

Electrokinetic and surface properties of some methacrylate-based copolymers

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Abstract: In this study, some electrokinetic and surface properties of MBAOM-GMA copolymers synthesized from 2-[(methoxy-1,3-benzothiazole-2-yl) amino]-2-oxoethyl methacrylate (MBAOM) and glycidyl methacrylate (GMA) monomers were investigated. Accordingly, (i) pH-dependent zeta (ζ) potential changes of the copolymers were investigated under a constant ionic strength (in 1.10^{-3} mol/dm³ NaCl) and the corresponding isoelectric points (*iep*) were determined, (ii) zeta potential changes depending on the salt concentration in the presence of mono-, di- and tri-valent metal salts were examined, (iii) contact angles (θ) of the copolymers with water were measured and their wetting behavior was assessed, and (iv) surface free energies (*SFE*) of the copolymers were determined by Acid-Base approach using Van Oss-Chaudhury-Good method. The compositions of the copolymers were 77% MBAOM - 23% GMA, 45% MBAOM - 55% GMA, and 19% MBAOM - 81% GMA. FeCl₃, CaCl₂, and KCl salts were used for the salt solutions for the zeta potential measurements. As a result, (i) it was determined that the chemical structure of methacrylate copolymers showed a decisive effect on both electrokinetic and surface properties, (ii) the hydrophobic character of copolymer increased with the increase of the GMA ratio, and correspondingly, the *SFE* decreased, and (iii) the *iep* of the copolymers varied between pH 3.1-3.7 depending on composition.

Keywords: methacrylate copolymer, zeta potential, contact angle, hydrophobicity, surface free energy

1. Introduction

The existence of polymers was first suggested by Hermann Staudinger in the 1920s, and in the following years, polymers have been used in almost every phase of our daily life. The main advantages of polymers are that they are light, resistant to corrosion, and easy to process (Saçak, 2005). One of the most important parameters determining the usage area of polymer materials is the functional groups they contain. The variety of functional groups affects the characteristics of polymers such as mechanical, thermal, wettability, and biological (Takahara, 1992). One of the methods applied to obtain functional polymers is chemical reactions on the side branch by making modifications to a known monomer. Some restrictions in the use of a polymeric material can be overcome by combining the monomer of this polymer with another monomer in a polymer chain. In this way, a material with much better properties can be obtained. This phenomenon is called copolymerization (Saçak, 2005). Copolymerization is also of great importance in terms of technology. It may be possible to design and prepare a polymeric product with the desired properties more efficiently by copolymerization. For instance, methacrylate-based polymers such as PMMA [poly(methyl methacrylate)], in general, constitute the most essential polymeric class and show desirable properties such as good optical properties (transparent, light transmittance 92%), low electrical conductivity, resistance to external conditions, strength, and high dimensional stability (Saçak, 2005; Ngai et al., 2017). Due to these properties, they are used instead of glass and products such as aircraft glasses, eyeglasses, lamps for automobiles, etc. However, in some cases, block copolymer materials such as PMMA-PEG poly(ethylene glycol) are used instead of PMMA to reduce the hydrophobic character, especially in the production of biomaterials such as contact lenses (Ko et al., 2017). The usage areas of block copolymers, especially methacrylate-based copolymers, are

increasing yearly. Typical applications of block copolymers can be given as high-impact-strength polymers, elastic fibers, elastomers, surfactants, permselective membranes, biomaterials, adhesives, sealants, and surface modifiers (Takahara, 1992). As is known, synthetic polymers (polyacrylic acid, sodium polyacrylate, ammonium polymethylmethacrylate, etc.) are also widely used as flocculants or deflocculants in mineral processing depending on their hydrocarbon chain length and ionic structure (Leja, 1982; Lu et al., 2005). On the other hand, polymer sieves can be given as another example of the use of polymers as solid materials in mineral processing. They have low surface energy and hydrophobic properties compared to metal sieves. Thus, their screening performance, corrosion resistance, and service life are higher than metals.

Concepts such as wettability, hydrophilicity/hydrophobicity, surface free energy (*SFE*), and zeta (ζ) potential can be considered among the most important surface properties of solids. These concepts are frequently encountered in many industrial areas such as mining, textile, aviation, automotive, petroleum, paper, pharmacy, medicine, plastic, paint, environment, construction, textile, food, agriculture, and metal. Some of the usage areas can be listed as follows; production of water-repellent (non-wetting) fabric in textile (Karaman and Uçar, 2016), coating the metal surface (with teflon, etc.) to obtain a non-stick surface in the metal industry (Arukalam et al., 2016; Gnedenkov et al., 2016), determination of the dyeability and print quality of the paper surface (Gao et al., 2015; Asano and Shiraishi, 2015), mineral beneficiation by flotation (Leja 1982), stabilization of emulsified products in food, cosmetics, and paint (Hiemenz 1986; Kapilashrami et al., 2004), drug formulations (Gönül, 2000), production of microfluidic devices such as microchips and determination of product quality in insulation material production (Hölck et al., 2012; Syakur et al., 2012; Falahati et al., 2014; Ngai et al., 2017), floor covering with hydrophobic materials (Evcin et al., 2018), obtaining a super hydrophobic product surface in the materials science (Chakradhar et al., 2011), production of hydrophobic coating materials in the automotive or aerospace industry (Dobrzanski, 2006; Zenkiewicz, 2007), and production of biomaterials (Ebnasajjad, 2011; Lung and Matinlinna, 2015). The explanation of phenomena such as adhesion, coating processes, printing, deinking, lubrication, dispersion, coagulation/flocculation, and flotation is based on concepts such as zeta potential, hydrophobicity, and surface energy.

Numerous studies have been reported to investigate the thermal, mechanical, and biological properties of methacrylate-based polymers, and copolymers (Erol and Soykan, 2002; Erol and Soykan, 2003; Schroeder et al., 2007; Sabaa et al., 2008). It was determined that polymers with high molecular weight and good thermal stability have good mechanical properties and that the change in the chemical structure of the copolymer also affects the biological properties. Although many studies (Caslavská et al., 2001; Walker et al., 2002; Fa et al., 2005; Mahabadi et al., 2006; Chen et al., 2006; Falahati et al., 2014) have reported on such properties of methacrylate-based polymers, studies of electrokinetic properties of methacrylate-based copolymers are limited. In the study of Erol et al. (2017), polymers were synthesized with the combination of 2-(4-nitrophenyl)-2-oxoethyl-2-methacrylate (NFM) and glycidyl methacrylate (GMA) in different ratios and it was determined that the point of zero charge (*pzc*) values of the obtained products were between 3.2 and 4.5. Additionally, as the ratio of polar NFM monomer in the copolymer increased, the zeta potential increased in the negative direction, and the contact angles with water decreased; the hydrophobic character decreased (Erol et al., 2017). On the other hand, several studies were reported on the hydrophobicity/hydrophilicity (or wettability) and *SFE* of different polymers such as epoxy, polytetrafluorethylene, polymethylmethacrylate, polyvinylchloride, and polystyrene (Lipatov and Feinerman, 1979; Van Oss, 1994; Adamson and Gast, 1997; Abbasian et al., 2004; Ma et al., 2007; Zenkiewicz, 2007; Chibowski and Terbilowski, 2009; Syakur et al., 2012; Ngai et al., 2017; Rymuszka et al., 2017; Evcin et al., 2018). These studies indicated that the chemical structure of the polymer is one of the most important factors that determines its surface wettability and *SFE*. Similarly, lots of studies were carried out on contact angle and *SFE* of different copolymers such as polystyrene(PS)-poly(hydroxylated butadiene) (PHBD), poly(2-hydroxyethyl methacrylate (PHEMA))-PS, polyethylene oxide (PEO)-poly(tetramethylene oxide) (PTMO), Methoxy poly(ethylene glycol) methacrylate (MPEGM)-PS, nitrophenyl methacrylate(NFM)-glycidyl methacrylate (GMA) (Teraa et al., 1990; Takahara 1992; Erol et al., 2017). According to the information obtained from these studies, it was seen that the molecular design of the copolymers directly affects their wettability and *SFE*.

In this study, the electrokinetic properties (zeta potential profile, isoelectric point (*iep*), potential determining ions, and indifferent ions) and surface properties (wettability and *SFE*) of novel functional methacrylate copolymers based on glycidyl methacrylate obtained from the various combination of 2-[(methoxy-1,3-benzothiazole-2-yl) amino]-2-oxoethyl methacrylate (MBAOM), and commercial monomers glycidyl methacrylate (GMA) were investigated. To our best knowledge, there is no study on the surface properties of these newly synthesized copolymers.

2. Materials and methods

2.1. Materials

In the experiments, MBAOM-GMA copolymers were obtained by using different ratios of glycidyl methacrylate (GMA) and 2-[(methoxy-1,3-benzothiazol-2-yl) amino]-2-oxoethyl methacrylate (MBAOM) monomers. The polymers were synthesized within the scope of an MSc thesis (Güldiken, 2017), and the synthesis process was as follows. MBAOM and GMA monomers were first put into polymerization tubes. Then, 2% by mass of the total monomer amount of azobisisobutyronitrile (AIBN) and three times the 1,4-dioxane were added to the tubes. Nitrogen gas was passed through the polymerization tubes for 5 min, their mouths were closed, and the polymerization reaction was carried out in an oil bath adjusted to 65°C. After the polymerization was completed, all of the copolymers were precipitated in ethanol. After the precipitated product was filtered and dried in the air, it was washed with pure water and dried again in the air. The composition ratios of the synthesized monomers in the initial mixture and post-synthesis copolymer are given in Table 1. The compositions of the prepared copolymer samples were determined by using the elemental analysis results. By using the nitrogen values in MBAOM units, the mole numbers and mole percentages of MBAOM and GMA units in the copolymer composition were calculated.

Table 1. The initial mixing ratios of the synthesized monomers and the composition ratios in the produced copolymer (Güldiken, 2017)

Initial mixing ratios of monomers (mol %)		Copolymer composition (mol %)	
MBAOM	GMA	MBAOM	GMA
15	85	19	81
50	50	45	55
90	10	77	23

The chemical structures of the copolymers are shown in Fig. 1. When the chemical structure of the MBAOM-GMA copolymer is examined, it is seen that the GMA unit contains fewer polar groups than the MBAOM unit. GMA has only carbonyl (-C=O) and epoxide rings as polar groups. In the MBAOM structure, there are many functional groups and heteroatoms such as carbonyl (-C=O), amide (NH-C=O), sulfur, and nitrogen (N, S) in the ring structure, and methoxy (CH₃-O) attached to the benzene ring.

Sodium chloride (NaCl, 99%), potassium chloride (KCl, 99%), calcium chloride (CaCl₂, 97%), iron chloride (FeCl₃, 97%) were purchased from Sigma Aldrich. Hydrochloric acid (HCl, 37%), sodium hydroxide (NaOH, 98%), ethylene glycol (HOCH₂CH₂OH, 99%), diiodomethane (CH₂I₂, 99%) were purchased from Merck.

2.2. Methods

Electrokinetic and surface properties were determined after the copolymer samples were ground to a size of approximately -0.3 mm in an agate mortar.

2.2.1. Determination of isoelectric point (*iep*) of copolymers

pH-dependent zeta potential profiles of each of the copolymers were obtained, and then their *iep* values were determined. Before the experiments, a 1 dm³ of 1 mol/dm³ NaCl stock solution was prepared, and two different concentrations (1.10⁻² mol/dm³ and 1.10⁻³ mol/dm³) of NaCl salt solutions were derived

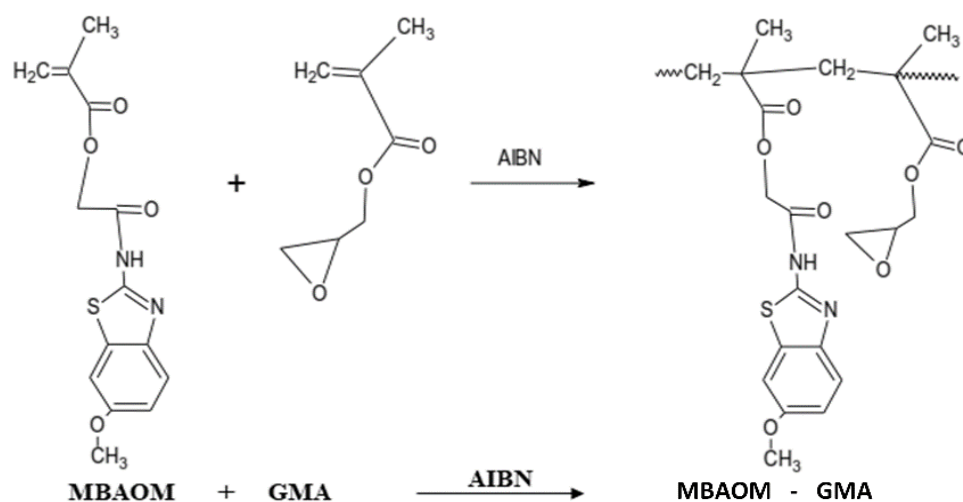


Fig. 1. MBAOM-GMA copolymer synthesis and chemical structure of the copolymer (Güldiken, 2017)

from this stock solution. Additionally, HCl and NaOH solutions at different concentrations (1.10^{-2} mol/dm³, 10^{-1} mol/dm³, 1 mol/dm³, 5 mol/dm³) were prepared for the pH adjustment. 80 cm³ of the prepared salt solution was added into a beaker, 0.015 g of the copolymer to be measured was added to it, and mixed for 30 min at 8000 rpm using an Ultra-Turrax IKA T25 digital homogenizer (Germany) to ensure a good dispersion. The prepared dispersion was then continued to be mixed at 700 rpm with IKA Basic RCT (Germany) magnetic stirrer until pH was adjusted and then stirred for 10 min after each pH adjustment. Two separate dispersions were used for the zeta potential measurements at acidic and basic pHs. A WTW 720 pH meter with ± 0.01 sensitivity was used for the pH measurements. Then, approximately 2 cm³ of dispersion was drawn with an injector and injected into the measuring cell of the Malvern Zetasizer Nano-Z (United Kingdom) zeta potential device and placed in its place. The device performs the zeta potential measurements using the Laser Doppler Electrophoresis method. Distilled water with a conductivity of ~ 2 $\mu\text{S}/\text{cm}$ was used for the preparation of acid, base, and salt solutions for all experiments.

2.2.2. Zeta potential measurements of copolymers dependent on metal salt type and concentration

In order to see the effect of different valent metal cations on the zeta potential of each of the copolymers, 1 mol/dm³ stock metal salt solutions of 1 dm³ KCl, CaCl₂, and FeCl₃ were prepared. Then, 1.10^{-5} , 1.10^{-4} , 1.10^{-3} , and 1.10^{-2} mol/dm³ solutions were derived from them, and the zeta potential measurements were carried out similar to the previous ones.

2.2.3. Contact angle measurements with different liquids (water, diiodomethane, and ethylene glycol) on copolymers

Hydrophobic character and surface free energy (*SFE*) of the copolymers were determined by performing a series of contact angle measurements using two polar (water and ethylene glycol) and one apolar (diiodomethane) liquids. The procedures performed are given below:

2.2.3.1. Sample preparation

Ground copolymer sample (~ 0.3 mm) was first dried in an oven at 60°C, and then 15 mm diameter smooth surface tablets were produced by using the laboratory type Specac GS15011 brand model hydraulic manual press. Produced tablets were placed in a desiccator in order not to be affected by ambient humidity and were kept there until measurement.

2.2.3.2. Preparation of the measuring liquid

Before starting the contact angle measurement, the Hamilton micro-syringe was cleaned first with hexane, then with acetone, and finally with distilled water. Then, it was cleaned twice with the liquid

to be used to measure the contact angle, and finally, the syringe was filled with the measuring liquid and placed in the compartment in the device.

2.2.3.3. Contact angle measurements

In the experiments, contact angle measurements were performed at room temperature using the sessile drop method with the KSV Attension ThetaLite TL 101 (China) optical tensiometer device. After a drop of liquid was dropped on the flat solid surface with a Hamilton micro-syringe, the contact angle formed by the liquid drop on the solid surface was measured with an optical camera depending on the time. The contact angle measurements were performed with liquid drops of 5-7 μL , and data of the fifth second were taken as contact angle values.

2.2.4. Determination of surface free energies (SFE) of copolymers

As it is known, while the surface tension of liquids can be measured directly with a device, a direct measurement is not possible for the SFE of solids. However, the SFE of the solid can be calculated using some mathematical equations after measuring the contact angles of polar and nonpolar liquids with known surface tension components with the solid surface (Erbil, 2006). Liquids with known surface tension values (Table 2) were used to calculate the SFEs of the copolymer samples by the Acid-Base (Van Oss-Chaudhury-Good) method. The contact angle measurements for the samples were performed on each copolymer surface with each of these liquids, and then the SFEs of the copolymers were calculated by the device according to the Acid-Base approach using the Van Oss-Chaudhury-Good method (Eq. 1).

Table 2. Liquids used in contact angle measurements (Erbil, 2006)

Liquid	Chemical structure	Polarity	γ	γ^{LW}	γ^{AB}
Water	H_2O	polar	72.8	21.8	51.0
Ethylene glycol	$\text{HOCH}_2\text{CH}_2\text{OH}$	polar	48.0	29.0	19.0
Diiodomethan (methylene iodide)	CH_2I_2	apolar	50.8	50.8	0

γ , Surface tension of the liquid (mJ/m^2)

γ^{LW} , Surface tension component (mJ/m^2) of the liquid resulting from the Lifshitz-van der Waals (LW) interaction potential

γ^{AB} , Surface tension component (mJ/m^2) resulting from the liquid's acid-base (AB) interaction potential

2.2.5. Calculation of SFE with acid-base approach using the Van Oss, Chaudry, and Good equation

SFE of the solids with the Van Oss, Chaudry, and Good (OCG) equation were calculated as follows. Eq. 1 was solved using the surface tension components of three different liquids and the measured contact angle values. Eq. 2 was then solved, and SFE (γ_s) of the solid was calculated using obtained results from Eq. 1 (Van OSS, 1986; Erbil, 2006):

$$1 + \cos \theta \gamma_L = 2 \left(\sqrt{\gamma_s^{\text{LW}} \gamma_L^{\text{LW}}} - \sqrt{\gamma_s^- \gamma_L^+} - \sqrt{\gamma_s^+ \gamma_L^-} \right) \quad (1)$$

$$\gamma_s = \gamma_s^{\text{LW}} + 2\sqrt{\gamma_s^+ \gamma_s^-} \quad (2)$$

where γ_s^{LW} is the surface energy (mJ/m^2) of the solid resulting from Lifshitz-Van Der Walls (Keesom, Debye, and London) interactions, γ_L^{LW} is the surface energy (mJ/m^2) of the liquid resulting from Lifshitz-Van Der Walls interactions, γ_s^+ and γ_L^+ are surface energies (mJ/m^2) resulting from Lewis acid (receiving electron) interaction of solid and liquid, γ_s^- and γ_L^- are surface energies (mJ/m^2) resulting from the Lewis base (electron donor) interaction of solid and liquid, respectively.

3. Results and discussion

3.1. pH-dependent zeta potential change and determination of iep of copolymers

The pH-dependent zeta potential profiles and the obtained iep of the copolymers of different composition ratios are shown in Fig. 2. The curves and the obtained iep values shifted to the right with the increase of the GMA ratio in the copolymer, and therefore the iep values of the copolymers containing 23%, 55%, and 81% GMA were found around pH 3.1, pH 3.3, and pH 3.8, respectively. This

is a clear indication that the electrokinetic character of the copolymer in water changes with the change in its chemical structure. The zeta potential values for the copolymer containing 23%, 55%, and 81% GMA at the same pH value (pH 4) were found around -22, -13, and -4 mV, respectively. As the GMA ratio increased, the negative surface charge of the copolymer decreased significantly. Therefore, the H^+ ion concentration is given to the media to neutralize the surface charge of the copolymer also decreased. In other words, at a higher pH value, an *iep* was reached. This can be explained by the fact that the copolymer becomes more hydrophobic with the increase of the GMA ratio. Therefore, its affinity toward water molecules and hydrogen/hydroxyl ions in water decrease. As known, hydrophobic polymers such as PMMA and PTFE do not contain reactive surface groups such as carboxyl (-COOH) and hydroxyl (-OH). Therefore, the origin of surface charge for the polymers mainly results from OH^- or H^+ adsorption onto the surface, depending on the pH of the media (Tandon et al., 2008; Falahati et al., 2014). Similar results were also obtained by Erol et al. (2017), in which the effect of structural changes in glycidyl-based methacrylate copolymers on the zeta potential was investigated. In the study, the pH-dependent zeta potential changes of NFM [2-(4-nitrophenyl)-2-oxoethyl-2-methacrylate] and GMA (glycidyl methacrylate) copolymers at different composition ratios were investigated. It was determined that the *iep* shifted to the right with the increase in the GMA ratio in the copolymer, and the pzc values of the copolymers with eight different structures changed between pH 3.2 - 4.5 (Erol et al., 2017). On the other hand, in the literature, it has been revealed that the *iep* of PMMA polymer varies between approximate pH 3 - 4 and that the electrolyte type in the media, ionic strength and ambient temperature should be considered in the zeta potential measurements (Caslavská and Thorman, 2001; Walker et al., 2002; Fa et al., 2005; Mahabadi et al., 2006). However, some studies determined that PMMA has always positive the zeta potential values at all pH values (3-11.5). In other words, there is no *iep* (Soper et al., 2002; Chen et al., 2006; Falahati et al., 2014). It was seen that very different zeta potential profiles and *iep* values are obtained in the literature, even for the same polymer material. This is essentially an indication that many factors can affect the electrokinetic properties of solids. These can be listed as follows; (i) the use of different measurement methods (electrophoresis, streaming potential, etc.), (ii) the polymer materials used may contain some unpredictable impurities arising from different production processes, (iii) some pre-treatments (acidic or heat treatment, surface polishing, etc.), (iv) some impurities that may be at the polymer-liquid interface during the measurement, (v) using a buffer solution during the measurement, ignoring the ionic strength of the media or using a different ionic strength media.

3.2. Effect of various metal salts on the zeta potential of copolymers

The effect of different metal cations on the zeta potential of the copolymers is given in Fig. 3. The zeta potential of the copolymers containing 23%, 55%, and 81% GMA was found to be -57, -50, and -45 mV, respectively. At the same time, $FeCl_3$ concentration was 1.10^{-5} mol/dm³. When the iron concentration increased to 1.10^{-4} mol/dm³, it was determined that it increased up to +39 mV, +34 mV, and +30 mV, respectively. The pH of the prepared $FeCl_3$ solutions varies between 2.85-4.27 depending on the concentration. At this pH range, there are not only Fe^{3+} ions but also ions such as $FeOH^{2+}$ and $FeOH^{2+}$. Therefore, such ferric hydroxyl-type ions can also adsorb on negatively surface-charged copolymers, compressing the electrical double layer (EDL) thickness, and causing a decrease in the zeta potential. It can be seen from Fig. 3 that Ca^{2+} ions also have a significant effect on the zeta potential of their copolymers. These ions can adsorb on the copolymer surface due to strong dipole-dipole, dipole-excited dipole interactions between Ca^{2+} ions and polar groups such as carbonyl (-C=O), S, and N of the copolymers. As a result, the zeta potential of copolymers containing 23%, 55%, and 81% GMA at 1.10^{-2} mol/dm³ $CaCl_2$ concentration decreased to around -16, -12, and -6 mV, respectively. For this reason, the Ca^{2+} ion can be considered as the specifically adsorbed ion for MBAOM - GMA copolymers. Monovalent K^+ ions, on the other hand, cannot adsorb on the copolymers due to the relatively weak electrostatic interaction and only collect into the EDL and compress the EDL, thereby reducing the zeta potential slightly. In summary, it was determined that the effect degrees of metal cations on the zeta potential were in the order $FeCl_3 > CaCl_2 > KCl$. It was found that 3+ valence metal cations (such as Fe^{3+}) showed a more significant effect on the zeta potential compared to 2+ and 1+ valence metal cations (such as Ca^{2+} and K^+). Trivalent Fe^{3+} ions are capable of reversing the sign of the zeta potential of all copolymers from negative to positive in a narrow concentration range. This shows that there is a powerful electrostatic

interaction between Fe^{3+} cations and negatively charged copolymers so that they can penetrate the stern layer, which forms the EDL of the copolymers. As known from the literature, metal ions with 3+ valence can adsorb specifically onto solids with negative surface charge, and they convert the surface charge to positive (Ersoy and Çelik, 2002). In a study, the effect of CaCl_2 and KCl salts on the zeta potential of PMMA was investigated, and similar results were obtained (Falahati et al., 2014).

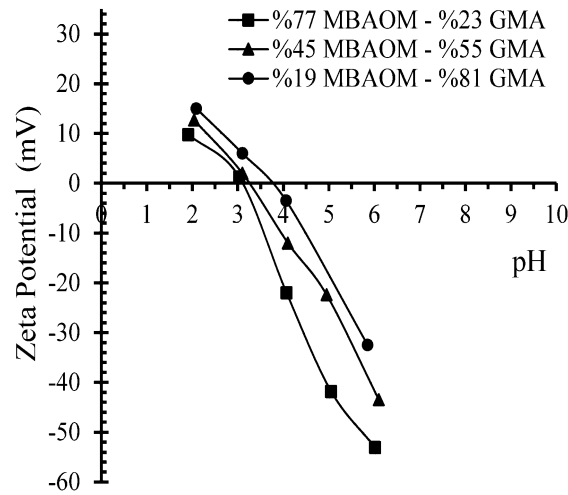


Fig. 2. pH-dependent zeta (ζ) potential profiles of copolymers (in 1.10^{-3} mol/dm³ NaCl solution)

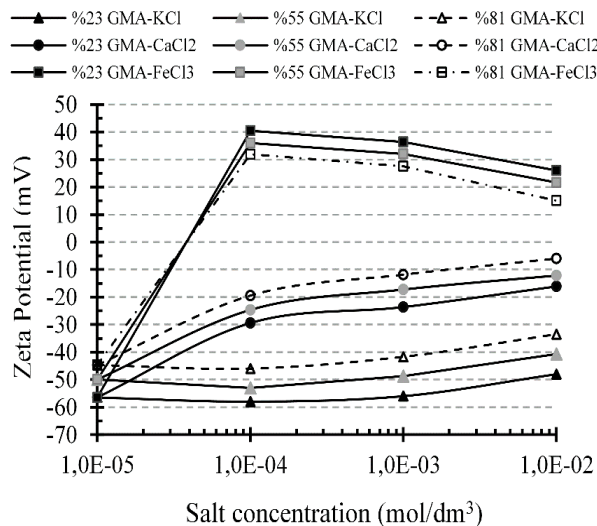


Fig. 3. Zeta (ζ) potential profiles of copolymers depend on salt concentration in the presence of different metal salts

3.3. Surface hydrophobic/hydrophilic properties of copolymers (contact angles, θ , with water)

As it is known, the most essential indicator of the hydrophobic character of a solid surface is the contact angle value of that solid surface with water. As the hydrophobic character of the solid surface increases, the contact angle increases. If the contact angle with water is 90° and above, that surface is called a hydrophobic surface (Leja, 1982; Erbil, 2006; Evcin et al., 2018). Related to the hydrophilic and hydrophobic concepts, Good and Van Oss (1992) expresses that "There is no question that hydrogen bonding is involved in hydrophilic behavior of solid surfaces and that its absence is correlated strongly with hydrophobic behavior". The measured contact angles for MBAOM-GMA copolymers with different monomer composition ratios used in this study are given in Fig. 4. As seen from Fig. 4, the contact angle value increases with the increase of the GMA ratio of the copolymer. While the contact angle of the copolymer with 23% GMA was $\sim 59^\circ$, it was determined that this value increased to $\sim 64^\circ$ in the copolymer containing 55% GMA and to $\sim 68^\circ$ in the copolymer containing 81% GMA. The GMA

monomer of the copolymer contains much fewer polar groups than the MBAOM monomer. While there is only carbonyl ($-C=O$) and epoxide ring as polar groups in the GMA unit, the MBAOM unit has carbonyl ($-C=O$), amide ($NH-C=O$), methoxy (CH_3-O) sulphur and nitrogen (N, S) groups (Fig. 1). For this reason, as the ratio of GMA increases in the copolymer structure, the polar character of the copolymer decreases. Therefore, its affinity for water decreases; that its hydrophobic character increases.

Similar to these results, in a study investigating the surface properties of glycidyl methacrylate-based NFM-GMA copolymers, it was determined that the contact angle of the copolymer with water increased. In other words, hydrophobicity increased with the increase of the GMA ratio of the copolymer. While the contact angle of the copolymer consisting of 100% NFM was 65° , this value increased to 88° for the copolymer consisting of 74% NFM - 26% GMA (Erol et al., 2017). On the other hand, while MBAOM-GMA-based copolymers showed contact angles varying between 59° - 68° , higher contact angles were measured for epoxy, and polyester-based polymers (Adamson and Gast, 1997; Evcin et al., 2018). This is due to the difference in the chemical structures of methacrylate polymers and the other polymers mentioned. The hydrophobic character of methacrylate polymers is relatively lower than some other polymers such as epoxy, PTFE, and polystyrene (Ma et al., 2007; Ngai et al., 2017; Evcin et al., 2018). In the literature (Takahara, 1992), it is stated that the wettability determined by using a water droplet on the dry polymer surface of the PHEMA-PS-PHEMA [(Poly(2-hydroxyethyl methacrylate))] triblock copolymer increases with the increase of HEMA mole fraction in the copolymer. In another study, the contact angle of PMMA polymer with water was measured as 72.5° , while they measured the contact angle of 33.5° and 40.4° for two different PMMA-PEG copolymers obtained with different techniques. They explained this decrease in contact angle with the presence of OH groups in the molecular structure of PEG (Ko et al., 2017). On the other hand, Ngai et al., (2017) measured the contact angles of 5 different methacrylate-based polymers and PS with water. As a result, they showed that the contact angles (θ) of the polymers changes depending on the chemical structure as PMMA (64°) < PEMA (poly(ethyl methacrylate)) (78°) < PIPMA (poly(isopropyl methacrylate)) (80°) = PPhMA (poly(phenyl methacrylate)) (80°) < PIBMA (poly(isobutyl methacrylate)) (85°) < PS (Polystyrene) (86°).

3.4. Surface free energies (SFE) of copolymers

The surface free energies (SFE) of the copolymers were calculated by the Acid-Base approach using the Van Oss-Chaudhury-Good method. Figure 5 revealed that the SFE decreased with the increase of the GMA ratio in the copolymer. This is because the GMA monomer contains fewer polar groups compared to the MBAOM monomer. The SFE value of the copolymer containing 23% GMA was ~ 45 mJ/m², while it was calculated as 26 mJ/m² for the copolymer with a GMA ratio of $\sim 81\%$. Similar results were obtained in the study of Erol et al. (2017), in which they investigated the surface properties of glycidyl methacrylate-based NFM(2-(4-nitrophenyl)-2-oxoethyl-2-methacrylate)-GMA (glycidyl methacrylate) copolymers. It was determined that the SFE of the copolymer decreased with the increase of the GMA ratio of the copolymer. In the literature (Good and van Oss, 1992; Busscher, 1992), SFE values of PMMA polymers calculated by the Acid-Base approach are given between 49-65 mJ/m² which is higher than those of MBAOM-GMA copolymers used in this work. When the molecular structures of PMMA and MBAOM-GMA were examined, it would be expected that the SFE of the 77%MBAOM-23%GMA copolymer with a high MBAOM ratio would be higher than that of PMMA. Because the number of H-bonding groups on the surface of PMMA is less than that of the MBAOM component. Therefore, the MBAOM-GMA copolymer is considered to be more hydrophilic than the other. However, according to the contact angle values, it was seen that this does not happen. This can be explained by some factors that are effective in determining the contact angle and SFE of solids, similar to the zeta potential measurements (Reynolds, 2005; Erbil, 2006). These are (i) factors related to solid material (heterogeneity in chemical structure, surface roughness, surface contamination, surface moisture), (ii) factors related to the measuring liquid (degree of purity, volatility of the liquid, contamination of the liquid, etc.), (iii) depending on the measurement conditions (drop volume, contact angle measurement time, pre-treatments such as washing and drying applied to the solid sample before measurement, different test liquids), and (iv) environmental factors (temperature, humidity, pressure, gaseous/dusty/smoky media). Considering and knowing all these factors while performing contact angle measurements is of great importance in terms of the reliability of the results obtained.

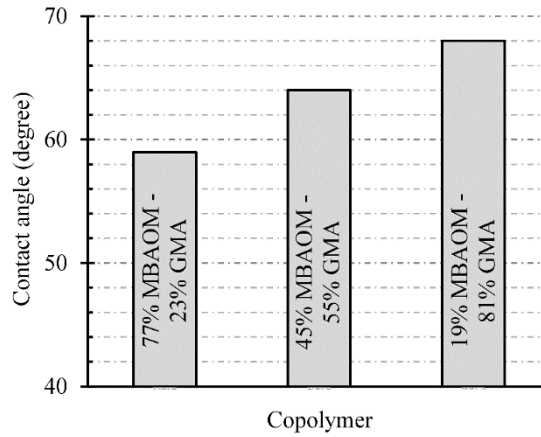


Fig. 4. Contact angle values of copolymers measured with water

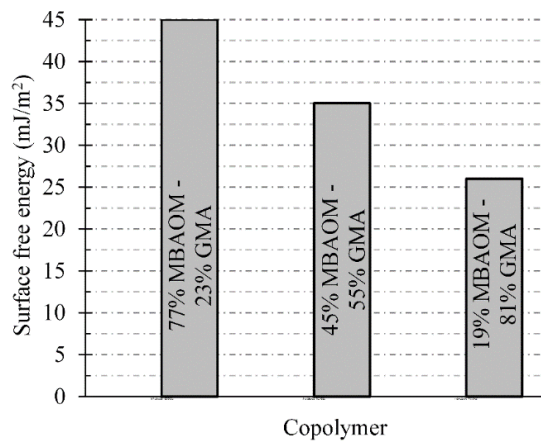


Fig. 5. Surface free energies of copolymers

3.5. Comparison of contact angles and surface free energies of copolymers

As is known, there is an inverse relationship between hydrophobicity and *SFE*, and if one increases, the other decreases (Erbil, 2006; Evcin et al., 2018). Therefore, an increase in the hydrophobic character of the copolymer means a decrease in the *SFE*, which was also revealed in Fig. 6. The highest contact angle (68°) and lowest *SFE* (26 mJ/m²) measured with distilled water were obtained by MBAOM-GMA copolymer containing 81% GMA. This is because the GMA monomer is more hydrophobic than the MBAOM monomer due to the fewer polar groups in its structure.

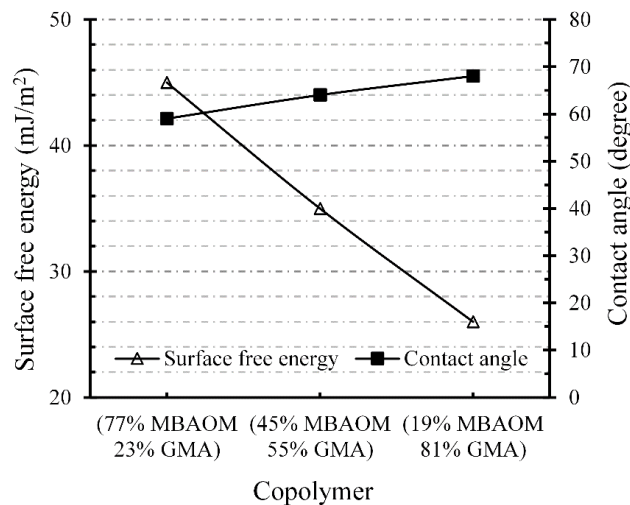


Fig. 6. Comparison of surface free energies and contact angles of copolymers

4. Conclusions

MBAOM (2-[(methoxy-1,3-benzothiazole-2-yl) amino]-2oxoethyl methacrylate)-GMA (glycidyl methacrylate) copolymers naturally have negative surface charge and the zeta potential in water. The change in the composition of the copolymer seriously affected the zeta potential. It was determined that the zeta potential decreased depending on the increase in the GMA ratio. This is because the GMA monomer has a more hydrophobic character than the MBAOM monomer. Namely, the number of polar groups is fewer.

The *iep* of the copolymers changed according to the GMA ratio, and the *iep* shifted towards a slightly higher pH as the GMA ratio increased. It was determined that the *iep* values of the copolymers containing 23%, 55%, and 81% GMA were around pH 3.1, pH 3.3, and pH 3.8, respectively.

The type and number of cations in the dispersion media played an important role in the zeta potential. When a small amount ($5 \cdot 10^{-5}$ mol/dm³) of FeCl₃ salt was added to the media, the surface charges of the copolymers changed from negative to positive. Other 2+ and 1+ valence cations (Ca²⁺, K⁺) did not show such an effect.

For MBAOM-GMA copolymers, H⁺ and OH⁻ are potential determining ions, Fe³⁺ and Ca²⁺ are ions capable of specific adsorption, and K⁺ and Na⁺ are indifferent ions.

According to the contact angle data, MBAOM-GMA copolymers were found to be relatively hydrophilic, unlike most other polymers. As the GMA ratio of the copolymer increased, the contact angle and thus its hydrophobic character increased. This was due to the chemical structure difference between GMA and MBAOM. The GMA monomer contains much fewer polar groups/atoms than MBAOM and its hydrophobic property was higher than MBAOM. The highest contact angle (68°) was obtained with the copolymer with the highest GMA ratio (81%).

The *SFEs* of the copolymers calculated by the Acid-Base approach using the Van Oss-Chaudhury-Good (OCG) method were compatible with the contact angle data. The *SFE* decreased as the GMA ratio of the copolymer increased. The lowest *SFE* value (26 mJ/m²) was obtained with the copolymer with the highest GMA ratio (81%).

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References

- ABBASIAN, A., GHAFARIAN, S.R., MOHAMMADI, N., FALLAHI, D., 2004. *The contact angle of thin-uncured epoxy films, thickness effect*. Colloids Surf. A: Physicochem. Eng. Aspects. 236, 133–140.
- ADAMSON, A.W., GAST, A.P., 1997. *Physical Chemistry of Surfaces (Sixth Edition)*. Wiley, New York.
- ARUKALAM, I.O., OGUZIE, E.E., LI, Y., 2016. *Fabrication of FDTS-modified PDMS-ZnO nanocomposite hydrophobic coating with anti-fouling capability for corrosion protection of Q235 steel*. J. Colloid Interface Sci. 484, 220–228.
- ASANO, H., SHIRAIISHI, Y., 2015. *Development of paper-based microfluidic analytical device for iron assay using photomask printed with 3D printer for fabrication of hydrophilic and hydrophobic zones on paper by photolithography*. Analytica Chimica Acta. 883, 55–60.
- BUSSCHER, H.J., 1992. *Wettability of Surfaces in the Oral Cavity, in: Modern Approaches to Wettability* (Eds: M.E., Schrader, Loeb, G.I.), Plenum Press, New York.
- CASLAVSKA, J., THORMAN, W., 2001. *Electrophoretic separations in PMMA capillaries with uniform and discontinuous buffers*. J. Microcolumn Separations. 13, 69–83.
- CHAKRADHAR, R.P.S., DINESH KUMAR, V., RAO, J.L., BASU, B.J., 2011. *Fabrication of superhydrophobic surfaces based on ZnO–PDMS nanocomposite coatings and study of its wetting behavior*. App. Sur. Sci. 257, 8569–8575.
- CHEN, R., GUO, H., SHEN, Y., HU, Y., SUN, Y., 2006. *Determination of eof of PMMA microfluidic chip by indirect laser-induced fluorescence detection*. Sens. Actuators, B, 114(2):1100–1107.
- CHIBOWSKI, E., TERPILOWSKI, K., 2009. *Surface free energy of polypropylene and polycarbonate solidifying at different solid surfaces*. App. Surf. Sci. 256, 1573–1581.
- DOBZANSKI, L.A., 2006. *Engineering Materials and Materials Design, Fundamentals of Materials Science and Physical Metallurgy*, WNT, Warsaw.

- EBNASAJJAD, S., 2011. *Handbook of Adhesive and Surface Preparation (Technology, Applications and Manufacturing)*, Elsevier Inc., Oxford.
- ERBİL, H.Y., 2006. *Surface Chemistry of Solid and Liquid Interfaces*. Blackwell Publishing Ltd, England.
- EROL, İ., SOYKAN, C., 2002. *Synthesis, characterization, and polymerization of new methacrylate esters having pendant amide moieties*. J. Macromol. Sci. -Pure App. Chem. A39, 405-417.
- EROL, İ., SOYKAN, C., 2003. *Synthesis and characterization of new aryl-oxycarbonyl methyl methacrylate monomers and their polymers*. React. Funct. Polym. 56, 147-157.
- EROL, İ., DEVRİM, D.N., ÇİFTÇİ, H., ERSOY, B., CİGERCİ, İ.H., 2017. *Novel functional copolymers based on the glycidyl methacrylate, synthesis, characterization and polymerization kinetics*. J. Macromol. Sci. -Pure App. Chem. 54(7), 434-445.
- ERSOY, B., ÇELİK, M.S., 2002. *Electrokinetic properties of clinoptilolite with mono and multivalent electrolytes*. Microporous Mesoporous Mat. 55, 305-312.
- EVCİN, A., ERSOY, B., UYGUNOĞLU, T., GÜNEŞ, İ., 2018. *The effect of different mineral additives on the wettability and surface energy of the epoxy floor coating material*. J. Fac. Eng. Arc. Gazi Univ. 33, 581-590 (in Turkish).
- FA, K., PARUCHURI, V., BROWN, S., MOUDGIL, B., MILLER, J.D., 2005. *The significance of electrokinetic characterization for interpreting interfacial phenomena at planar, macroscopic interfaces*. Phys. Chem. Chem. Phys., 7(4):678-684.
- FALAHATI, H., WONG, L., DAVARPANA, L., GARG, A., SCHMITZ, P., BARZ, D.P.J., 2014. *The zeta potential of PMMA surfaces in contact with electrolytes of various conditions, Theoretical and experimental investigation*. Electrophoresis. 35, 870-82.
- GAO, Z., ZHAI, X., LIU, F., ZHANG, M., ZANG, D., WANG, C., 2015. *Fabrication of TiO₂/EP super-hydrophobic thin film on filter paper surface*. Carbohydr. Polym. 128, 24-31.
- GNEDENKOV, S.V., SINEBRYUKHOV, S.L., EGORKIN, V.S., VYALİY, I.E., 2016. *Wettability and electrochemical properties of the highly hydrophobic coatings on PEO-pretreated aluminum alloy*. Surf. Coat. Technol. 307, 1241-1248.
- GOOD, R.J., VAN OSS, C.J., 1992. *The Modern Theory of Contact Angle and the Hydrogen Bond Components of Surface Energies in: Modern Approaches to Wettability* (Eds: M.E., Schrader, Loeb, G.I.), Plenum Press, New York.
- GÖNÜL, N., 2000. *Suspension and Emulsion Technology*. Ankara Univ., Ankara, Türkiye (in Turkish).
- GÜLDİKEN, A., 2017. *Synthesis and characterization of a new methacrylate polymers having pendant methoxy substituted thiazol arylamide*. M.Sc. Thesis, Afyon Kocatepe Univ., Afyon, Türkiye (in Turkish).
- HIEMENZ, P.C., 1986. *Principles of Colloid and Surface Chemistry (2nd Edition)*, Marcel Dekker Inc., New York.
- HÖLCK, O., BAUER, J., WITTLER, O., MICHEL, B., WUNDERLE, B., 2012. *Comparative characterization of chip to epoxy interfaces by molecular modeling and contact angle determination*. Microelectronics Reliability. 52, 1285-1290.
- KAPILASHRAMI, A., ESKILSSON, K., BERGSTRÖM, L., MALMSTEN, M., 2004. *Drying of oil-in-water emulsions on hydrophobic and hydrophilic substrates*. Colloids Surf. A; Physicochem. Eng. Aspects. 233, 155-161.
- KARAMAN, M., UÇAR, T., 2016. *Enhanced mechanical properties of low-surface energy thin films by simultaneous plasma polymerization of fluorine and epoxy containing polymers*. Appl. Surf. Sci. 362, 210-216.
- KO, J.S., CHO, K., HAN, S.W., SUNG, H.K., BAEK, S.W., KOH W.G., YOON, J.S., 2017. *Hydrophilic surface modification of poly(methyl methacrylate)-based ocular prostheses using poly(ethylene glycol) grafting*. Colloids and Surfaces B: Biointerfaces 158, 287-294.
- LEJA, J., *Surface Chemistry of Froth Flotation (Second Edition)*, 1982. Plenum Press, New York.
- LIPATOV, Y., FEINERMAN, A., 1979. *Surface tension and surface free energy of polymers*. Adv. Colloid Interface Sci. 11, 195-233.
- LU, S., PUGH, R.J., FORSSBERG E., *Interfacial Separation of Particles*, 2005. Elsevier, Amsterdam.
- LUNG, C.Y.K., MATINLINNA, P., 2015. *Surface Pretreatment Methods and Salinization in Handbook of Oral Biomaterials*, Ed. Jukka P. Matinlinna, CRC Press, London.
- MA, Y., CAO, X., FENG, X., MA, Y., ZOU, H., 2007. *Fabrication of super-hydrophobic film from PMMA with intrinsic water contact angle below 90°*. Polymer. 48(26), 7455-7460.
- MAHABADI, K.A., RODRIGUEZ, I., HAUR, S.C., VAN KAN, J.A., BETTIOL, A.A., WATT, F., 2006. *Fabrication of PMMA micro-and nanofluidic channels by proton beam writing: Electrokinetic and morphological characterization*. J. Micromech. Microeng., 16(7):1170-1180.
- NGAI, J.H.L., JOHNNY, HO, K.W., CHAN, R.K.H., CHEUNG, S.H., LEUNG, L.M., SO, S.K., 2017. *Growth, characterization, and thin film transistor application of CH₃NH₃PbI₃ perovskite on polymeric gate dielectric layers*. RSC Adv. 7, 49353- 49360.

- REYNOLDS, P., 2005. *Wetting of Surfaces* in: *Colloid Science (Principles, Methods and Applications)* (Ed: T. Cosgrove), Blackwell Publishing Ltd., Oxford.
- RYMUSZKA, D., TERPIŁOWSKI, K., STERNIK, D., TOMCZYŃSKA-MLEKO, M., GONCHARUK, O., 2017. *Ukraine wettability and thermal analysis of hydrophobic poly (methyl methacrylate)/silica nanocomposites*. *Ads. Sci. Technol.* 35, 560–571.
- SABAA, M.W., FARAG, Z.R., MOHAMED, N.A., 2008. *Thermal Degradation Behavior of Poly (vinyl chloride) in the Presence of Poly (glycidyl methacrylate)*. *J. App. Polym. Sci.* 110, 2205-2210.
- SAÇAK, M., 2005. *Polymer Technology*. Gazi kitabevi, Ankara, Turkiye (in Turkish).
- SCHROEDER, W.F., BORRAJO, J., ARANGUREN, M.I., 2007. *Poly (methyl methacrylate)-modified vinyl ester thermosets, Morphology, volume shrinkage, and mechanical properties*. *J. App. Polym. Sci.* 106, 4007-4017.
- SOPER, S.A., HENRY, A.C., VAIDYA, B., GALLOWAY, M., WABUYELE, M., and MC CARLEY, R.L., 2002. *Surface modification of polymer-based microfluidic devices*. *Anal. Chim. Acta*, 470(1): 87–99.
- SYAKUR, A., BE RAHIM, H., ROCHMADI, T., 2012. *Hydrophobic contact angle and surface degradation of epoxy resin compound with silicone rubber and silica*. *Electr. Electr. Eng.* 2, 284-291.
- TAKAHARA, A., 1992. *Block Copolymers and Hydrophilicity*, in: *Modern Approaches to Wettability* (Eds: M.E., Schrader, Loeb, G.I.), Plenum Press, New York.
- TANDON, V., BHAGAVATULA, S.K., NELSON, W.C., KIRBY, B.J., 2008. *Zeta potential and electroosmotic mobility in microfluidic devices fabricated from hydrophobic polymers, 1. The origins of charge*. *Electrophoresis.* 29, 1092–1101.
- TERAYA, T., TAKAHARA, A., KAJIYAMA, T., 1990. *Surface chemical composition and surface molecular mobility of diblock and random copolymers with hydrophobic and hydrophilic segments*. *Polymer*, 31(6), 1149-1153.
- VAN DE WETERING, P., SCHUURMANS-NIEUWENBROEK, N.M.E., VAN STEENBERGEN, M.J., CROMMELIN D.J.A., HENNINK, W.E., 2000. *Copolymers of 2-(dimethyl amino)ethyl methacrylate with ethoxytriethylene glycol methacrylate or N-vinyl-pyrrolidone as gene transfer agents*. *J. Controlled Release.* 64, 193–203.
- VAN OSS, C.J., 1994. *Interface Forces in Aqueous Media*. Marcel Dekker Inc., New York.
- VAN OSS C.J., GOOD R.J., CHAUDHURY, M.K., 1986. *The role of van der Waals forces and hydrogen bonds in hydrophobic interactions between biopolymers and low energy surfaces*. *Journal of Colloid and Interface Science*, 111(2), 378-390.
- WALKER, S.L., BHATTACHARJEE, S., HOEK, E.M.V., ELIMELECH, M., 2002. *A novel asymmetric clamping cell for measuring streaming potential of flat surfaces*. *Langmuir*, 18(6): 2193–2198.
- YAO, C.H., QI, L., JIA, H.Y., 2009. *A novel glycidyl methacrylate-based monolith with sub-micron skeletons and well-defined macropores*. *J. Mater. Chem.* 19, 767-772.
- ZENKIEWICZ, M., 2007. *Methods for the calculation of surface free energy of solids*. *J. Achieve Mater. Manuf. Eng.* 24, 137-145.