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Diffusion of Rigid Rodlike Molecules across Interfaces: Implications in Welding of Liquid Crystalline Polymers[†]

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The diffusion of long rigid rodlike (RRL) macromolecules in liquid crystalline concentrated solutions and melts is highly anisotropic, and restricted to their translation along the rod axis.[1] This could pose severe limitations on the interdiffusion of the constituent RRL molecules between two liquid crystalline polymeric bulks, when the molecular orientation is parallel to the interface. This has, in turn, serious repercussions in various operations, for instance, in the injection molding of the emerging "self-reinforcing thermoplastics". Poor weld strengths in the injection molding of such materials is known to be a common problem.[2,3] It is surprising that in spite of the importance of the problem, a quantitative analysis identifying the key molecular parameters which affect the welding of such materials has not been addressed at all. The simple heuristic analysis presented in this work hopefully makes a worthwhile beginning in this direction.

It is well known that when two compatible polymer surfaces at a temperature greater than their glass transition temperatures are brought into contact, interdiffusion of the chain segments occurring across the interface results in development of mechanical strength across the joint. Welding, crack healing, particle coalescence, injection molding weldlines, tack of elastomers, lamination of composites, coextrusion, etc. involve such interdiffusion of similar or dissimilar polymers. Besides, such interdiffusion is important in control of phase separation, and hence tailor-making of polymer blends and alloys.

Analysis of such healing processes at interfaces of flexible polymers is based on the celebrated reptation model of De Gennes.[4] Quantitative predictions have been made and verified experimentally, for the time (t) and polymer molecular length (L) dependence of the average monomer depth (x) and the number of bridges (p) across the unit area of the original interface, that may be related to the weld strength.[5,6] These analyses, by and large, have assumed the diffusion of flexible polymer molecules to be isotropic. However, extension and orientation of the macromolecular coils under the imposed flow during processing result in reduced diffusivity of the polymer molecules perpendicular to the direction of orientation. This anisotropic and shear-dependent diffusion of polymers in solutions and melts is now being increasingly studied, in view of the implications in a number of areas of pragmatic interest.[7,8] Although statements about the importance of the orientation of the macromolecules at the interface in determining the rates of interdiffusion during the welding of two polymers have been repeatedly made,[9,10] only Kim and Han[11] recently analyzed this problem in some detail. They considered the effect of the flow-induced orientation parallel to the interface on the rate of interdiffusion during coextrusion, where layers of two different polymer melts undergo welding and showed clearly the role of orientation. It is logical to expect that the effect of orientation and anisotropic diffusion will be far more important in processes involving RRL polymers. We can examine the possible reasons.

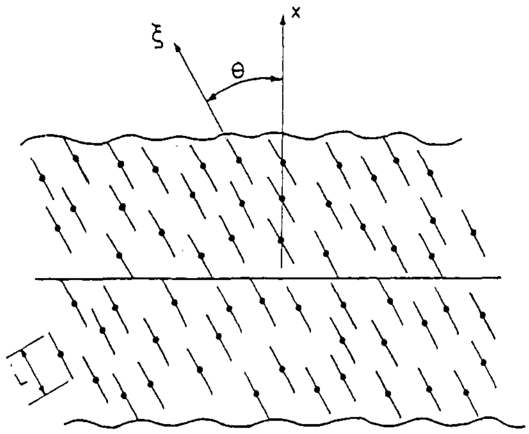

Figure 1. Model for healing at nematic liquid crystalline polymer interface. The filled circles represent centers of the rodlike molecules.

Firstly, even in the quiescent state, the RRL molecules undergo spontaneous transition (at high concentrations and low temperatures) to the nematic liquid crystalline state, displaying a very high degree of orientational order. Secondly, the large aspect ratio of RRL molecules, with severe "entanglements" from the neighboring molecules at their high concentrations and large molecular lengths, leads to their highly anisotropic diffusion.[1] While the translational diffusivity perpendicular to the rod axis vanishes rapidly ($D_{t\perp} \rightarrow 0$), the diffusivity parallel to the rod axis decreases only slowly ($D_{t\parallel} \approx L^{-1}$). This is in sharp contrast to isotropic translational diffusion for flexible molecules. Finally, the RRL polymers exhibit low rotational diffusivity (D_r), and hence a high degree of orientation even under relatively weak flows during processing.

Such diffusional characteristics have serious implications in the analysis of processes involving diffusion of RRL molecules. For example, reducing $D_{t\perp}$ and D_r with increasing molecular lengths during RRL polymerization leads to diffusional limitations on the rate of the polymerization reaction.[12] Also the flow-induced alignment facilitates the orientational requirement for rotational diffusion-controlled reactions.[13] As remarked earlier, although it has been recognized that the RRL polymers display very poor weld strengths,[2,3,14] no analysis, which gives an insight into the way the molecular attributes of the RRL molecules will influence the welding phenomena, has been reported. We address this problem here. In particular, we will consider the phenomenon of welding at the interface between two layers of the same monodisperse polymer, with the molecular orientation parallel in both layers but at an angle θ to the interface (Figure 1). We examine this albeit simplistic case, since the problem in its full generality is extremely difficult to solve.

Replacing $D_{t\parallel}$ by D hereafter, and denoting by ξ the distance along the molecular axis (Figure 1), the corresponding 1-D translational diffusion equation, assuming Fickian diffusion, is written as

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial \xi^2} \tag{1}$$

Considering uniform spatial distribution of molecules initially, the initial condition ($t = 0$) is

$$\begin{aligned} C &= 0 \quad \text{at } -L/2 < \xi < +L/2 \\ &= C_0 \quad \text{otherwise} \end{aligned} \tag{2}$$

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and the solution for number density is

$$C(\xi,t) = C_0\left[1 - \frac{1}{2}\left\{\operatorname{erf}\frac{L/2-\xi}{2(Dt)^{1/2}} + \operatorname{erf}\frac{L/2+\xi}{2(Dt)^{1/2}}\right\}\right] \quad (3)$$

Since all the molecules with centers defined by $-L/2 \le \xi \le +L/2$ pass through the original interface plane, the number of rods per unit area of the original interface plane is

$$n(t) = \int_{-L/2}^{+L/2} C(\xi,t)\,\mathrm{d}\xi \quad (4)$$

Substituting for C from eq 3 and simplifying

$$n(t) = C_0L - C_0\int_0^{L/2} \operatorname{erf}\frac{L/2+\xi}{2(Dt)^{1/2}}\,\mathrm{d}\xi \quad (5)$$

Further, using dimensionless time $\tau = Dt/L^2$, we get

$$n(\tau) \approx \rho_0\left(1 - 2\tau^{1/2}\int_{1/4\tau^{1/2}}^{1/2\tau^{1/2}} \operatorname{erf} z\,\mathrm{d}z\right) \quad (6)$$

where ρ_0 is the density of the bulk polymer.

The scaling law for molecular penetration along the molecular axis ξ for the 1-D diffusion is derived from

$$\langle\xi^2\rangle \approx 2Dt \quad (7)$$

or

$$\xi(t) \approx L^{-1/2}t^{1/2} \quad (8)$$

We estimate the relaxation time for welding by substituting $\xi \approx L/2$ and $t \approx t_R$ as

$$t_R \approx L^3 \quad (9)$$

The average monomer depth is obtained as

$$x(t) = \xi\cos\theta \approx L^{-1/2}t^{1/2}\cos\theta \quad (10)$$

and the number of chains $n(t)$ and bridges $p(t)$ per unit interface as

$$p(t) = n(t) \approx x(t)C_0 \approx \rho_0L^{-3/2}t^{1/2}\cos\theta \quad (11)$$

which yields the equilibrium value $p_0 \approx L^0\cos\theta$ at $t \to t_R$.

The scaling results for RRL polymers are summarized in Table I, along with the results for flexible molecules.[5] We note a stronger dependence of the average monomer depth x on t and L for welding of RRL polymers than for the welding of unoriented flexible polymers. This is because a chain segment of length l diffusing across the interface results in actual depth of penetration given by

$$\langle x^2\rangle \approx \langle l^2\rangle^m \quad (12)$$

with $m = 1/2$ for flexible polymers due to the Gaussian nature and $m = 1$ for RRL polymers.[1] This slower development of interpenetration depth for longer molecules in the case of RRL polymers has implications in blending of liquid crystalline polymers, where the interfacial thickness may determine the synergistic evolution of blend properties. Of even greater interest is the additional dependence (eqs 10 and 11) on θ, the molecular orientation relative to the interface. In particular, we note that for molecular orientation perpendicular to the interface ($\cos\theta = 1$), the interdiffusion is rapid, and for molecular orientation parallel to the interface ($\cos\theta = 0$), we have $x \approx 0$, corresponding to poor welding. It is interesting to note, however, that the fractional number of bridges relative to the bulk (i.e., p/p_0) is independent of θ, the molecular orientation. Again, it is remarkable that in spite of the differences in the diffusion mechanism of RRL and flexible molecules, the dependence of the number of bridges $p(t)$ on t and L is the same.

Table I
Transient Interdiffusion at the Polymer–Polymer Interface

interdiffusion property	symbol	oriented RRL polymer	unoriented flexible polymer[a]
average monomer depth	$x(t)$	$L^{-1/2}t^{1/2}\cos\theta$	$L^{-1/4}t^{1/4}$
number of chains	$n(t)$	$L^{-3/2}t^{1/2}\cos\theta$	$L^{-5/4}t^{1/4}$
number of bridges	$p(t)$	$L^{-3/2}t^{1/2}\cos\theta$	$L^{-3/2}t^{1/2}$

[a] From ref 5; L is the contour length.

Our analysis brings out the importance of molecular orientation at the interface during welding of liquid crystalline polymers. Although additional factors such as chain pull out, bond rupture, and crack propagation may contribute to the overall fracture mechanism and weld strength,[5] the present analysis may be considered to provide an indication of the key factors to the first level of approximation. For example, during injection molding, the fountain flow results in molecular orientation parallel to the interface at the weldline. The poor weld strengths observed[2,3] thus follow as a natural consequence. Our results will have implications on the mold and die design in the case of injection molding and coextrusion, where the flow pattern may be designed to yield orientation favorable to rapid welding. With the role of orientation being so crucial, appropriate external fields (e.g., magnetic electrical, etc.) may also have to be explored so as to yield orientation favorable for rapid welding of such systems.

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