

# Effect of a Methyl Substituent in the Polymerization–Crosslinking Treatment of Cotton with NMMA and NMA

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## Synopsis

An estimation of structures of reagent residues in cotton fabrics treated with *N*-methylolmethacrylamide (NMMA) and *N*-methylolacrylamide (NMA) and comparison of textile performance of the NMMA–cotton and NMA–cotton provide the basis for insight into the structure–performance relationship in these fabrics. The  $\alpha$ -methyl substituent, which constitutes the difference between NMMA and NMA, accounts for an altered composition of reagent residues in the treated cotton. The more attractive balance of strength–abrasion resistance with resilience for the NMMA–cotton seems to be a result of a lower degree of covalent crosslinking, which appears compensated by a higher elastic modulus in the NMMA network polymer.

## INTRODUCTION

We recently reported the polymerization–crosslinking of cotton with *N*-methylolmethacrylamide (NMMA) and *N*-methylolacrylamide (NMA) to achieve improved balances of textile performance properties in durable–press fabric.<sup>1–3</sup> These two treatments result in similar balances of properties, but in some cases significantly different specific values. The two reagents differ by a methyl group on the  $\alpha$ -carbon atom. Because of the methyl group, methacrylic derivatives generally (a) are more stable to hydrolysis and oxidation, (b) are less reactive, and (c) form polymers with higher moduli. These factors could be significant in treatment of cotton with NMMA and NMA. In this report, we examine the effects of the  $\alpha$ -methyl group in terms of the chemistry and textile performance of cotton fabric treated with NMMA and NMA.

## EXPERIMENTAL

### Materials

The fabric was a desized, scoured, and bleached 80 × 80 printcloth weighing 0.109 kg/m<sup>2</sup> (3.2 oz/yd<sup>2</sup>). Acrylamide (AA) and *N,N*-methylenebisacrylamide (MBA) were obtained from American Cyanamid Co., methacrylamide (MA) from Henley and Co., and ammonium persulfate (APS) from the Fischer Scientific Co. [Names of companies or commercial products are given solely for the purpose of providing specific information; their mention does not imply recommendation or endorsement by the U.S. Department of Agriculture over others

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not mentioned.] The solution of ammonium hydrogen sulfate (AHS) was prepared by mixing equimolar solutions of ammonium hydroxide and sulfuric acid. The softening agent was Velvetol 7727, a 17% emulsion of polyethylene (PE) from the Quaker Chemical Co. The wetting agent was Triton X-100 from the Rohm and Haas Co. Other chemicals were reagent grade.

## METHODS

Preparation of NMMA and NMA solutions was described in a previous publication.<sup>2</sup> In a typical durable-press finishing treatment, samples of printcloth were padded to 90–100% wet pickup, dried and cured on pin frames, machine laundered, and tumble dried. The pad bath compositions and the drying and curing conditions are listed in the table footnotes and figure legends.

## FABRIC ANALYSIS

Nitrogen content of treated fabric was determined on dry samples by the Kjeldahl procedure; formaldehyde by the chromotropic acid method.<sup>4</sup> Add-on was estimated from contents of nitrogen and formaldehyde in the fabric. Durable-press appearance rating was measured after one laundering and tumble drying cycle by comparing with standard replicas (AATCC-124-1967). Standard test methods were used to measure conditioned and wet wrinkle-recovery angles (WRA's) (ASTM D-1295-67), breaking strength and elongation (ASTM D-1682-64), Elmendorf tearing strength (ASTM D-1424-63), Stoll flex abrasion resistance (ASTM D-1175-71), and Accelerator abrasion resistance (AATCC 93-1978). All directional tests were carried out in the warp direction.

## RESULTS AND DISCUSSION

### Estimation of Structural Components from NMMA and NMA in Cotton

Estimates were made of the individual vinyl polymerization and etherification reactions of NMMA and NMA in cotton. When equimolar amounts of MA and AA were reacted in cotton with APS and small amounts of MBA, network polymers were formed and entrapped. The amounts of entrapped polymer (in terms of nitrogen bound in the modified fabric) were taken to be representative of the extents of MA-type and AA-type vinyl polymerizations that are characteristic of NMMA and NMA, respectively. The results are shown in Figure 1(a) as plots of bound nitrogen vs. cure time. Both MA- and AA-type vinyl polymerizations proceeded rapidly with APS catalysis at 160°C. At maximum reaction levels, the curve representing MA reaction is substantially lower in nitrogen content, indicating that MA-type monomer polymerizes in cotton less extensively than the AA-type monomer. Methyl substitution at the  $\alpha$ -carbon atom of the MA molecule hinders the rotation of the double bond, which in turn reduces the effectiveness of the vinyl group to polymerize. Accordingly, in radical-initiated reactions of NMMA and NMA with cotton, a lower percentage of vinyl groups of NMMA might be expected to undergo polymerization as compared to NMA; this assumes that *N*-methylol substitution has similar or small effects on reactivities of vinyl groups in NMMA and NMA.

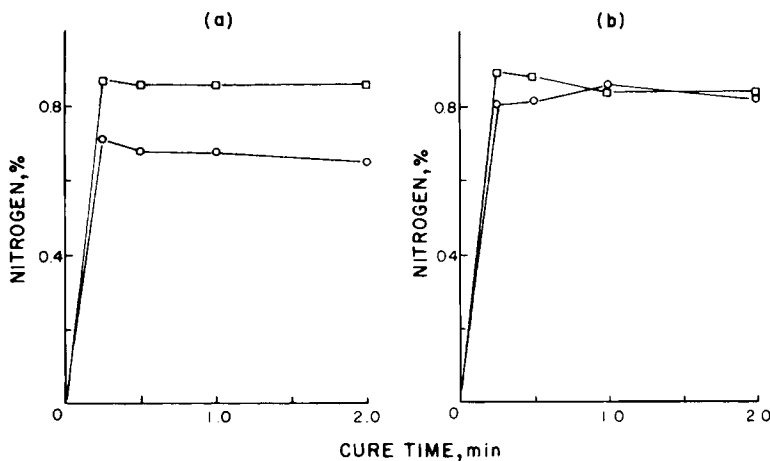


Fig. 1. Percentage of bound nitrogen vs. cure time for reactions in cotton fabric of (a) MA (O) and AA (□) and (b) NMMA (O) and NMA (□). Padded fabric was dried at 70°C for 6 min and cured at 160°C for 0.25, 0.50, 1.0, and 2.0 min. Reagent solutions consisted of (a) 8.5% MA or 7.1% AA with 0.5% MBA, 0.5% APS, and 0.05% Triton X-100 and (b) 11.4% NMMA or 10.0% NMA with 0.3% AHS, 0.03% hydroquinone, and 0.05% Triton X-100.

When equimolar NMMA and NMA were applied to cotton in the presence of an acid catalyst (AHS) and a small amount of radical inhibitor (hydroquinone), the reagents reacted exclusively by single-ended etherification with cellulosic hydroxyl groups. The extents of etherification in terms of bound nitrogen are shown as a function of cure time in Figure 1(b). In the absence of polymerization, etherifications of NMMA or NMA with cotton cellulose proceeded equally reaching identical levels in 1.0 min or longer.

The above studies indicate that the  $\alpha$ -methyl group of NMMA lowers the extent of vinyl polymerization but exerts little or no effect on etherification. However, when the reactions are caused to occur simultaneously, the effects become more complicated than when they occur separately. Actual results are shown in Table I, which summarizes the compositions of fabrics treated with (i) MA or AA and APS, (ii) NMMA or NMA and AHS, and (iii) NMMA or NMA and APS. Items (i) and (ii) in Table I involve polymerizations and etherification respectively, under separate and independent controls, whereas item (iii) involves the same reactions occurring simultaneously. The treatments were conducted with equimolar amounts of reagents and equal strengths of other active components, so that extents of reaction can be compared directly from the nitrogen and  $\text{CH}_2\text{O}$  bound in the fabric.

From data in (i) and (ii), nitrogen contents were the lowest for MA-APS-cotton and comparable for AA-APS-cotton, NMMA-AHS-cotton, and NMA-AHS-cotton. Thus, with the exception of the vinyl polymerization of MA (representative of NMMA), vinyl polymerization and etherification reactions of NMMA and NMA occurred to comparable extents. When vinyl and methylol groups of NMMA and NMA were catalyzed for simultaneous reaction in cotton, NMMA-cotton displayed slightly lower nitrogen and formaldehyde contents than NMA-cotton, as shown by data in (iii). The nitrogen contents of NMMA-APS-cotton and NMA-APS-cotton were higher than those of

TABLE I  
 Composition of Treated Fabrics<sup>a</sup>

Reagent	Catalyst	Cure time (min)	N (g-atom/100 g)	CH <sub>2</sub> O (mol/100 g)	CH <sub>2</sub> O/N (mol/g-atom)
	(i)				
MA	APS	1	0.049		
		2	0.046		
AA	APS	1	0.062		
		2	0.062		
	(ii)				
NMMA	AHS	1	0.061	0.059	0.97
		2	0.059	0.058	0.98
NMA	AHS	1	0.060	0.057	0.96
		2	0.060	0.056	0.95
	(iii)				
NMMA	APS	1	0.083	0.049	0.59
		2	0.082	0.049	0.60
NMA	APS	1	0.089	0.055	0.62
		2	0.087	0.052	0.60

<sup>a</sup> Padded fabric was dried at 70°C for 6 min and cured at 160°C for 1 and 2 min. Reagent solutions consisted of (i) 8.5% MA or 7.1% AA with 0.5 MBA, 0.5 APS, and 0.05% Triton X-100; (ii) 11.4% NMMA or 10.0% NMA with 0.3% AHS, 0.03% hydroquinone, and 0.05% Triton X-100; and (iii) 11.4% NMMA or 10.0% NMA with 0.5% APS and 0.05% Triton X-100.

NMMA-AHS-cotton and of NMA-AHS-cotton, respectively, but the opposite was true of formaldehyde contents.

The nitrogen contents in (iii) may arise from NMMA or NMA which undergoes (1) both polymerization and etherification, (2) polymerization with concomitant loss of CH<sub>2</sub>O, or (3) etherification only. Structures of units accounting for these types of bound nitrogen are shown in Figure 2, and are estimated quantitatively for the NMMA-APS-cottons and NMA-APS-cottons in Table II. The calculations were made with the assumption that a negligible number of formaldehyde crosslinks was formed under the reaction conditions. The estimated amounts of the three structural units for NMMA-APS-cottons and for NMA-APS-cottons are substantially different in the cases of Structure 1 and 3; there is less of Structure 1 and more of Structure 3 in the NMMA-cottons. There are practically identical amounts of Structure 2 in both NMMA- and NMA-treated fabrics. At similar molar levels of reagent treatment of cotton, NMMA-cotton contains a lower amount of covalent bonding from polymer to cellulose (Structure 1), less network polymer (Structures 1 + 2), and a higher amount of pendent monomer units (Structure 3). Polymer in the form of Structure 2 and pendent units in the form of Structure 3 do not contribute directly (through covalent crosslinks) to the development of fabric resilience, although they may serve as "inert" comonomer units, act as fillers for the cotton pores, or increase microfibrillar surface interactions, and thus enhance the effectiveness of network polymeric crosslinks.

The foregoing analysis indicates that polymerization and etherification of NMMA and NMA in cotton are different when these reactions occur simultaneously than when they occur individually. Simultaneous polymerization and etherification of NMMA and NMA in cotton result in an overall increase in the involvement of monomer over individual polymerization or etherification re-

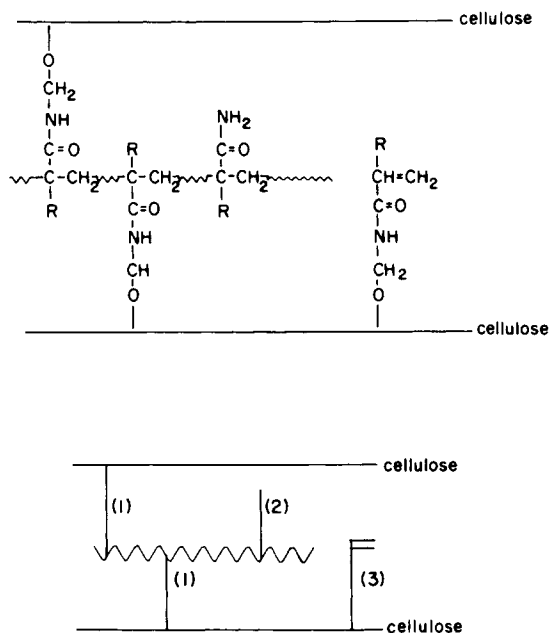


Fig. 2. Schematic representation of structural units from NMMA ( $R = \text{CH}_3$ ) or NMA ( $R = \text{H}$ ) in pores of cotton. Structural units are derived from (1) polymerization and etherification, (2) polymerization with concomitant loss of  $\text{CH}_2\text{O}$ , or (3) etherification only.

actions. However, a low amount of Structure 1 resulting from simultaneous reactions indicates a restriction of the etherification reaction once the monomer becomes a part of a polymeric chain. This restriction is more pronounced in the case of NMMA than for NMA. The presence of a substantial amount of pendent monomer units indicates that these units are not readily available to participate in vinyl polymerization. This restriction is greater for NMMA than for NMA. The more pronounced restrictions on the reagent molecule bearing the  $\alpha$ -methyl group are attributed to more restricted mobility of molecular segments of the NMMA unit resulting from steric, bulk, and hydrophobic contributions of the methyl group.

TABLE II  
Contributions of Various Structures to Nitrogen Contents of NMMA-APS-Cottons and NMA-APS-Cottons<sup>a</sup>

Reagent	N (mol/100 g)		
	Structure 1	Structure 2	Structure 3
1-min cure			
NMMA	0.015	0.034	0.034
NMA	0.028	0.034	0.027
2-min cure			
NMMA	0.013	0.033	0.036
NMA	0.027	0.035	0.025

<sup>a</sup> Structures 1, 2, and 3 are depicted in Figure 2. Calculations are based on data from Table I. Contributions: (2) polymerization with concomitant loss of  $\text{CH}_2\text{O}$  = (nitrogen content in iii) - ( $\text{CH}_2\text{O}$  content in iii); (1) both polymerization and etherification = (nitrogen content in i) - (contribution of 2); and (3) etherification only = ( $\text{CH}_2\text{O}$  content in iii) - (contribution of 1).

## EFFECTS OF NITROGEN VERSUS AIR ATMOSPHERES DURING CURING REACTIONS OF NMMA AND NMA IN COTTON

Effects of curing in inert atmosphere and in air on the reactions of NMMA and NMA with cotton were examined. Curing times of 1–6 min were used for treatments in heat-resistant bags filled with nitrogen (in the forced draft oven) and in the air atmosphere of the forced-draft oven. The two reagents were applied at equimolar concentrations of 11.4% NMMA and 10.0% NMA.

There is a trend toward higher nitrogen content and lower  $\text{CH}_2\text{O}/\text{N}$  ratio in the fabrics cured in nitrogen for 3 min or longer. Estimates of structural components (as in Table II) showed that amounts of Structures 1 and 2 are practically unchanged but that Structure 3 is reduced by 19% from curing NMMA and NMA in nitrogen. Fractions of reagent residues in Structures 1 and 2 are increased as a consequence of cures in nitrogen, indicative that vinyl polymerization proceeded more efficiently in nitrogen. Etherification was relatively unaffected by the change from air to nitrogen. The effects of curing atmosphere on selected textile properties of the fabric treated with NMMA and NMA at various curing times are summarized in Figure 3. The data plotted are for samples cured in nitrogen relative to samples cured in air. Samples cured in nitrogen show trends toward lower DP rating and comparable conditioned WRA but higher strength and abrasion resistance than samples cured in air. These trends are consistent with a shift to more polymerization (that is, relatively less etherification) in the balance between polymerization and etherification. Curves for NMMA are lower in level than those for NMA in Stoll flex abrasion resistance. A similar small difference in Accelerotor abrasion resistance appears to be real. Although the trends are erratic for breaking and tearing strength, the majority of data points for NMMA show lower ratios than those for NMA.

We conclude that the presence of nitrogen during cure caused shifts in the balance of polymerization and etherification reactions, that the resilience of treated cottons was unchanged or only slightly lowered (without significant differences between the NMMA- and NMA-cottons in this regard), that strength and abrasion resistance were affected advantagously (the greater effect being exerted on the NMA-cotton), and that the changes are consistent with a lower degree of sensitivity of the NMMA residues to oxidative attack during and subsequent to polymerization. The last point refers to the difference in sensitivity of methacrylic and acrylic double bonds to presence of oxygen during initiation and propagation of polymerization and to the difference in sensitivity to attack by oxygen at the  $\alpha$ -carbon atom.

### COMPARATIVE TEXTILE PERFORMANCE OF NMMA- AND NMA-Cottons

In the preceding sections, fabric treatments with NMMA and NMA were compared at a single equimolar concentration. Similar treatments with curing in nitrogen atmosphere were conducted with the reagents at four equimolar levels of concentration. Results are summarized in Table III. Data are presented as ratios of the specific property for the NMMA-cotton relative to that for the NMA-cotton. Add-ons of reagent were consistently lower from NMMA than

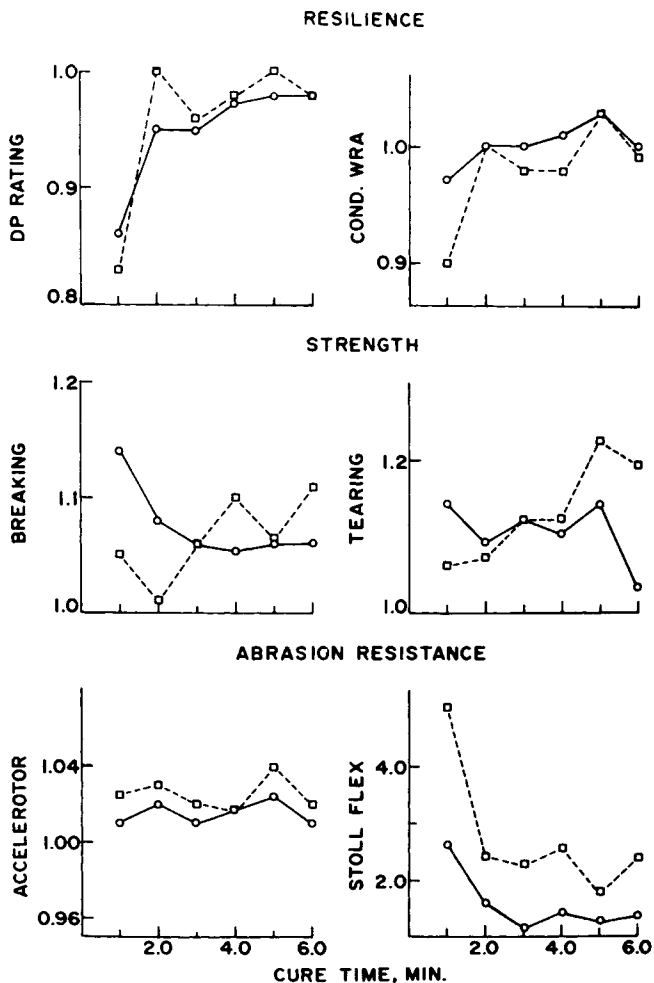


Fig. 3. Ratio of textile properties (nitrogen cure divided by air cure) vs. cure time for reactions of cotton fabric with NMMA (O) and NMA (□). Components in the pad bath were 11.4% NMMA or 10.0% NMA, 0.5% APS, 0.5% MBA, and 0.05% Triton X-100.

from NMA, more so with increasing reagent concentration, despite the higher (14%) weight concentration employed for NMMA. The  $\text{CH}_2\text{O}/\text{N}$  ratio for NMMA-cotton relative to that for NMA-cotton decreased with increasing reagent concentration, and the values were generally lower than unity. The “ $\alpha$ -methyl effect” described in a preceding section became more pronounced with increasing reagent concentration, that is, mobility in the NMMA unit became more restricted than that of the NMA unit.

For fabric resilience (DP rating and conditioned WRA), the ratios of NMMA-cotton performance to NMA-cotton performance were below unity but only slightly below at the three higher levels of reagent concentration. The ratios of strength and abrasion resistance were consistently higher than unity.

NMMA-cottons are consistently superior to NMA-cottons in balances of resilience and strength-abrasion resistance. The “ $\alpha$ -methyl effect” is considered critical to these differences. We propose that the increased moduli in the net-

TABLE III  
Textile Properties of NMMA-Cotton Relative to NMA-Cotton<sup>a</sup>

Reagent concentration <sup>b</sup> (wt %)		Retention of textile properties (NMMA/NMA) <sup>a</sup>							
		Composition		Resilience		Strength		Abrasion resistance	
NMMA	NMA	Add-on	CH <sub>2</sub> O/N	DP	Cond WRA	Breaking	Tearing	Stoll flex	Accelerator
5.7	5.0	0.88	1.15	0.94	0.89	1.06	1.08	1.94	1.01
11.4	10.0	0.80	0.98	0.98	0.98	1.13	1.10	1.97	1.03
17.1	15.0	0.76	0.93	0.97	0.97	1.12	1.06	2.13	1.07
22.8	20.0	0.74	0.94	1.00	0.97	1.20	1.12	1.82	1.12

<sup>a</sup> Pad bath contained NMMA or NMA in the quantities indicated above, 1.0% PE, and 0.05% Triton X-100. APS and MBA were also included at mole ratios of 0.022 and 0.033 respectively, relative to the methylol reagent present. The padded fabrics were dried at 70°C for 6 min and cured at 160°C for 5 min under nitrogen in heat-resistant plastic bags.

<sup>b</sup> Equimolar concentrations of reagents.

<sup>c</sup> The values were tabulated by dividing those for NMMA by those for NMA (for example, the CH<sub>2</sub>O/N ratio for the NMMA-cotton divided by CH<sub>2</sub>O/N ratio for the NMA-cotton.)

work polymer from NMMA compared to that from NMA is critical to the maintenance of high levels of resilience at reduced levels of network crosslinking with NMMA. We suggest that the higher elastic modulus in the NMMA network polymer counterbalances the lower level of network crosslinkages relative to resilience and that the rigidity in the network polymer of NMMA, being less restrictive than covalent crosslinkages, is less detrimental to strength-abrasion performance.

### Phosphate Salt Effects

Cotton fabrics were treated with NMMA or NMA and the usual supplementary agents in the presence of various amounts of phosphate salts. The addition of NaH<sub>2</sub>PO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> had little or no effect on the amount of bound nitrogen or on the CH<sub>2</sub>O/N ratio. Estimates of structural components showed Structures 1 and 2 unchanged and small decreases (13%) in amounts of structure 3. The structural change is similar to but smaller than that noted earlier in transition from air to nitrogen as the curing atmosphere.

The effects of phosphate salts on textile performance properties of these cottons are summarized in Figure 4. Each textile property, normalized to that of product with zero phosphate salt concentration, is plotted as a function of phosphate salt concentration. In both NMMA and NMA systems, resilience decreased and strength and abrasion resistance increased with the increase in phosphate salt concentration. At a given level of phosphate salts, decreases in DP rating were almost identical for NMMA and NMA series, decreases in conditioned WRA were smaller for NMMA samples, and increases in strength and abrasion resistance were consistently lower for the NMMA series, except in the case of breaking strength, for which the increases were comparable for both series at lower levels of phosphate salts. Overall, the improvements in the balance of resilience-strength and abrasion resistance because of phosphate salts were less pronounced for NMMA-cotton than NMA-cotton.

The beneficial effects of phosphate salts on the balance of textile properties are attributed to a shift of the balance of polymerization and etherification and



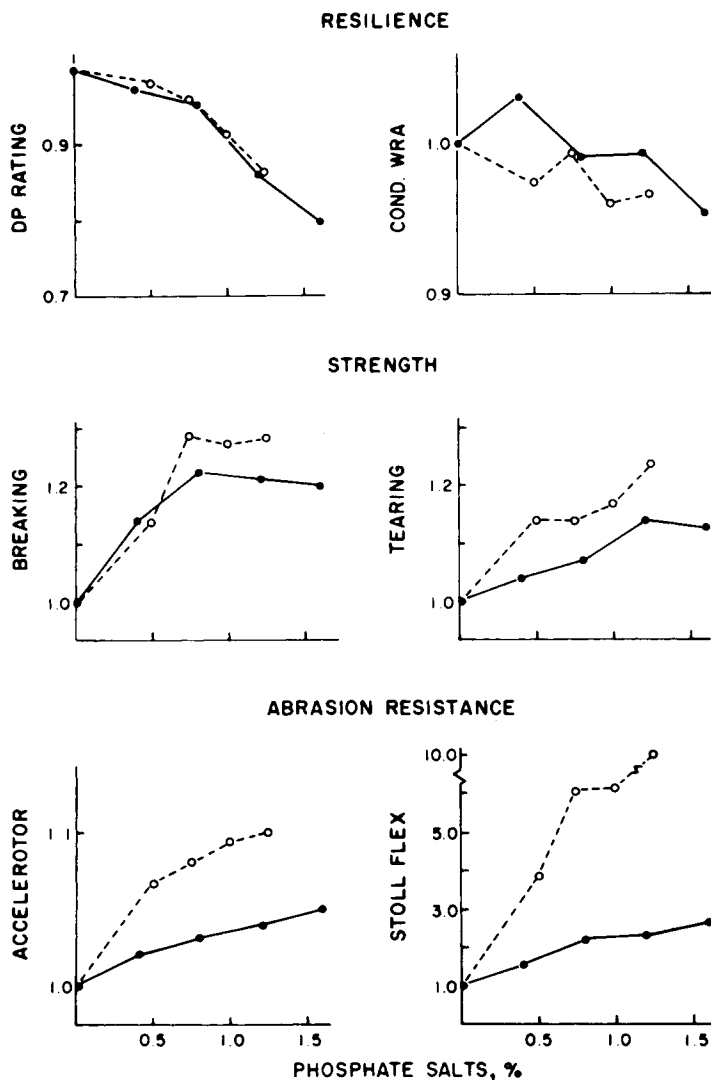


Fig. 4. Effects of phosphate salts on textile properties of NMMA-treated (●) and NMA-treated (○) cotton fabrics. Components in the pad bath were  $\text{NaH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$  at equal weight ratio and at indicated concentrations, 11.4% NMMA or 10.0% NMA, 0.5% APS, 0.5% MBA, 1.0% PE, and 0.05% Triton X-100. The padded fabric was dried at  $70^\circ\text{C}$  for 6 min and cured at  $160^\circ\text{C}$  for 4 min.

a change of the reaction rates involved.<sup>3</sup> Phosphate salts may operate by allowing most vinyl polymerization to occur before a substantial fraction of the reagent units is etherified to cellulose, which in turn enhances the network polymer-cellulosic surface interaction and facilitates more effective subsequent crosslinking. The fact that the improvement in textile performance because of phosphate salts is less pronounced for NMMA-cotton than NMA-cotton is consistent with NMMA's lower degree of reactivity. NMMA, having less reactive functional groups than NMA, is less responsive to the effects of phosphate salts on the reactions involved.

## SUMMARY AND CONCLUSIONS

We observed that: (a) MA-type monomers polymerized less extensively than AA-type monomers in cotton, whereas, in the absence of reaction involving the vinyl groups, the methylol groups of NMMA or NMA underwent etherification equally effectively with cellulosic hydroxyl groups; (b) when occurring simultaneously, both polymerization and etherification of NMMA or NMA were restricted, and the restriction was more pronounced for the etherification reaction and in the case of NMMA; (c) the NMMA- and NMA-treated fabrics cured in nitrogen, as compared to those cured in air, tended to shift the balance of polymerization and etherification toward the former and the products had higher strength and abrasion resistance (the elevation of abrasion resistance was more pronounced for the NMA series than the NMMA series); (d) cotton treated with NMMA displayed higher strength and abrasion resistance but comparable or slightly lower resilience than did the NMA counterpart; and (e) the addition of small amounts of phosphate salts in fabric treatments with NMMA or NMA improved fabric strength and abrasion resistance without significantly lowering the resilience (again, the effects were more pronounced in the case of NMA, changes attributed to the ability of the phosphate salts to delay etherification, to accelerate vinyl polymerization, and to shift the balance of reactions in favor of vinyl polymerization).

We propose that the hindrance of the methyl group to rotational motion in NMMA represses the occurrence of vinyl polymerization in cotton, which in turn slows the etherification between NMMA and cellulose. As a result, the crosslinking of cotton with NMMA is less extensive than with NMA. Indications are that this " $\alpha$ -methyl effect" moderated the degree of crosslinking, but that the crosslinking of NMMA with cotton remained adequate (the treated fabric displayed high levels of resilience). The higher elastic modulus of the network polymer from NMMA is believed to be the compensating factor that makes a high level of resilience possible at a moderated degree of crosslinking.

When polymerization and etherification occur simultaneously, the " $\alpha$ -methyl effect" has greater impact on the latter reaction. The methyl group in NMMA effects a delay and/or a shift of reactions involving the functional groups slightly in favor of the vinyl polymerization. The changes may be small but sufficient to ensure the development of crosslinks causing less structural embrittlement. Methyl substitution served as a built-in moderator; without it, the NMA system required various operations to achieve similar controls on reactions of the functional groups. In fact, because of its greater reactivity and excessive crosslinking, the NMA system was affected to a greater extent than the NMMA system when desirable controls were in effect (as evidenced by the greater improvements obtained for the NMA products when curing was changed from air to nitrogen atmosphere or when phosphate salts were introduced).

## References

1. S. P. Rowland, F. A. Blouin, and J. S. Mason, *Text. Res. J.*, **48**, 73 (1978).
2. F. F. Shih, N. R. Bertoniere, and S. P. Rowland, *Text. Res. J.*, **50**, 432 (1980).
3. F. F. Shih and S. P. Rowland, *Text. Res. J.*, to appear.
4. W. J. Roff, *J. Text. Inst.*, **47**, 309 (1956).

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