The Reduction of Orientation in Fibers Spun from Two-Phase Polymer Blends via the Introduction of Shear into Elongational Flow by the Presence of a Second Phase

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Synopsis

A model is proposed for the reduction of orientation in spun fibers of two-phase polymer blends. This is based on the introduction of shear into an elongational flow by the presence of a second phase. The requirement is that the dispersed phase should not deform to the same extent as the continuous phase so that the flow field in the region of each particle is perturbed. Around an isolated droplet of minor component, the shear rate in the continuous phase goes through a maximum when the extension rate in the droplet is around half that macroscopically imposed. The dependence of orientation reduction on concentration of dispersed phase is fitted well by assuming that the flow field around a particle is disturbed over a distance two to three times the particle diameter. In this case the maximum average shear rate around the particle is of the same order of magnitude as the elongation rate. The model proposed is consistent with all the observed features of orientation reduction during spinning of two-phase blends.

INTRODUCTION

It has recently been reported[1] that interesting and useful changes in fiber properties can result when small amounts of a selected, immiscible polymer are added to a polymer being melt spun. In particular, at a given rate of fiber wind up, the molecular orientation in the fiber can be reduced substantially in the presence of the additive. Since orientation increases with wind-up speed (WUS), the result is a blend fiber whose properties resemble those of the pure fiber spun at lower WUS. For this reason the effect has been called wind up speed suppression or WUSS. The significance can probably be more directly appreciated when it is thought of as orientation suppression. It is important commercially since it permits increased productivity at the same spinning speed.

The effect has been studied in detail[1] and any mechanism proposed for it has to be consistent with the following key facts:

1. In every case of WUSS the polymer additive is present as small (typically 1 μm) droplets which deform into fibrils during passage down the threadline.

2. A large range of immiscible polymers produce very similar WUSS in poly(ethylene terephthalate) (PET) despite chemical dissimilarity. Thus, liquid

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crystal polymers, poly(ethylene oxide), nylon 6,6 and alkathene are all effective.

3. The effect is not peculiar to PET but has been obtained in nylon 6,6 and polypropylene fiber spinning.

4. In PET the effectiveness of nylon 6,6 in WUSS increased with increasing viscosity of the nylon.

5. The process controlling WUSS must occur in the threadline since WUSS can be induced by changing threadline conditions, in particular temperature, while keeping other parameters constant.

6. There appears to be an optimum droplet size of around 1 μm for the minor phase which maximises WUSS.

7. WUSS increases with increasing WUS.

These key facts have been fully discussed[1] and no attempt at a comprehensive treatment is made here. Rather, this paper proposes a mechanism for WUSS and discuss its validity and implications.

It is likely that WUSS is a rheological effect. Many authors have examined the shear rheology of two phase polymer blends. Types of behavior observed vary greatly and this is considered elsewhere.[2] However, the relevance of such work to fiber spinning is limited since in spinning the flow is almost purely extensional. For rheologically complex fluids, such as polymer melts, it is at present impossible to predict behavior under extension from that in shear.

This is borne out by our own shear viscosity data for PET/nylon 6,6 blends.[2] These did not display any features which could help us to understand WUSS. Indeed we now believe that the phenomenon underlying WUSS is peculiar to elongational flows. In shear the velocity gradient is perpendicular to flow while in extension it is in the flow direction. Elongational flow is irrotational but shear flow has a strong rotational component. Thus a macromolecule will tend to rotate under shear and to become extended in the flow direction under elongation. It is the latter effect which leads to the development of molecular orientation during fiber spinning. At a molecular level WUSS is the reduction of this orientation.

When a small amount of one polymer is added to the melt of another it may change its rheology. Two classes of effect can be distinguished. The viscosity of the major phase may be changed by the complete or partial dissolution of the additive in it. Alternatively the presence of a second phase may modify the rheology of the fluid without changing the composition of the major phase. As has been discussed by Brody,[1] it is difficult to reconcile an effect of the first type with the key features of WUSS. The second type of behavior would fit much more readily with his observations. It has been proposed[1] that WUSS results from the use of an additive whose elongational viscosity is lower than that of the polymer being spun. The suggestion is that, for a given macroscopic deformation, the dispersed phase elongates to a greater extent than the continuous phase and that this results in a translational motion of one part of the matrix relative to another which leads to WUSS.

The model proposed here falls into the same category being based on the physical presence of a second phase. It differs from Brody's model in that it is the presence of fibrils generated from the deforming drops rather than the deformation process itself which is believed to result in WUSS and that it

does not require that the dispersed phase should deform to a greater extent than the continuous one.

The model puts the dependence of WUSS on particle deformation on a quantitative basis and predicts the form of its dependence on volume fraction. An explicit mechanism for the reduction of orientation during spinning of two-phase blends and hence for WUSS is suggested.

THEORY

Expressions have been derived[3] for the rheological behavior of dilute suspensions of high aspect ratio particles in power-law fluids. These predict lower elongational viscosities than those of equivalent suspensions in Newtonian fluids. The difference in behavior is a consequence of the shear field introduced around rigid, high aspect ratio, particles in a fluid undergoing extensional flow. If the fluid is shear thinning the stress arising from the presence of the particle is reduced. This provides the starting point for our model.

Consider an isolated rigid fibril in a fluid subjected to steady elongation. The cylindrical coordinate system has its origin at the centre of mass of the fibril. At sufficiently great distance from the fibril, say $r \geq r_{crit}$, the flow field is unperturbed steady extension so that

$$\frac{\partial V_z}{\partial z} = \dot{\epsilon} \tag{1}$$

where V_z = the component of velocity in the z direction and $\dot{\epsilon}$ = extension rate which is a constant in steady elongation.

The components of velocity are

$$V_Z = \dot{\epsilon} Z \tag{2a}$$

$$V_r = -\tfrac{1}{2}\dot{\epsilon} r \tag{2b}$$

$$V_\theta = 0 \tag{2c}$$

Close to the fibril, $r < r_{crit}$, the flow field is affected. In particular, $V_Z = 0$ at the particle surface. Comparison of this condition with eq. (2a) which holds for all $r > r_{crit}$ shows that V_Z must be a function of r for $r < r_{crit}$, except at $Z = 0$ when $V_Z = 0$ for all r.

For values of $|Z| > l/2$, where l is the length of the fibril, the flow field can be considered to be unaffected so that V_Z is a function of r only for $r < r_{crit}$ and $|Z| \leq l/2$.

In this region we have

$$\dot{\gamma} = \frac{\partial V_z}{\partial r} \neq 0 \tag{3a}$$

while outside it we have, by eq. (2)

$$\dot{\gamma} = 0 \tag{3b}$$

where $\dot{\gamma}$ is the shear strain rate.

Thus, the presence of a rigid fibril introduces shear into what would otherwise be a completely irrotational flow. In order to calculate V_Z as a function of r, the constitutive equation for the fluid is needed. For a polymer melt this is far from being a trivial problem. At constant Z the velocity profile, V_Z vs. r, might, for instance, be that shown in Figure 1(a) or it might be different in detail. We do know, however, that V_Z would vary monotonically from zero at $r = 0$ to $\dot{\epsilon}Z$ [by eq. (2a)] at $r \geq r_{crit}$. In Figure 1(a) $\dot{\gamma}$ is a function of r. A reasonable approximation to this and to other possible velocity profiles is Figure 1(b). Here we assume a constant value of $\dot{\gamma}$ at $r < r_{crit}$. This will allow us to calculate the effective shear rate around the fibril while remaining ignorant of its detailed dependence on r.

As can be seen from Figure 1(b),

$$\dot{\gamma} = \frac{\partial V_z}{\partial r} = \frac{\dot{\epsilon}Z}{r_{crit}} \tag{4}$$

r_{crit} may itself be a function of Z, but, in order to calculate an effective average shear rate, we assume it is a constant. Thus, there is a shear field

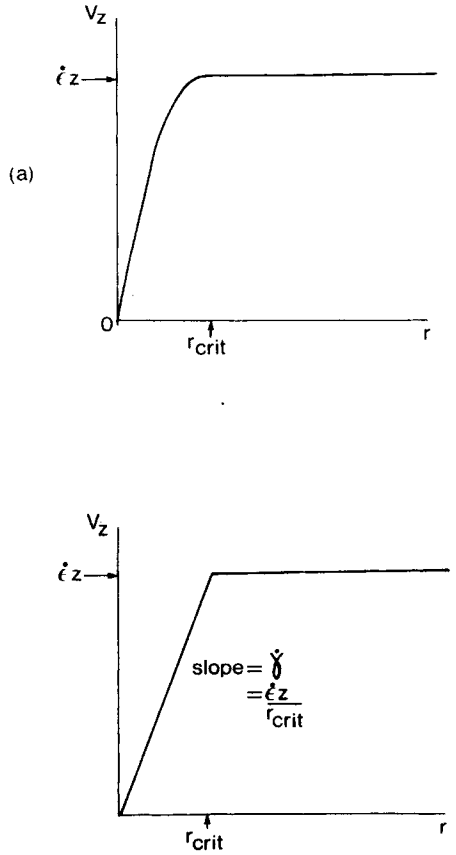

Fig. 1. Plots of V_z vs. r at constant z for an infinitely thin fibril in an extending fluid: (a) possible form for true velocity profile; (b) approximation to velocity profile.

around the fibril whose magnitude increases from zero at the center of mass of the particle to a maximum of

$$\dot{\epsilon} l/2r_{\text{crit}}$$

The average over the length of the fibril of the effective shear rate is, from eq. (4),

$$\dot{\epsilon} l/4r_{\text{crit}}$$

Now, consider the case where the fluid is a polymer melt. The effect of elongation on a polymer molecule is to extend it in the Z-direction. Under shear, on the other hand, a macromolecule will rotate. The effect of introducing shear into an extensional flow will be to take the molecular orientation out of the flow direction. If the macromolecule is in a fiber being spun the net result of the introduction of shear is a lowering of molecular orientation along the fiber axis, in other words, WUSS.

It has been demonstrated that shear could be produced if high aspect ratio, nondeformable fibrils, oriented in the flow direction, were present during fibre spinning; WUSS could result. In fact, WUSS is produced by the presence of deformable droplets of an immiscible polymer. Such inclusions can introduce shear by essentially the same mechanism as rigid fibrils provided that the particles do not deform to the same extent as the matrix. In steady elongational flow a polymer melt B is extended at a constant rate $\dot{\epsilon}$. If a droplet of a second polymer A is present in B, it may deform into a fibril at a rate $\dot{\epsilon}'$. In affine deformation $\dot{\epsilon}' = \dot{\epsilon}$ and the velocity field in B is completely unaffected by the presence of A. Clearly in this case no shear results from the presence of a second phase. However, $\dot{\epsilon}'$ may not equal $\dot{\epsilon}$ and shear can be introduced. A coordinate system with origin at the center of mass of A is again selected and the deforming particle is approximated by a cylinder of radius r' and length l.

Within A and by analogy with eqs. (1) and (2)

$$\frac{\partial V_z}{\partial z} = \dot{\epsilon}' \tag{5}$$

$$V_Z = \dot{\epsilon}' Z \tag{6}$$

l increases with time according to

$$\frac{dl}{dt} = V_z\left(\frac{l}{2}\right) - V_z\left(\frac{-l}{2}\right)$$

$$= \dot{\epsilon}' l$$

so that

$$l = l_0 \exp(\dot{\epsilon}' t) \tag{7}$$

where

$$l_0 = l \qquad \text{at } t = 0$$

$$= \text{diameter of undeformed droplet}$$

Far enough away from the particle, say $r > r_{crit}$, the flow of B is unaffected by the presence of A so that $V_Z = \dot{\epsilon}Z$. However, in fluid B immediately adjacent to the particle, i.e. at $r = r'$ and for $-l/2 \leq Z \leq l/2$, $V_Z = \dot{\epsilon}'Z$. As long as $\dot{\epsilon} \neq \dot{\epsilon}'$ there will be a finite shear rate $\dot{\gamma} = \partial V_z/\partial r$ in this region.

As discussed for the case of a rigid fibril, the details of the velocity profile are unknown but this does not really matter since it is the effective shear rate which is sought. The flow field is therefore approximated by assuming that $\dot{\gamma}$ is independent of r for $r' < r < r_{crit}$. In this case, within the region around the particle, B is subjected to a shear rate

$$\dot{\gamma} = \frac{(\dot{\epsilon} - \dot{\epsilon}')Z}{r_{crit} - r'} \tag{8}$$

$\dot{\gamma}$ is zero at the center of the particle and increases along the length of the fibril to a maximum of

$$\dot{\gamma} = \frac{(\dot{\epsilon} - \dot{\epsilon}')l}{2(r_{crit} - r')} \tag{9}$$

If $|\dot{\gamma}|$ is averaged along the length of the particle, then substitution of eq. (7) into eq. (9) yields

$$\dot{\gamma}_{ave} = \frac{|(\dot{\epsilon} - \dot{\epsilon}')|l_0 \exp(\dot{\epsilon}'t)}{4(r_{crit} - r')} \tag{10}$$

The absolute value is used because, whereas $\dot{\gamma}(z) = -\dot{\gamma}(-z)$, the sign of $\dot{\gamma}$ is immaterial with respect to its effect in lowering orientation. In this context only its magnitude is important.

Thus, fluid B in the volume $\pi \cdot r_{crit}^2 \cdot l$ around A is subjected to an effective average shear rate $\dot{\gamma}_{ave}$. As noted above, shear can reduce molecular orientation and so provide a mechanism for WUSS. Either subaffine ($\dot{\epsilon}' < \dot{\epsilon}$) or superaffine ($\dot{\epsilon}' > \dot{\epsilon}$) deformation could lower orientation. Only in the case of affine deformation when $\dot{\epsilon} = \dot{\epsilon}'$ is $\dot{\gamma}_{ave}$ zero.

Since the aspect ratio of the fibril increases steadily, $\dot{\gamma}_{ave}$ is a function of time or, equivalently, of total imposed strain $\epsilon = \dot{\epsilon}t$. Some knowledge of the form of $r_{crit} - r'$, the depth into the fluid surrounding a particle over which shear occurs, is required in order to determine conditions which maximize $\dot{\gamma}_{ave}$ at a given total strain ϵ. The possibilities that $r_{crit} - r'$ is independent of r' and therefore of $\dot{\epsilon}'$ and that $r_{crit} - r'$ is proportional to r' are considered. Since either subaffine or superaffine deformation can lead to finite $\dot{\gamma}_{ave}$, four cases are dealt with.

(a) $\dot{\epsilon}' > \dot{\epsilon}$, $r_{crit} - r'$ Constant.

$$\dot{\gamma}_{ave} = \frac{(\dot{\epsilon}' - \dot{\epsilon})l_0 \exp(\dot{\epsilon}'t)}{4(r_{crit} - r')}$$

Differentiating this with respect to $\dot{\epsilon}'$ (which is a measure of the extent of

particle deformation), we obtain

$$\frac{\partial \dot{\gamma}_{ave}}{\partial \dot{\epsilon}'} = \frac{l_0 \exp(\dot{\epsilon}'t)[(\dot{\epsilon}' - \dot{\epsilon})t + 1]}{4(r_{crit} - r')}$$

$$> 0 \tag{11}$$

so that $\dot{\gamma}_{ave}$ increases continuously with increasing $\dot{\epsilon}$.

(b) $\dot{\epsilon}' > \dot{\epsilon}$, $r_{crit} - r' = kr'$ Where k = Constant.

$$\dot{\gamma}_{ave} = \frac{(\dot{\epsilon}' - \dot{\epsilon}) l_0 \exp(\dot{\epsilon}'t)}{4kr'}$$

Now, r', the radius of the fibril, depends on total strain as

$$r' = r_0' \exp(-\dot{\epsilon}'t/2) \tag{12}$$

where $r_0' = r'$ when $t = 0$

$= l_0/2$ for an originally spherical drop

so that

$$\frac{\partial \dot{\gamma}_{ave}}{\partial \dot{\epsilon}'} = \frac{\exp(3/2\dot{\epsilon}'t)[1 + 3/2(\dot{\epsilon}' - \dot{\epsilon})t]}{2k}$$

$$> 0 \tag{13}$$

and again $\dot{\gamma}_{ave}$ increases continuously with increasing $\dot{\epsilon}'$.

(c) $\dot{\epsilon}' < \dot{\epsilon}$, $r_{crit} - r'$ Constant.

$$\dot{\gamma}_{ave} = \frac{(\dot{\epsilon} - \dot{\epsilon}') l_0 (\dot{\epsilon}'t)}{4(r_{crit} - r')}$$

$$\frac{\partial \dot{\gamma}_{ave}}{\partial \dot{\epsilon}} = \frac{[(\dot{\epsilon} - \dot{\epsilon}')t - 1] l_0 \exp(\dot{\epsilon}'t)}{4(r_{crit} - r')} \tag{14}$$

and $\dot{\gamma}_{ave}$ goes through a maximum when

$$(\dot{\epsilon} - \dot{\epsilon}')t = 1 \tag{15}$$

(d) $\dot{\epsilon}' < \dot{\epsilon}$, $r_{crit} - r' = kr'$.

$$\dot{\gamma}_{ave} = \frac{(\dot{\epsilon} - \dot{\epsilon}') \exp(3/2\dot{\epsilon}'t)}{2k}$$

$$\frac{\partial \dot{\gamma}_{ave}}{\partial \dot{\epsilon}'} = \frac{\exp(3/2\dot{\epsilon}'t)[3/2(\dot{\epsilon} - \dot{\epsilon}')t - 1]}{2k} \tag{16}$$

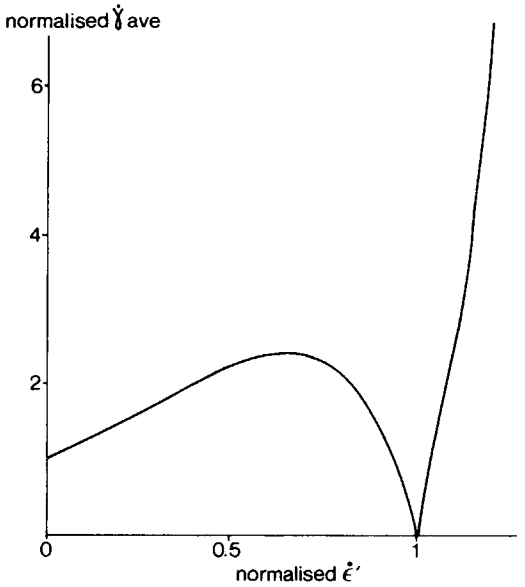

Fig. 2. Plot of $[4(r_{crit} - r')/l_0\dot{\epsilon}]\dot{\gamma}_{ave}$ vs. $\epsilon'/\dot{\epsilon}$ at constant total strain $\epsilon = 3$.

and $\dot{\gamma}_{ave}$ goes through a maximum when

$$(\dot{\epsilon} - \dot{\epsilon}')t = 2/3 \tag{17}$$

For a given $\dot{\epsilon}$ the value of $\dot{\epsilon}'$ which maximizes $\dot{\gamma}_{ave}$ depends on t and therefore on the total strain. For instance, at a total strain $\dot{\epsilon}t = 3$ and assuming that $r_{crit} - r'$ is a constant, the shear rate around a particle depends on the rate of deformation as shown in Figure 2. Since a rigid particle will still give rise to shear, there is a finite shear rate at $\dot{\epsilon}' = 0$ and $\dot{\gamma}_{ave} = 0$ only when $\dot{\epsilon}' = \dot{\epsilon}$. On either side of this point, shear rate rises rather steeply so that some WUSS may be possible even for deformations rather close to the affine.

WUSS is essentially orientation suppression. Before it is observed, there must be significant orientation so that some minimum value of $\dot{\epsilon}$ is necessary. This will, of course, depend on the system considered. Reduction in orientation will depend on the relative values of $\dot{\gamma}_{ave}$ and $\dot{\epsilon}$. Thus, if $\dot{\epsilon} \gg \dot{\gamma}_{ave}$, then the shear field will have little effect on orientation on the timescale on which stretching, and, therefore, orientation occurs. On the other hand, when $\dot{\epsilon} \ll \dot{\gamma}_{ave}$, the extensional stress will be completely averaged out in a coordinate system rotating with the macromolecule. Thus, no orientation will occur. The sensitivity of molecular orientation to shear will be greatest when $\dot{\gamma}_{ave} \sim \dot{\epsilon}$. Since molecular orientation is not wholly eliminated in systems manifesting WUSS, they are not in the regime $\dot{\gamma}_{ave} \gg \dot{\epsilon}$. This being the case, it ought to be possible to increase WUSS by maximizing $\dot{\gamma}_{ave}$. One approach would be to aim for maximum superaffine deformation. Unlike subaffine deformation, this is not commonly observed and the control of subaffine deformation seems a more promising route.

The condition maximizing $\dot{\gamma}_{ave}$ depends on total strain which increases down the threadline in fiber spinning. In order to promote WUSS, we need to

maximize shear in that part of the threadline where most of the orientation takes place. This is around the region where

$$\frac{V}{V_0} \sim \frac{1}{2}\frac{V_f}{V_0} \tag{18}$$

where V = threadline velocity, V_0 = initial velocity on exit from the die, and V_f = final velocity = WUS.

Typically V_f/V_0 is in the range 10–100 so that $\dot{\gamma}_{ave}$ should be maximized when V/V_0 is in the range 5–50. Now,

$$\epsilon = \dot{\epsilon}t = \ln V/V_0 \sim 1.6\text{–}3.9 \tag{19}$$

at this point. Substituting $\epsilon = \dot{\epsilon}t$ into eq. (15) yields

$$\dot{\epsilon} - \dot{\epsilon}' = \dot{\epsilon}/\epsilon \tag{20}$$

so that by eqs. (19) and (20) $\dot{\epsilon}'$ which maximizes $\dot{\gamma}_{ave}$ lies in the range $0.4\dot{\epsilon}$–$0.7\dot{\epsilon}$.

The sensitivity of the condition maximizing $\dot{\gamma}_{ave}$ to the form of $r_{crit} - r'$ is not terribly great. For example, at a total strain $\epsilon = 2$ eq. (17) leads to $\dot{\epsilon}' = 2\dot{\epsilon}/3$ while eq. (15) leads to $\dot{\epsilon}' = \dot{\epsilon}/2$. Similarly, when $\epsilon = 3$, eq. (17) yields $\dot{\epsilon}' = 7\dot{\epsilon}/9$ while eq. (15) gives $\dot{\epsilon}' = 2\dot{\epsilon}/3$. The actual behavior of $r_{crit} - r'$ is not expected to be far from the two possibilities considered. WUSS should therefore be maximized at levels of deformation of 1/2 to 3/4 that of the fiber as a whole.

In order to evaluate the actual maximum value of $\dot{\gamma}_{ave}$ by substituting $\dot{\epsilon}' \sim 0.4\text{–}0.7\dot{\epsilon}$ into eq. (10), it is necessary to estimate $r_{crit} - r'$. Until this is done, it is not known whether shear rates attainable during spinning are sufficiently high that they can reasonably be expected to give rise to WUSS.

So far only the shear field around an isolated particle in a fluid subjected to extension has been considered. In reality during the spinning of fibers from blends, many particles are involved. At low enough volume fraction of the minor phase A, the particles can be considered to be isolated from each other. In this situation there will be a finite volume of continuous phase, B, which undergoes shear around each particle. The total volume of B which is affected will simply be the sum of such volumes and will be proportional to φ, the volume fraction of A. Orientation suppression should depend on the proportion of B in which there is shear. Thus WUSS is expected to increase with φ. However, as φ increases, overlap will occur between those sheared volume elements of B around neighbouring fibrils of A. This means that the volume of B sheared will increase less rapidly with φ.

Approximating the deforming fibril by a cylinder, the ratio R of the volume element around a particle in which shear occurs to the volume of the particle is

$$R = (r_{crit}/r')^2 \tag{21}$$

Substituting

$$b = (r_{crit} - r')/2r' \tag{22}$$

where b is the ratio of the depth into B over which shear occurs to the diameter of the fibril, into eq. (21) gives

$$R = 4b^2 + 4b + 1 \tag{23}$$

If the system is divided into elements of volume Rv, where v is the volume of a single particle, then any such element containing one or more particles is sheared. This allows overlap between sheared volumes around adjacent fibrils to be taken into account. The aim is to ensure that the same volume is not counted more than once when the total volume sheared is calculated.

This can be done rather simply using the Poisson distribution. If particles are distributed randomly among an arbitrary set of volume elements then the probability, $P(n)$, of a volume element containing n particles is

$$P(n) = \frac{\mu^n}{n!}\exp(-\mu) \tag{24}$$

where μ = average number of particles per volume element.

For elements of volume Rv we have

$$\mu = \varphi R \tag{25}$$

There are limits to the use of the Poisson distribution. At very high φ it permits a finite value of $P(n)$ where $n > R$, i.e., it allows a greater number of particles into an element than the number whose combined volume is that of the element. This is obviously physically impossible.

At the volume fractions relevant to WUSS, this problem does not arise, and the Poisson distribution describes the behavior of real systems well. The volume fraction φ_{sh} of the material in which shear occurs is the fraction of elements of volume Rv containing one or more particles. This is particularly easy to calculate since

$$\sum_n P(n) = 1 \tag{26}$$

so that

$$\begin{aligned}\varphi_{sh} &= 1 - P(0) \\ &= 1 - e^{-\varphi R}\end{aligned} \tag{27}$$

φ_{sh} can be calculated as a function of φ for any value of R and therefore for any value of b [from eq. (23)].

WUSS is expected to be a function of $\dot{\gamma}_{ave}$ but for a given system and a given set of spinning conditions $\dot{\gamma}_{ave}$ should be more or less constant and WUSS should then increase with φ_{sh}. Figure 3 plots WUSS, as characterized by reduction in birefringence, against nylon concentration in PET. The data are taken from Ref. 1. The two solid curves are φ_{sh} vs. φ calculated from eqs. (27) and (23) for $b = 2$ and $b = 3$. This corresponds to the depth into the PET of the shear field being 2 or 3 times the fibril diameter. The calculated curves

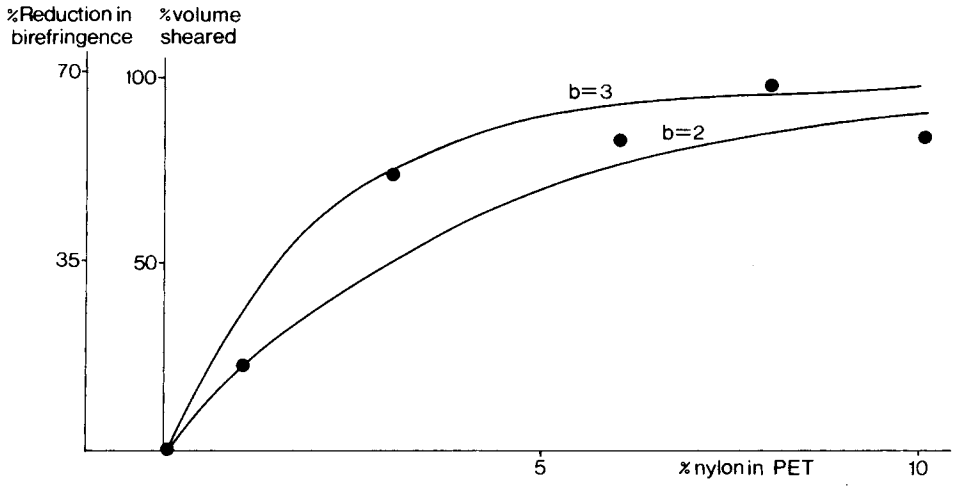

Fig. 3. Plot of WUSS vs. nylon content (data points) in PET and of volume fraction sheared versus concentration of minor component (solid curves) according to our model.

have been normalised so that $\varphi_{sh} = 1$ corresponds to the maximum observed birefringence reduction. This is the only arbitrary measure employed. The curves fits the data points very well. This implies that the simple relationship WUSS $\propto \varphi_{sh}$ holds. It is physically reasonable that the extent of WUSS should be proportional to the volume fraction sheared as long as $\dot{\gamma}_{ave}$ is independent of φ_{sh}. Figure 3 indicates that any change in effective shear rate occurring on overlap of shear fields round adjacent particles is too small to have a significant effect on WUSS. It is physically reasonable that the data are best fitted with the shear field around a particle extending 2–3 times the particle diameter into the matrix.

The self-consistency of the approach is now tested by calculating the order of magnitude of the maximum value of $\dot{\gamma}_{ave}$ expected from the value of $r_{crit} - r'$ corresponding to $b = 2.5$. If this is negligible, the model cannot predict WUSS.

Substituting eq. (22), with $b = 2.5$, into eq. (10), we obtain

$$\dot{\gamma}_{ave} = \frac{|(\dot{\epsilon} - \dot{\epsilon}'|l_0 \exp(\dot{\epsilon}'t)}{20r'} \tag{28}$$

Equations (28) and (12) yield

$$\dot{\gamma}_{ave} = \left(|(\dot{\epsilon} - \dot{\epsilon}')|/10\right)\exp(3/2\dot{\epsilon}'t) \tag{29}$$

From eqs. (19) and (20) it was calculated that, at a total strain $\dot{\epsilon}t$ in the region 1.6–3.9, $\dot{\gamma}_{ave}$ would be maximized with $\dot{\epsilon}'$ in the range $0.4\dot{\epsilon}$–$0.7\dot{\epsilon}$. Substituting $\dot{\epsilon}' = 0.5\dot{\epsilon}$ into eq. (29), together with $\dot{\epsilon}'t = 0.5\dot{\epsilon}t \sim 1.5$ yields

$$\dot{\gamma}_{ave} = 0.5\dot{\epsilon} \tag{30}$$

The model therefore predicts shear rates of a sufficiently high magnitude to give rise to WUSS. When WUSS is plotted against volume fraction at

constant WUS etc., as in Figure 3, it is at constant $\dot{\epsilon}$ and $\dot{\gamma}_{ave}$. WUSS is then proportional to the volume fraction sheared. The same qualitative dependence of WUSS on φ would hold under different conditions, but the high φ limit to WUSS would vary depending on $\dot{\gamma}_{ave}$.

EVIDENCE SUPPORTING THE MODEL

The phenomenon described should occur during elongation of suspensions of high aspect ratio particles or particles which do not deform affinely. However, significant effects are expected only when extension rates are high enough for molecular orientation. It has been found[4] that low volume fractions of a second fluid have no detectable affect on the elongational flow of a poly(ethylene oxide) (PEO) solution. This work was carried out on the Sangamo elongational viscometer on which extension rates were limited to less than 100 s^{-1}. Very little molecular orientation is likely at these rates in a comparatively low viscosity medium. Much higher extension rates are accessible on the cross-slot device of Keller and Odell[5] at Bristol University. Furthermore, the Bristol group can measure birefringence and thereby monitor orientation of macromolecules in solution directly.

In dilute solution, the onset of birefringence takes place when $\dot{\epsilon} \sim 1/\tau$, where τ is the relaxation time of the isolated macromolecule. τ depends on MW so that for a polydisperse material birefringence does not increase stepwise at a critical value of $\dot{\epsilon}$. Instead, birefringence vs. $\dot{\epsilon}$ is sigmoidal in form and the increase in birefringence becomes less abrupt the broader the MW distribution. At higher polymer concentrations entanglements between molecules complicate the behavior, and it can no longer be interpreted in terms of a distribution of simple τ values, each corresponding to a particular MW. Nevertheless, birefringence increases sigmoidally with $\dot{\epsilon}$. Thus, at low $\dot{\epsilon}$ there is very little molecular orientation, and most of the orientation takes place over some critical range of $\dot{\epsilon}$.

Dr. Odell kindly undertook to examine two fluids for us in his cross-slot device. These were a 3% solution of 900,000 MW PEO in concentrated sucrose solution and a 3% emulsion of silicone oil in the same. Intensity of birefringence is plotted vs. $\dot{\epsilon}$ in Figure 4 for both fluids. There is a small but significant difference between the two curves.

At a given strain rate the behavior of the emulsion resembles that of the solution at a lower extension rate. Since the solution is identical to the continuous phase of the emulsion, the silicone oil brings about "strain rate suppression." Equivalently, the birefringence at a given strain rate is reduced, demonstrating orientation suppression. Our model can explain this observation. During elongational flow in the device the oil droplets would deform into fibrils. Provided that deformation was not affine, this would generate shear in the surrounding PEO solution thereby reducing orientation.

Goddard predicts[3] that, at a given extension rate, the tensile stress in a suspension of fibrils should be lower if the fluid is shear thinning than if it is Newtonian. His argument is based on the introduction of shear so that stress is relatively low in shear thinning systems. Such behavior would parallel what we describe in terms of orientation suppression. On the other hand it would be restricted to shear thinning liquids. This limitation would not apply to

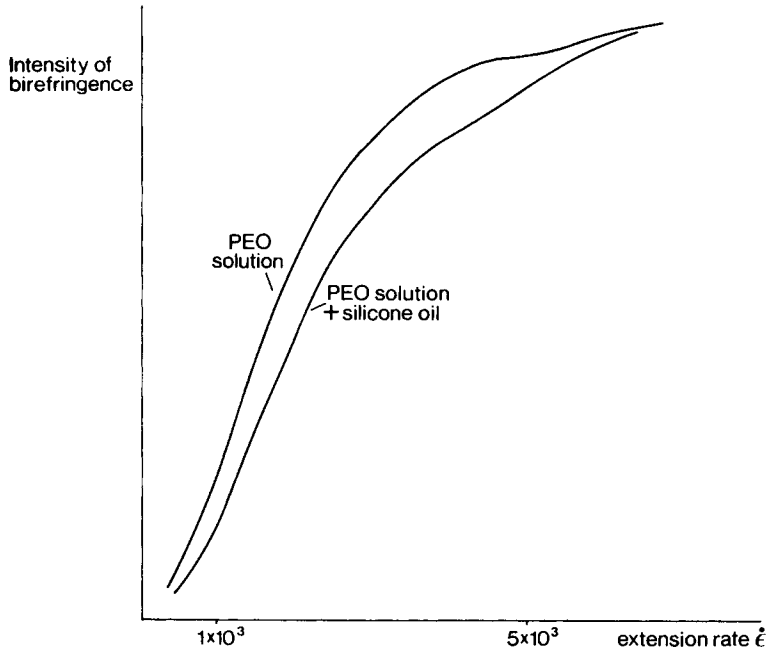

Fig. 4. Plots of birefringence versus $\dot{\epsilon}$ for PEO solution and for PEO solution containing silicone oil.

orientation suppression. Goddard's theoretical treatment is in qualitative agreement with published work[6,7] on fiber-filled melts. He cites elongational viscosity measurements on high density polyethylene (HDPE) both unfilled and filled with glass fiber. In pure HDPE, elongational viscosity was independent of $\dot{\epsilon}$ while in the filled HDPE it was a decreasing function of $\dot{\epsilon}$.

Interesting and relevant observations have been made on the fiber spinning of blends by Min et al.[8] Blends of polystyrene (PS) and polyethylene (PE) were melt spun and the orientation in the PE phase measured by WAXS. Orientation in the blends was lower than that in PE spun at the same stress. The authors suggest that the PS phase bears a disproportionately high part of the load so that the stress on the PE phase is reduced. This argument may well apply at higher PS levels where there is some continuity of the PS. However, substantial orientation reduction occurs at 10% PS when the PS is the dispersed phase. Thus, in Figure 20 of Ref. 8, the orientation of PE increases less rapidly with spinline stress when the PE contains 10% PE. Orientation reduction is clearly demonstrated. The authors recovered the PS fibrils from the spun blend and measured their diameters. Deformation was subaffine and approached affine deformation with increasing draw down ratio. Thus orientation suppression from subaffine deformation is convincingly demonstrated. Furthermore, spinline stress increases with draw down ratio so that as stress increases deformation increases towards the affine. The reduction in orientation when 10% PS is added to PE reported by these authors appears to go through a maximum as a function of spinline stress. Our model predicts precisely this behavior since, $\dot{\gamma}_{ave}$ will at first increase then fall off as affine deformation is approached. A similar experiment was carried out by the same

workers[9] on blends of PP with nylon 6. They found that the addition of 25% PP left nylon orientation unchanged. However, in this case the PP deformed affinely so that again the behavior is exactly as predicted by our model.

DISCUSSION

The introduction of shear through nonaffine deformation of the dispersed phase is consistent with and provides an explanation for the following observations:

1. *All system manifesting WUSS are two phase blends and in all cases the dispersed phase deforms into fibrils during spinning.* The presence of a second phase is an essential feature of our model. Although shear is introduced around particles which do not deform, the volume of continuous phase sufficiently close to a spherical particle to be influenced by it would be insignificant at the low volume fractions relevant to WUSS. Deformation into fibrils is then a prerequisite for WUSS.

2. *The effect is rather insensitive to the chemical nature of the minor components.* Our model predicts that it is the extent of relative deformation which controls WUSS. The physical properties of the components, rather than their chemical properties, are important.

3. *For nylon 6.6 in PET WUSS increased with nylon viscosity.* The particle size of the dispersed phase will increase with its viscosity. This could result in increased deformation. On the other hand, the tendency of a particle to deform may decrease with increasing viscosity. In either case the extent of deformation will be a function of particle viscosity. Since we predict WUSS will go through a maximum at some relative deformation, WUSS could either increase or decrease with minor phase viscosity. To predict the direction of the change, it is necessary to know the prevailing extent of deformation.

4. *WUSS depends on conditions in the threadline. Lowering the threadline temperature can induce WUSS.* According to the model, the mechanism underlying WUSS operates in that part of the threadline where orientation increases most. A drop in threadline temperature is likely to affect the relative deformation of the fiber components. This could increase WUSS to a detectable level.

5. *There seems to be an optimum particle size which maximizes WUSS.* Since the particle size affects deformation, a maximum in WUSS at some optimum subaffine deformation and therefore at some optimum particle size is predicted.

6. *WUSS increases with increasing WUS.* As reported in the literature[8] and discussed above, WUSS appears to go through a maximum with increasing WUS in the system PS/PE. In this case deformation approached affine deformation at higher WUS so that our theory would predict a maximum. If deformation is below the optimum level, WUSS will increase with WUS.

Thus, all the key features of WUSS can be interpreted via our model in physically reasonable ways. The essence of our model is the introduction of shear into an extensional flow by the presence of a second phase which does not deform at the same rate as the matrix. Affine deformation will produce no WUSS. Superaffine deformation would give the maximum scope for increased orientation suppression but is itself unlikely. On the other hand subaffine deformation is a common occurrence, and this can lead to orientation suppres-

sion. Optimization of WUSS is therefore a practical possibility via control of subaffine deformation.

Conditions maximizing WUSS themselves depend on WUS but for typical spinning conditions correspond to deformation such that the elongation rate of the particle is around one half to three quarters of that of the matrix. The model provides a physically sound mechanism for WUSS. It predicts the form of its dependence on additive volume fraction. Furthermore, it explains the dependence of the high volume fraction limit to WUSS on both WUS and the nature of the system.

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APPENDIX: NOMENCLATURE

b	ratio of extent of shear field around fibril to fibril diameter
l	length of fibril or deforming particle
l_0	diameter of undeformed particle = l at $t = 0$
R	ratio of sheared volume to particle volume
r, θ, Z	cylindrical coordinate system centered on isolated particle; in fiber spinning Z corresponds to direction of flow
r_{crit}	value of r above which the flow field around a particle is unaffected by its presence.
r'	radius of deforming particle
V	threadline velocity
V_0	initial threadline velocity
V_f	final threadline velocity
$V_Z(r, \theta)$	velocity in $Z(r, \theta)$ direction
v	volume of single particle
WUS	wind up speed
WUSS	wind up speed suppression
$\dot{\gamma}$	shear rate around particle = $\partial V_z/\partial r$
$\dot{\gamma}_{ave}$	the average magnitude of the shear rate in the region around a particle
ϵ	total strain; approximating $\dot{\epsilon}$ as being constant yields $\epsilon = \dot{\epsilon}t$
$\dot{\epsilon}$	extension rate in continuous phase = $\partial V_z/\partial z$
$\dot{\epsilon}'$	extension rate in deforming particle
μ	average number of particles per volume element
φ	volume fraction of additive
φ_{sh}	volume fraction subjected to shear
τ	relaxation time of an isolated macromolecule

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