A Technique for Stabilizing Polymeric Materials in an Annealed State

During attempts to improve the wrinkle recovery and other properties of wool, the concept of stabilization in an "annealed" or low-energy state was evolved.[1]   Annealing occurs slowly on prolonged storage under ambient conditions, or is achieved at a faster rate by heating the wool at constant water content.[2,3]   After annealing at high temperatures, slow cooling is needed to prevent rapid localized changes in moisture content which can cause deannealing.   We believe that the process of annealing involves rearrangement of labile hydrogen bonds to give a more stable (i.e., lower energy) molecular configuration.[1]

An annealed fabric possesses increased resistance to, and recovery from, deformations that occur during wrinkling, but the improvement is lost if the low-energy hydrogen-bonded network is disturbed by wetting or steam pressing.[1,3]   Hence a method for stabilizing the annealed state is required.   Treatment with crosslinking agents, e.g., formaldehyde, under appropriate conditions, enhances the annealing effect,[1] but the improvement is only partially stable to deannealing conditions such as wetting.   The purpose of this communication is to demonstrate that a much higher degree of stability can be conferred on wool and other textiles by in situ formation of a three-dimensional polymer network under annealing conditions.   The effects of the process on other chemical and physical properties will be discussed elsewhere.

Figure 1 shows that the degree of improvement in wrinkle recovery brought about by such polymer treatments depends on the humidity (and therefore the water content) at which the wool is annealed and stabilized.   Thus, the state of the wool–water system
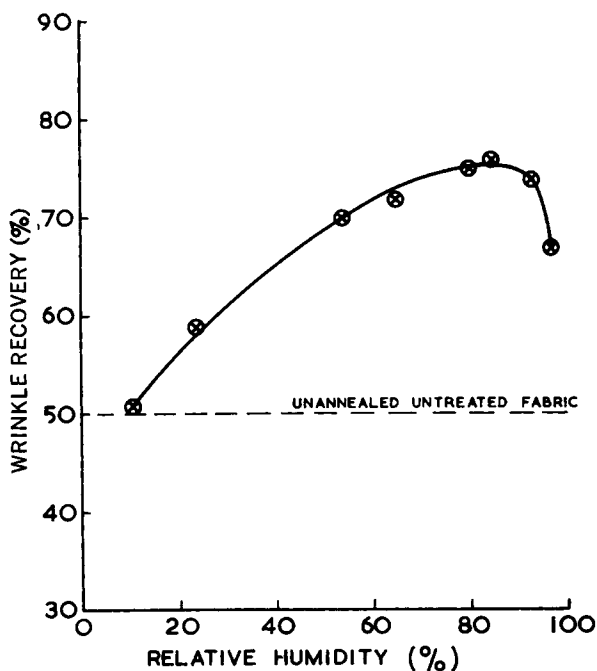

Fig. 1. Effect of relative humidity during annealing and stabilization on wrinkle recovery.   Wool fabric containing 6% resorcinol was conditioned at the various humidities, then heated for 1 hr at 100°C in a sealed tube containing 6% paraformaldehyde (on weight of wool).   For testing conditions, see footnote to Table I.

TABLE I
Effect of Annealing and Molecular Stabilization on
the Wrinkle Recovery of Textile Fabrics

Fiber[a]		Treatment	Wrinkle recovery,[c] %	
			After treatment	After deannealing[d]
Wool	1.	Untreated	—	52
	2.	Annealed[b] for 20 hr at 80°C and 65% R.H.	74	52
	3.	Annealed as (2), in presence of 5% paraformaldehyde (on weight of wool)	80	60
	4.	Wool containing 6% resorcinol treated as (3)	87	85
	5.	Wool containing 6% β-resorcylaldehyde treated as (3)	96	90
	6.	Wool containing 8% monomethylol melamine annealed for 20 hr at 90°C and 65% R.H. in presence of 9% paraformaldehyde	90	85
Cotton	7.	Untreated	—	27
	8.	Annealed for 60 hr at 60°C and 65% R.H., in presence of 5% paraformaldehyde	74	41
	9.	Cotton containing 5% resorcinol, treated as (8)	94	81
Silk	10.	Untreated	—	20
	11.	Annealed for 20 hr at 80°C and 65% R.H. in presence of 9% paraformaldehyde	50	20
	12.	Silk containing 5% resorcinol, treated as (11)	46	40
Nylon	13.	Untreated	—	43
	14.	Annealed for 20 hr at 80°C and 65% R.H. in presence of 9% paraformaldehyde	52	44
	15.	Nylon containing 5% resorcinol, treated as (14)	77	64

[a] Undyed plain-weave fabrics were used.

[b] Annealing was carried out by heating the fabric under the specified conditions in a sealed metal cylinder.

[c] Katz's Multiple Pleat Test[4] for wrinkle recovery was used. Fabrics were preconditioned for 24 hr at 65% R.H., 20°C, then subjected to a fixed deformation for 15 min at 85% R.H., 30°C; then % wrinkle recovery was measured after 15 min at 65% R.H., 20°C.

[d] Immersed in water at 20°C for 30 min, centrifuged, steamed for 10 sec and vacuumed for 10 sec on a steam press, then equilibrated with an atmosphere of 65% R.H., 20°C for 24 hr before measurement.

plays an important role in the annealing process. At low humidities, the molecular re-arrangements involved in annealing would not be expected to take place readily, because only a small quantity of relatively immobile water is present.[5] At very high humidities (and with wet wool), the wool–water system forms a mobile hydrogen-bonded network in which much of the sorbed water is in a state approaching that of liquid water.[5,6] This allows scope for molecular rearrangements, but the mobility of the system probably lowers the extent of annealing by reducing the differences in energy levels associated with different configurations.

At intermediate humidities, a favorable balance is apparently achieved between mobility and stability of the hydrogen-bonded network. The lubricating action of the sorbed water allows bond rearrangements to occur, but the rate of rearrangement is extremely slow unless elevated temperatures are employed.[3] Thus, when drying wet wool or wool of high moisture content to ambient conditions of, e.g., 65% R.H. and 20°C, the hydrogen-bonded network that forms as the fibers deswell will probably not have attained a minimum energy state by the time sorption equilibrium is reached. Such an unannealed (or deannealed) state is characteristic of wool as it is usually encountered in practice. Similar considerations would also apply to absorption of water or to any large changes in moisture content.

Conditions of 85% R.H. and 30°C were used for the test results presented in this communication. Similar results are obtained when other testing conditions are employed, except that the R.H. for annealing tends to change in the direction of the R.H. of testing. However, this correlation between maximum annealing and R.H. of testing is not absolute, probably because of the change of molecular mobility with change of water content, as discussed above.

The results in Table I show that the extent of annealing and stabilization varied for different textile fibers, but in all cases the wrinkle recovery was significantly improved. This is to be expected because all fibers have water sorption isotherms of a similar sigmoidal shape.[7] Thus, the general considerations discussed above will apply. The levels of annealing and stabilization obtained with the different fibers are probably influenced by the differences in amount of water sorbed at the various humidities. Obviously, other chemical and physical properties, such as accessibility to reagents and number and type of available reactive sites, will also affect the degree of improvement obtained with each fiber type.

So far, only those reagents capable of forming three-dimensional crosslinked polymers have given the large permanent improvements illustrated in Table I. It is believed that an impractical number of isolated crosslinks (such as those obtained using formaldehyde alone) would be required to prevent small segments of the molecular structure from moving to higher-energy configurations under the influence of deannealing conditions. To obtain a stabilized crosslinked network, one or more of the reacting species must be potentially at least trifunctional. Furthermore, the compound or compounds must be capable of reacting under conditions that are compatible with the annealing conditions or, if applied later, do not bring about deannealing. Thus, we have found that very little effect is obtained if the treatments are carried out under dry or wet conditions, as is the common practice for most crosslinking or polymer-forming textile treatments.

The general technique of forming a three-dimensional crosslinked structure under annealing conditions should be capable of improving the resistance to deformation of all polymeric materials that are capable of undergoing molecular rearrangements under the action of moisture and heat. Similar effects may also be possible with hydrophobic polymers under appropriate swelling and treatment conditions.

References

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