

The Resiliency and Modulus of Viscose Rayon as a Function of Swelling and Temperature*

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Fiber resiliency and stiffness are very important factors in the crease recovery of fabrics, and the effect of water on these properties influences fabric wash-wear behavior, especially with cellulosic fibers. This paper is concerned with the effect of absorbed water on the mechanical properties of viscose rayon fibers and how this effect may be modified by chemical treatment of the rayon.

Earlier studies¹ have shown that for a number of synthetic textile fibers there is a temperature range wherein the resiliency shows a minimum and the modulus shows a considerable decrease. These changes were believed to arise from a glass-rubber transition in the amorphous portion of the fibers. It has been shown by Bryant and Walter from tensile measurements² and by others³ that the glass transition temperature of fibers can be lowered by absorption of water. Bryant and Walter examined different textile fibers and found that the change in T_g brought about by immersion in water increased with the hydrophilic nature of the fiber. Rayon showed no minimum in resiliency in either the wet or the air-dry state over the temperature range studied. However, the resiliency of wet rayon decreased with decreasing temperature from 30 to 0°C., while in the same temperature range the modulus increased. These results were interpreted by Bryant and Walter as indicating a T_g of greater than 240°C. (the decomposition temperature) for the dry fiber and of less than 0°C. for the wet fiber. A second-order transition has been reported for wet rayon^{4,5} in the region of 45°C. based on force-temperature measurements, but the results are in error due to failure to apply a swelling correction.⁶ Transitions have also been reported for dry rayon at -20°C. from dielectric studies⁷ and in the region from -20 to -60°C. from dynamic mechanical measurements,⁸ but these are

not considered to be the primary transition. The absorption of a plasticizer by a polymer is known to reduce T_g ,⁹⁻¹¹ but a change of more than 240°C. is exceptionally large, and we considered this remarkable effect to warrant further study.

It follows from Bryant and Walter's suggestion that at intermediate degrees of water absorption the T_g of rayon should fall in the measurable range between 0 and 100°C. We have made resiliency and modulus measurements as a function of both water content and temperature. Control of the water content was achieved by immersing the yarn in acetone-water mixtures, in polymer-water mixtures, and in air of different relative humidities. The effects of "wet"-state and "dry"-state cross-linking of rayon on the above properties have also been determined.

EXPERIMENTAL

All measurements were made in a room maintained at 21°C. on 42-filament, 150-denier viscose yarn having 2.5 tpi of twist. The test samples had a gage length of 3 in. and their ends were glued to tabs of phenolic-impregnated paper with a cold-setting epoxide cement. Diamond-shaped holes were punched in the tabs to accommodate the hooks which held the sample during testing. Two conditioning treatments of the yarn were employed before testing. For experiments involving 5 min. soaking time in acetone-water solutions the yarn was conditioned in air at 65% R.H. and 21°C. In all other experiments the samples were dried for 10 min. at 150°C. in an oven and then desiccated over concentrated H_2SO_4 for 16 hr. Samples cross-linked in the "dry" state were prepared by winding the yarn onto a wire frame and soaking it for 5 min. in a 15% (w/w) solution of dimethylolethyleneurea containing 0.16% NH_4Cl as a catalyst. The yarn was removed from the frame, squeezed between rollers to remove surplus solution, re-

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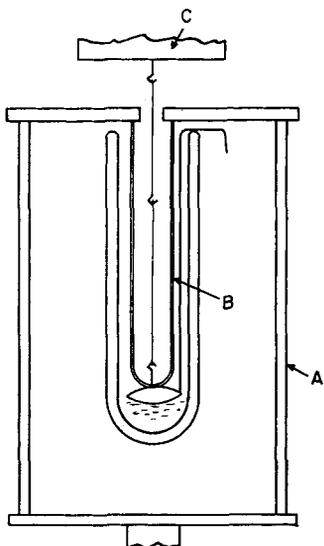


Fig. 1. Apparatus for measuring the tensile properties of yarn immersed in solution as a function of temperature.

wound on the frame taut, dried 10 min. at 100°C., and then cured 15 min. at 150°C. The yarn was soaked 15 min. in boiling water, washed for 45 min. in cold water, and allowed to dry in air. Yarn crosslinked "wet" was prepared in a way similar to that suggested by Morton,¹² by soaking 3-in. test samples, held taut on a frame, in a 36% (w/w) solution of HCHO in 1N H₂SO₄ for 10 min. at 80°C. The samples were washed for 30 min. in hot water, then for 30 min. in cold water, and then conditioned for testing.

The apparatus for measuring the resiliency and modulus of wet yarn as a function of temperature is shown schematically in Figure 1. It consists of a steel frame (A) bolted to the cross-head beam of an Instron tester. Suspended from this is a U-shaped stainless steel rod (B) which holds a small hook. The lower end of the sample is secured by this hook while the upper end is attached to the strain gage (C) by means of a steel wire hook. The steel loop and sample were immersed in the experimental solution contained in an unsilvered glass Dewar flask. Temperature was measured with a mercury thermometer and the solution was stirred manually by means of a wire stirrer. Just prior to the test the sample length was determined with a cathetometer by observation through the Dewar flask. Measurements were made (after 5 min. immersion time in this case) by subjecting the yarn to a stress-strain cycle to 4% strain at a rate of 6.6%/min. The resiliency was defined as the

percentage linear strain recovery at the end of the cycle, and the modulus as the stress at 4% strain in g./d. (referred to standard conditions). For measurements in the range of -40 to 21°C., the bath solution was introduced into the flask at the lowest temperature and allowed to warm up slowly. Samples were put into the bath when it reached the desired temperature and the exact temperature determined at the midpoint of the extension cycle. Bath temperatures in the range 21-98°C. were obtained by introducing the solution at a higher temperature and allowing it to cool slowly. The bath temperature in the Dewar flask changed so slowly that it remained essentially constant during the time taken to make a measurement.

Tensile measurements of yarn samples in a series of swelling solutions at 21°C. involved the use of a number of large test tubes. The sample was suspended in the appropriate solution inside the tube and held taut during the soaking period by means of an adjustable wire support at the upper end of the tube and a hook glued to the bottom of the tube with epoxide cement. Measurements were made after 4 hr. soaking time by clamping the tube to the Instron cross-head beam and attaching the upper end of the sample to the strain gage with a wire hook.

Two types of bath solutions were used, solutions of reagent grade acetone in deionized water and solutions of Pluronic L 44 in deionized water.

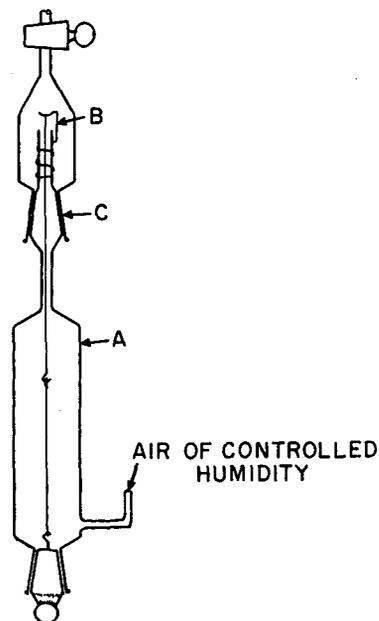


Fig. 2. Apparatus for measuring the tensile properties of yarn in a controlled atmosphere.

Pluronic L 44 is a copolymer of propylene and ethylene oxides supplied by the Wyandotte Chemicals Corp. It is a liquid with a molecular weight of about 2000 which is miscible with water in all proportions at 21°C. The relative humidity of air in equilibrium with the Pluronic solutions was determined with a Dunmore electric hygrometer which had been checked against standard salt solutions. The relative humidity over the acetone solutions was calculated from partial vapor pressure data in the literature.¹³

The apparatus used to obtain data in air is shown schematically in Figure 2. Air, dried first over magnesium perchlorate, was passed continuously through a sintered glass bubbler containing the appropriate H₂SO₄ solution,¹⁴ to control the relative humidity, and then into the glass vessel (A). The desiccated sample was introduced into (A) and one end attached to the lower hook. The other end was suspended from a hook attached to a wire support (B) which was adjusted vertically to make the sample taut. After 10 min. the flow of air was stopped, the cap (C) placed in position, and the vessel sealed. Periodically the air in the vessel was renewed by the same process. Measurements were made after conditioning for 3 days

which was found to be sufficient time to bring the sample to equilibrium within the range of experimental error. To make a measurement, the sample vessel was mounted on the cross-head of the Instron tester, the glass cap removed, and the wire hook attached to the strain gage. A flow of air was maintained through the sample vessel during the measurement to prevent outside air from entering. For data in air containing water and acetone vapor the acid solutions were replaced with acetone-water solutions.

RESULTS

The variation of resiliency and modulus with temperature for rayon yarn immersed in a series of acetone-water solutions is shown in Figure 3. As the water concentration of the solution is decreased, the resiliency curve is displaced to higher temperatures. A minimum in resiliency first appears in the 60% aqueous solution and occurs at 0°C. Minima also occur in the 40% solution at 10°C., in the 30% solution at 15°C., and in the 20% solution at 30°C. No minimum occurs in the 10% aqueous solution at temperatures up to 40°C. The decrease in modulus with temperature, which also first begins to appear in the 60% aqueous solu-

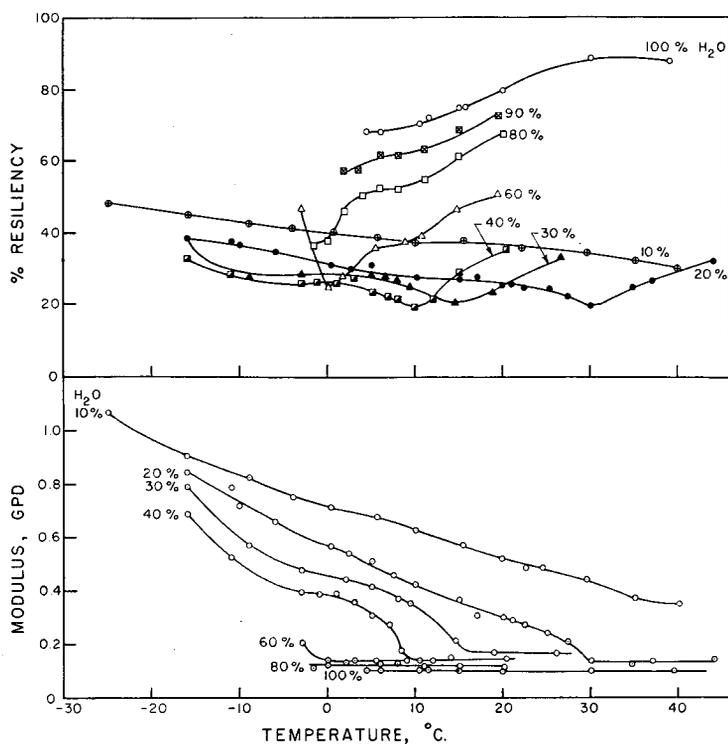


Fig. 3. The variation of resiliency and modulus with temperature for rayon yarn immersed for 5 min. in acetone-water solutions of various concentrations.

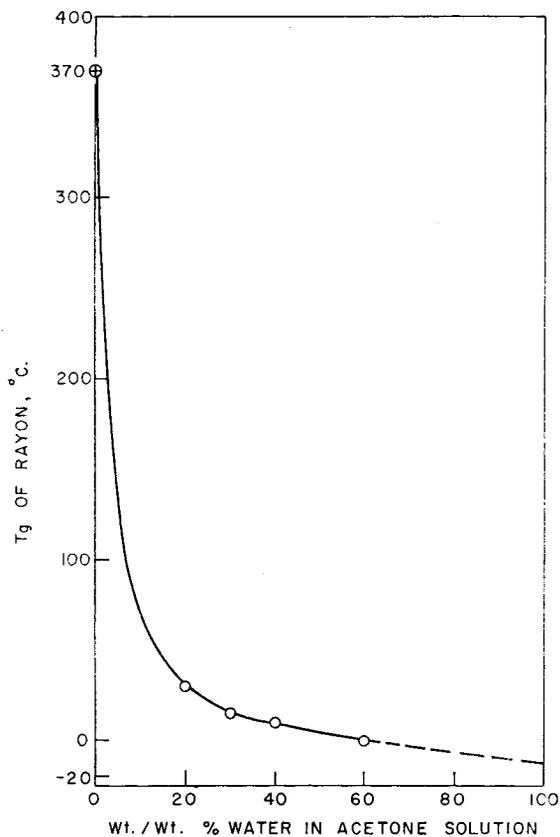


Fig. 4. The variation of the T_g of rayon with the water content of the bath solution. (\oplus) data of Kargin.¹⁵

tion, is observed to shift to higher temperatures with decreasing water content of the bath solution, and the modulus becomes constant with increasing temperature at the temperature at which the resiliency passes through a minimum. In Figure 4 the variation of T_g of rayon as a function of the water content of the bath solution is given. Bryant and Walter's results indicated that the T_g

for dry rayon is higher than 240°C., and recently Kargin and co-workers¹⁵ obtained an extrapolated value of 370°C. Figure 4 shows that the T_g is lowered to room temperature (21°C.) when rayon is immersed in an acetone solution containing approximately 27% water.

The resiliency and modulus of rayon in acetone-water solutions at 21°C. are shown in Figure 5. As the water content is increased the resiliency decreases substantially, passes through a minimum, and then increases almost to its original value. The modulus decreases considerably and then becomes constant in both solutions of more than 30% water content.

In the preceding experiments, "conditioned" yarn was immersed for 5 min. in the solution before measurement. Satisfactory reproducibility ($\pm 1\%$ resiliency) was obtained in this way. If the soaking time in the bath solution was increased, both the resiliency and modulus gradually changed, apparent equilibrium being reached within 4 hr. However, longer soaking times could not be studied because of frequent glue failure. The measurements made in acetone-water solutions at 21°C. were repeated with a 4-hr. soaking time and samples which, before being immersed, were desiccated as described in the experimental section instead of being conditioned in a standard atmosphere. The results are shown in Figure 6. The effect of the new procedure was to shift the minimum in resiliency to solutions of lower water content than before. This is consistent with greater fiber swelling during the longer soaking time.

Figure 7 shows the change in the shape of the cyclic stress-strain curves with increasing water content of the rayon. It is apparent that as the water content increases, the modulus decreases,

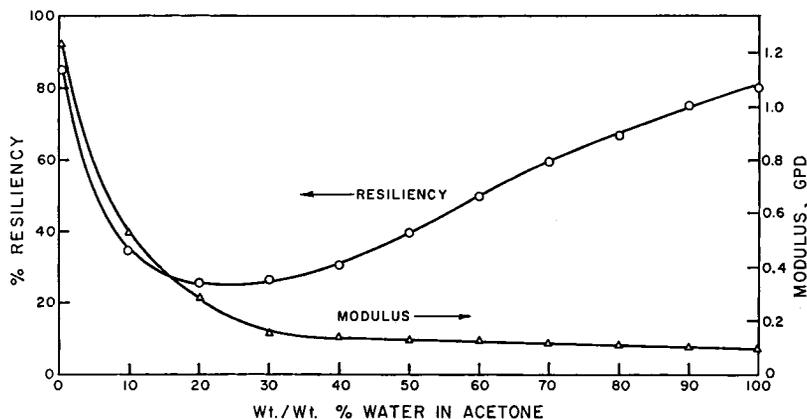


Fig. 5. The resiliency and modulus of conditioned rayon yarn immersed for 5 min. in acetone-water solutions at 21°C.

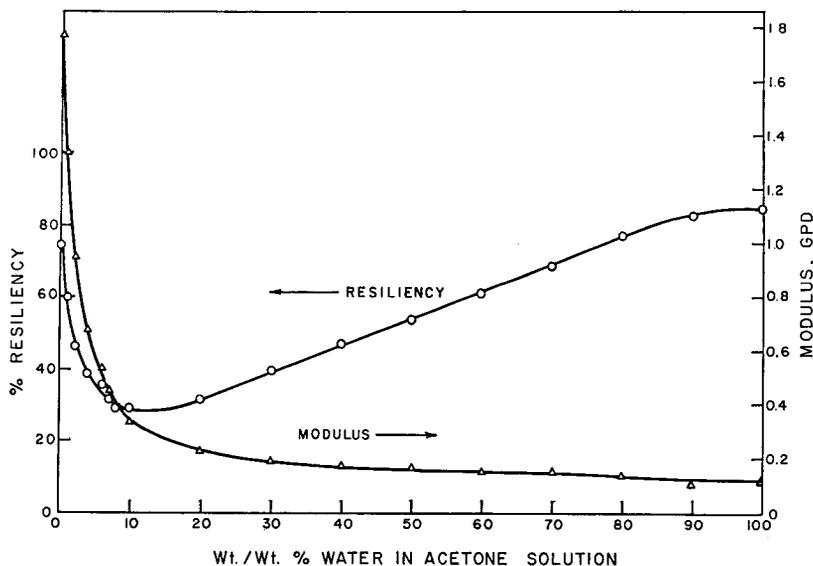


Fig. 6. The resiliency and modulus of dried yarn rayon immersed for 4 hr. in acetone-water solutions at 21°C.

and the viscous component of extension increases and becomes a maximum at the glass transition point. Further absorption of water results in a somewhat lower modulus and a considerably increased resiliency. The yield point in the stress-strain curve disappears at high water contents.

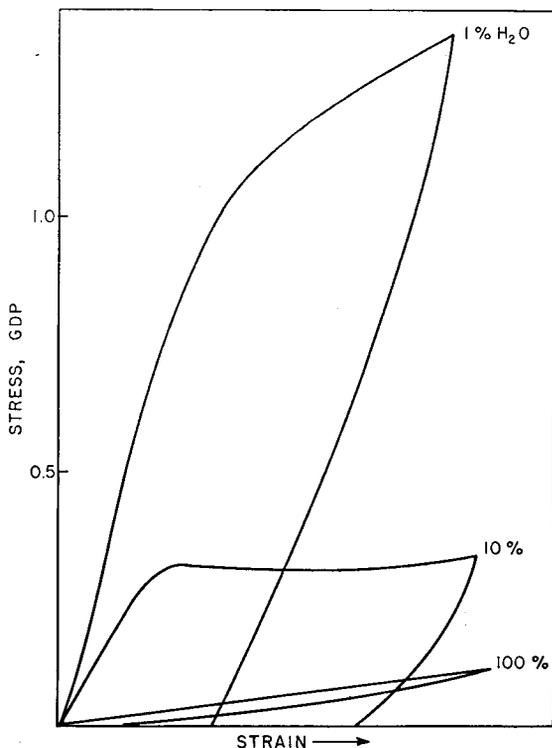


Fig. 7. Comparison of the cyclic stress-strain curves of rayon yarn extended 4% immersed in acetone-water solutions.

In Figure 8 the variation of resiliency and modulus with relative humidity are shown for rayon in air at 21°C. These results do not show a well-defined minimum. The resiliency decreases up to 50% R.H., remains almost constant up to 95% R.H., and then increases sharply to 100% R.H. The modulus changes in a similar way up to 90% R.H. and then decreases further up to 100% R.H. The values of resiliency and modulus at 100% R.H. are a little higher than those found in liquid water. The shapes of the stress-strain curves for these samples indicate that they are all below their T_g except at 100% R.H., which leads us to conclude that the T_g occurs between 95 and 100% R.H. The dotted line shows the expected resiliency calculated from the measurements made in acetone-water solutions based on literature data for the partial pressure of water over such solutions. The minimum in resiliency for the measurements in vapor occurs at 95% R.H. or higher while that calculated from solution data is in the region of 50–70% R.H.

Figure 9 shows the variation of resiliency and modulus for rayon yarn in air at 21°C. containing acetone-water vapor in equilibrium with the solutions used in the liquid-phase experiments. There is a big difference between the values obtained in the vapor state and those obtained in the corresponding solutions although the fugacities of acetone and water in the two environments are the same.

The variation in resiliency and modulus of rayon as a function of water concentration in solutions

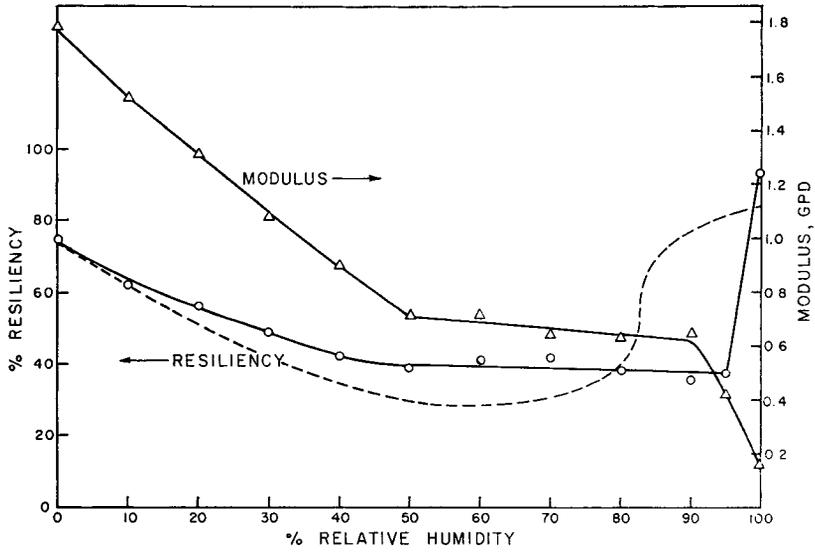


Fig. 8. The resiliency and modulus of dried rayon yarn in air as a function of relative humidity at 21°C.

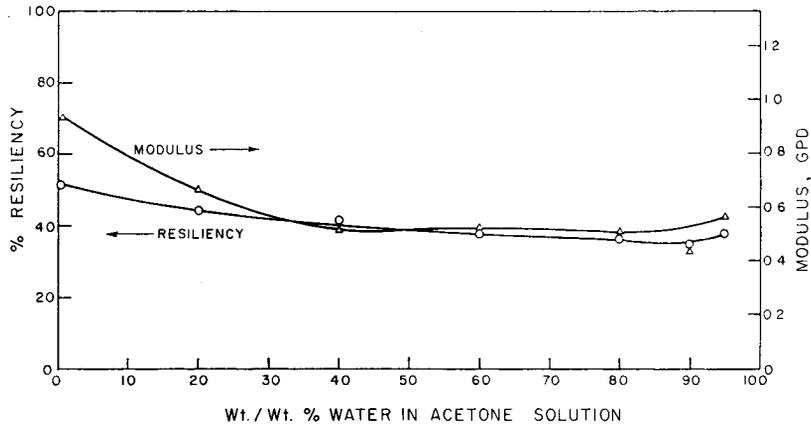


Fig. 9. The resiliency and modulus of dried rayon yarn in air as a function of acetone-water vapor concentration at equilibrium with acetone-water solutions at 21°C.

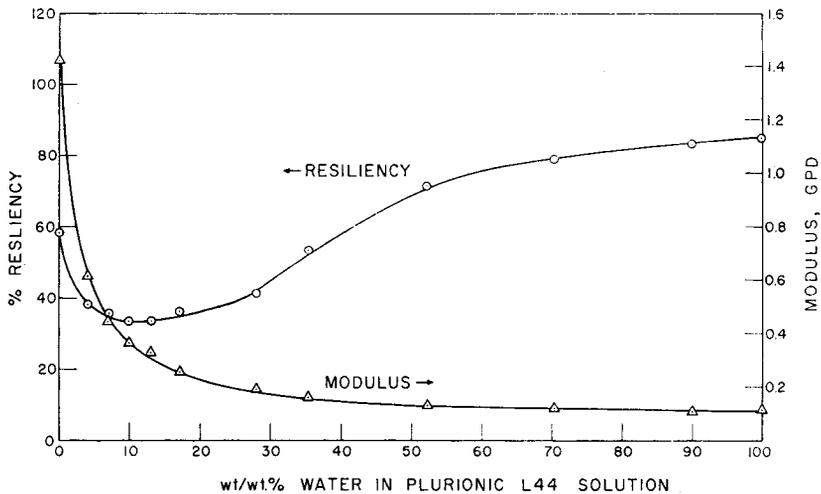


Fig. 10. The resiliency and modulus of dried rayon yarn immersed for 4 hr. in polymer-water solutions at 21°C.

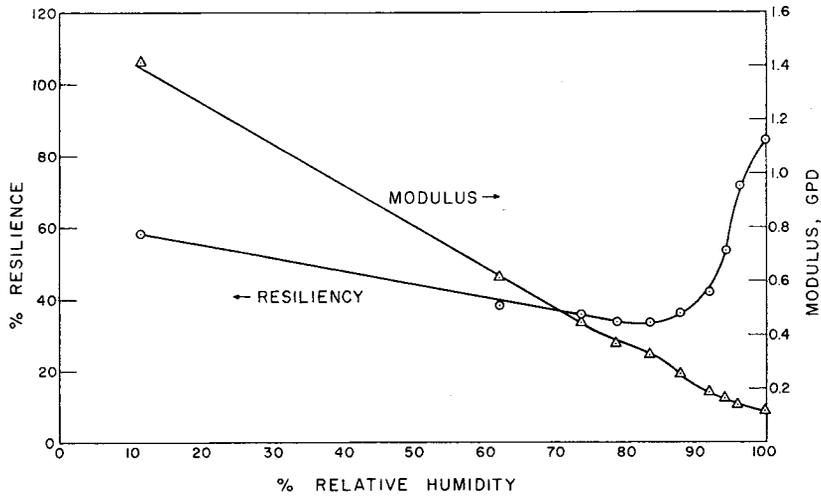


Fig. 11. The resiliency and modulus of dried rayon yarn in air as a function of relative humidity at 21°C., calculated from polymer-water solution data.

of Pluronic L 44 is shown in Figure 10. It seems justifiable to assume that the polymer molecule is too large to penetrate and swell the cellulose appreciably during the soaking time of the experiment. The changes in properties observed should therefore

reflect only the effect of water. The relative humidity of air in equilibrium with these polymer solutions was obtained, and the resiliency and modulus data from the solution measurements are plotted in Figure 11 against the R.H. measured for the corresponding solutions. These results are closer to those obtained in moist air than those

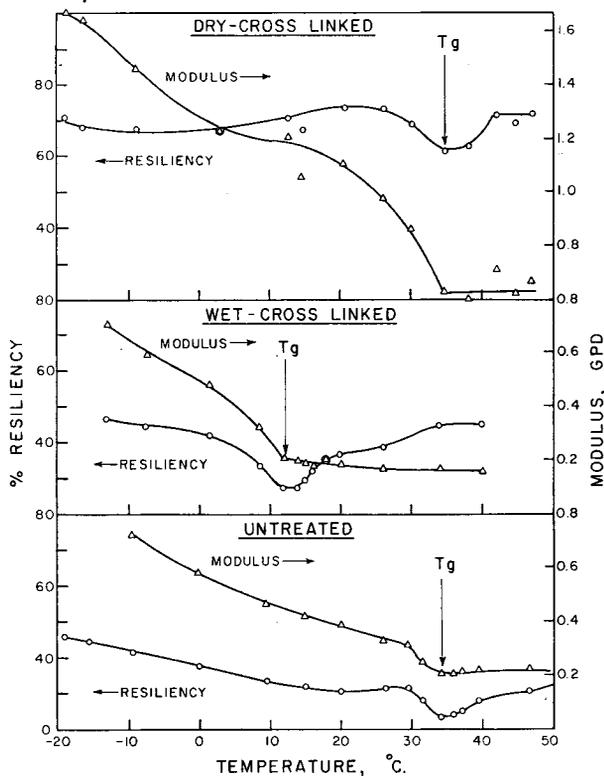


Fig. 12. Comparison of the variation of resiliency and modulus with temperature for untreated, wet-crosslinked, and dry-crosslinked rayon immersed for 5 min. in 10% aqueous acetone solution.

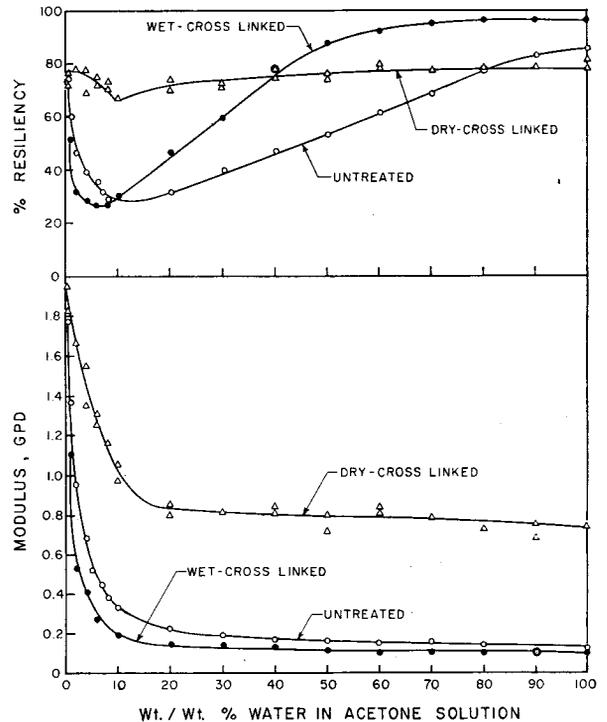


Fig. 13. Comparison of the resiliency and modulus of untreated, wet-crosslinked, and dry-crosslinked rayon immersed for 4 hr. in acetone-water solutions at 21°C.

calculated from the acetone-water solution data. The minimum in resiliency occurs at 84% R.H.

The effects of "wet"-state and "dry"-state crosslinking on the properties of rayon yarn are compared in Figures 12 and 13. Figure 12 shows the variation of resiliency and modulus as a function of temperature for untreated, wet-crosslinked, and dry-crosslinked rayon in 10% aqueous acetone solution. The T_g of both untreated and dry-crosslinked rayon is 34°C., while that of wet-crosslinked rayon is about 12–14°C. The values of resiliency and modulus are about the same for untreated and wet-crosslinked rayon, but those for dry-crosslinked rayon are much higher over the whole temperature range studied. In these experiments the untreated sample was soaked in water for 30 min. before conditioning in air at 65% R.H. and 21°C. In this way the untreated and treated samples all came to equilibrium water content from the wet state, thus avoiding hysteresis effects in water absorption. This preconditioning treatment accounts for the lower T_g of untreated rayon in these experiments compared to that observed earlier.

In Figure 13 the resiliency and modulus of untreated, wet-crosslinked, and dry-crosslinked rayon are compared as a function of water concentration in acetone solutions at 21°C. Wet crosslinking results in a shifting of the minimum toward solutions of lower water content, which corresponds to a lowering of T_g . It should be noted that the resiliency above T_g is considerably increased as a result of this treatment. The modulus changes for wet-crosslinked rayon are similar to those of untreated rayon except for the shift to lower water concentrations. Dry-state crosslinking increases the overall resiliency and decreases the depth of the minimum but does not shift its position. There is a corresponding decrease in the modulus in the region of T_g , but the modulus values are much higher than those of untreated rayon.

In general it was found that better results were obtained for the change in tensile properties with temperature when conditioned samples soaked for 5 min. in the acetone solutions were used rather than desiccated yarn immersed for 4 hr.

DISCUSSION

Measurement of modulus and resiliency with temperature appears to be closely related to dynamic mechanical tests which measure the response of a material to cyclic strains at a high frequency. From such tests it is possible to calculate an elastic modulus and the energy dissipation or

mechanical loss. In the region of a second-order transition in a polymer, the mechanical loss passes through a maximum and the dynamic modulus decreases sharply with increasing temperature. We can consider a decrease in resiliency to correspond to an increase in mechanical loss, and since the tensile modulus decreases with increasing temperature in the region where resiliency passes through a minimum, these changes also appear to characterize a second-order transition. Dynamic mechanical measurements of partially crystalline fibers reveal that there are often several second-order transitions which occur at temperatures below the crystalline melting point.¹⁶ The principal transition is usually considered to be the glass-rubber transition for the amorphous portion of the fiber. It is interpreted in molecular terms as arising from the onset of motion of rather large chain segments in the amorphous region. Lesser transitions occurring at lower temperature are associated with the segmental movement of the side chains. The second-order transitions observed by Brown¹ and by Bryant and Walter² from tensile measurements are most probably the principal amorphous transitions of the fibers concerned, since the changes in tensile properties are substantial and are found to be greater for fibers which are more amorphous in nature. Furthermore, the transition temperatures are close to, but lower than, those obtained from dynamic mechanical measurements for the amorphous transitions in the same polymers. The lower transition temperature is consistent with the change to be expected as a result of the longer time scale of the tensile measurements. It seems reasonable to assume that the second-order transition we have observed for partially swollen rayon is the principal amorphous transition due to the onset of motion in fairly large chain segments. The forces which restrain this motion arise from hydrogen bonds and van der Waals' forces between the cellulose chains. Increased thermal agitation at higher temperatures tends to reduce these restraining forces. At the transition temperature the maximum number of chain segments can respond to the applied strain during the time scale of the experiment, and the resiliency passes through a minimum. The assumption is made in our experiments that the changes in resiliency and modulus with temperature in a given bath solution are due mainly to increased thermal motion of chain segments and that the degree of cellulose swelling does not appreciably alter with temperature. This seems reasonable, since Passaglia¹⁷ and

Koppehele⁶ have shown that the temperature coefficient for the swelling of cellulose model filaments in water is negative and relatively small.

The decrease in T_g for rayon with increasing water content of the bath solution, and hence with increasing water content of the fiber, may be explained in the following way. Water swells the amorphous portion of the fiber, reducing the number of hydrogen bonds between chains and reducing van der Waals' forces. This assists the thermal process in reducing the restraining forces and enables the transition to occur at a lower temperature. A similar view has been put forward to explain the decrease in the temperature of the principal amorphous transition in nylon by absorbed water.³ When acetone-water solutions were used, the T_g of rayon could be practically observed only in the range of 0 to 40°C. The shape of the modulus and resiliency curves with temperature in the 10% aqueous solution indicate that the T_g is greater than 40°C. in this solution, and suggests that it will continue to increase with decreasing water content in the fiber. The work of Bryant and Walter² and, more recently, of Kargin¹⁵ indicates that the T_g of completely dry rayon is above its decomposition temperature, which is in the region of 240°C. If this is correct, then the absorption of water by rayon apparently does lower the T_g by over 240°C. Although this is a large change, it is not unreasonable when one considers that the water content of rayon at 100% R.H. is about 40%, and that absorption of 6.4% water by nylon reduces its T_g by 90°C.

From a consideration of the resiliency and modulus of rayon at 21°C., it is apparent that dry rayon is below T_g and wet rayon above. Evidently a second-order transition takes place as the fiber becomes wet. A comparison of Figures 4 and 5 shows that the minimum in resiliency which occurs in a bath solution of between 20 and 30% water content must correspond to the water content of rayon which lowers the T_g to the temperature of the experiment. The decrease in modulus and increase in the viscous flow component of extension up to the glass transition point, as shown by the cyclic stress-strain curves, is consistent with the view that water reduces the intermolecular restraining forces. Supporting evidence that a transition must occur as rayon absorbs water at 21°C. is given by force-temperature measurements which show that dry rayon has glasslike properties⁴ and by entropy stress studies that show wet rayon has rubberlike properties.¹⁷ These results indicate

that there is a concentration of absorbed water below which the elastic behavior of rayon is essentially glasslike and above which it is essentially rubberlike.

The change in tensile properties with soaking time in acetone-water solutions may be due to a two-stage absorption process involving an initial rapid stage followed by a slower second stage. Two-stage absorption has been described by Newns for the water vapor-cellulose system¹⁸ and by others for different systems.^{19,20} The experimental evidence suggests that the second stage is controlled by slow changes of the polymer structure. In acetone-water solutions absorption of acetone from solution probably also occurs. Hermans and Vermaas²¹ have shown that cellulose model filaments immersed in glycerol-water mixtures rapidly absorb water and then more slowly absorb glycerol, although anhydrous glycerol does not penetrate dry cellulose.

A number of factors may be involved in the difference between the observed behavior of rayon in air at different humidities and that calculated from solution data at corresponding fugacities of water. The glass transition observed in moist air occurs at 95% R.H. or higher while those calculated from polymer-water and acetone-water solution data occur in the region of 84% and 50-70% R.H., respectively. This shifting to lower relative humidities indicates greater swelling in the solution experiments. The greater shift, for acetone-water solutions, perhaps includes an effect due to the absorption of acetone, but it is very unlikely that polymer is absorbed from the polymer solutions. The big difference between the tensile behavior of rayon in acetone-water vapor and that in solutions having the same fugacities of acetone and water suggests that the physical state of the surrounding medium affects the mechanical properties. Treloar has shown experimentally that the absorption of water by cellulose increases with extension of the fiber and decreases with strain recovery.²² The position of the minimum in resiliency will depend not only on the amount of water present in the rayon at the commencement of the tensile tests, but also on the amount of water which is taken up during stretching and expelled during strain recovery. The latter is controlled by the rate of passage of water molecules across the cellulose surface during the time taken to perform the test. Experimental evidence indicates that this rate will be greater in acetone-water and polymer-water solutions than in humid air. However, the total increase in water by this process,

based on Treloar's measurements and assuming equilibrium conditions to exist for rayon in the liquid medium, is only about 2%, which is insufficient to account entirely for the shift in glass transition. Another factor to be considered is the possibility of structural differences arising in the cellulose from the absorption process in the two different states. Whatever the true explanation,

TABLE I

Relative humidity, %	Water content of rayon Challis, %		
	Untreated	Wet-crosslinked	Dry-crosslinked
10	3.08	3.43	2.92
30	5.94	6.47	5.58
50	8.78	9.54	8.00
70	11.77	13.19	10.91
90	18.29	20.49	18.02
95	19.41	23.08	20.59

it is interesting to note that up to 95% R.H. rubberlike recovery mechanisms play little part in the mechanical properties of rayon, and that in the range 50–95% R.H. rayon behaves as if it were in a glass-rubber transition region.

It is of considerable practical importance to know the effect of chemical modification of cellulose on the relationship between fiber resiliency and water content. Wet-state and dry-state crosslinking produce quite different changes in this relationship.

Wet-state crosslinking lowers the T_g of rayon in a given swelling medium, but does not appreciably alter the shape of the modulus curves. The depth of the resiliency minimum at 21°C. is unchanged, but the resiliency is greater at water contents greater than that which corresponds to the glass transition point. The lower T_g can be explained if we assume that the fibers swell more in the solutions as a result of the wet state crosslinking treatment. The increased swelling would lower the intermolecular forces between chains and decrease the T_g . A further reduction in T_g would result from intramolecular crosslinks which would satisfy some of the cellulose hydroxyls and reduce hydrogen bond forces between chains. It has been postulated that wet-state crosslinking of cellulose results in a greater ratio of intramolecular crosslinks to intermolecular crosslinks,²³ and the same may be true for the reaction with formaldehyde. Evidence for increased swelling is given by the greater water absorption of rayon fabric crosslinked

in the wet state as compared with untreated rayon, as shown in Table I. We have also observed that the reaction solution we used for wet-crosslinking rayon at 80°C. reduces the modulus of the yarn to a greater extent than water at 21°C. The moduli obtained under these conditions are among the data shown in Table II which suggest that the hot reaction solution may be able to penetrate some regions of the cellulose which are not accessible to water at 21°C. The greater swelling may be due to extensive hemiacetal formation occurring between cellulose hydroxyl groups and formaldehyde which would decrease hydrogen bonding between chains. The formation of intramolecular crosslinks and, perhaps, the deposition of polymer in the previously inaccessible regions will tend to maintain chain separation in these areas and consequently increase the degree of swelling possible when the sample is immersed in other swelling media. The increased resiliency occurring above T_g is probably due to intermolecular crosslinks assisting rubberlike recovery mechanisms.

Since dry-state treatment probably introduces a greater proportion of intermolecular crosslinks than wet-state treatment, it is surprising that it does not increase the T_g to some extent as a result of decreased segmental mobility. However, Table

TABLE II

Solution	Temp., °C.	Stress of rayon yarn at 25% strain after 5 min. immersion, g./d.
Water	21	0.522
36% HCHO	21	0.628
Water	80	0.481
36% HCHO	80	0.454
1N H ₂ SO ₄	80	0.441
36% HCHO, 1N H ₂ SO ₄	80	0.378

I indicates that the water absorption of rayon fabric is only slightly decreased by such treatment. It is possible that at this level of treatment there are sufficient crosslinks to stiffen the fiber and to reduce permanent viscous flow of the cellulose chains under strain, but not enough to prevent swelling of the chains between crosslinks and normal viscoelastic behavior in these regions. Analogous results were obtained by Boyd,²⁴ who found that crosslinking reduces the dielectric loss peak of nylon but does not change the transition temperature.

The results of this work may be of practical significance in relating the wash-wear properties of cellulosic fabrics to their wet and dry crease recovery. Our data indicate that these two extremes of water content provide an inadequate basis for prediction of wash-wear performance since a minimum in fabric resiliency occurs at an intermediate water content. The wash-wear performance is probably controlled by the depth of this minimum, the water content at which it occurs, and the method of drying used. Since washed fabrics in the course of drying must pass through T_g , at which point the crease resistance is probably at a minimum, drying methods which tend to crease the fabric at or near this critical water content will produce wrinkles in the fabric which will persist during the final drying process. The occurrence of a second-order transition in partially swollen rayon with the attendant mobility of rather large chain segments provides an explanation for the effectiveness of steam-ironing, since it has been postulated by Brown that the ironing temperature of fabrics is closely related to the glass transition temperature of the fibers.¹ The rapid loss of fabric creases during washing can be similarly related to relaxation recovery occurring at the glass transition point.

CONCLUSIONS

It has been shown from tensile measurements that a second-order transition occurs in partially swollen rayon which is thought to be the glass-rubber transition for the amorphous portion of the fiber. The T_g value decreases with increasing water content of the fiber, and the results support the view of Bryant and Walter that water lowers the T_g of dry rayon from above the decomposition temperature (240°C.) to below 0°C. for water-wet rayon. The effect is attributed to swelling of the amorphous regions and reduction of intermolecular forces between cellulose chains.

A glass-rubber transition occurs in rayon at 21°C. as water is absorbed. The transition point is marked by a minimum in resiliency and occurs at the water content which lowers the T_g to 21°C. Wet-state crosslinking lowers the T_g of rayon in a given aqueous swelling medium and increases the rubberlike elasticity above T_g . Dry-state crosslinking considerably reduces the minimum in resiliency and increases the modulus but does not affect the transition temperature in a given swelling medium.

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Synopsis

Resiliency and modulus measurements were made on viscose rayon yarn swollen to different extents in acetone-water mixtures. The resiliency was measured as a function of temperature and found to pass through a minimum at a temperature which is assumed to be the glass transition temperature (T_g) for the amorphous portion of the fibers. The effect of the degree of swelling on T_g was observed by changing the composition of the acetone-water mixture, and it was found that the T_g decreased with increased swelling. The plasticizing action of water apparently reduces the T_g from a value above the decomposition temperature (240°C.) for dry rayon to below 0°C. for water-wet rayon. At 21°C., the resiliency of rayon in acetone-water mixtures passed through a minimum as the water concentration changed. The concentration at the minimum corresponds to that which lowers the T_g to 21°C. Similar measurements were made on rayon immersed in polymer-water mixtures and in air at different relative humidities, and it was found that there were differences in the values of resiliency and

modulus at equal water fugacities in the three media. Wet-state crosslinking lowered the T_g of rayon and increased the rubberlike elasticity above T_g . Dry-state crosslinking did not change T_g but greatly reduced the depth of the resiliency minimum. Both the modulus and the resiliency were increased over most of the range of water content by dry crosslinking.

Résumé

On a fait des mesures de résilience et de module sur du fil de rayonne de viscose gonflé à différents degrés dans des mélanges acétone-eau. La résilience a été mesurée en tant que fonction de la température et on a trouvé qu'elle présentait un minimum à une température qu'on suppose être la température de transition vitreuse (T_g) pour les parties amorphes des fibres. On a observé l'effet du degré de gonflement sur T_g en changeant la composition du mélange acétone-eau et on a trouvé que T_g diminuait quand le gonflement augmentait. L'action plastifiante de l'eau réduit manifestement T_g d'une valeur supérieure à la température de décomposition (240°C) pour la rayonne sèche à une valeur inférieure à 0°C pour la rayonne humide. A 21°C la résilience de la rayonne dans des mélanges acétone-eau passe par un minimum quand on fait varier la concentration de l'eau. La concentration au minimum correspond à celle qui abaisse T_g à 21°C. Des mesures analogues ont été faites sur de la rayonne plongée dans des mélanges polymère-eau et dans l'air à différentes humidités relatives. On a trouvé qu'il y avait des différences dans les valeurs de résilience et de module pour des fugacités égales de l'eau dans les trois milieux. Des pontages à l'état humide abaissent T_g de la rayonne et augmentent l'élasticité caoutchouteuse au-dessus de T_g . Des pontages à l'état sec ne changent pas T_g mais réduisent considérablement la profondeur du minimum de résilience. Le module et la

résilience sont tous deux augmentés sur la grande partie du domaine de concentration en eau par un pontage à l'état sec.

Zusammenfassung

Messungen der elastischen Energie (Resilienz) und des Moduls wurden an Viskoserayongarn vorgenommen, das in Aceton-Wasser-Gemischen verschieden stark gequollen wurde. Die Resilienz wurde als Funktion der Temperatur gemessen und es wurde gefunden, dass sie bei einer Temperatur, die als die Glasumwandlungstemperatur (T_g) des amorphen Faseranteils angesehen wird, durch ein Minimum geht. Der Einfluss des Quellungsgrades auf T_g wurde durch Veränderung der Zusammensetzung des Aceton-Wasser-Gemisches ermittelt und es wurde gefunden, dass T_g mit steigender Quellung abnimmt. Die Weichmacherwirkung des Wassers vermindert offenbar T_g von einem Wert oberhalb der Zersetzungstemperatur (240°C) für trockenes Rayon auf unterhalb 0°C für mit Wasser befeuchtetes Rayon. Bei 21°C geht bei Änderung der Wasserkonzentration die Resilienz von Rayon in Aceton-Wasser-Gemischen durch ein Minimum. Die Konzentration beim Minimum ist die gleiche, die T_g auf 21°C vermindert. Ähnliche Messungen wurden an Rayon in Polymer-Wasser-Gemischen und in Luft bei verschiedener relativer Feuchtigkeit durchgeführt und es traten Unterschiede in den Werten für die Resilienz und den Modul bei gleicher Wasserfugazität in den drei Medien auf. Vernetzung im feuchten Zustand vermindert die T_g von Rayon und erhöht die kautschukartige Elastizität oberhalb T_g . Vernetzung im trockenen Zustand verändert T_g nicht, vermindert aber die Tiefe des Resilienz-Minimums sehr stark. Sowohl Modul als auch Resilienz stiegen bei trockener Vernetzung über einen Grossteil des Bereichs an Wassergehalt an.

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