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Effect of functional monomer GMA on the physical–mechanical properties of coatings from poly(BA–MMA) latexes

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Abstract Functional acrylic latexes based on the terpolymer of butyl acrylate (BA)–methyl methacrylate (MMA)–glycidyl methacrylate (GMA) were prepared with different amounts of GMA via semi-batch emulsion polymerization at 75 °C, using potassium persulfate as an initiator, sodium dodecylbenzene sulfonate as an emulsifier and sodium bicarbonate as a buffer. The latexes were characterized by laser light scattering, apparent viscosity, and proton magnetic resonance (^{1}H NMR) and Fourier transform infrared (FTIR) spectroscopies. Physical and mechanical properties of cured and uncured latex films were investigated. For uncured films, gel content, solvent resistance, flexibility, and adhesion of uncured films were improved using higher GMA in the feed, while the glass transition temperature (T_g), surface hydrophobicity, water resistance, tensile modulus and strength, and hardness were decreased. For cured films, higher T_g values, more gel content, improved water and solvent resistances, and enhanced hardness and adhesion, were obtained with increasing the GMA contents. Curing the latex films resulted in hydrophilic surfaces.

Introduction

In spite of using solvent-based coatings for many years, their application is limited by environmental problems associated with organic solvents (i.e., volatile organic compounds, VOCs). Latex technology is one of the successful approaches to eliminate VOCs in coatings. These types of coatings have several advantages over solvent-based coatings such as inexpensive, low odor, environmental-friendly, and fast drying [1], but suffer from lack of chemical resistance and mechanical properties. Recently, researchers have concluded that cross-linkable latexes can afford a performance similar to solvent-borne thermosetting systems [2].

For cross-linking reaction, it needs reactive functional groups, either at the surface or inside the latex particles. Frequent functional groups consist of carboxyl [3], hydroxyl [4], silane [5], amine and enamine [6], acetoacetoxy [7], melamine and aldehyde [8], isocyanate [9], and epoxy [10–16] groups. Monomers such as glycidyl acrylate (GA) and glycidyl methacrylate (GMA) can introduce epoxy groups to the latex particles.

The latex containing epoxy groups is an important and useful class of functional polymers due to the ability of the oxirane ring to react with large number of functional groups (e.g., carboxylic acid and their ammonium salt, hydroxyl, and amines) [2, 17, 18]. The reaction of oxirane ring with various nucleophiles is an opportunity for chemical modification of the base polymer [19–21].

The reaction of epoxy group with amines takes place at ambient temperature [22]. When a diamine is added to epoxy-functionalized latex in the dispersed state, the reaction begins as soon as the diamine can diffuse to reach the epoxy groups of polymer particles [18].

Latex containing GMA (co)polymers present various industrial applications (Table 1). In coatings, the epoxy groups can act as cross-linking sites and improves the mechanical properties, adhesion to the substrate and chemical resistance, as well as the abrasion resistance and general durability [18, 23, 24].

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Table 1 Representative applications of GMA-contained functional latexes

Application	References
Water-borne coatings	[1, 13, 14, 16, 18, 24, 25]
Adhesives (e.g., pressure sensitive adhesives and leather adhesives)	[10, 26, 27]
Biomaterials	[11, 28, 29]
Stationary phase for chromatography and extraction	[12, 30, 31]
Blending compatibilizer	[32, 33]
Surface modification	[29, 34, 35]
Properties modifier for other resins (i.e., melamine–formaldehyde and urea–formaldehyde resins, epoxy resins, and unsaturated polyester resins)	[13, 14, 16]

Fan et al. [13, 16] prepared latex with core–shell structure using methyl methacrylate (MMA) and butyl acrylate (BA) as core and 2-ethylhexyl acrylate (2EHA) and GMA as shell. They cured the latex by a water-soluble urea formaldehyde resin to improve the glass transition temperature (T_g), mechanical strength, and hydrophilicity.

Winnik and co-workers [1, 18] fully investigated the polymer diffusion and cross-linking rates during film formation of poly(BA–MMA–GMA) latexes. They found out even at the absence of a cross-linker, gel formation was occurred as soon as films were formed. This is comparable with the observations in our previous works [36–38]. Wu et al. [15] investigated the effect of GMA on the stability of core–shell latex consisted of BA as core and MMA/GMA mixture as shell. GMA improved the latex stability when its content in the latex exceeded 2%.

Gosh and Krishnamurti [27] developed water-borne cross-linkable pressure sensitive adhesives based of BA–GMA and 2EHA–GMA copolymers (with a maximum GMA of 5%) and investigated the swelling behavior and peel strength of prepared latexes before and after curing. Recently, Choudhary and coworker [10] also developed a latex based BA–MMA–GMA copolymer via seeded emulsion polymerization and studied its application as a pressure sensitive adhesive without curing of the epoxy groups.

According to our best literature survey, no study has investigated the effect of epoxy content and its curing on the physical and mechanical properties of epoxy-functional latex coatings. Therefore, we decided to prepare epoxy-functional latexes using GMA as the functional monomer to use for coating.

In this work, poly(BA–MMA–GMA) latexes prepared by semi-batch emulsion polymerization which carried out in three stages: seed stage, feed stage, and steady stage. The recipe used via these stages was previously optimized to reach furthermost monomer conversion [36]. Latex consisted of BA–MMA (40–60), which is a common formulation in commercial latexes, was preferred as the reference formulation. In the next formulations some portions of MMA in the feed was replaced with GMA to investigate the effect of GMA contents and cross-linking via epoxy groups aminolysis on the physical and mechanical properties of latexes and their coatings.

Experimental

Materials

Monomers butyl acrylate (BA, Fluka), methyl methacrylate (MMA, Merck), and glycidyl methacrylate (GMA, Merck) were used without purification. Potassium persulfate (KPS, Merck) as initiator and sodium dodecylbenzene sulfonate (SDBS, reagent grade, Merck) as emulsifier were used as received. Distilled water (DW) was employed as the continuous media. 1,4-Butylene diamine (BDA, Merck) was used as curing agent. Acetone and tetrahydrofuran (THF) as solvent and methanol as non-solvent (all from Merck) were employed.

Polymerization

Semi-batch emulsion polymerization were carried out at 75 ± 1 °C in a 500-mL 4-necked laboratory glass reactor fitted with a reflux condenser, 3-bladed stainless steel impeller stirrer, nitrogen inlet, and feeding tube. The recipes for preparing latexes are given in Table 2.

An initial charge of monomers (20% of total monomers), water, emulsifier (SDBS), and buffer (sodium bicarbonate) were added to the reactor. The reactor contents were brought to the 75 °C and purged with nitrogen for 30 min to remove any dissolved oxygen prior to the start of reaction. Then initiator, dissolved in 2.5 mL distilled water, was added to the reactor. After 1 h (seed stage), the rest of monomer (as a previously emulsified mixture) with a certain feeding rate of 64.2–65.2 mL/h was added to the reactor via a metering pump (feed stage). The reaction system was then maintained at the fixed bath temperature for 1 h to reach furthermost monomer conversion (steady stage).

Table 2 Recipes for preparing the poly(BA–MMA–GMA) latexes and their characteristics

Sample code	BA (wt%)	MMA (wt%)	GMA (wt%)	Conversion (%)	Particle size (nm)	PDI	Viscosity (cP)
S1	40	60	0	95.0	131.8	0.280	37
S2	40	50	10	95.6	153.9	0.262	38
S3	40	40	20	96.1	171.8	0.252	38
S4	40	30	30	96.0	211.7	0.261	37

Bath temperature 75 ± 1 °C. Initial charge (1 h): water 87.5 g, sum of monomers 28.0 g, SDBS 0.840 g, $NaHCO_3$ 0.700 g, KPS 0.263 g. Charge of feed stage (3 h): water 73.5 g, sum of monomers 114.0 g, SDBS 4.288 g

Characterization

Monomer conversion was determined gravimetrically [36]. The particle size distribution (PSD) was measured by a laser light scattering (LLS) system (Sematech, model SEM-633). Apparent viscosity was determined by a rotational viscometer (Selecta, model Visco Star R, Spain) with spindle R1 at 200 rpm.

The ^{1}H NMR spectrum was recorded by a 400 MHz FT-NMR spectrometer (Bruker Instruments, model Advance 400, Germany) at room temperature using $CDCl_3$ as a solvent and TMS as an internal standard. Infrared spectrum was obtained on a FT-IR spectrometer (Bruker Instruments, model Aquinox 55, Germany) in the 4000–400 cm^{-1} range at a resolution of 0.5 cm^{-1}. Sample's pellet prepared with KBr (FT-IR grade, Fluka).

Glass transition temperature (T_g) was determined using a differential scanning calorimeter (DSC, Netzach, model 200F-3 Maia, Germany). Samples were purified and cut into small pieces (~20 mg) and put into aluminum vessels. Sample vessels were initially heated from 20 to 110 °C at a heat rate of 10 °C/min under nitrogen atmosphere then cooled to −40 °C and again heated to 450 °C at a heat rate of 10.0 °C/min. Second scan were reported. The T_g values were estimated as the temperatures at the inflection-point of the change in the base-line. Theoretical T_g is predicted based on the Fox equation (Eq. 1), where w_{BA}, w_{MMA}, and w_{GMA} are weight fractions of monomers in the feed. T_{gBA}, T_{gMMA}, and T_{gGMA} are the glass transition temperatures for poly(BA) (−54 °C), poly(MMA) (105 °C), and poly (GMA) (94 °C), respectively.

$$\frac{1}{T_g} = \frac{w_{BA}}{T_{gBA}} + \frac{w_{MMA}}{T_{gMMA}} + \frac{w_{GMA}}{T_{gGMA}} \tag{1}$$

Latex films were prepared by casting on glass and aluminum sheets by thickness of about 300 μm. The surface of aluminum sheets was pre-treated by acetone washing, keeping in NaOH solution (1.0 M) for 1 h, washing with HCl (0.1 M) and finally washing with distilled water just before the film casting. Free stand films of the latexes (with thickness of 2 mm) were also prepared by casting on a poly(tetrafluoroethylene) mold. Latexes were cured by addition of 1,4-butylene diamine as curing agent just before film formation. For ensuring of full curing of latexes, curing agent was added with 1.33 mol ratio (4/3) of amine to epoxy. Additionally, for studding the effect of partially curing of the films, sample S4 was also cured with 0.67 molar ratio (2/3) of amine to epoxy in the latex. In the continue, uncured films are called as the same the corresponding latex codes (S1, S2, S3, S4) and cured films called based on their latex and amine/epoxy molar ratio used for the curing. For example, S2-Cured4/3 means films prepared from latex S2 which cured with amine/epoxy ratio of 4/3 (1.33).

Gel content of the prepared polymers was determined by using THF as an extraction solvent according to Eq. 2. Briefly, weighed samples (W_1, ~1 g) were immersed in 100 mL of THF under stirring at 25 °C for 3 days. For a complete extraction, fresh THF was replaced every day. Finally, the extracted samples were removed, dried, and weighed (W_2).

$$\text{Gel content} = \frac{W_2}{W_1} \times 100 \tag{2}$$

The absorption ratio (swelling ratio) of polymers in water and THF was also measured according to Eq. 3.

$$\text{Absorption ratio} = \frac{W_{swollen} - W_{initial}}{W_{initial}} \times 100 \tag{3}$$

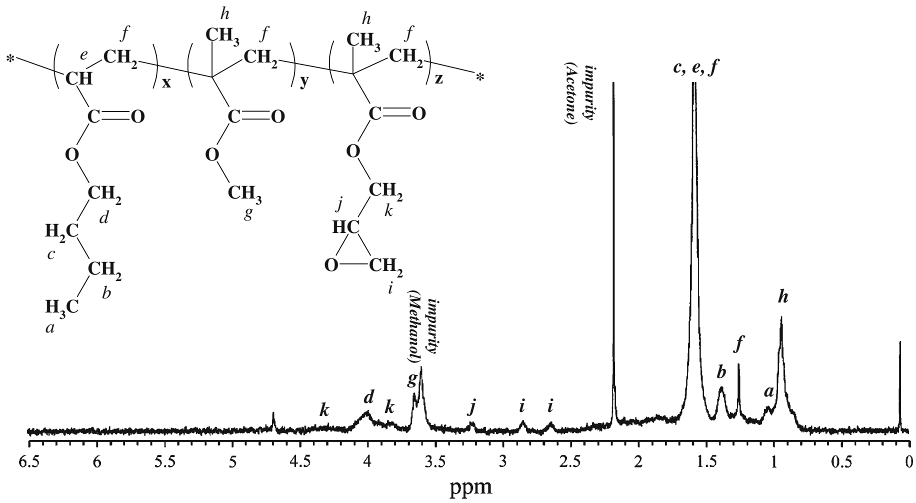
where $W_{initial}$ is initial weight of film sample and $W_{swollen}$ is weight of sample after swelling in solvent for 72 h.

Tensile properties of free films were investigated by a universal test machine (MTS, model 10/M, USA). Hardness of latex films was achieved by a pendulum hardness tester (Elcometer, model 3034, England) on könig mode. Pull off adhesion of films on the treated aluminum substrate was also attained by a pull off adhesion tester (Erichsen testing equipments, model 525, USA).

Results and discussion

Poly(BA–MMA–GMA) latexes was prepared and the effects of GMA contribution on the physical and mechanical properties of latexes and their uncured and cured films were investigated.

Fig. 1 ^{1}H NMR spectrum of sample S3 (BA–MMA–GMA of 40–40–20) dissolved in $CDCl_3$



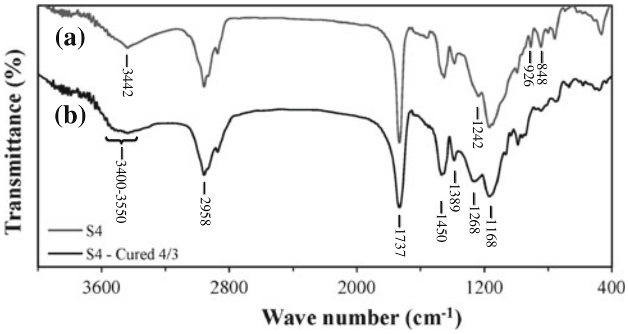


Fig. 2 Representative FTIR spectrums for (*a*) sample S4 and (*b*) sample S4-Cured 4/3

^{1}H NMR spectroscopy was used to study the molecular structure of prepared terpolymers. In Fig. 1, ^{1}H NMR spectrum of sample S3 (BA–MMA–GMA of 40–40–20) is typically shown. Chemical structure of prepared terpolymer is represented and all recorded peaks were indicated in the structure.

FTIR spectroscopy employed to investigate the curing reaction during film forming. Two FTIR spectra are given for sample S4 having BA–MMA–GMA of 40–30–30 before and after curing (Fig. 2). According to Fig. 2, epoxy group peaks (1242, 926, and 848 cm^{-1}) that are obvious for uncured sample (Fig. 2a, sample S4) are disappeared after curing (Fig. 2b, sample S4-Cured4/3). The peak at about 3440 cm^{-1} in Fig. 2a belongs to O–H bond produced via partially hydrolysis of GMA epoxy group during emulsion polymerization. Increasing of this peak in Fig. 2b (3400–3550 cm^{-1}) is due to producing of O–H and N–H bonds after curing. In addition, the peak at 1268 cm^{-1} is attributed to C–N bond appeared after curing (Fig. 2b).

The strong peaks appeared at 1737 and 1168 cm^{-1} are due to stretching vibration of C=O and C–O bonds, respectively. The bands of the aliphatic C–H stretching (at 2958 cm^{-1}) and C–H bending (at 1389 and 1450 cm^{-1}) are also observed in the spectra.

Latex characterization

Characteristics of prepared latexes are given in Table 2. As mentioned before, MMA contribution was partially replaced with GMA for samples S2–S4 (from 10 to 30%). Monomer conversion for all of polymerizations was higher than 95%. Particle size properties of latexes obtained from LLS data are available in Table 2. Higher mean diameter of polymer particles was resulted by increasing the GMA content in the feed, while particle size polydispersity (PSDI) remained invariable. The reason of increasing of particle size is attributed to adhesion and aggregation of polymer particles because of partially water-solubility of GMA. This is fully discoursed in our previous work [36].

Apparent viscosity of prepared latexes was also measured and recognized to be independent from monomers composition (Table 2). Fundamentally, for latexes with solid content lower than 60% (like our latexes with solid content of 49%), the apparent viscosity was near to that of the solvent, water [39].

Physical properties of the latex films

Physical properties of prepared films are given in Table 3. Theoretical values of T_g were calculated based on the Fox equation (Eq. 1) [40] and experimental values obtained from DSC. Interestingly, experimental T_g values for uncured films are predominantly higher than those we expected theoretically. The high experimental T_g values are due to some partially undesirable cross-linking reactions during emulsion polymerization of GMA and BA. The epoxy groups within the particles can partially be hydrolyzed to form a diol and result in internal cross-linking of

Table 3 Physical properties of films prepared from the poly(BA–MMA–GMA) latexes

Sample code[a]	GMA (wt%)	Theoretical T_g[b] (°C)	Experimental T_g[c] (°C)	Gel content (%)	Contact angle (θ)
S1	0	19.9	43.9	57.4	58
S2	10	19.3	31.7	77.4	45
S3	20	18.6	28.2	82.0	46
S4	30	17.9	26.2	85.4	46
S2-Cured4/3	10	–	46.7	83.8	<10
S3-Cured4/3	20	–	60.5	91.5	<10
S4-Cured4/3	30	–	76.9	93.1	<10
S4-Cured2/3	30	–	78.1	93.6	<10

[a] In the cured samples, the number 4/3 and 2/3 is the amine to epoxy molar ratio

[b] Theoretical T_g is predicted based on Fox equation

[c] Experimental T_g is obtained from DSC analysis

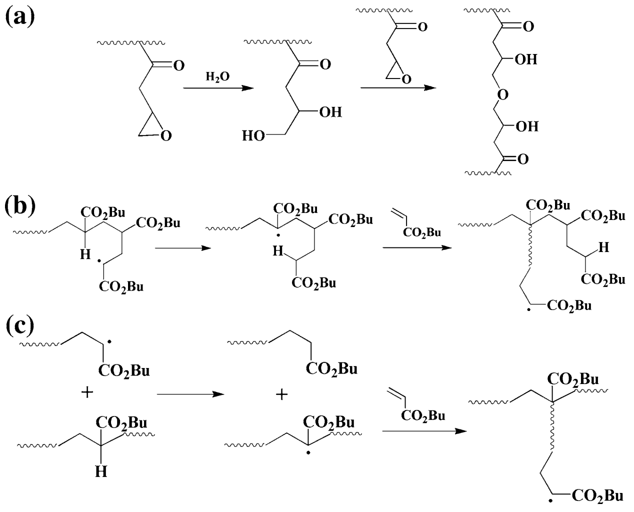


Fig. 3 Important side reactions occurred during the emulsion terpolymerization of BA, MMA, and GMA. Cross-linking reactions via **a** hydrolysis of GMA epoxy groups, **b** intra-molecular, and **c** inter-molecular hydrogen abstraction reaction of BA backbone

the latex particles [24, 25, 41] (Fig. 3a). Geurts et al. [41] mentioned that in butyl methacrylate (BMA)–GMA latex, 32% of epoxy groups hydrolyzed to diol within 1 year at ambient temperature.

The existence of small amount of dimethacrylates (100–200 ppm) in the commercial GMA monomers is confirmed by gas chromatography–mass spectroscopy (GC–MS) [41]. The dimethacrylates can be removed by distillation, but they may be formed again upon storage of monomer or during the polymerization.

The gel is also brought to form via hydrogen abstraction from backbone tertiary C–H bonds which occurs extensively in emulsion polymerizations of BA (Fig. 3b, c) [42–44]. Under starved conditions, a highly branched polymer (branches of 0.9–3.4%) containing 50–60% gel was formed [44].

By partial replacement of MMA with GMA in the feed (samples S2, S3, and S4), a decrease in theoretical and experimental T_g values of uncured films is observed. One reason is lower T_g of GMA homopolymer (94 °C) comparing to that of MMA homopolymer (105 °C). But this cannot be the main reason for the great difference of T_g value of sample S1 and other uncured samples (samples S2–S4). Probably, introducing of bulky GMA epoxy groups as polymer branches and theirs strict hindrance for polymeric backbone and plasticizing effect, caused higher free volume between polymer chains led to higher flexibility [45–47]. Therefore, T_g is higher in the absence of GMA (sample S1).

Curing of latexes during film formation resulted in increase of T_g values comparing to the uncured sample counterparts (Table 3). Cross-linking limits polymer chains mobility, leads to decrease in free volume and increase in T_g [45]. As expected, T_g values are raised with increase GMA content in the feed. This is due to higher cross-linking reactions and network density in the prepared polymeric films and so, lower flexibility of polymer chains [45]. Focusing on T_g values of samples S4-Cured4/3 and S4-Cured2/3, showed that partially cured film (S4-Cured2/3) had a higher T_g than the fully cured film (S4-Cured4/3). The reason is higher concentration of unreacted butylene diamine in sample S4-Cured4/3 (even after purification) which can act as a plasticizer between the polymer chains [48–50].

As observed from Table 3 data, higher GMA in the terpolymer resulted in higher gel content in the uncured films. It can be attributed to partially cross-linking reactions that was mentioned before. Curing reaction during film forming improved the gel content of films as high as 93% for sample S4-Cured4/3. Equal cross-linking density for samples S4-Cured4/3 and S4-Cured2/3 can be concluded from same gel content values. Therefore, amine/epoxy molar ratio of 2/3 (0.67) was adequate for a nearly complete curing. This is due to partially hydrolysis and consuming of epoxy groups during polymerization and is in agreement with the T_g values.

Contact angle can be set in a particular position of surface hydrophobicity. According to the water contact

Table 4 Mechanical properties of films prepared from the poly(BA–MMA–GMA) latexes

Sample code	GMA (wt%)	Water absorption (%)	THF absorption (%)	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Pendulum hardness (s)	Pull off adhesion (N/m^2)
S1	0	13.6	3051.6	497.8	27.5	7.9	95.7	1.05
S2	10	18.3	1097.6	202.7	10.0	175.1	33.6	1.79
S3	20	16.8	906.7	199.1	8.6	183.2	28.5	1.98
S4	30	15.1	616.3	92.8	4.4	276.4	14.8	2.13
S2-Cured4/3	10	3.3	169.7	–	–	–	105.6	3.48
S3-Cured4/3	20	2.7	117.8	–	–	–	144.0	3.92
S4-Cured4/3	30	2.6	65.3	–	–	–	191.4	4.42
S4-Cured2/3	30	3.0	78.4	–	–	–	186.3	4.13

angle (Table 3), GMA addition in samples decreased water contact angle and so the hydrophobicity of the prepared coatings, due to hydrophilic polar epoxy groups in GMA [51, 52]. Film's hydrophobicity was reduced sharply for cured films ($\theta < 10$). This observation is because of producing hydrophilic hydroxyl and amine groups in cured films via aminolysis of epoxy groups.

Mechanical properties of the latex films

For investigating the film resistance against aqueous and organic media, water and THF absorption tests were conducted. According to Table 4, both water and solvent (THF) resistances are improved using higher GMA and cross-linking. Surprisingly, uncured film without GMA (sample S1) had lower water absorption (13.6%) comparing to other uncured films contained GMA. This is due to the GMA polar epoxy groups resulted in moderately hydrophilic surfaces (samples S2–S4). However, among uncured films containing GMA (samples S2–S4), increasing of GMA portion in the feed from 10 to 30% brought about lower water absorption and, therefore, higher water resistance. It is due to more partial cross-linking occurrence. Water resistance was also improved for cured films, although the surface of cured films was hydrophilic. The cross-linking of polymer chains prevented the water to entrance the polymeric bulk and therefore, improved the water resistance. As a remarkable result of our research, incorporation of GMA moiety in the polymer backbone and curing of epoxy groups improved the solvent resistance by decreasing the solvent (THF) absorption from 3051% for sample S1 to 65% for sample S4-Cured4/3.

Tensile analysis was also carried out for the uncured free stand films (Table 4). According to Table 4, tensile modulus and strength were decreased by incorporation of GMA, but elongation at break was improved. Therefore, higher GMA resulted in films with more flexibility but less tensile resistance. These results are in agreement with determined T_g values (Table 3) which decreased with GMA increase.

Hardness values of the prepared latex films on glass sheet are also given in Table 4. For uncured films, a decrease in hardness values was observed by increasing GMA content, but for cured films hardness values improved with higher GMA content. This difference is related to T_g values. Generally, the higher the Tg value, the harder the polymer [53–55]. In this respect, a well-established relation between hardness and glass transition temperature of some polymers has been established [53]. Higher T_g accompanies with higher modulus and pendulum hardness.

Adhesion of the prepared latex films on pretreated aluminum sheet was evaluated by the pull off testing (Table 4). Results showed that the higher GMA content favored the adhesion of the uncured films of samples. Here, hydrogen bonding of GMA's epoxy moieties was the main explanation for bonding of coating to the aluminum substrate. This is the reason for improving the bond strength with the increased GMA content [27]. Another important inspection from pull off test is the type of failure. Adhesion failure type was observed for all of the uncured samples. The adhesion was improved by using higher GMA contents in the cured latexes. As it is obvious from the data (Table 4, pull off values), curing of the latex films led to about 2 times better adhesion. Curing the latex during film formation produced hydroxyl and amine groups in the polymer chains and increased hydrogen bonding and polar interactions between the coating and pretreated aluminum sheet [27]. Both adhesion and cohesion failure types were recorded for the cured samples. It implies that the adhesion forces between films and aluminum sheet was as strong as the cohesion forces in the films. Cohesion failure type was major for samples S4-Cured4/3 and S4-Cured2/3.

Conclusion

Functional latexes of poly(BA–MMA–GMA) with different GMA content were prepared via semi-batch emulsion polymerization. Increasing GMA content in the latexes resulted in higher particle size while particle size polydispersity index and apparent viscosity remained invariable. Uncured, partially cured and fully cured films were prepared to study the effect of GMA content and epoxy group curing on properties of the coating. Higher GMA content in uncured films improved the gel content, solvent resistance, flexibility, and adhesion; whereas T_g, surface hydrophobicity, water resistance, tensile strength, and hardness were reduced. For cured films, higher T_g, gel content, water and solvent resistances, hardness, and adhesion were achieved using higher GMA contents. Curing the latex films led to surfaces with increased hydrophilicity.

Thanks to the particular characteristics of the functional latexes, they can be formulated by incorporation of suitable ingredients such as pigments to prepare developed acrylic surface coatings with improved properties. In addition, the epoxy functionality possesses high potential for partial modification to many other functional groups such as carbonate and urethane groups with promising characteristics.

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