

Cellulose Derivatives Part-II Graft Copolymers of Cellulose With Methyl Methacrylate

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INTRODUCTION

Graft copolymers are high polymers, the molecules of which consist of two or more polymeric parts of different composition, chemically united together. Graft copolymers are important for specialised fields based on service requirements and where properties outbeat the cost. A grafted cellulose with various vinyl monomers will have the properties of resistance to microbiological attack, thermal and chemical stability, improved tear, burst and tensile strength, water repellancy, better hydrolytic resistance, stability to ultra violet and gamma radiation, resistance against bacterial attack, abrasion resistance, ion-exchange membranes and so many other properties.

During the past decade or so, nearly 900 patents were filed by some 150 different companies dealing with graft copolymers. Rayonier Company in 1961 introduced ethylene oxide grafted cellulose product under the trade name of "Ethylose" which finds use in coated papers, textiles, ceramics and food stuffs.

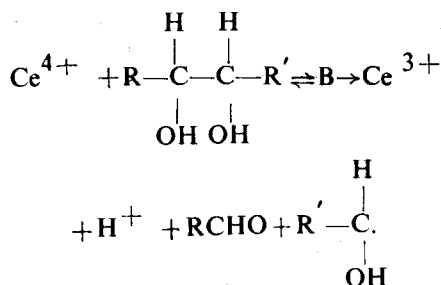
Similarly grafting of cellulose acetate with vinyl acetate produced a product which is easily mouldable having better mechanical properties and resistance to the action of prolonged boiling water.

Different methods of graft copolymer

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Three different graft copolymers of cellulose with methyl methacrylate were prepared using ceric ion redox system and under an atmosphere of nitrogen. The grafting efficiency and percentage grafting, under the conditions of reaction, were found to vary between 57.5-63.4% and 30.0-74.0% respectively. The paper also reports the degree of polymerisation of the homopolymer and of hydrolysed polymer from graft. The isolated graft copolymer of cellulose, the physical mixture of cellulose and homopolymer of methyl methacrylate as well as cellulose were examined by Infra-red spectroscopic study.

synthesis have been reported. The use of certain ceric salts for the introduction of free radicals has been widely followed. These ceric salts form very effective redox system in the presence of organic reducing agents like alcohols, thiols, glycols aldehydes and amines. The oxidation-reduction produces cerous ions and transient free radical species capable of initiating the well known vinyl polymerisation. In case of glycols, mechanism of initiation reaction in general can be written as follows :



Where Ce^{4+} represents ceric complex, B the ceratoglycol complex $\text{R}'\text{CHOH}$, a free radical. If a vinyl monomer is present, the free radical initiates polymerisation. Neimo and

Sihtola (1965) used acrylamide for grafting with cellulose.

The present paper reports the results obtained by the graft copolymerisation of cellulose with methylmethacrylate using ceric ion redox system in an atmosphere of nitrogen.

Experimental

Starting Materials : (i) Methylmethacrylate (MMA pure); (ii) Ceric ammonium sulphate (AR); (iii) Sulphuric acid (AR) and (iv) cellulose pulp of high alpha grade.

Synthesis of graft copolymers : Reactions were carried out in a round bottomed flask with a stirring arrangement under nitrogen atmosphere. The exact conditions for graft copolymerisation are given in Table I below :

Separation of homopolymer and grafted polymer

After the reaction, the product was filtered through a fritted glass crucible, washed thoroughly with water till free from the acid and dried. Homopolymer was extracted with

Table-1

Expt. No.	Wt. of cellulose (g)	Monomer MMA (ml)	Water (ml)	Ceric salt mg	Temp.	Time (Hrs.)
I	2.0	10.0	180	60 mg in 8.0 ml of 1M H ₂ SO ₄	30°C	6.0
II	10.0	45.0	600	380 mg in 40.0 ml of 1M H ₂ SO ₄	30°C	4.0
III	2.0	9.0	180	90 mg in 8.0 ml of 1M H ₂ SO ₄	25°C	4.0

acetone (30 hours). The polymer obtained was of satisfactory purity. A part of the synthesised products were subjected to hydrolysis with 72% sulphuric acid for obtaining the grafted MMA polymer.

Average M. Wt. and D. P. of the products: The viscosity of grafted polymethylmethacrylate and homopolymethylmethacrylate in acetone solution was determined at 25°C and values of intrinsic viscosities (η) were obtained. From the intrinsic viscosity, the average molecular weight and the degree of polymerisation (D. P.) were found out by the well known method.

Infrared spectra : Infrared spectras of various polymers viz. cellulose, homopolymer, hydrolysed graft polymer and physical mixture of cellulose and homopolymer, were recorded on standard infrared spectrophotometer using well known potassium bromide disc technique.

Percentage grafting and grafting efficiency

Grafting% = (Final cellulose wt.

$$\frac{-\text{Initial cellulose wt.}}{(\text{Initial cellulose wt.})} \times 100$$

$$\text{Grafting efficiency\%} = \frac{(\text{Wt. of grafted MMA})}{(\text{wt. of grafted MMA} + \text{wt. of Homo MMA})} \times 100$$

Results and Discussion

Results obtained on grafting reactions in an atmosphere of air and also in absence of air, were not very encouraging. The grafting reaction carried out in an atmosphere of nitrogen gave good results. From Table 2, it can be seen that under the reaction conditions the grafting efficiency varied between 57.5–63.4% and the percentage grafting obtained was as high as 74.0. The increase in the original weight of cellulose after extraction of homopolymer with acetone, represents the true graft. Further Table 2, gives the degree of polymerisation (D. P.) data for

homopolymer as well as for hydrolysed polymer from the graft.

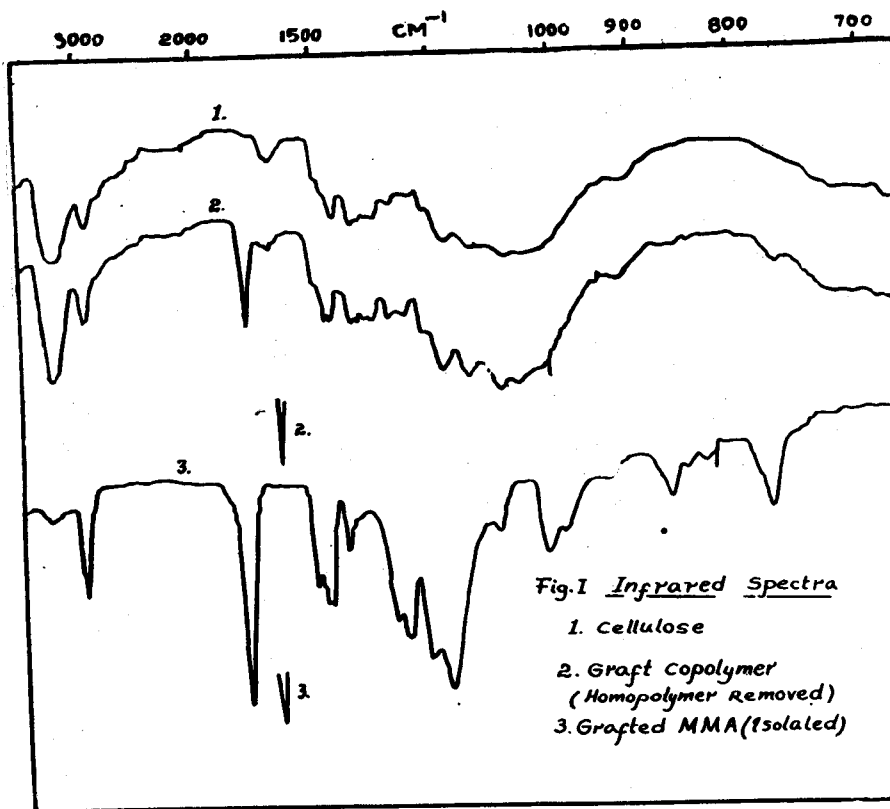
Figures I and II depict the I.R. spectra of 1. Cellulose; 2. graft copolymer (homopolymer removed) and 3. grafted methmethacrylate (isolated) while Fig. II gives I.R. spectra for 1. graft copolymer and homopolymer; 2. physical mixture of cellulose and homopolymer as well as 3. Methyl methacrylate homopolymer. Referring jointly to figs. I and II, it can be seen that the peak at 1725cm⁻¹ of ester (C=O) group and at 1640cm⁻¹ (C=O) is rightly missing in case of cellulose only while it is present in the rest of the spectra and especially in the sample freed from homopolymer by acetone, thus supporting the grafting reaction. The latter peak at 1640cm⁻¹ has been shown more distinctly by a separate slow scanning. The peak at approx. 3300cm⁻¹ which is due to secondary alcoholic group is, as expected, present in cellulose, other cellulose containing grafts and in physical mixture while it is rightly absent in the grafted MMA (isolated) and in MMA homopolymer.

Acknowledgements

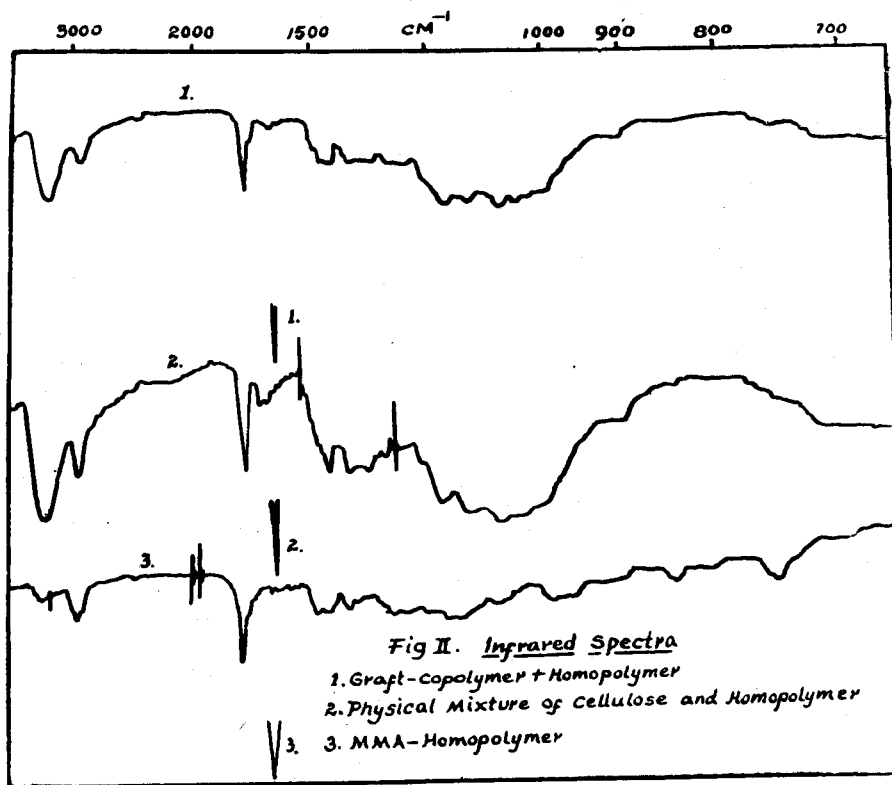
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Table-2

Expt. No.	wt. of cellulose (g)	Wt. of total grafted product (g)	Nett increase in wt. (g)	Wt. of extracted Homopolymer (g)	Wt. of true graft with cellulose (g)	Wt. of hydrolysed polymer from graft (g)	D.P. of Homopolymer	D.P. of Hydrolysed polymer from graft	Grafting Efficiency %	Percent grafting %
I	2.00	3.48	1.48	0.54	2.94	0.90	4159	3412	63.4	74.0
II	10.00	13.18	3.18	1.31	11.87	1.77	3981	3467	57.5	31.7
III	2.00	2.60	0.60	0.24	2.36	0.33	4365	3890	60.7	30.0



WAVELENGTH (Microns)



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References

1. Battaerd, H. A. J. and Tregear, G. W., "Graft copolymers" Interscience Publishers. A-division of John Wiley & Sons, New York, 1961.
2. Neimo, L. and Sihtola, H., *Paper and Timber*, 47, 369 (1965).
3. Mino, G. and Kaizerman, S., *J. Polymer Sci*, 31, 122, 242 (1958).
4. SCAN-C15: 62, *Paperi Ja Puu*, 44, 571 (1962).
5. Baysal, B., et al., *J. Polymer Sci.*, B1, 257 (1963).
6. Toda, T., *J. Polymer Sci.*, 58, 411 (1962).
7. Sobue, H., et al., *J. Polymer Sci.*, C2, 415 (1963).
8. Colthup, N. B. et al., "Introduction to infrared and Raman spectroscopy" New York: Academic press, 1964, 250 pp.