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Review
The application of the reptation hypothesis to polyelectrolyte biomaterials

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Recent studies have attempted to explain the processes which occur at fracture in glass-ionomer and zinc polycarboxylate cements in terms of the reptation hypothesis. This approach is reviewed, along with the theory itself. The current status of the theory is considered and the considerable doubt which exists about the validity of theory is highlighted. The failure of the theory to predict the relationship between fracture toughness and molecular mass found experimentally for glass-ionomers and zinc polycarboxylates is noted. These results, together with others from the wider realm of polymer physics, lead to the conclusion that the attempt to understand the fracture of polyelectrolyte biomaterials in such detailed theoretical terms is probably premature.

1. Introduction

The so-called reptation hypothesis has recently been applied to polyelectrolyte biomaterials as a means of understanding the processes occurring at the crack tip during fracture [1, 2]. It has also been used to explain aspects of the mechanical properties of polyelectrolyte dental cements as adhesives [3]. The theory has been claimed to be of use in understanding some of the mechanical properties of polyelectrolyte cements, in particular the molecular mass dependency of properties such as fracture toughness [1].

Despite this apparent usefulness, there are difficulties with the hypothesis. For example, the author of a recent book on polymer solutions states that the preference for the reptation model " . . . is too strong for the amount and range of reported experimental evidence" [4]. It is the purpose of this paper to examine the reptation hypothesis in some detail and explore the reasoning behind this remark.

2. The theory

The reptation hypothesis was developed by de Gennes in 1971 [5] and has since been expanded by Doi and Edwards [6]. It states that when the concentration of a polymer solution is high enough to produce dense chain entanglements, each chain is forced to wriggle in an anisotropic curvilinear mode. de Gennes called this motion "reptation" (from the Latin for creeping, which is also the root of the word "reptile") and since then it has been used to describe a number of aspects of bulk behaviour that involve motion of the molecules. These include self-diffusion in solution or the melt as well as viscoelastic flow at fracture.

The essence of the reptation hypothesis is that, under specified conditions, the movement of an individual polymer molecule can be modelled as that of a snake moving through a narrow tube. The tube arises due to the presence of all of the other polymer molecules. Though they are not entangled in the sense of being knotted, they are sufficiently closely entwined so as to maintain the tube in place over timescales that are long compared with the time it takes for the reptating molecule to pass through.

This model makes two major assumptions.

(i) That there is no lateral "wriggling" by the polymer molecule; in other words, the molecule is assumed to fit snugly inside the tube.

(ii) That there is no dynamic coupling of chains. In reality one would anticipate that forced motion of one polymer molecule, as occurs in plastic flow at the crack tip during fracture, would cause other molecules to be dragged along as well. Such co-operative motion is, however, ignored.

The mathematics of the reptation hypothesis is complicated but can be simplified to two straightforward predictions. They are:

$$D_S \propto 1/M^2$$

where D_S is the self-diffusion coefficient and M is the molecular mass, and

$$G_1 \propto M^2$$

where G_1 is the fracture toughness and, again, M is the molecular mass.

In both cases, the force to pull the chain through the putative tube is assumed to be frictional [4]. For fracture, the assumption is that the polymer chains are stretched, then pulled out of their tubes in the fracture plane. The idea has been applied to poly(methyl methacrylate) and poly(carbonate), where values for the molecular mass exponent of 2.5 have been held to support the theory [7]. The deviation from the value of 2 predicted by reptation theory was assumed to arise because of the polydispersity of the polymer samples.

In applying reptation theory to fracture, a limit is set to the range of molecular masses over which the inverse square relationship applies. It is argued that at high values of molecular mass, there comes a point at which the energy needed to pull the polymer molecule out of the tube is greater than the energy needed to fracture covalent C–C bonds along the polymer backbone. When that point is reached, G_1 no longer depends on M.

3. Application to polyelectrolyte cements

Reptation theory has been applied to the fracture of both glass-ionomers [1] and zinc polycarboxylates [2]. This approach has been justified on the grounds that cracks propagate through the polymeric matrix of these materials [1]. However, in the case of glass-ionomers, the fracture toughness was found to depend on (molecular mass)$^{1/2}$, i.e. the exponent was very different from the value expected from reptation theory. For zinc polycarboxylates, the exponent was found to be 1, again not the value required by the reptation hypothesis.

As noted earlier, reptation theory also predicts the existence of an upper critical molecular mass, above which there is no dependency of fracture toughness on molecular mass. For glass-ionomers, this critical molecular mass was found to be 1.08×10^6 [1]. However, for zinc polycarboxylates, using the same molecular mass range of poly(acrylic acid), no critical molecular mass was found. The relationship between fracture toughness and molecular mass was found to apply over the entire range that was studied [2]. These differences between the behaviour of glass-ionomers and zinc polycarboxylates have been useful in highlighting the structural differences between these materials [8], regardless of the appropriateness of the reptation model in describing this behaviour.

The theory of reptation makes a further prediction about the relationship between fracture toughness and molecular mass. Below the chain entanglement molecular mass, polymeric materials are predicted to have no detectable toughness [1]. However, the lowest molecular mass used in the study was 1.15×10^4, which is assumed to be close to the entanglement value of PAA, yet the cements made from this polymer were found to exhibit significant toughness [1].

Despite these problems, some success has been claimed for this approach [1, 2] with deviations being attributed to ionic interactions between the polymer molecules. Ionic interactions do, of course, occur in these systems, but the evidence is that when they do, they cause such substantial deviations from theory that it is doubtful if the polymer molecules can really be considered to be moving reptatively at all.

4. Problems with the reptation theory

Reptation theory has not merely run into trouble in its application to polyelectrolyte cements, there is also some doubt about its validity for any polymeric materials [4]. For example, in principle it does not apply to polydisperse systems [1], which means that it does not actually apply to any *real* material. However, as with several such mathematical models, this in itself may not necessarily require the model to be abandoned.

Other, more serious, difficulties become apparent when the model has been examined more closely. For instance, one essential assumption of the reptation model, stated explicitly by Doi and Edwards [6], is that the polymer molecule under consideration reptates in a tube fixed in space. The difficulty with this is that in concentrated solutions, melts, or even in solids undergoing fracture, all of the molecules are wriggling simultaneously. Hence the tube around each molecule is never really fixed, but instead is successively renewed by different molecules. This means the theory is not self-consistent.

If the notional tube around the particular polymer molecule is not fixed, there is the possibility that the size of the tube will fluctuate. This gives the principal polymer molecule the scope to wriggle in modes other than reptation. As Fujita remarks [4] " . . . we have no *a priori* reason to deny the possibility of such non-reptative chain motions."

Recently, too, experimental evidence has emerged that challenges the concept of reptation as applied to concentrated polymer solutions [9]. It is not straightforward to study the motion of polymer molecules in concentrated systems and complete theoretical calculation is hopelessly difficult. Hence there has been growing interest in computer simulation experiments as a means of studying the subject [4].

In such a typical study, Kolinski *et al.* [10] modelled polymer motions by considering a collection of random flight chains confined to a tetrahedral lattice. This enabled all possible conformational transitions in a polymer to be studied as elementary motions. The only constraints on the dynamics of this polymer chain came from the lattice and the excluded-volume of the polymer. Two important findings emerged from this study.

(i) That each molecule undergoes isotropic wriggling, i.e. moves non-reptatively.

(ii) The relationship between self-diffusion coefficient and molecular mass varied according to

$$D_s \propto 1/M^a$$

where a varies from 1.15 to 2.06 as the volume fraction of the polymer increased.

Taken together these findings lead to the conclusion that systems behaving non-reptatively can give the inverse square relationship with molecular mass under appropriate conditions. Hence the existence of such a relationship cannot be taken to *prove* that the polymer molecules are behaving reptatively.

Experimental studies on real polymer systems have been carried out that have cast doubt on the validity of the reptation hypothesis. In practice, it is difficult to make the necessary measurements directly, but an acceptable approach has been developed, using labelled polymers as tracers and forced Rayleigh scattering to study their diffusion coefficient, D_{tr}.

A typical study involving this approach was carried out by Wheeler *et al.* [11]. They studied poly(styrene) in dilute and semi-dilute solutions of poly(vinyl methyl ether) and found that the following relationship applied:

$$D_{tr} \propto 1/M^a$$

where a went from 0.55 to 1.9 as the concentration rose. By contrast, Kim *et al.* [12] found for poly(styrene) in toluene that the exponent a varied from 2 to 3 as the system became more dilute. Nemoto *et al.* [13] carried out a similar study using poly(styrene), this time with dibutyl phthalate as the solvent, and they found a value for a of 2.5 ± 0.1 for all values in the concentration range examined. In reviewing these results, Fujita [4] claims that none of these results can be accounted for by the reptation hypothesis, either in its original form as devised by de Gennes, or in modified form, involving tube renewal.

In the early work on the application of reptation theory to fracture, the experimental value of 2.5 for molecular mass exponent in the relationship to fracture toughness was taken to be a fair approximation of that required to confirm reptation [7]. The view of the authors of these more recent studies is that values of about 2.5 are not a good estimate of the value of 2 required by the reptation hypothesis. Thus there is considerable doubt that, even in the allegedly favourable case of poly(methyl methacrylate), the hypothesis reptation *really* describes the situation at fracture.

5. Conclusions

This review of the reptation hypothesis of de Gennes and its relationship to polyelectrolyte biomaterials leads to four main conclusions.

(i) That the model itself, though based on detailed mathematics, is actually a very crude representation of reality.

(ii) There are several other mathematical models which predict the result that the self-diffusion coefficient, D_s, is inversely proportional to the square of the molecular mass. Presumably, such theories would also predict the direct relationship between fracture toughness and the square of the molecular mass. Hence, such results cannot be taken as proof of the validity of the reptation model.

(iii) A few recent experimental results for studies of self-diffusion of polymers in solution give results that cannot be explained by the reptation hypothesis. To date, the number of such results is small, but the fact that experimental evidence is beginning to cast doubt on the theory ought to serve as a warning against adopting it uncritically.

(iv) Regardless of the applicability of the reptation theory to relatively simple polymers, it is clear that the theory does not describe the fracture behaviour of polyelectrolyte biomaterials particularly well. Deviations from the relationship predicted by the theory are considerable. Accordingly, studies of the relationship between fracture toughness and molecular mass for glass-ionomers and zinc polycarboxylates cannot be held to have proved that the polymer molecules move reptatively at the crack tip during fracture. In fact, the experimental evidence appears to point in the opposite direction: whatever motion the molecules may undergo at the crack tip during fracture it seems certain that it is not reptative.

Given the complexity of the structure of glass-ionomer and zinc polycarboxylate cements, the fact that a conceptually simple model does not apply to them should not be surprising. Moreover, in view of the debate still in progress concerning the validity of the reptation theory in polymer physics, attempting to use this theory to explain the behaviour of these materials is probably premature.

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