



CARBOXYMETHYL SODIUM ALGINATE: SYNTHESIS AND CHARACTERIZATION

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ABSTRACT

Sodium alginate, an important family of polysaccharides, was chemically modified by carboxymethylation to obtain the product Sodium salt of Partially Carboxymethylated Sodium Alginate. The Fourier Transform Infrared (FTIR) analysis and ¹H-NMR spectroscopy were used to confirm the chemical structure of the product. Thermal analysis (TGA/DSC) and Scanning Electron Microscopy (SEM) were also used to characterize the materials.

Keywords: Sodium alginate, Sodium salt of Partially Carboxymethylated Sodium Alginate, Characterization

INTRODUCTION

As renewable raw materials, polysaccharides have received major attention due to their advantages over the synthetic polymers such as non-toxic, biodegradable and low cost. Depending on the source, these polysaccharides have many impurities and molecular distributions. However, through purification and modification, useful products can be obtained [1-8].

Among various water-soluble polysaccharides, sodium alginate is one of the most industrially important polysaccharides [9]. It is composed of two 1→4 glycosidically linked monomers: β-D-mannuronic acid (M) and α-guluronic acid (G). The relative amounts of M and G, as well as their sequential arrangement along the polymer chain, is not fixed and varies greatly with the origin of the alginate, age of the algae and the method of extraction. Fig. 1 represents the structural characteristics of the alginates.

It is well known that Sodium Alginate (SA) chelates with divalent cations to form hydrogels. However, SA hydrogels suffer from low water absorbency and poor mechanical properties. In this work, therefore, we report only the chemical modification of SA by carboxymethylation and its characterization by using various techniques. This has been carried out in order to meliorate its compatible performance and chemical stability.

However, this synthesized carboxymethylated derivative of SA i.e. Sodium salt of Partially Carboxymethylated Sodium alginate (Na-PCMSA) has been further modified via graft copolymerization of acrylonitrile onto it using chemical and low energy radiation methods in order to evaluate the potential applications of the synthesized graft copolymers of Na-PCMSA as hydrogels and ion-exchange resins, the results of which will be published elsewhere.

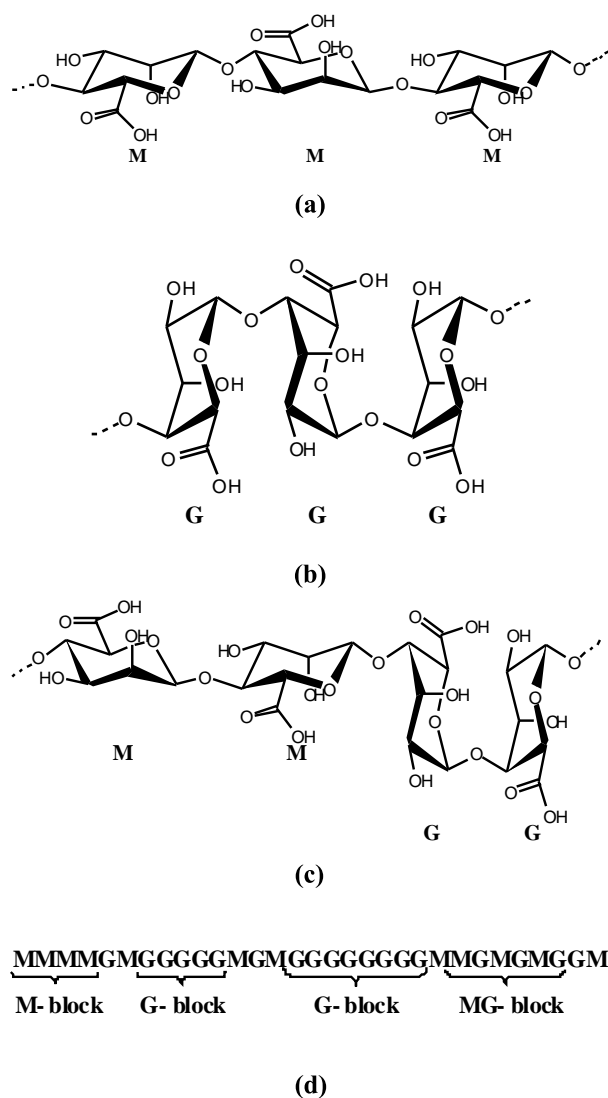


Fig.1: Structural characteristics of alginates:
(a) Repeating D-mannuronic acid
(b) Repeating L-guluronic acid
(c) Chain Conformation and (d) Block distribution.

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EXPERIMENTAL

Materials

Sodium alginate was kindly supplied by Loba Chemie Pvt. Ltd., Mumbai, India. Sodium monochloroacetate (Fluka, Switzerland) was used as received. Isopropanol used was of laboratory grade (SD Fine Chem. Ltd., Mumbai, India)

Nitrogen Purification

Nitrogen gas (supplied by the Indian Oxygen Company Ltd. Ahmedabad) was purified by passing through freshly prepared alkaline solution of pyrogallol (15g of pyrogallol dissolved in 100 mL of 50% NaOH solution).

Preparation of Sodium salt of Partially Carboxymethylated Sodium Alginate

The preparation of Na-PCMSA was carried out based on the procedures of Kamel et. al. [10] and Ragheb et. al. [11] with some modifications. The procedure adopted was as follows: In a three-necked flask equipped with stirrer, water condenser and a gas inlet tube, a fixed amount of sodium alginate was suspended in a known volume of isopropyl alcohol and the mixture was stirred for thorough mixing for one hour at 70°C. A known quantity of sodium monochloroacetate was then added once. Carboxymethylation of Sodium alginate in the presence of sodium monochloroacetate proceeds smoothly in the homogeneous medium without using sodium hydroxide. The reaction mixture was then further stirred for four and half an hour at 70°C. Temperature was controlled throughout the reaction by immersing the reaction flask in constant temperature bath and the reaction was carried out throughout under nitrogen atmosphere.

After completion of reaction, the isopropyl alcohol from the reaction mixture was poured off and the product, Na-PCMSA, was filtered through sintered glass G-2 funnel. The product was washed repeatedly with 95% aqueous methanol, to remove excess of salt and then with pure methanol and ether respectively. It was dried in a vacuum oven at 35°C.

CHARACTERIZATION

Determination of the Degree of Substitution (\overline{DS})

The average degree of substitution (\overline{DS}), which is the average number of carboxymethyl groups in the polymer, was determined by following the well known Acid-Wash method [12]. The value of the \overline{DS} of Na-PCMSA was found to be 0.605.

Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectra of SA and Na-PCMSA (\overline{DS} = 0.605) samples were taken in KBr pellets using Nicolet impact 400D Fourier Transform Infra Red Spectrophotometer.

$^1\text{H-NMR}$ Spectroscopy

$^1\text{H-NMR}$ spectra of SA and Na-PCMSA (\overline{DS} = 0.605) samples were taken in D_2O using Bruker 500 MHz

FT-NMR (Model: Advance - DPX500) in order to prove the introduction of Carboxymethyl groups in SA.

Thermo Gravimetric Analysis (TGA)

The thermal analysis of SA and Na-PCMSA (\overline{DS} = 0.605) samples was carried out in an inert atmosphere at a scan rate of 10°C/min with the help of the Mettler Toledo make thermogravimetric analyzer.

Differential Scanning Calorimetry (DSC)

The DSC analysis of SA and Na-PCMSA (\overline{DS} = 0.605) samples was carried out in an inert atmosphere at a scan rate of 10°C/min with the help of Mettler Toledo DSC 822 Differential Scanning Calorimeter.

Scanning Electron Microscopy

Model ESEM TMP+ EDAX, Philips make has been used to obtain the micrographs of SA and Na-PCMSA (\overline{DS} = 0.605) samples.

RESULTS AND DISCUSSION

Carboxymethylation is a well known derivatization process for polysaccharides, giving products in which the primary and/or secondary alcohol groups are etherified with carboxymethyl groups. Fig.2 represents the reaction scheme for the carboxymethylation of sodium alginate.

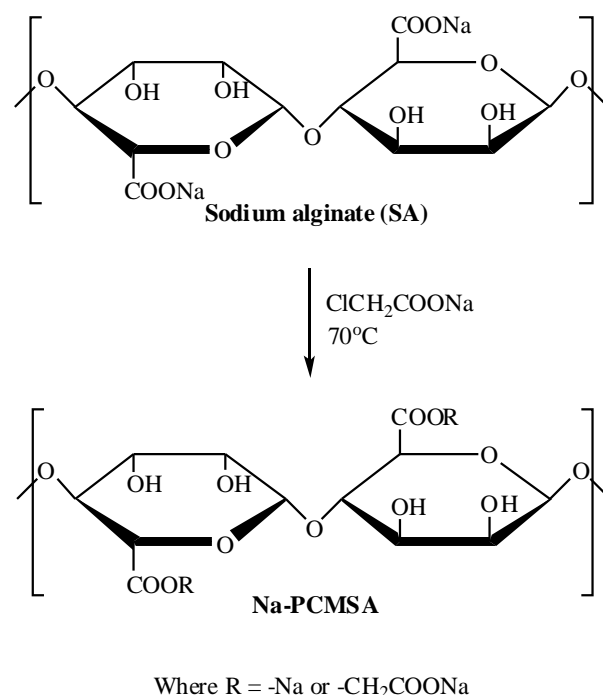
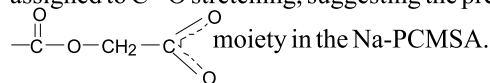


Fig.2: Reaction scheme for the synthesis of Sodium salt of Partially Carboxymethylated Sodium Alginate (Na-PCMSA).

FTIR Spectroscopy

The FTIR spectrum of SA is shown in Fig.3(a). The presence of a strong and broad absorption band at 3431 cm^{-1} is assigned to O-H stretching vibrations. The absorption band at $\sim 2933\text{ cm}^{-1}$ may be attributed to the -CH stretching. The peaks at around 1616 cm^{-1} and 1416 cm^{-1} , indicating the stretching vibrations of COO^- (asymmetric) and COO^- (symmetric) respectively. The C-O stretching is distributed in the absorptions at about 1126 cm^{-1} , 1093 cm^{-1} and 1030 cm^{-1} . All these absorption bands which have appeared in the figure are the characteristics of polysaccharide.

Fig. 3(b) represents the IR spectrum of Na-PCMSA (DS = 0.605). It is very interesting to note that the absorption peak at 1745 cm^{-1} is a strong one and is assigned to C=O stretching, suggesting the presence of



The presence of $-\text{COO}^-$ moiety present in Na-PCMSA is also evident from the absorption bands appeared at 1620 cm^{-1} and 1420 cm^{-1} [Fig. 3(b)]. However, interestingly the position and shape of that absorption bands are found to be somewhat different than those seen (for the same moiety which is also present) in the case of sodium alginate [Fig. 3(a)]. As expected the position and shape in the absorptions having contributions from $-\text{CO}$ stretching is also registered change in the Na-PCMSA.

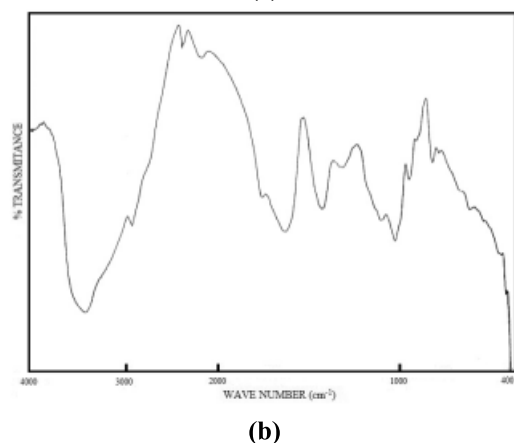
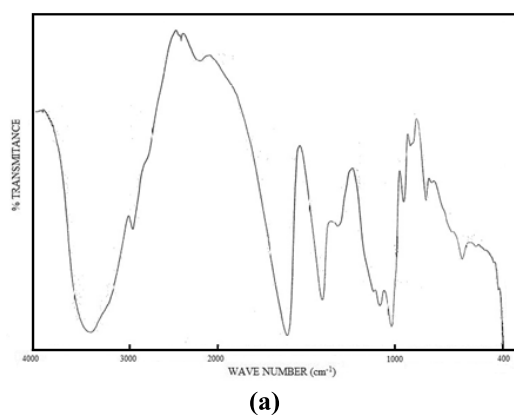


Fig.3: FTIR spectra of (a) Sodium Alginate (SA) and (b) Sodium salt of Partially Carboxymethylated Sodium Alginate, Na-PCMSA (DS = 0.605) samples.

$^1\text{H-NMR}$ spectroscopy

The $^1\text{H-NMR}$ spectrum of sodium alginate is shown in Fig. 4(a). As it can be seen from this figure that there is a signal at value of 5.04 ppm which is attributed to anomeric proton. The remaining protons (C-H) appear in the region 3.5-4.5 ppm. The -OH protons possibly are seen $\sim 4.81\text{ ppm} - 4.89\text{ ppm}$.

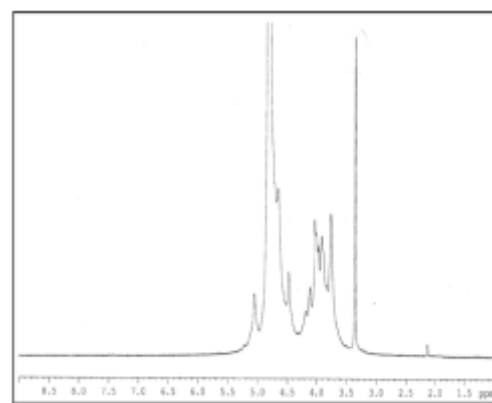
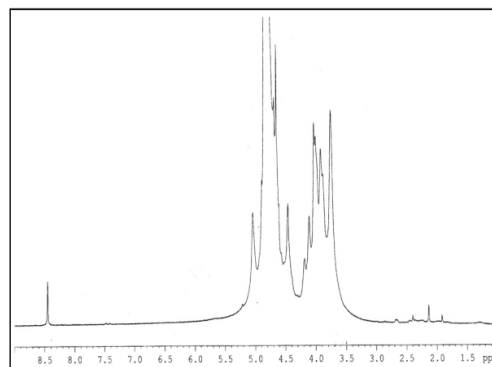


Fig.4: $^1\text{H-NMR}$ Spectra of (a) sodium alginate and (b) Sodium salt of Partially Carboxymethylated Sodium Alginate, Na-PCMSA (DS = 0.605) samples.)

Fig. 4(b) represents the $^1\text{H-NMR}$ spectrum of Na-PCMSA (DS = 0.605) which is practically similar to that of sodium alginate [cf. Fig. 4(a)] except that Na-PCMSA (DS = 0.605) has an additional resonance at 3.35 ppm [cf. Fig. 4(b)]. This additional peak is assigned to

CH_2 of $-\text{C}(=\text{O})-\text{O}-\text{CH}_2-\text{C}(\text{O})-$ moiety suggesting the formation of Na-PCMSA.

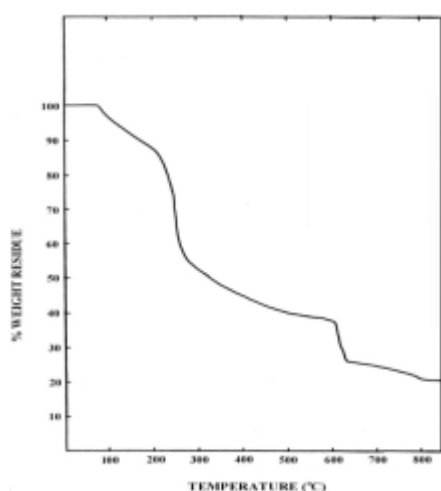
In conclusion, the appearance of the infrared absorption band at 1745 cm^{-1} and the proton NMR resonance at 3.35 ppm indicate beyond doubt about the introduction of carboxymethyl moiety in sodium alginate.

Thermal analysis

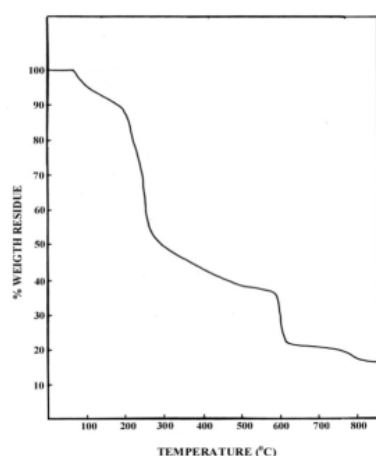
The thermal behaviour of SA and Na-PCMSA (DS = 0.605) samples is examined by a study of their

primary thermograms [Figs. 5 (a) and (b)]. In the samples, about 5-10% loss in weight was observed below 10°C. This was attributed to absorbed water and has not been taken into consideration while plotting the weight residue versus temperature curves.

Figs. 5(a) and 5(b) represent the primary thermograms for SA and Na-PCMSA ($\overline{DS} = 0.605$) samples respectively obtained at a scan rate of 10°C/min in nitrogen atmosphere. The overall degradation of SA [Fig. 5(a)] exhibits two distinct weight loss steps. The decomposition starts at 75°C and proceeds slowly up to 200°C. Beyond this temperature degradation proceeds at a faster rate up to 300°C and sample loses 35% of its original weight at this temperature. In the temperature range 300°C-550°C the sample degrades very slowly and loses 13.5% of its original weight. The second step of decomposition commences from 550°C and completes at 675°C and in this region the weight loss of about 14% is observed. The maximum rates of weight loss occur at 240°C and 620°C for first and second decomposition steps respectively. The overall degradation leaves about 20.5% residue.



(a)



(b)

Fig. 5: TG thermograms for (a) Sodium Alginate and (b) Na-PCMSA ($\overline{DS} = 0.605$) samples.

It can be further observed from the Fig. 5(b) that Na-PCMSA sample also involves two steps of degradation. The first step of degradation encompasses the temperature range from 70°C to 550°C, amounting to a loss of about 62.5 percent weight, exhibiting maximum rate of weight loss at 245°C. The second step of degradation exhibits the temperature range 550°C to 650°C involving about 16% weight loss with a maximum weight of loss occurs at 605°C. The sample leaves about 17% weight residue.

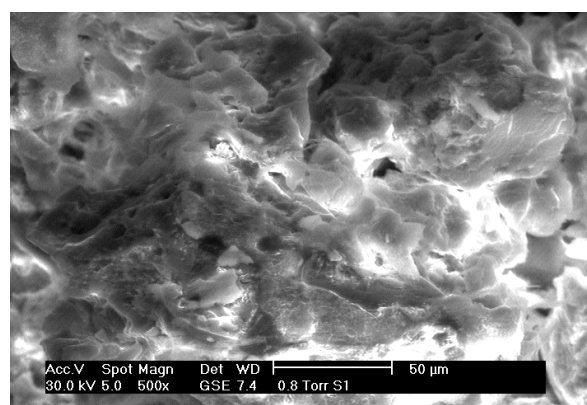
The values of the temperature characteristics derived from the corresponding thermograms [Figs. 5(a) and 5(b)] are presented in Table 1. The values of the transition data obtained from DSC scans (not shown) for both the samples are also reported in Table 1. The endothermic transitions appeared in the case of both the samples are due to moisture loss and the appearance of the two exothermic transitions is attributed to the decomposition of the respective samples.

Table 1: Thermal analysis of Sodium alginate and Sodium salt of Partially Carboxymethylated Sodium Alginate (Na-PCMSA, $\overline{DS} = 0.605$) samples.

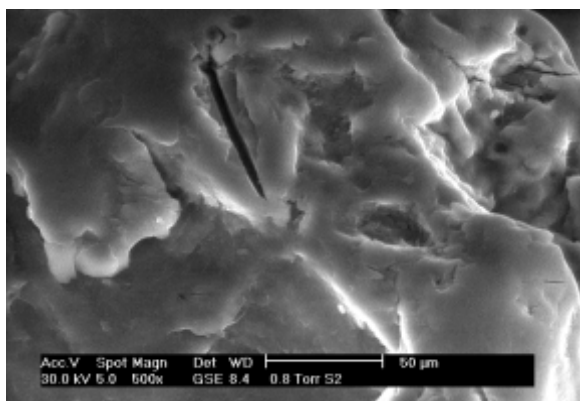
| Sample | T_i (°C) (IDT) | T_f (°C) (FDT) | T_{max} (°C) | | T_{10} (°C) | T_{50} (°C) | Transition Data from DSC | | |
|----------|---------------------|---------------------|----------------|--------|---------------|---------------|--------------------------|-----------------|-----------------|
| | | | Step 1 | Step 2 | | | T_1 (°C) | T_2 (°C) | T_3 (°C) |
| SA | 75 | 810 | 240 | 620 | 120 | 325 | 52.21 (endo) | 250.52 (exo) | 347.00 (exo) |
| Na-PCMSA | 70 | 810 | 245 | 605 | 175 | 295 | 52.90 (endo) | 257.33 (exo) | 349.50 (exo) |

Scanning Electron Microscopy (SEM)

Figs. 6(a) and 6(b) represent scanning electron micrographs obtained for SA and Na-PCMSA ($\overline{DS} = 0.605$) samples respectively. The micrograph of SA shows a rough surface with cavities. On the other hand upon carboxymethylation of SA, the morphology seems to be different indicating that the introduction of carboxymethyl groups in the sodium alginate moiety has taken place.



(a)



(b)

Fig. 6: Scanning Electron Micrographs of (a) Sodium Alginate and (b) Sodium salt of Partially Carboxymethylated Sodium Alginate, Na-PCMSA (DS = 0.605) samples (500X)

Conclusions

The carboxymethylation of sodium alginate was successfully carried out in order to synthesize Sodium salt of Partially Carboxymethylated Sodium alginate (Na-PCMSA) sample having $DS = 0.605$. The macromolecular characterization i.e. FTIR spectroscopy, 1H -NMR spectroscopy, thermal analysis and SEM proved that carboxymethylation did take place.

Acknowledgments

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REFERENCES

- [1] Singh, R. P., Nayak, B. R., Biswal, D. R., Tripathy, T. and Banik, K. (2003) Biobased polymeric flocculants for industrial effluent treatment. *Materials Research Innovations*, 7: 331-340.
- [2] Yuan, W., Yuan, J., Zhang, F. and Xie, X. (2007) Syntheses, characterization, and in vitro degradation of ethyl cellulose-graft-poly(epsilon-caprolactone)-block-poly(L-lactide) copolymers by sequential ring-opening polymerization. *Biomacromolecules*, 8: 1101-1108.
- [3] Qian, F., Cui, F., Ding, J., Tang, C. and Yin, C. (2006) Chitosan graft copolymer nanoparticles oral protein drug delivery: preparation and characterization. *Biomacromolecules*, 7: 2722-2727.
- [4] Trivedi, J. H. (2013) Synthesis, characterization, and swelling behavior of superabsorbent hydrogel from sodium salt of partially carboxymethylated tamarind kernel powder-g-PAN. *Journal of Applied Polymer Science*, 129: 1992-2003.
- [5] Trivedi, J. H., Jivani, J. R., Patel, K. H. and Trivedi, H. C. (2013) Modification of Sodium salt of Partially Carboxymethylated Tamarind Kernel Powder through Grafting with Acrylonitrile: Synthesis, Characterization and Swelling Behavior. *Chinese Journal of Polymer Science*, 31: 1670-1684.
- [6] Lin, H., Zhou, J., Yingde, C. and Gunasekaran, S. (2010) Synthesis, Characterization of pH- and Salt-Responsive Hydrogels Based on Etherified Sodium Alginate. *Journal of Applied Polymer Science*, 115: 3161-3167.
- [7] Shah, S. B., Ray, R., Patel, C. P. and Trivedi, H. C. (1994) Studies on Biodegradability of Sodium Alginate Graft Polyacrylonitrile. *Journal of Polymeric Materials*, 11: 85-88.
- [8] Pourjavadi, A., Zohuriaan-Mehr, M. J., Ghasempoori, S. N. and Hossienzadeh, H. (2007) Modified CMC. V. Synthesis and Super-Swelling Behavior of Hydrolyzed CMC-g-PAN Hydrogel. *Journal of Applied Polymer Science*, 103: 877-883.
- [9] Draget, K. I. (2009) Alginate, In: G.O. Philips, P. A. Williams Editions, *Handbook of Hydrocolloids*, 379.
- [10] Kamel, M., Abdel-Thalouth, I., Amer, M. A., Ragheb, A. and Nassar, S. H. (1992) Chemical Modification of Guar Gum Part I: Carboxymethylation in Aqueous Medium. *Starch/Strake*, 44: 433-437.
- [11] Ragheb, A. A., Kamel, M. Abdel-Thalouth, I. and Nassar, S. H. (1994) Chemical Modification of Guar Gum. Part 3: Carboxymethylation in non-Aqueous Medium. *Starch/Strake*, 46: 443-446.
- [12] Eyler, H. W., Klug, E. D. and Diephuis, F. (1947) Determination of Degree of Substitution of Sodium Carboxymethylcellulose. *Analytical Chemistry*, 19: 24-27.