STRUCTURAL STUDIES, REACTIONS, AND APPLICATIONS OF OXIDIZED CELLULOSES

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BY

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- ***Dedicated to my Late Parents***

CERTIFICATE

Certified that the work incorporated in the thesis entitled "Structural Studies, Reactions, and Applications of Oxidized Celluloses" by Vilas B. Chavan was carried out by the candidate under my supervision. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

AJVarma
A.J. Varma
Research Guide

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INTRODUCTION

I. INTRODUCTION

Cellulose is the most abundantly available naturally occurring organic material in the world. It is a naturally occurring polymer of glucose, and the accepted view is that it is a 1,4-ß-D-linked polyanhydro glucopyranose (Figure I.1). It is the principal constituent of the cell walls of higher plants, and provides them with their structural strength. It is estimated that 100 billion tonnes of cellulose in the form of renewable vegetation is produced every year on this planet. This translates into an availability of approximately 20 tonnes of cellulose for every person on earth (1). Indeed, the wide range of derivatisation of cellulose possible has given mankind a magnificent variety of products of academic interest as well as of industrial useage. It is more than a century since cellulose nitrate, cellulose acetate, cellulose xanthate, and many other derivatives were produced as industrial materials, and these continue to be important materials even today. Recent researchers have seen, expectedly, an ever-increasing interest in these materials, and development of new derivatives continues (2). Another major incentive for developing industrial materials based on renewable cellulose is that cellulose derivatives are generally considered to be biocompatible, biodegradable, environment-friendly, and non-toxic. Modern society is increasingly conscious of its responsibility to develop and use environment-friendly

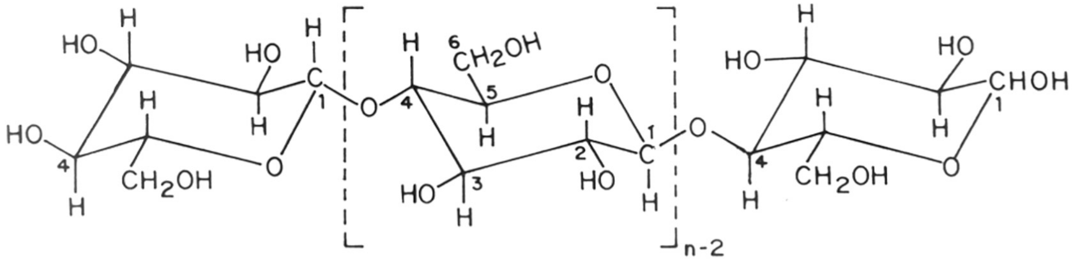

FIG. I·1: STRUCTURE AND CONFORMATION OF THE CELLULOSE MOLECULE materials, and several nations even have strong legislations in this regard.

Oxidation of cellulose to produce modified celluloses known as oxidized celluloses was first investigated in 1882 by Witz (3). This chemical modification of cellulose was seen to impart several desireable properties to cellulose, and therefore continues to be investigated till today (4-10).

A wide range of oxidising reagents such as sodium chlorite, potassium chromate, hypochlorous acid, sodium metaperiodate, nitrogen dioxide, nitrogen tetroxide, etc. are known to oxidise cellulose, and the structure and properties of the oxycellulose produced depends on the reagent used, its concentration, pH of the medium, reaction time, temperature, etc. For example, nitrogen tetroxide is known to oxidise the C-6 hydroxyl of cellulose to produce a carboxyl group, while sodium metaperiodate selectively cleaves the C-2 - C-3 bond to produce 2,3-dialdehyde cellulose. From the large number of possible oxidation products of cellulose, 2-3 dialdehyde cellulose, 2-3 dicarboxycellulose, and polyglucuronic acid have found interesting applications (1, 11-22).

Partial oxidation of cellulose can lead to a variety of polymers having different functional groups, such as aldehyde and carboxyl, in addition to the primary and secondary hydroxyl groups already present. This can increase the range of applications of cellulose for industrial applications. Oxidized cellulose has increased affinity for various dyes (12), and this has great significance for the textile industries. Fire resistant materials can be made from oxidized cellulose by reacting them with tris(hydroxymethyl) phosphine, alkylene oxide, and tris(aminoethyl) borate (13,14). Oxidized cellulose can have two carboxylate groups, and therefore can have applications in removal of heavy metals from aqueous solution by flocculation (15), and its good sequestering power for ions causing hardness in water results in its useage as a detergent builder (16). Oxidized celluloses show improved initiation characteristics compared to the unoxidised samples of cellulose in graft copolymerisation studies, and give larger yields of graft copolymers (17,18). Use of oxidized cellulose and as reaction-incorporated fillers in epoxy matrix have been shown to improve cure rates, prevent phase separation by chemically linking the filler and the polymer matrix, and eliminate the compounding step for addition of curing agent (19). Oxidized cloth has been shown to be useful for immobilising enzymes like collagenase in bandages for wound healing (20). Microbicides, which are safe and useful for textiles, coatings, and building materials, have shown 100% fungicidal effect when immobilized on oxidized cellulose (21). Oxidized cellulose, when converted to difluoroaminated dialdehyde cellulose, are useful in explosives and propellants (22).

Thus, it is clear that oxidized celluloses represent an important class of cellulose derivatives. Oxidation reactions result in a change in the molecular weight and molecular weight distribution, crystallinity and other structural features, solution properties, thermal properties, etc., of the resulting polymer molecule. A search of the literature showed that no detailed systematic study of the structure and properties of oxidized cellulose samples having incremental changes in their degrees of oxidation had ever been reported. In view of these lacunae, as well as their diverse applications and potential for further development as industrial materials, an investigation into the structure and properties of oxidized celluloses in the solid state as well as in solution seems to be warranted. Therefore, these aspects form the subject matter of this dissertation.

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SCOPE OF WORK

II. SCOPE OF THE WORK

As mentioned in the introduction, there is a great need to synthesize a series of oxidized cellulose samples having incremental changes in their degrees of oxidation. These samples are then to be systematically studied for their structural characteristics, reactions, properties, and applications, both in the solid state and in solution. In order to achieve these goals, the following studies were conducted, which represents the scope of this dissertation research:

1. Synthesis of 12%, 30%, 60%, 80%, and 98% 2,3-dialdehyde cellulose (based on glucose monomer units), using sodium metaperiodate as the oxidising reagent in aqueous dispersion of cellulose powder.

2. Synthesis of 12%, 30%, 60%, 80%, and 98% sodium 2,3-dicarboxylate cellulose, (based on glucose monomer units), using sodium chlorite as the oxidising reagent in aqueous dispersion of 2,3-dialdehyde cellulose.

3. Synthesis of 12%, 30%, 60%, 80%, and 98% 2,3-dicarboxy-cellulose (based on glucose monomer units), using ion-exchange resins and hydrochloric acid treatment in aqueous dispersion of sodium 2,3-dicarboxylate cellulose.

4. Synthesis of cellulose diamine by the reaction of 30% dicarboxycellulose, first with thionyl chloride in carbon tetrachloride dispersion, followed by reaction with 1,3-diaminopropane, also in carbon tetrachloride dispersion.

5. A wide-angle X-ray diffraction study of the crystallinity changes occurring in
   (i) pure cellulose powder (~ 85% α-cellulose)
   (ii) 30%, 60%, 80%, and 98% 2,3-dialdehyde cellulose
   (iii) 12%, 30%, 60%, and 98% 2,3-dicarboxycellulose
   (iv) 12%, 30%, 60%, 80%, and 98% sodium 2,3-dicarboxylate cellulose.

These studies were conducted using a Philips PW 1730 X-ray generator equipped with a CuK_α target and β Ni filter. Diffractometer scans over a 2θ range of 6-30° were taken.

6. High resolution solid state C-13 NMR studies with magic-angle spinning of the following cellulose and oxidized cellulose samples were studied:
   (i) pure cellulose powder (~ 85% α-cellulose)
   (ii) 30%, 60%, 80%, and 98% 2,3-dialdehyde cellulose
   (iii) 30%, 60%, 80%, and 98% 2,3-dicarboxycellulose
   (iv) 30%, 60%, 80%, and 100% sodium 2,3-dicarboxylate cellulose.

A Bruker MSL-300 NMR spectrometer was used to obtain solid state C-13 NMR spectra with cross polarization - magic angle spinning, operating at 75.47 MHz.

7. Thermogravimetric analysis (TG) of the following cellulose and oxidized cellulose samples were carried out:
   (i) pure cellulose powder (~ 85% α-cellulose)
   (ii) 30%, 60%, 80%, and 98% 2,3-dialdehyde cellulose
   (iii) 60%, 80%, and 98% 2,3-dicarboxycellulose
   (iv) 60%, 80%, and 98% sodium 2,3-dicarboxylate cellulose.

8. Differential thermal analysis (DTA) of the following cellulose and oxidized cellulose samples were carried out:
   (i) pure cellulose powder
   (ii) 30%, 60%, 80%, and 98% 2,3-dialdehyde cellulose
   (iii) 60%, 80%, and 98% 2,3-dicarboxycellulose
   (iv) 60%, 80%, and 98% sodium 2,3-dicarboxylate cellulose.

9. Polyelectrolyte behavior of 98% sodium 2,3-dicarboxylate in aqueous solution, with and without added sodium chloride was studied. For this purpose, reduced viscosity versus concentration studies using an

Ubbelodhe viscometer immersed in a constant temperature bath, was used to obtain the required data. In another study, a Brookfield viscometer model DV-1 was used to obtain Brookfield viscosity (in centiPoise) versus concentration data.

10. Rheological data for 1.5% and 3.0% aqueous solutions of 98% sodium 2,3-dicarboxylate cellulose was obtained by measuring Brookfield versus shear rate (using a Brookfield model DV-1 with digital read-out and plotting shear stress versus shear rate. For the latter study, a Ferranti-Shirley cone-plate viscometer was used at 200 to 800 rpm.
11. Practical application of polyelectrolyte characteristics of 98% sodium 2,3-dicarboxylate cellulose in aqueous solution was investigated by a flocculation study of aluminium sulfate dissolved in water. 1 X 10^{-3} moles/lit aqueous solutions of sodium 2,3-dicarboxylate cellulose and commercial sodium carboxymethyl cellulose were used to flocculate solutions of aluminium sulfate in the concentration range 5 X 10^{-3} to 1 X 10^{-1} moles/lit.

12. Practical application of polyelectrolyte characteristics of 98% sodium 2,3-dicarboxylate cellulose in aqueous solution was investigated by Ca^{++} ion binding studies. A calcium ion-selective electrode of Orion Research make along with a reference electrode was

used. A digital pH Ion meter (EILUK) of M/s. Global Electronics, Hyderabad, was used for obtaining the millivolt readings.

13. Practical application of oxidized cellulose and cellulosic diamines made from oxidized cellulose as reaction-incorporated fillers in polymer composites. An epoxy resin was blended with 10% by weight of pure cellulose powder, 30% 2,3-dicarboxycellulose, and 30% 2,3-dicarboxycellulose containing 8% chemically reacted 1,3-diaminopropane to obtain cure characteristics at 120°C using a Tecam Gelation Timer, Model GT4, manufactured by Techne (Cambridge) Ltd., England. In some experiments, 1,3-diaminopropane had to be added for obtaining cure times.

LITERATURE SURVEY

III.I X-RAY DIFFRACTION STUDIES OF CELLULOSE AND ITS DERIVATIVES

X-rays are generated in cathode-ray tubes when high energy electrons impinge on metal targets. X-ray diffractometry permits determination of crystalline states without destroying samples (1). X-rays made incident on the samples fixed on the axis of the spectrophotometer are diffracted by the sample. The intensities of the diffracted X-rays are plotted against the rotatio angle of the sample (Fig. III.1.1).

When X-rays are focused on a polymer sample, two types of scattering occur. If the sample is crystalline, the X-rays are scattered coherently, i.e., there is no change in wavelength or phase between the incident and scattered rays. Coherent scattering is commonly referred to as X-ray diffraction. If the sample is semicrystalline, the scattering is incoherent, i.e., there is change both in wavelength and phase. Incoherent scattering is referred to as diffuse diffraction (2).

For both experimental and theoretical reasons, it is useful to separate X-ray diffraction effects into small and wide angle according to the size of the angle of deviation from the direct beam, which is designated as 2θ. Small angle diffraction effect is observed at angle smaller than about

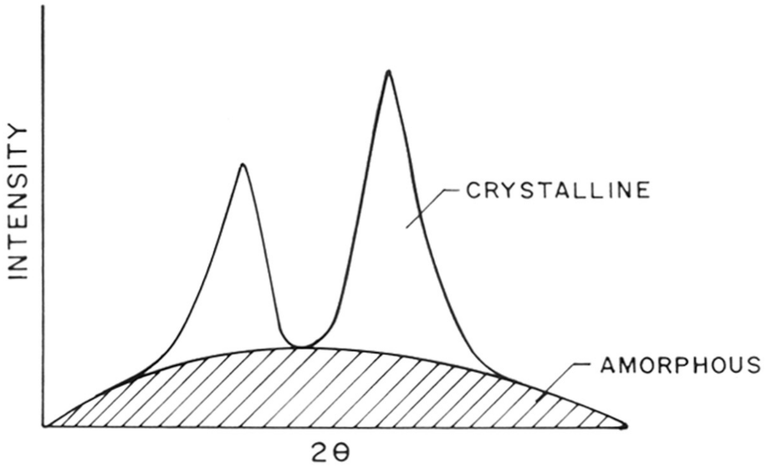


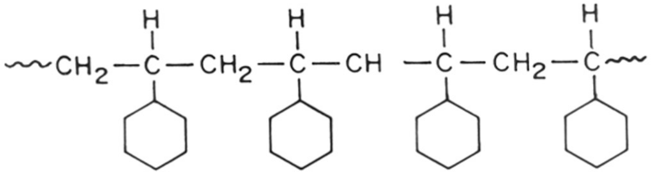
FIG. III·1·1: WAXD OF A SEMICRYSTALLINE POLYMER (Ref. 7)

2° or 3°. Wide angle diffraction effect is observed at larger angle up to 180°. Small angle diffraction is used for measuring thickness of tiny particles.

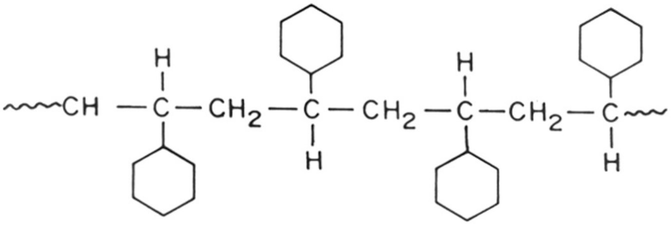
The X-ray diffraction method is a powerful tool for investigating the structure of polymeric compounds (1-7). Crystalline polymers are those whose molecules have geometric regularity. Semicrystalline polymers have crystalline and amorphous regions. Solid polymers can exist in an amorphous state characterized by disordered arrangements of molecules, and in a crystalline state characterized by three dimensional order. The X-ray method can distinguish between different crystalline forms of the same compound. Percentage crystallinity can be calculated by area measurements under the crystalline peaks and amorphous humps (4). The physical and mechanical properties of polymers are dependent on the degree of crystallinity. Both crystalline and amorphous polymers can be oriented, for example, by stretching the polymer at a high temperature and maintaining it in the stretched condition while rapidly chilling (8).

A semicrystalline polymer can be described by the percentage of crystallinity, the size, and size distribution of the crystalline regions and when oriented, by the degree of orientation of its crystalline and amorphous portion (9). Fig. III.1.2 shows the X-ray diffraction curve of partly crystalline isotactic polystyrene and Fig. III.1.2b shows similar curve for amorphous iotactic polystyrene which was obtained by melting and rapidly cooling a part of isotactic polymer. Both the curves are corrected for incoherent scattering by subtraction of the cross-hatched areas in the lower portion of figures. Curve III.1.2a, which was obtained with partly crystalline polymer, can be resolved into two parts corresponding to scattering by amorphous polymer (shaded) and to scattering by crystalline polymer (unshaded).

CHEMICAL STRUCTURE



isotactic polystyrene



syndiotactic of polystyrene

Cellulose is a crystalline and polymorphic compound. These polymorphic forms can be studied by X-ray diffraction methods. Each polymorphic form, when treated with chemical reagents, physical forces, or subjected to high temperatures, can either change its polymorphic form or undergo changes in its relative crystallinity. Wide-angle X-

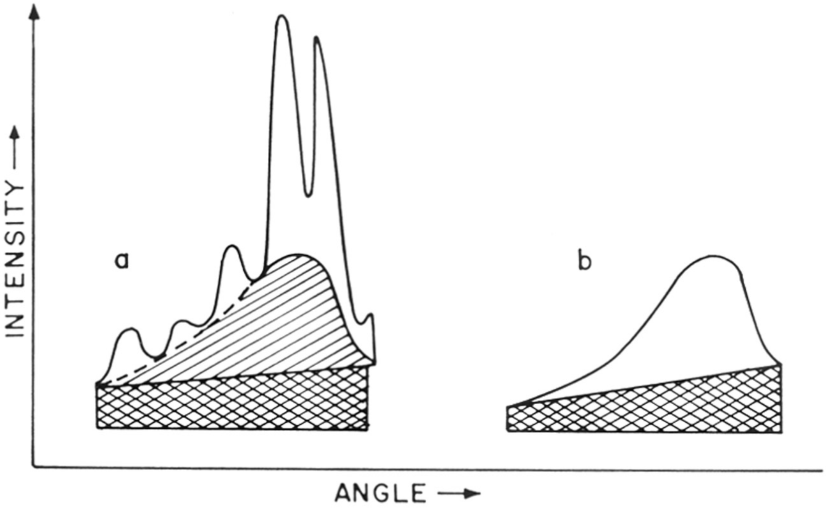


FIG. III·1·2: DIFFRACTION CURVE FOR POLYSTYRENE
a : PARTLY CRYSTALLINE , b : AMORPHOUS (Ref. 9)

ray diffraction is an effective tool to determine these changes (10-14).

Study of variety of samples of cellulose with crystallinity using different instrument such as Dynamic thermogravimetry, differential thermogravimetry (DTG) and Fourier Transform IR spectroscopy have been carried out (15,16). The data thus obtained compared the crystallinity index (C.I.) detected by these methods with the X-ray diffraction method. Cotton chemically modified with ethylamine (17), and wood treated with NH_3 at 140°C under high pressure (18) were studied by X-ray diffraction. In the latter case, it was shown that the cellulose existed as "Cellulose III" polymorph (19-21).

Davidson showed that the X-ray diagram of cellulose becomes more diffuse as the degree of oxidation with periodic acid increases. Cotton cellulose is decrystallized by periodate oxidation (22). It was estimated that the kinetics of decrease in crystallinity index (C.I.) is pseudo Zero order for over 60% of the reaction and is consistent with diffusion controlled mechanism. Mc-Burney (23) had studied oxidized cellulose samples by X-ray diffraction and intrinsic fluidity. These data indicate that oxidation most likely occurs in the amorphous region of the samples. A study on cellulose and periodate oxidized cellulose heated at temperatures of 120°C, 180°C, & 240°C for three hours showed that crystallinity decreases almost proportionately to the degree of oxidation of the starting cellulose (24). Nitrogen dioxide oxycellulose (25) was characterized for their acid-hydrolytic and enzymic degradation. It was observed that the crystalline region of cellulose was possibly oxidized while the crystallinity was maintained. However, the oxidation did not occur uniformly in the crystalline regions. It was concluded that oxidation occurred in the edge areas of the elementary fibrils.

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III.2 HIGH RESOLUTION SOLID-STATE CP/MAS C-13 NMR FOR STRUCTURE ELUCIDATION OF CELLULOSE AND ITS OXIDATION PRODUCTS

High resolution NMR spectra of solids have been reviewed in several texts (1-5). A large number of polymers which are not soluble in non-polar and non-interacting solvents, as well as crosslinked polymers, are now conveniently studied by solid state NMR using the cross-polarisation and magic-angle spinning technique.

In this literature review, the application of C-13 cross-polarisation, magic-angle spinning solid state NMR to the study of crystalline structure of cellulose, cellulose polymorphs, and cellulose derivatives has been brought out.

In order to obtain C-13 NMR in the solid state with a resolution close to that of solution spectra, several techniques have to be applied, such as magic angle spinning, cross-polarisation, and high power decoupling. In dilute spin system such as C-13 the total interactions encountered are shown in Eq.(1)

$$\text{H (total)} = (\text{Zeeman} + ({}^{1}\text{H} - {}^{13}\text{C dipolar}) + ({}^{13}\text{C} - {}^{13}\text{C dipolar}) + (\text{Chemical shift anisotropy}) \qquad (1)$$

The ^{1}H - C-13 interactions are decoupled using very high power decoupling fields at the proton resonance frequency.

The C-13 - C-13 dipole-dipole interactions are neglected, since the natural abundance of C-13 nucleic is very low (1.1%).

Magic-angle spinning

In the solution C-13 NMR spectrum of a molecule, the chemical shift of each carbon atom depends on its environment, and are the isotropic values obtained by averaging all possible orientations of the nucleus to the applied magnetic field, due to the random motion of the molecules.

However, in the solid state C-13 NMR spectrum for a single crystal, a single signal will appear at a position determined by the orientation of the nucleus to the magnetic field. For a polycrystalline solid all orientations are possible, and leads to a large number of signals. In order to average these signals their isotropic values, the sample has to be spun about an axis at an angle (known as the "magic-angle") of $\theta = 54.74°$, where θ is the angle between the spinning axis and the magnetic field vector. At $\theta = 54.74°$, the term $(3 \cos^2\theta - 1)$ becomes zero, giving rise to the single isotropic shift value, the same as for random motion of the molecule possible in solution. The small differences between the solid state and solution spectra are due to the structural and environmental differences prevailing in the two states.

Cross-Polarization

The technique of cross-polarization, discovered by Pines et al. (6), increases the signal-to-noise (S/N) ratio of the dilute nucleus being observed by first spin locking the proton and carbon spins for a time Tc known as the contact time. The magnitudes of the spin locking field H_{1H} and H_{1C}, are determined by the Hartmann-Han condition such that: $Y_C H_{1C} = Y_H H_{1H}$, where Y is the magnetogyric ratio. The total magnetization of the dilute spins is increased to a theoretical maximum of Y_H/Y_C, giving a corresponding increase in S/N. For the ^{13}C nuclei, the maximum increases in S/N is approximately four fold. In addition, the repeat time of the experiment depends only on the proton spin-lattice relaxation times which are much shorter than the carbon values leading to more efficient experiments.

The combined cross-polarization and magic angle spinning (CP/MAS) experiment was first reported by Schaefer and Stejskal (7). Since then, chemists, and particularly polymer chemists, have shown tremendous interest and dependence on this technique to elucidate structural information in the solid state.

The fundamental difference between solid state NMR and X-ray diffraction results is that NMR reflects short distance molecular interactions and therefore is far more likely to represent localised order or disorder than X-ray crystallography. Therefore, solid state NMR studies of crystalline and semi-crystalline polymers would complement the understanding achieved by X-ray crystallographic studies.

A number of structural features such as crystal structure, morphology and polymorphic forms, can be inferred by a study of C-13 NMR of cellulose by the cross polarization/magic angle spinning (CP/MAS) technique.

The groups of Atalla et al. (9) and Earl and VanderHart (10) simultaneously reported the CP/MAS C-13 NMR spectrum of cellulose. Atalla (9) investigated the spectra of highly crystalline Cellulose I and Cellulose II, as well as that of completely amorphous cellulose I. He noted that the C-1 resonances for the two polymorphic forms of cellulose and the C-4 resonance of cellulose II showed splitting into two lines of approximately equal intensities, providing evidence for the presence of two types of glycosidic linkages and the authors interpreted this as an alternation of nonequivalent glycosidic linkages along the chains. The spectrum of amorphous cellulose I had clearly different features from that of crystalline cellulose I, with all the peaks being broad and unresolved.

Earl and VanderHart (10) studied the CP/MAS spectrum of a dried sample of microcrystalline cellulose I. They measured the longitudinal, T_{1C}, and transverse, T_{2C}, relaxation times for the peaks in the spectrum, and derived several qualitative conclusions regarding the structure of cellulose I. The T_{1C} values showed that the molecular motions are in an intermediate range of glassy synthetic polymers and highly crystalline materials. The T_{1C} and T_{2C} data also showed a faster relaxation for the carbons in the upfield tail of C-6 relative to the sharp peak, and were interpreted as being the result of greater mobility for the carbons in the tail. The authors also felt that the splitting of C-4 into two separate resonances, the splitting of C-1 into two peaks of nearly equal intensity, and the shoulder on C-6 all point to the glucose monomer units being in two magnetically inequivalent environments.

These same authors, in a more recent paper (11) compared the spectra of cotton linters, ramie, and various hydrocelluloses prepared from cotton, bacterial cellulose, and algal cellulose, and found the same peak positions but observed differences in resolution of the C-4 and C-6 peaks. They ascribed these differences to the differences in the morphology of the samples. The peak positions of C-1, C-4, and C-6 are characteristic of different polymorphs of cellulose, and NMR is a useful tool to distinguish them.

Table III.2.1: C-13 chemical shifts (ppm relative to TMS) from the 22.6 MHz CP/MAS spectra of solid cellulose polymorphs (8,11).

	C-1	C-2, C-3, C-5	C-4	C-6
Cellulose I	105.0	74.1, 72.0	90.0	67.0
Cellulose II	107.9, 106.2	77.7, 76.0, 73.4	88.9	64.0
Cellulose IV	103.3	72.3	82.2	62.3

Fyfe et al. (8) reported the chemical shifts of cellulose oligomers (triose, tetraose, pentaose, and hexaose) and compared the chemical shifts to that of cellulose II. They found that beyond cellulose tetraose, increase in molecular weight did not significantly change the peak positions. These authors interpreted the near merging of the C-4 and C-6 peaks with the C-2, C-3, and C-5 "massif" in cellulose IV as being due to the low crystallinity of this polymorph.

In order to remove the uncertainties associated with conclusions from comparative studies of celluloses taken from different biological sources, Maciel et al. (12) used cotton linters for preparing four samples of different crystallinities by the mechanical degradation method of ball-milling. The sharp spectral features of the cotton linter spectrum progressively became broader as the crystallinity decreased. This confirmed the views of Earl and VanderHart. Zhbankov et al. (13) proposed a method for separating the signals in the NMR spectra of cellulose I and for calculating the degree of crystallinity of dry and swollen cellulose I. Sterk et al. (14) investigated 24 different samples of cellulose and calculated the crystallinity on the basis of relative intensity ratios.

Teeäär and Lippmaa (15) studied the C-13 spin-lattice relaxation times T_1 of hydrolyzed cotton cellulose and assigned the C2-C3-C5 peaks based on these data. Their relaxation data was very different to that obtained by Earl and VanderHart (10) with the observation that relaxation in the amorphous regions being much faster than in the crystalline part (indicating higher mobility). These studies of Teeäär were followed up by investigating the crystallinities by CP/MAS NMR and X-Ray diffraction methods (16).

Horii et al. (17,18) used a new approach to determine the torsion angles by C-13 isotropic chemical shifts and to characterize the complicated chain conformation of cellulose in the crystalline and non-crystalline regions. They carried out relaxation studies under a variety of conditions to arrive at their conclusions. They correlated chemical shifts to torsion angles, and analyzed the contributions of the crystalline and non-crystalline components in terms of spin-lattice relaxation times. A recent paper (19) has studied the influence of conformational and packing effects.

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III.3 THERMAL ANALYSIS OF CELLULOSE AND ITS DERIVATIVES

Thermogravimetric analysis is an important tool for the characterization of polymeric materials. By studying the results of different thermal methods of analysis (TG, DTA, DSC etc.) it is possible to elucidate important information such as oxidation stability, degradation kinetics, decomposition temperature, phase transitions, etc. (1-5).

Thermal studies of cellulose and its derivatives have been widely reported in literature; the degradation products are known to give a series of complex chemical reaction products. Whether an oxidizing atmosphere was present or an inert atmosphere, identical degradation processes occurred (6). Pyrolytic decomposition gave 65% tar, which contained 80% levoglucosan (1,6 anhydro-β-D-glucopyranose). Under vacuum, greater percentages of levoglucosan can be obtained (7). Below 200°C, the dominating reaction is oxidation, but at higher temperatures, depolymerisation is the main reaction (8). The discussion on mechanism of levoglucosan formation is based on transglycosylation (9) and free radical mechanisms (10). A detailed DTA study of pyrolysis of pure cellulose in air has been reported by Dollimore and Hoath (11). The thermal decomposition of cotton linters, viscose rayon, and bagasse pulp showed that the activation energies depended on the purity of the sample. Bagasse pulp had low activation energy due to the presence of pentosans and volatiles (12). Jain et al. have made detailed thermal analysis of cellulose and a large number of their derivatives and also investigated the charred residues, calculated the activation energies, and proposed a mechanism for acid-catalysed thermal degradation (13,14).

DTA and TGA of cellulose oxidized by use of periodate, periodate-chlorite, chromate,chromate-chlorite, hypochlorous acid, and hypochlorous acid-chlorite have been reported (15). Oxidation was found to generally destabilise cellulose. Greater destabilisation occurred for dicarboxycellulose than for the dialdehydecellulose (15). The activation energies for thermal degradation as well as the resistance to degradation decreased in the following order: nonoxidized cellulose, reduced dialdehydecellulose, carboxymethylcellulose, dialdehydecellulose, monocarboxycellulose, and tricarboxycellulose (16-18). In argon atmosphere, below 320°C nonoxidized cellulose was comparable to monocarboxycellulose and dialdehydecellulose; the degradation patterns of the latter two compounds are explained by dehydration, decarboxylation, decarbonylation, estorification reactions, and levoglucosan formation (17,18). Concentrations of aldehyde greater than 20 meq/100g of cellulose are required to cause noticeable destabilisation of cellulose (15). Oxidized cellulose having complex structures such as H_3PO_4-$NaNO_2$-oxycellulose were investigated (19). TGA curves of 40%, 90%, and 120%

(theoretical oxidation) in nitrogen atmosphere showed an abrupt peak at 250°C for the 40% oxidized sample, but no peak in the 450-500°C region, whereas for the 90% and 120% oxidized samples peaks at 250°C as well as in the 450-500°C region were observed. This showed that at 40% oxidation, very little dicarboxy structure was present (19).

The calcium salt of dicarboxycellulose is much more stable, while the aluminum salt is destabilised (15). The effect of counterions has also been recently discussed by Chinese researchers (20). Maekawa et al. (21) found that Zn salts of carboxycellulose had the highest thermal stability while Cu salts had the lowest stability. Ca salts were found to have anomalous thermal bahaviour, with a two-stage thermal decomposition (21).

Since the rate of heating of the sample can have a profound effect, a study was performed for weight loss and temperature profiles at different heating rates (22). Effect of the crystallinity of the cellulose sample has also been reported (23-24).

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III.4 RHEOLOGY OF POLYELECTROLYTES BASED ON CELLULOSE

Solution viscosity is a measure of the size of a polymer molecule in that particular solvent, being empirically related to the molecular weight by the following relationship (known as the Mark-Houwink relationship):

η = KM^a

M = Molecular weight of the polymer.

K = Constant for the given polymer for a particular solvent and temperature.

a = Function of the geometry of the molecule.

η = Intrinsic viscosity.

\`K´ and \`a´ are constants determined from the double logarithmic plot of intrinsic viscosity and molecular weight.

Rheology is defined as the science of the deformation and flow of matter and is concerned with the response of materials to mechanical force. The flow may be irreversible, reversible, elastic deformation, or a combination of both (1-12). Polymer rheology has received the most intensive attention of rheologists, and its importance is increasing. This may be attributable to the steadily increasing world demand for polymeric materials as a substitute for many natural materials (e.g. fiber, wood, metal, rubber).

A variety of forces are applicable to polymer deformation, and some of the basic terms used in rheology are defined briefly.

Shear stress (τ) is defined as the force (F) in dynes per unit of surface area (A) in square centimeters, that is,

$$\tau = \frac{F}{A}$$

Shear strain (γ) , is the amount of deformation of one plane with respect to another.

$$\gamma = \frac{X}{Y}$$

Resistance to shear is the shear modulus, G, which is the ratio of shear stress to shear strain.

$$G = \frac{\tau}{\gamma}$$

Shear rate ($\dot{\gamma}$) , is defined as the gradient of the velocity of the flowing liquid and it is given by,

$$\dot{\gamma} = \frac{d\gamma}{dt}$$

If the viscosity of a solution is independent of the rate of shear, it is said to be Newtonian, as shown in Fig. III.4.1.

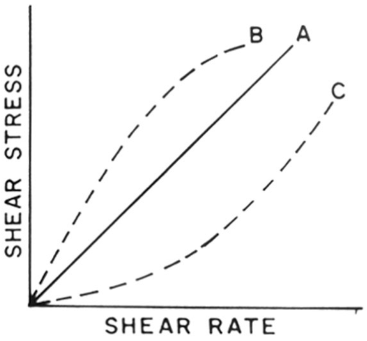


FIG. III·4·1 : TYPES OF SHEAR FLOW
A : NEWTONION , B : SHEAR THINING
C : SHEAR THICKNING (Ref. 1)

Curve A shows Newtonian behavior i.e. shear stress increases in proportion to the shear rate.

Curve B represents shear thinning behavior, i.e. a reversible decrease in viscosity with increasing shear rate.

Curve C represents shear thickening behavior i.e. one in which viscosity increases with increasing shear rate.

The dimensions of polyelectrolytes (polyions) are strongly dependent on its concentration in aqueous solutions; they are in highly extended form at low concentrations, and viscosity increases with increasing dilution. This is the typical behavior of a polyelectrolyte. Addition of simple salts decreases the viscosity of the polyelectrolyte. A typical plot of η_{sp}/C versus concentration is shown in Fig. III.4.2 (13,15).

The viscosity of a pseudoplastic liquid such as aqueous NaCMC solutions decreases with increasing shear rate (shear thinning) (16). Had it been a Newtonian liquid, a straight line would have been observed, as shown in Fig.III.4.3a which is continuously decreasing after going over to a high shear rate region as shown in Fig.III.4.3b is observed.

There have been a large number of publications in the area of solution properties of sodium carboxymethyl cellulose (NaCMC) (17-37), with which the solution behavior of sodium 2,3-dicarboxy cellulose can be compared.

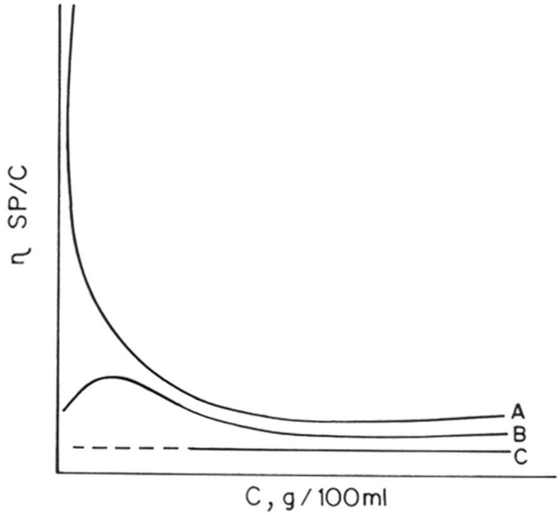
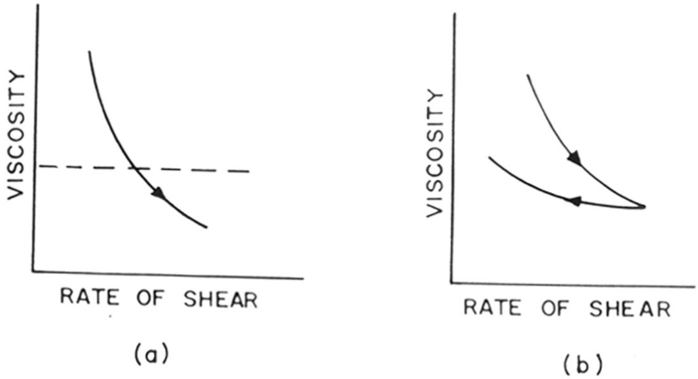


FIG. III·4·2: REDUCED VISCOSITY OF POLY (4-Vinyl-N-butyl pyridinium bromide) SOLUTION
A) WATER AS A SOLVENT B) 0·001N POTASSIUM BROMIDE AS A SOLVENT C) 0·03N POTASSIUM BROMIDE (Ref. 13, 14)



(a)

(b)

FIG. III·4·3: VISCOSITY VERSUS RATE OF SHEAR OF NaCMC
a) SHEAR THINING (—) NEWTONIAN (---)
b) SHEAR THINING LIQUID WITH THIXOTROPY (Ref. 16)

Fujita and Homma (34) studied the non-Newtonian solution behavior of dilute solutions of NaCMC at low shear rates (50-1000 sec^{-1}). In the salt free solutions, the n_{sp}/C versus shear rate curves showed an upward trend; the initial slope of each curve increased markedly with increasing dilution. The same plots for solutions with constant ionic strength (1.5 X 10^{-3} mole/l) were nearly straight lines, with the slopes of the straight lines decreasing with increasing dilution. The intrinsic viscosity at constant shear rates for the isoionic system was independent of shear rate. These studies showed the dramatic influence of addition of small amounts of neutral salt on the viscosity and its shear rate dependence. A more recent study (35) using rotational viscometry to study the rheological behavior of aqueous solutions of NaCMC and its derivatives methyl carboxymethyl cellulose and hydroxyethyl carboxymethyl cellulose with and without the addition of electrolytes like NaCl and $CaCl_2$ showed that the viscosity of all the solutions studied in the absence of added electrolyte decreased with increasing temperature. On the other hand, in the presence of added electrolyte, there was either an increase or decrease in viscosity depending on the cellulose ether type and concentration of the electrolyte. They found similar activation energy values (22.3-27.6 IJ/mol) of viscous flow of aqueous solution of all cellulose ethers in the absence of electrolytes, but there were significant differences in the presence of added electrolytes. This paper again underscores the dramatic influence of added electrolytes.

Narayan and Ramasubramanian (36) investigated the viscosity dependence of five polysaccharides - NaCMC, alginate, karaya, guar and xanthan - on concentration, shear rate, and temperature, and also calculated the apparent activation energy for flow. The polyanions (NaCMC and alginate) had high activation energies for flow at low shear rates, but decreased with increasing shear rate. The neutral polysaccharides had low activation energies which were independent of shear rate. Another difference between the two classes of polysaccharides was that the neutral polysaccharides like guar had high viscosities even at low concentrations, exhibiting a high degree of pseudoplasticity, while the polyanions NaCMC and alginate had high viscosities only at high concentrations with some dilational (polyelectrolyte) contribution. However, some neutral polysaccharides of complex structure also show such properties. deButts et al. (37) had earlier reported on the rheology of thixotropic and non-thixotropic pseudoplastic NaCMC solutions. They tried to unravel a molecular picture of NaCMC solutions. This molecular picture involved gel centers and electrostatic and hydrogen-bonding forces. The presence of polyvalent cations increased thixotropy, gelling, and precipitation, which further supported the molecular picture. A similar network structure and its dissolution behaviour was investigated recently (38). Thus, rheological studies have provided a sound basis to unravel the comformational and configurational properties of polymers.

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III.5 FLOCCULATION PROPERTIES OF POLYSACCHARIDE DERIVATIVES

The aggregation of small masses in liquid media is described as flocculation. It is a balance between electrical repulsion and van der waals forces of attraction as explained in the theory investigated by Deryagin and Landau and Verwey and Overbeek (DLVO theory) (1-3). The flocculants are classified as 1) inorganic, 2) synthetic organic products, 3) natural organic products, 4) synthetic polymeric products.

Flocculants have been used in very large scale in a wide variety of applications e.g. water treatment, oil recovery, soil stability etc. Naturally occurring organic polymers such as glue and starch have found wide use in the mineral processing area.

Polymeric flocculants have the following advantages: 1) flocs are larger, 2) they are stronger, 3) they are formed very fast, 4) salt concentration is not high therefore less sludge is generated.

Flocculation occurs by the following methods:

1) Bridging flocculation arising from adsorption on polymer chains (4-7). Here, in addition to ionic interactions, non-ionic interactions (hydrophobic bonding, H-bonding) also play an important role.

2) Charge neutralization mechanism can operate when the polymer and the particle have opposite charges (8-10).

Though charge neutralization goes a long way towards explaining the observed behavior, there are some effects of molecular weight and ionic strength also, which requires modified mechanisms. In water and effluent treatment, usually cationic polymers are used, since most particles are negatively charged.

Water soluble polymers are widely used for flocculating suspension of finely divided mineral either for clarification of the water or recovery of the solids (11). Selection of the flocculant is generally on trial and error basis. The study of the flocculant requires a knowledge of the surface chemistry of the mineral in water and mechanism of adsorption of the polymer. The use of chemical coagulation using alum to clarify water for drinking purpose is an ancient practice.

Naturally occurring compounds like alum have been used since long for clarification of water (12,13). However, a large number of natural polymeric flocculants such as glue, starch, cellulose and their derivatives are being used in many applications.

Cellulose derivatives are used as flocculant for recovery of Ag from waste water (14,15). NaCMC has been used as flocculating agent in sugarcane juice (16), surface water purification (17) and sludge removal (18) and for dewatering sludges (19).

The stability of silica solution was studied in the presence of adsorbing hydroxyethylcellulose and nonadsorbing sodium carboxymethylcellulose. The stage of aggregation was monitored by turbidity measurements. Flocculation due to polymer bridging was observed at low polymer addition, while at higher polymer concentration flocculation induced by depletion mechanism was observed (20,21). The red mud is flocculated using dextran and synthetic anionic polymer in the liquor. The liquor may be the primary settler slurry, the secondary clarification liquor or liquor from > 1 of the red mud washing stages (22). The process is especially useful where the liquors are high in carbonate content.

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III.6 BINDING OF CALCIUM BY POLYSACCHARIDE DERIVATIVES

The binding of relatively small ions to neutral or charged polymers is an important property of the polymer, and forms the basis of industrially useful materials on the one hand and biological model systems on the other. The strength of the complex so formed (1-3) can be described by an equilibrium constant, as follows:

$$M^{+2} + L^{-N} \rightleftharpoons ML^{2-N}$$

$$Km = \frac{[ML^{2-N}]}{[M^{+2}][L^{-N}]}$$

where

M = metal ion

L = ligand

N = valency

Use of ion-selective electrodes affords a convenient method of determining the stability constants (4,5). In recent years there has been tremendous industrial interest in utilising the calcium sequestering property of polysaccharide derivatives in the lucrative detergent business as a builder (6-13). Phosphorus-free detergent builders have been reported by the use of oxidized cellulose (7,8), dicarboxyglucan (9), carboxylated starches (13), and oxidized maltodextrins (10). Binding studies of Ca^{+2} and Mg^{+2} by 2,3-dicarboxyamylose and 2,3-dicarboxycellulose (DCC) have been investigated (11,12). DCC has also been investigated for the recovery of heavy metallic ions under mild conditions (12).

Theoretical work on the counterion binding for some polysaccharides has been reported (14,15). Thermodynamic parameters for the exchange of cations with sodium ions on cellulosic polyanions have been determined (16). These polyanions have similar properties to biological polyelectrolytes on the one hand and ion-exchange resins on the other, with respect to their ion-binding characteristics (16). Structural and conformational effects on the complexation of calcium by 2,3-dicarboxy derivatives of β-cyclodextrin, amylose, and cellulose have been studied by optical rotation data and dynamic light scattering studied (17). The dicarboxycellulose derivative showed a substantially larger change in conformation than the corresponding amylose and cyclodextrin (17).

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III.7 MODIFIED CELLULOSE USED AS REACTION INCORPORATED FILLER IN COMPOSITES

Fillers are materials incorporated into commercial polymers to improve their general properties, to induce specific characteristics, or to reduce the cost of the compound (even though certain physical properties may be somewhat impaired). They are often used to increase hardness, improve electrical properties, or alter the specific gravity (1-3). Fillers have always played an important role in the plastic industry.

The use of fibers (such as glass, carbon, kevlar) in plastics forms the basis for reinforced plastics.

The Characteristics of an ideal filler are:

1) Low cost
2) Availability
3) Low oil absorption
4) Good surface wetting and bonding
5) Good chemical resistance
6) High strength
7) Good moisture resistance

Fillers are also selected for their lack of effect on surface finish and processing equipment (e.g. lack of abrasive action on dies and mixing equipment) and for minimum deterioration of physical properties and absence of absorbed moisture and gases.

Classification of filler

Fillers may be divided into organic and inorganic groups, and each of them may be subdivided into fibrous and nonfibrous type.

Organic

Fibrous	Non-fibrous
Wood flour	Canbar blacks
Cotton flock	Graphite
Wood cellulose	Coconut shell
Sisal	Flour
Kevlar	Walnut shell
Carbon	

Inorganic

Fibrous	Non-fibrous
Asbestos	Silica
Glass fiber	Talc
	Mica
	Clay
	Calcium carbonate etc.

In many polymer-filler systems, certain types of compounds called coupling agents, are generally added in order to improve the properties of the product. These coupling agents are bifunctional compounds, one end of which reacts with the polymer matrix and the other end reacts with the filler. Thus, coupling agents are molecular bridges between the polymer matrix and the filler.

Use of Cellulosics as Fillers

Lignocellulosics are available in large quantities due to their natural abundance. They have been tried as reactive fillers in a variety of thermoset polymer systems (4,5). The cellulose part of lignocellulosics is generally considered to be the reactive molecule. Besides being inexpensive, lignocellulosics such as wood pulp fibers are often used to modify mechanical properties of polymeric composites (6). The polar nature of wood-based fillers and reinforcing agents affects adversely the adhesion to the plastic matrix (7,8). The plastics used here are HDPE, polypropylene, polystyrene, etc. Cellulosic fillers may be regarded as low reinforcing fillers comparable to untreated mineral product such as calcium carbonate. Apart from the advantage of the low density of cellulosic fillers, their lack of significant hardness is an important property, since the wearing out of processing equipment is minimised.

Wood pulp fibers possess strength and modulus properties which compare favourably with glass fibers when the difference in fiber densities are considered (9). It is usually difficult to disperse wood pulp fibers in non-polar hydrocarbon polymers such as polyethylene and polypropylene. However, the addition of carboxylic waxes aids dispersion and permits the incorporation of 40 to 50 weight percent fibers without difficulty. Although cellulosic fillers are widely used in the plastic industry in the form of ground wood floor, the large fiber aspect ratios of wood pulp fibers can impart significantly greater strength and modulus values to the composite (9). Recently, new approaches have been tried using benzoyl peroxide to crosslink polypropylene in polypropylene/wood flour composites (10) thereby achieving enhanced tensile properties for the composites. P. Cousin et al. (11) reported a similar result for the linear low density polyethylene (LLDPE) and hard-wood pulp system. Benzoyl-peroxide decomposes into radicals which attack the cellulose backbone, generating cellulosic radicals which may subsequently promote the grafting of cellulose to the polymeric matrix. Urea-formaldehyde resins are used to produce light coloured moulding compounds with α-cellulose as filler. This filler is essential to provide higher strength and mouldability (12). They exhibit good electrical properties and tracking resistance (13) studied stress in curing when wood flour and CM-cellulose are added to urea-formaldehyde resin adhesives or phenol-formaldehyde adhesives. The internal stress was found to decrease while the viscosity increased, thus facilitating their use on inclined surfaces. The curing of adhesive for bonding wood was studied in the presence of wood flour, and CM-cellulose fillers and polyvinylacetate dispersion (14). In general, addition of filler increased the curing time of the adhesion. Cellulose derivatives (15) have been mixed in acrylic polymer emulsion used as anticorrosive fillers for cables and additives. Cellulose is included in polymer compositions used for repairing wooden articles (16).

CMC was used as a filler in cement for water proofing coating. The latter controls the viscosity, surface activity, and colour of the material. The product has very high adherence to concrete, metal, wood and other construction material, is resistant to frosting, UV radiation, and salt solution (17). A ligand, modified with silane residue for attachment to a hydroxylated carrier, can be coupled to polymers and biopolymers for use in affinity chromatography (18). Artificial grindstones can be prepared by mixing of abrasive particles containing cellulose, polyvinyl alcohol, and pore forming materials reacting in the presence of a crosslinking agent and catalyst (19). Whetstones prepared from abrasive particles containing spherical or oval cellulose composite particles and thermosetting resin particle has given good result in polishing optical glass plates (20). The mechanical properties of natural rubber composites filled with short cellulose fibers were studied. Strong anisotropy caused by the fiber orientation is observed in the mechanical properties at high fiber loading (21). The nature of the interphase and how it changes when compatibilizing agents (alkyl succinic anhydride and maleated polypropylene) are used, have been investigated (22). This group also showed that the presence of compatibilizing agent enhanced stress transfer and increased interface thickness considerably, the most significant effect being obtained for the high molecular weight compatibilizers (23). Varma et al. have reported interesting results on modified celluloses as reaction incorporated fillers in epoxy matrix (24,25), while cellulose fibre activation by use of electrophilic reagents (glycidyl methacrylate, maleic anhydride, and succinic anhydride) has been gainfully used by Rozman et al. (26) in imparting improvements in fibre board properties in phenol-formaldehyde and methyl methacrylate systems.

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EXPERIMENTAL SECTION

IV.1 SYNTHESIS OF 2,3-DIALDEHYDE-CELLULOSES (DAC)

Material

Cellulose:

Hard wood cellulose powder (CP-100, Cellulose Products of India Ltd., Ahmedabad) of ~ 150 mesh fineness was used. It contained 80-85% alpha cellulose and an ether extract of 0.2% maximum. This cellulose was further purified before use, as follows:

500 g of cellulose CP-100 powder was taken in a 2 liter beaker and repeatedly washed with distilled water until the filtrate had a pH between 6.5-7.0. Finally the cellulose was washed with methanol, filtered, and dried in a vacuum oven at 60°C until constant weight was achieved.

Chemicals:

Sodium metaperiodate of 99.5% purity was supplied by Loba Chemicals, Bombay. Sodium thiosulfate (99.5%), Sodium hydroxide (98.5%), Sodium bicarbonate (99.5%), methanol (99.5%), and soluble starch were products of S.D. Fine Chemicals, Boisar. Potassium dichromate (99%) was supplied by Sarabhai Chemicals, Baroda, and potassium iodide (98.5%) by Ranbaxy Laboratories, Gurgaon. All these chemicals were used without further purification.

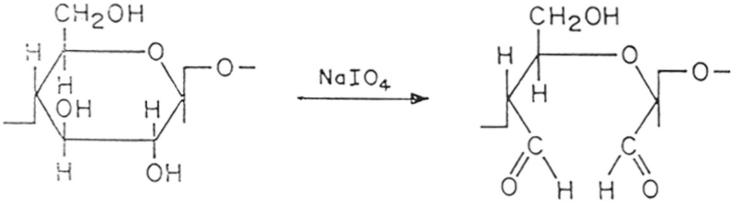
Synthesis of 12%, 30%, 60%, 80% and 98% 2,3-Dialdehydecelluloses:

In order to obtain different degrees of oxidation of cellulose viz. 12%, 30%, 60%, 80%, and 98% required quantities of cellulose powder dispersed in distilled water and Sodium metaperiodate dissolved in distilled water as shown in Table-IV.1.1 were slowly added over a period of 15 minutes (1,2). The pH at this stage was around 3.5. The reaction was carried out in the dark and the temperature maintained at 55°C for 6h. At this stage the temperature was brought down to room temp. Cellulose was filtered off, washed twice with distilled water and then with methanol, and finally allowed to dry in a vacuum oven at 60°C. Analysis of Sodium metaperiodate was carried out by the published methods (3) (Fig.IV.1.1).

Table IV.1.1

Qnantities of reagents required for synthesis of 2,3-Dialdehydecelluloses (DAC)

% oxidation of cellulose to obtain DAC	Quantities of cellulose used (g)	Quantities of Sodium metaperiodate used (g)	Total vol. of of dist. water in reaction mixture (mL)	Wt. of product obtained (g)
12	50	7.92	2000	43
30	50	19.80	2000	42
60	50	39.60	2000	40
80	50	53.00	2000	26
98	50	66.00	2000	15



I

II

I CELLULOSE
II 2,3-DIALDEHYDE CELLULOSE (DAC)

FIG.IV·1·1: SYNTHESIS OF 2,3-DIALDEHYDE CELLULOSE (DAC)

Preparation of 0.1N Sodium thiosulphate ($Na_2S_2O_3$) solution:

24.8 g (0.1 mole) of Sodium thiosulphate was weighed accurately, taken in a beaker and 100 mL distilled water was added. When Sodium thiosulphate was completely dissolved, the mixture was diluted in 1000 mL in a standard volumetric flask.

Preparation of 10% potassium iodide (KI) solution

100 g of potassium iodide was weighed accurately, taken in a beaker and 100 mL distilled water was added. When potassium iodide was completely dissolved, the mixture was diluted to 1000 mL in a standard volumetric flask.

Saturated solution of Sodium bicarbonate in water was prepared by the usual method.

Preparation of 0.1% starch solution:

0.1 g of soluble starch was added to 100 mL distilled water and boiled for 5 mins. This solution was freshly prepared before use.

Standardization of 0.1N Sodium thiosulphate ($Na_2S_2O_3$) solution

Procedure: A previously reported method was adopted (4). 0.1032 g (0.00035 mole) potassium dichromate was weighed accurately and taken in a stoppered conical flask with 100 mL distilled water. After potassium dichromate was completely dissolved it was acidified with 5 mL conc. HCl

(35%), and 20 mL 10% potassium iodide solution and 50 mL distilled water were added quickly and the flask was kept securely closed. It was kept in the dark for 20 minutes. Subsequently, it was titrated against approximately 0.1N $Na_2S_2O_3$ solution. During titration the solutions turned brown to pale yellow. At this point starch indicator was added and the solution became bluish green coloured. Dropwise addition of 0.1N $Na_2S_2O_3$ solution was continued. The endpoint was reached when the dichromate solution turned from greenish blue to light green colour.

$$1 \text{ mL } 1\text{N } Na_2S_2O_3 \equiv 0.04904 \text{ g. } K_2Cr_2O_7$$

$$\text{Normality of } 0.1\text{N } Na_2S_2O_3 = \frac{\text{Factor of } K_2Cr_2O_7 \text{ X Wt. of } K_2Cr_2O_7}{\text{Burette Reading}}$$

$$= \frac{20.39 \text{ X Wt. of } K_2Cr_2O_7}{\text{Burette Reading}}$$

$$\text{Factor} = \frac{1000}{\text{eq. wt.}}$$

(Equivalent weight of potassium dichromate 49.04)

Determination of Periodate Consumption Method by Thiosulphate Method

$$NaIO_4 + 7KI + 8HCl \longrightarrow NaCl + 7KCl + 4H_2O + 4I_2$$

Procedure: 1 mL of reaction mixture was added to 20 mL distilled water containing 10 mL cold saturated solution of Sodium bicarbonate and 20 mL of 10% KI solution. The solution was made acidic by addition of 5 mL conc. HCl (35%) and kept in the dark for 20 minutes. The liberated iodine was titrated with standard 0.1N $Na_2S_2O_3$ solution using starch as indicator. The end point was blue to colourless.

1 mL 1N $Na_2S_2O_3$ = 0.02675 g $NaIO_4$

1 mL 0.1N $Na_2S_2O_3$ = 0.002675 g $NaIO_4$

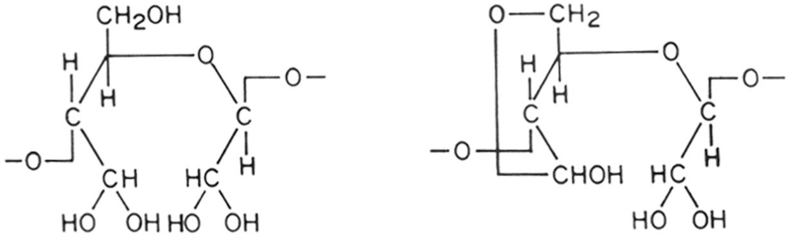
$$\text{g periodate} = \frac{\text{Burette Reading X 0.002675 X Total Volume}}{\text{mL of volume taken}}$$

I.R. Spectra of 2,3-Dialdehydecelluloses (DAC)

Infrared spectra of DAC's in nujol emulsion showed a carbonyl peak at 1710 cm^{-1} and 1650 cm^{-1}. It is well known (5) that 2,3-dialdehydecelluloses exist as hydrates and hemiacetals, as shown in Fig. IV.1.2. Figs. IV.1.3-IV.1.7 show the I.R spectra recorded for 12%, 30%, 60%, 80% and 98% DAC in nujol emulsion, and Fig. IV.1.8 is an overlapping spectra.

Solid State C-13 NMR Spectra of 2,3-Dialdehydecelluloses (DAC)

High resolution CP/MAS spectra were recorded on a Brucker MSL-300 spectrometer. In DAC, the aldehyde carbonyl carbon peak was not seen at 190 ppm because it was present in hemialdal form which borne out from the corresponding I.R. Actual spectra are presented in Section IV.6.



HYDRATE

HEMIACETAL

FIG. IV.1·2 : STRUCTURE OF 2,3-DIALDEHYDE CELLULOSE IN HYDRATED FROM AND HEMIACETAL FORM (Ref.5)

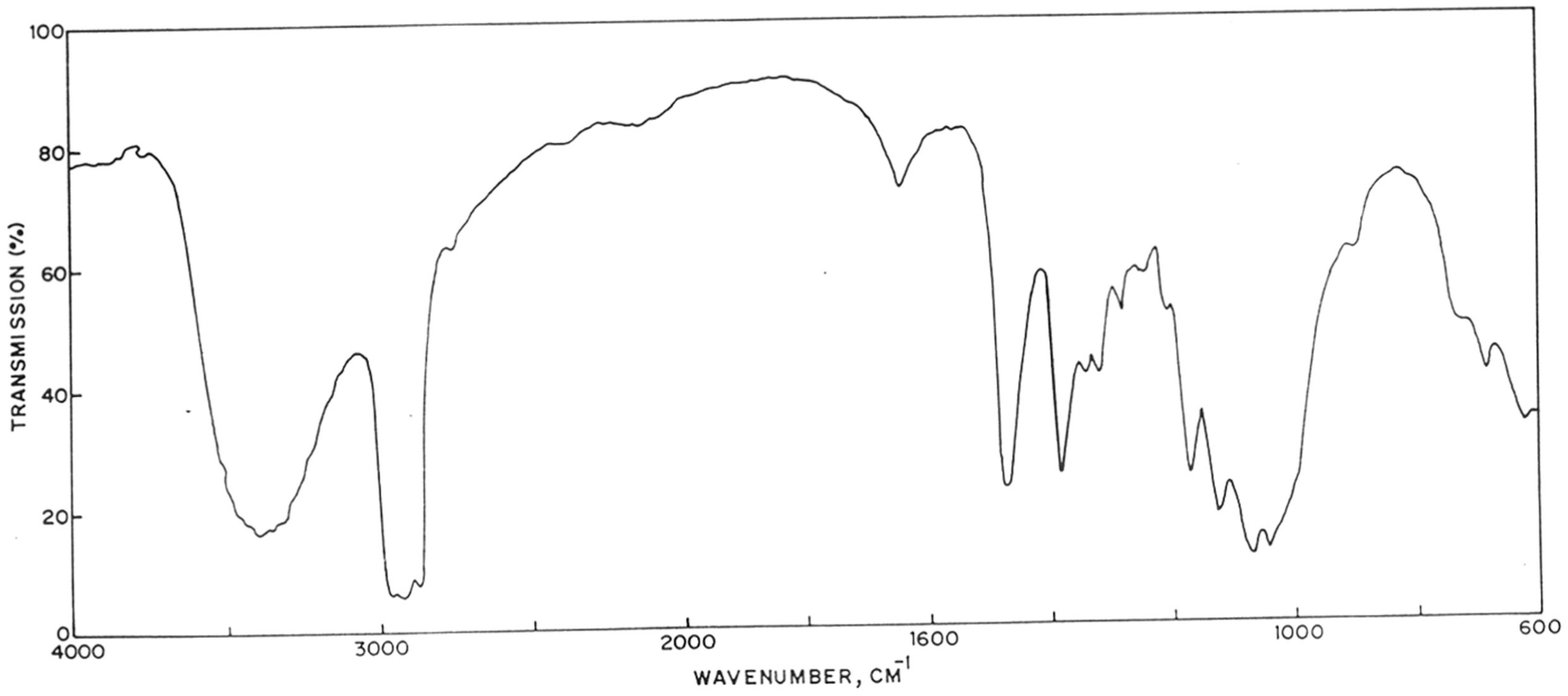


FIG.IV·1·3: IR SPECTRUM OF 12% DAC IN NUJOL

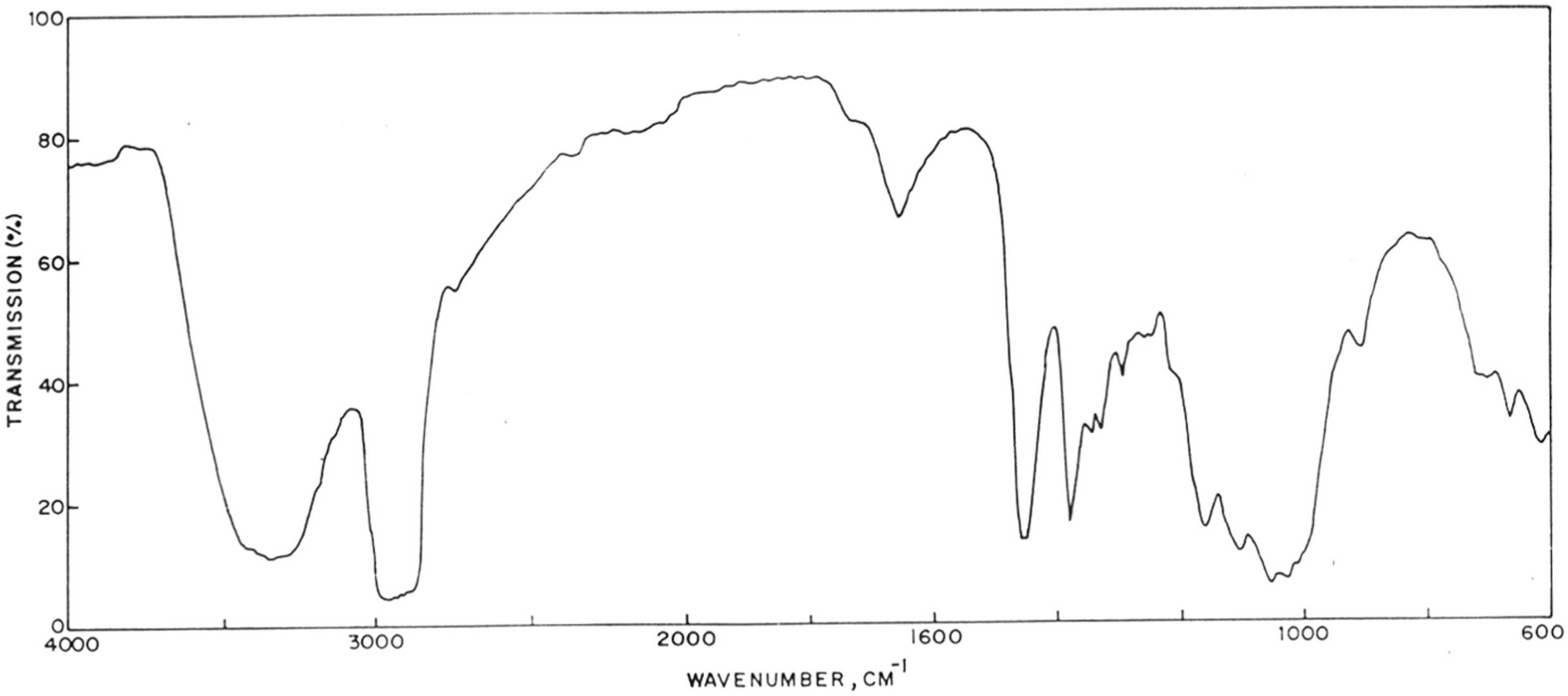


FIG. IV·1·4: IR SPECTRUM OF 30% DAC IN NUJOL

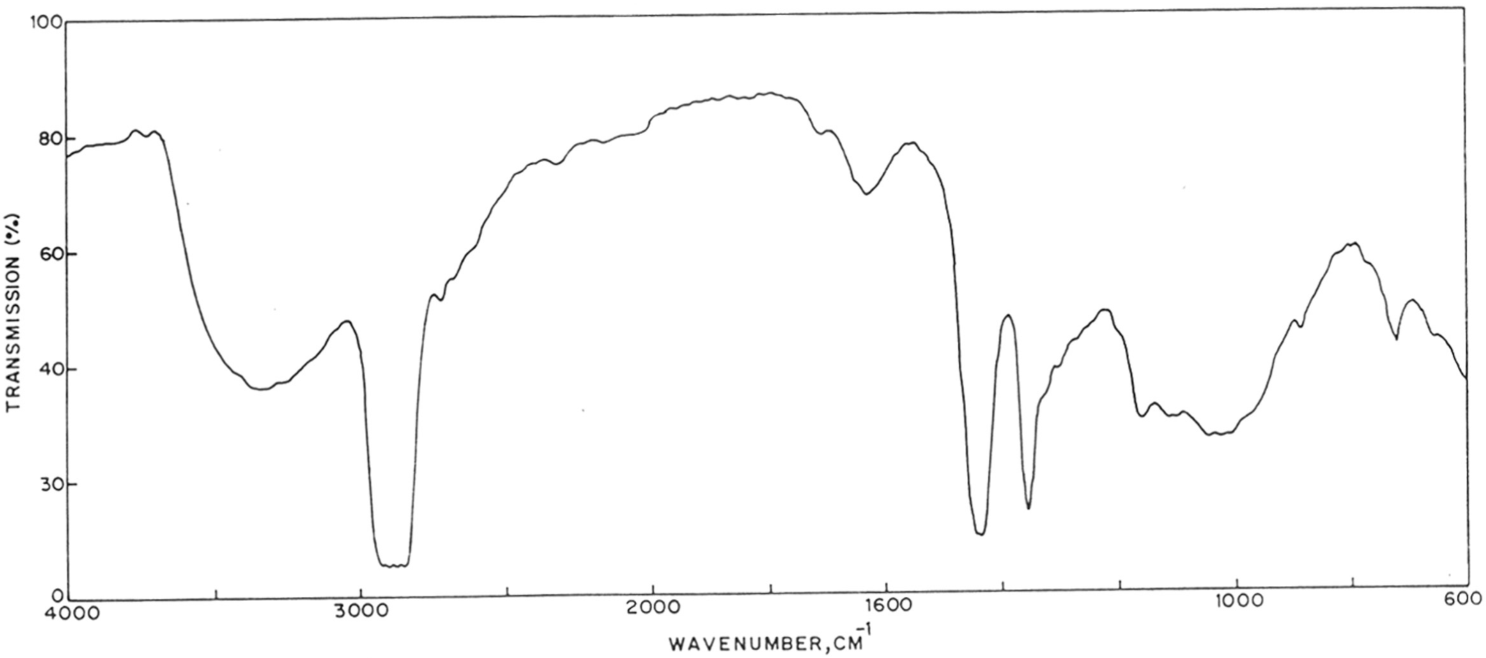


FIG. IV·1·5 : IR SPECTRUM OF 60% DAC IN NUJOL

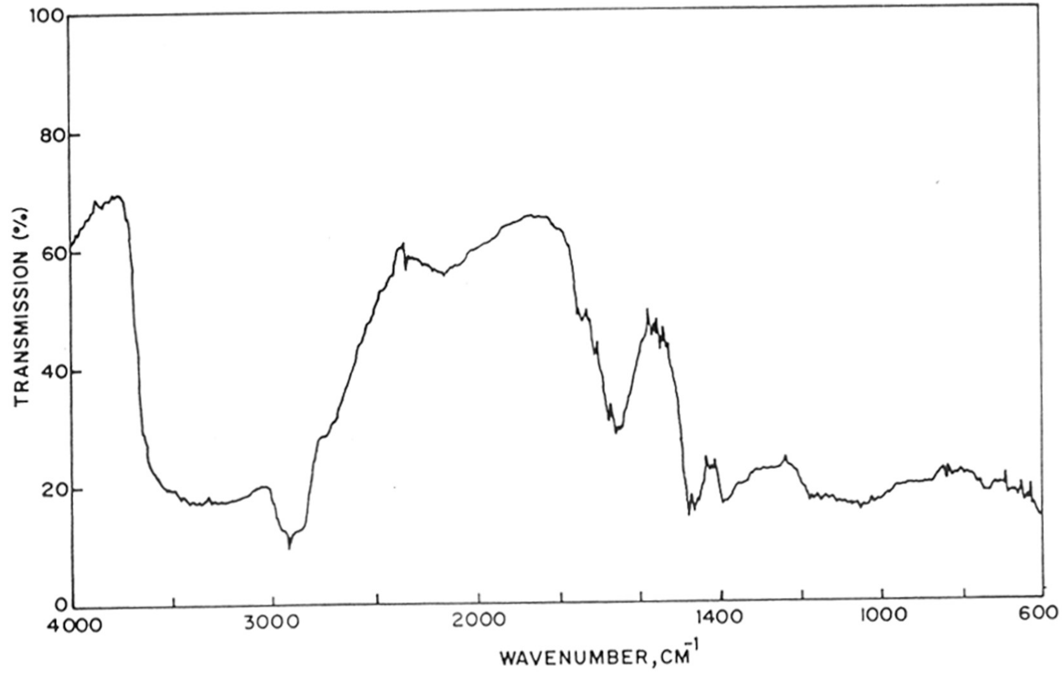


FIG. IV·1·6 : IR SPECTRUM OF 80% DAC IN NUJOL

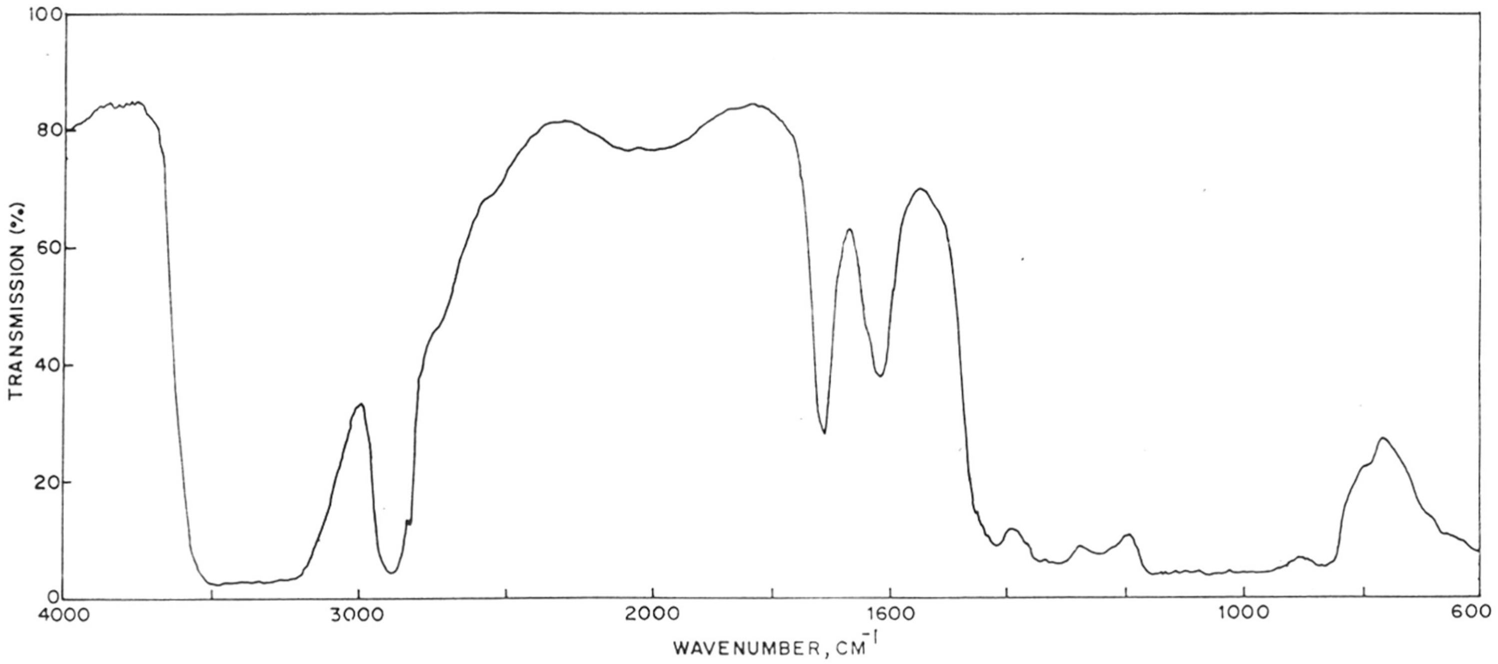


FIG. IV·1·7: IR SPECTRUM OF 98% DAC IN NUJOL

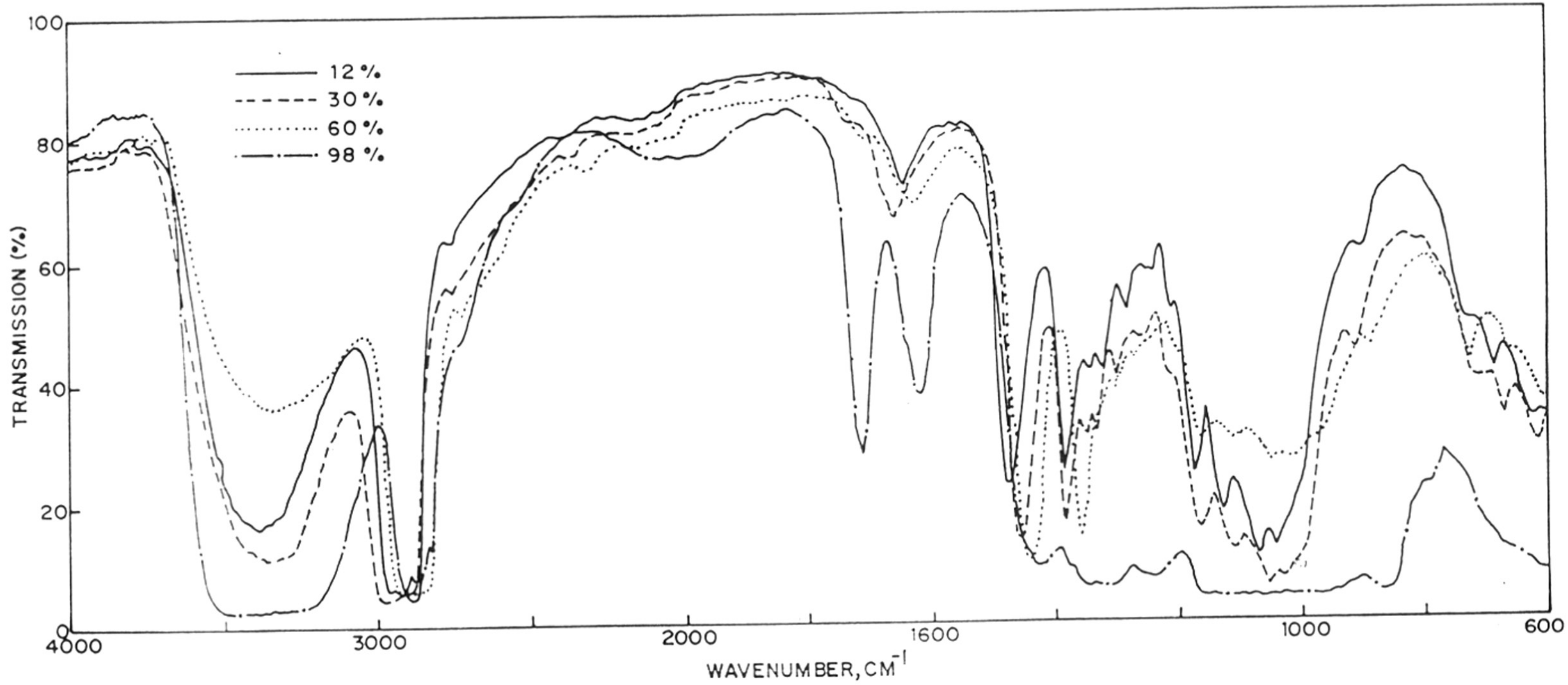


FIG. IV·1·8: OVERLAPPING IR SPECTRA OF 12%, 30%, 60% AND 98% DAC IN NUJOL

IV.2 SYNTHESIS OF SODIUM 2,3-DICARBOXYCELLULOSES (NADCC)

Material

2,3-Dialdehydecelluloses: 2,3-Dialdehydecelluloses (12%, 30%, 60%, 80%, and 98% based on glucose monomer units) were synthesized and characterized as described in Section IV.1.

Chemicals: Sodium chlorite of 76% purity was supplied by M/s. Vijay Chemicals, Poona, and acetic acid (glacial) (99.5%) by S.D. Fine Chemicals, Boisar, and they were used without further purification.

Assay of Sodium Chlorite ($NaClO_2$)

Procedure: A previously reported method was adopted (6). 0.1 g of $NaClO_2$ and 50 mL distilled water were taken in a stoppered conical flask. When a clear solution was obtained, 20 mL of 10% KI solution and 5 mL acetic acid solution were added. The flask was closed with a stopper and kept for 15 minutes in the dark. The liberated iodine was titrated against 0.1N $Na_2S_2O_3$ solution. When a pale yellow colour appeared, 2 mL of 0.1% starch solution was added, which resulted in a black bluish colour. At this stage 0.1N $Na_2S_2O_3$ was added dropwise till a colourless solution was obtained.

$$\% \text{NaClO}_2 = \frac{(V)\ (N)\ (2.26)}{\text{Wt. of sample taken}}$$

V = Volume of $Na_2S_2O_3$ solution

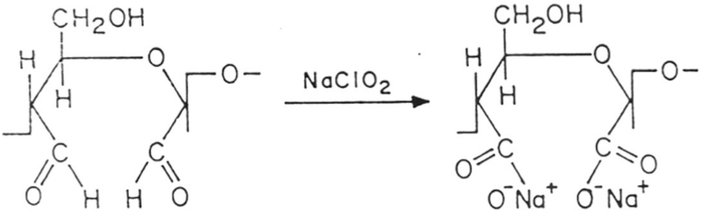
N = Normality of $Na_2S_2O_3$ solution

W = Wt. of the sample taken

Synthesis of 12%, 30%, 60%, 80%, and 98% Sodium 2,3-Dicarboxycelluloses

In order to obtain Sodium 2,3-Dicarboxycelluloses with different degree of oxidation viz, 12%, 30%, 60%, 80%, and 98% required quantities of dialdehydecelluloses were dispersed in distilled water. Details of quantities of reagents used are shown in Table-IV.2.1.To this was added aqueous Sodium chlorite solutions. The temperature was maintained at 20°C. Glacial acetic acid dissolved in distilled water was added dropwise, the temperature being maintained at 20°C (7) (Fig. IV.2.1).

The start of the oxidation was indicated by the formation of yellow colouration and evolution of ClO_2 gas. The reaction was continued for 7h until there was no further evolution of gas. Nitrogen gas was bubbled through the reaction mixture to remove dissolved gases. The pH of the reaction mixture was adjusted to 8.5 by addition of 10 N NaOH solution. The reaction product (the Sodium salt of 2,3-dicarboxy- cellulose) was precipitated by pouring into three volumes of ethanol. The precipitated solid was filtered, dried in vacuum at 60°C and purified by reprecipitation.



II III

II 2,3-DIALDEHYDE CELLULOSE (DAC)

III SODIUM 2,3-DICARBOXY CELLULOSE (NaDCC)

FIG.IV.2·1 : SYNTHESIS OF SODIUM 2,3-DICARBOXY CELLULOSE (NaDCC)

Table IV.2.1

Quantities of reagents required for synthesis of Sodium 2,3-Dicarboxycelluloses (NaDCC)

% oxidation of DAC to obtain NaDCC	Wt. of DAC (g)	Wt. of $NaClO_2$ (g)	Wt. of acetic acid (g)	Wt. of product obtained (g)
12	15	5.35	1.35	14.1
30	15	14.80	3.37	12.3
60	15	26.75	6.75	13.5
80	15	35.66	9.00	14.0
98	7	20.21	5.10	6.0

Sodium analysis of 98% Sodium 2,3-Dicarboxycellulose(NaDCC)

Solution of 98% NaDCC (concentration range 3-5 ppm) were tested for Na by use of Atomic Absorption Spectrophotometer model Z-8000 (HITACHI). Operating condition of analysis Sodium were : slit - 0.4 nm, wavelength 589.6 nm, lamp current 7.5 mA. Complete agreement between the experimental and theoretical value (i.e. 19.65% Sodium content) were obtained.

I.R. Spectra of Sodium 2,3-Dicarboxycelluloses (NaDCC)

Infrared spectra of NaDCC's in nujol emulsion showed a carboxylate peak 1610 cm^{-1}. Figs. IV.2.2-IV.2.6 show the I.R. spectra recorded for 12%, 30%, 60%, 80% and 98% NaDCC in nujol emulsion and Figs. IV.2.7 & IV.2.8 are overlapping spectra.

Solid State C-13 NMR spectra of Sodium 2,3-Dicarboxycelluloses (NaDCC)

High resolution CP/MAS C-13 NMR spectra were recorded on a Brucker MSL-300 spectrometer. The carbonyl peak was seen at 174.5 ppm; Actual spectra are presented in Section IV.6.

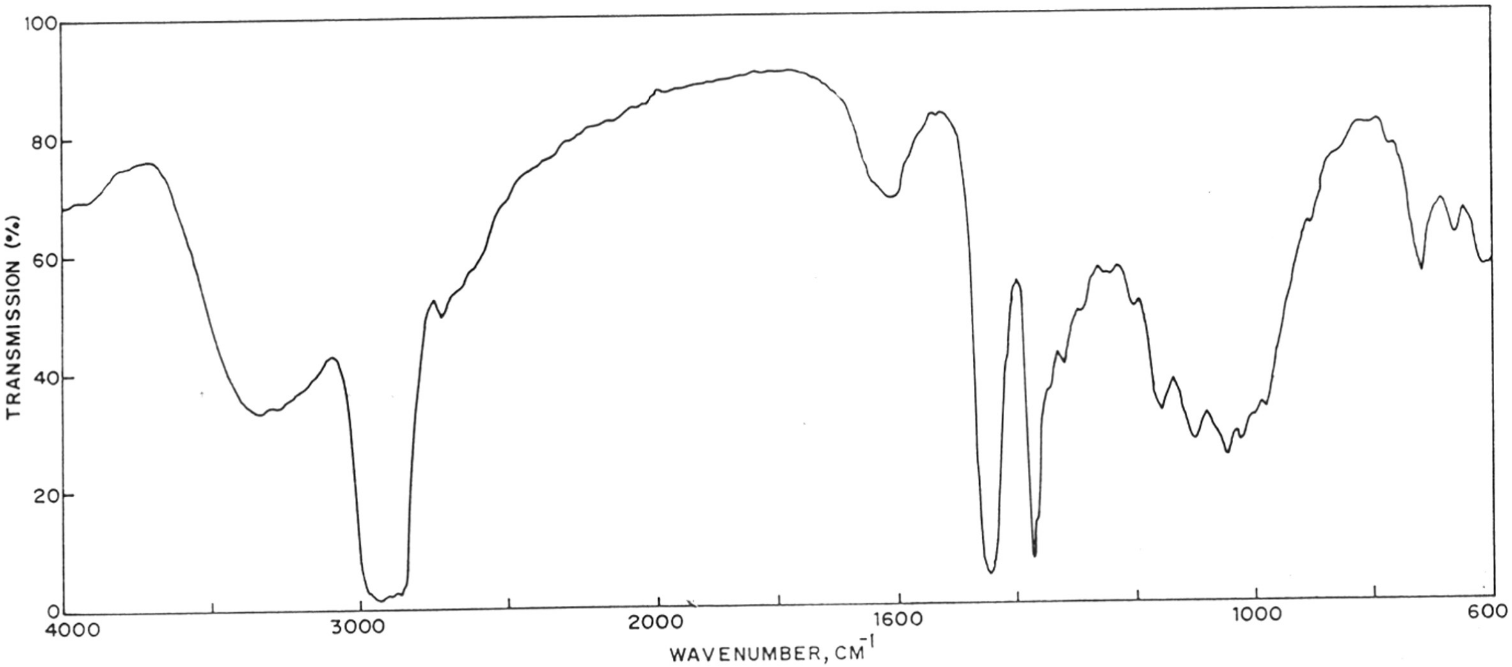


FIG. IV·2·2 : IR SPECTRUM OF 12 % NaDCC IN NUJOL

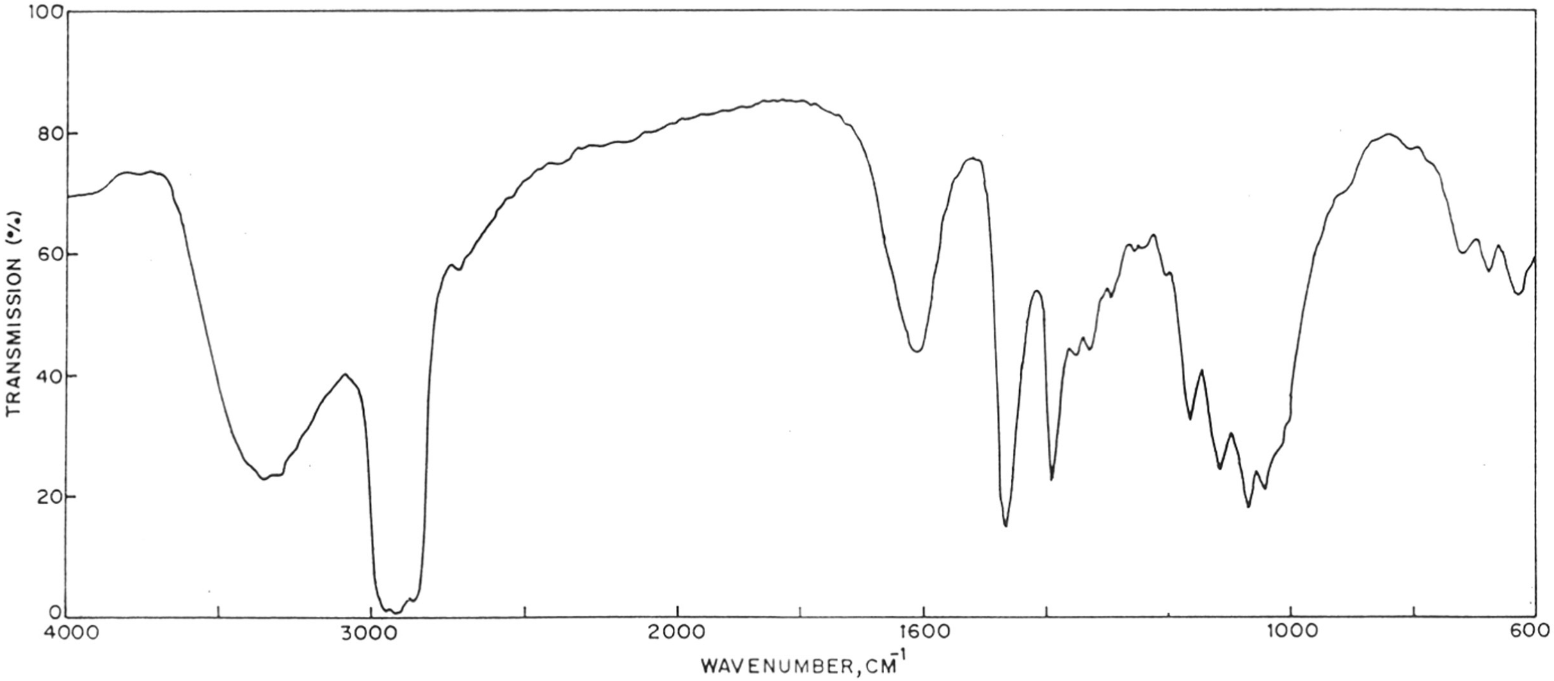


FIG. IV.2·3 : IR SPECTRUM OF 30% NaDCC IN NUJOL

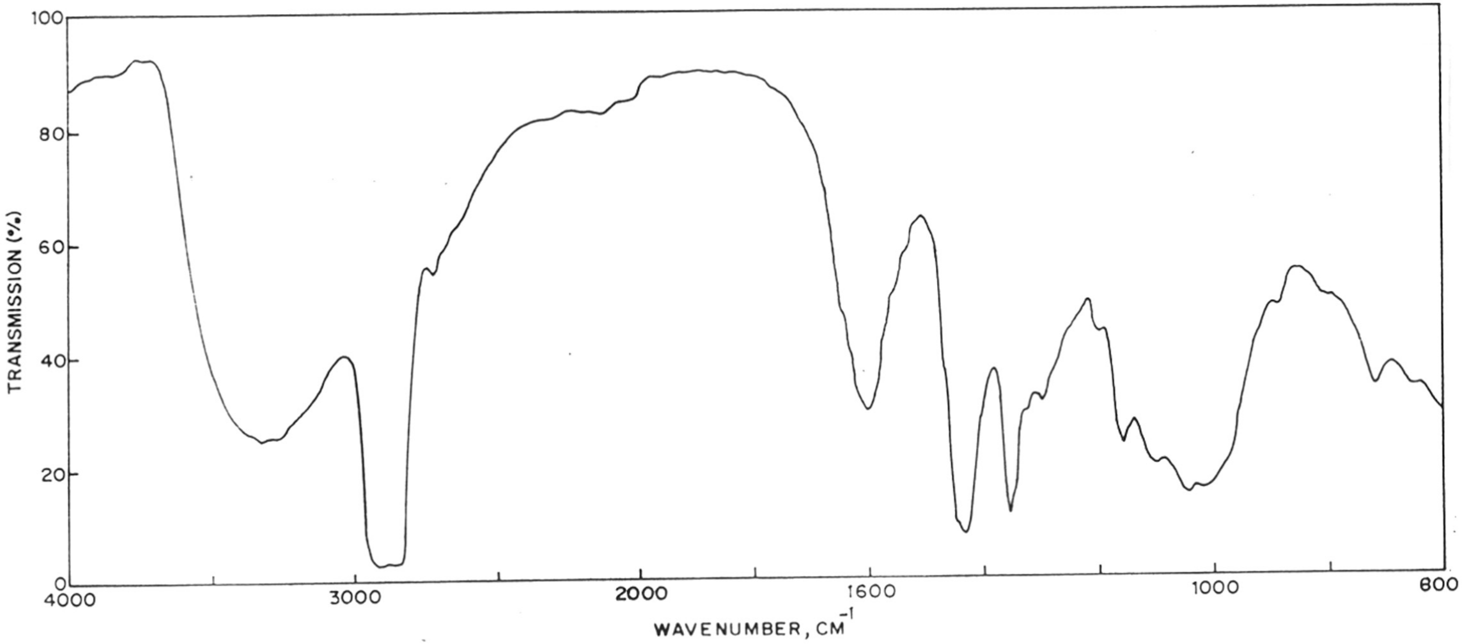


FIG. IV·2·4: IR SPECTRUM OF 60% NaDCC IN NUJOL

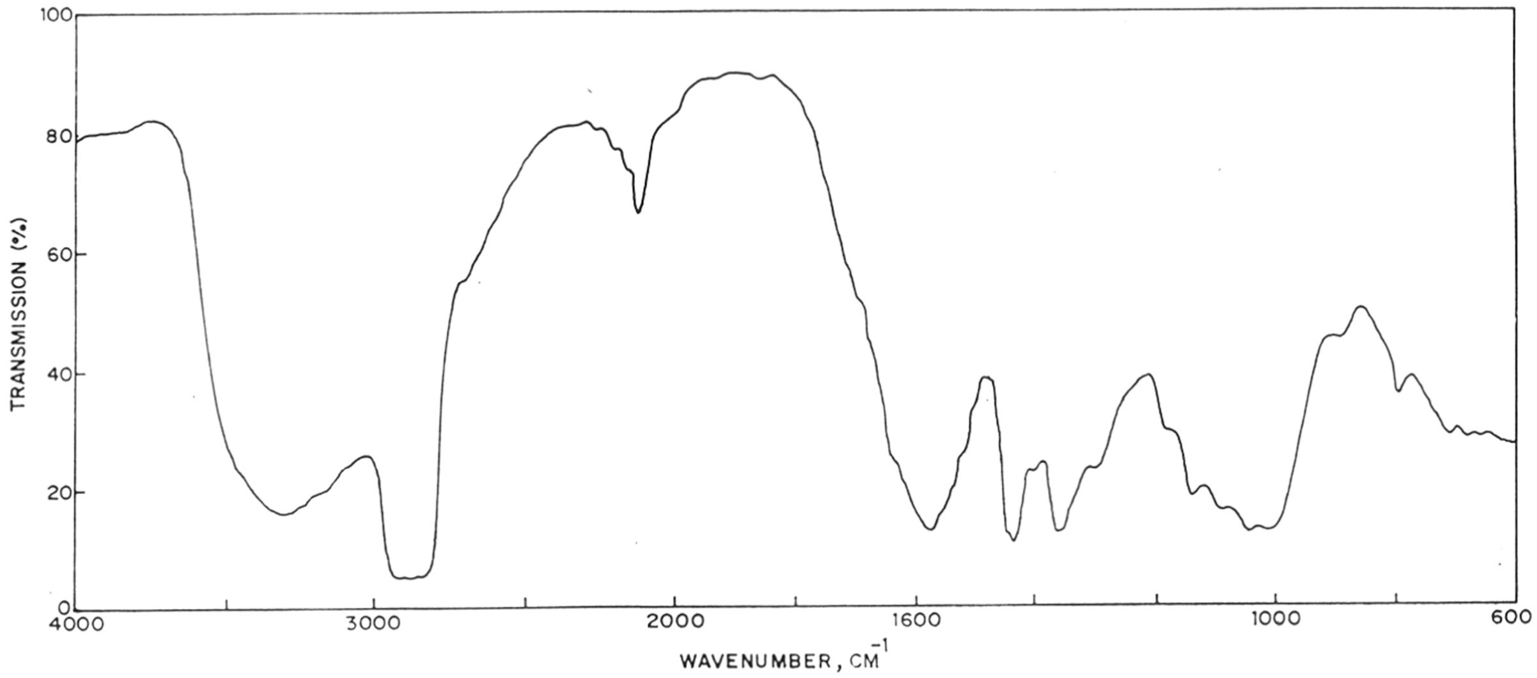


FIG. IV·2·5: IR SPECTRUM OF 80% NaDCC IN NUJOL

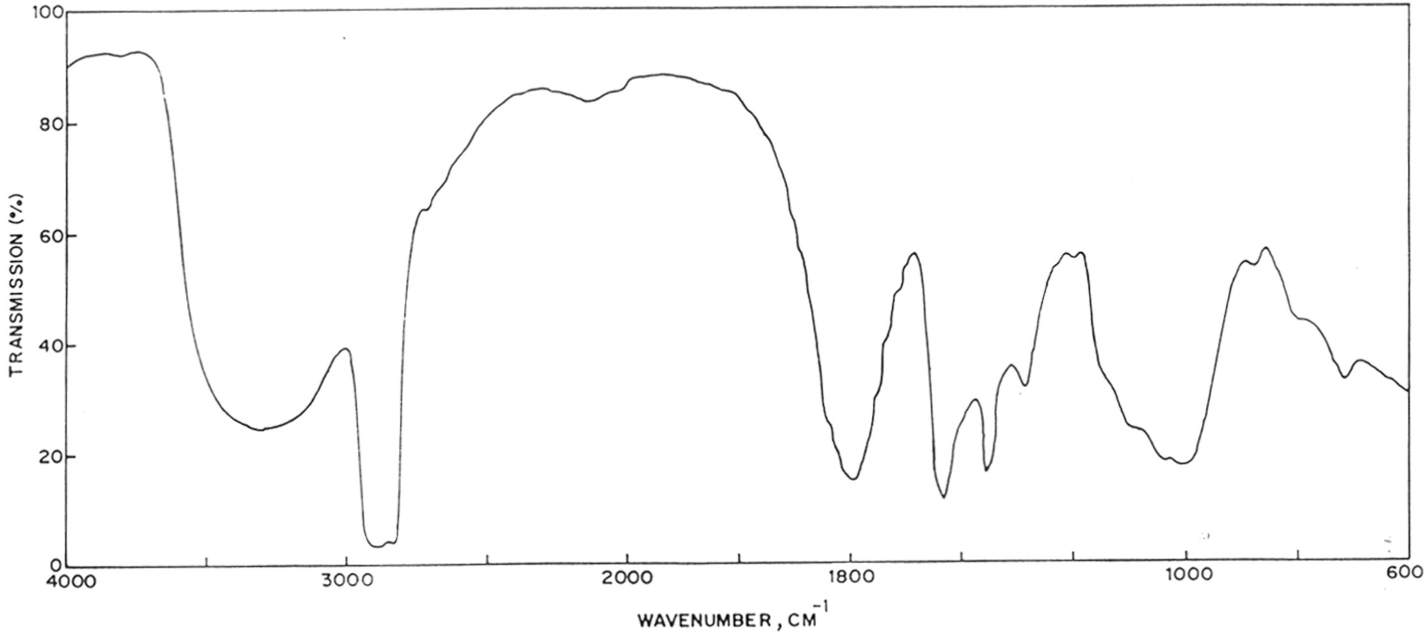


FIG. IV·2·6 : IR SPECTRUM OF 98% NaDCC IN NUJOL

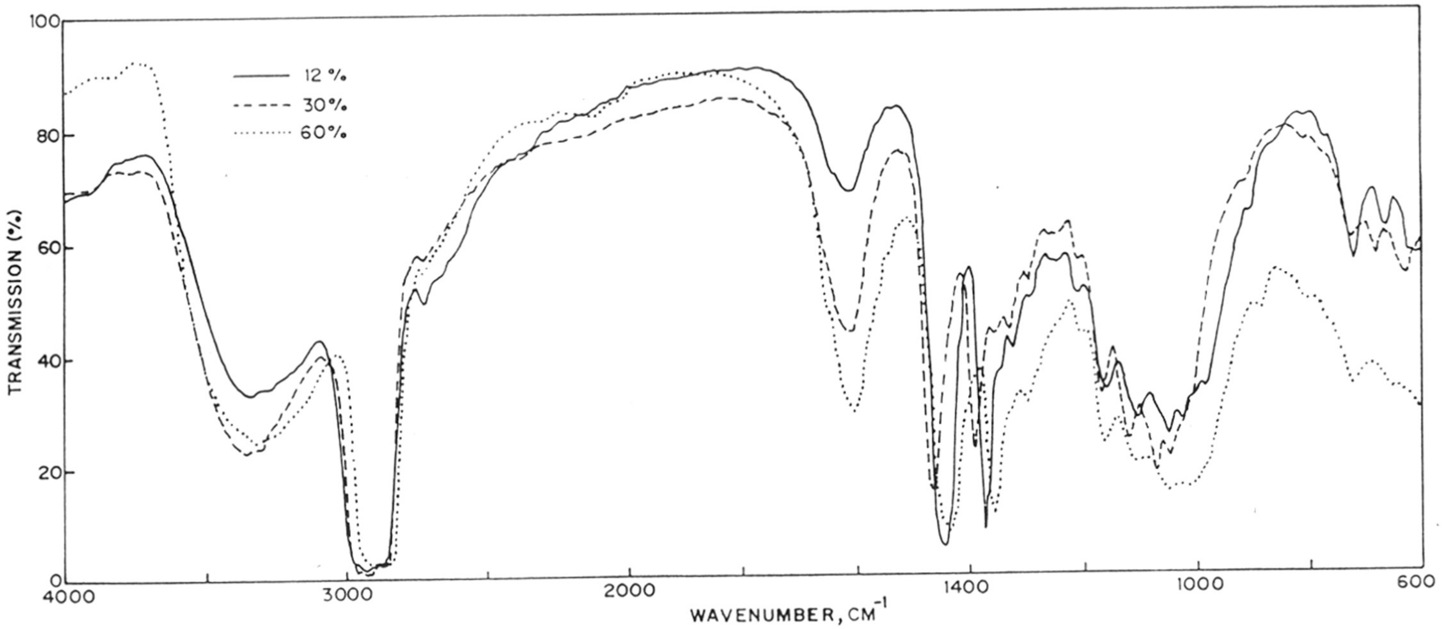


FIG.IV·2·7:OVERLAPPING IR SPECTRA OF 12%, 30%, 60% NaDCC IN NUJOL

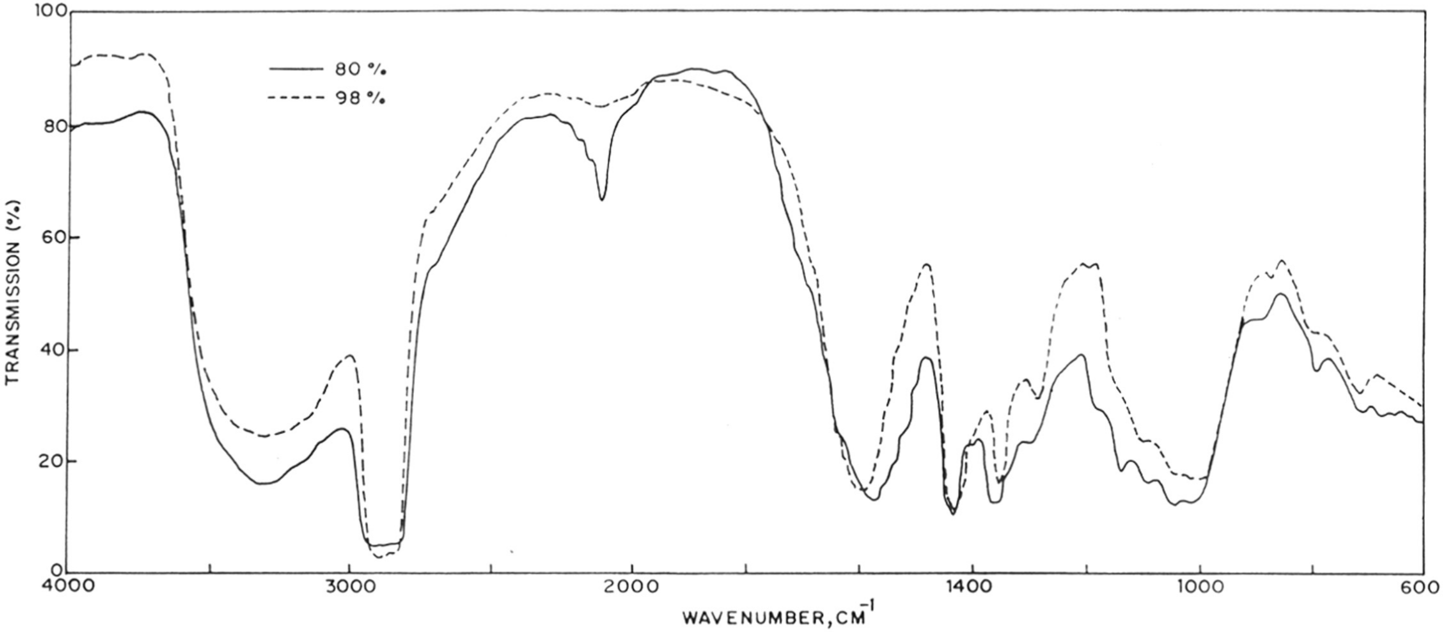


FIG. IV·2·8: OVERLAPPING IR SPECTRA OF 80% AND 98% NaDCC IN NUJOL

IV.3 SYNTHESIS OF 2,3-DICARBOXY-CELLULOSES (DCC)

Materials

Sodium 2,3-Dicarboxycelluloses: Sodium 2,3-Dicarboxycelluloses (12%, 30%, 60%, 80%, and 98% based on glucose monomer units) were synthesized and characterized as described in Section IV.2.

Chemicals: Sodium hydroxide (98.5%), Sodium Chloride (99.6%), and Hydrochloric acid (35%) were products of S.D. Fine Chemicals, Boisar.

Potassium hydrogenphthalate (99.5%), Bromocrysol purple indicator (pH range 5.2-6.8), phenolthelin indicator (pH range 8.3-10) were supplied by Glaxo laboratories, Bombay.

Dowex resin 50X8H^+ in 50-100 mesh size was supplied by Aldrich Chemicals, Milwaukee.

Synthesis of 98% 2,3-Dicarboxycellulose by H^+ ion-exchange resin

The method reported in published literature based on ion-exchange resin (7,8) was adopted for use. The procedure is as follows:

Activation of H$^+$-ion exchange resin

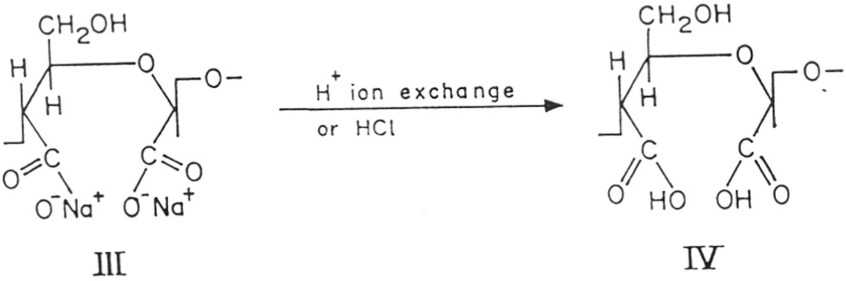
H$^+$ ion exchange resin (Dowex 50X8H$^+$, 50-100 mesh) was washed several times with distilled water. A glass column of 50 mm diameter and 240 mm height was taken and filled with the washed resin. Distilled water was passed over it and the elutant was collected dropwise until neutral pH was obtained. The resin so activated was used for the preparation of 2,3-Dicarboxycellulose.

7.0 g of 98% NaDCC was dissolved in 100 mL distilled water and loaded on the activated H$^+$ resin column. The column was eluted with distilled water until the elutant was neutral. The collected elutant was acidic. It was vacuum distilled at 50°C. The concentrated acid so obtained was dried in vacuum oven at 50°C. Yield: 4.57 g (80.3%).

Synthesis of 12%, 30%, 60%, and 80% 2,3-Dicarboxycelluloses

Since 12%, 30%, 60%, and 80% NaDCC were not water soluble, the method of ion-exchange resin could not be used for preparing the corresponding 2,3-Dicarboxycelluloses. Therefore a method based on treatment with HCl was used (1,7).

Required quantities of Sodium 2,3-Dicarboxy cellulose were dispersed in distilled water and 0.2N HCL was added under stirring till the pH was 3.5. The exact quantities are indicated in Table-IV.3.1. The solution was kept at 1°C in a freezer for 30 minutes and stirred occasionally with a glass



III SODIUM 2,3-DICARBOXY CELLULOSE (NaDCC)
IV 2,3-DICARBOXY CELLULOSE (DCC)

FIG.IV·3·1 : SYNTHESIS OF 2,3-DICARBOXY CELLULOSE (DCC) rod. The aqueous HCl was decanted and to this was added 30 mL distilled water, and stored in a refrigerator at 5°C for 24h. The product was washed several times with water until the wash was neutral. It was then filtered and dried in a vacuum oven at 60°C (Fig.IV.3.1).

In this manner, 2,3-Dicarboxycelluloses with different degree of oxidation viz. 12%, 30%, 60%, 80% were obtained.

Table IV.3.1

Quantities of reagents required for synthesis of 2,3-Dicarboxycelluloses (DCC)

% oxidation of NaDCC to obtain DCC	Wt. of NaDCC (g)	0.2N HCl (mL)	Wt. of product obtained (g)
12	5	20	4.5
30	5	60	4.2
60	5	120	4.0
80	5	135	4.5

Characterization of 2,3-Dicarboxycellulose by chemical method

A simple alkali-titration method described by Davidson and Nevell has been used here (9).

Preparation of 0.1N Sodium hydroxide (NaOH) solution

4.0 g Sodium hydroxide and 100 mL distilled water were taken in a volumetric flask, and after complete dissolution of Sodium hydroxide, dilution was carried out to 1000 mL.

Preparation of 0.1N Hydrochloric acid (HCl) solution

8.9 mL conc. HCl (35%) was diluted to 1000 mL in a volumetric flask with distilled water.

Standardization of 0.1N NaOH solution

The standard method of standardization (4) was used. 0.2 g potassium hydrogen pthalate was dissolved in 50 mL of distilled water and a drop of phenolpthalein indicator was added. The solution was titrated with the 0.1N NaOH solution prepared earlier, till a pink coloured end-point was obtained.

Calculation

$$\text{Normality of 0.1 NaOH} = \frac{\text{Wt. of KHP X factor KHP}^{*}}{\text{Burette Reading}}$$

$$= \frac{\text{Wt. of KHP X 4.898}}{\text{Burette Reading}}$$

$$\text{Factor} = \frac{1000}{\text{eq.wt.}} \quad \text{(Equivalent weight of KHP = 202.22)}$$

* KHP: Potassium hydrogen phthalate

Standardization of 0.1N HCl

To 10 mL of approximately 0.1N HCl solution prepared earlier was added 50 mL distilled water and the solution titrated against standard NaOH solution using phenolpthalein indicator (end point colourless to pink).

Procedure for titrimetric analysis of carboxy groups of 2,3-Dicarboxycelluloses (DCC)

Back Titration

To 0.1 g of 2,3-Dicarboxycellulose was added 40 mL of 0.1N NaOH solution, 1.0 g solid Sodium chloride and some quantity of distilled water. The mixture was kept overnight (18h) at room temperature. It was titrated with 0.1N HCl using Bromocresol purple indicator. The end point was indicated by a change in colour from violet to yellow.

Blank Titration

In a 250 mL conical flask all reagent were added except 0.1 g of 2,3-Dicarboxycellulose, and it was kept for 18 hours and titrated against 0.1N HCl using Bromocresol purple indicator. The end point was indicated by a change in colour from violet to yellow.

Calculation

% 2,3-Dicarboxycellulose =

$$\frac{R \times N \times W \times 100}{\text{Wt. of DCC taken} \times 1000 \times 2}$$

$$= \frac{R \times N \times 192 \times 100}{\text{Wt. of DCC taken} \times 1000 \times 2}$$

$$= \frac{R \times N \times 9.6}{\text{Wt. of DCC taken}}$$

Where,

R = (Blank-Back)

N = Normality of 0.1N HCl

W = M. Wt. of DCC (192)

I.R. Spectra of 2,3-Dicarboxylcelluloses (DCC)

Infrared spectra of DCC´s in nujol emulsion showed carboxyl peak at 1730 cm^{-1}. Figs. IV.3.2-IV.3.6 show the I.R. spectra recorded for 12%, 30%, 60%, 80% and 98% DCC in nujol emulsion, and Fig. IV.3.7 & IV.3.8 are the overlapping spectra.

Solid-state C-13 NMR spectra of 2,3-Dicarboxycelluloses (DCC)

High resolution CP/MAS C-13 NMR spectra were recorded on a Bruker MSL-300 spectrometer. The carboxyl carbon peak was seen at 169.6 ppm; Actual spectra are presented in Section IV.6.

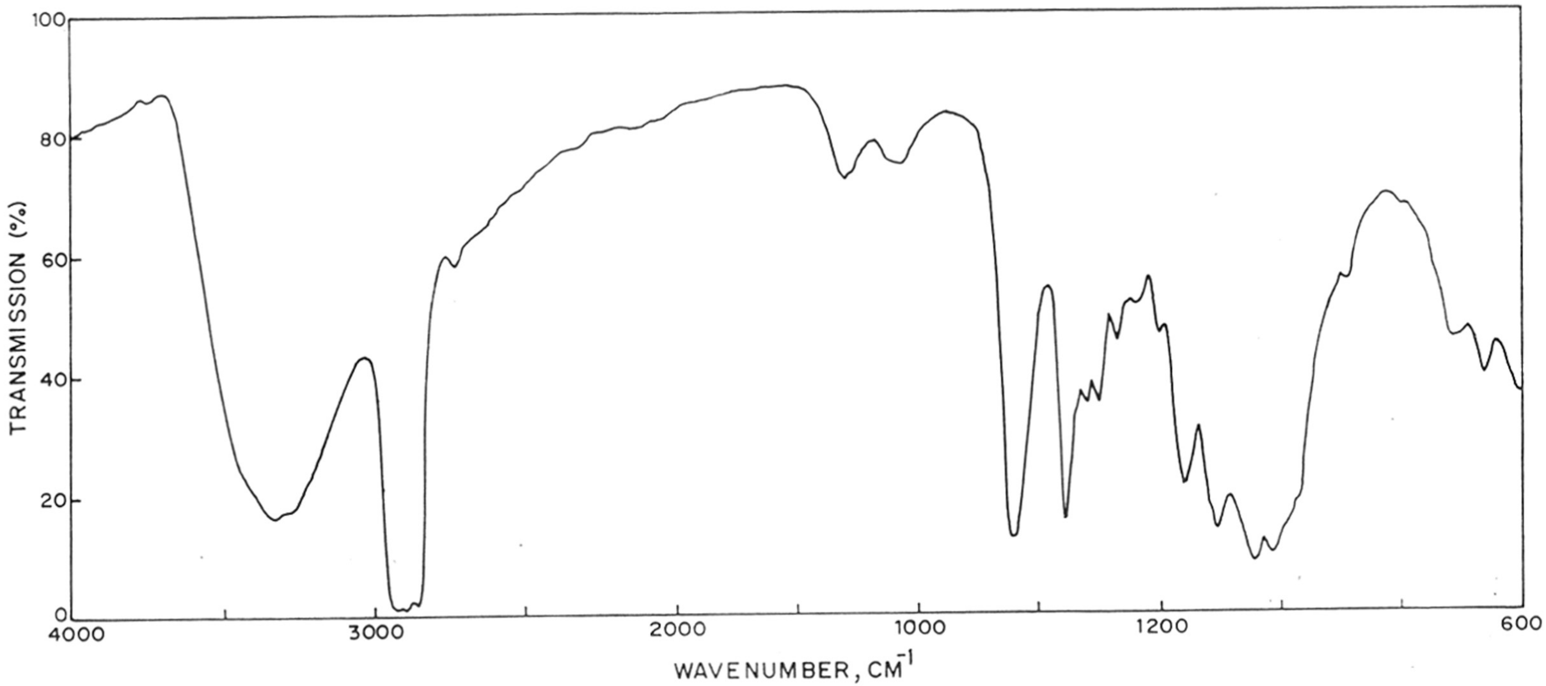


FIG. IV: 3·2: IR SPECTRUM OF 12 % DCC IN NUJOL

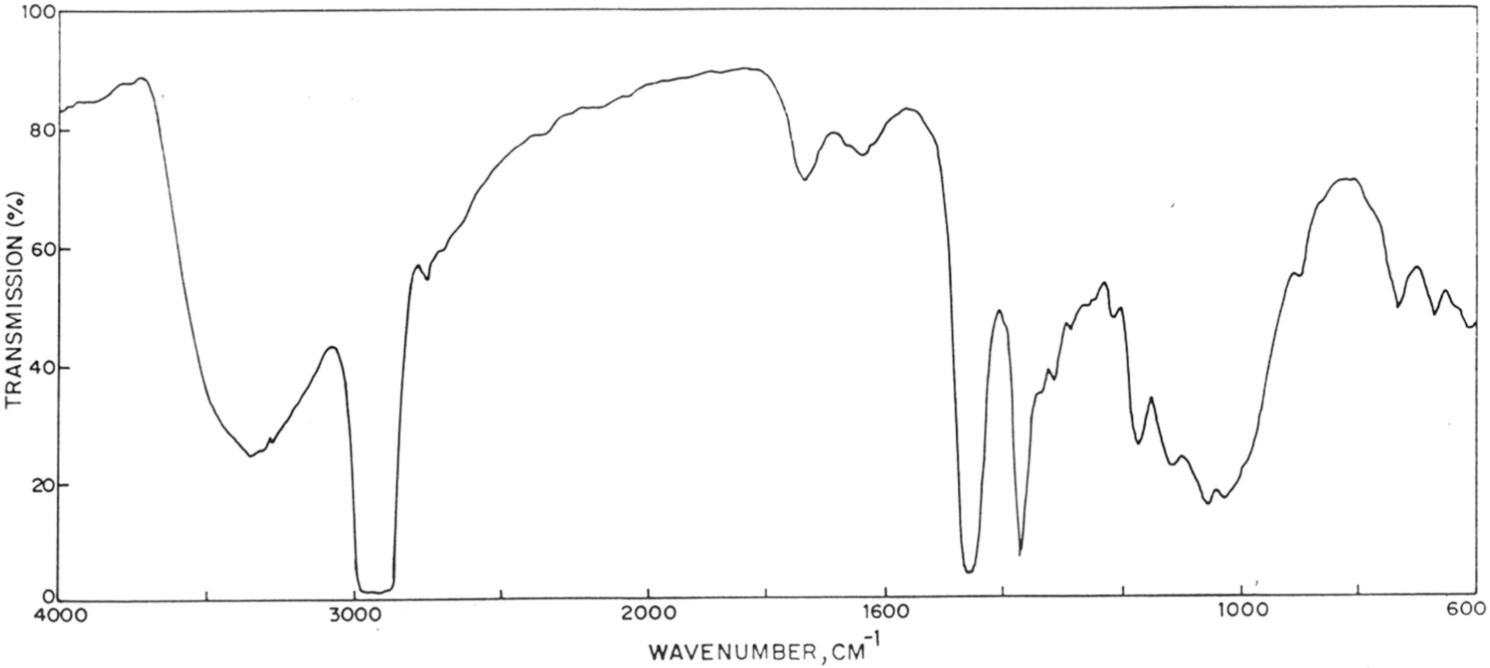


FIG. IV·3·3 : IR SPECTRUM OF 30% DCC IN NUJOL

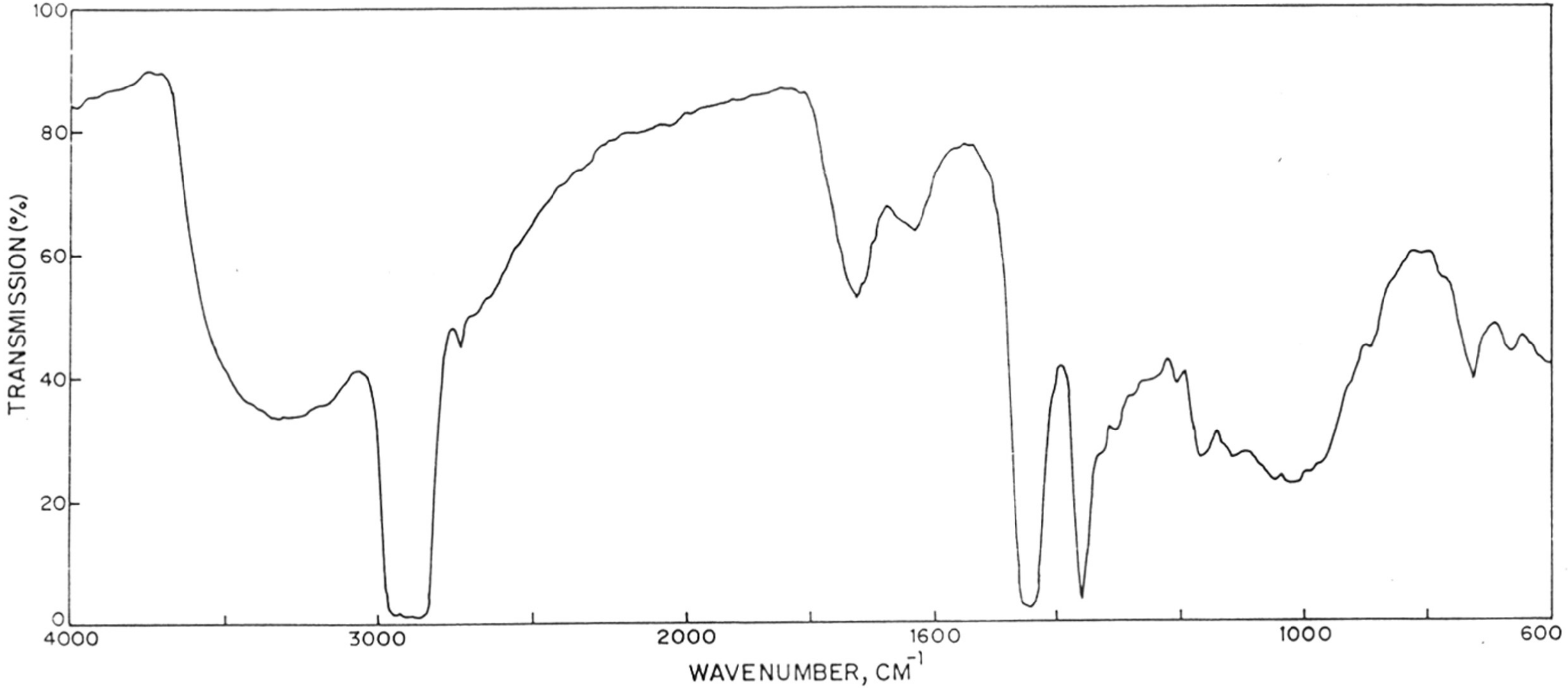


FIG. IV.3.4 : IR SPECTRUM OF 60% DCC IN NUJOL

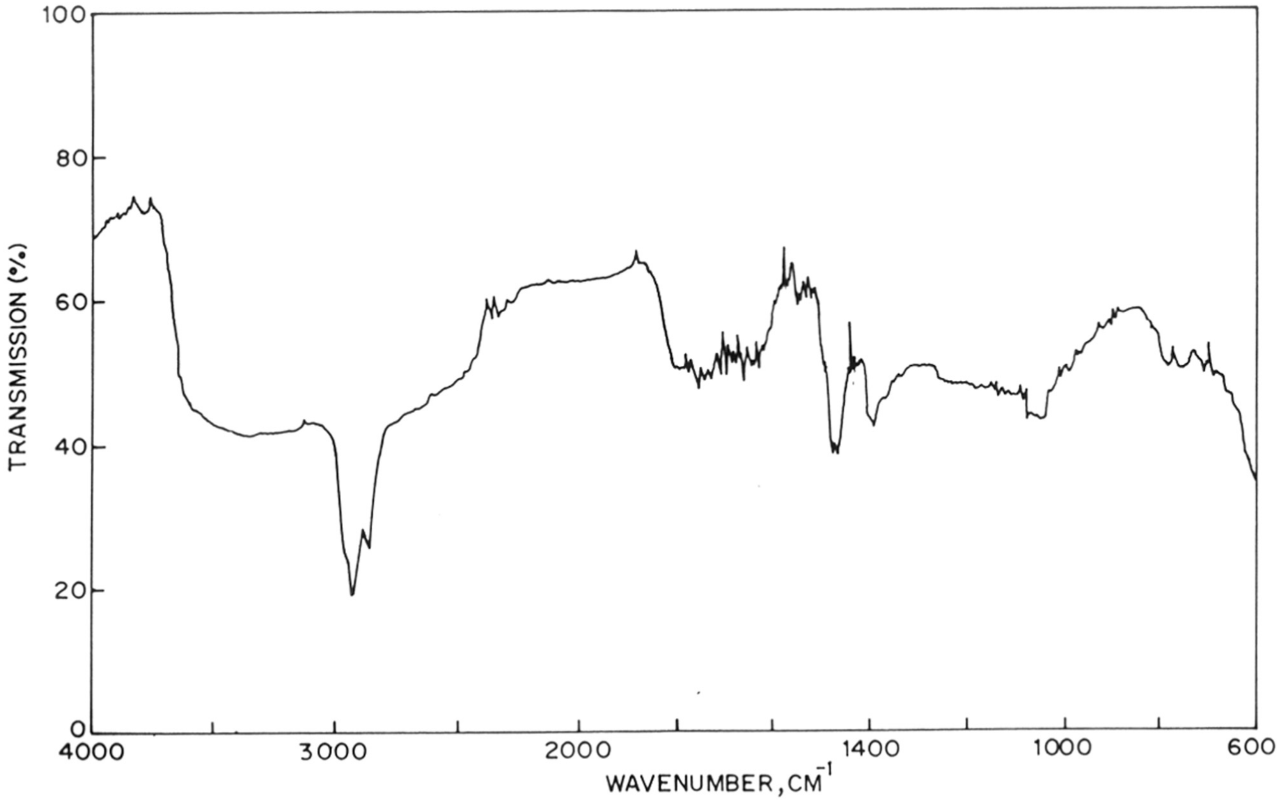


FIG. IV. 3·5 : IR SPECTRUM OF 80 % DCC IN NUJOL

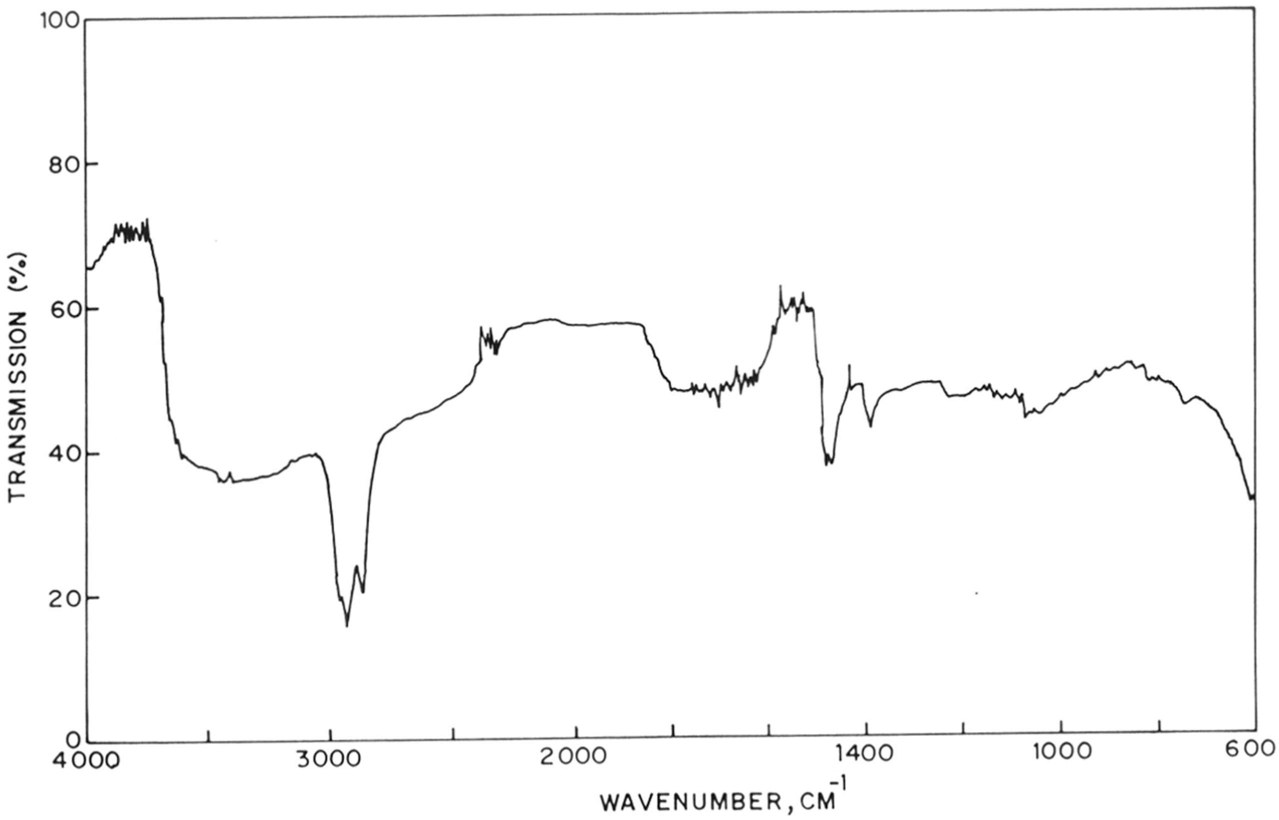


FIG. IV. 3·6: IR SPECTRUM OF 98 % DCC IN NUJOL

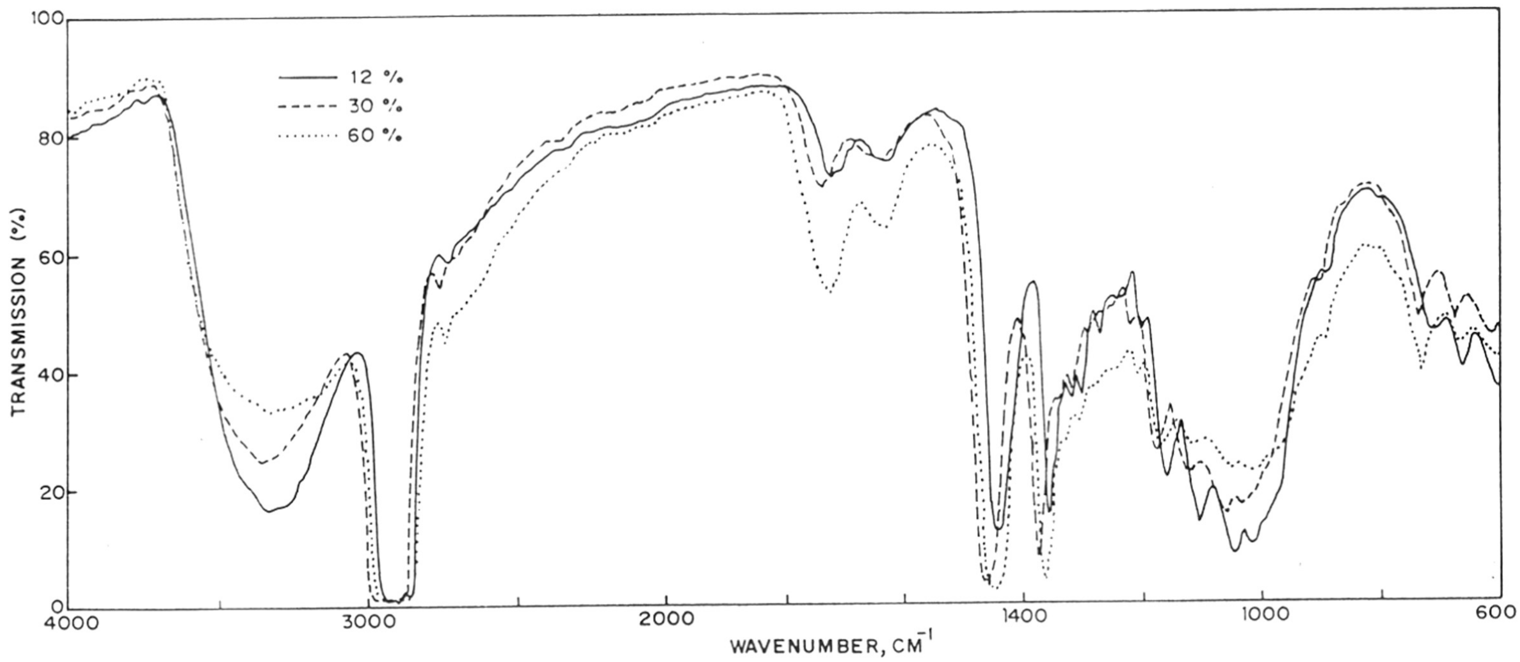


FIG. IV·3·7: OVERLAPPING IR SPECTRA OF 12%, 30%, 60% DCC IN NUJOL

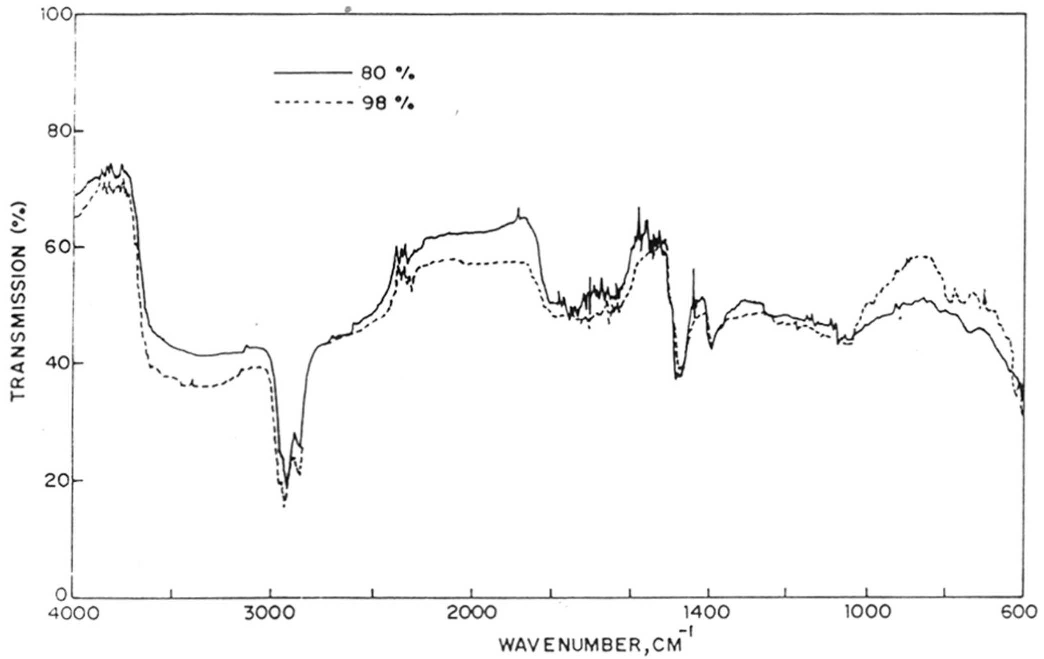


FIG. IV.3.8: OVERLAPPING IR SPECTRA OF 80% AND 98% DCC IN NUJOL

IV.4 SYNTHESIS OF CELLULOSIC DIAMINE

Material

Cellulose powder CP-100 was described in Section IV.1.

The synthesis of 30% 2,3-Dicarboxycellulose (i.e. 30% of the glucose monomer units were converted at 2,3-Dicarboxycellulose) was described in Section 3.

Chemicals

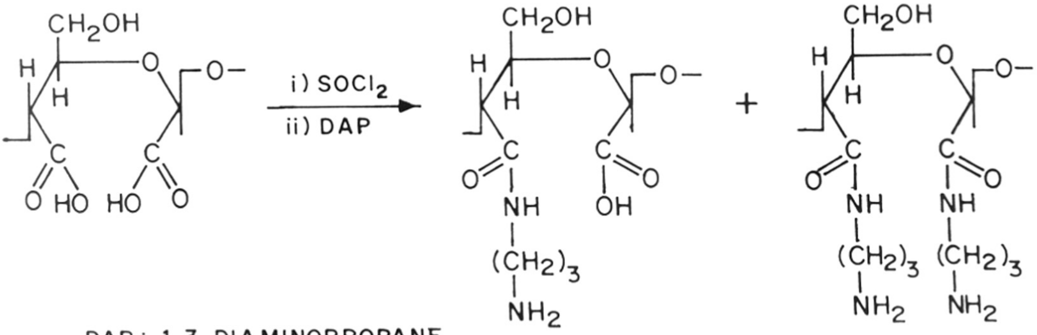
The epoxy resin (Araldite GY 250 based on bisphenol-A and epichlorohydrin of epoxy equivalent weight 192-196 and viscosity 225-275P at 21°C) was obtained from Ciba Geigy, Bombay. Diaminopropane (DAP) was procured from Aldrich, Milwaukee. Carbon terachloride (99.5%), Thionyl Chloride (99.5%), and Triethylamine (99%) were supplied by S.D. Fine Chemicals, Boisar. All these chemicals were used without further purification.

Synthesis of Cellulosic diamine

Procedure: 5.0 g of 30% 2,3-Dicarboxycellulose was dispersed in 15 mL CCl_4 and to this was added 25 mL thionyl chloride and refluxed for 5h to give the DCC acid chloride. Excess thionyl chloride was removed by vacuum distillation. 15 mL CCl_4 was added to the DCC acid chloride and heated to reflux. 1 mL Triethylamine was added, followed by the dropwise addition of 2.5 mL of diaminopropane dissolved in 10 mL CCl_4. This mixture was refluxed for 18h. The product was filtered, washed with water and methanol and dried to get 5.4 g 1,3-Diaminopropane-linked 2,3-Dicarboxycellulose. The amount of diaminopropane attached to the carboxy cellulose was estimated by weight gain which was 8% (Fig.IV.4.1).

I.R. spectra of 2,3-Diaminopropane-linked 2,3-Dicarboxycellulose

Infrared spectra (Fig.IV.4.2) of 1,3-Diaminopropane-linked 2,3-dicarboxycellulose in nujol emulsion showed carbonyl peak at 1675 cm^{-1} and the CONH peak at 3190 cm^{-1}.



DAP : 1,3-DIAMINOPROPANE

FIG. IV·4·1 : REACTION SCHEME FOR SYNTHESIS OF CELLULOSIC DIAMINE

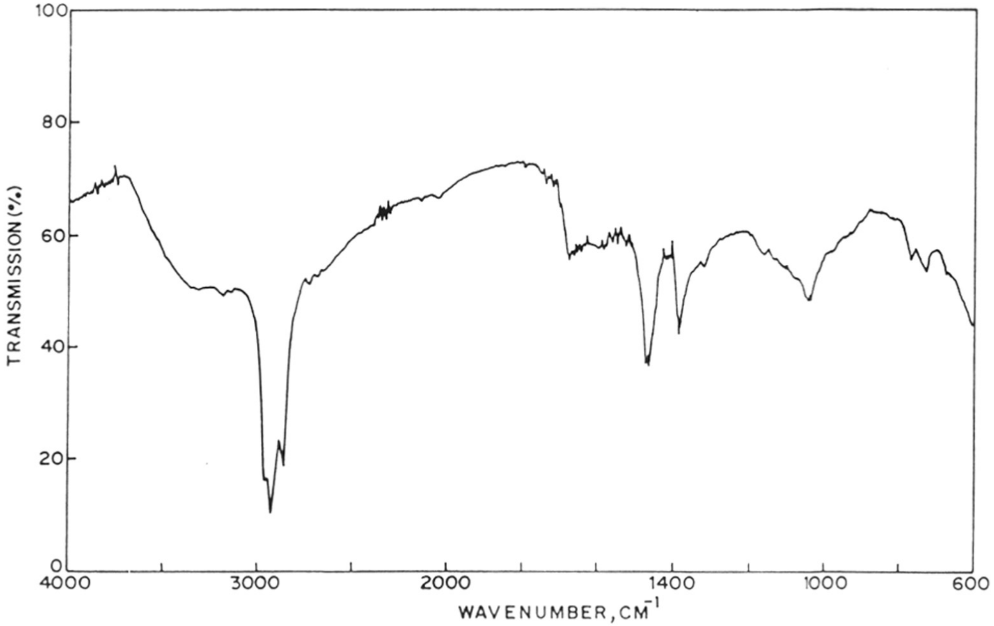


FIG. IV·4·2: INFRARED SPECTRUM OF 1,3-DIAMINOPROPANE-LINKED 2,3-DICARBOXY CELLULOSE

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IV.5 STUDY OF CRYSTALLINITY CHANGES IN OXIDIZED CELLULOSES

Introduction

Partial oxidation of cellulose can lead to a variety of polymers having different functional groups, such as aldehyde and carboxyl groups, in addition to the primary and secondary hydroxyl groups already present. This can increase the range of applications of cellulose. Oxidized cellulose has been recognised as an important material for use in chromatography (1). We have already demonstrated curing rate acceleration by the use of oxidized cellulose powder instead of ordinary cellulose in an epoxy matrix (2). Recently, we have prepared cellulosic diamines from oxidized cellulose and used these as reaction-incorporated fillers in an epoxy matrix, thereby completely eliminating the separate addition and compounding of a curing agent and simultaneously enhancing the curing rate and preventing phase separation of the filler and epoxy matrix (3).

Oxidation of cellulose causes changes in the structure and crystallinity of the resulting molecule, which affects its chemical and physical properties. Previously, we had briefly reported on the relative crystallinities of dialdehydecellulose (DAC) and heat treated cellulose (4). We have now extended study to include sodium dicarboxy cellulose (NaDCC) and dicarboxycellulose (DCC) which are obtained by further oxidation of DAC. We also report here the water absorption characteristics and thermal properties of these oxidized products. Solid state CP-MAS C-13 NMR spectra of these molecules also support the results (5).

Experimental

Materials

Hardwood cellulose powder (CP-100, Cellulose Products of India Ltd., Ahmedabad) of ~150 mesh was used. It contained ~85% alpha-cellulose and an ether extract of 0.2% maximum.

Preparation of 2,3-dialdehydecellulose (DAC) by periodate oxidation :

12%, 30%, 60%, 80% and 98% DAC was prepared by following the procedures previously reported (4), leading to cellulose molecules having 12%, 30%, 60%, 80% and 98% of their glucose monomer units oxidized. It is well known that periodate oxidation of cellulose leads to breaking of the C_2-C_3 bond of the glucose and formation of 2,3-dialdehydecellulose (6). Titrimetry was used to calculate the consumption of metaperiodate (7). Infrared spectra (nujol) in each case confirmed the presence of a carbonyl peak at 1710 cm^{-1}, and, as already reported (8), this peak was much smaller than expected due to hemiacetal linkages being formed. The carbonyl peak was also not seen in the solid state CP-MAS C-13 NMR spectra of the dialdehydecelluloses (9).

Preparation of sodium 2,3-dicarboxycellulose (NaDCC) :

Reaction of DAC with sodium chlorite to produce NaDCC was carried out by a reported method (10). The quantities of sodium chlorite and glacial acetic acid were adjusted according to the dialdehyde content of DAC. Thus 12%, 30%, 60%, 80% and 98% DAC were converted to 12%, 30%, 60%, 80% and 98% NaDCC. Characterisation was carried out by a reported procedure (11). Solid state CP-MAS C-13 NMR spectra showed the carbonyl peak at ~175 ppm (9). The spectrum IR shows the carbonyl peak at 1600 cm^{-1} as reported (8).

Preparation of 2,3-Dicarboxycellulose (DCC) :

12%, 30% and 60% DCC was prepared from the corresponding NaDCC by a method reported in Ref. 12. 80% and 98% DCC was prepared from the corresponding NaDCC was prepared by the method of Maekawa and Kosijima (10). Solid state CP-MAS C-13 NMR spectra showed the carbonyl peak at ~169 ppm. The IR spectrum shows a prominent carbonyl peak at 1730 cm^{-1}.

IR, NMR, TG, WAXRD

IR spectra were recorded using a Perkin Elmer 283 B IR spectrophotometer using nujol emulsions smeared on sodium chloride plates.

Solid state C-13 NMR spectra were recorded using a Bruker MSL-300 FT-NMR with proton decoupling.

Thermogravimetric Analysis was carried out using a

Netzsch STA 409 thermal analyser at a heating rate of 10^{o}C/min. with a 10 mg sample weight.

Wide angle X-ray Diffraction (WAXRD) spectra were obtained using a Philips PW 1730 X-ray generators equipped with a Cu K target and β Ni filter. Diffractometer scans over a 2 θ range of 6-30^{o} were taken.

Results and Discussion

Table IV.5.1 and Figures IV.5.1-IV.5.3 show that the X-ray diffraction peak at $2\ \theta = 22.7^{o}$ for the oxidized cellulose samples (DAC, DCC, NaDCC) decreases almost proportionately to the degree of oxidation of the starting cellulose, accompanied by slight line broadening. However, there are some important differences in their relative crystallinities. Figure IV.5.4 shows a plot of change in % relative crystallinity resulting from different oxidation levels of the cellulose, along with deviations from the idealised linear relationship between % oxidation and % crystallinity. For example, assuming that the starting cellulose has 100% crystallinity, 30% DAC has a residual crystallinity of 80%. This value would have been 70% had both the crystalline and amorphous regions of cellulose reacted with exactly equal facility. However, as expected, the amorphous regions and the exposed surface are more accessible to attack by the periodate. Since 30% NaDCC was produced by reacting 30% DAC with sodium chlorite, thereby

Table IV.5.1

Wide angle X-ray diffraction data for cellulose and oxidized celluloses: 2,3-dialdehydecellulose (DAC), 2,3-dicarboxy cellulose (DCC), and sodium 2,3-dicarboxycellulose (NaDCC)

Sample	Peak intensity at $2\theta = 22.7$ height (cms)	Full width of half maximum of $2\theta = 22.7°$ peak (degrees)	% crystallinity [100 x crystalline peak height at $2\theta = 22.7°$] (peak ht. of cellulose at $2\theta = 22.7°$
Cellulose	19.6	1.35	100
30% DAC	15.6	1.35	80
60% DAC	7.3	1.60	37
80% DAC	4.5	1.85	23
98% DAC	3.3	2.80	17
12% DCC	14.2	1.35	72
30% DCC	11.5	1.40	59
60% DCC	8.5	1.40	43
98% DCC	2.8	1.90	14
12% NaDCC	17.1	1.30	87
30% NaDCC	10.3	1.30	53
60% NaDCC	7.6	1.50	39
80% NaDCC	3.2	-	16
98% NaDCC	1.1	1.65	6

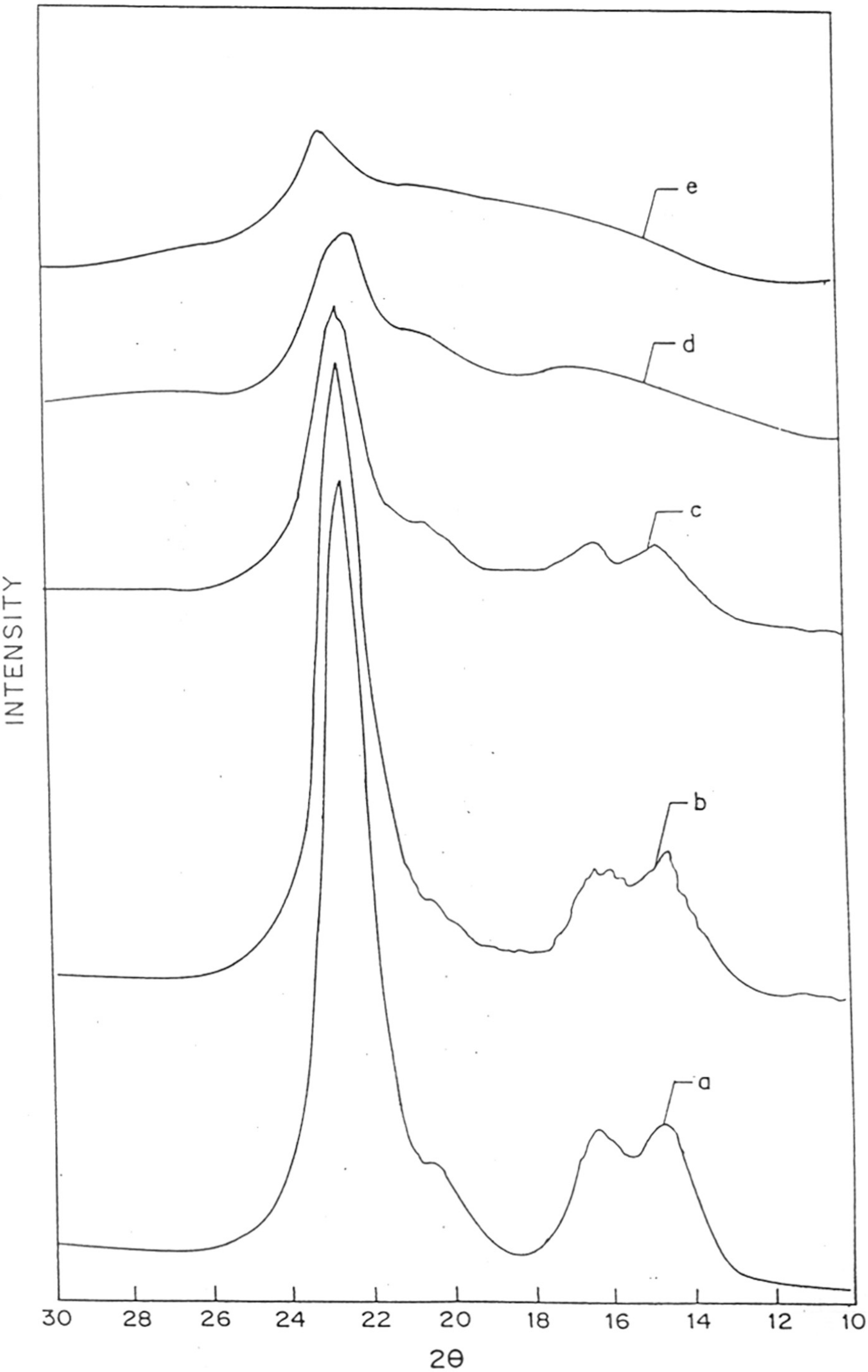


FIG.IV·5·1 : X-RAY DIFFRACTOGRAMS OF OXIDIZED CELLULOSE
a) CELLULOSE POWDER, CP-100 b) 30% DAC c) 60% DAC
d) 80% DAC e) 98% DAC

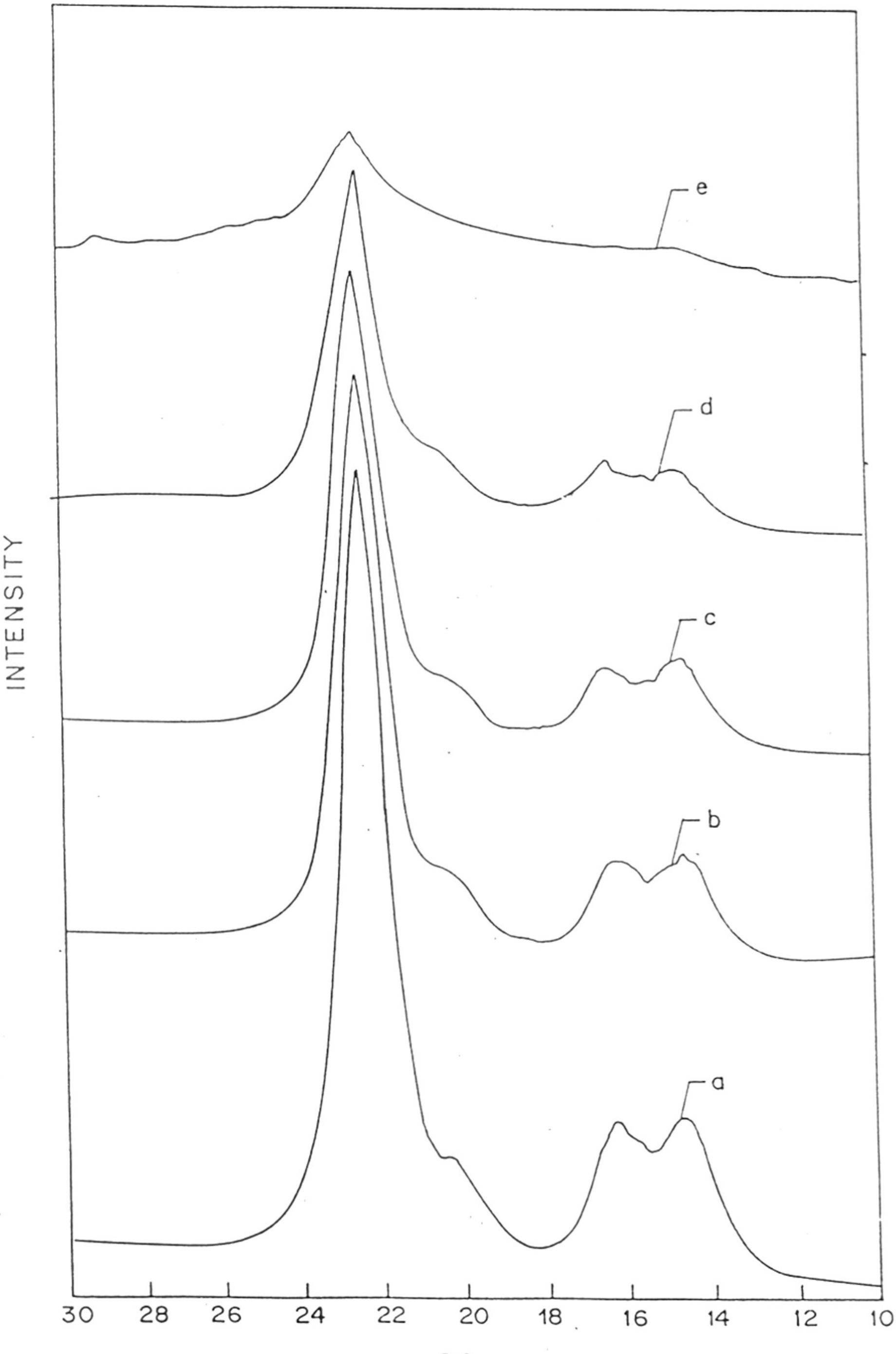
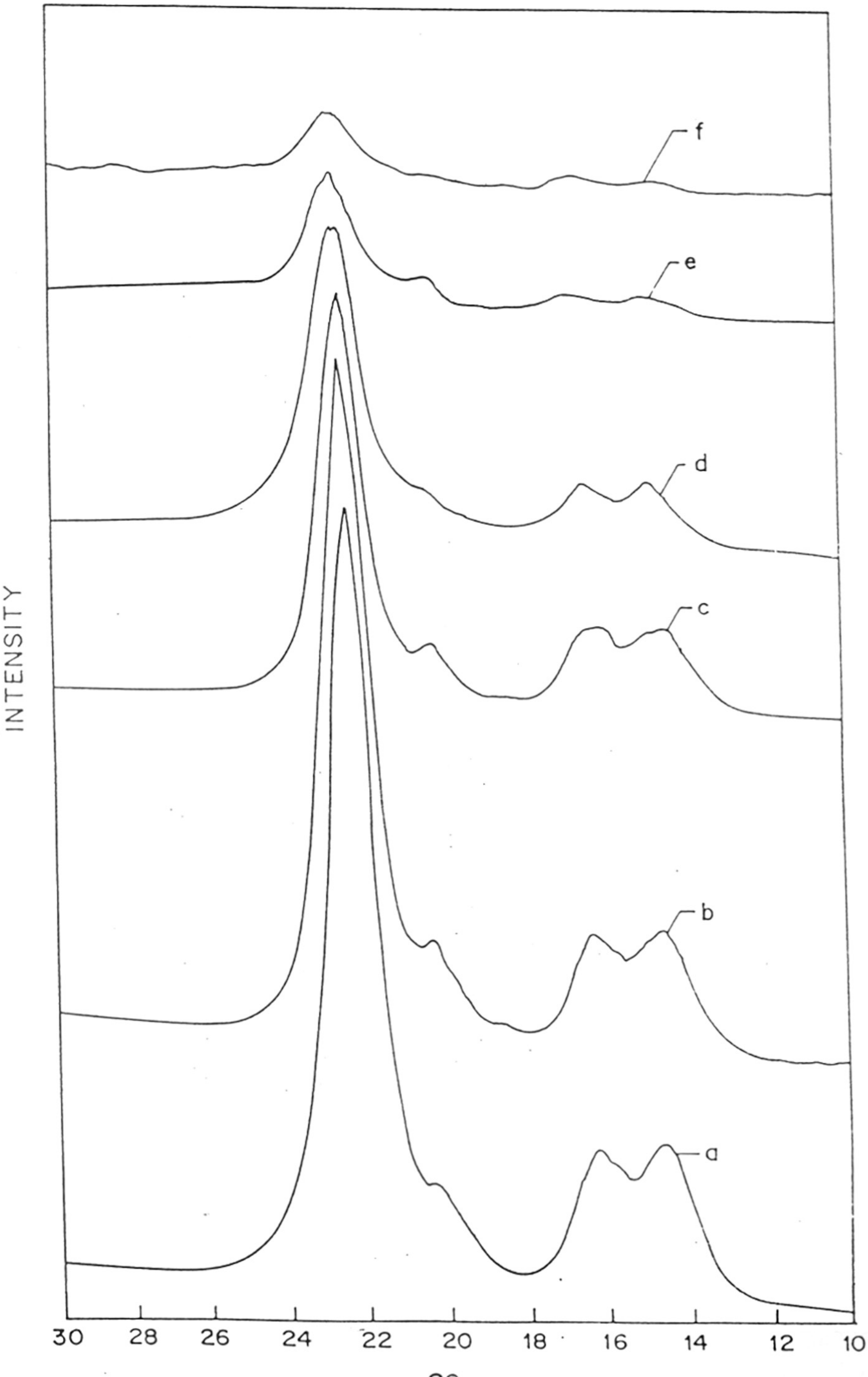


FIG.IV·5·2: X-RAY DIFFRACTOGRAMS OF OXIDIZED CELLULOSE
a) CELLULOSE POWDER, CP-100 b) 12 % DCC c) 30 % DCC
d) 60 % DCC e) 98 % DCC



FIG·IV·5·3: X-RAY DIFFRACTOGRAMS OF OXIDIZED CELLULOSE
a) CELLULOSE POWDER, CP-100 b) 12 % NaDCC
c) 30% NaDCC d) 60 % NaDCC e) 80 % NaDCC f) 98% NaDCC

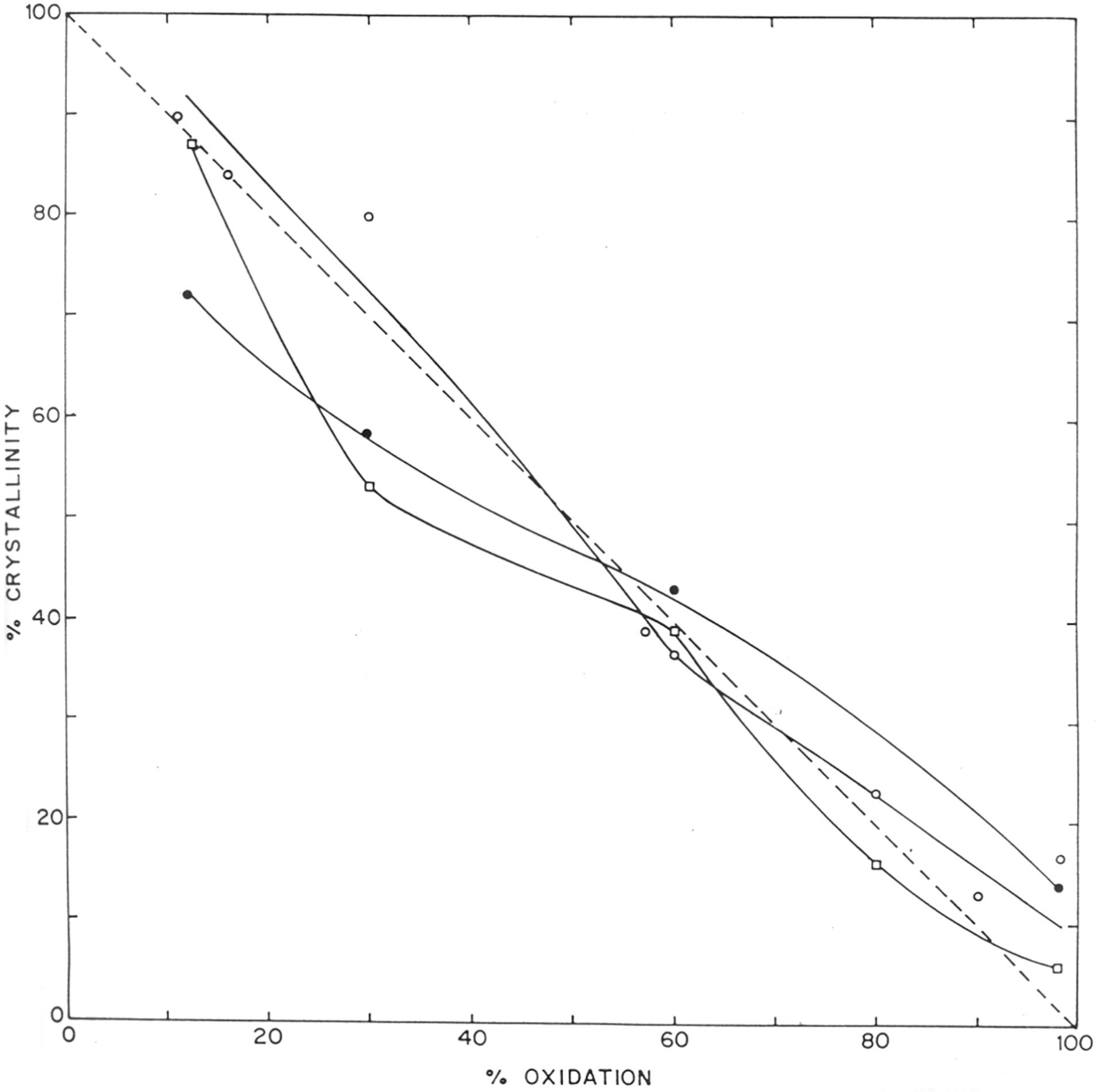


FIG.IV·5·4: CHANGES IN CRYSTALLINITY WITH DEGREE OF OXIDATION FOR DIFFERENT OXIDATION PRODUCTS OF CELLULOSE MEASURED AT 2θ = 22·7.° ○ DAC, ● DCC, □ NaDCC, ---- THEORETICAL oxidising the aldehyde functional groups to the sodium carboxylate functional group but leaving the hydroxyl functional groups intact, it may be expected that 30% NaDCC should have the same or similar crystallinity as 30% DAC. 30% NaDCC, however, has a residual crystallinity of only 53%, as compared to 80% for 30% DAC. This drastic decrease in the crystallinity of NaDCC may be due to polymer chain degradation in the acidic reaction environment in which it was synthesized as well as changes in the intermolecular H-bonding. This was ascertained at least for the 98% NaDCC which was found to be water soluble, and a viscometric study carried out showed its molecular weight to be in the region of only 6000 (13). 30% DCC, which was produced by acidification of 30% NaDCC (12), has almost the same crystallinity as 30% NaDCC. The slightly higher value observed may be due to improved inter-molecular H-bonding possible in 30% DCC, leading to structure formation. Below 20% oxidation levels, the observed crystallinities are close to the idealised linear relationship line, except for DCC (Fig.IV.5.4).

Above 60% oxidation, the observed crystallinities are again close to the idealised linear relationship line, except for 98% DCC and 98% DAC.

Table IV.7.2 shows the temperatures at which the major losses in weight occurs for cellulose and the oxidized celluloses. It was observed in thermogravimetric studies that at the initial stages of weight loss with heating (200°-400°C) almost all oxidized samples started to decompose at lower temperatures than the starting cellulose. This again reflects their lower crystallinity as compared to cellulose. However, the decomposition patterns became more complex with increasing oxidation (above 30%), and two stage decompositions occurred for all initial weight losses (up to ~400°). In the case of NaDCC, even the final weight loss temperature range (500°-650°C) showed two stages decomposition. The final weight loss of all DAC and DCC samples was in the 80-85% range, while for NaDCC the range was 30-70%.

The changes in the structure and crystallinity of oxidized celluloses are also indicated in the spectral features of the high resolution solid state CP-MAS C-13 NMR studies (5). A detailed paper on this aspect is also nearing completion (9).

In conclusion, it can be said that studies of the type reported in this paper are useful in understanding the structural changes that occur when cellulose is oxidized and in explaining structure property correlations with respect to thermal properties, solvent absorption, etc. This information is useful in planning applications of these products.

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APPENDIX

APPENDIX

X-ray diffraction comparisons of different oxidized cellulose derivatives (DAC, DCC, NaDCC) having the same degrees of oxidations.

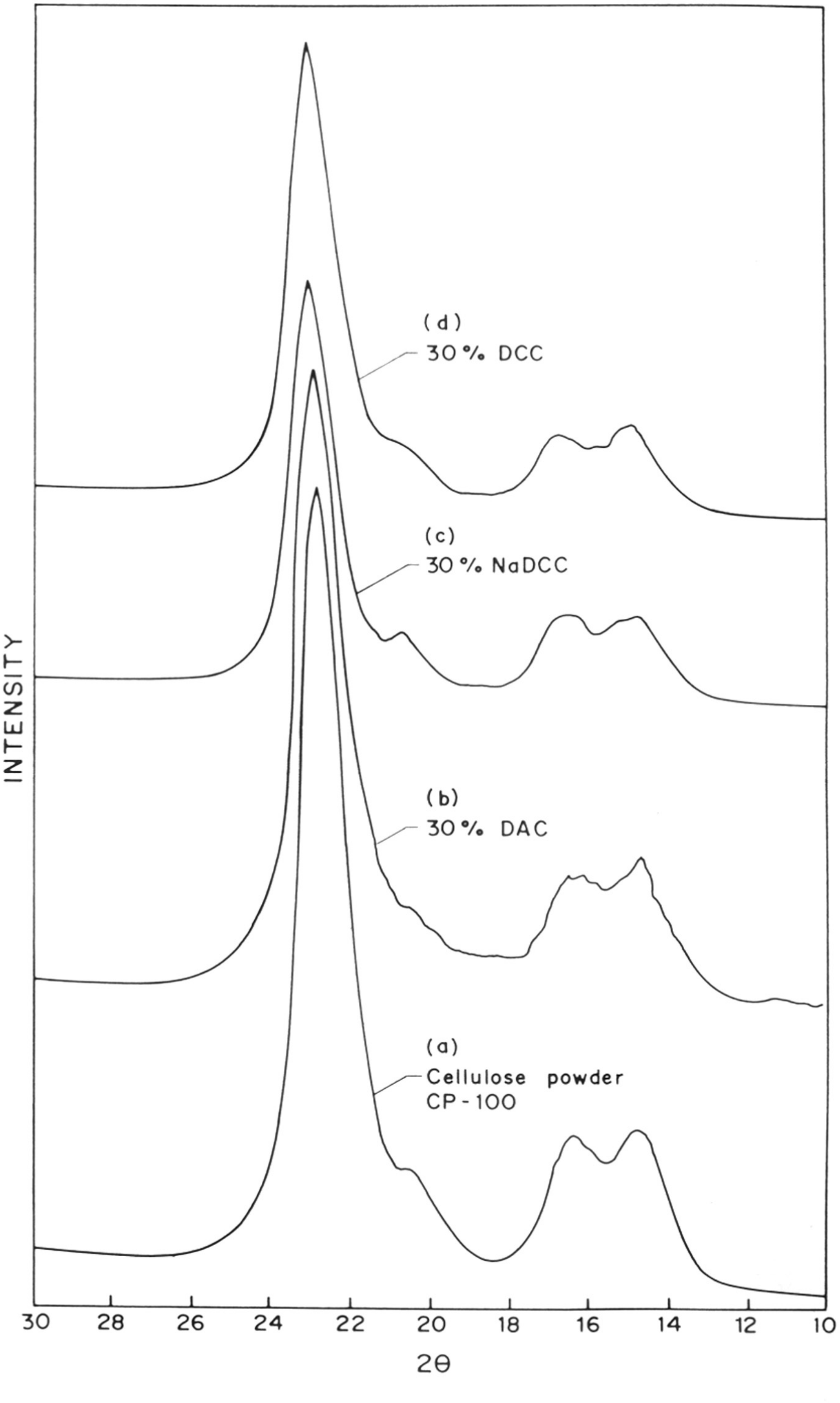

FIG.IV.5·5: X-RAY DIFTRACTOGRAMS OF OXIDIZED CELLULOSES
a) CELLULOSE POWDER, b) 30% DAC, c) 30% NaDCC,
d) 30% DCC

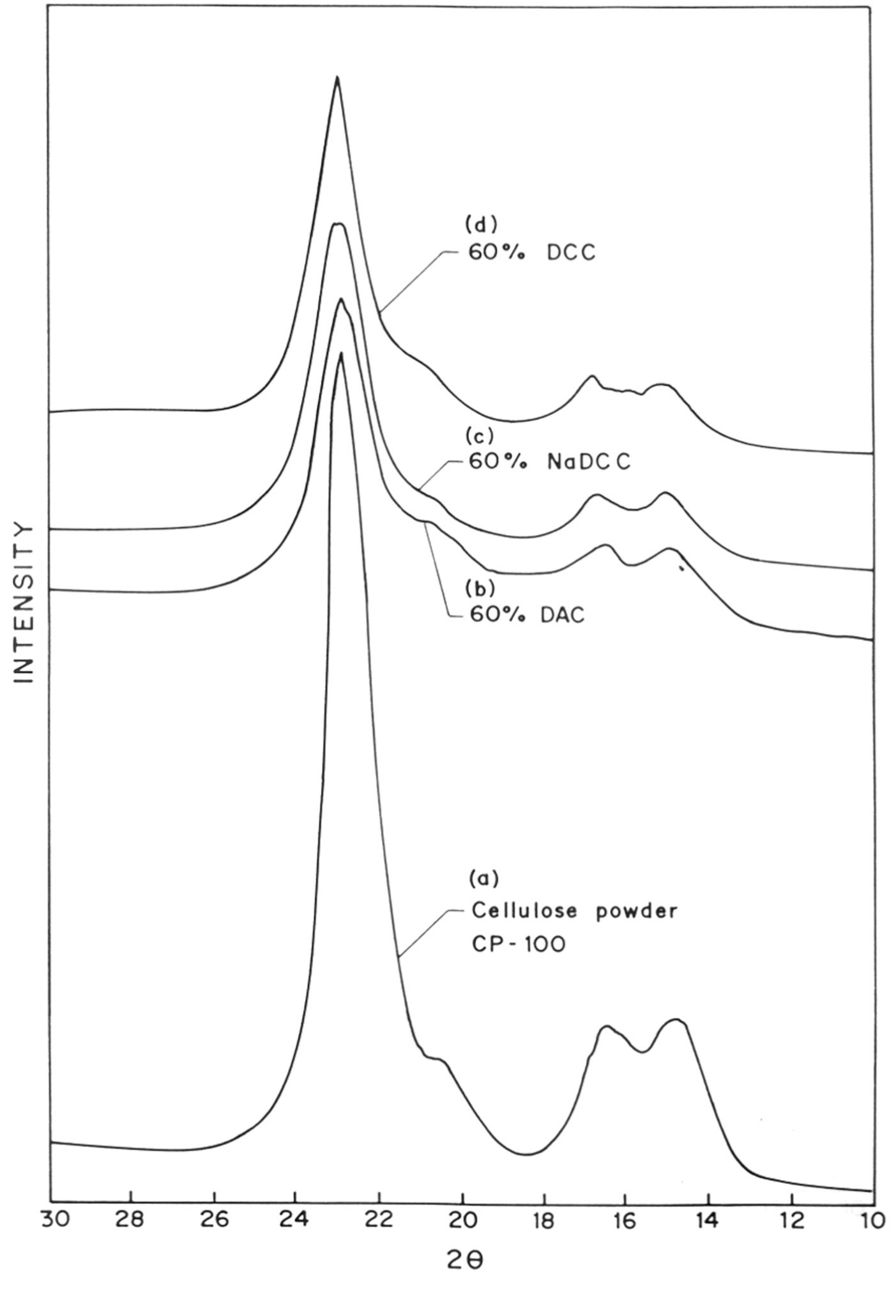

FIG. IV.5·6 : X-RAY DIFTRACTOGRAMS OF OXIDIZED CELLULOSES:
a) CELLULOSE POWDER CP-100, b) 60% DAC, c) 60% NaDCC,
d) 60% DCC

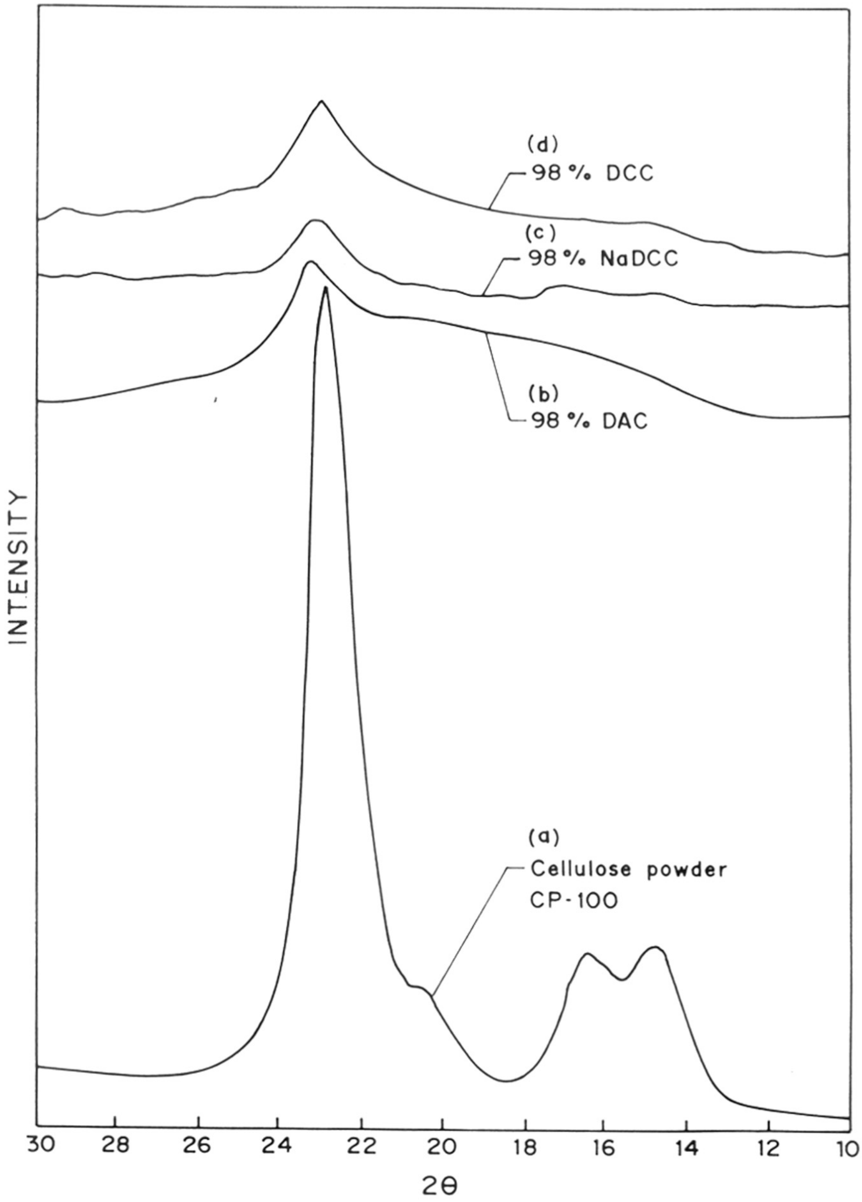

FIG.IV.5·7: X-RAY DIFTRACTOGRAMS OF OXIDIZED CELLULOSES:
a) CELLULOSE POWDER CP-100, b) 98 % DAC, c) 98 % NaDCC,
d) 98 % DCC

IV.6 HIGH RESOLUTION SOLID STATE CP/MAS C-13 NMR STUDIES OF CELLULOSE AND ITS OXIDIZED DERIVATIVES

Introduction

A large number of structural studies based on solid state C-13 NMR of crystalline and amorphous cellulose, cellulose polymorphs, and model compounds, have been reported in recent literature (1-6). The observations regarding the sensitivity of the spectra to the microcrystalline environment (1,2) is of great interest to scientists and technologists utilising cellulosic fibres and its modifications as reinforcements or fillers in composites. A change in the crystallinity of a polymer affects its physical properties. Fyfe et al. (5) briefly investigated the oxidized cellulose derivative dicarboxycellulose and found that the cellulosic portion of the spectrum (60-110 ppm) had the same general features as the starting cellulose. This was interpreted in terms of surface oxidation of the cellulose fibrils (5). This could be true of oxidized cellulose having low degrees of oxidation. However, at high degrees of oxidation wherein quantitative consumption of oxidising agent in relation to the cellulose occurs, there should not be much difference between the surface structure and the bulk structure. We have recently communicated our results on the crystallinity changes occurring in a series of dialdehydecelluloses (DAC), dicarboxycelluloses (DCC), and sodium dicarboxycelluloses (NaDCC), as studied by wide-angle X-ray diffraction (7,8). The results generally confirm our belief that atleast at higher oxidation levels (say around 60%) the chemical structure in the bulk and on the surface are not too different. With this as a base, then, we felt it would be of great interest to study the solid state C-13 NMR spectra of a series of oxidized celluloses with incremental changes in oxidation levels. We thus present in this paper, solid state C-13 NMR studies of 30%, 60%, 80%, and 98% oxidized DAC, DCC, and NaDCC.

Experimental

Materials

Cellulose powder CP-100 of 100 mesh fineness, was a product of Cellulose Products of India, Ltd., Ahmedabad. It had an α-cellulose content of ~ 85%, and ether extract was 0.2% max.

Oxidized Celluloses

The synthesis and characterisation of 30%, 60%, 80%, and 98% 2,3-dialdehydecelluloses (DAC), sodium 2,3-dicarboxylate celluloses (NaDCC), and 2,3-dicarboxycelluloses (DCC), is reported elsewhere in detail (7-10).

NMR

A Bruker MSL-300 NMR Spectrometer was used to obtain solid state C-13 NMR with CP/MAS, operating at 75.47 MHz. The spectra were recorded under matched Hartmann-Hahn conditions at 52 KHz, using a spectral width of 30 KHz and dipolar decoupling of 52 KHz. The Hartmann-Hahn match condition was adjusted using adamantane. The chemical shifts are referred to the low field CH carbon of adamantane taken as 37.3 ppm from TMS.

Results and Discussion

A wide-angle X-ray diffraction spectral study of oxidized cellulose samples (DAC, DCC, NaDCC) shows that the crystalline peak at 2θ = 22.7° decreases almost proportionately to the degree of oxidation of the starting cellulose (7,8). Figure IV.5.4 shows a plot of change in % crystallinity resulting from different oxidation levels of the cellulose. The reasons for the deviations from the idealised theoretical curve are explained in an earlier paper (7).

Considering the significant changes in the crystallinity of cellulose on oxidation, we felt it would be of interest to record their high resolution solid state C-13 CP/MAS NMR spectra and compare their structural features. Since periodate oxidation of cellulose leads to the cleavage of the C_2-C_3 bond of the glucose monomer unit, it would be of interest to see if any chemical shifts occur, as would be expected, particularly for the C_2 and C_3 carbons of DCC and NaDCC.

Table IV.6.1 lists the peak positions of the various peaks of cellulose and various oxidized celluloses, rationalised on the basis of peak positions assigned in literature for cellulose II (1,2,5). Surprisingly, there are no significant chemical shifts, even at high oxidation levels. The carbonyl peak of NaDCC appears around 174.5 ppm, while that of DCC appears around 169.5 ppm. The appearance of a ~ 174.5 ppm peak in DCC is due to incomplete exchange of the sodium ion of NaDCC by the ion-exchange resin.

For each series of spectra of increasing oxidation levels of DAC, DCC, and NaDCC (Figs. IV.6.1, 6.2 and 6.3), one notices an increasing trend towards formation of upfield shoulders on C_6, C_4 and C_1. At intermediate levels of oxidation we have mixtures of the original cellulose peaks superimposed on the peaks of the oxidized glucose monomer moeities. However, at 98% oxidation, we have an almost pure oxidized cellulose, and we expect to see a sharp spectrum like that of cellulose II (1). However, the 98% DAC gives a very broad spectrum, while the corresponding spectra of DCC and NaDCC are relatively better resolved. The sharp spectra of cellulose II is due to its high degree of crystallinity, and a continued decrease in crystallinity by oxidation leads to broad spectra. However, the type of broadness observed in "non-crystalline" oxidized cellulose is quite different from the uniform peak broadness of amorphous cellulose (1), since the former represent chemically and structurally new

TABLE-IV.6.1

CP/MAS C-13 NMR Chemical Shift Data of Cellulose and

Oxidized Celluloses (DAC, DCC, NaDCC)

Name of the sample	C_1	C_2	C_3	C_5	C_4	C_6	$\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}$
Cellulose	104.547	74.250	71.065	71.734	88.238	64.649	
30% DAC	104.438	74.039	70.724	71.574	88.130	64.444	
60% DAC	105.109	74.164	71.151	71.851	88.455	64.745	
80% DAC	103.656	74.135	71.119	71.719	88.376	64.830	
98% DAC	103.669	73.568	70.968	71.368	88.446	64.806	
30% NaDCC	104.859, 103.566	73.924	70.551	70.751	88.099	64.457	175.882
60% NaDCC	103.762	74.059	71.110	71.855	88.216	64.614	174.750
80% NaDCC	103.749	74.025	71.155	71.955	88.105	64.461	174.402
98% NaDCC	103.609	74.180	71.091	71.491	88.193	64.402	174.652
30% DCC	103.559	73.936	70.841	71.641	88.061	64.489	169.500
60% DCC	104.620	74.092	71.261	71.868	88.273	64.700	169.830
80% DCC	103.714	73.821	71.080	71.880	88.293	64.748	169.600 174.336
98% DCC	103.622	73.639	71.113	71.513	88.254	64.626	169.538 174.69

DAC - 2,3-Dialdehydecellulose

DCC - 2,3-Dicarboxycelluloses

NaDCC - Sodium 2,3-Dicarboxycelluloses

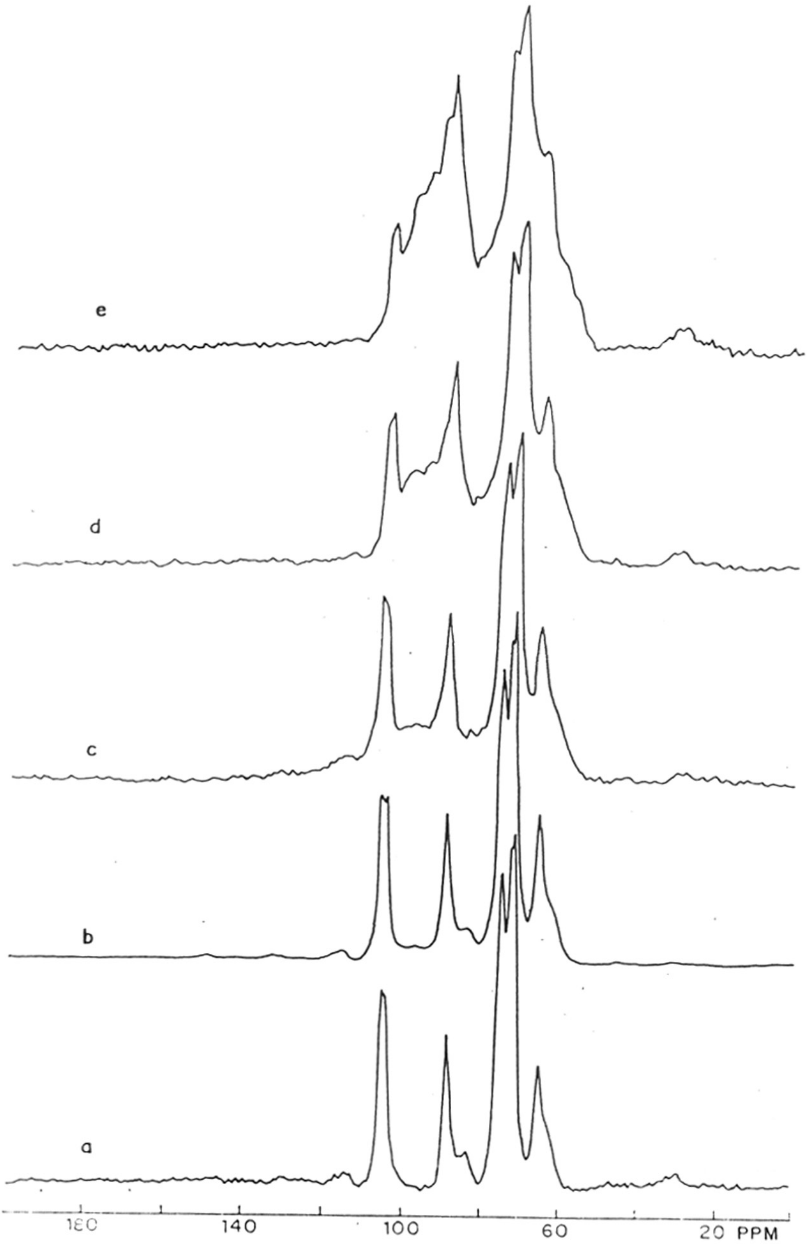

FIG.IV·6·1: COMPARATIVE Cp/MAS C-13 NMR SPECTRA SPECTRA OF 2,3 DIALDEHYDE CELLULOSE (DAC): a) CELLULOSE POWDER CP-100, b) 30% DAC, c) 60% DAC, d) 80% DAC, AND 98% DAC.

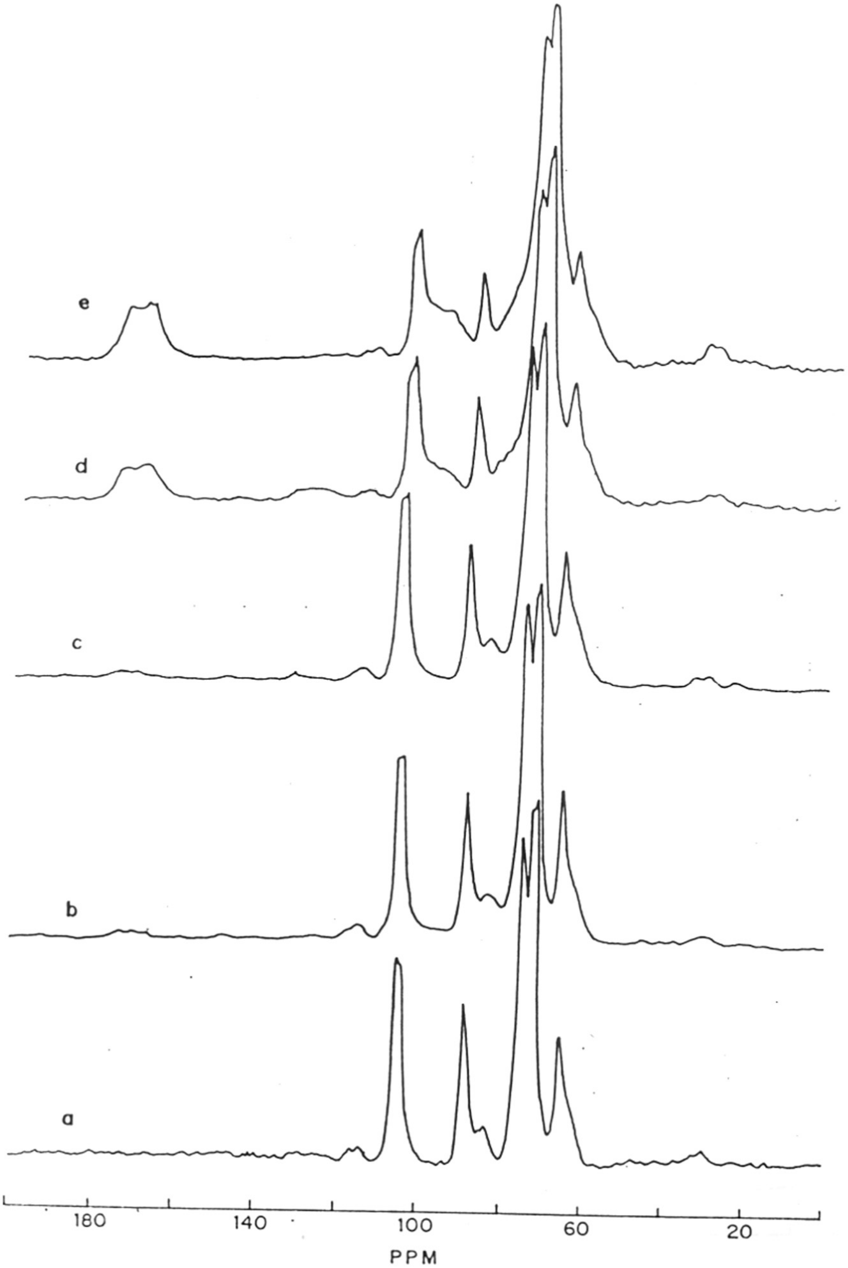

FIG. IV·6·2: COMPARATIVE Cp/MAS C-13 NMR SPECTRA OF 2,3-DICARBOXY CELLULOSE (DCC): a) CELLULOSE POWDER CP-100, b) 30% DCC, c) 60% DCC, d) 80% DCC AND e) 98% DCC

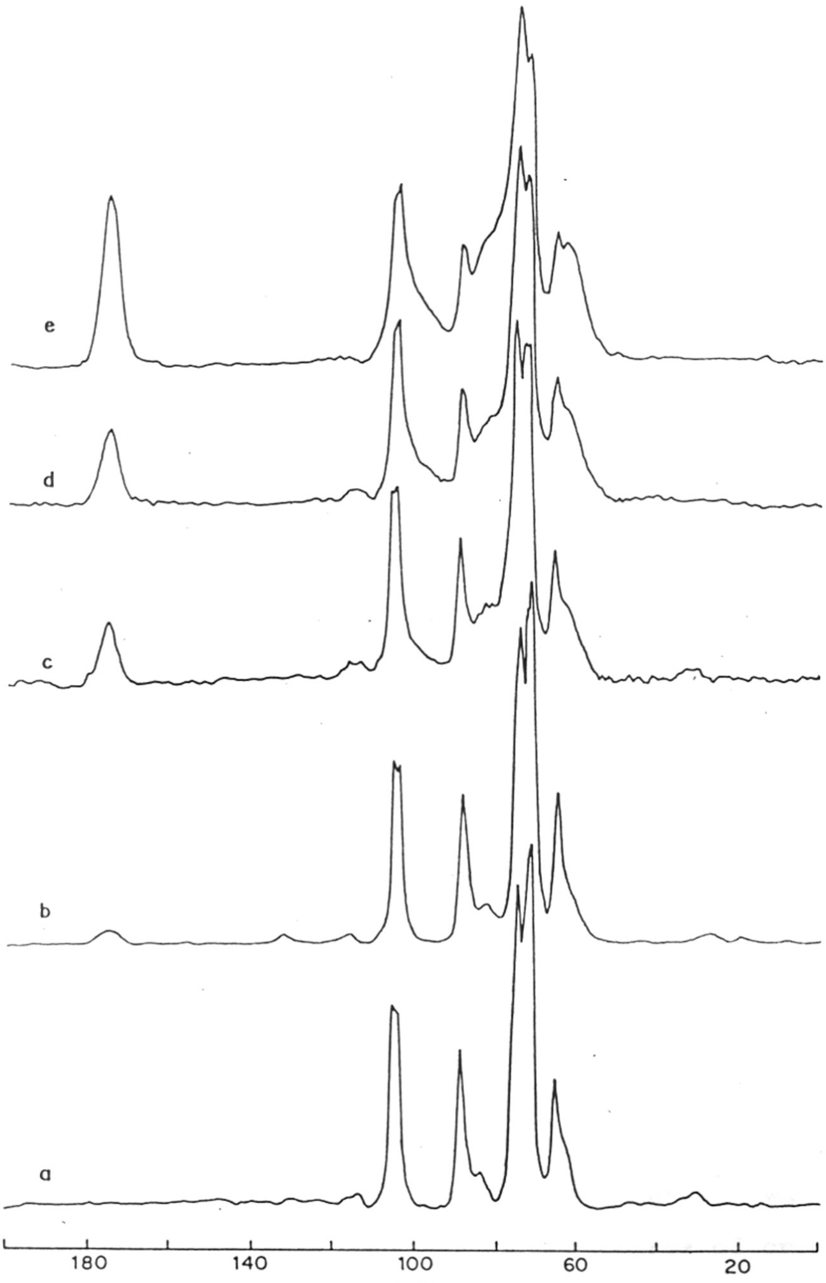

FIG. IV·6·3: COMPARATIVE Cp/MAS C-13 ~~NMR~~ SPECTRA OF SODIUM 2,3-DICARBOXY CELLULOSE : (NaDCC) a) CELLULOSE POWDER CP-100, b) 30 % NaDCC, c) 60 % NaDCC, d) 80 % NaDCC AND e) 98 % NaDCC molecules.

Comparison between the cellulose spectrum and that of 30% DAC, 30% DCC and 30% NaDCC (Figs. IV.6.1a, IV.6.1b, IV.6.2b, IV.6.3b) shows that there are practically no changes in the structural features, except for slight broadening of the small peak upfield of the C_4 peak at 88 ppm for the oxidized products. Apparently, at this lower degree of oxidation, many surface groups and amorphous regions get oxidized. The WAXRD data shows that for 30% DCC and 30% NaDCC, the residual crystallinity is much lower than that of 30% DAC, mainly due to polymer chain degradation (7). However, the NMR spectra do not show these differences in such a clear cut manner as WAXRD spectra.

In comparing the 60%, 80% and 98% oxidized celluloses with the cellulose II spectrum (Figs. IV.6.1-6.3), the observations are similar to that for the 30% oxidized samples, only now the upfield shoulders on C_6, C_4, and C_1 become increasingly more dominating. In the 30% oxidized celluloses only the peak upfield of the C_4 peak was noticeably broader.

Thus, oxidation of cellulose II leads to formation and broadening of peaks upfield of the C_6, C_4, and C_1 peaks of the cellulose II. Since increasing oxidation was shown to lead to a continual decrease in the degree of crystallinity (7), it can be inferred that the new broad peaks formed (upfield of C_6, C_4, and C_1) represent the amorphous content of the sample. Thus, CP/MAS C-13 NMR spectra of partially crystalline polymers can give an indication of their degree of crystallinity. We plan to similarly investigate a series of other polysaccharides and their derivatives.

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APPENDIX

APPENDIX

Additional CP/MAS C-13 NMR spectra of cellulose and its oxidized derivatives including comparisons of the different types of oxidised products (DAC, DCC, NaDCC) having the same degrees of oxidations.

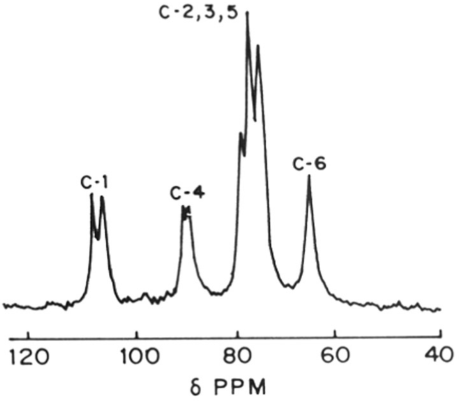

FIG. IV·6·4: CP/MAS C-13 NMR SPECTRUM OF HIGH CRYSTALLINE CELLULOSE

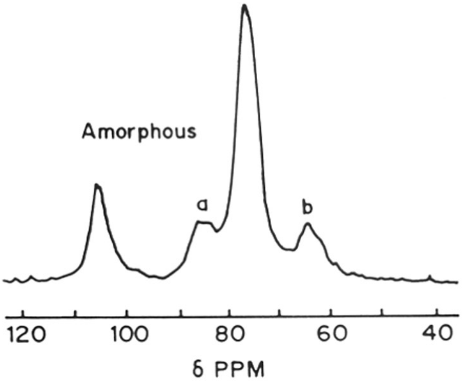

FIG. IV.6·5: CP/MAS C-13 NMR SPECTRUM OF AMORPHOUS CELLULOSE

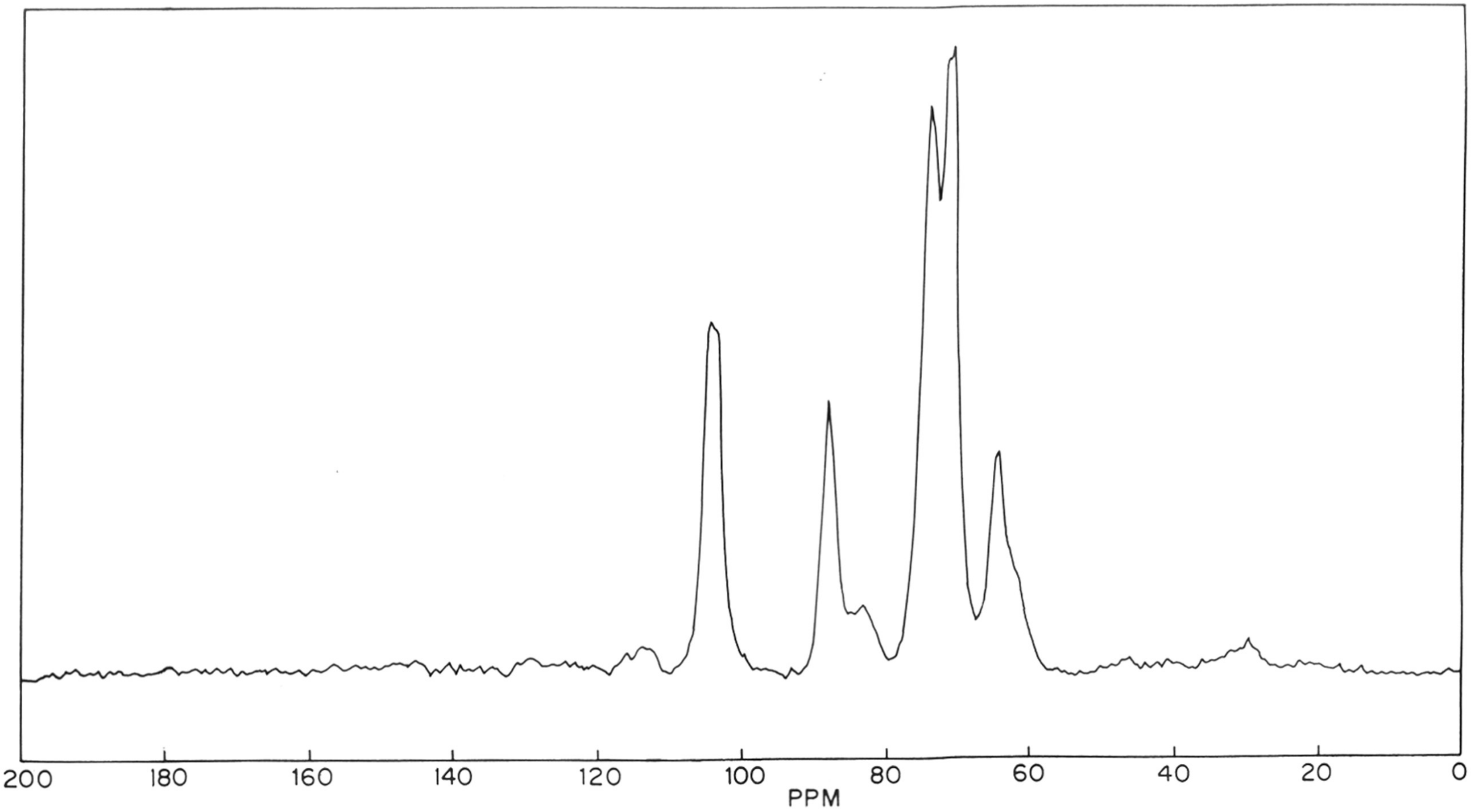

FIG.IV.6·6: CP/MAS C-13 NMR SPECTRUM OF CELLULOSE POWDER CP-100

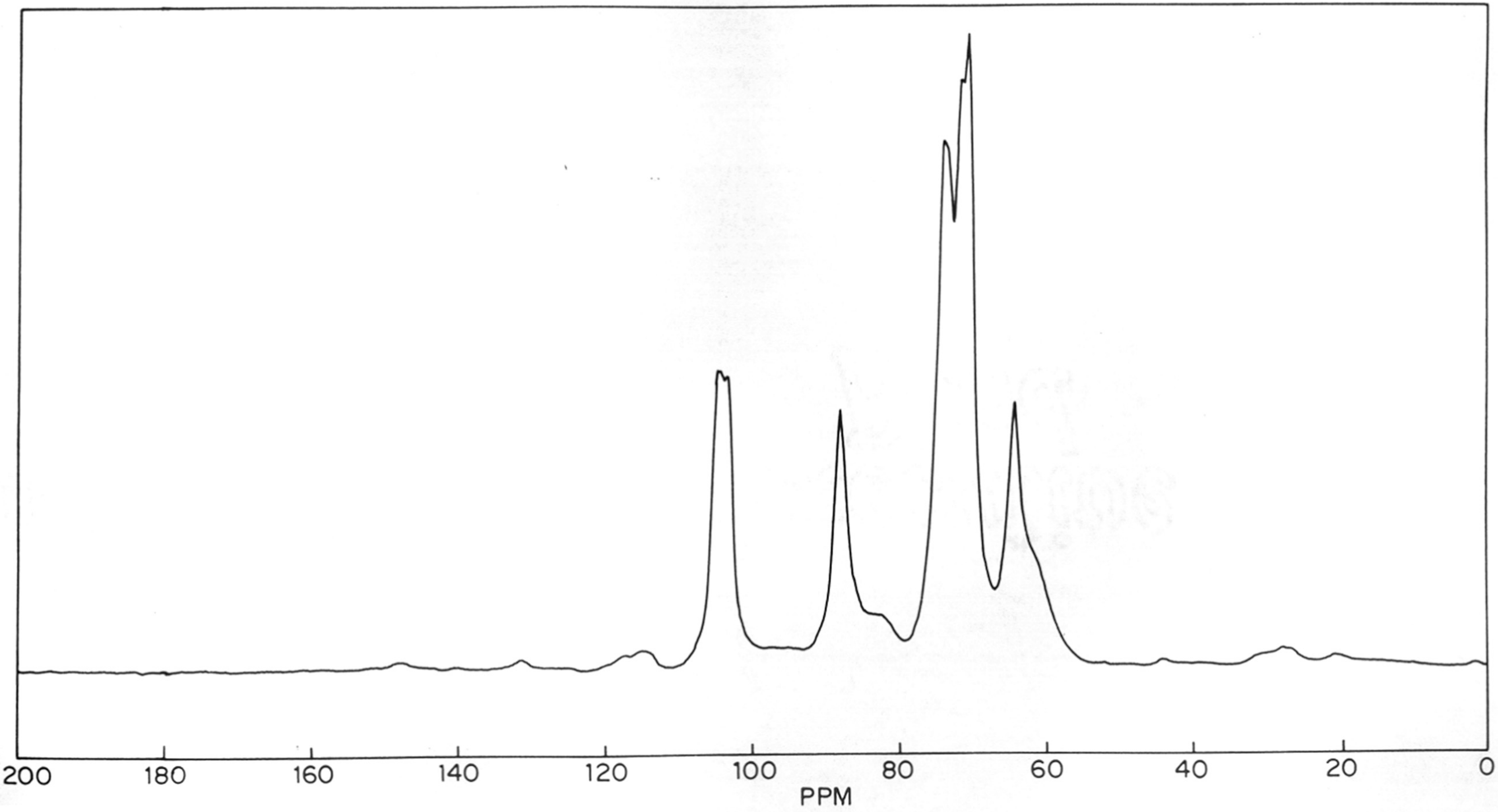

FIG.IV.6·7: CP/MAS C-13 NMR SPECTRUM OF 30% DAC

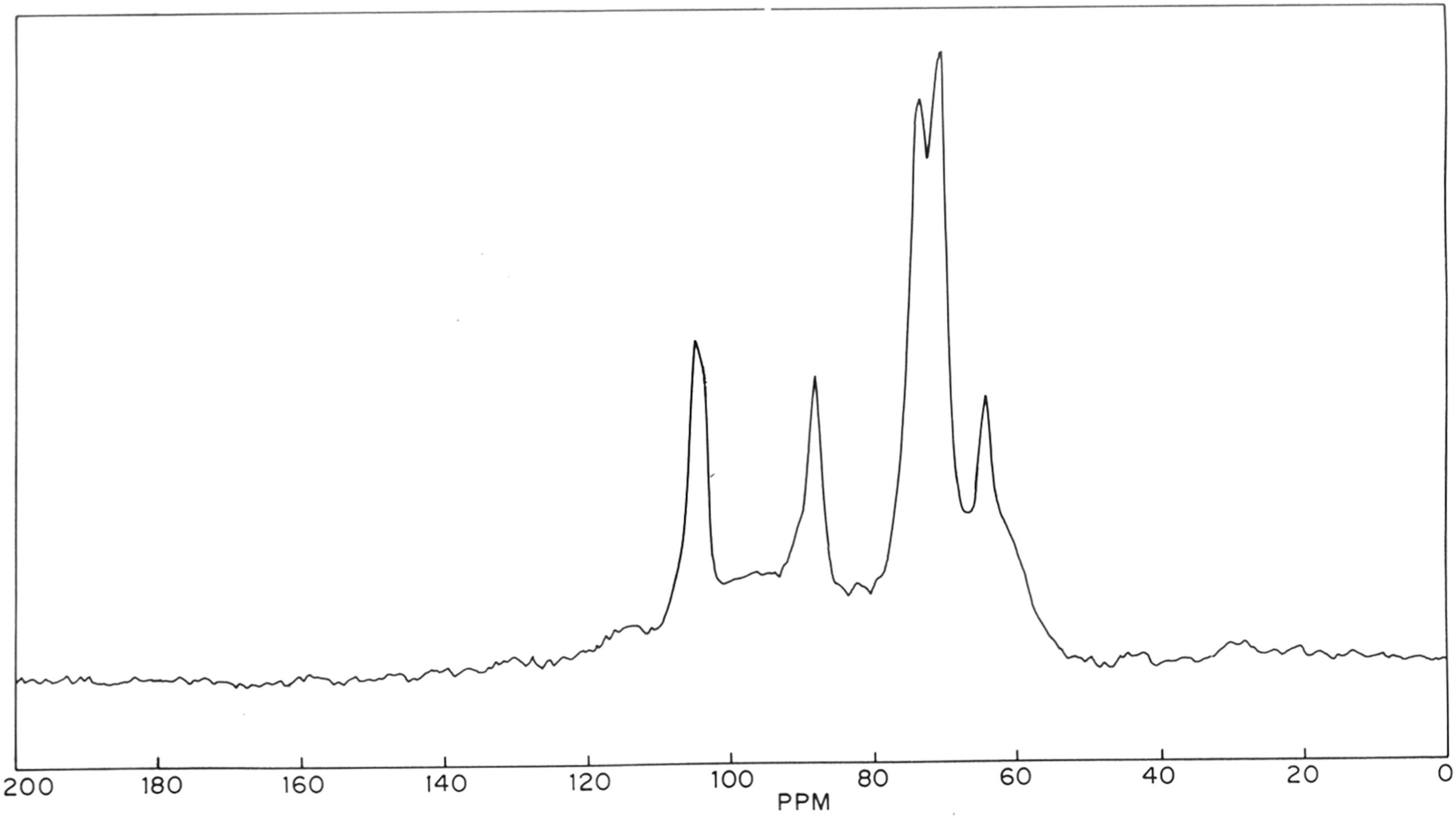

FIG.IV·6·8: CP/MAS C-13 NMR SPECTRUM OF 60% DAC

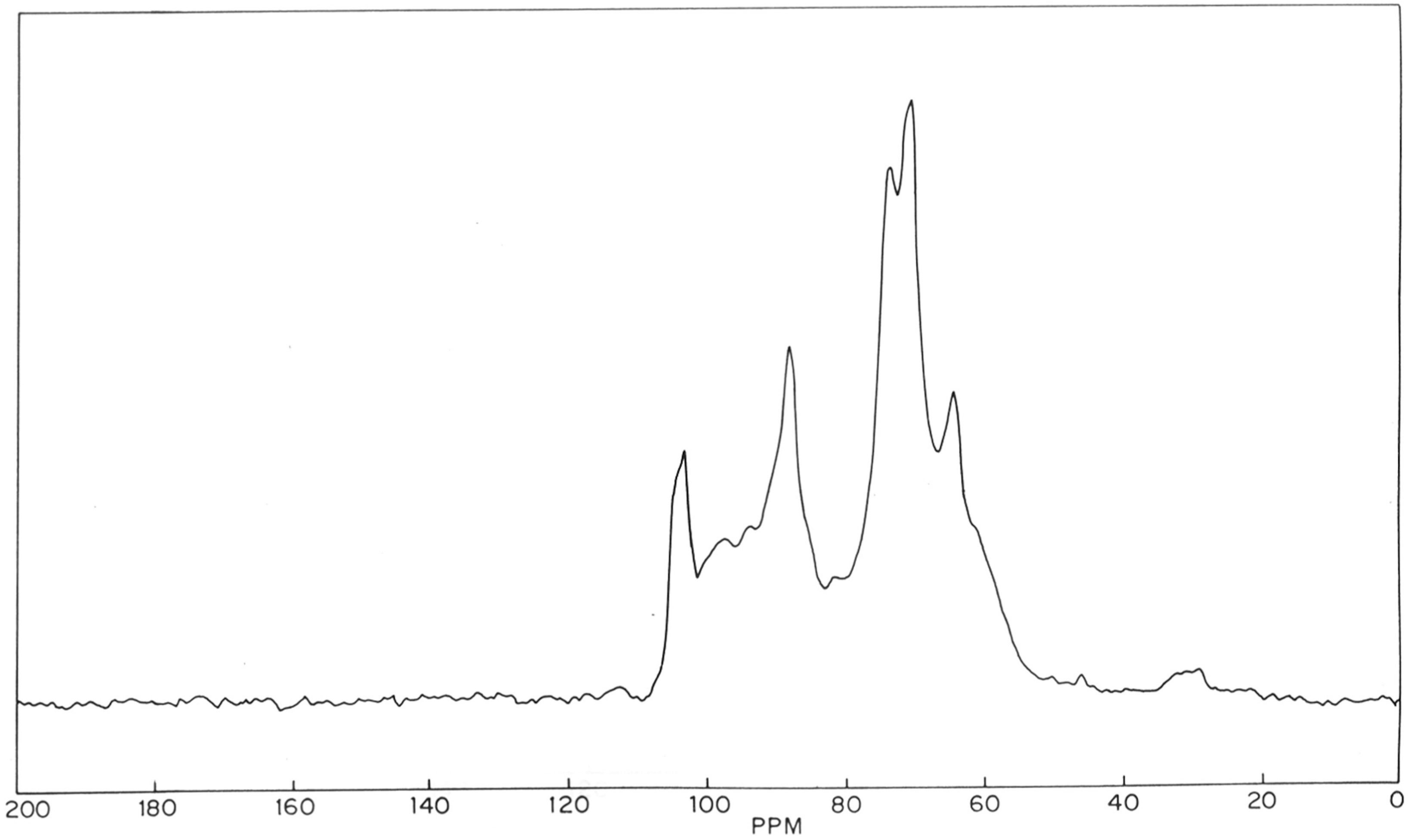

FIG.IV·6·9:CP/MAS C-13 NMR SPECTRUM OF 80% DAC

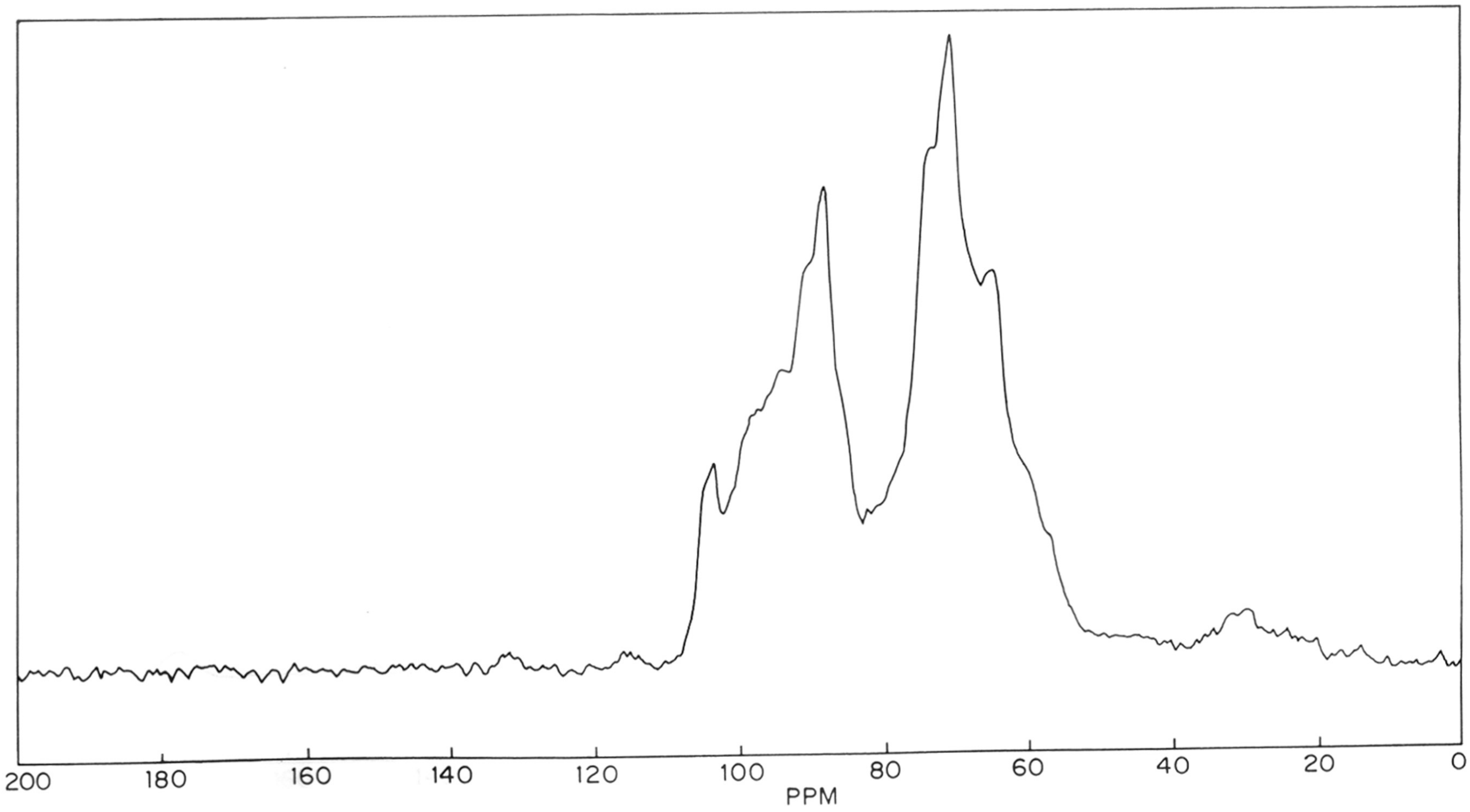

FIG. IV·6·10: CP/MAS C-13 NMR SPECTRUM OF 98% DAC

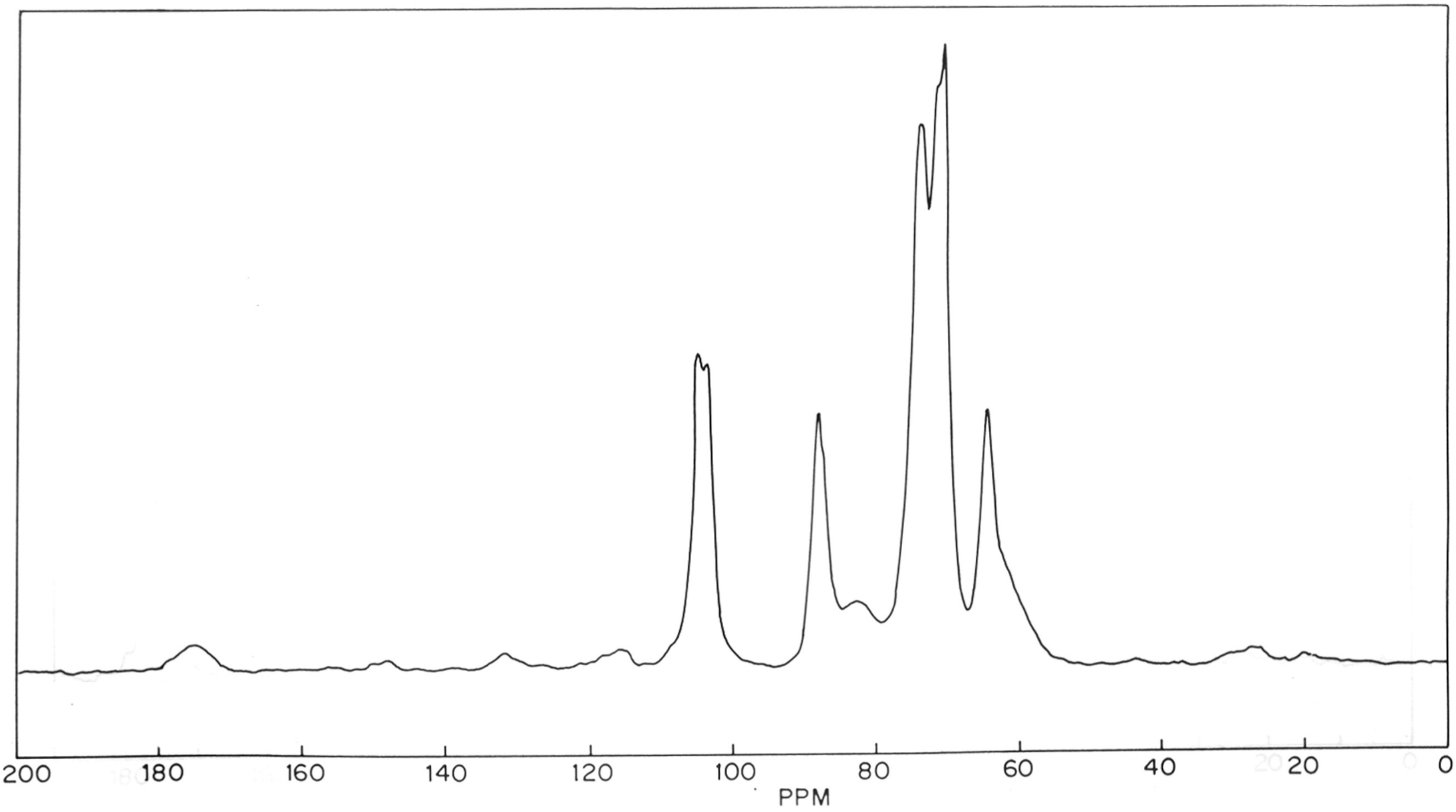

FIG.IV.6·11 : CP/MAS C-13 NMR SPECTRUM OF 30% NaDCC

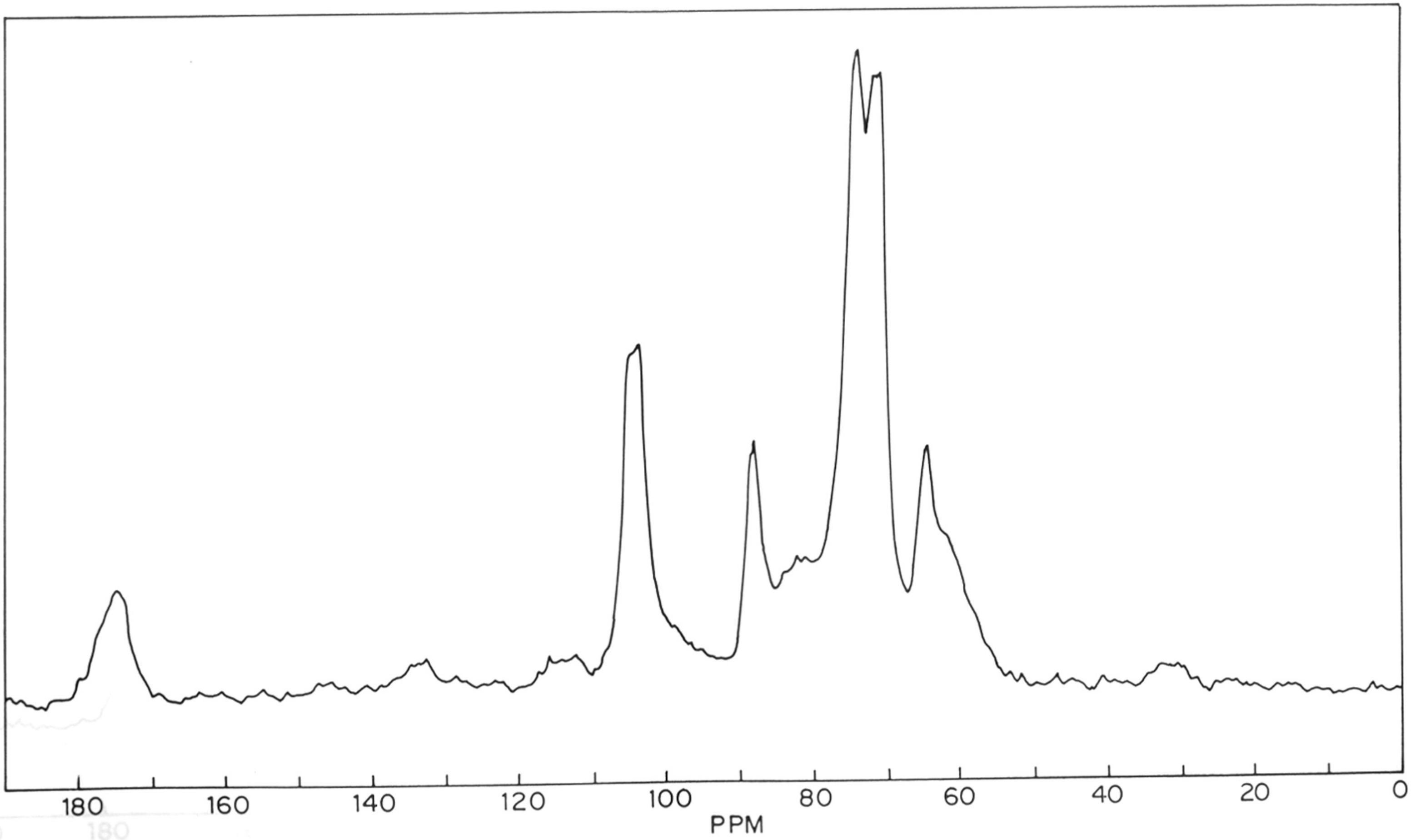

FIG. IV.6·12: CP/MAS C-13 NMR SPECTRUM OF 60% NaDCC

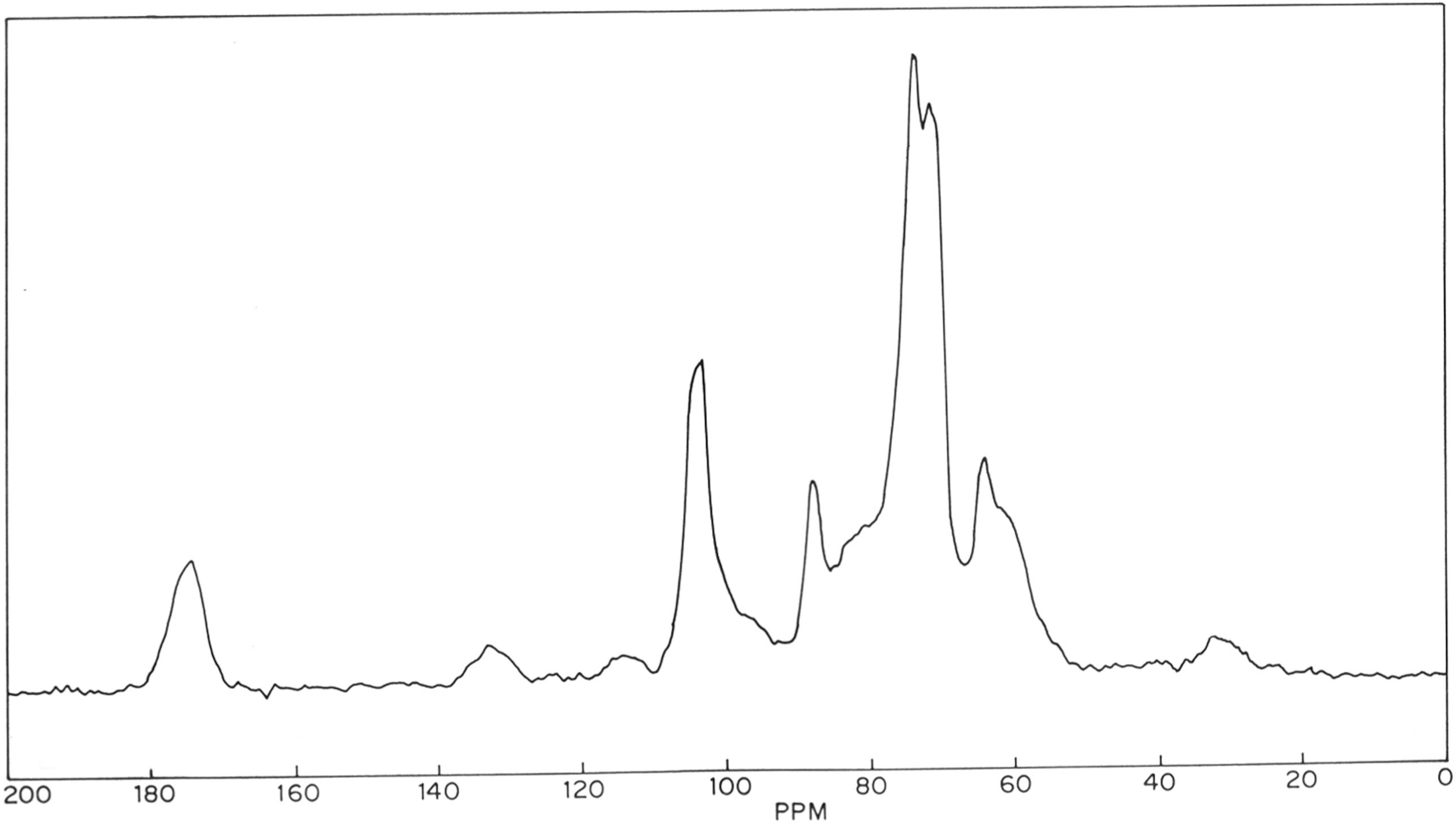

FIG. IV:6·13: CP/MAS C-13 NMR SPECTRUM OF 80% NaDCC

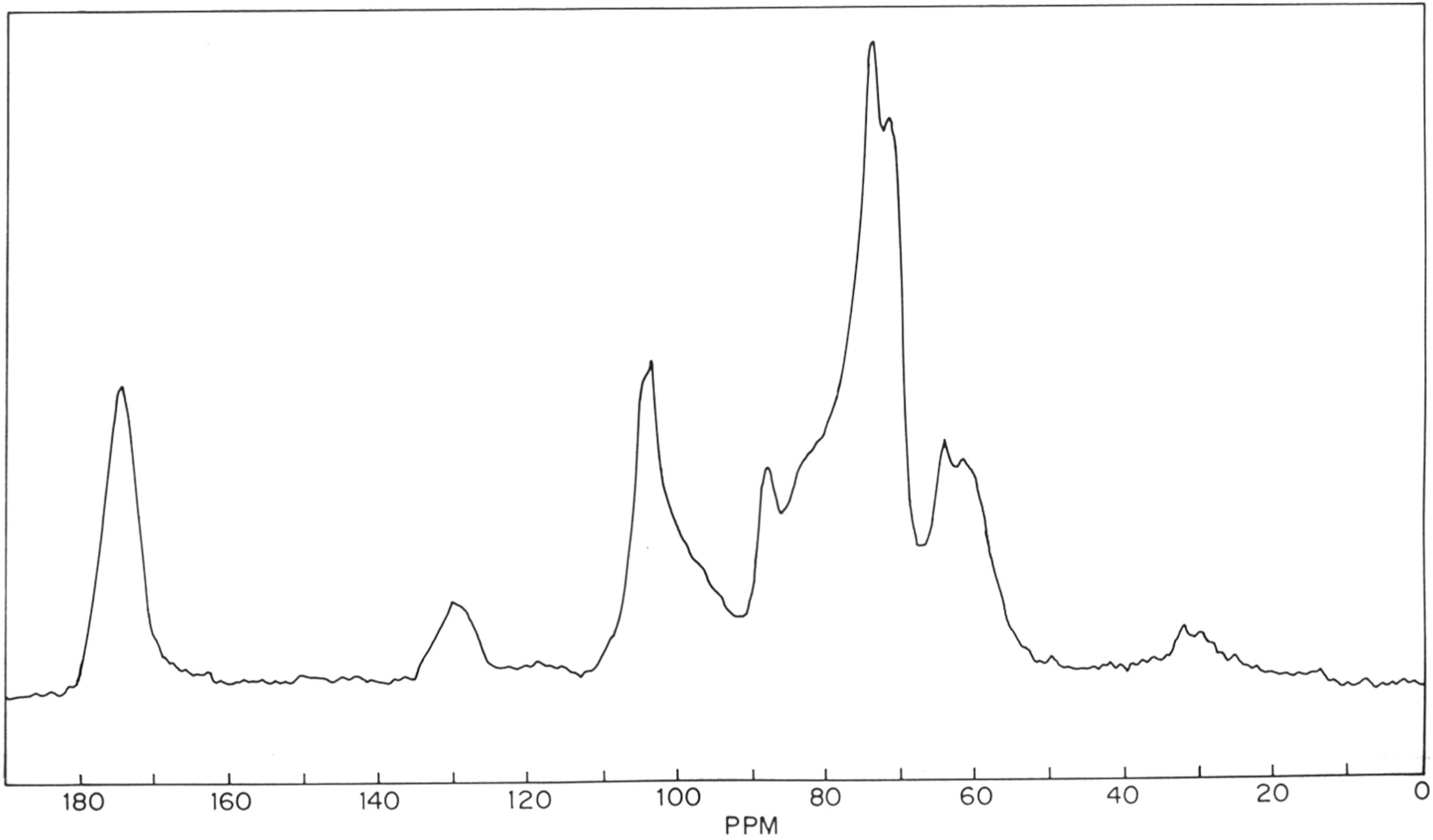

FIG. IV. 6·14 : CP/MAS C-13 NMR SPECTRUM OF 98% NaDCC

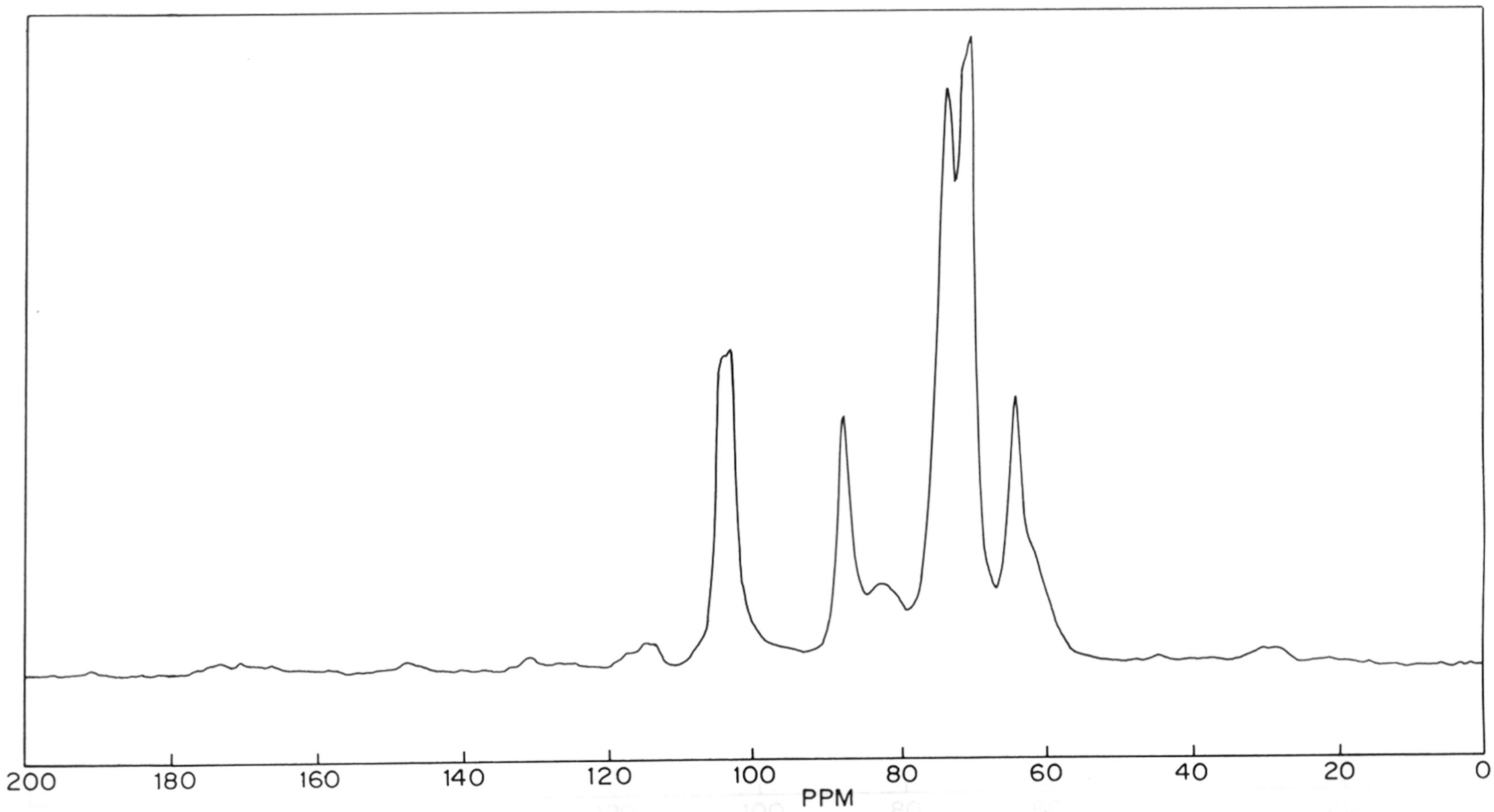

FIG.IV.6·15: CP/MAS C-13 NMR SPECTRUM OF 30% DCC

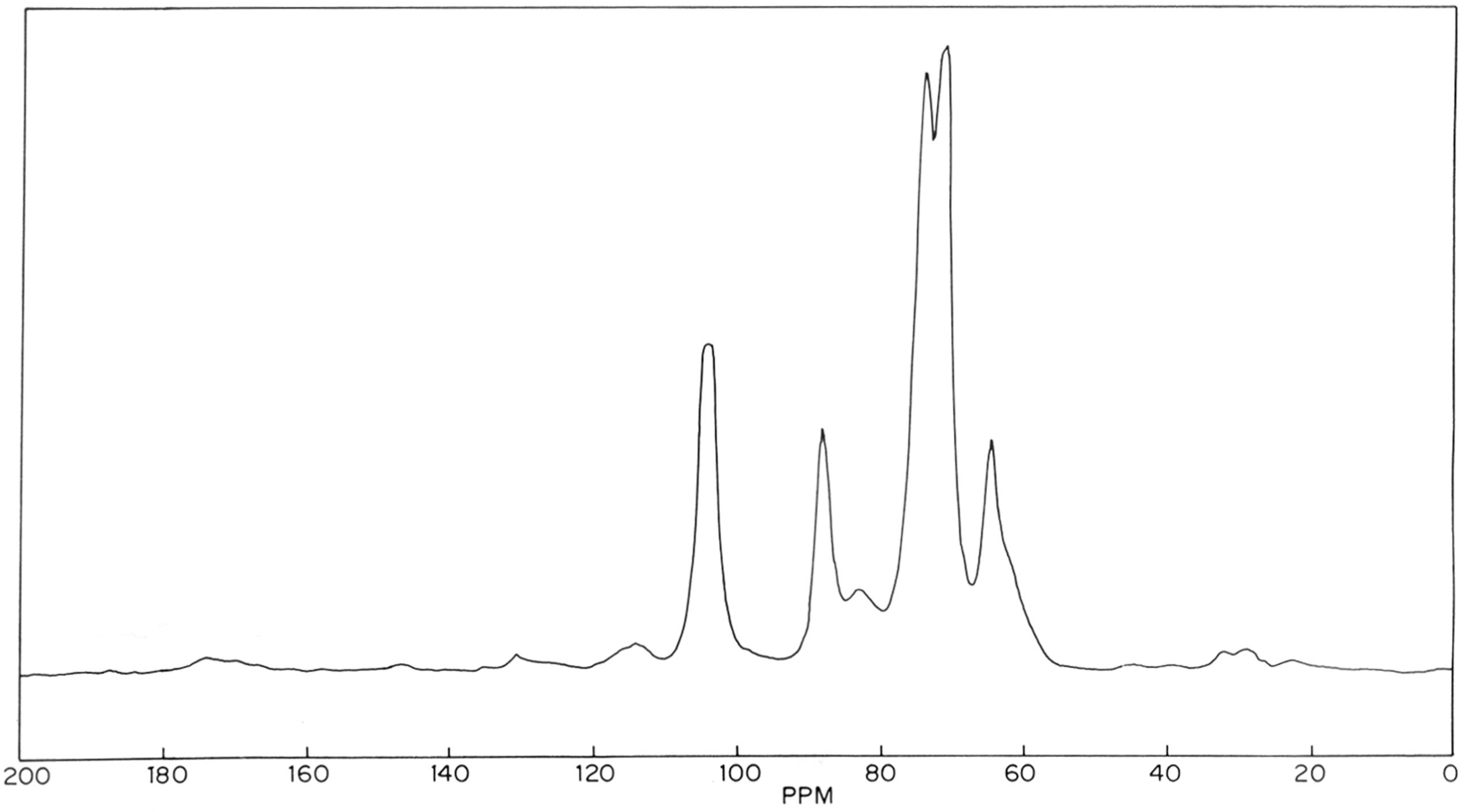

FIG. IV·6·16: CP/MAS C-13 NMR SPECTRUM OF 60% DCC

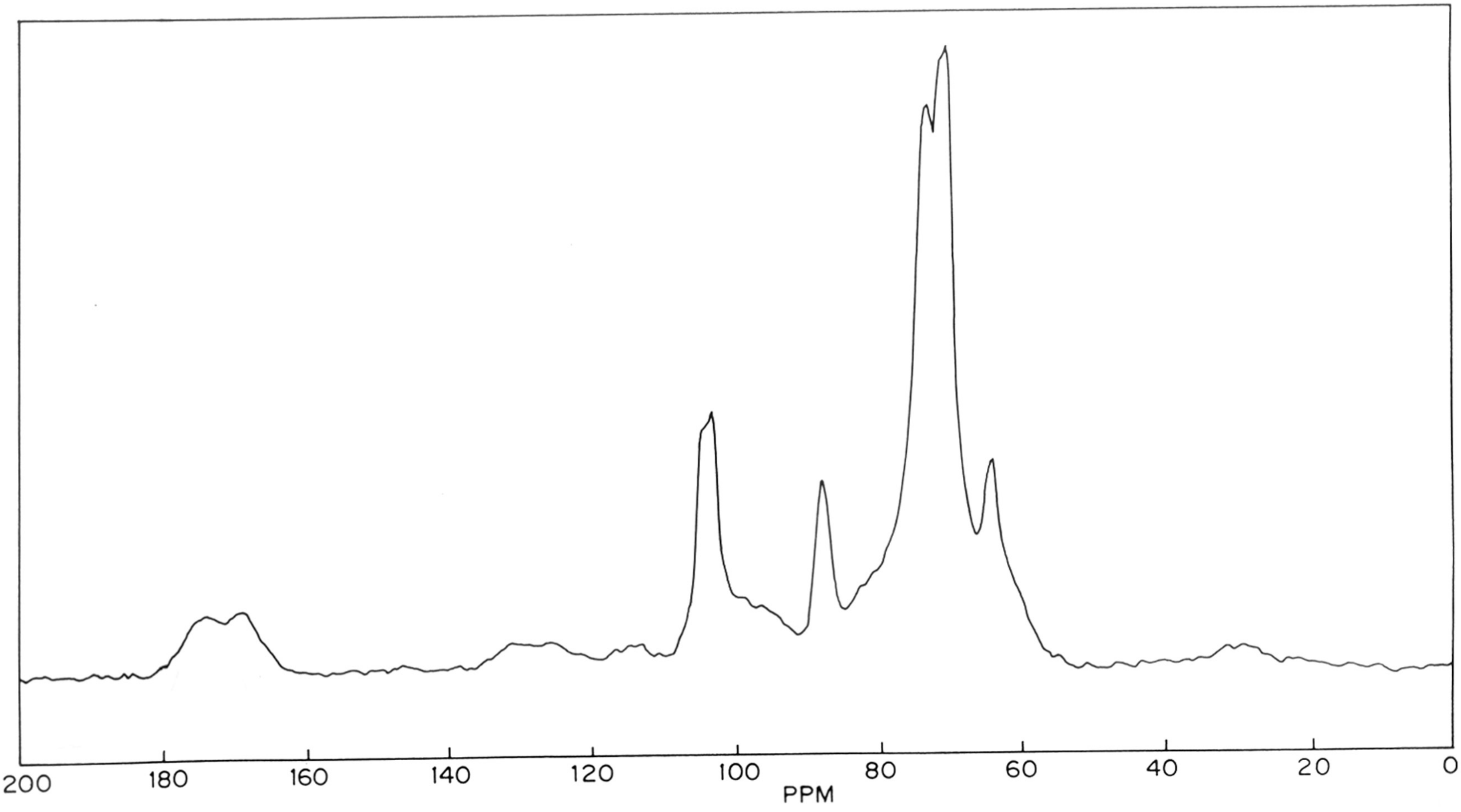

FIG. IV.6·17: CP/MAS C-13 NMR SPECTRUM OF 80% DCC

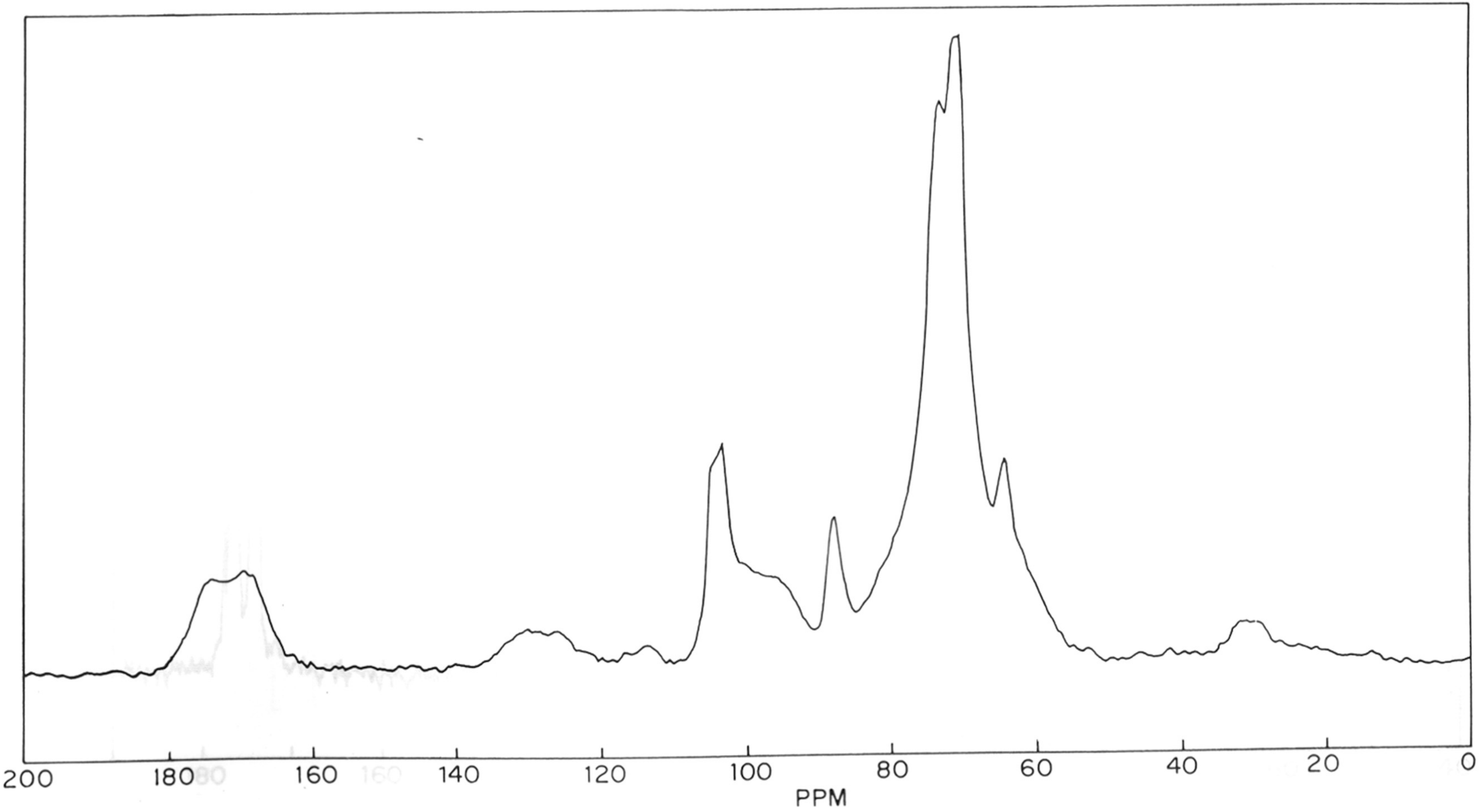

FIG. IV.6·18: CP/MAS C-13 NMR SPECTRUM OF 98% DCC

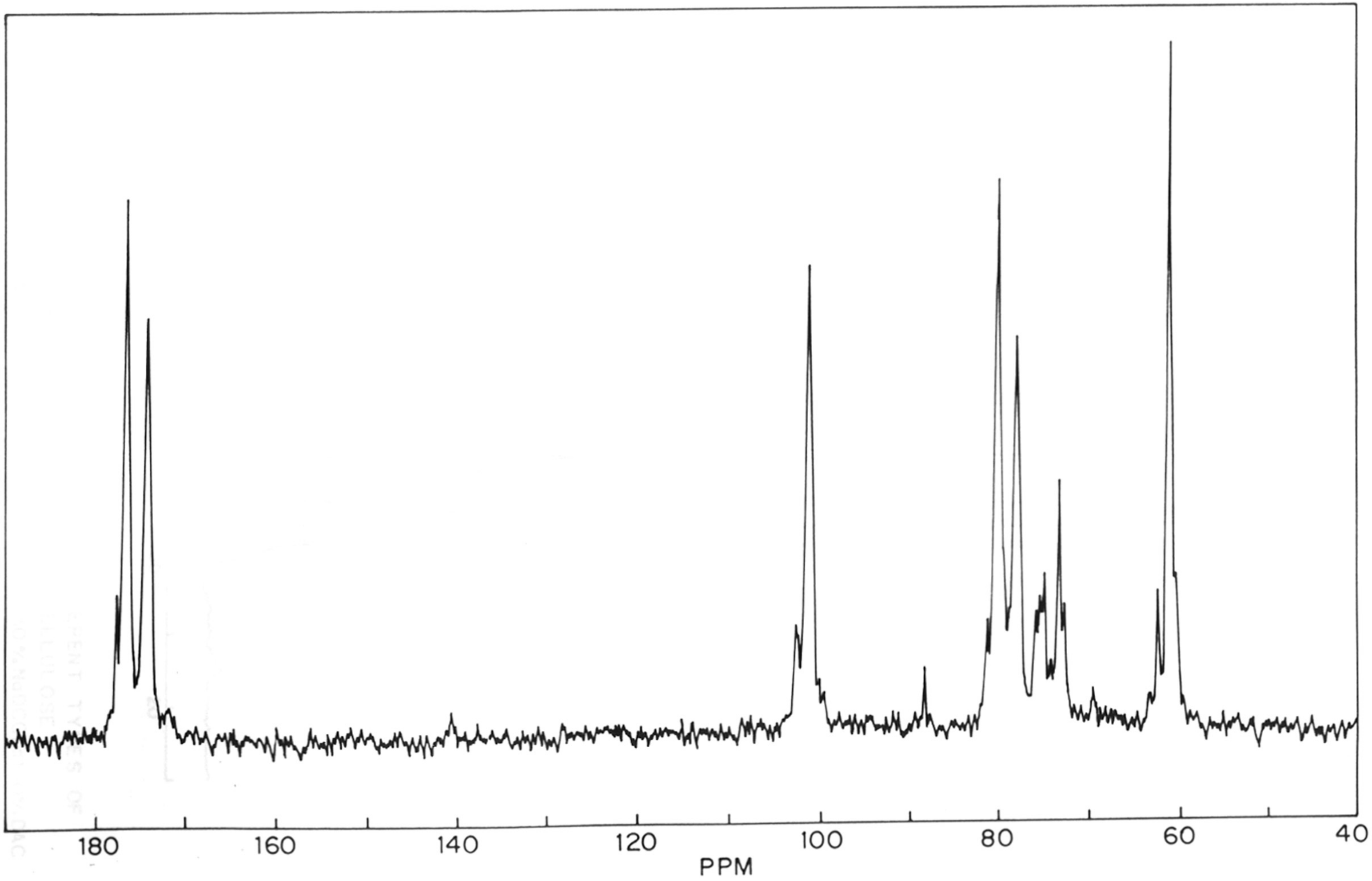

FIG. IV.6·19: CP/MAS C-13 NMR SPECTRUM OF 98% NaDCC IN AQUEOUS GEL FORM

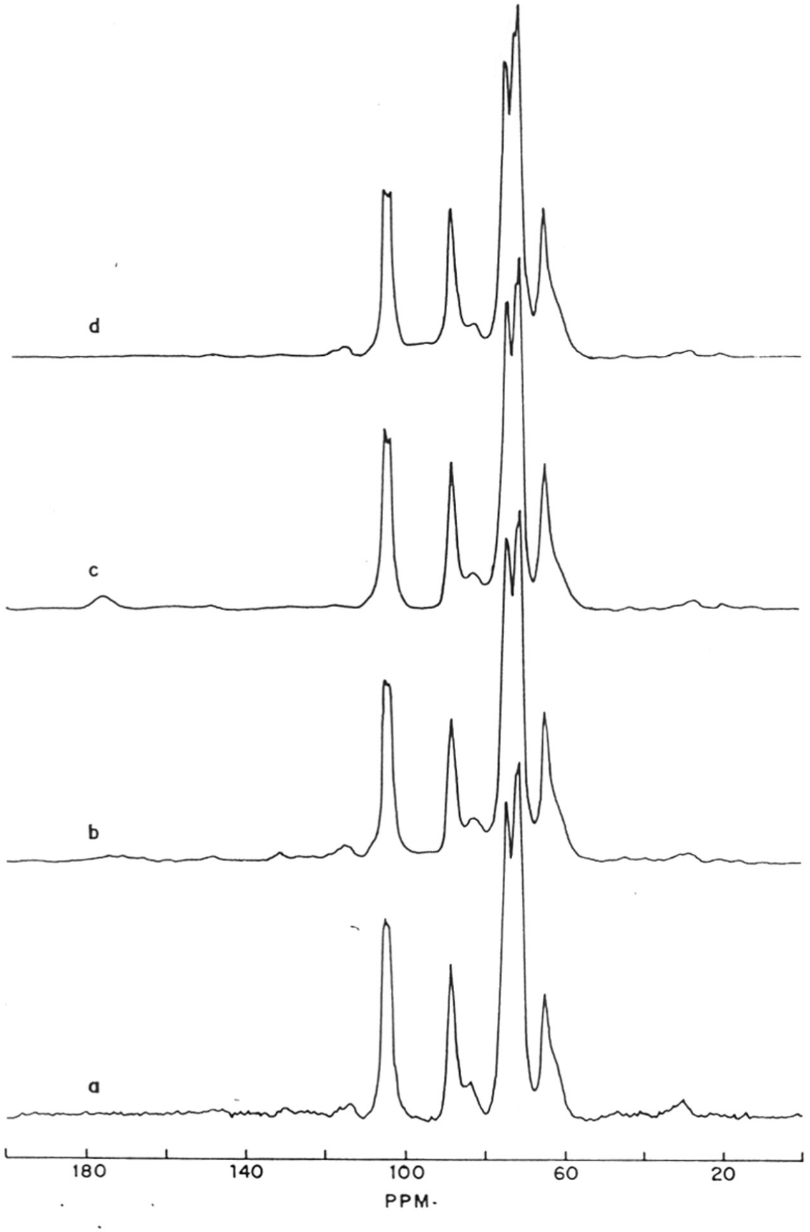

FIG. IV.6·20: COMPARATIVE CP/MAS C-13 NMR OF DIFFERENT TYPES OF 30% OXIDIZED PRODUCTS WITH PARENT CELLULOSE
a) CELLULOSE POWDER CP-100, b) 30% DCC, c) 30% NaDCC, d) 30% DAC

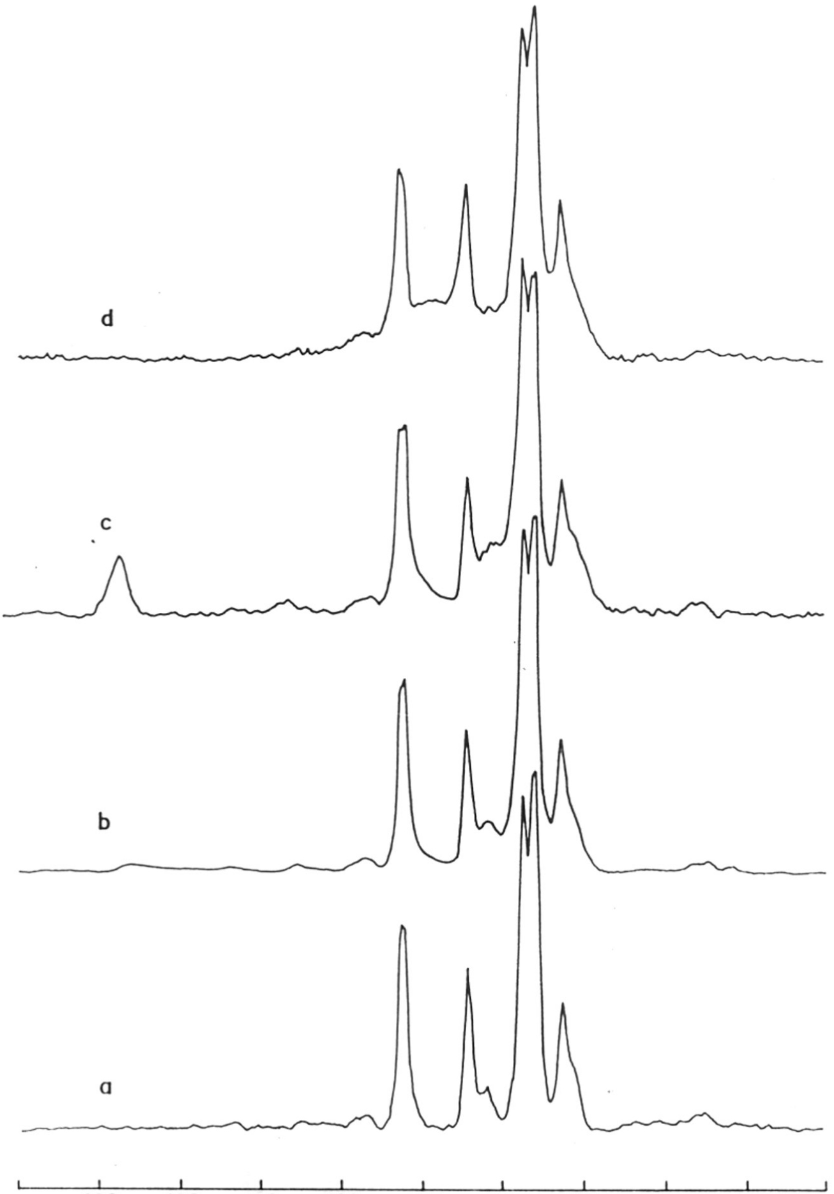

FIG. IV.6·21 : COMPARATIVE CP/MAS C-13 NMR SPECTRA OF DIFFERENT TYPES OF 60% OXIDIZED CELLULOSE PRODUCTS WITH PARENT CELLULOSE a) CELLULOSE POWDER CP-100, b) 60% DCC, c) 60% NaDCC, d) 60% DAC

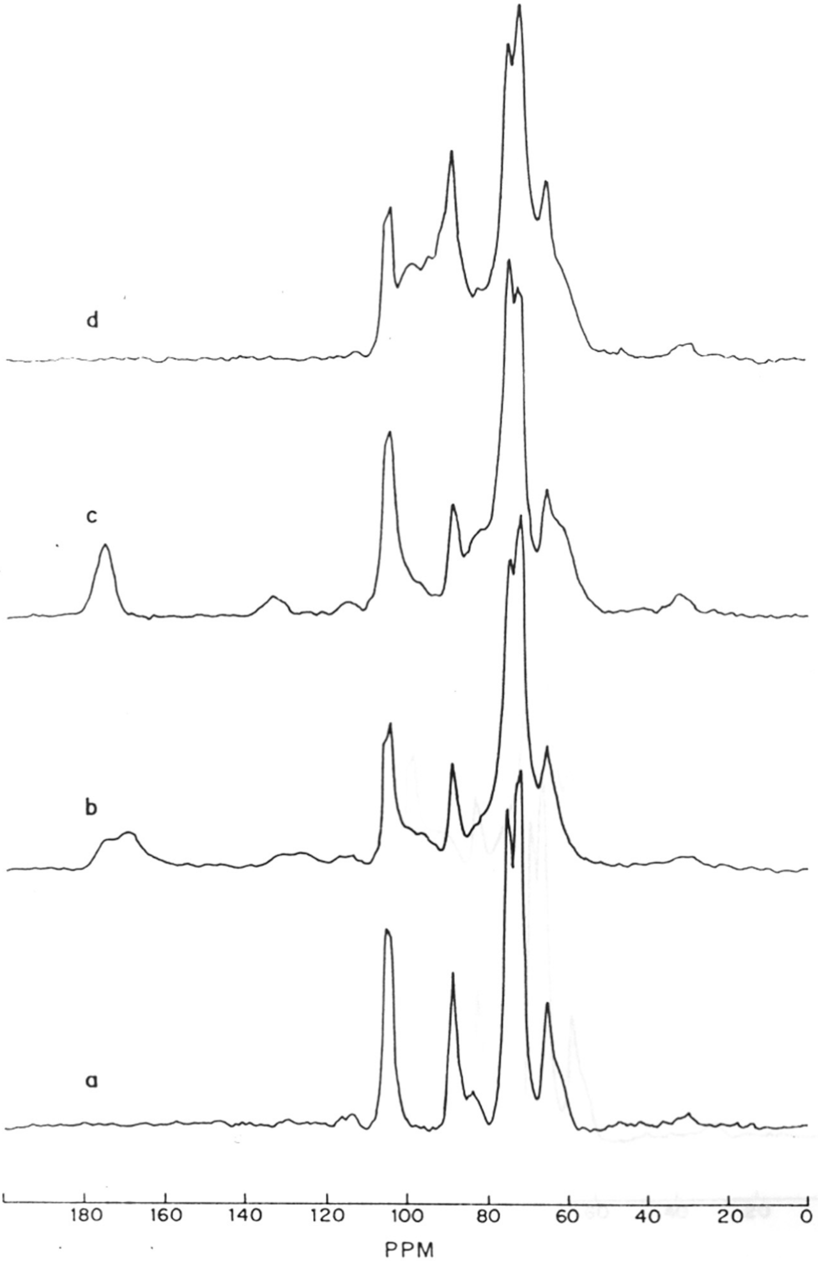

FIG. IV.6·22: COMPARATIVE CP/MAS C-13 NMR SPECTRA OF DIFFERENT TYPES OF 80% OXIDIZED CELLULOSE PRODUCTS WITH PARENT CELLULOSE
a) CELLULOSE POWDER CP-100, b) 80% DCC, c) 80% NaDCC, d) 80% DAC

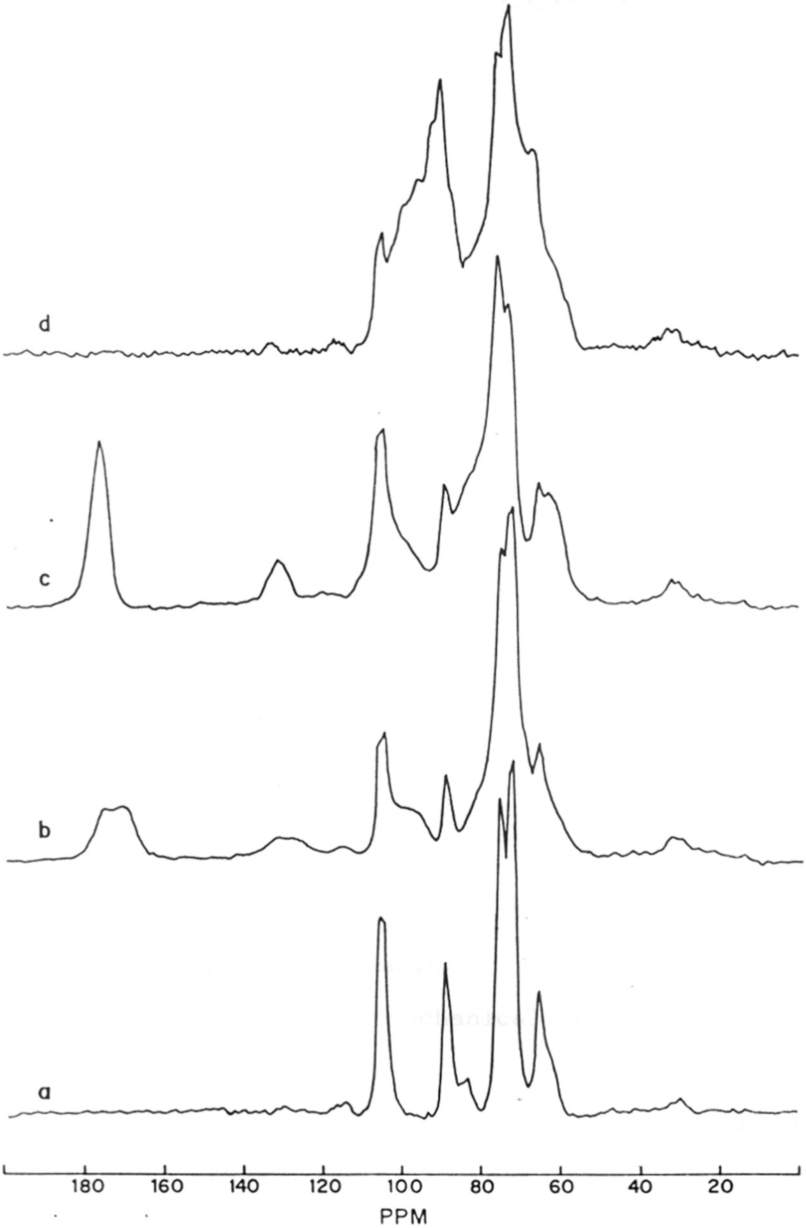

FIG.IV·6·23: COMPARATIVE CP/MAS C-13 NMR SPECTRA OF DIFFERENT TYPES OF 98% OXIDIZED CELLULOSE PRODUCTS WITH PARENT CELLULOSE a) CELLULOSE POWDER CP-100, b) 98% DCC, c) 98% NaDCC, d) 98% DAC

IV.7 THERMOGRAVIMETRIC ANALYSIS AND DIFFERENTIAL THERMAL ANALYSIS OF OXIDIZED CELLULOSES

Introduction

Oxidation of celluloses leads to a variety of structures, depending on the type of oxidising agent used. Of these, poly-glucoronic acid, 2,3-dialdehydecellulose, and 2,3-dicarboxycellulose have found interesting applications (1). Slight oxidation of cellulosic fabrics is known to improve dye binding. Cellulosic fibres such as jute, sisal, flex, ramie, etc. are being increasingly investigated as fillers, reinforcing agents and property modifiers in polymer composites (2). It is an established fact that the properties of the filled polymer systems depend greatly on the polymer-filler interaction. In order to obtain enhanced physical and chemical properties through the use of fillers, there should be bonding between the polymer matrix and the cellulosic filler (3). Processing of the polymer composite involves exposure of the cellulosic filler to high temperatures in air, leading to oxidation, a change in crystallinity, chemical, mechanical and thermal properties results. Further, extensive oxidation of cellulose can lead to water soluble polymers, thereby extending the range of applications of oxidized celluloses.

In this paper, we report the thermal properties of a series of systematically oxidized products of commercial cellulose powder, analogous to a homologous series. There have been reports in literature (1,4,5) on thermal analysis of oxidized celluloses. While our study adds to the literature, we have also noted differences in the results. Data on sodium 2,3-dicarboxycellulose are being reported for the first time. Further, considering the increasing usage and importance of renewable resource materials like cellulose, it is important to investigate their detailed properties. We have recently reported on the crystallinity studies of oxidized celluloses (6,7), polyelectrolyte and rheological behavior of the oxidized cellulose derivative sodium 2,3-dicarboxycellulose (8), and applications of cellulosic diamines (prepared from oxidized cellulose) as reaction-incorporated fillers in epoxy composites (9,10).

Experimental

Materials

The cellulose powder CP-100 was a commercial product of the Cellulose Products of India Ltd., Ahmedabad. It was a fine white powder, 93% of which could pass through a 240 mesh sieve, with the following specifications: bulk density, 0.3-0.4 gcm^{-3}; moisture at packing, 7% maximum; ash on a dry basis 0.5% maximum; α-cellulose 80-85%, pH 6.0-8.0; and ether extract 0.2% maximum. A pure variety of cellulose powder, Cellulose Pulver 123, was procured from Schleicher and Schull, West Germany, for comparing with cellulose CP-100 the %C and %H content in the bulk by usual elemental analysis (obtained by standard combustion methods), and on the surface (by X-ray Photoelectron Spectroscopy). This was also a fine white powder, 92% of it passing through a 200 mesh screen, and it contained 86% α-cellulose and ~ 14% hemicelluloses. The O/C ratio by elemental analysis was 0.91 for cellulose CP-100 and 0.94 for cellulose Pulver 123, the theoretical value for cellulose having the formula $(C_6H_{10}O_5)_n$ being 0.83. The hemicellulose xylan usually associated with cellulose has the formula $(C_5H_8O_4)_n$ with O/C = 0.80. The surface O/C obtained by X-ray photoelectron spectroscopy was 0.32 for cellulose CP-100 and 0.31 for Cellulose Pulver 123 (11). Thus, cellulose CP-100 is very close to cellulose Pulver 123 in chemical purity.

This cellulose CP-100 was used for preparing 30%, 60%, 80% and 98% (based on glucose monomer units) 2,3-dialdehydecellulose (DAC), sodium 2,3-dicarboxycellulose (NaDCC) and 2,3-dicarboxycellulose.

Preparation of 2,3-dialdehydecellulose (DAC) by periodate oxidation:

12%, 30%, 60%, 80% and 98% DAC was prepared by following the procedures previously reported (6), leading to cellulose molecules having 12%, 30%, 60%, 80% and 98% of their glucose monomer units oxidized. It is well known that periodate oxidation of cellulose leads to breaking of the C_2-C_3 bond of the glucose and formation of 2,3-dialdehydecellulose

(12). Titrimetry was used to calculate the consumption of metaperiodate (13). Infrared spectra (nujol) in each case confirmed the presence of a carbonyl peak at 1710 cm^{-1}, and, as already reported (14), this peak was much smaller than expected due to hemiacetal linkages being formed. The carbonyl peak was also not seen in the solid state CP-MAS C-13 NMR spectra of the dialdehydecelluloses (15).

Preparation of sodium 2,3-dicarboxycellulose (NaDCC):

Reaction of DAC with sodium chlorite to produce NaDCC was carried out by a reported method (16). The quantities of sodium chlorite and glacial acetic acid were adjusted according to the dialdehyde content of DAC. Thus 12%, 30%, 60%, 80% and 98% DAC were converted to 12%, 30%, 60%, 80% and 98% NaDCC. Characterization was carried out by a reported procedure (17). Solid state CP-MAS C-13 NMR spectra showed the carbonyl peak at ~175 ppm (15). The IR spectrum shows the carbonyl peak at 1600 cm^{-1}, as reported (14). Sodium content analysis for 98% NaDCC was carried out using a Hitachi model Z-8000 Atomic Absorption Spectrometer, and there was complete agreement between the calculated and theoretical values, i.e. 19.65% sodium content.

Preparation of 2,3-Dicarboxycellulose (DCC):

12%, 30% and 60% DCC was prepared from the corresponding NaDCC by a method reported in Ref. 12. 80% and 98% DCC was prepared from the corresponding NaDCC was prepared by the method of Maekawa and Kosijima (16). Solid state CP-MAS C-13

NMR spectra showed the carbonyl peak at ~169 ppm. The IR spectrum shows a prominent carbonyl peak at 1730 cm^{-1}.

Thermal Analysis

TG and DTA curves were obtained using a Netzch STA 409 thermal analyzer at a heating rate of 10°/min in air.

Results and Discussion

Using pure cellulose of Schleicher and Schull, Bhatnagar et al (18) observed a strong endothermic peak at 314°C, caused by dehydration, and formation and evaporation of volatile products. This was followed by a strong exotherm at 350° due to oxidation of products, and another strong exotherm at 468°C due to oxidation of the charred residues. The charred residues started to burn, and the burning was complete at 520°C. About 68% weight loss occurred around 314°C, and a total of 92% weight loss occurred around 500°C. Pataky et al. (1) observed similar results in thermogravimetry, although from their reported TG curve there seems to be ~100% weight loss at ~600°C. However, Ti, defined as the temperature at which half the ultimate weight loss occurs, was around 320°C in Bhatnagar´s case (18), and about 360°C for Pataky (1).

In our case we observed a single large endotherm at 323°C (Table IV.7.1). The endotherms before 323°C were negligible. A strong exotherm was observed at 501°C, a value

TABLE IV.7.1

Major temperature peaks in the DTA thermograms for cellulose and oxidized celluloses in air (DAC, DCC, NaDCC)

Sample	DTA Curve			
	Initiation Temp./°C	Peak Temp./°C	Termination Temp./°C	Nature of the DTA peak
Cellulose	302	323	345	Endo large
	440	501	546	Exo large
30% DAC	331	374	432	Exo large
	463	534	598	Exo large
60% DAC	303	325	357	Endo small
	446	548	602	Exo large
80% DAC	296	345	372	Exo small
	440	536	581	Exo large
98% DAC	213	270	287	Exo small
	350	420	441	Exo small
	457	578	627	Exo large
60% DCC	208	364	385	Exo small
	395	524	593	Exo large
80% DCC	187	229	264	Exo small
	285	334	361	Exo small
	372	445	516	Exo large
98% DCC	208	244	271	Exo small
	289	358	369	Exo small
	374	437	534	Exo large
60% NaDCC	178	201	259	Endo small
	497	538	636	Exo large
80% NaDCC	171	177	253	Endo small
	487	548	558	Exo large
	558	562	612	Exo large
98% NaDCC	173	196	226	Endo small
	243	266	293	Exo small
	337	364	374	Exo small
	578	603	647	Exo large

that is considerably higher than the exotherm values of 350°C and 468°C obtained by Bhatnagar (18). The final burning of charred residues was observed at 546°C. The Ti in our case was at 340°C, and the weight loss at 323°C was 65%. The ultimate weight loss was 85% at 536°C (Table IV.7.2).

Comparison of cellulose with DAC shows that the weight loss temperatures as well as DTA transitions is higher for DAC. The weight loss at around 323°C was 65% for cellulose and only 30% for 80% DAC and ~35% for 98% DAC. The final weight loss temperatures for DAC shift to higher temperatures. However, the weight loss for 60%, 80% and 98% DAC occurs in two steps in the initial stage of decomposition (Table IV.7.2) as opposed to a single step for pure cellulose and 30% DAC. The initial weight loss occurs at a lower temperature than cellulose. Therefore there seems to be lower thermal stability of DAC up to around 250°C (Table IV.7.2), as compared to cellulose. At higher temperatures, DAC seems to become more stable than cellulose. Parks (5) reported thermal destabilization of DAC especially at aldehyde content higher than 20 meq/100 g of cellulose. From the TGA curves reported by Pataky (1), it can be observed that at the initial stages of weight loss, DAC is less stable than cellulose, but at the later stages (beyond 50% weight loss for 90% DAC), DAC is more stable. Unfortunately, DTA curves were not reported by Pataky. Apparently, there is greater crosslinking possible for DAC's at higher temperatures.

Table IV.7.2

Thermogravimetric Data on Selected Cellulose and Oxidized Cellulose Samples (DAC, DCC, NaDCC)

Sample	Initial Weight Loss		Final Weight Loss		Temp. for half of final wt. loss Ti,°C
	Temp. (°C)	Wt.loss (%)	Temp. (°C)	Wt.loss (%)	
Cellulose	323	65	536	85	340
30% DAC	331	58	549	83	347
60% DAC	219,357	45	568	82	482
80% DAC	169,313	30	562	75	353
98% DAC	242,368	35	597	80	384
60% DCC	254,369	45	529	80	342
80% DCC	200,339	50	481	82	318
98% DCC	178,406	58	508	80	320
60% NaDCC	213,309	42	513,543	70	304
80% NaDCC	230,287	15	553,558	30	309
98% NaDCC	190,249,266	20	578,647	37	282

DAC : 2,3-Dialdehydecellulose

DCC : 2,3-Dicarboxycellulose

NaDCC : Sodium 2,3-Dicarboxycellulose

Note : Two or more temperatures indicated in each temperature column indicates two or more stages of decomposition.

The thermal stability of DCC is lower than DAC, in agreement with the results of Parks (5). For example, 60% DCC and 80% DCC show weight losses of 50% and 58% in the initial stages of decomposition, as opposed to 30% and 35% for the corresponding DAC´s (Table IV.7.2). Similarly, the DTA transitions of DCC occur at lower temperatures than for DAC (Table IV.7.1).

For NaDCC´s, the initial decomposition and weight loss occurs at lower temperatures than the corresponding DCC´s, but the final weight loss temperatures are not only higher than that of DCC´s, but also higher than DAC´s and cellulose. Also, the total weight losses for 80% NaDCC and 98% NaDCC were found to be only 30% and 37% respectively. Cellulose, all DAC´s, and all DCC´s had weight losses in the region of 80-85%. However, the Ti´s for all NaDCC´s are lower than all the other cellulose derivatives investigated (Table IV.7.2). The weight of sodium in 98% NaDCC is 19.65% of the total weight. Even if this factor is taken into account, and added to the observed 37% weight loss, the total weight loss would only be ~ 57%, which is still much lower than 80-85% weight loss observed per cellulose, 98% DAC, and 98% DCC. This points to the greater thermal stability of 80% and 98% NaDCC than the other oxidized derivatives. The thermal transitions of NaDCC´s shown by DTA are also shifted to lower values as compared to DCC, at the initial stages (Table IV.7.1). However, the NaDCC´s show higher DTA peak temperatures than cellulose and all its other oxidized derivatives studied, at the later stages of heating (above 500°C).

It should be mentioned that the molecular weights of the derivatives are in the following order : Cellulose > DAC´s > DCC´s > NaDCC´s. This is due to progressive oxidative degradation in their synthesis (8). The molecular weight may also have some effect on temperature stability. Figures IV.7.1a, IV.7.1b, IV.7.2a, IV.7.2b, IV.7.3a and IV.7.3b show superimposed thermal spectra (TG and DTA) of DAC´s, DCC´s and NaDCC´s, respectively. The shifts in positions of TG (Figs. IV.7.1a, IV.7.2a and IV.7.3a) can be clearly seen for each series of polymers produced by oxidation. The dramatic change in DTA spectra in going from 30% to 60% DAC, and similarly from 60% to 80% DAC, and 80% to 98% DAC is seen in Figure IV.7.1b. 30% DAC has two major exotherms, while 60%, 80% and 98% DAC have only one major exotherm. The DCC´s also have only one major exotherm (Figure IV.7.2b) and the same is true for NaDCC´s (Figure IV.7.3b).

The thermal analysis of the three series of oxidized celluloses (DAC´s, DCC´s and NaDCC´s) have shown consistent trends. Data of this type could be useful in ascertaining the usefulness of cellulosics in polymer composites for specific applications.

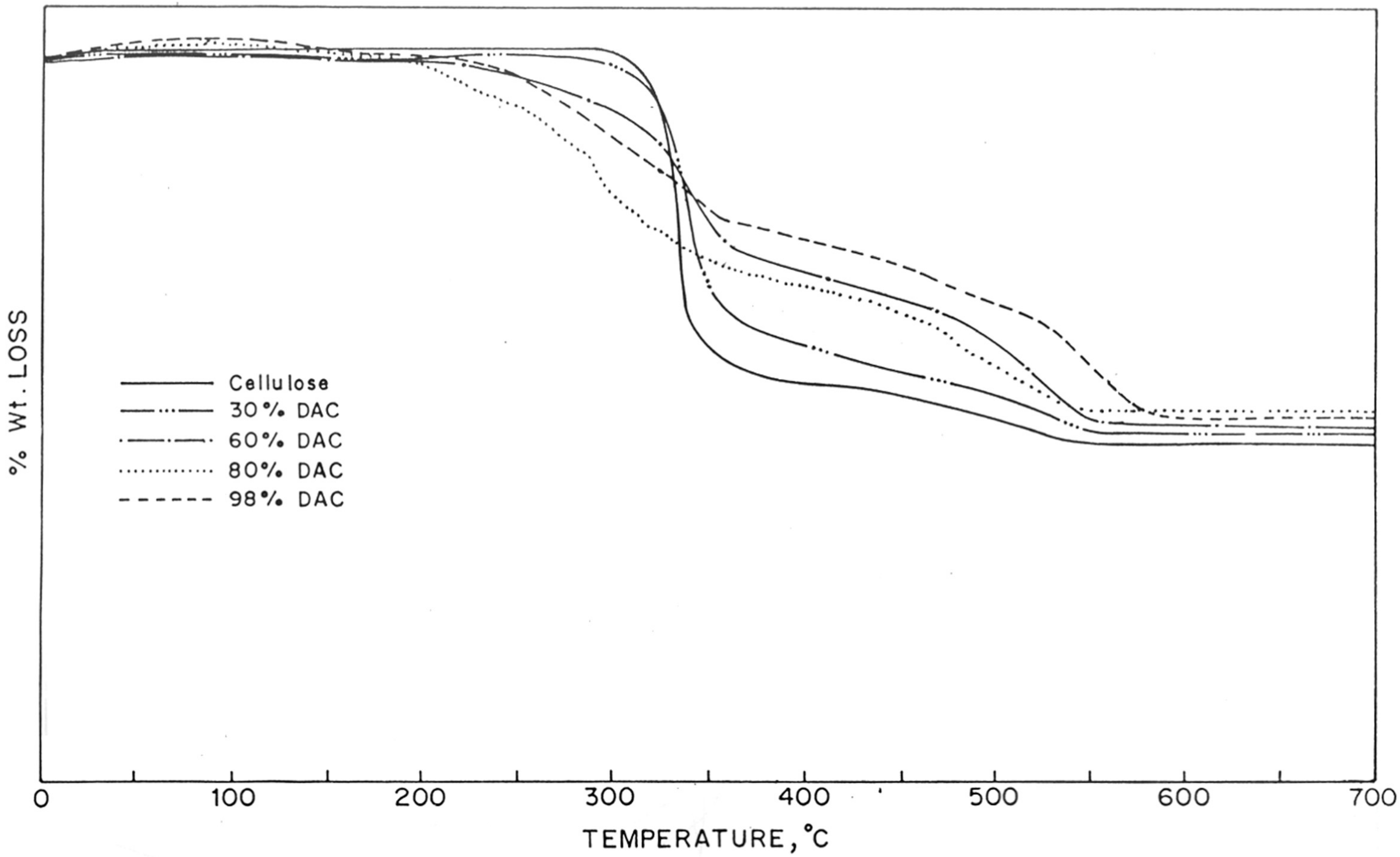

FIG.IV.7·1a : TG CURVES OF CELLULOSE POWDER CP-100, 30% DAC, 60% DAC, 80% DAC AND 98% DAC

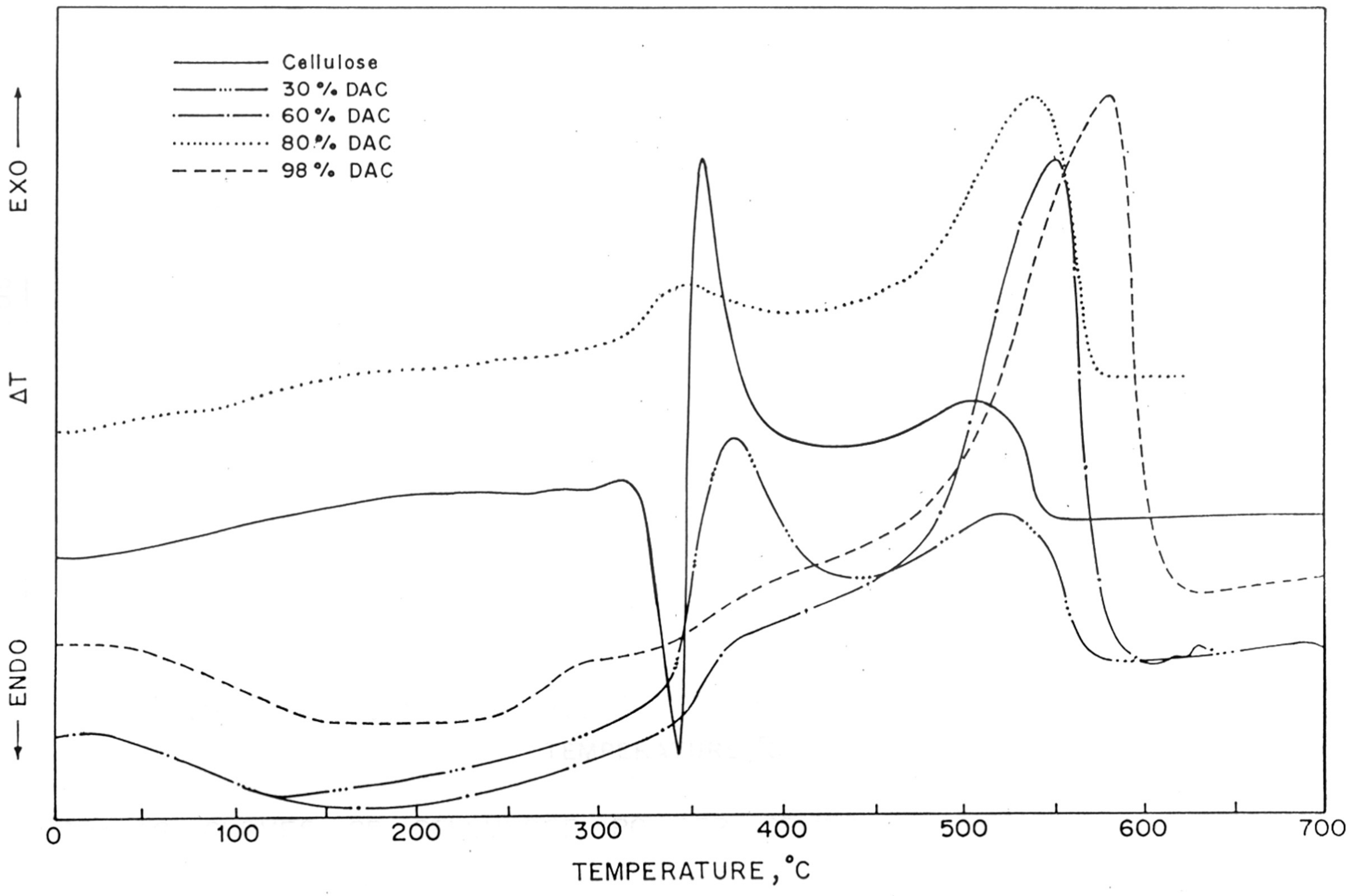

FIG.IV·7·1b : DTA PLOTS FOR CELLULOSE POWDER CP-100 , 30% DAC , 60% DAC , 80 % DAC

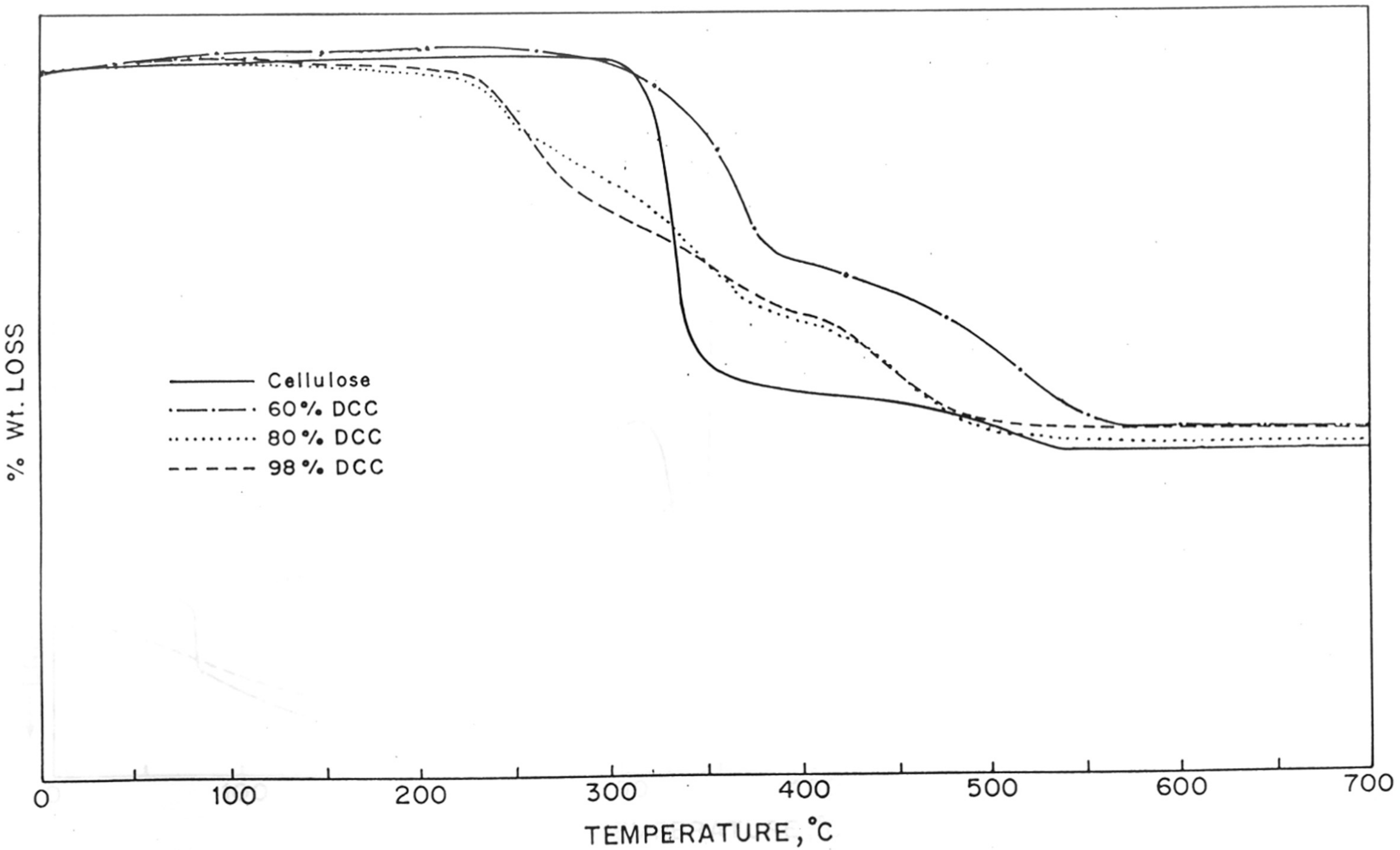

FIG. IV.7·2a : TG CURVES OF CELLULOSE POWDER CP-100, 60% DCC, 80% DCC AND 98% DCC

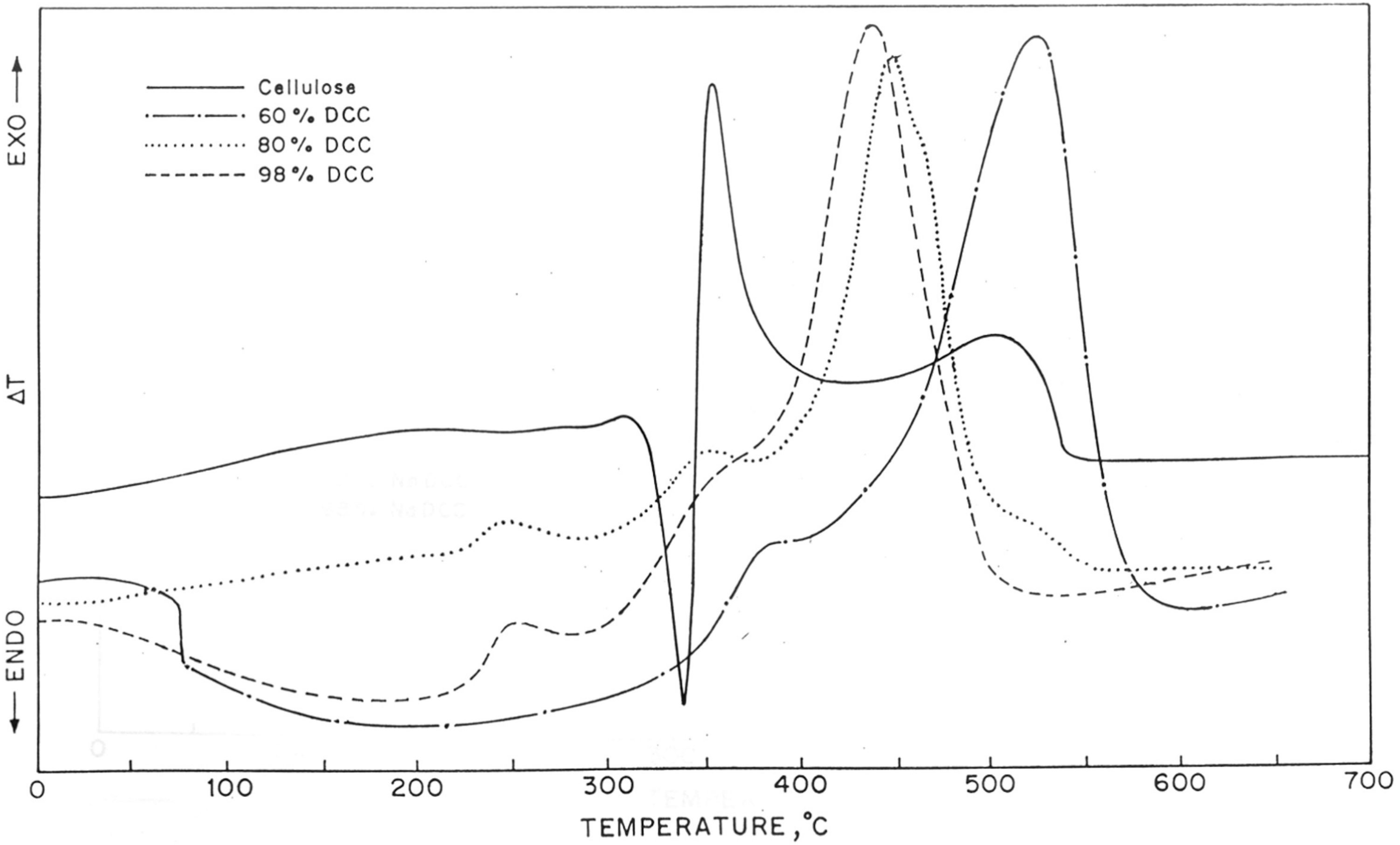

FIG.IV.7·2b: DTA PLOTS FOR CELLULOSE POWDER CP-100, 60% DCC, 80% DCC AND 98% DCC

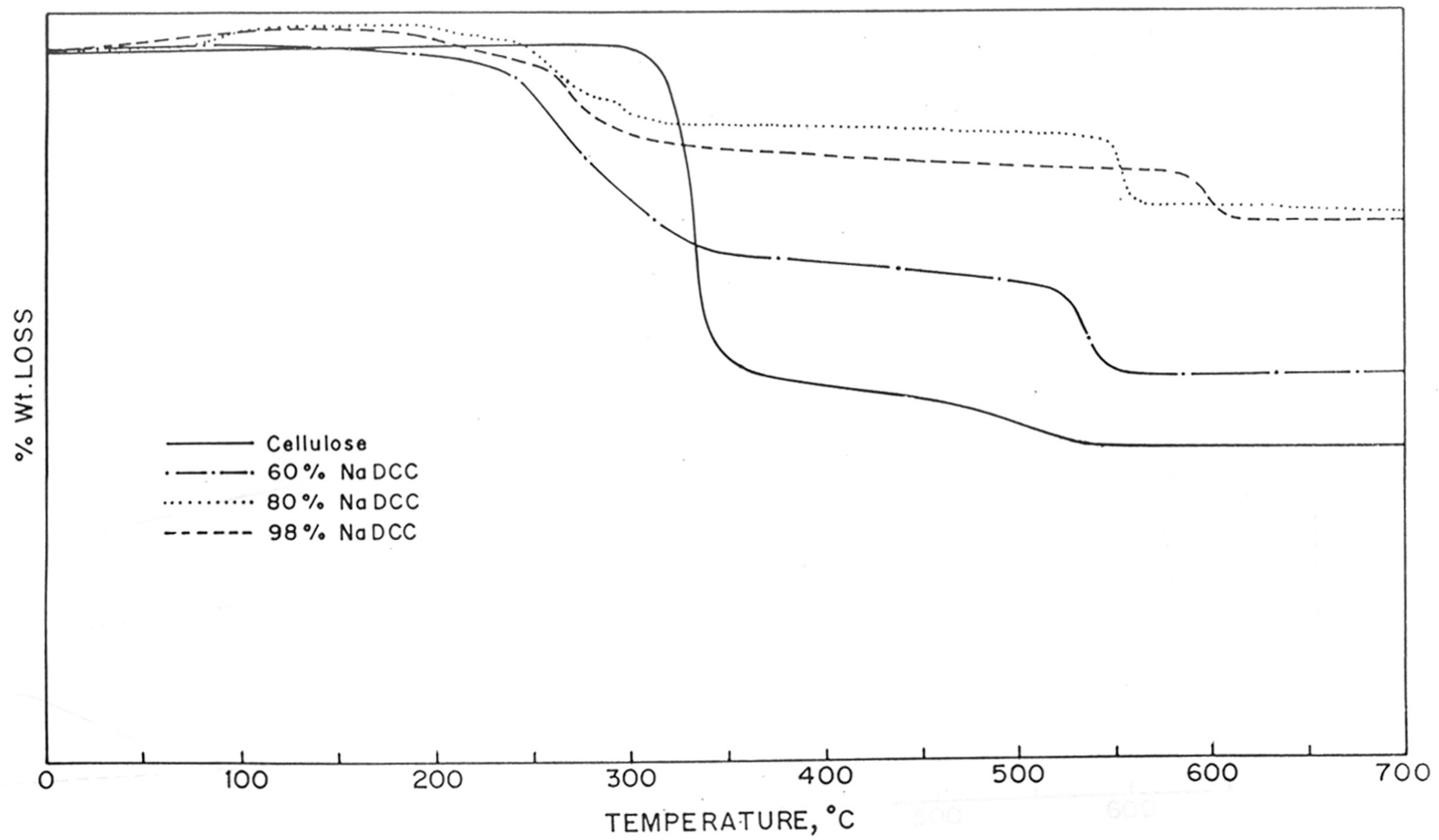

FIG.IV.7·3a : TG CURVES OF CELLULOSE POWDER CP-100, 60% NaDCC, 80% NaDCC AND 98% NaDCC

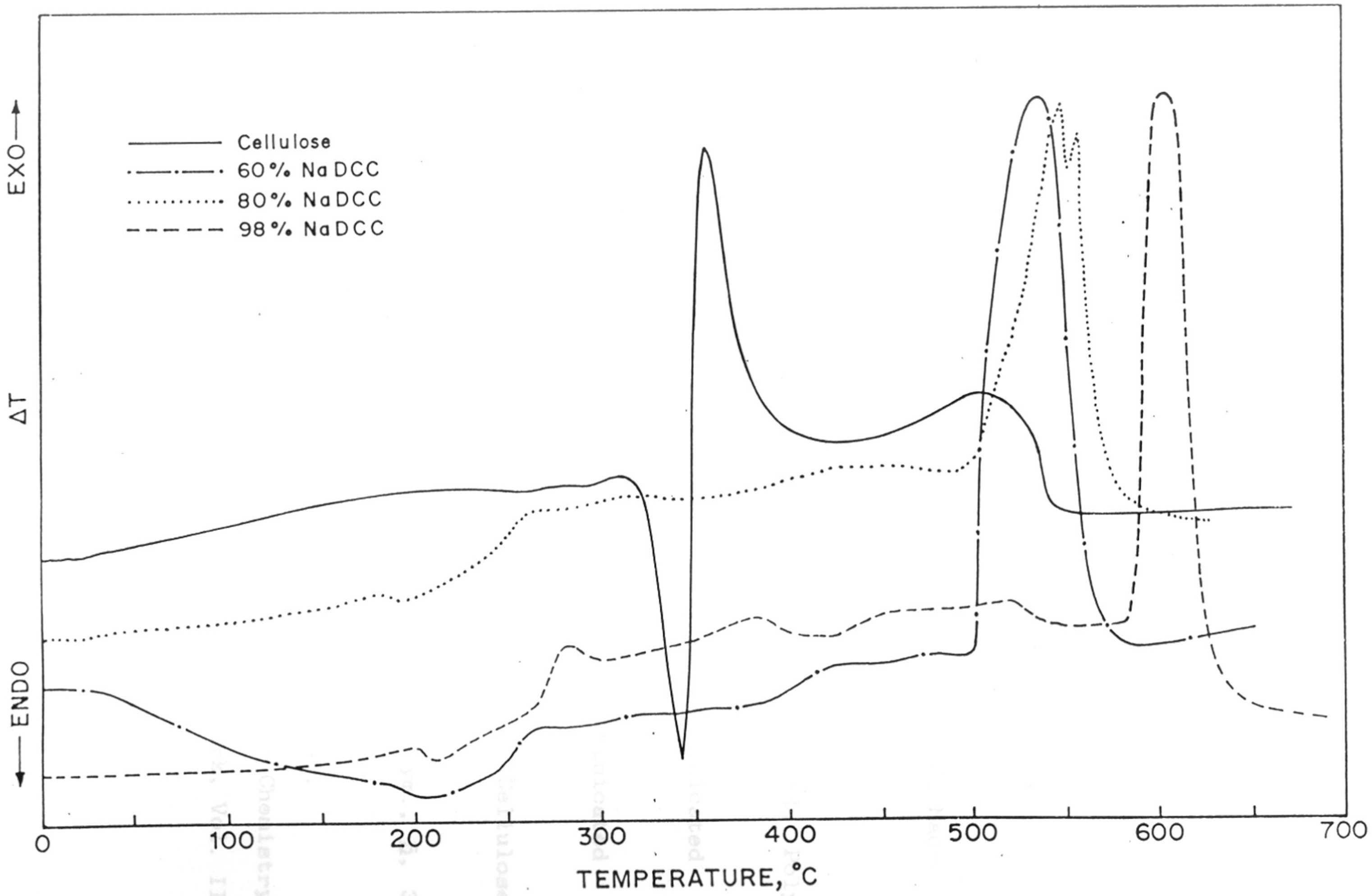

FIG.IV.7·3b : DTA PLOTS FOR CELLULOSE POWDER CP-100, 60% NaDCC, 80% NaDCC AND 98% NaDCC

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APPENDIX

APPENDIX

TG and DTA curve comparisons of different oxidised celluloses (DAC, DCC, NaDCC) having the same degrees of oxidations.

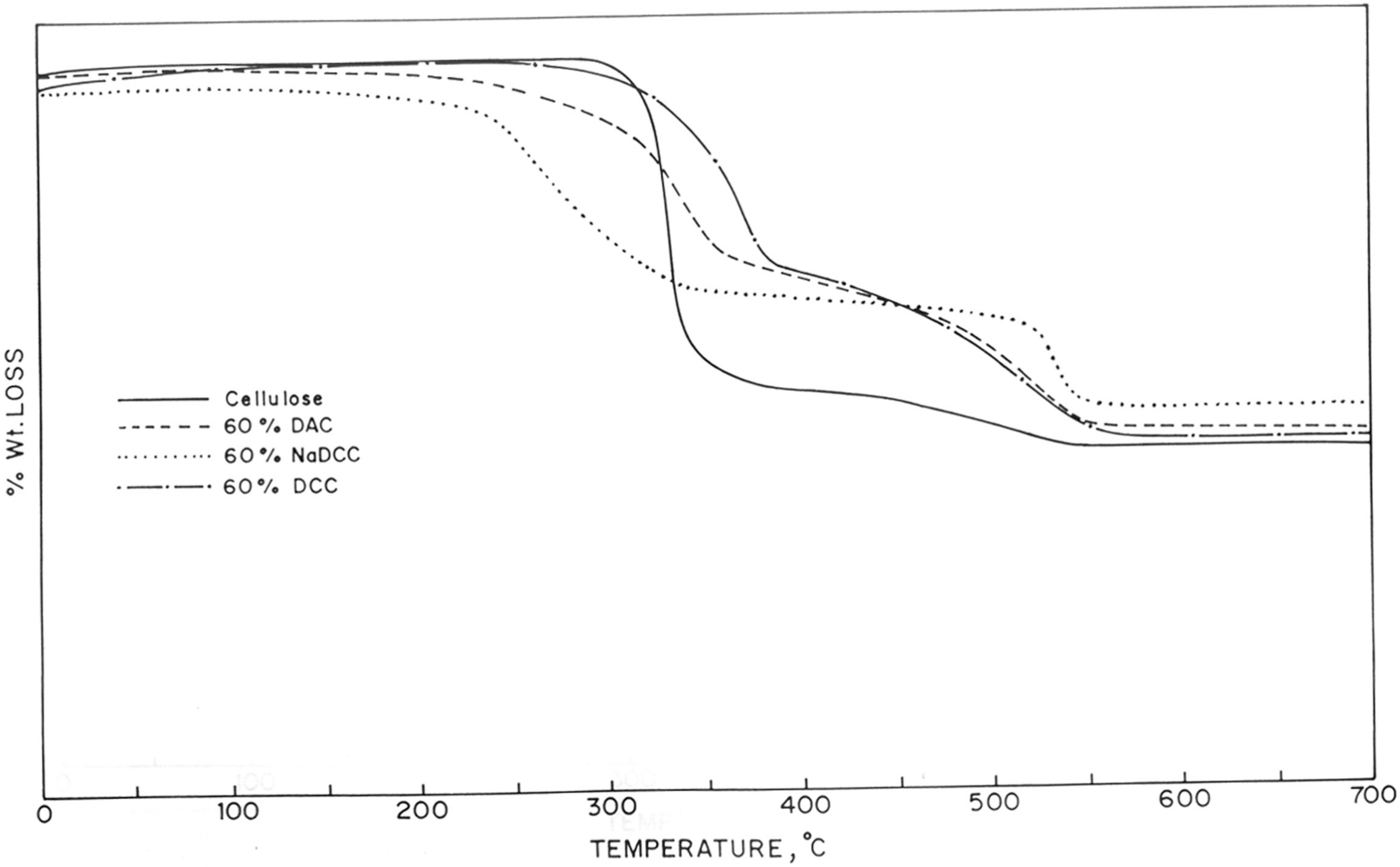

FIG.IV.7·4a: TG CURVES OF CELLULOSE POWDER CP-100, 60% DAC, 60% NaDCC AND 60% DCC

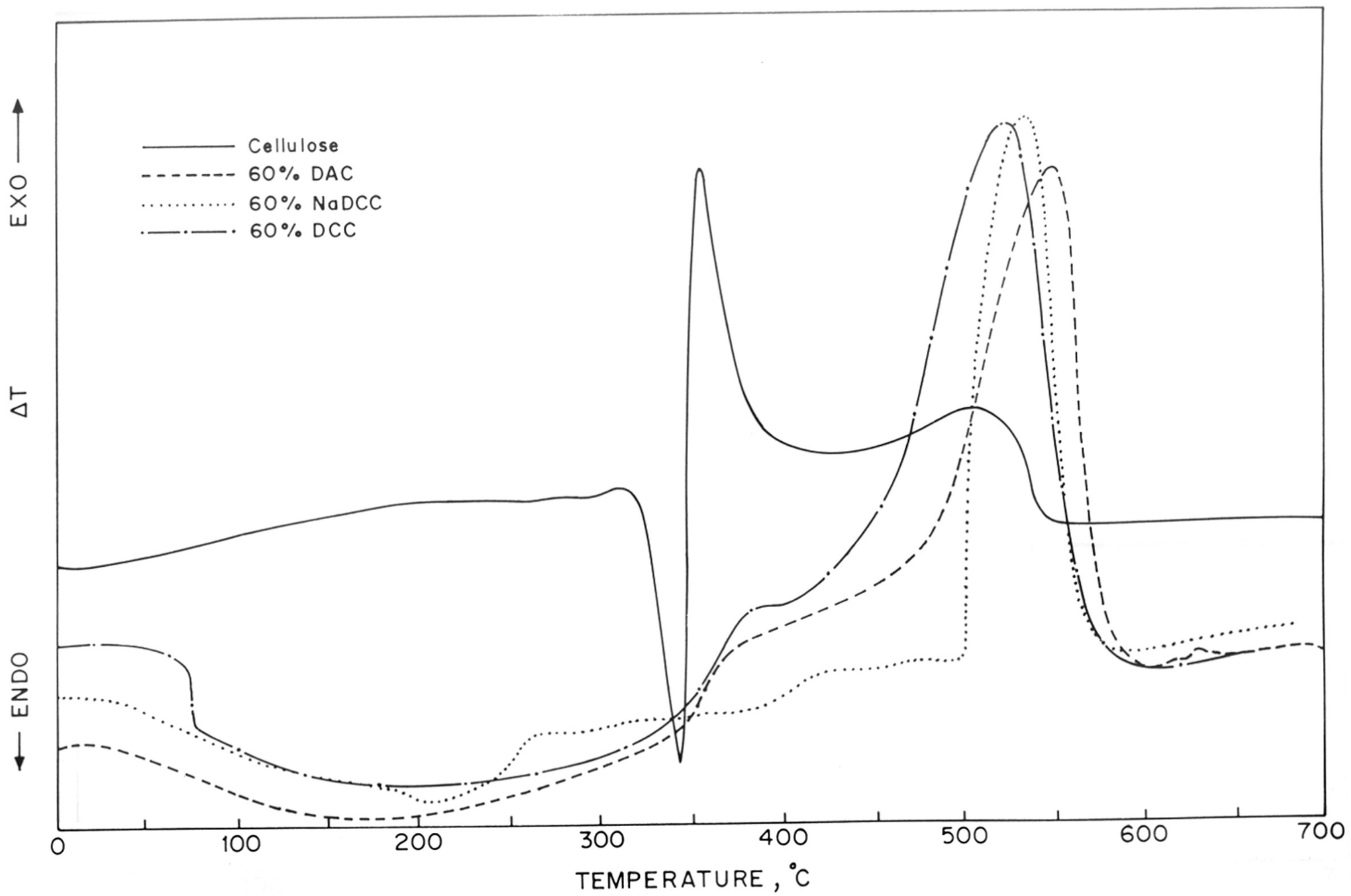

FIG.IV·7·4b : DTA PLOTS FOR CELLULOSE POWDER CP-100, 60% DAC, 60% NaDCC AND 60% DCC.

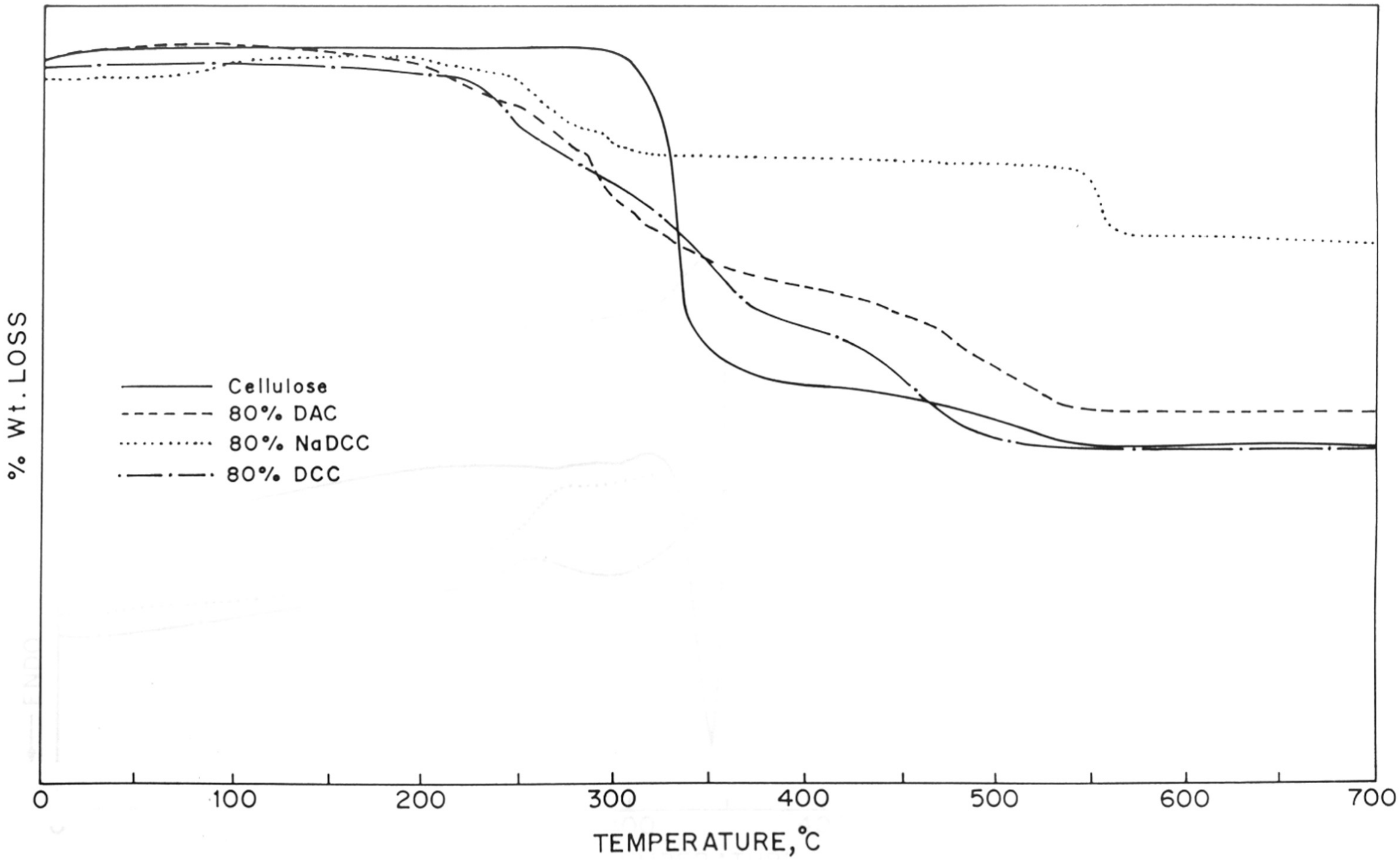

FIG. IV.7·5a: TG CURVES OF CELLULOSE POWDER CP-100, 80% DAC, 80% NaDCC AND 80 % DCC

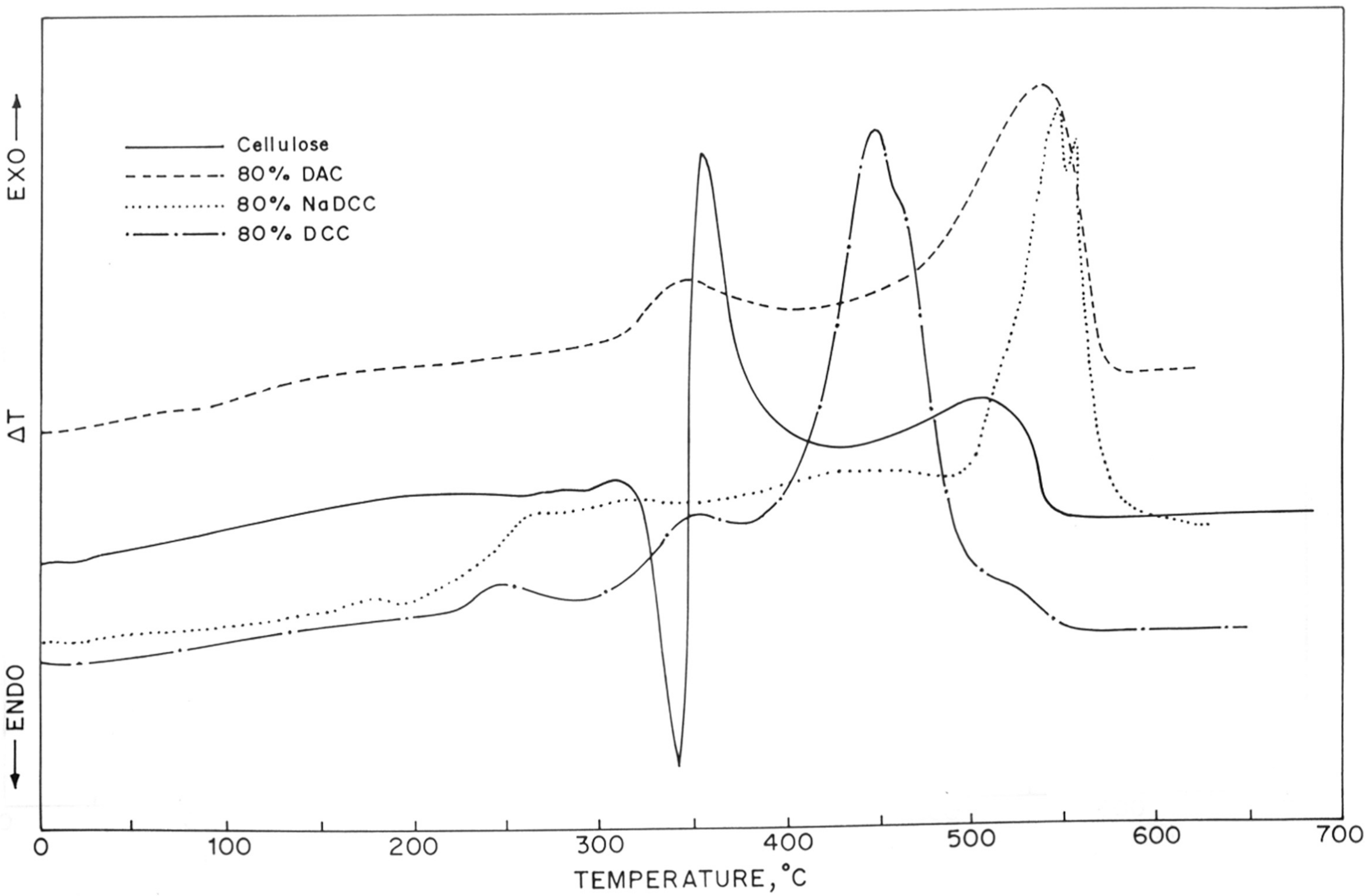

FIG.IV·7·5b:DTA PLOTS FOR CELLULOSE POWDER CP-100, 80% DAC, 80% NaDCC AND 80% DCC

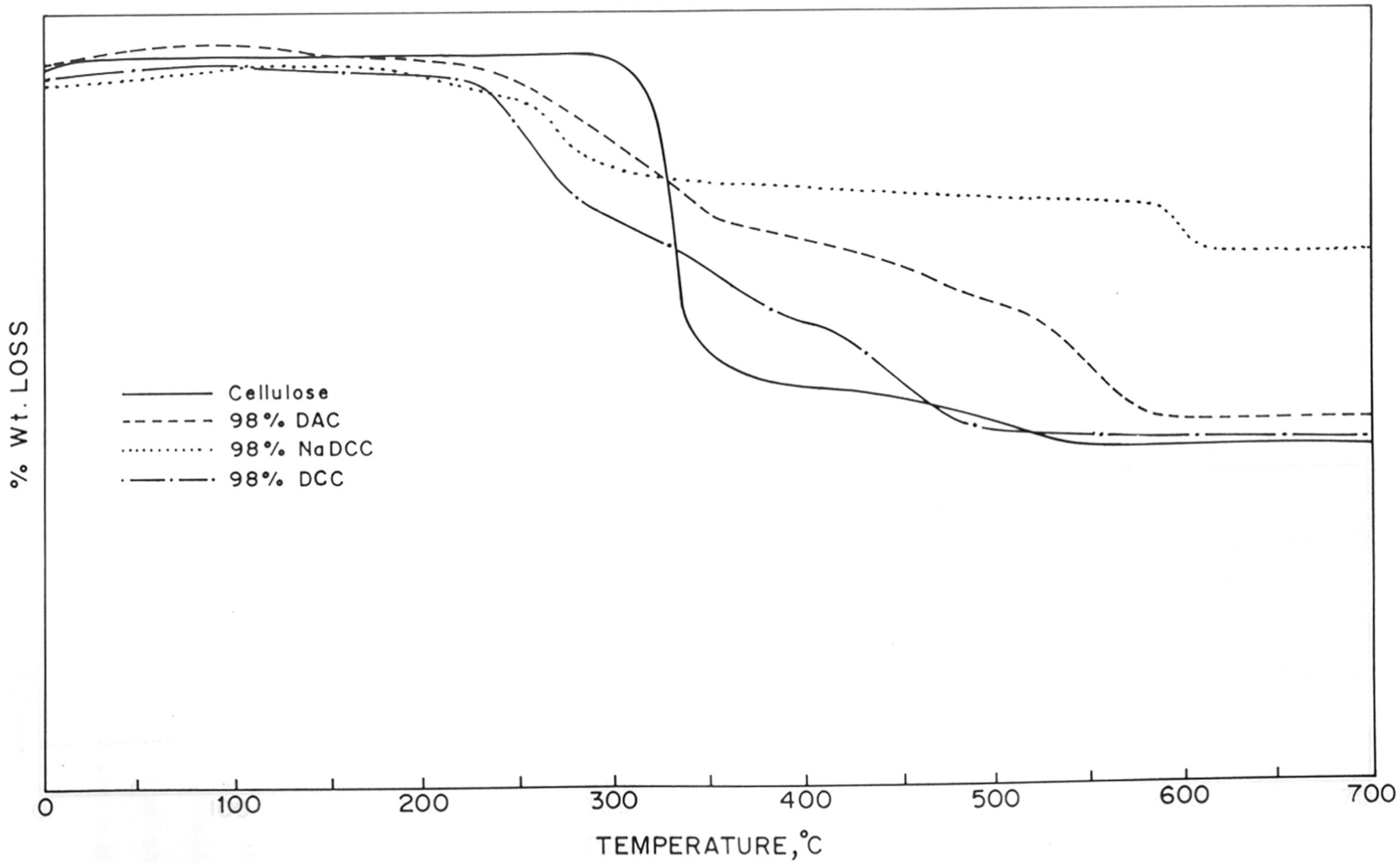

FIG. IV·7·6a: TG CURVES OF CELLULOSE POWDER CP-100, 98% DAC, 98% NaDCC, 98% DCC

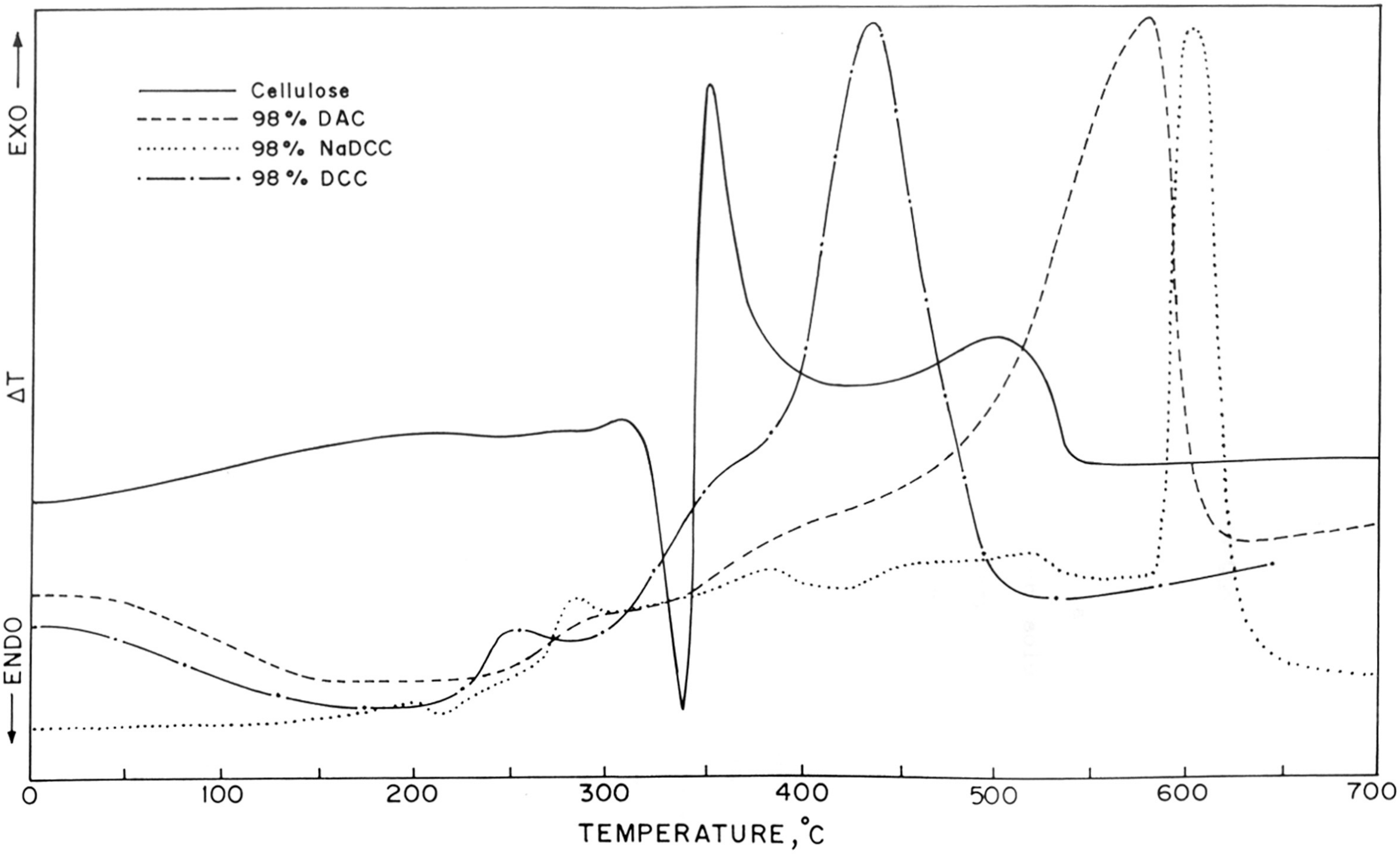

FIG. IV·7·6b: DTA PLOTS FOR CELLULOSE POWDER CP-100, 98% DAC, 98% NaDCC, AND 98% DCC

IV.8 POLYELECTROLYTE, RHEOLOGICAL AND FLOCCULATION PROPERTIES OF SODIUM 2,3-DICARBOXYCELLULOSE

Introduction

Cellulose derivatives constitute a very important segment of the world market for water soluble polymers. Their industrial applications cover a very wide range due to a variety of functional characteristics. Cellulose derivatives are generally considered to be biocompatible, biodegradable and non-toxic, and are derived from cellulose, which is the most abundant renewable resource produced by nature from a variety of plant life. It is estimated that 100 billion tonnes of cellulose in the form of renewable vegetation is produced every year on this planet (1). Amongst cellulose derivatives, sodium carboxymethyl-cellulose occupies perhaps the topmost position in terms of industrial usage. It is an anionic water soluble polyelectrolyte having a broad range of applications in the food, pharmaceutical, cosmetic, laundry, textile, paper, petroleum, detergent, and many other industries. It is therefore of great interest to search for new anionic derivatives of cellulose, which may out- perform sodium carboxymethyl-cellulose (NaCMC) in properties and economics. Salts of 2,3-carboxy cellulose have been prepared and some of their properties have been reported (2). However, their rheological behaviour has not been much investigated. As part of our on-going researches in the area of oxidized cellulose derivatives (3-5), we felt it would be of interest to synthesize water soluble sodium 2,3-dicarboxycellulose and investigate its rheological properties. The structure of this polymer is such that it does not have any anhydroglucopyranose units which constitute the cellulose chain. Therefore this polymer would not have the same degree of chain stiffness as sodium carboxymethylcellulose in which all the glucopyranose monomer units are intact. Further, this polymer would have two carboxylate functional groups per glucose monomer unit in fixed C_2 and C_3 positions, while NaCMC has the carboxylate group on C_6 position.

In this investigation, a series of sodium dicarboxycellulose (NaDCC) were prepared wherein the degree of oxidation of cellulose was 12%, 30%, 60%, 80% and 98%, based on anhydroglucopyranose units. Solubility studies indicated that only 98% NaDCC was water soluble. Hence it was selected for investigating its polyelectrolyte and rheological properties. Data on these aspects is presented in this paper, and the results compared with NaCMC.

Experimental

Synthesis of NaDCC

Stoichiometric quantities of sodium metaperiodate and cellulose powder were reacted in the dark at 55°C for 6 hrs to give the corresponding cellulose dialdehyde (6). The aldehydes were further oxidized with excess sodium chlorite and acetic acid at 20^{o}C for 7 hrs (3). After the reaction N_2 gas was bubbled to remove dissolved chlorine dioxide gas. Recovery of the product was carried out by usual work-up, as described in literature (6). The reaction scheme is shown in Figures IV.1.1, IV.2.1 and IV.3.1. The excess salt, if any, was removed by repeatedly dissolving the NaDCC in distilled water and precipitating in three times its volume of ethanol.

Sodium analysis of 98% NaDCC

Solutions of 98% NaDCC (concentration range 3-5 ppm) were tested for Na by use of Atomic Absorption Spectrophotometer model Z-8000 (Hitachi). Operating conditions of analysis were: slit 0.4 nm, wavelength 589.6 nm and lamp current 7.5 mA. Complete agreement between the experimental and theoretical value (i.e. 19.65% sodium content) were obtained.

Viscosity Measurements

An ubbelohde viscometer immersed in a constant temperature water bath maintained at 25^{o}C was used for all viscosity measurements. NaCMC and NaDCC concentrations in the range of 4.2×10^{-4} % to 1×10^{-1} % with and without added sodium chloride were studied. Flow time measurements were made in triplicate and the average value was taken for calculations.

For one study, a Brookfield Viscometer model DV-I with digital read out was used.

Rheological Study

A Ferranti-Shirley cone-plate viscometer was used for aqueous solutions of NaDCC at 200 to 800 rpm.

Procedure for Flocculation

10 mL of 1 x 10^{-2}M NaDCC was taken in a beaker containing 40 mL distilled water. In another beaker 10 mL of 1 M $Al_2(SO_4)_3$ was diluted with 40 mL distilled water, and added dropwise to the polymer solution under vigorous stirring for 10 minutes, and then left standing for 24 hrs. The flocculated materials was filtered using Whatman filter paper No.1, and dried at 50°C under vacuum and weighed. In a similar manner, flocculation of more dilute $Al_2(SO_4)_3$ solutions viz. 1 x 10^{-2}M, 5 x 10^{-2}M and 5 x 10^{-3}M and NaCMC solutions were carried out. The results are reported in Table IV.8.1.

Results and Discussion

Figure IV.8.1 shows that for an aqueous solution of NaDCC, the reduced viscosity increases continuously with a decrease in concentration when there is no salt added. This is the typical behaviour of a polyelectrolyte. With added salt also, the general trend is in agreement with reported results for NaCMC, Na-pectinate, etc (7,8). The general effect of addition of a simple salt is to depress the

Table IV.8.1

Flocculation data on the treatment of various concentrations of $Al_2(SO_4)_3$ dissolved in water with 1 x 10^{-3} moles/lit. aqueous solutions of NaCMC and NaDCC at room temperature. (Total volume of $Al_2(SO_4)_3$ solution and polymer solution was kept constant at 100 mL).

$[Al_2(SO_4)_3]$ (moles/lit.)	Wt. of flocculant using NaCMC (g)	Wt. of flocculant using NaDCC (g)
5 x 10^{-3}	3.44	2.45
1 x 10^{-2}	5.30	2.78
5 x 10^{-2}	7.21	2.97
1 x 10^{-1}	7.65	3.20

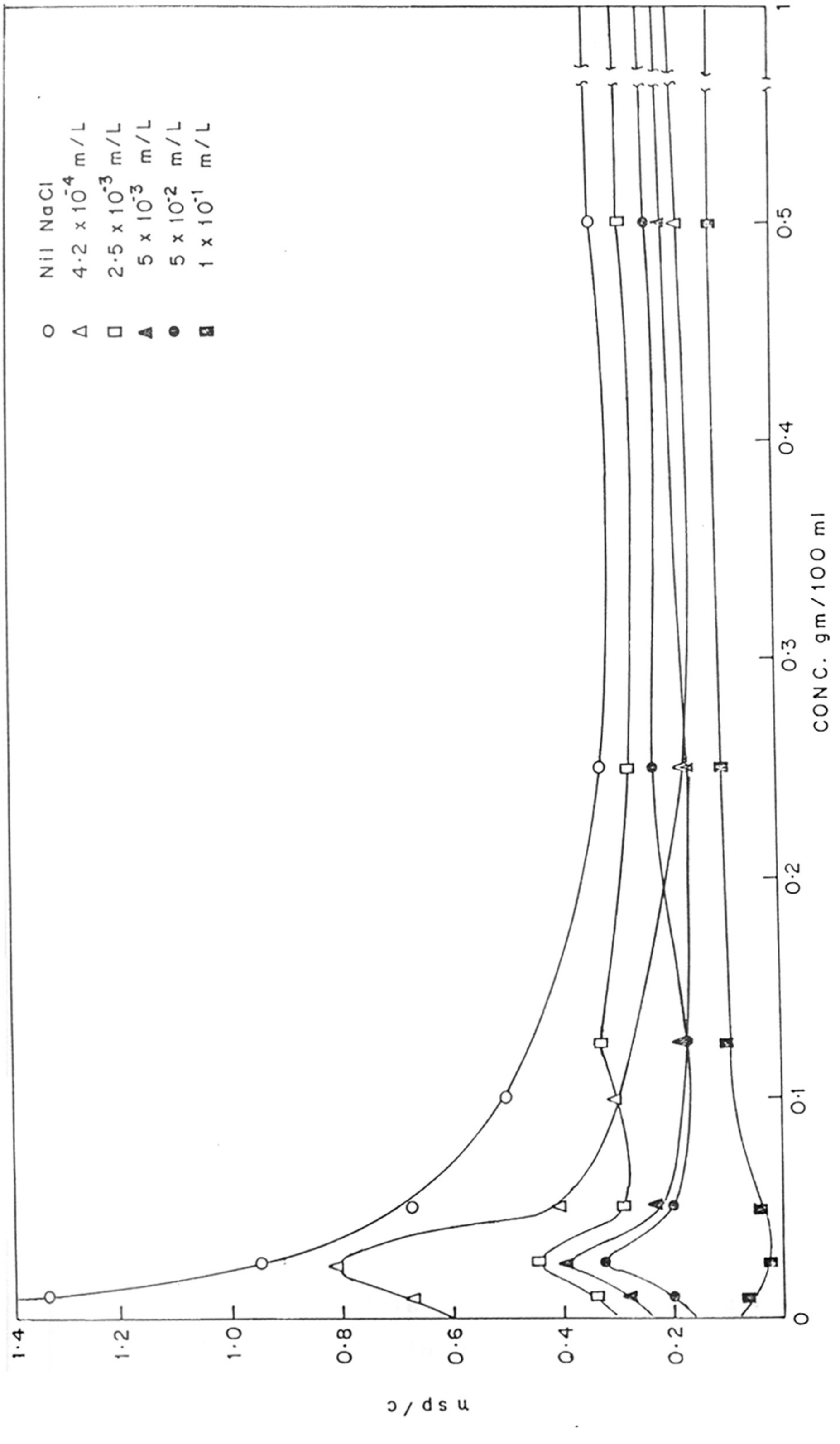

FIG.IV.8.1:REDUCED VISCOSITY η_{sp}/c Vs CONCENTRATION g/100 ml OF NaDCC IN AQUEOUS SOLUTION WITH AND WITHOUT ADDED NaCl.

viscosity of the polyelectrolyte solution over the entire range of concentrations (9). Due to severe chain degradation during the course of the oxidation reaction used in synthesizing NaDCC, the reduced viscosities observed were very low. Comparing the reduced viscosity data of NaDCC presented in Figure IV.8.1 with similar data on NaCMC of D.P. 417 reported by Fujita and Homma (7), we find that our values of reduced viscosities are lower by more than an order of magnitude under identical conditions (in the range of 30-50 times lower). Assuming similar values of "K" and "a" in the relationship $= KM^a$, the D.P. of NaDCC may be 8-14. In order to check that even in industrial applications NaDCC behaves like a polyelectrolyte, in spite of very low molecular weight, we studied the flocculation of multivalent salts like $Al_2(SO_4)_3$ using our low molecular weight NaDCC (viscosity 1.1 cP), and a commercial higher molecular weight NaCMC (viscosity 12 cP). The results are presented in Table IV.8.1. Apparently, the presence of two carboxylate groups close together on the NaDCC chain have a role to play in this flocculation.

K.S. Narayan and V. Ramasubramanian (10) studied the rheological behavior of aqueous solutions of NaCMC and sodium alginate in the concentration range of 3.0 to 3.5%. In both the cases, they observed a drop in viscosity with increasing shear rate. This is in contrast to our observation (Fig. IV.8.2) of increasing viscosity with shear rate. However, in our case the maximum viscosity of 3% NaDCC

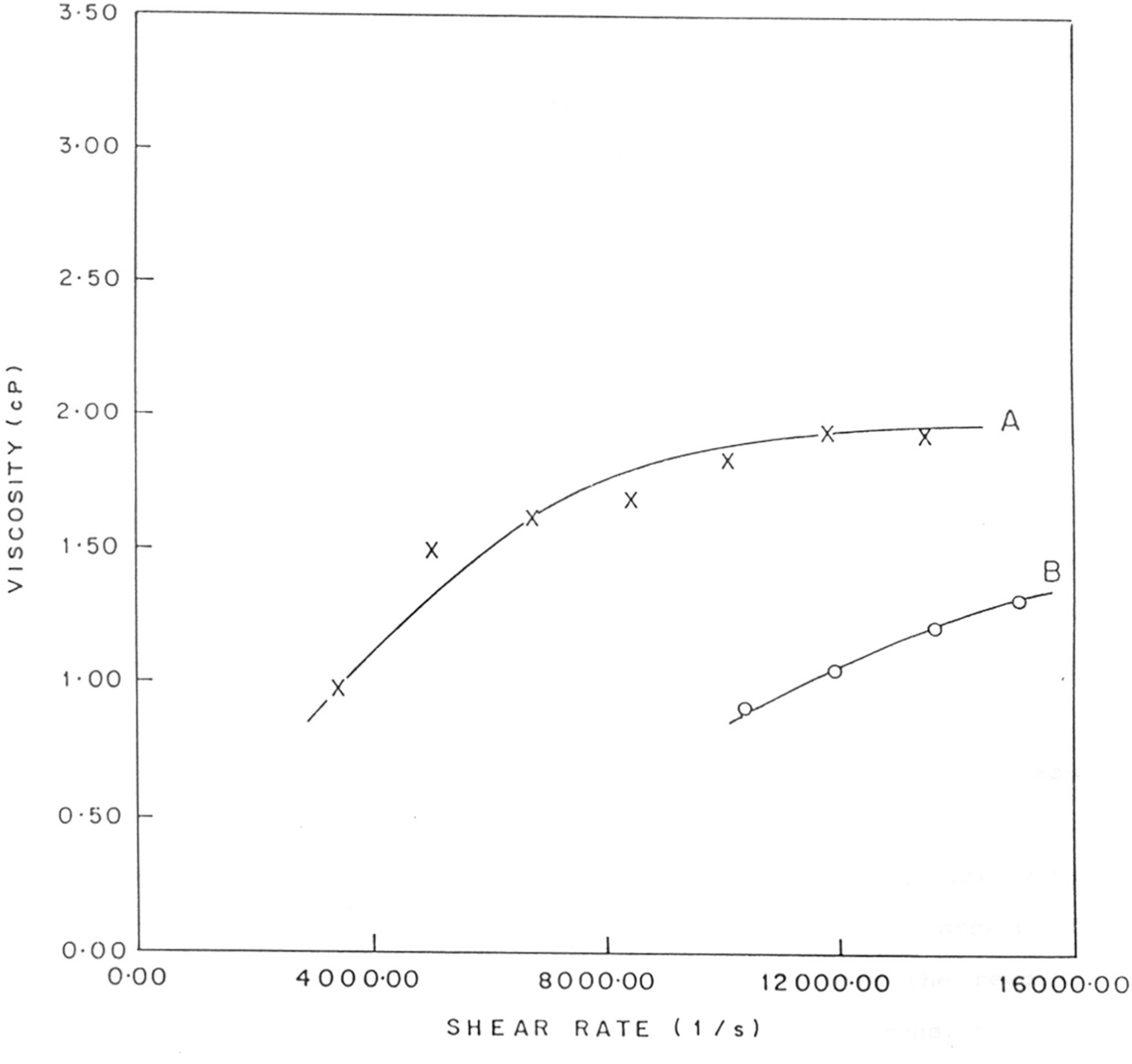

FIG.IV·8·2: BROOKFIELD VISCOSITY (cP) Vs SHEAR RATE (1/s) OF NaDCC IN AQUEOUS SOLUTION, A - 3% AND B - 1·5%

was only 1.94 centipoise (cP), and a very high shear rate (13500 sec^{-1}) was used. In the case of NaCMC for a 3.5% aqueous solution at 25°C, the viscosity was 3911 cP at a shear rate of 7.05 sec^{-1} dropping to 272 cP at a shear rate of 1142 sec^{-1} (10). Therefore, our observations pertain to a much higher shear rate region, and the two systems are not strictly comparable. We are now attempting to synthesize high molecular weight NaDCC (using noble metal catalyst systems), so that its solution properties can be compared to NaCMC. For the moment, however, the preliminary observations on the shear-thickening behaviour of NaDCC seems to be an exciting property.

A rheogram of shear stress versus shear rate for a 3% aqueous NaDCC solution is presented in Fig. IV.8.3. The shear stress is increased from 32.79 to 262.31 dynes/cm^2 and the corresponding shear rate goes up from 3400 to 13500 $sec.^{-1}$ Now, as the shear stress value is seen to decrease continuously, the shear rate is also seen to decrease, but has a value lower than what was observed earlier with increasing shear stress. For example, at a shear stress of 76.51 dynes/cm^2, the shear rate was 5075 when the reading was taken with continuously increasing shear stress, but was only 4230 when the reading was taken with continuously decreasing shear stress. The hysteresis loop is shown in Fig. IV.8.3. This behavior, again, was the reverse of what has been reported for NaCMC (11). It is well known that most

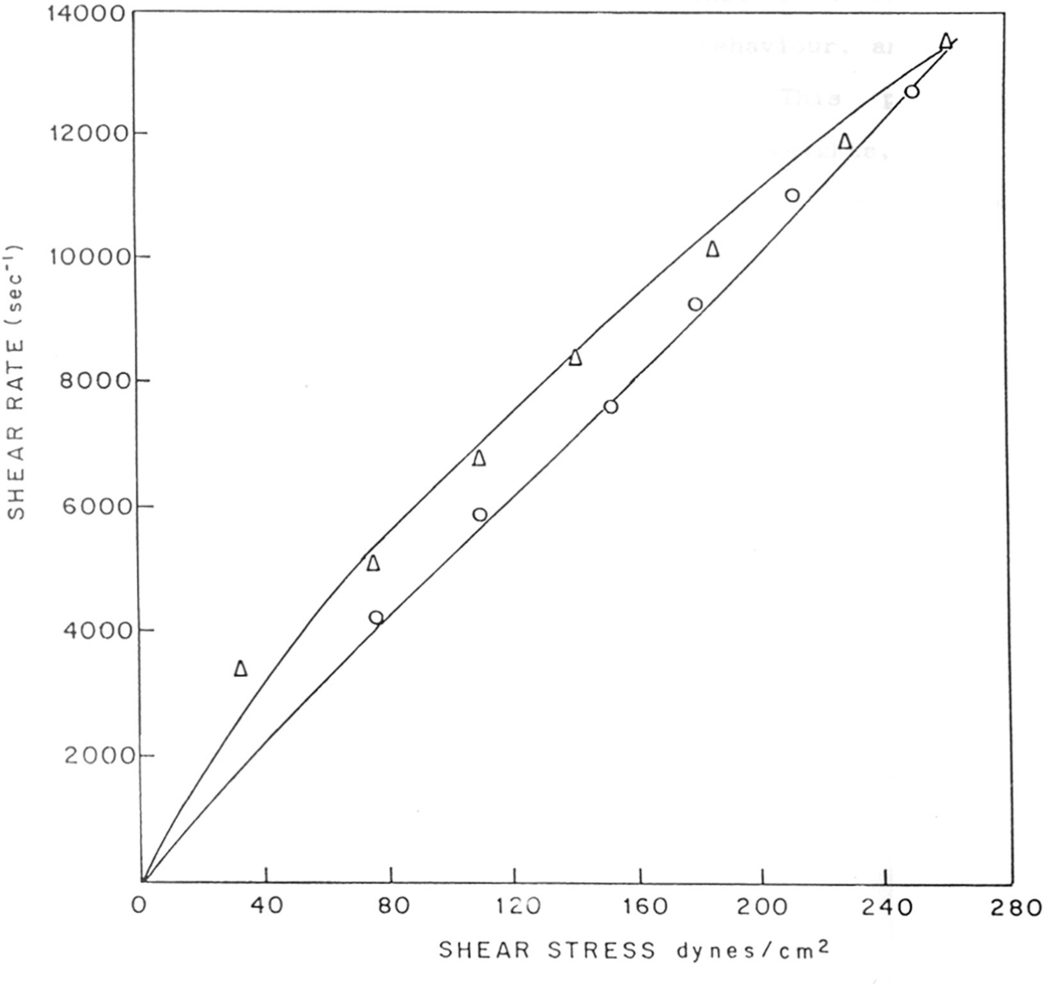

FIG.IV.8·3 : RHEOGRAM OF NaDCC SOLUTION

shear-thickening polymers contain functional groups which are capable of associating, both intramolecularly and intermolecularly, through ionic or dipolar interactions, H-bonding, insolubility in the medium, etc. There are reports of quantitative theories for explaining the phenomenon of shear-thickening in polymers (12).

In conclusion, it is clear that even low molecular weight NaDCC shows polyelectrolyte behaviour, and also some interesting rheological properties. This polymer, if synthesized with higher molecular weights, may have interesting rheological properties for industrial applications.

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APPENDIX

APPENDIX

$\eta_{sp/c}$ Vs. conc. curves of sodium carboxymethyl cellulose and sodium pectinate, obtained from literature, for comparing with sodium 2,3-dicarboxycellulose

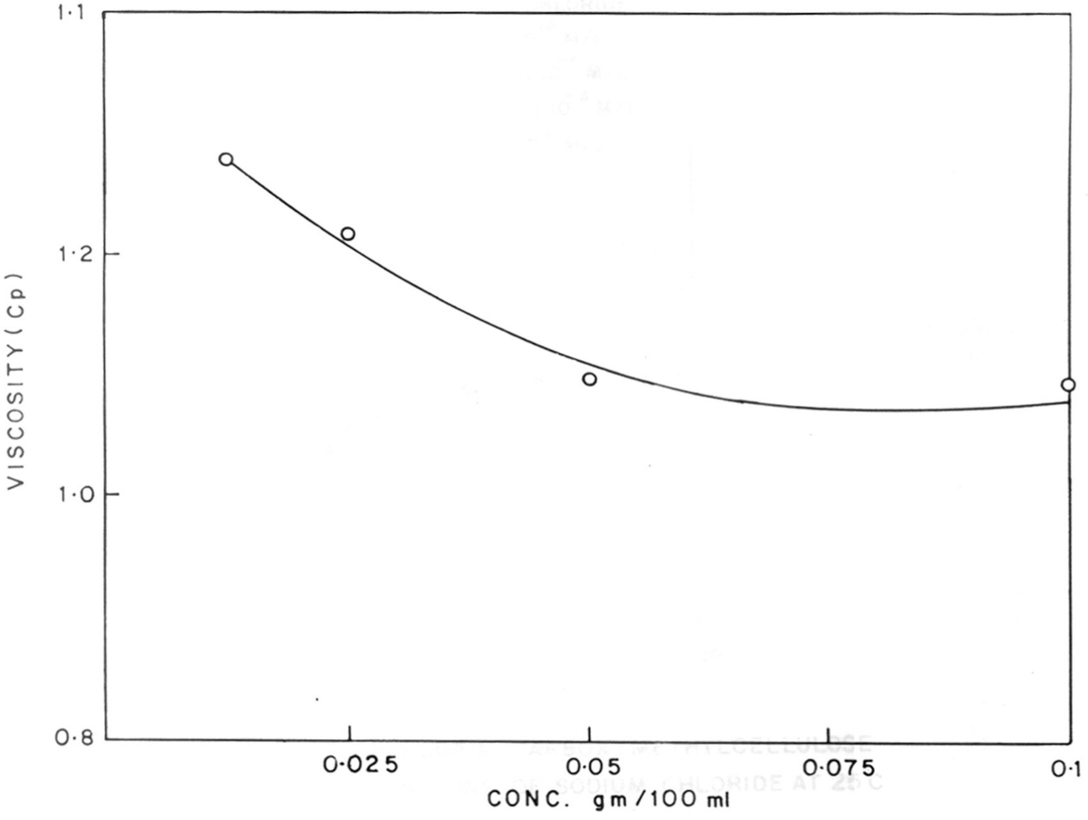

FIG.IV.8·4: BROOKFIELD VISCOSITY (CP) VERSUS CONCENTRATION (g/100 ml) OF NaDCC IN aq. SOLUTION

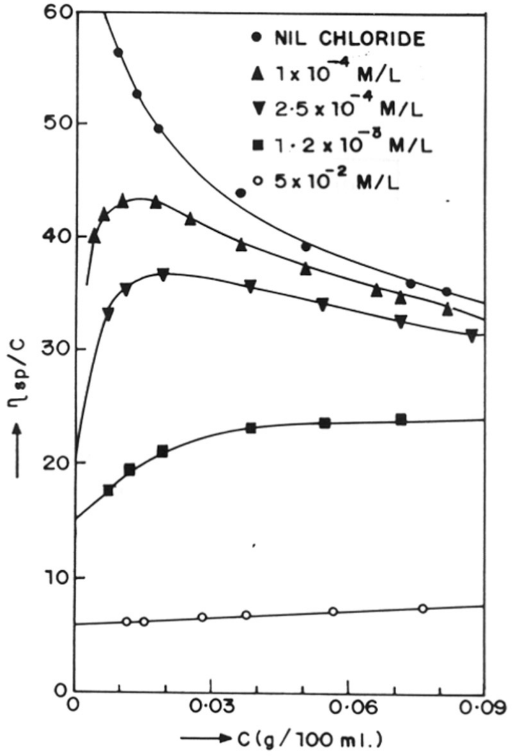

FIG.IV.8·5: η_{sp}/C vs. C FOR SODIUM CARBOXYMETHYLCELLULOSE (DP 417) IN SOLUTIONS OF SODIUM CHLORIDE AT 25°C

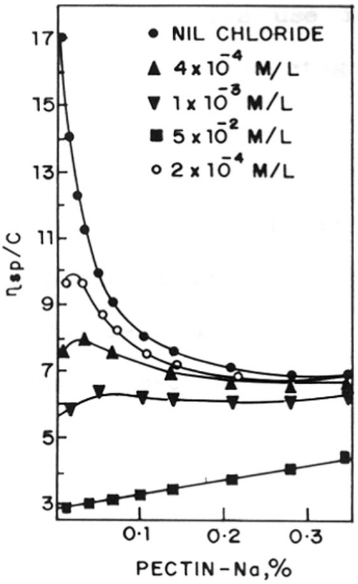

FIG. IV. 8·6 : η_{sp}/C AGAINST C FOR PECTIN–Na IN AQUEOUS NaCl SOLUTION OF VARIOUS CONCENTRATION (mole per liter)

IV.9 COMPLEXATION OF CALCIUM BY SODIUM 2,3-DICARBOXYCELLULOSE

Introduction

High calcium complexing strength by ligands is a prerequisite for a detergent builder. Sodium triphosphate (STP), is currently the main builder in detergent formulations. However, its use is considered to stimulate eutrophication in lakes and stagnant waters. This has lead to intense searches for substitutes of STP. It has been shown that the oxydiacetate moiety is a favorable structural feature for calcium complexation (1,2). Some oxidized polysaccharides (3,4) and alginates (5) have been shown to complex calcium. In view of the favorable structure of 98% sodium 2,3-dicarboxylate cellulose and its low molecular weight (6) which would facilitate biodegradation, we felt it would be of great interest to study calcium complexation by sodium 2,3-dicarboxylate cellulose.

Experimental

Materials:

Sodium 2,3-dicarboxylate cellulose (NaDCC) with 98% of the glucose monomer units having carboxylate functional groups in the C_2 and C_3 positions with the C_2-C_3 bond broken, was prepared by a procedure reported earlier (6).

Sodium carboxymethyl cellulose was a commercial product of MCA Chemicals Limited, Hyderabad, (India).

Potassium chloride, calcium chloride, sodium hydroxide, and hydrochloric acid (35%) were obtained from M/s. S.D. Fine Chemicals Ltd., Boisar, (India).

Equipment:

A digital pH/Ion meter (EILUK) was used for this work.

Calcium Ion-Selective Electrode along with Ag/AgCl type Double junction reference Electrode (Orion Research Inc., USA) was used for measurement of calcium ion concentrations. Potential measurements were made with a PH/Ion meter (EILUK).

Preparation of Standard Solution of 1000 PPM Ca^{2+}:

0.25 gms of $CaCO_3$ was dissolved in 10 ml of 4N hydrochloric acid solution. After diluting to 30 ml, the solution adjusted to pH 5 using 0.5N KOH solution in a 100 ml volumetric flask to give 100 ml solution.

Ionic Strength Adjuster (ISA):

2M KCl was prepared by dissolving the required amount of KCl in water. 1 ml of this solution was added to 50 ml of sample or standard solution before taking readings with the Ion Selective Electrode.

Preparation of Standard Solution of 1000 PPM:

98% sodium 2,3-dicarboxycellulose (NaDDC) and sodium carboxymethyl cellulose (NaCMC).

0.1 gm of each polymer was dissolved in 40 ml distilled water and then diluted to 100 ml in a volumetric flask.

Calibration Curve of Ca^{2+} ion Concentration using Ion Selective Electrode:

The 1000 PPM Ca^{2+} solution was used for preparing 1, 10 and 100 PPM solutions by appropriate dilutions in 100 ml volumetric flasks. Calcium ion selective electrode and reference electrode type were introduced in these solutions and millivolts readings recorded.

Calcium binding for 98% sodium 2,3-dicarboxycellulose (NaDCC) and sodium carboxymethyl cellulose (NaCMC).

100 PPM NaDCC solution was taken in a 250 ml beaker and standard 2.5 ml Ca^{2+} ion solution was added to it so that the final concentration of Ca^{2+} in the solution was 2.5 PPM. Using Ca^{2+} ion selective electrode and the reference electrode (mV) reading were taken on the ION meter. Other solution mixtures were studied in a similar fashion, such as

1) 100 PPM NaDCC containing 5 PPM Ca^{2+} ion,
2) 100 PPM NaDCC containing 10 PPM Ca^{2+} ion,
3) 100 PPM NaDCC containing 20 PPM Ca^{2+} ion.

The results are presented in Table-IV.9.1. Free Ca^{2+} ion were read off from the calibration curve.

Table IV.9.1

Calcium ion bound gram/gram to NaDCC and NaCMC (with $1X10^{-3}M$ KCl added for adjusting the ionic strength of the medium) final pH of solution 8.2.

Moles/lit	$[Ca^{2+}]$ Moles/lit	Free$[Ca^{2+}]$ Moles/lit	Bound$[Ca^{2+}]$ Moles/lit	Bound$[Ca^{2+}]$ g/g
NaDCC $4.2X10^{-4}$	$6.25X10^{-5}$	$3.75X10^{-5}$	$2.5X10^{-5}$	0.010
$4.2X10^{-4}$	$1.25X10^{-4}$	$6.25X10^{-5}$	$6.25X10^{-5}$	0.025
$4.2X10^{-4}$	$2.5X10^{-4}$	$1.20X10^{-4}$	$1.38X10^{-4}$	0.055
NaCMC $4.2X10^{-4}$	$6.25X10^{-5}$	$2.5X10^{-5}$	$3.75X10^{-5}$	0.015
$4.2X10^{-4}$	$1.25X10^{-4}$	$4.75X10^{-5}$	$7.75X10^{-5}$	0.031
$4.2X10^{-4}$	$2.5X10^{-4}$	$8.75X10^{-5}$	$1.60X10^{-4}$	0.065

Results and Discussion

Oxidation of cellulose to produce 98% 2,3-dialdehyde cellulose using sodium metaperiodate results in a reduction of molecular weight of the polymer. Continued oxidation of 98% 2,3-dialdehyde cellulose with sodium chlorite in glacial acetic acid to produce 98% sodium 2,3-dicarboxylate cellulose (NaDCC) resulted in further decrease in molecular weight (6). A 1% aqueous solution of 98% NaDCC had a Brookfield viscosity of only 1.1 centiPoise (cP), as opposed to 12.0 cP for the sodium carboxymethyl cellulose (NaCMC) sample used as a reference in these studies. It is estimated that the degree of polymerization of our 98% NaDCC is in the range of 10 to 15.

A comparison of the properties of NaCMC (viscosity 12.0 cP) and 98% NaDCC (viscosity 1.1 cP) in the binding of calcium ions (Table IV.9.1) shows that NaDCC is superior to NaCMC almost by an order of magnitude.

The binding constants of calcium ions obtained by using oxidized members of "the starch family" (maltodextrins, amylose, amylopectin, starch) for the lower degree of polymerization are in the range of log K = 2 to log K = 3.5 (2). These polysaccharides are claimed to be potentially useful in replacing sodium triphosphate in detergent formulations, especially in combination with zeolite NaA (2). The structure of NaDCC, shown in Fig. IV.2.1, shows that the ionised polymer with neighbouring carboxylate groups is also well suited for calcium complexation. Further work is in progress in our laboratory to derivatise NaDCC in such a way to improve the calcium binding constants. In an earlier work (6) we have shown the flocculation power of NaDCC with aluminum sulfate.

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APPENDIX

APPENDIX

Calcium complexation by oxidised cellulose (NaDCC)

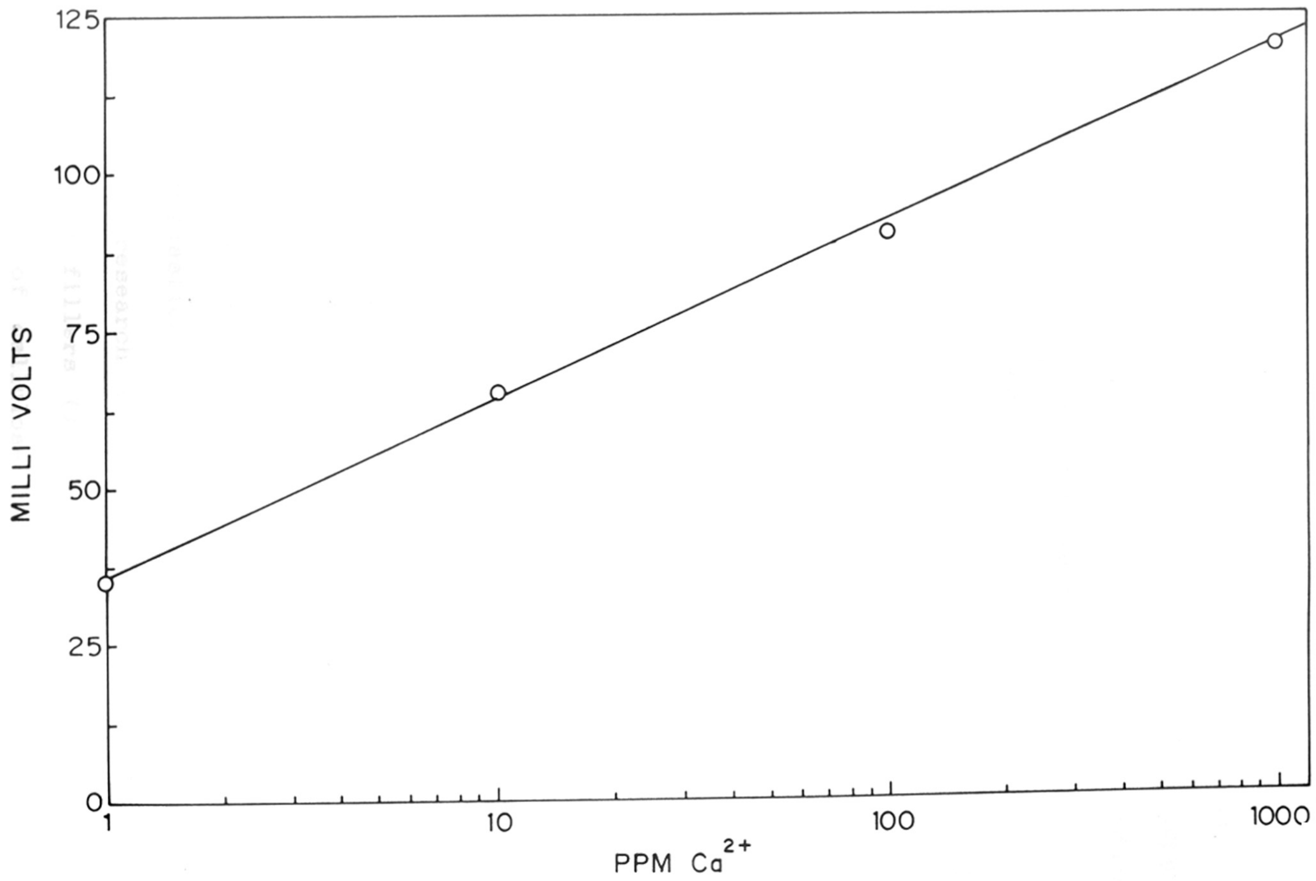

FIG.IV.9·1: CALIBRATION CURVE OF Ca^{2+} ION CONCENTRATION USING Ca^{2+} ION SELECTIVE ELECTRODE

IV.10 CELLULOSIC DIAMINES AS REACTION-INCORPORATED FILLERS IN EPOXY COMPOSITES

Introduction

Lignocellulosics, due to their natural abundance and low cost, have been used as fillers in a variety of polymer systems (1-6). Besides being inexpensive, lignocellulosics such as wood pulp fibres impart excellent mechanical properties to polymeric composites (7). However, thermoplastic matrixes, such as polyethylene, and thermoset matrixes, such as epoxies, and incompatible with cellulose and phase separation occurs with time. The weak interface between the cellulosic filler and resin may be strengthened by surface pretreatment of the cellulosic fibres with silane coupling agents (8) or by the use of surface modifier additives such as maleated waxes (9). Cross-linking the cellulosic filler with thermoplastics such as polypropylene and linear low density polyethylene to improve tensile properties of the composite and to prevent phase separation has also been successfully attempted (10,11).

Due to the vast potential for use of cellulosic fillers in thermoplastics and thermosets, our laboratory has undertaken research on modified celluloses as reaction-incorporated fillers (12,13). In this paper, we describe modification of cellulose by incorporating pendant amino groups along the cellulose polymer chain and its use as a reaction-incorporated filler for an epoxy thermoset system. Titanates have found specific application as coupling agents for inorganic filler systems (14), and silanes for a variety of other surfaces (8). Similarly, cellulosic fillers with pendant amine or other suitable functional groups can be used advantageously in composite systems.

Materials and Methods

Cellulose powder of 150-mesh fineness and containing ~85% alpha-cellulose was obtained from Cellulose Products of India Ltd., Ahmedabad. It was thoroughly washed with water and dried before use. The epoxy resin (Araldite GY 250 based on bisphenol-A and epichlorhydrin of epoxy equivalent weight 192-196 and viscosity 225-275P at 21°C) was obtained from Ciba Geigy, Bombay. Diaminopropane (DAP) was procured from Aldrich, Milwaukee.

The synthesis reaction scheme is shown schematically in Fig.IV.3.1. The synthesis of 30% 2,3-dicarboxycellulose (i.e. 30% of the glucose monomer units are converted at 2,3-dicarboxy derivative, Fig.IV.3.1), was adapted from the literature (12,15,16). Cellulose powder (140 g) was dispersed in 1500 ml distilled water in a flask fully covered with aluminium foil, and 56.2 g sodium metaperiodate dissolved in 400 ml distilled water was slowly added. This reaction mixture was maintained at 55°C with stirring in the dark for 6 h. At this stage, the reaction was stopped. The aqueous layer was decanted off, and the reaction product (30% 2,3-dialdehyde cellulose) was thoroughly washed with distilled water and dried. Of this 2,3-dialdehyde cellulose, 15 g were dispersed in 200 ml water. To this was added 14.8 g sodium chlorite dissolved in 70 ml water and the temperature was maintained at 20°C. Glacial acetic acid (3.54 ml) dissolved in 30 ml water was added dropwise, the temperature being maintained at 20°C. The start of the oxidation reaction was indicated by the formation of a yellow coloration and the evolution of ClO_2 gas. The reaction was continued for 7 h until there was no further evolution of gas. Nitrogen gas was bubbled through the reaction mixture to remove dissolved gases. The reaction product (the sodium salt of 2,3-dicarboxycellulose, was precipitated by pouring it into three volumes of ethanol. The precipitated solid was filtered, dried, and then reprecipitated by dissolving in water, and pouring into ethanol, to get pure sodium salt. To convert the sodium derivative to the acid form (Fig.IV.2.1), 6 g of sodium salt was taken in 60 ml of 0.1 M HCl, kept at ~1°C in a freezer for 30 min and stirred occasionally with a glass rod. The aqueous HCl was decanted, and to this was added 30 ml distilled water; the whole was stored in a refrigerator at 5°C for 24 h. The product, 2,3-dicarboxycellulose, (insoluble in water) was washed several times with water, until the wash was neutral. It was then filtered and dried. Dicarboxycellulose (5 g) was dispersed in 15 ml CCl_4 and to this was added 25 ml thionyl chloride and refluxed for 5 h to give acid chloride. Excess thionyl chloride was removed by vacuum distillation, CCl_4 (15 ml) was added to acid chloride, and heated to reflux. Triethylamine (1 ml) was added, followed by the dropwise addition of 2.5 ml diaminopropane dissolved in 10 ml CCl_4. This mixture was refluxed for 18 h. The product (Fig.IV.4.1) was filtered, washed with water and methanol, and dried to get 5.4 g of 1,3-Diaminopropane-linked 2,3-dicarboxycellulose. The IR spectrum showed the C = 0 peak at 1675 cm^{-1} and the CONH peak at 3190 cm^{-1}. The amount of diaminopropane attached to the carboxycellulose was estimated by weight gain. In the product abovesaid used for this study, the weight gain was 8%.

Gel times were obtained with a Tecam Gelation Timer, Model GS4, manufactured by Techne (Cambridge) Ltd., England.

Results and Discussion

Primary aliphatic amines were among the first chemicals to be accepted as curing agents for epoxy resins. They are generally used at or near stoichiometric ratio (i.e. one amine hydrogen for each epoxy group), and generally provide well-cured resins even at room temperature.

However, since the purpose of this study was to investigate the effect of primary aliphatic diamines chemically linked to cellulose on the cross-linking reaction of the epoxy compound, the concentrations of diaminopropane (DAP) selected are far below the stoichiometric requirement, which is 9.5 PHR (parts per hundred of resin) in this case. Table IV.10.1 shows that the gel times for curing the epoxy using DAP concentrations in the range 3.1 to 4.4 PHR, with or without 10 PHR cellulose filler present, are quite similar, with the gel times being consistently somewhat higher in the presence of cellulose. This indicates that, at the higher initial viscosity in the latter system, the mobility of DAP is somewhat decreased, which leads to a slightly greater reaction time.

Cellulose (10 PHR) and 10 PHR of 30% dicarboxycellulose with 0.9 PHR DAP added to the epoxy did not cure even after 2200 min. Therefore, these experiments were stopped at this stage. However, when the same quantity of DAP (0.9 PHR) was chemically linked to the 30% dicarboxycellulose (Fig.IV.4.1) then gel time was achieved in only 948 min (Table IV.10.1). This was possible now because the cellulose was also chemically linked to the epoxy, and a reasonable gel time was achieved even when the DAP content was less than 10% of the stoichiometric requirement of 9.5 PHR. In this case it is speculated that dicarboxyl and hydroxyl functional groups must have acted as accelerators. In the case of 10 PHR cellulose and dicarboxycellulose blended with 0.9 PHR DAP, phase separation of the celluloses from the epoxy resin was observed after about 1 h of reaction, indicating minimal progress in the cross-linking reaction and definitely no

TABLE IV.10.1

Gel times for the curing of epoxy with and without cellulose filler, using DAP as cross-linking agent and with cellulose-linked DAP at 120°C

Type of filler	Quantity of filler (PHR)	Quantity of DAP (PHR)	Gel time (min)
–	–	4.4	1
–	–	4.2	6
–	–	4.0	19
–	–	3.8	71
Cellulose	10	3.1	189
Cellulose	10	4.4	1
Cellulose	10	4.2	10
Cellulose	10	4.0	33
Cellulose	10	3.8	98
Cellulose	10	3.1	219
Cellulose	10	2.0	>1200
Cellulose	10	0.9	>2200[a]
30% carboxycellulose	10	0.9	>2200[a]
30% carboxycellulose containing 8% chemically reacted DAP	10	0.9 (in bound form)	948

[a] Phase separation was clearly observed after about one hour, indicating minimal cross-linking of epoxy and no participation of cellulose or carboxycellulose in the reaction. (In experiments, where low gel times are achieved through the use of higher concentrations of DAP, sufficient cross-linking occurs in the initial phase itself, thereby physically preventing cellulose from settling down into a separate phase.)

participation of the cellulose in the cross-linking reaction. The beneficial effect of chemically linking DAP to cellulose was further confirmed when it was seen that even when more than double the concentration of DAP (2.0 PHR) is used in un-linked form with cellulose (Table IV.10.1), the gel time is far greater than it is with 0.9 PHR DAP in the cellulose-linked form.

Although organic carboxylic acids are known to cure epoxy resins, in general, the reaction is sluggish unless phenolic accelerators or tertiary amine catalysts are used (17). In the case of 30% dicarboxycellulose, not only was the 10 PHR concentration far below the stoichiometric requirement, there were no phenolic accelerators or tertiary amine base catalysts present to aid the reaction. Therefore, like cellulose, dicarboxycellulose also did not take part in the cross-linking reaction. It might have been expected that DAP might react with the carboxycellulose, leading to cross-linking of the dicarboxycellulose with the epoxy resin, but that apparently did not occur in the present reaction system.

Conclusions

In summary, we can list the advantages of organic fillers (cellulosics, lignocellulosics) with built-in curing agents. These are:

(i) No phase separation of the modified filler due to incompatibility with the matrix resin, since the filler is also the curing agent.

(ii) No additional curing agent needed if sufficient reactive functional groups are created along the cellulose chain.

(iii) Significant decrease in the quantity of curing agent needed.

(iv) Greatly enhanced curing rate (gel time).

(v) Compounding step is avoided for separate addition of curing agent.

(vi) When the curing agent is chemically linked to the organic filler it also acts as a coupling agent.

Further work is continuing in our laboratory to mitigate another major disadvantage of lignocellulosics, namely, that of lack of high thermal stability. It is expected that results of these and other investigations (2-4,6) would ultimately lead to greater utilization of the inexpensive and abundantly available renewable resources (lignocellulosics) as fillers, without compromising on properties.

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SUMMARY OF THESIS

V. SUMMARY OF THESIS

Cellulose is the most abundantly available naturally occurring organic material in the world. It is a naturally occurring polymer of glucose, and the accepted view is that it is a 1,4-β-D-linked poly(anhydro-glucopyranose). It is estimated that 100 billion tonnes of cellulose in the form of renewable vegetation is produced every year on this planet. This translates into an availability of approximately 20 tonnes of cellulose for every person on earth.

Investigations into the structure of cellulose have been conducted for more than one hundred and fifty years, and due to this there has been constant progress in our understanding of the cellulose structure at the macro as well as molecular level. The wide range of derivatisation of cellulose possible has given mankind a magnificent variety of products of academic interest as well as of industrial usage. It is more than a century since cellulose nitrate, cellulose acetate, cellulose xanthate, and many other derivatives were produced as industrial materials, and these continue to be important materials even today. Recent researchers have seen, expectedly, an ever-increasing interest in these materials, and development of new derivatives continues. Another major incentive for developing industrial materials based on renewable cellulose is that cellulose derivatives are generally considered to be biocompatible, biodegradable, environment-friendly, and non-toxic.

Oxidation of cellulose to produce modified celluloses known as oxidized celluloses was first investigated in 1882 by Witz. This chemical modification of cellulose was seen to impart several desirable properties to cellulose, and therefore continues to be investigated till today. Partial oxidation of cellulose can lead to a variety of polymers having different functional groups, such as aldehyde and carboxyl, in addition to the primary and secondary hydroxyl groups already present. This can increase the range of applications of cellulose for industrial applications. Oxidized cellulose has increased affinity for various dyes, and this has great significance for the textile industries. Fire resistant materials can be made from oxidized cellulose by reacting them with tris(hydroxymethyl) phosphine, alkylene oxide, and tris(aminoethyl) borate. Oxidized cellulose can have two carboxylate groups, and therefore can have applications in removal of heavy metals from aqueous solution by flocculation, and its good sequestering power for ions causing hardness in water results in its usage as a detergent builder. Oxidized celluloses show improved initiation characteristics compared to the unoxidized samples of cellulose in graft copolymerisation studies, and give larger yields of graft copolymers. Use of oxidized cellulose and as reaction-incorporated fillers in epoxy matrix have been shown to improve cure rates, prevent phase separation by chemically linking the filler and the polymer matrix, and eliminate the compounding step for addition of curing agent. Oxidized cloth has been shown to be useful for immobilising enzymes like collagenase in bandages for wound healing. Microbicides, which are safe and useful for textiles, coatings, and building materials, have shown 100% fungicidal effect when immobilized on oxidized cellulose. Oxidized cellulose, when converted to difluoroaminated dialdehyde cellulose, are useful in explosives and propellants.

Thus, it is clear that oxidized celluloses represent an important class of cellulose derivatives. Oxidation reactions result in a change in the molecular weight and molecular weight distribution, crystallinity and other structural features, solution properties, thermal properties, etc., of the resulting polymer molecule. A search of the literature showed that no detailed systematic study of the structure and properties of oxidized cellulose samples having incremental changes in their degrees of oxidation had ever been reported. In view of these lacunae, as well as their diverse applications and potential for further development as industrial materials, an investigation into the structure and properties of oxidized celluloses in the solid state as well as in solution seems to be warranted. Therefore, these aspects form the subject matter of this dissertation.

Sections I, II, and III of the thesis deal with the introduction, scope of work, and literature survey, respectively, of researches in the field of oxidation products of cellulose. In particular, all published work on synthesis, wide-angle X-ray diffraction studies, NMR studies, thermal analysis and solution properties are reviewed.

Section IV of the thesis is the experimental research part. This section has been divided into ten sections.

Sections IV.1-3 deal with the syntheses of 2,3-dialdehyde cellulose (DAC), sodium 2,3-dicarboxylate cellulose (NaDCC), and 2,3-dicarboxycellulose (DCC). In each type of derivative, various degrees of oxidation - 12%, 30%, 60%, 80%, and 98% (based on glucose monomer units) were carried out, and the samples were characterised by periodate consumption, IR, and FT-NMR.

Section IV.4 relates to the synthesis of cellulosic diamines. In particular 30% DCC was reacted with 1,3-diaminopropane to give a cellulosic diamine, which was later admixed with an epoxy resin for use as a reaction-incorporated filler.

Section IV.5 represents an experimental investigation of the changes in crystallinity occurring due to incremental changes in the degree of oxidation of cellulose. Cellulose was oxidized to dialdehyde cellulose (DAC), sodium dicarboxy cellulose (NaDCC) and dicarboxy cellulose (DCC). Products having oxidation levels of 12%, 30%, 60%, 80%, 98% based on glucose monomer units, were obtained by adjusting the quantity of oxidizing agents. The wide-angle X-ray diffraction peak at $2\theta = 22.7°$ for the various oxidized cellulose samples which indicates the crystallinity of the cellulose, was found to decrease almost proportionately to the degree of oxidation of the starting cellulose. The differences in crystallinity between DAC, NaDCC and DCC of the same degree of oxidation are expected to result from differences in their H-bonding ability with adjacent molecules. This interpretation was supported by water absorption studies, NMR studies, and thermal analysis.

Section IV.6 deals with high resolution solid state CP-MAS C-13 NMR spectra of these same oxidized cellulose samples in order to investigate the changes occurring in the spectral features with increasing oxidation levels. For each series of spectra of increasing oxidation levels of DAC, DCC, and NaDCC, an increasing trend towards formation of upfield shoulders on C6, C4, and C1 is observed. Therefore it can be inferred that the new broad peaks formed represent the amorphous content of the oxidized cellulose sample. The actual comparative spectra of the oxidized celluloses are presented, along with the tabulated peak positions of each carbon atom. CP-MAS C-13 NMR spectra thus can be used as a tool to qualitatively get an idea of the degree of crystallinity of partially crystalline celluloses. It is possible to extend this study to other partially crystalline polymers.

Section IV.7 is a thermal analysis investigation of the above incrementally oxidized cellulose samples. Their thermogravimetric analysis (TG) and differential thermal analysis (DTA) were studied. It was found that oxidation generally destabilised cellulose at lower temperatures (below ~ 250°C), but at higher temperatures the oxidized products were found to be more stable. Cellulose, DAC´s, and DCC´s all showed final weight losses in the region of 80-85%. However, 80% NaDCC and 98% NaDCC showed weight losses of only 30% and 37%, respectively.

Section IV.8 deals with the polyelectrolyte behavior and rheological study of 98% NaDCC. The polyelectrolyte behavior of 98% NaDCC was compared to a commercial sample of sodium carboxymethyl cellulose (NaCMC), and sodium alginate. NaDCC showed typical polyelectrolyte properties, such as viscosity and flocculation of multivalent salts. Inspite of very low viscosity of aqueous NaDCC solution due to very low molecular weight, the flocculation of $Al_2(SO_4)_3$ from aqueous solutions using NaDCC was quite comparable to NaCMC. The rheological properties of NaDCC were in contrast to that of NaCMC reported in literature. This was because of the vast difference in their molecular weights, which resulted in their rheograms being investigated in very different shear rate regions. The NaDCC solutions showed slight shear thickening behavior. A rheological study of high molecular weight NaDCC is expected to lead to more interesting properties and applications, and currently our research is proceeding in this direction.

Sections IV.9 and IV.10 deal with applications of oxidized celluloses. Section IV.9 shows preliminary data on calcium binding by 98% NaDCC. It has been shown that the oxydiacetate moiety is a favourable structural feature for calcium complexation. Compounds having high complexation strength are useful as detergent builders. In spite of very low molecular weight (~ 6000) of 98% NaDCC, the calcium complexation power was found to be comparable to high molecular weight commercial sodium carboxymethyl cellulose (NaCMC).

Section IV.10 is an important study on the use of modified celluloses as reaction-incorporated fillers in thermosets. Cellulosic fillers were chemically modified by attaching pendant primary amine groups (diamino propane). The modified cellulose fillers were used for curing an epoxy resin (diglycidyl ether of bisphenol A). Gel times thus obtained were much less than systems containing unmodified cellulose. The advantages from the use of such modified organic fillers are discussed. Our investigations could encourage greater utilization of renewable lignocellulosic materials as reaction-incorporated fillers for polymer composites.

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

VI. CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

The conclusions drawn from the studies of WAXRD, High Resolution CP/MAS C-13 NMR, Thermal Analysis, Polyelectrolyte and Rheological Study, Calcium Binding and Flocculation Studies, and Applications of Cellulosic Diamines as Reaction-incorporated Fillers in an Epoxy Matrix are given at the end of each relevant section.

It is clear that this systematic synthesis and study of various oxidized cellulosic products (DAC, DCC, NaDCC), having incremental changes in their degrees of oxidation, using various analytical tools, has given us a comprehensive picture of the structural, physical, and chemical changes occuring on oxidation to various extents. Considering the importance and potential of applications of the products of oxidation of cellulose, this study would benefit scientists and technologists who wish to further develop the field of oxidized celluloses. It would be desireable to work on new mild chemical synthesis methods to prevent the chain degradation and thereby improve the polyelectrolyte properties of oxidized celluloses. New emerging techniques of analyzing the residual crystallinity of polymers like polyethylene and poly(oxymethylene) by C-13 inversion-recovery cross-polarisation NMR (IRCP) may be employed for gaining further insight into the structures of the oxidized celluloses.

LIST OF PUBLICATIONS

VII. LIST OF PUBLICATIONS

1. Cellulosic diamines as reaction-incorporated fillers in epoxy composites.
   A.J. Varma and V.B. Chavan.
   Cellulose **1**, 215-219(1994)

2. Thermal properties of oxidised cellulose.
   A.J. Varma and V.B. Chavan.
   Cellulose (Accepted for publication, Feb. 1995).

3. A study of crystallinity changes in oxidized celluloses.
   A.J. Varma and V.B. Chavan.
   Polym. Degradn. and Stab. (Accepted for publication, March 1995).

4. Polyelectrolyte and rhelogical properties of sodium 2,3-Dicarboxycellulose.
   A.J. Varma and V.B. Chavan.
   Carbohydr. Polym. (Accepted for publication, April 1995).

5. High resolution solid state CP-MAS C-13 NMR studies of cellulose and its oxidised derivatives.
   A.J. Varma, V.B. Chavan, P.R. Rajamohanan and S. Ganapathy.
   Cellulose (Communicated).

6. Calcium complexation by oxidised cellulose.
   V.B. Chavan, O.G.B. Nambiar and A.J. Varma.
   (Manuscript in preparation)

Papers Presented in Conferences/Symposia

1. Structure of cellulose - a material for future generation.
   A.J. Varma, V.B. Chavan, P.R. Rajamohanan and S. Ganapathy.
   Proceedings of the All India Conference on "New Dimensions in Science and Technology" at Banaras Hindu University, Varanasi, February 7-9 (1991), p.247.

2. Polyelectrolyte behaviour of sodium 2,3-dicarboxy-cellulose - an industrially important nature-derived polymer.
   A.J. Varma and V.B. Chavan.
   Paper presented at the Indian Chemical Congress (CHEMCON-91), Anna University, Madras, December 18-21 (1991).