# THE EFFECT OF BENZYL ALCOHOL ON THE GLASS TRANSITION TEMPERATURE AND DYEING BEHAVIOR OF WET COURTELLE S

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## SYNOPSIS

The effect of a model carrier on the glass transition temperature of wet acrylic filament was examined using dynamic mechanical analysis. The presence of the compound was found to reduce the $T_g$ of wet acrylic fiber by up to 29°C, thus demonstrating the plasticizing action of the carrier with respect to this polymer. The increase in dye uptake with carrier concentration was also found to be proportional to the reduction in $T_g$.

## INTRODUCTION

The glass transition temperature ($T_g$) of wet fibers has received surprisingly little attention considering the significance of this parameter with respect to a fiber's physical properties. The relative lack of investigation of the $T_g$ of wet fibers can be attributed to the practical difficulties that attend its measurement. Many of the methods previously employed, such as dynamic mechanical analysis (DMA), pulsed NMR, dilatometry and differential scanning calorimetry (DSC) [1–6], have been critically reviewed by Fuzek [7], who concluded that monitoring the change in elastic modulus of a fiber with temperature gave the most reliable results. A technique has been developed that enables the $T_g$ of acrylic filament to be measured under conditions that resemble those encountered in a dyebath; the technique, which employs a Du Pont 983 dynamic thermal analyzer and a novel method of mounting the test specimen, has shown [8, 9] that the $T_g$ of dry Courtelle S tow was reduced

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by 20°C in the presence of distilled water, thus demonstrating the plasticizing action of water on the fiber.

The dyeing and washing behavior of regenerated and synthetic fibers are markedly dependent upon temperature; the diffusion of dyes within such fibers depends on the segmental mobility of the polymer chains. Acrylic fibers are dyed with cationic dyes at temperatures above the $T_g$ of the fiber in order to facilitate dye diffusion; in contrast, the characteristic high wet fastness properties of the resultant dyeings can be attributed primarily to the relative absence of dye diffusion that results from such aqueous treatments (e.g., laundering) being carried out at temperatures below the $T_g$ of the fiber.

The addition of organic compounds, such as esters or phenols, to an aqueous dyebath, accelerates the commercially unacceptable slow rate of dye diffusion within hydrophobic fibers. The use of such "carriers" is mostly confined to polyester and triacetate fibers, owing to their compact structure, marked hydrophobicity, and low extent of swelling under aqueous conditions. Of the numerous suggestions that have been made over many years to explain carrier action, only one has been widely accepted, namely, that carriers plasticize the fiber.

The aim of this work is to determine the effect of a model carrier on the $T_g$ of wet acrylic fiber using DMA under conditions that resemble those encountered in dyeing.

## EXPERIMENTAL AND RESULTS

*Carrier.* Laboratory-grade benzyl alcohol (BDH) was used throughout this investigation as a model carrier for acrylic.

*Dye.* A commercial sample of CI Basic Blue 45, kindly supplied as Astrazon Blue 5GL (200%) by Bayer was used; the dye was not purified prior to use. The chemical constitution of the anthraquinone dyestuff is not disclosed in the Colour Index.

*Fiber.* Both Courtelle S tow and Courtelle S fabric, supplied by Courtaulds Plc, were used. Each type of fiber was scoured, rinsed, and dried prior to use as described previously [9].

*Equipment.* The dynamic mechanical properties of acrylic tow were measured at 1 Hz and 0.3 mm oscillation amplitude using a Du Pont Instruments 983 dynamic thermal analyzer interfaced to a 9900 Series computer thermal analyzer; details of the arrangement of the novel design of sample holder employed are provided elsewhere [9].

### Treatment of Acrylic Tow with Carrier

A 50 $cm^3$ aliquot of a stock aqueous (distilled water) buffer solution (270 $cm^3$ 0.2 *M* acetic acid/230 $cm^3$ 0.2 *M* sodium acetate) was placed in a 300 $cm^3$ capacity stainless steel dyepot. An appropriate volume of benzyl alcohol was then added to give a concentration of 10, 20, 30, 40, 50, 60, 70, or 80 g $L^{-1}$ and the solution made up to 100 $cm^3$ using distilled water; the pH of the treatment bath was 4.5. The sealed dyepot was housed in a Zeltex Polycolor PC1000 laboratory dyeing machine and the treatment bath allowed to reach thermal equilibrium at 80°C. A sample (1 g) of scoured acrylic tow was then added and treatment continued for 30 min at this temperature. The dyepot was then cooled to room temperature; the fiber sample and the residual treatment liquor were removed and placed, together, in a sealed glass container to await analysis.

### Measurement of $T_g$ of Wet Acrylic Tow

The length of the fiber sample was determined by the design of the cantilever clamps and the initial tension in the bundle of fibers was set arbitrarily by hand. The $T_g$ of dry acrylic fiber in air was found to be 90°C using the procedure described earlier [9]. The $T_g$ of Courtelle S tow in distilled water was measured using a bundle of initially dry, scoured filaments following the procedure recounted in a previous study [9]. The response of the bundle of filaments that were immersed in a third bath (400 $cm^3$) of distilled water is shown in Figure 1. The maximum in tan $\delta$ corresponds to a $T_g$ of 71.6°C, which closely agrees with previous values obtained for the same fiber under identical conditions [9]. The result (Fig. 1) confirms that distilled water reduced the glass transition temperature of dry acrylic fiber by some 20°C, thus demonstrating the plasticizing action of water.

The $T_g$ of Courtelle S filament which had been pretreated with benzyl alcohol was determined as follows. A bundle of pretreated filaments which had been stored in a sealed glass container, immersed in residual carrier treatment liquor, was secured between the clamps of the DMA. The mounted sample bundle was then immersed in 400 $cm^3$ of distilled water and the wet fibers heated over the temperature range 20–90°C. The hot distilled water was then replaced with 400 $cm^3$ of fresh distilled water and the cool (ambient) fibers heated once more over the same temperature range.

Figure 2 shows that the peak in tan $\delta$ occurred at approximately 43°C when a sample of fiber which had been pretreated with 50 g $L^{-1}$ benzyl alcohol was heated in the first bath of distilled water. This clearly demonstrates that benzyl alcohol has reduced the $T_g$ of the wet fiber by approximately 29°C and that of the dry fiber by almost 50°C. The plasticizing action of benzyl alcohol is also manifest by the broadening of the DMA spectrum (Fig. 2).

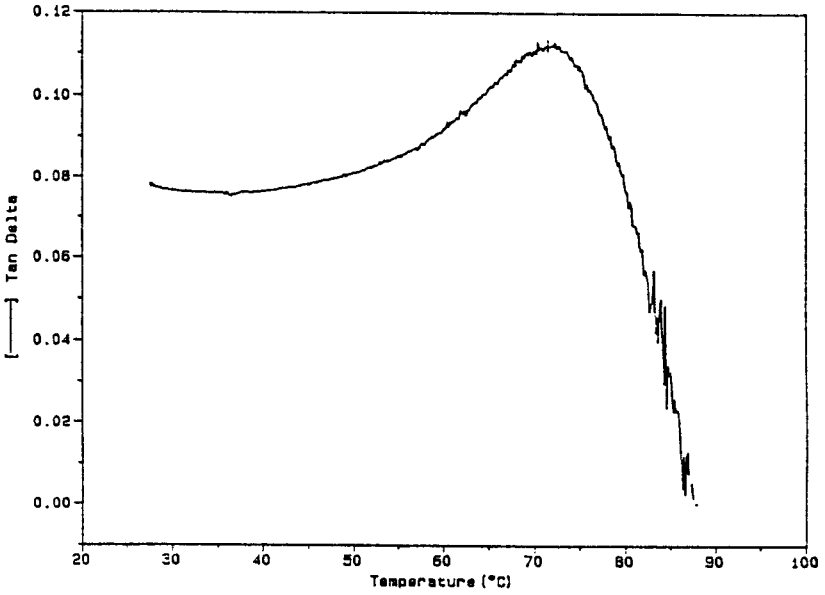


FIG. 1. DMA curve of wet fiber.

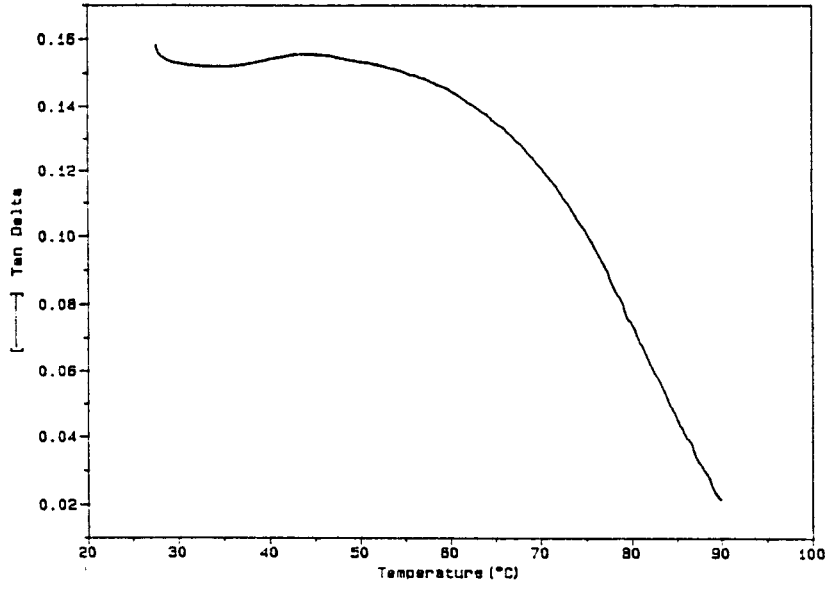


FIG. 2. DMA curve of 50 g $L^{-1}$ benzyl-alcohol-treated wet fiber.

The peak in tan $\delta$ obtained when the pretreated sample had been heated in the second bath of distilled water (Fig. 3) corresponds to a $T_g$ of 68.5°C, which closely approaches that obtained for the filaments in water. This virtual reestablishment of the $T_g$ in distilled water can be attributed to the benzyl alcohol having diffused out of the fiber during heating in water. Thus, the plasticizing action of the carrier is reversible, indicating that it entails only physical disruption of the molecular structure of the fiber.

## The Variation of $T_g$ with Carrier Concentration

Figure 4 shows the variation of wet $T_g$ of Courtelle S tow with concentration of benzyl alcohol applied. The nonlinear relationship clearly shows the presence of a minimum value for $T_g$ that corresponds to the aqueous solubility of the carrier at 80°C, the temperature at which pretreatment of the filament had been carried out.

## The Effect of Carrier on Dye Uptake

A 50 $cm^3$ aliquot of the stock aqueous acetic acid/sodium acetate buffer solution described above was placed in a 300 $cm^3$ capacity stainless steel

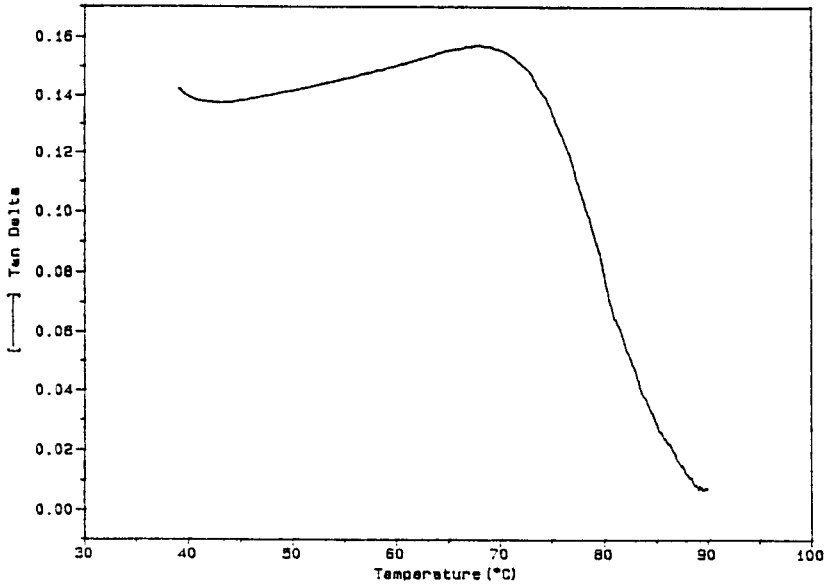


FIG. 3. DMA curve of the second run with the 50 g $L^{-1}$ treated sample.

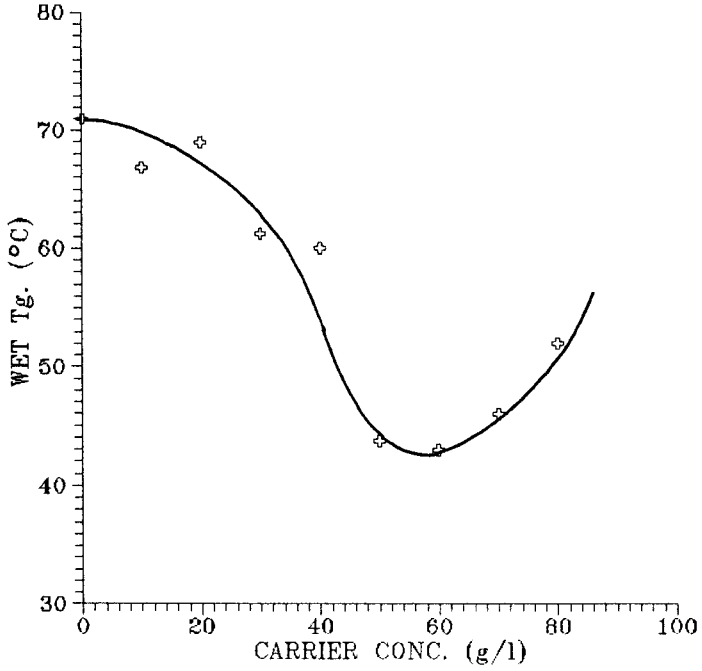


FIG. 4. Effect of carrier concentration on $T_g$ of wet fiber.

dyepot. A 20 $cm^3$ aliquot of a stock aqueous (distilled water) dye solution (2 g $L^{-1}$) was then added and an appropriate volume of benzyl alcohol was added to give a concentration of 10, 20, 30, 40, 50, 60, 70, or 80 g $L^{-1}$. The volume of the ensuing dyebath was then made up to 100 $cm^3$ using distilled water (the dyebath had a pH value of 4.5), the dye pot housed in a Zeltex Polycolor PC1000 laboratory dyeing machine and the dyebath allowed to reach thermal equilibrium at 80°C. A sample (1 g) of dry, scoured Courtelle S fabric was then added and dyeing carried out for 30 min at this temperature. The dyed sample was then removed, rinsed with warm water, and washed in 50 $cm^3$ of acetone for 5 min at 20°C to remove surplus dye and carrier. After drying in an oven at 40°C, the extent of dye uptake was determined using as ICS Micromatch color measurement system. The reflectance spectrum of the dyed sample was measured using a 10° standard observer, illuminant $D_{65}$ with specular component excluded and UV component included; the sample was folded so that measurement was carried out using a total of four layers of fabric. The corresponding K/S value at 640 nm was noted, this being the $\lambda_{MAX}$ of CI Basic Blue 45. Five measurements were made of each sample and

the average of these reflectance values was then used so as to minimize any error due to unlevel dyeing and/or sample presentation.

Figure 5 shows that benzyl alcohol increased the extent of dye uptake onto the fabric; a maximum value being achieved between 50 and 60 g $L^{-1}$ carrier, which corresponds to the maximum water solubility of benzyl alcohol at the dyeing temperature (80°C) employed.

### The Variation in K/S with $T_g$

Owing to the similarities between Figures 4 and 5 an examination of the relationship between the $T_g$ of wet Courtelle S tow and dye uptake onto Courtelle S fabric was made (Fig. 6). As expected, a linear relationship was obtained between the extent of dye uptake and $T_g$ of the wet fiber.

## DISCUSSION

The observed plasticizing action of water on acrylic fiber (Fig. 1) confirms the results obtained by other workers [10–13]; this effect can be attributed

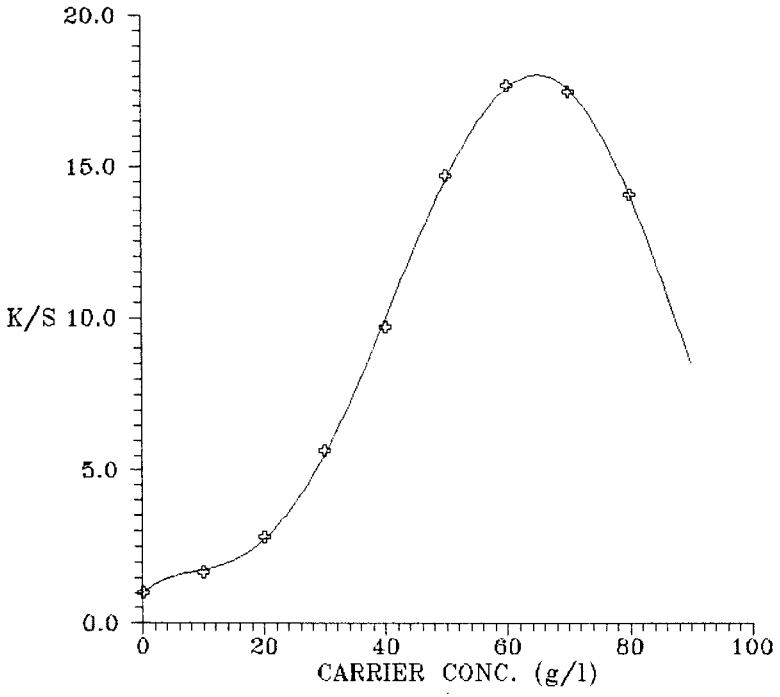


FIG. 5. Effect of carrier concentration on dye uptake.

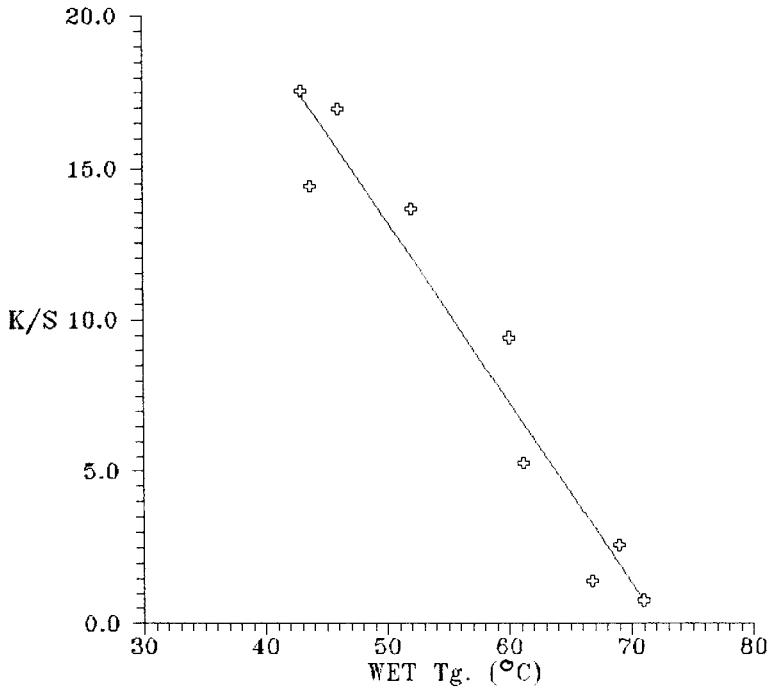


FIG. 6. Variation in dye uptake with $T_g$ of wet fiber.

to the adsorbed water molecules having disrupted the molecular structure of the fiber. The finding that benzyl alcohol reduced the $T_g$ of wet fiber (Fig. 4) demonstrates that the compound has caused further disruption of the physical structure of the substrate. It can be argued that the observed reduction in $T_g$ that accompanied an increase in concentration of carrier applied to the fiber up to 50 g $L^{-1}$ (Fig. 4) is due to a corresponding increase in concentration of benzyl alcohol adsorbed by the substrate; thus, the extent of plasticization at concentrations of benzyl alcohol which are lower than its maximum water solubility at 80°C increased with increasing concentration of carrier in the fiber. The maximum reduction in $T_g$ occurred at 60 g $L^{-1}$ benzyl alcohol which corresponds to the maximum amount of carrier adsorbed by the fiber and the maximum solubility of benzyl alcohol in water at 80°C. The observed increase in $T_g$ that occurred at carrier concentrations in excess of 60 g $L^{-1}$ (Fig. 4) is due to the maximum aqueous solubility of benzyl alcohol having been surpassed. At concentrations in excess of its water solubility, the carrier has greater affinity for the saturated, aqueous benzyl alcohol phase present in

the treatment bath than for the fiber. Consequently, carrier adsorption onto the substrate decreases with increasing concentration applied, as shown by the reduction in plasticization.

The enhancement in the uptake of CI Basic Blue 45 caused by benzyl alcohol (Fig. 5) can be attributed to the plasticizing action of the carrier on the fiber. The shape of the curve in Figure 5 is the antithesis to that of Figure 4, suggesting that maximum dye uptake onto Courtelle S fabric corresponds to the maximum reduction in wet $T_g$ obtained for Courtelle S tow. Thus, the observed increase in uptake of CI Basic Blue 45 that occurred at concentrations up to 50 g $L^{-1}$ benzyl alcohol can be attributed to an increase in plasticization of the wet fiber due to an increase in concentration of the carrier adsorbed. The maximum in dye uptake that occurred at 60 g $L^{-1}$ benzyl alcohol corresponds to the maximum amount of carrier adsorbed onto the substrate and the maximum water solubility of the carrier at the dyeing temperature used. The observed decrease in dye uptake found at concentrations of benzyl alcohol in excess of 60 g $L^{-1}$ can be attributed to a decrease in uptake of the carrier by the fiber and the concomitant decrease in $T_g$ reduction; alternatively, this decrease in dye uptake may, as proposed by Kim [14], be due to the dye having greater affinity for the saturated, aqueous carrier phase than the fiber.

The gradient of the linear relationship obtained between the extent of dye uptake and $T_g$ of the wet fiber (Fig. 6) is important since, if its value is the same for all carriers, then it can be concluded that plasticization is the only factor that determines carrier action and, therefore, that carrier efficiency is determined solely by the amount of carrier adsorbed by the fiber. However, if the value of this gradient differs for different carriers, then other factors, such as the dye's solubility in the carrier, will also contribute to carrier action.

## CONCLUSIONS

The presence of benzyl alcohol has been shown to enhance the uptake of CI Basic Blue 45 on Courtelle S fabric. The compound acts as a plasticizer, reducing the $T_g$ of the wet fiber. The degree of plasticization and the extent of enhancement of dye uptake were found to be proportional to the amount of carrier adsorbed by the fiber. This, in turn, suggests that the carrier functions as a diluent in that it facilitates dye diffusion within the fiber by disrupting the molecular structure of the substrate.

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