



Eco-Friendly and Non-Toxic Superabsorbent Hydrogel as Food Packaging Packets

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ABSTRACT

In response to the demand of alternative eco-friendly packaging materials for foods, hydrogels based on carboxymethyl cellulose (Na-CMC) emerges as water absorbent food packaging packets was prepared. Degree of substitution, intrinsic viscosity, degree of polymerization, and average number molecular weight of CMC were determined. The graft copolymerization of acrylamide onto carboxymethyl cellulose sodium salt in aqueous medium was performed with varying acrylamide ratios. The grafting was characterized by investigation means of FT-IR, X-ray diffraction, scanning electron microscope (SEM), elemental analysis, and thermal behaviour (TGA and DSC). The maximum water swelling capacity was 413% at 30.28 grafting degree. Migration test of residual acrylamide to fresh meat sample upon direct contact was done to ensure meat safety. The result revealed that, carboxymethyl cellulose grafted polyacrylamide copolymer (CMC-g-PAm) is safe and healthy for meat packaging during storage.

Key words: Hydrogel; Food packaging packets; Food safety; Acrylamide; Grafting

INTRODUCTION

Hydrogel constitute a group of polymeric materials, the hydrophilic structure of which renders them capable of holding large amounts of water in their three-dimensional networks. They have incredible applications in a wide variety of fields as drug delivery, pharmaceutical and food packaging [1]. Hydrogels can offer new challenges for the tailoring packaging materials with desirable properties as alternatives to petrochemical based packaging materials [2]. As expected, natural hydrogels were gradually replaced by synthetic types due to their higher water absorption capacity, long durability, biodegradability, and wide variable of raw chemical resources [3-4]. Liu et al [5] and Fishman et al [6] studied various attempts to develop food packaging wrapping materials using biopolymers like starch, gum, gelatin, whey protein, chitosan, alginate, pectin and others as promising biopolymers for many fields of manufactures hydrogel applications. Packaging hydrogels based on gelatin have been suggested as replaceable materials to petroleum based plastics [7-9]. Stefano et al [10] prepared composite films from gelatin and low-methoxyl pectin from simultaneous reversible and permanent polyion-complex hydrogels. Early research addressed cellulose and its derivatives in developing food packaging hydrogel. Cellulose derivatives such as carboxymethylcellulose (CMC) and hydroxypropylcellulose are of the numerous polymers known by their superabsorbent capacity that has been proposed for the preparation of biocompatible hydrogels [11]. Adriana et al [12] developed a breathable and biodegradable hydrogel film for food packaging application using synthetic polyvinyl pyrrolidone (PVP) and biopolymers carboxymethyl cellulose (CMC) to create PVP-CMC hydrogel films. Polyacrylamide hydrogel is a defined polymer prepared through controlled polymerization reaction of acrylamide. PAm has been widely used in food, water supply. However, major concern has been widely expressed because acrylamide used to produce polyacrylamide hydrogel is implicated as a potential mutagen and reproductive toxicant. It is, therefore, necessary to investigate the toxicity of residual monomer in PAm [13].

Accordingly, our aim in the present study is the development of eco-friendly food packaging materials based on grafting a candidate synthetic monomer (acrylamide) onto CMC and to identify the appropriate CMC/acrylamide monomer ratios to satisfactory safe and free acrylamide packaging material. CMC was perfectly prepared from wood pulp and alkali/monochloroacetic acid. The attained CMC was characterized with degree of substitution, intrinsic viscosity, degree of polymerization, and average number molecular weight

(Mn). The graft copolymerization of acrylamide onto (CMC) in aqueous medium was performed with varying acrylamide ratios. The grafting is confirmed by investigation means of FT-IR, X-ray diffractometry, SEM, TGA and DSC. These types of three-dimensional network of hydrogel packets will manage water and humidity in food packaging. The safety ensurance of residual acrylamide monomer migration upon hydrogel packets contact to the food was done.

EXPERIMENTAL SECTION

Materials and chemicals

Wood pulp has approximately 90 % alpha cellulose content. Monochloroacetic acid and acrylamide were obtained from Alpha Chemika (Bumbai). Potassium peroxodisulfate (KPS) was purchased from Sisco Research Laboratories PVT Ltd, Mumbai. Methanol, ethanol, sodium carbonate, isopropanol, sodium hydroxide, and sodium chloride are used as received. Desiccant paper packets were supplied from ICPACKS Co., Badr industrial area, Cairo, Egypt.

Preparation of CMC sodium salt

The heterogeneous preparation method of CMC sodium salt includes two steps, alkalization and etherification. In the alkalization step approximately (5 g) of wood pulp was added to flask (500 ml) followed by addition of (92.5 g) isopropanol and (3.7 g) water. Then, sodium hydroxide solution 30 % (w/v) was dropped to the reaction medium and macerated for 2 hours at 30 °C. The etherification step involves addition of appropriate amount of monochloroacetic acid and the reaction was macerated at 60 °C for 2 hours. Finally, the reaction was filtered and residue was suspended in methanol. The suspended CMC slurry was easily dissolved in distilled water, and then extracted with 95% methanol as precipitated solid, then dried under vacuum at 50 °C and ground [14].

Synthesis of grafted (CMC-g-PAm) three dimensional network copolymers

In three necks round bottom flask, appropriate amount of CMC was placed while stirring in under an inert gas. Determined amount of acrylamide monomer was completely homogenized with the mixture through vigorous stirring for 20 min. Sodium carbonate and potassium persulfate were added to the reaction mixture. Graft polymerization was occurred for 8 hrs at 80 °C, to reach complete conversion of polymerization. After that, reaction flask was immersed in an ice bath to drop down the temperature of the reaction medium to 25 °C, and precipitated in cooled ethanol. Prepared hydrogel was charged into soxhelt with acetone for 20 cycles to extract non grafted monomers and homopolymers. CMC-g-PAm was separated through sintered glass filters disc and dried in vacuum oven at 40 °C overnight. The graft percentage was determined related to the nitrogen content in all prepared samples. Gel content of the prepared hydrogel was defined by extraction using acetone. Weighted samples were packed in a cellulose thimble and each sample was replicated four times. The solvent extraction was carried out with 250 ml acetone for 20 cycles. After that, extracted samples were dried under vacuum and re-weighed. Percentage of gel content was calculated according to the following equation:

$$\text{Gel content \%} = (\text{weight after extraction} / \text{weight before the extraction}) \times 100$$

Characterization

Degree of substitution of CMC

The substitution degree of the attained of carboxymethyl cellulose sodium salt (Na-CMC) was determined as described. Na-CMC was stirred in acetone to be transformed to its acid form (H-CMC) by dropped 30 ml (6 M HCl per 10 g of the sample in aqueous medium), under stirring for half hour. Resultant solution was filtered and the precipitate was washed with (80 % methanol). After that, the precipitate was re-dispersed for further purification, filtered and followed by vacuum drying at 50 °C.

Accurately weight (0.5 g of the H-CMC) sample in 250 ml Elenmeyer flask and 100 ml distilled water was added and stirred. Sodium hydroxide solution (25 ml, 0.5 M) was poured and heated for 20 min. Heated solution was titrated with 0.3 M HCl in presence of phenolphthalein indicator. Titration experiment was replicated three times for precision results [15].

The DS was calculated using the equation below:

$$A = BC - DE / F$$

$$\text{Degree of substitution} = (0.162 \times A) / (1 - (0.058 \times A))$$

A: milli- equivalents of consumed acid per gram of specimen;

B: NaOH volume, ml;

C: NaOH concentration, mol;

D: equivalent HCl volume, ml;

E: HCl concentration, mol;

F: weight of sample;

162: formula weight of the anhydrous glucose unit (g/mole) and 58 is the net increase in the anhydrous glucose unit.

The intrinsic viscosity, degree of depolymerization, and average number molecular weight of Na-CMC

Intrinsic viscosity Na-CMC was carried out using Ubbelohde geometry at 25 °C. The polymer concentrations of the sample value of 2 % Wt. The typical five concentrations of sodium chloride from 0.4×10^4 to 1.6×10^4 mg/L were separately measured. The relation of viscosity versus concentration was extracted by extrapolating to zero concentration. The degree of polymerization (DP) of CMC can be obtained by the following equation:

$$DP = [\eta]/0.0066.$$

Molecular weights of the prepared polymers were determined by intrinsic viscosity $[\eta]$ values. Mark Houwink equation, $[\eta] = DKM^\alpha$ is applied for determined of molecular weight of linear polymers where K and α are constants for a particular polymer/solvent/temperature system [16].

Infrared spectroscopy (FT-IR)

Wood pulp, CMC and PAm, and CMC-g-PAm samples were investigated with FT-IR instrument (JASCO FT-IR-4100, Japan) with range from 400-4000 cm^{-1} .

X-ray diffractometry

X-ray diffraction patterns were obtained by using PAN analytical XPERTPR O Super X-ray diffractometer equipped with Co $K\alpha$. The tube operated at 45 kV, 9 mA.

Elemental Analysis of CMC-g-PAm copolymer

The grafting percentage was determined related to the nitrogen percent by elemental analysis. Thus, the grafting percentage in (CMC-g-PAm) copolymer can be determined by estimation nitrogen (N) content using Elemental analyzer (Vario El Elementary, Germany).

Topographic Investigation

SEM Model Quanta 250 FEG attached with EDX Unit (Energy Dispersive X-ray Analyses), with accelerating voltage 30 K.V., magnification 14x up to 1000000 and resolution for Gun.1n).

Swelling capacity

Weighted dry grafted polymer granules together were immersed in distilled water for 24 h. The granules were wiped using tissue paper and weighted again. Percentage of swelling ratio percentage was determined using the equation below [17]:

$$\text{Swelling ratio (\%)} = (\text{Swelled weight} - \text{Original weight}) / \text{Original weight} \times 100$$

Thermal behavior

TGA and DSC were tested using Perkin-Elmer Thermo gravimetric Analyzer Model TGA 7. TGA and DSC temperature run program from 50-650 °C and 25-200 °C respectively with heating rate 10 °C /min and flow rate 50 cm^3 under nitrogen atmosphere. The reference material was α - alumina.

Migration test of acrylamide

Meat samples preparation:

CMC-g-PAm hydrogel was packed in desiccant paper package and closed by Vacsy bag sealing unit. Meat samples (10 g) were kept in plastic packing upon contact with (0.2 g) of CMC-g-PAm hydrogel in desiccant paper package for different time 2, 4, 6, 8, and 10 days at 4°C. After the incubation time, the meat samples were allowed to determine the residual acrylamide monomer by HPLC.

Preparation acrylamide standard and Carrez solutions:

200 mg of acrylamide (Am) was dissolved in (50 ml) acetonitril to prepare stock solution of Am. Serially diluted of stock solution to prepare working standard solutions were stored at 4°C. The Carrez (I) solution was prepared by dissolving the (15 wt% in water) of potassium hexacyanoferrate in water and Carrez (II) was prepared by dissolving (30 wt% in water) zinc sulfate.

Acrylamide analysis: Triplicate samples of meat were analyzed according to the extraction method described. In brief, hydrogel sample (1g) was extracted by 20 ml of mM formic acid. The fate layer was separated using cooling centrifuge at 5000 rpm for 10 min. The clear supernatant was treated with Carrez I and Carrez II solutions (25 μl each). Following centrifugation at 10,000 rpm for 5 min, the extract was clean up by Oasis MCX cartridge. The first eight drops was discarded to prevent the dilution and the rest were collected in clean vial for HPLC analysis.

HPLC analysis:

HPLC-UV analysis was done on Waters millennium HPLC instrument equipped with UV-Vis detectors 274. The calibration standards and sample extracts were injected via a 20 μ l sample loop and the analytical separation was performed on an 250 mm x 4.6 mm, 5 μ m phenomenex C₁₈ using a mobile phase of acetonitril and water (3:7, V/V) at flow rate of 0.8 ml/min, and the detection wavelength was 210 nm. For more strong confirmation of the residual acrylamide monmer results, the DART-Plus instrument (USA) was used [13].

RESULTS AND DISCUSSION**Characteristics of prepared of Na-CMC**

Degree of substitution is key property of any derivatization reaction. DS of carboxylic group in carboxymethyl cellulose is represented as average number of hydroxyl group in cellulose building unit which was substituted by carboxymethyl group at C₂, C₃, and C₆. The attained Na-CMC sample has degree of substitution (0.65), intrinsic viscosity of the prepared Na-CMC (0.184), degree of polymerization (9.38×10^3), and average number molecular weight (1.69×10^6).

Fourier Transformer Infra-Red (FT-IR)

By comparing FT-IR spectra of wood pulp and CMC as original materials, in Figure (1); OH groups represent as a broad peak at around 3420 cm^{-1} either from cellulose or lignin. The peak at around 2922 cm^{-1} represents the C-H a symmetric stretching in aliphatic methyl. In wood pulp, a peak appears at around 1634 cm^{-1} is due to ester carbonyl stretching absorption band mainly arises from the carbonyl stretch in unconjugated ester, carboxylic, or ketone groups in hemicelluloses. High intense band appears at 1617 cm^{-1} and 1426 cm^{-1} may attributed to stretching and bending vibrations of carboxylate anion groups ($-\text{COO}^-$) in CMC. Characteristic peaks at around 2898 cm^{-1} and 2900 cm^{-1} which represents stretching vibration bands of active methylene group ($-\text{O}-\text{CH}_2-\text{COO}^- \text{Na}^+$) in CMC sodium salt. A band appears at approximately at 1458 cm^{-1} is due to bending vibration of C-H of methylene group (scissoring vibration). Wood pulp and CMC sample showed a band at 1059 cm^{-1} and 899 cm^{-1} which dominates the spectrum of cellulose linkages and β -glycosidic linkage. PAm and CMC-g-PAm copolymer were captured in Figure (1). The peak at around 3428 cm^{-1} is attributed to OH and NH₂. Peaks around 1712 cm^{-1} , 1671 cm^{-1} , and 1444 cm^{-1} are attributed to amide-I (C=O) on PAm chains, the overlap of ($-\text{COO}^-$) on the CMC backbone and the amide-II (N-H) on the PAm chains, and the C-N stretching in the graft copolymer [18].

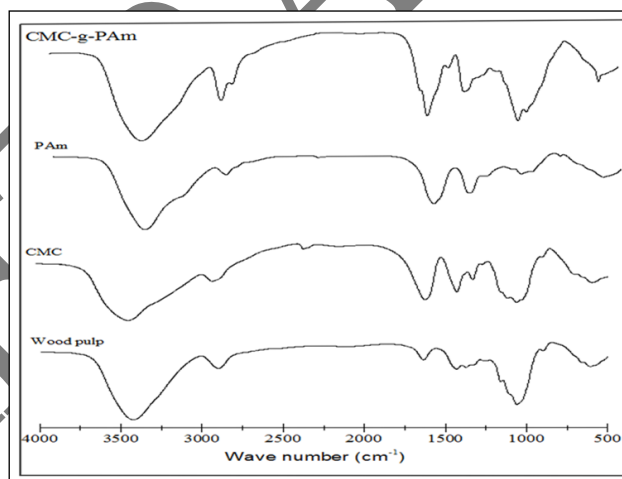


Figure 1: FT-IR spectra of wood pulp, CMC, PAm, and CMC-g-PAm copolymer

X-ray diffraction pattern (XRD)

X-ray diffraction pattern confirmation of wood pulp, CMC, and CMC-g-PAm was demonstrated in Figure (2) respectively. The wood pulp presented X-ray diffraction pattern as typically of cellulose I. In particular, the main diffraction pattern of cellulose, namely 101, 101^{*}, 002, and 040 are exhibit at diffraction angles 2θ around 14.9, 16.3, 22.5, and 34.6° respectively. However, cellulose sample presence, 101, 101^o diffraction planes of CMC overlapped with each other and formed one broad peak. This phenomenon was owed to the destruction of crystalline region. To investigate the final product further, it is demonstrated that, CMC has relatively weaker band at $2\theta = 20^\circ$ for the decreased of the ordered structure due to presence of carboxylate group substituent on cellulose backbone. There is a shift peak at $2\theta = 23^\circ$ in CMC-g-PAm corresponds to the position of $2\theta = 20^\circ$ observed in CMC pattern. Previous results may be point to morphological rearrangement of the polymer segment after grafting of acrylamide to CMC. In addition, there are two main peaks at position $2\theta = 32^\circ$ and $2\theta = 38^\circ$.

= 46° in CMC belong to hydrogen bonding of hydroxyl groups in CMC, their intensities decreased in CMC-g-PAm. This is evidence of grafting copolymerization on CMC backbone occurred through ether formation. Additionally, with grafting the peaks become broader and weaker indicating that, the structure of the grafting products become amorphous, therefore, it can be concluded from the XRD patterns that, the ordered structure of CMC has destroyed by grafting copolymerization [19].

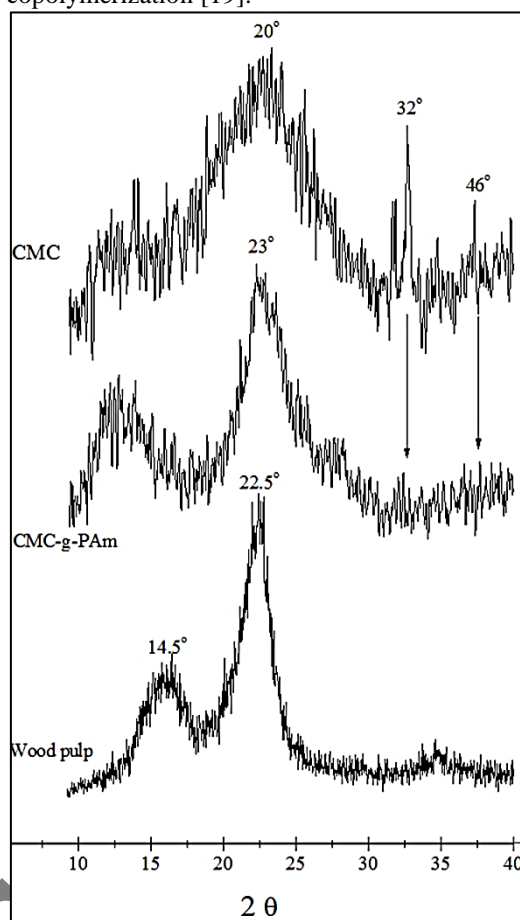


Figure 2: X-ray diffraction pattern of wood pulp, CMC, and CMC-g-PAm copolymer

Elemental analysis, gel content %, and degree of grafting %

Table 1: Elemental analysis results and grafting degree percent of CMC-g-PAm copolymers of various CMC: acrylamide weight ratios, AS₁ (1:1), AS₂ (1:2), AS₃ (1:3), AS₄ (1:4), AS₅ (1:5)

Sample code	N %	C%	H%	Gel content %	Grafting degree, %
AS ₁	1.74	41.8	6.86	28	8.87
AS ₂	5.938	34.86	6.18	91	30.28
AS ₃	5.22	40.02	6.95	83	26.6
AS ₄	5.54	43.98	7.81	66	28.27
AS ₅	5.25	46.74	1.36	52	26.77

Elemental analysis results of graft copolymer samples were presented in Table 1; in CMC-g-PAm copolymers. Considerable percentage of nitrogen content is indicated to the grafting of PAm segments on the cellulose backbone [20]. Different grafting ratios on CMC, highest percentage of nitrogen is observed in case of AS₂. Previous behavior can be presence with nice interpretation on the basis of short and longer segments of polyacrylamide on cellulose backbone. The grafting percentage of monomer on to natural polyelectrolyte CMC was measured after removing homopolymer by extracting with a solvent. The grafting percentage of monomer on CMC skeleton increases with increased concentration of monomer in all cases. However, polymer/monomer ratio 1:2 is considered the optimum for monomer grafting. Consequently gel fractions content results agree with the net results as shown in Table (1). Beyond, CMC/acrylamide monomer 1/2, grafting degree percentage comparatively decreased. This may be assigned to the reaction directed towards homopolymer formation.

Swelling capacity

The relationship between swelling ratio and degree of grafting of CMC-g-PAm copolymers percentages as a function of monomer concentration is shown in Figure 3. Clearly, swelling ratios increased considerably to certain extent, then they start to decrease with increasing of grafting degree. Na-CMC has high density carboxylic groups in structure formula which increase swelling capacity behavior of hydrogel. Presence of hydroxide, primary amine and carboxylic functional groups are responsible for increasing the hydrogel swelling as hydrophilic chains in grafted polymer [21-23]. The optimum grafting degree (30.28) gave the maximum swelling ratio (413 %).

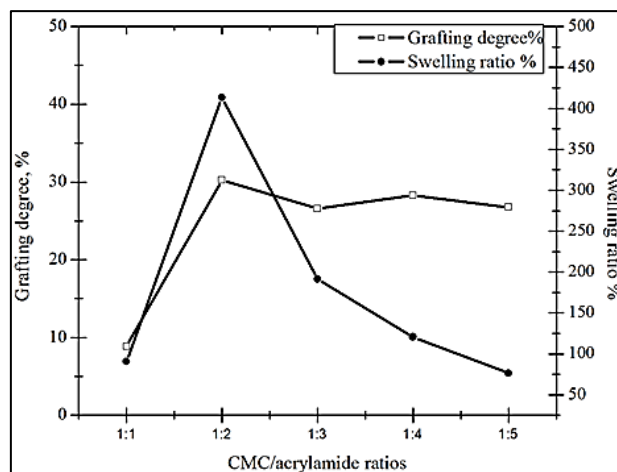


Figure 3: Swelling ratio - Grafting degree of CMC-g-PAm copolymer as a function of monomer concentration

Morphological investigation

SEM micrographs of CMC and the graft copolymer (CMC-g-PAm) are exhibited in Figure (4). It is clear that, the morphological structure of CMC differed from CMC-g-PAm. Surface topography of CMC before grafting showed a smooth structure, which has been changed to fibril form after grafting. It became more close to forest morphology. Thus, the comparison of these figures reveals that grafting has taken place. Grafting morphological structure of PAm over CMC topographic surface make high and deep polymer network as three dimensional networks copolymer.

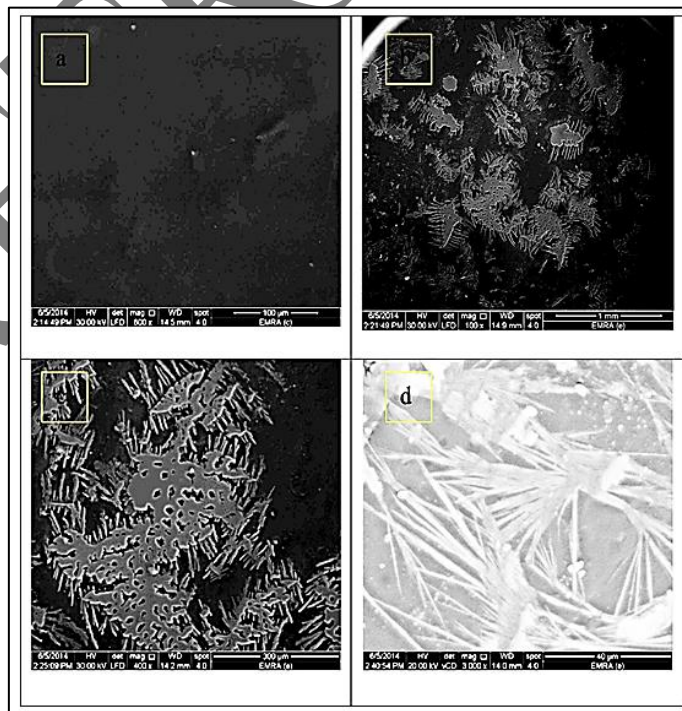


Figure 4: shows SEM micrographs for CMC (a) and CMC- g- PAm (b, c and d)

Thermal analysis

Thermal gravimetric analysis (TGA) is a characteristic technique in which materials is gradually decomposed over stages by heating. TGA curves are presented in Figure (5). CMC-g-PAm copolymer thermogrametric shows two stages of the polymer degradation. The first stage referring to thermal decomposition of CMC segment occurs in the 241-343 °C, with a weight loss of 13 %. The second stage occurs within 343-450 °C with weight loss 31% which may be related to degradation of PAm side segment. Moreover, pure CMC thermally degrade into two stages, the first within temperature range 265-320 °C with weight loss of 18%, the second decomposition stage within temperature range 320-450 °C with weight loss of 57%. Furthermore, pure PAm degrade into two stages, the first starts at temperature range of 111-250 °C with weight loss of 18%, the second stage begins at temperature range of 250-450 °C with weight loss of 74%. It is clear from the outlined results that, grafting of acrylamide to CMC backbone shows increasing thermal stability of the copolymer based on weight loss percent during heating. In CMC-g-PAm copolymer, weight loss percent in both two decomposition stages less significant than in pure CMC and PAm polymers.

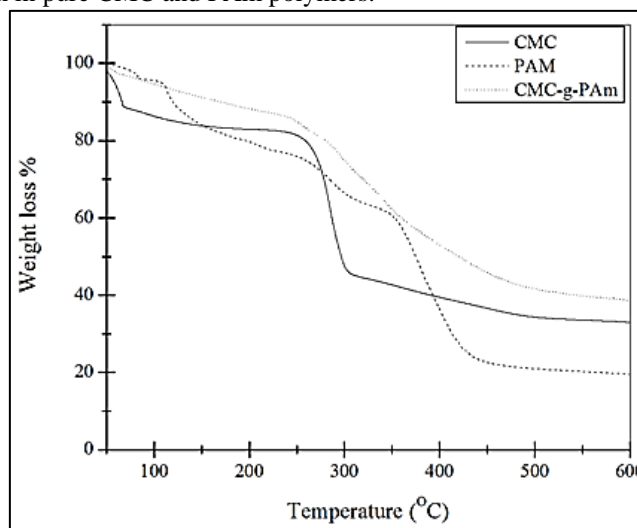


Figure 5: TGA pattern curve of CMC, PAm, and CMC-g-PAm copolymer

Differential Scanning Calorimetry (DSC)

As explained in Figure 6, DSC curve of CMC-g-PAm exhibits two endothermic peaks, the first peak at temperature 70 °C that could be attributed to T_g of the copolymer. This peak showed relatively some broadness may be due to the overlapping of the T_g transitions of the two polymers [24]. However, glass transition temperature of pure CMC and PAm were observed at around 97 °C, and 55 °C respectively. The other endothermic melting transition of CMC-g-PAm copolymer was observed at 260 °C. While in case of CMC and PAm, their T_m was observed at temperature 290 °C and 125 °C respectively. Since copolymerization of two homopolymers have significant impact on reducing the T_m of the copolymer and glass transition temperature mediated glass transition temperature of both homopolymers. It is strong evidence that grafting has been done.

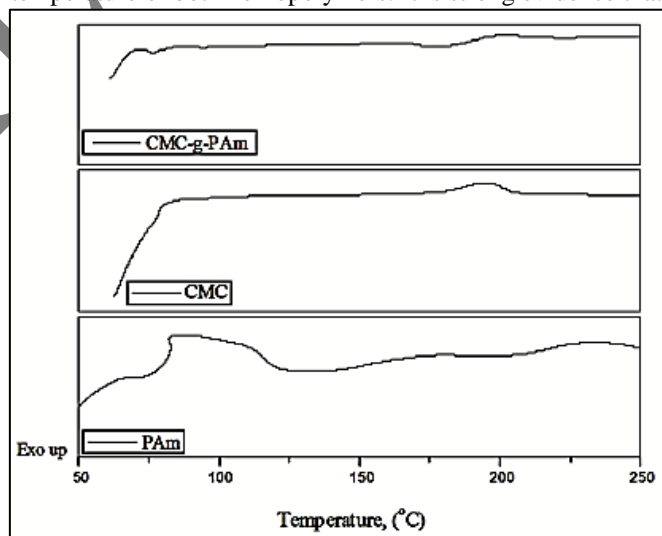


Figure 6: DSC thermogram of CMC, PAm, and CMC-g-PAm copolymer

Acrylamide residue

The common impurity in most synthesis process of polyacrylamide is the residual acrylamide monomer in range 1 to 600 ppm. Residual amount of monomer in PAm could be detected in range from <.01% to 0.1%. Additionally, measurement amounts were recorded at up level 0.02% to 0.03%. PAm is not significantly toxic in polymer form. Recently, an oral toxicity examination of PAm in rats recorded the maximum oral dose of 4.0 g/kg body weight was abided. In sub chronic toxicity experiment, dogs and rats feed with Polyacrylamide with gradually doses up to 0.464 g/kg body weight, which presence any indicators of toxicity. Over two years oral toxicity examination in dogs and rats fed diets charged with up to 5% PAm did not show any significant adverse effects. Acrylamide was classified as category 2 carcinogen and category 2 as mutagen by European Commission [25-26].

The experimental aimed to study the effect of migration of acrylamide from packing hydrogel to meat samples during different incubation periods. Acrylamide extraction from food entail with an extraction with acidified aqueous followed by cleaning up with SPE prior to HPLC-UV. The results indicated that the acrylamide residue in meat samples appeared that no acrylamide found in the samples at different incubation periods under this study. From the above studies, it is observed that the packing hydrogel is safe for meat packing. Also, to confirm the previous result we used the DART-Plus instrument to detect the acrylamide residue in meat samples and the results appeared that no acrylamide residue found in the samples (Mw. 72.06 g/mol). In conclusion from previous data the hydrogel packing material is recommended as the best method for keeping fresh food as meat.

CONCLUSION

CMC sodium salt was successfully prepared with degree of substitution 0.65. Intrinsic viscosity of the prepared Na-CMC 0.184, degree of polymerization 9.38×10^3 , and average number molecular weight 1.69×10^6 . An eco-friendly, safely, and healthy superabsorbent hydrogel packaging packets was prepared by free-radical graft copolymerization onto prepared CMC sodium salt. The ratios of acrylamide monomer content to CMC were studied. The optimal CMC / acrylamide ratio was (1/2), gave the maximum values of grafting degree (30.28), and swelling capacity (413%). Grafting was verified by means of FT-IR, SEM, X-ray diffraction patterns. The results confirmed that grafting reaction onto CMC skeleton has been done. Thermal analysis (TGA & DSC), in TGA, CMC-g-PAm copolymer showed weight loss percent less significant than pure CMC, and PAm. However, in DSC, T_g and T_m of copolymers was mediated of homopolymer of both CMC and PAm. Migration test showed no migrated residual of acrylamide monomer to meat during storage periods. Generally speaking, we can conclude that this type of food packaging packets is safe and efficient.

ACKNOWLEDGEMENTS

The authors are thankful for the support of technical research by Vacsy bag sealing unit as a gift from Zepter Co. Sweden.

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