

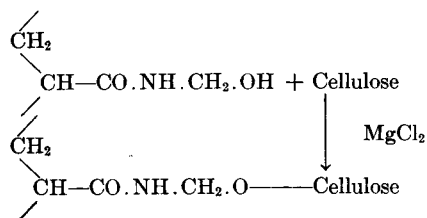
Crosslinking of Cellulose Modified with Polyacrylonitrile

Recently Kamogawa and Sekiya¹ and Gardon² reported studies of the crosslinking of cotton fabrics by using acrylamide as starting substance. The former polymerized acrylamide in cotton fabrics and gave it a secondary after-treatment with various reactive compounds such as formalin and adipamide; the methylolated product was then crosslinked with cellulose by the usual acid curing treatment. The latter followed a reverse procedure, that of crosslinking *N*-methylol acrylamide with cellulose; i.e., the methylolated acrylamide was first made to react with cotton with a mild acid catalyst and then was cured. This was then crosslinked with cellulose by the use of ammonium persulfate or potassium hydroxide, to bring about the reaction of the vinyl double bonds with cellulose hydroxyls.

In both cases there was reported a considerable improvement in the wrinkle recovery of the treated fabrics.

In our studies on the polymerization of acrylonitrile in cotton fabrics, crosslinking and improved fabric crease recovery were obtained through treatments essentially similar to those described above.

The nitrile group in polyacrylonitrile was first saponified to the amide by reaction with sodium hydroxide of varying concentrations.³ This then reacted with formaldehyde (30%) at 9–9.5 pH, to give the methylol which is known to react with cellulose under an acid curing treatment. It is interesting to note that, although the reaction of the polymer chain with cellulose can occur at one end only, viz.,



the treated fabrics exhibit considerable improvement in wet crease recovery, indicating the presence of polymer crosslinking with cellulose.

This would therefore substantiate the hypothesis that, during the polymerization process, the polymer is grafted to cellulose at the vinyl double bonds. Such a graft, when modified and made to react further with cellulose by the above method, would produce crosslinks and improve the wrinkle recovery of the fabrics.

Details of this work, together with other evidence supporting graft formation of polyacrylonitrile with cellulose will be published shortly.

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Adhesion Properties of Nylons

A study was undertaken to evaluate the characteristics of nylon adhesion to metal surfaces. These polymers were selected because they can be applied as hot-melt adhesives and are, therefore, one-component systems. Furthermore, they contain a single type of active group, the amide group. Adhesion strengths of nylon-metal joints were determined and the results were analyzed in the light of adhesion fundamentals. In this work, a series of linear nylons was studied and the role that mechanical properties of polymers play in dictating adhesive joint strength was investigated.

Three different adhesion tests—tensile, lap shear and impact—were used in these experiments, giving a better overall performance rating of the adhesive and enabled an objective examination of the results to be made. The tensile tests were a modification of the ASTM C297-52T procedure. However, a circular instead of a square contact area was used to eliminate corner effects. Lap shear strengths were obtained by rupturing (in tension) joints made by melting the polymer between two metal bars (4 in. × 1/2 in. × 1/4 in.) at 1/2 in. overlap. A test resembling the IZOD impact test was employed to obtain impact strengths. In all tests, the contact surfaces were first cleaned and smoothed with Carborundum silicon carbide paper (#400/w) on a flat surface. They were washed with acetone and water, and then given a chemical conditioning treatment. The aluminum and steel surfaces were treated as described by Black and Blomquist.¹ The copper surfaces were dipped in concentrated nitric acid and immediately washed with water. The polymers were then melted onto the blocks, and while still fluid were pressed together with minimum contact pressure, to insure proper spreading and joint formation.

Results of the adhesion tests are presented in Table I; data for polyethylene are included for comparison. Generally, with the exception of Nylon 48, adhesion strengths vary according to the amide content. Table I also lists some mechanical properties of the polymers. Comparison shows that a clear correlation exists between bulk mechanical strength of the polymeric adhesive and adhesive strength. These data confirm the known fact that rheological properties of adhesive materials are most important in dictating ultimate joint strengths of adhesives.² However, contrary to expectation, the ruptured joints were observed to exhibit partly boundary and partly cohesive failure. What must be assumed in this case, since it is known that the amide groups of nylon are capable of influencing both interfacial and bulk properties simultaneously, is that the boundary layer is initially sufficiently strong to support an external force. When a breaking stress is applied to the joint, the failure crack notably initiates in the bulk of the adhesive polymer and thus the adhesion strength reflects the bulk polymer strength. The rupture course proceeds in any direction by a tearing or peeling mechanism. The failure crack may then be expected to propagate along the metal-polymer boundary as well as in the layer of polymer. This latter step would be rapid and require little energy. This hypothesis suggests that a "threshold" of interfacial boundary strength may exist, by which is meant that, if the mechanical strength of the boundary layer is above that of the bulk polymer, interfacial properties would not be expected to influence the strength behavior of the composite joints. Similar views of adhesion are held by Bikerman.³

TABLE I
 Adhesion and Bulk Properties of Various Nylons

	[η] ^e	Amide content, %	Adhesion ^{a, f, i, k}					$\bar{\sigma}$ ^g	Impact IZOD—Al, ft. lb./in.	Bulk ^h		
			Tensile, psi			Lap shear aluminum, psi	Tensile strength × 10 ⁻³ , psi			Elongation, %	Elastic modulus × 10 ⁻⁵ , psi	
			Steel	Copper	Aluminum							
Nylon 6 ^b	0.95	38.0	10,400	10,600	9,600	4100	0.17	0.50	12.0	300	3.0	
Nylon 66 ^b	1.11	38.0	9,900	10,900	9,700	3800	0.28	0.30	10.5	90	4.0	
Nylon 48 ^b	0.76	38.0	4,300	5,100	4,100	2400	(-0.15)	0.20	4.3 ⁱ	3	2.1	
Nylon 610 ^b	0.93	30.6	7,700	9,000	8,300	3100	0.34	0.13	7.0	90	2.6	
Nylon 11 ^c	0.95	23.5	5,700	3,800	6,000	2600	0.16	0.18	8.5	120	1.8	
Polyethylene ^d	—	0.0	2,500	1,600	2,500	1100	0.14	0.12	4.4	11	1.5	

^a Adhesion values are for optimum melt temperatures (260–310°C.; polyethylene 200°C.).

^b Special unmodified samples.

^c Belding Corticelli Industries, 1100 series, Nylon 11, type 1107.

^d U. S. Industrial Chemicals Co., microthene powdered polyethylene.

^e Intrinsic viscosity in cresol at 30°C.

^f All adhesion results reported as averages of five or more determinations.

^g Poisson's ratio for Nylon 66 is approximately 0.4 (ref. 5).

^h Data obtained from commercial literature and ref. 6.

ⁱ Values are approximate (micro tensile test used).

^j Thickness of adhesive layer in the joints was kept in the plateau range of 1 to 5 mils.

^k Average deviations: tensile ± 800 psi; lap shear ± 300 psi; impact ± 0.05 ft. lb./in.

Of special interest is the adhesion behavior of Nylon 48. Although Nylon 6, Nylon 66, and Nylon 48 have the same amide contents, Table I shows that they differ, to varied extents, in adhesive and mechanical strength. This is not believed to be caused by molecular weight differences. In preliminary studies with Nylon 66, it was found that samples having intrinsic viscosities of 0.54 to 1.2 exhibited the same levels of adhesion strength. Therefore, it is assumed that Nylon 48 would also be reflecting ultimate mechanical properties at this level of intrinsic viscosity. It is known, however, that these three 38% amide-content nylons do not possess the same crystallinity. In fact, from an x-ray analysis the following qualitative rating was made: according to decreasing crystallinity, Nylon 48 \gg Nylon 66 $>$ Nylon 6. It therefore appears that polymer crystallinity is reflected in the adhesion (and mechanical) strength of nylons. This aspect of adhesion appears important and warrants further investigation.

The data presented may be used as the basis for a proposed one-parameter index of adhesion character. If we assume the adhesion tensile strength (ATS) to be proportional to Young's modulus⁴ and the adhesion lap shear strength (LSS) to be proportional to the shear modulus, we may define an "adhesion Poisson's ratio":

$$\bar{\sigma} = \frac{(\text{ATS})}{2(\text{LSS})} - 1 \quad (1)$$

The classic limits⁵ for Poisson's ratio are $0 \leq \sigma \leq 0.5$. Interestingly enough, the values of $\bar{\sigma}$, except for Nylon 48, fall into this range. It thus appears that the "adhesion Poisson's ratio" may be reflecting the mechanical properties of the polymers, at least in those cases in which the adhesion behavior reflects mechanical properties. If adhesion tensile strengths for all of the polymers on steel, copper, and aluminum are plotted against amide content, all of the points except those for Nylon 48 fall around a smooth curve.

Nylon 48 is, in fact, behaving anomalously. Further work is under way to explore the significance of the adhesion Poisson's ratio.

In summary, the nylons are shown to be good hot-melt adhesives. The adhesion tensile strength shows good correlation with the amide content and a rough correlation with the tensile strength. A new one-parameter index of adhesion character, the "adhesion Poisson's ratio," is proposed.

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