Chemical Degradation of Cellulosic Materials

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Introduction

Cellulose is by far the most abundant organic material in the world. It is the main constituent of most plants and as it is formed by photosynthetic processes it is a resource which is being constantly replaced. It is used by man, sometimes in a relatively pure form, sometimes in combination with other naturally occurring organic compounds, in a wide range of materials such as wood, paper, natural and synthetic fibres, textiles, plastics, adhesives, explosives and paints to mention only some of the many end products based on cellulose and lignocellulosic materials.

Cellulose in the form of cotton and linen has been used by man for many centuries. Over the last 100 years technological developments have resulted in wood and, to a lesser degree, bamboo and various agricultural materials becoming the major commercial sources of cellulosic materials. These are prepared by a variety of processes depending on the nature of the raw material and the end use of the isolated cellulose.

Over the past few decades a great deal of attention has been directed towards obtaining a better understanding of the chemical nature of cellulose and the ways in which it may be modified to give a wide range of products based on cellulose. The ways in which cellulosic materials may be modified by chemical treatments and by the actions of heat, light and general atmospheric conditions have also been studied in great detail. The present paper is directed towards reviewing some of these aspects and discussing in general terms some of the factors responsible for the degradation of cellulose.

Chemical Nature of Cellulose

The term "cellulose" may be used to describe an idealized chemical substance or it may be applied to various technical preparations which, when carefully purified, approach the ideal or theoretical chemical compound. However, even the best methods of preparation give a cellulose which contains a small percentage of material which cannot be considered as true cellulose. As will be discussed later the presence of these "impurities" can have a marked influence in promoting the degradation of technical cellulosic preparations.

Cellulose considered as a pure chemical substance may be described as a linear polymer formed from carbon, hydrogen and oxygen atoms. The cellulose chain consists of a large number of anhydroglucose units linked together through the one and four positions as shown in Figure 1. The chain

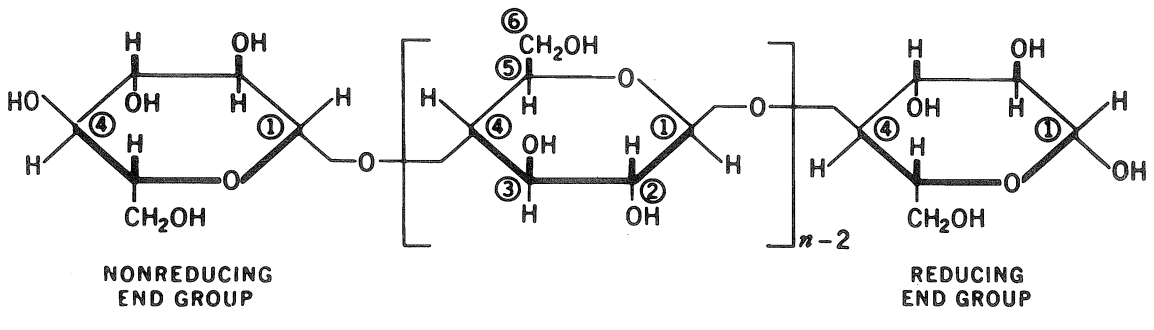

Figure 1. Structural formula for cellulose

has a non-reducing end group at one end and a reducing group at the other end. The repeating unit, n, may have values ranging from 50 to several thousand depending on the source of the cellulose and the methods used in its isolation and purification. If the value of n is high it is an indication that the cellulose has suffered little degrade during its isolation.

To appreciate the ways in which cellulose can be degraded, together with its ability to withstand various forms of chemical attack, it is necessary to consider both its chemical formula and its polymeric structure. A single cellulose chain may be modified by exposure to acidic or alkaline conditions both of which can reduce the chain length. Under oxidative conditions the hydroxyl groups in the molecule may be modified which in turn leads to an increase in solubility in various solvents accompanied by a reduction in chain length. Degrade of this nature is accelerated by light, by the presence of degraded cellulosic materials and is catalyzed by traces of some of the more common elements such as iron and manganese.

As against this the polymeric nature of cellulose tends to protect the cellulose from various forms of attack.

The cellulose chains are frequently arranged in an ordered sequence (crystalline structure) and in these zones the chance of chemical attack on the cellulose is greatly restricted. The high degree of permanence shown by cellulosic materials such as cotton, paper and the like may be attributed to the ordered structure of the cellulose. It must be appreciated that the cellulosic fibres that are seen in cotton or paper are built up from a complex of cellulose chains comprising both crystalline and non-crystalline regions which in turn aggregate into micelles, fibrils (which may be seen under high magnification in the light microscope) and finally into fibres. The general arrangement is illustrated in Figure 2.

The net result of this complex organization is a cellulose fibre which, although readily degraded by various chemical treatments, is much more durable than would be expected from an examination of its chemical formula as shown in Figure 1. Unless the chemical attack is such as to severely modify its polymeric structure the physical and chemical characteristics of the cellulose are not seriously impaired.

Degradation of Cellulose

The discussion so far has been directed towards the properties and nature of a theoretical or idealized cellulose. In this section it is proposed to examine the ways in which technical celluloses are affected by acids, alkalies, heat and light. This will be confined for simplicity to materials made from cotton, one of the purest forms of technical cellulose. Cotton materials in the form of thread or fabric remain intact after wetting whereas paper products may dissociate into individual fibres. Even if the cellulosic fibres have not been affected by the wetting treatment the structure of the paper will have been destroyed and will no longer be available for testing.

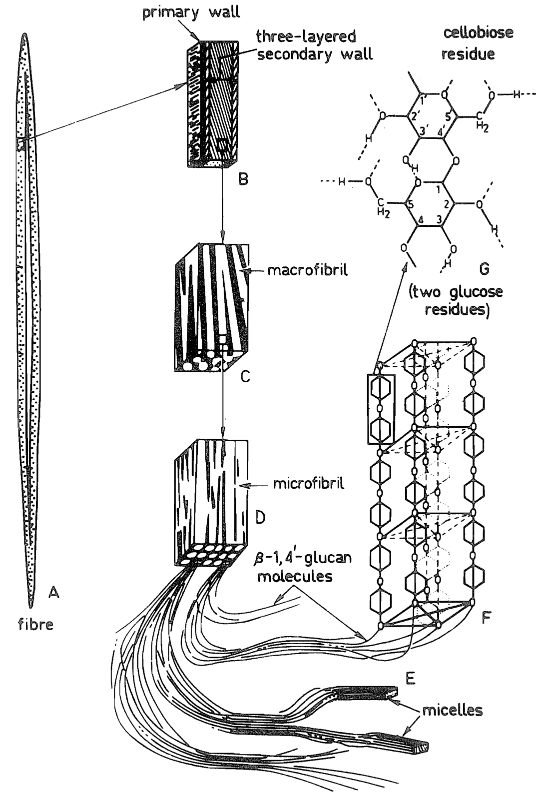

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Figure 2. Demonstrating the way in which the glucose units are built up into chains and then into micelles (crystalline regions), microfibrils, macrofibrils and finally into a fibre. It should be noted that the fibre itself has a complex layered structure.

Acid Attack (Hydrolysis). Cellulose is readily attacked by acids. The severity of the attack varies with the type of acid and the duration and temperature of the treatment. With mineral acids such as sulphuric or hydrochloric acid, prolonged treatment can result in complete depolymerization of the cellulose and its reduction to simple, water soluble sugars. The rate of attack varies according to the type of pretreatment given to the cellulose during its preparation. Any degradation during the preparative stage will accelerate the hydrolytic effect.

The acid attack results in a general weakening of the cotton thread or fabric. The loss in strength is directly related to the reduction in the chain length of the cellulose and the more severe the acid attack the greater the loss in strength. If the treatment conditions are sufficiently severe the fibrous structure is destroyed and the cellulose is reduced to a friable powder.

Oxidative Attack. The oxidation of cellulose may be brought about by a wide range of oxidizing agents. Whilst most of these are mainly of academic interest others, such as the hypochlorites, are widely used in the bleaching of the cellulose fibres used in fabrics and in paper. Efforts are made to control these bleaching operations so as to minimize the amount of chemical attack in the cellulose but any departure from the idealized conditions will result in some damage to the cellulose fibre. Molecular oxygen can also oxidize cellulose, the rate of the attack being greatly accelerated by alkaline conditions and elevated temperatures.

All forms of oxidative attack result in a modification of the cellulose, a shortening of the cellulose chain and in a weakening of the cellulose fibre. Only a small consumption of oxygen is required to produce this effect. For example, a consumption of between 1 and 2 per cent of oxygen per anhydroglucose unit can bring about a 50 per cent reduction in the tensile strength of cotton thread.

Light. It is well known that cellulosic materials are damaged by prolonged exposure to light. The visible signs are some degree of discolouration accompanied by a general loss in strength.

Two distinct mechanisms have to be considered. In one of these light energy is the factor responsible for the degradation of the cellulose but in the second type impurities in the cellulose and the presence of moisture and oxygen all contribute to the attack.

Photolysis — This effect is produced by high energy radiation in the ultra-violet range which breaks some of the chemical bonds in the cellulose chain. As it is produced only by light waves well beyond those encountered in normal daylight or artificial light, it is mainly of academic interest.

Photosensitization — These effects are produced by normal light, not by direct attack on the cellulose but by photosensitization of materials which have been added to the cellulose either directly or introduced during manufacture. This effect is commonly noted with some dyestuffs and is accelerated by the presence of moisture and oxygen. The effect is also produced by certain pigments such as zinc oxide and titanium dioxide both of which are used in certain grades of paper. As against this the effect may be prevented by the presence of very small amounts of certain metals.

This form of degradation can be attributed to a direct oxidation by atmospheric oxygen, together with the production of oxidizing materials produced by the interaction of light with the dyes or pigments. This form of attack proceeds rather slowly but it can lead ultimately to quite marked reductions in strength properties.

Heat. Cellulose is fairly stable to heat providing the initial moisture content is low. Tests have shown that heating at 140°C for up to 4 hrs produces only relatively small changes in chemical composition or in strength properties. If the heating is carried out in a moist atmosphere oxidative effects are apparent and there is a substantial reduction in strength properties.

Atmospheric Conditions. These may combine some or all of the conditions already discussed. The effect of atmospheric conditions on the strength of cotton fabrics is well illustrated by an experiment reported by Race (*J. Soc. Dyers Colourists* 65: 56 (1949)). Cotton yarn was exposed to the elements in a city environment in England in each month of the year and the amount of deterioration determined by measuring the tensile strength of the fabric before and after exposure. The most severe reduction in strength was during the winter. The cotton was found to have a pH of about 3 over the winter period whereas the pH was between 5 and 6 for the summer months. The high acid conditions would have been a major factor in the reduction in tensile strength. Some reduction in strength due to photochemical oxidation was also apparent during the mid-summer period.

General Discussion

Most of the descriptions in the previous sections illustrating the ways in which cellulose may be degraded, particularly those produced by hydrolytic and oxidative reactions, refer to relatively severe conditions such as treating the cellulose with solutions containing acids or oxidizing reagents. In many cases elevated temperatures were used to increase the reaction rates, the result being that the degrading of the cellulose was produced in a short period. However it has been shown that even under atmospheric conditions the amount of degrade can be appreciable if the right conditions of moisture content, acidity and oxygen are present. These are always present to some degree in atmospheres surrounding cellulosic products such as paper and fabrics unless quite extraordinary precautions are taken and some degrade must be expected although it might not become apparent for many years.

In addition, impurities which promote the breakdown of the cellulose are often present. Paper, for example, is usually sized to improve its resistance to water. Sizing is usually carried out during the manufacture of paper using a combination of rosin and alum. Alum is an acidic substance and as a result rosin-alum sized papers always have a slightly acidic pH. Over a period of time this acidity leads to a decrease in strength and the paper tends to become brittle. The effects are greatly increased if the paper is stored under conditions of either high humidity or high temperatures.

Bleached papers may show strong evidence of degrade after a relatively short period (10-20 years) if the bleaching operations have not been carefully controlled. In addition the presence of traces of bleach residues which are retained in the paper can accelerate the degradation processes.

Many paper grades are prepared from fibres which contain considerable quantities of lignin. Conventional newsprint, for example, is made from 20 per cent chemical pulp (relatively pure cellulose) and mechanical pulp which contains both lignin and cellulose. The darkening of newsprint on exposure to sunlight is due mainly to the presence of the lignin which rapidly darkens in the presence of light.

Although cellulosic products will inevitably degrade with the passage of time they can, under the right conditions, show a high degree of durability. Linen fabrics have been recovered from ancient grave sites and there are many examples of papers which are in good condition after many hundreds of years. It must be remembered that most materials now manufactured from technical celluloses are not intended to have a long life. Many paper products are discarded soon after use and in only a very few cases would a life of more than 50 years be a requirement. However, documents intended for immediate use may become of historic interest and the problem is how to store them so as to minimize degradation.

The best conditions for storage of cellulosic materials are a relatively low and constant humidity, a temperature around 20°C, protected from direct light and especially from ultra-violet radiation and in an atmosphere free from traces of sulphur dioxide and other acidic constituents. If special care is required air may be excluded and the material stored in an inert gas atmosphere such as nitrogen.

If it is known that the cellulosic material will be retained for a long period special attention may be given to its preparation. The cellulose must be prepared under conditions already outlined which will minimize degrade and in addition care must be taken with any materials that might be added. With paper, for example, it is possible to use alkaline sizing agents thus avoiding paper acidity and by using alkaline fillers such as calcium carbonate it is possible to obtain a high degree of protection against atmospheric acidity. Such paper stored under proper conditions of temperature, humidity and protected from light could be expected to last for some hundreds of years with little loss in strength.

Bibliography

Material for this paper has been collected from a number of sources. For readers requiring more details on the chemistry of cellulose, factors affecting the degradation of cellulose and the ways in which these modify cellulosic materials such as paper and fabrics, reference may be made to one or more of the publications listed below.

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