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The Effect of Anisotropy in Wet Spinning Poly(P-Phenyleneterephthalamide)

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Abstract

In this paper a description is given of series of experiments which demonstrate the effect of the anisotropy of poly(p-phenyleneterephthalamide) solutions in concentrated sulphuric acid on the tensile properties of wet spun yarn. It will be shown that, in agreement with the well-known rules for spinning processes, the orientation of the molecules produced by stretching essentially contributes to the mechanical properties of the spun yarn, whereas anisotropy tends to have an adverse effect on the formation of fibers.

Introduction

Solutions of the polymer poly(p-phenyleneterephthalamide), or abbreviated here as PPTA, in sulphuric acid very well satisfy the theory of FLORY [1] regarding solutions of rigid rod polymers. This theory predicts the formation of a liquid crystalline optically anisotropic phase above a certain concentration. As has been shown by HERMANS [2], at this transition the viscosity at low shear shows a discontinuity in that it decreases. On increasing shear, however, this discontinuity will vanish. This implies that the order of the rigid rodlike molecules in the solution produced by shear can overrule that for the liquid crystalline solution at low shear.

In a number of publications it is suggested that anisotropy is of advantage in spinning fibers [3],[4]. Evidently, such advantage has to be considered against the background fact that in all solution spinning processes the mechanical properties improve with increasing concentration [5]. Considering this general rule from the scarcely available experimental data published up to now, it can only be concluded that anisotropy has no effect at all on the properties of fibers.

Experimental

To compare the properties of PPTA yarn spun from diluted isotropic dopes with those of anisotropic concentrated dopes, a series of solutions in 99.8% sulphuric acid were prepared from a batch of PPTA polymer having an inherent viscosity (η_{inh}) of 4.2.

The polymer was prepared in accordance with the method described in [6]. The spinning machine consisted of a container, a spinning pump, a

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filter and a spinneret provided with 96 holes 75 μm in diameter. By means of a heating jacket the temperature of the unit was kept at 40°C. The dopes were spun into a water bath of 40°C at a jet velocity of 20 m/min. The spun yarn was collected on a winder, washed for 24 hours in a stream of cold water and dried. After twisting the yarns to 120 t.p.m., their properties were measured on an Instron tester.

In a first series of experiments, the yarns were collected at the same rate as that at which they were extruded. In a second series of experiments the denier of the filaments was kept constant by increasing the speed of collection. When spinning with a spinneret immersed in the water bath it was found that spin stretch ratios above about 2 could not be realized because of the very fast coagulation of the PPTA-sulphuric acid solutions in the water bath. This is a well-known situation in wet spinning processes. Higher stretch ratios are usually obtained either by adapting the spinning bath [5] or by placing the spinneret just above the bath (air gap spinning). The latter method is known from the spinning of acrylics and rayon [7] and was proposed for the wet spinning of wholly aromatic polyamides [8]. It was also used in the second series of experiments.

Another way of showing the effect of anisotropy is to compare the properties of yarns spun from low molecular weight isotropic solutions and from high molecular weight anisotropic solutions, using the same polymer concentration. For this experiment a series of 10% solutions of polymers having different molecular weights were prepared and spun into yarn at a spinstretch ratio of 1.5.

Results

The phase diagram of PPTA solutions in concentrated sulphuric acid is given in Figure 1.

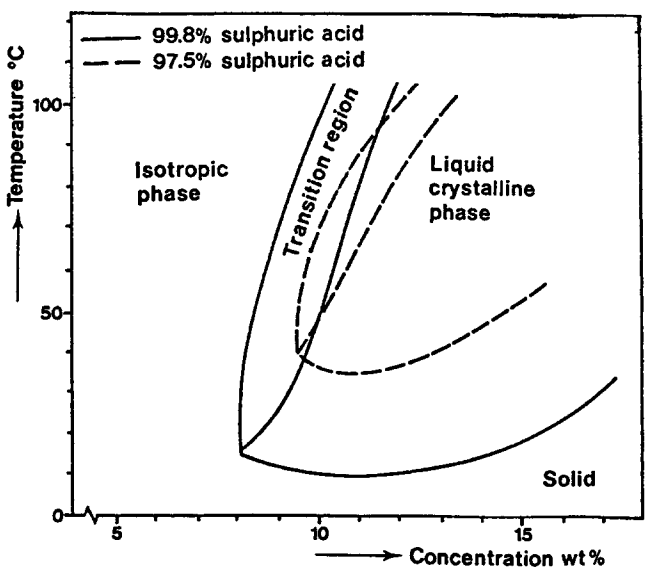

Figure 1 : Phase diagram of solutions of PPTA with n_{inh} of 4.2

The transition was determined on a polarizing microscope by recording the transmitted light on heating the sample at a rate of 2°C/min. In agreement with PAPKOV [9] a transition area was observed between the isotropic and the anisotropic phase.

Regarding the concentration of the sulphuric acid it should be noted that anisotropic solutions of PPTA can be obtained in sulphuric acid having a strength of about 96% or higher. In view of the degradation of the polymer in sulphuric acid suitable concentrations range from 97 to 100%.

The rheological behaviour of the solutions at 40°C is shown in Figure 2. This figure clearly demonstrates the viscosity maximum at low shear as a result of the transition to the liquid crystalline phase. On increasing shear the maximum shifts to lower concentrations. These results are in good agreement with the observations made by HERMANS [2] and support the suggestion made by CIFERRI [10] regarding the overruling effect of shear on the order of the molecules. GULRICH [4] in his search for a "jump" in the fibre properties by passing from the isotropic into the anisotropic phase came to the same conclusion.

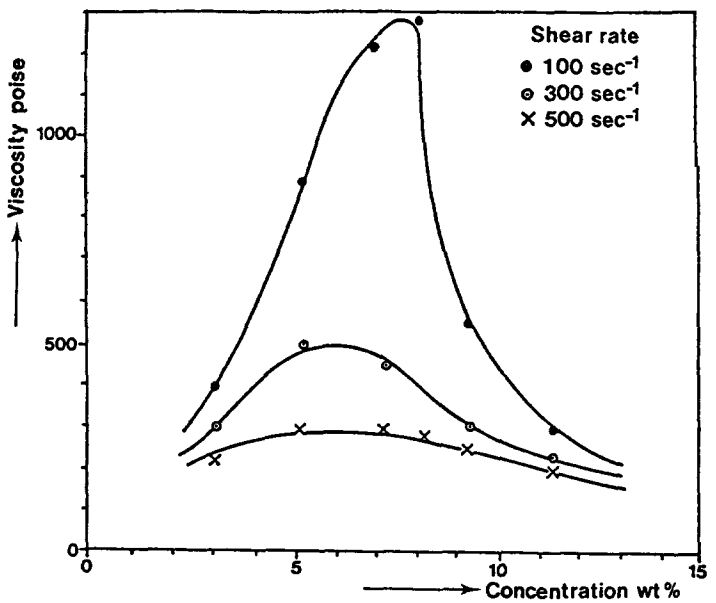

Figure 2: Viscosity of solutions with PPTA with a n_{inh} of 4.2 in concentrated sulphuric acid at different shear rates at 40°C

The properties of the spun yarns are shown in the Figures 3, 4 and 5. The situation in which the yarns were collected at the same rate as that at which they were extruded, i.e. at a spin stretch ratio of 1, is represented in Figure 3. In these series of experiments both the modulus and the tenacity show a maximum before the transition to the anisotropic phase. Figure 4 shows the results for the situation in which the filament denier is kept constant by increasing the spin stretch ratio with the concentration. Evidently, upon increasing the spin stretch ratio the orientation increases

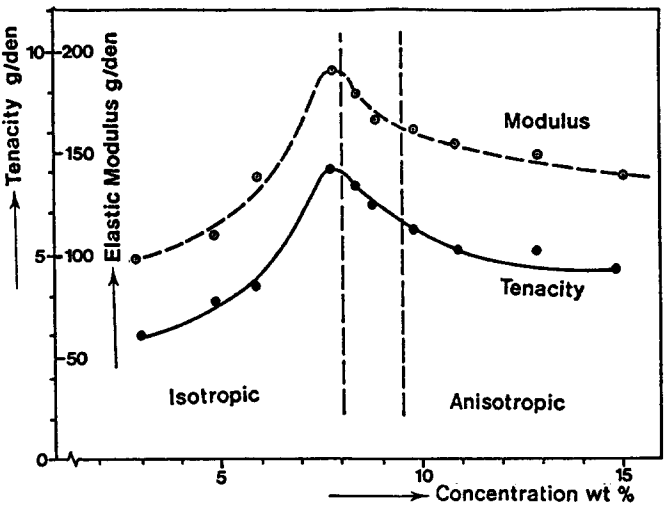

Figure 3: Properties of as-spun PPTA yarn spun from solutions in concentrated acid at 40°C and at a spin stretch ratio of 1.

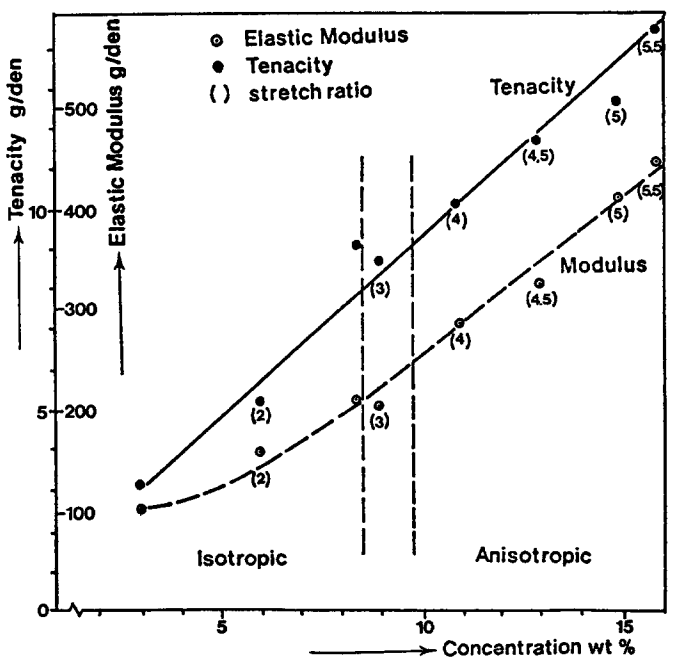

Figure 4: Properties of PPTA yarn spun from concentrated sulphuric acid solutions at 40°C with the spin stretch ratio being increased in proportion to the concentration.

and consequently also modulus and tenacity of the spun yarn.

Another way of showing the effect of anisotropy on the tensile properties of PPTA is to compare the tensile properties of yarns spun from low molecular weight isotropic solutions and from high molecular weight anisotropic solutions, using the same polymer concentration. The results of these experiments are shown in Figure 5.

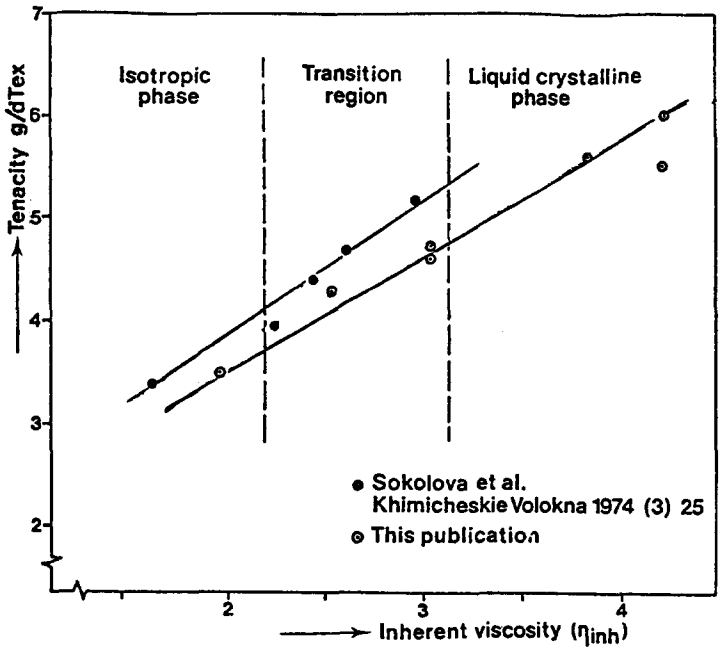

Figure 5: Tenacity of as-spun PPTA yarn spun from 10% solution in concentrated sulphuric acid at a spin stretch ratio of 1.5.

Discussion

It will be evident that an effect of anisotropy is to be sought in a difference in orientation of the molecules in the filaments spun from isotropic and anisotropic solutions. This effect can be observed by the change of the elastic modulus or the tenacity. As appears from the work of NORTHOLT [11] the modulus is a direct measure of orientation.

The difference sought between isotropic and ansitropic solutions will be the most pronounced in spinning under the conditions of low shear and extensional stresses. This appears clearly from Figure 2, which shows that this difference vanishes with increasing shear. At higher shear rates the initially isotropic solutions also become anisotropic, which is a well-known effect occuring in a stream of polymer solution [12].

For these reasons the first series of experiments, performed at the lowest spin stretch ratio, i.e. 1, will be the most revealing as far as the effect of anisotropy is concerned.

The results found for this situation are summarized in Figure 3. For the iso-

tropic solutions both the modulus and tenacity show the normal behaviour of wet spinning solutions, viz. the higher the concentration the better the mechanical properties obtained.
In contrast with this general rule for solution spinning processes the use of anisotropic solutions is attended with the properties declining with increasing concentration. In view of the relation between modulus and orientation this can only point to a decrease of the degree of orientation as a result of the formation of liquid crystals.

In the second series of experiments the denier of the filaments was kept constant by increasing the spin stretch ratio in propertion to the concentration. The effect of filament denier on tenacity is therefore eliminated. Both modulus and tenacity show the normal behaviour of a steady increase with the stretch ratio (Figure 4).
At the transition to the anisotropic phase no significant discontinuity could be observed. Obviously, the obstructing effect of the liquid crystals disappears on increasing the spin stretch ratio.
The same conclusion can be drawn from Figure 5, which shows the tenacity in relation to the molecular weight of PPTA yarns spun from 10% solutions at a spin stretch ratio of 1.5. Apparently, the results found are in good agreement with those of Sokolova et al. [13] and do not show any discontinuity upon passing from the isotropic into the anisotropic region.
From similar experiments GULRICH [4] concluded that as a result of the overruling influence of concentration and shear under normal spinning conditions no effect of anisotropy can be observed.

From the above it can be concluded that, in agreement with the well known rules for spinning processes, the orientation of the molecules produced by stretching essentially contributes to the mechanical properties of the spun yarn, whereas anisotropy tends to have an adverse effect on the formation of fibers.

Like for other polymers also for spinning PPTA the optimum conditions have to be sought in highly concentrated solutions of high molecular weight polymer and the use of high spin stretch ratios. These optimum mechanical properties also can be realized at a low spin stretch ratio and in hot-drawing the as-spun fibers. [10] A combination of both, the use of an air gap to realize high spin stretch ratios and hot drawing, has been proposed in a Monsanto patent [8]. In illustration Figure 6 shows the experimental data found for these various methods in the literature.

Hence, irrespective of the method, the ultimate tenacity that can be obtained finally only depends on the molecular weight. A few years ago WILFONG and ZIMMERMAN [14] mentioned this factor as the main source for the steady improvement of strength.
As has been outlined by MARK [15] this improvement will continue until a limiting strength is approached which is for all polymers reached at a degree of polymerization of about 600.
Although we are past the stage of the initial rapid increase, a further increase in strength may still be expected as a result of further increasing the molecular weight of the polymer.

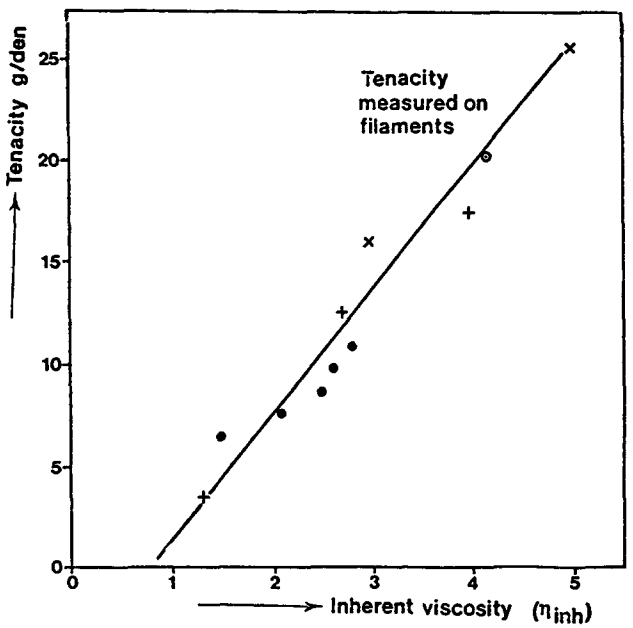

Figure 6: Tenacity of PPTA filaments in relation to the molecular weight made by different spinning and drawing methods.
+ US patent 3 671 542, wet spinning and hot drawing.
• Sokolova et al. [13]: Wet spinning and hot drawing.
x US patent 3 767 756: air gap spinning.
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