The Relationship Between Molecular Parameters and Polymer Distribution and the Ability of a Polymer to Improve the Resilience of Cotton Fabrics

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Synopsis

Elastic properties are found to be critical parameters for polymers which improve the wrinkle resistance of cotton fabric. Those molecular factors which result in optimum recovery of a polymer film from distortion (i.e., stretching) are shown to be directly related to the ability to improve fabric wrinkle recovery. Further, those molecular factors which inhibit the tendency of a polymer to form ordered structures allow the inherent flexibility of the polymer to be utilized in storing energy of distortion. This energy is then available, if the polymer is properly distributed on the fabric, to help overcome the fabric's frictional resistance to recovery. The most advantageous distribution of polymer is one in which interfiber and interyarn elastic bridges are formed.

INTRODUCTION

In previous work of this series[1] it was shown that in polymer treatments of cotton fabrics, elastic recovery properties of the polymer are the primary factors determining whether or not the resiliency (wrinkle recovery) of the fabric will be improved. Walsh et al.[2] also reported similar conclusions after investigating the change in properties of cotton fabric treated with polymer of varying degrees of stiffness or softness.

On a molecular scale, various groups or fragments of molecules reduce or increase the elasticity of a given polymer in a predictable manner.[3] Therefore, the trends in resiliency of polymer-treated fabric should also be predictable based on a knowledge of the chemical composition of the polymer. In this paper we used model systems to substantiate this expectation through the examination of two facets of elastomeric polymers: the tendency to crystallize and the crosslink density. Also, because the elastic recovery properties must be coupled with the recovery properties of the fabric, the distribution of the elastomer on fibers and yarns of the fabric were examined by scanning electron microscopy.
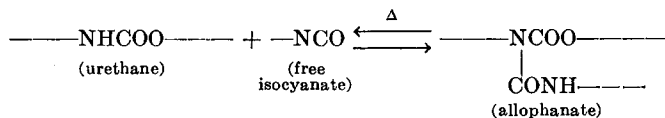
EXPERIMENTAL AND RESULTS

A variety of polymers, especially polyurethanes, were used as model compounds to demonstrate the effect of various structural properties on an elastomer's ability to affect fabric resiliency. With only moderate effort one can be quite versatile in synthesizing polyurethanes providing that appropriate "prepolymers" are available. These form the basic repeating units of the polymer between urethane linkages (—NH—CO—O—). Such prepolymers as polyethers, polyesters, polybutadienes, and polysiloxanes were used in preparing our samples, but the results from only a few of these are reported here.

The polyurethanes were prepared using methods described or referenced by Saunders.[3] Fabric samples were prepared and tested by standard techniques, as described earlier.[1]

The Tendency to Crystallize

The tendency of a polyurethane to crystallize can be controlled in a number of ways, many of which are one means or another of controlling interchain separation. Poly(ethylene oxide) glycols (PEGs) were used as the prepolymers in preparing a series of chain-branched polyurethanes, the chain branching serving as one means of effecting interchain separation. These polymers were obtained from Matheson, Coleman, and Bell in various molecular weight ranges, from 90 to 6750, "capped" with toluene diisocyanate (TDI) to form reactive prepolymers, and were then chain-extended by polymerization with 1,2,6-trihydroxyhexane. The triol introduces a certain degree of chain separation, owing to chain branching during polymerization, and helps to prevent crystallization and subsequent loss of elasticity. Extension with a diol, on the other hand, would have no such effect. In addition, the chain branching introduced by a triol leads to a covalently crosslinked polymer network. In the case of a diol, allophanate rather than urethane linkages provide the major source of crosslinks under the experimental conditions employed, and these are readily broken upon moderate heating[3]:

$$
\underset{\text{(urethane)}}{\text{——NHCOO————}} + \underset{\substack{\text{(free} \\ \text{isocyanate)}}}{\text{—NCO}} \overset{\Delta}{\underset{}{\rightleftarrows}} \underset{\substack{\text{(allophanate)}}}{\overset{\text{——NCOO————}}{\underset{\text{CONH————}}{|}}}
$$

In one experiment it was found that when polyurethanes prepared with a PEG of MW = 1000 and extended with either the triol or 1,4-butanediol were applied to cotton printcloth, wrinkle recovery angle was improved from about 200° (conditioned, warp plus filling directions) to about 240° for both polymers at add-on levels up to about 5%, but above this only the triol-extended polymer maintained the improved wrinkle recovery. The diol-extended polymer imparted no improvement in recovery at these higher levels. Triol-extended PEGs of other molecular weights exhibited similar behavior, but PEG-1000 was found to be the most efficient, im-

parting recovery angles of up to 260° at add-on levels as low as 10%. This polymer had a glass transition temperature (T_g) of $-50°C$.

Bulky pendant groups can also serve to prevent interchain crystallization. In an attempt to investigate the effect of this aspect of polymer structure on the ability to improve wrinkle recovery, both poly(propylene oxide) and poly(ethylene oxide) of the same molecular weight of 1000 were capped with TDI and diol-extended and then applied to cotton printcloth. At about the 10% add-on level, the poly(propylene oxide)-treated printcloth exhibited a wrinkle recovery angle of 240°, while the poly(ethylene oxide)-treated printcloth had a recovery of only 215°. In this case, chain lengths of the polymers were similar but not equal. Also, it was observed that after remaining under conditions of 68°F and 65% relative humidity for three months, both polymer-treated samples exhibited wrinkle recovery angles of about 240°. This effect was reproducible, and we have no explanation for it.

Another means of introducing chain branching is through the reaction between a trifunctional amine and a carboxy-containing polymer,[4] the resulting structure being similar to that of a triol-extended diisocyanate. A butadiene–acrylonitrile copolymer having several pendent carboxyl groups along its chain (B. F. Goodrich's HYCAR 1562X103, $T_g = -25°C$) was applied to printcloth at several levels of add-on, and the recovery angles were measured. Similar samples were also heated in a vacuum oven into which triethylenetetramine (TETA) was introduced and allowed to react. In both sets of samples conditioned wrinkle recovery angle increased with add-on to about 7%, after which only those which had been cured with TETA continued to rise in wrinkle recovery. These results are shown in Figure 1 and again illustrate the improvement in wrinkle recovery that can be imparted by improved interchain separation.

The above observations show the effect of preventing chains from approaching each other close enough to form crystalline areas. Similar results can be expected from measures which tend to reduce the attraction of the polymer chains for each other. Polar groups contribute more to this intermolecular attraction, or "molar cohesive energy," than do non-polar groups.[3] All else being equal, molecular groups having high molar cohesive energy increase the tendency to crystallize in linear polymers and lead to high glass transition temperatures, hardness, and reduced elasticity in branched polymers. In a number of trials, fabric treated with polymers containing increasing numbers of polar groups, such as urea and urethane groups, generally imparted decreasing improvement in wrinkle recovery.

Crosslink Density

In polyurethanes, the crosslink density can be altered by varying the segmental molecular weight of the prepolymers which are extended with a triol to form the resulting branched polymer. As crosslink density decreases, the segmental molecular weight increases. Thus, when the poly-(ethylene oxide) glycols were "capped" with TDI and extended with 1,2,6-
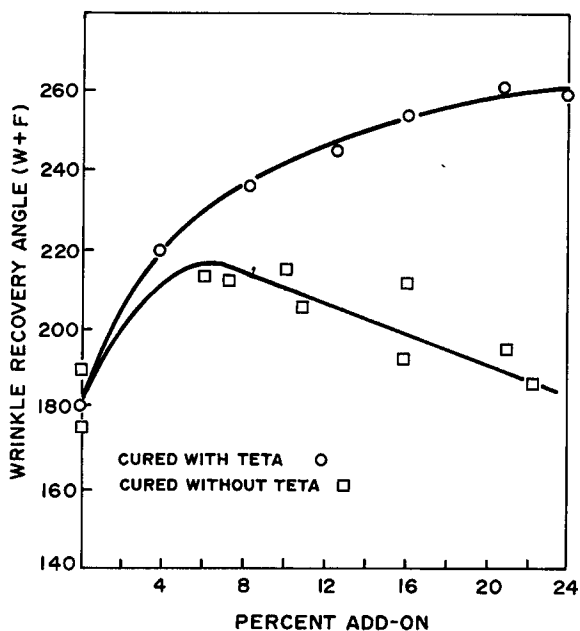
Fig. 1. Effect of chain separation in a butadiene–acrylonitrile copolymer cured at 150°C.

hexanetriol, in effect a crosslink was created at each branch point within the polymer. If each urethane linkage resulted in a branch point, the density of crosslinks would be a maximum for a given prepolymer and would increase as the molecular weight of the prepolymer decreased. The chain extension reactions were carried out in such a manner as to realize as high a crosslink density as possible, and the several resultant polymers of varying segmental molecular weight were applied to printcloth and their conditioned wrinkle recovery angles measured as before. The results, plotted against the molecular weights of the original prepolymers, are shown in Figure 2.

The T_g is a sensitive measure of the elasticity of a given polymer. Therefore, according to the proposed model, T_g should be a minimum for the polymer which imparted the greatest improvement to fabric resiliency. Figures 2 and 3 show this polymer to be the polyurethane which was synthesized from PEG prepolymers of molecular weight 1000. The T_g's of the polyurethanes used to construct both Figures 2 and 3 were obtained by applying them to braids made from cotton yarn and then observing their torsional motion as a function of temperature. This is known as torsional braid analysis (TBA)[5] and yields T_g values which are closely related to the effect of the respective polymers on resilience of cotton fabric. The results are shown in Table I, and, as expected, a minimum value for T_g is seen to occur near the segmental weight of 1000. Literature T_g values for the original PEGs are also shown in Table I, and it can be seen that the trend
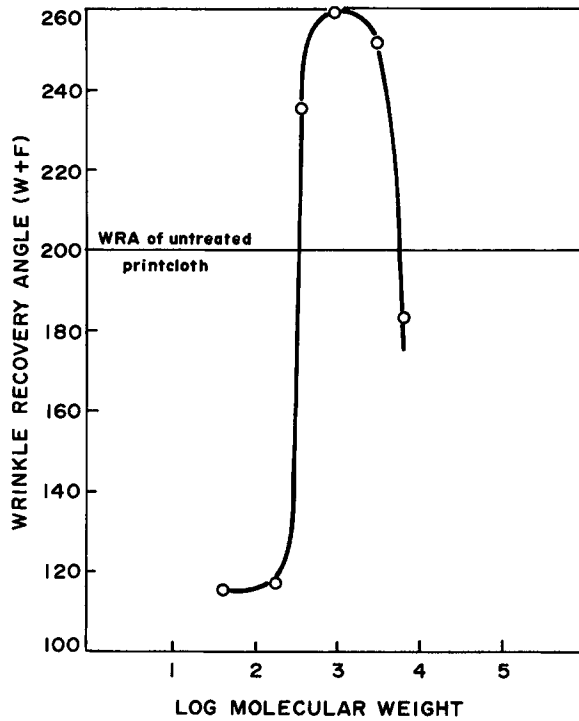
Fig. 2. Effect of crosslink density, as a function of molecular weight between crosslinks, on the wrinkle recovery of polyurethane-treated cotton printcloth.

in polyurethane T_g values does not derive from the T_g values of the original glycols.

Scanning Electron Microscopy

Four samples were selected for determining the distribution of a polymer by observations with a Cambridge scanning electron microscope (SEM).

TABLE I
Glass Transition Temperatures of Poly(ethylene Oxide) Glycols[6] and of Triol-Extended Polyurethanes Made from Them

PEG MW	Glycol (ref. 6)	Triol-extended polyurethane
90	−85	+115
194	−72	+73
400	−55	+15
600	+146	a
1000	−40	−50
1450	−34	a
3350	−20	−41
6750	−17	+40

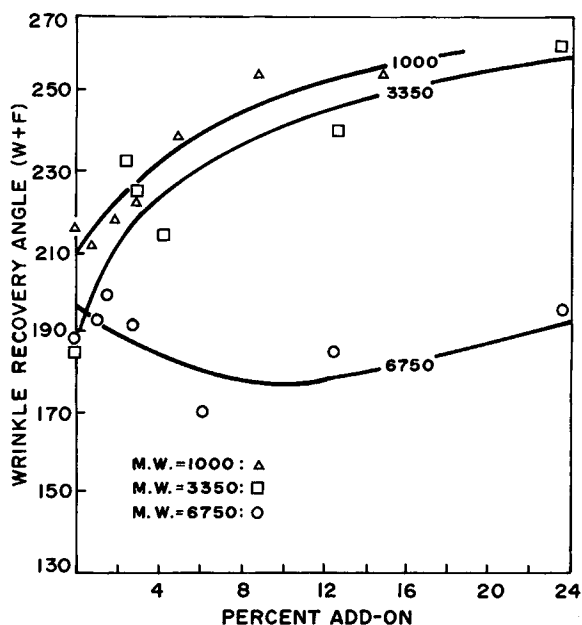a Values for which adverse experimental conditions prevented reliable data from being taken.

Fig. 3. Effect of molecular weight between crosslinks on the wrinkle recovery of cotton printcloth. M.W. is the molecular weights of the prepolymers, and thus the molecular weight between crosslinks— or crosslink density—of the final polymer as applied to the fabric.

Two of the samples were prepared by treatment with General Electric's polysiloxane SE-54, and two by treatment with Rohm & Haas's polyacrylate K-3. The polysiloxane causes a gradual increase in fabric recovery with increasing add-on, while the polyacrylate causes a more rapid increase. Both polymers improve the resiliency of cotton printcloth to about the same extent at add-on levels of above 10%, imparting wrinkle recovery angles of 270°. These samples were prepared and tested according to standard methods, as described previously.[1]

Samples were chosen for study such that both polymers were represented by both a low and a higher add-on level, and such that one of the polyacrylate samples and one of the polysiloxane samples had nearly the same wrinkle recovery values at nearly the same add-on levels. Representative results are described in Table II and shown in Figures 4 to 7.

The electron micrographs show little difference between samples of low (about 5%) and high (about 10%) add-on. This is especially true for the polyacrylates (Figs. 6 and 7). However, the character of the distribution is quite different between the polyacrylates and the polysiloxanes. The "caking" of the polysiloxanes indicates that much of the polymer distributes itself in such a way as to be ineffectual in coupling its recovery forces to those of the fabric. The poorly distributed portion is thus less effective in improving fabric resiliency. This polyacrylate, on the other hand, produces a rapid improvement in wrinkle recovery, and this observation

<div align="center">TABLE II</div>

Treatment	Add-on	WRA	Observations
SE-54 Polysiloxane	6%	250°	"caked" deposits of polymer, small numbers of fiber–fiber bridges
	11%	270°	same general appearance as the 6% sample, somewhat more "caking"
K-3 Polyacrylate	4%	270°	more uniform distribution than in the SE-54 case, very little "caking," large number of fiber–fiber bridges, some extending over large portions of the length of a fiber
	12%	270°	similar to the 4% sample

correlates well with the fact that the polymer is more uniformly distributed and forms many fiber-to-fiber bridges.

Apparently, because of its greater polarity, the polyacrylate wetted cellulose surfaces better than the polysiloxane. Therefore, it adhered better and its recovery forces apparently coupled more effectively. Surprisingly, the relatively nonpolar polysiloxane wetted the cotton fibers rather well (Fig. 8) compared to what had been expected. Smooth, uniform distribution occurred, accompanied by interfiber bridging.

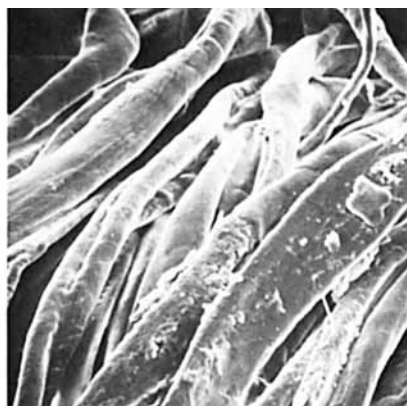Fig. 4. Scanning electron micrograph of 6% polysiloxane-coated fibers.

Fig. 5. Scanning electron micrograph of 11% polysiloxane-coated fibers.

DISCUSSION

It has been shown that of the bulk properties which describe the behavior of a polymer, those related to its elasticity are directly related to its ability to improve the resiliency of a fabric to which it is applied.[1,2] The present work has extended these observations to show that the same holds true on a molecular scale: those factors affecting the ability of a

Fig. 6. Scanning electron micrograph of 4% polyacrylate-coated fibers.
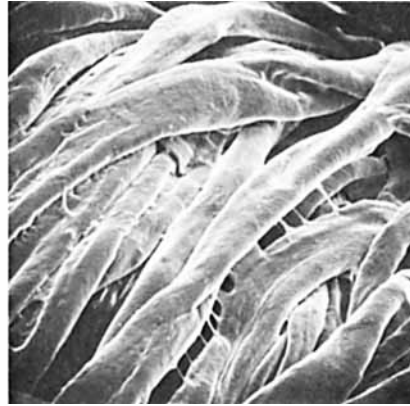
Fig. 7. Scanning electron micrograph of 12% polyacrylate-coated fibers.

polymer to recover from distortion primarily determine its ability to impart resiliency to fabric. An elastic polymer must be able to store a large proportion of the energy of any distortion imposed upon it and be able to efficiently utilize that energy to recover its original configuration. In all cases, it was seen that those conditions which result in improved wrinkle recovery of the treated fabric also result in the ability of the polymer system to store a large amount of negative free energy upon undergoing distortion, this free energy being the energy which thereby becomes available to effect recovery. Using such considerations, the best results were obtained when polymers were used which contain a large number of inherently highly flexible molecular units. For example, polysiloxanes, which according to Saunders[3] are among the most highly flexible polymers, were found to yield among the highest wrinkle recovery angles.[1] Ether

Fig. 8. Scanning electron micrograph of 11% polysiloxane-coated fibers. Magnification twice that of other figures.

linkages are also highly flexible,[3] and because of this and the availability and ease of handling of the poly(ethylene oxide) glycols, they were chosen for the major portion of the study.

Some evidence was presented inferring that bulky substituent groups helped to prevent crystal formation and thereby aided in retaining the inherent flexibility of the polymer. Likewise, the proper number of cross-linking branch points were found to enhance the retention of this inherent flexibility, presumably also through the mechanism of preventing ordered structures from forming, i.e., T_g was lowest for the polymers imparting the most increase in wrinkle recovery. When the molecular weight between crosslinks becomes too large, the branch points no longer serve to separate more than a small portion of the polymer chains, and order begins to increase and imparted resilience begins to decrease. Conversely, when the branch points begin to occur too close together, crosslink density and ordering increase, again leading to decreased ability to impart resiliency. Figure 2 illustrates these effects especially well.

Conditions which maintain interchain separation result in entropy being maximized in the unstressed polymer, thus providing a maximum driving force to return it to its original state of disorganization whenever a distortion (which must, in such cases, result in increased ordering) is imposed on the fabric and, through the fabric, on the polymer. A distorting stress such as is imposed by wrinkling, will, however, cause the polymer chains to slip relative to each other unless some retaining force is provided in the form of either crosslinks or entanglements. This latter case has been observed in studies with oleoylated cellulose, wherein the long flexible oleoylated side chains can tangle with each other or with the cellulose chains.[7]

Crosslinking, of course, provides a degree of organization to the polymer, and so it is found that the desired results are also dependent upon there being a balance between the crosslink density required to reduce chain slippage to zero and that required to keep polymer organization to a minimum. This can be seen from the fact that the wrinkle recovery passes through a maximum in Figures 2 and 3. Chain slippage results in high-stress decay and high permanent set, and therefore in decreased recovery.[1]

It is concluded that the same theoretical considerations concerning the requirements for good elastic recovery in polymers also govern the ability of polymers to improve fabric resiliency. Also, the given elastic recovery forces of a polymer must in some way be coupled to the fabric recovery mechanisms and that the degree and manner of this coupling is also important in determining the ultimate resiliency obtainable. The polymer must be distributed on the fibers and yarns of the fabric as to favor this coupling of forces. The numerous fiber-to-fiber bridges found in the polyacrylate-treated samples (Table II) provide a means by which the elastic behavior of the polymer can directly influence the recovery of the fabric in the manner suggested by Steele.[8] Steele presented evidence that

the primary recovery mechanism of polyacrylate-treated fabrics operates through the formation of interyarn adhesive bonds.

In summary, it appears that polymer treatments can be devised which could lead to much higher levels of fabric resiliency than have so far been observed, provided that certain criteria are met. These criteria require that a highly flexible polymer must be used and that a certain degree of crosslinking must be effected within the polymer to yield the optimum elastic recovery. Beyond this, techniques must be employed which will cause the polymer to form interfiber and interyarn bridges and to adhere well to the fiber surfaces. This latter criterion, adhesion, will be the subject of a later paper.

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