

Impact of Carboxymethyl Cellulose-Bentonite Combination on Paper Performance

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Abstract

Aim of study: The purpose of this research is to evaluate the effects of applying CMC-BEN (carboxymethyl cellulose-bentonite) mixes to the surface of paper, both in terms of their impacts on paper qualities and the mixing ratios at which they were formed.

Material and method: The production of CMC-BEN mixes was prepared by combining the components at the following rates: 1/1, 1/0.5, 1/0.25 and 1/0.1. Simple coating technique was utilized in order to apply the mixes to the surfaces of the paper. Strength performances of the papers, as well as their antibacterial activities, FTIR patterns, COBB values, and SEM views were evaluated.

Main results: The solution absorption diminished with the addition of BEN to the CMC structure. The wet strength properties decreased in 100% CMC and CMC-BEN coated papers, and the dry strength and COBB values increased.

Research highlights: On the surface of the paper, mixtures based on CMC and CMC-BEN were applied, each of which was made using a different mixing ratio. It was found that the CMC-BEN mixture had a positive impact on the paper's dry strength, but it had a negative impact on wet strength properties.

Keywords: Surface treatment, paper, polymer

Karboksümetil Selüloz-Bentonit Kombinasyonunun Kağıt Performansına Etkisi

Öz

Çalışmanın amacı: Bu araştırmanın amacı, CMC-BEN (karboksümetil selüloz-bentonit) karışımlarının kağıt yüzeyine uygulanmasının hem kağıt kalitesi üzerindeki etkilerini hem de karışım oranları açısından etkilerini değerlendirmektir.

Materyal ve yöntem: CMC-BEN karışımlarının üretimi, bileşenlerin belirtilen oranlarda karıştırılmasıyla gerçekleştirilmiştir: 1/1, 1/0.5, 1/0.25 ve 1/0.1. Karışımların kağıt yüzeylerine uygulanması basit kaplama tekniği kullanılarak gerçekleştirilmiştir. Kağıtların sağlamlık özellikleri yanında antibakteriyel aktiviteleri, FTIR diyagramları, COBB değerleri ve SEM görüntüleri incelenmiştir.

Temel sonuçlar: CMC yapısına BEN ilavesiyle çözelti absorpsiyonu azalmıştır. %100 CMC ve CMC-BEN kaplı kağıtlarda ıslak sağlamlık özelliklerinin azalmış, kuru sağlamlık ve COBB değerleri artmıştır.

Araştırma vurguları: CMC ve farklı karışım oranlarında üretilen CMC-BEN esaslı karışımlar kağıt yüzeylerine uygulanmıştır. CMC-BEN karışımının kağıdın kuru sağlamlık ve su emme özelliklerine olumlu yönde katkı sağladığı ancak ıslak sağlamlık özelliklerine ise olumsuz etki ettiği tespit edilmiştir.

Anahtar Kelimeler: Yüzey işleme, kağıt, polimer

Introduction

Paper production technology is a broad product process involving complex mechanisms based on diverse chemical and physicochemical processes. Different types of paper exist for different uses, such as sanitary, packaging, household, and different application processes are employed depending on the desired properties of the paper. In these applications, coating the paper

surface with different polymer components is important in terms of making the paper more resistant to liquids in the application area and improving water vapor permeability and gas barrier properties. Synthetic polymers such as polypropylene (PP), low density polyethylene (LDPE), and polystyrene (PS) are commonly used in paper surface coating processes. However, although these synthetic polymers are inexpensive and simple to apply onto paper surfaces, they negatively impact the



recycling process of the paper they are used in and create serious environmental problems with high amount of microplastics. Therefore, academic research has focused on biodegradable, non-toxic, and biodegradable polymers as alternatives to synthetic polymers in surface coating processes for paper materials. These biopolymeric surface coating materials have been employed in a number of investigations using cellulose derivatives (Afra et al., 2016; He et al., 2021; Jin et al., 2021), starch (Larotonda et al., 2005; Váscenez et al., 2009; Du et al., 2011; dos Santos et al., 2025; Zhang et al., 2025), chitosan (Kjellgren et al., 2006; Liu et al., 2022; Amarin-da-Silva et al., 2024), alginate (Jiang et al., 2014; Wu et al., 2018; Chen et al., 2025; Sam et al., 2025), and combinations of these polymers with various chemical additives.

CMC, a prevalent cellulose derivative, is a highly soluble, anionic polymeric substance. This polymer was initially produced in 1918, but its commercial use was not assessed until 1920 (Rahman et al., 2021). Cellulose and its derivative CMC, have analogous chemical structures. The sole structural difference is that the hydrogen ions in the hydroxyl group of cellulose are substituted by carboxyl groups in the CMC structure. The polymer's attributes, including its derivation from abundant cellulosic polymers, cost-effectiveness, modifiable rheological properties, and versatility in producing various forms through blending with different polymeric components, facilitate its application across diverse sectors, ranging from biomedical fields to the food industry, and from the paper industry to the plastics sector. Among the proposed use cases for CMC, its primary industrial use is the production of papers. It is widely used in the paper industry for multiple functions, such as increasing the strength characteristics of paper (Fatehi et al., 2010; Mazhari Mousavi et al., 2017; Zhang et al., 2022; Cao et al. 2025), modifier for fillers (Mousavipazhouh et al., 2018), improving surface characteristics to elevate print quality and ink retention (Gençoğlu et al., 2010; Rezaneshad et al., 2025), and thereby facilitating more efficient color dispersion on the surface.

BEN is a naturally occurring mineral belonging to the montmorillonite family, characterized by a wide range of chemical characteristics. This mineral typically exists in two distinct forms: the sodium form, which expands in water, and the calcium form, which does not. This clay, abundant in aluminum and magnesium, predominantly consists of colloidal silica and possesses a soft, porous structure. The primary attributes of BEN include its elevated specific surface area (700-800 m²/g) (Kobayashi et al., 2017), substantial cation exchange capacity (80-150 meq/100g) (Caglar et al., 2009), significant thermal stability, and high Young's modulus. Moreover, its significant swelling capacity, adhesive properties, and reactivity with diverse chemical structures render it advantageous in other domains, including drilling, pharmaceuticals, and biomedical applications (Chokri et al., 2025).

This investigation involved the preparation of CMC-BEN based composites at various mixing ratios (1/1, 1/0.5, 1/0.25 and 1/0.1), which were then applied to conventional standart filter paper. The following parameters of papers were examined: density, coating solution absorption, dry-wet paper strength, water uptake values, air permeability (Gurley technique), degradation rates, antibacterial efficacy, FTIR spectrum, and micromorphological views.

Material and Methods

Materials

The base papers utilized for coating with CMC and CMC-BEN mixtures were standard filter papers branded as Schleicher & Schuell 5891, possessing a grammage of 85 g/m² and a pore size ranging from 12 to 25 µm. CMC (Mw:700.000, Sigma Aldrich) and BEN (Hydrocol OB) was purchased from Ciba Specialty Chemical Inc. (Bradford/United Kingdom). Deionized water was employed in all experiments, with the exception of the evaluation of the wet strength of papers.

Methods

Preparing CMC-BEN Solutions

CMC-BEN solutions were prepared by integrating a specific amount of BEN into a 1% CMC solution to get final mixing ratios of

1:1, 1:0.5, 1:0.25, and 1:0.1. Subsequent to the incorporation of the requisite amount of BEN, the CMC-BEN mixing solutions were subjected to mixing with a high-shear homogenizer for 4 minutes at 10.000 rpm.

Coating of CMC-BEN Solution onto Papers

The application of CMC-BEN solutions to paper surfaces was performed via dipping, followed by the bar coating method. The first test papers were submerged in a CMC-BEN solution for 30 seconds, and the excess solution was removed. An iron rod coated with silicone was applied to the paper surface twice without physical pressure to ensure uniform distribution of the coating solution. Surface-treated samples underwent drying at 90 °C for 25 min. in an oven. All paper assessments were performed after a 24-hour acclimatization period at 50% relative humidity and a temperature range of 22-25 °C.

Density and Coating Absorption on Paper Surface

The densities of the papers after coating were ascertained by the principal method of converting volume fraction to weight. Following calibration, the coated papers were assessed, and the total volume was quantified using a micrometer. The absorption capabilities of pure CMC and CMC-BEN solutions on paper after coating were evaluated via determining the mass changes of the material pre- and post-coating. Absorption rates were calculated with Equation 1 below.

$$\text{Absorption Rate (\%)} = \frac{[M_t - M_o]}{[M_o]} \times 100 \quad (1)$$

where;

Mt: Sample weight after coating (g)

Mo: Sample weight before coating (g)

FTIR Experiment

The FTIR spectra analyzed the chemical interactions between coating formulations and cellulose fibers, with tests performed using the Bruker Alpha instrument in the range of 400–4000 cm⁻¹ with a spectral resolution of 2 cm⁻¹.

Strength, Water Uptake (COBB) Performances

The Karl-Frank 800 Pendulum device was utilized to evaluate the dry and wet tensile strengths of both treated and untreated papers, adhering to the TAPPI T 404 om-87 standard. After a 0.5 min., 3min. and 5min. immersion of paper strips in water, the wet strength of the papers was evaluated. The COBB test was utilized to evaluate the water absorption of the test papers over a 60-second period, in accordance with the TAPPI T 441-om 98 standard.

Antibacterial Performances

The disc diffusion method was utilized to assess the bacterial resistance of paper against *S. aureus* and *E. coli*. Bacteria grown on enriched media for BHA (*S. aureus*) and SS (*E. coli*) were transferred to agar media via the switch process, leading to their proliferation across the agar medium. Samples with a diameter of 1 cm were placed in the bacterial habitat, and after a 24-hour incubation at 35 °C, the inhibitory zones in the agar medium were measured and averaged.

Micro Views

SEM images of the papers were examined using an FEI Quanta FEG 450 instrument (USA). Samples were coated with gold-palladium prior to measurements.

Results and Discussion

Density and Solution Absorption

The variations in density and solution coating absorption rates of the CP and CMC-BEN papers are depicted in Table 1. Upon examination of the density data, it is evident that both 100% CMC and CMC-BEN based papers exhibit higher density values than CP. Paper treated with 100% CMC showed an increase in the density value from 0.05 g/cm³ for CP to 0.0565 g/cm³. During the examination of papers that had been treated with solutions based on CMC-BEN, it was discovered that the density values were higher than those of CP, but they were lower than those of papers that were composed entirely of CMC. Upon examination of papers treated with CMC-BEN based solutions, it was observed that the density values were superior

to those of CP although inferior to those of papers composed entirely of 100% CMC. The maximum solution absorption was recorded in papers treated with 100% CMC at 5.66%, whilst the minimum rate was noted in CMC-BEN 1/0.5 coated papers at 5.02%. The table illustrates that the density variations in the treated papers correspond closely with the absorption of the CMC-BEN solution by the papers. Upon general examination of Table 1, it is evident that neither the density nor the solution absorption values exhibit substantial variation. In paper constructions, the measured volume change due to surface application is less significant than the weight change, resulting in greater density readings compared to CP. The absorption rates of the solutions applied to the paper surfaces were lower compared to those of papers treated with 100% CMC. The elevated concentration of BEN in CMC-BEN based formulations adversely impacted the absorption of the surface coating solution onto the paper substrate. Nonetheless, the surface absorption values of the mixtures generated at mixing ratios of 1/0.25 and 1/0.1 exhibit a rise once more. This is seen as an additional aspect demonstrating that CMC interacts more readily with cellulose surfaces owing to its very hydrophilic nature. The decrease in absorption rate at elevated BEN concentrations is attributed to the swift interaction of BEN molecules with CMC during the mixture manufacturing, which obstructs sites of reaction and diminishes CMC's efficacy. The absorption of CMC into cellulosic fibers happens through hydrogen bonding, and the presence of BEN adversely impacts the hydrogen bond-forming ability of CMC, resulting in reduced solution absorption (Mazhari Mousavi et al., 2017).

Table 1. Density and Solution absorption rates of CP and coated papers

Sample	Density (g/cm ³)	Absorption Rate (%)
CP (control paper)	0.0501	-
CMC 100%	0.0565	5.66
CMC-BEN 1/1	0.0544	5.36
CMC-BEN 1/0.5	0.0522	5.02
CMC-BEN 1/0.25	0.0531	5.12
CMC-BEN 1/0.1	0.0537	5.28

FTIR

Figure 1 illustrates the transitions that occur in the chemical structure of papers that have been coated with CP, 100% CMC, CMC powder and mixing ratios of 1/1 and 1/0.1. When analysed the CP, peaks between 3000 cm⁻¹ and 3750 cm⁻¹ are often attributed to the stretching vibrations of O-H groups, with the peak at 3340 cm⁻¹, identified as 3331.70 cm⁻¹ in our analysis, associated with the chemistry functions of OH groups, as reported by Sathishkumar et al., (2013). C=C stretching vibrations are responsible for the peaks that were observed at 2899 cm⁻¹, which were observed as 2894.48 cm⁻¹, and the peak that was found at 2019 cm⁻¹, which was noted as 2013.55 cm⁻¹ in this experiment (Jonoobi et al., 2010; Otenda et al., 2022). It has been established by Liu et al., (2011) and Md Salim et al., (2021) that the peak at 1635 cm⁻¹, which shifted to 1639.12 cm⁻¹ in this analysis, is connected with fluid that has been adsorbed. –CH₂ scissoring and –OH bending vibration are the vibrations that are attributed to the bands that are located around 1419 cm⁻¹ and 1328 cm⁻¹, respectively. The presence of the band at a frequency of 1059 cm⁻¹ can be attributed to the stretching of the >CH–O–CH₂ bond (Yadav et al., 2013; Liu et al., 2014). According to this study, the stretching and bending vibrations of CH₂ and -CH, -OH, C–O–C vibrational frequency, and C–O bonds in cellulose are responsible for the peaks that were identified at 1426.91, 1364.17, 1158.76, 1040, and 895.38 cm⁻¹, respectively (Jonoobi et al., 2010; Xu et al., 2013; Hospodarova et al., 2018; Otenda et al., 2022). During the course of this investigation, the FTIR diagrams of powdered CMC were analyzed, and the distinctive FTIR peaks of 1050 cm⁻¹, 1440 cm⁻¹, and 1600 cm⁻¹ were found to be present at 1053 cm⁻¹, 1426 cm⁻¹, and 1640 cm⁻¹ respectively. It was determined that these peaks represent the asymmetric and symmetrical modes of carboxylate ions, respectively, as well as the stretching of C–O bonds (Ge et al., 2018). The FTIR diagrams of surface-coated and CP behaved almost exactly the same way, despite the fact that there were some little differences in the peaks as the intensities decreased during the experiment. The paper coated with 100% CMC clearly shows that the characteristic

peak at 1640 cm^{-1} , which is associated with CMC, lost its density after the addition of BEN to the composition. This shift in peak intensity was found to be more prominent when the mixing ratio was 1/1 with a greater quantity of BEN. On the other hand, when the mixing ratio was 1/0.1 with the least amount of BEN, the peak intensity was found to be

extremely close to the equal intensity. It was discovered that the identical condition occurred in the 1426 cm^{-1} peak, which is another typical peak of CMC. It is clear that there is a significant interaction between CMC and BEN, as evidenced by the changes in the characteristic peaks of CMC as well as the variations in peak intensities (Li et al., 2025).

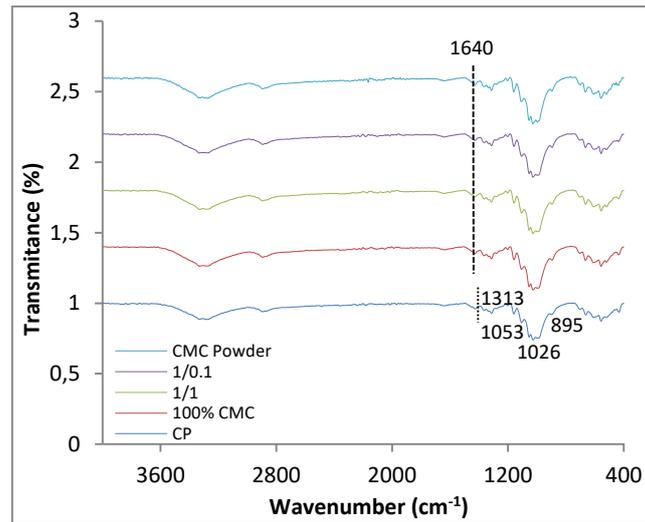


Figure 1. FTIR diagrams of CP, CMC powder and coated papers

Strength and Water Uptake (COBB) Performances

The findings of the dry strength, wet strength, and COBB performance of the papers are displayed in Figures 2-4. As can be shown in Figure 2, papers that have been treated with 100% CMC and a mixture of CMC-BEN have a more favorable impact on their dry strength qualities when compared to CP. When compared to CP, the dry strength of the paper surface increased by 66.6% when it was coated with 100% CMC. The dry strength increased from 2.1 kNm/kg to 3.5 kNm/kg. The dry strength values, on the other hand,

were found to be roughly equivalent at a variety of CMC-BEN blending ratios, as can be seen rather well in the figure. However, this value is relatively near to that of papers generated with other mixture ratios. The dry strength value of papers produced at a CMC-BEN mixture ratio of 1/0.1 was determined to be 3.6 kNm/kg. As can be shown in Figure 2, the incorporation of BEN into the CMC composition did not result in a visible variation in the dry strength characteristics of the paper materials, and the main effect on dry strength performances was obtained by the CMC.

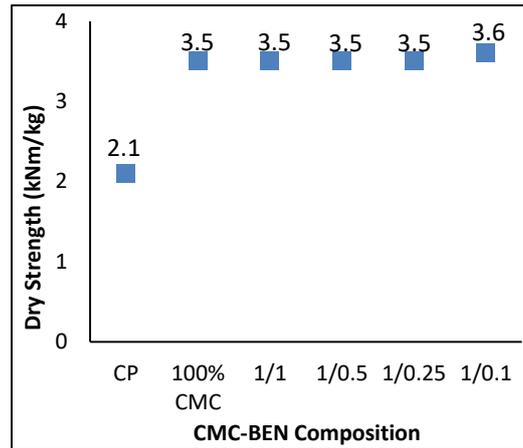


Figure 2. Dry strength values of papers

CMC and CMC-BEN coated papers exhibited a considerable decrease in wet strength values (Figure 3) as compared to CP, in contrast to the dry strength values that were observed. After 30 seconds, the wet strength values of CP were found to be the highest, measuring 4.6 kNm/kg. On the other hand, the lowest value was seen in papers coated with a mixture ratio of 1/0.1 CMC-BEN, which measured 0.3 kNm/kg by the end of 3 minutes. As can be observed from the image, both CMC and BEN have a negative impact on the wet strength qualities of the paper. An anionic cellulose precursor known as CMC is typically chosen for use in a variety of applications within the paper manufacturing industry. These applications include coating, wet zone chemical treatment, surface bonding, and filler changes (Blomstedt et al., 2007; Shen et al., 2010). In accordance with the findings of Hashem et al., (2025), the incorporation of CMC into the manufacturing process of paper at a rate ranging from 0.5 to 1% leads to a 15% enhancement in the paper's strength attributes. As stated by Baker (2025), the incorporation of CMC results in an increase in the number of hydrogen bonds that exist between CMC and cellulose fibers, hence enhancing the dry strength of the paper. In contrast to the dry strength values, the wet strength properties of CMC and CMC-BEN coated papers are significantly lower. It is true that the structures of CMC and BEN are hydrophilic. However, the water that is present in the CMC structure and is applied to the surface of the paper weakens the bonds at the contact points of the fibers on the paper

surface. This has a negative impact on the bond strength and, as a result, the wet strength qualities of the paper. As the amount of time that the paper samples were submerged in water increased, the water molecules weakened the bonds that were present in the fiber contact point region. This resulted in a decrease in bond strength, which in turn led to even stronger wet strength values.

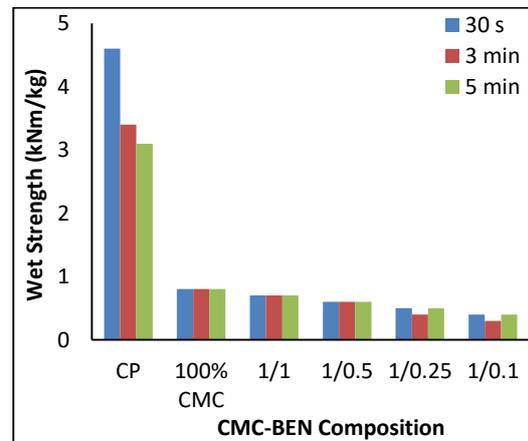


Figure 3. Wet strength values of papers

In addition to the wet strength properties of the paper, the COBB test was utilized to determine the total water absorption of the substance. The findings of this measurement are depicted in Figure 4. It was discovered that sheets based on 100% CMC and CMC-BEN had higher COBB values when compared to CP. It was found that the maximum COBB value was 104 g/m² in CMC-BEN additive papers that were generated at a 1/1 blend ratio. On the other hand, this value was found to be 79.6 g/m² for CP. The highest COBB values were achieved in papers that were generated

with the highest mixing ratio of 1:1. This was due to the fact that both CMC and BEN have a high hydrophilic nature. According to Li et al., (2026), the hydrophilic behavior of BEN is a result of the powerful bonds that take place between interlayer cationic ions and water molecules. These relationships make it possible for BEN to effectively adsorb nuclear ions that are dissolved in water.

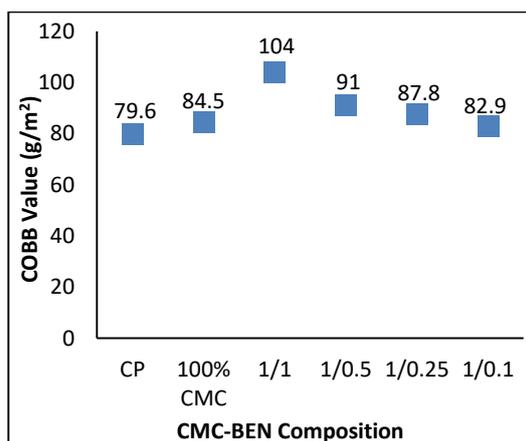


Figure 4. COBB performances of papers

Antibacterial Activities

In a variety of paper applications, antibacterial qualities are becoming increasingly significant. This is especially true in the case of food packaging materials, which are becoming an increasingly important consumer product. Sanitary papers and papers used for packaging food are two of the most prominent examples of these applications. On the other hand, as can be seen in Figure 5, which provides visuals of the antibacterial activity performance of the papers, neither CP nor CMC-BEN based papers were found to exhibit any antibacterial activity versus *S. aureus* and *E. coli*. Generally speaking, pure CMC does not exhibit any antibacterial activity against bacteria such as *S. aureus* and *E. coli* (Han and Wang, 2017). In a similar vein, antibacterial activity experiments were carried out on CMC-ZnO-based papers. The results showed that CMC-coated papers did not exhibit any antimicrobial properties. On the other hand, the incorporation of ZnO into the structure led to a rise in resistance against both *S. aureus* and *E. coli* bacteria (Kurtuluş, 2025). Following the findings of the research carried out by Oliveira et al., (2023), it was discovered that the inhibition rates of Na-BEN

in hybrids produced by incorporating essential oils into the framework of BEN were approximately 20% for both *S. aureus* and *E. coli*. Furthermore, it was found that the antibacterial activity improved with growing quantities of essential oil in the composition. It is believed that the absence of any antibacterial activity in these CMC-BEN based papers is due to the highly hydrophilic nature of CMC, which enables it to easily bind to the surface of the paper and reduce the effectiveness of BEN through the hydrogen bonds that it forms. This is despite the fact that BEN clay, in contrast to CMC, demonstrates a low level of antibacterial activity.

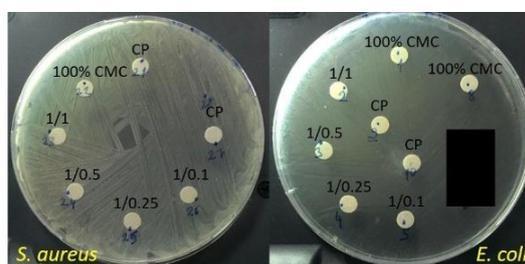


Figure 5. Antibacterial activity test results

SEM Images

Figure 6 illustrates the SEM views of CP and also papers coated with 100% CMC and 1/0.5 mixing ratio of CMC-BEN mixture. CP and 100% CMC coated paper have surface photographs that clearly demonstrate that the surface morphology of CMC coated papers is more homogenous and softer than that of CP. The coarser fibers that are readily apparent in the CP structure are noticed in a surface morphology that is more homogenous and smoother when the CMC surface coating is applied. An examination of the scanning electron microscopy (SEM) picture of CMC-BEN coated papers with a mixing ratio of 1/0.5 reveals that the strong surface coating effect of CMC is immediately apparent. Due to the fact that CMC has a highly hydrophilic structure, it quickly interacts with cellulosic fibers. As a result, it is difficult to clearly detect the presence of BEN in the structure; the BEN that is present on the surface of the paper is indicated by a red arrow. The conclusion is that the coarser fiber structure that was observed in the CP composition is transformed into a more homogeneous structure with the addition of CMC, and that

CMC forms a softer structure on the surface of the paper. This is demonstrated by the views obtained from the SEM. The high hydrophilic effect of CMC, which enables it to rapidly attach to the surface, made it difficult to detect the presence of BEN on the

paper surface. This was due to the fact that the paper surface was coated with CMC. The CMC-BEN mixture filled the micro-gaps in the structure of the paper and coated the fiber surfaces, which resulted in an increase in the paper's homogeneity.

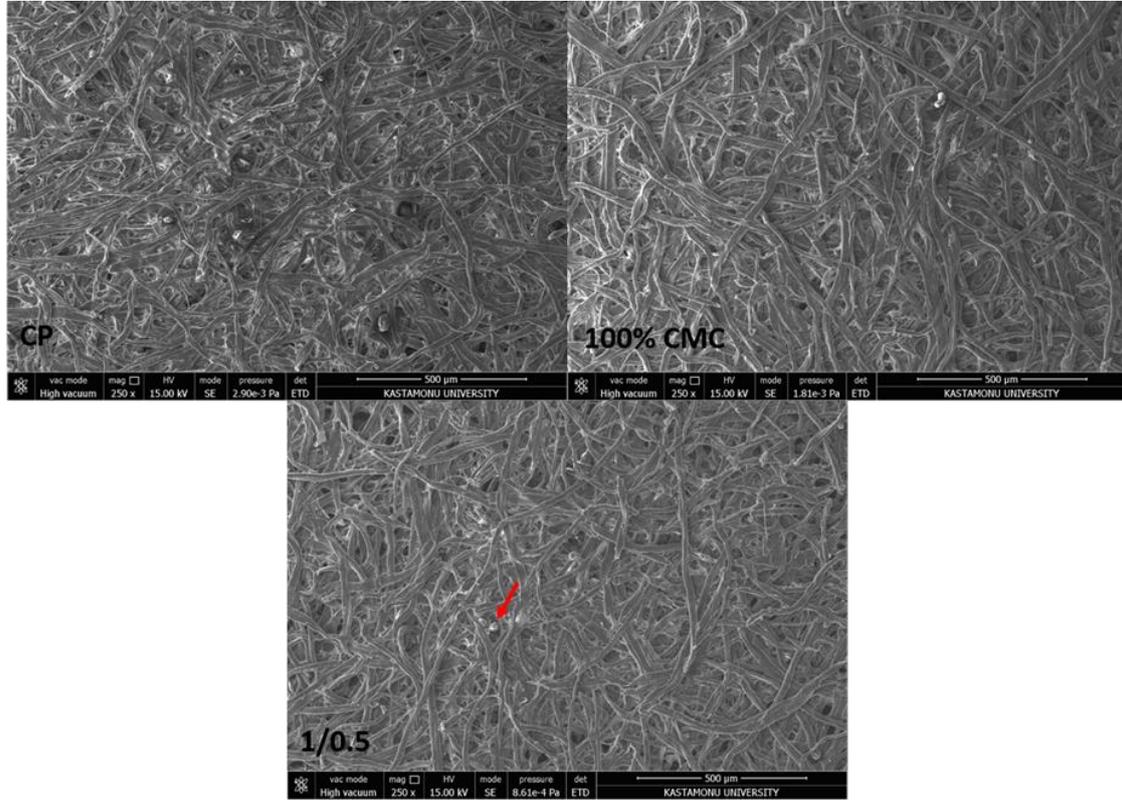


Figure 6. SEM Images of CP (250 X), 100% CMC (250X), and 1/0.5 (500X) coated papers

Conclusion

For the purpose of this investigation, CMC-BEN mixes that were produced with different mixing ratios were applied to the surface of paper, and the resulting changes in the properties of the paper were investigated. The application of CMC-BEN to the surface of the paper has been found to result in an increase in the density values of the paper. Additionally, it was noticed that the coating procedure yields higher absorption when solutions containing a high percentage of CMC are used. Nonetheless, none of the papers, including CP, exhibited resistance to *S. aureus* and *E. coli* bacteria; although the dry strength and COBB properties of the papers were enhanced by CMC-BEN treatment, the wet strength values were adversely impacted.

Ethics Committee Approval

N/A

Peer-review

Externally peer-reviewed.

Author Contributions

Conceptualization: O.Ç.K.; Investigation: O.Ç.K.; Material and Methodology: O.Ç.K.; Visualization: O.Ç.K.; Writing-Original Draft: O.Ç.K.; Writing-review & Editing: O.Ç.K. All authors have read and agreed to the published version of the manuscript.

Conflict of Interest

The authors have no conflicts of interest to declare.

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