

Methylene Cellulose

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Introduction :

FORMALDEHYDE can react with cellulose, i.e. anhydro- β -glucose-chain molecules (within textile fibres), to form a chemically new compound, called methylene cellulose. Many research workers and technicians have studied the properties—chemical and physical—of methylene cellulose and exploited the same for technical purposes. The work has been covered by various patents but a few references are available which discuss the chemistry of methylene cellulose.

The reaction of formaldehyde with cellulose was first reported by Eschali¹ in 1906. Cross and Bevan² verified Eschali¹'s work and suggested that some structural modification of cellulose took place in the reaction. Meunier and Guyot³, Wood⁴, Schenk⁵, Saegusa⁶ and Dillenius⁷ studied the physical and physico-chemical properties of methylene cellulose and concluded that there was a chemical reaction between cellulose and formaldehyde, forming a cross-link between two anhydroglucose chains. Vogel⁸ found out the molecular weight of methylene cellulose. Grunfest and Gagliardi⁹ studied the conditions under which the reaction could take place. Cameron and Morton¹⁰ studied various compounds, which react with cellulose and have presented an evidence which demonstrates the existence of cross links in methylene cellulose. Goldthwait¹¹ studied the reaction in two separate non-aqueous systems—glacial acetic acid and acetone. Wagner and Pacsu¹² prepared methylene cellulose by reacting cellulose and gaseous formaldehyde under pressure. They studied the constitution of methylene cellulose and tried to give its

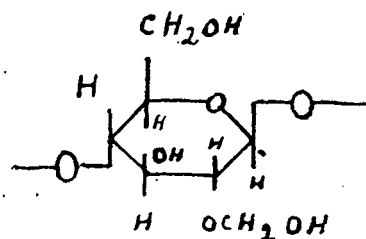
correct configuration. Recently, Steele¹³ has used infra-red spectra of methylene cellulose to elucidate its structure. It is proposed in this article to present a brief review of the tremendous amount of work done in this field by various workers.

Methods of preparation :

Various reactions are possible when formaldehyde reacts with cellulose. They may be classified as follows :—

- (i) Addition,
- (ii) Dehydration and
- (iii) Polymerisation.

(i) Addition of formaldehyde molecule takes place at the available hydroxyl group in the anhydroglucose chain-molecules, giving a compound having a formula :—

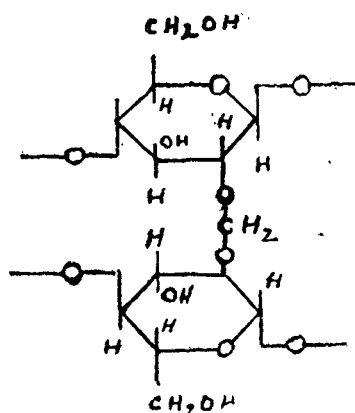


This reaction takes place under mild conditions, such as neutral or alkaline pH and low temperatures. The addition product is not stable to washing.

(ii) Dehydration reaction is possible under drastic conditions, which should remove a water molecule per molecule of formaldehyde. Acidic conditions, high temperatures, etc. are the favourable conditions for dehydration. The com-

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pound, methylene cellulose, thus obtained is stable to boiling water and alkalis and has a formula:—



(iii) Polymerisation of formaldehyde is a side reaction with the reaction of formaldehyde with cellulose. These polymerised compounds are removed from methylene cellulose by boiling it with 20% ammonia. Polymerisation takes place when formaldehyde is used in excess.

Methods of preparation of methylene cellulose may be summarised as follows:

(i) Formaldehyde or its polymer is dissolved in water and acidified with acids or compounds which liberate acids at high temperatures. Cellulose (cloth or yarn) is treated with the solution, excess of the solution is removed and then the wet cellulose is heated at 90-150°C for 1-10 mins. Gruntfest and Gagliardi⁹ have studied various catalysts and their rôle in the reaction. Up to 3% combined formaldehyde is obtained by this method.

(ii) Cellulose is treated with a solution of formaldehyde or its polymer in non-aqueous mediums¹¹ such as acetone or glacial acetic acid and an acid catalyst, under reflux for four hours to get a 0.5-1.5% combined formaldehyde.

(iii) Cellulose is dipped in boric acid solution (1-10% strength) and dried at low temperatures. It is then heated in a sealed tube with paraformaldehyde i.e. a polymer of formaldehyde, at

110-150°C, when 6-7% combined formaldehyde is obtained.

(iv) Soda-cellulose is treated with dichloro-dimethyl sulphate or chloromethoxy sulphonyl chloride in ether. This method gives maximum amount of combined formaldehyde i.e. 17% which corresponds to monomethylene ether of cellulose.⁴

(v) Cellulose, dipped in concentrated sulphuric acid (sp. gr. 1.7) containing 15% paraformaldehyde for five minutes, reacts with formaldehyde to give a product containing 6-7% combined formaldehyde. This can further be treated as in the method (iv) to give 17% combined formaldehyde.⁴

(vi) Cellulose is treated with formalin, which is saturated with hygroscopic substances such as calcium chloride, aluminium chloride etc. Hydrochloric acid is added as a catalyst.¹⁴

Practically, most of the patented processes are modifications of the above methods.

After the preparation of methylene cellulose, it is washed with alkali at boil to remove the uncombined formaldehyde or its polymer. Addition products of formaldehyde and cellulose which are not stable to washing, are also removed in alkaline washing.

Constitution of Methylene Cellulose:

Methylation and analysis of methylated products (after hydrolysis) by paper chromatographic methods is the standard method¹⁵ used to determine the constitution of carbohydrates. The same method was adopted by Wagner and Pacsu¹² for methylene cellulose. Their conclusions are as follows:—

(i) Methylation of methylene cellulose shows that one molecule of formaldehyde condenses with two hydroxyl groups of the anhydroglucose chains to form a methylene bridge. None of the bridges are formed from the polymers of formaldehyde.

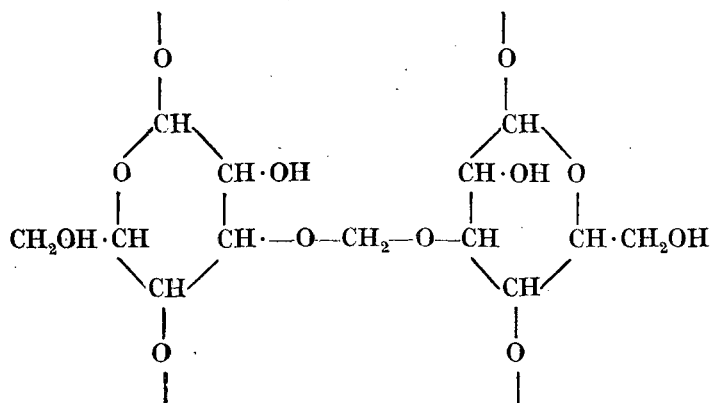
(ii) Formaldehyde reacts selectively with the secondary hydroxyl groups of the anhydroglucose in the formation of methylene cellulose.

(iii) All methylene bridges are formed between hydroxyl groups of different glucose residues.

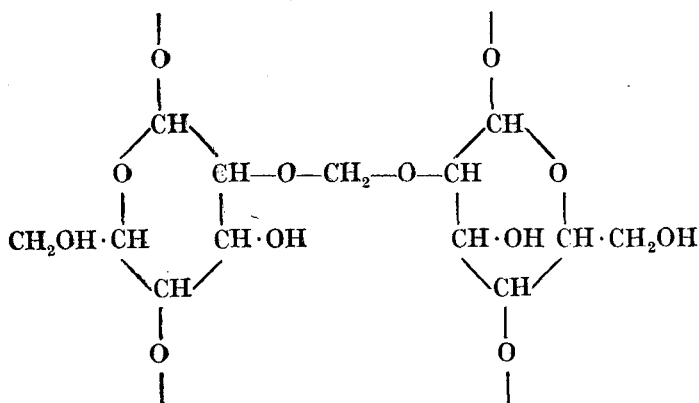
(iv) The radical change in the textile and physical properties observed after

methylenation of cellulose, indicates that these glucose residues must, usually, have been on different chains but no direct proof of this postulation has been obtained.

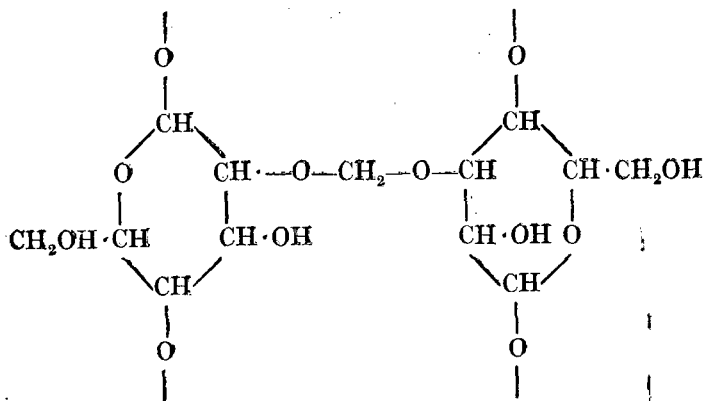
(v) Methylene bridges are either all carbon atoms number 2:3 linkage or a mixture of atoms number 2:2 and 3:3 linkages. The available data does not allow a definite choice between these possibilities :—



3 : 3 Methylene
Cellulose



2 : 2 Methylene
Cellulose



2 : 3 Methylene
Cellulose

Properties of Methylene Cellulose :

Properties of methylene cellulose vary from sample to sample. They are governed by the amount of combined formaldehyde, which varies according to the method of preparation and the condition of cellulose before methylenation. Methylenation causes three major changes in the structure of cellulose, namely :—

- (i) It reduces the number of available hydroxyl groups.
- (ii) New links are introduced between the neighbouring anhydroglucose chains. The new links are stronger than the hydrogen bonds present in the cellulose.
- (iii) Acid used (as a catalyst) in the process hydrolyses the anhydroglucose chains at 1:4 positions.

All the modifications in the properties of cellulose due to methylenation are either due to one or all of the above changes. Modifications will increase with increasing formaldehyde content.

A. Physical Properties :

(i) *Rigidity* : Methylene cellulose shows more rigidity than cellulose because of the added cross links. It gives lower elongation than cellulose, when a load is applied to it. Saegusa⁶ has found out the relation between the combined formaldehyde content and elongation upto break.

Methylene cellulose shows quicker recovery in the limits of reversible elongation (primary creep) than cellulose because of the presence of stronger cross links. Improved crease-resistance of methylene cellulose is due to the quicker recovery in the limits of reversible elongation.

(ii) *Tensile Strength* : Methylene cellulose becomes brittle by the increased rigidity. Beyond the limits of reversible

elongation (i.e. after the yield point), the structure of methylene cellulose collapses. Acid used in the reaction (as a catalyst) hydrolyses the anhydroglucose chains.⁸ The tensile strength of methylene cellulose is lower than that of cellulose because of its brittleness, and of the hydrolysis of the chains due to the catalyst.

The loss in strength due to methylenation depends on the rigidity of cellulose before methylenation. Cotton-cellulose shows more loss in strength than regenerated cellulose on methylenation. Unmercerised cotton loses more strength than mercerised one. Before methylenation, the rigidity of cotton is higher than that for regenerated cellulose. It increases further, on methylenation due to the new cross links. Regenerated cellulose swells excessively on wetting and thus loses strength. Its wet strength is improved by methylenation which introduces new cross bonds and reduces the swelling on wetting.

B. Physico-Chemical Properties :

(i) *Moisture absorption* : Some of the available hydroxyl groups are blocked by methylenation. As they are the seats of moisture absorption, methylene cellulose shows lower moisture content than cellulose. 1.5% combined formaldehyde reduces the moisture content of cotton by 1%.

(ii) *Swelling* : Added cross links in methylene cellulose reduce its swelling to a great extent. Cross links in methylene cellulose do not allow the molecules of the swelling medium to enter inside the anhydroglucose chains. Even traces of combined formaldehyde can reduce the swelling to a great extent. Water imbibed (in methylene cellulose) on wetting is much less than that by cellulose.

If cellulose is in a swollen state during methylenation, the product obtained is a

swollen methylene cellulose. This methylene cellulose swells in normal swelling agents and can take up direct dyes. Water content, during methylenation, determines the condition of the final product (swollen or non-swollen). Non-swelling type of methylene cellulose is obtained as the water content in the reaction system is decreased. (A fabric shrinks to a less extent if the excessive swelling of warps and wefts is prevented). In technical preparations of methylene celluloses, non-swelling type is required, which can be prepared by various methods. In one method¹⁵ hygroscopic substances are included in the formaldehyde bath which prevents swelling which is due to the water present in the treating bath. In another method, non-aqueous solvents are used in which cellulose does not swell.¹¹ Swollen type of methylene cellulose (marketed as "Organdie") is obtained by using a concentrated sulphuric acid bath. In anti-shrink finishing processes, the fabric is padded with formalin and an ammonium salt and dried at a low temperature. The 'dry' cloth is then heated at high temperatures, when methylene cellulose is formed, which does not swell in water.

(iii) *Solubility*: Swelling precedes dissolution in the case of fibrous materials. Because of restricted swelling, due to the presence of cross links, methylene cellulose is insoluble in solvents, such as cuprammonium hydroxide, which are used for cellulose. Methylene cellulose, containing a high percentage of combined formaldehyde, does not swell in caustic soda of mercerising strength. Strong acids, such as sulphuric acid, break the methylene ether linkages and facilitate dissolution of the products. Taking the advantage of the rupture of methylene linkages by nitration, Vogel⁸ found out the viscosity of an acetone solution of nitrated methylene cellulose.

(iv) *Dyeing*: Swelling type of methylene cellulose shows same dyeing

properties as cellulose. Non-swelling type of methylene cellulose does not take direct dyes from salt bath as it does not swell in water. If the dye is present on cellulose before methylenation, it cannot come out of the pores and does not wash away in washings. This principle is used to increase the washing fastness of some of the direct dyes.

(v) *Rotting*: Methylene cellulose is more resistant to microbiological attack than cellulose. Goldthwait¹¹ tested methylene cellulose and cellulose for microbiological rotting, by burying in a soil, which was active enough to destroy cellulose within a week. Methylene cellulose retained 80% of its strength after three weeks and 50% after five weeks. According to him, 10-20% loss in tensile strength, observed after methylenation, could easily be tolerated if the treatment was found to postpone for a sufficient time a much greater loss from microbiological rotting.

C. Chemical Properties:

Methylene cellulose is not affected by alkalies, water and very dilute acids at room temperatures. It is stable to 20% ammonia, even at boil. Sulphuric acid (1N) at boil destroys the methylene ether linkages, thereby liberating formaldehyde. Methylene cellulose is inert to chemical reagents. Effects of various oxidising and other reagents are not studied much, because of its inertness. When methylene cellulose is treated with periodic acid, only one-third of the theoretical quantity of periodic acid is consumed. Methylene ether linkages partially inhibit the penetration of the periodic acid.¹²

Technical importance:

The chemistry and preparation of methylene cellulose are studied intensively because of its technical possibilities. Eschali¹, the pioneer in this field, used the reaction of formaldehyde with

cellulose to improve the wet strength of regenerated cellulose. In 1919 Barrett¹⁶ used it successfully in anti-crease process. Then, hundreds of patented processes were evolved which claimed number of improvements in cotton and regenerated cellulose, such as, resistance to—shrinkage, elongation, dyeing, creasing, rotting and swelling; controlled parchmentation with acids; permanent mechanical effects such as embossed, glazed etc. Thus the formation of methylene cellulose is one of the methods to produce a number of permanent finishes.

Cellulose becomes brittle on methylenation and shows lower tensile and tear strengths. High acidity and high temperatures involved in the process and volatility of formaldehyde necessitate a close control of the process and demand a special equipment. Because of the inherent drawbacks in methylenation, the process is not much used in textile finishing. Recent trend is to use compounds such as glyoxal which are less volatile than formaldehyde. Use of thermosetting urea — and melamine — formaldehyde resins¹⁸ is widely made in preference to formaldehyde alone. Polyfunctional substances, such as polyisocyanates,¹⁹ are increasingly used to cross link the cellulose molecules within textile fibres and so produce permanent finishes.

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