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Short communication

Solid state thermal degradation behaviour of graft copolymers of carboxymethyl cellulose with vinyl monomers

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ABSTRACT

The graft copolymer of sodium carboxymethyl cellulose (CMC) with acrylamide (ACM), dimethylacrylamide (DMA), *N*-vinyl pyrrolidone (NVP), 2-acrylamido-2-methyl-1-propane sulphonic acid (AMPS) and vinyl caprolactum (VCL) were synthesized in nitrogen atmosphere by employing redox initiators. The integral procedural decomposition temperature (IPDT) of CMC and its graft copolymer with ACM, DMA, AMPS, NVP and VCL have been found to be 274 °C, 375 °C, 421 °C, 404 °C, 466 °C and 331 °C, respectively. The higher value of IPDT showed more thermal stability. Among all five graft copolymers, the graft copolymer of CMC with NVP is thermally more stable and VCL grafted copolymer was found least thermally stable. The higher char yield and final decomposition temperature (FDT) were obtained in the case of more thermally stable graft copolymer. All five graft copolymers have shown more than one T_{max}, which suggests that degradations were multistep process.

1. Introduction

CMC is a water-soluble anionic linear polysaccharide and is prepared by the partial substitution of the —OH groups of glucose repeating unit of cellulose at 2, 3, and 6 by carboxymethyl group. Among the natural polymers sodium carboxymethyl cellulose (CMC) is also known as cellulose gum and by other trade names water soluble cellulose ether. CMC polymers are made up of a linear β-(1 → 4)-linked (fig. 1) glucose unit that exhibit poly-electrolytic characteristics due to the presence of weakly acidic groups [1]. To modify the structure and properties of natural polymers i.e. CMC can be achieved by one of the most perfect method i.e. process of graft copolymerization through environmentally benign methodology i.e. by conventional free radical polymerization [2].

The carboxymethyl group in cellulose increases the swellability of cellulose [3] which leads to their unique applications in various industries, such as the paper [4] and textile processing industries [5]. The basic properties that enhance its commercial value are its ability to thicken water, suspend solids in aqueous media, stabilize emulsions, absorb moisture from the atmosphere, and form films. For example, the graft copolymer of sodium carbxoymethyl cellulose-g-polyacrylamide is used as flooding material to enhance crude oil recovery. Since sodium carboxymethyl cellulose-g-acrylamide is amphoteric copolymers, which contains both acidic and basic groups along with the macromolecular backbone, Their uses range from paper manufacturing and water treatment, through oil recovery [6,7], to soil modification and medical applications. Out of these applications one of the great disadvantages is the reduced biodegradability of the graft copolymer because of the drastic change in original structure of the substrate as well as synthetic polymer content in the product. Hydrophobically modified carboxymethyl cellulose are used as thickener, which having good water solubility, salt resistance, heat resistance and anti-shear viscosity property. The cationic polymers exhibit effective shale inhibition but suffer from weak mud performance, bad compatibility, and high toxicity to aquatic organisms. The graft copolymers with amphoteric nature are in demand in the oil-field industry to develop environmentally acceptable polymeric additives that can combine cationic and anionic polymer behavior advantageously and overcome the limitations inherent in the aforementioned additives [8]. Thus, polysaccharide (sodium carboxymethyl cellulose) based graft copolymers were found to have multifunctional characteristics as oil-field-drilling mud additives with respect to shale inhibition, viscosity building, and filtration control [9,10]. The properties and applications of grafted carboxymethyl cellulose depend on the type of vinyl monomer grafted by the process of graft copolymerization; the physical and chemical

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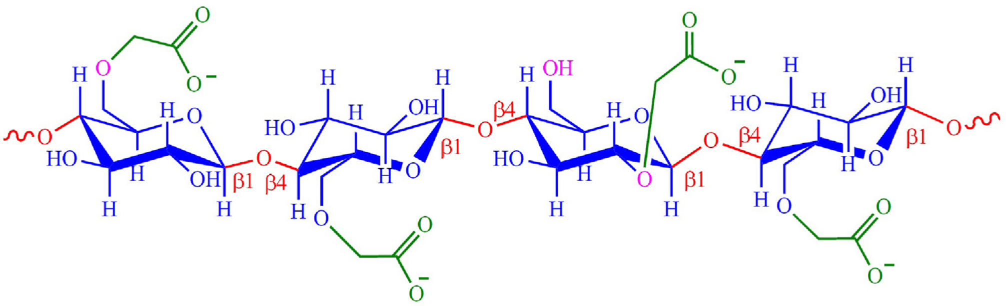


Fig. 1. Structure of Carboxymethyl cellulose anion.

properties of synthetic monomers are superimposed on the properties of natural polymer. Therefore, it was thought to be worthwhile to graft amide and sulphonic acid based vinyl monomers onto carboxymethyl cellulose with different redox pairs. For this the five vinyl monomers were choosen viz. acrylamide, dimethyl acrylamide, 2-Acrylamido-2-methyl-1-propane sulphonic acid (AMPS), *N*-vinyl-2-pyrrolidone and *N*-vinyl caprolactum due to their wide range of usages in industries [11–16]. In-spite of graft copolymers wide range applications, there is always a problem of biodegradation of materials, which could be solved by selecting appropriately thermally stable graft copolymers. Recently, few researchers have attempted to study the thermal degradation behavior of polymeric substrates [17–20] before going to study other essential application of synthetic polymers, because thermal analysis could solved selection of polymers.

In view of the above, a study of the thermal degradation of CMC and its graft copolymers with ACM, DMA, AMPS, NVP and VCL was undertaken. Hence, In the present communication, we are discussing the thermal degradation behaviour of CMC, and their graft copolymers viz. CMC-g-ACM, CMC-g-DMA, CMC-g-AMPS, CMC-g-NVP & CMC-g-VCL. Furthermore, literature survey reveals that polymers [21], copolymers [22] and graft copolymers of natural polysaccharide [23–29] show the variable thermal stability with respect to vinyl monomers and authors failed to find out the reason of variable thermal stability reported by other workers. Our study report can be used to select thermally stable polymeric materials for end-use applications with improved product quality. This prompted us to study the thermal stability of graft copolymers obtained by addition of various vinyl monomers on to carboxymethyl cellulose substrate.

2. Experimental

2.1. Materials

Acrylamide (ACM), Dimethylacrylamide (DMA), *N*-vinyl pyrrolidone (NVP), 2-acrylamido-2-methyl-1-propane sulphonic acid (AMPS), *N*-vinyl caprolactum (VCL) and Sodium carboxymethyl cellulose (CMC) were purchased from Aldrich Co., USA. The liquid state vinyl monomers were purified by distillation under reduced pressure, while solid vinyl monomers were purified by re-precipitation into respective solvents at very low temperatures and dried in vacuum. The other reagents like sulphuric acid and methanol, acetone and redox pair reagents were purchased from Merck India.

2.2. Instrumentation

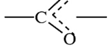
FT-IR spectra on KBr disc were recorded on a Varian Excalibur 3000 (Palo Alto, CA) spectrophotometer in the region 400–4000 cm^{-1}. Thermogravimetric analysis of polymers were carried out on a Make/Model Perkin Elmer, Diamond thermo gravimetric analyzer at a heating rate of 10 °C/minute in an Alumina crucible and the flow of nitrogen gas was 20 ml/min, keeping the sample mass ≈10 mg for each analysis. The integral procedural decomposition temperature (*IPDT*) was calculated by Doyle method [30] which accounts the whole shape of the curve and it sum up all of its dips and meanderings in a single number by measuring the area under the curve.

2.3. Procedure for graft copolymerization

For each experiment, the solution of sodium carboxymethyl cellulose (CMC) was prepared in a reactor by adding the calculated amount of CMC (Table 1) in required amount of triple distilled water. The calculated amount of vinyl monomer, sulphuric acid and solution of reductant (Table 1) were added into the prepared solution of CMC and a slow stream of oxygen free nitrogen gas was passed for 30 min. After 30 min, a known amount of de-aerated solution of oxidant (Table 1) was added to initiate the graft copolymerization process. The reactions were performed under a continuous flow of purified nitrogen gas. After a desired interval of time (Table 1), the reaction was stopped by letting air into the reaction mixture. The graft copolymer was precipitated by pouring the reaction mixture into water methanol mixture (1:3) for CMC-g-ACM, CMC-g-AMPS & CMC-g-NVP and 1:2 for CMC-g-DMA & CMC-g-VCL (solvent composition was chosen according the nature of polysaccharide and monomer). The precipitated graft copolymer was washed several times with distilled water to remove the unreacted monomers. The graft copolymer was dried and weighed. The homopolymer was separated by soxhlet extraction. For graft copolymerization reactions following redox pairs have been used to synthesize the graft copolymers viz: Peroxymonosulphate/Thiourea for CMC-g-DMA and CMC-g-NVP, Bromate/Thiourea for CMC-g-AMPS and CMC-g-VCL, Ferrous/Bromate redox pairs for CMC-g-ACM.

3. Results and discussion

3.1. Evidence of grafting: fTIR spectroscopy

The spectra (fig. 2) of CMC shows band at 3566 cm^{-1} due to O—H stretching vibration with hydrogen bonding. The band at 2926 cm^{-1} is due to C—H stretching vibration and at 1616 cm^{-1} is due to C—O stretching vibration of  $-\mathrm{C}(\cdots\mathrm{O})_2-$ group. The bands around 1419 and 1338 cm^{-1} are assigned to $-CH_2$ scissoring and —OH bending vibration, respectively. The band at 1062 cm^{-1} is due to CH—O—CH_2 stretching. On comparing the IR spectra of CMC and grafted CMC with different vinyl monomers (fig. 2), we have found that the additional absorption bands corresponding to the amide-I group (C═O stretching) in CMC-g-ACM, CMC-g-DMA, CMC-g-NVP, CMC-g-VCL and CMC-g-AMPS (fig. 2) at 1663 cm^{-1}, 1647 cm^{-1}, 1690 cm^{-1}, 1692 cm^{-1} and 1651 cm^{-1}, respectively.