

Orientation Suppression in Fibers Spun From Polymer Melt Blends

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Synopsis

The addition of very small amounts of carefully selected polymers by melt blending has been found to radically change the flow properties at spinning of conventional polymers such as polyethylene terephthalate, nylon 66, and polypropylene. This has a large effect on spun properties, especially at high wind-up speeds. The additive polymers used have included liquid crystal polymers, polyethylene, polyethylene glycol, and nylon 66. A major phenomenon is a considerable lowering of spun orientation, or wind-up speed suppression. In order to activate the non-liquid crystal polymers to achieve this effect special spinning conditions are necessary. The decrease in orientation can potentially lead to large increases in spinning productivity. The mechanism is viewed as being nonuniform extensional flow in a two-phase system and not molecular interaction.

INTRODUCTION

Whereas compatible polymer blends can generally be treated as additive systems, incompatible polymers may provide surprises, particularly in the field of rheology. For instance, the viscosity may be lower than either pure component over a broad concentration range, as had been found by Han for polystyrene/polypropylene¹ and polystyrene/HDPE² blends.

Of great interest and potential, however, is the very curious behavior that is becoming increasingly evident in the literature where small amounts of one polymer are added to another. This produces a large decrease in the shear viscosity of the major component as measured by capillary and rotational rheometers. The viscosity of polypropylene can be reduced by small additions of various polymers,³ (e.g., about 2% of polycarbonate gives a particularly large drop of about 70%). Small amounts of ethylene/propylene/hexadiene terpolymers considerably reduce the viscosity of a fluoroe-lastomer and vice versa, with a broad flat minimum in between, the EPDM acting as a processing aid in injection moulding.⁴ Lipatov et al. has found that small amounts of polycarbonate give a large decrease in the viscosity of polystyrene,⁵ and he has also studied a number of other immiscible systems and found similar behavior.⁶ Utracki has also found similar behavior for small concentrations of nylon 66 in polyethylene terephthalate, (e.g., there is a minimum in viscosity at 10% nylon).⁷ Recently it was found that small additions of thermotropic liquid crystal polymers lowered the viscosity of various polymers, which facilitated injection moulding.⁸ The work in this paper has explored the effect of these viscosity changes on the high-speed spinning of melt-spun fibers.

EXPERIMENTAL

The polyethylene terephthalate (PET) and nylon 66 were ICI commercial grades. The LCPs (liquid crystal polymers) used had abbreviated codes for convenience. They were CO, a copolymer of 6-oxy-2 naphthalene and *p*-oxybenzene,⁹ CLOTH, copoly chloro-1,4-phenylene-ethylene-dioxy-4,4'-dibenzoate terephthalate,¹⁰ and X7G, copoly ethylene terephthalate/*p*-oxybenzoate.¹¹ The polyethylene used was ICI Alkathene Grade 23, and the polyethylene glycol was Union Carbide Carbowax PEG 20M. Melt viscosities of these polymers at the temperature of measurement and a shear stress of 10^4 Pa are given in Table I.

The PET had an intrinsic viscosity of 0.63 dL/g measured in ortho-chlorophenol. The nylon 66 had a relative viscosity of 40, measured on a 8.4% solution in 90% formic acid compared with formic acid alone. The CO melted at 260°C to give an anisotropic melt as observed in a polarizing microscope fitted with a hot stage. The CLOTH melted at 220°C to give a melt which was anisotropic up to 320°C. The melt flow index of the polypropylene was 66, measured at 230°C under a load of 2.16 kg.

Spinning was performed on a screw-fed laboratory melt spinner. Polymer blending was done in two ways. Either chip blends were used directly or preblending was done with a screw extruder which produced a lace which was then cut into chips. The melt extrusion temperatures for PET and nylon 66 were 290–300°C. Shear processes occurred at spinning during passage of the blend through the pack and spinneret which further reduced the size of the dispersed phase. Therefore, samples of extrudate immediately after exit from the spinneret, when all such processes were complete, were taken for measurement of the globular size of the dispersed phase. Microtome sections were made and examined under the microscope.

Birefringence values were measured with a compensator and polarizing microscope. Instron measurements were made using a gauge length of 10 cm and a strain rate of 200%/min.

RESULTS

The effect of the addition of 3% of the LCPs CO and CLOTH to PET on the spun orientation of the PET, measured as birefringence, is shown in Figure 1. It can be seen that these LCPs considerably lowered the spun orientation of the PET at high WUS (wind-up speed), the effect increasing with WUS. The result of adding the LCPs is that fibers spun at high WUS

TABLE I

Polymer	Temperature (°C)	Melt viscosity (PaS)
PET	280	250
Nylon 66	285	80
CO	270	600
CLOTH	270	5
Alkathene 23	180	12
PEG 20M	100	15

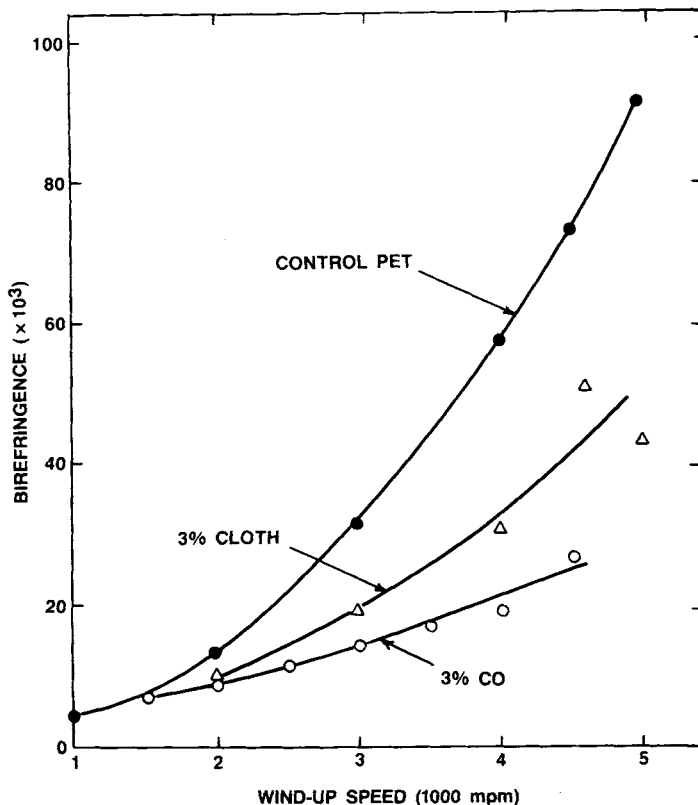


Fig. 1. The birefringence of spun fibers of PET blends with 3% CLOTH and 3% CO compared with the control. (mpm = meters per minute).

appear as if they were spun at a lower WUS, and for this reason the effect has been termed WUS suppression or WUSS. The intrinsic viscosities of the PET in the blend fibers were the same as the control, and so the molecular weight was not changed.

The effective reduction in WUS also considerably changes the boiling water shrinkage of the spun yarn, as shown in Figure 2. The inverted U of the control is flattened and truncated, consistent with an expansion of the abscissa scale.

The extension-to-break of the control PET decreases with WUS, as shown in Figure 3, and so WUSS should have increased the extension to the value of the control at the equivalent lower WUS. However, the extension of the blend fibers was lower than predicted. This is because although the molecular network orientation is reduced so that it has the potential for higher final extension, flaws prevent this being attained. This can be demonstrated by the stress-strain curves (specific stress—corrected for linear density) shown for the three WUS in Figure 4. The locus of termination of stress-strain curves of the control PET at lower WUS has been drawn in Figure 4 as dashed lines called the *theoretical extension*. The stress-strain curves of the blend fibers lie considerably below the control, indicating WUSS, but they do not reach their theoretical extension because they are terminated early by flaws. The extrapolated intersection with the dashed line gives the

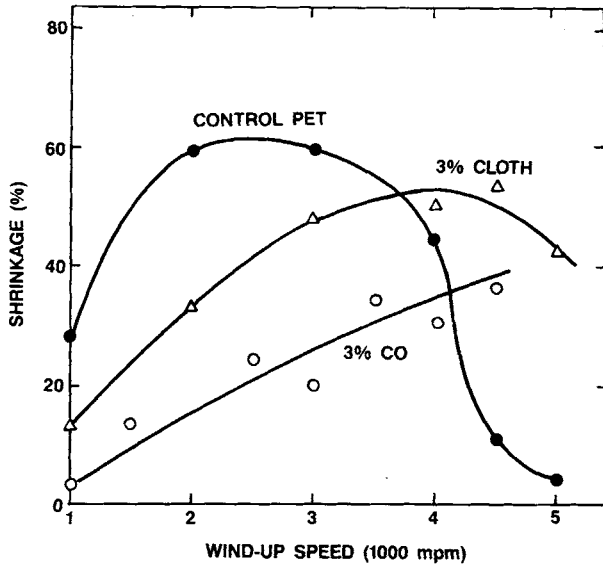


Fig. 2. The boiling water shrinkage of spun fibers of PET blends with 3% CLOTH and 3% CO compared with the control.

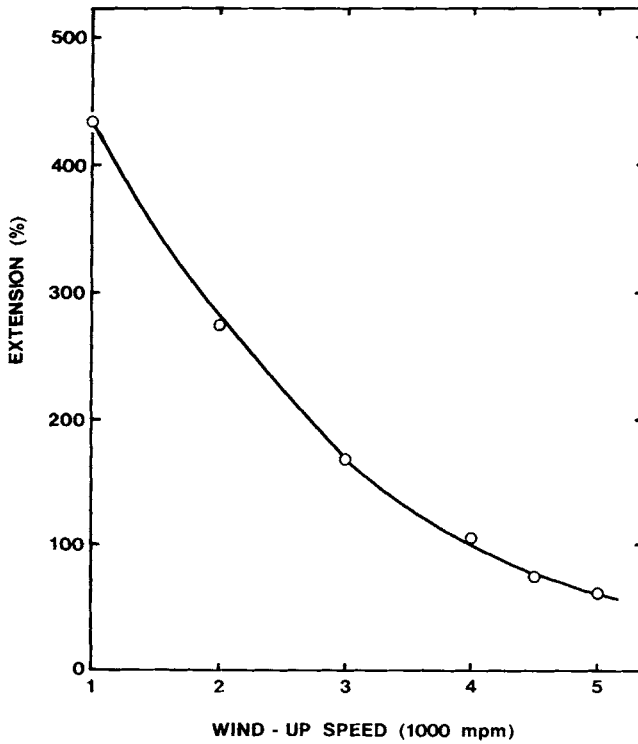


Fig. 3. The extension-to-break of PET as a function of wind-up speed.

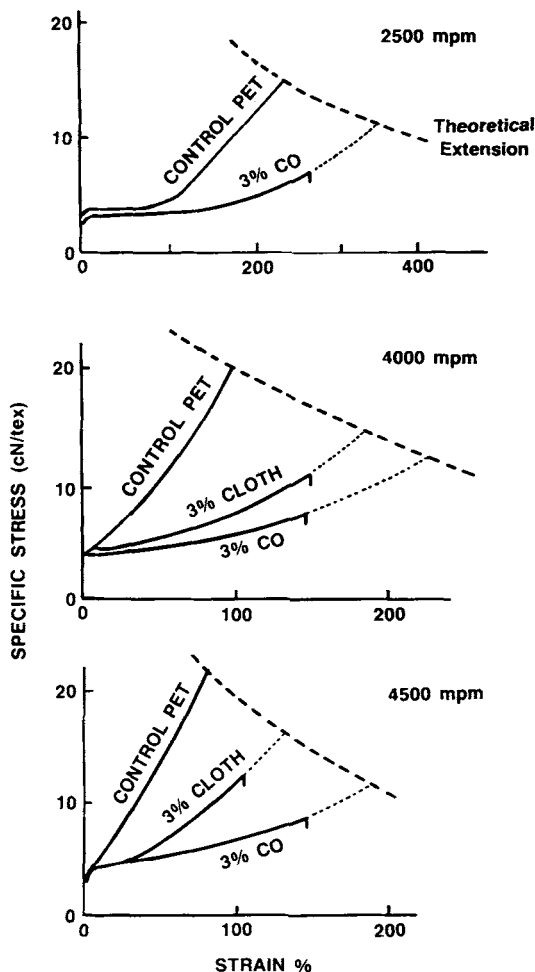


Fig. 4. Stress-strain curves of fibers of PET blends with 3% CLOTH and 3% CO spun at 2,500, 4,000, and 4,500 mpm compared with the control. The locus of theoretical extensions of the control PET is shown as dashed curves.

theoretical extension they would have if they were flawless. These values agree well with the extension of the control in Figure 3 at the lower equivalent WUS given by the lower birefringence in Figure 1, as shown in Table II. This shows that the stress-strain curves of the blend fibers are indeed those that would be expected from the spun orientation. Early termination of stress-strain curves is evidence for the presence of flaws.

A similar effect of WUSS with PET was obtained by using other very low viscosity additives, such as 3% Alkathene 23, a low-viscosity polyethylene, and Carbowax PEG 20M, polyethylene glycol, as shown in Figure 5, but only using special spinning conditions. WUSS could only be obtained if the PET spinning threadline was relatively cool. This is difficult to quantify in general because it depends on the particular spinning conditions used.

TABLE II

WUS (mpm)	LCP	Lower equivalent WUS from Fig. 1 (mpm)	Extension of control at lower equivalent WUS (%)	Extrapolated extension in Fig. 4 (%)
2500	CO	1800	310	340
4000	CLOTH	3000	170	180
	CO	2400	230	230
4500	CLOTH	3300	140	130
	CO	2700	200	190

A cooler threadline can be produced by reducing the throughput per spinneret hole, giving a thinner threadline which cools more rapidly. For a melt temperature of 300°C, there was virtually no WUSS when the throughput per hole was 98 g/h, but when the throughput was reduced to 40 g/h the results in Figure 5 were obtained. The same results were produced by reducing the melt temperature to 285°C and blowing quench air on the threadline. Because of the sensitivity to the threadline environment, these results would be qualitatively the same but quantitatively different on another spinning machine. In contrast the LCPs gave the WUSS shown in Figure 1 under all conditions used, and were not temperature sensitive.

It was found that the effect was not limited to low-viscosity additives. The addition of conventional nylon 66 (relative viscosity 40) to PET produced

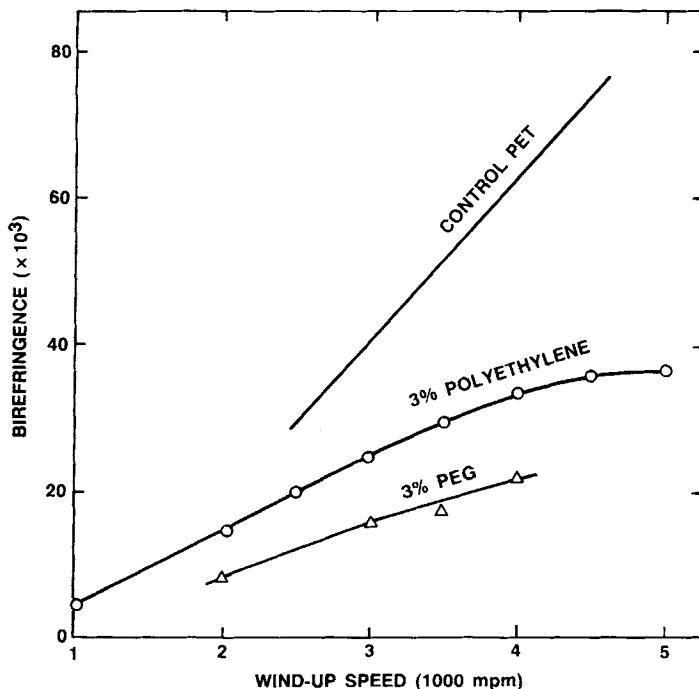


Fig. 5. The birefringence of spun fibers of PET blended with 3% polyethylene and 3% polyethylene glycol after "activation" by cooling the threadline.

similar results, as shown in Figure 6, but only when the threadline was cooled. Thus when the throughput was 240 g/h per hole there was no WUSS, but when the throughput was reduced to 96/g/h per hole the results in Figure 6 were obtained. The effect on the spun shrinkage was as dramatic as for the LCPs, as shown in Figure 7. These results also show that very small amounts of nylon 66 are very effective.

This time it was found that flaws did not limit the extension as with the LCPs and that the theoretical extension could be obtained, as shown in Figure 8. This is important commercially. The ability to spin a lower orientation at the same WUS should increase the spinning productivity, the spinning machine throughput, as discussed in Ref. 12, and as has been shown by the use of pentaerythritol.¹³ This is because the draw ratio to reach a final fixed diameter can be increased, and therefore a larger diameter fiber can be spun. If a spun filament has a breaking strain of e , the maximum draw ratio is $(1 + e)$. If a blend fiber has a larger breaking strain e' , it can be subjected to a larger draw ratio $(1 + e')$. To make drawn filaments of equal linear density at these maximum draw ratios the linear densities of the spun filaments must be proportional to $(1 + e)$ and $(1 + e')$, respectively. The percent increase in spinning throughput is there-

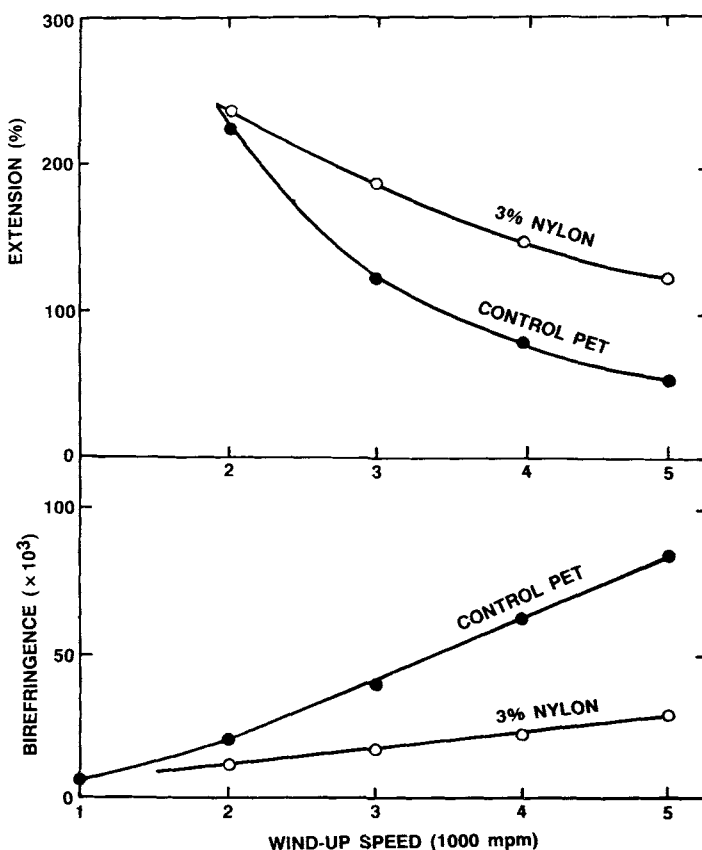


Fig. 6. The extension-to-break and birefringence of spun fibers of PET blended with 3% nylon 66 when the nylon 66 is "activated," both showing WUS suppression.

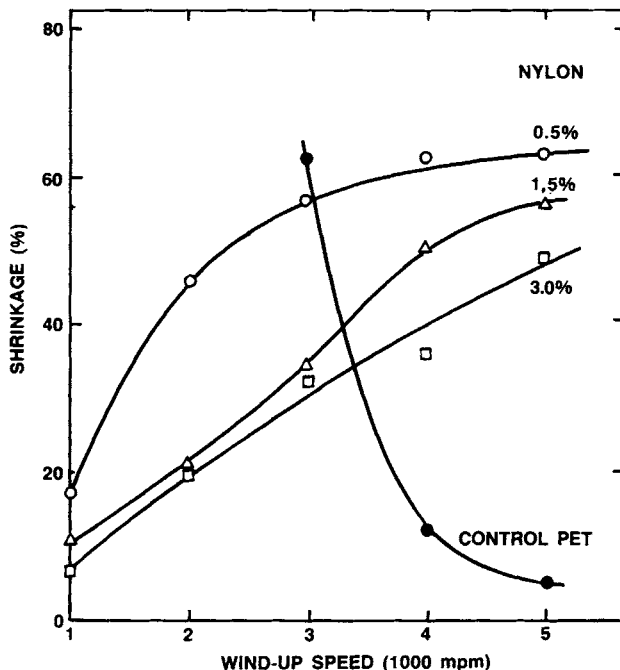


Fig. 7. The boiling water shrinkage of spun fibers of PET blends containing 0.5, 1.5, and 3.0% nylon 66 when "activated" compared with the control.

fore $100[(1 + e') - (1 + e)] / (1 + e)$. The increase by using 3% nylon 66 is potentially quite large, being 50% at a WUS of 5000 mpm.

When the effect of the molecular weight of the nylon 66 added to the PET was examined it was surprisingly found that an increase in the molecular weight increased the degree of WUSS. Increasing the relative viscosity of 3% nylon 66 in PET progressively, with estimated values of 26, 44, 47, and 57 in the spun fiber reduced the birefringence accordingly from the control value of 0.070 to values of 0.051, 0.027, 0.017, and 0.015, respectively.

So far the effect of additives to PET has been demonstrated, but the effect appears to be universal since similar effects were found for nylon 66 and polypropylene. To demonstrate WUSS some parameter has to be chosen which changes monotonically with WUS. For PET the birefringence is very convenient, but for nylon 66 there are changes in orientation after spinning due to further crystallization, and so the birefringence is not representative of the true spun state. A stable property is extension-to-break, and even though this may be limited by flaws as discussed above, an increase in extension is evidence for WUSS. The results for nylon 66 are shown in Figure 9, and considerable WUSS was obtained. As for PET large increases in spinning productivity are potentially possible, 6% CO giving a 40% increase at a WUS of 4000 mpm.

For polypropylene the presence of flaws restricted the extension to values lower than the control, but another convenient parameter demonstrating WUSS could be obtained from the stress-strain curves. These do not superpose on each other as do those for PET,¹⁴ and the stress at a given strain

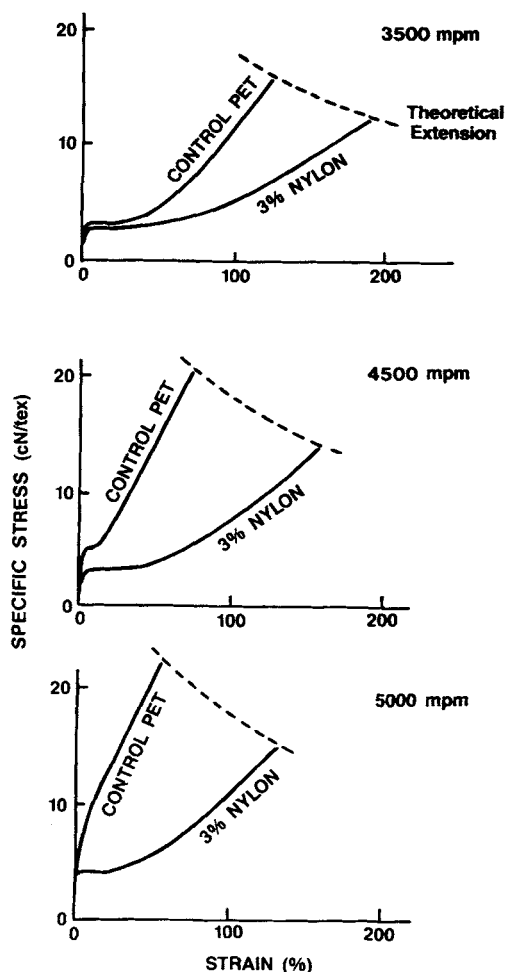


Fig. 8. Stress-strain curves of fibers of PET blended with 3% nylon 66 spun at 3,500, 4,500, and 5,000 mpm compared with the control. The locus of theoretical extensions of the control PET is shown as dashed curves.

increases with WUS. The stress at 50% strain was therefore chosen as a suitable parameter and the values obtained by LCP blends is shown in Figure 10, demonstrating appreciable WUSS.

DISCUSSION

The mechanism has to be consistent with a number of key experimental facts:

1. The two blend polymers are immiscible in every case. Examinations of the polymer blends on exit from the spinneret show the additive phase is present as globules a few microns in diameter. These can be observed in fracture surfaces of the blends as spheres, and also seen in optical micrographs of sections of the blends.

2. There is a large range of very disparate polymers chemically which behave almost identically as additives.

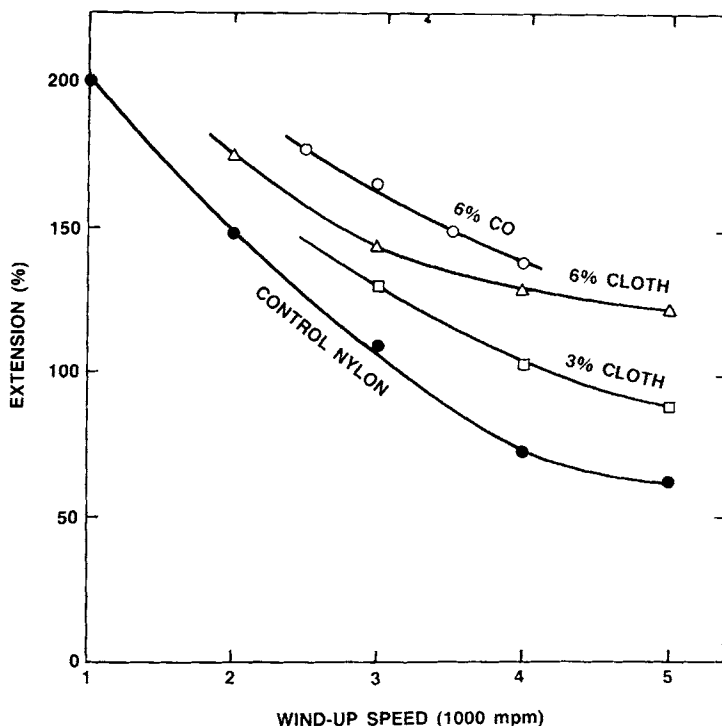


Fig. 9. The extension-to-break of spun fibers of nylon 66 blends with 6% CO, 6% CLOTH, and 3% CLOTH compared with the control, showing WUS suppression.

3. Increase in molecular weight of the nylon 66 increased the degree of WUSS.

4. The process which leads to WUSS occurs in the threadline, not the pack or spinneret. This is because WUSS of non-LCP blends is "activated" on cooling the threadline using quench air, while keeping the melt temperature constant.

5. Immediately after exit from the spinneret the additives are present as globules, but these have been deformed into microfibrils in the spun fiber, as can be seen optically or by solution of the matrix. Without such deformation WUSS does not occur.

6. There seems to be an optimum size of these globules of about $1\mu\text{m}$ for maximum WUSS.

7. Increasing the WUS increases the degree of WUSS.

The prevailing view of the majority of previous workers for the reduction of shear viscosity by small amounts of additive is that the effect occurs at a molecular level, with interpenetration of molecular segments lowering intermolecular attraction and thus facilitating mutual displacement (e.g., Ref. 3). Lipatov determined χ , the thermodynamic interaction parameter, by inverse gas chromatography, and found that a positive increase in χ corresponded with a low viscosity.⁶ Utracki seems to take two viewpoints, in again proposing partial solubility for nylon 66/PET blends, but also seeming to take another view in postulating readily deformable droplets of nylon 66 which form shear-dependent structures.⁷ Han does not invoke

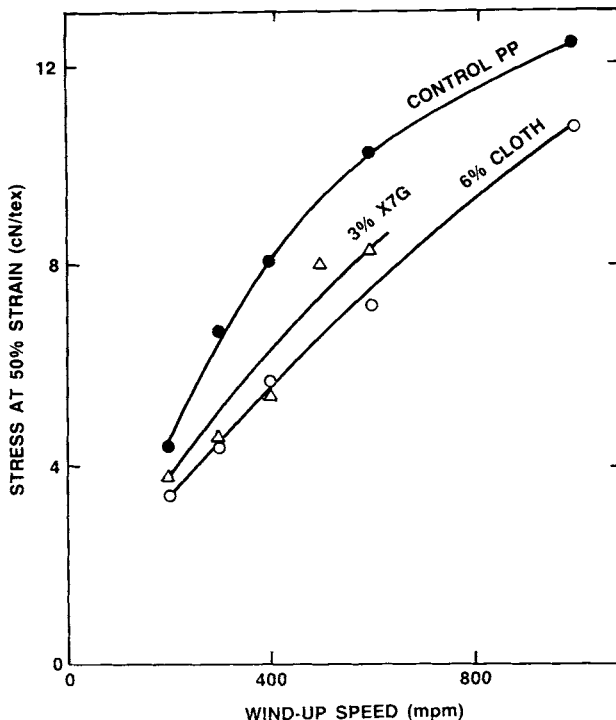


Fig. 10. The stress at 50% strain of spun fibers of polypropylene (PP) blends with 3% X7G and 6% CLOTH compared with the control, showing WUS suppression.

molecular interactions at all but proposes a mechanism in extensional flow where if polystyrene is the minor phase it stretches more than the HDPE because of its lower viscosity.²

This macrorheological model is the one that is considered most likely for WUSS, i.e., a two-phase system in which the deformation of the droplets is the key factor, rather than a single phase in which the additive molecules are in solution, and viscosity reduction is obtained by molecular interaction. The list of experimental observations above seems to be incompatible with a molecular mechanism; in fact these results seem to be just the kind that would be sought for and cited to disprove such a mechanism! Immiscibility suggests that very few molecules can be in solution in the major phase, and therefore they must be very potent to produce such large degrees of WUSS. Longer molecules from higher molecular weight would be expected to be less easily diffusible, not more. Why would cooling the threadline enhance solubilization of the additive? What is the common feature of so many different additives? It seems most likely that the effect is related to the geometry of the globules—the size, and the apparent necessity for the deformation into microfibrils.

If the rheology of the spinning threadline is the factor of importance it is extensional viscosity not shear viscosity that should be considered. Unfortunately, only shear viscosity has been measured by previous workers. Measurements of the extensional viscosity of these polyblend systems at the extensional shear rates during spinning would provide very valuable information, but are not yet experimentally accessible.

The course of deformation of the globules into microfibrils at 4000 mpm has been analyzed for CO and polyethylene blends with PET by removing sections of the threadline with a special two bladed cutter device, and examination of these sections in the microscope. The conditions were such that the polyethylene gave WUSS. Concurrent temperature measurements of the threadline were made with an infrared pyrometer. Both the CO and polyethylene remained as spherical particles a few microns in size down to about 10 cms below the spinneret when the temperature of the threadline had fallen to about 260°C. At this point the globules rapidly elongated within about 5 cm to become about 8 μm in length, and thereafter continued to elongate further. This suggests highly nonaffine deformation, but this would have to be confirmed in a more thorough experiment. What can be concluded is that the deformation appears to occur at about the normal solidification point of the PET. In other words the deformation is imposed on the additive by the expected behavior of the matrix, regardless of the very different nature of these two additives.

Considering therefore the overall fate of the additive in the threadline, there are three states that have to be considered: (i) globules, (ii) the transition to "liquid" microfibrils, and finally (iii) the liquid microfibrils themselves. It is not thought possible that a small concentration of liquid spheres alone could have such a large effect on the rheology. Considering the final stage of the parallel microfibrils, these cannot interact laterally in extensional flow by definition. This therefore leaves the transition from globules to liquid microfibrils as the key factor.

If the extensional viscosity of the additive polymer was less than a certain threshold value it can be envisaged that the matrix would deform without impedance, although differently from normal because of the geometrical irregularity. It would then not matter which additive was used—they could all be considered the same. Taking this idea further, the extreme situation would be when the relative viscosity of matrix to additive was such that the globules could be considered as holes. A simple experiment was performed to show that such holes can lead to surprising results. Holes were punched in a rubber sheet which was then stretched by 150%. Very non-affine deformation was obtained, as shown in Figure 11. The pattern of transverse markings showed that the extensional type of deformation in such a system is very high around the holes and low between. Classical

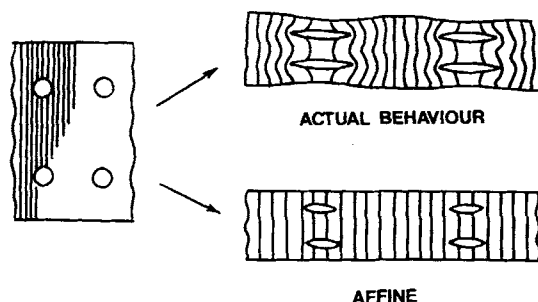


Fig. 11. The extensional deformation of a rubber sheet containing holes when stretched 150%. Below is the expected affine deformation and above is that actually observed.

mechanics shows that there is a stress concentration at the edges of holes in solid sheets when such sheets are stressed. This stress attenuates to the level in the sheet over a distance of a few diameters. If these stresses were generated in a fluid they could not be sustained, and would therefore be translated into fluid flow of the sort seen in the rubber sheet.

Nonuniform extensional flow does not by itself explain the WUSS effects that are obtained, but there is an unexpected result which is very significant. It is shown diagrammatically in Figure 12. Each cell on the extreme left represents a region containing a hole, the holes being staggered. It is assumed that only the regions around these holes can deform, and the rest of the matrix does not. The width of the cells is therefore kept constant. On extension, in order to preserve continuity at the interfaces there has to be a contraction obtained by a rearrangement of the "waisted" cells, leading to the final tessellated situation. Assuming the high flow regions around the holes have a draw ratio of 9.0 gives an overall draw ratio of 2.5, represented by boundaries that can be drawn around the periphery of the cells before and after deformation, even though most of the matrix does not draw. Thus, because of the lateral contraction the matrix is translated as well as being extended, giving a lower increase in overall orientation by effectively converting extensional flow into shear.

It is of course very difficult to produce small holes in a polymer fluid, and the use of a polymer blend offers an easy route to such "holes." There is another favorable aspect of these polymer holes. Compared with gas bubbles the interfacial surface tension will be much reduced, and so deformation of the polymer globules will be much easier.

The effect in Figure 12 is achieved because the holes are staggered the maximum amount. The more they become adjacent the less the degree of tessellation after deformation, and the greater the overall orientation. Staggering therefore enhances the effect and vice versa. For low concentrations of additive the globules will be a large distance apart relatively, and thus will be highly staggered, since statistically they are not likely to be adjacent. This explains why such surprisingly small concentrations of additive are so effective, as shown in Figure 7. As the concentration increases, the dis-

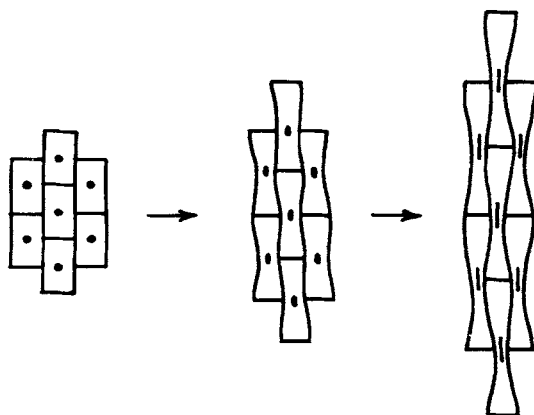


Fig. 12. Diagrammatic representation of the progressive deformation of blends with staggered high flow regimes.

tance between the globules decreases and more become adjacent, reducing the value of their contribution.

In this highly simplified model there are thus two related variables, the distance between the globules and their concentration, which of course determines this distance. Thus

$$\text{WUSS} \propto cd \quad (1)$$

where c = concentration of additive globules

d = distance between globules

Consider a spherical globule of diameter D in a unit cell of side A . The concentration c of globules is given by

$$c = \frac{\pi}{6} \left(\frac{D}{A} \right)^3 \quad (2)$$

and

$$A = \frac{0.81 D}{c^{0.33}}$$

The distance d between spheres is $A-D$, whence WUSS

$$\begin{aligned} &\propto Dc^{0.67} (0.81 - c^{0.33}) \\ &\propto c^{0.67} (0.81 - c^{0.33}) \end{aligned} \quad (3)$$

for a given value of D , where D is assumed independent of c .

So far this theory has been tested on the PET/nylon 66 system, and the results are shown in Figure 13. The effect of concentration of nylon 66 (relative viscosity 40) in PET on the percent reduction in birefringence at

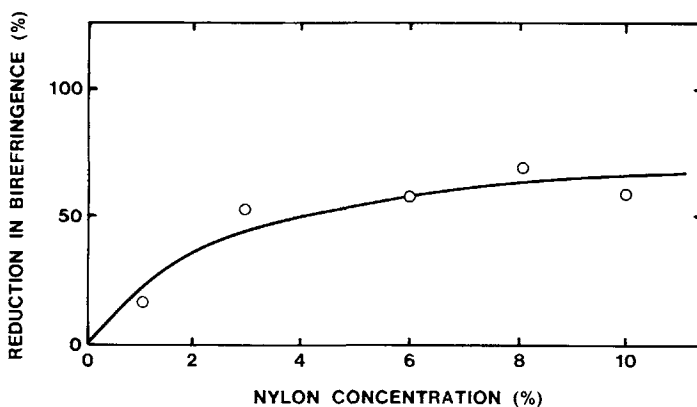


Fig. 13. Reduction in birefringence for PET at 3,000 mpm as function of nylon 66 concentration. The points have been experimentally determined. The curve has been drawn using the expression $\text{WUSS} \propto c^{0.67} (0.81 - c^{0.33})$, scaled so that the value at 6% nylon 66 is the same as that experimentally determined.

3000 mpm (i.e., degree of WUSS), is shown by the experimental points. The expression for WUSS above has been calculated, omitting the unknown constant and assuming that D does not change, and scaled so as to give the same result at 6% nylon 66 as obtained experimentally. The curve then shown in Figure 13 is that given by this theoretical expression. It can be seen that this simple theory fits the experimental results extremely well.

A geometrical mechanism involving extensional flow also explains other observations. The activation of low-viscosity polyethylene by lowering the temperature can be ascribed to the different temperature responses of the extensional viscosities, which raises the relative viscosity above a critical value. Even though the polyethylene used had an extremely low *shear* viscosity, its branched nature can produce very different relationships between *extensional* viscosity and stress,¹⁵ so that its actual viscosity could be higher than anticipated. In contrast LCPs worked under all process conditions used. The extensional viscosity of LCPs is probably always low, and so the relative viscosity ratio will always be high.

A connection with the effect of the size of the globules can be obtained from the work of Han.¹⁶ He measured the extent of deformation of droplets of one polymer solution in another flowing into channels, and found it depended on the Weber number, We , where $We = (\eta\dot{\gamma}a)/\sigma$, where η is matrix viscosity, $\dot{\gamma}$ is shear rate, a is droplet size, and σ interfacial tension. Assuming there is more WUSS the greater the droplet deformation, there is a geometrical contribution in terms of diameter. An optimum may arise because of a balance between diameter and shear rate. Another important factor is the interfacial tension. The lower this value by suitable choice of polymers, the greater the globule deformation.

CONCLUSIONS

Small amounts of immiscible polymers can lower the orientation of PET, nylon 66, and polypropylene fibers spun at high WUS. The degree of lowering, or WUSS, increased with WUS. LCPs are particularly effective in producing WUSS for different threadline temperatures, but non-LCP additives need a relatively cool threadline, dependent on the spinning conditions used. The mechanism governing WUSS takes place in the spinning threadline, and is connected with deformation of globules into microfibrils. A theory which considers the additive globules to deform as holes in non-uniform extensional flow yields an expression which fits very well the experimental results for degree of WUSS as a function of additive concentration.

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