

Tensile Recoveries of Cotton Modified with and without Crosslinks

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Synopsis

When effect of the substrate is nullified, resiliency can be defined as a function of strain, time, and humidity. Determination of improvement in the immediate, or rapid, tensile recovery readily delineates differences due to chemical modifications. Delayed recovery is usually less improved than immediate. Crosslinking cotton with dimethylol-ethyleneurea (DMEU) increases tensile strain recovery as the number of crosslinks increase, reduces dependency of recovery upon external strain, and produces maximum recovery at about 65% R.H. Noncrosslinking treatments produce limited increases in tensile strain recovery. Measurements on yarns crosslinked with DMEU and then hydrolyzed indicate that incalculably few residual links may contribute to tensile recovery. *N*-Methylol-*N'*-methylethyleneurea treated cotton displays physical blocking and water swelling which aid recovery. Oleoyl chloride esterified cellulose has tensile recovery probably due to molecular entanglements. Its delayed or viscoelastic recovery is the most improved with immediate recovery being the least improved. The higher the moisture regain, the greater tensile modulus reduction under wet conditions. Crosslinking with DMEU under dry conditions lessens this reduction in modulus. Improvements in the tensile recovery of strain and energy, for all samples and with varied conditions of humidity and strain, correspond linearly with unit slope.

INTRODUCTION

Previous evaluations of the changes in textile fibers due to chemical modifications concerned mainly strength and elongation.^{1,2} Now, resiliency commands greater interest. Methods of improving the elastic recovery of cellulose were devised earlier in the present century.^{3,4} Generally, bifunctional chemical reagents effectively bind cellulose chain molecules by primary valence bonds. The introduced crosslinks increase the resiliency, dimensional stability, and wrinkle resistance of the fabric.

Applications of idealized rubber-elasticity concepts to resiliency were visualized independently by Eyring,⁵ Karrer,⁶ and others. Significant progress in establishing the reason for fabric and fiber elasticity has since been made by different researchers.⁷⁻⁹ However, there is need to understand further the mechanism of recovery and the effects of different treatments upon the cotton fiber itself. The elastic recovery of chemically modified cottons under various environmental conditions should be known

to develop the optimum treatments for best performance. In this report, recovery from essentially pure tensile strain is given for chemically modified yarns. Variations in tensile recovery are delineated for the parameters of applied strain, recovery time, and relative humidity. The fiber modifications vary from a typical commercial crosslinking treatment to substitutions by monofunctional, grafted groups.

EXPERIMENTAL

Samples

A Deltapine 15 cotton was processed into a 14/3 (126 tex) yarn with a twist multiplier of 3. The low twist multiplier was chosen to emphasize the properties of the single cotton fibers composing the yarn¹⁰ and to facilitate penetration of the modifying solutions. The cotton was obtained as a greige yarn and was ethanol-extracted before treatments. Before being tested, all untreated samples were washed by the same procedure used for the treated samples.

Treatments were selected to determine which components of fiber recovery were due to structure fixation, such as afforded by crosslinking nitrogenous agents, and which components were due to mechanical blocks, such as produced by noncrosslinking chemical modifications. All yarns were treated under slack conditions.

The samples are grouped into three sets.

Set I. Four reference samples were the greige yarn, the control yarn extracted with alcohol, a yarn treated with zinc nitrate, and an alcohol-extracted yarn degraded for 4 hr. with 2*N* HCl at 23°C.

Set II. Two crosslinked samples were obtained by application of dimethylol ethyleneurea (DMEU), a commercial finishing agent, with zinc nitrate as the catalyst. The treatment consisted of soaking skeins of yarn in the aqueous solution, centrifuging to 80% wet add-on, repeating these two procedures, drying at 80°C. for 10 min., curing at 160°C. for 5 min., rinsing in running tap water, and finally drying at 60°C. for 30 min. Two concentrations of the agents were applied: 3% and 8%. By the method of Frick et al.,¹¹ yarn samples prepared in this manner had 0.1 and 2.6 crosslinks per 100 anhydroglucose units, respectively. They are designated DMEU-3 and DMEU-8.

Set III. Three samples considered to be noncrosslinking modifications of the yarns were prepared. First, DMEU-treated yarns were acid hydrolyzed to remove the crosslinks. This treatment was designed to leave an amount of the nitrogen comparable to that in the yarn sample DMEU-3. Analysis showed the sample contained equal molar proportions of formaldehyde and ethyleneurea residues, an indication that no crosslinks remained after hydrolysis. Samples prepared in this manner are estimated to have a degree of substitution of 3 per 100 anhydroglucose units.

The second sample in this group was a cotton yarn treated with *N*-methylol-*N'*-methylethyleneurea (MMEU). This monomethylol compound

TABLE I
Properties of Yarns

Sample	Code	Bound		Density		Moisture regain, % ^a	Strength		Crease recovery of fabrics			
		N, %	HCHO, %	Vol., g./cc. ^a	Linear, tex ^b		Standard		Wet		Standard	Wet
							Tenacity, g./tex	Strain, %	Tenacity, g./tex	Strain, %		
Untreated greige	G	—	—	1.555	131	6.5	14.8	10.0	16.8	16.8	Poor	Poor
Extracted control	C	—	—	1.551	134	7.0	18.6	12.9	17.2	14.4	Poor	Poor
Zinc-treated	Z	—	—	1.550	131	6.5	16.8	12.4	16.8	14.5	Poor	Poor
Acid-degraded	A	—	—	1.550	132	6.8	13.8	11.0	14.3	13.5	Poor	Poor
3% DMEU-treated	3	0.50	0.61	1.548	131	6.3	11.8	9.3	10.1	8.8	Fair	Poor
8% DMEU-treated	8	1.02	1.53	1.544	135	5.4	8.3	7.9	7.4	8.3	High	Medium
Hydrolyzed	H	0.50	0.51	1.544	127	7.5	9.2	9.3	8.4	10.6	Poor	Poor
MMEU-treated	M	0.85	0.52	1.542	129	7.1	15.9	8.2	14.2	14.4	Poor	Poor
Oleoylated	0	0.00	0.00	1.370	191	3.3	2.1	11.2	2.2	11.8	Fair	Fair

^a Dry mass per unit volume.^b Also, weight fineness in milligrams per meter at standard conditions of 65% R.H., 70°F.^c At standard conditions.

was applied by the pad, dry, and cure method. Its degree of substitution was also 3 per 100 anhydroglucose units, the same as the hydrolyzed sample. Because of the similarity in structure between MMEU and DMEU,¹² this sample was considered to closely resemble a cotton treated with DMEU without crosslinks.

The third sample in this group was obtained by treatment of yarns with oleoyl chloride in a dimethylformamide solution^{13,14} at 60°C. to a 36% add-on by weight. The degree of substitution of this oleoylated sample was 0.3.

The properties of these samples are presented in Table I.

Nitrogen content was determined by the Kjeldahl method. Formaldehyde content was determined by the digestion and distillation methods according to Roff¹⁵ and Frick et al.¹¹ The mass per unit volume (volumetric density) was determined in a dry density-gradient column by the method of Orr et al.¹⁶ Textile properties are the mass per unit length (linear density); moisture regain determined under standard conditions by the ASTM method;^{17a} strength, to be discussed in a later section; and generalized crease recovery according to the Monsanto method.^{17b} The last is for cotton print cloth treated as indicated.

Microscopy

Comparative structural changes of untreated, crosslinked, and non-crosslinked samples were observed by use of light and electron microscopes. Whole fibers were immersed in 0.5*M* cupriethylenediamine (CED) and observed with the light microscope. The resultant swelling and dissolution are indicative of the amount of crosslinking and uniformity of treatment.

A Phillips EM 100 electron microscope was used for observation of cross-sectioned specimens prepared by the method of Rollins and Tripp.¹⁸ To judge the location of chemical reactants, fibers, preswollen in an equi-volume mixture of ethylene glycol and water, were subsequently embedded in a methacrylate mixture. Polymerization of the methacrylate within the fiber caused separation of the lamellae where the polymerization forces exceeded crosslinking forces.¹⁹

Tensile

The mechanical measurements were made on an Instron tester with associated integrating circuit and environmental chamber. The rate of loading was so adjusted for each sample that the time required for a direct break would be approximately 40 sec. The direct, noncyclic load-elongation curve and the energy to break (i.e., toughness) were determined.

Recoverable deformation after short and long time delays was measured at several locations along the load-elongation curve.²⁰ Immediate recovery *I* is the recovery after the specimen is returned to zero load at the same rate at which the load was applied. The average time for these samples was 7 sec. Delayed recovery *D* allows essentially complete re-

traction by the slower moving elements. Total recovery T is then measured after a 60-min. relaxation period. Total recovery is the sum of immediate and delayed recoveries. Each recovery is calculated as a percent of the strain applied. Percentage permanent set is therefore equal to 100 minus total recovery.

The tensile recovery measurements were made at more than four loads for each sample. Three successive loadings were 10, 25, and 65% of the previously determined mean breaking loads. An additional measurement for each sample was the tensile strain recoveries separately determined at $1/2$ of the mean breaking load. Recoveries were also measured at other selected loads. Accuracy and reproducibility were best at intermediate strains and above 1.5% strain. Automatic integration gave the fraction of energy immediately recoverable.

Each sample was evaluated under atmospheric conditions of 35, 65, and 95% R.H. These same tests were repeated with the yarns in a wet state. With the temperature maintained at 70°F., 65% R.H. is defined as standard conditions—sometimes referred to as “dry” for wash-wear fabrics. The wet condition is considered to approximate 100% R.H. All specimens were tested at a 10-in. gage length. At least five specimens per sample were used to determine average tensile recovery values and at least 15 specimens per sample to determine average tensile break values. Duplicate sets were repeated under standard and wet conditions.

RESULTS AND DISCUSSION

Microscopy

Tripp et al.²¹ have shown that crosslinking does not affect the appearance of a cotton fiber examined microscopically, but does alter its solubility in CED. Untreated cotton swells and dissolves in 0.5M CED, leaving a small noncellulosic residue, whereas cotton extensively crosslinked by DMEU does not swell. In the sample treated with DMEU and then hydrolyzed, possible residual crosslinks remain; fibers do swell; and, partial dissolution occurs. Cotton fibers treated with the monofunctional MMEU dissolve rapidly. Fibers treated by esterification behave differently from either extracted or crosslinked cottons. Oleoylated cotton disintegrates in spots along the fiber length finally leaving a transparent residue. This behavior is similar to that of partially acetylated cotton.²²

Although dissolution is a useful index of chemical bonding, the presence of crosslinks within a single cotton fiber is identified more effectively by the polymerization of methacrylate. Electron micrographs of sections of cotton fibers embedded in methacrylate after being preswollen in ethylene glycol and water are shown in Figure 1. The control cotton (Fig. 1A) shows a distinct separation of the laminated structure of the fiber. With a low level of crosslinking (Fig. 1B), fibers showing no laminated cross sections are observed in addition to fibers approaching the appearance of the control cotton. The occurrence of both types in the same sample usually indicates

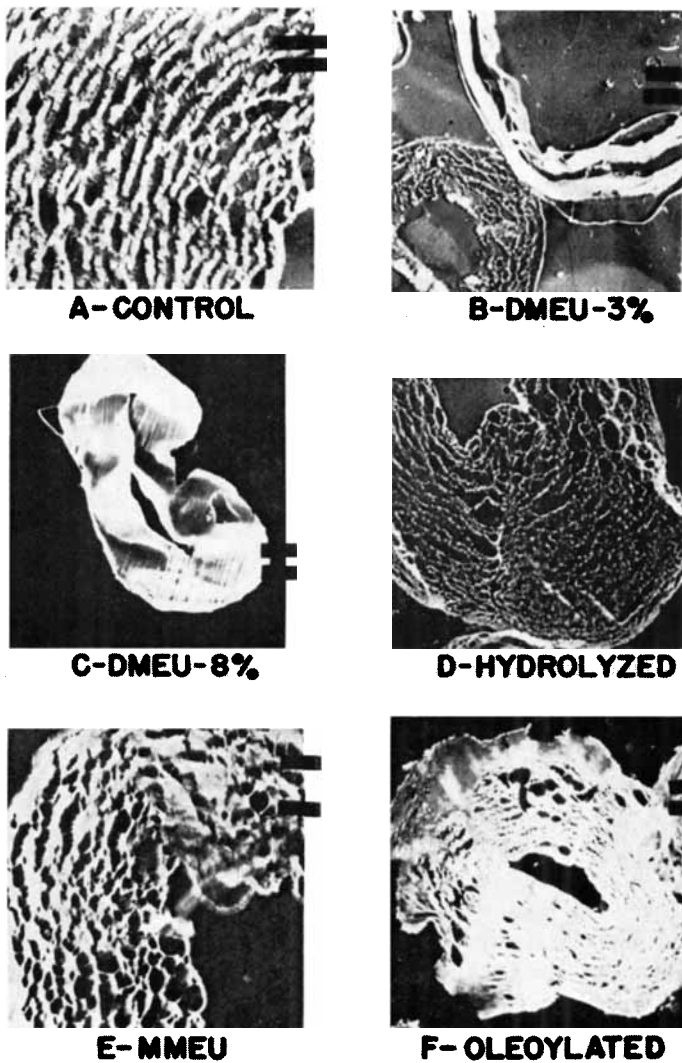


Fig. 1. Electron micrographs of thin sections from cotton fiber samples preswollen in ethylene glycol and water and embedded in methacrylate. (Marks represent 1- μ distance.)

a nonuniformity or small extent of treatment. For the extensively cross-linked DMEU samples yielding commercial wash-wear properties (Fig. 1C), all fibers show a compact nonswelling structure. In the sample for which the DMEU was stripped from the cotton (Fig. 1D), lamellar separation is again pronounced. Cotton treated with MMEU (Fig. 1E) has layer separation, expanded lumen, and some radial restriction. Displaying limited swelling, the oleoylated fiber is distended, and the fibrillar character appears fused (Fig. 1F). Cellulosic esters are known to swell in the methacrylate, and lamellar separation may depend upon the degree of substitution.²²

Strength

The mean mechanical values from direct breaks, characterizing each sample under standard and wet conditions, are listed under strength in Table I. Tenacity is a linear stress calculated by dividing the breaking load in grams by the linear density in tex. Strain is the increase in length per unit original length, often termed per cent elongation in textiles. In Figure 2A are shown the mean load-elongation curves determined after the chemically modified samples and their control curves were conditioned in a standard atmosphere. Curves determined while the yarns were wet are shown in Figure 2B. The slope of each curve is an index of the tensile modulus of the yarn.

Dry-cure, crosslinking treatments increase the modulus of the yarns and practically eliminate the changes due to different humidity conditions. The control and hydrolyzed samples display noticeably lower moduli under wet as compared to standard conditions. This decrease in modulus upon wetting corresponds to the moisture regain, as given in Table I, a confirmation that the absorption of water influences a fiber's stress-strain relation. There is an extreme decrease in slope of the load-elongation curve for the MMEU treated cotton when tested under wet conditions but a complete lack of such change in the oleoylated sample. The MMEU and oleoylated cottons have high and low moisture regain, respectively.

Losses in the breaking load and elongation of chemically modified cottons are generally expected when fiber elements are fixed in positions unfavorable for equitable stress distribution. Oleoylated yarns suffer an additional loss

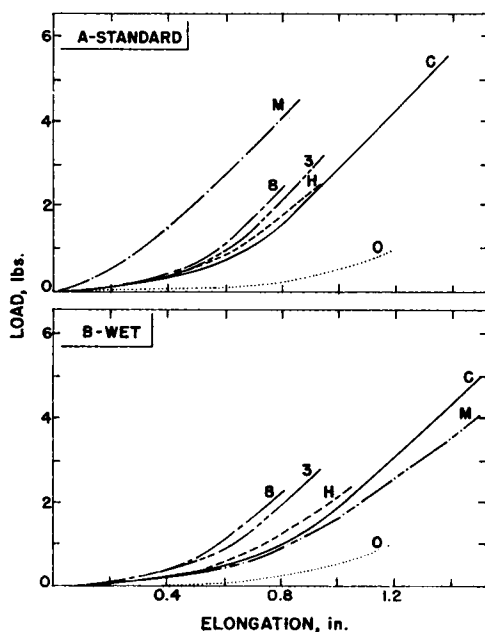


Fig. 2. Load-elongation curves for control and treated yarns under standard and wet conditions.

TABLE II
Immediate and Total Tensile Strain Recoveries of Yarns

Strain	R.H., %	Untreated greige		Extracted control		Zinc-treated		Acid-degraded		3% DMEU-treated		8% DMEU-treated		Hydrolyzed		MMEU-treated		Oleoylated	
		I, %	T, %	I, %	T, %	I, %	T, %	I, %	T, %	I, %	T, %	I, %	T, %	I, %	T, %	I, %	T, %	I, %	T, %
0.02	35	53	95	43	91	42	89	—	—	44	95	47	97	41	95	50	95	40	97
	65*	52	93	40	91	41	87	42	88	49	95	53	96	43	93	54	95	39	96
	95	39	89	38	89	38	89	—	—	36	95	40	97	36	96	37	96	35	97
0.04	Wet	29	81	34	83	39	83	34	84	36	83	40	90	39	90	36	90	35	88
	35	45	84	37	79	36	78	—	—	42	85	46	93	43	88	47	86	41	97
	65	42	81	36	78	34	75	36	76	48	92	55	96	43	86	49	83	41	95
0.06	95	34	76	32	77	33	76	—	—	36	86	44	89	40	92	39	85	35	95
	Wet	30	71	33	74	35	75	34	75	39	74	46	85	44	85	38	79	40	84
	35	38	71	33	68	31	67	—	—	38	74	46	90	41	79	33	75	46	93
$1/2$ of break	65	35	66	32	65	29	63	32	62	42	83	53	93	41	79	38	68	45	93
	95	30	66	29	65	30	63	—	—	36	78	45	85	42	86	39	73	41	90
	Wet	29	64	33	67	35	68	34	67	40	72	49	80	48	81	40	71	41	88
$1/2$ of break	35	45	85	33	68	33	67	—	—	42	83	47	92	42	86	47	87	44	95
	65	40	78	33	69	30	66	31	65	48	89	54	96	43	85	48	84	44	94
	95	30	62	28	57	28	57	—	—	38	83	44	89	42	88	39	73	40	91
Wet	29	59	33	66	34	67	34	63	40	74	47	84	45	82	40	70	42	81	

* Standard humidity.

in breaking load due to acid degradation, or perhaps to the high add-on. Retained strength can be much higher when the oleoylation mixture contains pure pyridine as an acid scavenger.¹⁴ However, it is hypothesized that with or without pyridine, strain to break is retained because of the entanglement of the long-chain oleoylated cellulose molecules and the lateral expansion of the yarn. The bulky nature due to this esterification is implied in Table I by a decrease in volumetric density concurrent with an increase in linear density (weight fineness). Such a swelling could also increase the helix angle of the fiber in the yarn and thus increase elongation.

Components of Strain and Recovery

Mark and Press ably present the basic forces that retard deformation and cause recovery in high polymers. There may be as many as seven forces.²³ Like many polymers, cotton does not show the instantaneous linear recovery of an idealized crystalline material. It displays instead a relatively rapid, immediate recovery or primary creep superimposed upon a long-range secondary creep. To resolve the concomitant effects of these recovery forces, resiliency is ideally divided into three types: immediate elastic recovery, delayed viscoelastic recovery, and nonrecoverable plastic elongation or permanent set.

Experimental tensile strain recoveries are summarized for these nine samples in Table II. Immediate and total recoveries from four strains after conditioning under four humidities are tabulated.

The recoveries and strength of the untreated greige, extracted control, and zinc-treated yarns are essentially the same at 70°F. under 35, 65, 95, and 100% R.H. The only differences are slight superiorities in recovery for the greige under low humidities and for the extracted and zinc-treated yarns under wet conditions. A possible explanation for this improvement is that adsorbed water may improve the strain distribution by swelling or lubricating the extracted fibers and thus increase their recoveries at high humidities. As seen in Table I, losses in breaking strain, approaching those of hydrolyzed-DMEU and oleoyl chloride-treated cottons, are displayed by the acid-degraded yarn. Yet, the tensile strain recoveries under standard and wet conditions are the same for the acid degraded and extracted control yarns. Because the differences due to chemical modifications are much greater than the differences among the reference yarns, the extracted, unmodified cotton will be the only control referred to in the following discussions.

These results confirmed that: (1) conditions such as heat of treatment, mechanics of process, or wetting by reagents are not in themselves responsible for the increased strain recoveries observed in chemically modified cottons; (2) purification of cotton increases the uniformity of succeeding treatments rather than improving recovery of the control itself; and (3) the recoveries accompanying the residual crosslinks in hydrolyzed-DMEU yarns and bulking in oleoylated yarns are not due to acid degradation.

Strain-Strain Recovery

Extensive data are available regarding the crease recovery of crosslinked cottons but considerably less information has been released on their more definitive tensile recoveries. Tensile recovery was originally represented as the retraction of a hypothetical set of springs and dash-pots. Or, recovery is considered due to the return of polymolecular networks to their original spatial conformation because of the intermolecular bonding forces. To profit most from such theories, the fundamental properties that are also basic to applications must first be characterized for various chemically modified cottons over a range of environments.

Figure 3 presents the immediate and total tensile strain recoveries as functions of the applied strain for the control and 8% DMEU-treated yarns. Such strain recovery diagrams are extrapolated by dots to the mean breaking strain of the cycled specimens. In Figure 3A the total strain recovery of the control, extracted cotton when measured under standard atmospheric conditions is 50% at about 8% strain. Immediate and total recovery curves (*I-C*, *T-C*) show the consistently decreasing recovery for increasing strain that is typical of such viscoelastic materials as unmodified cotton. For comparison, the graph also shows recovery curves (*I-8*, *T-8*) for the extensively treated DMEU cotton. Recoveries significantly increase. In seconds, recovery of the treated sample (*I-8*) at the region of

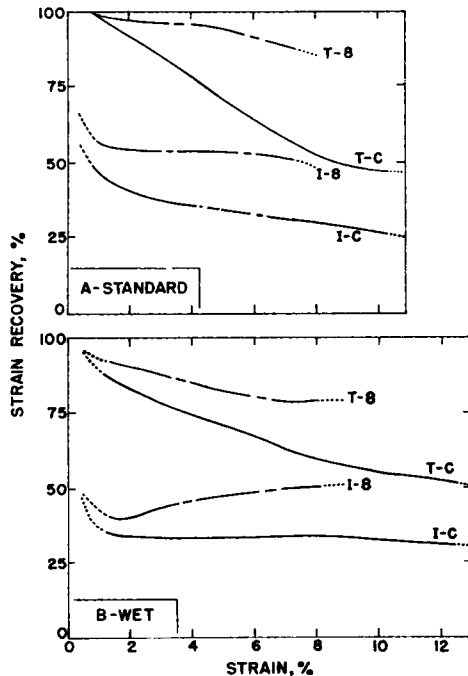


Fig. 3. Immediate (*I*) and total (*T*) recoveries as a function of strain for control (*C*) and DMEU-8 yarns under standard and wet conditions.

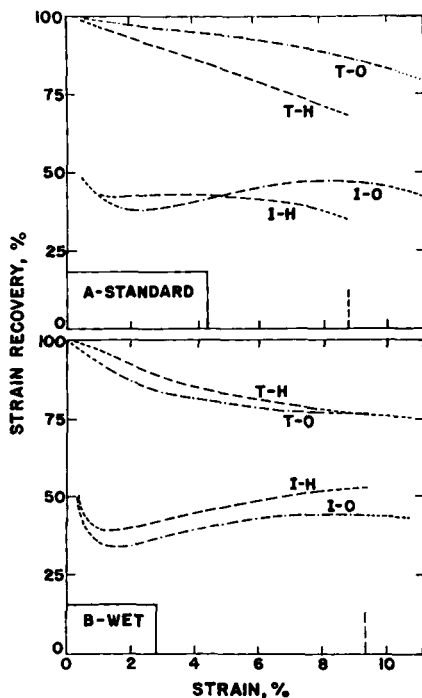


Fig. 4. Immediate (*I*) and total (*T*) recoveries as a function of strain for hydrolyzed-DMEU (*H*) and oleoylated (*O*) yarns under standard and wet conditions.

8% strain approximates the control's recovery after 1 hr. delay (*T-C*). Also the recoveries of the crosslinked sample are more nearly independent of applied strain than are those of the control.

Even though there is less difference under wet conditions (Fig. 3*B*), the crosslinked cotton has significantly greater recovery than the control. At low applied strain under wet conditions, the immediate tensile strain recovery of the 8% DMEU-treated yarn (DMEU-8) approaches a minimum. Whereas such a minimum may be due to recovery-strain interactions, this recovery value is needed to describe the resiliency of the fiber.²⁴ This minimum can also be an important factor in the wrinkling of crosslinked cottons during laundering. The recovery of the extracted control tested under wet conditions is less dependent upon strain than under dry conditions, an indication that water swelling aids recovery.

The recovery of the 3% DMEU-treated sample (DMEU-3), a cotton crosslinked to a lesser degree, is less than that of the DMEU-8 sample.

The preceding results are typical of pad-dry-cure treated cottons and extend similar results determined for cotton crosslinked by the conventional formaldehyde treatment.²⁵

Figure 4 presents representative tensile strain recoveries as a function of strain for two noncrosslinking treatments. Generally, the recoveries of the hydrolyzed-DMEU and oleoylated cottons are less than those of the well-

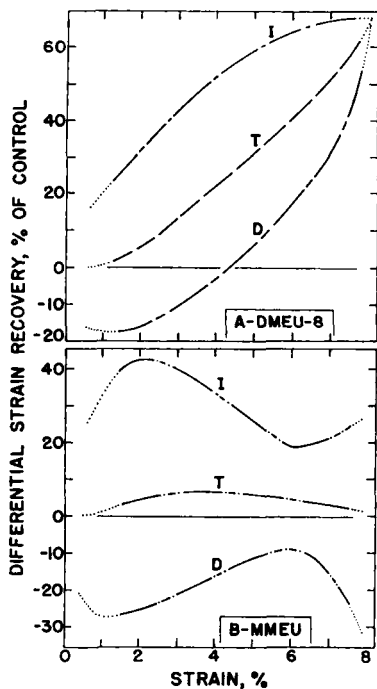


Fig. 5. Changes of immediate (*I*), delayed (*D*), and total (*T*) recoveries as a function of strain for DMEU-8 and MMEU yarns under standard conditions.

crosslinked cotton, but greater than those of the control. Under standard conditions (Fig. 4A), an increase in strain has less detrimental effects upon oleoylated than upon hydrolyzed cotton. Because of its low modulus and bulky, loose structure, oleoylated cellulose may not evince irrecoverable displacements equal to those of hydrolyzed-DMEU cotton, until a high strain is reached.

The effects of water on these recoveries are shown in Figure 4B. The immediate recovery for the hydrolyzed-DMEU (*I-H*) cotton approximates the same type of recovery as a DMEU-treated cotton. The recoveries of MMEU-treated cotton are usually less than those of the oleoylated and hydrolyzed-DMEU cottons.

More informative than the strain recovery diagrams of Figures 3 and 4 is the difference in recovery between a modified sample and its control, expressed as a per cent of the recovery of the control when both samples are measured under the same parameters. Such differential tensile strain recoveries are presented as a function of strain in Figure 5 for standard atmospheric conditions. The zero line represents the extracted control. Typically, the changes due to crosslinking treatments result in a continuous improvement of the tensile strain recovery for increasing strains. In Figure 5A, the greatest improvement in DMEU-8 cotton is displayed in immediate recovery. This result implies that the quick acting, springlike, elastic force enhances the behavior of wrinkle-resistant textiles. In com-

parison with the control, the immediate recovery of DMEU-8 cotton improves more than delayed recovery. Delayed tensile strain recovery does not improve until a significant strain (ca. 4%) is reached. It is as if the structure must first be firmed by an external force before the full benefit of crosslinking is achieved.

MMEU-treated cotton, whose properties have been changed by a substitution rather than crosslinkage, presents in Figure 5B differential tensile strain recoveries contrasting to those of the DMEU-8 sample. There is no continuous improvement with increasing strain. Total recovery reflects the lack of improvement in delayed recovery. An obvious hypothesis is that without crosslinks mechanical blockage cannot withstand the increasing external strain and irreversible slippage occurs among the subfiber elements. In rheological models, this MMEU modification is analogous to imposing dissipative blocks in parallel with the spring and dash-pot that represent delayed recovery.

The recoveries for the DMEU-3 and hydrolyzed-DMEU samples are similar to but less than those for the DMEU-8 sample. Tensile strain recoveries, especially immediate, improve with increasing crosslinks. Presentations such as Figure 5 tend to nullify effects of the substrate and emphasize results due to the chemical modification itself. Hence, differential tensile strain recovery becomes a sensitive index of the small resiliency due, perhaps, to the incalculably few residual crosslinks within the fiber. The added groups provided by both the hydrolyzed-DMEU and the MMEU treatments are about the same size. Oleoylation gives larger and more effective groups than those due to the MMEU treatment. Determinations on the oleoylated sample show that its recovery is achieved by a different mechanism which can be better discussed in the next section. Hence, in addition to numerical changes, differences in the reaction of individual recovery components to increasing strain exist for different chemical treatments.

Humidity-Strain Recovery

The absorption of water vapor by a textile fiber produces significant variations important in both basic and applied research. Previous discussions of standard and wet conditions are now extended to the extreme relative humidities of 35 and 95%. Figure 6 presents the recovery from 4% strain as a function of the relative humidity. Both the total and immediate recoveries of the DMEU-8 sample remain higher than the comparable recoveries of the control. The immediate strain recovery of the pad-dry-cure sample, however, shows more dependency upon moisture content than does the control. This result is in agreement with the crease recovery measurements of Gill and Steele.²⁴ Table II presents data for other samples and other strains. Under all humidities and strains, the tensile recoveries of both the hydrolyzed-DMEU and the MMEU-treated cotton yarns are greater than those of the extracted control with minor exceptions at 2% strain.

Figure 7A presents differential tensile strain recoveries for the DMEU-8

sample after recovering from a 4% strain. The zero line represents the extracted control. Again, the immediate tensile strain recovery is improved more than the delayed recovery. Although the crosslinks that

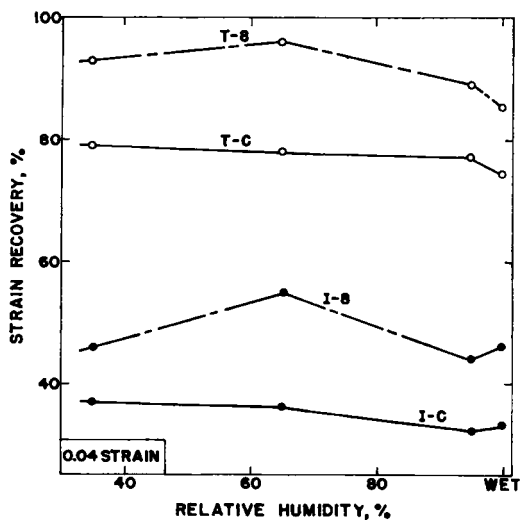


Fig. 6. Immediate (*I*) and total (*T*) recoveries from 4% strain as a function of humidity for control (C) and DMEU-8 yarns.

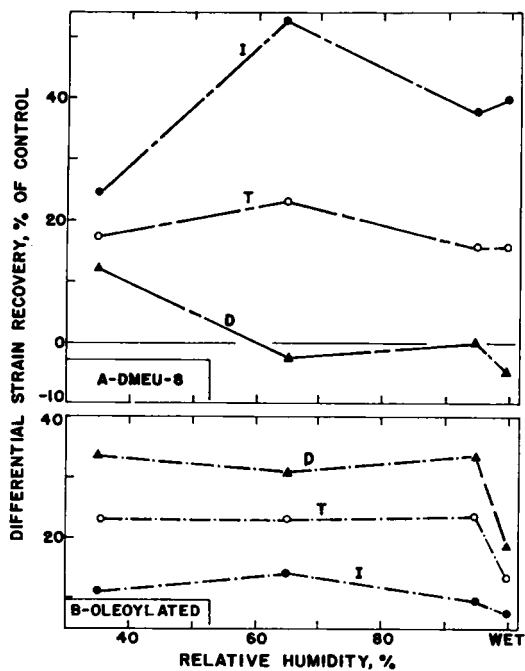


Fig. 7. Changes of immediate (*I*), delayed (*D*), and total (*T*) recoveries from 4% strain as a function of humidity for DMEU-8 and oleoylated yarns.

convert some set and delayed recovery into rapid recovery forces are effective at all humidities, they are most effective for this DMEU treatment in the region of 65% R.H. Under wet conditions the possible increase in recovery due to swelling does not overcome the loss in recovery due to the destruction of natural links by the water molecules. The latter allows irreversible dislocations in regions of the fiber that were not crosslinked in the collapsed state. Below 65% R.H., immediate tensile strain recovery is reduced, probably because limited absorption of water does not permit lubrication or swelling pressure to fully aid recovery. These results are reflected in the crease recovery of fabrics and extend similar data on other pad-dry-cure treatments.

The changes due to humidity for both DMEU samples at other strains generalize the preceding results. The improvement in resiliency of cotton fiber for this wash-wear treatment is due principally to the improvement in the immediate tensile strain recovery. Also, light and electron microscopic observations support the view that a decrease in swelling ability, a property related to moisture regain, and a decrease in lamellar separation correspond to an increase in the dry recovery of fibers modified in a non-swollen state.

The tensile properties of oleoylated cellulose are less dependent upon water vapor than are those of other cottons. The unusual nature of the recovery due to oleoylation is illustrated in Figure 7B. In addition to displaying less variation in recovery over the same range of humidities, the oleoylated cotton achieves limited resiliency by having its greatest improvement in delayed recovery. Uniquely, oleoylated cotton has an improvement in delayed tensile strain recovery at all strains. This result implies that its resiliency from structural changes without crosslinking and without water swelling is due mostly to an improvement in viscoelastic elements. These results are in agreement with the concept of achieving limited recovery through chemico-physical blocking. Hypothetically, the long flexible oleoylated side chains may tangle with each other or with the cellulose chains. Some of these hindrances would be strong enough to cause a rubberlike retraction. Such recoveries would have a longer delay than would those due to primary, crosslinked valences. Hence, if a treatment similar to oleoylation is introduced for wash-wear, it would have the best opportunity for success where a long time was allowed for recovery.

The comparative effect of relative humidity on the differential, immediate tensile strain recovery of cotton yarns with different chemical modifications is shown in Figure 8. Improvements in recovery are presented for 6% rather than 4% strain to show that such results are generally true at more than one strain. The recovery again is the most improved for the cross-linked DMEU-8 cotton, but the hydrolyzed-DMEU and MMEU samples also have some improved recoveries. The dependency on environmental moisture of the latter two samples is different from that of the DMEU-8 sample. With this DMEU sample, the maximum improvement in recovery again occurs in the region of 65% R.H. The hydrolyzed-DMEU

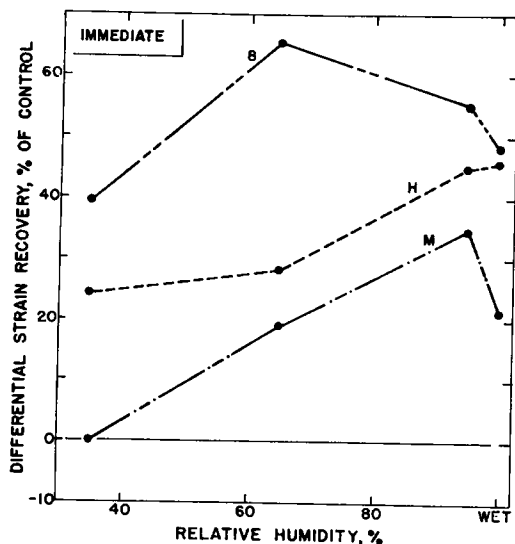


Fig. 8. Increases of immediate recovery from 6% strain as a function of humidity for DMEU-8, hydrolyzed-DMEU (H), and MMEU (M) yarns.

fibers, which have grafted groups to keep the fiber structure open and possibly also have a minute number of residual crosslinks, continue to improve with increasing humidity. Mechanically, this behavior is analogous to that of cotton crosslinked with formaldehyde while swollen. This result for MMEU cotton also indicates the assistance that water absorption renders "elastic" recovery for part of the delayed recovery is transferred to immediate recovery.

As seen from Table II, the relations among immediate, delayed, and total tensile strain recoveries of hydrolyzed-DMEU and MMEU-treated yarns are similar to those of DMEU-treated yarns. The noncrosslinked samples seem to be more affected by friction, stress distribution, or Poisson's deformation ratio than the DMEU samples.

Energy and Strain Recoveries

In Figure 9 is shown differential immediate tensile strain recovery as a function of the differential immediate tensile energy recovery for these samples when retracting under standard and wet conditions from strains corresponding to one-half of their breaking loads. The control data are located at the origin. A decrease occurs only for greige cotton under wet conditions. The line, constructed by the method of least squares, is represented by the equation:

$$S = 1.00E + 1.58$$

where the differential recoveries are represented by S for strain and E for energy. The correlation coefficient is 0.96. Similar results occur at other strains and under different humidities. This graph extends results

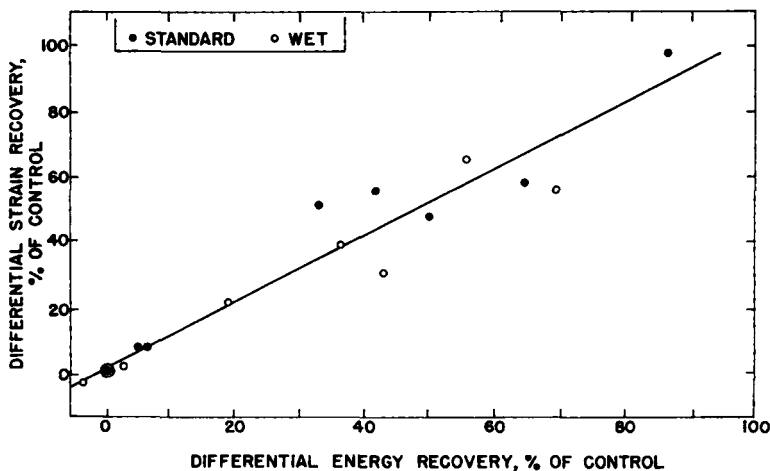


Fig. 9. Increases in strain recovery as a function of increases in energy recovery from $1/2$ breaking loads for modified and unmodified yarns.

published for formaldehyde modifications of cotton²⁵ and is in agreement with the data of Beste and Hoffman.²⁶ Such direct correspondence indicates that the same principles control both recoveries. A unit improvement in recovery for strain gives the same for energy. Therefore, conclusions regarding strain recovery appear equally applicable to energy recovery. Even though toughness is decreased, an improvement in recoverable energy and strain may also imply an improvement in mild abrasion resistance.²⁷

This relation of recoveries may have practical importance in the wash-wear industry. Although tensile strain recovery delineates various chemical modifications better than crease recovery,²⁸ measurements of strain recovery consume more time and manpower. Modern tensile testers with automatic integration of the load-elongation and recovery curves yield direct indices of the energy per unit weight for the same effort expended in measuring breaking load. Therefore, for present routine evaluations, measurements of energy recovery may be considered as a substitute for determinations of strain and crease recoveries. Energy recovery is more easily measured than the former and is more definitive than the latter.

CONCLUSIONS

1. Understanding how various chemical modifications cause different mechanical changes aids current efforts to improve textiles. Resiliency, a property in which improvement is desired, is difficult to characterize by a single value. A tensile strain recovery test, well defined spatially and rheologically, enables an explicit description of strain and recovery divided into their three components: elastic, which is immediate recovery from deformation and reflects the reaction due to primary valence bonds; viscoelastic, which is time-delayed recovery and reflects the movement of large

molecular segments or subfiber elements; and plastic, which is the irreversible breakage of introduced and natural bonds.

The changing of plasticity into elasticity is one of the primary avenues for improving recovery. The increase in total recovery is due principally to the increase in immediate recovery. Viscoelasticity is the least improved. Modifications that increase elastic recovery and reduce plastic set have practical advantages. Samples discussed in this report, especially the cotton highly crosslinked by dimethylol ethyleneurea, conform to the above description over broad ranges of external parameters. The single exception is the sample esterified with oleoyl chloride in which viscoelasticity is most improved.

2. The improvements in strain and energy recoveries appear equivalent. These measurements display a linear correspondence with a unit slope. Hence, measurements of energy recovery may be an accurate and convenient substitute for measurements of crease recovery angle.

3. Recoveries exhibited by the greige and extracted control samples (not chemically modified) are essentially equal, recoveries of the greige being slightly higher under low humidities and those of the extracted slightly higher under high humidities. Tensile recoveries of unmodified cotton are no less dependent upon strain than upon humidity. Tensile recoveries clearly demonstrate the improved resiliency due to chemical modification.

4. Differences in tensile recovery due to strain, time, and humidity enable characterization of the type and extent of chemical treatments. Of the measurements presented, immediate tensile strain recovery is the most sensitive and the most improved. Relations among the components of strain recovery generally remain the same with changes in humidity and strain for all samples except the esterified yarn.

DMEU, crosslinking cellulosic chains with covalent bonds, reduces irreversible slippage even under the influence of an external longitudinal force. These crosslinks reduce the dependency of recovery upon strains and produce a maximum in tensile recovery at about 65% R.H.

Cotton fibers crosslinked with DMEU have tightly bound lamellae and also have improved tensile recoveries. MMEU and hydrolyzed-DMEU cottons do not display tightly bound lamellae or greatly improved dry recoveries. Oleoylated cotton displays limited bound lamellae and moderately improved tensile recoveries.

5. Tensile moduli are reduced by wetting. This change is less with the crosslinked cottons. Oleoylated cotton, which has an unusually low modulus, does not change with humidity. Usually, the higher the moisture regain, the greater the modulus change.

6. Crosslinks increase wet and dry tensile recoveries. Wet tensile recovery is enhanced by increasing ability of the fiber to swell in water. Swelling prevents or makes reversible the dislocations that may occur at low humidities. There is a minimum of immediate recovery when both low strain and wet conditions occur.

7. Limited, but real, increases in tensile strain recovery were accomplished without crosslinks. Results with hydrolyzed-DMEU cotton show that residual crosslinks may contribute to strain recovery. The MMEU sample displays tensile strain recoveries due to water swelling. Oleoylated cellulose has improved recovery as a result of the blockage due to molecular segments larger than those conferred by other treatments. Oleoylated cotton is the least sensitive to moisture and its delayed recovery is the most improved.

An ideal wash-wear treatment should produce very high recovery independent of both water vapor and applied strain. Of the treatments evaluated, only that with DMEU, an agent used commercially, approaches this ideal.

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Use of a company name and/or product by the Department does not imply approval or recommendation of the product to the exclusion of others that may also be suitable.

References

1. J. N. Grant, *Textile Res. J.*, **26**, 74 (1956).
2. R. S. Orr, L. C. Weiss, A. W. Burgis, and J. N. Grant, *Textile Res. J.*, **27**, 966 (1957).
3. X. Eschaliere, French Pat. 347,724 (1906), U. S. Pat. 995,852 (1911).
4. T. H. Morton (to Courtauld's Ltd.), U. S. Pat. 2,243,765 (1941).
5. H. Eyring, *J. Chem. Phys.*, **4**, 283 (1936).
6. E. Karrer, *Protoplasma*, **8**, 475 (1933).
7. J. L. Gardon, *J. Appl. Polymer Sci.*, **5**, 734 (1961).
8. R. S. Orr, J. J. Hebert, L. C. Weiss, R. H. Tsoi, and J. N. Grant, *Am. Dyestuff Repr.*, **54**, 896 (1965).
9. G. C. Tesoro, *J. Appl. Polymer Sci.*, **5**, 721 (1961).
10. R. S. Orr, A. W. Burgis, and J. N. Grant, *Textile Res. J.*, **31**, 550 (1961).
11. J. G. Frick, Jr., B. A. K. Andrews, and J. D. Reid, *Textile Res. J.*, **30**, 495 (1960).
12. J. G. Frick, Jr., B. A. Kottes, and J. D. Reid, *Textile Res. J.*, **29**, 314 (1959).
13. K. Matschat, *Textil-Rundschau*, **16**, 580 (1961).
14. J. B. McKelvey, R. R. Benerito, and R. J. Berni, *Textile Res. J.*, **35**, 365 (1965).
15. W. J. Roff, *J. Textile Inst.*, **47**, T308 (1956).
16. R. S. Orr, L. C. Weiss, H. B. Moore, and J. N. Grant, *Textile Res. J.*, **25**, 592 (1955).
17. American Society for Testing Materials, Committee D-13: (a) D629-57T, (b) D1295-60T, Philadelphia, Pa. (1961).
18. M. L. Rollins and V. W. Tripp, *Methods in Carbohydrate Chemistry*, Vol. III, Academic Press, New York, 1963, pp. 356-63.
19. W. A. Reeves, R. M. H. Kullman, J. G. Frick, Jr., and R. M. Reinhardt, *Textile Res. J.*, **33**, 169 (1963).
20. R. S. Orr, A. W. Burgis, J. J. Creely, T. Mares, and J. N. Grant, *Textile Res. J.*, **29**, 355 (1959).
21. V. W. Tripp, A. T. Moore, and M. L. Rollins, *Textile Res. J.*, **31**, 295 (1961).
22. V. W. Tripp and R. Giuffria, *Textile Res. J.*, **24**, 757 (1954).
23. H. Mark and J. Press, *Rayon Textile Mo.*, **24**, P297, P339, P405 (1943).
24. R. A. Gill and R. Steele, *Textile Res. J.*, **32**, 338 (1962).

25. Gulf Coast Committee (J. G. Frick, Jr. and Louis C. Weiss, Cochairmen) AATCC Intersectional Technical Competition, *Am. Dyestuff Repr.*, **52**, P952 (1963).
26. L. F. Beste and R. M. Hoffman, *Textile Res. J.*, **20**, 441 (1950).
27. D. D. Gagliardi and A. C. Nuessle, *Am. Dyestuff Repr.*, **40**, P409 (1951).
28. T. F. Cooke, J. H. Dusenbury, R. H. Kienle, and E. E. Lineken, *Textile Res. J.*, **24**, 1015 (1954).

Résumé

Lorsque l'effet de substrat est annulé, la résilience peut être définie en fonction de la tension, du temps et de l'humidité. La détermination de l'amélioration du recouvrement immédiat ou rapide après étirement, souligne rapidement les différences dues à des modifications chimiques. Le recouvrement retardé est généralement moins amélioré que le recouvrement immédiat. Le pontage du coton au moyen du diméthyléthylèneurée (DMEU) accroît le recouvrement après étirement à mesure que le nombre de ponts augmente; il réduit la dépendance du recouvrement à l'égard de la déformation externe et produit un maximum de retrait à environ 65% d'humidité relative. Le traitement non pontant produit un accroissement limité du recouvrement après étirement. Des mesures sur des fils pontés au moyen du DMEU et ensuite hydrolysés indiquent qu'extrêmement peu de ponts résiduels peuvent néanmoins contribuer au recouvrement. Le coton traité à la *N*-méthylol-*N'*-méthyléthylèneurée montre un blocage physique et un gonflement à l'eau qui facilite le recouvrement. La cellulose estérifiée au chlorure d'oléyle présente un phénomène de recouvrement après étirement probablement dû aux enlacements moléculaires. Son recouvrement retardé ou viscoélastique est fortement amélioré alors que le recouvrement immédiat l'est le moins. Plus le regain d'humidité est élevé, plus la réduction du module-tension est élevée également dans des conditions humides. Le pontage avec le DMEU dans des conditions sèches diminue la réduction du module. Pour tous les échantillons et dans des conditions variées d'humidités et de tension, les améliorations de recouvrement en tension et l'énergie se correspondent linéairement avec une tangente unitaire.

Zusammenfassung

Bei Ausschaltung des Einflusses des Substrats kann die Elastizität als Funktion von Verformung, Zeit und Feuchtigkeit definiert werden. Die Bestimmung der Verbesserung der unmittelbaren oder raschen Zugerholung lässt leicht durch chemische Modification bedingte Unterschiede erkennen. Die verzögerte Erholung wird meist weniger verbessert als die unmittelbare. Die Vernetzung von Baumwolle mit Dimethyloläthylenharnstoff (DMEU) erhöht mit steigender Zahl an Vernetzungsstellen die Zugverformungserholung, setzt die Abhängigkeit der Erholung von der äusseren Spannung herab und führt zu einer maximalen Erholung bei etwa 65% relativer Feuchtigkeit. Eine Behandlung ohne Vernetzung erzeugt eine begrenzte Zunahme der Zugverformungserholung. Messungen an mit DMEU vernetzten und dann hydrolysierten Garnen zeigen, dass offenbar eine geringe, unterhalb der Berechenbarkeitsgrenze liegende Anzahl restlicher Bindungen zur Zugerholung beiträgt. Mit *N*-Methylol-*N'*-methyläthylenharnstoff behandelte Baumwolle zeigt physikalische Blockierung und Wasserquellung, welche die Erholung fördern. Mit Oleoylchlorid veresterte Zellulose besitzt eine, wahrscheinlich durch Molekülverschlingungen bedingte Zugerholung. Ihre verzögerte oder viskoelastische Erholung ist die am stärksten verbesserte, bei einer am wenigsten verbesserten unmittelbaren Erholung. Je grösser die Feuchtigkeitsaufnahme, umso stärker wird der Zugmodul unter Feuchtigkeitseinwirkung herabgesetzt. Eine Vernetzung mit DMEU unter trockenen Bedingungen schwächt diese Herabsetzung des Moduls ab. Die Verbesserung der Zugerholung in Bezug auf Verformung und Energie verläuft bei allen Proben und bei varierten Feuchtigkeits- und Verformungsbedingungen linear mit einer Einheitsneigung.

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