The stress–strain relationship in polymer glasses

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The concept of the entanglement of polymers in condensed situation being represented by slip links is here extended to polymer glasses. It is argued that the whole polymer chain is divided into smaller parts which are effectively tethered but have considerable internal freedom. This leads to bounds to the strain which the glass can sustain before it crazes and then fractures. It also offers a ready explanation of the return to the undeformed state upon heating above the glass temperature.

(Keywords: polymer glasses; crazing; entanglements; slip links; glass transition)

INTRODUCTION

The authors are honoured to be invited to contribute to this volume dedicated to the late Leslie Treloar. The senior author learned much from Professor Treloar during his time in Manchester and will always remember the dedicated energy with which Treloar attacked the experimental problems of rubber elasticity[1].

The present paper discusses how ideas current in rubber elasticity can be extended to glass problems, and finds a new way to look at, and employ, the fact that, although a random flight chain must have an end-to-end separation R where

$$\langle \boldsymbol{R}^2 \rangle = Nl^2$$

where thare are N links each of length l, and the maximum extension must be $\boldsymbol{R}^2 = N^2 l^2$, i.e.

$$\frac{\boldsymbol{R}^2_{\max}}{\boldsymbol{R}^2_{\text{random}}} = N$$

Now N is a very large number, and this observation is unlikely to be of direct experimental consequence except perhaps in elongational flow. Nevertheless we believe it can play a key part in understanding glass behaviour.

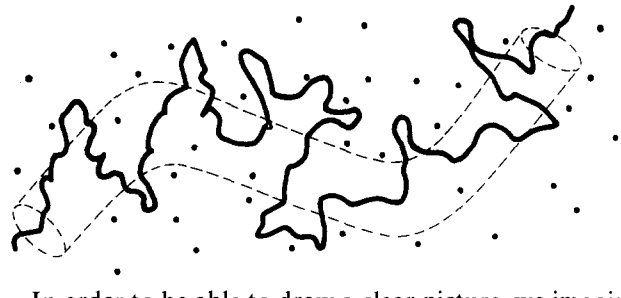
The paper will discuss a view of the entanglement of chains in rubbers, or any condensed phase of polymers, and then discuss how these ideas can be extended to glasses, providing a qualitative explanation of the stress–strain relationship for glasses and of the recovery mechanism.

The authors have been able to draw on the extensive literature concerning glassy polymers which is summarized in the distinguished book by Professor Haward[2].

THE ENTANGLEMENTS OF POLYMERS

The basic idea is contained in *Figure 1*.

Figure 1



In order to be able to draw a clear picture, we imagine all the chains but one being intersected by the plane of the picture and are represented by dots. One polymer happens (without loss of generality) to be in the plane end is shown in *Figure 1*. Consider the ends of the polymer fixed and enquire after its freedom. One can consider a topological skeleton of the polymer which we call the primitive path[3,4] which loosely speaking will be the locus taken up by polymer if it is drawn in at its ends until it is taut. There are various ways of imagining the role of this primitive path. It can be considered the axis of a diffuse tube[5] representing a confining potential, approximately harmonic, for the polymer.

Another way is to consider that there are slip links[6] at the ends of the steps of the primitive path, so that *Figure 1* becomes replaced by *Figure 2*. These slip links are

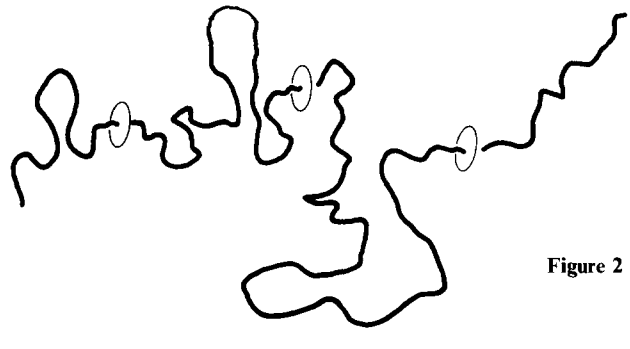


Figure 2

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embedded in and represent the large number of other chains and are regarded as effectively fixed in the medium. Between the slip links the polymer has much freedom but any excursion into the material must return on the same path (see *Figure 3*).

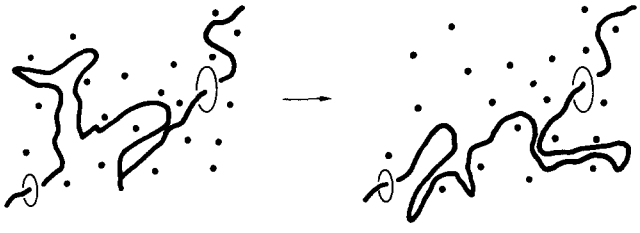


Figure 3

This picture can be quantified and the entropy of a polymer with fixed ends confined by a network has been established[7,8] following earlier approximate discussions[9–11]. A review of the problems of the quantitative prediction of primitive path concepts in rubber elasticity is given in ref. 12.

Now consider the consequences of this picture for rubber elasticity where the end points of the above pictures are the permanent crosslinks, but between them are a series of slip links so that the locus joining the slip links is itself a random flight but now with a step length a. If between the crosslinks there are N Kuhn lengths, and N_{pp} steps of the primitive path, i.e. N_{pp} (or more precisely $N_{pp}-1$) slip links

$$\langle \boldsymbol{R}^2 \rangle = Nl^2 = N_{pp}a^2$$

so that if the contour lengths are

$$L = Nl \quad , \qquad L_{pp} = N_{pp}a$$

$$L_{pp} = L\left(\frac{l}{a}\right)$$

The quantity a is a function of the density of 'contour length' of the material, and can be varied by swelling the rubber when it depends on the concentration by a power slightly greater than unity. Some remarkable correlations can then be made between the plateau modulus of different polymers[13,14].

The detailed modulus of the rubber is affected in two ways. If we argue that the polymer can slip through the slip link by a certain amount related to a, then under deformation this sliding distance will *increase* with the result that the rubber gets softer[15,16]. If one now further strains the material, there comes a point where the chains between the slip links are fully extended.

Between two slip links there are N/N_{pp} Kuhn lengths, so that when the spatial separation $\boldsymbol{r}$ is increased to $(\lambda_1 x, \lambda_2 y, \lambda_3 z)$ with

$$\langle \lambda_1^2 x^2 + \lambda_2^2 y^2 + \lambda_3^2 z^2 \rangle = \frac{N}{N_{pp}} l^2 \underline{\lambda}^2$$

$$\underline{\lambda}^2 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$$

full extension is reached at

$$\left(\frac{N}{N_{pp}}\right)^2 l^2 = \left(\frac{N}{N_{pp}}\right) l^2 \underline{\lambda}^2$$

i.e.

$$\lambda^2 = N/N_{pp}$$

Typical values for

$$\left(\frac{N}{N_{pp}}\right)^{1/2}$$

are around five, so the picture is consistent with the experimental increase in modulus at extensions of this order. Notice that $\lambda^2 = N$ would be an enormous extension, and it has long been appreciated that if the effect is present, it must be confined to segments, and is often quoted for crosslinks which happen to be close along the chain. Here however we are suggesting that the omnipresence of topological constraints make the effect universal. Of course other things happen at large extensions in particular crystallinity, but the increase in modulus is found in polymers not given to crystallizing easily.

The final approximation offered by Edwards and Vilgis[16] for these two effects is a free energy of

$$F = F_c + F_s$$

$$F_c = \tfrac{1}{2} N_c \left\{ \frac{\sum \lambda_i^2 (1-\alpha^2)}{1 - \frac{\alpha^2}{3}\sum \lambda_i^2} - \log\left(1 - \frac{\alpha^2}{3}\sum \lambda_i^2\right) \right\}$$

$$F_s = \tfrac{1}{2} N_s \left\{ \sum \frac{\lambda_i^2 (1-\alpha)(1+\eta)}{(1+\eta\lambda_i^2)\left(1 - \frac{\alpha^2}{3}\sum \lambda_i^2\right)} - \log(1+\eta\lambda_i^2) - \log\left(1 - \frac{\alpha}{3}\sum \lambda_i^2\right) \right\}$$

$$N_s = (Vc/al^2)(c_x + 2c)^{-1} c_x$$

Although an approximation is the problem this does have reasonable agreement with experiment.

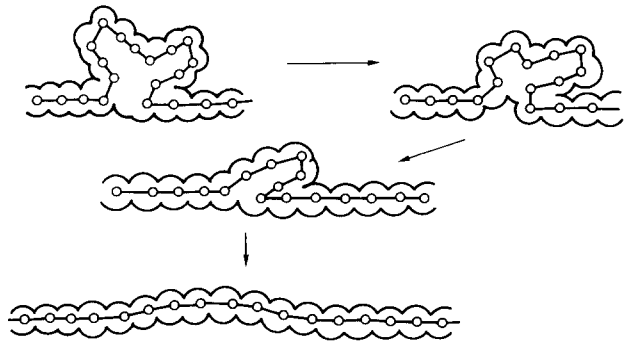
We now turn to see if these ideas can help in understanding glass behaviour.

STRESS–STRAIN RELATIONSHIP FOR GLASS

As the polymer melt is cooled (or otherwise has its density increased) it passes through the glass transition. Glass formation is easy for polymerized materials because the basic diffusion process is reptation which involves the slow Brownian motion of the chain down the tube, i.e. along the primitive path (with new tube being created by an emerging end, or the old tube being destroyed by a retracting end). Reptation is a tiny part of the many different degrees of freedom of the polymer, but it is the motion which allows creep. At the glass transition creep ceases, reptation ceases, but the other degrees of freedom keep going albeit more slowly as the temperature diminishes and/or the density increases. An easy way to visualize this is to imagine that the slip link points tighten to the extent that slipping is no longer possible. This could be due to an increasing constriction, or it could be due to slow local crystallinity developing in the chain, making it impossible for the chain to slip through the slip link. Or it could be due to the creation of quite new constrictions along the length of the chain. For whatever

reason our picture now is of a polymer 'pinched' at a series of points along its length. Some of these pinches will be weak, and as the material is stressed will open, permitting an easier stress–strain relationship than that at zero stress strain. This is familar with all frictional systems, the initial modulus is higher than that at finite strain. But other pinches are very strong and will hold. This now means that the primitive path segments will extend under stress, but will do so irreversibly as the polymer is being drawn over potential barriers by the stress. A picture to illustrate this is given in *Figure 4*,

Figure 4



where the slack in the primitive path in the first picture is pulled out to reach the last picture. A rough contour of the potential energy is sketched around the polymer and this field is climbed to move from one picture to the next.

When one reaches the fully extended condition the strain is

$$\lambda = \left(\frac{N}{N_{pp}}\right)^{1/2} = \frac{a}{l}$$

where now a can be shorter than in the melt because of the effects (extra pinches, chain thickened by crystalline region etc.) of the colder denser environment.

When one passes this strain the material will craze. This crazing itself can be studied by the above concepts since it can be regarded as the consequence of the checking of cracks by the full extension of chains which have not up to that point been fully extended[17]. Thereafter the material has no further capability of strain and suffers brittle fracture.

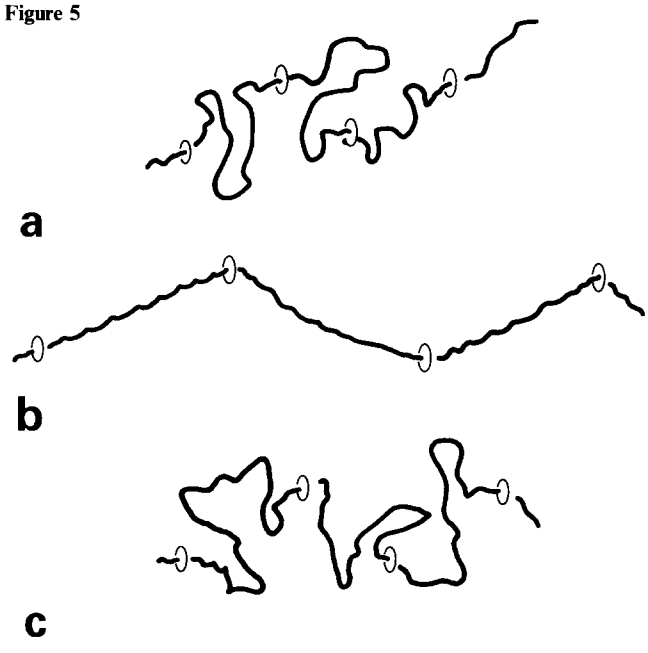
THE RECOVERY PROCESS

Suppose we study a glass which is strained but not fractured, and heat the glass back through the glass transition to the melt.

We have argued that the 'slip links', or the 'tube' are consequences of the topology of the entanglements. The slack of the chain which is taken up on straining, and the development of pinches and of crystallinity, do not violate this topology. It follows that on returning to the melt the topological specification of the material is unaltered except in as much as some withdrawal may have taken place at the ends of the chains.

In *Figure 5* from the initial (a) to the fully extended (b) the chain has slipped out of the last link so that on heating its return to (c) will not be to the identical shape (a) but one which retains a memory of the shape (b).

Figure 5



These remarks include the effects of patches of crystallinity for crystallinity retains the topological specification of the chain except near the end points. We therefore find a simple explanation of the well known recovery process.

CONCLUSIONS

The difficulty with the above picture is in making it quantitative. For melts Doi and Edwards[4] argued that an effective friction coefficient, and the step length, gave a total specification of the viscoelasticity of the melt or to be more precise it is possible to produce a theory of viscoelasticity with only these two parameters, and one naturally explores that theory before embarking on adding new parameters to overcome failings of the simplest theory.

When we come to study the glassy state, the stress–strain relationship is already non-linear in its initial phase, and the only easy prediction is that if there are no extra pinches or crystalline accretions, the full extension of the glass up to fracture will be the same as that of the rubbers. This must however be an overestimate and more parameters appear describing all the various concepts described in this paper. The authors hope to offer a quantitative analysis in due course, but it is clear that it will never be as simple as the melt.

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