



Synthesis and Characterization of Emulsion Polymerizable Surfactant Based on Ethoxylate Alcohol Maleate

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Abstract

A novel maleate surfmer was synthesized through the esterification of alcohol ethoxylate ethylene oxide propylene oxide (EO/PO) block copolymers with maleic anhydride. The structure of the non-ionic maleate ethoxylate surfmer was confirmed by mass spectrum analysis, the critical micelle concentration (CMC) of the prepared surfmer was found to be 0.0053 mol/l whereas its polymerization reaction order was found to be (1.44) for vinyl acetate (VAc) and (1.3) for butyl acrylate (BuA). The volume average diameter D_v^- of poly (VAc) and poly (BuA) decreases with increasing surfmer concentration; however, the latter shows a slightly bigger particle size under the same conditions. The number of polymer particles (N_t) was found to increase with increasing surfmer concentration. When compared to poly (BuA), poly (VAc) has more defined and spherical particles. Increasing the surfactant concentration from 4.2×10^{-3} to 8.4×10^{-3} (mol/l) reduces the surface charge density of poly(BuA) and poly(VAc) from 115 to 81 and 85 to 36 microcolumb, respectively. Besides, Poly (BuA) shows greater surface charge density and greater stability than poly (VAc) at the same concentration. The obtained results recommend the use of prepared EO/PO maleate surfmer for the development of high-solid lattices of (VAc) homopolymer and poly(VAc/BuA) copolymers for superior adhesion, water resistance, and mechanical stability when compared with similar commercial types of wood adhesive and emulsion paint.

Keywords: Polymerizable surfactant; Maleate surfmer; Surfactant monomers; Emulsion polymerization; CMC and morphology.

1. Introduction

A significant number of studies have been undertaken on emulsion polymerization using surfmers [1-5]. These molecules present the advantage of combining the physical behaviour of surfactants with the reactivity of monomers to achieve the best latex characteristic for several applications. The polymerizable moiety of these surfmers can be permanently reacted with the polymer chain via a covalent bond, limiting their migration to the latex surface or being desorbed from polymer particles [6, 7]. Using surfmer improves the stability, particle size distribution, surface charge density, and surface functionality of latex particles. These latexes are important in various fields such as paints, adhesives [8], paper coatings, inks, textile sizing, and polymer nanocomposites [9-11]. Anionic, cationic, and non-ionic surfactants have been reported to have a wide range of structures that differ for polar functional groups (that is, hydrophilic and lipophilic balance) and

the location of the polymerizable moiety [12-16]. Styrene, acrylic, methacrylic, and acrylamides are examples of traditional polymerizable groups used in the synthesis of surfmers [17].

It has been established that for the surfmer to perform well in the emulsion polymerization process, it must have limited solubility in water, moderate reactivity at the beginning of the process of polymerization to avoid burring the inner polymer particles, and substantial reactivity at the end of polymerization to be anchored onto particle surfaces [18]. Maleic surfactants are the most promising among the described structures because they are easy to prepare and do not enter homopolymerization [1, 19]. The paint industry is a huge consumer of polymer latex formed by emulsion polymerization. The surfactants are essential to the stability of the latex during and after the polymerization reaction, but at the same time, surfactants introduce performance problems in the final coating as they tend to form surfactant clusters in

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drying latex films, which migrate to the polymer-air and polymer-substrate interfaces, causing weak films toward water resistance and adhesion. Moreover, during the storage of the latex, surfactants tend to live in the polymer particles, where they coagulate and finally precipitate. Esteban et al. [8] investigated the water sensitivity of films made from high-solids content acrylic latexes, with a particular emphasis on the role of the surfactant used in the synthesis step. The performance of films obtained from latex stabilized by non-ionic surfmers was compared to that of acrylic latex stabilized with conventional non-ionic and anionic surfactants. Latexes stabilized with reactive surfactants were reported to have significantly better resistance to both water permeability and water vapour permeability, increasing the durability of the films. Atomic force microscopy images suggested that the defects created by surfactant migration in the latexes stabilized with conventional surfactants promoted the permeation of water by capillarity [8]. Previous work [9–13] shows that the type of surfmer (anionic, cationic, or non-ionic) affects the character of produced polymers. Moreover, the hydrophobic and lyophobic backbone structure of the surfmer controls the rate of the reaction, morphology, and stability of the produced lattices. So, the emulsion polymerization must consider the affinity of a certain type of monomer to a specific type and structure of surfmer.

This work aims to synthesize a novel surfactant monomer (Surfmer) to be used in emulsion polymerization. The use of the prepared surfmer enables the fabrication of polymer latex with unique physicochemical characteristics, including improved adhesion and water resistance, and prolonged shelf life.

2. Materials and methods

2.1 Materials

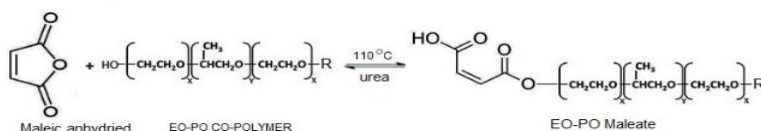
Vinyl acetate (VAc) monomer (stabilized with 14 ppm hydroquinone) was supplied by BDH, and butyl acrylate (BuA) monomer (stabilized with 14 ppm hydroquinone) was provided by Merck-Schuchart, Germany. Both (VAc) and BuA were distilled before use and stored at -20°C . Potassium persulphate (KPS)

initiator, supplied by Labmerk chemicals (India), was recrystallized from water by methanol, and the final crystals were vacuum-dried. Sodium bisulfite (lab grade) is provided by S.D. Fine Chemicals (India). Potassium hydroxide, maleic anhydride, acetone, methanol, and hydroquinone (Quinol) were products of the El-Nasr Pharmaceutical Chemical Company (Adwic), Egypt. The polyethylene oxide-propylene oxide (EO/PO) block copolymer is a non-ionic emulsifier known as TERGITOL surfactant a product of DOW Chemical Company. All the water used was purified by distillation. Calcium carbonate (EJSF) and EJ2 were supplied by Omya Green Egypt. Lomon Billions China provided the titanium dioxide LOMON-996 (rutile type). Dispex N40, an anionic dispersing agent (sodium salt of polymeric carboxylic acid), was supplied by Allied Colloids Limited, England. Antifoam (commercial type) England Commercial Poly (VAc) (EMULTEX 4030) is the product of Synthomer Middle East Company Ltd. Eagle Resins Egypt manufactures commercial poly (VAc) Eagle H (480/50), a non-plasticized poly (VAc).

2.2. Synthesis

2.2.1. Synthesis of the non-ionic EO/PO maleate

In a 250 ml 3 neck flask equipped with a magnetic stirrer, condenser, and thermometer EO/PO maleate surfmer was prepared by the esterification of alcohol ethoxylate ethylene oxide propylene oxide (EO/PO) block copolymer by reacting with maleic anhydride in the presence of urea at the stoichiometric amount of EO-PO block copolymer TERGITOL (EO/PO) alcohol ethoxylate and maleic anhydride at 110°C in 50 min [1]; the stirring rate was adjusted at 200 rpm, hydroquinone (HQ) was added to prevent polymerization of the double bond by the effect of high temperature of esterification [24]. An isotropic solvent, such as xylene, was used to speed up the removal of water from the reaction, which increased yield and reduced reaction time. The products were then washed and dried in a vacuum.



Scheme (1): Schematic diagram representing the synthesis of EO/PO maleate surfmer.

The EO/PO maleate surfmer prepared as shown in Scheme (1) was confirmed using mass spectrometry analysis (Figure 1), and the CMC of the maleate ethoxylate surfmer was higher than that of the conventional surfactant, which was found to be 0.0053 mol/l, which is a normal value conceded to anionic surfactants. However, due to the very high molecular weight and the long chain of the ethoxylate backbone, some foaming characteristics were observed during the titration.

2.2.2. Synthesis of polyvinyl acetate by semi-continuous technique:

In this process, the amount of emulsifier (the prepared surfmer) was dissolved in distilled water and charged into 250-ml three-necked flasks. The monomer and initiator were added separately at a rate of about 20 ml/hr using two separating funnels. The polymerization reaction was carried out at 70 °C for 2 hours using automatic stirring at 200 rpm.

2.2.3. Emulsion polymerization of VAc and BuA monomers using EO/PO maleate surfmer

Acetone sodium bisulfite (ASBS) adduct (as a redox initiator) was prepared by the addition reaction of sodium bisulfite on the carbonyl group of acetone [20, 21]. The emulsion polymerization of VAc and BuA has been carried out in a 250 ml 3 neck flask through batch polymerization technique with different surfmer concentrations of 1.0, 1.5, and 2.0 grams which is equivalent to concentrations 4.2, 6.3, and 8.4 $\times 10^{-3}$ mol/l in presence of redox initiator system KPS/ASBS [6.25×10^{-3}]/[12.5×10^{-3}], respectively. The order of addition was as follows: water, emulsifier, initiator, and either VAc or BuA monomer. The polymerization reactions were carried out at 70°C ($\pm 1^\circ\text{C}$) in an automatically controlled water bath. All the experiments were run with mechanical stirring at 200 rpm; this speed is in the range where the agitation has no noticeable effect on the rate of polymerization.

2.3. Characterization of the prepared surfmer

The critical micelle concentration (CMC) for surfmers was determined by conductivity measurements using a conductivity meter (Janeway 4510). Plotting the relationship between surfmer concentration (mol/l) versus conductivity in (micro-Siemens) of surfmer solution at different temperatures 23°C and 70°C, CMC was determined at the point of significant change in conductivity at a given surfmer concentration. The polymerization technique and a number of polymer particles per unit volume of water were carried out as previously mentioned [22,23].

The polydispersity and morphological characteristics of polymer particles were calculated by using a transmission electron microscope (TEM) of ZESIS type model EM10, Germany, and computerized image analyzer equipment (BILDANALYZE IBAS 1 and 2) to find the maximum diameter (D_{max}), circular diameter (D_{circle}), the deviation from spherical morphology ($D_{\text{circle}}/D_{\text{max}}$), and the number of polymer particles per unit volume of water (N_t). The stability of emulsion latex particles was investigated using conductometric titration to determine the surface charge density (SCD), which provides information about the emulsion's storage life (JANEWAY 4510). A conductivity meter and (JANWAY 1000) hotplate and stirrer. The rate of polymerization (R_p) values were calculated from the slope of these curves for 30–50% conversion by applying the following equation:

$$R_p = \frac{p}{V M t} \text{ (mol/l.sec)} \dots (1)$$

where (p) is the weight of the polymer formed at time (t) in the second, (V) is the volume of the aqueous phase in litres, and (M) is the molecular weight of the monomer. A transmission electron microscope (TEM) of Zeiss type model EM.10, Germany, was used to measure the average diameter (D_i) of different polymer latex particles. The microscope is operated at 60 kV, has a magnification range of 1000–10,000, and it has computerized image analysis equipment (BILDANALYZE IBAS 1 and 2). The blue bar length is equivalent to 1 cm.

The surface charge density (SCD) of the polymer lattices can be calculated as follows:

$$SCD = \frac{\text{Amount of charges (coulomb) in one gm}}{\text{The specific surface area (SSA) of one gm}} \dots (2)$$

Conductometric titration was used to determine the number of charges present on the surface of one gramme of polymer latex, and the specific surface area of latex particles (SSA) can be calculated using the following equation:

$$SSA = \frac{3}{a\rho} \text{ (cm}^3/\text{gm)} \dots (3)$$

where (a) represents the radius of polymer particles, which can be determined from TEM (transmission electronic microscope) measurements, and (ρ) is the density of polymer particles. Shear strengths are measured by a universal tensile testing machine, and the speed of the lower jaw is 50 mm/min. This test is designed specifically for wood glue made from a vinyl acetate homopolymer. The water resistance of the prepared lattices was investigated by applying a latex film to clean glass panels of appropriate dimensions using a film applicator of 60. Keep it for one week to

cure completely in a dry, clean place. On the dry, clear latex film, put a single drop of water and start counting the time until the film's water resistance fails by noticing that the film starts to become milky as the water starts to penetrate the polymer film; this then becomes the maximum water resistance.

3. Results and discussion

3.1. Preparation and Characterization of the (EO/PO) Maleate

A new polymerizable non-ionic surfactant with a reactive double bond has been synthesized by the esterification of alcohol ethoxylate ethylene oxide propylene oxide (EO/PO) block copolymer by reacting with maleic anhydride in the presence of urea at 110°C in 50 min [1]. Stoichiometric equivalent amounts were used, and hydroquinone (HQ) was added to prevent the polymerization of the double bond. The EO/PO maleate surfmer has been verified by using mass spectrum analysis (Figure 1).

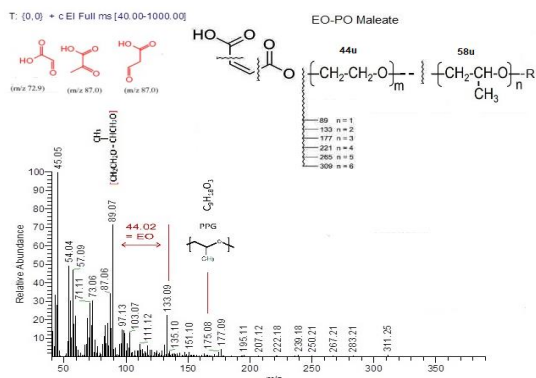


Figure 1. mass spectrum graph for EO/PO maleate surfmer

3.2. Determination of the critical micelle concentration (CMC)

The CMC was determined using the conductometric method [25]. Figure 2 shows the relation between the concentration (mol/l) of the surfmer and the corresponding conductivity data in coulomb at two different temperatures: 23°C and 70°C. The value of CMC was found to be independent of temperature and equal to 0.0053 mol/l. It shows a lower CMC value, which may be due to the presence of a free acidic anionic group in the EO/PO maleate surfmer.

3.3. Kinetic study of the emulsion polymerization of VAc and BuA monomers using EO/PO maleate surfmer

Figure 3 (A&B) shows the conversion-time curves of poly (VAc) as well as poly (BuA), respectively, using different concentrations of EO/PO maleate surfmer. Figure 3A depicts the poly (VAc) conversion time curves using various concentrations of EO/PO maleate surfmer; the R_p values at 30-50% conversion at surfmer concentrations of 2.4, 3.6, and 8.4 $\times 10^{-3}$ mol/l

were calculated from the slope of these curves; the maximum VAc conversion is approximately 85% and occurs after nearly 50 minutes of the reaction.

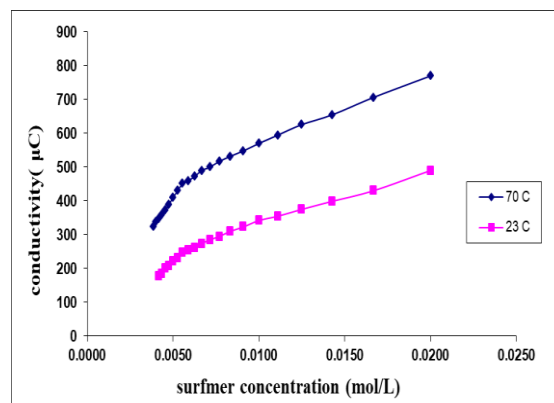


Figure 2. Determination of the critical micelle concentration (CMC) of (EO/PO) maleate surfmer at 23°C and 70°C using conductivity measurements in μC .

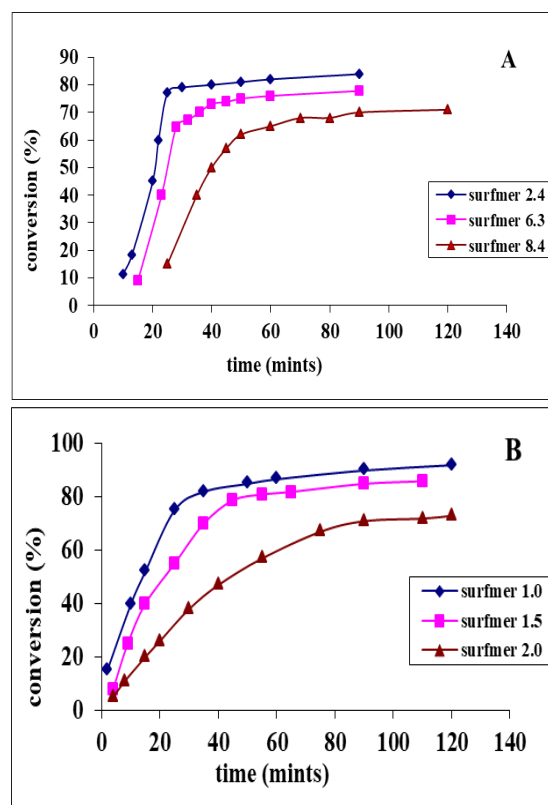


Figure 3. conversion – time curves of: (A) poly (VAc) and (B) poly (BuA) using different concentration of EO/PO maleate surfmer concentration 4.2, 6.3 and 8.4 $\times 10^{-3}$ Mol/l.

Figure 3A and B show the conversion-time curves of poly (VAc) as well as poly (BuA), respectively using different concentrations of EO/PO maleate

surfmer. Figure 3A shows the conversion time curves of poly(VAc) using different concentrations of EO/PO maleate surfmer, the R_p values were calculated from the slope of these curves at 30–50% conversion at surfmer concentrations 2.4, 3.6, and 8.4×10^{-3} mol/l; the maximum VAc conversion is about 85% and after almost 50 min of the reaction.

Figure 3B shows the conversion-time curve of emulsion polymerization of BuA using different concentrations of 1.0, 1.5, and 2.0 gm, equivalent to concentrations of 4.2, 6.3, and 8.4×10^{-3} of EO/PO maleate surfmer. It is clear that the rate of emulsion polymerization of VAc using EO/PO maleate is nearly close to the rate of emulsion polymerization of BuA, and the rate of the polymerization decreases with increasing surfmer concentration for both monomers. This is consistent with a wide range of literature [6, 9, 19, 23–28], but we can see that at concentrations near the CMC value, the converting rate is high, reaching 80% after 50 min. of the reaction, indicating that the VAc monomer has a somewhat higher self-affinity to that surfmer than the BuA monomer.

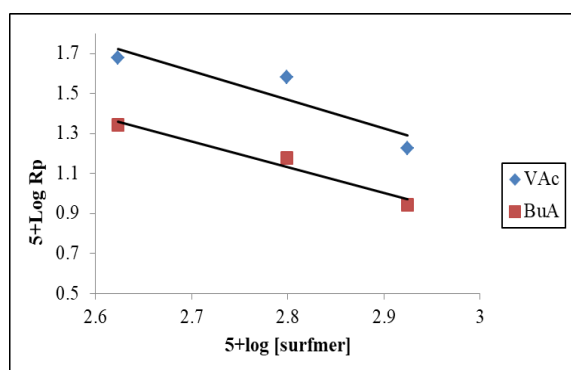


Figure 4. Determination of R_p of poly (VAc) & poly (BuA) using EO/PO maleate surfmer

The above results clearly show that the VAc monomer has a little more tendency for polymerization with EO/PO maleate surfmer than the BuA monomer. This could be because the VAc monomer is more water soluble (20 mol/l) than the BuA monomer (6 mol/l). Furthermore, the anionic characteristics of the maleate surfmer help in the fast nucleation of both monomers through the anionic moiety with a considerably fast and constant propagation rate.

Figure 4 shows the double logarithmic plot of R_p versus surfmer concentrations. The order of the emulsion polymerization of VAc using EO/PO maleate surfmer was calculated from the slope and found to be 1.44. This value is comparable to that of BuA (1.3).

3.4. Morphological characteristics of PolyVAc and PBuA emulsion polymer particles using (EO/PO) maleate surfmer

Figure 5 depicts TEM images of polymer particles from PolyVAc and PBuA emulsion polymers. The detailed morphological parameters of poly (VAc) and poly (BuA) emulsion particles are shown in Table 1. The data in this table show that both polymers show the same morphological effects at the same surfmer concentration. They have particle sizes that are nearly similar in terms of volume average diameter (D_v), maximum diameter (D_{max}), number of polymer particles per unit volume of water (N_t), D/D polydispersity index, and D_{circle}/D_{max} deviation from spherical morphology.

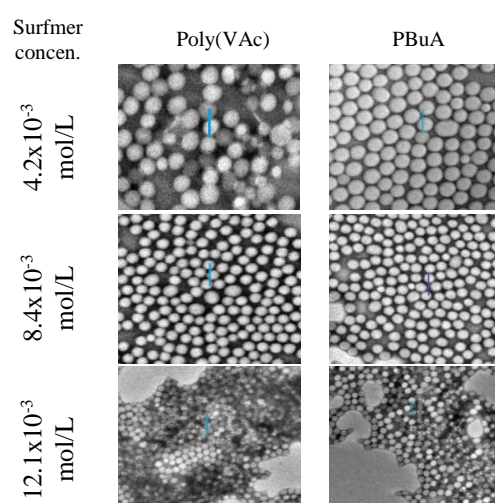


Figure 5 Effect of different surfmer concentration on the size of the emulsion latex particles of poly (VAc) and poly (BuA) lattices prepared at 70°C in the presence of redox initiator KPS/ASBS [6.25×10^{-3}]/[12.5×10^{-3}], respectively.

The data in Table 1 and Figure 5 show that increasing the surface concentration reduces D_v while increasing the number of polymer particles per volume of water N_t . The D_{circle}/D_{max} also decreases by increasing surfmer concentration, which means fewer spherical particles were obtained. The volume average diameter D_v ranges from 278 to 455 nm for poly (VAc) particles and from 312 to 562 nm for poly (BuA) particles that are fabricated using EO-PO maleate surfmer. The yield of a larger particle size is recommended for special applications in water treatment and medical applications compared with that produced by conventional surfactants, which normally range from 80 to 250 nm [29]. It is also clear that both poly (VAc) and poly (BuA) show polydispersity particles; the data disclose that poly (VAc) particles are more defined and spherical (92–96%) as compared to those of poly (BuA) (85–89%).

3.5. Stability of emulsion lattices of polyvinyl acetate and polybutyl acrylate using EO/PO maleate as surfmer.

Table 2 shows the surface charge density of poly (VAc) and poly (BuA). Increasing the surfmer concentration decreases surface charge density and

consequently reduces the stability of emulsion lattices for both polymers [29]. It is also obvious that the poly (BuA) emulsion shows greater stability and greater surface charge density than the surface charge density of poly (VAc) at the same concentration of EO/PO maleate surfmer.

Tables 1. Effect of different Maleate ethoxylate surfmer concentration on the $D\bar{v}$, $D\bar{w}/D\bar{n}$, N_t , the D_{max} , D_{circle} and D_{circle}/D_{max} (the deviation from the spherical dimensions) of the emulsion latex particles of PolyVAc and PBuA lattices Prepared at 70°C in the presence of redox initiator KPS/ASBS [6.25×10^{-3}]/[12.5×10^{-3}] respectively.

Monomer	VAc (1.16 mol/l)			BuA (1.1 mol/l)		
	4.2	6.3	8.4	4.2	6.3	8.4
Surfmer $\times 10^{-3}$ mol/L	4.2	6.3	8.4	4.2	6.3	8.4
$D\bar{v}$ (nm)	455.5	352.91	278.6	562.38	476.9	312.6
$D\bar{n}$ (nm)	451.3	347.19	268.8	556.18	461.9	299.5
$D\bar{w}$ (nm)	461.85	358.48	288.2	570.7	489.9	325.2
$D\bar{w}/D\bar{n}$	1.023	1.033	1.072	1.026	1.06	1.09
N_t ($\times 10^{14}$)	1.85	3.35	5.68	1.62	2.84	4.67
D_{max} (nm)	6.721	6.765	5.876	7.253	6.458	5.918
D_{circle} (nm)	6.485	6.48	5.39	6.49	5.65	5.082
D_{circle}/D_{max} (%)	96.48	95.84	91.66	89.46	87.55	85.86

Table 2. Effect of different EO/PO Maleate surfmer concentrations on the stability and surface charge density in microcoulombs (μC) of emulsion latex particles of PolyVAc and PBuA lattices Prepared at 70°C in the presence of redox initiator KPS/ASBS [6.25×10^{-3}]/[12.5×10^{-3}].

Monomer	VAc (1.16 mol/l)			BuA (1.1 mol/l)		
	4.2	6.3	8.4	4.2	6.3	8.4
Surfmer concentration $\times 10^{-3}$ mol/L	4.2	6.3	8.4	4.2	6.3	8.4
Surface charge density (SCD) μC	85.69	63.71	36.78	115.17	92.66	82.57

3.6. Polymerization of vinyl acetate by semicontinuous technique used in industrial application

The semicontinuous polymerization method was used to prepare poly (VAc) homopolymer and its copolymer with poly (BuA) of 50% solid content, as recommended by almost all industrial applications that use high solid concentrations; the polymerization recipe is shown in Table 3.

Emulsion paint can be made by using a high-shear mixer for good pigment and extender dispersion, and other ingredients with the poly(VAc) emulsion paint are as stranded paint formulation as ASTM ®. The most important applications of emulsion polymers are their use as water-borne coatings and as adhesives, and latex paints were used for interior and

exterior coatings. In the present work, both the poly (VAc) and poly (BuA) lattices were prepared. Poly (BuA) lattices are very tacky, and it will be very difficult to incorporate them in paint application (non-film forming). For this reason, the BuA monomer should be copolymerized with another monomer (VAc monomer), to incorporate it into paint application.

Table 4 shows the shear strength of prepared homopolymer lattices using EO/PO maleate was 135 kg/cm², which is nearly similar to the commercial-grade EAGEL 480/50, which shows 139 kg/cm² using universal tensile strength testing equipment and higher than that made with conventional surfactant (Pluronic F108®).

Table 3. The recipe of the emulsion polymerization of applicable poly(VAc)/ poly(BuA) lattices

Ingredients	Function	Amount (gms)	Concentration mol/l
VAc or/and BuA	monomers	VAM 35+ BuA 15	1.2×10^{-3}
Surfmer	Emulsifier/monomer	1.5 gm	6.3×10^{-3}
KPS/ASBS	Redox initiator	0.168 / 0.2025	[6.25×10^{-3}]/[12.5×10^{-3}]
Distilled water	Dispersing medium	50	5000 ml

Table 4. Comparison of shear strength between adhesive lattices formulation with different types of surfactants

Ingredients	Latex [poly (VAc)] 50% using classical (Pluronic F108) ®	Commercial latex EAGL H (480/50) ®	Latex [poly (VAc)] 50% using (EO/PO) maleate surfmer 1.5 gm
Poly (VAc)	70	70	70
CaCO ₃	18	18	18
DIBP	1	1	1
Water	10	10	10
Defamer	1	1	1
Total	100	100	100
Shear strength (Kg/cm ²)	98	139	135

3.7. Test of water resistance for prepared lattice using a water spot test

Apply a film of the latex to be tested on clean glass panels of suitable dimensions using a film applicator of 60 μ . Keep it for one week to cure completely in a dry, clean place. On the dry, clear latex film, put a single drop of water and start counting the time until the film's water resistance fails by noticing that the film starts to become milky as the water starts to penetrate the polymer film; this becomes the maximum water resistance.

Table 5 compares the water-resistance of poly(VAc) latex (50%)/EO-PO maleate surfactant (1.5gm), with that of poly(VAc) latex (50%)/classical surfactant Pluronic F108 (1gm); and with poly(VAc) latex (50%)/commercial latex EAGL H (480/50) (50%). Superior water resistance for poly (VAc) prepared using EO/PO maleate as a surfmer was obtained over the other two types examined. This

Table 5. Results of water-resistance of the lattices film

Type of latex	Latex [poly (VAc), 50%] Using classical surfactant, Pluronic F108 (1gm)	Commercial latex EAGLE H (480/50) 50%	Latex [poly (VAc), 50%] Using (EO/PO) maleate surfmer (1.5 gm)
Water spot test sec.	12	22	45

superiority may be due to the presence of a hydrophobic maleate group in this surfmer.

3.8. The properties of poly (VAc & BuA) copolymer and its application in emulsion paint

The commercial poly (VAc) latex (emultex 4030) ®, a product of Synthomer Co., was chosen for comparison with the prepared paint formulation. The paint film properties of both the prepared and commercial poly (VAc) emulsion paints are illustrated in Table 6.

Table 6 shows the adhesion, hardness, and washability for poly (VAc/BuA) 35:15 co-polymer, 50% solid content using EO/PO maleate 1.5 gm in comparison with poly (VAc/BuA) 35:15 co-polymer, 50% solid content using classical surfactant 1 gm PLURONIC F108. It is clear from this table that, poly (VAc/BuA)/EO/PO maleate has superior washability and adhesion as compared to those of poly (VAc/BuA)/Pluronic F108.

Table 6. Properties of paint produced from emulsion lattices

Type of emulsion paint	Emulsion paint latex (VAc/BuA) Using classical surfactant (Pluronic F108)	Commercial latex EMULTEX 4030 Emulsion paint	Emulsion paint latex (VAc/BuA) using(EO/PO) maleate surfmer 1.5 gm
Drying time(mint)	5	5	5
Adhesion *	0B	2B	3B
Hardness	98.5	88.2	86.5
Thickness (μ)	120	120	120
Washability(cycle)	27	98	135

*ASTM reference adhesion test

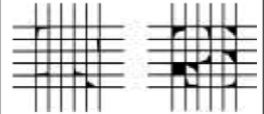
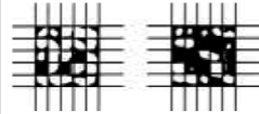
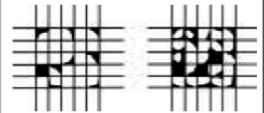
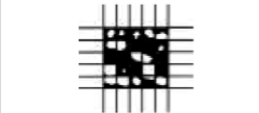
ISO Class: 2/ASTM Class: 3B The coating has flaked along the edges and/or at the intersections of the cuts. A cross-cut area significantly greater than 5%, but not significantly greater than 15%, is affected.		ISO Class:4/ASTM Class: 1B The coating has flaked along the edges of the cuts in large ribbons, and/or some squares have detached partly or wholly. A cross-cut area significantly greater than 35%, but not significantly greater than 65%, is affected.	
ISO Class: 3/ASTM Class: 2B The coating has flaked along the edges of the cuts partly or wholly in large ribbons, and/or it has flaked partly or wholly on different parts of the squares. A cross-cut area significantly greater than 15%, but not significantly greater than 35%, is affected.		ISO Class: 5/ASTM Class: 0B Any degree of flaking that cannot even be classified by classification 4.	

Table 6 also demonstrates that the paint prepared from a co-polymer of poly (VAc/BuA) using EO/PO maleate as the surfmer has better properties than other commercial types, with good adhesion characteristics (3B), very good hardness balanced between adhesion and cohesion forces, which provides pilling resistance, and the highest washability properties among the tested samples (135 cycles); thus, it is clear that using maleate surfactant provides an advantage over using a traditional surfactant.

Conclusion

A new polymerizable non-ionic surfmer (EO/PO) Maleate was successfully synthesized by the esterification and verified by mass spectrum. The CMC of this new surfmer was measured using conductivity and found to be 0.0053 mol/l. A course of emulsion polymerization of vinyl acetate and butyl acrylate using (EO/PO) maleate as a new surfmer was studied with three different surfmer concentrations. The order of the polymerization reaction of vinyl acetate (1.44) was found to be slightly higher than that of butyl acrylate (1.3). The volume average diameter D , the maximum diameter (D_{max}), the number of polymer particles per unit volume of water (N_t), $D/D_{polydispersity}$ index, and the D_{circle}/D_{max} deviation from spherical morphology were measured and calculated. The D was found to decrease with increasing surfmer concentration; also, the D was nearly the same when using both BuA monomer and VAc under the same conditions. The poly VAc shows better morphology with (EO/PO) maleate surfmer than poly (BuA); the two of them show monodisperse particles. Increasing surfactant concentration also reduces the surface charge density of the emulsions produced, lowering their stability; poly(BuA) emulsions are more stable than poly(VAc) emulsions. The presence of the hydrophobic group in surfmer increases the water resistance of poly (VAc) films, increases the washability of poly (VAc/BuA) films, and increases the shear strength of poly (VAc) adhesive. From these data, it can be concluded that the used ionic EO/PO maleate surfmer not only affects the course of the emulsion polymerization process but also improves the physicochemical properties of the produced polymer films. Emulsion lattices show better storage stability than conventional surfactant types due to the non-migration of surfmer to the surface compared to classical surfactant types.

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