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Effect of CuO Nanoparticle concentrations on the surface roughness parameters and swelling rate of PVP/CMC polymer nanocomposite

Sh.Younis[1], A.M.Abdelghany[2], D. M. Ayaad[1]

[1]*Chemistry Department, Faculty of Science, Mansoura University, Mansoura, 35516, Egypt.*

[2]*Spectroscopy Department, Physics Research Institute, National Research Center, 33 Elbehouth St., Dokki, 12311, Giza, Egypt.*

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Abstract: Flexible thin films of 80w t% carboxymethyl cellulose (CMC) 20 wt% Polyvinylpyrrolidone (PVP) with copper oxide (CuO) variable mass fraction dopant were successfully synthesized. The effect of dopant CuO concentration was studied on correlation to the roughness parameters and swelling rate behavior of the studied nanocomposite. All doped samples were compared to their parent undoped polymeric blend of CMC/PVP. Obtained data shows the concentration dependence on the studied sample physical parameters. Studied samples characteristics suggest possible use in different medical, catalytic and optical applications.

keywords: carboxymethyl cellulose (CMC); Polyvinylpyrrolidone (PVP); Copper oxide (CuO); Roughness parameters; Swelling rate.

1. Introduction

Polymer blending attract the curiosity of several scientists within the last decades because of their superior characteristics among their separate polymer networks and wide applications [1-3]. In addition, doping of polymeric matrices with inorganic materials [4] or nanomaterial [5] may result in new applications. Humidity sensors are being employed in a growing range of industrial processes and environmental control applications. The development of sensing materials has sparked a lot of attention as the demand for water vapor management grows. Because of their low cost and ease of production, chemical sensors are in high demand in industry and environmental science. Humidity measurements in industries are crucial since they might impact the product's commercial cost as well as the workers' health and safety [6, 7].

Because of its high environmental stability, simple processability, reasonable electrical conductivity, and diverse physics in charge transport mechanism, PVP remains crucial among conjugated polymers. Because of the existence of the stiff pyrrolidone group, it is an amorphous polymer with high glass transition temperatures (Tg) up to 170 °C. It has great wetting capabilities in solution and rapidly forms films. This makes it suitable for use as a coating or as a coating additive [8, 9]. Controlled medication release technologies and electrochemical devices are two of its other applications (batteries, displays) [10].

Carboxyl methyl Cellulose (CMC) is a biocompatible and biodegradable anionic polymer obtained through chemical modification of natural cellulose. Furthermore, CMC might be employed as fat substitutes in situations where non-digestible fibers are present [11].

Scanning electron microscopy was used to evaluate the surface roughness characteristics and swelling rate of polymeric nanocomposite (CMC/PVP/ CuONPs) in this work. The information gathered was utilized to propose synthesized samples for medication administration or sensing purposes.

2. Experimental Work

2.1. Sample preparation

Parent undoped thin films of carboxymethyl cellulose / Polyvinylpyrrolidone (CMC/ PVP) (80/20wt%) in addition to another sample that doped with minor concentrations of variable mass fraction copper oxide (CuO) were successfully synthesized via traditional solution casting route using distilled water as a common solvent. Copper oxide nanoparticles (CuONPs) were successfully synthesized via the laser ablation route in aqueous media. Clean copper target immersed in distilled water subjected for Nd:YAG nanosecond pulsed laser adopting 1064 nm beam of width 6 nm and power 4 Watt with pulse frequency 10Hz [12]. The concentration of CuNPs in the solution was determined using absorption spectroscopy. Sample nomination and composition were listed in the table (1).

Table (1) sample nomination and composition

Sample	Nominal Composition		
	CMC	PVP	CuO × 380 ppm
	Wt%		
Blend	80	20	0
Cu1	80	20	1
Cu2	80	20	2
Cu3	80	20	3
Cu4	80	20	4
Cu5	80	20	5

The surface morphology of the synthesized thin films was investigated using a scanning electron microscope (SEM) (Quanta Field emission FEG 250 Netherlands) operated at 30 kV voltage. A (2cm×2cm) piece of the dry sample was immersed in a buffer solution of constant pH ranging between 4 and 9 and incubated at 37 °C for 24 h until the samples reached the equilibrium state of swelling. The swollen films were weighted before (W_d) and after immersion (W_s). The swelling ratio was calculated using [13]:

$$Swelling\ ratio(\%) = \frac{W_s - W_d}{W_d} \times 100$$

3. Results and Discussion

3.1. SEM analysis

SEM permits to form a quantitative analysis of different morphological aspects of a corroded surface, including estimating surface roughness, characterizing the corrosion pits (their dimension and shape), locating the corrosion, and determining the morphology of corrosion products (such as oxides).

The SEM of samples' surface and cross-section regulate by the casting/solvent evaporation technique. Mixing of different polymers can happen upon evaporation of the solvent, out coming change in the polymeric matrix, and that a perfect interaction among polymers realize before and after incorporate with amoxicillin drug.

Figure (1.a-d) reveals exemplified SEM micrographs of the studied samples. The analyzed sample micrographs were used to calculate surface parameters including average roughness (R_a), Root mean square roughness (R_q), the maximum height of the roughness (R_t) maximum roughness valley depth (R_v), maximum roughness peak height (R_p), and Average maximum height of the roughness (R_{tm}).

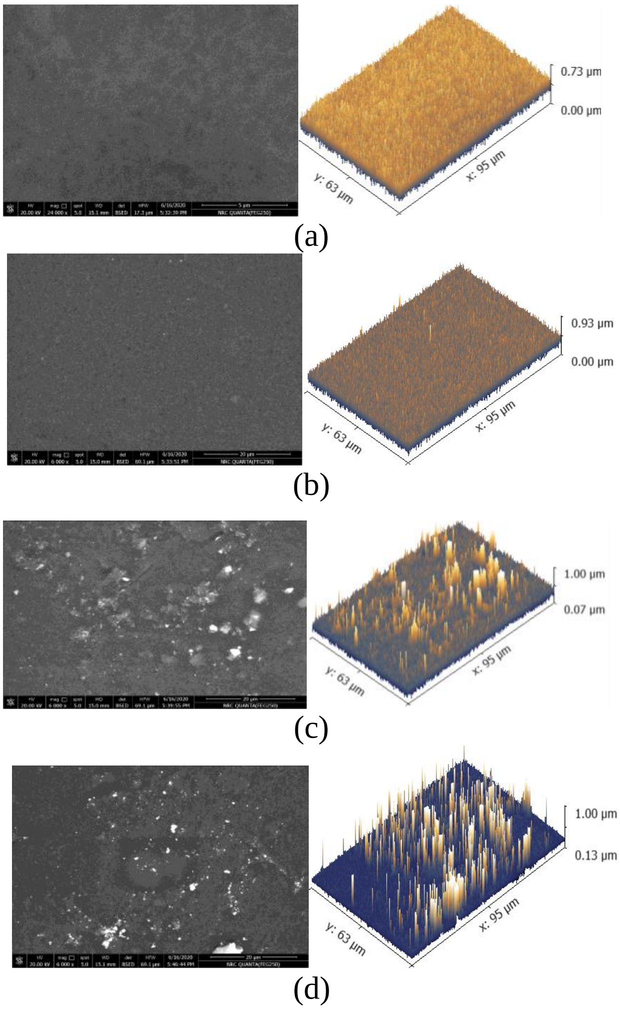

Figure (1.a:d) SEM of CMC/PVP (80:20) with CuO nanoparticles (a) BlendCu0, (b) Cu1, (c) Cu3, and (d) Cu5.

It was clear that the roughness parameters values that were normally categorized as amplitude, spacing, and hybrid parameters [14] were increased with increasing copper oxide nanoparticle contents as summarized in Table (2). The sudden change in roughness parameters of the sample Cu5 suggests the formation of copper oxide clusters shown in SEM micrographs figure (1.d).

Table (2) roughness parameters of the studied samples

Sample	R_a	R_q	R_t	R_v	R_p	R_{tm}
Blend	37.1	47.1	350.2	170.5	180.2	264.8
Cu1	38.7	48.9	354.8	173.3	181.6	269.4
Cu2	40.0	50.5	338.1	157.6	180.5	248.9
Cu3	35.5	45.6	339.4	150.5	188.9	284.8
Cu4	40.9	51.9	405.6	224.6	180.7	318.8
Cu5	26.7	45.3	684.9	234.1	450.8	335.9

Obtained data may be used to identify the suitable application at which studied samples can be used. An increase in roughness parameters combined with the increase of the surface area suggests the possible use of studied samples as a catalyst with high surface area in industrial applications or drug delivery and wound healing applications in medical applications especially with CuONPs that have superior antibacterial characteristics [15].

3.2. Swelling rate test

The skin topmost layer is biologically described as stratum corneum and features of its structure such as homeostasis, intercellular lipid, permeability barrier, and cohesion, etc. These features are controlled by many agents including the pH of the skin. pH of healthy and normal skin is in the range of 5.0–6.0, so the stratum corneum is recognized as the acid mantle. The range of 5.0–6.0 is described the healthy and normal skin pH, so the stratum corneum is recognized as the acid mantle. Sebaceous glands, eccrine glands, apocrine glands, epidermal cells, gender, and age are agents that affect acid mantle pH. If the skin pH is unbalanced, it leads to many disorders like skin illness (irritation and inflammation) as well as reduced cell cohesion and permeability barrier in the stratum corneum [16]. The swelling behavior is essential for polymer films used for wound healing because fluid uptake is a key agent during tissue regeneration. Swelling is a usual phenomenon of the interaction of a Polymer with solvent. Insertion of such liquid within polymer matrix tends to swell it. This could be either reversible or irreversible [17-19]. Many times, some polymers tend to absorb moisture which tends to change the associated properties. The total moisture insertion is not always reversible.

Figure (2) explains the swelling behavior of CMC, PVP, and its blend. This data revealed that PVP does not have a good adsorption capacity [20]. With increasing the pH values, the swelling rate of PVP decreased.

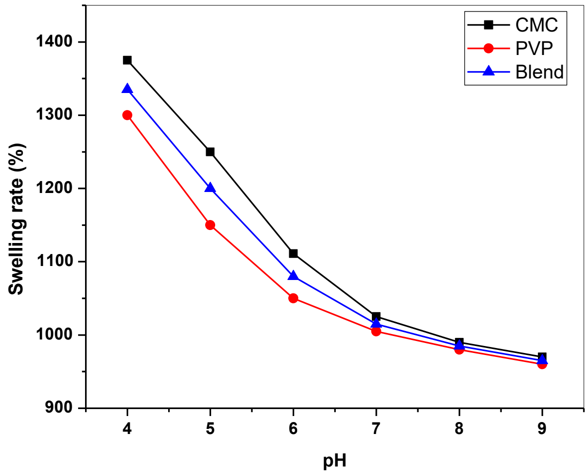

Figure (2) Swelling ratios of pure CMC, PVP, and its blend with various pH values.

CMC is recognized by its water-absorbing, its swelling ability, and its biocompatibility. So CMC curve shows the good swelling behavior of it. With increasing the pH, the swelling behavior of carboxymethyl cellulose decreased. So these results encourage using CMC for the treatment of severe wounds and can be used for the preparation of hydrogel in the treatment of chronic wounds like diabetic foot ulcers [18]. By adding CMC to PVP, the swelling behavior of CMC decreases by increasing the PVP concentration and it is proved by the blend curve in figure (2). These types of films can be utilized for antibiotic drug delivery or as injectable drug delivery carriers.

Figure (3) shows the various swelling rates of CMC/PVP blend at different values of pH (4.0, 5.0, 6.0, 7.0, 8.0, and 9.0) after adding different concentrations of CuO NPs to this blend. There is a change in the swelling ratio of the blend has been noticed when placed in various pH of the aqueous solution. At (pH 4.0- 6.0), the swelling ratios of the system decrease by increasing the concentration of CuONPs. When the pH values increased the swelling behavior decreased due to the increase of cross-linked, rigidity of network and compact structure of the blend due to intra/inters molecular interaction which decreased swelling and solubility of CuO nanoparticles.

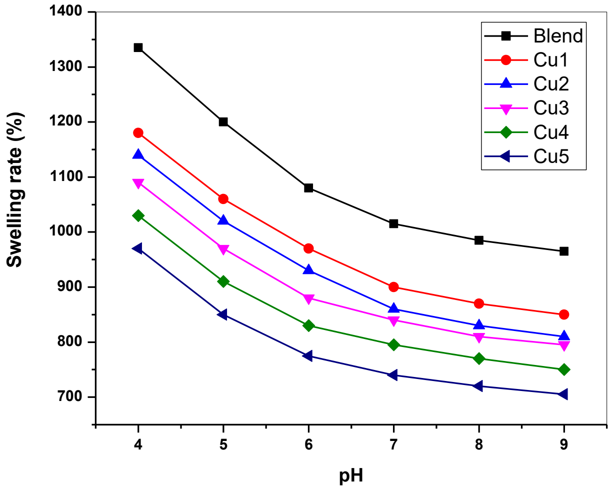

Figure (3) Swelling ratios of (CMC/PVP) blend with different concentrations of CuO NPs against various pH values**.**

4. Conclusions

20wt%CMC/80wt%PVP flexible thin films and other samples of the same composition containing minor dopent of CuONPs were synthesized via ordinary casting route adopting water as a common solvent. It seems that both blending and addition of CuONPs to the studied blend causing an increase in surface roughness parameters and a decrease in the swelling rate of the studied nanocomposites. Both phenomena may arise and be interpreted in the shade of crosslinking process that causes a delay in the swelling process. effect resulting in a decrease in the swelling rate. Obtained data shows the concentration dependence on the studied sample physical parameters. It was also noted that samples containing up to 1000 ppm of CuNPs nearly have the same behavior. Such concentration was recommended for possible use in different medical, catalytic and optical applications.

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