INVESTIGATING THE EFFECT OF MICROWAVE IRRADIATION TIME, POLYETHYLENE GLYCOL CONCENTRATION AND pH ON THE PROPERTIES OF Mg-BASED BACTERIAL CELLULOSE NANOBIOCOMPOSITE

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This paper is dedicated to my supervisor, late Dr. Faranak Mohammad Kazemi

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Mg-based bacterial cellulose nanobiocomposites (Mg-BCN) were produced assisted by microwave irradiation. In this study, the effects of the concentration of starter molecules, solution pH, and microwave irradiation time (MIT) on the properties of Mg-BCN were investigated. Tensile strength, structural properties, morphology and thermal stability of the nanocomposites were evaluated. According to the obtained results, an increase in the concentration ratio of starter molecules, pH, and MIT increased the formation of MgO, in comparison with $Mg(OH)_2$. The nanocomposites synthesized with the 1:2 and 2:1 concentration ratio of magnesium acetate to polyethylene glycol, at pH 11 and with 3 minutes of MIT, had the largest tensile strength and crystallinity. Meanwhile, the opposite results were obtained with 1:1 and 1:0 ratios, at the mentioned pH and time. According to FESEM analysis, at pH = 9, the nucleation rate decreased and smaller particles were formed. Moreover, the results showed decreased possibility of agglomeration in the presence of polyethylene glycol (PEG). TGA results indicated that the thermal stability of all Mg-based nanocomposites is higher than that of pure cellulose. In addition, the maximum weight loss temperature in all treatments involving PEG was higher than in the case of the samples treated without PEG.

Keywords: nanobiocomposites, microwave irradiation time, polyethylene glycol concentration, Mg-based bacterial nanocomposites

INTRODUCTION

Bacterial cellulose (BC) can be used in drug packaging, drug release and tissue replacement in the body, owing to its capability of gradual hydrolytic decomposition. The advantages of bacterial cellulose fibers as natural polymers, which make them preferable to synthetic polymers, include their eco-friendliness, renewability and availability.[1,2] Other properties of BC are their mechanical and thermal stability, water holding capacity, and heat resistance.[4] Natural fibers, such as bacterial cellulose, have been used in a wide variety of applications, such as medicine, drug industry, environmental remediation and oil industries.[3,5]

The application of microwave irradiation is popular in organic synthesis, due to the ability to control the reaction rate, efficiency in energy consumption, and lower environmental impact, along with rapid initial heating and the production of high-pressure areas in the reactive sites.[6] Studies of the microwave-assisted organic synthesis have demonstrated the unique ability of microwave irradiation to accelerate the chemical processes, change the structure and composition of nanoparticles, and reduce the duration and energy costs. This method has been found to often offer flawless hydrothermal synthesis products.[7]

Magnesium (Mg) is one of the constituent elements of the human body. Mg is also one of the most important elements in many of the biochemical reactions that are present in living processes in the environment. The valuable applications of basic magnesium composites in industry and the environment are confirmed, also Mg composites have been demonstrated as economic, environmentally friendly and sustainable materials with antimicrobial activity.[8] Specifically, in the paint and textile industries, considerable amounts of dyes enter the effluents of factories, and Mg-based composites have been investigated and found efficient as dye adsorbents for wastewater remediation.[9]

Here, we describe a simple route for the preparation of Mg-based bacterial cellulose nanobiocomposites. Also, we study the effect of microwave irradiation time (T_{MI}), pH, and concentration ratio of magnesium acetate (MgOAc) to polyethylene glycol (PEG) on the tensile strength, morphology, and thermal stability of nanocomposites.

EXPERIMENTAL

Material

Purified bacterial cellulose (BC) sheets were purchased from NNP Co., Iran. The concentration and size of BC sheets were 1% w/v and 250×100×2 mm, respectively. Also, aqueous NH_3 (25%), polyethylene glycol 600, $Mg(CH_3COO)_2$ and MgOAc were purchased from Merck Co.

Sample preparation

In this study, different concentration ratios of MgOAc to PEG (four ratios), microwave irradiation time (1, 3, 7 min), and pH (pH = 9.0 and 11.0) were considered as variable factors. Dip coating was used for preparation of basic magnesium nanocomposites in the solutions with specific fractions of magnesium acetate, polyethylene glycol, and ammonia. Then, the samples were removed from the solution, washed and dried in a freeze dryer for 24 hours. The reaction parameters are shown in Table 1.

Characterization of samples

Fourier transform infrared spectroscopy

The FTIR of dried BC was performed on a NEXUS 870 analyser, equipped with a DTGS detector and a Golden Gate Micro-ATR. The spectra were scanned in the 4000–400 cm^{-1} region, with an average of 15 scans, with a resolution of 2 cm^{-1}.

Mechanical properties

Tensile strength and elongation at break were measured using a Testometric machine model M350-10ct (Type DBB MTCl, Testometric Co., Rochdale, England), according to ASTM D 882-02 standard. The freeze-dried samples were cut into rectangular slabs in a size of 100 mm × 10 mm × T, where T was the thickness of samples. The loading rate was 5 mm/min. We tested five replicates for each sample.

Thermogravimetric analysis (TGA)

TGA analysis of the samples was carried out using a TGA Instrument 931 thermal analyzer (TA Instruments). The scan rate of 20 K/min over a temperature range of 20–600 °C was applied. All tests were performed under the flow rate of 50 mL/min of N_2 gas.

X-ray diffraction spectrometry (XRD)

The XRD spectra of the samples were measured by a Rigaku Ultima IV device, with a tube voltage of 40 kV and amperage of 40 mA, using a Cu LFF lamp in the 2θ range of 5-80 degrees.

Table 1
Treatment conditions used in the study

Nr	Radiation time (min)	pH	Concentration ratio	Nr	Radiation time (min)	pH	Concentration ratio
1	1	9	2:1	13	1	9	1:1
2	3	9	2:1	14	3	9	1:1
3	7	9	2:1	15	7	9	1:1
4	1	11	2:1	16	1	11	1:1
5	3	11	2:1	17	3	11	1:1
6	7	11	2:1	18	7	11	1:1
7	1	9	1:2	19	1	9	1:0
8	3	9	1:2	20	3	9	1:0
9	7	9	1:2	21	7	9	1:0
10	1	11	1:2	22	1	11	1:0
11	3	11	1:2	23	3	11	1:0
12	7	11	1:2	24	7	11	1:0

Field emission scanning electron microscopy (FESEM)

The surface morphology, shape and structures of basic magnesium bacterial cellulose nanobiocomposites were investigated by scanning electron microscopy. This imaging was obtained with a Hitachi S-4160 Scanning Electron Microscope (FESEM, 20 kV).

RESULTS AND DISCUSSION

To investigate the chemical structure and functional groups of Mg-based bacterial cellulose nanobiocomposite samples obtained under the conditions specified in Table 1, the FT-IR analysis of the samples was performed in the range of 400-4000 cm^{-1} (Fig. 1a-b). As may be noted, the broad band at 3350 cm^{-1} is related to the OH stretching of cellulose and the bands at about 2893 cm^{-1} are assigned to the symmetric and asymmetric stretching of the alkyl groups of cellulose and starter materials, magnesium acetate and PEG.[10] The strong intensity bands at about 1450 and 1620 cm^{-1} are due to starter molecules too. The strong intensity bands in the 980-1200 cm^{-1} region and the medium intensity bands at 1260 and 960 cm^{-1} assigned to different movement of cellulose, including C-C, C-O, and CH_2-OH stretching and C-H, OH, and C-O bending. These findings agree with earlier results reported in previous work.[11]

In the nanocomposites, Mg-O stretching of MgO and $Mg(OH)_2$ was observed in the region of 400-800 cm^{-1}, that at a higher wavenumber being due to $Mg(OH)_2$.[9,12] Two bands at 662 and 621 cm^{-1} assigned to the stretching of Mg-O in $Mg(OH)_2$ and MgO, respectively can also be seen in the spectra in Figure 1. These two bands appear along with the other normal modes due to deformation of the six-member rings of cellulose coupled with some other movements, such as bending of C-C-OH and rocking of CH_2. According to Figure 1a, the band intensity of the mentioned bands for samples with 1:2 and 2:1 ratios is higher than that for the samples with 1:1 and 1:0 ratios. So, the content of Mg as MgO and $Mg(OH)_2$ in 1:2 and 2:1 ratios is higher than that in 1:1 and 1:0 ratios. Also, it can be stated that pH alone does not have a significant effect on the interactions and crosslinks with OH cellulose groups.

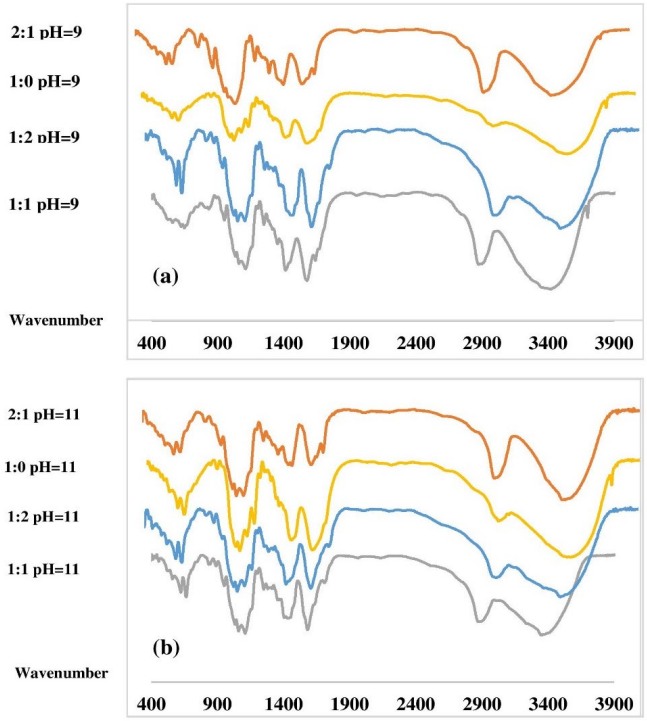

Figure 1: FTIR spectra of synthesized nanobiocomposites during 3 min, at (a) pH 9, (b) pH 11

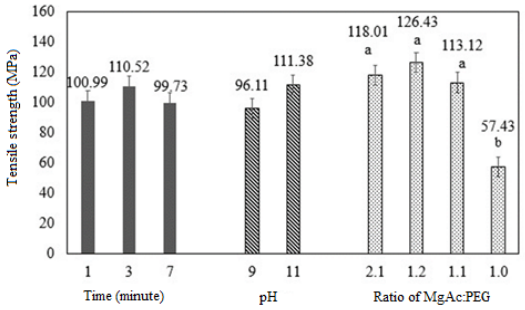

Figure 2: Effect of MgAc:PEG ratio, irradiation time and pH on tensile strength of nanocomposites

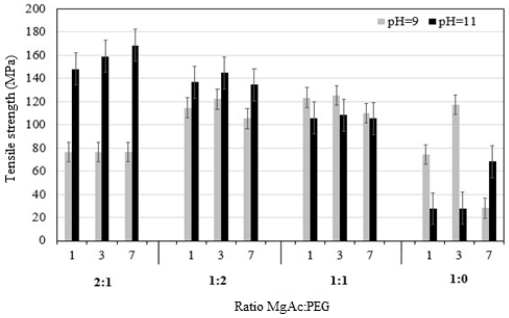

Figure 3: Interaction effect of MgAc:PEG ratio and pH during microwave irradiation treatment for different times on tensile strength

In addition, the weak intensity, narrow band at 3700 cm^{-1} is assigned to OH stretching of $Mg(OH)_2$, which is in agreement with the research reported by Zidane *et al.*[13] As shown in Figure 1, the content of $Mg(OH)_2$ in the samples with ratios of 1:1 and 1:0 is higher than that in the samples with 1:2 and 2:1 ratios. It seems that the amount of $Mg(OH)_2$ depends on the variables of irradiation time, ratio, and pH.

Also, we examined the effect of different parameters in the synthesis of nanocomposites on their tensile strength. These parameters included the ratio of MgAc:PEG, irradiation time and pH. The results obtained are shown in Figures 2 and 3.

Figure 2 shows the influence of each variable parameter on the tensile strength of the nanocomposites. Observing the data presented in this figure, it can be concluded that the nanocomposites synthesized with pH=11 have higher tensile strength, compared to those synthesized at pH = 9. Also, the nanocomposites prepared with the ratio of 1:0 of $Mg(CH_3COO)_2$ to PEG have the lowest tensile strength. Thus, the pH and ratio variables have the greatest effect on the tensile strength.

Figure 3 shows the interaction effect of concentration and pH during microwave irradiation treatment on tensile strength. As this figure shows, in the concentration ratios of 2:1 and 1:2, the nanobiocomposites synthesized with pH = 11 have higher tensile strength. Also, the highest value is related to the ratio of 2:1 and treatment time of 3 and 7 minutes. PEG, as non-ionic surfactant, covers the surface of the synthesized crystals and prevents them from clumping.[14] It also possesses the ability to form more ionic interactions and crosslinks with the OH groups of cellulose by increasing the pH of magnesium ions. Thus, the tensile strength increased when the ratios of 2:1 and 1:2 were used. Thus, higher resistance is supposedly obtained when PEG is used in the synthesis and the material density increases. This factor can be attributed to improved dispersion of the nanoparticles in the presence of polyethylene glycol and thus, better stress distribution. Also, the synthesized nanobiocomposites also showed quite high strength in the ratio of 1:0 (without PEG) at pH = 9. However, as the pH increased over 9, the nucleation rate increased as well and larger particles were formed, and in the absence of PEG, the probability of agglomeration was much higher and hence tensile strength decreased significantly. The mentioned results agree with the work reported by Wang *et al.*[15,16]

Figure 4 shows the XRD patterns of nanobiocomposites synthesized using different concentration ratios, at pH = 9, with irradiation time of 3 min. According to Scheurell *et al.*,[17] the peaks at 2θ = 17, 32, 36, 44, 50, 58, 61, 64, and 68 degrees are related to $Mg(OH)_2$, while the peaks at 37, 43, and 63 are due to MgO, respectively. Magnesium acetate peaks at 2θ = 8°, 10°, are also seen in some treatments. In addition, in the corresponding samples with concentration ratios of 2:1 and 1:2, the presence of MgO is more obvious than that of $Mg(OH)_2$, while in the samples with 1:1 and 1:0 concentrations the existence of $Mg(OH)_2$ is significant. The existence of MgO and $Mg(OH)_2$ at pH=11 for different concentration ratios agrees with the results obtained at pH = 9 (see Fig. 5). These results also agree with the findings of FTIR analysis.

As shown in Figures 4 and 5, nanobiocomposites with a 2:1 ratio had the highest crystallinity, which increased slightly with increasing pH (51.27% at pH = 9 and 54.78% at

pH = 11). In fact, at higher concentration ratios (2:1 and 1:2), as the pH increased, the nucleation rate increased. As has been mentioned previously,[18] PEG coatings of the nanoparticles have a great role in preventing agglomeration. In the samples without PEG, due to penetration of magnesium acetate and formation of hydrogen bonds with cellulose, the crystallinity decreased, in comparison with that of pure cellulose.

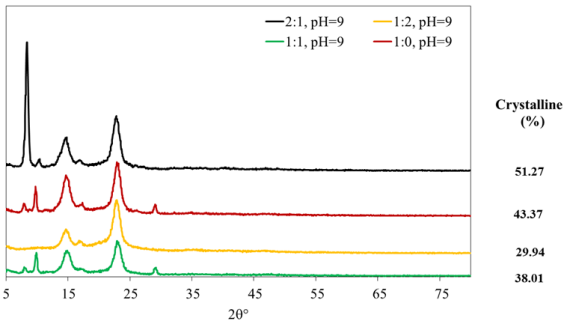

Figure 4: XRD patterns of nanocomposites synthesized with different MgAc:PEG ratios, irradiation time of 3 min and pH 9

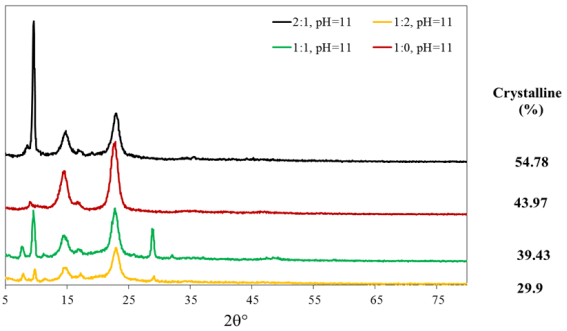

Figure 5: XRD patterns of nanocomposites synthesized with different MgAc:PEG ratios, irradiation time of 3 min and pH 11

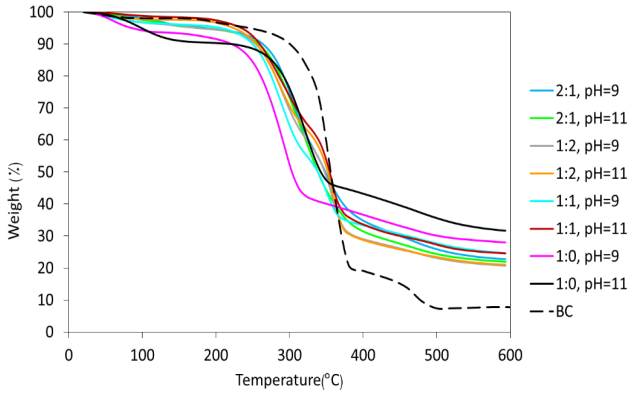

Figure 6: TGA thermograms of different formulations (irradiation time =3 min, BC – bacterial cellulose)

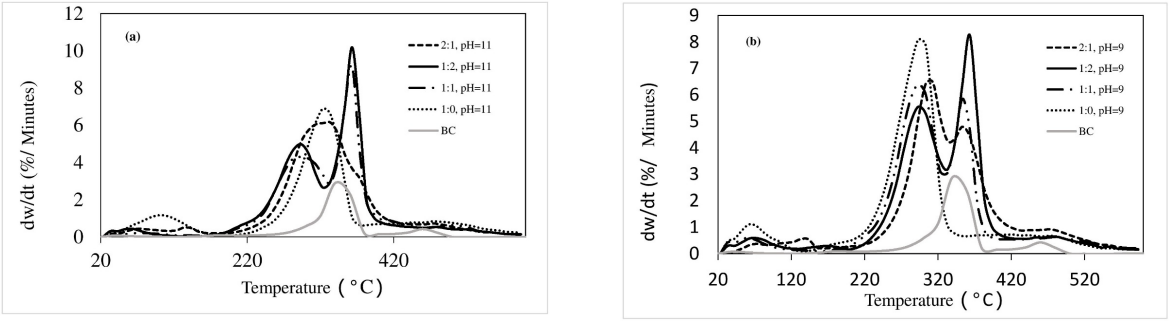

Figure 7: DTG thermograms of different formulations (irradiation time =3 min, and pH = 9 (a), and pH = 11 (b), BC is bacterial cellulose)

Figure 6 shows the weight loss and thermal stability of our specimens, compared with those of bacterial cellulose (BC). The weight loss of the samples at temperatures in the range of 150 to 200 °C is due to moisture evaporation during the experiment. From 250 to 350 °C, the degradation of cellulose occurs, along with the decomposition of glucose units and formation of carbon residues. The sample prepared with the ratio of 1:0, at pH = 9, shows the highest weight loss, which can be attributed to its severe degradation because of the absence of PEG.[16]

According to Figure 6, samples with 2:1 and 1:2 ratios show a lower decreasing slope, which can be attributed to the presence of polyethylene glycol 600. The chemical compounds of PEG 600 begin to degrade at 200 °C.[19] As shown in Figure 7, the optimized samples lose weight at lower temperature than bacterial cellulose. However, they lose less weight than the control sample, BC. Specimens containing PEG at 293 and 363 °C had the highest weight loss per minute, which is believed to have a very high effect on the adsorption of MgO on the surfactant that causes hydrogen bonding to the OH groups. It binds to the MgO, thereby reducing weight.[20]

Specimens containing PEG had the highest weight loss per minute at 293 °C and 363 °C, and their final weight loss temperature (363 °C) was higher than that of pure cellulose (340 °C), indicating increased thermal stability. Meanwhile, in the sample without PEG, only one phase of thermal degradation is observed for the samples prepared at pH = 9 and pH = 11, occurring at 293 °C and 323 °C, respectively.

The initial drop in the sample weight can be attributed to the loss of the adsorbed solvent molecules and secondly to the significant loss of weight due to the decomposition of polyethylene glycol, which increased the thermal stability of coated MgO from 300 to about 500 °C.

SEM images in Figure 8 show the presence of round and angular microcrystals and nanocrystals of MgO and $Mg(OH)_2$ on the materials. Concentrations of 1:1 and 1:0, as well as pH 11, lead to the formation of larger crystals, which may be related to MgO oxidation and $Mg(OH)_2$ formation. Studies show that, as the size of the crystals increases, the mechanical strength decreases.[18] The decrease in particle size in these nanobiocomposites may also be the reason for the higher resistance of these nanobiocomposites. Their crystallinity was also lower than that achieved for the samples prepared with the concentration of 2:1. On the other hand, as the pH increases, the nucleation rate increases and the particles are more likely to clump. In the absence of PEG (ratio of 1:0 and pH=11), the intensity of aggregation and coalescence increases.[21] In general, the final properties of nanocrystals are strongly dependent on their shape, and aggregation may have a significant influence.

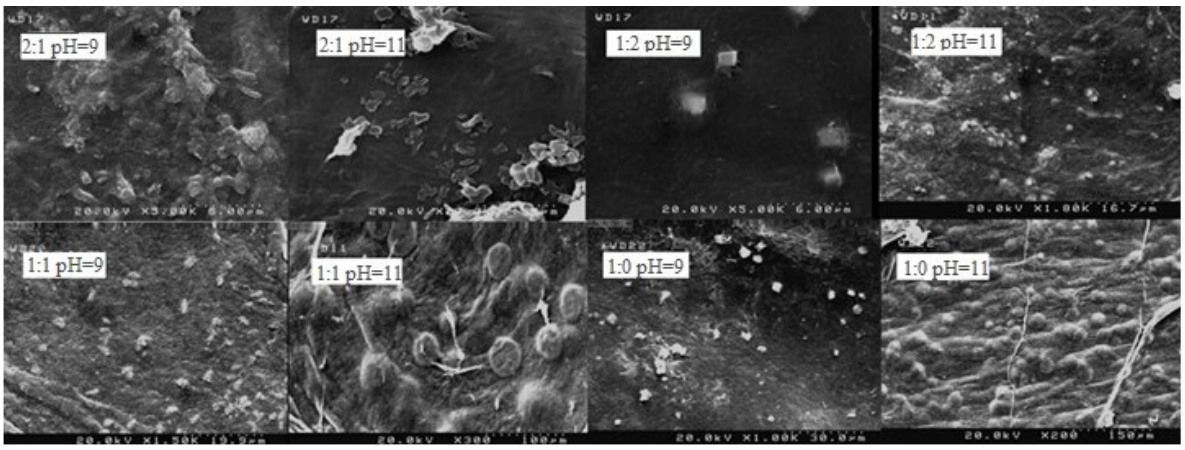

Figure 8: FESEM micrographs of nanocomposite samples

CONCLUSION

The effect of the concentration ratios of MgOAc to PEG, solution pH and microwave irradiation time on the properties of Mg-based bacterial cellulose nanocomposites was studied. The results showed that at higher pH value (pH=11), at irradiation time of 3 min and 2:1 and 1:2 ratios, the tensile strength of composites and their crystallinity were improved. In addition, the weight loss of the composites was lower than that of the control bacterial cellulose, and their thermal stability was increased. Among the composites, the samples prepared with the ratio of 1:0 had the lowest weight loss.

According to the FTIR spectra of the samples, a correlation was noted between the intensity of the bands at 662 and 621 cm^{-1} and the pH and concentration ratio of the material. Also, the intensity of the band at 3697 cm^{-1}, assigned to the OH stretching of $Mg(OH)_2$, was influenced by the considered variables. Thus, for the material prepared at the lower pH and treatment time of 3

min, the intensity of the mentioned band increased. Thus, the possibility of $Mg(OH)_2$ formation is increased compared to MgO formation. According to these results, there is a favourable interaction between bacterial cellulose and $Mg(OH)_2$ nanoparticles.

A decrease in the tensile strength of the nanobiocomposite could be attributed to rising particle size and lower crystallinity of the samples. Also, in the absence of PEG, the nucleation rate rose and the particle agglomeration increased, which led to a decrease in the composite's tensile strength.

According to the obtained results, bacterial cellulose can be a suitable substrate for the synthesis of magnesium hydroxide and magnesium oxide particles. In addition, the synthesized magnesium-based bacterial cellulose nanocomposites had high tensile strength and high thermal stability. Thus, they could be used in applications requiring such characteristics. By changing of the synthesis conditions, especially the pH and the concentration of MgOAc and PEG, the size of $Mg(OH)_2$ and MgO particles can be controlled, and thus, the final properties of the materials.

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