

# THERMAL ANALYSIS OF ACRYLIC FIBERS\*

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## ABSTRACT

This is a comprehensive survey of our work during the past thirteen years on the thermal analysis of acrylic fiber, including some recent, unpublished results.

## INTRODUCTION

It is usually possible to get much information about the structure and properties of a material when it is undergoing changes of states. Thermal analysis is such a method for studying the polymer structure, including that of fibers.

The major methods employed here for the thermal analysis of acrylic fibers as reported in this article are TMA and DSC, aided sometimes by other methods like thermomicroscopy, thermal X-ray diffraction and IR analysis. The medium in which the acrylic fibers are immersed may be air, inert gas or a suitable solvent.

Acrylic fibers are chosen as the object of study since they possess predominantly an amorphous structure which is quite glassy below its glass transition temperature and has a moderate degree of paracrystallinity. Such a structure is rather sensitive to heat and shows a wide distribution of order. However, the methods developed in our study of acrylic fibers may be adapted to other fibers as well.

## THERMAL ANALYSIS OF ACRYLIC FIBERS IN THE DRY STATE

### 1. *Thermomechanical analysis (TMA)*

#### (1) Instrumentation and methods

The instrument used in this work for determining the thermomechanical properties of the various acrylic fibers is an improved model of the thermomechanical analyzer designed and constructed in our laboratory designated as type XRF-2<sup>[1]</sup>. It is built on the extensometer principle, both the length change and force application can be controlled positively. The length is measured by means of a precision screw operated by a servo-step motor and the force is measured by means of an automatic electronic balance. The temperature-shrinkage and the temperature-shrinking stress curves are recorded on a X-Y recorder. The temperature rise is usually controlled at a rate of 1 to 10°C/min. As fiber samples, either a single fiber or a strand of multi-filaments will do. In this work, a strand of 10 filaments is usually used. Films can be cut into narrow strips in required direction and tested like fibers.

In order to make our instrument working, it is necessary to apply a slight initial tension, e.g.,

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0.5—1.0 mg per denier, to the fiber. Such relatively slight tension will not affect the free shrinking of the fiber.

Recently a further new model of TMA is designed, with some novice features. It is provided with a microprocessor and designated as XRF-3<sup>[2]</sup>

## (2) General description

In the present paper, we shall report the results of our study on the static thermomechanical analysis of fibers. The chief items of static TMA are thermal shrinkage and thermal shrinking stress, the former being measured at small fixed tension and the latter at fixed length. These are special cases of thermal creep and thermal stress relaxation when the initial tensions applied are very small. Modulus can be calculated from these quantities.

Some typical experimental results will be given below. Fig. 1a and b are the TMA thermograms of PAN and PAC\* fibers respectively. For the shrinkage and shrinking stress of 12 acrylic samples of different composition and modes of formation, the reader is referred to an original article<sup>[3]</sup>.

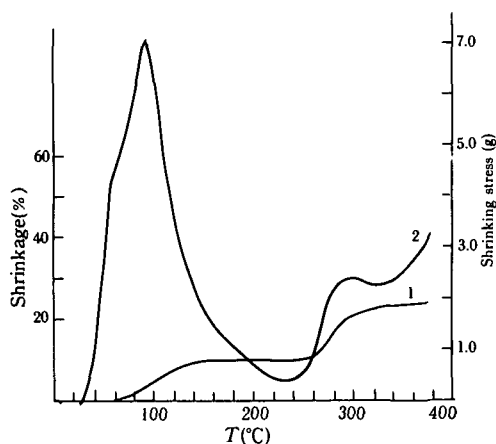


Fig. 1a Thermal shrinkage and thermal shrinking stress curves of PAN fiber, sample: No. 12, 10 filaments

AN = 100%, 25d

1. Shrinkage; 2. shrinking stress

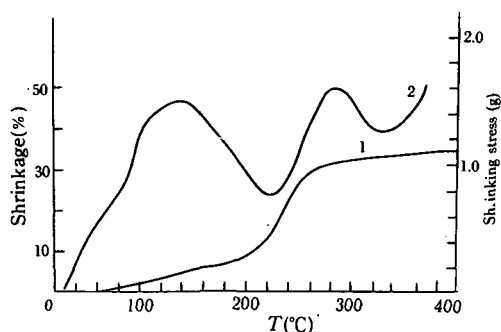


Fig. 1b Thermal shrinkage and thermal shrinking stress curves of acrylic fiber, sample: No. 6, 10 filaments

AN:MA:IA = 93:5.7:1.3, 10.2d

The thermal shrinkage of acrylic fibers usually occurs in two stages as the temperature is gradually raised. This is in concord with the single phase, double-bonded theory of acrylic fiber texture, a model first proposed by other authors<sup>[4,5]</sup>. In the case of PAC fibers, the first stage thermal shrinkage seldom exceeds 10%, reflecting microbrownian motion of chain segments in the amorphous, which is still much restricted by the existence of paracrystalline regions. The thermal shrinkage of the second stage which usually reaches 50% is obviously due to motion of macromolecular chains in the paracrystalline regions. However it is much complicated by the occurrence of oxidation and cross-linking at the end of the second stage. In the case of PAN fibers, the total shrinkage seldom exceeds 30%, still occurring in two stage.

If the fiber has been subjected after formation to a heat-setting process in the relaxed state,

\* Abbreviation of polyacrylonitrile copolymer, a term originated in German literature.

shrinkage must have already occurred during setting. Hence, the fiber will no longer show any substantial shrinkage, but instead may even show a slight elongation at the initial stage of heating.

It should be noted that the initial shrinking stress is frequently a revelation of the internal stress frozen in the texture of the fiber during formation processes, and is usually released first upon gentle heating of the fiber. In the shrinking stress curve, it usually appears as a shoulder.

### (3) Effects of applied tension

In the process of rising temperature, the relation between the length changes and tension is particularly marked. When the tension applied is relatively small, length change usually appears as a shrinkage; if the applied tension is big, it may then appear as an elongation as illustrated in Fig. 2.

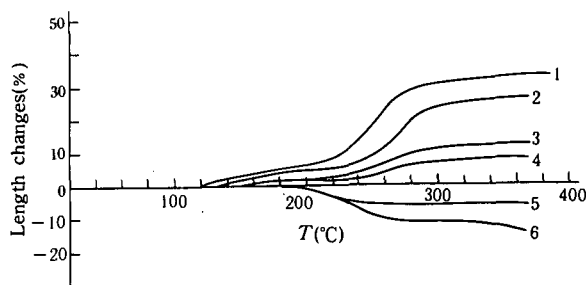


Fig. 2 Influence of tension on the thermal shrinkage

- |             |             |             |
|-------------|-------------|-------------|
| 1. 10 mg;   | 2. 200 mg;  | 3. 500 mg;  |
| 4. 1000 mg; | 5. 1550 mg; | 6. 1750 mg; |

Sample: No.6, 10 filaments, 1.02 denier each

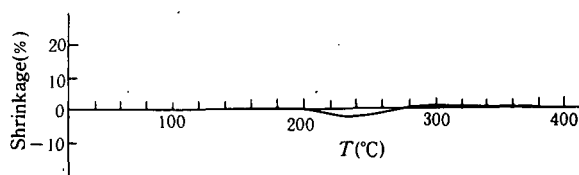


Fig. 3 Thermal shrinkage behavior under a stress which is the mean of the peak and trough values

Sample: No. 6, 10 filaments, 1.02d each

If we impose on the sample used in Fig. 1b, an amount of tension equal to the mean of the peak and the trough values, i.e., approximately 0.108g/den, then we obtain a thermal shrinkage curve shown in Fig. 3. The length changes fluctuate only slightly between shrinkage and elongation, but the absolute value does not exceed 3%.

From this result, a hint is obtained that if we could impose a programmed tension just equal to that required by thermal shrinking stress curve, the resulting shrinkage curve would exactly coincide with the horizontal axis, i.e., no length change at all.

### (4) The thermal relaxation of the peak shrinking stress

As the temperature is increased, micro-brownian motions of the macro-molecular segments become more and more vehement; physical linkages between the macromolecules in the amorphous region begin to break, resulting in the release of frozen internal stress. At the same time, loosening of intermacromolecular linkages will result in shrinkage, causing also an increase of shrinking stress which will subside down at a point when the linkages left are no longer sufficient to

sustain the shrinking stress already generated. With further rise of temperature, the shrinking stress will relax very rapidly to a minimum.

#### (5) Effects of composition and structure of acrylic fibers on shrinking stress

The thermal shrinking stresses of 5 acrylic fiber samples of different composition and mode of formation are shown in Fig. 4. The height and position of the first peaks vary a great deal among themselves because of the variation of composition and structure among fibers, while the second peaks which are definitely due to cyclization agree quite well in temperature. Curve 3 is the shrinking stress curve of a commercial PAC fiber (Jinlun). It lacks the first peak since it is well set in steam; at about 250°C there is a shoulder, due to the change of texture in the paracrystalline region; the rapid rise of shrinking stress around 290°C shows that the cyclization is accompanied by crosslinking.

#### (6) Different effects of air and nitrogen on relaxation of shrinking stress

In Fig. 5 are shown two shrinking stress curves, one in air and the other in nitrogen<sup>[6]</sup>. The

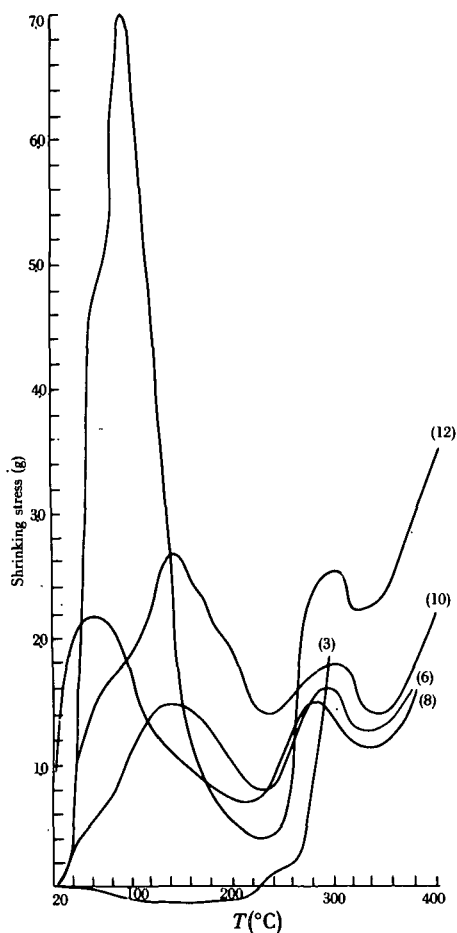


Fig. 4 Shrinkage stress curves of typical acrylic fibers in air<sup>[6]</sup>

No. 3, commercial Jinlun, 91.5% AN, 10 filaments, 3d each;  
No. 10, 98.5% AN, DMSO process, 10 filaments, 0.81d each;  
rest, already given before

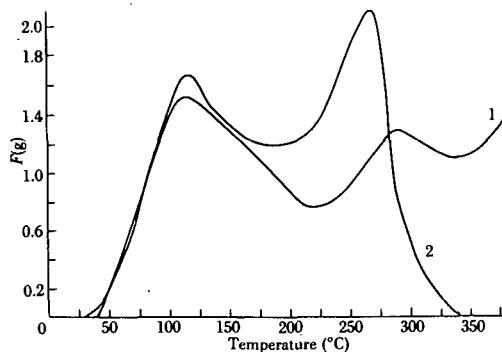


Fig. 5 Thermal shrinking stress curves of PAC fiber in various atmosphere  
1. in air, 2. in nitrogen

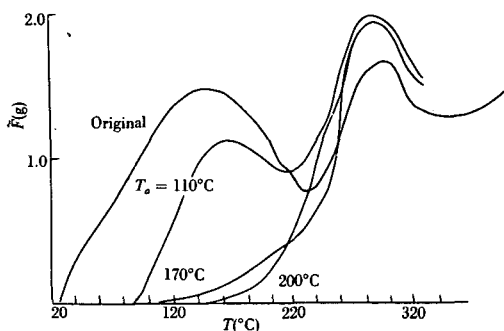


Fig. 6 Effect of the annealing temperature on the thermal shrinking stress of PAC (93% AN) fiber, No. 6

peak in air will relax to only a certain extent but that in nitrogen will relax completely, showing that no crosslinking has been formed yet at this temperature.

(7) Thermal shrinkage modulus

The thermal shrinkage  $S$  and the thermal shrinking stress  $\Delta\sigma$  can be correlated into a modulus  $E_s$  by the equation<sup>[7]</sup>

$$E_s = \Delta\sigma/S \tag{1}$$

It is a function of temperature and reflects mechanical properties of fibers.

(8) Effects of annealing on shrinking stress

As shown in Fig. 6, shrinking stress of a fiber can be removed by giving it a heat treatment under relaxed state. As the temperature of annealing is increased step by step, internal stress is usually eliminated first, followed by shrinking stress due to change of texture upon heating. The shrinking stress generated by cyclization is caused by a change of chemical structure, rather than a change of texture; so it is not removed by annealing.

2. Differential Scanning Calorimetry (DSC)

Examples of DSC thermogram in air of a number of acrylic fibers of different composition and mode of formation (same as those shown in Fig. 4) are shown in Fig. 7, while those for the same set of samples in  $N_2$  shown in Fig. 8.

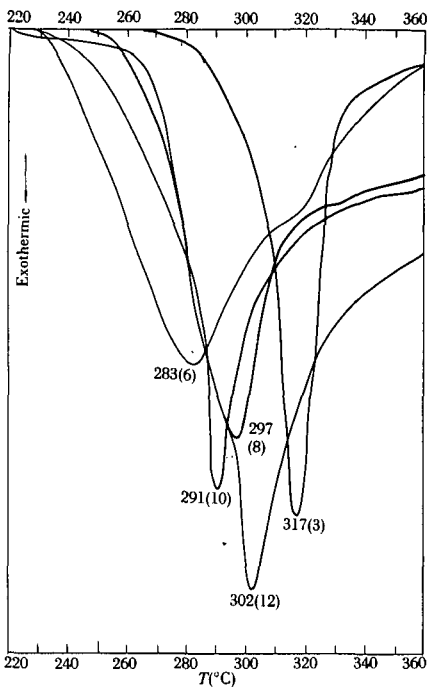


Fig. 7 DSC thermograms of typical acrylic fibers in air

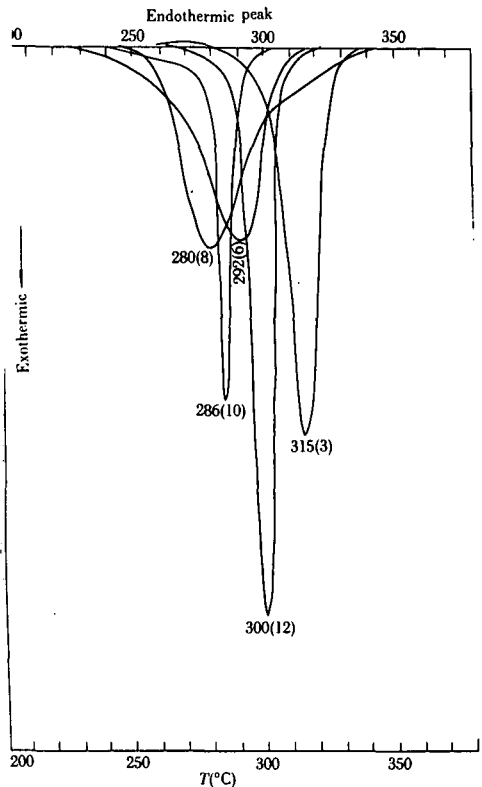


Fig. 8 DSC thermograms of typical acrylic fibers samples in  $N_2$

Samples: No. 3, No. 6, No. 8, No. 10, No. 12

Some particulars are noteworthy:

(1) The samples No. 6, 8 and 10 constitute one group in which some acidic or amide groups are present (No. 6, 10, itaconic acid; No. 8 amide groups because these are prepared by the  $\text{HNO}_3$  process), which are catalysts for cyclization, hence lowering the temperature of cyclization. No. 12 is pure PAN; it possesses a higher temperature of cyclization. No. 3 is commercial Jinlun which uses sodium methyl-allylsulfonate as its third component which might act as inhibitors for cyclization.

(2) The DSC thermograms in air are always wider than those in nitrogen because of oxidation. All the DSC peaks are due to cyclization which are highly exothermic. In the region between 250—300°C, there should be small endothermic peaks due to dissociation of intermolecular bonds in the paracrystalline region, but, except in the case of Jinlun (No. 3) where these two peaks are relatively widely separated (see Fig. 8), they overlap with each other, and hence can not be seen even when the DSC thermograms are taken in nitrogen.

(3) The second shrinking stress peak of TMA in air [see Fig. 4 (6)] coincides closely with the corresponding DSC exothermic cyclization peak in nitrogen, and so is also with the same DSC peak in air, the latter being a little lower in temperature (see Figs. 7 and 8).

## THERMAL ANALYSIS OF ACRYLIC FIBERS IN THE SWOLLEN STATE

Thermal analysis of acrylic fibers may be conducted in the swollen state, thus gaining several advantages, chiefly:

(1) The action of heat is enhanced, making the responses of fiber to heat quicker and more sensitive.

(2) The temperature of transition is lowered by the action of solvents, thus avoiding certain chemical reactions like cyclization to occur. This makes the thermal analysis of swollen fibers particularly suitable for studying the original texture of the fiber step by step without premature modification by the heating program of the thermal analysis itself.

(3) The detrimental effects of oxygen are automatically avoided due to the presence of solvents.

(4) Certain minute morphological structures, which are otherwise undetected, can be observed under a thermomicroscope by the presence of a suitable solvent.

(5) In the case of DSC, the test can be conducted in a sealed capsule, thus raising the temperature to a point above the boiling point of the solvent without vaporization and extending the range of analysis up to complete disruption of the fiber texture.

### 1. *Typical TMA thermograms of swollen acrylic fibers*

The TMA thermograms of a PAC fiber Jinlun, variously heat-treated after formation, are given in Fig. 9. The swelling agent used is 80% aqueous DMF. In Fig. 10 is the same type of curve for PAN fiber; because of the higher order of this fiber, the concentration of the swelling agent must be raised to 93% in order to keep the temperature of shrinkage maximum somewhat below the boiling point of the solvent. The two stage character of these thermograms can always be observed due to double-bonded structure.

Between the two stress peaks, sometimes the stresses increase and sometimes relax. The mechanism to be quite complex, but we are now able to account for it, at least, qualitatively in light

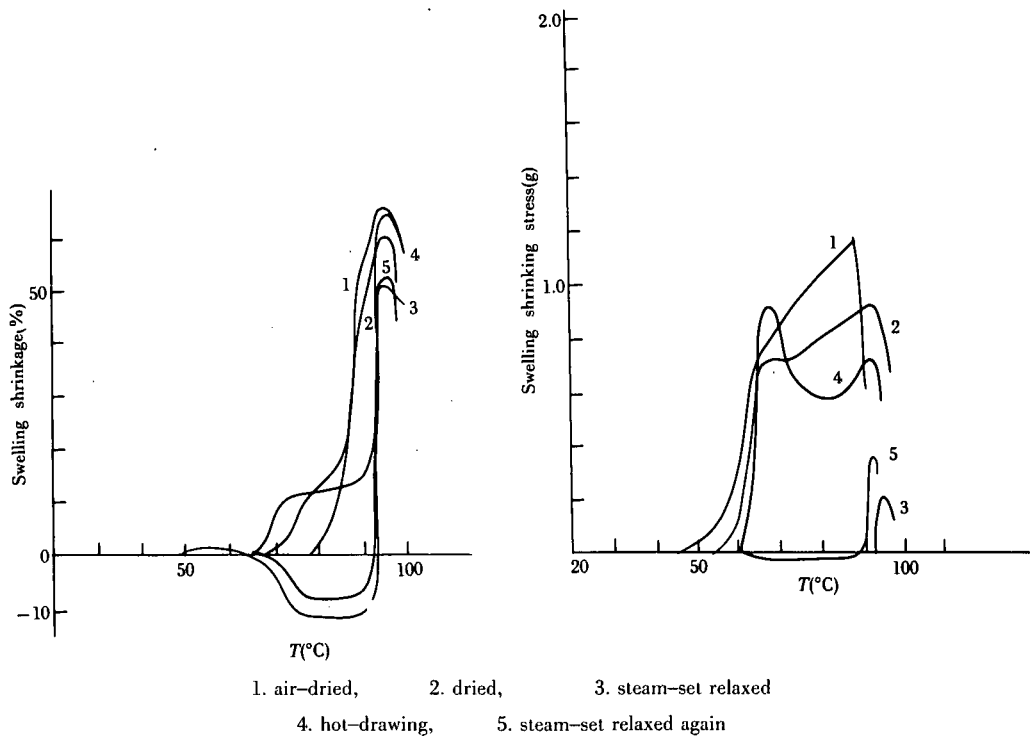


Fig. 9 Thermal swelling shrinkage and shrinking stress curves of Jinlun fibers, Samples: No. 1—5 (80% DMF), 10 filaments AN : MA : MAS = 91.7 : 7 : 1.3

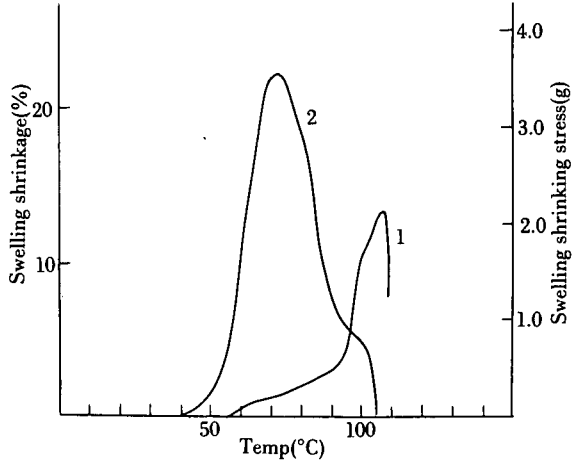


Fig. 10 Thermal swelling shrinkage and shrinking stress curve of PAN fiber, Sample: No. 12, 10 filaments AN = 100%, 25d (93% DMF)  
1. shrinkage; 2. shrinking stress

of all the data obtained from TMA and DSC. The general principle is that the shrinking stress is a reaction of the texture still remaining after swelling against the growing thermal shrinkage in the process of temperature rise; if the remaining texture is not strong enough, the existing shrinking stress will relax instead of growing further.

In Fig. 10, showing the shrinking stress curve for PAN fiber, the paracrystalline stress peak

does not develop well, but only appears as a shoulder. This is apparently an indication that in the texture of PAN fibers there are relatively little number of entanglements to sustain the growing stress; hence the stress relaxes rapidly to zero.

## 2. Thermal shrinkage of a swollen PAC fiber as a measure of orientation<sup>[8]</sup>

The orientation of an acrylic fiber must be closely related to its thermal swelling shrinkage. By comparing with the orientation measured by X-ray diffraction and by dichroism of an acrylic fiber, we came to the conclusion that

$$S' = S_0 \overline{\cos^2 \alpha}, \quad (2)$$

where  $S'$  is the measured shrinkage of an acrylic fiber during thermal swelling,  $\overline{\cos^2 \alpha}$  is the average square cosine of the angle of orientation and  $S_0$  is a constant equal to the shrinkage of a fiber sample with perfect orientation. It is interesting to note that the orientation of an acrylic fiber sample as measured by dichroism and by X-ray diffraction differ very little, showing that the orientation of the amorphous region and the crystalline region is nearly the same. This is a peculiarity of PAC fiber.

## 3. Load elongation behavior of swollen acrylic fibers—basis of single-phase double-bonded texture<sup>[9]</sup>

At an intermediate temperature of about 80°C, the amorphous region is already completely penetrated by the solvent, but the paracrystalline region remains intact. The macromolecules in the amorphous regions will tend to coil and contract freely while the intact paracrystalline regions will act as big cross-linking junction points. If the macromolecular segments connecting the paracrystalline regions are long enough to bridge over the crystallites, then the system will behave exactly like a rubber with good elastic and recovery properties. Experiments show that the swollen fiber under such conditions exhibits more than 240% extension yet still with complete recovery, in agreement with expectations. This fact will serve as a basis of our belief of a single-phase double-bonded theory of acrylic fiber texture; no evidence of phase separation has ever been observed. The small difference of orientation between the amorphous and paracrystalline region serves as another evidence of single-phase structure.

## 4. Thermomicroscopical work on swollen acrylic fibers

Quite interesting phenomena can be observed during the swelling process of an acrylic fiber. For fibers of high drawing ration, many streaks corresponding to the direction of orientation of the fibrils can be seen on the surface of the fiber<sup>[8]</sup>. A segment of fiber will show very beautiful wriggling motion, like a wounded earthworm, apparently due to unevenness of contraction in the different parts of the fiber. Such phenomenon will remain only a few seconds, showing very sharp transition. The degree of swelling is very considerable, showing around 100 times increase of diameter. The existence of skin and microfibrils is quite marked in all these microphotographs.

## 5. DSC of swollen acrylic fiber<sup>[10]</sup>

This method is accomplished by using a sealed cell easily done by pressing together an aluminium cover onto the cell containing sample and solvents. A hand screw press is needed in this operation.

In a previous literature<sup>[10]</sup> were shown thermograms of various samples of PAC fiber in

aqueous DMF solution. From these, it can be seen that annealing, especially steaming under relaxed conditions, will enhance the paracrystalline peak in both amount and sharpness, i.e., the peak area, or the amount of heat, will grow and the half breadth of the peak, which means distribution of order, will diminish. Stretching, in the contrary, will disrupt the paracrystalline structure.

The effects of the pressure of saturated steam used during heat-treatment are similar to that of temperature.

Indeed from the characteristics of the swollen DSC thermograms we can infer the processing conditions of commercial PAC fibers. There were also shown the swollen DSC thermograms of five imported PAC fiber samples. The differences among them are so big that these thermograms can be used for identification purposes.

## RECENT DEVELOPMENTS IN THE THERMAL ANALYSIS OF ACRYLIC FIBERS

There are several topics of interest, the results of which are still unpublished or just in press.

1. *Shrinkage, shrinking stress (integral) and shrinkage modulus in one program of temperature rise by means of TMA XRF-3*<sup>[2]</sup>

TMA XRF-3 is an improvement of TMA XRF-2 by providing the latter with a microprocessor. The construction of TMA XRF-2 is shown in Fig. 11.

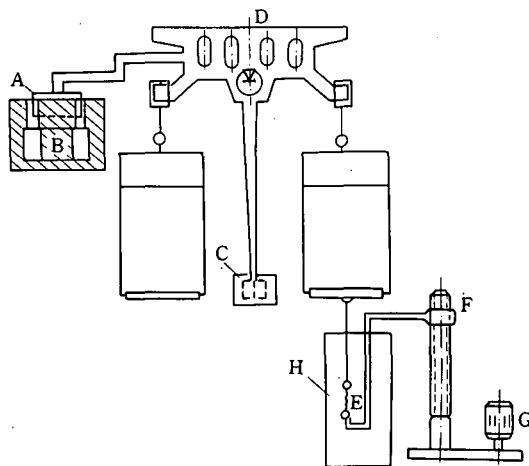


Fig. 11 A sketch of the model XRF-2 "Multi-Function Thermo-mechanical Analyzer for Fibers and Films"

- |                                    |                     |
|------------------------------------|---------------------|
| A. Coil                            | B. Permanent Magnet |
| C. Silicon Photoelectric Generator |                     |
| D. Balance                         | E. Fiber Sample     |
| F. Transmission Mechanism          |                     |
| G. Step Motor                      | H. Heating Furnace  |

In XRF-2, the shrinkage is measured by keeping the stress at a small fixed value, while the shrinking stress is measured at a constant length, but in XRF-3 these two operations are combined. In any thermomechanical process, using our analyzer, the change of stress is always the cause and the change of length the effect. In the operation of model XRF-2 TMA, the thermal shrinkage is actually controlled by the photoelectric signal which is the result of the change of

stress in the sample. During the determination of the thermal shrinkage curve at constant length, the stress signals are always there. The problem is to extract them out to get an increment of stress  $\Delta\sigma$  corresponding to each shrinkage increment  $\Delta s$ . This is accomplished in model XRF-3 by a clever process of conducting the shrinkage in a big number of successive steps. For each step, the sample is first allowed to experience an increment of stress  $\Delta\sigma$  which is quickly allowed to relax through a small shrinkage  $\Delta s$ . These small increments of stress and shrinkage are memorized in the microprocessor. During the small interval of shrinkage, stress generation will of course be stopped for which, however, a correction can be easily made, assuming that the stress generation is always linear during these short intervals. The process is repeated step by step during a programmed temperature rise, and the resulting values of  $\Delta\sigma$  and  $\Delta s$ , kept in the memory of the microprocessor, are integrated into a thermal shrinking stress curve and thermal shrinkage curve respectively. The former is, however, a stress-temperature curve without relaxation which is entirely different from the one obtained by XRF-2 at constant length as has been illustrated in all other shrinking stress curves given above. The thermal shrinking stress and thermal shrinkage curves obtained by XRF-3 are shown in Figs. 12 and 13.

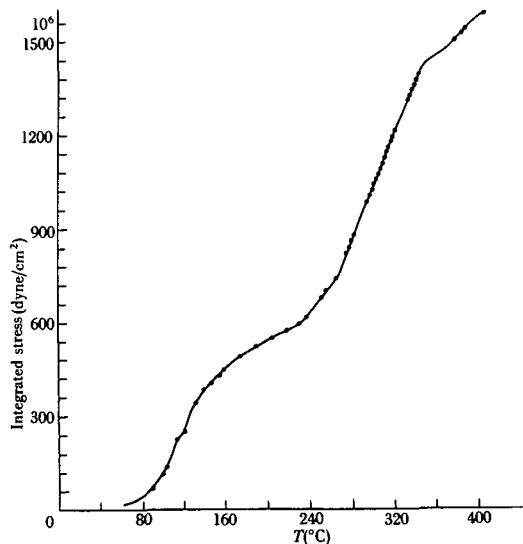


Fig. 12 Thermal shrinking stress,  
integrated with little relaxation  
Sample: PAC #6

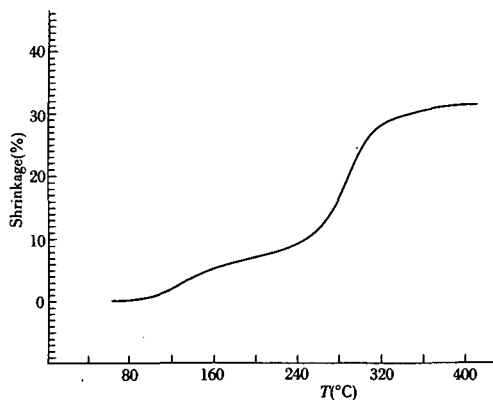


Fig. 13 Thermal shrinkage curve  
Sample: PAC fiber, #6

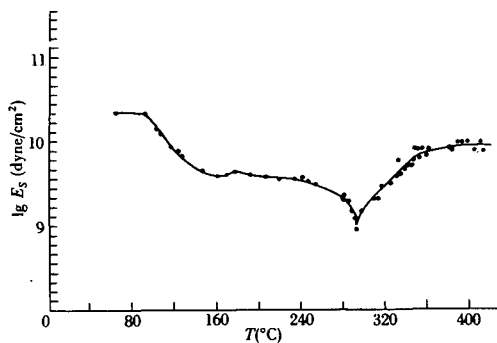


Fig. 14 Shrinkage modulus Sample: No. 6, PAC

A special merit of XRF-3 is: from each pair of  $\Delta\sigma$  and  $\Delta s$  values at a certain definite temperature, a modulus value can be calculated. The change of the cross sectional area of the fiber during progressive shrinkage can be calculated and applied to each  $\Delta\sigma$  value, taking Poisson ratio as 1/2. From the data so obtained, a temperature-shrinkage modulus curve (see Fig. 14) can be plotted in 1.5 hr. at a temperature-rising rate of 5°C/min through an interval of temperature rise of 400°C. This is far quicker and more convenient than the classic process of making a master curve by static thermomechanical measurements<sup>[11]</sup>.

## 2. Creep, relaxation and relaxation modulus (creep compliance)

If an external tension is applied to the sample during the thermomechanical analysis, we have then creep and relaxation of stress. The modulus value so obtained is the relaxation modulus<sup>[7]</sup> or, more precisely, its reciprocal the creep compliance (Fig. 15). This is a special feature of model XRF-3 instrument, due to the use of an electronic analytical balance as a force measuring device in conjunction with a microprocessor.

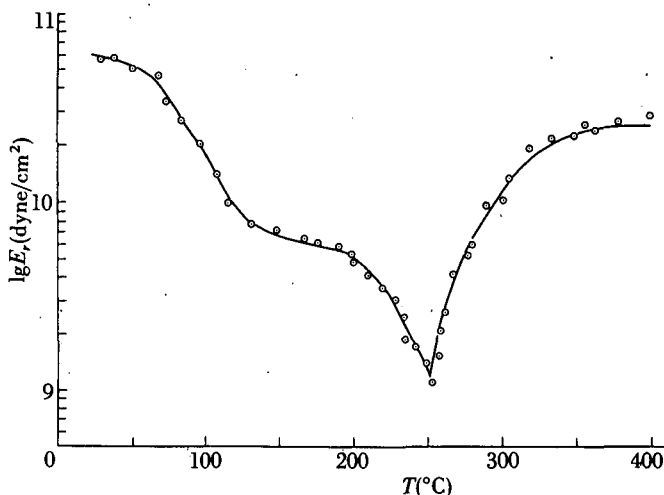


Fig. 15 Relaxation modulus

Sample: No: 6, PAC fiber, 10.2den., 10 filaments,  
rate of temperature rise, 5°C/min

## 3. Study of cyclization reaction by shrinking stress

The sample of acrylic fibers under fixed tension is lowered into the heating tube already adjusted to a definite constant temperature. The sample will quickly attain this temperature; this instant is reckoned as zero time. The shrinking stress owing to cyclization will grow according to the curve shown in Fig. 16. In this way the kinetics of the cyclization reaction can be studied. This work is still in progress.

## 4. DSC thermograms of swollen acrylic fibers as a means of ascertaining texture, order and the distribution of order

### (1) Physical meaning of the terms

The term "Texture" is here used as a synonym of supermolecular structure, chemical structure being excluded. It usually consists of several elements, namely, crystallinity, crystallite size, crystalline perfection and orientation. Fiber scientists have long attempted to express these ele-

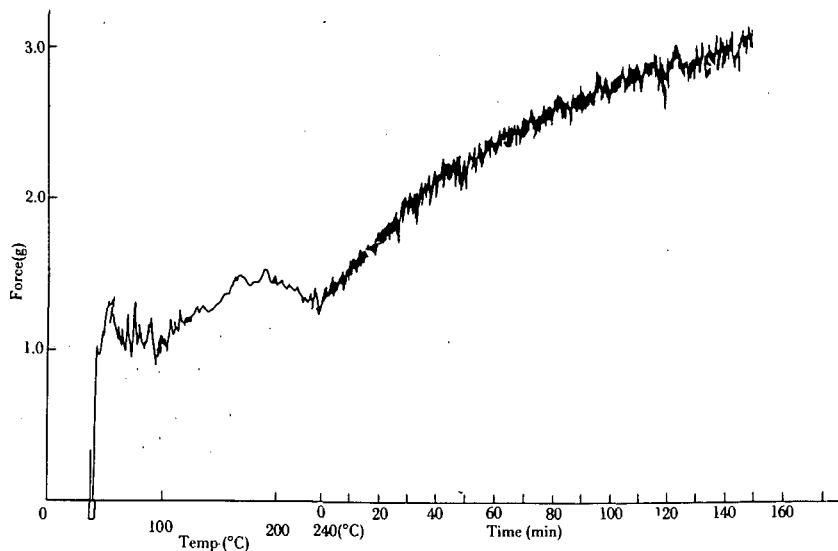


Fig. 16 Illustration of cyclization reactions by means of change of thermal shrinking stress

ments by a unified concept, called lateral order<sup>[12]</sup>. The merits of this concept is that the term can be used to include both amorphous and crystalline regions in the material, perfect crystallinity represents the highest order and perfect amorphicity represents the lowest order, but neither actually exists in a real fiber. Order is always a distribution. The term lateral order requires defining. Lateral means interchain relation in a direction cross-wise to the molecular chain axis. It has nothing to do with the chain orientation relative to the fiber axis, although high orientation is generally associated with high order. The word "lateral" may be omitted for simplicity.

Although the concept of order is nice, its physical significance is still ill-defined. Moreover, experimental methods of measuring order are still not well developed and yield no unambiguous results.

To explore the order and its distribution in a fiber, we generally employ a reagent which is composed partly of a swelling agent and partly of a non-swelling agent. The penetrating power of the reagent, or better expressed, the accessibility of the fiber to the reagent is related to the concentration of the swelling agent in the reagent, or in just the same sense, to the temperature of the reagent, both increasing concentration and increasing temperature promoting accessibility of the reagent to regions of higher order in the fiber. Cellulose is an example<sup>[13]</sup> for which assessment of order and its distribution can be conducted by increasing concentration which is usually a process rather difficult to fulfill continuously. Moreover, the attainment of equilibrium with changing concentration is through diffusion which is usually a slow process. The application of the method of increasing temperature is less affected by these drawbacks; it is actually a process of thermal analysis of swollen fibers.

The spread of the DSC peak is apparently an indication of the distribution of order or crystalline imperfection since perfect crystalline order is unique and cannot show distribution. Therefore peak spread is a characteristic of paracrystallinity. Excessive diminution of crystallite size will lead to the same results. All crystalline imperfection will cause a decrease of peak temperature, and vice versa.

The distribution of order in the various regions of the fiber material is usually ascertained by

the amount of physical or chemical responses that occur during the process of exploration (increasing concentration or increasing temperature). For the present, we will only concentrate our attention to those methods where physical responses occur as in the case of acrylic fibers.

(2) An early work for estimating lateral order distribution of PAC fibers by swollen DSC<sup>[10]</sup>

When a sample of acrylic fiber is immersed in an 80% aqueous DMF solution and gradually heated, the solvent penetrates step by step into the regions of higher and higher order in the texture of the fiber. In this process heat is continuously absorbed which represents the energy required to loosen the bonds between the macromolecular chains. This amount of energy is taken up at different energy levels, corresponding to different temperatures which means different order. The relative amounts of energy taken at different levels represent the relative amount of material present in the regions of different order, i.e.

$$\Delta H_j = h_j \cdot \Delta W_j \quad (3)$$

where  $\Delta H_j$  represents heat change due to the component  $j$ , while  $h_j$  the bond energy and  $\Delta W_j$  the amount of material of the same component. At that time, our equipment and technique used was still quite crude that we had not paid sufficient attention to the peaks other than the main one, and furthermore we had not attempted to give the DSC thermogram a really quantitative explanation.

(3) Different regions in the texture of acrylic fibers as evidenced by thermal analytical data<sup>[14]</sup>

With a more refined DSC instrument, we are now able to obtain more precise and well-defined DSC thermograms of swollen acrylic fibers (Fig. 17). These thermograms are however, still influenced by the variation of the concentrations of solvents and the rate of temperature rise.

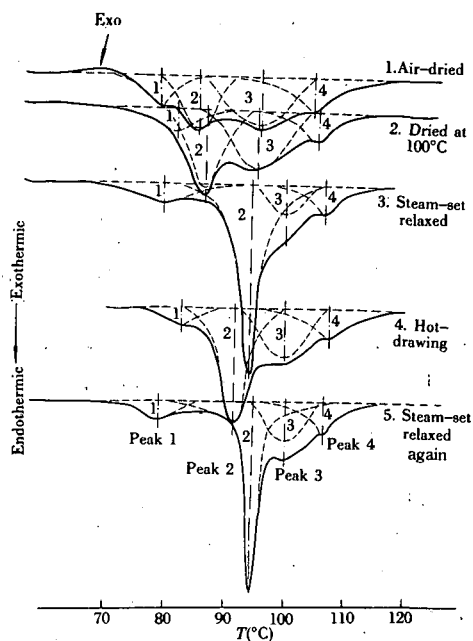


Fig. 17 The effects of different after-heat treatment on DSC thermograms of PAC fibers, with peaks separated

Note: In thermogram 1, the small exothermic peak is indicated by an arrow.

By a joint examination of the parallel TMA and DSC results of the various acrylic fibers in aqueous DMF solutions as given above, it is quite clear that in the texture of acrylic fibers there are always an amorphous region and paracrystalline region of varying intermolecular bond energy depending on the composition of fibers and on the process of formation and heat treatment.

The first peak in the TMA thermogram is apparently due to the amorphous region which contains a big number of relatively small junction points with a certain size distribution. The second peak originates from the swelling of the paracrystalline region which reveals itself as a shrinkage and shrinking stress in TMA, and a sharp endothermic peak in DSC.

Before complete dissolution, there is nearly in every case a kink on the DSC thermogram, which was neglected in our early work. We have now sufficient experimental evidences to show that this kink is due to the entanglement of the macromolecular chains in molecules, the loosening of which requires a definite amount of energy of disentanglement.

The nature of the third peak remains somewhat obscure. Probably it represents the dissolution of the swollen paracrystalline region, which usually follows swelling. The magnitude of this peak might be related in some way to the second and fourth peaks, i.e., to texture of the paracrystalline region and to entanglements.

(4) Bond energy of the different peaks as an expression for the distribution of order

Happily, bond energy values can be obtained from the DSC thermogram by a simple separation of peaks as is done in Fig. 17, the only assumption taken here is that each of the peaks possesses a normal distribution, and hence must be symmetrical on both sides. The bond energy values of the four peaks for five PAC fiber sample are listed in Table 1.

Table 1 The swelling heat of DSC peaks

| Sample |       | Swelling |       | heat  |       | (kcal/mol.) |  |
|--------|-------|----------|-------|-------|-------|-------------|--|
| No.    | $W_2$ | $H_2$    | $Q_1$ | $Q_2$ | $Q_3$ | $Q_4$       |  |
| 1      | 6.0   | 1.8      | 0.182 | 0.350 | 0.476 | 0.266       |  |
| 2      | 6.4   | 2.6      | 0.224 | 0.476 | 0.560 | 0.196       |  |
| 3      | 3.1   | 6.5      | 0.196 | 0.952 | 0.164 | 0.162       |  |
| 4      | 4.5   | 3.9      | 0.125 | 0.658 | 0.364 | 0.210       |  |
| 5      | 2.8   | 6.4      | 0.112 | 0.812 | 0.280 | 0.196       |  |

$W_2$ ,  $H_2$  are the relative width and height of the paracrystalline peaks

In equation (3) given above, the quantity that can be measured is the bond energy  $\Delta H_j$  values, i.e., the product  $h_j \cdot \Delta W_j$ ; since  $h_j$  is still not known, the distribution of  $\Delta W_j$  in various regions of the texture is still not ascertained. Since the properties of the material are concerned mostly with the bond energy values, it appears more appropriate to employ the distribution of  $\Delta H_j$  directly as a measure of the distribution of order, the levels of which is represented by the temperature at which this amount of  $\Delta H_j$  is absorbed. In other words, the DSC thermograms of swollen fibers can be used directly as a measure of the distribution of order. The situation may be more clearly represented as follows:

**Table 2** Analysis of order

| Peak No.<br>region of<br>the tex-<br>ture | 1st peak<br>amorphous<br>region                   | 2nd peak<br>paracrystalline | 3rd peak<br>region            | 4th speak<br>entanglements     |
|-------------------------------------------|---------------------------------------------------|-----------------------------|-------------------------------|--------------------------------|
| energy<br>designa-<br>tion                | energy of<br>secondary<br>bonds dis-<br>sociation | energy of<br>swelling       | energy of<br>dissolu-<br>tion | energy of dis-<br>entanglement |

The concept of regions is still retained; each region possesses its own distribution of order. The neighboring region may overlap with each other in some degree.

#### (5) Effects of molecular length on entanglements

The energy required for disentanglement is closely related to the length of the macromolecules (Fig. 18). This result is an indication that assignment of the 4th peak to entanglements is correct. It may be noted that the fourth peak occurs at a temperature when the fiber has been already disrupted completely.

The use of the 4th peak of the DSC thermogram of swollen acrylic fiber as a means of studying entanglement may be of great consequence since it attacks the problem from the energy point of view rather than from the force point of view (viscosity)<sup>[15]</sup>. From recent literature, a number of articles concerning entanglements and reptation can be found. Further study of this problem is in active progress in our laboratory.

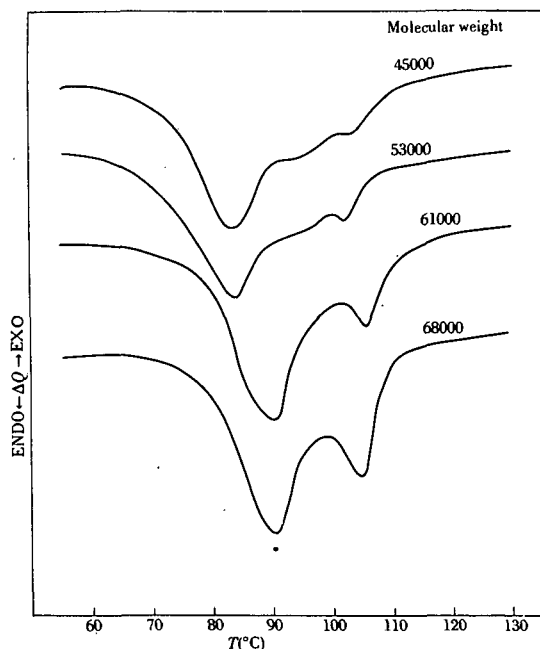


Fig. 18 Swelling DSC diagrams of acrylic fibers with different molecular weights. 80% DMF; Heating rate, 10°C/min.

## CONCLUDING REMARKS

It might be said that, by thermal analysis of acrylic fibers, many details in the texture of this fiber have been revealed. We arrive at a deeper understanding of the texture of acrylic fibers. The merits of the joint application of the two thermal methods, TMA and DSC, are quite obvious. The physical meaning of the term "order" are becoming more defined. Better experimental method of measuring order and its distribution are being developed. The importance of swollen DSC method for studying entanglements is finally emphasized.

**Keywords:**

Thermal shrinkage; Thermal shrinking stress; DSC of swollen fibers; Shrinkage modulus; Fibers texture

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