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Study of mass redistribution associated with the drawing process of polypropylene fibres

M. M. El-Tonsy, A. M. Shaban, and I. M. Fouda

Physics Department, Faculty of Science, Mansoura University, Mansoura, Egypt

SUMMARY

A fine system for measuring the density of fibres has been constructed. The measuring technique was based on the concept of vibrating strings . Density of polypropylene fibres , originally drawn to known ratios, was measured. The fibre diametre was measured by the laser forward diffraction technique. Behaviour of fibre density at different draw ratios and different molecular orientations was discussed. The bundle model for the polymeric microstructure was recommended in this study in order to explain the mass redistribution associated with the drawing process of the polypropylene fibres. X-ray diffraction technique was used to explain the share of crystalline phase in the mass redistribution process. The applicability of Gladston-Dale equation to mechanically drawn fibres was discussed.

I . INTRODUCTION

The phenomena of drawing represents a series of variations upon a theme, or rather several themes, for there are so many relevant variables, including the temperature of drawing, its strain rate , initial morphology and molecular mass distribution, among others (1) .

Thus, density of polymeric fibres is one of the physical parameters which is affected by the drawing process as well as the mechanical constants (2) . The most important parameters with which to characterize an anisotropic property of an oriented, polycrystalline polymer is the fraction of each phase presented, the intrinsic property of each phase , and the orientation function of each phase.In general,the fraction of each phase present in the polymer can be determined by the density or X-ray diffraction measurements.

The density of the polymer sample may be determined by any standard experimental methods (3) including pycnometry, hydrostatic weighing and use of a density gradient tube (4).

In this work , the density of polypropylene fibres(pp),with different draw ratios, was measured to estimate the variation due to the drawing process, and on the other hand, to describe how these variations may lead to understanding the molecular structure response to the applied uniaxial drawing force. The density of polypropylene fibres has been measured using a resonance technique based on the theory of vibrating strings.

II.EXPERIMENTAL

II.a. Density Measurement

1. Set-up of the constructed measuring system

When a string is stretched by a tensional force T and put in contact with a vibrator which vibrates at right angle to the axis of the string, a difinite length l of the string will vibrate stationary as the resonance condition between frequencies of vibrator and string is achieved. Let f_o be the resonance frequency then (5)

$$f_o = (p / 2l) (T / m)^{1/2} \qquad (1)$$

where p = number of resonance modes within the string's length l (p = 1 for the fundamental mode) and m = mass per unit length of the string .Thus the fibre has been clamped at one end while the other end (connected to a small scale pan) passes over a small frictionless pulley, Fig. (1). The clamp C and pulley W are fixed to an optical bench B. An electromagnetic pulse transmitter (vibrator) T , as well as Piso-crystal transducer R,are also fixed tightly to B. The fibre sample S is tightened by mass M and left to be in contact with T and R . The vibrator T is stimulated by a sinusoidal electric pulses from the adjustable frequency pulse generator G . Pulses from G are also supplied to the frequency counter FC , to be counted and to the first channel CH1 of the double-beam cathod ray oscilliscope , to be taken as reference wave . The frequency of the vibrator T was increased , from zero, up to the resonance frequency f_o at which points on the sample (from T to R) were vibrated with the same frequency f_o . Thus R receives pulses with a maximum amplitude. Pulses from R were magnified by the Pre-amplifier whose out-put signals were supplied to the second channel CH2 of the CRO. So, the received wave on CH2 possesses maximum amplitude only at resonant modes of the fibre (odd modes were shown out of phase , while even modes were observed in phase with the reference wave) when the vibrator's frequency was ascendingly changed. Using such a system allows one to determine the fundamental resonance frequency f_o of a certain length l of the fibre (l = distance between T and R) when it is loaded by a mass M gm.Then the mass per unit length m of the fibre under test could be calculated from equation (1).Accurate value of m could be obtained as an average over several modes of resonance. From the obtained value of the mass per unit length m, one easily calculate the density ρ of the fibre material from the relation

$$\rho = m / \pi r^2 \qquad (2)$$

where r is the radius of the cylendrical fibre.

2. Measurement of the fibre diameter

In present work, the fibre diameter d was measured by the technique of laser beam forward diffraction (6 , 7).
In this method the following formula was used :

$$d = \pm \lambda L / x \qquad (3)$$

where d is the fibre diameter, $\lambda = 632.8$ nm the wavelength of the He-Ne used ; x , the distance from the centre of the obtained diffraction pattern to the first minimum and L is the distance between the fibre and the screen on which the pattern was produced . Each sample was examined at several positions and the average value of d was considered.

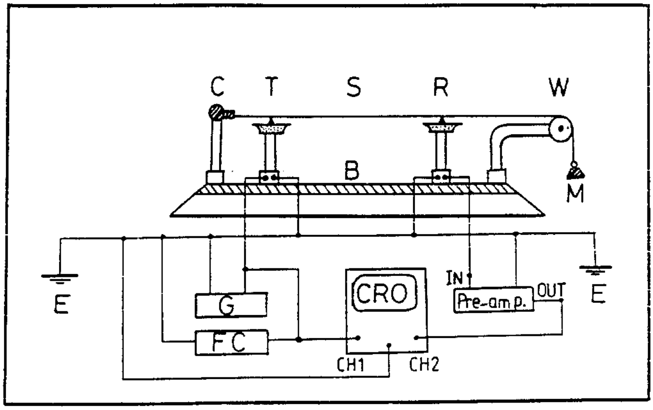

Fig.(1) Schematic diagram for the the density measuring system S sample under test, C clamp, T electromagnetic transducer, R piso-crystal transducer, W pulley, M weight, B optical bench, E earthing line,G function generator, FC frequency counter(±0.1 Hz), CRO dual-beam cathod ray oscillescope and Pre-amp. low noise pre-amplifier.

II. b . X-ray Diffraction Measurement

The ivestigation of the present crystalline phases and their ratio in polypropylene fibres was done using the X-ray diffraction technique . Diffraction patterns were done with Shimadzo X-ray diffraction DX30 with conventional Cu - $K\alpha$ ($1.542\ \mathring{A}$) .

III . RESULTS AND DISCUSSION

Polypropylene fibre samples, which were originally drawn to the ratios 1 , 3 , 3.5 ,4.5 and 5.2 x , were used in this work to study its density behaviour .

Fig. (2) shows the fibre density as a function of the draw ratio . It is found that Polypropylene fibres drawn to 3.5 x have the highest density value , while the density goes to, nearly, a steady value as the draw ratio reachs 5.2 . This increase in pp-density by drawing may be a consequence of the increased volume fraction of the intermicrofibrillar taut tie molecules (8). So, it is essential to study the density of fibres at different draw ratios in order to produce fibres sufficiently strong and light .

Birefringence is an excellent property to be used for the study of orientation in polycrystalline polymer .Hamza and Kabeel (9) have measured the optical properties of the same drawn polypropylene fibre samples . Their data showed an increase in the mean birefringence (Δn_a) up to , nearly , steady value by increasing the draw ratio. In order to study the relation between molecular chain orientation and the mass distribution in drawn pp-fibres , the data given in reference (9) for Δn_a was plotted versus the measured fibre density o, in this work.

Fig. (3 , I) shows that as the molecular chains are more oriented parallel to the direction of deformation, they also are distributed in more compact structure (higher density), according to a non-linear behaviour . The produced compact structure was then discomposed, linearly , while chains continued their better orientation parallel to the direction of deformation, Fig. (3 , II) .

The behaviour shown in Fig. (3) can be considered as a resultant output of variations occuring in both crystalline and non-crystalline phases of the medium due to the drawing process.

III a. Contribution of the crystalline phase

In order to estimate the contribution of crystalline phase in the observed mass redistribution of pp-fibres due to a drawing process, it was essential to detect crystal phases that have been formed during its manufacture process . X-ray diffraction pattern of the undrawn samples (draw ratio = 1) showed that three crystal phases were formed during the solidification of the pp-melt, Fig. (4 . a). Samuels (10) showed that most of the crystal reorientation and crystal share in pp-birefringence were occured through the first drawing effect (at draw ratio $\simeq$ 2). Higher drawing didn't affect neither crystal orientation nor birefringence due to the crystal phase.Therefore, one may decide that the density peak in Fig. (3) is free from any effect due to the crystalline phase reorientation. Extension of the X-ray diffraction measurements over pp-fibre samples with higher draw ratios, showed that the ratio of crystalline phase to the whole medium

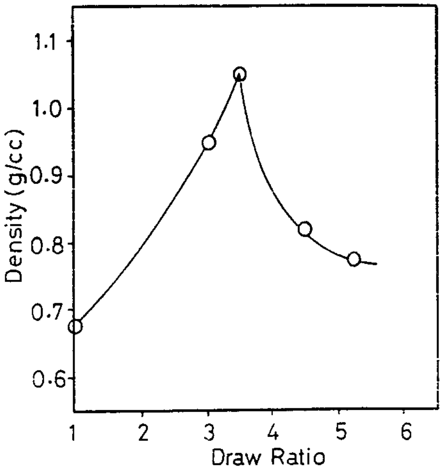

Fig.(2) pp. fibre density vs. draw ratio.

decreased by increasing the draw ratio , Fig.(4b & c). This decrease in the crystalline phase volume may be due to the defolding of lamellar regions that were formed during the initial annealing of the spun fibres (10).

IIIb Contribution of the non-crystalline phase

In order to estimate the contribution of the non-crystalline phase to the mass redistribution of pp-fibres due to drawing , a suitable structural model should be recommended .

The behaviour shown in Fig. (3) may be discussed on the bases ofthe bundle model of polymer structure where the polymer chains are extended to form bundles. In the bundle model , it was supposed that the bundle length is much longer than the length of the macromolecules that make up the bundle(11).

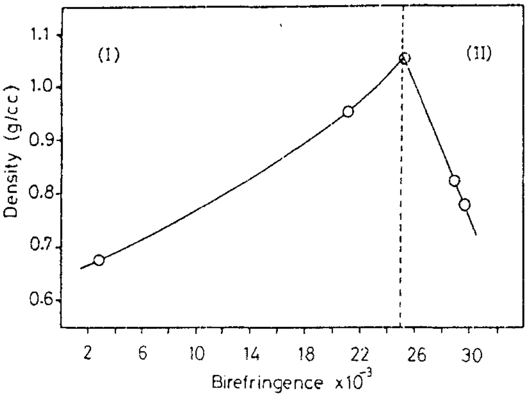

Fig. (3) Correlation between pp-fibre density and optical birefringence.

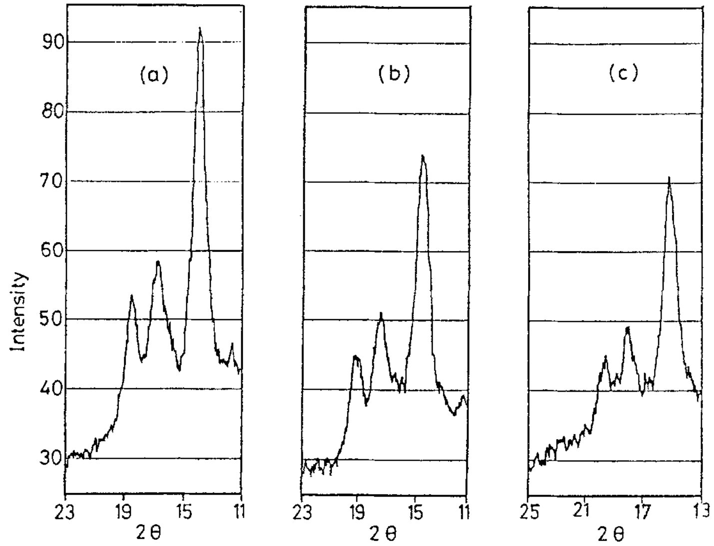

Fig. (4) X-ray diffraction patterns of drawn pp- fibres.

Fig.(5) shows the expected macromolecular distribution in the samples under test when they are acted on by a drawing stress . Fig .(5 a) is a less ordered and less package of pp- macromolecules which may be the domenant structure of the low drawn sample . Further drawing causes the macromolecules to be more parallel to the direction of deformation (more ordered) and in the same time more compact (more dense) . The higher molecular package is due to ;1-more straightening of molecular chains and 2- displacing chains with respect to each other in such a way that the end to end separation of each two trained molecules becomes too small, Fig. (5b). This structure is the most probable one at the peak point in Fig. (3). Further drawing produces orientation parallel to the direction of deformation while the molecular chains end to end separation is increasingly causing a reduction in the molecular package (density), Fig.(5c). This behaviour describes the linear drop in the density while the molecular orientation was more improved , Fig. (3-II).

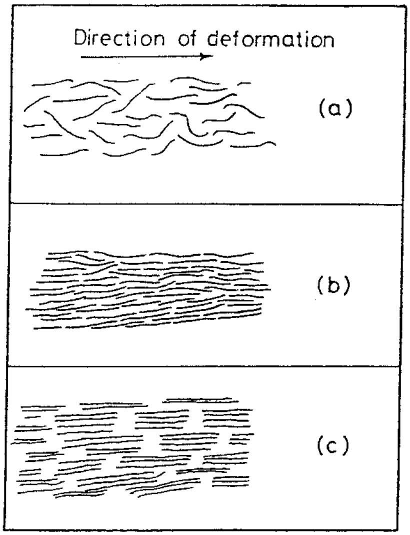

Fig. (5) Expected macromolecular orientation in drawn pp.

Data given in Ref. (9) for the mean parallel and perpendicular refractive indices ($n_a^{\parallel}$ & $n_a^{\perp}$) were used to calculate the isotropic refractive index n_{iso} of the drawn pp-fibre samples . The concept of the isotropic refractive index was discussed in details by Hannes (12) where

$$n_{iso} = 1/3 \; (n_a^{\parallel} + 2 \, n_a^{\perp})$$

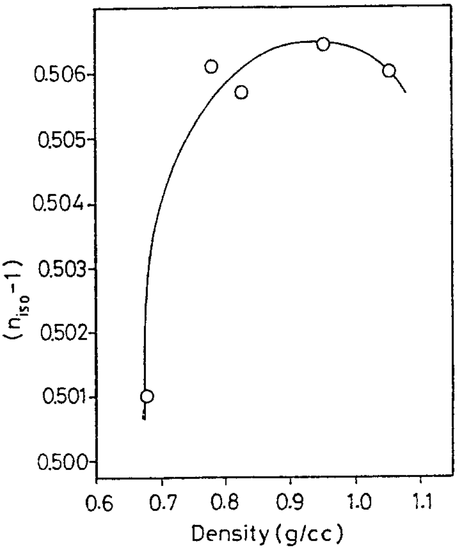

Fig. (6) The non-linear variation of n_{iso} with density.

Fig .(6) gives the relation between (n_{iso} - 1) and the density o of drawn pp-fibre samples . It is found that (n_{iso} - 1) changes non-linearly with ρ which means a remarkable shift from the well known Gladston equation:

$$(n_{iso} - 1) / \rho = k \qquad (4)$$

where k is a constant, i.e. k will be a function either in the density or in the draw ratio when the structure of pp-medium is deformed mechanically.

IV . CONCLUSION

From the above studies, following conclusions may be drawn
1. The density measuring system , that constructed in present work , has good accuracy to detect small variations in the density. This resonance technique is quick , non-distructive and accurate (expected error is below = 1 %). Except the critical selection of the loading mass , M , this technique would be much easier than the others . (Too heavy mass causes serious deformations in the sample's structure, while too light mass causes fast attenuation for the applied vibrations and accordingly the condition of stationary propagation may not be achieved.)

2. The density of polypropylene fibres is , remarkably, changed due to a drawing process .

3. The density of pp-fibres showed a sharp peak at the draw ratio 3.5 . This means a serious structural variations at this draw ratio .

4. The density of pp-fibres varies non-linearly with the optical birefringence. This means that the reorientation of polymeric chains due to drawing is associated with a mass redistribution .

5. The analysis of obtained results showed that the bundle model for polypropylene microstructure was a suitable structural model for interpretation of the mechanical response of pp-fibre structure .

6. From the X-ray diffraction patterns , it was found that crystalline phases of pp-fibres have a weak effect on the mechanism of the mass redistribution associated with the drawing process .

7. The decrease in crystallized volume , Fig.(4) , and the steady value of birefringence at the high draw ratios of pp-fibres may indicate that the defolded chains were extended directly parallel to the drawing direction.

8. The isotropic refractive index of drawn pp-fibres was found to change non-linearly with the fibre density . This

leads to the non-applicability of Gladston-Dale equation .

We conclude from the above results that the practical importance of these measurements provides acceptable view for the structural features of drawn pp-fibres and the mechanism of variations associated with the drawing process . Also from these studies, there is no doubt that mechanical properties of pp-fibres are a function of the density as well as the molecular orientation .

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