

Synthesis and Characterization of Carboxymethylcellulose Graft Copolymer by Free Radical Polymerization

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ABSTRACT

Aqueous graft copolymerization of N-vinyl caprolactam onto carboxymethylcellulose has been carried out in inert atmosphere using free radical initiator. The resulted graft copolymer was found to be a hydrogel.

Keywords : CMC, NVCL, Bromate / Thiourea

INTRODUCTION

The terms gels and hydrogels are used interchangeably by food and biomaterials scientists to describe polymeric cross-linked network structures. Gels are defined as a substantially dilute cross-linked system, and are categorized principally as weak or strong depending on their flow behaviour in steady-state (Ferry, 1980). Edible gels are used widely in the food industry and mainly refer to gelling polysaccharides (i.e. hydrocolloids) (Phillips & Williams, 2000). The term hydrogel describes three-dimensional network structures obtained from a class of synthetic and/or natural polymers which can absorb and retain significant amount of water (Rosiak & Yoshii, 1999). The hydrogel structure is created by the hydrophilic groups or domains present in a polymeric network upon the hydration in an aqueous environment.

This chapter reviews the preparation methods of hydrogels from hydrophilic polymers of synthetic and natural origin with emphasis on water soluble natural biopolymers (hydrocolloids). Recent advances in radiation cross-linking methods for the preparation of hydrogel are particularly addressed. Additionally, methods to characterize these hydrogels and their proposed applications are also reviewed.

Mechanism of Network formation

Gelation refers to the linking of macromolecular chains together which initially leads to progressively larger branched yet soluble polymers depending on the structure and conformation of the starting material. The mixture of such poly disperse soluble branched polymer is called 'sol'. Continuation of the linking process results in increasing the size of the branched polymer with decreasing solubility. This 'infinite polymer' is called the 'gel' or 'network' and is permeated with finite branched polymers. The transition from a system with finite branched polymer to infinite

molecules is called 'sol-gel transition' (or 'gelation') and the critical point where gel first appears is called the 'gel point' (Rubinstein & Colby, 2003). Different types of gelation mechanism are summarized in Figure 1. Gelation can take place either by physical linking (physical gelation) or by chemical linking (chemical gelation). Physical gels can be sub categorized as strong physical gels and weak gels. Strong physical gel has strong physical bonds between polymer chains and is effectively permanent at a given set of experimental conditions. Hence, strong physical gels are analogous to chemical gels. Examples of strong physical bonds are lamellar microcrystals, glassy nodules or double and triple helices. Weak physical gels have reversible links formed from temporary associations between chains. These associations have finite lifetimes, breaking and reforming continuously. Examples of weak physical bonds are hydrogen bond, block copolymer micelles, and ionic associations. On the other hand, chemical gelation involves formation of covalent bonds and always results in a strong gel. The three main chemical gelation processes include condensation, vulcanisation, and addition polymerisation.

Classification of hydrogel

Hydrogels are broadly classified into two categories:

Permanent / chemical gel: they are called 'permanent' or 'chemical' gels when they are covalently cross-linked (replacing hydrogen bond by a stronger and stable covalent bonds) networks (Hennink & Nostrum, 2002). They attain an equilibrium swelling state which depends on the polymer-water interaction parameter and the crosslink density (Rosiak & Yoshii, 1999).

Reversible / physical gel: they are called 'reversible' or 'physical' gels when the networks are held together by molecular entanglements, and / or secondary forces including ionic, hydrogen bonding or hydrophobic interactions. In physically cross-linked gels, dissolution is prevented by physical interactions, which exist between different polymer chains (Hennink & Nostrum, 2002). All of these interactions are reversible, and can be disrupted by changes in physical conditions or application of stress (Rosiak & Yoshii, 1999).

Characterization of Hydrogels

FTIR

FTIR (Fourier Transform Infrared Spectroscopy) is a useful technique for identifying chemical structure of a substance. It is based on the principle that the basic components of a substance, i.e. chemical bonds, usually can be excited and absorb infrared light at frequencies that are typical of the types of the chemical bonds. The resulting IR absorption spectrum represents a fingerprint of

measured sample. This technique is widely used to investigate the structural arrangement in hydrogel by comparison with the starting materials (2004; Mansur et al., 2004; Torres et al., 2003).

Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) :SEM can be used to provide information about the sample's surface topography, composition, and other properties such as electrical conductivity. Magnification in SEM can be controlled over a range of up to 6 orders of magnitude from about 10 to 500,000 times. This is a powerful technique widely used to capture the characteristic 'network' structure in hydrogels (Aikawa et al., 1998; Aouada et al., 2005; El Fray et al., 2007; 2004; Pourjavadi & Kurdtabar, 2007).

Other techniques

The main methods used to characterise and quantify the amount of free and bound water in hydrogels are differential scanning calorimetry (DSC) and nuclear magnetic resonance (NMR). The proton NMR gives information about the interchange of water molecules between the so-called free and bound states (Phillips et al., 2003). The use of DSC is based on the assumption that only the free water may be frozen, so it is assumed that the endotherm measured when warming the frozen gel represents the melting of the free water, and that value will yield the amount of free water in the hydrogel sample being tested. The bound water is then obtained by difference of the measured total water content of the hydrogel test specimen, and the calculated free water content (Hoffman, 2002). Thermogravimetric analysis (Lazareva & Vashuk, 1995; Singh & Vashishth, 2008; Torres et al., 2003), X-ray diffraction (2008; Mansur et al., 2004), sol-gel analysis (Janik et al., 2008; Rosiak, 1998; Wach et al., 2003b; Xu et al., 2002) etc. are also used to confirm the formation of cross-linked network gel structures of hydrogel.

Application of hydrogel

Hydrogel of many synthetic and natural polymers have been produced with their end use mainly in tissue engineering, pharmaceutical, and biomedical fields (Hoare & Kohane, 2008). Due to their high water absorption capacity and biocompatibility they have been used in wound dressing, drug delivery, agriculture, sanitary pads as well as trans-dermal systems, dental materials, implants, injectable polymeric systems, ophthalmic applications, hybrid-type organs (encapsulated living cells) (Benamer et al., 2006; Nho et al., 2005; Rosiak et al., 1995; Rosiak & Yoshii, 1999).

EXPERIMENTAL

MATERIALS:

Carboxymethylcellulose(CMC), Thiourea, -vinyl Caprolactam (NVCL), Potassium bromate, distilled water, acid solution, N₂ gas, three neck reactor and other instruments.

Procedure for Graft copolymerization:

Paste of CMC was prepared by addition of 20 mg of cmc and 6 mL of water in a three neck reactor. Then acid solution(1.065mL) was added in it, after that 0.139g NVCL was added to it. To maintain the molar solution of reaction 4 mL of water was added to the reaction mixture. The three neck reactor was connected with the N₂ gas vessel. For half an hour N₂ was allowed to flow in it. After 30 minutes M/100(0.0128g) of potassium bromate was added to the reaction mixture and the mixture was heated at a constant temperature of 40°C for two and half hours. The N₂ gas was passed continuously in the reaction mixture for two and half hours. After completion of the reaction solution was cooled down and then poured into Methanol(40 mL) and grafted CMC precipitates out, which on further dried and characterized by FTIR and TGA. The graft copolymer was found to be pale yellow in colour and insoluble in H₂O, CH₃OH, DMSO, Acetone, CHCl₃, HCl and THF. At high temperature it is also insoluble in above solvents while it is soluble in NaOH.

RESULTS AND DISCUSSIONS

FTIR Analysis of CMC

The infrared spectra analysis has been done to prove grafting. For this the IR spectra of ungrafted and grafted samples in KBr pellets have been recorded on Varian Excalibur 3000 (Palo Alto, CA) spectrophotometer in the region 400 to 4000 cm⁻¹.

The band appeared at 3304.51 cm⁻¹ was due to O-H stretching in CMC molecule. The band appeared at 2924.9 cm⁻¹ was due to C-H stretching of CH₃. The band appeared at 1601.85 cm⁻¹ was due to C=O stretching. The band at 1374 & 1416 cm⁻¹ was due to C-O-H bending. The band at 1155 & 1115 cm⁻¹ was due to C-O stretching. The band at 718 & 604 cm⁻¹ was due to C-H bending (out of plane).

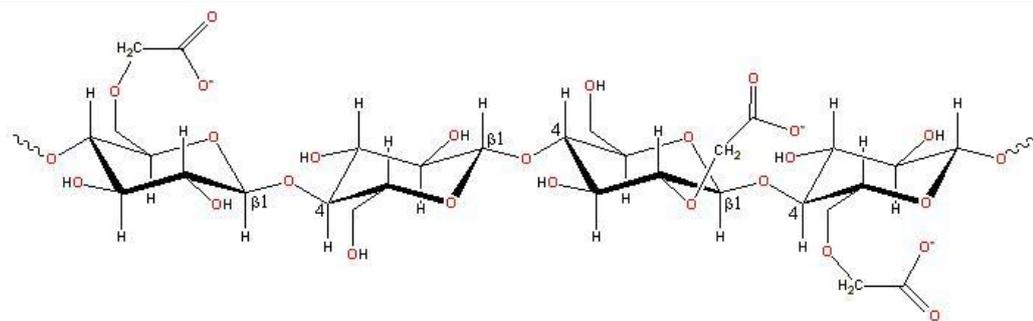


Fig.-1 : Structure of Carboxymethylcellulose

FTIR Analysis of CMC-g-Poly (N-Vinyl Caprolactam)

The band appeared at 3404.59 cm^{-1} was due to O-H stretching. The band at 2924.9 cm^{-1} was due to C-H stretching of CH_2 . The band at 1738.94 cm^{-1} was due to C=O stretching. The band at 1639 cm^{-1} was due to N-H bending. The band at 1429.8 & 1374 cm^{-1} was due to C-O-H bending. The band at 1123.1-1063.39 cm^{-1} was due to C-H stretching. The band at 673-579 cm^{-1} was due to C-H bending.

Thermogravimetric Analyses of Carboxymethylcellulose

The degradation of carboxymethylcellulose started at about 135.3°C. The degradation occurred in two stages *i.e.* from 135.3°C to 283.1°C and from 283.1 to 385.2°C. About 40% weight loss occurred between 200 and 400°C. The rate of weight loss increases on increasing the temperature upto 285.0°C, but decreases thereafter. The polymer decomposition temperature (PDT), final decomposition temperature (FDT), temperature at which maximum degradation (T_{max}) and integral procedural decomposition temperature (IPDT) were found to be 135.3, 385.2, 283.1 and 294.5°C respectively. Table 1 and 2 reveals that weight loss in the temperature range 400 to 700°C is almost constant. The char yield of 38% was obtained at 924°C. The DTA curve of sodium carboxymethylcellulose shows an endothermic peak with gradual decrease in weight and a broad band with fluctuations at 304°C and 413.1°C. It may be due to decarboxylation of carboxy group of carboxymethylcellulose.

Carboxymethylcellulose-g-Poly(N-vinyl Caprolactam)

Carboxymethylcellulose-g-Poly(N-vinyl Caprolactam) graft copolymer has been obtained by grafting N-vinyl caprolactam onto carboxymethylcellulose using BrO_3^- /thiourea redox couple. The graft copolymer began to degrade at about 180°C. However, 10% weight loss is observed upto 100°C may be attributed to the absorbed water. The degradation appears to be two-stage process *i.e.* from 233.9°C to 312.7°C and from 312.7 to 462.2°C. The rate of weight loss increased with an increase in temperature upto 268.7°C and gradually decreases thereafter. Again increase

in the rate of weight loss has been observed from 325°C to 377.1°C and thereafter it decreases (Table 1 & 2). Therefore, two T_{max} 's are obtained at 268.7°C and 377.1°C. The polymer decomposition temperature (PDT) is 233.92°C; *i.e.* 98.62°C higher than that of carboxymethylcellulose and final decomposition temperature (FDT) of carboxymethylcellulose-g-Poly(N-vinyl Caprolactam) is also higher than sodium carboxymethylcellulose. The weight loss of carboxymethylcellulose-g-Poly(N-vinyl Caprolactam) in lower temperature range *i.e.*, 180°C to 268.7°C, is due to the elimination of CO₂ molecule from the carboxymethylcellulose backbone. It is confirmed by the T_{max} of ungrafted carboxymethylcellulose value which is nearly same as grafted carboxymethylcellulose. At 975°C, a char yield of 15% has been obtained. The IPDT, T_{max} , and FDT values of carboxymethyl cellulose-g-Poly(N-vinyl Caprolactam) suggests that it is thermally more stable than carboxymethyl cellulose

Table- 1
Thermogravimetric Analyses of Graft Copolymer

Sample Code	PDT (°C)	FDT (°C)	T_{max} (°C)	IPDT (°C)	DTA Curves
					Exo peaks (°C)
C ₁	135.30	385.20	283.10	294.50	—
C ₂	233.92	432.14	268.70 & 377.11	370.16	—

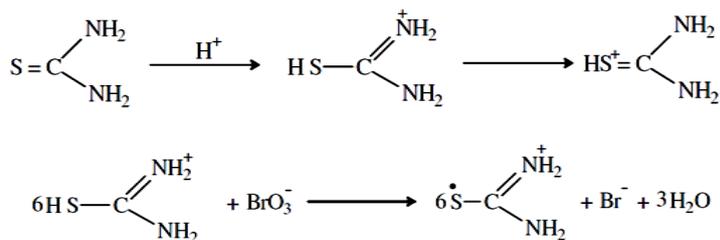
Table-2
Decomposition Temperature (TD)

% weight loss / Temp. °C	10%	20%	30%	40%	50%	60%
C ₁	270.00	284.00	296.00	382.00	740.00	904.00
C ₂	109.82	259.84	315.53	362.25	400.2	461.84

Where C₁ = Carboxymethylcellulose, C₂= Carboxymethylcellulose-g-Poly(N-Vinyl Caprolactam)

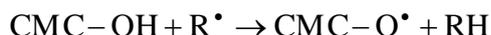
REACTION MECHANISM

On the basis of experiments, following tentative mechanism has proposed for the system. It is assumed that in presence of hydrogen ion, thiourea gets protonated, which reacts with bromate ion to give isothiocarbamide radicals. These radicals abstract hydrogen atom from the backbone (CMC) molecule producing carboxymethylcellulose free radicals. The monomer molecules which were near vicinity of the reaction sites, become acceptor of carboxymethylcellulose macro radicals resulting in chain initiation and thereafter themselves become free radicals donor to neighboring molecules thus grafted chain grows. Termination of chain occurs by coupling to yield graft copolymer.



Scheme-1 : Formation of Primary Free Radicals by redox couple

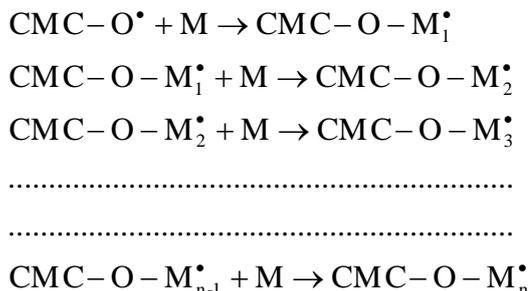
Initiation:



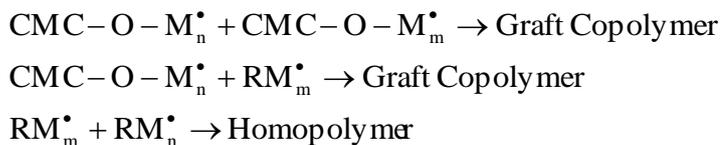
where



Propagation



Termination:



CONCLUSION

The monomer was N-Vinyl Caprolactam (NVCL) and polymer was carboxymethylcellulose(CMC). Potassium bromated was an oxidizing agent and thiourea was a reducing agent. They reacted in acidic media and produces radicals. The radicals attack on CMC and NVCL produces CMC graft copolymer. On the basis of IR spectra and data it is concluded that CMC-graft copolymer has formed.

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