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THE CHEMO-ENZYMATIC MODIFICATION OF CARBOXYMETHYL CELLULOSE AND ANTIOXIDANT ACTIVITY EVALUATION

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INRODUCTION

Carboxymethyl cellulose (CMC) has been allowed to be used as an additive in many kinds of food because of its security, hydrophilicity, gelling and film forming properties **[1]**. Laccases (EC 1.10.3.2) belong to the blue-copper family of oxidases. Laccases can monoelectronically oxidize suitable substrates, such as lignin, phenols, and aromatic or aliphatic amines, to the corresponding radicals in the presence of molecular oxygen (O2), can also be oxidized using a mediator together with a laccase **[2]**. Mediators usually have a low molecular weight and act as an electron shuttle. The TEMPO/laccase/O2 oxidation system was first applied to low-molecular-weight alcohols and sugars to prepare the corresponding oxidized compounds containing carboxyls, ketones, and aldehydes **[3]**.

In this study, we determine the optimum oxidation conditions to prepare oxidized Carboxymethylcellulose with high C6-carboxylate contents using the TEMPO/laccase/O2 system at room temperature in water under neutral conditions.

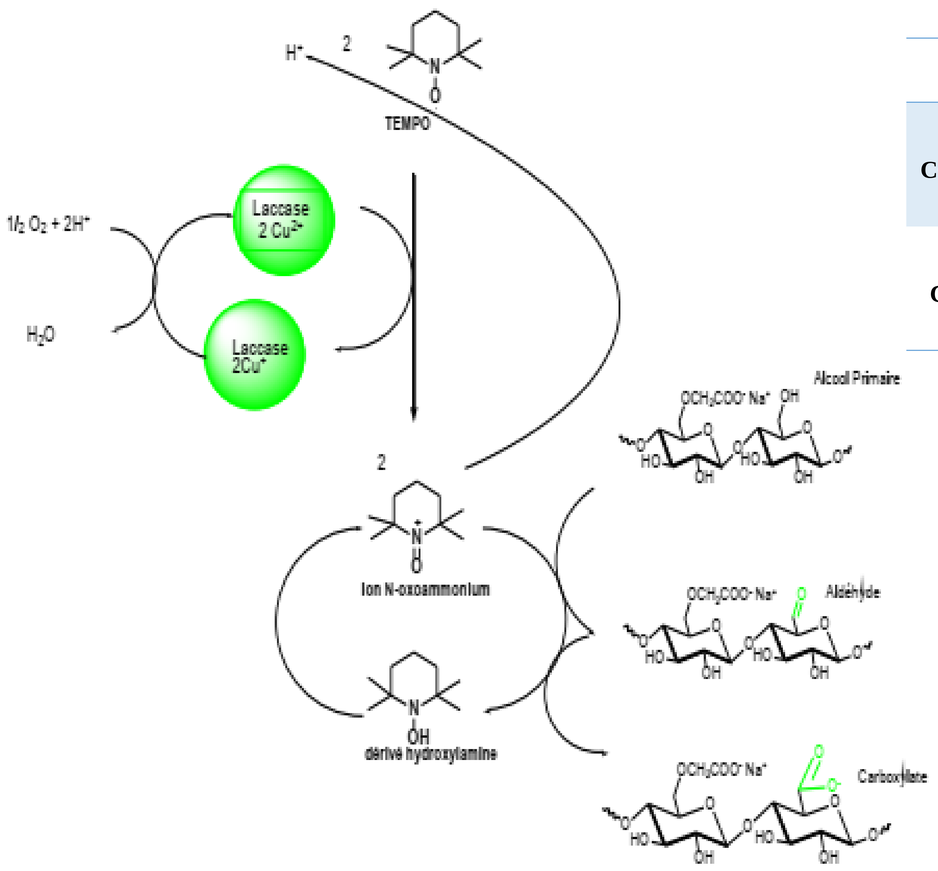


Figure 1: proposed catalytic oxidation reaction of CMC by the TEMPO/Laccase/O2 system at pH=4.5 in aqueous medium **[4]**.

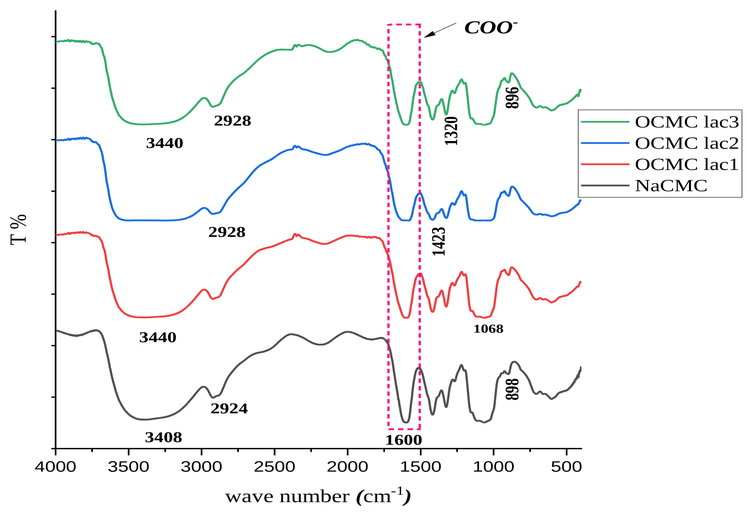


Figure 2 : IR-TF spectrum of Na CMC and oxidized CMC.

Table 1: contents of aldehyde and carboxyl groups in oxidized CMCs.

Compound	CMC	$OCMC_{lac1}$	$OCMC_{lac2}$	$OCMC_{lac3}$
COOH(meq/g)	3,39	0,92	1,02	1,17
COH(meq/g)		16,88	8,22	3,8

RESULTS AND DISCUSSION

In the TEMPO/laccase/O2 oxidation system, laccase oxidizes both TEMPO and *N*-hydroxyl-TEMPO (reduced TEMPO) to the *N*-oxoammonium compound ($TEMPO^+$), which can in turn oxidize primary hydroxyl groups to aldehyde and carboxyl groups. However, under the experimental conditions, $TEMPO^+$ molecules accumulate in the buffer solution, because the oxidation of TEMPO proceeds in the presence of laccase and O_2.

After oxidation, we observe the intensification of some peaks compared to the spectrum of the unoxidized compound. Moreover, we found that the peak of the band at 3408 cm^{-1} (OH elongation vibrations) is shifted to about 3431cm^{-1} while the strong absorption at 1600cm^{-1} in the oxidized sample is due to the carboxylate groups in their sodium salt form **[5]**.

As demonstrated in SEM images the CMC particles that are spherical shaped with different diameters in a very wide range (between 100 nm and 10µm) were obtained. The particles were not filtrated before imaging to acquire the true information about the CMC particles.

the scavenging evaluation against hydrogen peroxide with ascorbic acid as a positive control had shown that our products exhibited a good antioxidant behavior. In the interval of 0.05–5.0 mg/mL, the scavenging rate of CMCox is ranged from 12,03% to 88,37% and the IC_{50} value for eliminating hydrogen peroxide was disclosed to be 2,09mg/mL **[6]**.

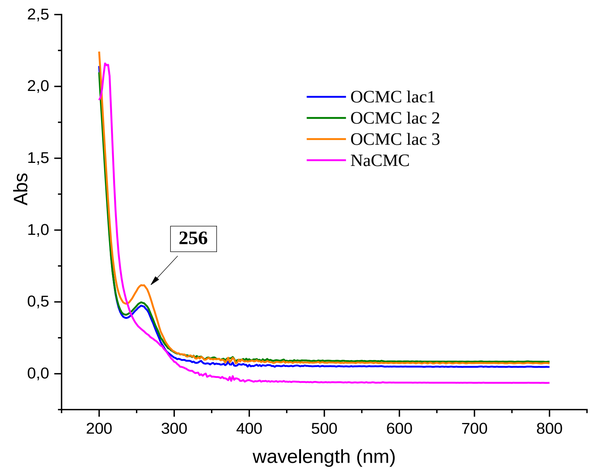
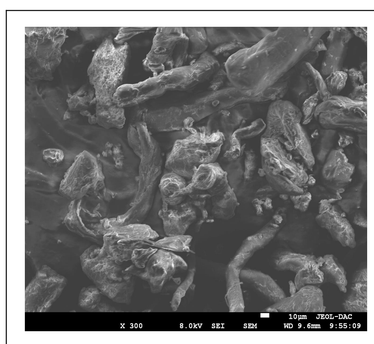


Figure 3 : UV-Vis spectrum of NaCMC and oxidized CMC



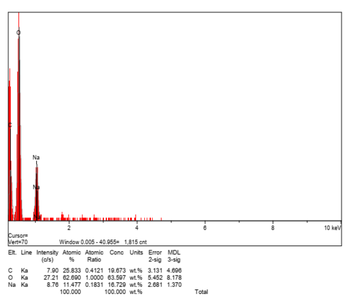
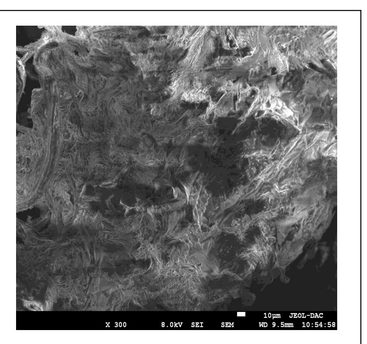


Figure 4 : SEM graph and EDX distributions of NaCMC.



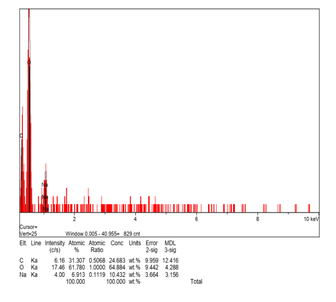


Figure 5 : SEM graphs and EDX distributionsof oxidized CMC.

Table. 2: IC50 values (mg/mL) of the studied materials.

compounds	IC_{50} (mg/mL)
OCMC lac 3	**2,09**
Ascorbic acid	**1,112**

CONCLUSION

In this work the film based on carboxymethyl cellulose was modified by the TEMPO-laccase redox system. The antioxidant, structural and morphological characteristics of films were investigated. The infrared spectroscopy analysis allowed to identify the newly formed functional groups through the positions and intensities of the different absorption bands present on the different measured spectra. The oxidation by the TEMPO/Laccase system induces the amplification of some peaks compared to the spectrum of the non-oxidized compound. According to antioxidant results, the CMCs have a free radical scavenging effect produced by the method using hydrogen peroxide; H_2O_2, but this action is inferior to that of the standard, Ascorbic acid. This new product can be used in many applications in the fields of drug delivery, biomedical imaging, cancer therapy, and chemical sensing

References

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