
DETERMINATION OF THE T_g OF WET ACRYLIC FIBERS USING DMA

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SYNOPSIS

A method is described for determining the glass transition temperature of both dry and wet acrylic filament. The method involves the use of dynamic mechanical analysis and a novel method of mounting the test specimen. The presence of water was found to reduce the T_g of dry acrylic fiber by 20°C, thus demonstrating the plasticizing action of water upon the polymer

INTRODUCTION

Dyeing is most commonly carried out from aqueous dyebaths. Water, in addition to serving as a vehicle for dye transportation and as a solvent for many dyes, also functions as a swelling agent or a plasticizer of fibers. The plasticizing action of water on textile fibers refers to the lowering of the glass transition temperature of the fiber. At temperatures below T_g , amorphous or semicrystalline polymers behave as rigid solids or glasses in which the segmental mobility of the polymer chains is effectively zero. As the temperature is increased, the segmental motion of the macromolecular chains increases, and at high temperatures (above T_g) the material behaves as a highly rubbery liquid. T_g denotes the temperature at which the transition from glassy to rubbery behavior occurs and is attended by marked changes in the mechanical, electrical, and thermodynamic properties of the polymer.

Several techniques, namely, thermomechanical analysis (TMA), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA), have been developed to determine the glass transition temperature of polymers.

Such methods record the property-temperature response of the polymer from which the position of T_g can be identified by some convenient point on the resulting property-temperature plot. Since the transition from glass to rubber is reversible, such methods can be performed on heating as well as cooling, although the results, to some extent, depend on the conditions of test and the particular technique employed.

DMA monitors the temperature dependence of mechanical stress/strain and loss behaviour ($\tan \delta$) as a function of the frequency of the oscillating deformation force applied. For a perfectly elastic material, the applied stress and measured strain is perfectly in phase and thus no losses occur (i.e., $\tan \delta$ is zero). This condition is closely approached by amorphous polymers at temperatures below their T_g since the composite macromolecular chains are effectively frozen into one configuration. As T_g is approached, mobility of the polymer chains increases until, at a given temperature, the relaxation time for chain mobility coincides with the frequency of the applied stress. At this particular point, the polymer absorbs mechanical energy and the damping factor (loss $\tan \delta$) reaches a maximum value. Thus the glass transition temperature can be identified as the point of maximum damping on a plot of $\tan \delta$ versus temperature at the particular frequency under consideration.

The rate of dye diffusion within hydrophobic fibers is markedly dependent on the segmental mobility of the polymer chains; therefore, the transition from glassy to rubbery state that occurs at T_g is accompanied by a marked increase in rate of dyeing. Since dyeing is usually carried out under aqueous conditions, the T_g of wet fibers is of great importance to dyers. Although the effect of temperature on the physical properties of fibers has received much attention, relatively little work has been carried out under dyebath (i.e., wet) conditions. The aim of this work is to develop a method of determining the T_g of acrylic fiber under aqueous conditions so as to provide an accurate description of the effect of this parameter on dyeing and, as discussed in a later paper at this conference, to determine the effect of various dyebath components on this parameter.

EXPERIMENTAL AND RESULTS

Fiber. A commercial sample of Courtelle S tow, supplied by Courtaulds Plc was used. The fiber was scoured prior to use by immersion in a stirred, aqueous (distilled water) solution containing 0.5 g L^{-1} Sandozin NIE (Sandoz) and 0.5 g L^{-1} tri-sodium phosphate for 120 min at 40°C using a liquor to goods ratio of 40 : 1. The scoured fiber was then thoroughly rinsed using distilled water until the wash-off was of constant pH (6.0) and allowed to dry in the open air.

Equipment. The dynamic mechanical properties were measured at a constant frequency of 1 Hz and a constant oscillation amplitude of 0.3 mm (peak–peak) using a Du Pont Instruments 983 dynamic mechanical analyzer interfaced to a 9900 Series computer thermal analyzer; Figure 1 shows a schematic representation of the instrument.

Conventionally, one arm of the DMA is electromagnetically driven at a constant frequency and amplitude and the resulting flexure of the sample is monitored using a linear, variable displacement transducer (LVDT) mounted on the driven arm. The power required to maintain both the system in forced oscillation and the phase difference between the applied load and sample response is recorded during the experiment and then converted into the appropriate modulus and damping parameters by knowledge of the sample geometry and instrument calibration constants. The sample is surrounded by an oven which enables measurements to be made in the temperature range 170–500°C. The frequency of mechanical deformation may be held constant between 0.1 and 10 Hz or, alternatively, the sample may be allowed to vibrate at its resonant frequency.

Figure 1 shows that the conventional sample-mounting geometry does not allow materials of low flexural stiffness, such as fibers, to be examined. This difficulty was overcome using a novel design of clamp assembly (Fig. 2) whereby a bundle of filaments was tensioned between the jaws of a fixed holder while the driven arm of the DMA was used to bow the midpoint of the sample in a dual cantilever. Owing to this unusual deformation mode,

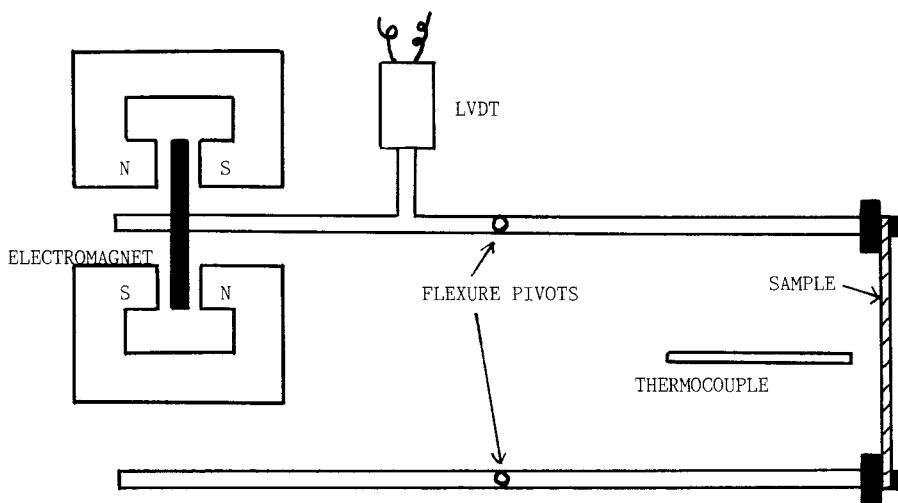


FIG. 1. Du Pont 983 DMA (schematic).

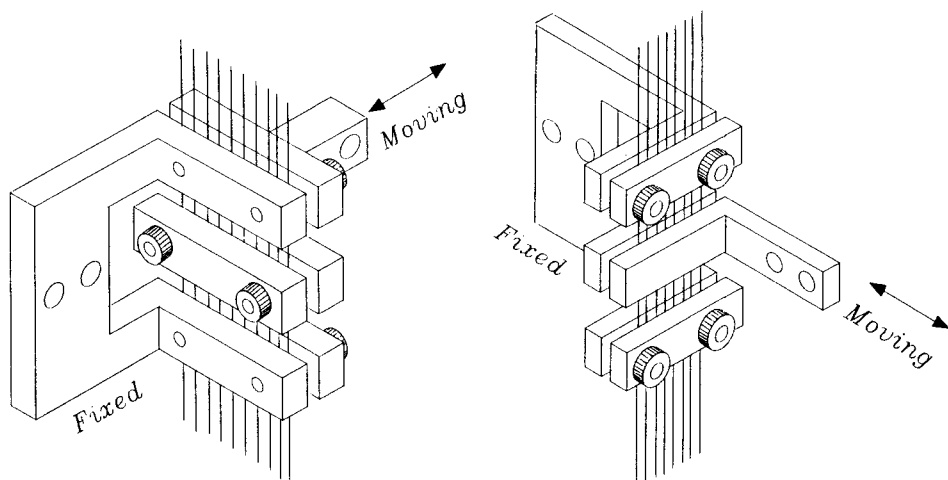


FIG. 2. Dual cantilever clamp assembly.

the modulus values generated by the computer software are no longer quantitative. The damping factor (E'/E'') is independent of both sample geometry and, to a first approximation, instrument calibration. The change in $\tan \delta$ as a function of temperature can therefore be used to monitor the viscoelastic behavior of the sample. In order to determine the T_g of wet fibers, a stainless steel liner was fitted inside the oven and, by turning the instrument on one side and filling this liner with water, the fiber sample could be completely immersed and heated at a controlled rate without the fibers drying out. A heating rate of $2^\circ\text{C}/\text{min}$ was found to be satisfactory even with the presence of water in the oven liner. Mechanical agitation of the water gave little improvement in heat transfer and was not employed owing to increased noise in the instrument output.

Determination of T_g

The length of the fiber sample used was determined by the design of the clamps, the resulting tension in the bundle of fibers being set arbitrarily by hand. The T_g of dry fiber was determined by securing a bundle of dry, scoured filaments between the two clamps; the fiber was then heated in air over the temperature range $40\text{--}120^\circ\text{C}$ to remove the fibers' thermal history. The clamps were then retightened and the sample reheated in air over the same temperature range. Figure 3 shows a plot of damping factor ($\tan \delta$) versus temperature for dry Courtelle S filament in air. The peak in $\tan \delta$ corresponds to a T_g of 92°C which closely agrees with determinations on the same material made using both DSC and TMA under comparable conditions.

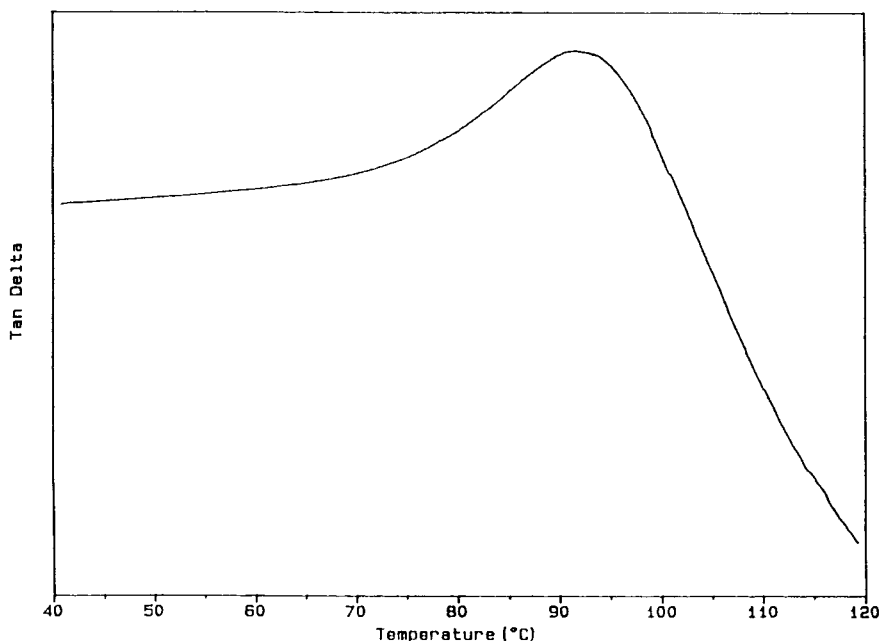


FIG. 3. DMA curve of dry fiber in air.

The T_g of wet fiber was measured using a bundle of dry, scoured filaments which had been heated in air, as described above, over the range 40–120°C in order to remove their thermal history. The cool (ambient) clamp assembly containing the filament bundle was then immersed in 400 cm³ of distilled water and the wet fibers were heated over the temperature range 40–90°C. The hot distilled water was then replaced with 400 cm³ of fresh distilled water and the cool (ambient) fibers heated once more over the same temperature range; this procedure was repeated a further time. It was found that the peak in $\tan \delta$ occurred at 75°C when heating had been carried out in the first bath of distilled water and at 72°C in the cases of both the second and third baths of water. The response of the bundle of filaments that were immersed in the third bath of distilled water is shown in Figure 4. Repeat measurements demonstrated that, provided that there are no chemical or physical differences between specimens, the position of T_g was reproducible to better than $\pm 1^\circ\text{C}$.

DISCUSSION

Many practical difficulties attend the measurement of the T_g of wet fiber; the material must be maintained at a known moisture level and not allowed to

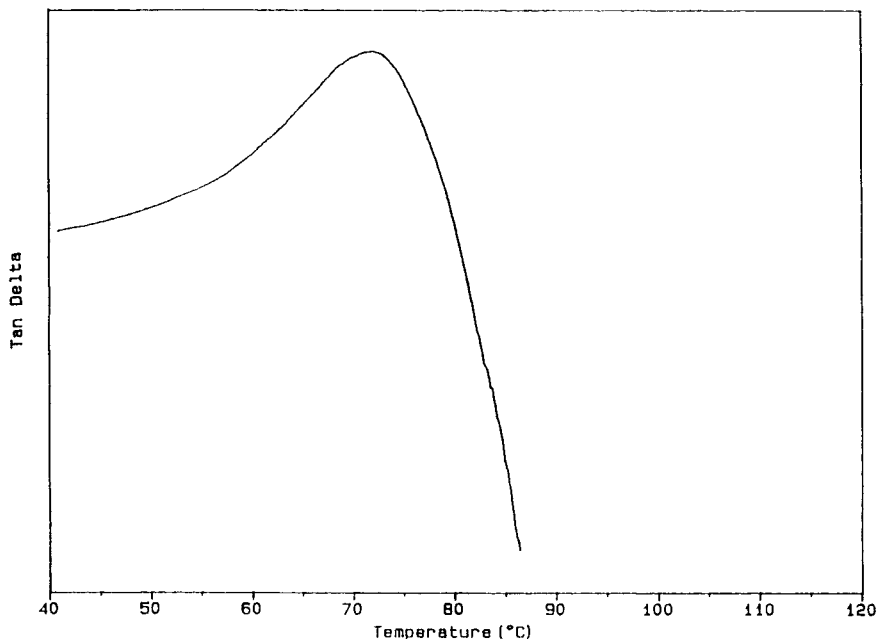


FIG. 4. DMA curve of wet fiber in water.

dry out throughout the course of the experiment. In this context, acrylic fiber has received little attention although Gur-Arieh and Ingamells [1] related the extension in length of Acrilan filament to T_g reduction and showed that the T_g of such filaments was reduced from 90°C in dry air to 57°C in water. Bell and Murayan [2] developed a DMA technique and showed that the T_g of an acrylonitrile-vinyl acetate copolymer was reduced from 128°C in dry air to 80°C at 100% relative humidity. Hori et al. [3] used DSC to show that the T_g of four kinds of acrylic fiber decreased with increasing water content and approached an almost constant value for all four fibers. A review by Fuzek [4] concludes that monitoring the change in elastic modulus (E') of a fiber with temperature gives the most reproducible results.

The 20°C difference in T_g obtained between dry and wet Courtelle S fibers in this work clearly demonstrates the plasticizing action of water. The finding that maximum reduction in T_g of the dry fiber (i.e., 20°C) was not achieved until the second and third heating in distilled water suggests that the filaments were not saturated with water at the end of the first heating phase.

CONCLUSIONS

Dynamic mechanical analysis has been shown to be a suitable technique for determining the glass transition temperature of acrylic filament when im-

mersed in water by means of the use of a novel method of mounting the fibers. The observed reduction in T_g of the fiber, caused by the presence of water, clearly shows the plasticizing action of water. The ability of the technique to measure T_g of the fiber when totally immersed in an aqueous environment will enable a study to be made of the effect of various dyebath additives on the T_g of acrylic fibers under conditions similar to those encountered in dyeing.

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REFERENCES

- [1] Z. Gur-Arieh and W. C. Ingamells, *J. Soc. Dyers Colour.*, **90**, 8 (1974).
- [2] J. F. Bell and T. Murayan, *J. Appl. Polym. Sci.*, **12**, 1795 (1968).
- [3] T. Hori, H. Khang, T. Shimuzu, and H. Zollinger, *Text. Res. J.*, **58**, 227 (1988).
- [4] J. F. Fuzek, in *Waters in Polymers*, ACS Symposium Series, 127, Am. Chem. Soc., Washington, DC, 1980, p. 515.