

Letters

The solution and regeneration of cellulose using novel solvent systems

Increasing concern over the established processes used in cellulose solution and regeneration is based on environmental factors, corrosion problems and difficulties arising from the inherent instability of products formed during intermediate stages. Several methods are used in cellulose solution formation, most of which are long established. These include xanthation, regeneration from solutions in metal-amine complexes, hydroxyethylation to produce an ill-defined hydroxyethyl cellulose and so on. Each of these has its own particular disadvantages most of which are well known and give rise to the concern mentioned above.

More recent attempts at cellulose solution include solubilization (a) by dinitrogen tetroxide^{1,2} dissolved in a variety of non-aqueous solvents at reduced temperatures; (b) by sulphur dioxide and diethylamine dissolved in acetonitrile or dimethyl sulphoxide³; (c) by an alkaline solution of Cadoxen (tris-ethylene diamine cadmium dihydroxide)⁴ and (d) by solution in cyclic amine oxides, a system which is claimed to act as a solvent for other natural polymers⁵. None of these developments would appear to have any commercial potential since they possess some of the unsatisfactory characteristics associated with the established methods.

A more promising system, based on the solution of cellulose in a dimethyl sulphoxide/paraformaldehyde non-aqueous mixture has been proposed by Johnson⁵. This system is claimed to be efficient in the solution of various forms of cellulose. The major disadvantage here is the use of dimethyl sulphoxide as a cosolvent.

It is of paramount importance that systems devised as possible replacements for cellulose xanthation processes should produce true solutions of cellulose in a minimum number of stages. These solutions should be stable over reasonable periods, from which regeneration can take place, on demand, in a non-corrosive medium. On regeneration, there should be relative ease of solvent recovery, reduced

environmental problems and the production of the cellulose in a desirable sheet or fibre form.

Our attempts to satisfy these objectives concern cellulose methylation, its solution via the methylol derivative and ultimate regeneration. We have considered various feasible routes to methylation and wish to record our investigations to date.

High quality wood pulp, kindly supplied by Transparent Paper Ltd, Bury, Lancashire, UK, containing a high level of α -cellulose was used throughout this work. This pulp was finely divided then treated with a solution of sodium hydroxide (20%) with the temperature maintained at 25°C. Such treatment removes alkali-soluble components. The treated material was washed with dilute acetic acid until neutral and then with copious amounts of water before storing overnight in distilled water to ensure complete removal of traces of alkali. After removing all extraneous water, the cellulose was dried under reduced pressure, and stored in a desiccator, under vacuum, until required.

The solvents used in the programme, dimethyl sulphoxide, dimethylformamide, pyridine and tetrahydrofuran were thoroughly purified by established methods before use. Storage over selected drying agents was carried out so as to preclude the possibility of trace amounts of water interfering with the attempts at methylation. Paraformaldehyde was used as the source of formaldehyde for the same reason.

Typically, 100 g of solvent containing a dispersion of 1 g of cellulose were set-up in a flask equipped with a condenser, drying tubes and means of efficient agitation. Formaldehyde was generated by heating paraformaldehyde and introducing the ensuing formaldehyde into the reaction flask which was maintained at the reflux temperature of the system. Heating of the paraformaldehyde was continued until 8 g had decomposed and had been supplied to the reaction flask.

Application of the above technique

using dimethyl sulphoxide as solvent (reflux temperature, 280°C) produced a clear solution after 15 h. For the other three solvents no solution was apparent, the product appearing as a finely divided mass. The reflux temperatures employed were dimethylformamide at 152°C, pyridine at 115°C, and tetrahydrofuran at 65°C. However treatment of each of these reaction mixtures with an excess of dimethyl sulphoxide at room temperature produced immediate solution. This indicates that methylation of cellulose takes place to some degree in each of the solvents studied. However, the methylolated cellulose is only soluble in dimethyl sulphoxide. Regeneration of the methylolated cellulose by treatment with water or methanol is easily achieved, though the nature of the product is greatly dependent on the concentration of methylolated cellulose in the solvent. Thus it is possible to generate the product in either film or powder form.

Attempts at drying the films or fibres after regeneration, or the products isolated immediately after reflux, resulted in the emission of formaldehyde and the formation of products which were insoluble in dimethyl sulphoxide, and appeared as discontinuous gels. It is clear that crosslinking occurs on heating which results in the insolubility of the cellulose.

The mechanism by which cellulose dissolves in dimethyl sulphoxide/formaldehyde is dependent on the formation of the methylol derivative. As formaldehyde is generated in the system, a portion of it reacts with the cellulose hydroxyl groups with the primary hydroxyl groups being favoured. The solvent serves two functions before complete solution occurs. It must promote swelling of the cellulose and also help stabilize any intermediates formed during reaction. Such intermediates are hemiacetal containing units stabilized by hydrogen bonding. This enhancement of stability is a major factor in the case of dimethyl sulphoxide based solutions. One might anticipate that such stabilization would

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reduce tendencies toward crosslinking. On heating, this stabilization is overcome and crosslinkage becomes a predominant feature in the absence of dimethyl sulphoxide. The contribution by hydrogen bonding may explain the lack of solubility of the methylolated celluloses in solvents other than dimethyl sulphoxide since the formation for hydrogen bonds will be less likely.

Regeneration of the methylolated celluloses and drying of the films produced samples of good tensile characteristics, good dimensional stability but reduced flexibility. Certain of our objectives have been achieved. These include the production of methylolated cellulose in a range of commercially acceptable solvents. The methylolated

celluloses are sufficiently substituted to allow solution in dimethyl sulphoxide and subsequent regeneration in a desirable form whether as films or fibres. The main restriction is that the methylol derivative must not be allowed to become dry before regeneration is completed. The complete system of cellulose solution and regeneration, presented here, offers many advantages when compared to the xanthation process which is in use. Examples include greater ease of recovery of non-aqueous solvents for recycling and a much reduced corrosion problem.

Work is continuing, aimed at a more complete characterization of the intermediate and final products of this type of reaction, and an extension of the range of solvents for the methylol

derivatives.

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Melting behaviour of stress crystallized high density polyethylene

Introduction

The relation between the observed melting point of polymers and their crystalline morphology is of topical interest. The purpose of the present Letter is to draw attention to past work in our laboratories on the melt extrusion of high molecular weight linear polyethylenes which gave discrete melting points of over 150°C.

Most of this work was carried out on experimental polyethylene grades with a weight-average molecular weight of about 300 000 and a melt flow index ≈ 0.008 : (measured at 190°C/2.16 kg ASTM D/238 6S-T). The polymer was extruded through different die geometries at various melt temperatures. At melt temperatures of 160°C, the polymer could be readily extruded in a normal fashion and on solidification became opaque. When the melt temperature was reduced to about 148°C, the melt swelled up excessively on leaving the die, and a very high haul-off load was required to draw it back to the same cross-section as the die. Although the extrudate had a poor surface, it was more transparent and considerably stiffer than that made at 160°C. There was a gradation in the degree of transparency across the cross-section, the exact pattern of transparency depending on the configuration of the die design. It was the more transparent parts of the section that showed the melting point curiosity with which we are concern-

ed. With the simplest die geometries, such as a slot die having a 1 mm gap, 10 mm width with a 10 mm land length, there was a tendency for the process to be unstable and, in particular, for the die to block after a short period. Special die configurations were therefore developed in order to eliminate this tendency to instability. These included dies which accelerated the inside layers of the melt more rapidly than the outside layers and those in which the central layers were held at lower temperatures than the outside layers. Details of these dies are given in refs 1 and 2. All these dies gave extrusions at about 148°C which contained transparent regions with a high melting component.

Experimental

Thin samples of about 2 mg were cut from the extrudates and examined in a Perkin-Elmer DSC2 scanning calorimeter operating with a helium quench gas. In most cases the samples were scanned with a heating rate of 80°C/min to above their melting point.

Some of the 148°C extrudate was treated in fuming nitric acid for 74 h at 65°C using the method of Palmer and Cobbold³. After thoroughly washing in distilled water and drying under vacuum, the embrittled solid was disintegrated ultrasonically and the debris was examined in an electron microscope.

Results

Figure 1 shows a superposition of the d.s.c. scans for extrudates drawn from melts of 160°C and 148°C respectively. The 160°C extrudate gave a single melting peak at 135°C, whereas the 148°C extrudate gave a double peak, one centred at 132°C and another at 152°C. The relative areas of these peaks varies with position in the extrudate. In the most transparent parts we have found that up to about 10% of the total area of the melting endotherm can be associated with the high temperature peak.

The precise shape of the melting endotherm varies with the heating rate. At rates lower than 80°C/min an inter-

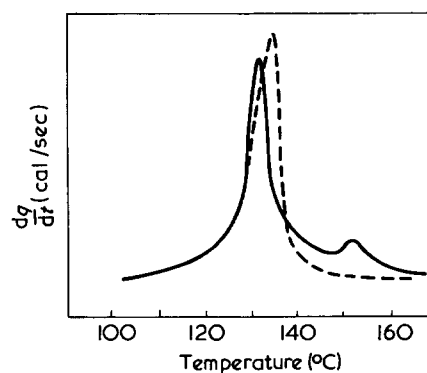


Figure 1 D.s.c. melting endotherms of extrudates: —, extruded at 148°C; ---, extruded at 160°C