

RESEARCH PAPER

Synthesis and Characterization of High Flux and Antibacterial Film Nanocomposite Based on Epoxy-Zeolite NaA

Shahabadin Khademi¹, Masood Hamadiani^{1*}, Behrooz Roozbehani², Nahid Khademi³

¹ Institute of Nano Science and Nano Technology, University of Kashan, Kashan, Iran

² Fuel and Petrochemical Engineering Research Center, Abadan Institute of Technology, PUT, Abadan, Iran

³ Environmental Health Engineering, Shiraz University of Medical Sciences, Shiraz, Iran

ARTICLE INFO

Article History:

Received 06 August 2019

Accepted 14 October 2019

Published 01 January 2020

Keywords:

Antibacterial

Epoxy resin

Nanocomposite

Thermal stability

Water softening

ABSTRACT

A high flux thin-film nanocomposite membrane epoxy/ zeolite NaA nanocomposite films prepared by using ultrasonic mixing and spin coating. The synthesized nanocomposites film was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), thermal gravity analysis (TGA), and FTIR spectroscopy. Water softener and water flux characteristics of the epoxy/ zeolite NaA nanocomposite film investigated. The results show the water softener, and hydraulic permeability of the membranes, remarkably improve by the wt.% of the zeolite NaA loading. Antibacterial activity was investigated by use modification of zeolite NaA with silver ions (Ag^+) and copper ions (Cu^{2+}) for nanocomposite.

How to cite this article

Khademi Sh, Hamadiani M, Roozbehani B, Khademi N. Synthesis and Characterization of High Flux and Antibacterial Film Nanocomposite Based on Epoxy-Zeolite NaA. J Nanostruct, 2020; 10(1): 177-184. DOI: 10.22052/JNS.2020.01.019

INTRODUCTION

Polymers due to properties and low cost are widely used in various industries application, but, polymers have the low total strength and poor fraction toughness which limit their applications in structural components [1-3]. Numerous fillers use to improve properties polymer such as nano-clay, zeolite, carbon black, carbon nanotubes compound with the polymers epoxy resin is a thermoplastic polymer which has unique properties such as excellent adhesion, chemical resistance, and high tensile strength [4-7]. Adding nanoparticles such as zeotype materials in the matrix of polymer improve the thermal stability of the produced composite [8-12]. Industrial applications of epoxy-based polymer materials are extensive and include adhesives, coatings and composite materials such as fiber and fiberglass [13].

Hard water has high concentrations of Ca^{2+} and Mg^{2+} ions and has serious problems for the

industry also limit its use. Due to cation exchange ability zeolites can reduce water hardness [14]. The use of zeolites in polymers makes it easy to separate them from solutions and reduce their cost considerably [15].

Zeolite NaA incorporated into the polyamide polymer matrix improves membrane permeability and silver exchange zeolite-polyamide nanocomposites exhibit antibacterial properties [4].

Zeolites are crystalline microporous and mesoporous structures of alumina silicates, which have high porosity. These structures have three-dimensional pore and cavities. Zeolite cavities have the negative charge that neutralized by cation elements. These cations are often loosely bound and easily replaceable, supplying increase to the ion replacement properties of zeolites without damaging the zeolite framework [16-18].

* Corresponding Author Email: hamadani@kashanu.ac.ir

Zeolite NaA displays the LTA (Linde Type A) structure. The pore diameter is small at 4.2Å and has the larger cavity of minimum free diameter 11.4Å. The general formula for zeolite materials is $M_x / n [(Al_2O_3)_x (SiO_2)_y] mH_2O$. For zeolite LTA, the Si to Al ratio is one and the pores size of its related to the type of counter cation (K^+ , Na^+ and Ca^{2+}). One application of Na-LTA zeolites is in detergent as water softener. It can also be with the ion exchange process and the replacement of silver ions in the structure zeolite the antibacterial property given to the specimen [17, 19, 20].

The target of this work was to expand the thin high-performance nanocomposite membranes with the combination of the zeolite NaA and epoxy polymer for effective calcium removal from water also to improve the water permeability at the same time. NaA zeolite ion exchange with silver and copper were used to improve the antibacterial nanocomposite membrane.

MATERIALS AND METHODS

Epoxy resin (based bisphenol A type, KFR-120, Kukdo Chemical), modified amine hardeners, tetraethylorthosilicate (TEOS, 98 wt. %), aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$), ethanol (EtOH, 99 wt. %), and solid NaOH were obtained from Merck.

Synthesis of Zeolite NaA

First 4. 5 ml of TEOS and 5 g of aluminum nitrate were added to 20 ml of the ethanol/water solution mix gently until aluminum nitrate was completely dissolved. Then 25 ml of 0.25 M sodium hydroxide were added to the previous solution gently mix until the gel is created. Then gel is heated under microwave radiation at 100 °C for 1 minute. After crystallization, the product solid was separated by centrifugation, washed by deionized water several times, dried overnight at 105 °C. To improve antibacterial properties of nanocomposites first Na ion in the structure of zeolite exchanged with Ag and Cu. 1 g of the zeolite were added separately to 0.01 M solutions of $AgNO_3$ and $Cu(NO_3)_2$ then was put under reflux at 90°C for 16 h with magnetic stirring. Silver and cooper ions exchange with sodium ions and produce Ag-LTA zeolite and Cu-LTA. The product solid was separated by centrifugation, washed by deionized water several times, dried overnight at 105 °C.

Synthesis of zeolite NaA/epoxy nanocomposite films

Various loading ratios ranging from 0 to 3 wt.% of the zeolite NaA added into epoxy and curing agent mixtures. The mixture was sonication for 30 minutes subsequently de-gassed at 25 °C for 1 h under the vacuum. Nanocomposite films were fabricated on the glass layer by spin coating process at 1000 rpm for 60 s and aging at 60 °C for 10 min. 1% wt% Ag-LTA and Cu-LTA zeolite were added to the epoxy mixture for investigated the antibacterial activity of the nanocomposite.

Membrane performance evaluation

The calcium ion absorption performance for nanocomposite and composite films were evaluated by a bench-scale cross-flow filtration system with a total internal volume of 50 mL and an active surface area of 15 cm². The water flux was computed at the pressure of 2 bar at 25 °C. The water flux (J) and ion removal (R) membranes were determined using the following equations [16, 21]:

$$J = \frac{V}{A \times \Delta t} \quad (1)$$

$$R(\%) = \left(1 - \frac{C_p}{C_f} \right) \times 100 \quad (2)$$

V is the volume of permeate water (L), A is the effective surface membrane area (m²), Δt is the filtration time (h), C_p (mg/L) and C_f (mg/L) are the salt concentration of penetration and feed solutions, respectively. The feed water contained 300 mg/L $CaCl_2$ solution.

The NaA zeolite that dispersed into the cross-linked epoxy polymer capable as the ion exchanger, adsorption Ca^{2+} and releases Na^+ . Calcium solutions were prepared using $CaCl_2 \cdot 2H_2O$.

Antibacterial assay

For antibacterial activities, E. coli and S. aureus were selected according to the standard method 24 hours cultured to obtain a logarithmic growth phase. Mueller-Hinton agar is employed for growth medium [22]. 1ml each bacterium was added to the culture medium and then cultured on a plate surface with the sterile swabs. zeolite AgA/ epoxy and zeolite CuA/ epoxy nanocomposite was prepared the centimeter square and placed on the

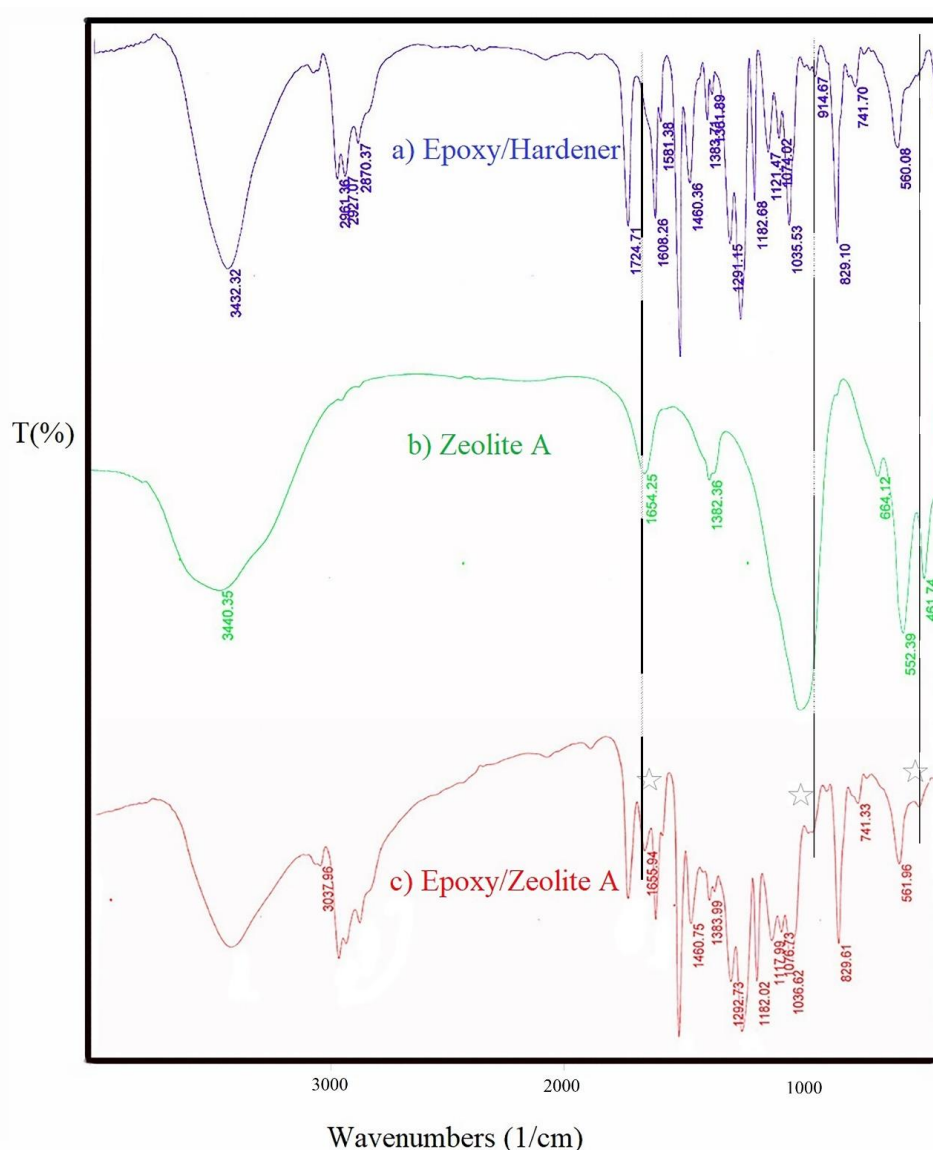


Fig. 1. FTIR curves of (a) epoxy cross-linked, (b) zeolite NaA and nanocomposites incorporated 3wt% zeolite NaA.

culture medium and incubated at 37 °C for 24 h. Antibacterial activity investigated by measuring the diameter of inhibition zone (DIZ) [23].

RESULTS AND DISCUSSION

The bonding interactions between the cross-linked epoxy and zeolite NaA nanoparticles were analyzed employ a Perkin Elmer, Fourier Transform Infrared (FTIR), from 4000 to 400 cm^{-1} using a thin layer of the sample on a 25×4mm KRS-5 disc. Fig. 1 shows the FTIR spectra of cross-linked epoxy, zeolite and epoxy nanocomposite (containing 3 wt.% zeolite nanoparticle) in the range of 4000-

400 cm^{-1} . Fig. 1a the peak of the oxirane ring observed at 915 cm^{-1} which attribute to the C-O of the oxirane group [24-26]. However, in Fig. 1c the oxirane ring peaks disappear, perhaps reacted with the OH on the surface of the zeolite. The peaks at 990 cm^{-1} and 462 cm^{-1} correspond to the asymmetric stretching vibration of inner tetrahedral and the bending vibration modes of T-O bonds in TO4 tetrahedral of zeolite structure (where T = Si or Al), respectively. The peak at 1655 cm^{-1} is attributed to the bend vibration of OH group in the adsorbed water on zeolite pore [27].

Fig. 2(a)–(c) show the SEM (Philips XL-30ESM)

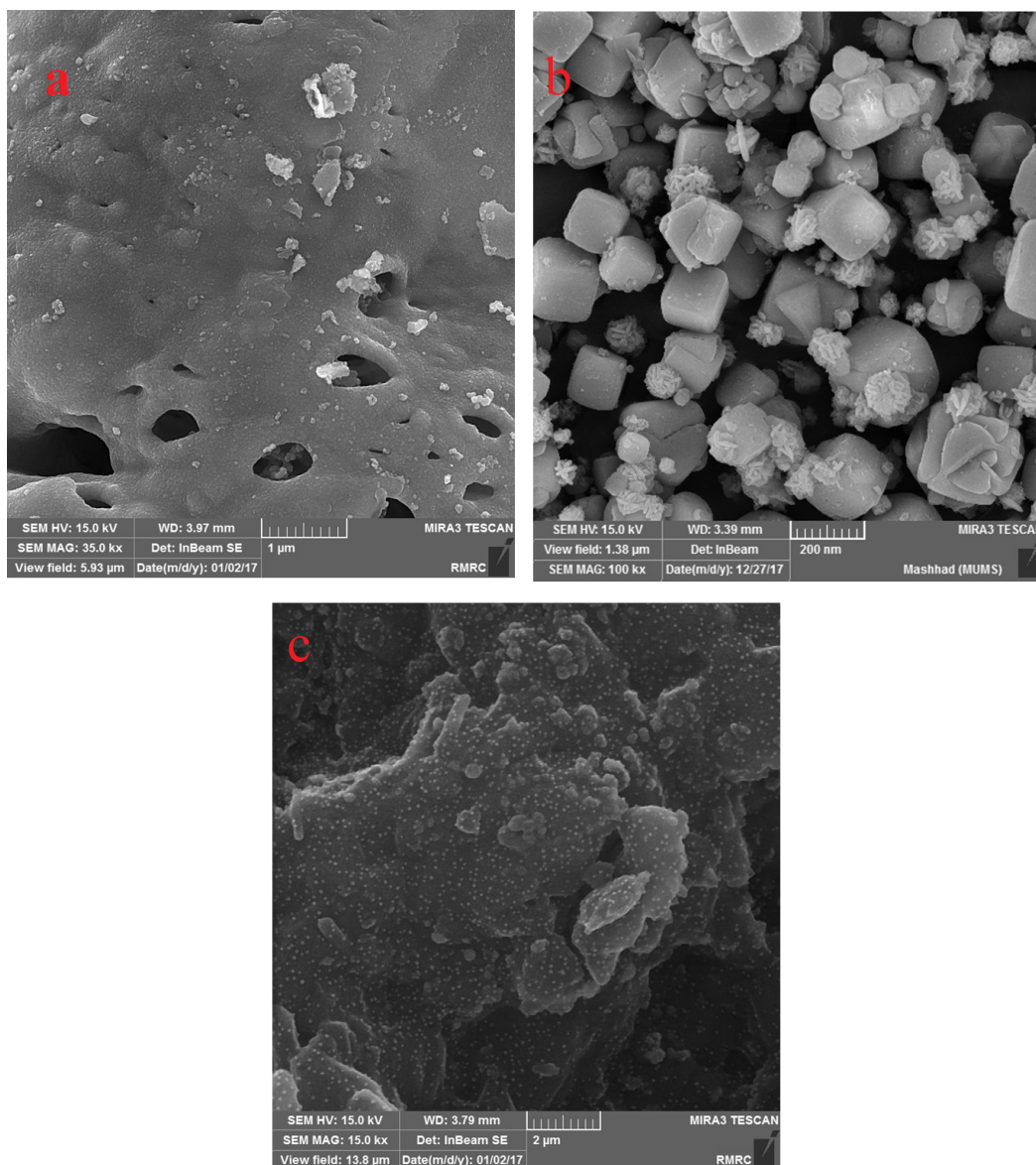


Fig. 2. SEM images of (a) epoxy cross-link, (b) nano-zeolites synthesized by microwave method at 100°C and (c) the 3wt% zeolite NaA-epoxy nanocomposites.

top surface of synthesized epoxy polymer, zeolite, and nanocomposite (containing 3 wt.% zeolite nanoparticle). Fig. 2b shows synthesized zeolite NaA has cubic morphology and flower-like with slightly different sizes. Fig. 2c depicts the morphology of surface nanocomposite, clearly seen zeolite uniformly distributed in the polymer matrix.

Crystallinity and structure of nanocomposite and zeolite, were analyzed employing an were recorded by a Philips, X-ray diffractograms using Ni-filtered Cu K α radiation. XRD was used to

investigate the structure of zeolite NaA/epoxy nanocomposite as shown in Fig. 3. The XRD patterns show the zeolite NaA has a crystalline phase and the nanocomposite has an amorphous phase. XRD patterns of zeolite NaA match well with that of standard Na₉₆Al₉₆Si₉₆O₃₈₄216H₂O (JCPDS-No. 39-0222).

The TGA of epoxy polymer and zeolite NaA/epoxy nanocomposite depict in Fig. 4. The results of the thermal gravimetric analysis (TGA) shows that adding zeolite improves the composite thermal stability. In the Fig. 4a, shows the thermal

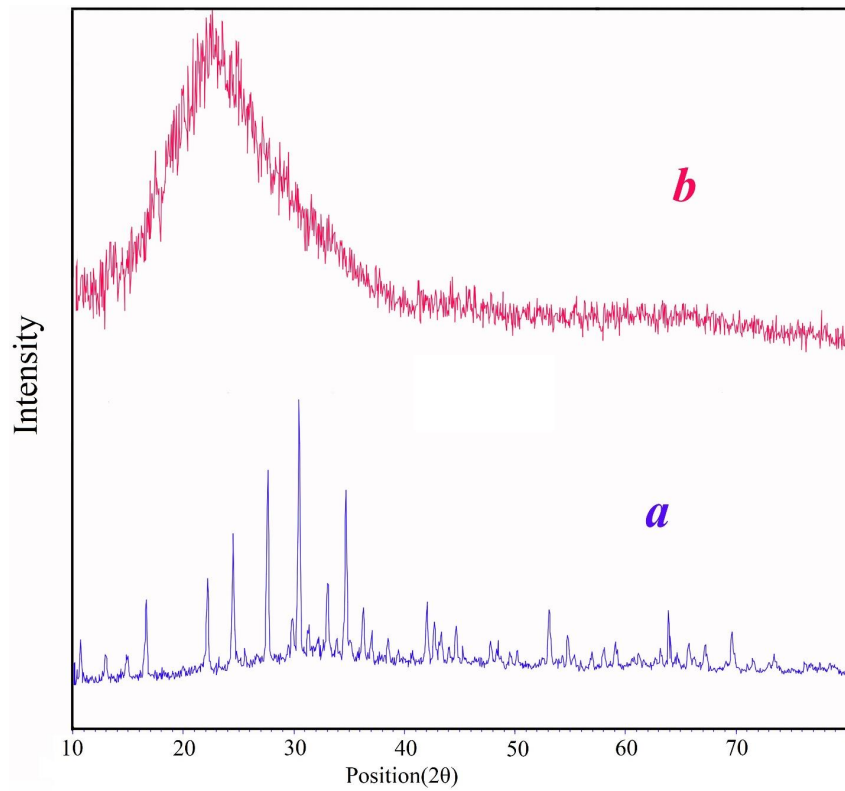


Fig. 3. XRD patterns of (a)zeolite NaA nanoparticles and (b)the 3wt% zeolite NaA-epoxy nanocomposites.

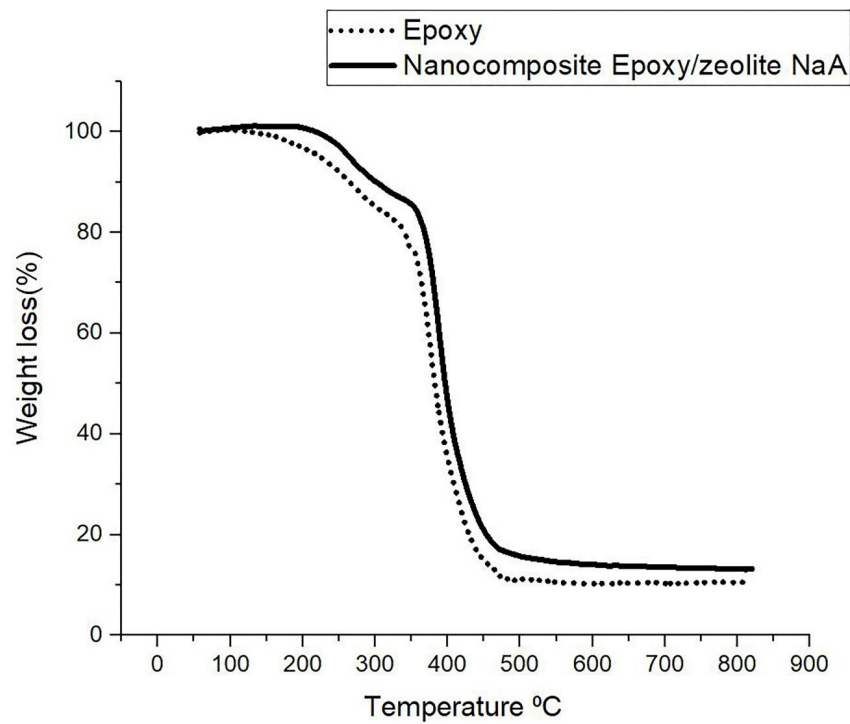


Fig. 4. TGA curves of pristine epoxy cross-linked and nanocomposites incorporated 3wt% zeolite NaA.

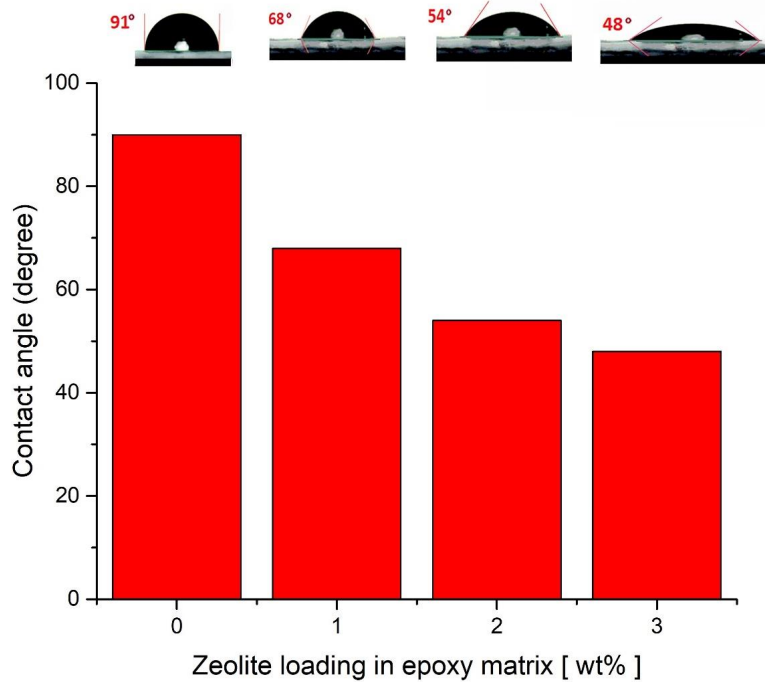


Fig. 5. Effects of wt% zeolite NaA loadings on separation performance of epoxy crosslink (300 mg L aqueous CaCl₂ solution) at 25 °C and 2 bar.

decomposition of the epoxy polymer starts at 350 °C, while the nanocomposite decomposes at 400 °C. Zeolite materials have thermal and chemical stability [15]. Zeolite Na can absorb carbon dioxide and reduces emissions of carbon dioxide from burning polymer.

The water contact angle values of the epoxy cross-linked membrane and epoxy cross-linked membrane containing various amounts of nano zeolite NaA in organic phase exhibit in Fig. 5. NaA zeolite is very hydrophilic and cation exchangeable could improvement interaction between the nanocomposite surface and the polar water, thereby increasing the water flux and reduced the contact angle in the epoxy films [14, 28]. The pure epoxy cross-linked membrane showed a high contact angle of 91°. after the incorporation of zeolite NaA nanofiller the contact angle of epoxy cross-link membranes decreases, with increase zeolite NaA loading from 1 wt% to 3 wt%, which means the improve of membrane surface hydrophilicity.

The Fig. 6 show the effect of zeolite weight loaded into the matrix of the cross-linked epoxy polymer on water permeability, cation adsorption of the nanocomposite. Increase the amount of zeolite loaded into the polymer matrix from 0 to 3

wt.% increases the water flux from 10 to 54 L/m² h. The NaA zeolite dispersed into the matrix cross-linked epoxy films creates a new flow path for water crossing through this film. Therefore, adding NaA zeolite into epoxy polymer increases water absorption and permeability [29, 30]. Increasing the amount of zeolite loaded in the range of 0 to 3 wt.% into the cross-linked epoxy polymer matrix increases the absorption of calcium ion from 4 to 99 percentage.

The image in Fig. 7 illustrates the antibacterial activity of AgA zeolite /epoxy and CuA zeolite / epoxy nanocomposites. The results of the study showed the growth inhibition zone for AgA zeolite/epoxy nanocomposites is 1 mm larger than the CuA zeolite/epoxy nanocomposite. Increased antibacterial properties of nanocomposites due to the release of Ag⁺ and Cu²⁺ ions to the medium containing bacteria.

CONCLUSION

Nanocomposite epoxy/zeolite NaA film was prepared by loaded of zeolite NaA in the epoxy matrix and homogenization by ultrasonic. Water flux and thermal stability of the membranes significantly enhanced by incorporation of zeolite NaA. The evaluation of the antibacterial properties

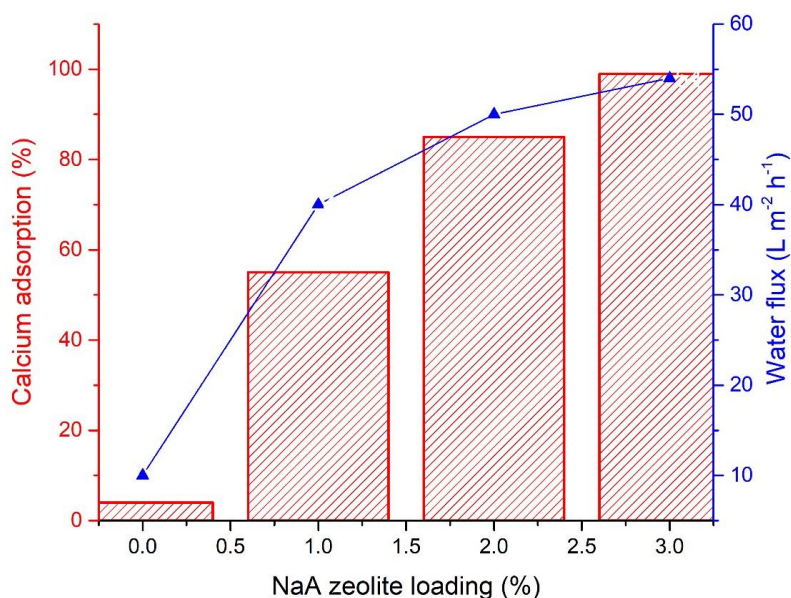


Fig. 6. Effects of wt% zeolite NaA loadings on water contact angle of epoxy cross-linked and nanocomposites.

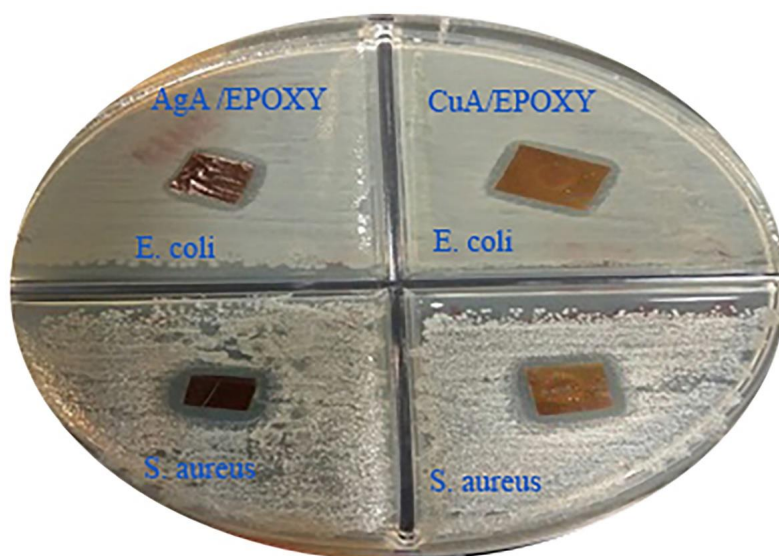


Fig. 7. Images of antibacterial activity of epoxy nanocomposites contain AgA zeolite and CuA zeolite assays on agar plates a case study on *E. coli* and *S. aureus*.

of the nanocomposite containing AgA and CuA zeolite the membrane against *E. coli* and *S. aureus* indicated antibacterial activity.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

REFERENCES

1. Qi Z, Tan Y, Gao L, Zhang C, Wang L, Xiao C. Effects of hyperbranched polyamide functionalized graphene oxide on curing behaviour and mechanical properties of epoxy composites. *Polymer Testing*. 2018;71:145-55.
2. Coleman JN, Khan U, Blau WJ, Gun'ko YK. Small but strong: A review of the mechanical properties of carbon nanotube-polymer composites. *Carbon*. 2006;44(9):1624-52.
3. Philip S, Keshavarz T, Roy I. Polyhydroxyalkanoates:

- biodegradable polymers with a range of applications. *Journal of Chemical Technology & Biotechnology*. 2007;82(3):233-47.
- Lind ML, Ghosh AK, Jawor A, Huang X, Hou W, Yang Y, et al. Influence of Zeolite Crystal Size on Zeolite-Polyamide Thin Film Nanocomposite Membranes. *Langmuir*. 2009;25(17):10139-45.
 - Saba N, Tahir P, Jawaid M. A Review on Potentiality of Nano Filler/Natural Fiber Filled Polymer Hybrid Composites. *Polymers*. 2014;6(8):2247-73.
 - Mirmohseni A, Zavareh S. Preparation and characterization of an epoxy nanocomposite toughened by a combination of thermoplastic, layered and particulate nano-fillers. *Materials & Design*. 2010;31(6):2699-706.
 - Gupta N, Lin TC, Shapiro M. Clay-epoxy nanocomposites: Processing and properties. *JOM*. 2007;59(3):61-5.
 - Baykara H, Martinez MC, Rey DV, Urbina DS, Paredes C, Rigail-Cedeño A, et al. Preparation and Determination of Antimicrobial Property of Cation-Exchanged Ecuadorian Natural Zeolite to be Used as Filler for Polyethylene and Polypropylene Matrices. *Journal of Polymers and the Environment*. 2017;26(6):2566-78.
 - Ramirez S, Chan K, Hernandez R, Recinos E, Hernandez E, Salgado R, et al. Thermal and magnetic properties of nanostructured densified ferrimagnetic composites with graphene - graphite fillers. *Materials & Design*. 2017;118:75-80.
 - Mohd Radzuan NA, Yusuf Zakaria M, Sulong AB, Sahari J. The effect of milled carbon fibre filler on electrical conductivity in highly conductive polymer composites. *Composites Part B: Engineering*. 2017;110:153-60.
 - Bourbigot S, Le Bras M, Delobel R, Bréant P, Tremillon J-M. 4A zeolite synergistic agent in new flame retardant intumescent formulations of polyethylenic polymers — study of the effect of the constituent monomers. *Polymer Degradation and Stability*. 1996;54(2-3):275-87.
 - Tantekin-Ersolmaz ŞB, Atalay-Oral Ç, Tatlier M, Erdem-Şenatalar A, Schoeman B, Sterte J. Effect of zeolite particle size on the performance of polymer-zeolite mixed matrix membranes. *Journal of Membrane Science*. 2000;175(2):285-8.
 - Li Y, Wong CP. Recent advances of conductive adhesives as a lead-free alternative in electronic packaging: Materials, processing, reliability and applications. *Materials Science and Engineering: R: Reports*. 2006;51(1-3):1-35.
 - Xue Z, Li Z, Ma J, Bai X, Kang Y, Hao W, et al. Effective removal of Mg²⁺ and Ca²⁺ ions by mesoporous LTA zeolite. *Desalination*. 2014;341:10-8.
 - Cho CH, Oh KY, Kim SK, Yeo JG, Sharma P. Pervaporative seawater desalination using NaA zeolite membrane: Mechanisms of high water flux and high salt rejection. *Journal of Membrane Science*. 2011;371(1-2):226-38.
 - Ji Y-L, An Q-F, Weng X-D, Hung W-S, Lee K-R, Gao C-J. Microstructure and performance of zwitterionic polymeric nanoparticle/polyamide thin-film nanocomposite membranes for salts/organics separation. *Journal of Membrane Science*. 2018;548:559-71.
 - Pan S, Meng X, Wang Z, Yan Y, Xiao F-S. An efficient synthesis of NaA zeolite membranes from direct crystallization of gel-dipped macroporous alumina tubes with seeds. *Journal of Materials Chemistry A*. 2018;6(22):10484-9.
 - Kim D, Jeon MY, Stottrup BL, Tsapatsis M. para -Xylene Ultra-selective Zeolite MFI Membranes Fabricated from Nanosheet Monolayers at the Air-Water Interface. *Angewandte Chemie*. 2017;130(2):489-94.
 - Schüth F, Schmidt W. Microporous and Mesoporous Materials. *Advanced Materials*. 2002;14(9):629-38.
 - Wan Y, Zhao. On the Controllable Soft-Templating Approach to Mesoporous Silicates. *Chemical Reviews*. 2007;107(7):2821-60.
 - Fateme Seyedpour S, Rahimpour A, Mohsenian H, Taherzadeh MJ. Low fouling ultrathin nanocomposite membranes for efficient removal of manganese. *Journal of Membrane Science*. 2018;549:205-16.
 - Khanom R, Parveen S, Hasan M. Antimicrobial Activity of SnO₂ Nanoparticles against Escherichia Coli and Staphylococcus Aureus and Conventional Antibiotics. *American Scientific Research Journal for Engineering, Technology, and Sciences (ASRJETS)*. 2018;46(1):111-121.
 - Alsammarraie FK, Wang W, Zhou P, Mustapha A, Lin M. Green synthesis of silver nanoparticles using turmeric extracts and investigation of their antibacterial activities. *Colloids and Surfaces B: Biointerfaces*. 2018;171:398-405.
 - K. Madhup M, K. Shah N, R. Parekh N. An Investigation of Abrasion Resistance Property of Clay- Epoxy Nanocomposite Coating. *Material Science Research India*. 2018;15(2):165-78.
 - Goyat MS, Rana S, Halder S, Ghosh PK. Facile fabrication of epoxy-TiO₂ nanocomposites: A critical analysis of TiO₂ impact on mechanical properties and toughening mechanisms. *Ultrasonics Sonochemistry*. 2018;40:861-73.
 - Awad SA, Fellows CM, Mahini SS. Effects of accelerated weathering on the chemical, mechanical, thermal and morphological properties of an epoxy/multi-walled carbon nanotube composite. *Polymer Testing*. 2018;66:70-7.
 - Ali S, Amalia S, Fasya AG. Synthesis and Characterization of Zeolite Y From Bagasse Ash with Hydrothermal Temperatures Variations Using The Sol-Gel Method. *ALCHEMY*. 2015;4(1).
 - Ma N, Wei J, Liao R, Tang CY. Zeolite-polyamide thin film nanocomposite membranes: Towards enhanced performance for forward osmosis. *Journal of Membrane Science*. 2012;405-406:149-57.
 - Fedosov DA, Smirnov AV, Shkirskiy VV, Voskoboinikov T, Ivanova II. Methanol dehydration in NaA zeolite membrane reactor. *Journal of Membrane Science*. 2015;486:189-94.
 - Baheri B, Shahverdi M, Rezakazemi M, Motaee E, Mohammadi T. Performance of PVA/NaA Mixed Matrix Membrane for Removal of Water from Ethylene Glycol Solutions by Pervaporation. *Chemical Engineering Communications*. 2014;202(3):316-21.