

# The Effect of Heat Setting on the Structure and Mechanical Properties of Poly(ethylene Terephthalate) Fiber. III. Anelastic Properties and Their Dependence on Structure

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## Synopsis

Viscoelastic parameters for poly(ethylene terephthalate) (PET) fibers heat set under different conditions were determined at 110 Hz between room temperature and about 200°C. The correlation of dynamic mechanical properties with structure and their dependence on the temperature of the measurement are discussed. It was found that in addition to the structural parameters such as degree of crystallinity, crystallite and amorphous orientation, etc., morphological factors such as size and distribution of crystallites also influence the dynamic mechanical properties. The activation energy of the  $\alpha$ -transition is reported, and the effect of the distribution of relaxation times on the activation energy is discussed.

## INTRODUCTION

There have been a number of studies on the viscoelastic behavior of drawn and undrawn poly(ethylene terephthalate).<sup>1-19</sup> The purpose of our investigations was to examine the effect of heat-setting parameters, such as temperature and time of heat setting, with the filaments held under taut or free conditions, on the loss modulus, storage modulus, and  $\tan \delta$  and the dependence of these viscoelastic parameters on the temperature of measurement. An attempt was also made to understand how the various structural parameters, which were reported<sup>20</sup> in part I, affect these dynamic mechanical properties. The activation energy of the  $\alpha$ -transition was determined by using two methods, viz., from the half-width of the loss modulus–reciprocal temperature curve or from the area of the loss modulus–reciprocal temperature curve,<sup>9</sup> using a single relaxation time or a distribution of relaxation times. The two methods were critically assessed.

## EXPERIMENTAL

### Sample Preparation

The details of sample preparation were given<sup>20</sup> in part I. In brief, commercial multifilament PET yarn was heat set under free (FA) and taut (TA) conditions in a silicone oil bath maintained between 100 and 220°C for times varying from 1 to 60 min. The samples, on being taken out of the bath, were quenched in air.

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In one case, the 60-min set of samples, the cooling rate was varied by allowing the yarn to cool in the bath itself over a period of 12 hr. The experimental specimens were prepared by combining four multifilament yarns into a strand, and the gauge length was kept as 4 cm.

### Dynamic Mechanical Properties

Dynamic measurements were made on a direct-reading viscoelastometer, the Rheovibron model DDV-II, which was operated at a frequency of 110 Hz between room temperature and 200°C. Samples were heated at 3°C/min under relaxed conditions. Measurements of the dynamic force and  $\tan \delta$  were made at increments of 10°C, except near the transition region where measurements were made at smaller increments of temperature. From the dynamic force, the length, and the cross-sectional area, the complex modulus was calculated. The value of  $\tan \delta$  being small, the storage and loss modulus are approximately given by the following expressions:

$$\text{storage modulus } E' = E^*$$

and

$$\text{loss modulus } E'' = E^* \tan \delta$$

where  $E^*$  is the complex modulus.

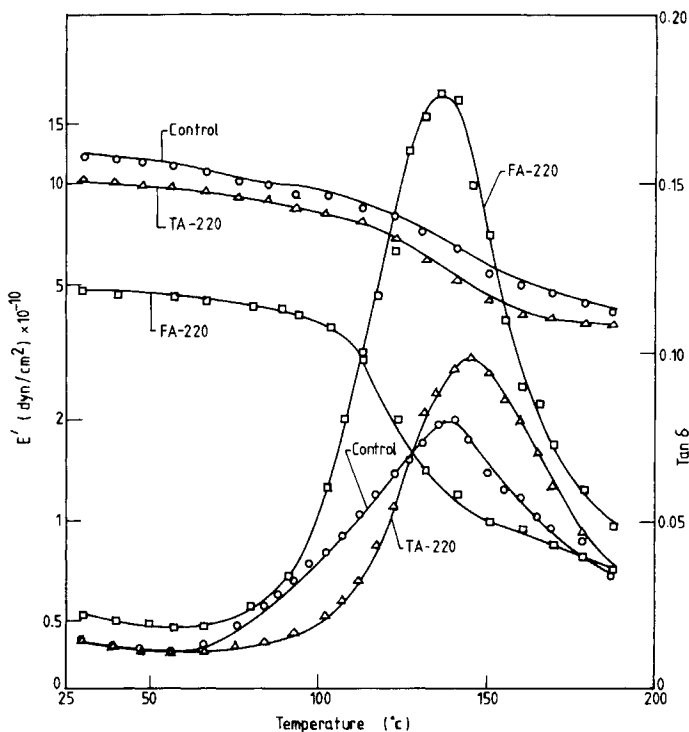


Fig. 1. Temperature dependence of storage modulus and  $\tan \delta$  for control, FA-220°C, and TA-220°C samples (heat set for 30 min).

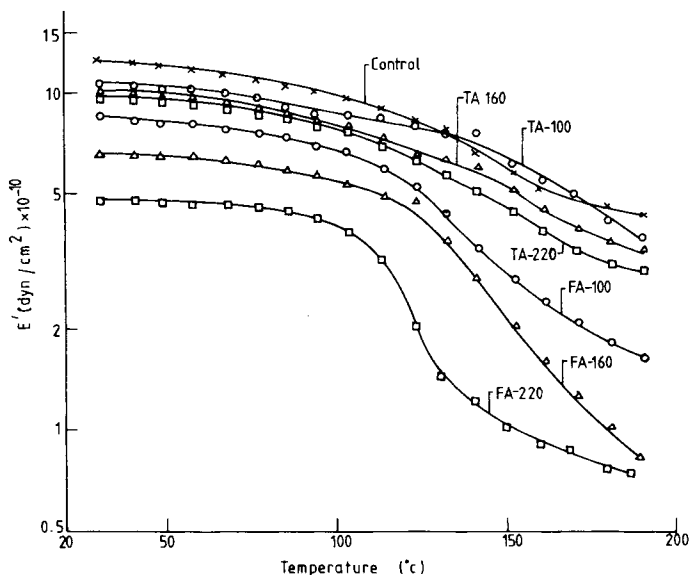


Fig. 2. Temperature dependence of storage modulus for control and heat-set samples (heat set for 30 min).

The  $\tan \delta$  measurements were made for samples annealed for 1, 30, and 60 min (slowly cooled). However, the storage modulus measurements were made only on samples heat set for 30 min while free to relax and held taut at constant length.

## RESULTS AND DISCUSSION

### Effect of Heat-Setting Parameters

To illustrate the typical data obtained, the dependence of  $\tan \delta$  and the storage modulus on the temperature of measurement for the control sample and the samples heat set at 220°C for 30 min while free to relax (FA 220) and held taut at constant length (TA-220) is given in Figure 1. The dependence of the storage modulus on temperature of measurement for the control sample and some heat-set samples is shown in Figure 2. The loss modulus data for the control sample and for the samples heat set at 220°C for 30 min while free to relax and held taut at constant length are plotted in Figure 3. The maximum amplitude of  $\tan \delta$  is shown as a function of heat-setting temperature in Figure 4. The areas of the loss modulus-reciprocal temperature curves are shown in Figure 5 as a function of heat-setting temperature. From an examination of Figures 1 to 5, the following points emerge:

- (1) The storage moduli of all the heat-set samples, broadly speaking, are less than the storage modulus of the control sample (Figs. 1 and 2).
- (2) The storage moduli of all the free-annealed samples are less than the storage moduli of the taut-annealed samples (Fig. 2).
- (3) The rate of decrease of storage modulus with temperature of measurement is relatively more in the free-annealed samples (Fig. 2).
- (4) The loss curve for the control sample is relatively more broad than for the heat-set samples (Figs. 1 and 3).

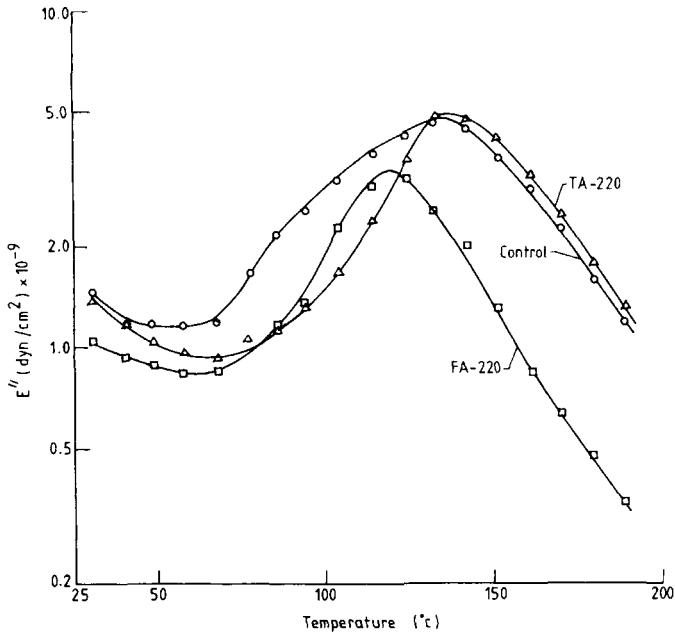


Fig. 3. Temperature dependence of loss modulus for control, FA-220°C, and TA-220°C samples (heat-set for 30 min).

(5) The maximum amplitudes of  $\tan \delta$  for free-annealed samples are almost twice the control value. The values of this parameter for the taut-annealed samples are close to the control value (Fig. 4).

(6) The maximum amplitude of  $\tan \delta$  increases slightly with increase in heat-setting temperature both for the free- as well as for taut-annealed samples (Fig. 4).

(7) The area of the loss modulus-vs.- $1/T$  curve decreases slightly with increase in heat-setting temperature in free- as well as in taut-annealed samples. This area is relatively smaller for the free-annealed samples. The area for the control sample is the highest (Fig. 5).

The above points clearly indicate that the state of the yarn during heat setting, viz., whether it is held in the free or taut state, has a predominant effect on the anelastic properties of heat-set PET fibers. It was shown in part II that this factor plays an important role in the case of the elastic modulus also. It has al-

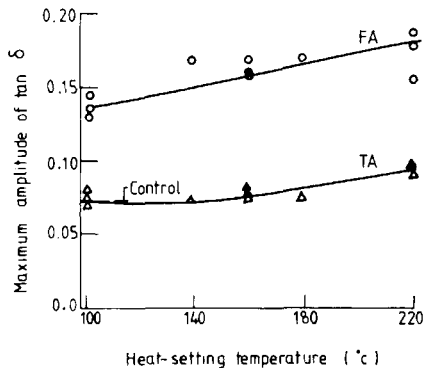


Fig. 4. Dependence of maximum amplitude of  $\tan \delta$  curves on heat-setting temperature.

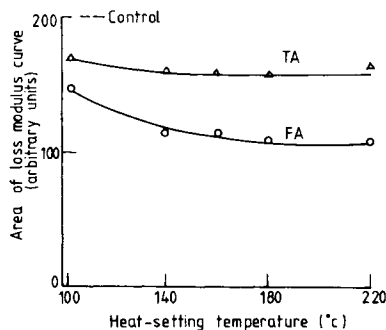


Fig. 5. Area of loss modulus-vs.- $1/T$  curves as function of heat-setting temperature.

ready been established<sup>20</sup> in part I that in these samples the major differences in the structural parameters are mainly in terms of orientation and that the other structural parameters such as crystallinity, crystallite size, etc., are not very different for these two sets of samples at corresponding heat-setting temperatures. Therefore, orientation will be expected to play an important role in controlling these dynamic mechanical parameters. Since the  $\alpha$ -transition is related to the glass transition temperature, which in turn will be dominated by the state of the amorphous phase, the orientation of the amorphous phase will be relatively more important. As shown later, this expectation turns out to be correct.

The  $\tan \delta$  values are relatively high in the free-annealed samples (Fig. 1) and are indicative of the faster rate of the decrease in modulus in these samples. Also the temperature at which the  $\tan \delta$  peak appears increases with the initial increase in crystallinity up to about 35 to 40% and then decreases with further increase in crystallinity. This is in agreement with the results of Illers and Breur,<sup>6</sup> according to whom a crystallinity increase of up to 30% is accompanied by an increase in temperature at which the  $\tan \delta$  peak occurs and further increase in crystallinity decreases the peak temperature. It was pointed out that when the fiber has a low crystalline content, a large number of small crystals are distributed over the amorphous matrix, giving rise to relatively more hindrance to molecular mobility. This results in an increase in temperature at which the  $\tan \delta$  peak appears. With further growth of crystallites at higher heat-setting temperatures, smaller crystals either merge together or merge with bigger crystals to form relatively large crystals, as shown<sup>20</sup> in part I, with comparatively less hindrance to molecular mobility. Hence, the  $\tan \delta$  peak appears at relatively low temperatures. It might be concluded that the main factors which influence the temperature at which the  $\tan \delta$  peak occurs are (a) crystallinity and (b) crystallite size, which determine the amount and distribution of the amorphous phase, and (c) amorphous orientation.

The maximum amplitude or the peak value of  $\tan \delta$  for free- and taut-annealed samples is plotted as a function of amorphous orientation,  $fa$ , in Figure 6(a) and as a function of  $(1 - \beta)(1 - fa)$  in Figure 6(b). The peak value of  $\tan \delta$  decreases with increase in amorphous orientation factor [Fig. 6(a)]. Since the viscoelastic phenomena are expected to be governed by the amount and orientation of the amorphous phase, a plot of the peak value of  $\tan \delta$  versus  $(1 - \beta)(1 - fa)$  can give useful information since the latter parameter contains information on both aspects of the amorphous phase. Figure 6(b) shows that an increase in amorphous

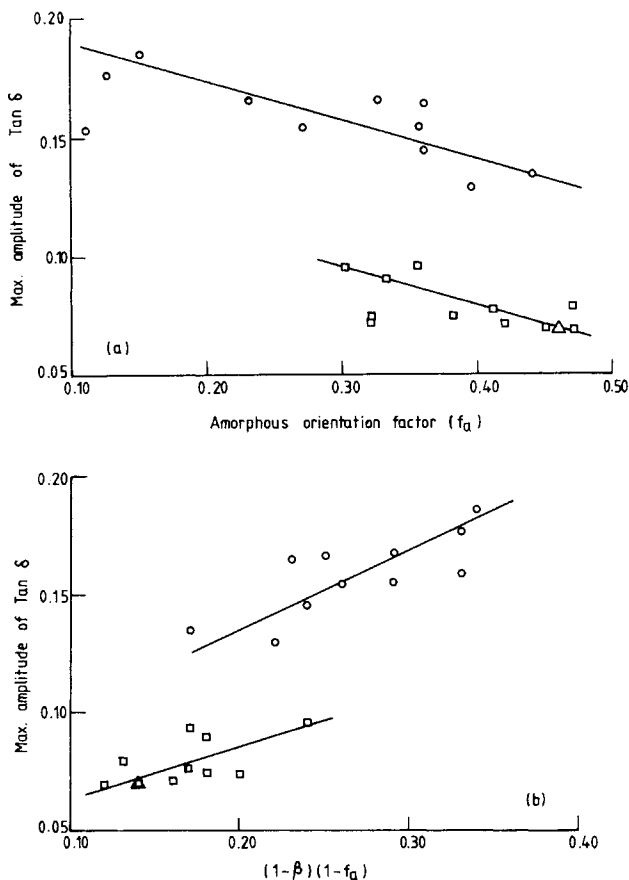


Fig. 6. Dependence of maximum amplitude of  $\tan \delta$  on (a) amorphous orientation factor and (b) on  $(1-\beta)(1-f_a)$ : ( $\Delta$ ) control; (O) FA; ( $\square$ ) TA.

content and its degree of randomness increases the maximum value of  $\tan \delta$ . Higher orientation of the amorphous region leads to straightening of the chains. The more ordered chains allow more efficient transfer of stress and thus reduce dissipation of energy, thereby reducing the maximum amplitude of  $\tan \delta$ . A point to be noted from these figures is that though the variation of  $\tan \delta_{\max}$  with  $f_a$  or with  $(1-\beta)(1-f_a)$ , both for free- and taut-annealed samples, shows similar behavior, the magnitude of a  $\tan \delta_{\max}$  can differ markedly for the free- and taut-annealed samples for the same orientation factor. Since this difference cannot be explained on the basis of amorphous content or its orientation, these results suggest that morphological factors such as the arrangement of crystals within the amorphous regions in the two sets of samples can be important. This point will now be discussed.

In samples in which the amorphous regions and crystal boundaries are sharply defined, as in an ideal two-phase material, the amorphous phase will play a relatively more important role and the response to an applied force in this case will have a higher viscoelastic component compared to a sample in which the amorphous regions are distributed without any sharp boundaries, though the two samples may have identical amorphous orientation. The value of  $\tan \delta_{\max}$  will

be larger in the former sample. The present results thus support the models for free-annealed and taut-annealed samples shown in Figures 7(a) and 7(b).

The modulus of the taut-annealed samples is higher than the modulus of the free-annealed samples (Fig. 2). Therefore, for the same applied stress, the strain in the taut-annealed sample will be relatively smaller than in the free-annealed sample. The loss modulus of taut-annealed samples, which is given by the ratio of the out-of-phase component of stress to the maximum strain amplitude, will therefore be higher assuming that the differences in the phase angle,  $\delta$ , between the free- and taut-annealed samples are, relatively speaking, less important. This assumption appears to be reasonable, and the results shown in Figures 3 and 5 are thus explained.

The early investigators of viscoelastic behavior in polymers based their conclusions<sup>23-27</sup> on the measurements of mechanical loss as given by  $\tan \delta$ , which they termed internal friction. The validity of this parameter as a measure of mechanical relaxation was questioned by Illers and Koseford.<sup>28</sup> These authors and many others<sup>6,29-31</sup> consider that the loss modulus  $E''$  is the more appropriate parameter for this purpose and that  $E''_{\max}$  is the more realistic measure of the relaxation intensity. Later workers<sup>32,33</sup> have however stated that  $\tan \delta$  is the more appropriate parameter.  $\tan \delta$  is a measure of the phase lag,  $\delta$ , which is essentially a function of the viscoelasticity of the sample. The loss modulus, on the other hand, is given by  $E' \tan \delta$  and thus combines the viscoelastic component ( $\tan \delta$ ) along with the mechanical resistance to the applied forces ( $E'$ ). Therefore,  $\tan \delta$  would appear to be a more appropriate parameter for the measurement of mechanical loss and the relaxation intensity. The area of the  $\tan \delta$ -temperature curve is a more representative measure of the loss or dissipation of energy and will be expected to be higher in free-annealed samples, as is found to be the case in the present studies (e.g., see Fig. 1).

The present observations can also be explained in terms of the strength of the relaxation which is conventionally defined<sup>22</sup> as

$$\frac{\text{relaxed strain} - \text{unrelaxed strain}}{\text{unrelaxed strain}}$$

where relaxed and unrelaxed strains are the limiting strains for a constant stress with respect to the  $\alpha$ -transition, and these are related to the relaxed and unre-

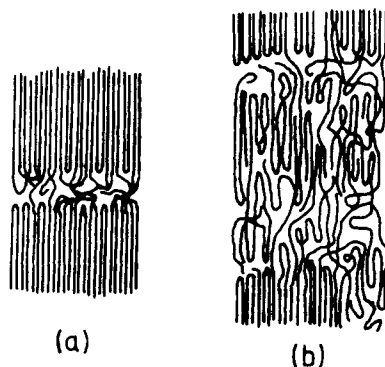


Fig. 7. Schematic representation of the arrangement of ordered and disordered regions in (a) free-annealed and (b) taut-annealed samples (taken from Ref. 22).

laxed moduli. The taut-annealed samples have a structure close to that of the control in which there is no distinct phase separation [Fig. 7(b)]. In free-annealed samples, on the other hand, there is a more distinct phase separation and the amorphous regions are relatively more relaxed [Fig. 7(a)]. As the temperature of measurement is increased, the glassy amorphous phase becomes rubbery and the modulus shows a large drop. In taut-annealed samples, on the other hand, the drop in modulus is much less. The relaxation strength is therefore relatively high for the free-annealed samples.

### Activation Energy

Procedures for determining activation energy using a single relaxation time model and for a distribution of relaxation times have been reported by McCrum, Read, and Williams.<sup>9</sup> The activation energy  $H$  can be obtained from a plot of loss modulus vs.  $1/T$ , using the following expression<sup>9</sup>:

$$\int E'' d\left(\frac{1}{T}\right) = (E'_U - E'_R) \frac{\pi R}{2H} \quad (1)$$

where the left-hand side represents the area of the loss modulus-vs.- $1/T$  curve,  $E'_U$  and  $E'_R$  are the values of unrelaxed and relaxed storage modulus, and  $R$  is the gas constant. The activation energy  $H$  for a single relaxation time model can also be computed from the half-width of the loss modulus-vs.- $1/T$  curve and is given by the following expression<sup>9</sup>:

$$H = \frac{2.303R \log(r \pm (r^2 - 1)^{1/2})}{1/T_r - 1/T_m} \quad (2)$$

where  $T_r$  is the temperature corresponding to a value of  $\tan \delta_r$  arranged near  $T_m$ ,  $T_m$  is the temperature of  $\tan \delta_{\max}$ , and  $1/r = \tan \delta_r / \tan \delta_{\max}$ .

Activation energies for the  $\alpha$ -transition determined for the samples heat set for 30 min from the area [eq. (1)] and width [eq. (2)] of the loss modulus-vs.- $1/T$  curve using a single relaxation time model are listed in Table I. From this table

TABLE I  
Activation Energy of the  $\alpha$ -Transition for Samples Heat Set for 30 Min

Sample	Activation energy using single relaxation time model, kcal/mole		Activation energy using a distribution of relaxation times from width measure- ment with $\xi = 0.2$ , kcal/mole
	From area measurement	From width measurement	
Control	109	12.0	80.0
FA-100	112	15.7	104.0
-140	116.7	19.5	129.0
-160	121.0	19.5	129.0
-180	109.3	21.0	139.0
-220	91.0	15.7	104.0
TA-100	95.0	11.6	76.9
-140	96.8	13.0	86.0
-160	111.0	14.0	94.1
-180	91.5	14.0	92.7
-220	88.4	16.4	108.7



we observe that the activation energies determined from the area are much higher than those determined from the width. The activation energies for unoriented amorphous, unoriented crystalline, and oriented crystalline PET samples were reported to be 184, 124, and 97 kcal/mole, respectively, by Thompson and Woods.<sup>2</sup> The activation energies determined from area measurements for the present set of samples, which are oriented crystalline fibers, are similar in magnitude to that given by Thompson and Woods.<sup>2</sup> To see why the activation energy determined from measurements of width and area give different results, the present data were analyzed in terms of a model involving a distribution of relaxation times. It has been shown<sup>9</sup> that the expression for activation energy from the area of the loss modulus-vs.- $1/T$  curve for a distribution of relaxation times approximates that for a single relaxation time for very small relaxation times. The region of interest in these investigations is the  $\alpha$ -relaxation which appears between 100 and 200°C. In this region the latter assumption may be quite justified. Therefore, eq. (1) would be expected to hold for a distribution of relaxation times also. The values of activation energy as given in Table I determined from the area of the loss modulus curves are therefore approximately true for a distribution of relaxation times also. Activation energy from the width of the loss modulus-vs.- $1/T$  curve for a distribution of relaxation times is given by<sup>9</sup>

$$H = \frac{2.303R \log (\alpha \pm (\alpha^2 - 1)^{1/2})}{\xi(1/T_r - 1/T_{\max})} \quad (3)$$

where  $\alpha = [2 + \cos (\xi\pi/2)]$  and  $0 < \xi \leq 1$ ;  $\xi$  is unity for a single relaxation time and zero for a complete distribution of relaxation times. The activation energy was calculated using eq. (3) for various values of  $\xi$ , and the activation energies for  $\xi = 0.2$  are included in Table I. These were found to be quite close to those determined from the area measurements, as seen from Table I. This indicates a wide relaxation time distribution, but it is quite possible that for these various heat-set samples, the distribution of relaxation times will not be the same. In fact, by taking suitable values of  $\xi$  for different samples, the activation energy values from the two methods can be matched. The present exercise suggests that when activation energy is determined from area measurement, the distribution of relaxation times is implicitly accounted for, and this method is therefore perhaps more meaningful and hence will be considered in further discussion.

The values of activation energy for one set of samples, as calculated using eq. (1), are plotted in Figure 8 as a function of heat-setting temperature. It is observed that the value of activation energy of the control sample is intermediate between those for free- and taut-annealed samples. The activation energy for free-annealed samples is higher than that for the taut-annealed samples. A phenomenological explanation of the higher activation energy in free-annealed samples can be given. The activation energy  $H$  using eq. (1) is given by

$$H = \frac{(E'_U - E'_R)\pi R}{2 \int E'' d(1/T)}$$

and is thus inversely proportional to the area of the loss modulus-vs.- $1/T$  curve and proportional to the difference between the unrelaxed and relaxed modulus. For the free-annealed samples, the difference between unrelaxed and relaxed modulus is higher than that for the taut-annealed samples, as was shown earlier. These factors thus contribute to the higher activation energy for free-annealed

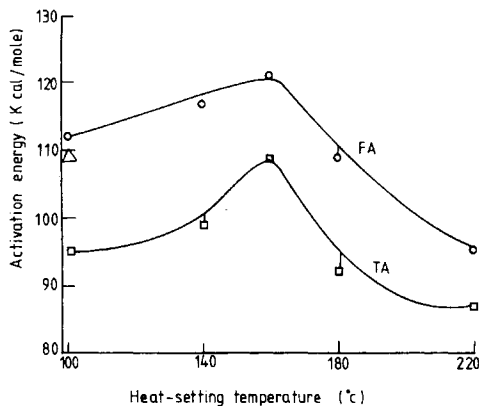


Fig. 8. Activation energy as function of heat-setting temperature for free- and taut-annealed samples heat set for 30 min: ( $\Delta$ ) control; (O) FA; ( $\square$ ) TA.

samples. The lower area of the loss modulus-vs.- $1/T$  curve and higher difference between  $E'_U$  and  $E'_R$  for the free-annealed samples were already explained earlier on the basis of structural factors.

Another notable observation from Figure 8 is that in both free- and taut-annealed samples, the activation energy initially increases with increasing heat-setting temperature and then decreases. A possible explanation of this observation is as follows: As stated earlier, the temperature at which the  $\tan \delta$  peak appears initially increases with increase in heat-setting temperature and later shifts to lower temperatures, as has been reported by other authors also.<sup>6</sup> As explained earlier, this could be attributed to the constraints to molecular mobility, which are large at intermediate heat-setting temperatures because of the presence of a large number of small crystals. At low heat-setting temperatures, though the crystallites are small in size, their number is not very large. The amorphous regions form the predominant phase in the fiber. The mobility is therefore relatively high. At high heat-setting temperatures, though the crystallinity is high, the size of the crystals is also relatively large and the amorphous regions have considerable mobility. The activation energy for this relaxation is a measure of the energy required to take the fiber from a glassy to a rubbery state, which can, for example, be achieved by creation of a free volume for segmental motion. Thus, the above structural and morphological factors are expected to have a considerable influence on the value of the activation energy, as is indeed found to be the case.

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