Sonic Modulus in a Porous System

INTRODUCTION

Acrylic fibers are often produced by a wet-spinning process in which the method of production results in a spun fiber containing microvoids. Subsequent operations include a stretching of the fiber, followed by a drying treatment in which radial contraction of the fiber occurs. As a consequence, the finished fiber has a compact structure with no apparent microvoids.

For some time, methods have been sought which would allow the orientation of the chain molecules to be determined. Birefringence is not an adequate method of orientation measurement in these acrylic fibers because the maximum birefringence is very low and the porous structure can lead to birefringence contributions. X-Ray diffraction does not provide extensive information because of the lack of meridional diffraction maxima. Consequently, interest has been generated in the use of sonic velocity measurements since this technique has been used successfully to determine the molecular orientation in a number of polymers.[1,2] Paul[3] has examined the orientation of acrylic fibers and has established correlations between spinning conditions and orientation parameters obtained from sonic velocity measurements. Paul comments that there are no good theories to indicate how the sonic velocity depends on porosity even in unoriented polymers. The purpose of this note is to show that the sonic velocity in a porous unoriented system can be predicted. The extension to the case of oriented chains is also discussed.

MODULUS OF A POROUS, UNORIENTED SYSTEM

The behavior of the sonic modulus of a porous, unoriented system in response to a change in void content may be understood with reference to the work of Kerner.[4] This author has shown how the elastic properties of a composite may be calculated. The composite is considered to be a collection of grains suspended in a homogeneous matrix. In the present case, the "grains" are the pores and the matrix is the acrylic polymer. The bulk modulus of the composite k_0 is given by

$$k_0 = \sum \frac{k_i v_i}{3k_i + 4\mu_1} \Big/ \sum \frac{v_i}{3k_i + 4\mu_1} \tag{1}$$

where the subscript i refers to the grain and the subscript 1 to the matrix, μ_1 is the shear modulus of the matrix; and v_i is the volume fraction of the species i. In the present case, $k_1 \gg k_i$, and eq. (1) becomes

$$k_0 = \frac{4\mu_1 k_1 v_1}{3k_1 + 4\mu_1 - 3k_1 v_1}. \tag{2}$$

The shear modulus of the composite is given by

$$\mu_0 = \mu_1 \frac{\sum^{i\neq 1}\left[\frac{\mu_1 v_i}{(7-5\sigma_1)\mu_1 + (8-10\sigma_1)\mu_i} + \frac{v_1}{15(1-\sigma_1)}\right]}{\sum^{i\neq 1}\left[\frac{\mu_i v_i}{(7-5\sigma_1)\mu_1 + (8-10\sigma_1)\mu_i} + \frac{v_1}{15(1-\sigma_1)}\right]} \tag{3}$$

where σ_1 is the Poisson ratio of the polymer matrix. Since $\mu_1 \gg \mu_i$ the equation simplifies to

$$\mu_0 = \mu_1 \frac{1}{1 + \frac{15(1-\sigma_1)(1-v_1)}{(7-5\sigma_1)v_1}}. \tag{4}$$

The ratio $15(1 - \sigma_1)/(7 - 5\sigma_1)$ is relatively insensitive to σ_1; it changes from 2.0 to 1.67 as σ_1 goes from 0.2 to 0.5.

Since the material is isotropic, Young's modulus E_0 may be expressed as

$$E_0 = \frac{9k_0\mu_0}{\mu_0 + 3k_0} \tag{5}$$

Substitution of eqs. (2) and (4) into eq. (5) gives finally

$$E_0 = \frac{36\mu_1 k_1 v_1}{3k_1 + 4\mu_1 - 3k_1 v_1 + 12k_1 v_1 \left[1 + \frac{15(1 - \sigma_1)(1 - v_1)}{(7 - 5\sigma_1)v_1}\right]} \tag{6}$$

as the expression for the modulus of the porous unoriented material. The influence of the pores enters through the volume fraction v_1. Equation (6) may be used to predict Young's modulus of a porous fiber or film, provided the volume fraction of polymer v_1 and the material constants μ_1, k_1, and σ_1 are known.

EXPERIMENTAL

The polymer used was a copolymer of acrylonitrile and vinyl acetate containing about 7% by weight of the latter. The polymer was dissolved in dimethylacetamide (DMAc) to give a solution containing 27.5% polymer by weight. This solution was pumped to a 100-hole spinneret immersed in a liquid bath containing 55% DMAc and 45% water by weight maintained at 40°C. The aqueous DMAc solution coagulates the filaments.[5] A quantity of fiber was allowed to collect at the bottom of the spin bath. These fibers were washed in water at room temperature to remove solvent and were then freeze-dried using liquid nitrogen. The mode of treatment preserved the fibrillar structure characteristic of wet-spun fibers at this point of processing,[6,7] and the method of spinning ensured that the fibers were unoriented.[3]

The sonic velocity in the fibers was determined with a KLH pulse propagation meter at room temperature using a tensile load of 0.05 g/den. The relation between the sonic modulus and the sonic velocity determined experimentally[2] is

$$E = 11.3c^2 \tag{7}$$

where E is the sonic modulus in g/den and c is the sonic velocity in km/sec. Fibers with different porosity were prepared by heating the spun fiber to different temperatures under relaxed conditions. The bulk density of the fibers was measured at room temperature by a mercury displacement method to give v_1. The measurements indicated that a treatment at 120°C gave a completely collapsed fiber, i.e., $v_1 = 1$. The sonic modulus of the completely collapsed fiber was used to obtain a k_1 of 50 g/den and μ_1 of 18.7 g/den by assuming that σ_1 was $1/3$. Equation (6) was then used to give values of E_0 for different v_1 values.

RESULTS AND DISCUSSION

Figure 1 shows how the sonic modulus varies with the polymer fraction v_1. Since the fibers were heated under relaxed conditions, there is no chance that orientation occurred during collapse. In addition, the density of the polymer, measured with liquids that wet the fiber, shows no change with change in porosity, indicating that the crystallinity stays constant. Therefore, the change in sonic modulus seen in Figure 1 is primarily due to the change in porosity of the fiber.

Table I gives the sonic moduli for the fibers of different void content. Also given is the sonic modulus calculated on the basis of eq. (6). It is seen that there is good agreement between the calculated and measured values. This agreement indicates that the

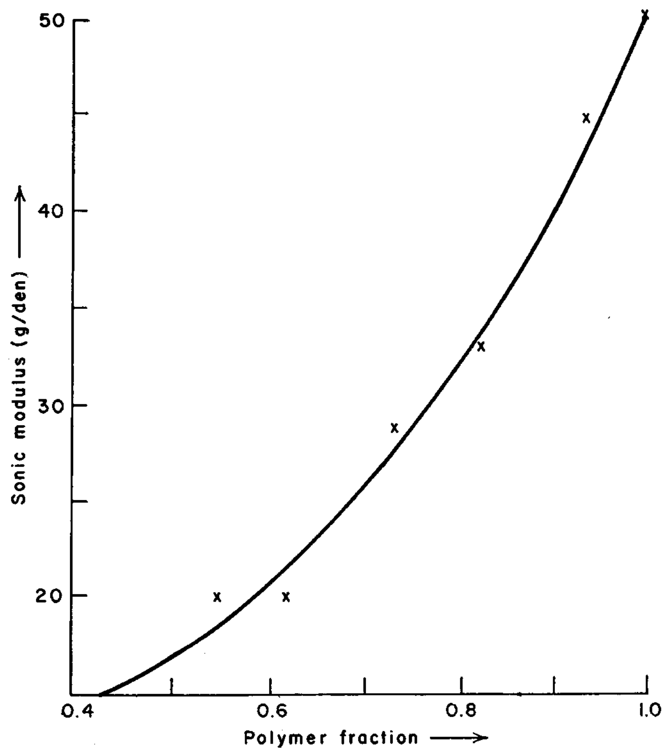

Fig. 1. Variation of sonic modulus with polymer volume fraction for unoriented acrylic fibers.

pores act as a filler and that the mechanism of sound propagation is the same in both the porous and the collapsed systems.

The treatment of the modulus of an oriented porous system has not yet been quantitatively attempted. The sonic modulus may be written symbolically as

$$E \doteq E(x, \beta, v_1) \tag{8}$$

where x is the crystallinity, β characterizes the orientation of crystalline and noncrystalline regions, and v_1 is the polymer fraction. As already mentioned, the density of the

TABLE I
Experimental and Calculated Sonic Moduli for Unoriented Acrylic Fibers of Different Porosity

Polymer fraction v_1	Experimental sonic modulus, g/den	Calculated sonic modulus, g/den
0.445	15.1	14.4
0.555	20.0	19.3
0.625	20.0	22.9
0.733	28.7	29.0
0.828	33.1	35.4
0.940	45.0	44.3
1.000	50.0	50.0

polymer is not a strong function of the conditions of treatment, and there is some evidence to suggest that acrylics may be regarded as a single-phase material.[8] Even with this simplification, the problem is still difficult because Kerner's treatment and eq. (5) only apply to unoriented systems. It may be possible to utilize the treatment of Moseley,[2] in which the polymer is regarded as made up of a number of units and the contribution from each unit is summed to give the modulus of the fiber, as long as it is realized that the modulus of a unit is a function of the porosity of the fiber.

CONCLUSION

It has been shown that the sonic modulus in a porous system (acrylic fiber) can be calculated by means of Kerner's equation. The results indicate that the pores act simply as a filler. This treatment is applicable to any porous system as long as the physical constants of the matrix are known. The extension to oriented, porous systems is complicated and has not yet been carried out. Finally, it should be pointed out that the effect of porosity is not confined to the sonic modulus but, for example, is seen with moduli taken from Instron load–extension curves.

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