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Synthesis and Characterization of Emulsion Polymerization of Acrylate Monomers

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ABSTRACT

A recently developed successful approach to achieve the balance of properties involves the copolymerization of film forming monomers like acrylates and methacrylates. The copolymerization of acrylate based monomer having different alkyl group offers the opportunity to study the effect of the alkyl substituents on the polymer properties. The objective is to study their copolymerization behavior with acrylate or combination of acrylates of varying chemical nature using free radical initiator and to correlate the composition of the copolymers with their physical properties suitable for its use as coating on hard surfaces.

Keywords: Acrylate, Emulsion, Copolymerization, Coating

1. INTRODUCTION

The copolymerization of acrylate or methacrylates having different alkyl group offers the opportunity to study the effect of the alkyl substituents on the polymer properties. The usual effect of increasing the side chain length in methacrylate and acrylate derived from straight and branched chain alcohols is expected to affect the rate of copolymerization, as well as thermal, mechanical and optical properties of the copolymers. MMA can copolymerize with variety of vinyl monomers[1-4] like methyl acrylate (MA), ethyl acrylate (EA), ethyl hexyl acrylate (EHA), ethyl hexyl methacrylate (EHMA), styrene (St), etc. to yield copolymers with improved

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flow behavior, better impact strength, heat and abrasion resistances. The ability to tailor the rigid and stable methacrylates alone or in combination with acrylates to fit specific application requirements such as outstanding clarity, dimensional stability, and unusual chemical and light stability of this class of materials has spurred its growth and have made methacrylic esters a prime candidate for numerous and diverse applications. These copolymers find applications as paints, automotive coatings, viscosity index improvers, medicines, adhesives and substitute for glass in solar collectors.

Coatings based on acrylic esters are being used since last four decades via solvent evaporation mechanism for the formation of film on different substrates. Because of environmental hazards related to solvent evaporation and its cost, the ambient cured water borne systems are emerging as one of the better option for achieving superior properties in high performance applications. The increasing cost of solvents that simply evaporate and disappear from coating is another driving force for the development of water-borne industrial coatings. From among the commonly used binders in organic coatings, the acrylic type resins is one of the most common class of resins which find application as binders. Acrylic resins may be used alone or as blend with other resins to form the suitable binder system for coatings. Binders are the backbone of any paint. It is the only component that must be present; other components included optionally, depending on the desired properties of the cured film. The binder imparts adhesion, binds the pigments together and strongly influences properties such as gloss potential, exterior durability, flexibility and toughness. Binders include synthetic or natural resins such as acrylics, vinyl-acrylics, vinyl acetate/ethylene (VAE), polyurethanes, polyesters, melamine resins, epoxy or oils.

2. MATERIALS AND METHOD

2. 1. Experimental Materials

Monomers methyl methacrylate (MMA), butyl acrylate (BA) (Aldrich) and ethyl hexyl acrylate (EHA) were purified before use by alkali wash method. Free radical initiator potassium persulfate (KPS; Thomas Baker) and emulsifier sodium lauryl sulphate (SLS; Thomas baker) were used as received. Deionized water was used throughout the experimental work.

Polymerization

The polymerization reactions were carried out in 500 mL three necked round bottom flask equipped with reflux condenser, stirrer, dropping funnel and thermometer. Polymer latex samples were prepared by thermally initiated free radical polymerization of MMA with BA or EHA. The Polymerization reaction was carried out at 70 ±1 °C, using SLS as emulsifier and KPS as initiator for 3h. The percentage conversion of polymers are varied with the monomer feed ratio in previous study [5]. The actual feed compositions and designations of polymers are given in Table 1 and 2.

2. 2. Physical properties

The physical properties of copolymers were studied as a coated film. The polymers were coated by deposition of a small amount of synthesized latex on glass and metal plates, which were air-dried at 60 °C.

(i) Hardness

Pencil hardness measurements have been used by the coatings industry for many years to determine the hardness of clear and pigmented organic coating films. The hardness of the films was measured according to ASTM: D 3363 test method [6]. In this test the pencil is held firmly against the film at a 45° angle (point away from the operator) and pushed away from the operator in a 6.5-mm (1⁄4-in.) stroke. The process is started with the hardest pencil and continued down the scale of hardness to either of two end points: one, the pencil that will not cut into or gouge the film (pencil hardness), or two, the pencil that will not scratch the film (scratch hardness). The films on the coated mild steel panels were tested for its scratch hardness using H, 2H and 4H pencils.

(ii) Adhesion test

Adhesion of the dried latex film was determined according to ASTM D3359 [7] by using crosscut adhesion tester. These test methods cover procedures for assessing the adhesion of coating films to metallic substrates by applying and removing pressure-sensitive tape over cuts made in the film. An X-cut is made through the film up to the substrate and, pressure-sensitive tape is applied over the cut. The tape is then removed, and adhesion is assessed qualitatively on the 0 to 5 scale.

(iii) Flexibility

Flexibility of the dried latex film was measured according to ASTM D522 [8] with ¼ inch mandrel bend tester (Sheen Instrument, U.K.) consisting of a rotating panel-bending arm 180° around.

(iv) Gloss

Gloss is a measure of the coated surface to reflect light and it is an important property of coating when the purpose is to provide aesthetic or decorative look to the surface. Gloss of the films was measured at 60º angle of reflectance using a digital mini gloss meter (Sheen, UK) calibrated against internal standard of known refractive index and the results are reported in gloss unit (GU) as per ATSM D523-99 [9].

Table 1. Feed composition of monomers (MMA/BA) used during the synthesis

Polymer code	Mole ratio of monomers		Weight percentage of monomers		Amount of MMA (g)	Amount of BA (g)
	MMA	BA	MMA	BA		
SA_1	9	1	90	10	43.75	6.25
SA_2	8	2	80	20	37.9	6.25

SA_3	7 3	70	30	32.3	17.1
SA_4	6 4	60	40	27.0	23.0
SA_5	5 5	50	50	21.9	28.1

Table 2. Feed composition of monomers (MMA/EHA) used during the synthesis.

Polymer code	Mole ratio of monomers		Weight percentage of monomers		Amount of MMA (g)	Amount of EHA (g)
	MMA	EHA	MMA	EHA		
SE_1	9	1	90	10	41.5	8.5
SE_2	8	2	80	20	34.2	15.8
SE_3	7	3	70	30	28.0	22.0
SE_4	6	4	60	40	22.5	27.5
SE_5	5	5	50	50	17.6	32.4

3. RESULTS AND DISCUSSION

3. 1. Physical properties of polymer latex

The films of the copolymer latexes synthesized using varying feed composition of MMA:BA and MMA:EHA were prepared by coating the latexes on glass and metal panels. The properties viz. hardness, adhesion, flexibility, gloss and water resistance of coated films were evaluated and the results have been summarized in Table 3 and 4.

Hardness: Hardness of polymer latex coated films were determined by using pencil hardness tester with a calibrated set of drawing leads ranging from 6B (softest) to 6H (hardest). The sharpened pencil with circular flat lead end was fixed to the hardness tester and pushed away in a 6.5 mm stroke on the coated surface. The process of testing was started with the hardest pencil (6H) and subsequently the pencils of lower hardness were used to check scratch behavior of the polymer films was observed. The hardness of the films prepared by copolymer latexes

are given in Table 3 and 4. It was observed that the pencil hardness of the coating based on PMMA was 4H, which has not decreased in case where SA_1 and SA_2 latexes and were used as coatings. Whereas it decreased to 3H in case of SE_1 and SE_2 latex coatings. The hardness of the coating decreased with the increase in BA and EHA content in the feed used for synthesis of copolymers. The hardness for $SA_3$and SE_3coating was 2H, and it was H for SA_4 and SA_5 coatings. The hardness of the films prepared using the copolymers based on SE_4 and SE_5 were found to be H and films were soft in nature, therefore their use in coating is limited and SE_3 was found to be better because of its average hardness. From the above results it is clear that the latexes based on homopolymers of MMA and that the copolymers containing higher MMA content were too hard for uses in common coating applications. The hardness of the films prepared by using the copolymers based on 6:4 and 5:5 molar ratios of MMA:BA and MMA:EHA were found to be lowest and these films were quite tacky and soft and therefore their use in general applications as coating is not very satisfactory. In view of the above results for the films prepared using feed ratio7:3 MMA: BA (SA_3) and MMA:EHA (SE_3) was found to be very significant due to the fact that films will hard in nature. The result shows that the hardness of the coating decreased with the increase in BA and EHA content in the feed used for the synthesis of copolymers. From the above results it is apparent that the latexes based on homopolymers of MMA and that the copolymers containing higher MMA content were quite hard and brittle and not suitable for end use of coating applications.

Adhesion: The synthesized polymeric latexes were checked for their adherence on the metal surface by using the cross hatch adhesion tester. The coating prepared by using polymeric materials which adhere well to the substrate on which they are applied. A variety of established method can be used to determine how well a coating is bonded to the substrate. The cross hatch test is a simple, and easy to check adhesion behavior of coatings on the substrate. The adhesion for SA_4 and SA_5 films were 3B which decreased to B for SA_1 and 2B for SA_2 and SA_3 film. The SA_4 and SA_5 latexes had good adhesion property among all the prepared copolymer latexes. The adhesion property depends on the copolymer composition and glass transition temperature (Tg). PMMA polymer latexes have B adhesion value while PBA had 5B, highest adhesion among all the synthesized latexes. The reason for lower adhesion of PMMA is its higher Tg (110 °C) while PBA have lower Tg (-54 °C). As the concentration of BA in copolymer of MMA-BA increases, adhesion also increases. The reason for strong adhesion of SA_4 and SA_5 latexes films, due to their low glass transition temperature [10]. The cross hatch test is a simple way to check adhesion behavior of coatings on the substrate. The cross hatch adhesion tester is used to check the adherence of synthesized polymer latexes films on metal surfaces. The adhesion for all the synthesized polymer films quantitatively ranged between B to 5B where B shows the poor adhesion which increased to 5B. PMMA polymer latexes have lowest adhesion among all the synthesized polymer latexes while PEHA discuss polarity had highest adhesion 5B. The reason for lower adhesion of PMMA is its higher glass transition temperature. The adhesion for SE_5 films was 4B which decreased to 3B for the films based on SE_3 and SE_4. The adhesion for SE_2 and SE_1 was 2B and B, respectively. The SE_5 latexes had good adhesion property among all the prepared copolymer latexes due to which such copolymer systems are not suitable for the coatings on exterior surfaces. The films prepared by SE_3 and SE_4 are seems to be appropriate for coating applications because of good adhesion and comparatively hard nature. From the above results it could be said that as the concentration of BA and EHA in the copolymer increases, adhesion increases due to their lower value of glass transition temperature.

Flexibility: Flexibility is the ability of a material to be bent without cracking or undergoing another failure. The more common way for determining a coatings flexibility, or percentage elongation, is to bend a thin gauge coated steel panel around a mandrel as described by ASTM D522 (test method for mandrel bend test mandrel size ¼' attached organic coatings) The result of flexibility for all the polymer latexes are given in Table 3 and 4. Based on this qualitative measurement it is apparent that the film became flexible as the concentration of higher acrylates in the copolymer increased. The film of PMMA polymer latexes cracked on bending whereas the PBA films pass the mandrel test. The films of SA_1 and SA_2 did not pass the mandrel test whereas the films of SA_3, SA_4, and SA_5 pass the flexibility test indicating that SA_1 and SA_2 film were comparatively harder. The three films exhibit good flexibility and adhesion. This could be attributed to the open molecular structure (non-compact) and distance between chains in the cured film of copolymer latexes. The film of PEHA is soft in nature and passes the flexibility test easily. The film of SE_1 copolymer lattice did not passes the test because of hard in nature while the film prepared by other copolymer latexes viz. SE_2, SE_3, SE_4, and SE_5 passes the flexibility test. The results it was found that the incorporation of EHA monomer increases the flexibilty of the polymer latexes because of its branched chain structure.

Gloss: Waterborne coating compositions such as paints containing emulsion-polymerized binders are frequently applied to substrate for decorative as well as for protective reasons. Fundamental appearance parameter is the gloss of the dried coating. In many instances high gloss is required and this has been difficult to achieve with paints based on aqueous emulsion polymers. The gloss is measured of the cured film at 60° angle of reflectance using Triglossometer. The numerical values of the gloss of the cured films of latexes based on PMMA, SA_1, SA_2, SA_3, SA_4, and SA_5, have been presented in Table 3. The gloss values are plotted as a function of monomer ratio in Figure 1. It could be seen that the gloss of the films lies between 32 to 95 GU. The values of gloss of the cured films based on PMMA, SE_1, SE_2, SE_3, SE_4, and SE_5, have been presented in Table 4 and the gloss values are plotted as a function of monomer feed ratios (Figure 2). It could be seen from the Figure that the gloss of the polymer latexes lie between 32 to 95 GU. It is apparent from the data that the gloss of the coatings decreased with the increase in BA and EHA content in monomer feed. This might be a consequence of the hindered film formation. The results of all the above physical properties show that the films of MMA based latexes with higher acrylate incorporation had acceptable properties for coating applications where the combination of high hardness and high flexibility is required.

Table 3. Physical properties of polymer films

Polymer	Hardness	Adhesion	Gloss	Flexibility
PMMA	4H	B	95	Cracked
PBA	H	5B	32	Pass
SA_1	4H	B	80	Fail
SA_2	4H	2B	78	Fail
SA_3	3H	2B	76	Pass

SA_4	2H	3B	65	Pass
SA_5	H	3B	55	Pass

Table 4. Physical Properties of the Coated Films

Polymer	Hardness	Adhesion	Gloss	Bend Test
PMMA	4H	B	95	Cracked
PEHA	H	5B	30	Pass
SE_1	3H	B	78	Hard
SE_2	3H	2B	75	Pass
SE_3	2H	3B	72	Pass
SE_4	H	3B	61	Pass
SE_5	H	4B	57	Pass

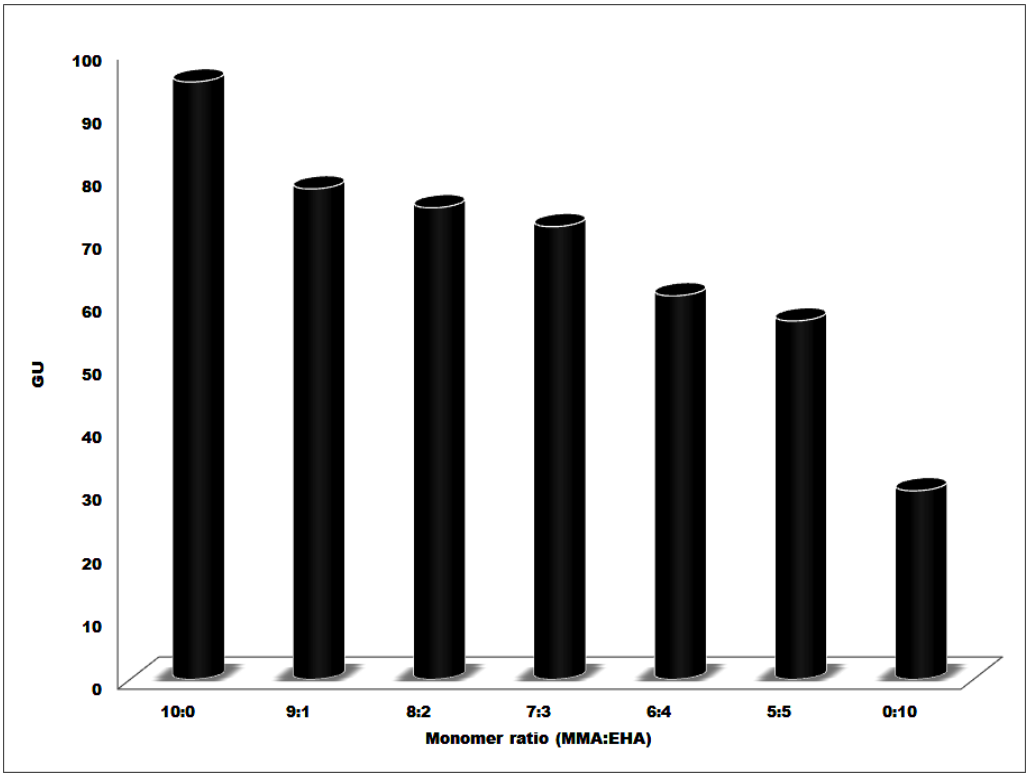

Figure 1. Effect of EHA content on the Gloss of MMA-EHA copolymer.

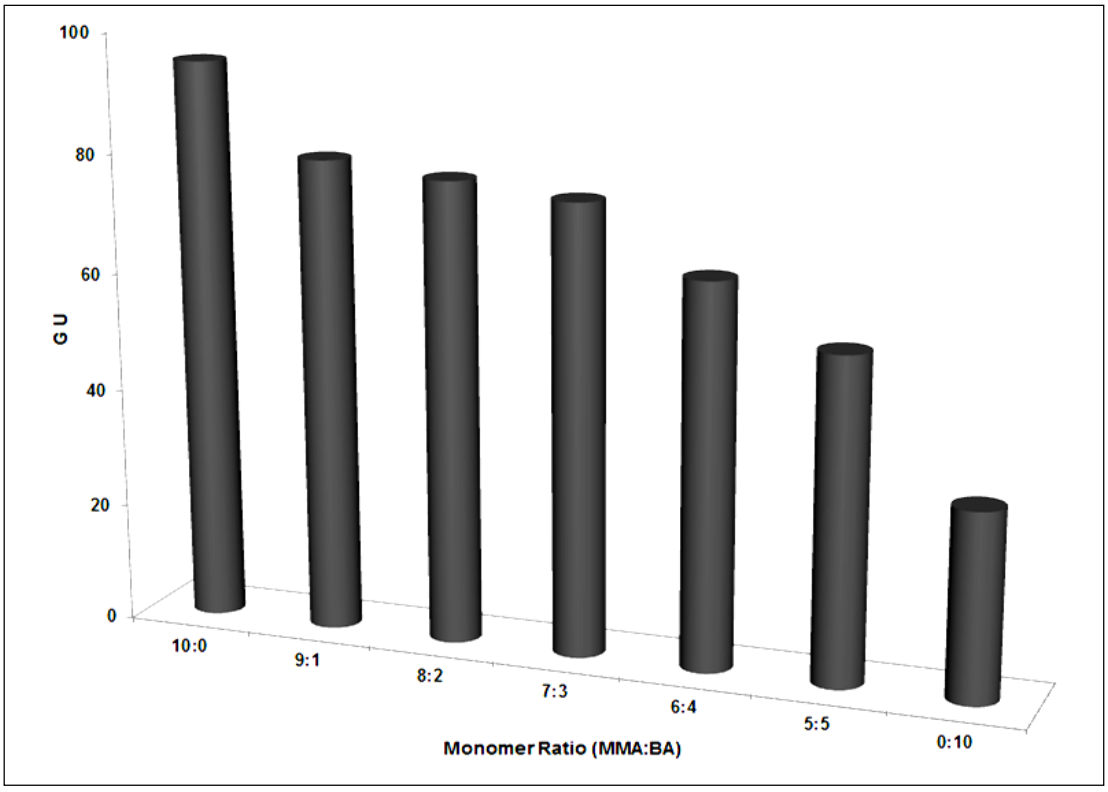

Figure 2. Effect of BA content on the Gloss of MMA-BA copolymer.

4. CONCLUSIONS

The physical properties viz. hardness, adhesion, flexibility and gloss of polymer films were evaluated by ASTM standards. It was observed from the results that the physical properties of the films were affected by the molar ratio of monomers used during their synthesis. The films had good flexibility with the higher content of BA or EHA in the feed whereas gloss decreased. The acceptability of latexes for coating applications was assessed by comparing their physical properties. It was observed that the copolymer latexes synthesized with 7:3 and 6:4 MMA: BA molar ratios had more suitability for their use in coatings. While in case of MMA: EHA copolymers the suitable molar ratios for coating application were 8:2 and 7:3.

References

[1] C. Laureau, M. Vicente, M. J. Barandiaran, J. R. Leiza and J. M. Asua, *J. Appl. Polym. Sci.* 81 (5) (2001) 1258.

[2] M. D. Gower and R. A. Shank, *J. Appl. Polym. Sci.* 93 (6) (2004) 2909.

[3] Mayer, T. Pith, G. H. Hu and M. Lambla, *J. Polym. Sci. Polym. Phys.* 33 (1995) 1781.

[4] M. D. Bhabhe, P. S. Galvankar, V. M. Desai and V. D. Athawale, *J. Appl. Polym. Sci.* 56 (4), (1995) 485.

[5] S. Bajpai, I. Nigam, and J.S.P. Rai J. Appl. Polym. Sci., 112(4) (2009) 2374.

[6] ASTM D 3363-00. 'Test Methods for Film Hardness by Pencil Test' in Annual Book of ASTM Standard (1994).

[7] ASTM D 3359-93. 'Test Methods for Measuring Adhesion by Tape Test' in Annual Book of ASTM Standard (1994).

[8] ASTM D 522-88. 'Test Methods for Mandrel Bend Test of coatings' in Annual Book of ASTM Standard (1989).

[9] ASTM D 523-99. 'Test Methods for Specular Gloss' in Annual Book of ASTM Standard (1999).

[10] Chapman and Hall, Surface Coating, Raw Materials and their usage, London, Vol. 1, Chap. 24, (1992) 356.