

Effects of Heterogeneous Acetylation and Methylation on Mechanical Properties of Isotropic Cellulose Film

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INTRODUCTION

Very few attempts to relate the molecular structure of regenerated celluloses to their mechanical properties have met with much success, but the model which has been most extensively considered is that of the network theory. This has been developed by Hermans,¹ among others, on the basis of a network of cellulose molecules held together at junction points by hydrogen bonding. The nature of such junction points should vary continuously over a wide range of size, degree of order and, presumably, of strength, extending from relatively large crystalline regions (micelles) down to completely random junctions. The conclusions to be derived from such a picture are necessarily vague; nevertheless, no better model is available at present and the work described here is derived from a consideration of this model.

Under mechanical deformation it seems reasonable to assume that the junction points in the less ordered regions would be weaker and would tend to break preferentially, while at the same time, during deformation, new junction points could form by intermolecular hydrogen bonding, particularly in the nonordered regions. This effect would result in a resistance to the recovery of the system to its original state, and could be the main cause of the permanent deformation of air-dry regenerated cellulose structures at strains above the yield point.

The strongest experimental support for this type of reasoning is the effect of water on the mechanical properties of regenerated cellulose. For example, deformation established in the air-dried state largely disappears with immersion of the cellulose in water, and redrying. In fact, most of the effects

of water on mechanical properties can be interpreted as due to a decreased intermolecular cohesion in parts of the cellulose structure and, according to the above network theory, this would reasonably be expected to result from breaking of the hydrogen bonds in the less ordered junction points.

According to the above reasoning, the mechanical, and particularly the elastic, properties of cellulose would be considerably changed if the strength of the intermolecular bonding in the non-ordered regions could be sufficiently reduced. Attempts were therefore made to change the nature of such interchain bonds by methylation and acetylation of the hydroxyl groups. Initially, these derivatives were effected preferentially in the non-ordered regions, but higher extents of reaction, up to cellulose triacetate, were also studied. Isotropic films were used throughout, in order to eliminate changes in mechanical properties due to orientation effects.

EXPERIMENTAL

Isotropic Cellulose Films

Cellulose triacetate (OAc, 44.6%; DP 543), prepared from cotton linters, was supplied by Courtaulds Ltd., Coventry, England. This material was cast into films from 3% w/v solution in chloroform, 100 ml. being used for a rectangular mercury surface 28 × 22 cm., and then the films were saponified as described by Dlugosz and Michie.² Only the center portions (ca. 14 × 10 cm. after saponification) of such films were used throughout. Film thicknesses, air-dry, were ca. 0.04 mm. Dlugosz and Michie² have shown that films prepared in this way are practically isotropic.

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Methylation

Air-dry cellulose films (6 samples, 14 × 10 cm.) were kept under a mixture of 1.0*N* potassium hydroxide (500 ml.) and dioxan (250 ml.) at room temperature for 10 min. A sample was removed as a blank and then a solution of dimethyl sulfate (40 ml.) in dioxan (200 ml.) was added with gentle stirring and left at room temperature for 2 hr. The films were then transferred to fresh alkali and the procedure repeated. After each stage a film was removed, washed overnight in water, and then air-dried between sheets of filter paper. The results are shown in Table I. Treatments 4 and 5

TABLE I
Methylation of Cellulose Films

	Treatment no.				
	1	2	3	4	5
OMe Zeissel, %	2.35	4.4	7.7	11.3	16.3
Degree of substitution	0.13	0.235	0.42	0.64	0.93

were each left for ca. 10 hr. in the methylation solution. The x-ray diagrams obtained from the methylated films indicated no marked change in crystallinity between samples 1 and 5.

Reacetylation

The conditions of reacetylation were similar to those described by Vermaas and Hermans,³ except that carbon tetrachloride was used as a nonsolvent instead of ether. Vermaas and Hermans, and also Happey,⁴ showed that this type of heterogeneous acetylation caused preferential attack on the nonordered regions.

Air-dry cellulose films (ca. 14 × 10 cm.) were covered with water for 10 min., then kept for 1 hr. periods successively in 25, 50, and 75% acetic acid, glacial acetic acid and, finally, a 4:1 (v/v) mixture

TABLE II
Acetylation of Cellulose Films

Series no.	Duration, hr.	Acetyl content, %	DS
A	0.5	4.65	0.18
A	1.0	6.2	0.25
A	2.0	7.85	0.32
A	4.5	13.1	0.57
A	6.0	24.5	1.22
B	1.0	13.7	0.60
B	4.0	33.4	1.87
B	6.0	39.3	2.41
B	24	44.6	2.97
B	48	44.7	2.99

of carbon tetrachloride and acetic anhydride. The films were next transferred to a mixture of carbon tetrachloride (1 liter) and acetic anhydride (250 ml.) at 0°C., to which 0.17 ml. of concentrated sulfuric acid had just been added. The mixture was kept at 2 ± 1° with occasional gentle agitation, and at intervals films were transferred to 95% ethanol; after standing at room temperature for 4 hr. they were left under fresh 95% ethanol overnight and then air-dried at room temperature for several days. Between 4.5 and 6 hr. of acetylation the temperature of the reaction was allowed to rise slowly to 15° (series A). In a second experiment (series B) the above procedure was repeated with the acetylation mixture at room temperature (21 ± 2°) throughout. The films increased in area to a maximum and subsequently decreased somewhat as acetylation proceeded.

Acetyl contents were determined in the manner described by Vermaas and Hermans,³ the results are shown in Table II.

Degree of Polymerization

For cellulose samples, the viscosity [η] of a 0.5% solution in cuprammonium hydroxide at 25° was calculated by the method of Calvert and Clibbens,⁵ and from this, the DP.⁶ Samples of acetylated celluloses (ca. 0.08 g.) were shaken with cuprammonium hydroxide solution (15 ml.) and cuprous chloride (ca. 0.02 g.) at room temperature overnight, and the viscosity of the resulting solution was used to calculate DP as above.

These determinations showed that the cellulose films (DP 687) had a considerably greater molecular weight than the original cellulose triacetate (DP 543), and this suggests that some extraction of low molecular weight material occurs during the saponification and subsequent washing of the triacetate films.

Mechanical Tests

All results were obtained on a Cambridge extensometer at 21 ± 0.5° and at a constant rate of extension (0.065 mm. sec.⁻¹; 65 ± 2% for air-dry measurements). Films were cut with a pair of parallel-mounted razor blades to give samples of ca. 45 × 2.15 mm., which allowed a constant test length of 30 mm. All the results shown represent the mean of five determinations. Sample dimensions were determined by direct microscopic measurement of thickness and width, the latter being found constant within experimental error. Break-

ing and yield loads are expressed as kg. mm.⁻² referred to the original cross-sectional area, and extensibility at break as the percentage increase in length. The yield point of the stress strain curve was taken as the point where the tangent to the curve makes an angle of 45° to the horizontal.

All films were quite brittle, and air-dry breaking measurements were particularly irreproducible, showing variations within a particular film of up to ca. ±15%, apparently due to variable initiation of breaks on a constant stress strain curve. Breaking measurements in water were more reproducible (ca. ±5%), and the yield load was particularly reproducible (<±5%).

Wet measurements were carried out with the same type of sample (test length, 30 mm. air-dry) under water at 21 ± 0.5° at constant rate of extension, 0.264 mm. sec.⁻¹. All wet load measurements are related to the approximate wet cross-sectional area *A'* which is calculated, on the assumption that swelling is isotropic, from the expression

$$A' = A(1 + 2s)$$

where *A* is the air-dry cross-sectional area and *s* is the fractional increase in length after immersion for 10 min. All wet strain measurements are expressed as percentage increase in length on initial length, measured after immersion for 10 min.

"Elastic" recovery measurements were also carried out at constant rate of extension (0.065 mm. sec.⁻¹) on the Cambridge extensometer, as described by Meredith,⁷ with a 30 sec. duration of maximum strain and 60 sec. under zero load.

In some of the results described below, two values were given for properties corresponding to DS = 0, in each case these referred to untreated film (shown thus, X) and to a blank (shown thus, 0) that has received a single treatment in the absence of dimethyl sulfate (in the case of methylation) or of sulfuric acid (in the case of acetylation).

TABLE III

Young's Moduli of Acetylated and Methylated Celluloses

Substituent	DS	Modulus × 10 ⁻¹⁰ , dynes cm. ⁻²
Methyl	0.23	3.5
Methyl	0.93	3.3
Acetyl	0.59	3.5
Acetyl	1.87	2.8
Acetyl	2.41	2.9
Acetyl	2.99	3.0
Original cellulose		3.3

Young's modulus values were determined on the Cambridge extensometer with samples 2.2 mm. wide; test length 100 mm., and at constant rate of loading, 6.8 g. sec.⁻¹. The resultant load-elongation curves were linear over the range 0.1–0.5% extension, and the moduli remained constant over four cycles from 0–0.6% extension. The results are expressed in Table III and each result represents the mean of four cycles on each of three different samples. Reproducibility was ca. ±10%.

Water Sorption

Samples of film (ca. 0.02 g.) were dried at 60° and 20 mm. Hg over phosphoric oxide to constant weight (20–30 hr.) then kept at 65% and 21° until constant weight was again attained (7–10 days).

RESULTS AND DISCUSSION

Breaking Load, Air-dry

The effects of acetylation and methylation on the air-dry breaking load are shown in Figures 1 and 2. Both acetylation and methylation cause a slight,

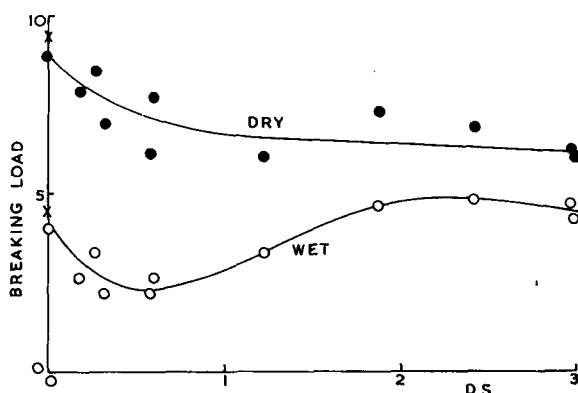


Fig. 1. Effect of acetylation on the breaking load.

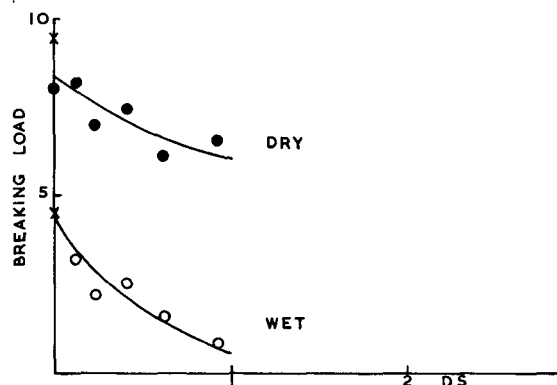


Fig. 2. Effect of methylation on the air-dry breaking load

but significant, fall in strength in the early stages of reaction. The continued slight fall in strength with progressive acetylation, however, may be due to hydrolytic degradation during the acetylation reaction (acetylation to DS 2.99 reduced the DP from an initial value of 687 for the cellulose film to 430). Fully reacetylated film prepared in this way has a considerably lower strength than an isotropic film cast from the original cellulose triacetate before saponification and reacetylation. The heterogeneous acetylation of viscose with ketene⁸ also results in hydrolysis and a fall in strength, but the results of this type of experiment may be influenced by changes in orientation during acetylation.

Breaking Extension (Extensibility), Air-Dry

Both acetylation and methylation reduce the air-dry extensibility (Figs. 3 and 4). Some slight trend in this direction might be attributed to a decrease in molecular weight. In addition, in the case of acetylation the moisture regain falls pro-

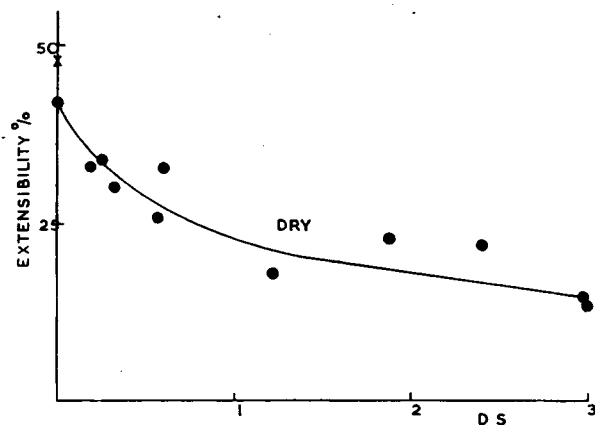


Fig. 3. Reduction of air-dry extensibility by acetylation.

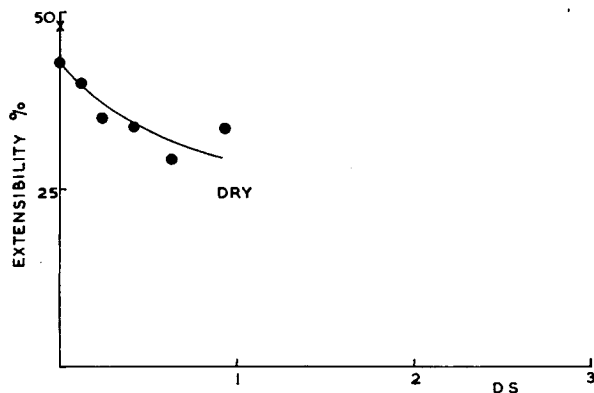


Fig. 4. Reduction of air-dry extensibility by methylation.

gressively with the introduction of acetyl groups and some decrease in extensibility may be attributed to a decreased plasticization by water.

Breaking Load in Water

The effects of acetylation and methylation on the breaking load in water are shown in Figures 1 and 2. In both cases the introduction of substituents into the nonordered regions results in a rapid decrease in wet strength.

The x-ray diffraction showed no marked change in crystallinity and only a very slight decrease in the 101 spacing due to methylation between DS 0 and 0.93. It is known, however, that further methylation can produce a water-soluble methyl cellulose. Furthermore, water solubility implies either a sufficient reduction in crystallinity or the production of crystalline regions which are disrupted by water. Although, therefore, the decrease in wet strength with methylation is most simply interpreted in a qualitative sense, as an approach to water solubility, the x-ray results give no marked indication of a concurrent decrease or disruption of crystalline regions. The extensive penetration of the crystalline regions by methylating agents and, subsequently, by water, which presumably results in the water solubility of more highly methylated films and which would be shown by x-ray diffraction, must be assumed to occur only above DS 0.9. The mechanical properties of the wet films are much more sensitive to this type of change, however, and may result from changes in the smaller and less ordered crystalline regions.

Progressive acetylation, however, results in an increase in wet strength above DS ca. 0.6. At the same DS the stress-strain curve in water first begins to show a yield point; the yield load thereafter increases with extent of acetylation (Fig. 9). These effects on wet strength and yield point in water both indicate the formation of a part of the structure which is resistant to the effect of water, and this probably corresponds to the formation of intermolecular acetate-acetate polar bonds which are not disrupted by water. Similarly, the resistance of intermolecular acetate-acetate bonds to penetration by water results in the high wet strength of cellulose triacetate film. The formation of acetate-acetate junction points, therefore acts in opposition to the solubilization effect in determining the effect of acetylation on wet strength and it results in the minimum given in Figure 1.

The heterogeneous acetylation of viscose by ketene has also been shown⁷ to produce a minimum

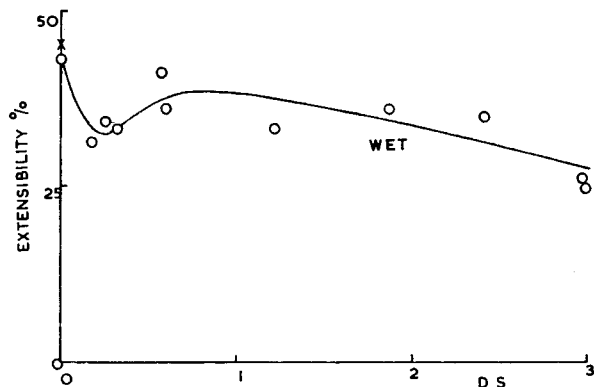


Fig. 5. Effect of acetylation on the extensibility in water.

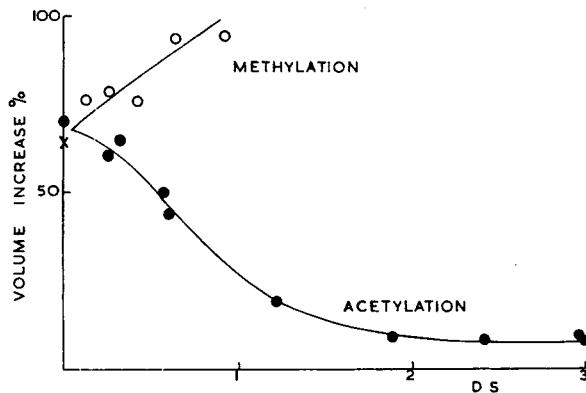


FIG. 7

Fig. 7. Increase in volume on immersion in water.

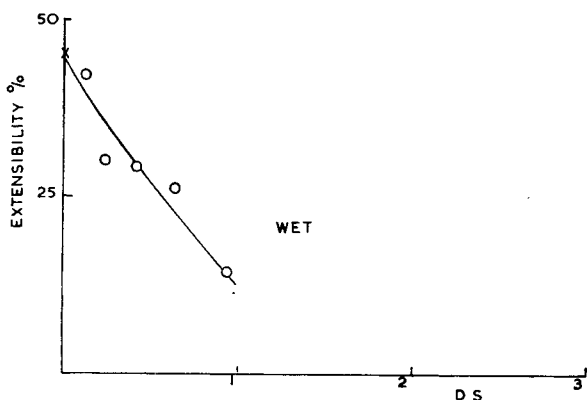


Fig. 6. Effect of methylation on the extensibility in water.

in the wet strength curve similar to Figure 1. The heterogeneous methylation of cotton⁹ has considerably less effect on the wet strength than was found for isotropic cellulose, and the differences, in this case, may arise from the differences in supracrystalline structure.

Breaking Extensions (Extensibility), Wet

The results are shown in Figures 5 and 6. The continuous decrease in extensibility with methylation (Fig. 6) is accompanied by an increase in the swelling volume and represents an approach to water solubility. The minimum in the acetylation curve (Fig. 5) also corresponds to the effects on wet strength discussed above. The slight fall in extensibility at high extents of acetylation is probably due to hydrolytic degradation during acetylation.

Swelling Volume in Water

Figure 7 shows the increase in volume on immersion in water at 21°. The results are calculated from increase in sample length, assuming isotropic swelling. The increase in swelling volume with

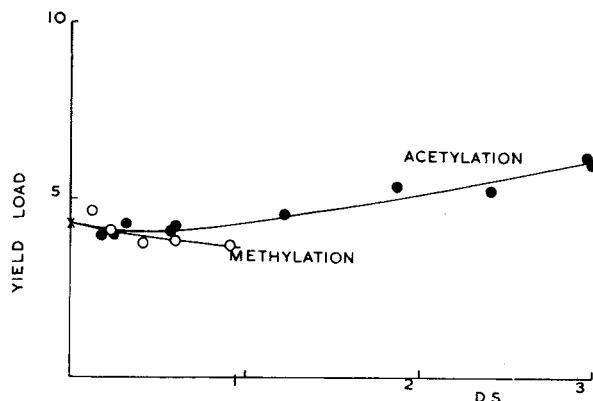


Fig. 8. Air-dry yield load insensitivity to acetylation and methylation.

methylation represents an approach to infinity at the DS corresponding to water solubility. The form of the curve of swelling volume against extent of acetylation is in accordance with the effects discussed in the section on wet strength.

Yield Load, Dry

Figure 8 shows that the yield load at 65% RH is relatively insensitive to both acetylation and methylation.

Yield Load, Wet

Neither cellulose nor any of the partially methylated celluloses showed a yield point in the stress-strain curves in water. With progressive acetylation, however, a marked yield point appeared at DS 0.6 and the yield load increased continuously with further acetylation (Fig. 9). This effect has been discussed above and probably corresponds to the increasing formation of intermolecular acetate-

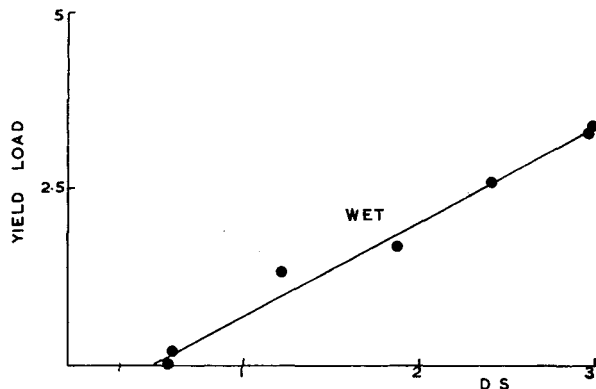


Fig. 9. Effect of acetylation on yield load in water.

acetate polar bonds of varying degrees of order, which are not disrupted by water.

Elastic Recovery

Figure 10 shows no marked dependence on acetylation or methylation in the recovery from strains above 5%. These results suggest that the simple network analogy, described in the Introduction, is not sufficient to explain the mechanical properties of cellulose and its derivatives. Mark and Tobolsky¹⁰ have discussed the theoretical intermolecular cohesive forces in cellulose acetate, cellulose, and the polyamides, and have concluded that the "specific molar cohesions" (for a length of 5 A.) are respectively 4800, 6200, and 5800 cal/mole⁻¹. Trimethyl cellulose would be expected to have an even lower cohesive energy than cellulose triacetate. Nylon, however, has a far higher elastic recovery from all strains than cellulose or the above-mentioned derivatives; whereas the argument based on the molecular network suggested that high elastic recovery should be associated with weak intermolecular cohesion.

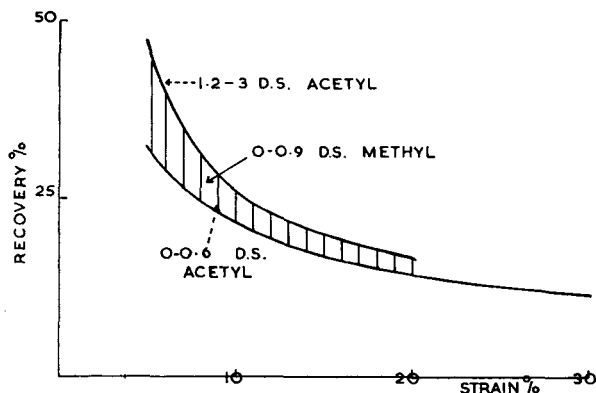


Fig. 10. Elastic recovery from strains.

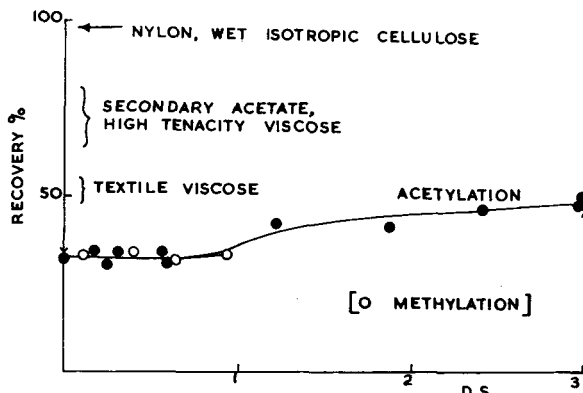


Fig. 11. Elastic recovery from 5% strain.

It seems that, at least in the air-dry state, the mechanical behavior of cellulose and its derivatives differs in some fundamental way from that of the synthetic polymers of high elastic recovery, such as nylon. The differences may arise from several sources that may be interrelated, such as molecular stiffness, distribution of dipoles along the molecule, and supracrystalline structure. For example, the regenerated cellulose may form a type of microfibrillar network² in which the mechanical properties would still be dependent on cohesions between adjacent microfibrils that could be disrupted by water. Such structures would, however, be expected to behave differently from a molecular network in other respects.

Figure 11 shows the elastic recovery of several representative textile materials, determined by Meredith.⁵ These results suggest that the general effect of increased orientation in cellulose is to increase the elastic recovery from a given strain. The same effect has also been noted with nylon.¹¹ In addition, the high recovery of isotropic cellulose in water is noteworthy. This provides support for the suggestion¹ that resistance to recovery is dependent on intermolecular hydrogen bonding in the nonordered regions during deformation, since this type of bonding would not be possible in water. To verify this, an air-dried sample of isotropic cellulose film was extended 20% for 30 sec. and then released. After 1 hr. at 65% RH and 21°, 21.7% of the strain had been recovered. The sample was then immersed in water at 21° for 10 min. and left to air dry for 18 hr.; 82% of the strain was recovered. The sample was then immersed in water at 21° for 10 min. and left to air dry for 18 hr.; 82% of the strain was recovered. This process probably corresponds to the disruption of some of the nonordered intermolecular hydrogen

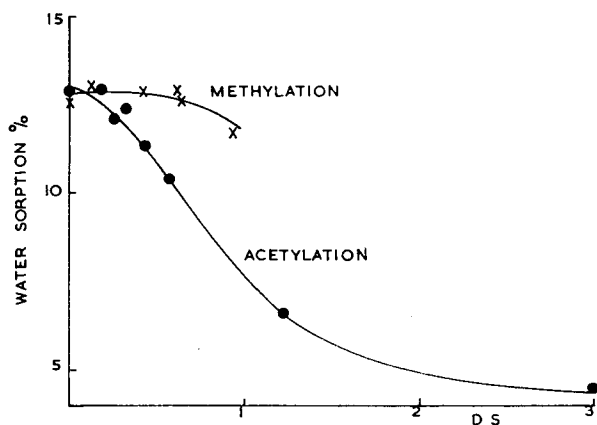


FIG. 12

Fig. 12. Decrease in water content with progressive acetylation.

bonds which were formed during the original deformation. Such behavior might be expected both in the Hermans type of molecular network and in a microfibrillar network.

Acetylated celluloses appear to have intrinsically slightly better recovery properties than cellulose itself. There is no evidence which assists the interpretation of this effect, which could be due to such factors as differences in water content, differences in molecular stiffness due to different intramolecular polar bonding, or differences in supracrystalline structure.

Young's Modulus (Air-Dry)

The results of Table III show no significant change of modulus on partial methylation, while progressive acetylation produces a barely significant decrease although, in the absence of other effects, the decrease in sorbed water due to acetylation would be expected to be accompanied by an increase in modulus. Variation of intermolecular interaction would not be expected to have any marked effect on Young's modulus if no breaking of junction points is involved in elastic deformation. However, on the basis of the network theory, the results given in Table III presumably also imply that there is no extensive change in the relative number of junction points throughout the process of acetylation.

Water Sorption

Figure 12 shows that there was a rapid decrease in water content at 65% RH with progressive acetylation. Methylation up to DS 1, however, produces very little change in water sorption, despite

the drastic effect on swelling volume over this range. Effects of sorbed water on extensibility and Young's modulus are considered in the appropriate sections.

CONCLUSIONS

The effects of acetylation and methylation on the mechanical properties of regenerated cellulose cannot be interpreted solely on the basis of Hermans' molecular network structure.¹ The mechanical properties are certainly dependent on intermolecular cohesions in the nonordered regions and this dependence is shown up particularly by the effects of swelling in water. However, the elastic recovery of acetylated and methylated cellulose and of cellulose itself is very low in comparison with nylon, for example, although the intermolecular cohesive forces are probably similar in all of these cases. This suggests that some other factor prevents the comparison of cellulose and its derivatives with nylon on the basis of cohesive forces in a simple molecular network. Relevant differences between the two types of polymer, which might produce such differences in elastic recovery, are molecular stiffness, spacing of dipoles along the polymer, and the postulated microfibrillar network structure² in regenerated cellulose.

In acetylated cellulose films the intermolecular acetyl-acetyl bonds appear to be relatively stable to water, but in methylated cellulose the intermolecular cohesions are extensively disrupted by water with attendant effects on mechanical properties.

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Synopsis

The effects on mechanical properties of heterogeneous acetylation and methylation of isotropic cellulose films have been studied. The effects on breaking load, extensibility, yield point, elastic recovery, and initial Young's modulus in the air-dry state were very small. It is concluded that these properties are not markedly influenced in cellulose derivatives by variation of the nature of the intermolecular cohesive forces in the way that might have been anticipated from the analogy of a simple molecular network. It is suggested that the lack of effect of such treatments, and also the cause of the low elastic recovery in cellulose and its derivatives, may be connected with molecular stiffness, dipole distribution, and supracrystalline structure. Cellulose and its derivatives are contrasted with nylon in this respect. The effects of methylation or acetylation on mechanical properties in water are much more extensive and are attributed to a solubilizing effect which, in the case of progressive acetylation, is ultimately opposed by the formation of acetate-acetate intermolecular bonds that are relatively stable to water.

Résumé

On a étudié les effets de l'acétylation et méthylation hétérogène sur les propriétés mécaniques de films isotropiques de cellulose. Les effets sur la tension de rupture, l'extensibilité, le point de déformation plastique, le recouvrement élastique, et le module initial de Young dans l'air sec étaient très petits. On en conclut que ces propriétés ne sont pas influencées de façon marquée dans des dérivés cellulosiques par variation de la nature des forces de cohésion intermoléculaire, comme on aurait pu anticiper à

partir de l'analogie avec un réseau moléculaire simple. On suggère que le manque d'effet de tels traitements, et aussi la cause du faible recouvrement élastique dans la cellulose et ces dérivés, peut être relié à la rigidité moléculaire, la distribution dipolaire, et la structure supracristalline. Sous cet angle la cellulose et ces dérivés contrastent avec le nylon. Les effets de l'acétylation ou méthylation sur les propriétés mécaniques dans l'eau sont bien plus appréciables et sont attribués à un effet de solubilisation, qui, dans le cas de l'acétylation progressive, est ultérieurement opposé par la formation de liens intermoléculaires acétate-acétate qui sont relativement stables à l'eau.

Zusammenfassung

Es wurde der Einfluss der heterogenen Acetylierung und Methylierung von isotropen Cellulosefilmen auf die mechanischen Eigenschaften untersucht. Der Einfluss auf Bruchbelastung, Dehnbarkeit, Fließgrenze, elastische Rückfederung und anfänglichen Elastizitätsmodul unter trockener Luft war sehr gering. Daraus wurde geschlossen, dass diese Eigenschaften bei Cellulosederivaten durch Änderung der Natur der intermolekularen Kohäsionskräfte nicht merklich beeinflusst werden, welchen Einfluss man aus der Analogie mit einem einfachen Molekülnetz erwartet hätte. Es wird angenommen, dass das Fehlen eines Einflusses einer solchen Behandlung und auch der Grund für die geringe elastische Rückfederung bei Cellulose und ihren Derivaten mit der Steifheit der Moleküle, der Dipolverteilung und der suprakristallinen Struktur zusammenhängt. Cellulose und ihre Derivate werden in dieser Hinsicht dem Nylon gegenübergestellt. Der Einfluss der Acetylierung oder Methylierung auf die mechanischen Eigenschaften in Wasser ist wesentlich stärker und wird auf einen Solubilisierungseffekt zurückgeführt, dem bei fortschreitender Acetylierung schliesslich die Bildung von gegen Wasser relativ beständigen intermolekularen Acetat-Acetat-Bindungen entgegenwirkt.

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