

## Thermoplasticity of Acetylated Cotton Yarn as Influenced by Degree of Substitution, Temperature, and Other Factors\*

J. J. CREELY, P. HARBRINK, and C. M. CONRAD, *Plant Fibers Pioneering Research Laboratory, Southern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture, New Orleans, Louisiana*

### Synopsis

The relative degree of thermoplasticity of acetylated cotton yarns has been determined by a technique developed for the purpose. The interfering contribution of hydrogen bonding could be eliminated by a wetting-out process. The yarns were acetylated to degrees of substitutions ranging from 0.77 to 2.93. Heat setting was applied either in vacuum or at atmospheric pressure in the presence of water vapor at temperatures in the range of 110–225°C. The thermoplasticity observed over a period of 30 days was permanent but readily removable by another application of heat setting. The effect of degree of substitution upon thermoplasticity could be represented by sigmoidal curves beginning at about  $DS = 1$  and increasing rapidly and asymptotically to a maximum at about  $DS = 2.25$ . In vacuum or water vapor the maximum thermoplastic response occurred at 175°C., but the response was greater with water vapor. Under vacuum heating a very distinct minimum response occurs at 180°C., due to second-order transition effect. Upon heating in the presence of water vapor a distinct minimum response occurs at 200°C. with secondary minima at 150 and 120°C. Prior crystallization (by heating to 200–225°C.) greatly reduces thermoplasticity due to reduction of the amorphous component, but does not completely eliminate it.

### INTRODUCTION

The thermoplastic nature of certain chemically modified cottons has been referred to in several publications from this division.<sup>1-5</sup> In those studies, thermoplasticity was demonstrated in a qualitative manner by the pleating of fabrics with a heated pressing iron<sup>1</sup> or by their mechanical behavior as a function of temperature.<sup>2-5</sup>

The mechanical tests demonstrating thermoplasticity usually involve a softening and eventual flow as the temperature increases from the glassy to the rubbery transition region. Accelerated flow is attributed to increasing segmental motion of the molecular chains in the amorphous regions.

\* Paper presented at the 147th Meeting of the American Chemical Society, Philadelphia, Pa., April 5–10, 1964.

The presence of an amorphous state in chemically modified cottons has been demonstrated in most cases by x-ray diffraction patterns<sup>2-3, 6-8</sup> which indicate loss of the original crystal structure of native cellulose and the presence of only a diffuse type of scattering. Upon annealing at elevated temperatures this amorphous material changes partly to a crystalline lattice, characteristic of the cellulose derivative.<sup>6</sup>

Because of a greatly increased interest in thermoplastic fibers, including chemically modified cottons, and in reversible crosslinks for which thermoplasticity might serve as an alternative, more information is needed about the thermoplasticity of chemically modified cottons, including techniques for measurement. The present study was undertaken to permit fuller evaluation of the thermoplastic behavior of partially acetylated cotton yarns, as influenced by degree of substitution, temperature, and the plasticizing effects of water vapor.

## MATERIALS AND METHODS

### Samples

The samples used in this study were prepared from scoured 7/1 combed Deltapine cotton yarns of approximately 3 twist multiplier. The acetylation of the samples has already been described.<sup>6</sup> Four yarns, acetylated to degrees of substitution (DS) varying from 0.77 to 1.59 by the PA (partial acetylation) process, and six yarns to DS of 1.11 to 2.93 by the FA (fully acetylated) process were available for study.

### Measurement of Thermoplasticity

Briefly, the experimental technique, as finally worked out, consisted in winding the yarns spirally on cylindrical rods of small diameter, heating at a temperature in the plastic region under the selected conditions, cooling, unwinding, and looping the yarns, and determining the overall length of the retracted loop (Fig. 1). The retracted doubled length, expressed as a percentage of its uncoiled doubled length, is used as an arbitrary measure of the degree of thermoplasticity of the yarn.

In preparation for winding, an approximately 6-ft. length of yarn is cut and knotted at each end. At about 15 in. from one end it is clamped to one end of a yardstick. The other end of the yarn passes over a grooved roller fixed at the opposite end of the yardstick and is held taut with a 22-g. weight. A 24-in. length of the yarn near the center of the length is now marked off for future use in fixing the loop length. One end of the yarn is tied to a 1/8-in.-diameter stainless steel rod, 12 in. long, and the entire length is wound onto the rod at a spacing of 16 twists/in. The winder, a modification of one ordinarily used for yarn-appearance boards, is equipped with a tension device to apply a uniform tension of 10 g. to the yarn. Finally, the other end of the yarn is tied to the rod with a loop knot to prevent unwinding.

For vacuum heating conditions, the yarn samples, on the rods, are placed in a vacuum oven and evacuated to 2–3 mm. Hg. Heating is commenced, and after the desired temperature (measured with a mercury-filled thermometer) is reached, the heat is maintained for 10 min. The heat is turned off and the oven allowed to come to room temperature.

For water vapor heating, the yarns, on the rods, are placed in the same oven, containing at the bottom a supply of water more than sufficient, when converted into vapor, to fill the oven compartment. The oven is heated rapidly to the selected temperature, whereupon the excess water is distilled off through a side tube at atmospheric pressure leaving behind

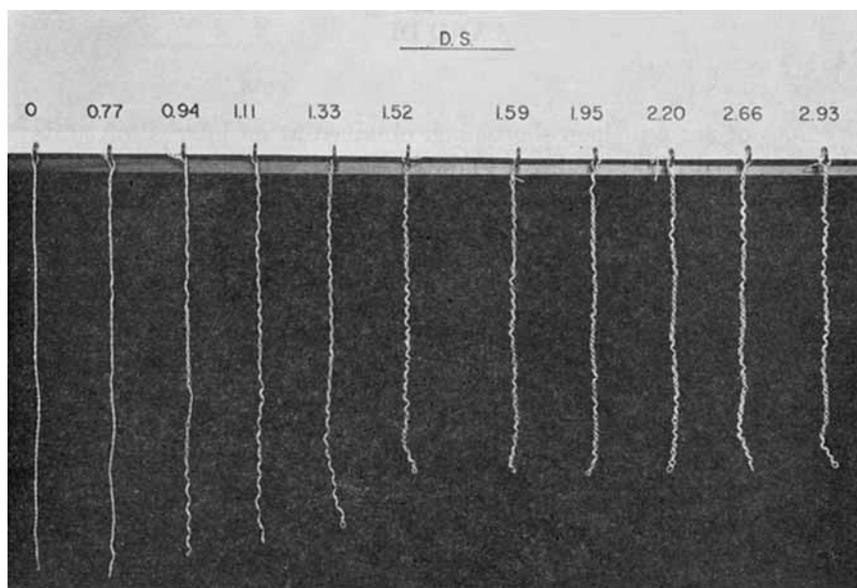


Fig. 1. Loops of acetylated yarns heat-set at 175°C. in the presence of water vapor, wet out, and dried under 100 g. tension.

only water vapor. After exposure for 10 min. at the required temperature the heat is turned off. No vacuum is used in this case.

After heating under the selected conditions, the yarns are cooled and while still wound on the rods are immersed for 30 minutes in water containing 0.1% Alkamerse wetting agent. The purpose of this step is to reduce hydrogen-bonding effects in the noncrystalline regions which, as will be shown below, would otherwise introduce complications. At the end of the wetting period the yarns are unwound from the rods. The 24-in. marks, previously mentioned, are brought together and securely tied with a cord to make a doubled loop 12 in. long. The wet loop is hung on a hook on a rack, loaded with a 100-g. weight, and is allowed to dry for 4 hr. under standard atmospheric conditions of 70°F. and 65% R.H. The weight is then removed.

After exposure in the standard atmosphere for 2, 15, and 30 days the 100-g. weight is again hung on the yarn for 30 sec. and removed, allowing the yarn to relax for 30 sec. This brief weighting before measurement removes certain shape distortions, probably caused by drying irregularities, and improves the reproducibility of the retracted length measurements. A 200-mg. weight is next hung on the suspended loop on the rack, and the distance between extremities of the yarn is measured to the nearest 0.05 in. with a 12-in. rule. The per cent loop shortening is then taken as the percentage of the contracted length divided by the original length (12.0 in.).

## RESULTS AND DISCUSSION

### Reproducibility of Measurements

Values of per cent loop shortening, obtained at an interval of 30 days after heat treatment, are listed in duplicate in Table I for samples heated under vacuum (2–3 mm. Hg) at three levels of temperature. Differences between replicates where each set of samples was heated as an independent group were taken (to remove DS correlation) and the differences averaged. Standard errors of the means and the *t* values were also computed. The *t* values for the 0.05 and 0.01 levels of significance of means of 11 yarn specimens, are also recorded in Table I.

By reference to the *t* values for the replicates and their comparison it was concluded that no significance is to be attached to the means of differences between samples heated at 150°C. and that the means of differences at 175°C. and 225°C. were just significant at the 5% level. Based on analysis of variances of more extensive data a standard error of 0.557 would be expected for means of differences of sets of 11 yarn specimens. If the latter figure is used, the means of difference between replicates at 175°C. and 225°C. would not be significant. Perhaps the precision is about as good as can be expected with this type of material.

### Hydrogen-Bonding Effects

Although it seems to be well established that the hydrogen bonds between the molecules in the crystalline regions of native cellulose fibers are quite stable,<sup>9</sup> this is not true of those in the noncrystalline regions. These are considered to be transient and strongly influenced by the amount of moisture present in the cellulosic structure. The beautiful deuteration experiments of Marrinan and Mann<sup>10</sup> are pertinent in this connection and point to the accessibility of the amorphous regions and the ease with which the hydrogen atoms in these regions can be replaced by deuterium atoms and vice versa. Presumably, hydrogen bonds are broken in these regions before replacement can occur.

It was considered that a part of the apparent thermoplastic effects might be due to hydrogen bonding,<sup>11</sup> fixed in the amorphous regions of the

TABLE I  
Precision of Measurement of Per Cent Loop Shortening after Heat Fixing at Various Temperatures. Measurements Made after 30 Days

DS	Loop shortening, %					
	150°C.		175°C.		225°C.	
	(a)	(b)	(a)	(b)	(a)	(b)
0	1.7	1.7	2.5	1.3	1.7	3.5
0.77	2.5	1.7	3.3	0.8	5.8	6.7
0.94	3.3	1.8	4.6	2.7	7.9	9.2
1.11	4.2	3.8	7.5	7.7	11.7	12.5
1.33	5.0	4.9	15.0	10.8	12.5	17.5
1.52	5.8	6.9	15.0	12.6	15.7	16.7
1.59	6.7	5.9	18.3	17.5	17.8	19.2
1.95	10.8	10.7	18.3	18.2	19.3	19.2
2.20	12.5	15.0	20.0	21.0	20.8	20.0
2.66	12.5	16.7	20.8	21.4	21.2	20.8
2.93	14.2	15.9	23.3	22.1	21.3	21.7
Means of differences						
Standard error						
<i>t</i> value <sup>a</sup>						

<sup>a</sup>  $t_{95} = 2.23$ ;  $t_{91} = 3.17$ .

fibers by the relatively high temperatures used in heat setting. These bonds would behave as crosslinks, tending to maintain the coiled state, thus contributing to yarn loop shortening and confusing the results. Such hydrogen bonds, if present, should be relatively easily broken by thorough wetting out with water. This is believed to be supported by the comment of Marrinan and Mann<sup>10</sup> that deuterated samples must be protected from the moisture of the air lest they "become rehydrogenated almost completely in the normal laboratory atmosphere in a few minutes." To become rehydrogenated many hydrogen bonds would have to be broken.

To test the possible hydrogen-bonding effect, four sets of yarn samples of different degrees of substitution were wrapped on rods and heated, two at 175°C. under vacuum and two at 125°C. with steam. One set from each heating condition was wetted out 30 min. in water containing wetting agent, while the other set was not wetted out. The samples were then conditioned as previously described, and the per cent retraction was determined in the usual manner.

The per cent retractions increased approximately 10% between 2 and 15 days but then remained essentially constant. The results after 30 days exposure, presented in Table II, show strong reductions of loop shortening due to wetting out. Since the *t* values are highly significant at the 1% level, it was concluded that the wetting-out step must be included in the technique.

TABLE II  
Effect of Wetting Out on Loop Shortening of Heat-Set Acetylated Cotton Yarns.  
Measurements Made after 30 Days.

DS	Loop shortening, %					
	Heated at 175°C. under vacuum			Heated at 125°C. with water vapor		
	Not wetted	Wetted	Difference	Not Wetted	Wetted	Difference
0.00	2.5	1.9	0.6	7.5	2.1	5.4
0.77	10.6	2.1	8.5	15.8	1.9	13.9
0.94	17.1	3.7	13.4	18.5	2.4	16.1
1.11	17.5	7.6	9.9	21.7	3.3	18.4
1.33	22.4	12.9	9.5	25.2	6.5	18.7
1.52	22.0	13.8	8.2	22.5	10.0	12.5
1.59	27.5	17.9	9.6	26.5	12.7	13.8
1.95	24.2	18.3	5.9	28.7	15.8	12.9
2.20	26.8	20.5	6.3	25.4	16.7	8.7
2.66	27.5	21.1	6.4	29.2	17.5	11.7
2.93	27.9	22.7	5.2	32.1	20.4	11.7
Means	20.55	12.95	7.59	23.01	9.94	13.07
Standard Error			0.99			1.18
<i>t</i> <sup>a</sup>			7.67			11.07

<sup>a</sup> *t*<sub>05</sub> = 2.23; *t*<sub>01</sub> = 3.17.

### Permanence of the Thermoplastic Effect

The permanence of the loop shortening of heat-set acetylated yarns was established by a series representing each degree of acetyl substitution and heat-set at temperatures of 150, 165, 175, 185, and 225°C. Since the results for the five temperatures changed in an essentially parallel way they were averaged and taken as a single value for each exposure period. In the results presented in Table III it will be noted that loop shortening continues for a number of days, increasing by about 17% between 2 and 15 days and another 3% between 15 and 30 days. Tentatively a 30 day exposure was selected for subsequent comparison of data.

TABLE III  
Mean Per Cent Loop Shortening after Different Intervals of Exposure to the Standard Atmosphere (70°F., 65% R. H.)

DS	Loop shortening, %		
	2 days	15 days	30 days
0	0.92	1.60	1.54
0.77	1.74	2.36	2.56
0.94	2.46	3.52	3.68
1.11	4.58	6.24	6.96
1.33	6.68	8.72	9.10
1.52	8.72	10.78	10.98
1.59	12.18	14.36	14.10
1.95	13.58	14.64	16.14
2.20	16.30	18.26	18.54
2.66	17.10	19.26	19.38
2.93	18.08	20.18	19.86
Means	9.30	10.90	11.17
Means, %	100.0	117.2	120.0

### Demonstration of Thermoplastic Effect

A truly thermoplastic effect should be reversible, i.e., a thermoplastic yarn after being heat-set in one form should again respond to comparable heat treatment to assume a new and different shape. Thermoplasticity is a property that is peculiar to amorphous but not to truly crystalline solids. Since it has been established that acetylated cottons crystallize substantially during heating to temperatures of 175°C. or higher,<sup>6</sup> we may raise the question as to whether acetylated cotton yarns are really thermoplastic in the usual sense or, due to crystallization above 175°C., are essentially thermosetting. Some experiments were carried out to throw light on these questions.

A series of yarns (A) representing all acetyl substitutions, were wound on the rods, heat-set under vacuum at 225°C., cooled, wet out, and exposed in the standard atmosphere for 30 days. A second series of equal lengths of the same yarns (B) were loosely mounted in the fully extended

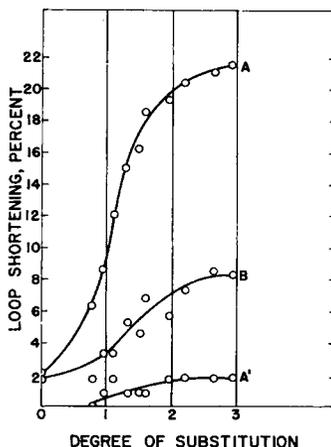


Fig. 2. Effect of annealing upon loop shortening: (A) control, heat-set at 225°C. under vacuum; (B) yarn specimens heat-set at full length at 225°C. under vacuum, cooled, and heat-set as in (A); (A') loops from (A) extended full length on a rack and again heat-set at 225°C. under vacuum.

unwound condition on a rack and heated at the same time in the oven. After cooling, the yarns of this series were wound on rods and heated a second time under the same conditions of vacuum and temperature as before. After cooling, these yarns were likewise wet out, and exposed under standard atmospheric conditions for 30 days. The per cent retraction of both series A and B was then determined. Finally, the yarns of the first series (A) were, after measurement, extended to full loop length on a rack and heated a second time under vacuum at 225°C. These yarns were likewise cooled, wet out, exposed under standard conditions and the retraction measured after 30 days (A'). Figure 2 represents the per cent retraction when the yarns were wound on the rods and processed in the usual way. Figure 2B shows the residual per cent retraction which can be induced after the yarns are first crystallized and heat-set without winding, and Figure 2A' represents the results for series A after crystallization and after the spiral is removed by a second period of heat setting in the extended state.

The above results reveal several important facts. First, a preliminary heat setting in the extended state at a temperature which induces crystallization greatly limits the amount of retraction that can be subsequently achieved by winding on the rods and heat setting. Second, when a high degree of retraction has been induced by coiling and heat setting (Fig. 2A), this may in spite of crystallization be almost completely removed by extending the loops to full length, stretching, and again heating (Fig. 2A') This latter effect demonstrates the truly thermoplastic nature of the phenomenon and shows that, crystallization notwithstanding, considerable amorphous cellulose acetate remains. At the same time it supports our belief that nearly all if not all of the loop shortening due to hydrogen bond-

ing in the coiled form has been broken by the wetting-out process and re-distributed, since almost none of the original retraction remains. The difference between values represented by Figures 2A' and 2B may be due to the slight tension placed on the previously heat-set yarn loops used in obtaining Figure 2A when extending them to their full length for the treatment represented by Figure 2A', or to additional crystallization induced by the tensioning process.

### Effect of Degree of Substitution and Temperature on Thermoplasticity

After preliminary test conditions had been established, a more comprehensive series of experiments was undertaken on yarns of the different degrees of acetylation in a vacuum oven at a range of temperatures. The loop lengths were measured after exposure for 2, 15, 30 days, the latter being plotted in Figure 3. When plotted against degree of substitution the data yielded sigmoidal curves. They were accordingly fitted by least squares with third-degree polynomial curves. In Figure 3 for the 125 and 150°C. curves, the individual observations are shown, but the inclusion of all individual observations for curves at the other temperatures was not considered feasible. From the curves it is evident that yarns with degree of substitution below  $DS = 1$  are poorly thermoplastic; between  $DS = 1$  and  $DS = 2.25$  the increase of thermoplastic response of the yarns is nearly proportional to substitution. Above  $DS = 2.25$  the loop shortening becomes asymptotic.

Examination of the positions of the curves shows that increasing thermoplasticity is not proportional to temperature. The reason for this becomes more obvious when the same loop shortening data are plotted against temperature (Fig. 4). Here it is seen that loop shortening reaches a maximum at 175°C. and is followed by a distinct minimum at 185°C.

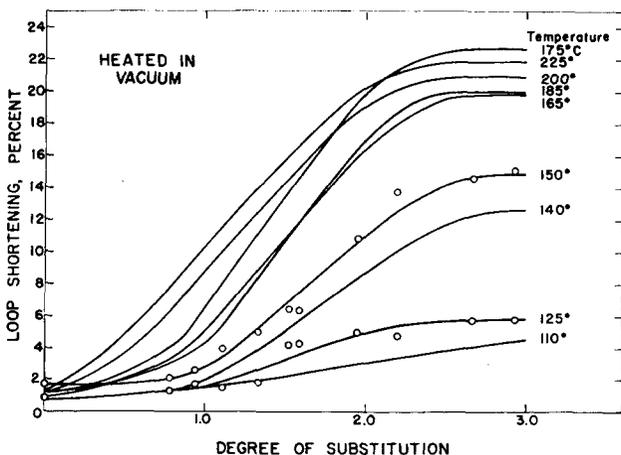


Fig. 3. Per cent loop shortening of acetylated cotton yarns as a function of degree of substitution. Measured 30 days after heat setting.

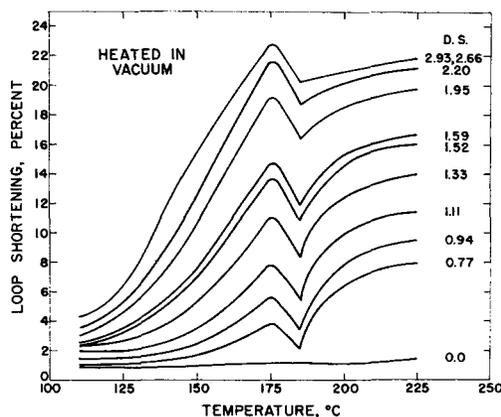


Fig. 4. Per cent loop shortening of acetylated cotton yarns as a function of temperature. Measured 30 days after heat setting.

This minimum appears to be associated with the second-order transition temperature which has been repeatedly observed at about  $180^{\circ}\text{C}$ .<sup>2</sup> The mechanical compliance reaches its greatest value at this temperature. Above  $185^{\circ}\text{C}$ . the shortening again proceeds asymptotically to a secondary maximum at  $225^{\circ}\text{C}$ . At the two higher substitutions the loop shortening reached at  $225^{\circ}\text{C}$ . is less than that at  $175^{\circ}\text{C}$ .; but at lower substitutions it is greater though by no means as great as that at the higher substitutions. The degree of loop shortening is generally proportional to substitution to  $\text{DS} = 2.25$ , above which little increase is observed.

### Effect of Water Vapor on Thermoplasticity

Since the effect of water vapor on the heat setting of textile fibers is well known,<sup>12</sup> it was of considerable interest to determine the effect also of moisture upon the thermoplastic behavior of acetylated yarns.

The data, again fitted by least squares to polynomial curves, are presented in Figure 5 as a function of substitution and in Figure 6 as a function of temperature. The curves of Figure 5 resemble those of Figure 3, except that the loop contraction is considerably higher for a given temperature and degree of substitution; the increase at  $175^{\circ}\text{C}$ . averaged 33%. Stated in another way, the presence of water vapor decreases the temperature for a given loop shortening in general by 30–35°C.

Again, it is observed that the height of the curves is not entirely progressive with temperature. When loop shortening is plotted against temperature (Fig. 6) important dips in the curves are observed at 200, 150, and  $120^{\circ}\text{C}$ . The approaches to the peaks and valleys appear to be gradual and not due to sudden irregularity in the data. It should be noted also that the valley which appeared at  $180\text{--}185^{\circ}\text{C}$ . in the family of curves from the vacuum-heated samples (Figure 3), where a second-order transition was inferred, is missing. With water vapor plasticization one should

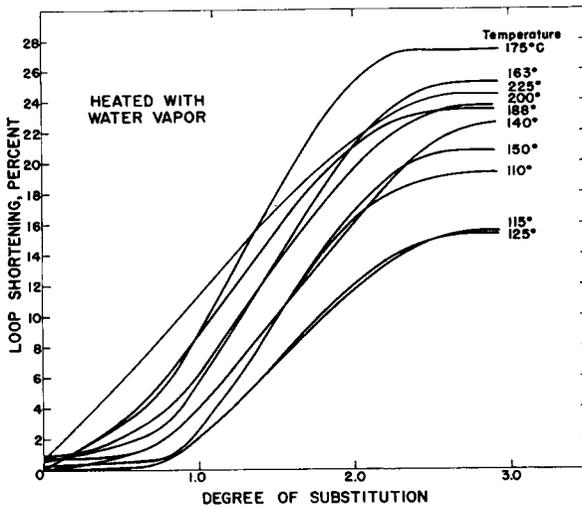


Fig. 5. Effect of water vapor at different temperatures on loop shortening as a function of substitution. Measured 2 days after heat setting.

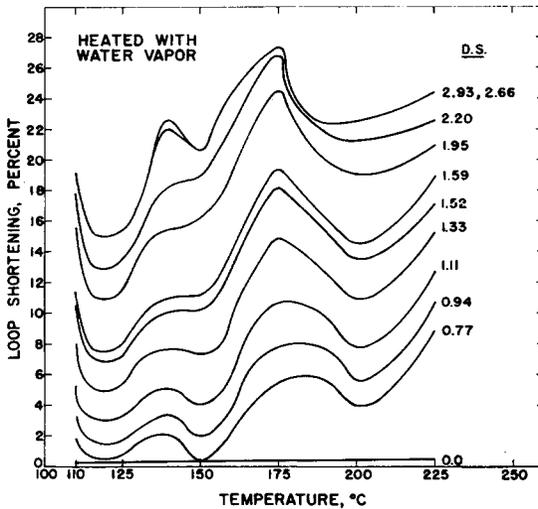


Fig. 6. Effect of water vapor on loop shortening of acetylated cotton yarns of different acetyl substitutions as a function of temperature. Measured 2 days after heat setting.

expect this to relocate at a lower temperature, and this is confirmed by the minimum at  $150^{\circ}\text{C}$ .

Before attempting an explanation of the position of the several valleys in Figure 6 one must consider the possible effect of the moisture on the crystalline structure of the acetylated cellulose and the temperature at which crystallization takes place. Diffractograms prepared according

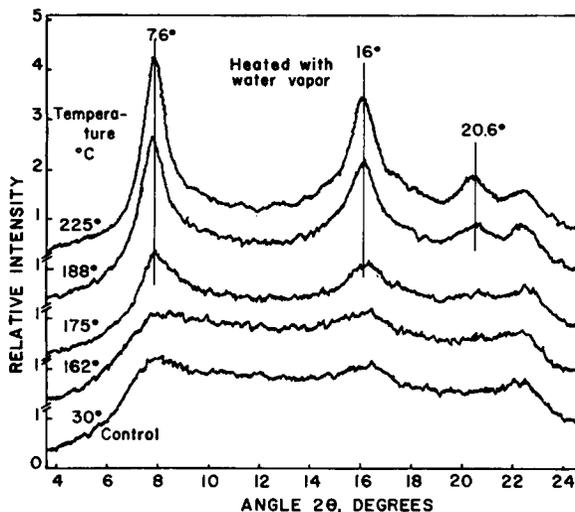


Fig. 7. Diffractograms of acetylated cotton yarn heat-set at the indicated temperature in the presence of water vapor.

to methods previously described<sup>6</sup> from portions of the yarn acetylated to  $DS = 2.93$ , are presented in Figure 7. It will be observed that water vapor has induced no changes in the crystalline structure of the diffractograms below  $175^{\circ}C$ ., the temperature at which crystallization has previously been observed to begin.<sup>6</sup> Above this temperature, crystallization of the cellulose acetate appears to be progressive and comparable to that observed in samples heated dry.

Returning now to consideration of Figure 6, the valleys in the family of curves may be tentatively interpreted as being associated with second-order type phenomena. The valley at  $150^{\circ}C$ . in these curves probably corresponds to that of  $180$ – $185^{\circ}C$ . in Figure 3, although from the data here reported the correspondence and extent of reduction cannot be established with any certainty. Large changes of transition temperature due to moisture have been deduced by Gill and Steele<sup>13</sup> for unmodified celluloses and by Bryant and Walter<sup>14</sup> for cellulose semi- and triacetates and other fibers. Furthermore, a wide range of transition temperatures previously has been associated in the literature with cellulose acetates.<sup>2</sup> The additional valleys observed in Figure 6 may correspond to some of these other reported transition temperatures.

### SUMMARY

The thermoplasticity of partially acetylated cotton yarns, varying in acetyl substitution from  $DS = 0.77$  to  $2.93$  was measured in the presence and absence of moisture at various temperatures by a technique developed during the study. The contribution of hydrogen bonds in the amorphous regions to heat setting, which could partly mask the thermoplasticity

measurements, was more or less completely eliminated by a wetting-out and weighting procedure.

Thermoplasticity is strongly influenced by degree of acetylation, being slight below  $DS = 1$  and rising rapidly and asymptotically to a maximum at about  $DS = 2.25$ .

Thermoplasticity is strongly influenced by temperature. Under vacuum the response is slight below  $150^{\circ}\text{C}$ ., rises rapidly to a maximum at  $175^{\circ}\text{C}$ ., dips to a minimum at  $180\text{--}185^{\circ}\text{C}$ . and then rises again. In the presence of water vapor the thermoplastic response begins at a lower temperature and reaches a maximum at  $175^{\circ}\text{C}$ .; this maximum averages 33% greater than that of the vacuum-heated samples. At any given degree of substitution and temperature approximately the same thermoplastic response is reached at a temperature about  $35^{\circ}\text{C}$ . below that required for the same effect in the vacuum-heated samples. These curves show minima at 120, 150, and  $200^{\circ}\text{C}$ . The minima are interpreted as second-order transition phenomena.

Crystallization of the cellulose acetate seems to play little or no part in the thermoplastic response at temperatures up to  $175^{\circ}\text{C}$ . However, thermoplasticity is strongly reduced if crystallization first is deliberately induced by heating the acetylated yarn to temperatures above the crystallization temperature. Even in highly crystallized yarn the heat-set state can be almost completely reversed by again heating under suitable conditions.

Use of a company and/or product name by the Department is for the information of the reader and does not imply endorsement over other products which may also be suitable.

Appreciation is expressed to E. Fred Schultz, Jr. for assistance with the curve fitting.

### References

1. Buras, E. M., Jr., S. R. Hobart, C. Hamalainen, and A. S. Cooper, Jr., *Textile Res. J.*, **27**, 213 (1957).
2. Conrad, C. M., P. Harbrink, and A. L. Murphy, *Textile Res. J.*, **33**, 784 (1963).
3. Conrad, C. M., D. J. Stanonis, P. Harbrink, and J. J. Creely, *Textile Res. J.*, **30**, 339 (1960).
4. Demint, R. J., J. C. Arthur, Jr., A. R. Markezich, and W. F. McSherry, *Textile Res. J.*, **32**, 918 (1962).
5. Klein, E., D. J. Stanonis, P. Harbrink, and R. J. Berni, *Textile Res. J.*, **28**, 659 (1958).
6. Conrad, C. M., and J. J. Creely, *J. Polymer Sci.*, **58**, 781 (1962).
7. Creely, J. J., and C. M. Conrad, *Textile Res. J.*, **32**, 184 (1962).
8. Creely, J. J., D. J. Stanonis, and E. Klein, *J. Polymer Sci.*, **37**, 43 (1959).
9. Hermans, P. H., *Contribution to the Physics of Cellulose Fibers*, Amsterdam Elsevier, 1946, pp. 41 ff.
10. Marrinan, H. J., and J. Mann, *J. Appl. Chem.*, **4**, 204 (1954).
11. Huggins, M. L., *J. Chem. Educ.* **34**, 480 (1957).
12. Press, J. J., *Ann. N. Y. Acad. Sci.*, **67**, 952 (1957).
13. Gill, R. A., and R. Steele, *J. Appl. Polymer Sci.*, **5**, 589 (1961).
14. Bryant, G. M., and A. T. Walter, *Textile Res. J.*, **29**, 211 (1959).

### Résumé

On a déterminé le degré relatif de thermoplasticité de fils de coton acétylé au moyen d'une technique élaborée à cet effet. L'interférence due à la contribution des liens hydrogènes peut être éliminée par un processus de déshumidification. Les fils ont été acétylés à des degrés de substitution s'étalant de 0.77 à 2.93. On a appliqué le traitement à chaud tant dans le vide qu'à pression atmosphérique en présence de vapeur d'eau entre 110 et 225°C. La thermoplasticité observée sur une période de 30 jours était permanente mais aisément éliminable au moyen d'une nouvelle application du traitement à chaud. L'influence du degré de substitution sur la thermoplasticité pourrait être représentée par une courbe sigmoïde partant de  $DS = 1$  et augmentant rapidement puis asymptotiquement jusqu'à un maximum à environ  $DS = 2.25$ . Dans le vide ou dans la vapeur d'eau, le maximum de réponse thermoplastique a lieu à 175°C, mais cette réponse est plus grande dans le cas de la vapeur d'eau. Lors du chauffage soud vide, un minimum de réponse apparaît distinctement à 180°C et est dû à l'effet d'une transition de second ordre. Lors du chauffage en présence de vapeur d'eau, un minimum de réponse est discernable à 200°C avec des minima secondaires à 150° et 120°C. Une cristallisation préliminaire (par chauffage à 200-225°C) qui réduit fortement la thermoplasticité, est due à la diminution de la teneur en composant amorphe; elle ne l'élimine cependant pas complètement.

### Zusammenfassung

Der relative Thermoplastizitätsgrad acetylierter Baumwollgarne wurde nach einem eigens für diesen Zweck entwickelten Verfahren bestimmt. Der störende Beitrag der Wasserstoffbindung konnte durch einen "Wetting-out"-Prozess ausgeschaltet werden. Die Garne wurden zu einem Substitutionsgrad von 0,77 bis 2,93 acetyliert. Hitzebehandlung wurde entweder im Vakuum oder bei Atmosphärendruck in Gegenwart von Wasserdampf bei Temperaturen im Bereich von 110 bis 225°C angewendet. Über einen Zeitraum von 30 Tagen wurde eine permanente Thermoplastizität beobachtet, die jedoch durch eine weitere Hitzebehandlung leicht zum Verschwinden gebracht werden konnte. Der Einfluss des Substitutionsgrades auf die Thermoplastizität konnte durch s-förmige Kurven dargestellt werden, welche bei etwa  $DS = 1$  begannen und rasch asymptotisch zu einem maximalen Wert bei  $DS = 2,25$  anstiegen. Im Vakuum oder in Wasserdampf wurde die höchste Thermoplastizität bei 175°C erreicht, sie war jedoch in Wasserdampf grösser. Beim Erhitzen im Vakuum tritt ein auf dem Einfluss einer Umwandlung zweiter Art beruhendes, sehr ausgeprägtes Plastizitätsminimum bei 180°C auf. Beim Erhitzen in Gegenwart von Wasserdampf tritt ein deutliches Minimum bei 200°C auf, mit Sekundärminima bei 150 und 120°C. Vorhergehende Kristallisation (durch Erhitzen auf 200-225°C) setzt die Thermoplastizität wegen des Rückganges der amorphen Komponente stark herab, beseitigt sie aber nicht vollständig.

Received July 13, 1964