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Synthesis and characterization of the poly(GMA-*b*-EG) block copolymer containing epoxy-resin by redox polymerization

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Keywords:
Epoxy-based block copolymer;
glycidyl methacrylate,
redox polymerization,
polyethylene glycol,
dispersity.

Abstract: In this study, poly(glycidyl methacrylate-*block*-ethylene glycol) [P(GMA-*b*-EG)] epoxy-based copolymer was synthesized and evaluated by redox polymerization. For this purpose, poly(GMA-*b*-EG) block copolymer containing epoxy-resin was synthesized by redox polymerization of glycidyl methacrylate using polyethylene glycol (PEG-3000) macroinitiator in the presence of cerium ammonium nitrate [$Ce(NH_4)_2(NO_3)_6$] catalyst. The synthesized epoxy-based copolymer was characterized by FTIR, ^{1}H-NMR, DSC, TGA, and SEM spectroscopic methods. The molecular weight of the epoxy-based copolymer was also determined by GPC. The epoxy-based copolymer has a relatively narrow molecular weight and distribution. The DSC result showed that the glass transition temperature value of the epoxy-based copolymer was 28 °C, different from that of the homopolymer. SEM analysis showed that the surface morphology of PEG and epoxy-based copolymers was different. It has been proven by TGA analysis that the epoxy-based copolymer has two different decomposition temperatures of 160 °C and 400 °C.

Redoks Polimerizasyonu ile Epoksi Reçine İçeren Poli(GMA-*b*-EG) Blok Kopolimerinin Sentezi ve Karakterizasyonu

Anahtar Kelimeler:
Epoksi bazlı blok kopolimer,
glisidil metakrilat,
redoks polimerizasyonu,
polietilen glikol,
dispersite.

Özet: Bu çalışmada, poli(glisidil metakrilat-*blok*-etilen glikol) [P(GMA-*b*-EG)] epoksi bazlı blok kopolimer redoks polimerizasyonu ile sentezlendi ve değerlendirildi. Bu amaç için, polietilen glikol (PEG-3000) makrobaşlatıcı kullanılarak glisidil metakrilatın seryum amonyum nitrat [$Ce(NH_4)_2(NO_3)_6$] katalizörü varlığında redoks polimerizasyonu ile epoksi reçine içeren poli(GMA-b-EG) blok kopolimeri sentezlendi. Sentezlenen epoksi bazlı kopolimer FTIR, ^{1}H-NMR, DSC ve SEM gibi spektroskopik yöntemlerle karakterize edildi. Epoksi bazlı kopolimerin moleküler ağırlığı da GPC ile belirlendi. Epoksi içeren kopolimer, nispeten yüksek molekül ağırlığına ve dar molekül ağırlığına dağılımına (dispersity) sahipti. DSC sonucu, epoksi bazlı kopolimerin camsı geçiş sıcaklığı değerinin homopolimerden farklı olarak 28 °C olduğunu göstermiştir. SEM analizi, PEG ve epoksi bazlı kopolimerlerin yüzey morfolojisinin farklı olduğu söylenebilir. Epoksi bazlı kopolimerin 160 °C ve 400 °C gibi iki farklı ayrışma sıcaklığına sahip olduğu TGA analizi ile kanıtlanmıştır.

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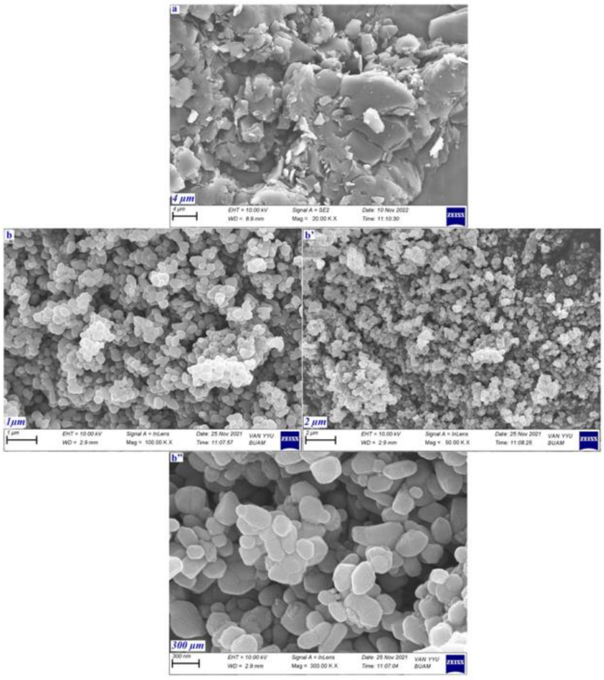
GRAPHICAL ABSTRACT



1. INTRODUCTION

Resin is a plastic that becomes heat resistant as a result of a series of chemical reactions. The use of plastic resins both in daily life and in some technological fields is increasing. Glycidyl methacrylate (GMA) is an important commercial monomer because it contains the epoxy functional group that allows many reactions. GMA-based copolymers are of great importance in biotechnological applications since the epoxy group can be easily converted to other functional groups. In addition, homogeneous and heterogeneous polymer networks can be prepared with GMA used in coatings, matrix resins and adhesives (Wang et al., 2022; Liu et al., 2022; Waly et al., 2020; Klimow et al., 2022; Wang & Hutchinson, 2008; Muzammil et al., 2017; May, 1988; Matt et al.,2021; Kovar et al., 1982; Yılmaz & Coşkun, 1982). Polyethylene glycol (PEG) is a straight or branched chain polymer in which oxygen and ethylene units are sequentially bonded to each other. PEG is a polymer preferred especially for medical uses because of its hydrophilic, non-toxic and biocompatibility. Since its hydrophilicity, biodegradability and mechanical properties can be improved, it has a wide range of uses. Polyethylene glycol is a polymer used especially in the pharmaceutical and biomedical field. PEG is prone to chemical modification, binding to another molecule and surface. It increases the size of the molecule it binds to and changes its solubility (Chen, 2008; Zhou, 2003; Li & Kao, 2003; Göktaş et al., 2014; Öztürk et al., 2014). Redox systems are widely used as initiators in radical polymerization and results are obtained in a very short time. Compared to other methods, its main advantage is processing at very mild temperatures. This indicates that it can minimize possible side reactions. Ce(IV) or permanganate combined with a hydroxyl or carboxyl group-containing reductant are more commonly used initiators (Çakmak, 1993; Hazer et al., 1992; Çakmak, 1995; Öztürk & Çakmak, 2007; Göktaş, 2019a; Göktaş, 2020; Göktaş & Deng, 2018). A block copolymer is a chemically bonded end-to-end form of two or more polymer chains. These chain segments follow each other along the main chain. Block copolymers in various structures such as linear diblock (AB), triblock (ABA or ABC), pentablock (ABABA), multiblock or segmented copolymers are available in the literature (Öztürk et al., 2010; Öztürk et al., 2016; Göktaş & Aykaç, 2020; Öztürk et al.,2016; Öztürk et al., 2013; Göktaş & Olgun, 2019; Göktaş, 2019b).

In this study, GMA was polymerized by redox polymerization on PEG, which is a suitable initiator for redox polymerization due to the hydroxyl group at its end, in the presence of $Ce(NH_4)_2(NO_3)_6$ catalyst and poly(glycidyl methacrylate-*block*-ethylene glycol) [P(GMA-*b*-EG)] epoxy-based block copolymer was obtained. The interpretation of the results of redox polymerization is presented in detail in the manuscript.

2. MATERIALS AND METHODS

2.1. Chemicals

The glycidyl methacrylate, ethylene glycol (PEG-3000), and cerium ammonium nitrate $[Ce(NH_4)_2(NO_3)_6]$ were received from Aldrich and used as received. Methanol and *N*,*N*-dimethylformamide (DMF) were received from Carlo Erba and used as received.

2.2. Analyzes

Molecular weights and molecular weight distributions of the synthesized epoxy-based copolymer were determined by a PL-GPC 220 and HPLC-Shimadzu; LC-20AD gel permeation chromatography (GPC) using THF as solvent. The functional groups, Fourier transform infrared spectroscopy (FTIR) spectra of the synthesized epoxy-based polymer and initiator were recorded with a Spectrum 100 Model FTIR Perkin Elmer spectrometer in transmit mode with a scanning speed of 4000 to 550 cm-1. Structure characterization of the synthesized epoxy-based block copolymer and initiator, ^1H-nuclear magnetic resonance (^1H-NMR) spectra using DMSO as a solvent, was performed with a Bruker Ultra Shield Plus, ultra-long retention time 400 MHz NMR spectrometer. Thermal analyses of the synthesized polymers were performed using the Lab SYS EVO TGA/DSC thermogravimetric analysis (TGA) device and differential scanning calorimetry (DSC) with the heating rate of 10 °C/min under Argon gas protection. TGA consists of a sample pan sup- ported by a delicate balance. It is possible to examine the surface morphology of polymeric materials with high molecular weight by scanning electron microscopy (SEM) method. SEM images of the epoxy-based copolymer were taken using a Scanning Electron Microscope ZEISS SIGMA 300 FESEM with Energy X-ray Spectroscopy (EDX).

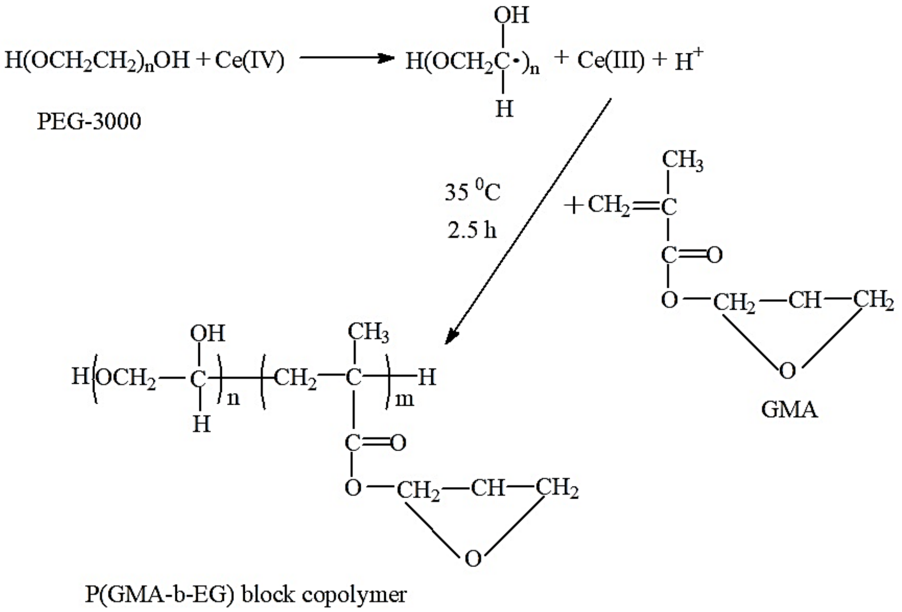
2.3. Synthesis of epoxy-based block copolymer by redox polymerization

Poly(glycidyl methacrylate-*block*-ethylene glycol) [P(GMA-*b*-EG)] epoxy-based block copolymer, via redox polymerization of glycidyl methacrylate using polyethylene glycol (PEG-3000) macroinitiator, was prepared. For redox polymerization, a vial was equipped with 3 g of glycidyl methacrylate (GMA), 2 g of polyethylene glycol (PEG-3000), and 2.5 g of $Ce(NH_4)_2(NO_3)_6$ (as a catalyst). The vial was placed in a water bath at 35°C for polymerization and stirred for 2.5 h. Then, the vial content, to precipitate P(GMA-*b*-EG) epoxy-based block copolymer, was dropped into excess of methanol. Poly(GMA-*b*-EG) epoxy-based block copolymer was dried in the vacuum oven at room temperature.

3. RESULTS AND DISCUSSIONS

3.1. Synthesis of poly(glycidyl methacrylate-*block*-ethylene glycol) block copolymer containing epoxy resin

In this study, poly(glycidyl methacrylate-block-ethylene glycol) [P(GMA-b-EG)] block copolymer containing epoxy resin was obtained by redox polymerization of glycidyl methacrylate in the presence of $Ce(NH_4)_2(NO_3)_6$ using a catalyst and PEG macroinitiator. The glycidyl methacrylate monomer conversion was calculated from the weight of the epoxy-based polymer dried at the end of polymerization. The polymerization conversion of the GMMA monomer onto polyethylene glycol is 70 wt. %. The synthesis route of the block copolymer is shown in Scheme 1.



Scheme 1. The poly(GMA-*b*-EG) epoxy-based block copolymer synthesis route.

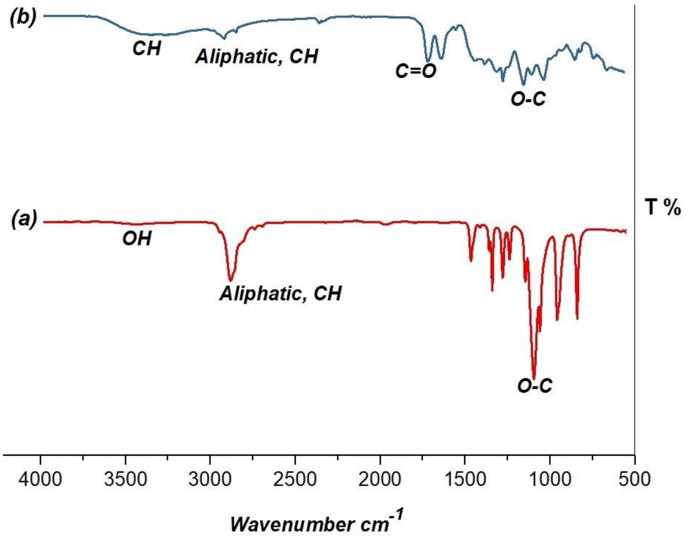


Figure 1. FTIR images of polyethylene glycol (PEG-3000) **(a)**, poly(GMA-*b*-EG) epoxy-based block copolymer **(b)**.

The FTIR image of polyethylene glycol shown in Figure 1a, ascribes the characteristic peaks of 3316 cm^{-1} for –OH groups, and aliphatic –CH groups at 2950 cm^{-1}. The FTIR results of P(GMA-*b*-EG) epoxy-based block copolymer in Figure 2b also show the characteristic bands of –CH of epoxy groups at 3269 cm^{-1}, aliphatic –CH groups at 2918 cm^{-1}, –C=O vibration at 1720 cm^{-1}, –O-C vibration at 1156cm^{-1}. The ^{1}H NMR results of the polyethylene glycol in Figure 2a ascribes 3.2 ppm for $-O\underline{H}$, and 3.4 and 3.5 ppm for $-OC\underline{H}_2$. Typical ^{1}H-NMR results of the P(GMA-*b*-EG) epoxy-based block copolymer shows in Figure 2b, 1.2 ppm for $-C\underline{H}_3$ of the GMA block, 2.4 and 2.5 ppm for $-C\underline{H}_2$, $-C\underline{H}$ and $-O\underline{H}$ of the PEG and GMA blocks, 3.2 and 3.3 ppm for $-OC\underline{H}_2$ of the PEG and GMA blocks, 4.1 ppm for $-OC\underline{H}_2$ of the GMA block.

The molecular weight of the epoxy-based block copolymer was determined by GPC. GPC curves for poly(GMA-*b*-EG) epoxy-based block copolymer was demonstrated in Figure 3. The molecular weight of the epoxy-based block copolymer was found to be *Mn*= 20808 g/mol by GPC. The dispersity value of the epoxy-based block copolymer was found 1.69. Thermal properties of the poly(GMA-*b*-EG) epoxy-based block copolymer investigated by differential scanning calorimetry (DSC). The glass transition temperature (*Tg*) of poly(GMA-b-EG) epoxy-based block copolymer was found by the DSC analysis. The *Tg* value for the epoxy-based block copolymer was observed as 28 °C. It can also be explained by the reduction of homopolymer formation and the high rate of epoxy-based block copolymer formation. The *Tg* curve is shown in Figure 4. Weight loss by TGA analysis of the epoxy-based block copolymer started at 25°C and ended with two degradations at 600°C. TGA and derivative thermogravimetry (dTG) of poly(GMA-*b*-EG) epoxy-based block copolymer is as shown in Figure 5. The poly(GMA-*b*-EG) epoxy-based block copolymer has two weight-loss stages in the range of 160 °C and 400 °C which can be attributed to the decomposition temperatures (T_d) of the PEG and PGMA blocks, respectively (in Figure 5). The surface morphology of the epoxy-based block copolymer was investigated by SEM analysis. The SEM images of epoxy-based block copolymer are given in Figure 6. SEM analysis displayed that the surface morphology of the epoxy-based block copolymer consisted of two different phases. SEM surface morphology of the epoxy-based block copolymer has clear surface properties and can form a continuous phase.

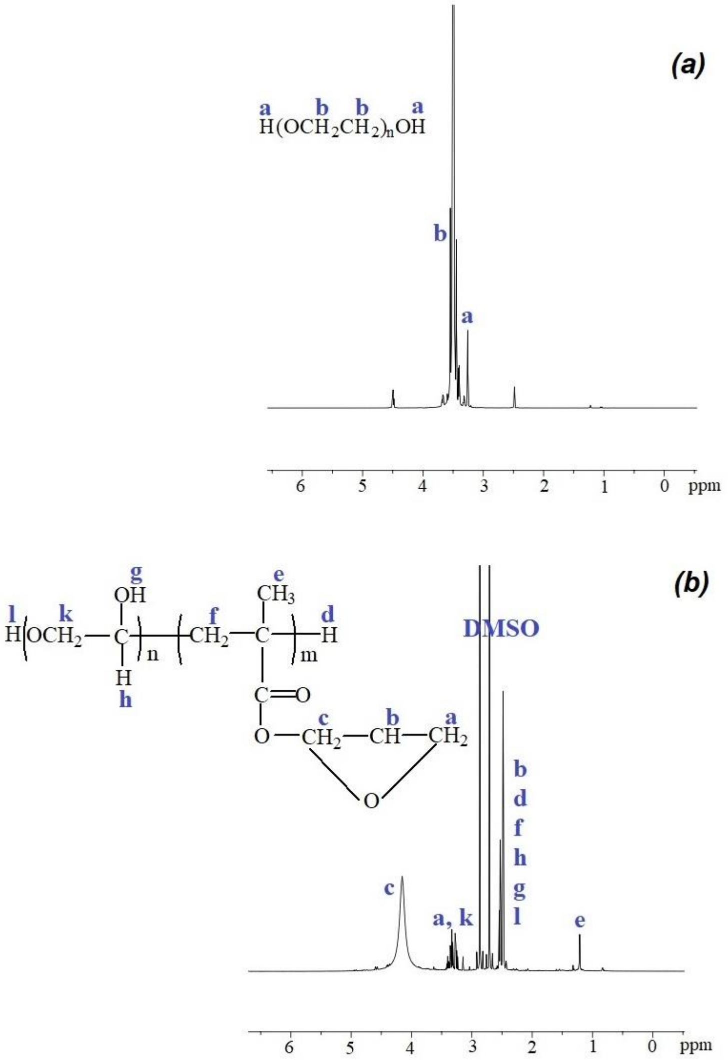


Figure 2. ^{1}H NMR images of polyethylene glycol (PEG-3000) **(a)**, poly(GMA-*b*-EG) epoxy-based block copolymer **(b)**.

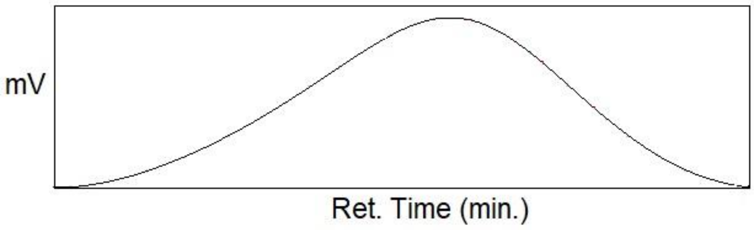


Figure 3. GPC diagram for poly(GMA-*b*-EG) epoxy-based block copolymer.

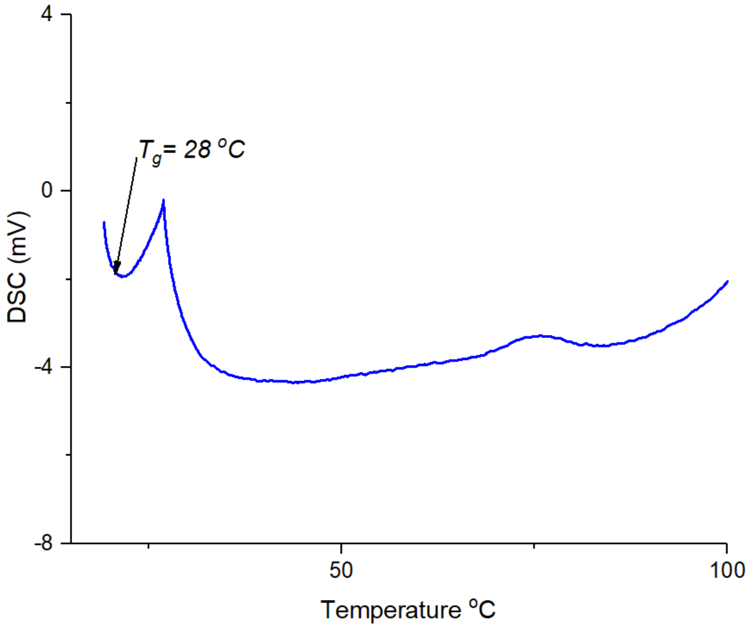


Figure 4. DSC result of poly(GMA-*b*-EG) epoxy-based block copolymer.

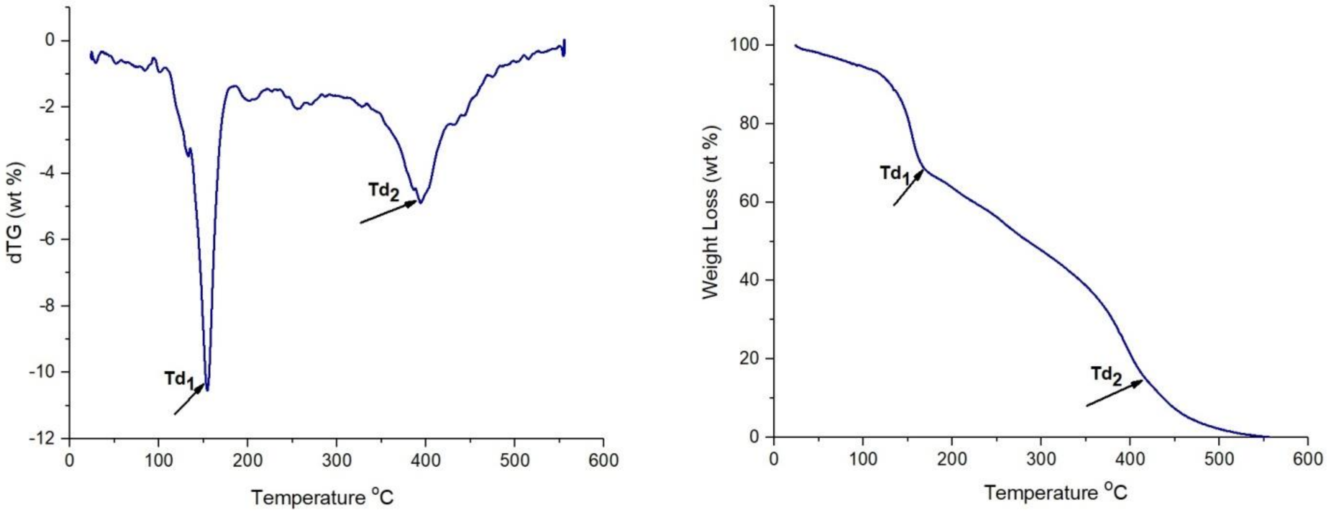


Figure 5. TGA and dTG curves of poly(GMA-*b*-EG) epoxy-based block copolymer.

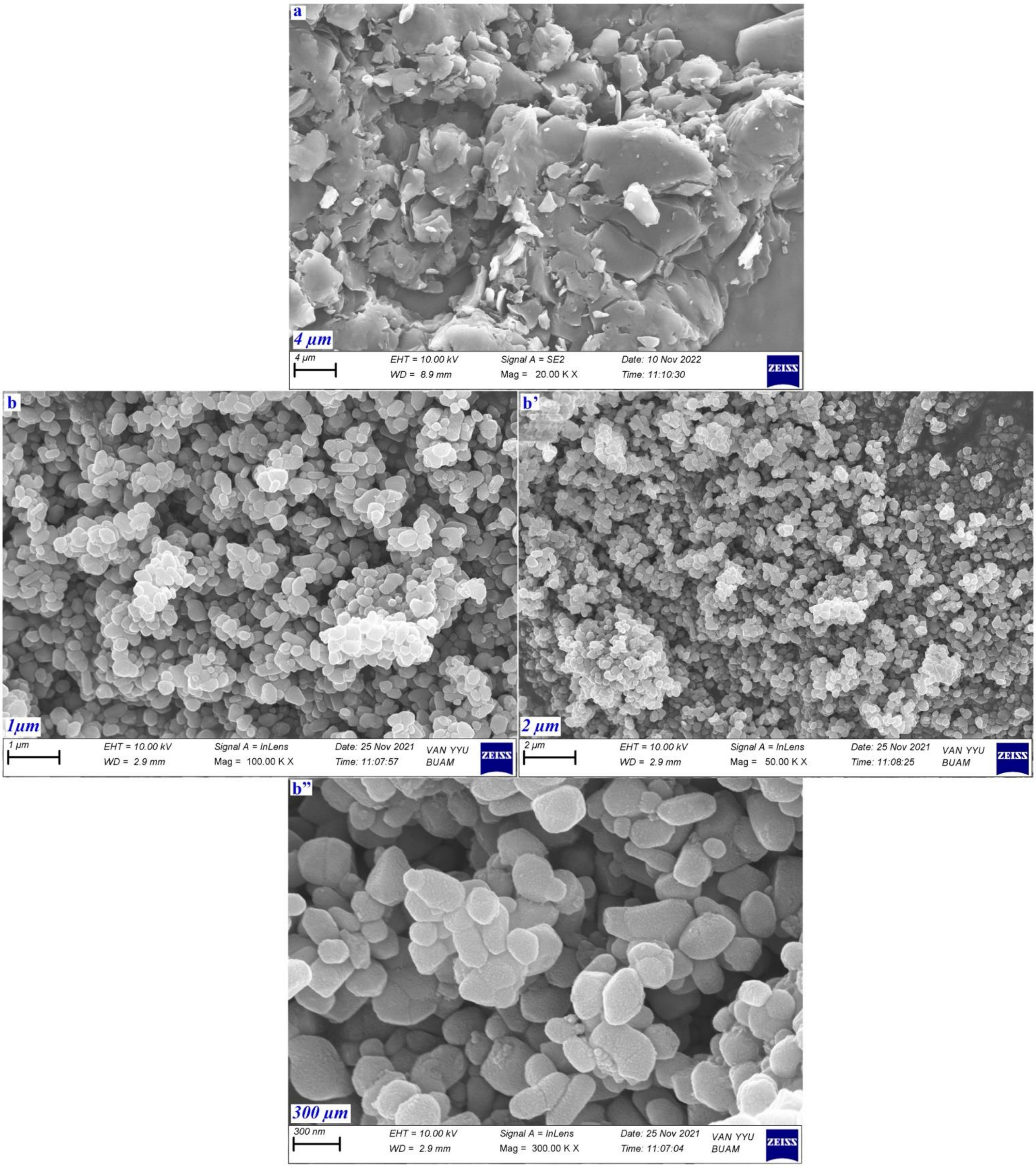


Figure 6. SEM images of PEG **(a)** and poly(GMA-*b*-EG) **(b, b', b")** epoxy-based block copolymer.

4. CONCLUSION

In this study, poly(glycidyl methacrylate-block-ethylene glycol) [P(GMA-b-EG)] block copolymer containing epoxy resin was obtained by redox polymerization of glycidyl methacrylate in the presence of $Ce(NH_4)_2(NO_3)_6$ a using catalyst and PEG macroinitiator. This method is an inexpensive and effective method for synthesizing block copolymers. The DSC result showed that the glass transition temperature value of the poly(GMA-*b*-EG) epoxy-based block copolymer was 28 ºC, different from that of the homopolymer. The SEM analysis demonstrated that the surface morphology of the PEG and epoxy-based copolymers differed. The fact that the epoxy-based copolymer has two different decomposition temperatures such as 160 °C and 400 °C has been proven by TGA analysis. The synthesized epoxy-based block copolymer can be used in various biotechnological applications because many reactions can be performed on the GMA units in poly(GMA) or copolymers to form new functional groups.

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5. REFERENCES

Cakmak I. (1993). Preparation of multiphase block copolymers by redox polymerization process. 2: Polymerization of acrylonitrile by the manganese(III)-poly(ethylene glycol) redox system. Die Angew. Macromol. Chem. 211(1), 53-60.

Cakmak I. (1995). Synthesis of block copolymers by redox macro initiators. Macromol Rep. 32(1) 197-206.

Chen J. (2008). Molecular Recognition in Terms of a Dimensionless Index. 2. Thermodinamic Patterns of Intromolecular Interactions of PEG and Its Alcohol Substrates. Journal of Physical Chemistry, 112(6) 1706-1711.

Göktaş M. (2019). Synthesis and characterization of poly (styrene-b-methyl methacrylate) block copolymers via ATRP and RAFT. J. Inst. Sci & Tech. 9(1), 139-149.

Göktaş M. (2019). Synthesis and characterization of various block copolymers using PMMA-Br macroinitiator. Chem. Papers, 73(9), 2329–2339,

Göktaş M. (2020). Synthesis and characterization of temperature-responsive block copolymers using macromonomeric initiator. Chem. Papers, 74(7), 2297–2307.

Göktaş M., Aykaç C. (2020). Synthesis and characterization of poly(ε-caprolactone)-b-poly(acrylamide) block copolymers. J. Inst. Sci & Tech. 10(2), 1154-1162.

Göktaş M., Deng G. (2018). Synthesis of Poly(methyl methacrylate)-b-poly(N-isopropylacrylamide) Block Copolymer by Redox Polymerization and Atom Transfer Radical Polymerization. Indones. J. Chem. 18(3), 537–543.

Göktaş M., Olgun B. (2019). One-step synthesis and characterization of poly(ε-caprolactone)-b-poly(N-isopropylacrylamide) thermo-responsive block copolymers via RAFT and ROP techniques. Polym. Sci. Series B. 61(4), 421–429.

Göktaş M., Öztürk T., Atalar M.N., Tekeş A.T., Hazer B. (2014). One-Step Synthesis of Triblock Copolymers via Simultaneous Reversible-Addition Fragmentation Chain Transfer (RAFT) and Ring-Opening Polymerization Using a Novel Difunctional Macro-RAFT Agent Based on Polyethylene Glycol. J. Macromol. Sci. Part A-Pure and Appl. Chem. 51(11), 854-863.

Hazer B., Çakmak İ., Denizligil S., Yağcı Y. (1992). Preparation of multiphase block copolymers by redox polymerization. Angew. Macromol. Chem, 195(1), 121-127.

Klimow V.V., Kolyaganova O.V., Bryuzgin E.V., Navrotsky A.V., Novakov İ.A. (2022) Effect of the Composition of Copolymers Based on Glycidyl Methacrylate and Fluoroalkyl Methacrylates on the Free Energy and Lyophilic Properties of the Modified Surface. Polymers, 14, 1960.

Kovar J., Navratilova M., Skursky L. (1982) Immobilization of horse liver alcohol dehydrogenase on copolymers of glycidyl methacrylate and ethylene dimethacrylate. Biotechnol. Bioeng. 24, 837–45.

Li J., and Kao W. J. (2003). Synthesis of Polyethylene Glycol (PEG) Derivatives and PEGylated-Peptide Biopolymer Conjugates. Biomacromolecules, 4(4), 1055-1067.

Liu X., Hou G., Zheng H., Li W. (2022) Preparation of Wool-g-Glycidyl Methacrylate with a Constructed –SH Groups/Ammonium Persulfate Redox System and Characterization. MATERIALS SCIENCE (MEDŽIAGOTYRA), 28 (3).

Matt L., Liblikas I., Bonjour O., Jannasch P., Vares L. (2021). Synthesis and anionic polymerization of isosorbide mono-epoxides for linear biobased polyethers. Polym. Chem. 12(41), 5937–5941.

May C.A. (1988). Epoxy resins chemistry and technology. New York: Marcel Dekker.

Muzammil E. M., Khan A., Stuparu M.C. (2017). Post-polymerization modification reactions of poly(glycidyl methacrylate)s. RSC Adv. 88 (7) 55874–55884.

Öztürk T., Atalar M.N., M Göktaş., B Hazer. (2013). One-Step Synthesis of Block Graft Copolymers via Simultaneous Reversible-Addition Fragmentation Chain Transfer and Ring-Opening Polymerization Using a Novel Macroinitiator. J. Polym. Sci. Part A Polym. Chem. 51(12), 2651–2659.

Öztürk T., Çakmak İ. (2007). Synthesis of Block Copolymers via Redox Polymerization Process: A Critical Review. Iranian Polym. J. 16(8), 561-581.

Öztürk T., Göktaş M., Hazer B. (2010). One-Step Synthesis of Triarm Block Copolymers via Simultaneous Reversible-Addition Fragmentation Chain Transfer and Ring-Opening Polymerization. J. Appl. Polym. Sci. 117(12), 1638–1645.

Öztürk T., Göktaş M., Hazer B. (2011). Synthesis and Characterization of Poly(methyl methacrylate-blockethylene glycol-block-methyl methacrylate) Block Copolymers by Reversible Addition-Fragmentation Chain Transfer Polymerization. J. Macromol. Sci. Part A-Pure and Appl. Chem. 48(1), 65-70.

Öztürk T., Kayğın O., Göktaş M., Hazer B. (2016). Synthesis and Characterization of Graft Copolymers Based on Polyepichlorohydrin via Reversible Addition-Fragmentation Chain Transfer Polymerization. J. Macromol. Sci. Part A-Pure and Appl. Chem. 53(6), 362–367.

Öztürk T., Yavuz M., Göktaş M., Hazer B. (2016). One-step synthesis of triarm block copolymers by simultaneous atom transfer radical and ring-opening polymerization. Polym. Bull. 73(6), 1497–1513.

Waly A.İ., Khedr M.A.M., Ali H.M., Ahmed İ.M. (2020) Chemical Functionalization of Cellulose-Poly(Glycidyl-Methacrylate) Graft Copolymer with Two Different Poly Amino Compounds. Egypt J Chem. 63 (7) 2673 – 2682.

Wang B., Wang P., He B., Liu S., Ye Q., Zhou F. (2022) Fabrication of ionic liquid-functionalized polystyrene nanospheres via subsurface-initiated atom transfer radical polymerization for anti-fouling application. Progress in Organic Coatings 171, 107044.

Wei Wang W., Hutchinson R.A. (2008). PLP/SEC/NMR Study of Free Radical Copolymerization of Styrene and Glycidyl Methacrylate. Macromolecules, 41(23), 9011-9018.

Yılmaz S., Coşkun M. (2018). Poly(glycidyl methacrylate-co-styrene): Synthesis, Characterization, Reaction With Aminated MWCNT and Thermal investigation. El-Cezerî Journal of Science and Engineering, 5(2) 537-546.

Zhou S. (2003). Biodegradable poly(e-caprolactone)-poly(ethylene glycol) block copolymers: characterization and their use as drug carriers for a controlled delivery system. Biomaterials, 24(20), 3563-3570.