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Techniques for the Evaluation of the Drawing Behavior of Experimental Fibers

K. TREGONNING* and E. DYSON, *Schools of Textiles, University of Bradford, Bradford, Yorkshire, England*

Synopsis

Equipment and techniques are described which have been developed for determining the drawing behavior of fibers from novel polymers which are available only in very small quantities. Emphasis is placed upon information obtained from the stress–strain diagrams of the fibers during drawing. A parameter, the reinforcement factor, is described which reflects the degree of orientation induced by drawing short lengths of fiber in a discontinuous manner. This parameter exhibits maxima at various combinations of temperature and draw rate, and the relationship between the corresponding temperatures and draw rates is shown to be logarithmic. The parameter is used to predict temperatures and draw rates which will give fibers having a high degree of orientation and good tensile properties when drawn continuously. The application of these techniques to give acceptable fibers from poly(*m*-phenylene adamantane-1,3-dicarboxamide) is described. This material is of interest as one possessing a high degree of thermal stability, and the best fibers produced to date have a tenacity of 4.0 g per denier, an initial modulus of 60 g per denier, and a break extension of 16.0%.

INTRODUCTION

After extrusion of a polymer melt or solution to form a filament, the filament is usually stretched to several times its initial length. It is this process which, by inducing molecular or crystallite orientation, is largely responsible for determining the characteristic mechanical properties of the fiber.

The drawing of polymeric materials as a phenomenon has been investigated by many workers and the drawing properties of synthetic fibers which are already commercially established have been examined in detail. However, although several publications concerning new fibers have been made available, little has been published on the techniques used to evaluate the fiber-forming potential of new materials.

The present paper describes techniques that have been developed for the evaluation of fibers which, because of their experimental nature, are only available in small quantities. The application of the techniques in the evaluation of fibers from poly(*m*-phenylene adamantane-1,3-dicar-

* Present address: U. K. Atomic Energy Authority, Dounreay, Caithness, Scotland, United Kingdom.

boxamide) (mPAD) is described in detail. This fiber, which is of interest because of its thermal stability, has been described elsewhere,[1] and the polymer repeat is shown in Figure 1. Because of the experimental nature of the polymer, it was available in only very small quantities (7.0 g in total), and this greatly influenced the techniques employed.

Drawing behavior can be described by several parameters, the most common being mode of drawing, i.e., whether cold, hot, or plastic flow.[2] Others are draw ratio at break, breaking stress, yield stress, and, in the cold-drawing mode, natural draw ratio. The variables affecting these parameters are numerous, but the most important are temperature and rate of drawing. Other factors which can be important are denier, moisture content, degree of crystallinity, and preorientation.[3,4] Because of the limited supplies of material (which made control of the secondary variables difficult), the variables which received the most attention in the present studies were temperature and draw rate. mPAD is essentially amorphous

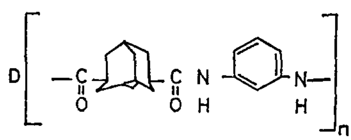

Fig. 1. Poly(*m*-phenylene admantane-1,3-dicarboxamide).

in the as-spun state,[5] and so one would expect to be able to apply molecular concepts, particularly Boltzmann's principle of time–temperature superposition. If the drawing characteristics of short lengths of fibers could be used to indicate those combinations of temperature and draw rate which give maximum orientation, then extrapolation of these optimum values would suggest appropriate conditions for the continuous drawing of longer lengths of fiber.

The experimental procedure is based on this philosophy and is divided into two stages:

1. Short lengths of fiber are drawn, using a tensile testing machine, at various rates and temperatures. A reinforcement parameter which can be obtained from the load–extension characteristics is used as a qualitative measure of the induced degree of orientation. The corresponding temperatures and rates at which maximum reinforcement occurs are noted and plotted semilogarithmically. This enables the range of corresponding temperatures and rates within which fibers are to be continuously drawn to be decided upon.

2. Continuous filaments are drawn on a small-scale drawing machine at rates and temperatures decided by the previous experiments, and the properties of the drawn fibers are determined. In addition to tensile properties, a molecular orientation factor is measured using a sonic modulus technique.

APPARATUS AND INSTRUMENTATION

Apparatus Used to Determine Load–Extension Characteristics of Fibers During Drawing

The basic equipment used was an Instron Universal Tensile Testing Machine, Model T.M.-M. A specially designed hot plate and fiber mounts were used with the Instron to draw short lengths of fiber at different rates and temperatures. This small-scale drawing rig enables fibers to be drawn in intimate contact with a hot surface, thus simulating to some extent the conditions found in continuous drawing. The apparatus is illustrated in position on the Instron cross head in Figure 2. The body of the device is constructed almost entirely from asbestos composite, employing a narrow brass strip to transfer heat from a 100-watt cartridge heater to the fiber being drawn. The upper half of the device has freedom of movement in a direction perpendicular to the fiber to allow the heated surface to be moved quickly up to the mounted fiber.

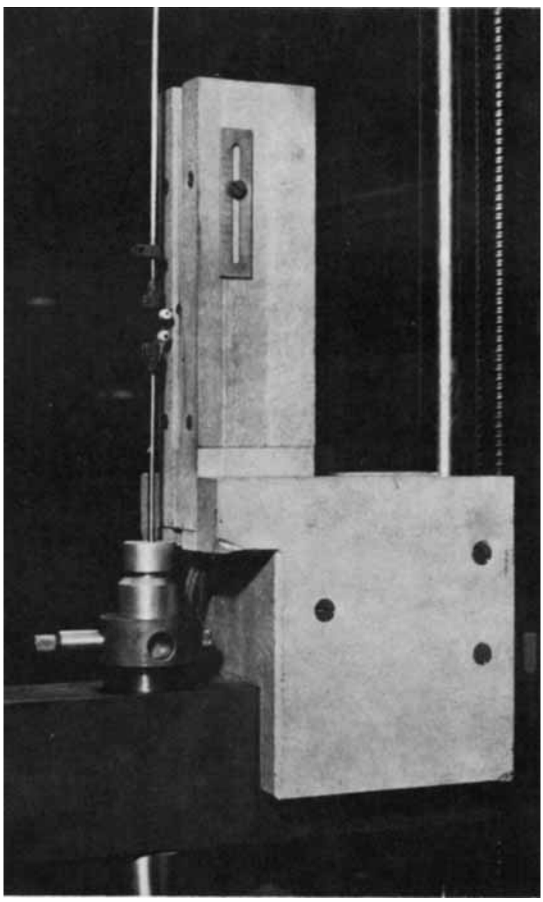

Fig. 2. Small-scale equipment for determining load–extension characteristics of fibers.

The temperature of the brass strip is controlled by a stepless controller between ambient temperature and 400°C to an accuracy of ±1°C. The positioning of the thermocouple hot junction on the brass strip and the sectional shape of the strip itself ensure that a good indication of the surface temperature of the brass is obtained without danger of interference with the fiber or fiber mounts during drawing.

The fibers are mounted for drawing on small P.T.F.E. capstan drums attached to two stainless-steel extension tubes, which are in turn connected to the Instron load cell and cross head, respectively. A small counterweight attached to the upper extension rod provides a small positive pressure between the P.T.F.E. capstan and the brass strip to ensure intimate contact between fiber and strip during drawing.

Continuous Drawing Apparatus

The apparatus used for the continuous drawing of filaments is shown in Figure 3. The mode of operation is that the feed rollers feed filament onto a hot plate, and the draw rollers take up the filament at a speed greater than that of the feed rollers by an amount equal to the applied draw ratio. Both halves of the machine are driven from one fractional horsepower d.c. motor with speed controller which is mounted on the output unit. The motor drives a master selsyn which is connected to a slave on the input unit, and this slave drives the feed rollers. The motor drives the output rollers and take-up unit through a mechanical variable-ratio unit. Thus, draw rate and draw ratio can be controlled independently by adjusting the motor speed and the variable ratio unit, respectively. This arrangement of the drive between input and output rollers permits their relative positions to be varied widely so that drawing can take place over hot plates of various lengths or alternately around a heated pin.

Normally, to string up the apparatus, filament is taken from a package on a free-running spindle, wrapped several times round the feed rollers (to

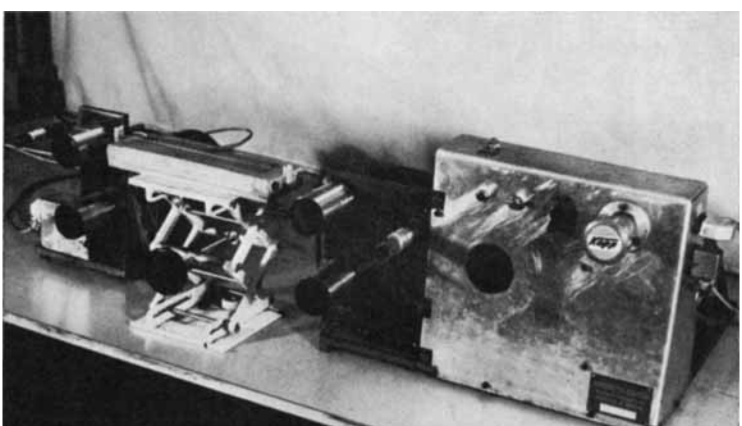

Fig. 3. Continuous-drawing apparatus.

avoid slippage), passed over the hot plate, and wound several times round the draw rollers and then onto the take-up package. When only a very limited quantity of as-spun fibers is available, too much filament was wasted using this method; so undrawn filament is fed onto the upper feed roller prior to drawing by reversing its direction of rotation, and the drawn fiber is collected on the upper draw roller and later packaged by hand.

Heat was applied to the fiber during drawing by an 8-in. convex brass hot plate whose temperature was controlled between ambient and 400°C by a stepless controller.

Measurement of Molecular Orientation

Several techniques are available for measurement of molecular orientation in drawn fibers, the commonest being measurement of optical birefringence. However, this technique is tedious, involving a large number of measurements in order to obtain a statistically meaningful orientation factor. Use of this technique would have involved further complications if applied to mPAD fibers because of their noncircular cross sections.

In recent years, several workers have used acoustic methods of measuring molecular orientation and have observed good correlation between birefringence and molecular orientation as measured by this technique.[6–9] It was felt that this would be a good method of obtaining an orientation factor for drawn mPAD filaments. The method involves velocity of sound measurements in oriented and unoriented samples of a fiber. Moseley's equation[8] for molecular orientation (α) is

$$\alpha = 1 - (C_u/C)^2$$

where C_u is the velocity of sound in the unoriented filament and C is the velocity of sound in the orientated filament. Alternatively,

$$\alpha = 1 - E_u/E$$

where E_u is the sonic modulus of the unoriented filament and E is the sonic modulus of the oriented filament.

To measure the sonic modulus experimentally, a filament is laid across two notched piezo-electrical crystals and tensioned by a small weight. One crystal is fed with a sinusoidal voltage and the resultant acoustic signal is transmitted by the filament to the second crystal whose output is amplified and displayed on a cathode ray oscilloscope. The input signal is varied in frequency until resonance occurs in the filament and the frequency is accurately measured using a digital counter. Under these conditions, the velocity of the acoustic signal in the filament is the product of resonant frequency and twice the separation of the transducers. The transducers used in the present instance had almost uniform response over the range 700 to 3.5 kHz; and with a transducer separation of 50 cm, this enabled sonic noduli between 3.6 and 120 g/den to be measured, a more than adequate range.

LOAD–EXTENSION DRAWING

Choice of Reinforcement Parameter

The degree of reinforcement as discussed by Thompson[2] reflects the general reinforcing effects of orientation and crystallization induced in a fiber by drawing and is usually described by the stress in the fiber as it is being drawn. The degree of reinforcement at break obtained from a load–extension diagram would be as follows:

$$\frac{\text{breaking load} \times \text{draw ratio at break}}{\text{initial denier}} \text{ g/den.}$$

In the absence of strain-induced crystallization, this would reflect the degree of orientation induced at break.

During the early stages of the work, the use of the above parameter was made prohibitive by denier variation from filament to filament. However, although breaking stress is an increasing function of the degree of orientation, it is a decreasing function of temperature. Yield stress is also a decreasing function of temperature; and although it is to a lesser extent a function of the secondary variables previously mentioned, if the above parameter were divided by the yield stress, this might be expected to offset the temperature effects. The resulting dimensionless parameter, namely,

$$\text{reinforcement factor} = \frac{\text{breaking load} \times \text{draw ratio at break}}{\text{yield load}}$$

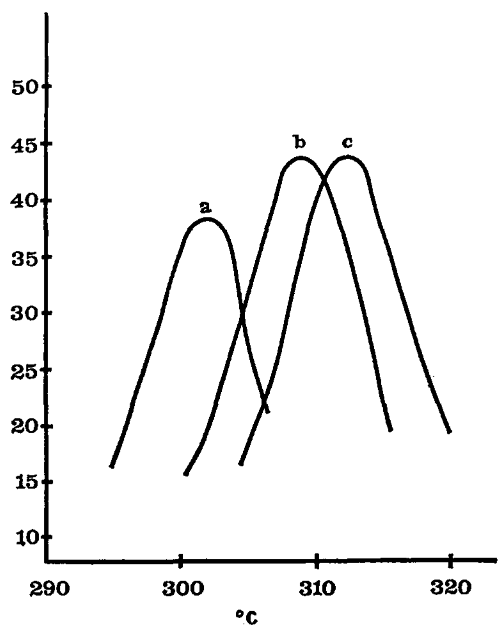

Fig. 4. Degree of reinforcement at break temperature at draw rates of (a) 1,000 % min^{-1}; (b) 5,000 % min^{-1}; (c) 10,000 % min^{-1}.

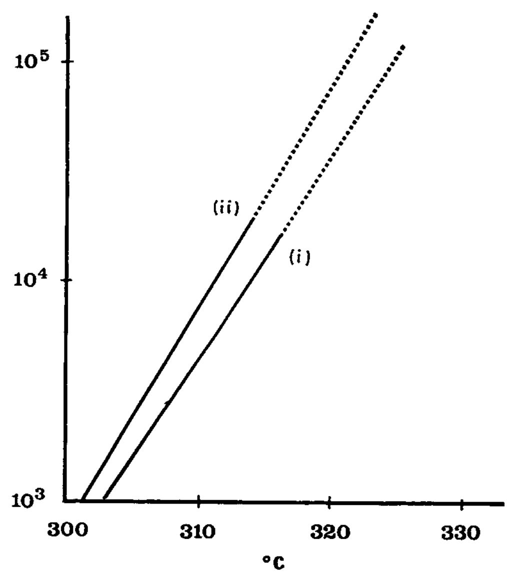

Fig. 5. Draw rate vs. position of maximum reinforcement on temperature axis: (i) early samples of mPAD; (ii) best sample of mPAD.

would be independent of denier (neglecting the effect of denier on yield stress and breaking stress). It was felt that this parameter was at least as valid as the first parameter, and it was used to describe reinforcement in the present studies.

The values of the reinforcement factor for the best sample of mPAD fibers (sample 4 of Table I) are shown in Figure 4. It can be seen that the reinforcement factor exhibits maxima at increasing temperatures as the rate is increased. The temperature–rate coordinates of the peaks are plotted for each of the different fiber types using a logarithmic rate scale in Figure 5. A straight line can be drawn through the rate–temperature coordinates, which makes possible extrapolation to the higher values of rate and temperature that are characteristic of continuous drawing.

CONTINUOUS DRAWING

Problems Associated with the Understanding of Continuous Drawing in Terms of Small-Scale Drawing Parameters

Extrapolation from the small-scale discontinuous drawing experiments can only be used to define the area within which the continuous drawing trials are to be carried out if an expression for draw rate in the continuous mode is found that corresponds to the draw rate applied by the Instron.

Several difficulties are involved in extrapolation between discontinuous and continuous drawing, even assuming that the extrapolation to high rates is valid. The temperature distribution in the discontinuous-drawing hot plate was reasonably constant over that length of the heated strip within which fibers were drawn. Two separate effects concerning temperature exist in the case of continuous drawing. One is the temperature gradient along the filament as it contacts the hot plate, the other is the transverse gradient within the filament due to the finite time required for the filament to reach its final temperature. This means that a complex situation can exist in which the filament draws at different rates, by varying amounts, on different regions of the hot plate, and that the length of the hot plate over which drawing takes place may vary with temperature. However, because of the characteristic properties of the polymer, which has been the main study to date, i.e., poly(*m*-phenylene adamantane-1,3-dicarboxamide), which does not draw at room temperature, the problem was simplified. Because of the critical dependence of draw ratio and tension on temperature, it is likely that most of the drawing will take place at maximum temperature. Problems of instability associated with spontaneous switching from hot drawing to plastic flow under certain conditions have been reported by Marshal and Thompson.[10] These problems were not expected to arise because filaments of mPAD would need to be drawn into the breaking region in order to correlate with the results obtained from the Instron experiments. For this same reason, problems associated with the cold-drawing mode and the possibility of the applied draw ratio being less than the natural draw ratio[10] would present no difficulty.

In order to derive an expression for draw rate, the length of the drawing zone (L) was assumed to be the length of the hot plate. It should be pointed out that although the filament travels some distance into the hot plate before it reaches maximum temperature, it also retains heat beyond the hot plate. If one assumes that a particle in the fiber moves with a constant acceleration through the drawing zone, it becomes possible to obtain a simple expression for draw rate in terms of L, draw ratio, and input roller speed:

$$\text{average draw rate} = \epsilon/\tau \text{ min}^{-1}$$

where ϵ is the total strain imposed by drawing and τ is the residence time in minutes in the drawing zone.

But

$$\epsilon = \text{D.R.} - 1$$

and

$$\tau = \frac{L}{{}^1/_2(V_1 + V_2)}$$

where D.R. is the draw ratio and V_1 and V_2 are the feed and draw roller speeds, respectively.

Therefore,

$$\text{rate} = \frac{(\text{D.R.} - 1)(V_2 + V_1)}{2L} \ \text{min}^{-1}$$

$$= \frac{V_1(\text{D.R.}^2 - 1)}{2L} \ \text{min}^{-1}$$

or

$$\text{rate} = \frac{50V_1\ (\text{D.R.}^2 - 1)}{L} \ \%\ \text{min}^{-1}$$

This expression is an approximation to the average draw rate of a filament drawing continuously over a hot plate, but in fact the draw rate imposed by the Instron in the small-scale drawing experiments is the average rate; so, in this sense, use of the equation is valid.

DRAWING OF POLY(*m*-PHENYLENE ADAMANTANE-1,3-DICARBOXAMIDE) FIBERS

Samples of mPAD fibers were received at various stages in the development of the spinning process. The general properties of these samples are listed in Table I, sample 4 consisting of the best fibers produced to date.

The samples were produced on a small-scale wet-spinning machine;[13] and after a comprehensive evaluation of the process when used for the spinning of mPAD, the following method was adopted. A 25% w/w spinning solution was prepared by dissolving the polymer in dimethylformamide containing 5% lithium chloride. After filtering, extrusion took place through a five-hole spinneret, the holes having a diameter of 75 microns. The spin bath was a 60% w/w mixture of dimethylformamide

TABLE I
Properties of As-Spun Fibers

Sample no.	Filament denier	Tenacity, g/d	Break extension, %	Initial modulus, g/d	Sonic modulus, g/d	Fiber cross section
1	25.0	0.17	10.4	4.2	13.6	circular section extensive sponge-like void structure
2	23.5	0.42	47.1	16.7	—	near-circular section, one central void or several radial voids
3	20.0	0.28	46.2	11.4	15.5	
4	59.4	3.53	68.4	20.5	30.0	dumbbell section, complete absence of voids

in water at a temperature of 10°C. After coagulation, the filaments were passed through a hot water bath to remove residual solvent and were then packaged before further washing in distilled water and drying in a forced-draught oven.

Experimental Procedure

A softening point of 294°C for mPAD has been quoted by Flavell,[11] and Sewell[12] obtained a T_g of 311°–317°C. It was decided in the first instance to examine a temperature range of 285° to 330°C in the event this range was sufficient to observe the whole spectrum of drawing behavior from cold drawing to plastic flow.

Single filaments were drawn on the Instron using the specially designed hot plate and fiber mounts described above at temperatures between 285° and 330°C and at three different rates. A gauge length of 1 cm was used throughout, and in each case ten samples were drawn under each set of conditions. The maximum speed of both the Instron cross head and the pen recorder chart was 100 cm/min, which meant that a maximum draw ratio of 10,000 min^{-1} could be employed giving a strain sensitivity of 100% cm^{-1} on the chart. A lower limit of 1,000% min^{-1} was set because at the

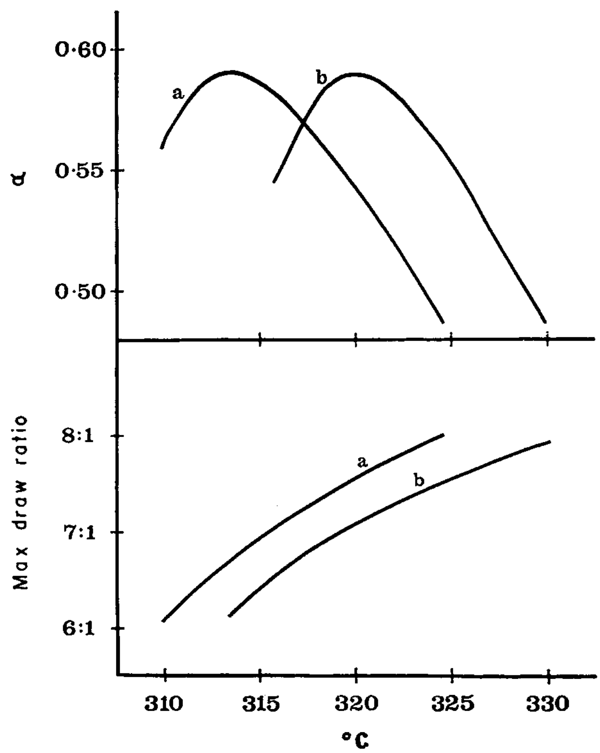

Fig. 6. Molecular orientation and maximum draw ratio vs. temperature for mPAD for draw rates of (a) 30,000 % min^{-1}; (b) 100,000 % min^{-1}.

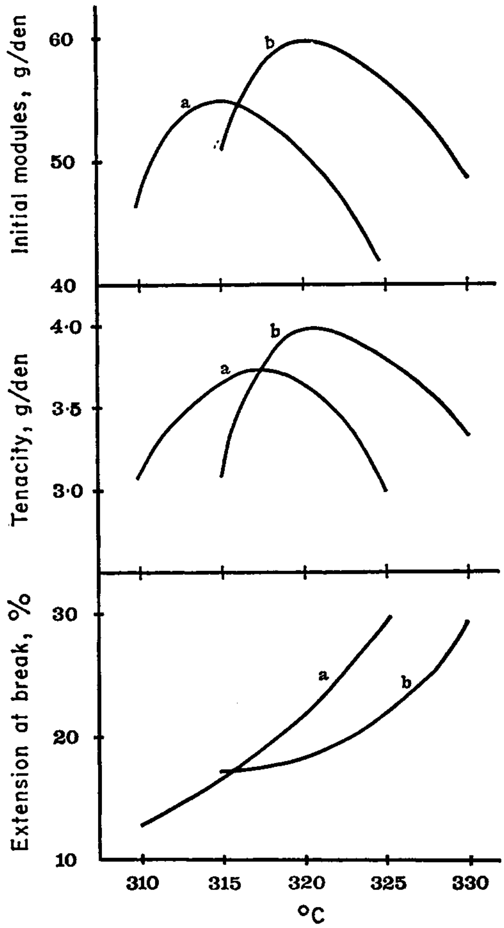

Fig. 7. Tensile properties of mPAD drawn to maximum draw ratio at rates of (a) 30,000 % min^{-1}; (b) 100,000 % min^{-1}.

higher temperatures longer residence times against the hot plate made the P.T.F.E. drums soft and sticky. The load–extension diagrams obtained were examined, and the three different drawing modes were observed; for example, at a draw rate of 10,000% min^{-1}, cold drawing occurred below 305°C, hot drawing at 315°C, and plastic flow at 330°C. Draw ratio at break was measured, as was the reinforcement factor.

Draw ratio at break and reinforcement factor were plotted against temperature for the various qualities of mPAD at the different rate values.

Fibers from samples 2, 3, and 4 were drawn continuously; attempts were made to draw filaments from sample 1, but because of their poor tensile properties and nonuniformity no useful results could be obtained. Filaments were drawn at temperature intervals of 5°C about the extrapolated peak reinforcement region, at rates between 20,000 and 100,000% min^{-1}. By using the draw ratios at break measured in the small-scale drawing experiments as a guide, a trial-and-error method was used to find the maximum draw ratio at a particular set of rate–temperature coordinates to within 0.1. Single filaments approximately 1.5 m in length were drawn, and a number of filaments (between about 3 and 6) needed to be drawn before the maximum draw ratio was found. Drawing runs at the critical conditions were repeated to guard against spurious breakages due to weak spots. After drawing, the filaments were removed from the top draw roller and packaged by hand, then stored in a desiccator prior to evaluation.

Sonic modulus measurements were made on the drawn filaments and the acoustic orientation factor determined. Tensile properties were also evaluated using the Instron, correlation between these and the extrapolated optimum reinforcement being of more practical importance. Figures 6 and 7 show maximum draw ratio, acoustic orientation factor, and tensile properties of sample 4 plotted against temperature for two different draw rates, and similar curves were obtained for sample 3. Difficulties in the spinning process, the effects of which did not become apparent until after drawing when the remaining as-spun fibers were tested, complicated the situation where sample 2 was concerned, and the tensile results were not very good. However, sonic modulus was observed to follow the same pattern of behavior as the orientation-dependent properties of samples 3 and 4. These orientation-dependent properties were seen to exhibit maxima in a similar manner to the reinforcement factor.

Samples of drawn filament were submitted for x-ray analysis, but the results did not indicate any significant degree of crystallinity.[5]

DISCUSSION

One of the most striking results of the small-scale drawing experiments on mPAD is the narrow temperature range within which the whole spectrum of drawing behavior is observed. The narrowness of this temperature range helped in the identification of the optimum reinforcement temperature at a given rate and probably accounts for the well-defined reinforcement-versus-temperature curves.

The reinforcement factor was a useful concept in that it exhibited a maximum as drawing temperature was increased, and the position of this maximum on the temperature axis increased with increasing draw rate. This time dependence of whatever mechanism the factor describes would indicate that the effect is molecular in origin. On this assumption, Boltzmann's principle of time–temperature superposition would predict that the temperature–log rate coordinates of the reinforcement peaks would lie on a straight line, and this was found to be the case.

The orientation-dependent properties of the continuously drawn filaments have been observed to exhibit maxima as the drawing temperature was varied. The temperature–log rate coordinates of these maxima are such that the same straight line can be drawn through these coordinates and the temperature–log rate coordinates of the maximum reinforcement values. This indicates that the choice of the reinforcement factor was also successful in that it was qualitatively representative of the degree of orientation induced.

The small-scale and continuous-drawing behaviors of the several fiber samples were seen to be essentially similar but differing in detail. One particularly obvious difference is in the relationship between maximum draw ratio (small-scale drawing) and temperature for samples 3 and 4. For the latter, maximum draw ratio continues to increase into the plastic flow zone, whereas for the former, maximum draw ratio levels off with temperature at a rate of 10,000% min^{-1} and actually decreases with increasing temperature at lower rates. This may be because sample 3 has a void structure which makes breakage of the filaments more likely in the unstable region of plastic flow. The effect would become more exaggerated at lower temperatures and rates because higher temperatures would induce void collapse more easily, and the effect of voids would be less apparent. The maximum degree of reinforcement and the maximum values of orientation-dependent properties all show a marked increase with increased temperature and rate for sample 3, while these increases are only slight in the case of sample 4. The presence or absence of voids may again be partly responsible for this, but not entirely since sample 4 has no apparent void structure, yet tenacity and initial modulus are slightly higher at the higher rate and temperature values. It may be that although x-ray analysis of drawn fibers indicates no significant crystallization, there has been sufficient crystallization, together with collapse of microvoids, to account for these slight increases, and the effect is exaggerated in the case of sample 3 by the presence of macrovoids.

An interesting point is that drawn fibers from sample 4 have a lower orientation factor than similar fibers from sample 3, which is an inherently weaker material. Fiber strength is generally supposed to increase with increasing molecular weight, all other effects being constant. Polydenmaya[8] demonstrated this for polycaproamides of varying molecular weights, and the effect was particularly marked when fibers were not drawn. It is clear from Table I that the predominant parameter affecting the strength of the various as-spun filament is fiber quality rather than molecular weight, and so it would appear that it is possible for a fiber spun from a lower molecular weight material to have a lower molecular orientation factor after drawing than fiber from a higher molecular weight material and yet have higher strength because of better homogeneity in the as-spun state. However, sonic modulus is dependent on void fraction, and it follows that improvement of the sonic modulus on drawing sample 3 is not only dependent on induced orientation, but also on void collapse due to increased thermal activity and the packing effect of drawing. Therefore, the possibility remains that sample 3, although weaker, has a higher orientation than sample 4. What does become apparent is that although α may be a valid representation of molecular orientation for a particular sample, it does not necessarily lend itself to quantitative comparison between different samples.

CONCLUSIONS

To evaluate the drawing properties of experimental fibers available only in small quantities necessitates the use of special techniques. In particular, substantial information can be obtained from drawing experiments of a discontinuous nature which use only short lengths of as-spun fiber. If the fiber is essentially amorphous, then by application of suitable approximations information obtained from the load–extension characteristics of fibers during drawing can be used to decrease appreciably the range of conditions under which continuous-drawing experiments need to be carried out. The techniques used were particularly successful when applied to mPAD fiber because of the high T_g of this polymer, the critical dependence of drawing behavior on temperature, and the lack of crystallinity in the drawn fibers. The success of the work is reflected in the fact that fibers having reasonably good mechanical properties, comparable with commercial synthetic fibers, were produced from only 7.0 g of polymer, particularly when one realizes that only a proportion of the fibers produced was suitable for drawing experiments. Further improvement in the properties of mPAD fiber will probably come from work on all three aspects of fiber production, i.e., properties of the polymer, the spinning process, and the drawing process.

The techniques which have been described would not necessarily meet with the same success if applied to other experimental fibers, but it is felt that the techniques which have been described would provide a valuable method of preliminary evaluation.

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