

Reactivity of N-Methylolacrylamide in Treatment of Cotton Under Ultraviolet Light

ROBERT M. REINHARDT and JETT C. ARTHUR, JR., *Southern Regional Research Center, Science and Education Administration, U.S. Department of Agriculture, New Orleans, Louisiana 70179*

Synopsis

N-Methylolacrylamide (NMA) and cotton react readily under ultraviolet light when the treatment is carried out in an atmosphere of nitrogen. Reaction is almost completely inhibited by the oxygen in air. Polymerization inhibitors such as the methyl ether of hydroquinone (MEHQ) retard, but do not prevent, reaction. Longer radiation times, i.e., higher radiation doses, overcome the inhibitory effect of MEHQ. A photosensitizer such as biacetyl can increase the rate and efficiency of NMA-cotton treatments, especially with short radiation times (low radiation doses). Relatively low ratios of photosensitizer to monomer produce such effects.

INTRODUCTION

N-Methylolacrylamide (NMA) has been used in various treatments of cotton by free-radical processes, including those initiated by chemical, thermal, and radiation means.¹ Radiation treatments from gamma, electron beam, and ultraviolet sources have been carried out. NMA was utilized in these radical-initiated treatments because of its ready reactivity and amenability to textile finishing. It is particularly well suited to textile finishing because it is water soluble, is essentially nonvolatile, has relatively low toxicity, is not unpleasant, and reacts rapidly.

In a study to utilize ultraviolet radiation treatment in producing wrinkle resistant cotton fabrics,² it was noted that inclusion of many salts capable of catalytic action in subsequent thermal treatment did not interfere with graft polymerization of NMA with cotton. A number of other observations were made on the reactivity of NMA in treatments of cotton under ultraviolet light. These observations, including reactivity of NMA in treatments in the presence of sensitizer and inhibitor, are described in this paper.

EXPERIMENTAL

Ultraviolet radiation treatments were carried out in a Rayonet Photochemical Reactor Model RPR-100 equipped with tubes that emit about 85%–90% of the light in the 300-nm range at about 21 UV W.³ The fabric used was 80 × 80 cotton printcloth that had been desized, scoured, and bleached. Aqueous solutions containing the indicated reagents were applied by soaking the fabric and adjusting the wet pickup to 80%–90% by passing the fabric through pad rolls. Wet pickup was determined by weighing the fabric before and after applying the solution. The solution-wet fabric was mounted on a wire support, placed in a quartz vessel which was then flushed with nitrogen (unless otherwise noted), and

radiated in the reactor. Temperature of the vessel was 25°C, rising slightly during radiation to about 40°C for the longest radiation time. After radiation, the fabric was washed with warm water in an automatic home-type washing machine and tumble dried.

Fabrics were analyzed for nitrogen content by the Kjeldahl method.⁴ Treatment efficiency was calculated from nitrogen content of the treated fabric, wet pickup, and nitrogen content of the solution applied.

Two commercial NMA products (Proctor Chemical Co.) were used, both available as 60% aqueous solutions. One contained no inhibitor; the other, 100 ppm of the methyl ether of hydroquinone (MEHQ). The photosensitizer used, biacetyl (2,3-butanedione), was obtained from a laboratory supply house. The treatment solutions also contained magnesium chloride, about 1.7%, needed for subsequent experiments with the fabrics but which does not affect reactions under ultraviolet radiation.²

In general, all treatments reported here were carried out with aqueous solutions containing, by weight, 10% NMA and 1.7% $MgCl_2$. In experiments that included the inhibitor, its concentration was about 17 ppm of treatment solution. (With twice the concentration of inhibitor, essentially similar results were obtained.) For treatments with sensitizer, amounts of biacetyl were added to the solution so that the molar ratio of biacetyl to NMA was 1:500, 1:200, or 1:100, i.e., concentrations by weight of 0.017%, 0.043%, or 0.085%, respectively.

RESULTS

Efficiencies of ultraviolet radiation treatments of cotton with NMA and of treatments that included inhibitor or sensitizer as functions of radiation time (0.5 to 10 min) are shown in Figure 1. Sensitizer concentration in this experiment was 0.043%, or equivalent to a molar ratio of biacetyl to NMA of 1:200.

The effect of the molar ratio of sensitizer to NMA on efficiency of the radiation treatment is indicated in Figure 2. Time of radiation was 0.5 min in these treatments.

In Figure 3, the efficiencies of treatments at molar ratio of sensitizer to NMA of 1:200 carried out in nitrogen or air are contrasted.

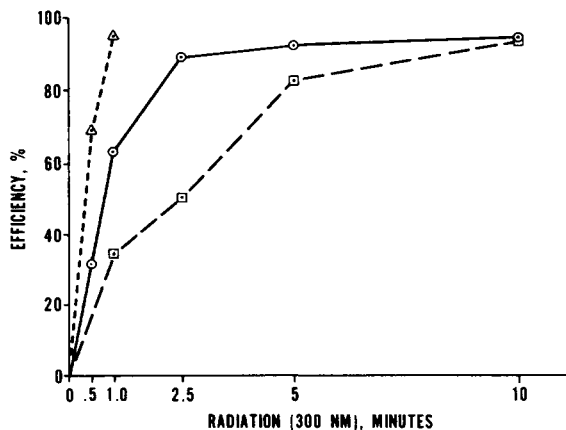


Fig. 1. Treatment efficiency as function of time of ultraviolet radiation. NMA = N-methylol-acrylamide: (○) NMA; (△) NMA plus sensitizer; (◻) NMA plus inhibitor.

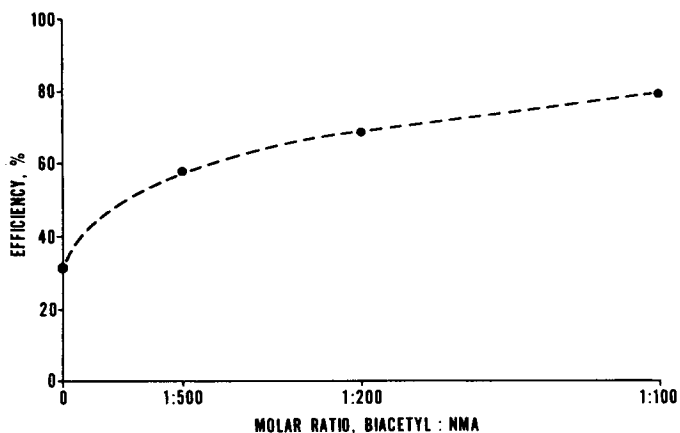


Fig. 2. Treatment efficiency as function of sensitizer concentration.

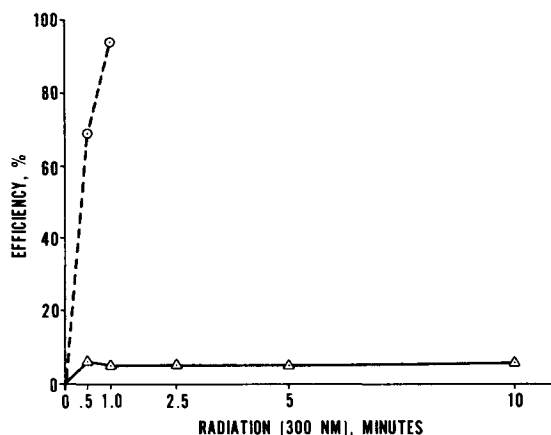


Fig. 3. Treatment efficiency in nitrogen and in air with sensitizer present: (○) in nitrogen; (△) in air.

DISCUSSION

NMA is a very reactive monomer for grafting to cellulose under the initiating action of ultraviolet light (Fig. 1). A grafting efficiency of about 89% was achieved in 2.5 min of ultraviolet radiation. However, some modification of this reactivity was possible through inclusion of a sensitizer or inhibitor in the treatment solution. In the presence of sensitizer, a treatment efficiency of about 94% was achieved in only 1 min of radiation. The polymerization inhibitor retarded the rate of the grafting reaction but did not completely prevent reaction.

From the data presented in Figure 1, treatment efficiencies with the three formulations in 1 min of radiation were:

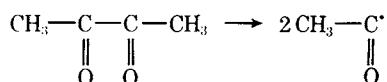
	Treatment efficiency, %	Relative efficiency
NMA + sensitizer	94.1	1.48
NMA	63.4	1
NMA + inhibitor	34.4	0.54

Thus, at this radiation level it was possible to alter efficiency of the NMA by about $\pm 50\%$ by including a sensitizer or inhibitor in the treatment solution applied to the cotton fabric. The reaction probably is not the same with sensitizer present as in its absence. In the latter case, grafting of NMA to cotton through radical sites on the cellulose molecules is believed to be the principal reaction. When cotton is modified by graft polymerization, in the absence of sensitizer and in the presence or absence of inhibitor, the modified fibers have lower degrees of stiffness than when cotton is modified by homopolymerization. When sensitizer is present, the homopolymerization reaction could predominate, although grafting of polymer to cotton through termination of the propagating polymer chain by reaction with the cellulose molecule is possible.¹

In longer radiation treatments, despite the presence of inhibitor, grafting of NMA proceeds to high efficiency levels. An efficiency of greater than 90% was achieved in 10 min of radiation time.

These observations indicate that the reactivity of NMA in ultraviolet radiation treatments is such that the deactivating effect of an inhibitor is overcome in longer radiation times and that the activating effect of a sensitizer is important only in relatively short radiation times. Thus, by adjustment of the radiation treatment (time or dose), an inhibited NMA could be used without removing the inhibitor. Sensitizers are beneficial only if very short radiation times are desired or if the radiation dose available is limited to a low level.

The amount of sensitizer used in conjunction with the NMA affected the efficiency of the treatment, as seen in Figure 2. However, the increase in reaction afforded by the sensitizer diminished as its concentration was increased. Although the abscissa of Figure 2 is expressed as the molar ratio of biacetyl:NMA, the ratios of potential radicals to monomer were twice these values. Upon photolysis, biacetyl dissociates to give two acetyl radicals:



Hence, because of effective propagation of the polymerization reaction after initiation, relatively high levels of polymerization are produced by each radical initiation. The influence of high concentrations of sensitizer thereby becomes less pronounced for polymerization initiation and may become a competing factor in chain termination.

The inhibitory effect of oxygen is much greater than that of commonly used inhibitors such as MEHQ. Furthermore, as seen in Figure 3, inhibition by oxygen (in air) completely overcomes the effect of added sensitizer. This oxygen inhibition is in sharp contrast with the efficient reaction obtained in similar treatments in a nitrogen atmosphere.

SUMMARY

Reaction of cotton with NMA in treatments initiated by ultraviolet radiation proceeds readily in a nitrogen atmosphere, but is almost completely inhibited by the oxygen in air. Polymerization inhibitors such as MEHQ retard but do not prevent reaction. The inhibition from MEHQ contained in the treatment

is overcome with longer radiation times, i.e., higher radiation doses. Sensitizers such as biacetyl can increase the rate and efficiency of NMA-cotton treatments. These effects are most pronounced in short radiation times (or low radiation doses) and with relatively low ratios of sensitizer to monomer.

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 not mentioned.

References

1. J. C. Arthur, Jr., *Adv. Macromol. Chem.*, **2**, 1 (1970).
2. R. M. Reinhardt and J. C. Arthur, Jr., Abstr. Pap., Am. Chem. Soc., 174th National Meeting, Chicago, Illinois, August 28-September 2, 1977, CELL 19.
3. J. A. Harris, J. C. Arthur, Jr., and J. H. Carra, *J. Appl. Polym. Sci.*, **22**, 905 (1978).
4. Association Official Analytical Chemists, *Official Methods of Analysis*, 12th ed., Washington, D.C., 1975, p 15.

Received May 1, 1978

Revised October 19, 1978