SYNOPSIS

SOME STUDIES IN THE APPLICATION OF RESINS TO COTTON

Reaction products of urea and formaldehyde ranging in composition from monomethylol urea (MMU) to dimethylol urea (DMU) have been used in textile industry to reduce creasing and shrinking of fabrics made from natural and regenerated cellulose. Considerable work is available in literature on the effect of process variables such as resin concentration, catalyst type and concentration, curing time and temperature etc. on the properties of the treated fabric. Little work has been published on the chemistry of the polymerisation of DMU within the fibre (10,11). It is known that the fabrics treated with DMU with different catalysts show some differences in properties. So far little attempt has been made to relate these to the polymer structure formed within cellulose.

Another problem requiring elucidation is the mechanism by which the resin polymer formed within cellulose brings about changes in fabric properties. It has been shown that the crease recovery of the treated fabric is due to the improved elasticity of the fibre resulting from the resin treatment (2, 4). Two major theories have been advanced to explain the improved crease recovery of cellulosic fabrics. According to the "deposition theory" (5,7,8) improvement in the fibre elasticity is caused by the presence of a hard, amorphous resin, accompanied perhaps by hydrogen bond formation between the NH groups of the resin and the hydroxyl
groups of cellulose. According to the "cross link" theory the resin polymer forms cross links with the hydroxyl groups of neighbouring cellulose chains through covalent bonds (1,3,6). The subject is still controversial.

The present investigation was undertaken to study the chemistry of the polymerisation of DMU within the cellulose fibres in presence of different catalysts giving a wide range of pH. The changes in the fibre properties obtained by the treatments have been examined in terms of the polymer structure. The possibility of cross linking of the polymer with cellulose has also been studied. The use of insolubility of the treated cellulose in cuprammonium hydroxide as a test for covalent cross linking of cellulose has been critically investigated.

The methods used in these studies were as follows:

(a) Analytical methods for determination of nitrogen and formaldehyde present as methylol (\(>\text{N}.\text{CH}_2\text{OH}\)) formaldehyde and methylene (\(>\text{N}.\text{CH}_2\cdot\text{N}<\)) formaldehyde.

From these analytical data, it was possible to construct the most probable structures of the polymer formed under various conditions of catalysis.

(b) Physical and mechanical properties of the treated fabric, such as crease recovery, tear strength, moisture regain, water imbibition, cuprammonium insolubility and wash-fastness of the finish.
These were related to the structure of the polymer determined as in (a) above.

(c) Alkaline hydrolysis of the DMU polymer formed within cellulose.

This was an attempt to throw some light on the contribution of the $\geq NCH_2O\geq$ cellulose cross-links to the crease recovery by taking advantage of the different rates of hydrolysis of $\geq NCH_2OR$ and $\geq NCH_2N\geq$ bonds.

(d) Microscopic studies of the swelling behaviour of DMU treated fabrics in cuprammonium hydroxide solution:

Photomicrographs of the treated fabrics swollen in cuprammonium hydroxide solution were taken. This study would provide evidence for cross-linking of the resin polymer with the cellulose.

(e) The equation derived by O'Brien and van Loo (9) for cellulose formaldehyde system for correlating wrinkle recovery improvement and concentration of the reacted agent, has been investigated for fabric treated with DMU in presence of different catalysts.

(f) Periodate oxidation of fabric treated with DMU and different catalysts has been studied.
CONCLUSIONS:

It has been found from the above studies that no one structure can be assigned to the DMU polymer in presence of different catalysts. The polymer formed with strongly acidic catalysts such as hydrochloric acid, tartaric acid and ammonium sulfate is highly cross-linked, whereas with other catalysts it is essentially linear.

Cross-linking of the polymer with cellulose is not a necessary requirement for high fabric crease recovery in the former case.

The structures proposed here are in agreement with our present knowledge of the chemistry of urea formaldehyde resins. They offer a reasonable explanation of the wide difference in washfastness of the UF finish obtained with different catalysts.

Formaldehyde liberated during drying and curing reacts with the cellulose in the presence of acid catalysts and a small but significant amount of formaldehyde is detected in the fabric after complete removal of the resin by acid hydrolysis. This formaldehyde present as methylene bridges, renders the acid hydrolyzed fabric insoluble in cuprammonium hydroxide.

The use of insolubility in cuprammonium hydroxide as a test for covalent cross-linking of cellulose has been thoroughly investigated. It is concluded that at least with DMU treated celluloses, this test cannot be applied.
DMU polymer formed in presence of magnesium chloride catalyst, within cellulose under drying conditions (110°C for 8 minutes) does not cross-link with cellulose, but does so under curing conditions (150°C for 5 minutes) as evident from the swelling behaviour of the treated fabric.

The rate study of periodate consumption of the DMU treated fabric confirmed the proposed structures.
REFERENCES:

10. Rumens, W., Textile Praxis 6, No. 10, 743 (1951)