps a memory of its history through a much larger dislocation density (Fig. 7h) which readily provokes the large Baushinger effect observed experimentally. Furthermore, we have shown [5] that this phenomenon is completely recoverable by dislocation relaxation and/or annihilation as the specimen is heated near T_g for a sufficient time. Unlike in metallic crystals, the shrinkage of dislocation loops on unloading is much more efficient in glassy polymers, because of the extensive chain orientation induced by plastic shear [29], the excess free energy of extended chains being added to the own line energy.

5. Conclusions

Modeling the original features of polymer plasticity has stimulated a very animated debate in the international polymer community for more than 30 years. Taking benefit of more accurate mechanical testing systems, microstructure investigation instruments and fast modeling tools, authors have particularly argued on whether or not dislocations could exist in macromolecular glasses. It is now clear that the problem must be addressed specifically at the different scales of the microstructure, typically: macroscopic, mesoscopic and microscopic. At each scale, results reveal evidence of plastic instability and plastic shear fronts, although rigorous dislocation topology is formally difficult to describe due to the absence of long range order in the undeformed material.

Whatever the answer to this open problem, it is important to recall here the assertion formulated by Gilman [16]

as early as 1968: “the concept of dislocations in glassy materials is not just a forced analogy but is desirable because it allows the flow properties of these structures to be discussed in a more organized way than otherwise possible. That is, it provides a simple means for describing the correlations that must exist between adjacent elementary shear processes”. Following this author, we consider that the development of dislocation models in glassy polymers has been very fruitful to many respects, even though some ones are still doubtful on the actual existence of these defects at the microscopic scale.

References

- [1] F. Spaepen, *Acta Metall.* 25 (1977) 407.
- [2] B. Crist, in: R.N. Haward, R.J. Young (Eds.), *The Physics of Glassy Polymers*, 2nd Edition, Chapman & Hall, London, 1997, Chapter 4, pp. 155–212.
- [3] Z.H. Stachurski, *Progr. Polym. Sci.* 22 (1997) 407–474.
- [4] C. G'Sell, A.J. Gopez, *J. Mater. Sci.* 20 (1985) 3462.
- [5] C. G'Sell, H. El Bari, J. Perez, J.Y. Cavallé, G.P. Johari, *Mater. Sci. Eng. A* 110 (1989) 223.
- [6] J. Grenet, C. G'Sell, *Polymer* 31 (1990) 2057.
- [7] J. Weertman, *Bull. Seismol. Soc. Am.* 54 (1964) 1035.
- [8] J.C. Savage, in: F.R.N. Nabarro (Ed.), *Dislocations in Solids*, Vol. 3, North-Holland, Amsterdam, 1980, pp. 251–339.
- [9] C. G'Sell, in: H.J. McQueen, J.P. Bailon, J.I. Dickson, J.J. Jonas, M.G. Akben (Eds.), *Strength of Metals and Alloys*, Pergamon, Oxford, 1986, pp. 1943–1982.
- [10] A.S. Argon, V.V. Bulatov, P.H. Mott, U.W. Suter, *J. Rheol.* 39 (1995) 377.
- [11] P.H. Mott, A.S. Argon, U.W. Suter, *Philos. Mag.* 67 (1993) 931.
- [12] M. Theodorou, B. Jasse, L. Monnerie, *J. Polym. Sci. Pol. Phys. Ed.* 23 (1985) 445.
- [13] C.F. Fan, *Macromolecules* 28 (1995) 5215.
- [14] J.C.M. Li, J.J. Gilman, *J. Appl. Phys.* 41 (1970) 4248.
- [15] A.S. Argon, *Philos. Mag.* 28 (1973) 839.
- [16] J.J. Gilman, in: A.R. Rosenfield, G.T. Hahn, A.L. Bement Jr., R.I. Jaffee (Eds.), *Dislocation Dynamics*, McGraw Hill, New York, 1968, pp. 3–25.
- [17] P.B. Bowden, S. Raha, *Philos. Mag.* 29 (1974) 149.
- [18] J.C.M. Li, in: *Metallic Glasses*, ASM, Metals Park, Ohio, 1978, p. 224.
- [19] J.C.M. Li, *Met. Trans.* 9A (1978) 1353.
- [20] B. Escaig, in: B. Escaig, R. Groh, L.P. Kubin, J.L. Martin (Eds.), *Dislocations et déformation plastique*, Editions de Physique, les Ulis, 1979, 261 pp.
- [21] J.M. Lefebvre, B. Escaig, *Polymer* 34 (1993) 518.
- [22] B. Escaig, *Pol. Eng. Sci.* 37 (1997) 1641.
- [23] C. Somigliana, R. C. Accad. Lincei 23 (1914) 463.
- [24] J. Perez, in: B. Escaig, C. G'Sell (Eds.), *Plastic Deformation in Amorphous and Semi-Crystalline Materials*, Editions de Physique, les Ulis, 1982, pp. 265–285.
- [25] M.B.M. Mangion, J.Y. Cavallé, J. Perez, *Philos. Mag.* 66 (1992) 773.
- [26] R. Quinson, J. Pérez, M. Rink, A. Pavan, *J. Mater. Sci.* 32 (1997) 1371.
- [27] C. G'Sell, J.J. Jonas, *J. Mater. Sci.* 16 (1981) 1956.
- [28] W.G. Johnston, *J. Appl. Phys.* 33 (1962) 2716.
- [29] C. G'Sell, A. Souahi, *J. Eng. Mater. Technol.* 119 (1997) 223.