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MOLECULAR STRUCTURE AND OPTICAL ATTRIBUTES OF (Na-CMC/SA) NATURAL POLYMER BLEND

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ABSTRACT. Biopolymers are referred to the bio-degradable polymer that is derived from living organisms in nature or synthesized from renewable materials but needs polymerization. There are consisting of monomeric units that bond together through a covalent bond to obtain large molecules. A biopolymeric blend of sodium carboxymethyl cellulose/sodium alginate (Na-CMC/SA) film was prepared by the casting/solvent evaporation method. In addition to the molecular structure, the optical and molecular geometry of the collected films were characterized. XRD of binary blend investigated the interaction and miscibility among two biopolymers. FTIR of the blend spectrum explicated the conferring of the two polymer group's vibrations. UV/Vis and optical studies appeared a peak in the binary at the wavelength (227 nm) which explained the high combination between two polymers. Molecular geometry clarifies the assignment of vibrational spectra of pure polymers which implied the important role of the (C=O) group as eventful regions for the two polymers.

KEY WORDS: Sodium carboxymethyl cellulose, Sodium alginate, Na-CMC/SA, FTIR, XRD, UV/Vis

INTRODUCTION

Casting solution is applied to develop membranes by casting technique. The principal components of the solution system are polymer, solvent, and diverse additives can be also appended. The proper choice of the polymer must be soluble in the selected solvent which is strictly related to the final membrane application. Even the selection of the solvent is based on specific prerequisites but is not arbitrary. Various modifiers in the casting solution allow adjusting film properties based on the final film performances and utilization, although the lowest concentrations of used additives [1].

Sodium carboxymethyl cellulose is advertised as odorless and tasteless fibrous or granules powder with hygroscopic properties that are white, slightly yellowish, or greyish (off-white). It is practically insolvable in ethanol but easy to be dissolved in hot or cold water which yielded with water a viscous colloidal solution. Na-CMC has received more attention owing to its low price (abundance), aptitude to form membranes, better biocompatibility, super water solubility, and swell susceptibility [2-4].

Sodium alginate has many attractive physical and biological properties, such as low price compared to natural casings, linear, hydrophilic, high availability, solubility in water, moisture reservation, excellent biocompatibility, perishable, and higher viscosity. Alginates have favorable film-forming properties the thin layer in the alginate solution can eliminate the thin film of moisture by evaporation and is impermeable to oil and fat but can help them to redissolve in water-by-water vapor. The biocompatibility of sodium alginate has been evaluated broadly in vivo and in vitro which depends upon the alginate composition and purity level [4-7].

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Although sodium carboxymethyl cellulose is high solubility, and good physiochemical and biological properties, it needs adding another polymer to enhance its mechanical and morphological properties. So, blended two polymers with each other or more promote featured properties from the interaction with another polymer.

Lee *et al.* [8], encapsulated curcumin to sodium alginate/carboxymethyl cellulose blend as an upgraded drug-carrying system. The upgraded system is characterized by (FT-IR), (SEM), and (XRD) which exhibited the compatible interaction between curcumin and biopolymer. They concluded that the percentage of curcumin release increased with increasing carrier concentration. Nwabor *et al.* [9], encapsulated Crude ethanolic with sodium alginate–sodium carboxymethyl cellulose (CMC) for the food system and biomedical application. They characterized the matrix by morphology, micromeritics properties, particle size, physicochemical parameters, and antimicrobial activity testing. These tests appeared good encapsulant properties that kept bioactive extract. Da Silva Júnior *et al.* [10], an integrated polymeric blend of sodium carboxymethyl cellulose and sodium alginate comprised carbon dots as a stable eco-friendly membrane. They characterized the matrix by transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transforms infrared spectrophotometer (FTIR), mechanical tests, and other tests. Therefore, these tests appeared to have good completion of the synthesized membranes due to the residence of polymers. Mohamad *et al.* [11], developed a hydrogel (Na-CMC/SA) as a wound bandage. They resulted in the clear homogeneity of the hydrogel formulation. So, this hydrogel is utilized for highly suppurating wounds due to its traits. Salama *et al.* [12], prepared a ternary system of carboxymethyl cellulose/sodium alginate/chitosan biguanidine hydrochloride as an edible film. Prepared films confirmed by using FTIR, XRD, TGA, WVP, mechanical, and antibacterial properties which showed some changes in structures, mechanical and antibacterial properties improvement of studied films after adding chitosan biguanidine hydrochloride. Hameed *et al.* [13], prepared copper oxide nanoparticles (CuO NPs) loaded with carboxymethyl cellulose and sodium alginate matrix (CMC/PEO). They are characterized by using XRD, SEM, and UV-Vis which appeared significant changes upon the addition of CuO NPs, especially in the energy gap which shifts toward lower frequency. Also electrical and dielectric analysis enriched after adding different content of CuO NPs. So, this study showed that nanocomposite membranes are optimistic for supercapacitors applications.

This study was aimed to prepare a biopolymer blend and to investigate the characterization, and evaluation of the structural changes of the prepared system as molecular structure and optical properties.

EXPERIMENTAL

Materials

Sodium carboxymethyl cellulose rendered about (99.5%) of the purity percentage, solid physical state, and white powder color. From a (German Company, Engineering Chemistry), and (Carlroth Co.) were attained sodium carboxymethyl cellulose (Na-CMC) and sodium alginate (SA) respectively.

Binary blend preparation

Each of the (Na-CMC) and (SA) virgin polymers liquefy by stirring in (50 mL) of distilled water. Then polymer solutions were blended, stirred for one hour, cast on Petri plates, and incubated at 50-degree Celsius for several days. The preparation process showed in Figure 1.

Characterization of studied samples

XRD verified information about the nature (crystal/amorphous) lattice arrangement which appeared for pure polymers and the binary blend was executed adopting a (PANalytical X'Pert

Pro XRD). IR absorption bands position alteration was inspected by adopting a (Nicolet™ iS™ 10 FTIR Spectrometer). Samples' optical characteristics were ascertained by adopting the (Jasco Inc. UV/Vis-spectrometer V-570). The computed (HOMO) and (LUMO) orbitals of the samples were secured from the (Gaussian program).

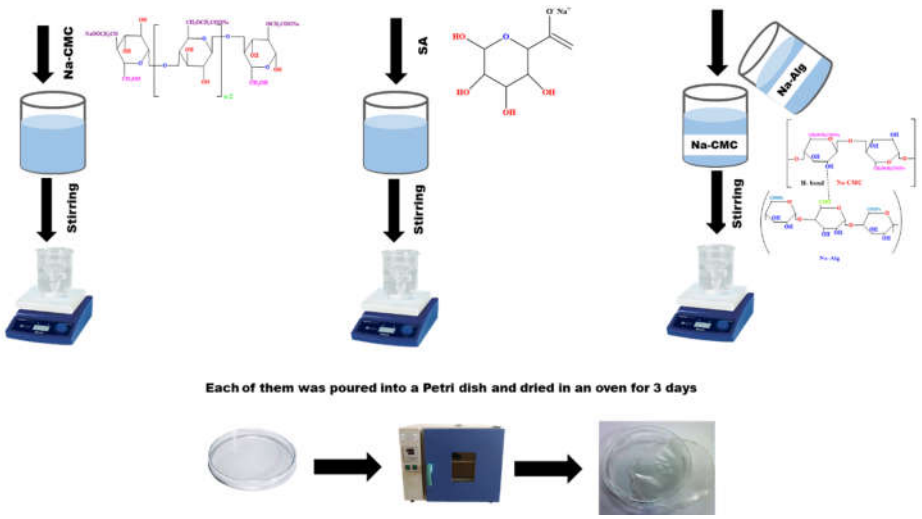


Figure 1. Flow chart of the sample preparation by standard solution cast technique and flexibility of the blend polymer films: Preparation of single films and binary films.

RESULTS AND DISCUSSION

XRD scans

X-ray patterns of virgin polymers (Na-CMC and SA), and binary blend film (Na-CMC/SA) are displayed in Figure 2. Each of the biopolymers could have its crystal domain in their thin films that indicate the reflection images of the non-crystalline feature. An immense peak at an angle (22°) exhibited and indicated the amorphous structure of the Na-CMC spectra spectrum [4, 13, 14, 15, 16]. An amorphous feature at an angle (21°) manifested the SA pattern [4, 17]. The blend manifests the immense band at $2\theta = 21.6°$ that is allocated to the amorphous aura of the two virgin polymers [4, 18]. Finally indicate from the blending the amorphous polymers have a flexible polymeric backbone and investigate the interaction and miscibility among two biopolymers.

FTIR analysis

Figure 3 displays the FT-IR spectra of virgin polymers and polymer blends. The collected fingerprint groups of the samples are recorded in Table 1 [2, 19, 20, 21]. The creation of the hydrogen bond between the two virgin polymers is implied by the linking between the hydroxyl groups of two polymers, as shown in Sketch 1. Succeed by the disappearance C-H stretching peak and the sharpness of the asymmetric (COO^{-}) stretching vibration due to the SA component in the blend matrix [7, 21, 22]. The polymer blend spectrum elucidated the contribution of the virgin polymer group's vibrations.

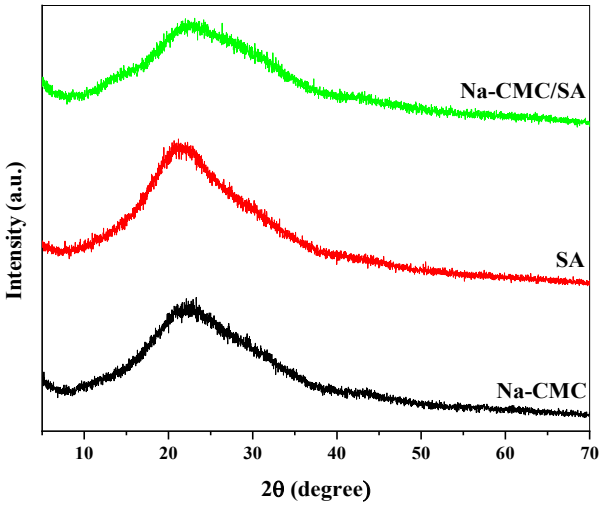


Figure 2. XRD pattern of virgin polymers, and polymer blend.

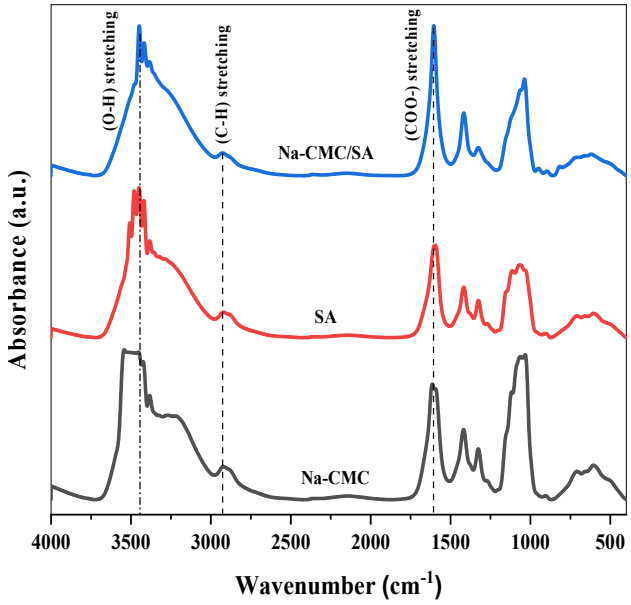


Figure 3. FTIR spectra of virgin polymers and polymer blend.

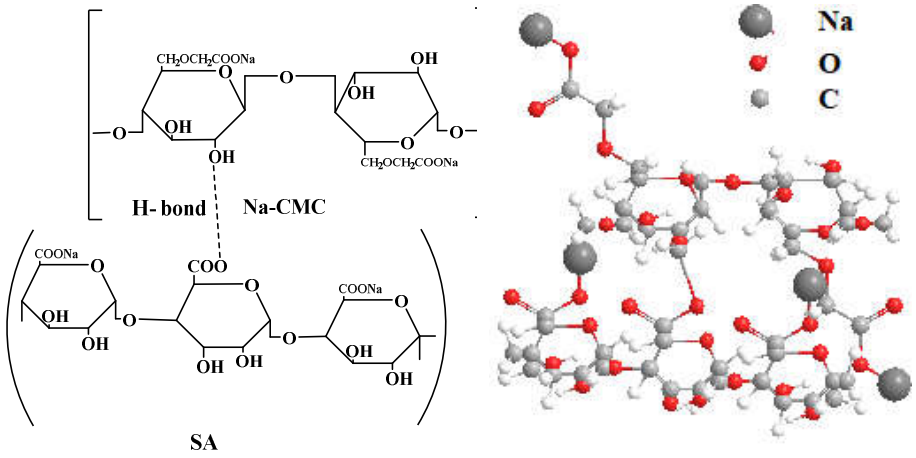
UV/Vis studies

Figure 4 exhibits the UV/Vis spectra of virgin polymers and polymeric blend film that lie inside the range of invisible UV region. The Na-CMC, SA, and Na-CMC/SA membranes have an

absorption rate of 234, 227, and 227 nm, which potentially owing to the charge-relocate complexes' presence for the Na-CMC and polymer blend cases and the (π–π*) transition of the carbonyl groups (C=O) for SA case [7, 13, 16, 23-26].

Table 1. The bands position of virgin polymers and polymer blend.

Sodium carboxymethyl cellulose		Sodium alginate		Blend	
ν (cm^{-1})	Assignment	ν (cm^{-1})	Assignment	ν (cm^{-1})	Assignment
3541	O-H vibrations	3450	O-H vibrations	3400	O-H vibrations
3380	Aliphatic fractions C-H [$\nu_{as}(CH_2)$, $\nu_s(CH_2)$, respectively]	2912	Aliphatic fractions C-H	2919	C-H stretching
2926	N-H stretching	1600	Antisymmetric stretching ν_{as}(Coo-)	1605	Asymmetric COO- stretching
1613	Asymmetric carboxylate ν_s(C=O)	1417	Symmetric stretching ν_s(Coo-)	1417	Symmetric COO- stretching
1417	Symmetric carboxylate ν_{as}(C=O)	1325	Antisymmetric stretching (C-O-C)	1040	Glycosidic linkages in polysaccharides
1327	Symmetric stretching vibration of alkyl groups	-	-	-	-
1034	Distinctive peaks of the glucopyranose ring	-	-	-	-



Sketch 1. Interaction mechanism of two virgin polymers.

Optical properties studies

Figure 5 showed the optical properties studies as (a) absorption coefficients (α), (b and c) direct and indirect band gap (E_g^d and E_d^{in}), and (d) Urbach energy (E_U) and collected in Table 2:
(1) The absorption coefficients (α) can be estimated by Beer-Lambert's formula [25-27]:

$$\alpha(\lambda) = \frac{2.303\ A}{d} \quad (1)$$

where A and d represent the absorbance and the film's thickness, respectively.
(2) The power (m) indicates the transformation of the direct and indirect at m = 0.5 and 2, respectively. Furthermore, the bandgap can be determined as follows [13, 25-27]:

$$\alpha h\nu = A\,(\,h\nu - E_g)^m \tag{2}$$

where (hν) refers to the photon energy, E_g represents the bandgap and A is the band tailing parameter.

(3) The refractive index (n) can be calculated as follows [13, 28]:

$$\frac{n^2-1}{n^2+1} = 1 - \sqrt{\frac{E_g^{in}}{20}} \tag{3}$$

(4) The Urbach energy (E_U) can be predicted utilizing the subsequent equational statement [29]:

$$\alpha(h\nu) = \alpha_{\circ} exp\left(\frac{h\nu}{E_U}\right) \tag{4}$$

where (α_o) is a constant and (E_U) is the Urbach energy.

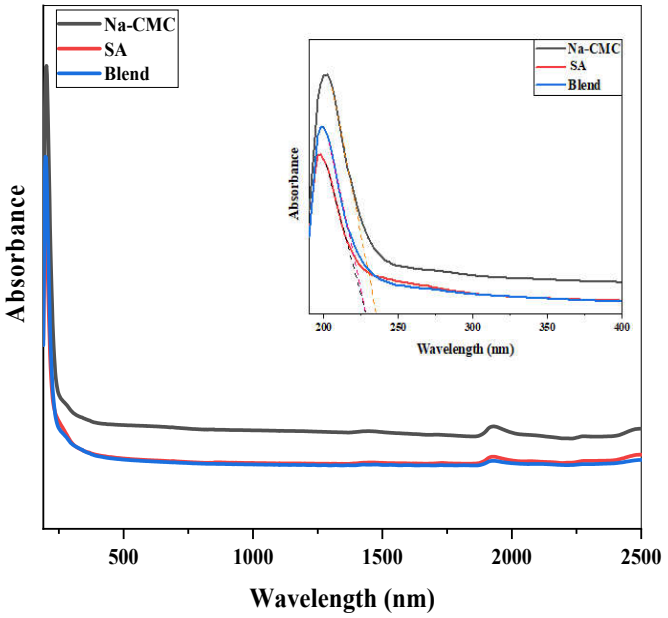


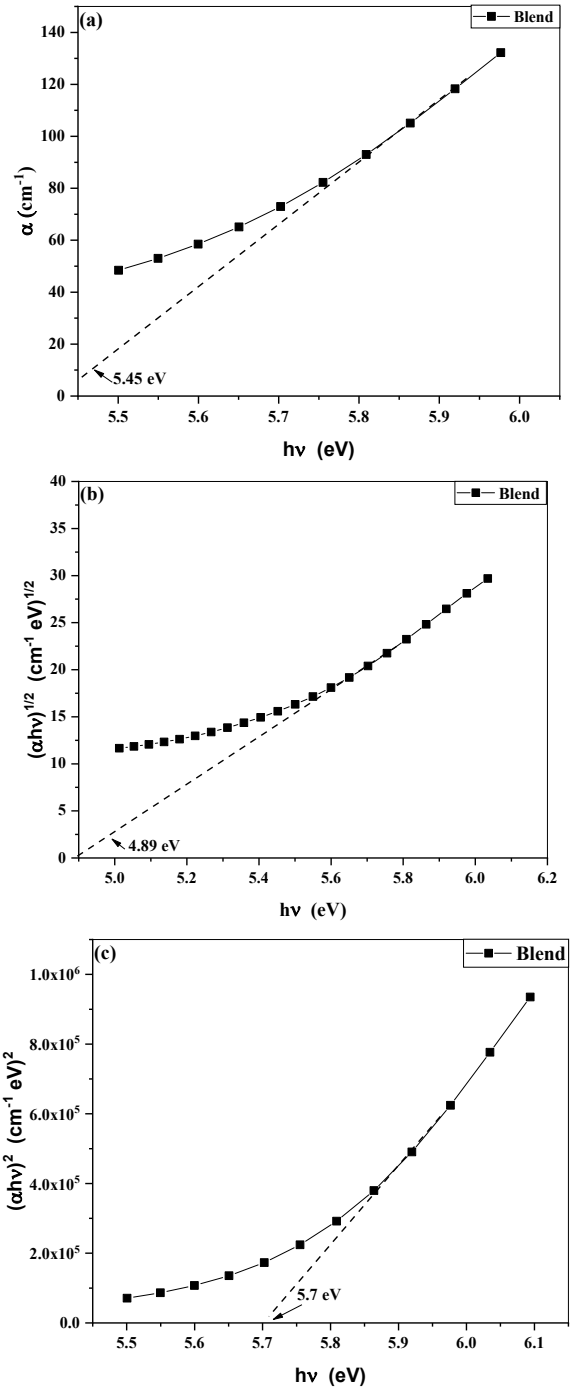
Figure 4. UV-Vis spectra of virgin polymers, and polymer blend.

Table 2. Optical parameters for the prepared blend.

Samples	α (cm^{-1})	E_g^d (cm^{-1} eV)^2	E_g^{in} (cm^{-1} eV)^2	E_U	n
Na-CMC/SA	5.45	4.89	5.7	2.97	1.82

Molecular geometry

The computed (HOMO/LUMO) orbitals of the virgin samples secured using the Gaussian program in addition to those reported in Table 3 were demonstrated in Figure 6. The (LUMO) of Na-CMC is situated in the carboxylate group (-COO) however the (HOMO/LUMO) orbitals of SA are located at (–COONa) [26, 27, 30]. As a result, the carboxylate group served as a crucial eventful site for virgin polymers.


(a)
Blend
α (cm^{-1})
5.45 eV
hν (eV)
(b)
Blend
(αhν)$^{1/2}$ (cm^{-1} eV)$^{1/2}$
4.89 eV
hν (eV)
(c)
Blend
(αhν)^2 (cm^{-1} eV)^2
5.7 eV
hν (eV)

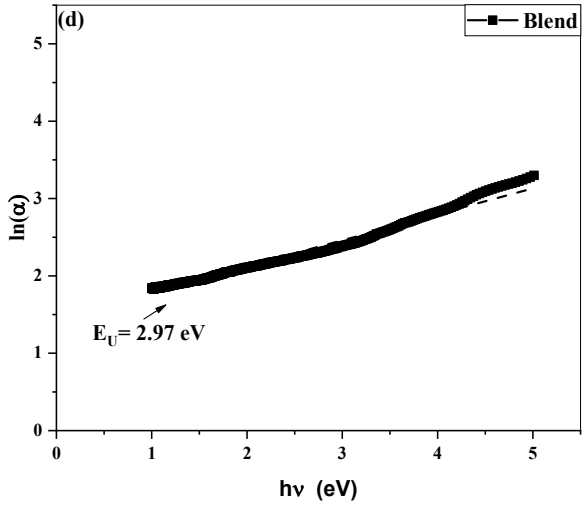


Figure 5. Optical properties estimation curves for polymer blend.

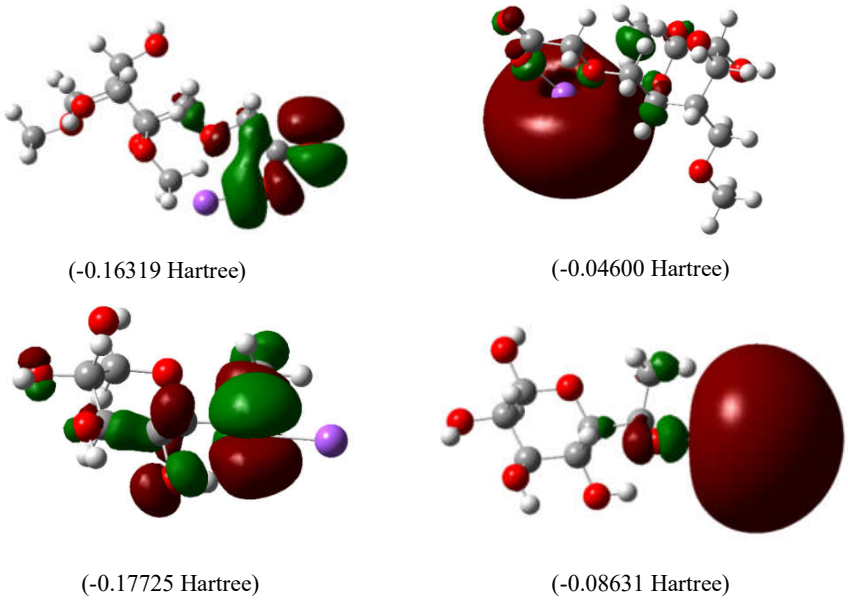


Figure 6. (a) Na-CMC and (b) SA monomers' molecular orbitals.

Table 3. Chemical parameters of virgin polymers.

Virgin polymer	HOMO energy (eV)	LUMO energy (eV)	$\Delta E = (E_2 - E_1)$ (eV)
(Na-CMC)	-4.44	-1.25	3.19
(SA)	-4.82	-2.35	2.47

CONCLUSION

Structural, optical, and spectroscopic investigations for the prepared samples have been studied in the present work. The following conclusions have been extracted. The XRD pattern of the polymer blend manifests the immense band at an angle (21.6°) that is allocated to the two virgin polymers' amorphous aura. The FTIR spectra elucidated the contribution of the virgin polymer group's vibrations. From UV-Vis spectra, the blend has a summit at (227 nm) which agreed with (COO−) stretching vibration at about 1600 cm^{-1} corresponded to FTIR spectra. Molecular geometry indicated the carboxylate group served as a crucial eventful site for virgin polymers. Therefore, this obtained results in this work demonstrated that the polymeric blend seems to be a promised candidate in many applications, especially in biomedical applications.

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