

Reinforcement Factors in Fibers from Block Copolyamides and Polyamide Blends

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Synopsis

The modulus of a fiber can be increased by plying with it a higher-modulus fiber. In this case, the modulus of the combination is characterized by a springs-in-parallel model, and the modulus of the composite is a linear function of the per cent of the second fiber in the composite. Another method of obtaining reinforcement is to melt-blend a higher-modulus polymer with the substrate polymer. With polyamides, this leads to a certain degree of amide interchange and block copolymer formation which depends on the compatibility of the polymers as well as on the usual kinetic factors. If the dispersion of the higher-modulus polymer is such that aggregate size is relatively large (e.g., $\geq 500 \text{ \AA}$) and if the adhesion between the two polymers is good, a springs-in-parallel-type reinforcement is the best which can be obtained. In melt-blend polyamides, a "nonclassical" phenomenon in reinforcement has been noted when the diameters of the dispersed aggregates are $\leq 500 \text{ \AA}$ and when there are a relatively high number of hydrogen bonding sites on both polymer components. In this case, it appears that moduli appreciably higher than predicted from a springs-in-parallel model are obtained as well as higher than expected T_g values. A mechanism is proposed to account for this "nonclassical" behavior along with data to support it. Another type of anomaly is observed when the components of the blend are isomorphous. In this case, the reinforcement is considerably less than expected.

INTRODUCTION

Nylon yarns are generally characterized by high-strength potential, toughness, and abrasion resistance. On the other hand, nylon 66 or other linear aliphatic polyamides tend to have moduli which are low for a number of important end uses such as tire cord. In addition, glass transition temperatures (T_g) lie in the range of room temperature to 80°C (depending on moisture content), and this results in a number of undesirable attributes such as tire flat spotting propensity. In an effort to upgrade the modulus and T_g of such polyamides while maintaining their other desirable attributes, effort has been directed to the use of reinforcing agents. Among

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the methods which can be used for reinforcement are (a) fiber blends (i.e., plying a high modulus fiber with the fiber which requires reinforcement), (b) co-spinning the lower-modulus polymer with a higher-modulus polymer in a sheath-core relationship, or (c) blending a higher-modulus polymer into the lower-modulus substrate. The latter approach differs from the first two in that the high-modulus component is dispersed in the form of small discontinuous fibrils, whereas in the first two cases we have for all practical purposes continuous lengths of each component.

For the situation of essentially infinite lengths of parallel components, the modulus of the aggregate is a linear weight average of the moduli of the components, i.e.,

$$M = f_1M_1 + f_2M_2. \quad (1)$$

For the case of discontinuous fibrils with good adhesion between the components, the modulus of the composite would be expected to approach that described by eq. (1) in the limit of an infinite ratio of length to diameter (l/d). For low values of l/d , the modulus of the composite would be expected to be somewhat lower.

Equation (1) predicts that a graph of modulus versus composition for elements in parallel should be a straight line connecting the individual components. On the other hand, frequently one is concerned with a measurement which is a reflection of compliance ($1/M$) rather than modulus, and a graph of compliance versus composition would show a deviation from a straight-line relation as indicated in Figure 1. For example, the flat spotting propensity of a tire cord has been shown to be related to the difference between the compliance at tire operating temperature and the compliance at room temperature.¹ Thus, a reinforced tire

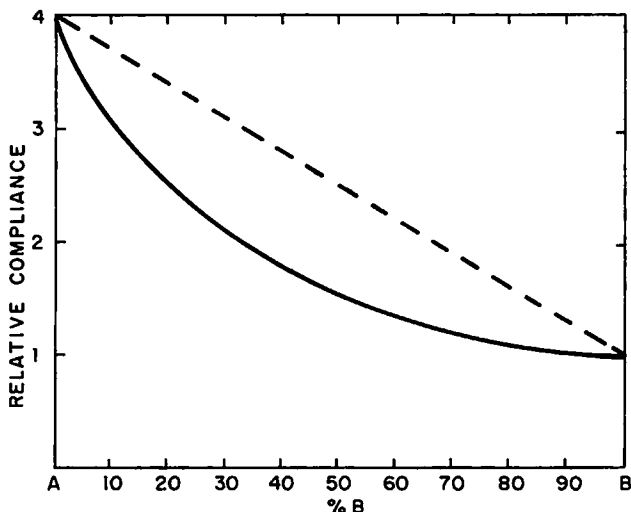


Fig. 1. Compliance vs. composition (springs-in-parallel).

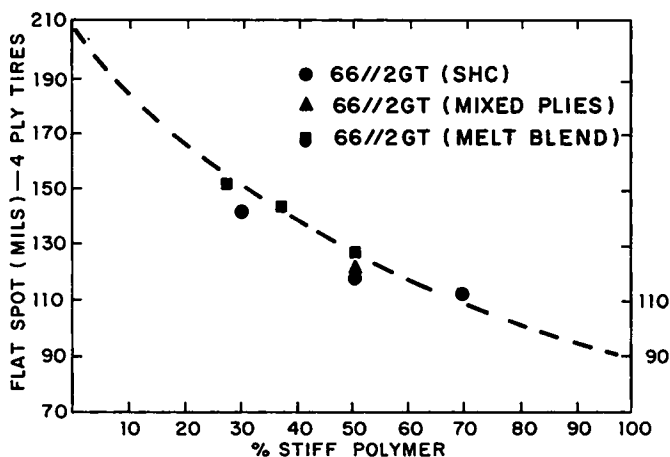


Fig. 2. Flat spotting of reinforced nylon 66.

cord which consists essentially of elements in parallel would show a faster than linear decrease in flat spot as the per cent of the reinforcing agent was increased. Examples of such reinforcement can be shown in the system of nylon 66 blended with poly(ethylene terephthalate) (2GT). One can see that the flat spot versus composition relationship is essentially the same for the 66/2GT composites, whether they be concentric sheath-core yarns, melt-blend yarns, or combinations in a tire of separate plies of nylon 66 and 2GT (Fig. 2). This behavior can be termed "classical." In this paper, we will describe a study of reinforcement of nylon 66 by blending stiff, high- T_g polyamides at low degrees of amide interchange in which an unusual extent of reinforcement has been observed beyond that which could be expected on the basis of existing reinforcement theories.

EXPERIMENTAL

It has been known for a long time that interchange in polyamide blends, such as nylon 66 and 6, is slow enough to permit a reasonable degree of control and that it takes more than 8 hr at 285°C to achieve true randomness, as indicated by melting point.² The polyamide blends described here were prepared by feeding polymer flake through each of two screw melters into a mechanical polymer mixer and from there to a conventional melt spinning unit.³ Two types of blends were encountered. First there were blends in which the melts were compatible as judged by transparency of the blends and interchange rates equal to those predicted from rate constants derived from model studies. In these blends (e.g., nylon 66 with the polyamide from *m*-phenylenediamine and adipic acid [MPD-6] or with 6I isophthalamide), holdup time in the melt was controlled so that the per cent interchange based on the stiff polymer component generally did not exceed 3%, and thus the average chain length of this component exceeded 200 Å. Since the number of interchanges must be the same

for both components, the per cent interchange based on the nylon 66, which was always the major component, usually did not exceed 0.8% so that its average chain length exceeded 550 Å. The melting point of the blend was thus within one or two degrees of that of nylon 66 homofiber.

Amide interchange was determined by a turbidometric titration with H₂O of solutions of fibers in 98% formic acid.³ Calibration curves for this procedure were obtained from interchange rate constants determined from a study of model compounds (details of this study will be given in a future publication) and from data on random copolymers (e.g., nylon 66 with 1–10% 6I) both of which gave equivalent results.

Data on the glass transition for fibers from the blends were obtained from dynamic mechanical measurements on dry fibers at a strain frequency of 0.1 cycles per second, with a strain amplitude of $\pm 0.8\%$. The temperature of maximum work loss is referred to as T_g .

Flat spot results are obtained either from a laboratory test which simulates the stress and temperature cycles appropriate to a passenger tire operating at high speeds³ or from actual tire data. A close correlation has been established between the predictions of the laboratory test and tire data.

RESULTS AND DISCUSSION

In work with compatible blends of ring-containing, high- T_g polymers with nylon 66, the effect of increasing degrees of amide interchange on flat spot level was about 2.5 mils per per cent interchange (based on the minor component) for a blend containing 20% stiff polymer. The rate of interchange was proportional to the carboxyl endgroup concentration of the melt and, for example, with 6I dispersed in nylon 66, was in the range of 1–2% per 5 min of holdup time at 285–300°C. There is evidence that the stiff polymer in the solid fiber is aggregated, even though such aggregates could not always be readily seen in the electron microscope. Indirect evidence and reasoning which support the conclusion that aggregates of the minor component exist in fibers from compatible melt blends are:

1. The components are generally not isomorphous and the melting points of the stiff polymers were frequently less than those of the major component (i.e., nylon 66). Since x-ray analysis shows that the major component generally forms its normal crystal structure, one would expect that crystallization of the major component should force consolidation of the reinforcing polymer. However, since the matrix becomes fairly rigid at this point and since a block copolymer is formed, long-range migration of the reinforcing polymer to form large aggregates would not be possible.

2. Amide interchange rate in the solid fiber at 231°C for a typical blend (e.g., nylon 66 with 6I) was only 1.4% in 16 hr, whereas a low molecular weight amide (*n*-hexylcaproamide) dispersed in nylon 66 gave 40% interchange in 16 hr at the same temperature. The fact that solid-phase polymerization rates are quite fast in the fiber at the same tempera-

ture does not make it plausible that mobility factors alone are involved and points to incompatibility in the solid fiber as a more reasonable explanation.

3. At higher concentrations of the minor component (in the range of 30-40%), one can actually see the aggregates in a Stereoscan microscopic examination of the fiber surface.

Some of the blends studied were of polyamides which were not compatible in the melt, and aggregates were readily seen in electron micrographs of fiber cross sections. In such blends, the aggregate size in the melt is a function of degree of incompatibility and the mixing shear stress. Aggregate size and l/d in the drawn fiber depend, in addition, on the degree of attenuation from the spinneret to the drawn yarn and on whether stresses in drawing are sufficient to rupture the aggregates. In these incompatible blends, the per cent amide interchange tends to be lower because of the lack of intimate contact between the components.

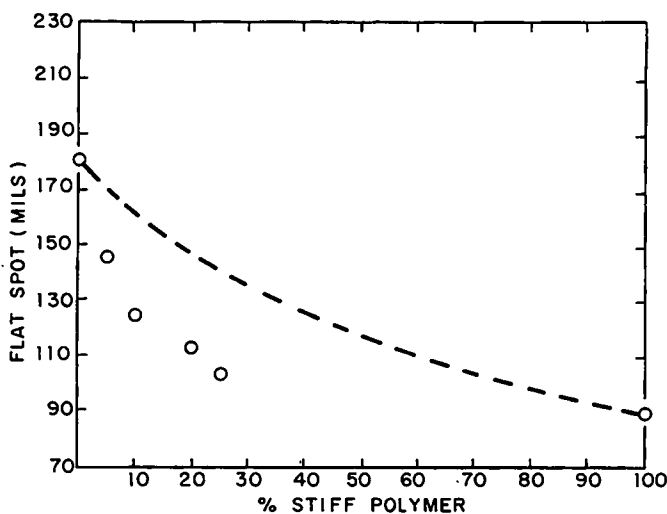


Fig. 3. Flat spotting (0.7% H₂O) of compatible melt blends of nylon 66 with 6I or MPD-6.

We consider first the mechanical properties of fibers from compatible blends. Tire flat spot data for melt blends of nylon 66 with 6I or with MPD-6 at various composition levels are plotted in Figure 3. The dashed curve represents the relationship from Figure 2 which is the best that might be expected from a classical "springs-in-parallel" type of reinforcement. It should be noted that the observed flat spots are considerably below this curve. The corresponding positive deviation from "ideality" in the modulus-versus-composition relationship is shown in Figure 4. The point for 100% stiff polymer is deduced from the orientation in the blend of the stiff polymer in comparison with the modulus-versus-orientation relationship for the high-modulus homopolymer. The

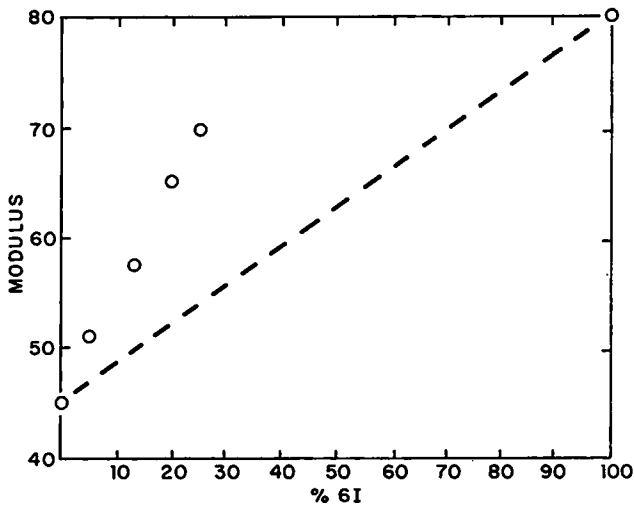


Fig. 4. Moduli of blends of nylon 66 with 6I.

very rapid increase in T_g (i.e., temperature of maximum work loss) for these systems is shown in Figure 5.

To explain this unusual degree of reinforcement, we have invoked the following hypotheses: (1) One or more layers of the lower modulus polymer are firmly bound to the reinforcing polymer and tend to act as if they were stiff polymer. The existence of an immobilized layer of substrate molecules on a reinforcing agent has been indicated in NMR studies of rubber reinforced with carbon black.⁴ Abnormally high dynamic elastic moduli have also been observed in blends of polystyrene with polyethylene and attributed to the existence of a diffuse interphase layer.^{5,6}

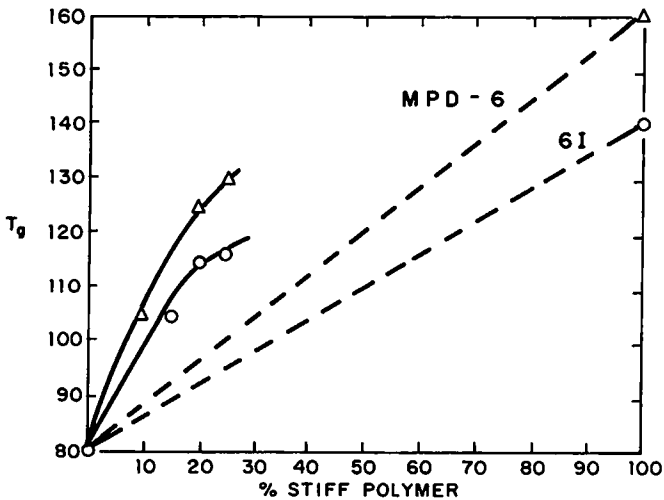


Fig. 5. T_g of melt blends of nylon 66 with 6I or MPD-6.

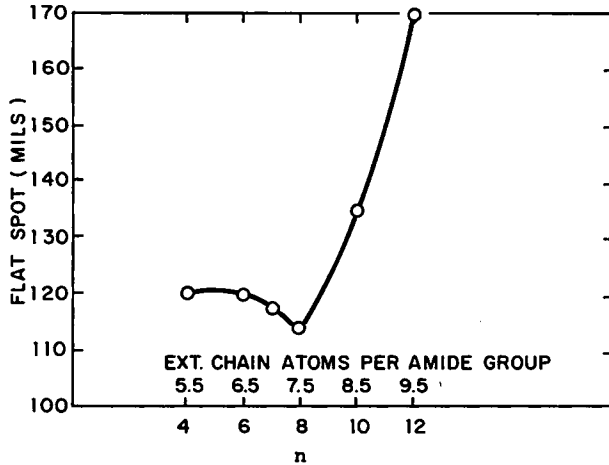


Fig. 6. Effect of hydrogen bonding on reinforcement in blends of nylon 66 with 15% n-I.

(2) The weight fraction of this surface layer is only appreciable when the stiff polymer aggregates are quite small in diameter (especially when less than 100 Å). (3) A relatively high frequency of hydrogen bonding sites is required on both components. Further discussion and elaboration of these hypotheses follow.

To study the effect of hydrogen-bonding frequency, a series of isophthalamides (4-I to 12-I) were blended with nylon 66 at the 15% blend level. The flat spotting propensity of these blends was determined by the laboratory procedure which has been shown to correlate well with actual tire flat spot data. These results are summarized in Figure 6. It can be seen that beyond 8-I the degree of reinforcement falls off very rapidly and much more than would be expected on the basis of the continuous reduction in stiff polymer modulus with progressive reduction in ring content.

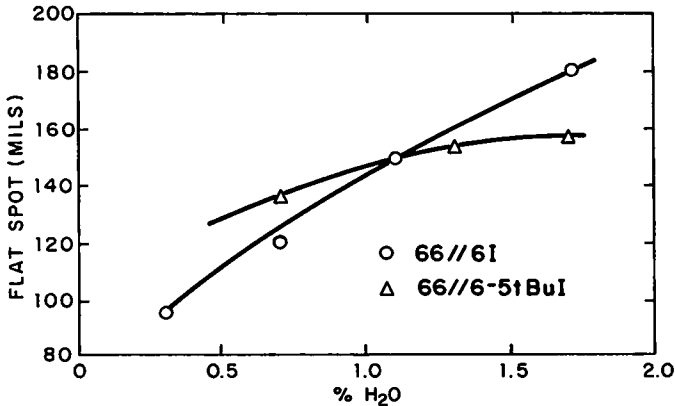


Fig. 7. Moisture sensitivity of blends of nylon 66 with 15% of 6I or 6-5t-BuI.

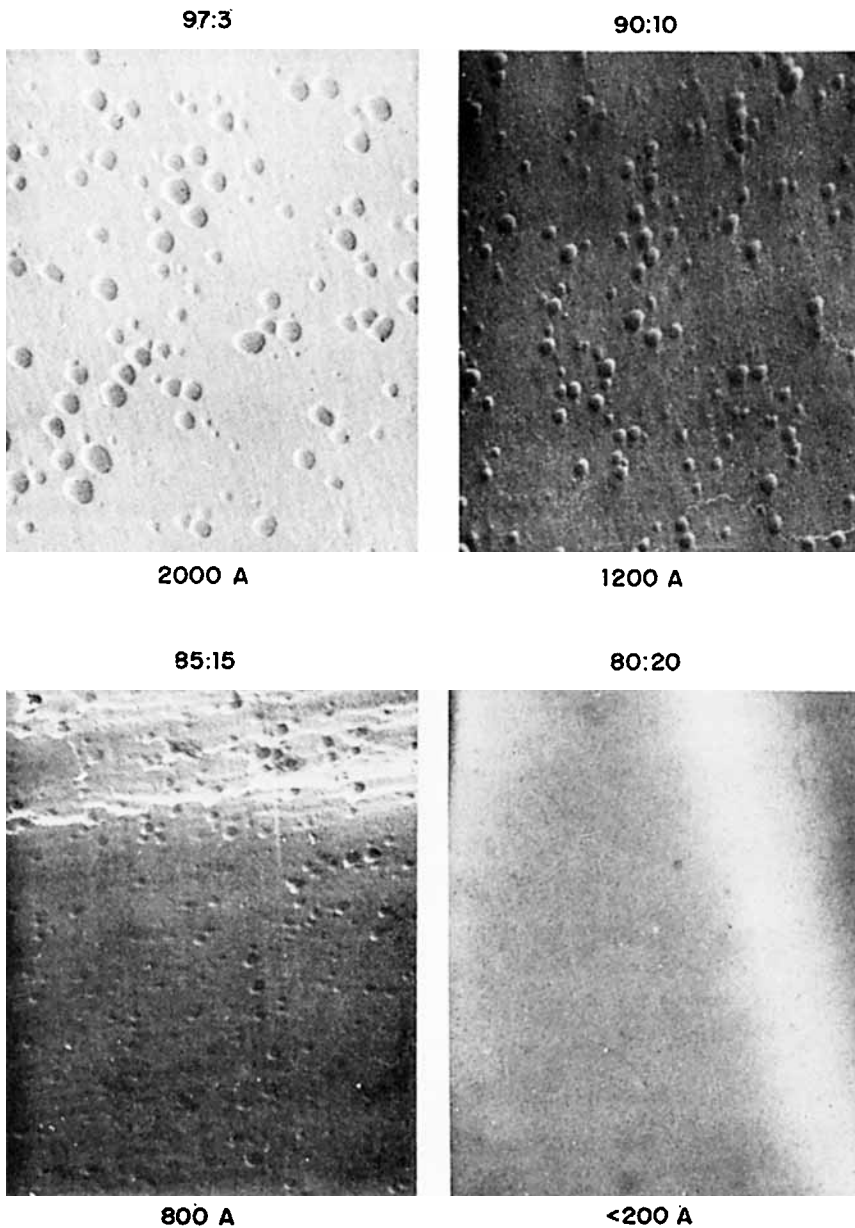


Fig. 8. Electron micrographs ($27,000\times$) of nylon 66 blended with 15% of various 6-5t-BuI/6I random copolymers.

Thus, it appears that the critical amide frequency for obtaining non-classical reinforcement is about one amide group per eight to nine extended chain atoms.

The importance of having small aggregates is shown by the following series of experiments. One of the difficulties inherent in the nylon 66/6I

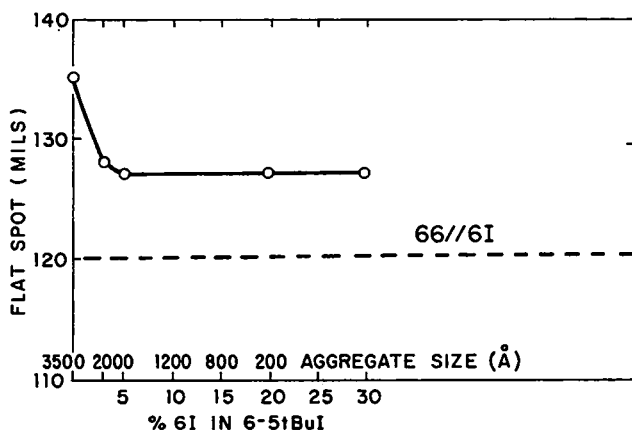


Fig. 9. Flat spotting of melt blends of nylon 66 and 20% 6-5*t*-BuI copolymers.

blends is a high sensitivity of the degree of reinforcement to fiber moisture content. This is shown in Figure 7. On continued investigation, it was found that placing a *tert*-butyl group in the 5-position of isophthalic acid resulted in a considerable reduction in moisture sensitivity (Fig. 7). However, the degree of reinforcement at low moisture content was not as great as with 6I, even though 6-5*t*-BuI appears to have a higher T_g than 6I. Microscopic examination of the fiber cross sections, as well as visual observation of blended melts, showed that these polymers were incompatible and aggregate sizes in the range of 3000 Å were observed. In addition, it was found that the orientation of the 6-5*t*-BuI in the drawn fiber was not as high as for 6I. It was reasoned that copolymerizing a certain amount of 6I into the 6-5*t*-BuI might result in significantly im-

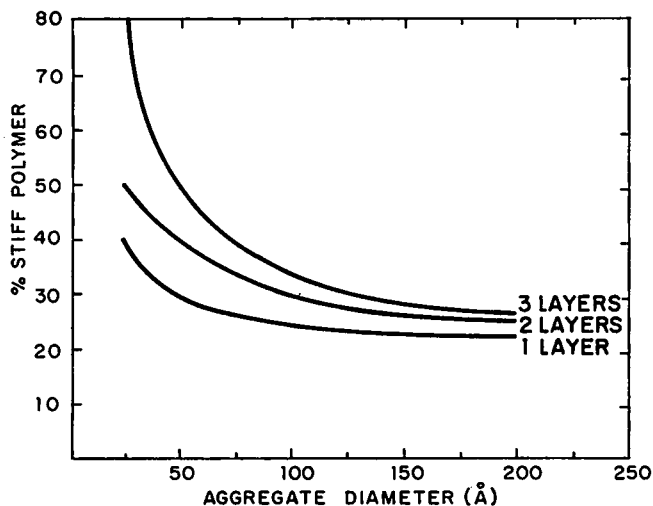


Fig. 10. Effective "per cent stiff polymer" vs. aggregate diameter for 20% blend (5 Å layer).

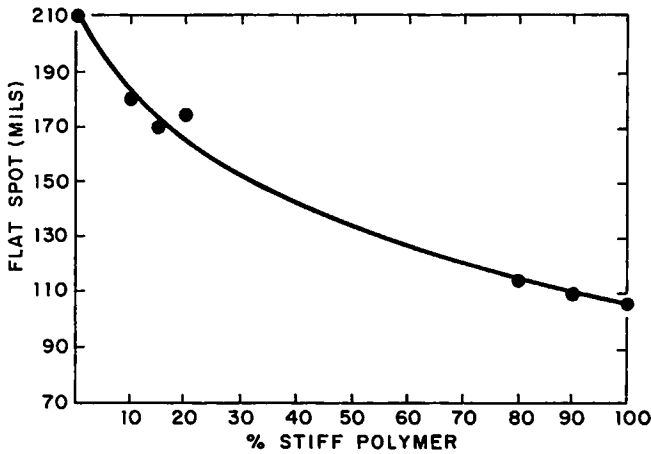


Fig. 11. Flat spotting of blends of nylon 66 with 2Me6T.

proved compatibility and thus increase the degree of reinforcement. The photographs in Figure 8 show that a marked increase in compatibility results as 6I content of the stiff polymer is increased up to 20%. The effect of this reduction in aggregate size on flat spot is shown in Figure 9, and one can see that there is a significant effect. At 6I contents up to 20% in the stiff polymer, there is no significant increase in moisture sensitivity so that the improvements carry through at the higher moisture contents which are normally encountered in tire operation. The increased compatibility also promoted increased orientation of the stiff polymer component.

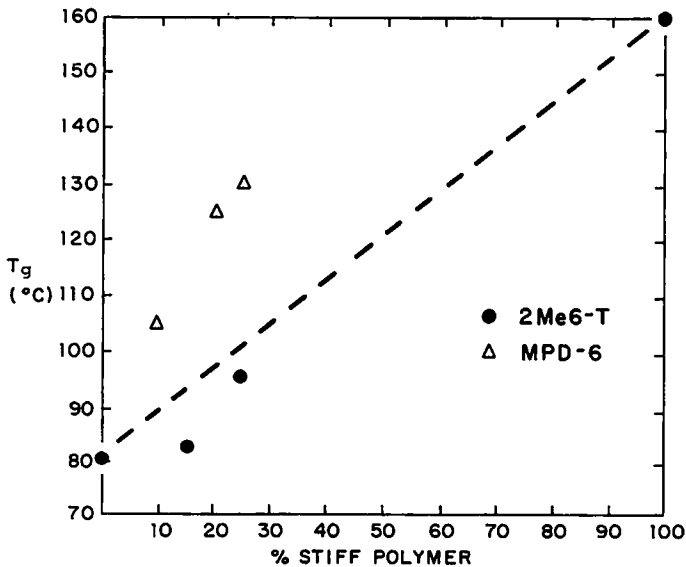


Fig. 12. T_g of blends of nylon 66 with 2Me6T.

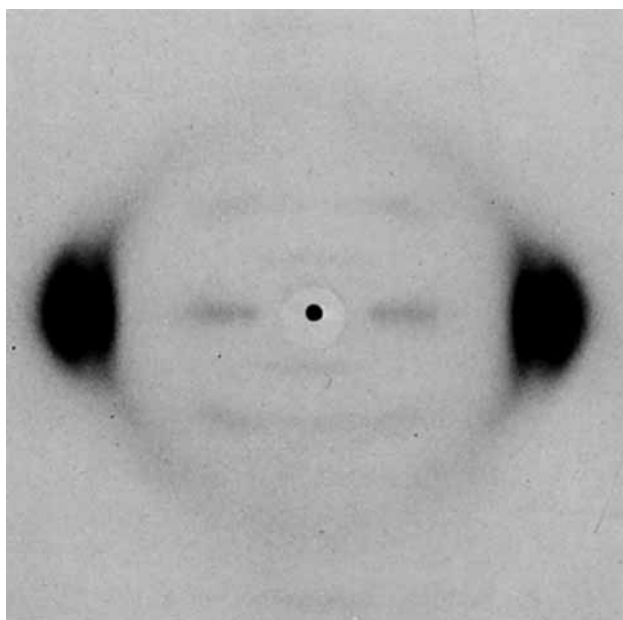


Fig. 13. X-Ray diagram of nylon 66 at room temperature.

We have calculated the "effective stiff polymer content" versus aggregate diameter for a 20% blend assuming a single bonded 5-Å layer of the lower-modulus polymer. We have also made the calculation for the cases where it is assumed that the layer effect propagates out to two or three layers. These are summarized in Figure 10. It can be seen that a dramatic increase occurs for aggregate diameters less than 100 Å. Of course, the actual situation might involve bonded layers which decrease gradually in T_g , so that the effective number of high T_g layers calculated might be less than the number of true layers of progressively decreasing T_g .

We can summarize the requirements for "nonclassical" or superreinforcement as follows: (1) a bonding site frequency larger than one per eight to nine extended chain atoms; (2) aggregate diameters less than 500 Å and preferably less than 100 Å; and (3) the greatest possible aggregate l/d .

In the course of this investigation, another unusual effect was observed. When the polyamide based on 2-methylhexamethylenediamine and terephthalic acid (2Me6T) was used as the reinforcing agent, the reduction in flat spot propensity was not nearly as great as that observed with the previously described blends, in spite of the fact that this terephthalamide is even higher in modulus as a homofiber than the other polymers. These results are shown in Figure 11. Similarly, the increase in T_g was also disappointingly small (Fig. 12). Further investigation of this blend showed that it was subject to a rather unusual crystallization behavior. In the first place, it should be noted that nylon 66 undergoes a crystalline transition above 160°C from its normal triclinic form to a hexagonal

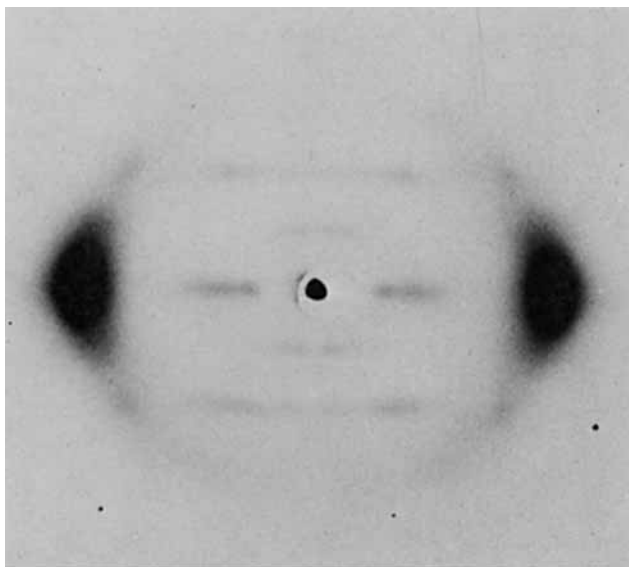


Fig. 14. X-Ray diagram of nylon 66 at 180°C.

form (Figs. 13 and 14). It was observed in the blends with progressively increasing concentrations of 2Me6T that an increasing hexagonal character was present in the blend yarns at room temperature. Evidently, because of the isolength relationship between nylon 66 and the stiff polymer and the high melting point of the latter, the two polymers were cocrystallizing, and the presence of the not quite isomorphous stiff component was inhibiting the normal transition to the triclinic form (Fig. 15). In contrast, the 66/6I blend shows the normal nylon 66 triclinic crystal structure (Fig. 16). The interpretation which we prefer to account for the relatively poor reinforcement in this system is that (a) cocrystallization wastes some of the

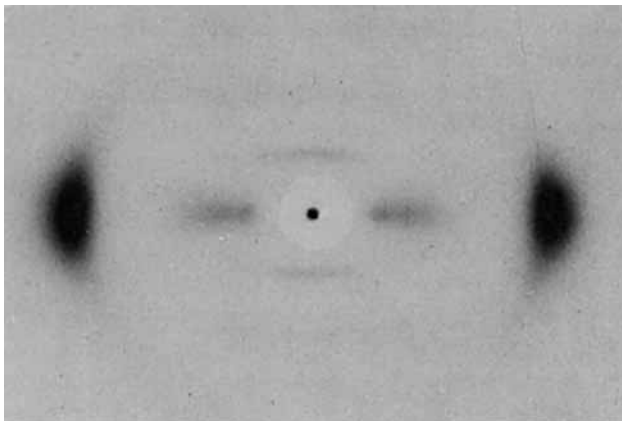


Fig. 15. X-Ray diagram at room temperature of the blend of nylon 66 with 20% 2Me6T.

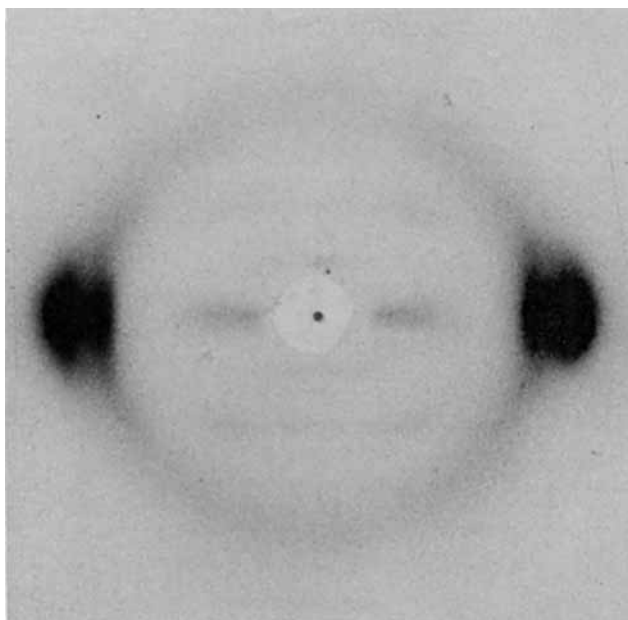


Fig. 16. X-Ray diagram at room temperature of melt blend of nylon 66 with 20% 6I.

stiff polymer by placing it in the nylon 66 crystal which already has an extremely high modulus, and (b) it is not possible to form the type of aggregate structure which seems to be most effective. Thus, we must invoke an additional requirement for optimum reinforcement, that is, absence of isomorphism.

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