



## Synthesis and Characterization of the thin films Containing Polyaniline - Carboxymethyl Cellulose Composites

A. M. Aboelkheir<sup>a</sup>, A. M. Abdelghany<sup>b\*</sup>, D. M. Ayaad<sup>a</sup>, M. Y. A. Abdelaal<sup>a</sup>



(a) Chemistry Department, Faculty of Science, Mansoura University, Mansoura, 35516, Egypt

(b) Spectroscopy Department, Physics Division, National Research Center, 33 Elbehouth st., 12311, Dokki, Giza, Egypt

### Abstract

Flexible polymer composite films comprising carboxymethyl cellulose (CMC), polyaniline (PANI) and silver nanoparticles (AgNps) were successfully fabricated through an in-situ polymerization method. The composite structure of the fabricated film was confirmed by X-ray diffraction and infrared spectroscopy, indicating the successful incorporation of AgNps into the CMC/PANI blend. The scanning electron microscope (SEM) images have indicated a homogenous loading and dispersion of AgNps into the CMC/PANI blend. The optical parameters such as band gap ( $E_g$ ) was determined using the UV optical absorbance. The inclusion of AgNps and PANI has enhanced the optical properties of the CMC polymer, providing a new composite suitable for energy conversion systems, solar cells, biosensors, and nonlinear optical applications. The electrical properties of the composites were examined using temperature-dependent DC conductivity within 293–373 °K. The composites with increasing AgNps in the PANI-CMC composites show the enhancement in the higher crystallinity, thermal stability, and higher electrical conductivity. The antimicrobial properties were evaluated with the aid of agar diffusion tests. The results showed distinct zones of inhibition against major microorganisms.

**Keywords:** Polyaniline; Nanocomposites; CMC; Solid-state polymerization; conducting polymer.

### 1. Introduction

In the industrial, research, and medical sectors, conductive polymers have a range of applications such as anticorrosion, static electromagnetic and coating shielding. Electric composites of the second generation have applications such as batteries for solar cells, transistors, LEDs, etc. In the engineering and science world, controlled low cost, conductivity, high-temperature resistance and ease of preparation make these materials attractive [1-2].

Polyaniline (PANI) is a traditional conducting polymer known for acid/base modification for its controllable conductivity, mechanical flexibility and environmental stability. It has potential applications such as electromagnetic shielding systems, lightweight battery electrodes, sensors, anti-corrosion coatings, etc. [1-6]. There is a significant opportunity for polymer composites such as PANI, whose electrical conductivity can be modified for the desired process and other characteristics are attractively

combined. Several novel techniques for the preparation of nanostructured PANI in the form of nanotubules, dispersions, nanofibers and nanowires have been developed over the past few years [7-9]

Thus, for many studies on conductive blends, the PANI and its composites have served as an impetus for obtaining a wide variety of conductivities that can be optimized for different potential applications provided the varied weight fractions of the conducting polymer (10-11). Thus, we can obtain new materials with improved processability and controllable conductivity by blending PANI with other polymers or fillers (12-14).

Because of their various applications in science and technology (15), nanocomposites of cellulose and its derivatives -based electrolytes (16) used in various fields due to it enhanced the mechanical properties (18). Because of its environmentally attractive sources and properties, cellulose, amongst other natural biopolymers, has gained a great deal of research interest in material science. The beneficial cellulose

\*Corresponding author e-mail: [a.m\\_abdelghany@yahoo.com](mailto:a.m_abdelghany@yahoo.com) (A.M. Abdelghany)

Receive Date: 12 June 2021, Revise Date: 26 July 2021, Accept Date: 28 July 2021

DOI: 10.21608/EJCHEM.2021.80402.3981

©2022 National Information and Documentation Center (NIDOC)

characteristics involve, for example, non-abrasive processing characteristics, renewability, high specific strength, biocompatibility, biodegradability and abundance. Additionally, recent developments are more based on investigating the relation between properties, performance and modification of these products that are derived from cellulose for various numerous applications that result in reduced the use of chemicals. Among cellulosic ethers, since they have high solubility, good chemical resistance and toxicologically hazardous, CMCs are very essential cellulose derivatives. CMC is a cellulose anionic carboxymethyl ether obtained by the alkali catalyzed chloroacetic acid cellulose reaction that has been widely used in various fields as a thickening and stabilizing agent. The polar carboxyl group's added to make the cellulose highly hydrophilic, soluble and chemically reactive, while it can sustain the tasteless, non-toxic, and biodegradable properties of cellulose. Thus, by its grafting modification <sup>(19)</sup>, CMC is beneficial in manufacturing eco-friendly polymer products and its application in superabsorbent fields is attractive and promising.

It is in this regard that we have synthesized new polymer composites containing PANI-CMC composites using different weight percentages of PANI to explore polymers with precisely defined molecular structures and to further explore composition relationships. The crystallinity and structural properties of the polymer composites films were studied by X-ray diffraction (XRD) patterns and Fourier transform infrared spectroscopy (FTIR).

The surface morphology was indicated by scanning electron microscopy (SEM). The temperature dependence of the composites' DC conductivity was determined in the 300-500 K temperature range. Characterization and conductivity studies indicate that the composites of PANI-CMC can be usefully used as a biodegradable polymer composite in various applications.

## 2. Experimental

### 2.1. Materials

Aniline sulfate was purchased from Alfa Aesar, Mwt =284.34, ammonium peroxydisulfate (APS) was obtained from Riedel-deHaen, Mwt =228.2, Carboxymethyl cellulose (CMC) was purchased from Sigma-Aldrich, Mwt = 90.000. All solutions were synthesized via deionized water in aqueous media.

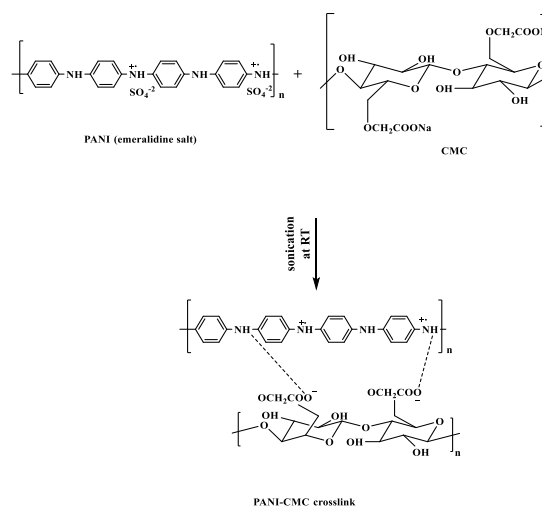
## 2.2. Experimental methods

### Synthesis of PANI-CMC composite films

At room temperature, all films were synthesized through the in-situ polymerization method. 0.5g of (C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>).H<sub>2</sub>SO<sub>4</sub> (aniline sulphate), 0.2g of an oxidizing agent (ammonium peroxydisulfate) and 0.5g of CMC were mixed. The mixture was ground until it turns from white to a dark green color. For this purpose, PANI-CMC composites were synthesized in the distilled water. During polymerization, 0.5g of CMC was added to the homogenous mixture gradually with continuous stirring. Distilled water and methanol were used to remove unreacted chemicals. After washing, the thin films were dried in an oven at 500C for 2 days. The mentioned preparation technique was repeated with various concentrations of aniline sulphate and APS as shown in table. I.

**Table. I.** The composition of PANI-CMC composites

| Samp les       | Aniline sulphate (g) | Ammonium Peroxysulphate (APS) (g) | Carboxymethyl cellulose sodium salt (NaCMC) (g) | (APS) concentration percent (W/W)% |
|----------------|----------------------|-----------------------------------|---|------------------------------------|
| S <sub>1</sub> | 0.5                  | 0.2                               | 1   | 11.7                               |
| S <sub>2</sub> | 0.25                 | 0.1                               | 1   | 7.40                               |
| S <sub>3</sub> | 0.125                | 0.05                              | 1   | 4.2                                |
| S <sub>4</sub> | 0.1                  | 0.04                              | 1   | 3.5                                |
| S <sub>5</sub> | 0.05                 | 0.02                              | 1   | 1.8                                |



**Figure 1** the mechanism of the interaction between PANI -CMC composites

### 2.3. Testing and analysis

#### Fourier transform infrared (FTIR)

FTIR spectra were recorded using the Thermo Scientific Nicolet iS10, USA FTIR spectrometer in a wavelength range of 400 to 4000  $\text{cm}^{-1}$  in an  $\text{H}_2\text{O}$ -purged environment with a mercury cadmium telluride detector.

#### X-ray diffraction analysis

The typical parameters used were 32 scans with a resolution of 2  $\text{cm}^{-1}$ . X-ray diffraction (XRD) spectrum was indicated using DIANO corporation-USA equipped with  $\text{Cu-K}\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ , 15 kV within the Bragg's angle ( $2\theta$ ) in the range of 5–80°.

#### Ultraviolet/visible (UV/Vis)

Ultraviolet/visible (UV/Vis) absorption spectra were measured by using the spectrophotometer (V-570 UV/Vis-NIR, JASCO, Japan) in the wavelength region of 190–1100 nm.

#### Morphological study

Morphological characterization was visualized via energy-dispersive spectroscopy (SEM/EDX) (SEM-JEOL JSM 6510 LV, USA).

#### E. DC conductivity

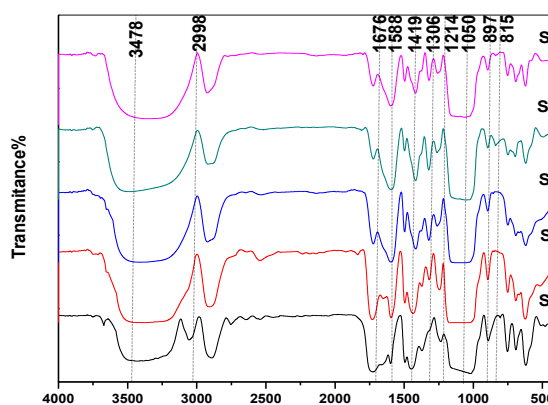
The electrical conductivity was determined using autoranging millimeter (METRISO 5000A, USA) of accuracy  $\pm 0.5\%$ .

## 3. Results and discussion

### 3.1. FTIR spectra of PANI-CMC nanocomposites

Figure 2 indicated the presence of small-shift characteristic bands of both PANI and CMC, thus confirming the association of PANI with CMC during the composite formation. Hydrogen bonding between the PANI dopant ions and the CMC polar molecules is the main force for this interaction. This mechanism of interaction has been schematically described in Figure 1. The corresponding bands indicated at 1588, 1410, 1306, 1214, 1050 and 897 respectively for the polyaniline salt. The band observed at 3478  $\text{cm}^{-1}$  and 2998  $\text{cm}^{-1}$  respectively is due to -OH stretching, N-H stretching vibration of composite compounds and -CH stretching. The PANI N-H band at 3478  $\text{cm}^{-1}$  in the composite showed a weak interaction between the PANI NH and the composite CMC carboxylic group.

The bands at 1588  $\text{cm}^{-1}$  and 1410  $\text{cm}^{-1}$  can be assigned to C=N stretching vibration of quinoid ring C=C stretching vibration of benzenoid ring modes, respectively. The formation of the polymer composites is further indicated by the difference in depth of characteristic PANI bands in the composite, a decrease in depth of 1214  $\text{cm}^{-1}$  band and an increase in depth of 1306  $\text{cm}^{-1}$ . The bands at 1050  $\text{cm}^{-1}$ , attributed to a protonated conducting vibration mode ( $-\text{NH}\bullet+\text{=}$ ) structure in the PANI spectrum are overlapped by the strong CMC absorption bands. In the spectrum, the band of out-of-plane deformation of C-H on a 1,4-disubstituted ring at 803.73  $\text{cm}^{-1}$  is also well observed. This indicates an increase in the electron density ( $\pi$ -electron delocalization) of PANI chains, contributed to an increase in the composite conductivity.

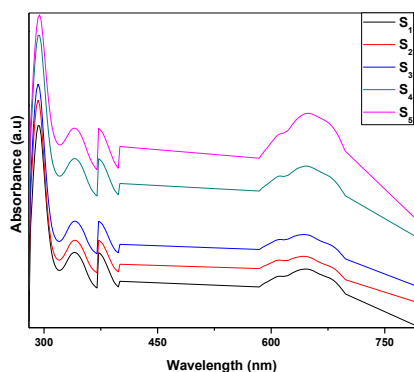


**Figure 2** FTIR spectra of PANI-CMC composites

### 3.2. UV. Visible spectroscopy

Figure 3 showed three specific bands of PANI, one of which was attributed to  $\pi-\pi^*$  at 340 nm in the benzenoid units. The second peak at 372 nm was related to the excitation of polaron- $\pi^*$  transitions in quinoid units. The third peak at 642 nm was due to the excitation transitions in quinoid units in the extended tail of the polymer chains. The spectra of PANI-CMC composites display a sharp peak at 292 nm attributed to anilinium cation, which becomes sharper as PANI decreases, whereas the other peak at 600–640 nm appears to be sharper but is essentially unchanged. The absorption peak of the CMC is about 292 nm, with sharpening at 320–330 nm, which may be a combination of PANI and CMC peak. The peak at maximum absorption shifted to a higher wavelength as the percentage of PANI in the CMC matrix decreased. It indicated that the binding energy is decreasing and charge delocalization is becoming easier. The neutral polymer backbone is used during the doping process.

Electrons can pass through conduction bands after converting to a charged-conjugated system. The polaron and bipolaron band transitions were previously thought to be responsible for the sharp band peak at 372 nm (a characteristic of protonated PANI). As a result, it is verified that the protonated form of PANI is present in all composites studied. The results are confirmed with that obtained from FTIR analysis.



**Figure 3** UV-Vis spectra for PANI-CMC composites.

### 3.3. DC conductivity

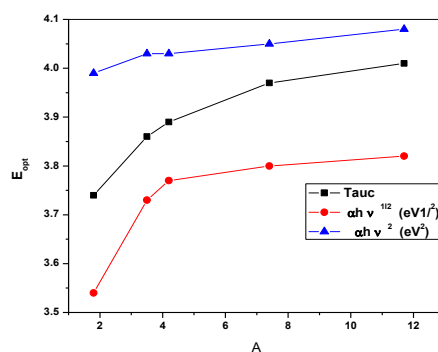
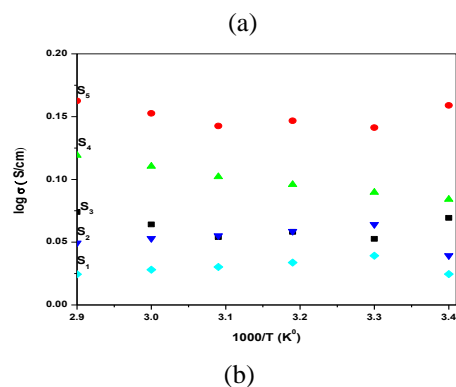
Figure 4 (a) indicated DC conductivity for PANI-CMC composite thin films in the room temperature range 293 to 373 OK. The electrical conductivities of thin films at 373 OK were 0.05, 0.11, 0.46 and 0.64 S/cm, respectively.

This means that the electrical conductivity of thin films was prepared with various amount of PANI dopant indicated the same trend regardless of temperature, in which the conductivity of the resulting thin films increased with decreasing PANI concentration. By decreasing the concentration of PANI, the mobility of ions increased and the thickness (D) of the resulting film decreased. The resistance is inversely proportional to the thickness. The results confirmed that the resistance of the composites increased with decreasing the concentration of PANI as well as the optical band gap decreased as shown in figure 4 (b). The results also confirmed by SEM images. The average grain size of the thin films decreased and this confirmed by decreasing the sharpness of the XRD peaks.

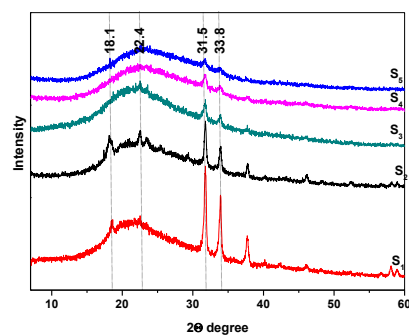
### 3.4. X-ray diffraction (XRD)

The characteristic semi-crystalline structure in PANI was assigned to the diffraction peaks at  $2\theta = 31.5^\circ$  and  $33.8^\circ$ . The periodicity parallel and

perpendicular to polyaniline chains is indicated by the peaks  $2\theta = 33.8^\circ$ . The CMC structure had broad peaks at  $2\theta = 18.1^\circ$  and  $22.4^\circ$ . Because of the structural ordering of PANI in the CMC matrix, the intensity of the PANI diffraction peak in PANI-CMC composites was significantly reduced, as shown in figure 5. The intensity of the diffraction peak was reduced by lowering the PANI concentration in the composites. The uniform dissolving of PANI in the CMC matrix improved  $\pi$ -electron delocalization of the composites during the formation of PANI-CMC composites in the aqueous medium.



**Figure 4** (a) DC conductivity (b) optical energy gap of PANI-CMC composite

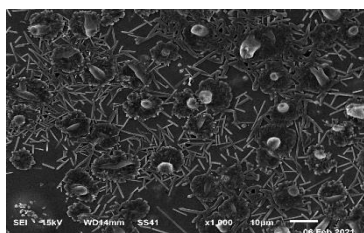


**Figure 5** XRD spectra of PANI-CMC composites.

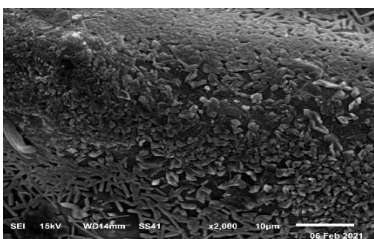
### 3.5. Microstructure of the prepared polymers

Figure 6 indicated that the morphology of the composite films is dependent on the PANI content. By decreasing the PANI content the films seem to become more impregnated into the hydrogel matrix. Thus it can be observed that the CMC surface had a hydrophilic nature that enabled the formation of a uniform dispersion of the hydrophobic PANI clusters. The surface of S5 revealed a well-arranged, smoother and more compacted structure than S1. SEM images indicated the enhancement of the mechanical properties of the polymer composites.

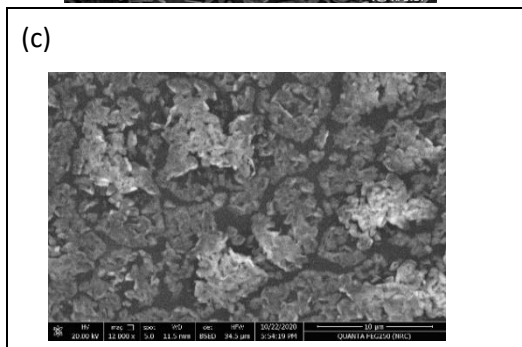
(a)



(b)



(c)



**Figure 6** SEM analysis of (a) S1, (b) S3 and (c) S5 polymer composites

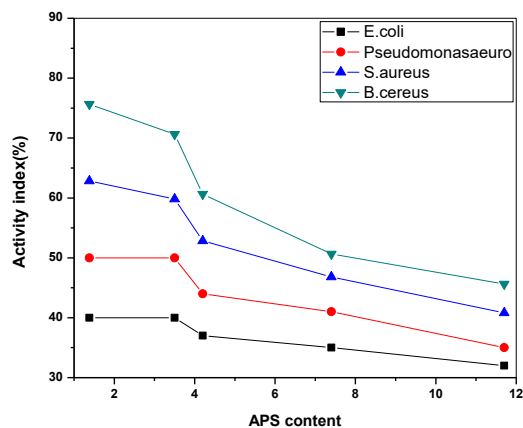
### 3.6. Antimicrobial activity

Figure 7 showed the effects of the PANI-CMC composites on the antimicrobial properties. All the samples had a higher degree of antimicrobial suppression due to the formation of amides from the condensation of carboxylic acid groups of CMC with PANI amino groups as observed in table II. The higher antimicrobial activity of PANI-CMC composites may be due to the highly positive electrostatic interactions

between the charged molecule and the cell surface that had been negatively charged. Strains of bacteria including *E. coli* that have an extracellular capsule, contain a less negative charge and are less susceptible to adsorption by the PANI-CMC composites surface, which is positively charged.

**Table II** Antibacterial activity tests of PANI-CMC composites against different types of bacteria.

| NO. | Sample         | <i>E. coli</i> |       | <i>Pseudomonas aeruginosa</i> |       | <i>S. aureus</i> |       | <i>B. cereus</i> |       |
|-----|----------------|----------------|-------|-------------------------------|-------|------------------|-------|------------------|-------|
|     |                | (mg/ml)        |       |                               |       |                  |       |                  |       |
|     |                | D (mm)         | A (%) | D (mm)                        | A (%) | D (mm)           | A (%) | D (mm)           | A (%) |
| 1   | S <sub>1</sub> | 12             | 32    | 12                            | 35    | 11               | 34    | 11               | 55    |
| 2   | S <sub>2</sub> | 13             | 35    | 14                            | 41    | 13               | 40    | 12               | 60    |
| 3   | S <sub>3</sub> | 14             | 37    | 15                            | 44    | 15               | 46    | 14               | 70    |
| 4   | S <sub>4</sub> | 15             | 40    | 17                            | 50    | 17               | 53    | 16               | 80    |
| 5   | S <sub>5</sub> | 15             | 40    | 17                            | 50    | 18               | 56    | 17               | 85    |
|     | Ciprofloxacin  | 37             | 100   | 34                            | 100   | 32               | 100   | 20               | 100   |



**Figure 7** antimicrobial activity of PANI-CMC composites.

### 4. Conclusion

PANI-CMC polymer composites were prepared through in-situ polymerization method, and their electrical properties, surface morphology, thermal behavior and spectral characterization were investigated. The incorporation of conducting PANI into biopolymer CMC improved processability and the achievement under readily accessible conditions of the necessary properties, such as surface morphology and thermal stability. Morphological analysis showed that the CMC forms a network of PANI particle. The surface modification and improved electrical conductors of the PANI-CMC composites are likely to be caused by such a network. The XRD patterns

demonstrated that the PANI-CMC composites are given an amorphous nature by CMC. By decreasing PANI concentration in the polymer composites, the electrical conductivity of the composites increased; this could be due to an increase in the mobility of the charge carriers. The present research on PANI-CMC composite preparation is eco-friendly and cost-effective. In various fields, such as photovoltaic devices, fuel cells, nanoelectronics, and sensors, these hybrid composites can find potential applications.

## 5. References

1. Moraes, S. R. and A. J. Motheo. "PANI-CMC: preparation, characterization and application to corrosion protection", *Molecular Crystals and Liquid Crystals*, Vol. 448, pp. 261-863 (2006).
2. Fahmy, Y., Fahmy, T. Y. A., and Mobarak, F., Agricultural residues (wastes) For manufacture of paper, board, and miscellaneous products: Background overview and future prospects. *International Journal of ChemTech Research*, 10, 424-448(2017). doi:10.5539/ibr.v10n8p31
3. El-Sayed, N. S., Moussa, M.A., Kamel, S. and Turky, G. "Development of electrical conducting nanocomposite based on carboxymethyl cellulose hydrogel/silver nanoparticles@ polypyrrole", *Synthetic Metals*, Vol. 250, pp. 104-114 (2019).
4. Tanzifi, M., Yarak, M. T., Karami, M., Karimi, S., Kiadehi, A. D., Karimipour, K. and Wang, S. "Modelling of dye adsorption from aqueous solution on polyaniline/carboxymethyl cellulose/TiO<sub>2</sub> nanocomposites", *Journal of colloid and interface science*, 519, pp. 154-173 (2018).
5. Gautam, V., Singh, K. B. and Yadav, V.L. "Preparation and characterization of green-nanocomposite material based on polyaniline, multiwalled carbon nano tubes and carboxymethyl cellulose: for electrochemical sensor applications, *Carbohydrate polymers*, Vol. 189, pp. 218-228 (2018).
6. Ahmed, H., Khattab, T. A., Mashaly, H. M. El-Halwagy, A. A. and Rehan, M. "Plasma activation toward multi-stimuli responsive cotton fabric via in situ development of polyaniline derivatives and silver nanoparticles". *Cellulose*, Vol. 5, pp 2913-2926 (2020).
7. Li, J., Fang, W. R., Tait, L., Sun, L. and Zhao, L.Q., "Preparation of conductive composite hydrogels from carboxymethyl cellulose and polyaniline with a nontoxic crosslinking agent", *Rsc Advances*, Vol. 86, pp. 54823-54828 (2017).
8. Basavaraja, C., Kim, J. K., Thinh, P. X. and Huh, D. S. "Characterization and DC electrical conductivity of the composite films containing polyaniline-carboxymethyl cellulose" *Polymer composites*, Vol. 9, pp. 1541-1548 (2012).
9. Fahmy, Y., Fahmy, T. Y., Mobarak, F., El-Sakhawy, M., and Fadl, M. Agricultural residues (wastes) for manufacture of paper, board, and miscellaneous products: Background overview and future prospects. *International Journal of ChemTech Research*, 10(2), 424-448 (2017). DOI:10.5281/zenodo.546735.
10. Fahmy, Y. E. H. I. A., and Mansour, O. L. F. A. T. On Carboxymethylation of cellulose. I. Dissolving carboxymethylation and analysis of the all-over dissolution rate. *Indian Pulp and Paper*, 20(9), 535-40 (1966).
11. Fahmy, Y., and Mansour, O. On Carboxymethylation of cellulose. III. Influence of type of alkali cellulose, average degree of polymerization and temperature on the reaction rate. *Indian Pulp and Paper* 21(7):449, 451-3, 455 (1967).
12. Fahmy, Y., and Mansour O. On Carboxymethylation of cellulose. IV. Rheological and filtering properties of CMC solutions. *Indian Pulp and Paper*, 21(10), 627-31, 634-5, 639 (1967).
13. Nagaty, A., Mansour, O. Y., and Fahmy, Y. A. Carboxymethylation of Cellulose Acetate, 27(2), 68-70 (1973). <https://doi.org/10.1515/hfsg.1973.27.2.68>