



Synthesis of a novel siloxane-based crosslink agent and its application in emulsion copolymerization of butyl acrylate and methyl methacrylate

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Abstract

Improving water-based polymer's properties using silicon compounds is strongly noticed nowadays. A novel siloxane-based crosslink agent was synthesized using oligomeric polydimethylsiloxane (PDMS) hydroxyl-terminated. The crosslinker was used for emulsion copolymerization of methyl methacrylate (MMA), butyl acrylate (BA), and acrylic acid (AA). Incorporation of the crosslinker in the structure of the copolymer increased the average latex particle size (from about 165 to 207 nm) and as a result, the viscosity of the latexes was dramatically decreased (from 212 cP to 83 cP). The crosslink density of the latexes, meanwhile, was raised (from about 7–60%). Electrostatic stability of the latexes was improved in the presence of the crosslinker (zeta potential from -31.7 mV to -49.5 mV and the average mobility of the latexes particles from -2.4 $\mu\text{m/s/V/cm}$ to -3.8 $\mu\text{m/s/V/cm}$). The crosslinking agent affected both the initial decomposition temperature and residual weight fraction of the copolymer (from 353 to 406 °C and from about 0.5 w% to 12.4 w% respectively). A morphological study of the latexes was carried out using transmission electron microscopy (TEM), scanning electron microscopy (SEM), and atomic force microscopy (AFM) techniques. The addition of the crosslinker, led to a decrease in the contact angle (from 70 to 39 degrees) of the latexes film formed.

Keywords Emulsion copolymerization · Crosslink agent · PDMS · Copolymerization · Butyl acrylate · Methyl methacrylate

Introduction

Due to the rising consciousness of safety and ecological concerns, emulsion polymerization has been increasingly noticed [1]. Polyacrylic material has several applications owing to its specific properties, such as transparency, excellent film forming, gloss, and relatively low cost [2–6]. However, to develop their applications for a wider range, their weatherability, abrasion resistance, and chemical and thermal stability need more improvement [7].

Silicon polymers, due to their excellent properties, such as high flexibility and gas permeability, appropriate thermal stability, and low surface energy, are increasingly employed in polymer industries [6]. Silicon compounds, especially

polydimethyl siloxane (PDMS), are materials which are widely used to modify polyacrylates and obviate some of their drawbacks. Since the Si-O bond has higher bond energy and longer bond length compared to the C-C bond, the thermal stability and molecular flexibility of PDMS are significantly greater than organic polymers such as polyacrylates. Furthermore, the helical structure of the PDMS chain whose methyl groups arrange outer and rotate around the main chain leads to a bulky structure with relatively low cohesive energy [7–15]. There are several synthesis approaches for incorporating PDMS into polyacrylate polymers such as emulsifiers, grafting agents, and crosslink agents [11].

Physical and chemical stability as well as weather and abrasion resistance improvement of a latex film can be enhanced employing incorporating a crosslinker in the emulsion polymerization process [4]. Using crosslinkers in the emulsion polymerization process permits control of particle morphology and improvement of mechanical properties of its obtained latex. Using a PDMS compound as a crosslinker is a wise and efficient strategy to benefit from both of privilege silicon and crosslinking and thereby

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avoid the problem of phase incompatibility between organic-inorganic phases [16].

In the last two decades, many studies have been conducted in the field of properties synergy of organic-inorganic polymers, especially modifying the properties of water-based polymers using PDMS and efforts have been made to overcome incompatibility between organic-inorganic phases [6, 8, 17–21]. Reza Erfani Ghorbani et al. have used a PDMS silanol terminated as a surfactant in the emulsion polymerization of vinyl acetate and butyl acrylate. Thermal stability, T_g , latex viscosity, and colloidal stability were increased with the addition of PDMS as a surfactant [22]. Divinyl-terminated polysiloxane was used by Qipeng Zheng and Minghua Wu to modify polyacrylates via a mini-emulsion polymerization process. Experimental results showed an increase in hydrophobicity and toughness of the films obtained from crosslinked latex [11]. In another research, seeded emulsion polymerization of MMA and BA in the presence of polymerizable polysiloxane was carried out. Good storage stability, high electrolyte resistance of the latex, and appropriate mechanical stability of composite lattices were reported [3]. Weili Li et al. have modified a PDMS with γ -methacryloxy propyl trimethoxyl silane and employed it in emulsion polymerization of acrylates monomers. The incorporation of the modified PDMS in the polymer structure caused an improvement in weather-proofing and anticorrosion properties, high and low-temperature stability, and toughness [13].

In the present work, a novel siloxane-based crosslinker compound was synthesized and used in the semi-batch emulsion polymerization of BA, MMA, and AA. The effect of the synthesized crosslinker was investigated on thermal stability, electrostatic stability, crosslink density, particle size, particle morphology, contact angle of its film, and viscosity of obtained latex.

Experimental

Materials

Butyl acrylate and methyl methacrylate as main monomers and acrylic acid as functional monomers were purchased from Petro Chem Co, Dubai, UAE, and used as received. Nonylphenol ethoxylate (KENON20) as a nonionic surfactant was attained from Kimyagaran Emrooz Chemical Industries, Arak, Iran. Anionic surfactant dioctyl sulfosuccinate (DOSS) and polydimethylsiloxane hydroxyl-terminated (HO-PDMS-OH, $M_n \sim 550$, viscosity ~ 25 cSt) were attained from Sigma-Aldrich, Saint Louis, USA. Ammonium persulfate (APS) as a thermal initiator and sodium bicarbonate

as a buffer were acquired from Aldrich, Lancaster, UK, and Merck, Germany, respectively. Maleic anhydride and sodium hydride were purchased from Merck, Germany. Tetrahydrofuran (THF) as a solvent was obtained from Dr. Mojallali Industrial Chemical Complex Co. Iran.

Synthesis of maleate terminated PDMS (M-PDMS-M)

A solution was prepared with dissolving HO-PDMS-OH (0.08 mol, 44 g) in dried THF (150 mL, in a 250 mL round-bottom flask). The flask was immersed in an ice bath and sodium hydride (0.16 mol, 3.84 g) was gradually added to the solution. The reaction was carried out under an Ar atmosphere and agitation via a magnetic stirrer. After completion of the sodium hydride addition, the temperature was increased to ambient temperature, and maleic anhydride (0.16 mol, 15.6896 g) was slowly transferred to the reaction mixture. The reaction was carried out in the same conditions for a further 3 h. Reaction progress was monitored using the thin-layer chromatography technique. As the reaction was completed, its solvent was evaporated. The precipitate was washed several times using a dried THF and filtered (yield $\sim 60\%$) [9]. Procedure of the reaction is shown in Fig. 1.

Synthesis of copolymer latexes

Polymerization was carried out in a conventional 1 L glass reactor, equipped with a mechanical stirrer, dropping funnel, thermometer, and reflux condenser. Deionized water (DW), emulsifier, buffer, and about 5% of the monomer mixture were used as an initial charge. As the reactor temperature reached to 70 °C about 30% of APS solution was injected into the reactor. When the reacting emulsion turned to a bluish color, the rest of the monomer mixture and the initiator solution were added dropwise through the two feeding inlets over about 3.5 h. Polymerization was performed at a constant temperature (73 ± 2 °C) with using a digital circulation oil bath and stirrer rate of 200 rpm. After the monomer feed completion, the temperature was raised to 80 °C, and the condition was kept for a further 30 min. The content of the reactor was cooled to the ambient temperature. The final pH of the latexes was adjusted (pH = 7–8) using a liquid ammonia solution. The way of adding the crosslinker to the polymerization system was that first, the required amount of M-PDMS-M was dispersed in a small amount of DW, and then in the first or second half time of the monomers feeding period, gradually added to the system. A typical recipe for the semi-batch emulsion copolymerization is given in Table 1.

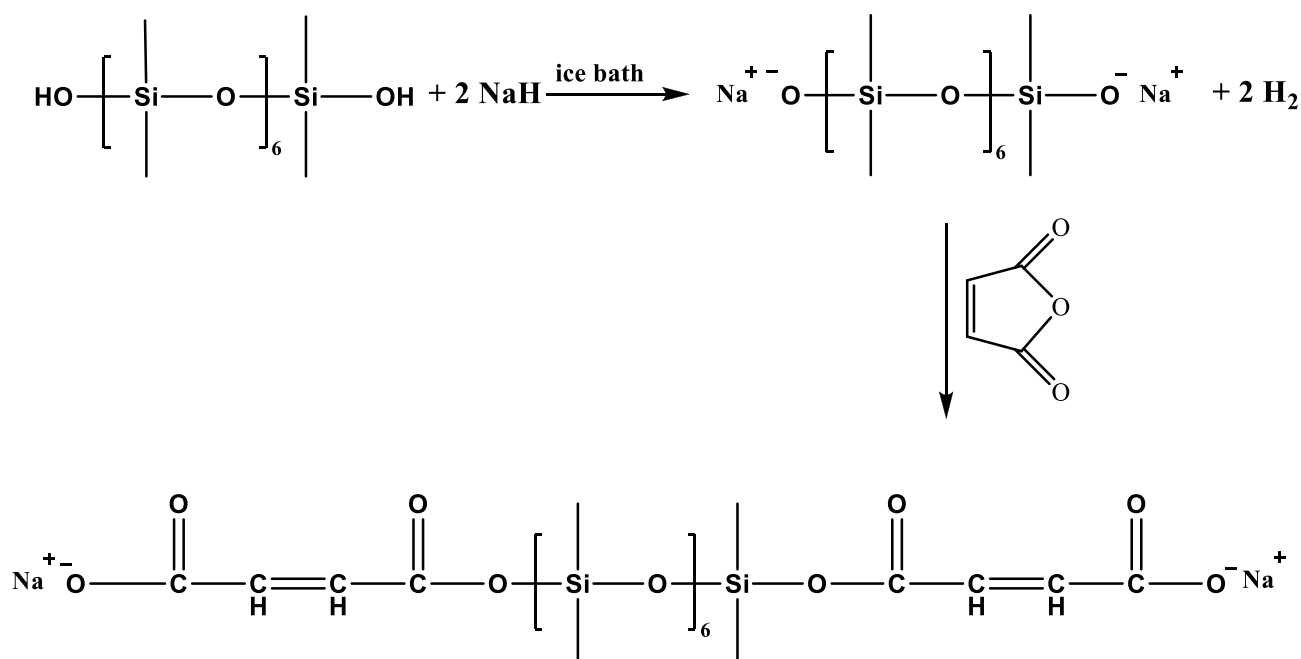


Fig. 1 Schematic synthesis procedure of Maleate Terminated PDMS (M-PDMS-M)

Characterization

The copolymer samples were tested using the ATR-FTIR technique (FTIR Thermo Nicolet, AVATAR 370 A, USA) after extraction of polymer from latexes by solvent (ethyl methyl ketone)/anti-solvent (DW) method. To investigate morphology of the latexes, TEM analysis (FEI/PHILIPS Model CM120, acceleration voltage 120 kV, Netherlands) was used. To characterize the surface shape of the latexes and the morphological features, AFM (Full plus model, Ara Research Company, Iran) was employed. SEM study was carried out using the FE-SEM

Table 1 Recipe for the BA-MMA copolymer latex synthesized through semi-batch emulsion polymerization

Ingredients	Initial charge (g)	Feed (g)
BA	7.5	141
MMA	6.1	115.4
AA	0.3	5.1
DOSS	3.5	-
KENON 20	7.5	-
APS	0.2	0.6
Sodium bicarbonate	0.6	-
DW	300	-
Crosslinker (M-PDMS-M)	-	4.1–16.5

apparatus (Tescan Company, model Mira3, Czech Republic). The TGA analysis (METTLER TOLEDO-TGA, Mettler, Switzerland) was used to study the thermal stability of the synthesized copolymers in the range of 25–800 °C. Due to the investigation of the colloidal stability of the latexes, the value of zeta potential and electrophoretic mobility of the particles were measured using a zeta potential analyzer (CAD, Zeta Compact, France). All measurements were carried out at a temperature of 22 °C and pH=8. The samples were diluted greatly before tests. The particle size was measured using a particle size analyzer (Cordouan, model Vasco3, France). Before examination, the samples were diluted with deionized water with a ratio of 10:1 (water/latex). After 48 h, the water contact angle of the films which were prepared on a glass, was attained using the sessile drop method with a goniometer (Static model, Adecco, Iran). The viscosity of the final copolymer latexes was determined with using a digital rotational viscometer (Brookfield, Model DV-III, USA) with spindle number 62 and rpm 30, at a temperature of 27 °C. To investigate the crosslink density of the synthesized latexes, a 200 µm thickness film of the latexes was coated on a polyethylene sheet. About 0.4 g of the dried films were placed in 50 mL of ethyl methyl ketone. After 48 h the samples were filtered and dried at a temperature of 60 °C for 2 h, and the crosslink density of the latexes was calculated gravimetrically [23].

Results and discussion

Chemical structure characterization

The molecular structure of HO-PDMS-OH and M-PDMS-M were characterized using FTIR spectrums (Fig. 2). The IR spectra of HO-PDMS-OH showed strong peaks at about 1261 cm^{-1} and 799 cm^{-1} which is related to the deformation of the $-\text{CH}_3$ group (in $\text{Si}-\text{CH}_3$) and $\text{Si}-\text{C}$ vibration, respectively. Wide and strong absorptions at about 1097 cm^{-1} and 1019 cm^{-1} belong to asymmetric and symmetric stretching of $\text{Si}-\text{O}-\text{Si}$ in the siloxane chain. Due to the strong electron donation of the siloxane chain and the reduction of $\text{O}-\text{H}$ bond polarity, the absorption of the hydroxyl group is very weak at about $3700-3600\text{ cm}^{-1}$ [24]. The appearance of a strong broad band at about $3600-3000\text{ cm}^{-1}$ ($-\text{OH}$ group), strong absorptions in 1705 , 1667 , and 1572 cm^{-1} (carbonyl groups), appeared peak at 1432 cm^{-1} which is attributed to $\text{C}=\text{C}$ vibration, and the weak absorption at 3050 cm^{-1} which is assigned for $\text{H}-\text{C}=\text{C}$ bond stretching, validate the structure of M-PDMS-M. A comparison of HO-PDMS-OH and M-PDMS-M spectrums confirms the

successful synthesis of the crosslinker. It is worth mentioning that a relatively great shift of $\text{C}=\text{O}$ absorption (at 1572 cm^{-1}) can be explained by a synergic effect of the siloxane chain and $\text{C}=\text{C}$ bond that weakens the carbonyl bond. The ATR-FTIR spectrums of the basic copolymer and the crosslinked polymer are shown in Fig. 3(a), (b) respectively. Extremely strong and wide band at about $3700-2800\text{ cm}^{-1}$ which is related to the acidic $-\text{OH}$ group, deformation of $\text{C}-\text{O}$ peak at about 1133 cm^{-1} due to overlapping with $\text{Si}-\text{O}-\text{Si}$ vibrations and appeared peak at 1636 cm^{-1} which can be assigned for $\text{C}=\text{O}$ group in the M-PDMS-M structure are evidence to the incorporation of the crosslinker in the copolymer structure. The structure of crosslinked copolymer is presented in Fig. 4.

Particle size and viscosity

The use of cross-linking agents significantly reduced the viscosity of the resulting latexes. The addition of the crosslinker, however, affects the average particle size of the obtained latex to higher values (from 165 to 207 nm). The surfactant-like structure of M-PDMS-M causes its migration

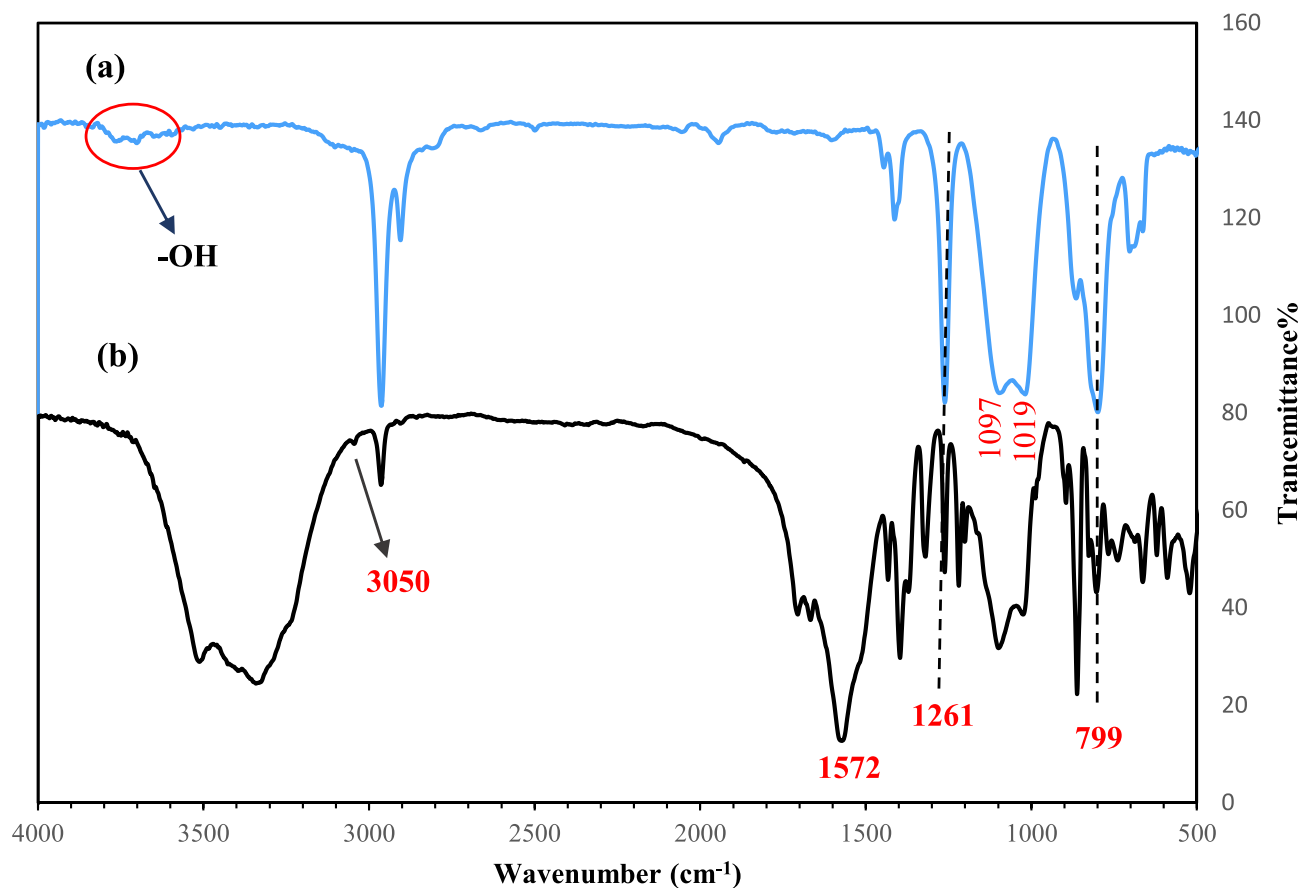


Fig. 2 FTIR spectra of a HO-PDMS-OH and b M-PDMS-M

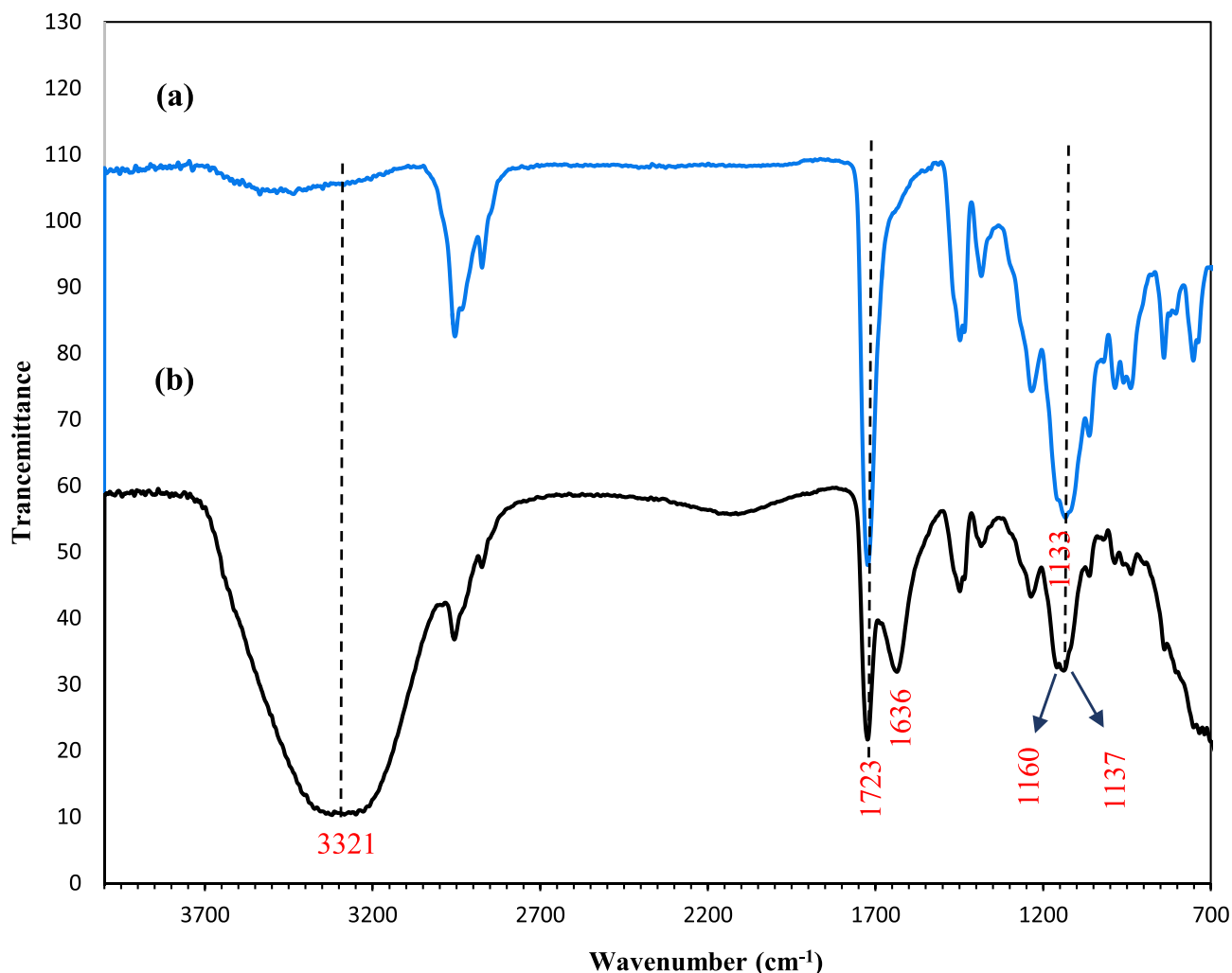


Fig. 3 ATR-FTIR spectra of **a** MMA-BA copolymer and **b** crosslinked MMA-BA copolymer

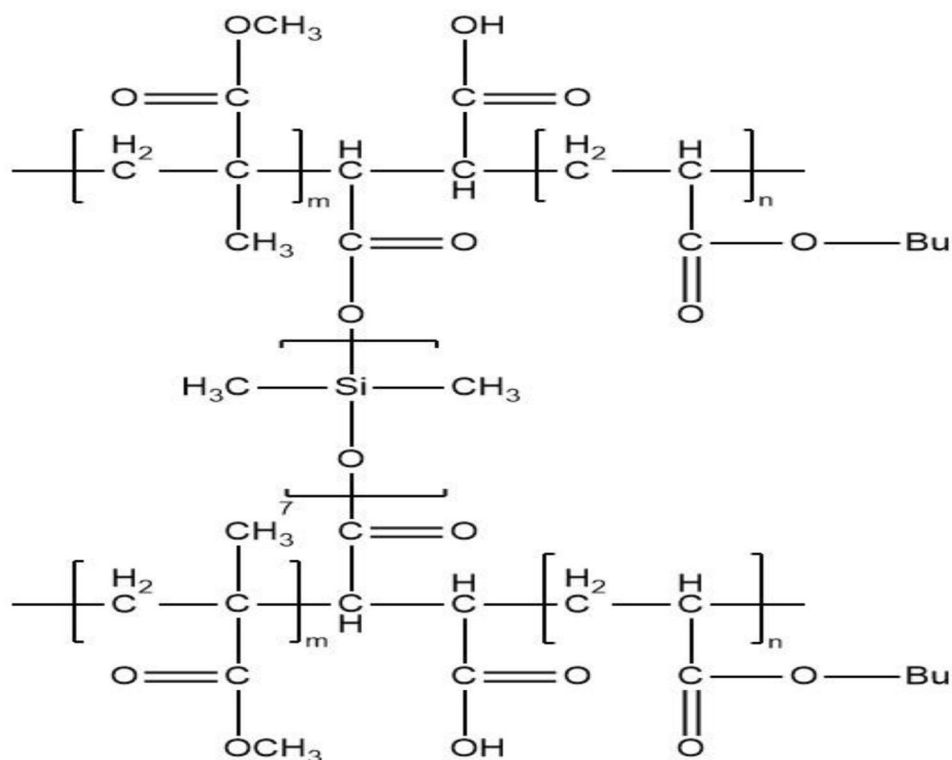
to surface of the latex particles and can lead to the inter-particle polymerization via its two $-C=C-$ bonds, which results in particle aggregation and an increase in particle size (Fig. 5). Furthermore, the long chain of the crosslinking agent can be considered as the reason for the increase in the size of the latex particles. It seems that the main reason for the decrease in the viscosity is the increase in the average size of the crosslinked latexes (Fig. 6). As the average size of the latex particles increases, total surface area and efficient interactions between particles decrease and consequently lead to a viscosity reduction [25]. The colloidal properties of the latexes are presented in Table 2.

Colloidal stability

Zeta potential has an important role in the characterization of electrophoretic stability of solid-liquid dispersions. The higher absolute numerical value of zeta potential and

particle mobility indicate the greater electrostatic stability of latex against coagulation [26, 27]. To evaluate the influence of the crosslinker on the colloidal stability of the latexes, zeta potential and average mobility of the latex particles were measured (Table 2). The results indicate that when the crosslinker was added in the first half of the monomers injection time, absolute value of average zeta potential (from -31.7 mV to -49.5 mV) and particle mobility (from -2.4 $\mu\text{m/s/V/cm}$ to -3.8 $\mu\text{m/s/V/cm}$) and subsequently colloidal stability of the latexes were increased significantly, however, when the addition was done in the second half of the polymerization time, both the absolute values of average zeta potential and the particle mobility decreased slightly (zeta potential from -31.7 mV to -25.3 mV and mobility from -2.4 $\mu\text{m/s/V/cm}$ to -1.8 $\mu\text{m/s/V/cm}$). According to the Smoluchowski equation (Eq. 1), the zeta potential (ζ) of a colloidal dispersion and its particle mobility (μ) have an inverse relationship

Fig. 4 Structure of crosslinked MMA-BA copolymer



with the viscosity (η) of the dispersion. In this equation, ϵ_r and ϵ_0 are the relative permittivity of electrolyte solution and the permittivity of vacuum, respectively [28]. Therefore, the drastic decrease in viscosity in the presence of the cross-linking agent can be considered as the reason for the significant increase in zeta potential and the consequent more stability of the latexes.

$$\mu = \frac{\epsilon_r \epsilon_0 \zeta}{\eta} \quad (1)$$

The addition of M-PDMS-M in the second half of the monomer feeding causes the functional groups at both ends of the chain to appear on the surface of the latex particles. The presence of these functional groups has probably

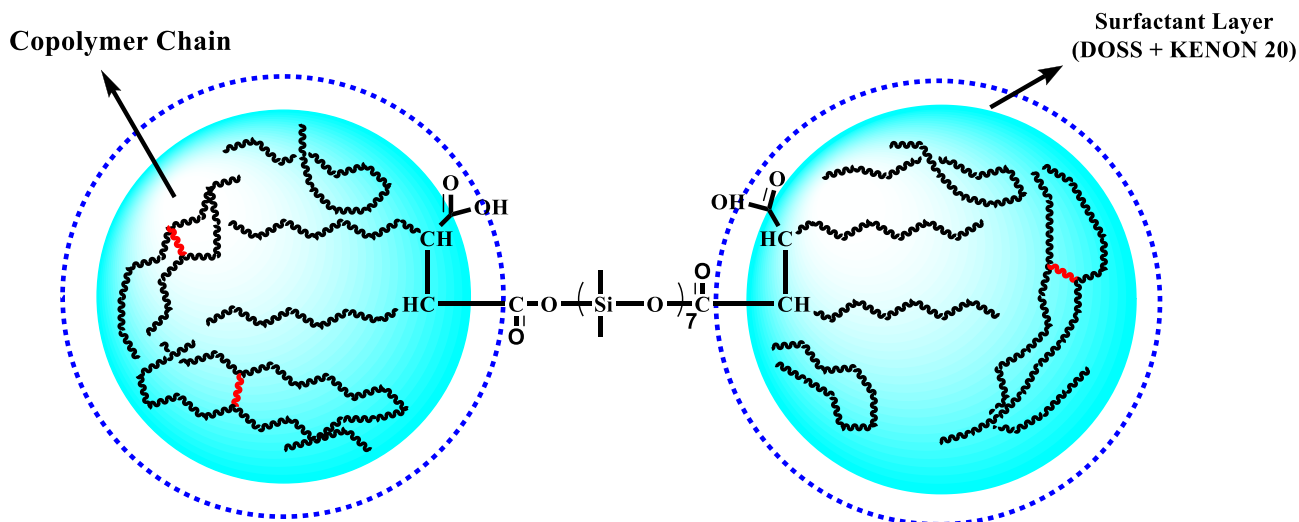


Fig. 5 A model of inter-particle crosslinking

Fig. 6 Effect of the crosslinker concentration on the viscosity of latexes and average particle size

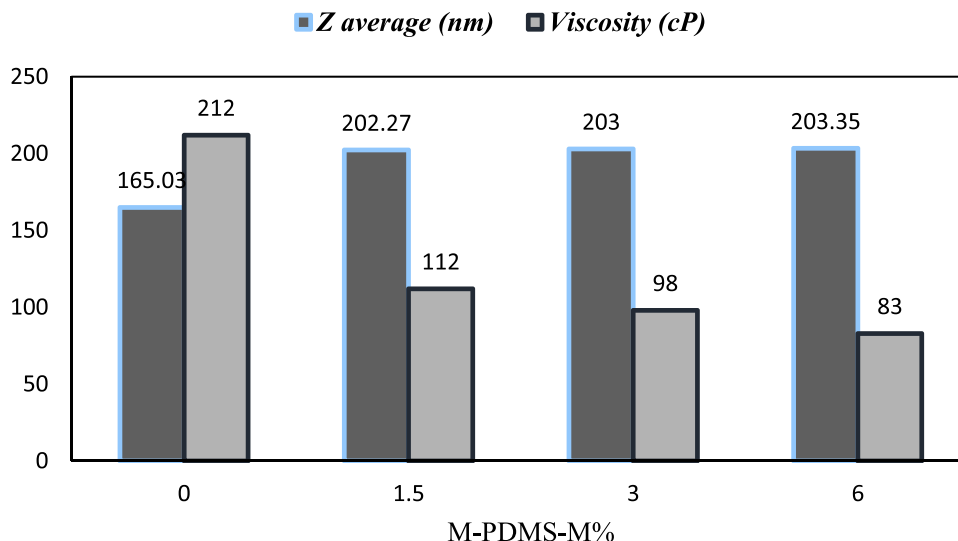


Table 2 Colloidal properties of the latexes

Product code	M-PDMS-M%	Crosslink density (%)	Zeta potential (mV)	Average particle mobility (μm/s/V/cm)	Z average (nm)	Polydispersity index (PDI)
S ₀	0	6.9	-31.7	-2.4	165.03	0.34
^a S _{1.5}	1.5	48.5	-44.9	-3.4	202.27	0.37
S' _{1.5}	1.5	29.9	-25.3	-1.8	207.33	0.33
S ₃	3	59.7	-46.3	-3.5	203.00	0.34
S ₆	6	60.1	-49.5	-3.8	203.35	0.32

^a In S_{1.5}, S₃, and S₆ samples, crosslinker was added in the first half time, and in S'_{1.5} it was fed in the second half time of monomers feeding period

strengthened the attraction forces between the particles and reduced the zeta potential and mobility of the particles. It should be noted that all measurements were conducted at pH = 8.

Thermogravimetry analysis

Thermal stability of the copolymers in the temperature range of 25–800 °C with a scanning rate of 10 °C. min⁻¹ were studied (Table 3; Fig. 7). According to the S₀ sample (base

copolymer) thermogram, the main loss of weight starts from temperature of around 370 °C and up to 420 °C at which the polymer has lost about 95% of its weight. The initial weight loss in this temperature range can be related to the scission of possible weak head-to-head linkage in the polymer structure and, with a further increase in temperature degradation of the copolymer chain occurs. The final decomposition can be attributed to random failure of the polymer chains [29]. Compared to the base copolymer, thermal stability of crosslinked copolymers was improved significantly (from 353 to 406 °C), and the highest thermal stability was found for the s'_{1.5} sample (Table 3). The initial, midpoint and the final degradation temperature of this sample, compared to the base polymer sample, was about 53 °C, 44 °C and 40 °C higher, respectively. The residue at 800 °C was increased from 0.52 w% for the base polymer to 12.41 w% for the s'_{1.5} sample.

Table 3 Thermal characteristics of the copolymer samples

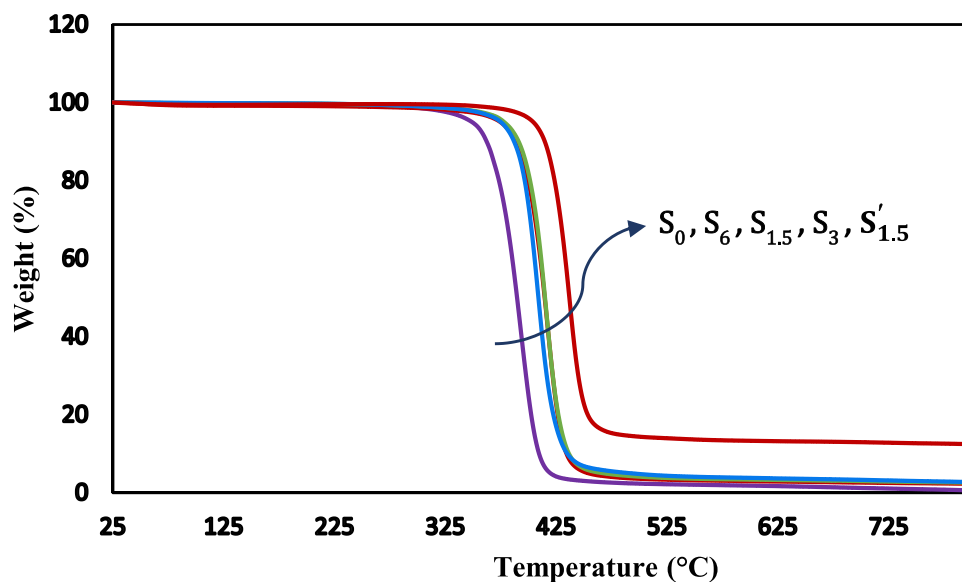
Product code	T _i (°C)	T _M (°C)	T _f (°C)	Remaining mass at 800 °C (w%)
S ₀	353.0	394.0	455.0	0.52
S _{1.5}	378.0	418.0	478.0	2.28
S ₃	380.0	418.0	481.0	2.54
S ₆	378.5	410.0	475.0	2.68
S' _{1.5}	406.0	438.0	495.0	12.41

T_i Initial degradation temperature, T_M Maximum degradation temperature, T_f Final temperature

Morphological study

TEM micrographs of the blank copolymer (S₀) and the crosslinked polymers (S_{1.5}-S₆) clearly illustrate the differences between the size and contrast of the latex particles (Fig. 8). The darker color of the particles indicates a compression of

Fig. 7 TGA curves of the copolymers (see Table 3). Curves $S_{1.5}$ and S_6 overlap



the polymer chains as a result of crosslinking. All the latex particles have a relatively regular spherical shape.

AFM is a powerful technique for studying high resolution images of polymer surfaces [30] which was used to obtain both two-dimensional and three-dimensional images of the latex surface. The boundary of particles was gradually eliminated, and the roughness of the latex surface was reduced by the participation of the crosslinker in the copolymer structure (Figs. 9 and 10). With increasing the concentration of the M-PDMS-M, the latex surface has become smoother and more uniform.

Investigation of FE-SEM micrographs revealed that in the copolymers containing cross-linking agent, especially $S_{1.5}$ and $s'_{1.5}$ (Fig. 11), the shape of the particles is more regular, and their surface is more smoothed. In samples S_3 and S_6 , due to the high percentage of the crosslinker used, it seems that the latex particles are connected, and chemical bonds have been formed between them.

Water contact angle

In the structure of the cross-linking agent there are both hydrophobic groups (the siloxane chain) and hydrophilic groups (the acidic and the ester functional groups at both ends of its chain), which have opposite effects on the water contact angle. It was found that the end polar groups had a greater effect on the contact angle than the siloxane part. Therefore, with an increase in concentration of the crosslinker in the structure of MMA-BA latexes, the contact angle of the obtained films with water decreased (Fig. 12). The reason for this can be related to the formation of hydrogen bonds between acidic and ester functional groups (in structure of the crosslinker) and water molecules. The contact angle obtained for the $s'_{1.5}$ sample was equal to 42.5 degrees, which was much less than the expected value due to the presence of the functional groups on the surface of the latex particles.

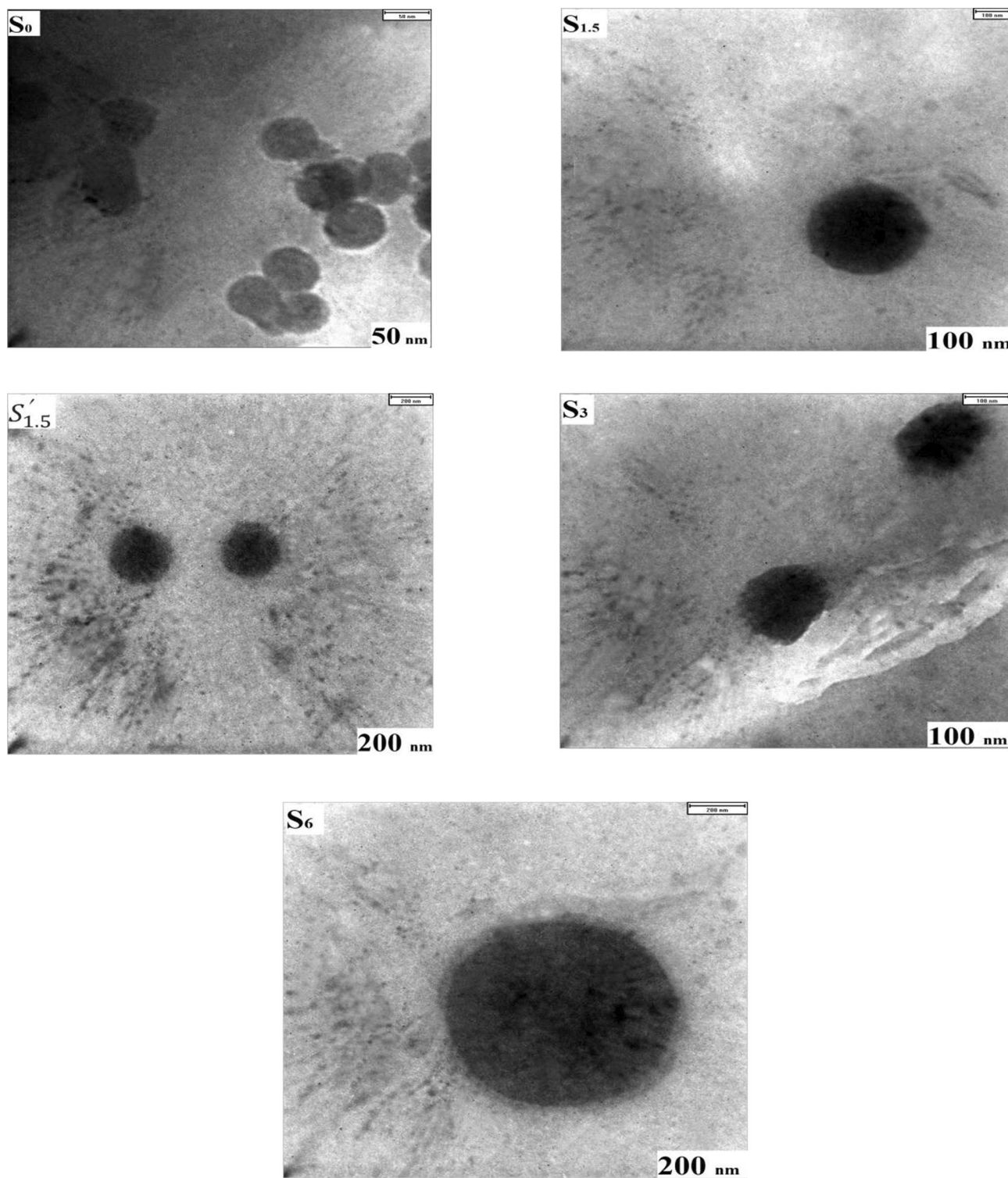


Fig. 8 TEM micrographs of the latexes

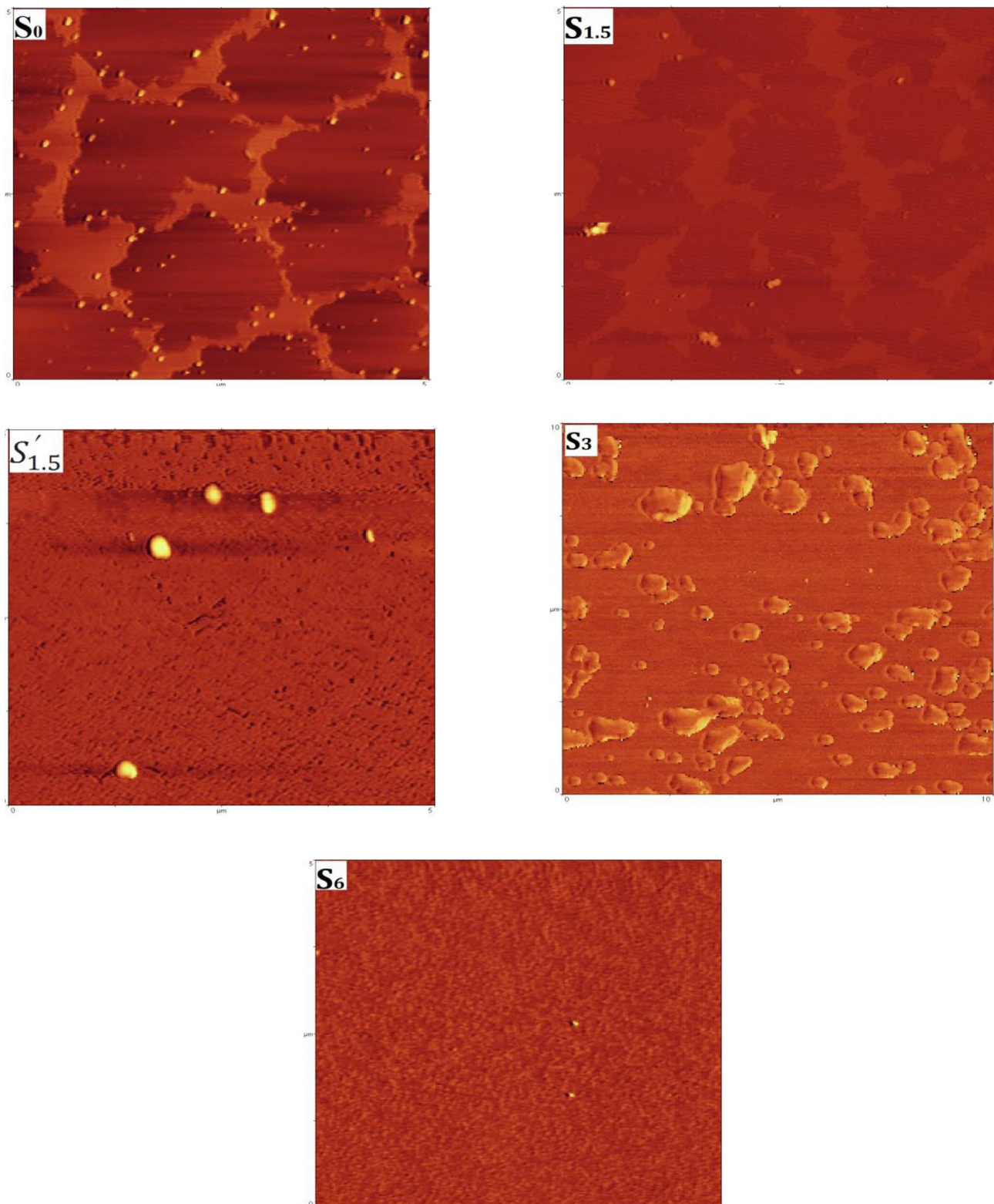


Fig. 9 AFM 2-dimensional photographs of the latexes

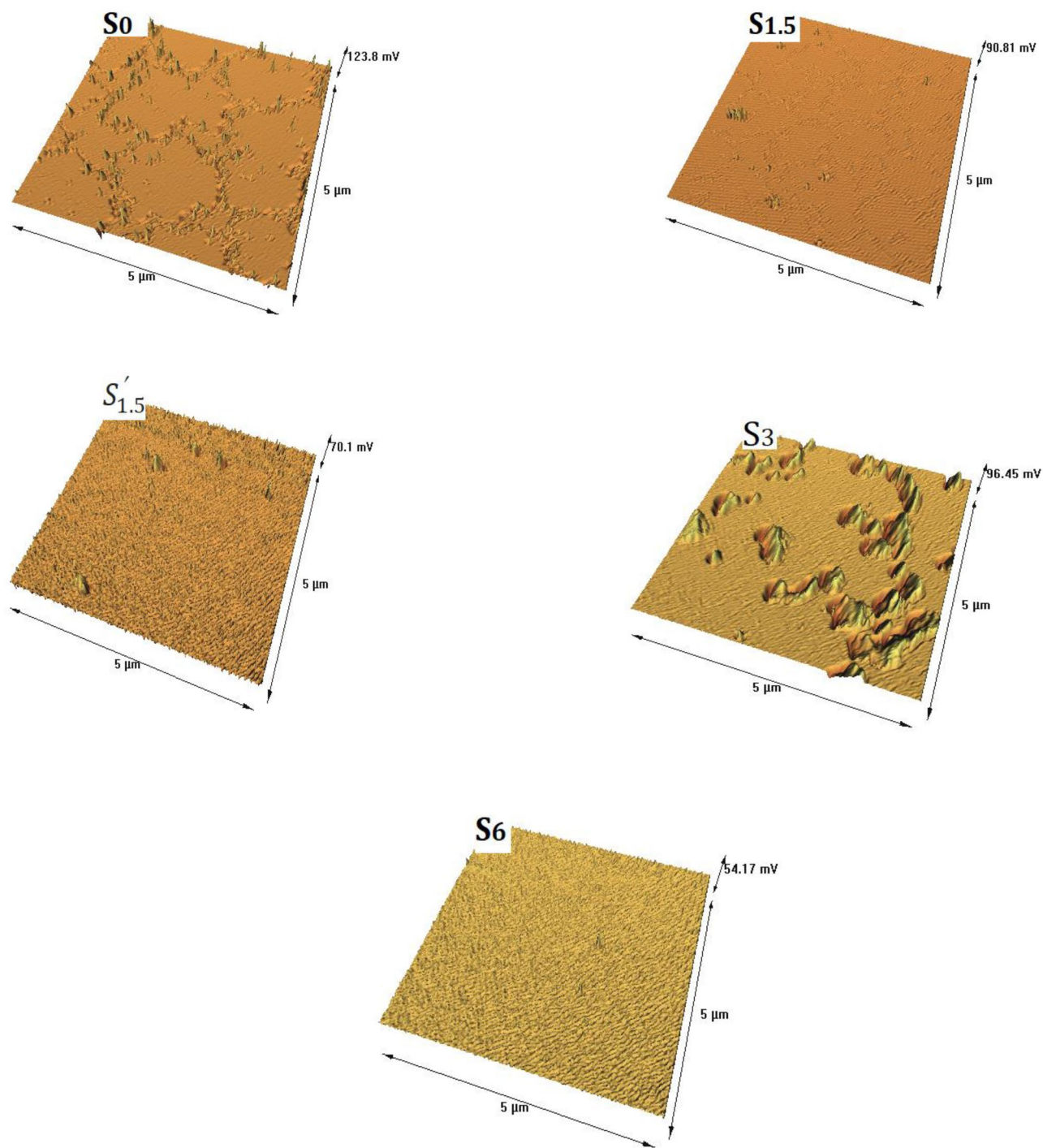


Fig. 10 AFM 3-dimensional photographs of the latexes

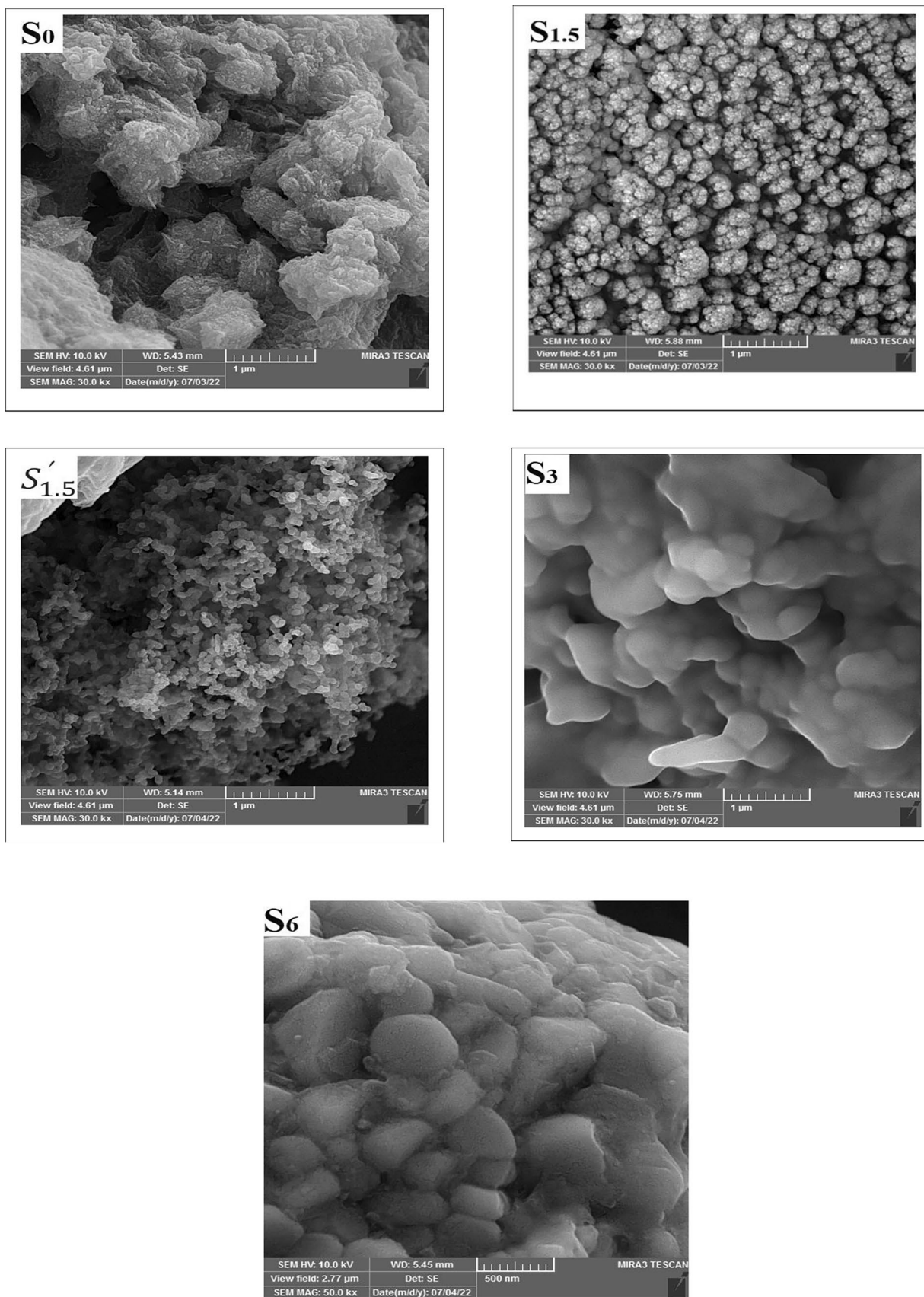
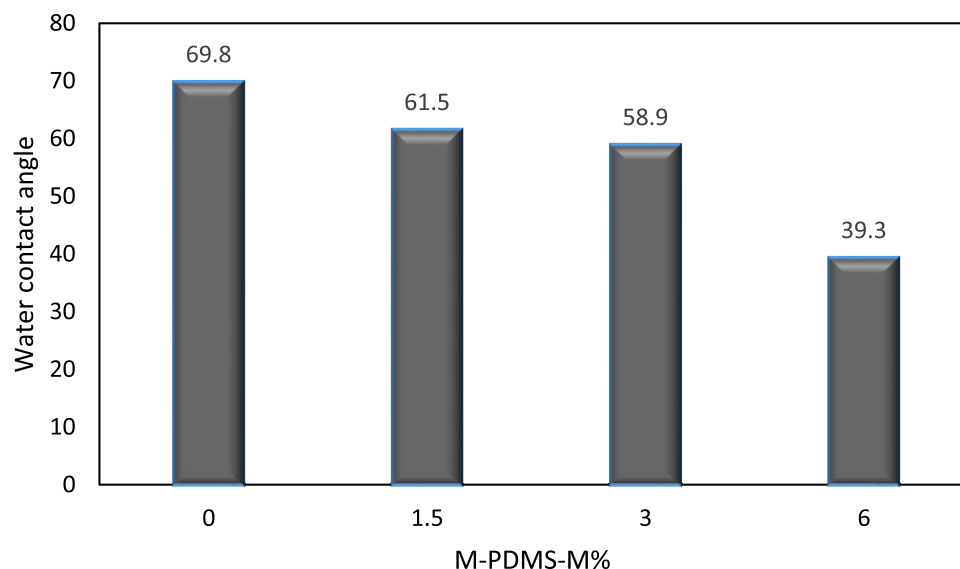


Fig. 11 FE-SEM photographs of the latexes

Fig. 12 Water contact angle of the copolymer films

Conclusion

A novel siloxane-based crosslinking agent was synthesized and used in an emulsion polymerization of MMA/BA. Incorporation of the crosslinker in the polymer structure improved many properties of the obtained copolymers. Crosslinking of the polymer chains led to an increase in particle size (from 165 to 207 nm) and decreased viscosity of the latexes (from 212 cP to 83 cP). Electrostatic stability of the latexes was improved dramatically (zeta potential from -31.7 mV to -49.5 mV), and thermal stability of the copolymers enhanced significantly (initial degradation temperature from 353 to 406 °C). TEM, SEM, and AFM photographs showed an improvement in uniformity of the latex particles and the smoothness of their surfaces. The water contact angle of the polymer was meaningfully decreased by using the crosslinker in the reaction.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10965-023-03807-2>.

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Author contributions We certify that the submission is not under review at any other publications and the figures and tables in the manuscript are the original work of the authors.

Declarations

Conflict of interest The authors declare no conflict of interest.

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