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Research Article

Investigation of Surface Properties of Eggshell based Kappa-Carrageenan-Polyvinyl Alcohol Nanobiocomposite Coated Low Alloyed Steel Foam

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Abstract

In this study, we developed a novel eggshell based kappa-carrageenan-polyvinyl alcohol nanobiocomposite coated low alloyed steel foam. The prepared nanobiocomposite was preferred as a coating function on the distribution of particles on the low alloyed steel foam. The scanning electron microscopy (SEM), stereo microscope, and fourier transform infrared spectroscopy (FT-IR) techniques were used to determine the chemical and surface properties of the nanobiocomposite and nanobiocomposite coated low alloyed steel foam. According to the characterization results, we observed that the nanobiocomposite coated low alloyed steel foam had a uniform controlled morphology. Furthermore, the mean surface roughness values of uncoated low alloyed steel foam and nanobiocomposite coated low alloyed steel foam were measured as 4.48 µm and 4.61 µm, respectively. Consequently, we showed that the nanobiocomposite was uniformly coated onto the surface of the micropore channel of the low alloyed steel foam. Based on these results, eggshell based kappa-carrageenan-polyvinyl alcohol nanobiocomposite is a promising nanomaterial for surface modification of the low alloyed steel foam with a controlled and homogeneously distributed surface feature in biomedical applications using a green approach.

Keywords: Nanobiocomposite, Steel foam, Coating nanomaterial.

Yumurta Kabuğu Bazlı Kappa-Karragenan-Polivinil Alkol Nanobiyokompozit Kaplı Düşük Alaşımlı Çelik Köpüğün Yüzey Özelliklerinin İncelenmesi

Öz

Bu çalışmada, yeni bir yumurta kabuğu bazlı kappa-karagenan-polivinil alkol nanobiyokompozit kaplı düşük alaşımlı çelik köpük geliştirdik. Hazırlanan nanobiyokompozit, düşük alaşımlı çelik köpük üzerindeki partiküllerin dağılımında kaplama görevi ile tercih edilmiştir. Nanobiyokompozit ve nanobiyokompozit kaplı düşük alaşımlı çelik köpüğün kimyasal ve yüzey özelliklerini belirlemek için taramalı elektron mikroskobu (SEM), stereo mikroskop ve fourier dönüşümlü kızılötesi spektroskopisi (FT-IR) teknikleri kullanıldı. Karakterizasyon sonuçlarına göre, nanobiyokompozit kaplı düşük alaşımlı çelik köpüğün homojen kontrollü bir morfolojiye sahip olduğunu gözlemledik. Ayrıca kaplanmamış düşük alaşımlı çelik köpüğün ve nanobiyokompozit kaplı düşük alaşımlı çelik köpüğün ortalama yüzey pürüzlülük değerleri sırasıyla 4.48 µm ve 4.61 µm olarak ölçülmüştür. Sonuç olarak, nanobiyokompozitin düşük alaşımlı çelik köpüğün gözenekli yapısının yüzeyi üzerine düzgün bir şekilde kaplandığını gösterdik. Bu sonuçlara dayanarak, yumurta kabuğu bazlı kappa-karagenan-polivinil alkol nanobiyokompozit, yeşil bir yaklaşım kullanılarak biyomedikal uygulamalarda kontrollü ve homojen olarak dağıtılmış bir yüzey özelliğine sahip düşük alaşımlı çelik köpüğün yüzey modifikasyonu için umut verici bir nanomalzemedir.

Anahtar Kelimeler: Nanobiyokompozit, Çelik köpük, Kaplama nanomalzemesi.

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1. Introduction

Nanotechnology applications have remarkable advancements in all disciplines of scientific fields (Kumar et al., 2018). Especially, nanobiocomposites have remarkable advantages and great potential to use as new coating nanomaterials especially due to their surface, physical, biological, and chemical properties in material technologies (Youssef and El-Sayed, 2018; Pan et al., 2018). With this approach, polymeric nanoparticles, metal / metal oxide nanoparticles, nanocomposites, nanofibers, and nanotubes have been developed in surface modifications of materials. Considering nanobiocomposites as advanced technological materials, preparation methods, synthetic strategies, techniques, surface and chemical properties of nanocomposites have been popular in several fields of applied nanotechnology (Hong et al., 2017; Asen and Shahrokhian, 2017).

Recently, with the increase in the search for lightweight materials, metal foams which are a class of engineering materials developed (Dukhan, 2013). Metallic foams can be produced in different porosity from many metals and alloys (Bafti and Habibolahzadeh, 2010; El-Hadek and Kaytbay, 2008; Smith et al., 2012; Paserine et al., 2004). Among these, steel foams draw attention due to their various superior properties such as low thermal conductivity, resistance to high operating temperatures, high specific strength, high energy absorption properties, as well as low production costs (Bekoz and Oktay, 2012). The current usage areas of steel foams are generally in the mechanical, aerospace and automotive industries (Smith et al., 2012). However, metallic foam materials have many properties that are not discovered and need to be investigated (Banhart, 2001). Successful expansion of usage areas of metallic foams depends not only on the invention of new methods to produce an inexpensive and improved quality of the metallic foams but also on a detailed understanding of their properties such as weldability and coating properties, as well as the improvement of their mechanical and microstructural properties (Banhart, 2001; Shirzadi et al., 2004; Smith et al., 2012).

When the studies in the literature are examined, it has been seen that there are many studies in which steel foams are produced by different methods and their mechanical and microstructural properties are investigated (Park and Nutt, 2001; Szyniszewski et al., 2014; Castro and Nutt, 2012). However, research on the coatability of steel foams has not been found. Therefore, the main purpose of this study is to fill this gap in the literature. For this purpose, in this study, steel foam produced from Cu-Ni-Mo pre-alloyed water atomized Distaloy AB powder was used as the substrate material with the space holder-water leaching method. The copper content in the steel powder provides the formation of the liquid phase in the sintering process and increases the strength of the part. Nickel content reduces the amount of elongation of the sintered part, while molybdenum gives the sintered part high compressibility (Bekoz and Oktay, 2014). This low alloyed powder provides dimensional stability and good green strength and can be sintered at lower temperatures than other steel alloys. The Cu-Ni-Mo-based low alloyed steel is generally used in automotive parts. In this study, we prepared eggshell-based kappa-carrageenan-polyvinyl alcohol nanobiocomposites as a green coating nanomaterial to modify the low alloyed steel foam. The chemical property and surface morphology of the material were investigated using different techniques such as scanning electron microscopy (SEM), stereo microscope, and fourier transform infrared spectroscopy (FT-IR).

2. Material and Method

2.1. Materials

Steel powders were purchased from Höganäs Company (Sweden). The chemical composition of pre-alloyed Distaloy AB steel powders was presented in Table 1.

Table 1. Chemical composition of pre-alloyed Distaloy AB steel powder

Element	*Cu*	*Ni*	*Mo*	*Fe*
wt.%	1.5	1.75	0.5	Balanced

Carbamide, paraffin wax, zinc stearate, and fine graphite were purchased from Merck Company (Germany). Eggshell (white) was obtained from a traditional farm (Pendik). Kappa-carrageenan (sulfated plant polysaccharide) was purchased from Sigma Aldrich Company (Germany). Polyvinyl alcohol (PVA, Mw of 60.000 gmol-1), and ethanol (purity ≥99.8%) were purchased from Merck Company (Germany).

2.2. Characterization

The scanning electron microscopy (SEM) (FE-SEM, JEOL 63335F) with a gold coating at 20 kV accelerating voltage and, stereo microscope, and fourier transform infrared spectroscopy (FT-IR) techniques (Perkin Elmer Spectrum Two FTIR Spectrometer) using a KBr powder in the spectral range of 4000 cm^{-1} to 500 cm^{-1} with a resolution of 4 cm–1 using 8 scans) were used to determine chemical and surface properties of the prepared nanobiocomposite and nanobiocomposite coated low alloyed steel foam. The total porosity content of low alloyed steel foam samples was determined using Archimedes' Principle. Measurements were performed on a Sartorius precision balance equipped with a density determination kit. In order to determine the open and closed porosity ratios of the samples, the samples were dipped in paraffin boiling at 150 ºC, the ratios were determined by weight measurements before and after immersion. The surface roughness values of steel foam specimens before and after coating was carried out using a SJ-201P model Mitutoyo surface roughness measurement device.

2.3. Preparation of Eggshell based Kappa-Carrageenan- Polyvinyl Alcohol Nanobiocomposite

In our previous study, we reported the preparation method of the eggshell based kappa-carrageenan- polyvinyl alcohol nanobiocomposite (Sanrı-Karapınar et al., 2020). The eggshell was cleaned with destilled water and dried using a microwave oven at 720 W for 10 min. The powder was added in water/ethanol solution (25 mL/25 mL) and dried for 5 min using a microwave oven. The sample was dissolved to 50 ml of glacial acetic acid/ultrapure water (1mL/49mL) solution and sonicated for 1 h at 35% amplitude-frequency. 5 g of PVA was dissolved in 50 ml of destilled water at 80°C and kept at 25°C for 5 days in a dark room. 0.1 gr of kappa-carrageenan was dissolved in 50 ml of destilled water. PVA and kappa-carrageenan solutions were mixed and the eggshell was added to the polymer blend. The sample was sonicated for 1 h at at 35% amplitude-frequency. Finally, it was was filtered using a 0.22 micron of sterile filter and stored in a sterile container at room temperature.

2.4. Preparation of Low Alloyed Steel Foam

Low alloyed steel foam as the substrate material for coating was produced by the space holder-water leaching method in powder metallurgy. In this method, low alloyed steel foam is prepared by going through the stages of the powder mix preparation, green strength foam preparation and then sintering for the final metallic foam part. First, rounded and irregularly shaped pre-alloyed steel powders were with an average particle size of 112 µm and a size distribution between 45 µm and 150 µm. The carbamide particles used as space holders in the study and they are irregular in shape and sieved in the size range of +710 -1000 µm. In addition to steel powders and carbamide in the powder mixture, zinc stearate and fine graphite were used as a lubricant and paraffin wax solution was used to help green strength. 0.8 wt.% zinc stearate and 0.4 wt.% fine graphite were added the steel powder as powder premix. This mix was mixed manually with paraffin wax (2 wt.%) solution. In order for the carbamide to be coated homogeneously with the powder premix, it was mixed in a turbula type mixer for 60 minutes as 80% of the carbamide and the %20 of the powder premix. Before sintering stage, carbamide particles coated with a steel powder mixture were compressed in a hydraulic press to prepare the green strength steel structure. The compression was done at 200 MPa in the cylindrical stainless steel mold with 10 mm in diameter and approximately 12 mm in height. The green parts were kept in distilled water at room temperature for 30 minutes to leach the carbamide particles. Finally, low alloy steel foams were produced by sintering at 1150 ºC for 60 minutes in a laboratory tube furnace.

2.5. Preparation of Eggshell Based Nanobiocomposite Coated Low Alloyed Steel Foam

In order to prepare for the coating process, cylindrically shaped steel foam samples were sliced with EDM (Electrical Discharge Machining). The process parameters for the cutting process are given in Table 2.

Table 2. Process parameters of the cutting process

Parameters	Value
Peak current	3 A
Pulse-on time	50 µs
Pulse-of time	30 µs
Open-circuit voltage	60 V
Wire feed speed	5 m/s
Wire	CuZn37 with 0.15 mm diameter

After the cutting process, the dust was removed from the surface of the parts with compressed air. Sliced samples thickness are approximately 0.5 cm. Then, thinly sliced low alloyed steel foams were dipped in the prepared nanobiocomposite solution at room temperature for 5 minutes. Finally, drying was carried out at 50 °C with a %30 relative humidity for 3 hours. Weight measurements were made on the pre and post-coating samples, and a post-coated weight gain of at 3.15 mg was determined.

3. Results and Discussion

3.1. Characterization of Eggshell based Kappa-Carrageenan- Polyvinyl Alcohol Nanobiocomposite

SEM micrograph of the nanobiocomposite is given in Figure 1. The SEM results were showed that the prepared nanobiocomposite had a nano-scale uniform distribution with fibrous structures less than 100 nm in diameter. The FTIR spectra of the nanobiocomposite is given in Figure 2. FTIR Furthermore, the characteristic FTIR peaks of the nanostructure were observed at 3400 cm−1 (–OH functional groups), 3199 cm−1 (–OH functional groups), 2913 cm−1 (–CH stretching), 2856 cm−1 (–CH stretching), 1726 cm−1 (–C=O groups), 1640 cm−1 (–C=O groups), 1455 cm−1 (C=O bonds), and 1050 cm−1 (C=O bonds). In our previous study, it was reported that there was a chemical interaction between -OH groups of polymer matrix and and C = O groups of eggshells to obtain the nanostructure (Sanrı-Karapınar et al., 2020).

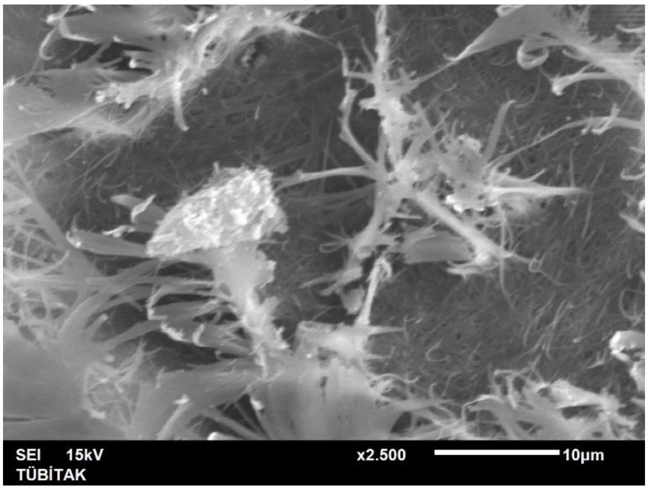

Figure 1. SEM micrograph of eggshell based kappa-carrageenan-polyvinyl alcohol nanobiocomposite.

3.2. Characterization of Low Alloyed Steel Foam

Stereo microscope image and SEM image of sintered steel foam are given in Figure 3 (a) and (b), respectively. The pore distribution of the steel foam samples was generally uniform. In the sintered product, the pores are separated from each other by the pore walls. No cracks were observed in the pore walls and the structure of the pores is similar to the structure of carbamide which is used as a space holder. The values of various pore properties of the uncoated low alloy steel foam are given in Table 3. The mean size and mean sphericity values were determined by the image analyzer software from the SEM image.

Table 3. Pore properties of uncoated low alloyed steel

Property	Value
Total Porosity	%75
Open Porosity	%57
Closed Porosity	%18
Mean Size	618 µm
Mean Sphericity	0,57

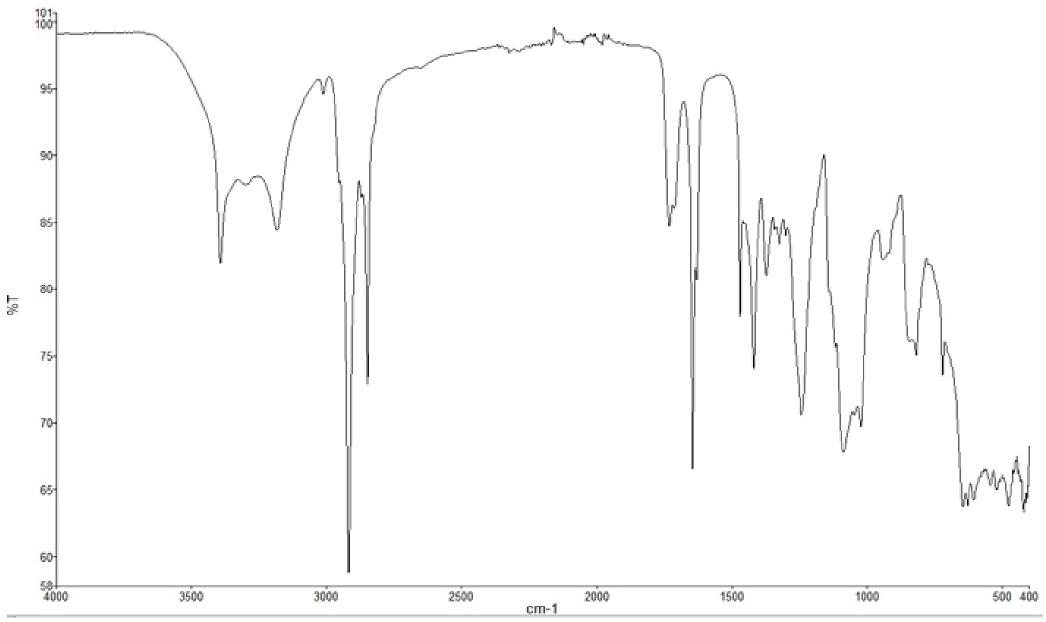

Figure 2. FTIR spectra of eggshell based kappa-carrageenan-polyvinyl alcohol nanobiocomposite.

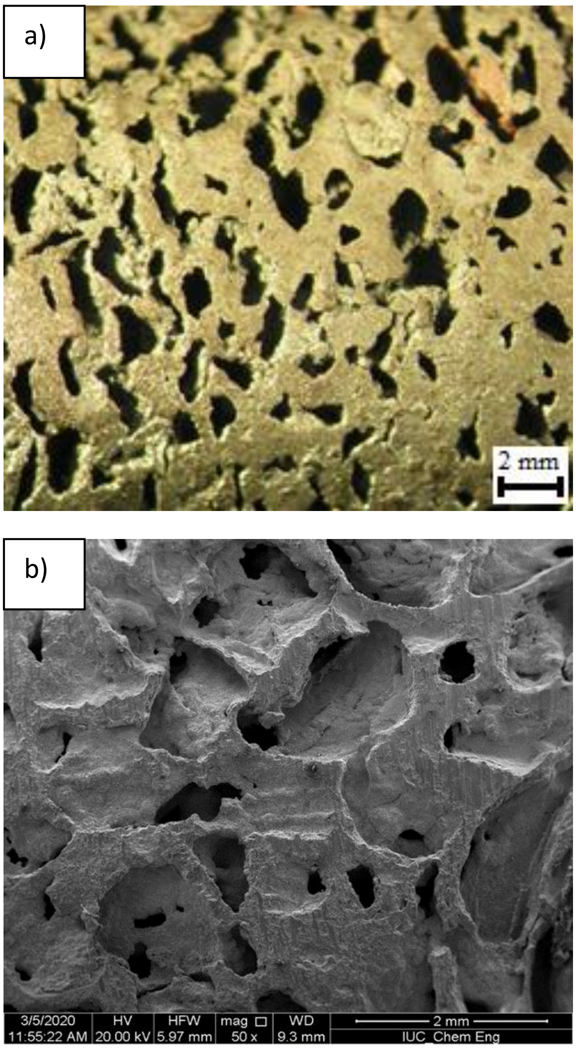

Figure 3. Images of low alloyed steel foam using a (a) stereo microscope and (b) SEM technique

3.3.Characterization of Nanobiocomposite Coated Low Alloyed Steel Foam

The SEM image of the uncoated surface and eggshell based kappa-carrageenan-polyvinyl alcohol nanobiocomposite coated surfaces at different magnifications are shown in Figure 4. It is seen that the post-coating structure is denser than the pre-coating structure. This can be explained by the coating of the microporous structure with a nano-sized coating. When the coating structure is examined at high magnification, it is seen that a flat and leafy structure is formed. Karakuş et al. (2020a), coated 17-4 PH stainless steel foam with Kappa-Carrageenan/PVA/ES nanobiocomposite using a dip coating technique, and explored the surface characteristics. They reported that the coating was uniformly distributed over the porous form. In another study of the Karakuş et al. (2020b), examined coated 17-4 PH stainless surface with ZnO nanoparticles, and obtained similar results.

The mean surface roughness values of uncoated steel foam and eggshell based kappa-carrageenan-polyvinyl alcohol nanobiocomposite coated foam were measured as 4.48 µm and 4.61 µm, respectively. Normally, the surface of the steel foam is rougher, but the surface roughness value is low due to laser cutting. There was no significant change after coating. In Figure 5, the image of the pore walls and the coating of the coated steel foams is given. According to the measurements taken from the microstructure image, the coating thickness values are between 13 and 18 µm. When the images are examined; the coating process was effective. No cracks were observed along the coating surface, but large numbers of micropores formed in the pore walls. Although the macropores appear to be isolated from each other, they are actually connected by micropores in the cell walls. Karakuş et al. (2021), studied the surface characterization of coated 17–4 PH stainless-steel foam with CMC/Chitosan-α-Fe_2O_3 nanoparticles (NPs). The authors found that the average surface roughness value coated stainless steel foam to be between 4.59–5.91 µm, and the coating thickness values to be between 15 and 30 µm. The results indicated similar trends in porous structures.

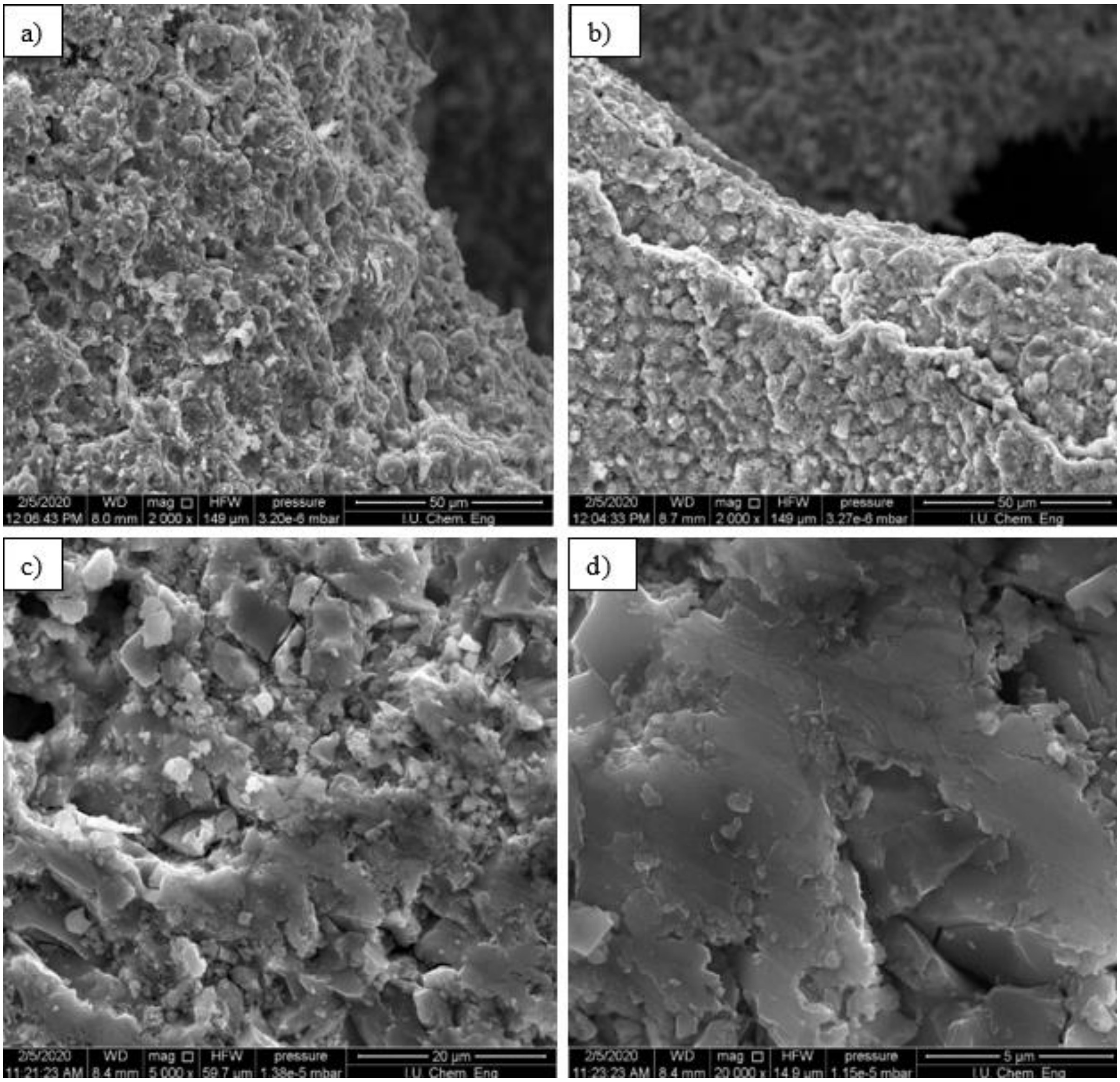

Figure 4. The SEM images of uncoated surface (a) and coated surfaces at different magnifications (b, c, d).

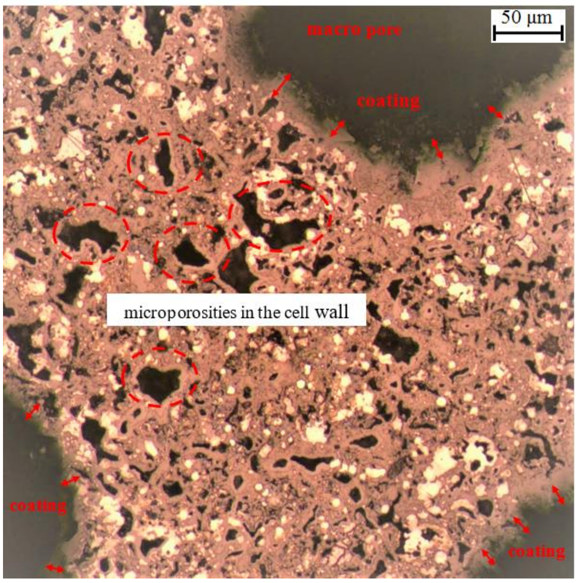

Figure 5. Cross-sectional surface microstructure of the nanobiocomposite porous coating on Cu-Ni-Mo based steel foam substrate

4. Conclusions and Recommendations

For the first time in literature, we demonstrated that eggshell based kappa-carrageenan-polyvinyl alcohol nanobiocomposite could be successfully coated on the steel foams. The surface properties of uncoated and coated foams were investigated usind SEM techniques.

Cross-sectional microstructure images and SEM micrographs showed that the steel foam was successfully covered with the nanobiocomposite to fabricate a novel organic–inorganic hybrid nanomaterial. Consequently, it was clear that the nano-coating was constructed uniformly on the surface of the material with a higher than 95% in the 13-18 µm coating thickness range. Overall, these experimental results showed that nano-foam construction of the nano-coating containing eggshell based kappa-carrageenan-polyvinyl alcohol nanobiocomposite and low alloyed steel foam provided a green and efficient approach for use in biomedical applications.

Metal coating process was performed without any detrimental effect on the steel foam parts at identical coating condition. In the light of the reviewed literature, further theoretical and experimental research is required on the characteristic effects such as pore ratio, shape and distribution on the coating characteristic of steel foams. We hope that this study will help researchers working on the subject.

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