Communications to the Editor

Entanglements at Polymer Surfaces and Interfaces

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Entanglements restrict the mobility of the polymer molecules in the bulk and in concentrated solutions and are at the basis of many of the unique and unusual dynamic properties of polymers. Qualitatively, one can envision an entanglement as a crossing of polymer chains which, when subjected to a strain, remains intact and hence mechanically active. The molecular weight of the polymer between the cross-link points, M_e, is normally obtained from the real part of the dynamic modulus, i.e., the storage modulus. It is, in fact, M_e which underlies many of the theoretical treatments of the diffusion and viscoelasticity of molten polymers. For example, the reptation model,[1,2] which has met with great success in describing the diffusion of polymer chains in the melt, describes the snakelike motion of polymer chains along their own contour and uses M_e to define the tube within which the polymer chain can diffuse. For polymers with molecular weights below M_e, the motion of the chain is unrestrained and the chain diffuses in a Rouse-like manner. In addition, the high strain and failure properties of solid polymers, as for example the natural draw ratio[3] and crazing,[4] are profoundly influenced by M_e. Failure properties, such as toughness, depend critically upon the ratio of the molecular weight of the polymer to its M_e.[5] Many more examples of the unique properties of polymers can be traced to M_e.

While it is simple to draw a schematic picture of entangled polymer chains, it is far more complex to define quantitatively an entanglement. A number of recent authors[6−9] have suggested that, in the bulk, entanglements, and hence M_e, are controlled mainly by the packing of the polymer chains. They proposed that the volume of space pervaded by a single chain of molecular weight M_e is a fixed constant of the order of 10 times the hard core volume occupied by the chain. The actual values of the constant depends upon the definition of the pervaded volume. Their arguments, which are supported by experimental evidence,[10] are based on the idea that packing defines the constraints placed on the motion of a single chain by the surrounding chains.

A tremendous amount of attention has focused recently on the surface and interfacial behavior of polymers. Consider, now, the situation at the surface of a polymer or at the interface between two immiscible polymers or between a polymer and another solid. It is, of course, the M_e of a polymer chain at the surface or interface and not in the bulk which controls the interfacial characteristics of the polymer. Three examples where M_e at the interface can influence the response of a polymer are as follows: (i) the initial stages of interdiffusion between two polymers which control the rate at which the mechanical strength of the interface develops with time; (ii) the mechanical coupling of chains at an interface between two immiscible polymers where copolymers are used to strengthen the interface; and (iii) the extent to which polymer chains at a surface can be aligned mechanically.

It is our intent to suggest that the entanglement concept of the bulk can be extended to the near-surface or interfacial regions of polymers. However, since polymer chains pack differently in the vicinity of a surface or interface than in the bulk, their degree of entanglement must also be different. Recently, a number of simulations on chains close to an impenetrable interface have appeared.[11−15] The results of these simulations can be well described by a model proposed previously by Silberberg.[16,17] The local configurations of only those polymer chain segments close to the interface are altered from the bulk configuration by contact with the interface. The interface effectively acts as a reflecting plane where the chain trajectory that would have occurred across the plane is reflected back into the polymer. This process does not perturb the projection of the radius of gyration parallel to the plane but causes a decrease in the radius of gyration normal to the plane. This reflection causes a depletion in the number of chains that have their center of mass closer than one radius of gyration from the interface. The decrease in the z-component of the radius of gyration normal to the interface, coupled with a slight, if any, increase in the component of the radius of gyration in the plane parallel to the interface, means that the volume pervaded by a given chain length is smaller close to the wall than in the bulk. Hence, the entanglement density near the interface must be less than that in the bulk.

It is worth noting that the published simulations do not all agree on the conformations of surface chains; for example, Wang and Binder,[13] Kumar et al.,[13] and Pakula[18] suggest there is no change in the radius of gyration close to the interface. If this is the case, then the entanglement density would not change. However, the volume pervaded by a polymer chain is not spherical but, rather, ellipsoidal and is, therefore, an anisotropic object. In the bulk, the ellipsoids can sample all different orientations and, on average, the chain sweeps out a spherical volume. Thus, in the bulk, one can calculate the radius of gyration from the axes of the ellipsoid. Near an interface, on the other hand, the rotation of the ellipsoid is restricted, which, in turn, limits the volume available to the chain. In the extreme case, for a polymer chain with its center of mass located a distance corresponding to the minor axis of the ellipsoid away from the interface, the effective volume available to the chain is markedly reduced and, hence, the effective radius of gyration of the chain is reduced. Thus, even in the extreme case where there is no deformation of the chain dimensions near the interface, there is a restriction in the volume available to the chain.

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For simplicity, consider a polymer with molecular weight M where $M \gg M_e$. In such a situation, chain ends can be ignored since their concentration is small. The volume pervaded by a single chain is given by[10]

$$V_0 = A\langle R_g{}^2\rangle^{3/2}$$

$$V_0 = A'\left(\frac{M}{m}\right)^{3/2} a^3 \tag{1}$$

where A and A' are constants, a is the size of a segment with molecular weight m, and $\langle R_g{}^2\rangle^{1/2}$ is the root mean square radius of gyration of the chain. V_p, the total volume occupied by a chain, is given by

$$V_P = \left(\frac{M}{m}\right) a^3 \tag{2}$$

Now, the entanglement molecular weight, M_e, is defined as the molecular weight where V_0/V_P is a constant, B. Therefore

$$M_e = m\left(\frac{B}{A'}\right)^2 \tag{3}$$

With respect to a bulk melt, the dimensions of any chain sections of molecular weight M centered at the interface are unperturbed in a direction parallel to the interface and are compressed normal to the interface. It is not obvious how to define the dimension of the chain normal to the surface in a quantitative manner. Qualitatively, however, the dimension will be approximately halved. Consequently, the pervaded volume is roughly one-half that in the bulk, which is equivalent to dividing A' in eq 1 by 2. Hence, from eq 3, M_e in the vicinity of an interface is approximately 4 times that in the bulk.

Independently, from the work of Silberberg,[16,17] an estimate of the pervaded volume of a chain close to an interface can be obtained. For a chain centered at the wall, it was shown that the z-component of $\langle R_g{}^2\rangle^{1/2}$ normal to the interface is reduced by a factor of $(1 - 2/\pi)^{1/2} = 0.603$ after reflection. The pervaded volume would be reduced by the same factor. This is in very good agreement with the results obtained from the qualitative arguments above.

While it is clear that M_e must be increased in the vicinity of a surface, the question remains as to how far this effect propagates away from the interface. Since entanglements are controlled by the packing of a continuous length of chain, then one could argue that the effect could only propagate over a distance corresponding to the root mean square end-to-end distance of a chain with a molecular weight equal to the bulk M_e. This distance corresponds to the tube diameter used in reptation arguments, which, for common polymers, varies from 3 to 8 nm.[10] Müller et al.[19] have approximated the distance over which the volume pervaded by a chain is perturbed by comparing the z-component of the radius of gyration, $\langle R^2_{g,z}(z)\rangle^{1/2}$, at a depth z from the surface to one-third the bulk radius of gyration, $\langle R^2_{g,bulk}\rangle^{1/2}/3$, as a function of the reduced depth, $z/\langle R^2_{g,bulk}\rangle^{1/2}$. In this way, a universal curve is seen which is near unity at a reduced depth of unity. As the reduced depth approaches zero, so too do the number of chains with their center of gravity at that reduced depth. Thus, the main contribution to the segment density comes from chains having their center of mass at $z \sim \langle R^2_{g,bulk}\rangle^{1/2}$. It is over this distance, which varies by $N^{1/2}$, where N is the number of segments in the chain, that one would expect to see some perturbations to the average volume pervaded by the chains.

The increase in M_e, for the arguments presented above, are strictly valid for the modifications to the chain packing in the vicinity of an impenetrable interface. Similar increases in M_e should, therefore, be found in any situation where the reflection hypothesis is applicable. Two examples immediately come to mind. The first is at a free surface which effectively acts as an impenetrable interface due to the energetic costs of having a rough interface. The second is at the interface between two immiscible polymers where enthalpic interactions between the polymers force the interface to be sharp. As discussed by Müller et al.,[19] the minimization of the number of contacts per chain between the two polymers should perturb the chain configuration at the interface. This should, also, be relevant at the interface between two identical polymers during the initial stages of interdiffusion.

The implication of a reduced entanglement density at the free surface of a glassy polymer on the mechanical response of the near-surface region of the polymer is profound. This situation is complicated, to some extent, by the fact that the glass transition temperature, T_g, of the polymer in the near-surface region may be different from that of the bulk.[20−24] There is evidence that the near-surface T_g may be as much as 50 °C lower than the bulk value. In general, entanglements significantly influence the high strain properties of a material. Both the "natural draw ratio" and the extension of craze fibrils are controlled by the ratio of the contour length of a chain of molecular weight M_e to its root mean square end-to-end distance. These extension ratios increase with $M_e{}^{1/2}$ and, consequently, should increase by a factor of $\sim$3 close to a free surface.

The reduced entanglement density at an interface provides a possible explanation of several different recent experimental observations and lends itself to a direct experimental test. Since the entanglement density controls the elongation ratio of deformation zones in polymer films,[22] one would expect that the elongation ratio would increase as the film thickness was decreased below twice the tube diameter. Consequently, deformation studies on ultrathin films can provide a direct piece of information that can test this hypothesis. Such experiments, using electron microscopy, are in progress and will be reported elsewhere.

A commonly used technique to produce alignment of liquid crystals is to place the liquid crystal in contact with a polymer surface that has been rubbed with a felt cloth under very small loads.[26] In this procedure, which is currently used in the production of flat panel displays, the liquid crystal is seen to form a monodomain aligned in the buffing direction. Recent experiments have quantitatively shown that, after buffing, the polymer chains in the near-surface region are aligned in the buffing direction even though the buffing is done hundreds of degrees below the glass transition temperature of the bulk.[27] The extent of alignment of the chains in the near-surface region is quite high, far more than can be obtained with the bulk specimen by uniaxially stretching a film. The ease of alignment of the near-surface chains is an indication that the drawing stress of the chains in the near-surface region is lower than that in the bulk which would result from a reduction in the entanglement density near the surface. In addition, the orientation of the chains propagates only $\sim$5 nm away from the surface, which is, also, consistent with the arguments presented above.

The strength of the interface between two immiscible polymers is controlled by the extent to which chains can couple across an interface. For glassy polymers, if the interface is not very weak, the strength is controlled by the number of chains that cross the interface and entangle with chains on the opposite side of the interface. One means of enhancing the adhesion between the two layers is to place a random or a block copolymer at the interface.[28] The copolymers are chosen so that one block mixes well with one homopolymer and the other block mixes well with the other homopolymer. If the entanglement molecular weight of the polymer near the interface is increased by at least a factor of 3, then the molecular weight of each block must be approximately 3 times the bulk M_e to produce substantial entanglements. This is in keeping with experimental observations.[29,30]

Finally, in a recent study on the interdiffusion of polystyrene (PS) with perdeuterated polystyrene (d-PS), a rather rapid interdiffusion of the polymers was seen at early times.[31-33] The experiment consisted of taking a layer of PS and placing this in contact with a layer of d-PS. The samples were then heated above the T_g of the polymer to allow interdiffusion, and neutron reflectivity was used to probed the interfacial broadening. At the shortest interdiffusion times, a rapid broadening of the interface of ~4.5 nm was observed. Up to roughly the relaxation time between entanglements, the broadening was effectively independent of temperature. If, as suggested above, the entanglement density in the vicinity of the initial interface is lower than that of the bulk, then one would expect a rapid intermixing of the two layers over a distance corresponding to approximately 2 times the tube diameter. This very rapid intermixing would then be followed by the normal diffusion of chains across the interface. This is consistent with the experimental observation.

It has been suggested that the entanglement density in the vicinity of an interface is markedly reduced. This surface effect, resulting from a reduction in the volume pervaded by a chain at the interface, should propagate at most a radius of gyration away from the surface, whereupon the normal entanglement density should be recovered. This reduced entanglement density provides a plausible explanation for several recent experimental observations and has implications in other areas such as friction and lubrication.

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