

Modified CMC: Part1-Optimized Synthesis of Carboxymethyl cellulose-g-Polyacrylonitrile

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ABSTRACT

As the first part of a continued research on conversion of carboxymethyl cellulose-sodium salt (CMC) to useful biopolymer-based materials, large numbers of cyanide functional groups were introduced onto CMC by grafting with polyacrylonitrile (PAN). The graft copolymerization reactions were carried out under nitrogen atmosphere using ceric ammonium nitrate (CAN) as an initiator. Evidence of grafting was obtained by comparing FTIR spectra of CMC and the graft copolymer as well as solubility characteristics of the products. The synthetic conditions were systematically optimized through studying the effective factors including temperature and concentrations of initiator, acrylonitrile monomer, and CMC. The overall activation energy for the grafting was estimated to be 39.7 kJ/mole. Finally, the CMC-g-PAN copolymer was characterized thermally by using differential scanning calorimetry and thermogravimetric analysis methods.

Key Words:

carboxymethylcellulose;
acrylonitrile;
polysaccharide;
ceric ion;
graft polymerization.

INTRODUCTION

Cellulose is the most abundant, renewable biopolymer, which is very promising raw material, available at low cost for preparing of various functional polymers. Carboxymethyl cellulose sodium salt (CMC) is the first water soluble ionic deriv-

ative 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 [1]. It is widely used in pharmaceuticals,

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detergents, cosmetics, foods, paper and textile industries due to its viscosity-increasing and emulsifying properties [1]. However, it may need to be further modified for some special applications.

Among diverse approaches that are possible for modifying polysaccharides, grafting of synthetic polymer is a convenient method for adding new properties to a polysaccharide with minimum loss of its initial properties [2]. Graft copolymerization of vinyl monomers onto polysaccharides using free radical initiation, has attracted the interest of many scientists. Up to now, considerable works have been devoted to the grafting of vinyl monomers onto the substrates, specially cellulose [3]. Among grafted monomers, acrylonitrile (AN) has been the most frequently used one, mainly due to its highest grafting efficiency [2,4], which is improving thermal resistance of the graft copolymer [5] and also subsequent alkaline hydrolysis of the grafting product to obtain water absorbents [2,6].

The literature survey, however, reveals that few of these modifications deal with chemical grafting of a pre-modified polysaccharide such as CMC. Ceric initiated grafting of vinyl monomers such as: methyl acrylate, ethyl acrylate, and ethyl methacrylate [7,8], AN/methyl methacrylate mixture [9], acrylamide (AAM) [10,11], and 4-vinylpyridine [12,13] onto CMC has been reported. Dimethylaminoethyl methacrylate (DMAEMA) [14], AAM/DMAEMA mixture [15], AAM/dimethyloctyl(2-methacryloxyethyl) ammoniumbromide [16], and diallyldimethylammonium chloride [17], has been grafted onto CMC by L.M. Zhang et al., using different initiators.

Acrylic acid has also been photografted onto CMC [18]. In addition, N-vinyl-2-pyrrolidone [19] and its mixture with AAM [20] has been graft copolymerized onto mixtures of CMC/hydroxyethyl cellulose to prepare cellulosic membrane with special biological effects. However, to our knowledge, no report has been published on the optimization of AN graft polymerization onto CMC using ceric-saccharide initiating system. It is as a part of our research program on CMC modification to prepare materials with metal-ion adsorption [21,22] or water-absorbing characteristics [23]. Here, we report the optimized CAN-induced synthesis of CMC-g-polyacrylonitrile under an inert atmosphere.

EXPERIMENTAL

Materials

Sodium carboxymethyl cellulose (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 1g sample heated at 60°C normal pressure, 15 h; then 13.33 kPa (100 torr), 5 h to be 9.0%. Ceric ammonium nitrate (CAN, Fluka) was used without purification. Acrylonitrile monomer (Merck) was distilled before use.

Graft Polymerization

The CAN solution was prepared by dissolving 2.74 g ceric ammonium nitrate in 50.0 mL of 1.0 N HNO₃. Generally, 3.50 mL of this stock solution (0.10 M) was used for each experiment except for those, whose effect of initiator concentration was studied.

The CMC solution was prepared in a 100 mL two neck flask equipped with magnetic stirrer, gas inlet, and reflux condenser. Total volume of the aqueous solution was 57 mL in all experiments. To control the reaction temperature, the flask was placed in a water bath at desired temperature. A gentle stream of purified N₂ was purged through the system during the reaction.

Desired amount of AN monomer was added to the flask and the mixture was heated at given temperature and stirred for 10 min. Then a given volume of the initiator solution was added to the mixture. The mixture was continuously stirred at desired temperature until completion of the reaction was held (2 h), where no temperature and viscosity increase was observed. After adding hydroquinon solution (0.5 wt%, 2 mL), cooling to room temperature, and adding few droplets of a molar sodium hydroxide solution to neutralize the remaining acid, the product was then precipitated in excess amount of methanol while stirring mildly for ten minutes. The product was filtered, washed thoroughly with methanol and dried at 50°C for 1 h. For separating the polyacrylonitrile (PAN) homopolymer, 0.50 g of the crude product was added to 50 mL of dimethylformamide (DMF) and stirred gently at 30°C for 24 h. After centrifugating and decanting the supernatant (PAN in DMF), CMC-g-PAN was precipitated in methanol, and washed thoroughly with it, and dried at 50°C to reach a constant weight.

Instrumental Analysis

Polysaccharide-*g*-PAN samples as KBr pellets were characterized by using a Mattson-1000 FTIR spectrophotometer.

A simultaneous thermal analyser (STA-625, Reometric Scientific) was used for differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). All thermal analyses were accomplished under purified N₂ gas (flow rate 10 mL/min). The heating rate was 20°C/min.

RESULTS AND DISCUSSION

Grafting Evidences

The simplest method to prove the formation of CMC-*g*-PAN is based on the solubility difference of 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 then with water for 24 h, an insoluble solid was still remained. A CMC/PAN physical mixture dissolved completely when it treated in the same manner. 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 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 cm⁻¹ in IR spectra of graft copolymers is a certain evidence of grafting. This absorption band arises from stretching vibration mode of the nitrile (C≡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, presence of appreciable amounts of nitrile groups in our reaction products after extraction, is an additional proof for grafting of polyacrylonitrile onto the polysaccharide.

Optimization of Polymerization

Since polymerization variables determine the extent of grafting and homopolymer amount, certain factors affecting the grafting parameters were investigated to

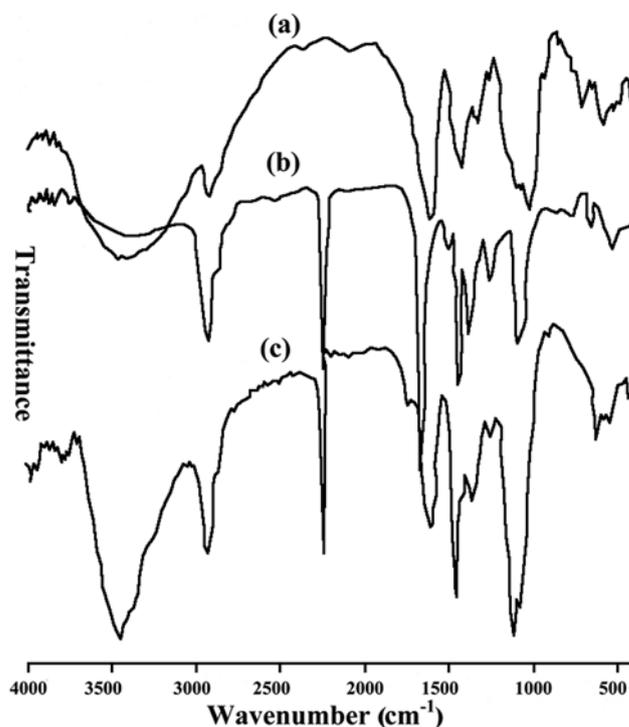


Figure 1. FTIR spectra of (a) CMC, (b) PAN and (c) CMC-*g*-PAN.

achieve the optimum condition of polymerization. Therefore, we optimized the grafting of acrylonitrile onto CMC in homogenous aqueous media by changing temperature, initial concentrations of monomer, initiator, and relative amount of the substrate. Our preliminary studies showed no considerable dependence between the reaction time and the grafting extent, within the range of the amount of used reactants.

The conversion value as well as grafting parameters i.e., homopolymer content (Hp), grafting ratio (Gr), and grafting add-on values was calculated by using following equations [5]:

$$\text{Conversion} = (W_3 - W_0) / W_1 \quad (1)$$

$$\text{Gr} = W_3 / W_0 \quad (2)$$

$$\text{Hp} = W_2 / (W_2 + W_3) \quad (3)$$

$$\text{Add-on} = (W_3 - W_0) / W_3 \quad (4)$$

Where W_0 , W_1 , W_2 , and W_3 are weight of initial substrate, monomer charged, homopolymer extracted, and homopolymer-free graft copolymer, respectively.

Effect of Temperature

We study the influence of reaction's bath temperature

on grafting parameters, so grafting of AN onto CMC was carried out at six temperature, ranging from 20 to 55°C. These results are given in Table 1. Grafting ratio percentage (%Gr) is increased with elevation of temperature from 20 to 35°C, then decreased. At 35°C, maximum grafting ratio (Gr=533%), minimum homopolymer content (13%) and highest add-on value (81.2%) was obtained. Improvement of grafting temperature up to 35°C can be attributed to the following factors: increased number of free radicals formed on the polysaccharide backbone, increased propagation of the graft copolymerization onto the substrate, enhanced diffusion of monomer and initiator into and onto backbone structure, and increased in mobility of monomer molecules and their higher collision probability with backbone macroradicals [24]. However, Gr was decreased as the bath temperature was raised beyond 35°C. This can be accounted for chain radical termination at higher temperatures. Premature termination of growing chains and instability of the ceric-saccharide complex [5] are presumably another reasons for reduced amount of Gr beyond 35°C. The PAN homopolymer formation is minimum at the bath temperature of 35°C.

Mechanism and Rate of Grafting

It has been shown that the anhydroglucose units are predominantly oxidized through C₂-C₃ bond cleavage which is induced by Ce⁴⁺ ions. Therefore, a general reaction scheme for grafting, in analogy with the one that is previously proposed [5,24] may be as follows (Scheme 1).

The reactive vicinal OH groups form a complex

Table 1. Grafting parameters from the graft polymerization^a of acrylonitrile onto CMC at different temperatures.

Temperature, °C	Conversion, %	Gr%	Hp%	Add-on%
20	22.4	222.2	41.1	55.0
25	57.1	411.1	15.9	75.7
35	81.1	533.3	14.6	82.1
45	59.2	422.2	17.4	76.3
50	32.6	277.8	48.9	64.0
55	4.1	122.2	78.0	18.2

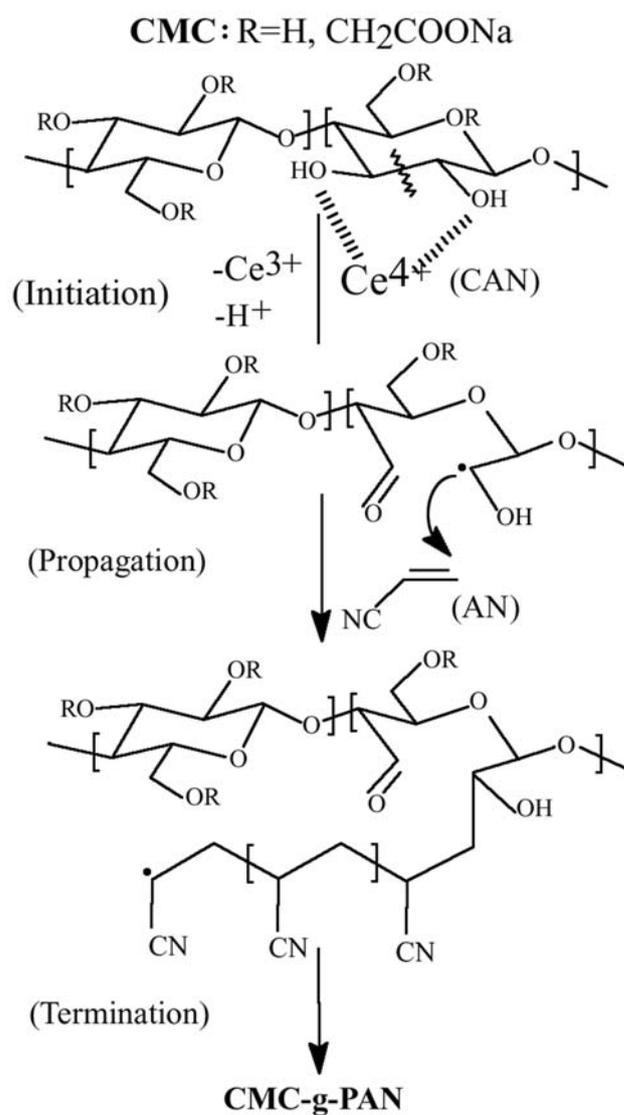
^a Reaction conditions: (CMC) 0.50 g (0.45 g dry basis), (water) 50.0 mL, (AN) 3.0 mL, (CAN) 5.35 mmol/L, (time) 2 h.

with ceric ion. This complex may dissociate, and giving rise to free radical sites onto the polysaccharide backbone and these radicals initiate the graft polymerization.

The rate of grafting (R_g) may be evaluated as measures of the rate of monomer disappearance by using the following expression [25].

$$R_g \text{ (mol L}^{-1}\text{s}^{-1}\text{)} = 1000W_3/MTV \quad (5)$$

M (gmol⁻¹) is the molecular weight of monomer. T and V stand for total reaction time (s) and total volume



Scheme 1. A brief proposed mechanism for ceric-induced grafting of polyacrylonitrile (PAN) onto carboxymethyl cellulose sodium salt (CMC).

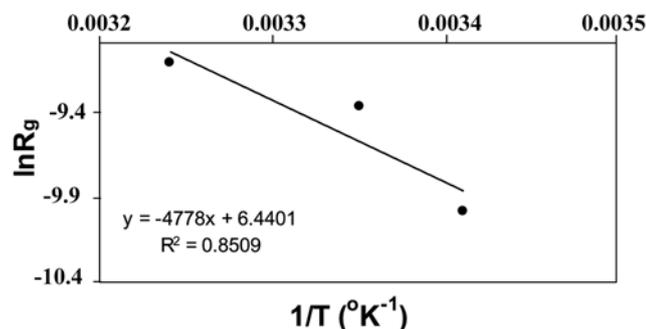


Figure 2. Plot of $\ln R_g$ vs. $1/T$ for estimating the activation energy of the graft polymerization reaction.

(mL) of reaction mixture, respectively.

Overall activation energy of grafting (E_a) may also be estimated from the temperature data through plotting $\ln R_g$ versus $1/T$ (K^{-1}) for the initial portion of the temperature data that are given in Table 1. The slope of this Arrhenius plot (Figure 2) lead to a rough estimation of E_a of grafting using the relationship slope = $-E_a/R$; where R is the universal gas constant. Therefore, E_a was found to be 39.7 kJ/mole (9.5 kcal/mole).

Effect of Initiator Concentration

The grafting dependence on CAN concentration can be concluded from Figure 3. The highest grafting ratio

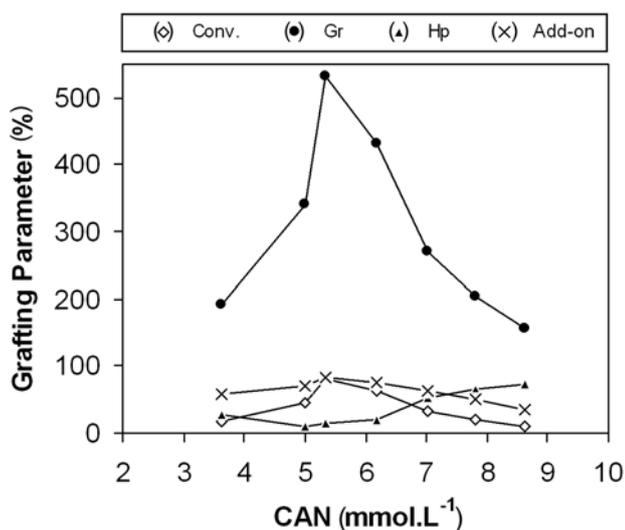


Figure 3. Variation of grafting parameters for the graft polymerization of acrylonitrile (AN) onto CMC versus different concentration of the initiator (CAN). Reaction conditions: (CMC) 0.50 g, (water) 50.0 mL, (AN) 3.0 mL, (temp.) 35°C, (time) 2 h.

(533%) was achieved at 0.0055 mol/L of CAN where homopolymer content was 14.6%. Increased CAN concentration resulted in more radical sites on the polysaccharide backbone that in turn led to higher Gr and add-on values and lower homopolymer formation. However, since the CAN initiator solution is used in dilute HNO_3 , at CAN concentration higher than 0.006 mol/L, a more acidic pH probably causes partial termination of the macroradicals formed on CMC. As a result, increased free radicals on CMC are compensated by partial termination of the macroradicals. Thus Gr and add-on values were diminished at higher amounts of the initiator.

Effect of Monomer Concentration

The effect of monomer amount on the grafting reaction was studied at various concentrations of AN while other effective factors were unchanged. Grafting parameter variations are changed by the amount of charged monomer (Table 2). The grafting extent is significantly increased due to more availability of monomer for grafting. However, beyond a certain Gr value, i.e., 533% at 4.25 %wt AN, the trend is reversed, i.e., the conversion and the grafting efficiency (G_e) were decreased, and homopolymer content was increased noticeably from 14.6% to 73%. Thus, acrylonitrile in an amount of 2.4 g (4.25 wt%) was recognized as an optimum monomer concentration.

Effect of Substrate Concentration

The relationship between grafting parameters and CMC concentration is summarized in Table 3. Maxi-

Table 2. Grafting parameters from the graft polymerization^a of acrylonitrile onto CMC at different amount of the monomer.

Acrylonitrile, wt%	Conversion, %	Gr%	Hp%	Add-on%
2.87	18.7	166.7	48.3	40.0
3.57	49.0	317.8	19.7	68.5
4.25	81.1	533.3	14.6	81.2
4.93	51.4	420.0	19.2	76.2
5.59	28.1	300.0	50.4	66.7
6.25	10.3	182.2	72.9	45.1

^(a) Reaction conditions: (CMC) 0.50 g, (water) 50.0 mL, (CAN) 5.35 mmol/L, (temp.) 35°C, (time) 2 h.

Table 3. Grafting parameters from the graft polymerization^a of acrylonitrile onto CMC at different concentration of the substrate.

CMC, wt%	Conversion, %	Gr%	Hp%	Add-on%
0.32	2.3	162.2	88.5	38.3
0.63	9.0	216.7	76.8	61.7
0.94	20.8	285.2	54.7	64.9
1.25	49.6	430.5	20.5	76.7
1.56	81.1	533.3	14.6	81.2
1.87	51.7	329.6	29.9	69.6

^(a) Reaction conditions: (water) 50.0 mL, (AN) 3.0 mL, (CAN) 5.35 mmol/L, (temp.) 35°C, (time) 2 h.

imum grafting rate and the lowest homoPAN formation was observed at 1.0 g (1.56 wt%) CMC, while other reactants including, monomer, initiator, and temperature were kept constant. Beyond this value, both grafting ratio and add-on values are reduced considerably. This behavior is attributed to availability of more grafting sites for initiation of graft copolymerization at higher concentration of the substrate (from 0.32 to 1.56 wt% CMC). However, upon further increase in the substrate concentration, increase in the reaction medium viscosity, restricts the movements of macroradicals that is leading to decrease in grafting ratio and add-on values. It also may be attributed to deactivation of the macroradical growing chains (e.g., by transfer reactions, combination and/or interaction with the primary radicals) soon after their formation.

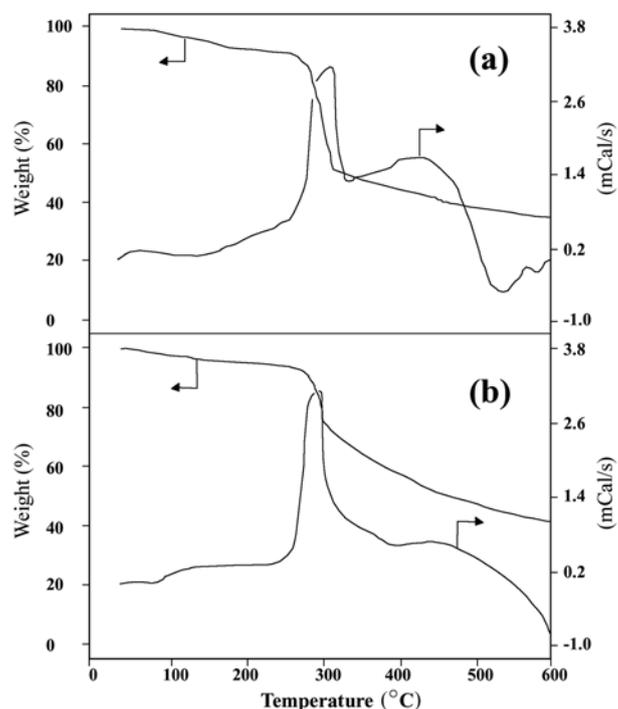


Figure 4. DSC/TGA thermograms of CMC; (a) before and (b) after polyacrylonitrile grafting.

Thermal Characterization

Thermal data obtained from DSC and TGA traces are presented in Table 4. The initial CMC exhibits two distinct weight losses in its thermogravimetric curve. The first one is in the range of 42-196°C peaking at 146°C is associated with loss of water (9.1 wt%), and the second one is in the range 263-328°C with maximum decomposition rate at 303°C (weight loss 40%).

Table 4. Thermal characteristics of the CMC substrate and the CMC-g-PAN copolymer (Heating rate 20°C/min. under N₂).

Sample	DSC		TGA				
	Temp. (°C)	ΔH ^a (J/g)	T _f ^b (°C)	WLC _f ^c	On-set (°C)	IPDT ^d (°C)	Char yield at 600°C (wt%)
CMC	134.3	Negligible	146.3	9.1%	276	412	35.2
	315.6	-291.1					
	418.0	-52.7					
CMC-g-PAN	80.0	Negligible	296.2	11.1%	279	446	42.0
	292.0	-302.0					

^(a) Enthalpy change, (-): exothermic; ^(b) Temperature at the first weight loss of the corresponding peak of the DTG curve;

^(c) The first weight loss, wt%; ^(d) Integral procedural decomposition temperature.

Grafting of polyacrylonitrile makes the grafted CMC hydrophobic. A weak endothermic transition in DSC (80°C) and a little absorbed water in TGA indicate that the graft copolymer CMC-g-PAN is much more hydrophobic than the non-grafted substrate.

The value of IPDT (integral procedural decomposition temperature) [26], as a means of summing up the whole shape of the normalized data curve of TGA, was also calculated to get a more semiquantitative data regarding the relative thermal stabilities. Although no appreciable difference is observed between initial decomposition temperature (on-set TGA data) of the non-grafted and grafted substrate, but according to char yield and IPDT values, thermal stability of the grafted CMC is certainly improved in comparison with CMC itself. It may be attributed to formation of conjugated cyclic systems consisting -C=N- groups from the pyrolytic addition reaction of adjacent nitrile groups [27] in the case of CMC-g-PAN. The important feature of this conjugation is sudden evolution of a large amount of heat (302 J/g).

CONCLUSION

A doubly modified cellulose, carboxymethyl cellulose-g-polyacrylonitrile, was prepared using ceric-initiated graft polymerization of acrylonitrile (AN) onto CMC. The synthetic conditions were systematically optimized through studying the effective factors including temperature, concentrations of the initiator, the monomer AN, and the substrate CMC.

The effects of the individual factors were investigated by calculating the grafting parameters i.e., grafting ratio (Gr), add-on value, homopolymer content (Hp), and conversion. Under optimum conditions (CMC 1.56 wt%, AN 4.25 wt%, CAN 5.35 mmol/L, reaction bath temperature 35°C, reaction time 2 h), the grafting parameters were achieved as 533%, 81%, 14%, and 81%, respectively.

The hydrophobically modified CMC exhibited higher thermal stability in comparison with un-modified CMC. The PAN-grafted CMC may be a good candidate for manufacturing of molded plastics, ionexchange resins, and plastic films and using in cosmetics. On the other hand, since non-biodegradable plastic waste are known as an ecological threat, such natural polymer-

based plastics in fact, is the need of today's. Hence, improving the thermal stability of the cellulose would make them suited better, for instance, in molded articles.

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