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The Influence of Barium Ferrite Nanoparticles on Morphological and Mechanical Properties of Ethyl Cellulose Based Nanocomposites

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Abstract:

This study presents preparation and characterization of ethyl cellulose based nanocomposites. Successful use of simple solvent casting technique provided nanocomposites with high loads of barium ferrite magnetic nanopowder in the polymer matrix, promising significant improvement of mechanical properties. Investigation of morphology revealed formation of agglomerates that are still on nanoscopic level. Nanocomposite thin films with a higher content of the magnetic powder showed substantial enhancement of break strength, elongation and microhardness compared to the pure ethyl cellulose, which was the primary aim of this research.

Keywords: Barium ferrite; Ethyl cellulose; Nanocomposite; Mechanical properties.

1. Introduction

Air separation has is widely used for oxygen production and air enrichment in different industrial fields, from chemical production to medical devices [1]. Generally speaking, the most commonly applied methods for air separation can be divided into two major categories, cryogenic and non-cryogenic. Among them, cryogenic distillation and pressure swing adsorption are the oldest and the most employed techniques for the oxygen-enriched air production [2, 3]. Although these techniques provide high oxygen purity, they also require high production cost and energy consumption, which is a major drawback nowadays when industry is turning its focus on more environmental friendly processes. Employment of membrane technology for gas separation is still relatively young approach, but with a high prospect in the future [4, 5]. Earlier types of membranes were dominantly composed of ceramic and metallic materials. The named classes of materials offer excellent mechanical and thermal properties, but also involve high operating costs [6, 7]. Advances in polymer science and engineering have opened possibilities for their use in the membrane technology for gas separation, offering simple processing, low cost materials, with potentially high-purity oxygen product. Polymer based membranes are already being widely used for

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micro-, ultra- and nanofiltration [8]. One of the polymers with potentials for the use in membrane technology is ethyl cellulose. It is a hydrophobic polymer used widely as a coating material, as well as a matrix material in medicine for the controlled drug release [9]. Major drawback for their use lies in poor mechanical performance. Overall, the mechanical properties of polymers are poor compared to ceramic and metallic materials, and therefore, various reinforcements are required. It is well known that by introduction of nanoparticles in the polymer matrix a significant enhancement of modulus of elasticity and toughness can be obtained. Ethyl cellulose based nanocomposites with both metallic and ceramic nanoparticles have already been presented in several studies [10, 11]. Especially interesting is a new emerging class of membranes called *magnetic membranes*, which can be utilized for separation of O₂/N₂ gas mixture, using their magnetic nature for the separation. However, all of the aforementioned studies report only limited or even insufficient data on material's mechanical behavior. Since materials with potential use in membrane technology must withstand specific and often demanding operating conditions, it is of an essence to investigate their mechanical performance.

Results of this study show the influence of magnetic nanoparticles' content on mechanical and morphological properties of the processed nanocomposites in the form of thin films, obtained by the simple, low cost solution casting technique. Different concentrations of magnetic barium ferrite (BaFe₁₂O₁₉) nanoparticles were incorporated in ethyl cellulose (EC) matrix in order to establish the most promising nanocomposite for further research.

2. Materials and Experimental Procedures

2.1. Materials

Ethyl cellulose (EC) used as a matrix material, solvents used for the preparation of thin films, toluene (99 % purity) and ethanol (99 % purity) and (barium ferrite) BaFe₁₂O₁₉ nanopowder were all purchased from Sigma-Aldrich.

2.2. Preparation of EC and EC- BaFe₁₂O₁₉ thin films

Ethyl cellulose (EC) flat films of thickness 77 – 100 μm and magnetic BaFe₁₂O₁₉ nanoparticle loaded EC films of thickness 82 – 112 μm (depending on the filler content) were prepared by polymer solution casting method. The 3 wt% EC solution in 40:60 ethanol/toluene mixture was poured into a Petri dish, and left to evaporate at room temperature for 24 h. Similarly, the magnetic nanocomposite membranes were made by pouring the 3 % ethyl cellulose solution with the dispersed BaFe₁₂O₁₉ nanopowder (<100 nm) into a Petri dish, and then evaporated for 24 h. The nanocomposite membranes with 10.0 and 20.0 wt% of barium ferrite powder content in dry polymer membrane were obtained. The membranes were removed from the Petri dish (with some distilled water), and subsequently dried at 40 °C for 24h.

2.3. Characterization of EC and EC-BaFe₁₂O₁₉ thin films

The morphology of the prepared EC and EC-BaFe₁₂O₁₉ thin films was investigated using a Field Emission Scanning Electron Microscope (FESEM, TESCAN MIRA 3XMU). The observed fracture surfaces were sputtered with gold for enhanced conductivity. The size distribution of BaFe₁₂O₁₉ nanoparticles was obtained through the analysis of the FESEM images by using the *Image Pro Plus 6.0* software Media Cybernetics, Inc. The Fourier Transformed Infrared (FTIR) spectra of all the samples in the form of KBr discs were recorded in transmission mode between 4000 and 400 cm⁻¹ with a resolution of 4 cm⁻¹, on Bomem MB-102 FTIR spectrometer. Microhardness tests on all the studied films were

performed using Vickers microhardness tester “Leitz, Kleinhartepuffer DURIMET I”, at load of 4.9 N [12-14]. The tensile tests were also performed on all of the obtained thin films, using universal testing machine, Shimadzu Autograph AG-X (Japan), in accordance with the ASTM D3039 standard [15].

3. Results and Discussion

3.1. FESEM analysis

FESEM micrographs of pure EC, EC-10%BaFe₁₂O₁₉ and EC-20%BaFe₁₂O₁₉ are presented in Fig. 1 (a, b and c). As it can be seen on Fig. 1a, FESEM image of pure EC thin film displays smooth surface without pores. Fig. 1b shows that for 10 wt% filler content, magnetic nanoparticles form agglomerates, which is in accordance with the expectations, considering high surface energy of magnetic nanoparticles and their incompatibility with the polymer matrix. In the nanocomposite film with 20 wt% content of nanoparticles, FESEM revealed thicker agglomerates (Fig. 1c).

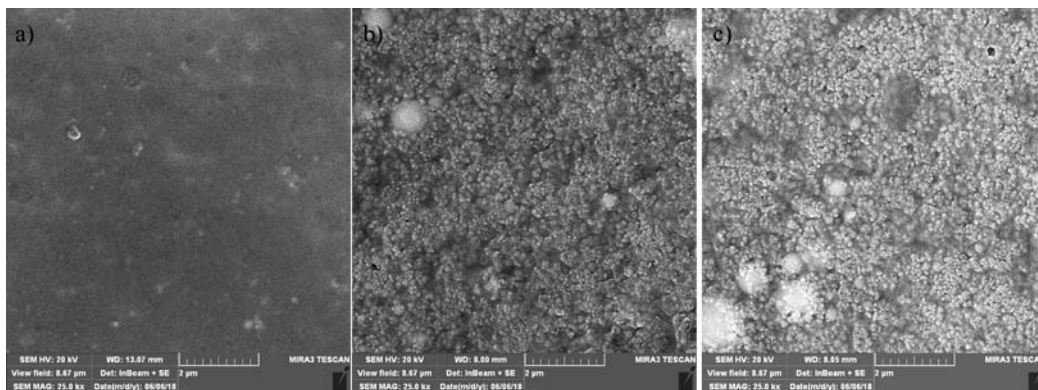


Fig. 1. FESEM images of: a) pure EC, b) EC-10%BaFe₁₂O₁₉ and c) EC-20%BaFe₁₂O₁₉ thin films.

Image analysis showed that the average nanoparticle diameter was 75 nm, with more than 50% nanoparticles with diameters below 60 nm. Software analysis is performed by identification of objects and clusters based on color contrast. Particle size distribution obtained after software image analysis is presented in Fig. 2.

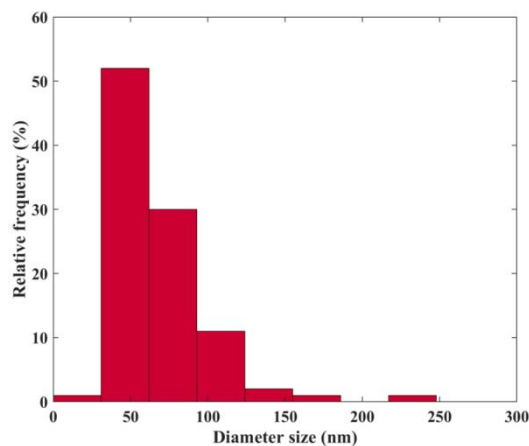


Fig. 2. Particle size distribution.

Agglomerates are varying in size, from 227 nm to 746 nm, which is still below classic micrometer particle size traditionally used as reinforcement. These findings indicate that magnetic BaFe₁₂O₁₉ nanoparticles could serve as an effective reinforcement in higher concentration despite the formation of agglomerates.

3.2. FTIR analysis

The FTIR spectrum for EC shows a distinct peak at 3477 cm⁻¹, which is due to the –OH groups present in the cellulose [16]. The peaks at around 2978 and 2867 cm⁻¹ may be originating from –CH stretching. Bending of –CH₃ can be seen at 1378 cm⁻¹, while –CH₂ bending shows at 1456 cm⁻¹. The peak at 1111 cm⁻¹ comes from C–O–C stretch in the cyclic ether. Both spectrums show similar peaks, indicating that there was no interaction between ferrite and polymer.

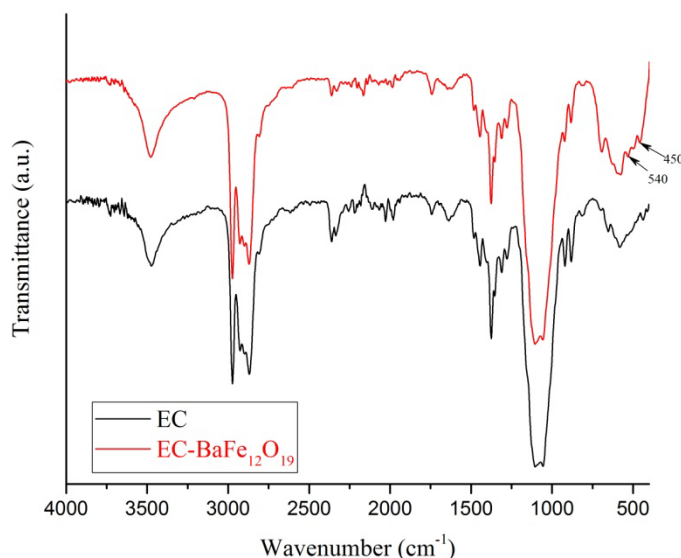


Fig. 3. FTIR spectra of pure EC and EC-BaFe₁₂O₁₉ thin films.

Barium ferrite was identified with two characteristic bands at 540 cm⁻¹ and 450 cm⁻¹, which are associated with intrinsic metal–oxygen stretching vibrations (Fe→ O, Ba ↔ O) at tetrahedral and octahedral sites of the spinel lattice, respectively [17]. Considering that, apart from these two bands which do not appear in the spectrum of pure EC, there are only subtle differences between the obtained spectrums; it can be assumed that nanoparticles remained stable during processing in the polymer [18].

3.3. Microhardness test

Micro Vickers hardness gives insight into the uniformity of magnetic nanoparticle dispersion through the polymer matrix in the processed nanocomposite. It has been revealed that pure EC films have a microhardness of 21 MPa, while the addition of 10 wt% of nanoparticles leads to the 5 % increase. Sample with 20 wt% of BaFe₁₂O₁₉ nanoparticles gives significant rise of 14 % microhardness value, compared to the pure EC, indicating that solvent casting is a suitable method for the processing of nanocomposite thin films based on EC.

Fig. 4 shows indents of all the samples. As it can be seen, indents are without inhomogeneity and cracking of the material.

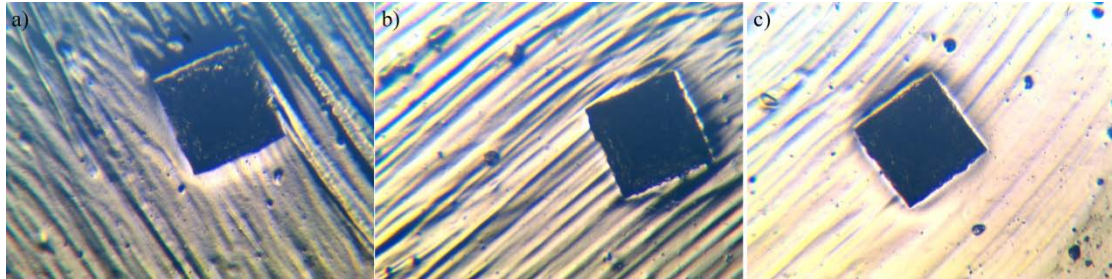


Fig. 4. Indent image for: a) pure EC, b) EC-10%BaFe₁₂O₁₉ and c) EC-20%BaFe₁₂O₁₉ thin films.

3.4. Tensile test

Fig. 5 presents the results obtained from the tensile tests. As the Fig. shows, break strength increased by 48 % for the sample with 10 wt%, and by 21 % for the sample with 20 wt% of BaFe₁₂O₁₉ nanoparticles, compared to the pure EC thin film.

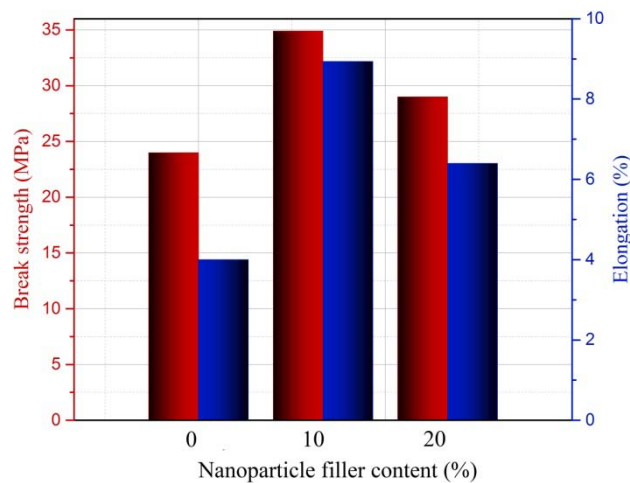


Fig. 5. Tensile test results for pure EC and EC-BaFe₁₂O₁₉ thin films.

Elongation rose from 6.4, over 7.4 to 9.0 % for pure EC, EC-20%BaFe₁₂O₁₉ and EC-10%BaFe₁₂O₁₉ respectively. These findings are in accordance with FESEM analysis, where thick clusters of nanoparticles were observed, indicating that after 10 % of nanoparticle loading, stacking of clusters prevails through the volume of the matrix, making the bonding between the polymer and nanoparticles more difficult. The consequence is decreased mechanical strength and lower elongation value. However, even with this possible phenomenon, mechanical performance of potentially ‘overloaded’ nanocomposite is still superior compared to the matrix itself. These findings and observations lead to the conclusion that simple solution casting of polymer nanocomposite thin films with magnetic particles results in enhancement of mechanical properties of the starting material. Since barium ferrite is both ceramic and magnetic material, as filler it serves two purposes. One of which is the discussed enhancement of mechanical properties and the other is role of the magnetically active component. As the filler content has an influence both on magnetic and mechanical

properties it is obvious that the magnetic performance will be limited by the optimal filler content from the mechanical properties point of view.

4. Conclusion

This research presented processing and characterization of nanocomposite based on polymer ethyl cellulose and magnetic nanoparticles of barium ferrite. The aim was to build nanocomposite material with significantly enhanced mechanical properties compared to pure polymer matrix, in order to expect the material to withstand potential operating conditions. Investigation of morphology using field emission microscopy revealed that nanoparticles tend to build agglomerates below microscopic scale, which opens a possibility of incorporation of high concentration of particles in nanocomposite with potential satisfactory mechanical performance. Infrared spectroscopy proved that nanoparticles of barium ferrite remain stable in ethyl cellulose during processing, indicating that solution casting is an appropriate processing technique for preparation of nanocomposite thin films. Microhardness test revealed significant increase in hardness value, up to 14 % compared to the pure EC, showing further that the chosen technique is appropriate. Finally, tensile test revealed desired mechanical improvement in the form of 48 % and 21 % percent rise of tensile strength for nanocomposites with 10 % and 20 % of nanoparticles, respectively. Small drop of tensile strength could point to stacking of barium ferrite particles through the volume of the matrix, which could lead to a decrease in mechanical performance. However, this result is still significantly higher compared to the pure ethyl cellulose. Summary of results shows that these easily processed nanocomposites with relatively high content of magnetic nanoparticles have mechanical properties that encourage further research for their potential application in different fields, among which is membrane technology.

Acknowledgments

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5. References

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Садржај: Ова студија представља припрему и карактеризацију нанокомпозита на бази етил целулозе. Успешна употреба једноставне технике изливања обезбедила је нанокомпозите са великим уделом магнетног нанопраха баријум ферита у полимерној матрици, обећавајући значајно побољшање механичких својстава. Истраживањем морфологије откривено је формирање агломерата који су и даље на наноскопском нивоу. Нанокомпозитни танки филмови са већим садржајем магнетног праха показали су значајно повећање прекидне чврстоће, издужења и микротврдоће у поређењу са чистом етил целулозом, што је био главни циљ овог истраживања.

Кључне речи: баријум ферит, етил целулоза, нанокомпозити, механичка својства.

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