

## Radiation-Induced Graft Copolymerization of Acrylonitrile onto Carboxymethylcellulose and Modification of its Chemical Structure

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### ABSTRACT

The monomer, acrylonitrile, was graft copolymerized onto Carboxymethylcellulose (CMC) using  $\gamma$ -rays as initiator. The reactions were carried out in a homogenous aqueous medium. After removal of the homopolymer, the graft copolymer was characterized by FTIR spectroscopy. The structure of pure pectin and grafted with monomer was also characterized by TGA analysis. The thermal properties of pure pectin and grafted with monomer were evaluated with a simultaneous thermal analysis system. The results showed that the thermal stability of grafted polyacrylamide samples was remarkably improved. A plausible mechanism of grafting has also been suggested. The effect of various factors affecting on grafting, i.e. dose of  $\delta$ -rays and concentration of the monomer and polysaccharide as well as the reaction temperature were studied by conventional methods to achieve the optimum grafting parameters.

**Key words:** Carboxymethylcellulose, acrylonitrile, graft copolymerization,  $\gamma$ -irradiation, modification.

### Introduction

Graft copolymerization is an attractive means for modifying base polymers because grafting frequently results in the superposition of properties relating to the backbone and pendant chains. Considerable interest has been focused on chemical modification by free radical graft copolymerization of hydrophilic and hydrophobic vinyl monomers biopolymers such as polysaccharides [1-3]. These biodegradable and low cost graft copolymers, with new properties, can be used in many applications such as textiles, paper industry, agriculture, medical treatment and also in petroleum industry as flocculants and thickening agents [4,5].

Graft copolymers are prepared by first generating free radicals on the polysaccharide backbone and then allowing these radicals to serve as macroinitiators for the vinyl monomers. Graft copolymerization can be carried out with different initiator systems. Among them, potassium persulfate, ammonium persulfate, benzoyl peroxide, azobisisobutyronitrile, and ceric ammonium nitrate are widely used for the synthesis of graft copolymers [6,7].

Radiation grafting technology is well established and accepted by industry. Radiation polymerization, radiation crosslinking and controlled degradation of

polymers comprise most of commercial applications of radiation technology [8].

The chosen polysaccharide for modification, i.e. Carboxymethylcellulose (CMC), is the most well-known and most important type of polysaccharide. Carboxymethylcellulose sodium salt (CMC) is the first water soluble ionic derivative of cellulose prepared in 1918 and produced commercially in the early 1920's in Germany. It has been the most important ionic cellulose ether with a worldwide annual production of 300,000 tons. It is widely used in pharmaceuticals, detergents, cosmetics, foods, paper and textile industries due to its viscosity-increasing and emulsifying properties. However, it may need to be further modified for some special applications.

Of the monomers grafted, acrylonitrile has been the most frequently used one, mainly due to its highest grafting efficiency [9,10], improving the thermal resistance of the graft copolymer [12], and also the subsequent alkaline hydrolysis of the grafting product to obtain water absorbents [13].

The present report describes graft copolymerization of acrylonitrile onto CMC backbone, initiated by  $\gamma$ -rays.

### 2. Experimental:

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### 2.1 Materials:

Sodium carboxymethylcellulose (CMC, Brookfield viscosity 30.3 mPa.s in 1% aqueous solution at 25 °C) was purchased from Fluka (degree of substitution, DS 0.70-0.85). Its moisture content was determined (for a one-gram sample heated at 60 °C normal pressure, 15 h; then 100 torr, 5h) to be 9.0%. Acrylonitrile monomer (Merck) was distilled before use.

### 2.2 Grafting procedure:

Graft copolymerization of acrylonitrile onto carboxymethylcellulose was carried out with  $\gamma$ -rays initiator. In a 100 mL flask, certain amount of CMC (0.5-3.0 g) was dissolved in 50 mL of degassed distilled water. The flask was placed in a water bath with desired temperature (60 °C). A given amount of monomer, AN (1.5-5.0 g), was added to the flask and the mixture was stirred for 15 min. The cold mixture was removed into a 250 mL aluminium tube. The inner wall of aluminium tube was covered with aluminium foil. The tube was closed tightly with the foil and paraffin film. The tube was then irradiated under  $\gamma$ -rays according to the desired total doses.

### 2.3 Homopolymer extraction:

The graft copolymer was freed from polyacrylonitrile (PAN) homopolymer, by pouring 0.50 g of the product in 50 mL of dimethyl formamide solution. The mixture was stirred gently at room temperature for 24 h. After complete removal of the homopolymer, the copolymer was filtered, washed with ethanol and dried in oven at 50 °C to reach a constant weight.

### 2.4 Evaluation of grafting parameters:

The grafting parameters used to characterize the nature of the copolymer are defined with the weight basis expressions as reported by (Fanta1986). The percentage of grafting ratio (Gr%) stands for the weight percent of the graft copolymer synthetic part (PAN grafted) formed from initial sodium hyaluronate used.

$$\text{Grafting ratio}(\%Gr) = \frac{\text{Weight of grafted polymer}}{\text{Weight of substrate}} \cdot 100$$

The percentage of grafting efficiency (Ge%) stands for the grafted PAA formed from initial monomer charged.

$$\text{Grafting efficiency}(\%Ge) = \frac{\text{Weight of grafted polymer}}{\text{Weight of polymer formed}} \cdot 100$$

The percentage of Add-on (Ad%) is the weight percent of the grafted PAN of the graft copolymer.

$$\text{Add on}(\%Ad) = \frac{\text{Weight of grafted polymer}}{\text{Weight of graft copolymer}} \cdot 100$$

The percentage of homopolymer (%Hp) denotes the weight percent of the homopolymer formed from initial monomer charged.

$$\text{Homopolymer}(\%Hp) = 100 - \%Ge$$

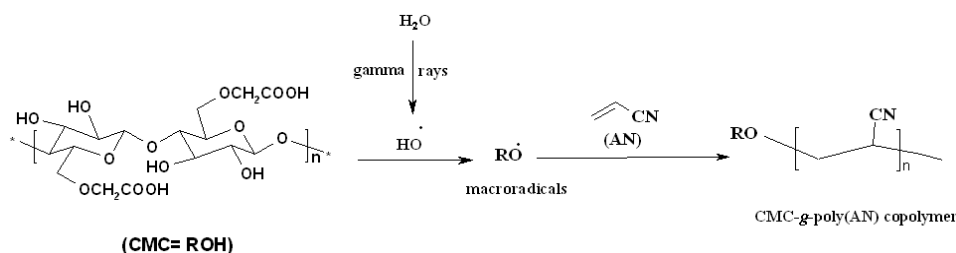
### 2.5 Instrumental analysis:

FTIR spectra of samples in the form of KBr pellets were recorded using an ABB Bomem MB-100 FTIR spectrophotometer. Irradiation was carried out using  $\gamma$ -rays from  $^{60}\text{Co}$  source, in a Gammacell-220 (Nordion, Canada) with a dose rate of 1.6 kGy/h, in air and at room temperature. The dose rate was determined by the conventional Fricke dosimeter. Thermogravimetric analyses (TGA) were also performed on a Universal V4.1D TA Instruments (SDT Q600) with 8–10 mg samples on a platinum pan under nitrogen atmosphere. Experiments were performed at a heating rate of 20 °C/min until 600 °C.

## RESULTS AND DISCUSSION

### 3.1 Graft copolymerization mechanism:

The mechanism of grafting acrylonitrile (AN) onto carboxymethylcellulose (CMC) using  $\gamma$ -rays as an initiator is shown in the Scheme 1. It should be mentioned that during the irradiation of AN, CMC and water ternary mixture, most of the energy is absorbed by water and only a very small fraction by other components. Thus, the initiation occurs mainly by an indirect effect. Hydroxyl radicals, formed during irradiation, add to one side of the AN double bond and leads to the formation of an unpaired spin on the other side of the vinyl bond. In this way, homo polymerization of AN is initiated. Attack of OH radicals on CMC would lead almost solely to the break age of C–H bonds. This fact is very well known from radiation chemistry of alcohols and carbohydrates in aqueous solution. A much more probable pathway is the addition of a AN molecule (not a radical) to the CMC-based radical, followed by polymerization leading to the growth of a branched chain.



**Scheme 1:** A brief proposed mechanism for  $\gamma$ -rays-induced grafting of poly(AN) onto CMC.

### 3.2 FTIR spectroscopy:

The simplest method to prove the formation of CMC-g-PAN is based on the solubility difference of the graft copolymer and the homopolymer, PAN. CMC and PAN are soluble in water and DMF, respectively. When a reaction product was Soxhlet-extracted with DMF and alternately with water for 24h, an insoluble solid was still remained. A CMC/PAN physical mixture was dissolved completely when it was treated in the same way. Therefore, it is obvious that the graft copolymer obtained was not a simple physical mixture, but some chemical bonds must exist between the CMC substrate and PAN macromolecules.

The PAN grafting was also confirmed by the differences between FTIR spectra of the substrate and that of the graft copolymer. Figure 1 shows the FTIR spectra of the CMC substrate, polyacrylonitrile (PAN) and the CMC-g-PAN graft copolymer freed from homoPAN. The existence of a sharp intense peak at  $2246\text{ cm}^{-1}$  in IR spectra of the graft copolymers is a certain evidence of grafting. This absorption band arises from stretching vibration mode of the nitrile ( $\text{C}\equiv\text{N}$ ) groups. Most of the other peaks are related to the carbohydrate backbone. Since PAN could be extracted nearly completely from a physical mixture of PAN and polysaccharide by DMF, the presence of appreciable amounts of nitrile groups in our reaction products after extraction is an additional proof for grafting of polyacrylonitrile onto the polysaccharide.

### 3.3. Thermogravimetric analysis:

TGA curves for pure CMC and CMC-g-poly(AN) copolymer are shown in Figure 2. The grafted CMC has shown improvement in thermal stability as clear from TGA curve. The initial decomposition temperature of the CMC on grafting was increased from  $147$  to  $406\text{ }^\circ\text{C}$  with maximum decomposition rate at  $523\text{ }^\circ\text{C}$ , in comparison to original decomposition temperature of  $328\text{ }^\circ\text{C}$  of CMC. These observations have clearly indicated that grafting of CMC-g-poly(AN) copolymer has improved the thermal stability of CMC, Zhang, [14].

### 3.4. Effect of polysaccharide concentration:

Figure 3 shows the effect of CMC concentration on the grafting parameters. With increasing the CMC amount, more reactive grafting sites are formed which are favourable for grafting. This can account for initial increment in grafting parameters up to  $8.0\text{ wt}\%$  of CMC value. Beyond this amount, the grafting values were diminished. This may be ascribed to the increase in viscosity that restricts the movement of the monomer molecules in a relatively small volume of the reaction mixture of  $50\text{ mL}$ , and the termination reaction between macroradical-macroradical and macroradical-primary radicals as well.

### 3.5. Effect of $\delta$ -rays dose:

Graft copolymerization was studied at various doses of  $\delta$ -rays by keeping other reaction conditions constant. As shown in Figure 4, the %Ge and %Gr increase with increasing in the doses of  $\delta$ -rays and reach at a maximum value. Further increase of doses of  $\delta$ -rays beyond  $30\text{ kGy}$  disfavoured the grafting parameters. A relatively high dose of  $\delta$ -rays may cause a reduction of %Ge and %Gr due to increase in the number of CMC free radicals terminated prior to AN addition. Furthermore, homopolymer formation at higher doses of  $\delta$ -rays which compete with the grafting reaction for available monomer could lead to decrease in the %Ge and %Gr.

### 3.6. Effect of monomer concentration:

The effect of AN concentration on the grafting parameters is presented in Figure 5. In the initial stages, though both %Ge and %Gr rise with increase in AN concentration, but beyond certain concentration of monomer,  $0.6\text{ mol/L}$ , the grafting parameters decrease. The initial increase in grafting parameters could be associated with the greater availability of monomer molecules in the vicinity of CMC macroradicals. The decrease of %Gr and %Ge with further increase in the AN concentration may be explained as follows [15]: (a) preferential homopolymerization over graft copolymerization, (b) increasing the viscosity of reaction medium, which hinders the movement of free radicals, and (c) increase in the chance of chain transfer to monomer molecules [13].

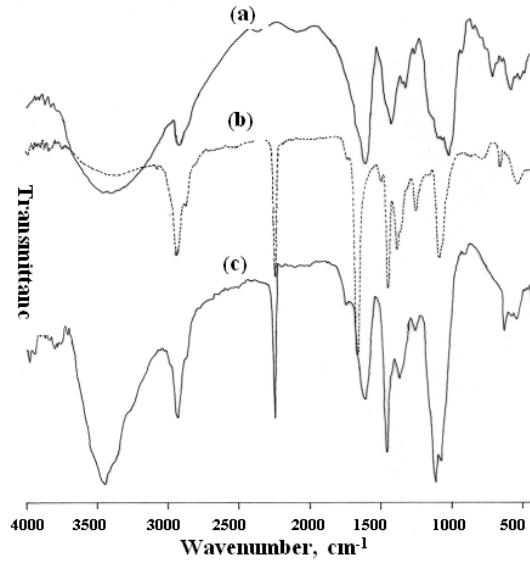


Fig. 1: FTIR spectra of (a) CMC and (b) PAN, (c) homopolymer-free CMC-g-PAN.

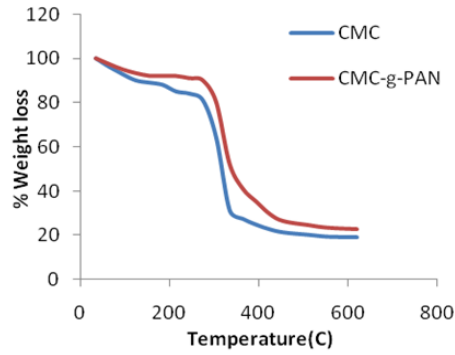


Fig. 2: TGA thermograms of (A) pure CMC and (B) homopolymer-free CMC-g-PAN copolymer. Heating rate 20 °C/min, under N<sub>2</sub>.

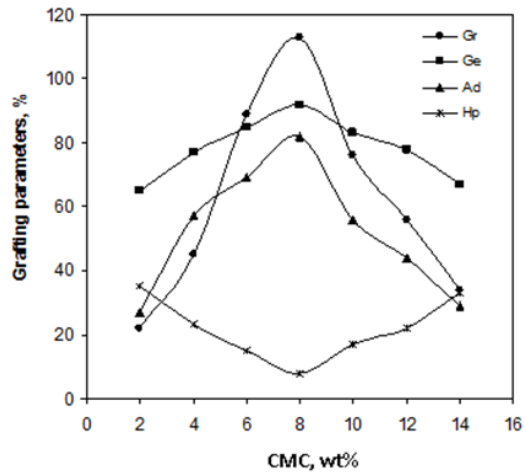


Fig. 3: Effect of polysaccharide concentration on the grafting parameters.

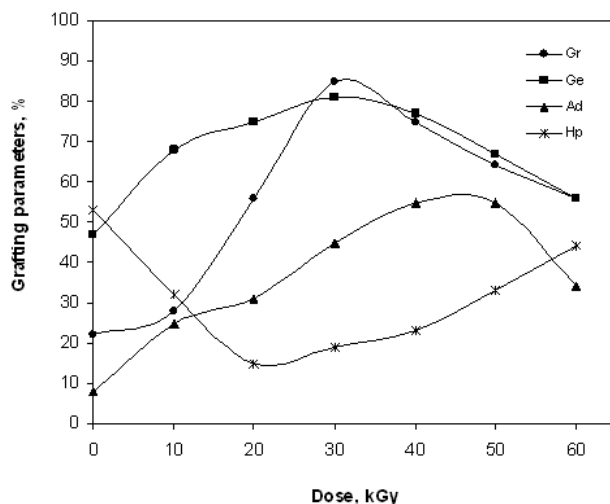


Fig. 4: Grafting parameters as functions of doses of  $\delta$ -rays.

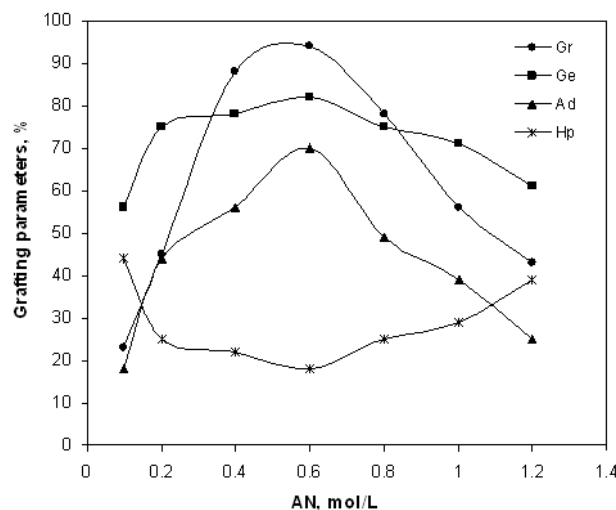


Fig. 5: Effect of the monomer concentration on the grafting parameters.

4. Conclusion:

The polysaccharide, Carboxymethylcellulose was graft copolymerized with synthetic monomer, acrylonitrile, using  $\delta$ -rays as efficient free radical initiators. In order to prove that monomer molecules were grafted, FTIR spectroscopy and TGA analysis were used. The synthetic conditions were systematically optimized through studying the influential factors including, doses of  $\delta$ -rays as well as concentration of the monomers and polysaccharide. The effect of the individual factors was investigated by calculating the grafting parameters. Overall, the grafted polysaccharide may be a candidate for manufacture of moulded plastics, ion exchange resins, and plastic films and in cosmetics. On the other hand, since non-biodegradable plastic waste is known as an ecological threat, such natural polymer-based plastics

in fact, are the need of time. Hence, improving the thermal stability of the polysaccharides would make them better suited for, for instance, moulded articles.

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