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Characterization of Fibers by Dynamic Thermoacoustical Analysis

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ABSTRACT

Dynamic thermoacoustical analysis has been described for the characterization of certain physicochemical properties of fibers. The method consists of a continuous measurement of the propagation time of constant frequency sonic pulses transmitted through the sample which is being held under light tension and heated under programmed temperature. The sonic pulses are generated by subjecting a piezoelectric crystal with electrical pulses of 7 kHz frequency. Dynamic thermoacoustical curves were obtained with a variety of synthetic fibers and cellulose fiber. The fibers were heated from room temperature to their respective melting points or decomposition temperature. Theoretical principles are discussed with respect to the relationship between sonic responses and the fundamental properties of polymers. The dynamic viscoelastic equation, based on Maxwell-Wiechart model for polymers, has been combined with sonic pulse propagation equation in order to relate the sonic response with the viscoelastic parameters of unoriented and oriented polymers. It is shown that the sonic response under dynamic heating condition is influenced by two factors: 1) orientation of polymer molecules and 2) sonic viscoelastic function of the polymer. It has been further demonstrated that the orientation of fibers practically remained unchanged on heating under the experimental conditions examined. The dynamic thermoacoustical curves for fibers revealed only the characteristic viscoelastic properties of polymers as a function of temperature.

INTRODUCTION

Thermoanalytical techniques in the field of polymer characterization have been rapidly expanding. The instrumentation on commonly known techniques such as differential thermal analysis (DTA) and thermogravimetric analysis (TGA) have been improved to a great extent during recent years while newer methods are constantly being introduced into the field. Among the newer methods, thermomechanical analysis (TMA) and torsional braid analysis (TBA) have been found to be extremely useful in characterizing certain physicomechanical properties of polymers. Although the overall polymer characterization capabilities have been greatly improved by these modified and newer techniques, there are still many characteristic properties of polymers which cannot be determined by the conventional thermoanalytical techniques. Therefore, the exploration of newer techniques to obtain hitherto undetermined properties of polymers is still very important.

The thermal-sonic technique, which is the subject of discussion of this paper, would determine the viscoelastic behavior of polymers under dynamic heating condition. The technique is somewhat analogous to rheovibron measurements but differs in many respects in theory and practice.

The use of sonic techniques for determining structure-property relationships in polymers was first reported by Ballou and Smith [1] in 1949 and the technique was further advanced by Charch and Moseley [2, 3].

In this work the main principle of the technique suggested by Ballou and Smith [1] has been adapted to develop a method for studying the viscoelastic properties of polymers under dynamic heating conditions. Also a theory has been developed to relate the sonic response to certain fundamental properties of polymers.

In broader terms, dynamic thermal analysis comprises techniques of measuring certain properties of material while it is being heated at constantly increasing temperature. The present technique consists of measurements of sound velocity in polymer while the polymer is being heated under a programmed rate. It therefore, falls under the general category of dynamic thermal analysis. The technique will be referred to as "dynamic Thermoacoustical analysis."

EXPERIMENTAL

Dynamic Thermoacoustical Analysis

In principle, the method consists of a continuous measurement of the propagation time of sonic pulses of constant frequency (7 kHz) through the sample which is being held under light tension and heated at programmed temperature. In the present investigation the samples were heated from ambient temperature to the respective melting points or decomposition.

The experimental set-up is shown in Fig. 1. In the figure, A represents the heating block of a Du Pont 900 DTA where H represents the heating element and T_2 and T_3 represent the reference and sample wells, respectively. Two additional holes (T_1 and T_4) were drilled all

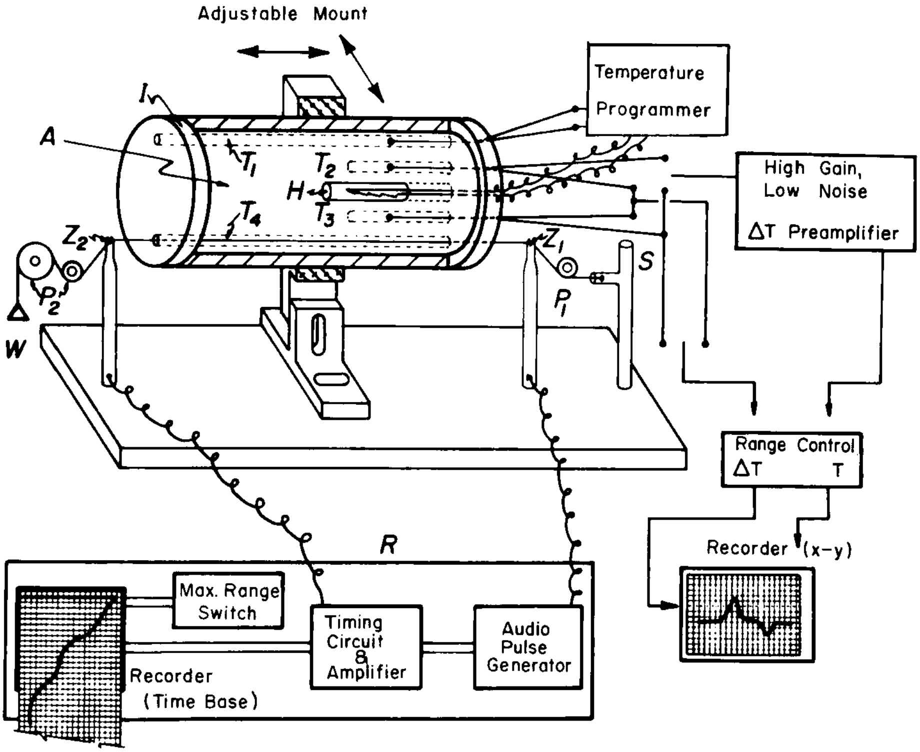

FIG. 1. A schematic representation of dynamic thermoacoustical system.

the way from one end to the other through the heating block. The heating block was thoroughly insulated by putting asbestos caps on both ends and covering the rest with asbestos tape. Melting point tubes, open on both ends, were inserted into the holes T_1 and T_4. The heating block was mounted horizontally and thermocouples were inserted in T_1, T_2, and T_3. These thermocouples were connected to different terminals of the Du Pont DTA cell as shown in the Fig. 1. The fiber sample was tied at one end to a clamp S, passed under a pulley P_1 and on a notched ceramic piezoelectric crystal transducer Z_1, through the hole T_4, and supported by another identical piezoelectric crystal Z_2 and a set of pulleys P_2 and finally terminated at a suspended weight of 5 g. The piezoelectric crystals were connected to an electrical pulse generating and recording device, R. The distance between Z_1 and Z_2 was 3.6 cm, which was kept constant throughout the experiment. The piezoelectric transducers and the pulse generating and recording devices were the parts of an instrument known as Pulse Propagation Meter, Model PPM-5R, manufactured by H. M. Morgan and Co., Cambridge, Massachusetts. The maximum range switch of the instrument was modified to obtain a time response as high as 2000 μsec.

As soon as the pulse propagation meter is activated, the electrical pulses of 7 kHz frequency are transmitted to the piezoelectrical crystal Z_1. The crystal lattice of Z_1 then begins to vibrate at the same frequency as the electrical pulses, and thus the electrical pulses are converted to sound pulses. Piezoelectricity is a means of converting electrical energy into mechanical energy and vice versa. The sound pulses are transmitted through the fiber sample to the crystal Z_2, which reconverts the sound pulses back to electrical pulses. As soon as this reconversion takes place, an internal timing circuit in the instrument is closed and the recorder instantaneously records the time required for pulses to propagate from Z_1 to Z_2. Knowing this propagation time and the distance between Z_1 and Z_2, one can calculate the velocity of sound through the sample. However, in the present technique it is necessary to record the pulse propagation time only; the velocity conversion is not required.

For dynamic thermoacoustical analysis the sample was heated in air atmosphere at a programmed rate of 20°C/min. The system temperature was continuously recorded on a DTA chart whereas the sonic response was simultaneously recorded on a time base recorder provided with the pulse propagation meter. The abscissa of the original sonic chart was later converted to a temperature scale.

Simultaneous DTA and Dynamic Thermoacoustical Analysis

In the case of simultaneous differential thermal analysis and dynamic thermoacoustical analysis, the fibers were cut into small pieces by using a Wiley mill with 60 mesh screen, and 5 mg of this sample was poured into a melting point tube. The tube was then placed into the sample cavity T_2; and a thermocouple, as shown in Fig. 1, was inserted into the sample. Similarly, in the reference cavity T_3, a melting point tube containing reference glass beads was inserted. The reference thermocouple was then embedded into the glass beads. For thermoacoustical analysis, the set-up was the same as that described in the preceding section.

On heating the metal block A, the DTA curve of the sample was obtained on the X-Y recorder of the DTA instrument and a thermoacoustical curve of the sample was obtained on the time base recorder of the PPM-5R.

Samples

The following fiber samples were used: nylon 610 mono filament (0.023 mil), nylon 66 filament (70/30), Alrac nylon 4 filament, Vylor mono filament (2750 denier), Dacron polyester filament (70/34), Fortrel polyester filament (70/36), Teflon filament (1200/180), rayon filament (900/100), cotton spun yarn, and glass filament.

Dacron polyester, Teflon, and all nylon filaments, except nylon 4, were manufactured by Du Pont. Nylon 4 was supplied by Alrac Division of Radiation Research Corp. Vylor, which contains nylon 66 and nylon 610, was also manufactured by Du Pont. Fortrel polyester was supplied by Celanese Corp. Rayon fiber was supplied by American Viscose and cotton yarn was obtained from Coats and Clark. The glass fiber was that used in torsional braid apparatus, supplied by Chemical Instruments Corp.

RESULTS AND DISCUSSIONS

Dynamic Thermoacoustical Curves

A sketch of a hypothetical dynamic thermoacoustical curve is shown in Fig. 2. The pulse propagation time for a distance of x cm of the sample at room temperature is represented by the horizontal portion of the curve AB. As long as the distance x is kept constant, AB remains parallel to the abscissa. The velocity of sound through the material at 25°C is equal to $(x/120) \times 10^6$ km/sec. The temperature programming of the DTA apparatus is initiated at B. As long as the sample remains physically and chemically unchanged, the curve continues to indicate a horizontal line. At C the sample begins to transform to a different phase and the curve deviates from the base line. A change toward the upward direction indicates the lowering of the sound velocity. It is

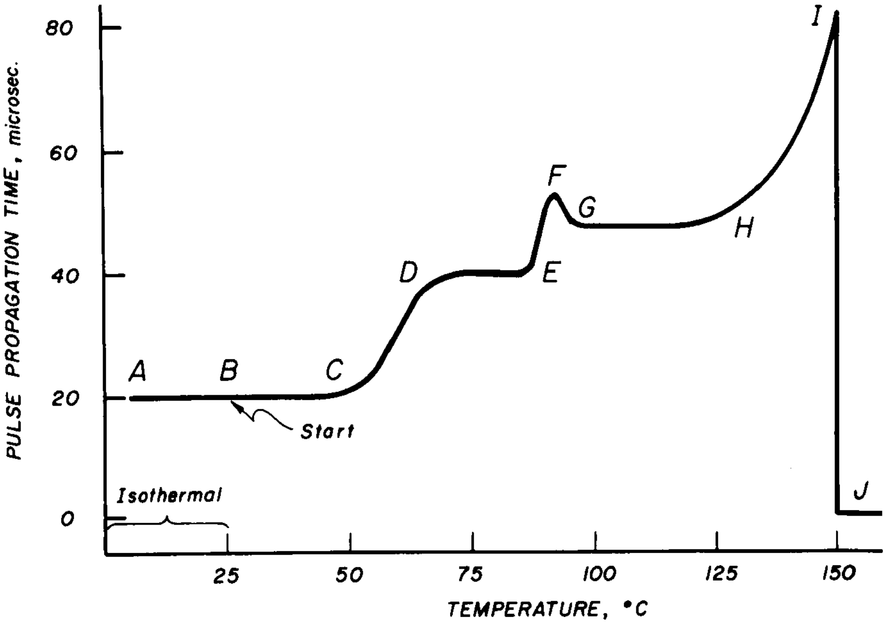

FIG. 2. A hypothetical dynamic thermoacoustical curve.

known that the velocity of sound is highest in solid, lowest in gas, and intermediate in liquid. Therefore, one may assume that the upward trend of the curve would indicate the change of polymer from compact form to relatively fluid form or, in other words, an increase of molecular motion of polymers. An opposite phenomenon is indicated by the downward trend of the curve FG. The sample at G is certainly in a less fluid state than at F. Again G to H shows no physical or chemical change in the sample. At H the sample reveals the premelting behavior. As the melting starts there is a sharp upward trend of the curve until the sample breaks at I due to the actual melting. The recorder pen drops immediately to zero, indicating thereby a discontinuity of the pulse propagation path.

In the case of a metal wire, the interpretation of the thermoacoustical curve is much simpler. For a metal, the sonic velocity is related to Young's modulus according to

$$C = (Y/D)^{1/2}$$

where C is the sonic velocity, D is the density of the metal, and Y is the Young's modulus. Therefore, the entire curve can be interpreted as the

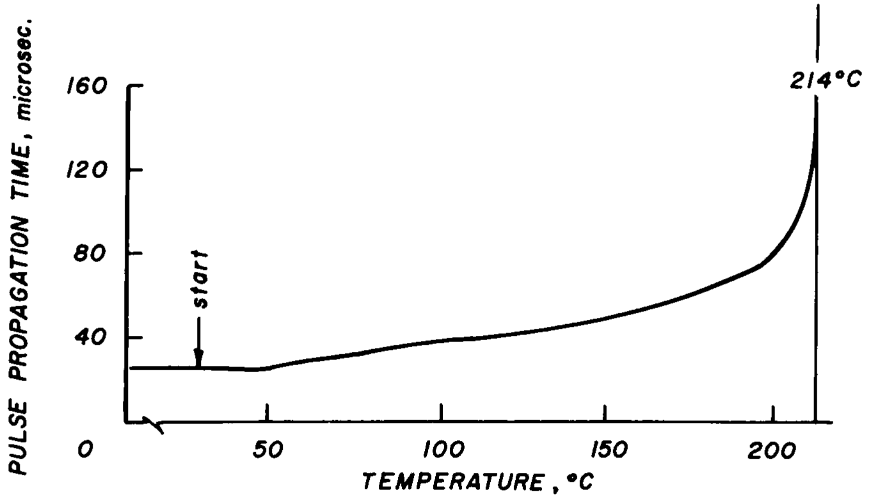

FIG. 3. Dynamic thermoacoustical curve of nylon 610 (draw ratio 3.5 to 1) in air.

change of Young's modulus or the density. In the case of polymers, the interpretation is not as simple due to the viscoelastic behavior of the material. However, before entering into any theoretical discussion it should be more interesting to review some of the experimental curves of synthetic and natural fibers.

The thermoacoustical curve of nylon 610 filament drawn to a ratio of 3.5 to 1 is shown in Fig. 3. The beginning of the temperature programming is indicated in the figure by an arrow. The curve shows a distinct upward deviation from the baseline at 45° C. It levels off again at 55° C. This deviation is attributed to the glass transition temperature of nylon 610. Premelting behavior of the polymer is revealed by the upward trend of the curve above 150° C. The melting is indicated by the sharp upward trend of the curve and then an instantaneous drop to the zero line. It is important to note that above the glass transition temperature the pulse propagation time increased continuously with the rise of temperature. Prior to melting, however, the propagation time increased at an accelerating rate.

The behavior of undrawn nylon 610 and drawn nylon 610 at different draw ratios has been compared in Fig. 4. The increase of pulse propagation time near T_g is more pronounced in the case of the undrawn fiber. The fiber drawn to a ratio of 3.5 to 1 shows relatively insignificant change at the time scale indicated in the figure. Another deviation in the curve of undrawn nylon 610 was observed at 160° C.

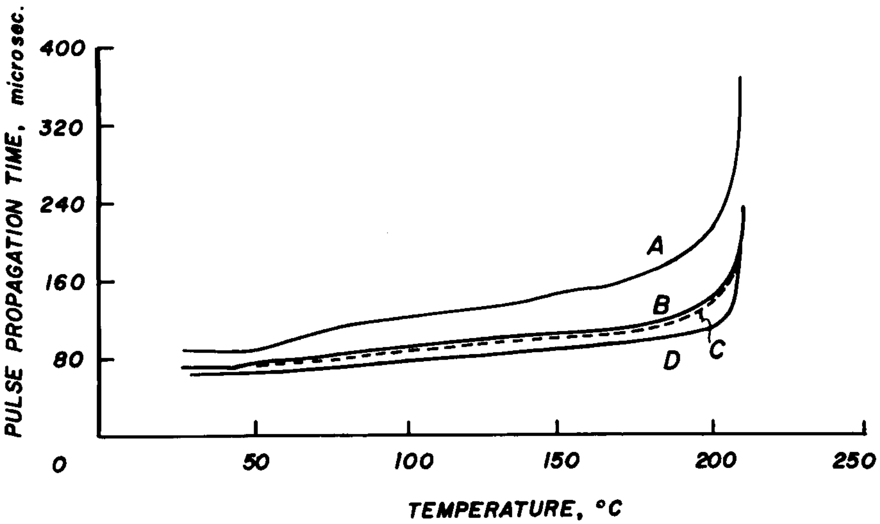

FIG. 4. Dynamic thermoacoustical curves of undrawn and drawn nylon 610 in air. (A) Undrawn. (B) Draw ratio 2:1. (C) Draw ratio 2.5:1. (D) Draw ratio 3.5:1.

This change may be associated with certain crystal structural changes. The premelting behavior of undrawn and drawn fibers appeared to be similar and melting of the polymer occurred at the same temperature in all cases. It should be noted that the curves shifted downward as the draw ratio was increased. This shift toward the lower pulse propagation time or, in other words, toward the higher sonic velocity has been attributed to the increase of the degree of orientation of the polymer molecules with the increased draw ratio. A theoretical consideration on this aspect is given later in this paper.

Thermoacoustical curves of a variety of synthetic fibers are shown in Fig. 5. These curves were all obtained under the same condition and at the same scale sensitivity. The curves of nylon 4, nylon 66, and nylon 610 all show different characteristic natures. Dacron and Fortrel polyester fibers behaved differently at temperatures below 100°C, but above 100°C both of them behaved identically. By comparing the curves, the thermoacoustic behavior of polyester fibers seemed to be somewhat similar to nylon 66. Teflon behaved similar to nylon 4 between 100 and 175°C. However, above 175°C it continued to rise upward at the same rate whereas the nylon 4 curve shows a change in rate. Also, Teflon melted at a lower temperature than nylon 4.

The thermoacoustical behavior of a glass fiber indicates no

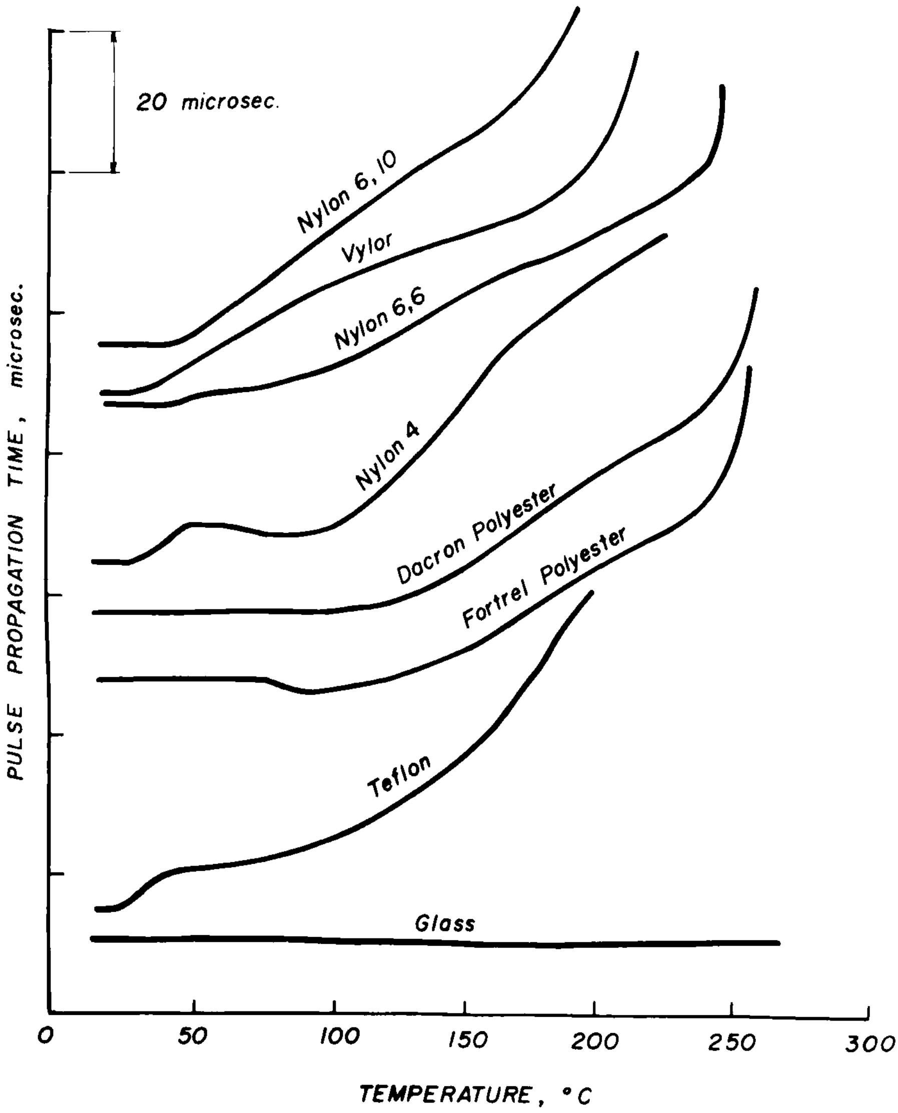

FIG. 5. Dynamic thermoacoustical curves of synthetic fibers in air.

significant change in the temperature range shown. The horizontal straight curve for glass fiber further indicates that the curves for synthetic fibers are actually showing the characteristic features of the fibers and are not just experimental artifacts.

Cellulose fibers, such as cotton and rayon, do not melt but decompose at temperatures above 300° C. Cotton and rayon are chemically the same (polymer made up of cellobiose units) but differ in their morphological structure, degree of crystallinity, and degree of polymerization. They are hard to differentiate by differential thermal analysis or by thermogravimetric analysis. The dynamic thermoacoustical curves of cotton and rayon are shown in Fig. 6. They are distinctly different, particularly above 250° C. Rayon shows a distinct peak at about 340° C, whereas cotton shows a series of overlapping peaks at higher temperatures. These peaks can be attributed to the decomposition of cellulose fibers. Because of a variety of chemical changes at the decomposition temperature, such as polymer scission and end-group unzipping, the velocity of pulses was slowed down, resulting in a peak. The right-hand side of the peak indicates the resumption of the original speed as the chemical changes were over and the cellulose molecule was converted to a stable carbonized form. Again, the curve of glass fiber has been included as a reference.

A simultaneous thermoacoustical curve and differential thermal analysis curve was obtained with nylon 610 by the technique described in the experimental section. For the thermoacoustical curve the sample was mounted as shown in Fig. 1, and for DTA the sample was cut into small pieces. Both curves were obtained simultaneously as shown in Fig. 7.

Theoretical Interpretation

The dynamic thermoacoustical technique and some of the experimental curves have been discussed. It is now important to investigate what the thermoacoustical curve reveals and how these sonic pulse propagation responses can be related to fundamental polymer properties. In order to develop a theory, the Maxwell-Wiechert model [4] for polymers has been considered as the basis. The model, shown in Fig. 8, consists of a very large (or infinite) number of Maxwell elements (spring and dashpot) coupled in parallel. In the figure, E_i and τ_i are the modulus and relaxation time, respectively, of the i-th element where i ranges from 1 to m and $\eta_i^{(t)}$ is the viscosity in tension, which is linearly related to the shear viscosity η. When strain s is applied to the model, a stress f will be developed. It must be remembered that the only observables are the external strains s and the overall stress f. The partial stress f_i and the quantities E_i and τ_i are not microscopically observable.

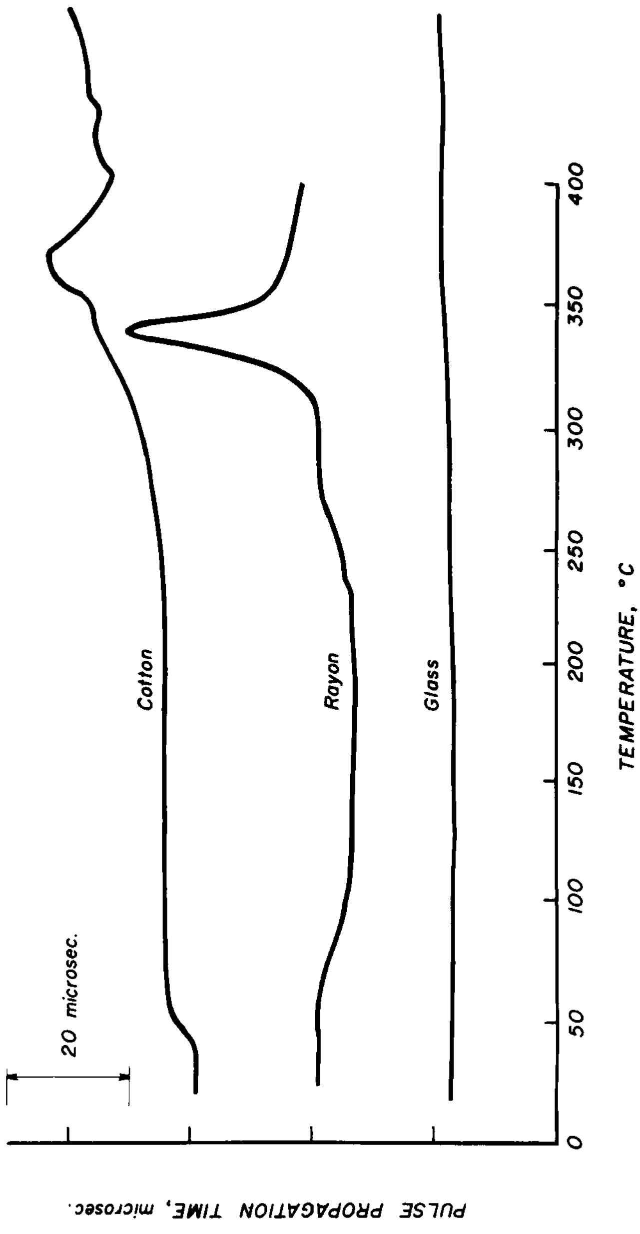

FIG. 6. Dynamic thermoacoustical curves of cellulose fibers in air.

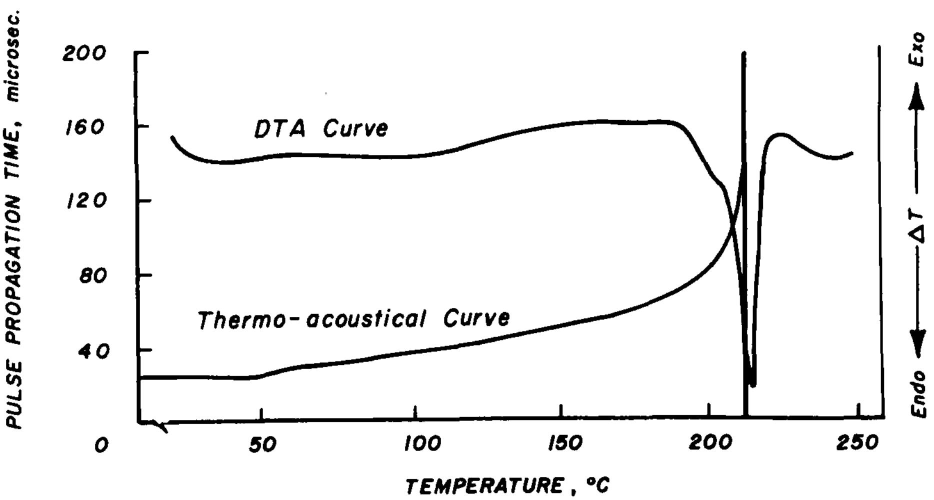

FIG. 7. Simultaneous DTA and dynamic thermoacoustical analysis of nylon 610 in air.

Assuming that a cube of viscoelastic material (Maxwell-Wiechert model) of unit dimensions is attached to an external mass and the whole system is subjected to forced oscillations, an equation can be deduced to define the viscoelastic stress set-up in the material in terms of the complex dynamic modulus [5]. Tobolsky and Eyring [6] separated the real and imaginary parts of the equation and defined the dynamic modulus (E_{dyn}) of the material as follows:

$$E_{dyn} = \sum_{i=1}^{m} \frac{E_i \, \omega^2 \, \tau_i^2}{1 + \omega^2 \, \tau_i^2} \tag{1}$$

where ω is the frequency of the applied stress.

When sonic pulses of frequency ω are transmitted through a polymeric material, the dynamic modulus can be defined by the equation cited above. Nolle [7] deduced a separate relationship between the dynamic modulus and the velocity of pulse propagation for an unoriented polymer:

$$E_{dyn} = \rho c^2 \omega^2 (\omega^2 - \alpha^2 c^2)/(\omega^2 + \alpha^2 c^2)^2 \tag{2}$$

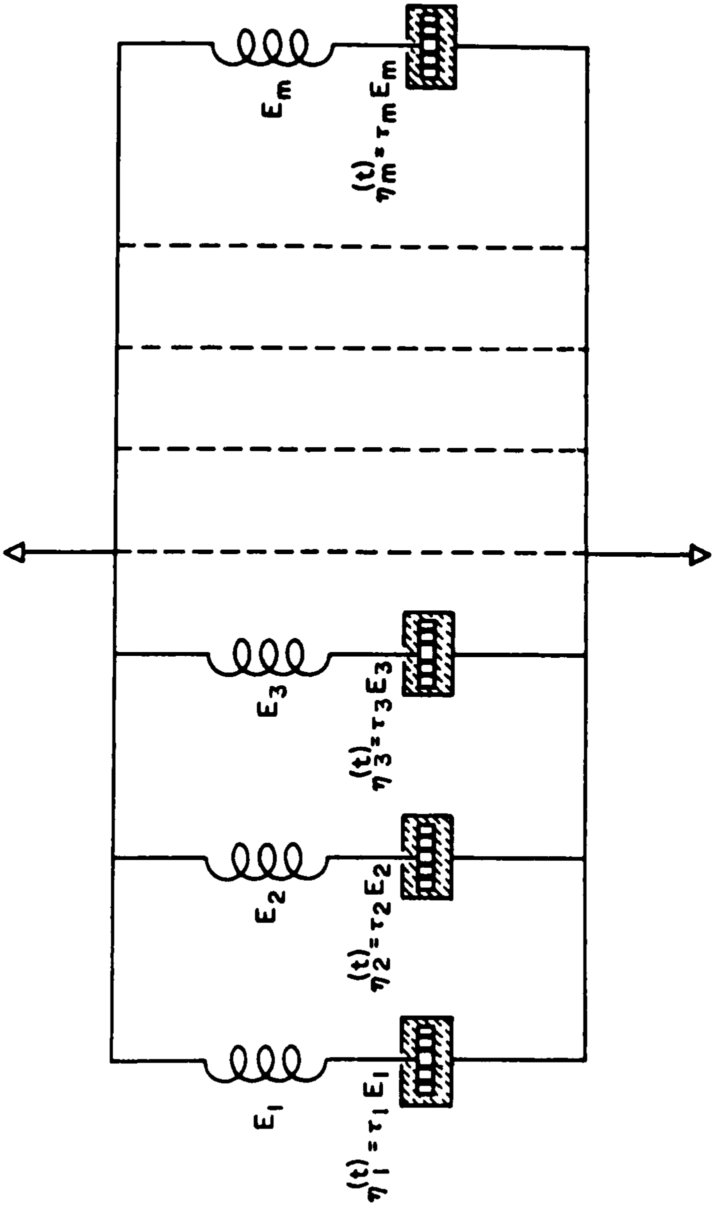

FIG. 8. Maxwell-Wiechert model for polymers.

where ρ is the density of polymer, c is the velocity of sound, and α is attenuation. For small damping, α is very small and the Eq. (2) reduces to

$$E_{dyn} = \rho c^2 \tag{3}$$

For an unoriented polymer, by combining Tobolsky and Eyring's equation (Eq. 1) with Nolle's equation (Eq. 3) the following equation results:

$$\rho c^2 = \sum_{i=1}^{m} \frac{E_i \omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2} = \sum_{i=1}^{m} \frac{E_i \tau_i^2}{1/(\omega^2 + \tau_i^2)} \tag{4}$$

If, however, the elements of the model have a very high relaxation time (τ_i) and the frequency of stress ω is also very high, Eq. (4) reduces to

$$\rho c^2 = \sum_{i=1}^{m} E_i \tag{5}$$

Since a polymer block contains elements of different τ values ranging from very low to very high values, let us assume that a fraction of elements have τ values so high that their relaxation is not responsive to sonic waves of frequency ω, and the rest of the elements have relatively lower τ values and the relaxation of these elements is responsive to sonic waves. In the former case the sound waves will propagate according to Eq. (5) whereas in the latter case the waves will propagate according to Eq. (4). Let us assign the latter fraction as β and the former as $(1 - \beta)$. The propagation of sound pulses through a polymer consisting of these two broadly classified groups of elements is illustrated in Fig. 9. The elements having low τ values are represented by open circles and their relaxation time is designated by τ_i, and those of high τ values are represented by solid circles and their relaxation time is designated as τ_j. The velocity of sound will be influenced by the combined effect of all these elements. Assuming that they are randomly distributed, the ultimate sound velocity through the polymer can be obtained by applying Urick's approximation [8]. The resultant equation is

$$\frac{1}{\rho c^2} = \frac{\beta}{\sum_{i=1}^{m\beta} \frac{E_i \omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2}} + \frac{1 - \beta}{\sum_{j=1}^{m(1-\beta)} E_j} \tag{6}$$

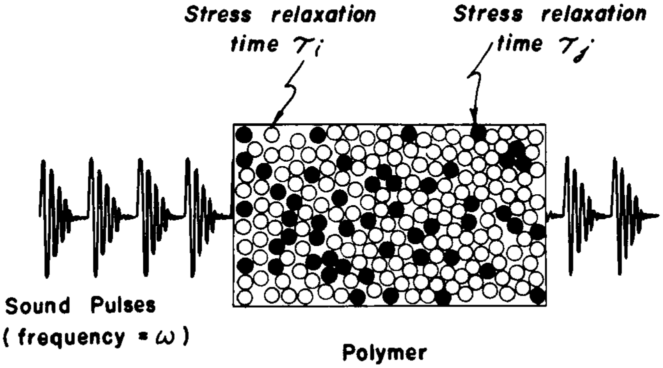

FIG. 9. A schematic showing pulse propagation through a polymer consisting of broadly classified elements (○) Elements of low relaxation time, τ_i. (●) Elements of high relaxation time, τ_j.

where subscripts i and j represent the elements of low and high τ values, respectively. This equation is applicable to nonoriented polymers only.

For oriented polymer molecules Moseley [3] derived a relationship between velocity of sound and molecular orientation:

$$c_\theta = \frac{2}{3} \frac{c^2}{\sin^2 \theta} \tag{7}$$

where θ is the angle between the direction of the propagation of sound and the molecular axis as shown in Fig. 10. c_θ is the velocity of sound in the direction as shown in Fig. 8, and c is the velocity in the same nonoriented polymer.

Therefore, for oriented polymer molecules that exist in fibers, Eqs. (6) and (7) can be combined. Hence

$$\frac{1}{c_\theta^2} = 0.67 \sin^2 \theta \left[\frac{\rho\beta}{\sum\limits_{i=1}^{m\beta} E_i \sin^2 \delta_i} + \frac{\rho(1-\beta)}{\sum\limits_{j=1}^{m(1-\beta)} E_j} \right] \tag{8}$$

where δ_i is the phase angle between the stress and the strain and

$$\tan \delta_i = \omega\tau_i$$

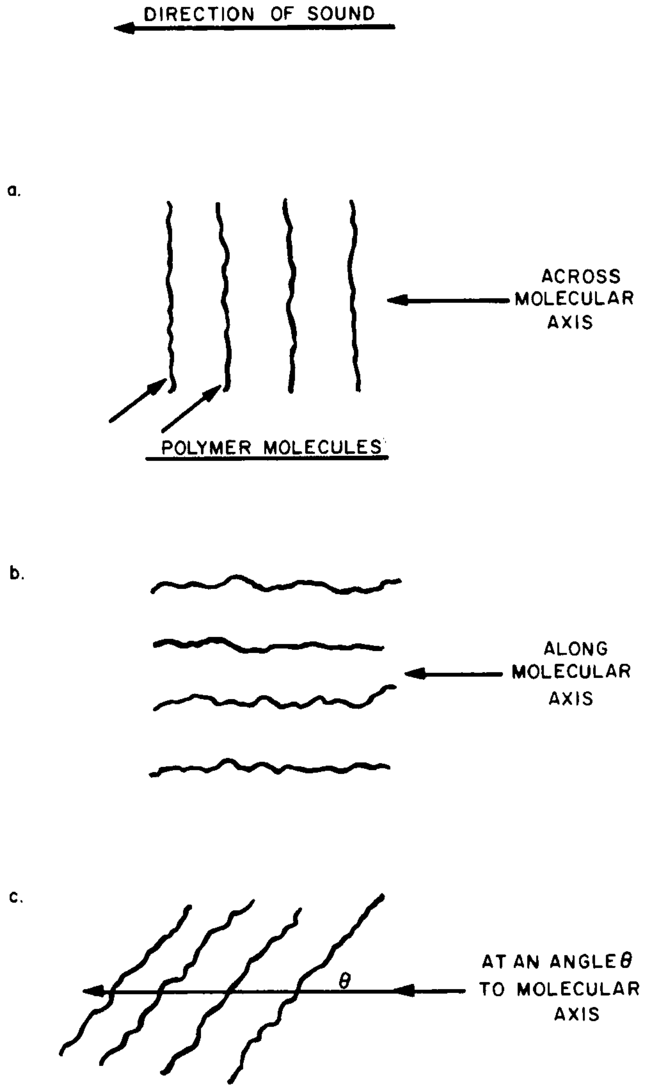

FIG. 10. Possible modes of sound transmission in polymers [3].

By changing c_θ to pulse propagation time, μ, for a fixed length, χ, of the sample, we get

$$\mu = 0.82\chi \sin\theta \left[\frac{\rho\beta}{\sum_{i=1}^{m\beta} E_i \sin^2 \delta_i} + \frac{\rho(1-\beta)}{\sum_{j=1}^{m(1-\beta)} E_j} \right]^{1/2} \tag{9}$$

This is the final relationship between the pulse propagation time and the viscoelastic parameters of a polymer. In Figs. 2 to 6, all the curves represent μ, which is a function of orientation and viscoelastic parameters vs temperature. For simplicity and practical consideration, let us write the equation as

$$\mu = 0.82\chi \sin\theta\, \epsilon_s \tag{10}$$

where ϵ_s is defined as a sonic viscoelastic function of the polymer at a constant sonic frequency ω, and this function is equal to

$$\left[\frac{\rho\beta}{\sum_{i=1}^{m\beta} E_i \sin^2 \delta_i} + \frac{\rho(1-\beta)}{\sum_{j=1}^{m(1-\beta)} E_j} \right]^{1/2}$$

Thus it can be inferred from Eq. (10) that as the fiber sample is heated at a constant rate, the thermoacoustical curves will be influenced by 1) the change in orientation of the polymer molecules and 2) the change in the viscoelastic properties of the polymer.

Experiments were conducted with repeated heating and cooling of nylon 610 to investigate the effect of heating on the orientation of polymer molecules. Figure 11, Curve A, represents the first heating of nylon 610 filament. The sample was allowed to cool slowly and found to indicate the same pulse propagation time μ at room temperature as that of the original sample. The second heating is represented by Curve B. On cooling after the second heating the propagation time was back to the original value. A similar phenomenon was also observed on heating a third time and cooling at room temperature. Since the sample was not mechanically disturbed during the heating and cooling process, it was expected that any changes in the orientation during heating would have shown some residual effects even after cooling the sample to room temperature. Any changes in the orientation should have been reflected as a displacement of the curve at room temperature after the second

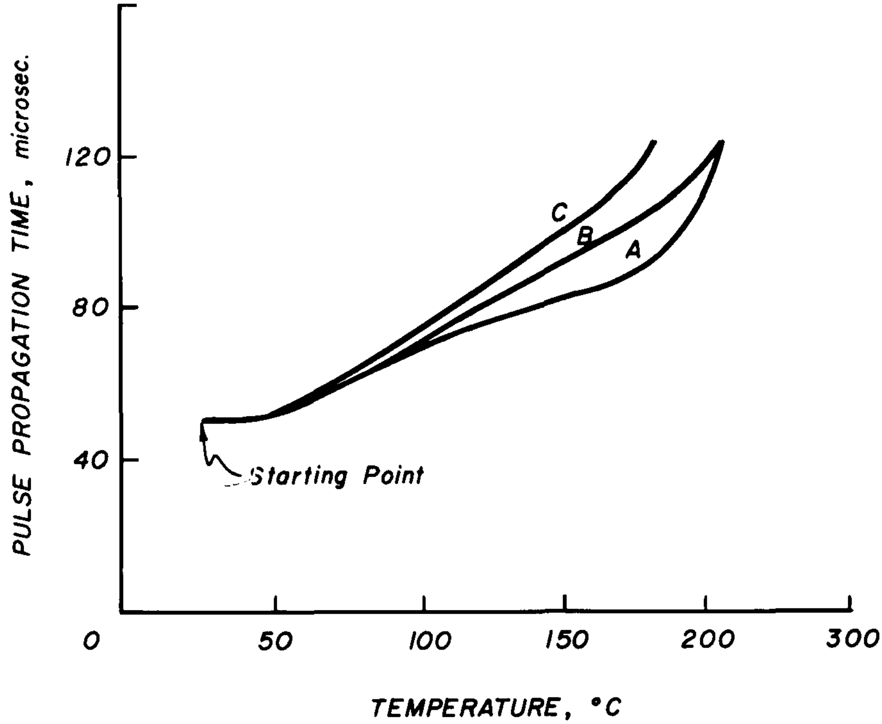

FIG. 11. Dynamic thermoacoustical curves of nylon 610 under repeated heating. (A) First heating. (B) Second heating. (C) Third heating.

and third cooling (refer to Fig. 4 also). Experimental curves show no such displacement. The fact that the first, second, and third heating curves do not coincide with each other at higher temperatures can be attributed to certain irreversible changes in the viscoelastic properties of the polymer. These experiments strongly suggest that the orientation of the polymer molecules in the fiber does not undergo any significant change under these experimental conditions. Therefore, it can be concluded that the sonic response under dynamic heating condition would enable us to characterize the fibers in terms of their viscoelastic responses to heat.

CONCLUDING REMARKS

The main purpose of this work is to demonstrate that acoustical measurement under dynamic heating conditions can be used for characterizing certain physicochemical properties of polymers. A theorectical relationship was derived between the sound propagation time, the viscoelastic properties of polymers, and the orientation of molecules. This relationship should be useful for the interpretation of dynamic thermoacoustical curves of fibers and other polymers.

However, further development is required in the experimental technique, particularly in the instrumentation. More precise measurements can be made by inserting the entire fiber mounting set-up and both piezoelectric transducers inside the heating chamber. In order to do this, selection of appropriate transducers which could stand temperature up to 600/700°C is important. Atmospheric control and an ability to cool the furnace below room temperature are also essential. In brief, to build a standard instrument the experimental set-up shown here must be modified.

The theoretical relationship derived here could be further simplified by separating the orientation factor and viscoelastic function so that they can be analyzed independently. The sonic viscoelastic function could be solved further to determine the individual parameters such as elastic modulus, dynamic viscosity, and stress relaxation time. Many of these proposed modifications can be achieved if the amplitudes of the pulses are also continuously measured along with the velocity.

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