

ABSTRACT

Many polysaccharides play an important role in the field of science and technology due to their unique properties. The polysaccharides are renewably available from natural and microbial resources and they are biodegradable and nontoxic. Water-soluble polymers based on grafted polysaccharides have drawn much attention in the recent decades because of their controlled biodegradability, shear stability and high efficiency as turbulent drag reducers, viscosifiers and flocculants. The graft copolymers show better performance in flocculation than the ungrafted polysaccharides, which is due to the better approachability of the grafted acrylic chains to the colloidal particles. The viscosity of the graft copolymers also increase than that of the base polysaccharides, because of the presence of the longer grafted acrylic chains.

The aim of the present investigation was to synthesize some water-soluble graft copolymers of polyacrylamide and carboxymethyl cellulose (CMC), in presence of ceric ammonium nitrate (CAN) as initiator. Further, it was envisaged to synthesize a series of graft copolymers with variation in the number and length of PAM chains by varying the concentration of acrylamide and CAN.

The CMC, PAM and the synthesized graft copolymers were characterized by various materials characterization techniques like elemental analysis, viscometry (intrinsic viscosity and absolute viscosity), infrared spectroscopy (IR), scanning electron microscopy (SEM), thermal analysis (TGA/DSC) and x-ray diffraction (XRD). The flocculation characteristics of graft copolymers were evaluated in three synthetic effluents, namely, kaolin, iron ore and silica suspensions. The characteristics of the best performing graft copolymer were then compared with those of the various commercially available flocculants in the national and international market.

The carboxymethyl cellulose-g-polyacrylamide and amylopectin-g-polyacrylamide were partially hydrolysed by the treatment with certain amount of alkali. The series of hydrolysed products of both grafted carboxymethyl cellulose and amylopectin were synthesized with varying the experimental conditions in order to establish the flocculation efficiency with expansion and straightening of

the grafted flexible PAM chains. During hydrolysis the $-\text{CONH}_2$ groups of PAM chains are converted to $-\text{COO}^-$ groups. The repulsion between the adjacent negatively charged groups leads to chain expansion.

The hydrolysed graft copolymers show better flocculation performance than the corresponding graft copolymers. The shear viscosity of the aqueous solutions of hydrolysed carboxymethylcellulose-g-polyacrylamide (Hyd CMC-g-PAM) and hydrolysed amylopectin-g-polyacrylamide (Hyd AP-g-PAM) at low shear rates increases several hundred times than that of the corresponding graft copolymers. The hydrolysed products were characterized by elemental analysis, IR spectroscopy, neutralization equivalent, SEM, thermal analysis, XRD and rheological techniques.

By varying the concentration of acrylamide and CAN, six grades of CMC based graft copolymers were synthesized (CMC-g-PAM 1 to CMC-g-PAM 6). The variation of synthetic parameters is reflected in the intrinsic viscosity of graft copolymers. The results of elemental analysis, IR spectroscopy, thermal analysis, XRD, SEM etc. establish the proof of grafting. In the series of graft copolymer based on CMC, the one with fewer and longer PAM chains was found to be most effective in all the three suspensions. When the flocculation efficiency of the graft copolymer was compared with that of some of the commercial flocculants, the synthesized graft copolymer was found to be best in performance in most of the cases.

During partial alkaline hydrolysis of PAM grafted CMC and amylopectin (AP), it is possible to control the carboxyl content by controlling the reaction parameters, e.g. time, temperature and concentration of alkali. The hydrolysed products show better flocculation performance than the unhydrolysed product in kaolin and iron ore suspension. However, in silica suspension no settling behaviour is observed due to the highly negative charges of the particles of the suspension. Further the hydrolysed product, which has certain amount of carboxyl content but is still having flexible grafted chains showed better flocculation performance than others having the higher carboxyl content and complete loss of flexibility. On hydrolysis, the $-\text{CONH}_2$ groups of the graft copolymer were converted to $-\text{COO}^-$

also increase. The former enhances the flocculation and the latter decreases the flocculation due to increasing repulsion between flocculant and negatively charged particles. Even though the former effect is dominant, only at optimum hydrolysis, there will be largest enhancement in flocculation characteristics.

The chains become straightened by repulsion of adjacent negatively charged groups increasing the hydrodynamic volume and as well as the intrinsic viscosity. The changes in absolute viscosity are due to changes in dimensions of the molecules and the polarity of the grafted chains. At low shear rate, the shear viscosity of hydrolysed graft copolymers is much more than that of the corresponding graft copolymer and the base polysaccharides. All the aqueous solutions of polysaccharides, grafted polysaccharides and hydrolysed grafted polysaccharides show non-Newtonian pseudoplastic behaviour. This marked shear thinning behaviour of polysaccharide solutions are explained by the conformational states of polymer molecules. The domains of associated polysaccharide chains exist at rest or at low shear and are stabilized by hydrogen bonds. On shearing, the extent of aggregation is reduced resulting in a lower solution viscosity.