

# Synthesis and Characterization of Butyl Acrylate/Methyl Methacrylate/Glycidyl Methacrylate Latexes

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**ABSTRACT:** The butyl acrylate (BA)/methyl methacrylate (MMA), and glycidyl methacrylate (GMA) composite copolymer latex was synthesized by seeded emulsion polymerization technique taking poly(methyl methacrylate) (PMMA) latex as the seed. Four series of experiments were carried out by varying the ratio of BA : MMA (w/w) (i.e. 3.1 : 1, 2.3 : 1, 1.8 : 1, and 1.5 : 1) and in each series GMA content was varied from 1 to 5% (w/w). The structural properties of the copolymer were analyzed by FTIR, <sup>1</sup>H-, and <sup>13</sup>C-NMR. Morphological characterization was carried out using transmission electron microscopy (TEM). In all the experiments, monomer conversion was ~99% and final copolymer composition was similar to that of feed composition. The incorporation of GMA into the copolymer chain was confirmed by

<sup>13</sup>C-NMR. The glass transition temperature ( $T_g$ ) of the copolymer latex obtained from the differential scanning calorimetry (DSC) curve was comparable to the values calculated theoretically. With increase in GMA content, particles having core-shell morphology were obtained, and there was a decrease in the particle size as we go from 2–5% (w/w) of GMA. The adhesive strength of the latexes was found to be dependent on the monomer composition. With increase in BA : MMA ratio, the tackiness of the film increased while with its decrease the hardness of the film increased. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 549–557, 2010

**Key words:** acrylic copolymer; adhesion; latex particles; seeded emulsion polymerization; T-peel strength

## INTRODUCTION

Acrylate copolymers with functional groups have their prime importance due to their versatile applications. A vast literature and patents are available regarding the adhesive properties of acrylate copolymers in lamination of paper to film,<sup>1</sup> film to film<sup>2,3</sup> and in tapes and labels as pressure sensitive adhesives (PSA). The effect of composition of acrylic latex in PSA and laminating adhesives to cellulosic substrates is well reported in the literature. Lovell<sup>4</sup> and Mayer et al.<sup>5</sup> studied the effect of polymeric particles formed by polymerization of butyl acrylate (BA)/acrylic acid (AA) and butyl acrylate (BA)/methyl methacrylate (MMA), and acrylic acid (AA) copolymers having core-shell morphology on the shear and peel strength. They observed that the end properties of the latex particles are mainly influenced by the comonomers present in the shell. Laureau et al.<sup>6</sup> prepared copolymers using varying amounts of 2-ethyl hexyl acrylate and MMA and investigated the effect of copolymer composition on the adhesive perform-

ance (tack, shear, peel). Gower and Shanks<sup>7</sup> studied the effect of varied monomer composition of latex with same glass transition temperature on the adhesive performances and peeling master curve for acrylic PSA. Similarly, the adhesion of MMA based acrylic latex to the cellulosic substrates and the influence of structure to adhesion were studied by McLaren<sup>8</sup> and Bhabhe et al.<sup>9</sup> Mao and Reegan<sup>10</sup> studied the effect of acrylic content on the adhesive strength (peel strength) of ethyl acrylate (EA)/BA/MMA system for a nonpressure sensitive adhesive and found that peel strength increases with increase in the length of the side chain of polymer.

Makati<sup>11</sup> reviewed the fundamentals of adhesive lamination, performance requirements of adhesives and approach to develop new one-component water-based laminating adhesives. So in this study, an approach was made to synthesize acrylate-based latex for laminating adhesives by modifying the technology utilized for aqueous PSA. Low  $T_g$  polymer latexes are very useful in adhesive and coating applications because of their film-forming behavior in the absence of the added VOCs. But the films, they form are very soft, weak, and tacky. Practical application of low  $T_g$  latex requires post application cure to introduce cross-linking in the film. For cross-linking reaction, it requires reactive functional groups, either at the surface or inside the particles. Useful functional

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groups include carboxyl, hydroxyl and epoxy groups. Carboxyl and hydroxyl groups are generally introduced to the latex particle with methacrylic acid and 2-hydroxyethyl (meth)acrylate as comonomers and epoxy group through glycidyl methacrylate (GMA) monomer. But the latex containing epoxy groups represents an important class of useful material because of the presence of oxirane ring. The reactivity of oxirane ring toward various nucleophiles is helpful for chemical modification of the basic polymer. Thus the epoxy group provides the cross-linking site, and also increases the adhesive properties of the polymer.<sup>12</sup> The aim of the present work was to investigate systematically the effect of functional monomer and the composition of soft and hard monomer on the performance properties of emulsions.

The article describes the preparation of BA/MMA/GMA copolymer latex by seeded emulsion polymerization method. The GMA content was varied from 1 to 5% (w/w) and in some cases up to 10% (w/w) for varying ratio of BA : MMA. Structural, molecular and thermal characterizations were done using FTIR, <sup>1</sup>H- and <sup>13</sup>C-NMR, GPC, and DSC. The effect of feed composition on monomer conversion, molecular weight, particle size, glass transition temperature and more specifically upon the T-peel strength of the laminates prepared, using these latexes was investigated.

## EXPERIMENTAL

### Materials

BA, MMA, and GMA of commercial grade (Fluka, Germany); ammonium persulphate (APS; CDH, India), sodium bicarbonate and dodecyl mercaptan (Aldrich, Germany) were used as received. Dowfax 2AI (sodium salt of dodecyl disulphonate diphenyl ether; Dow Chemical Co., USA) and OT-50 (sodium salt of di-octyl sulfosuccinate; Cytec) were used as surfactants in the polymerization. Liquid ammonia solution (Qualigens, India) was used to adjust the final pH of emulsion. De-ionized water was used throughout the reaction.

### Synthesis of PMMA seed latex

The seed latex was prepared by semicontinuous emulsion polymerization at 80°C using the recipe given in Table I. All the reactions were carried out in a 2-L four-necked glass reaction flask fitted with a nitrogen inlet, a reflux condenser, a thermometer and the stirrer was inserted through the middle neck. 0.89 g of Dowfax 2AI (surfactant) and 0.2 g of NaHCO<sub>3</sub> (buffer) were dissolved in 260.0 g of water and added to the reactor. The mixture was thoroughly stirred under nitrogen purging for 1 h before the monomer feeding and then heated to 80°C.

TABLE I  
Recipe for Seed Preparation

Raw materials	Amount (g)
DM water	290.0
Surfactant (Dowfax 2AI)	0.89
NaHCO <sub>3</sub>	0.5
MMA	124.0
Initiator (APS)	0.58
Stirring speed (rpm)	150
Temperature (°C)	80
Reaction time (h)	3

12.4 g of MMA and 2 mL of 3% (w/w) initiator (APS) solutions were charged into the reactor with continuous stirring. After 30 min, continuous feeding of monomer and initiator was done at a constant rate for about 3 h. The mixture was further stirred for another 3 h to complete the polymerization (99% conversion). The latex thus obtained was characterized for percentage conversion, molecular weight, particle size, particle size distribution and % coagulum. The latex had an average particle diameter of 55.9 nm, weight average molecular weight ( $M_w$ ) of  $1.05 \times 10^5$  g mol<sup>-1</sup> and 1.4% (w/w) gel content.

### Synthesis of seeded copolymer emulsion

Initially the required amounts of seed latex [0.1% (w/w) of final latex] and 120.0 g DI water were charged to the reactor. The mixture was heated to 80°C while being stirred and purged with nitrogen (approx for 1 h), followed by addition of APS solution [2.5 mL of 7% (w/w) solution]. The monomer mixture (total amount = 560 g) was pre-emulsified with 12.0 g of surfactant (Dowfax 2AI and OT-50) and then fed into the reactor at a constant rate for ~ 3 h. The initiator solution was also continuously fed throughout the reaction. The principal monomers were BA and MMA and the functional part was GMA. GMA 25% (w/w) was added with the pre-emulsion and rest was added at the end of the monomer pre-emulsion feeding. The reaction was kept at 80°C for an hour after the monomer feeding to complete the polymerization of remaining monomer. It was then cooled down to room temperature. The final pH of the latex was adjusted using liquid ammonia solution. The final seeded latex was filtered through a mesh of 200 μm.

To evaluate the effect of composition, several copolymer samples were prepared by varying the ratio of monomers (BA : GMA) in the feed. GMA content was varied in the range of 1–5% (w/w). BA : MMA (w/w) ratio was taken as 3 : 1, 2.3 : 1, 1.8 : 1, and 1.5 : 1. The samples were designated as B-X, C-X, D-X, and E-X where B, C, D, and E represent BA : MMA ratio of 3 : 1, 2.3 : 1, 1.8 : 1, and 1.5 : 1 and X represents the numerical (1, 2, 3, and 5) % (w/w) of GMA in the copolymer respectively. The

**TABLE II**  
**Details of Polymerization Conditions and Sample Code**  
 (Seed Latex = 1 g, Total Monomer = 560.0 g, Mixture of Dowfax 2AI and OT-50 Surfactant = 12.0 g, CTA = 1.4 g, APS = 2.8 g, DM Water = 445.0 g)

Sample code	Amount of reactants (g)			
	BA	MMA	BA : MMA	GMA
B-1	420.0	134.4	3 : 1	5.6
C-1	386.4	168.0	2.3 : 1	5.6
D-1	358.4	196.0	1.8 : 1	5.6
E-1	330.4	224.0	1.5 : 1	5.6
B-2	414.4	134.4	3 : 1	11.2
C-2	386.4	162.4	2.3 : 1	11.2
D-2	355.6	193.2	1.8 : 1	11.2
E-2	330.4	218.4	1.5 : 1	11.2
B-3	411.6	131.6	3 : 1	16.8
C-3	380.8	162.4	2.3 : 1	16.8
D-3	352.8	190.4	1.8 : 1	16.8
E-3	324.8	218.4	1.5 : 1	16.8
B-5	403.2	128.8	3 : 1	28.0
C-5	378.0	157.9	2.3 : 1	28.0
D-5	344.4	187.6	1.8 : 1	28.0
E-5	319.2	212.8	1.5 : 1	28.0
B-8	392.0	123.2	3 : 1	44.8
B-10	380.8	123.2	3 : 1	56.0

BA, butyl acrylate; MMA, methyl methacrylate; GMA, glycidyl methacrylate.

sample codes along with their monomer composition are given in Table II. Apart from these, two more experiments were carried out by taking 8 and 10% (w/w) of GMA keeping the ratio of BA and MMA as 3 : 1 by weight.

## Characterization

### Monomer conversion

The monomer conversion was calculated gravimetrically. Samples were withdrawn during the polymerization, to a preweighed aluminum foil and dried at 105°C in a preheated oven till a constant weight. In this study, the fractional weight conversion is defined as the fraction of monomer that had been polymerized.

### FTIR

Infrared spectra were recorded using Nicolet Impact 400D FTIR Spectrometer. The samples for FTIR spectroscopy were prepared by the freeze-drying technique. Powdered samples were mixed with KBr powder to make pellets for recording FTIR spectra of the samples.

### NMR

<sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded using a Bruker spectrophotometer operating at 400 MHz

using CDCl<sub>3</sub> (spectroscopic grade) as solvent and tetramethyl silane (TMS) as an internal standard at ambient temperature.

### Particle size determination

The particle size and particle size distribution was measured by dynamic light scattering (Malvernizer; 2000). To measure the particle size and particle size distribution, the samples were diluted using de-ionized water.

### Gel content

The gel content of prepared latex samples was determined gravimetrically. For this purpose, latex was dried in an air oven at ~ 100°C for ~ 1 h. The dried polymer film of known weight was placed in a screw capped bottle and then tetrahydrofuran (THF) was added and the bottle cap was tightened properly. It was stirred and then left undisturbed for 24 h. After 24 h, the solution was filtered using a preweighed G-4 crucible. It was washed with fresh THF to remove any soluble particle. Finally it was dried in air oven at 120°C for 1 h and weighed. The gel content was calculated using the following equation:

$$\text{Gel content (\%)} = \frac{W_g}{W_p} \times 100$$

where  $W_g$  = weight of insoluble polymer (g) and  $W_p$  = weight of dried polymer taken initially (g).

The gel content of each sample was determined at least three times and the average value was taken.

### Molecular weight determination

The molecular weight ( $M_n$  and  $M_w$ ) and molecular weight distribution of the soluble fraction of polymer was determined by using Waters size exclusion chromatography (SEC). A differential refractive index detector was used. Three columns with pore sizes of 10<sup>2</sup>, 10<sup>4</sup>, and 10<sup>6</sup> Å (Waters HR<sub>2</sub>, HR<sub>4</sub>, and HR<sub>6</sub>) and THF at a flow rate of 1 mL/ min were used. Narrow polystyrene standards having molecular weight ranging from 4 × 10<sup>2</sup> – 10 × 10<sup>6</sup> were used for calibration.

### Glass transition temperature

The glass transition temperature ( $T_g$ ) of dry polymer samples was measured using DSC; Universal V3. 9A, TA Thermal Analyser. DSC scans were recorded in the temperature range of -50 to 150°C at a heating rate of 10°C/ min. In the first heating run the samples were heated from -50 to 150°C and then quench cooled and the DSC scans were again recorded at a

heating rate of 10°C/ min. Second heating scans were used to determine the glass transition temperature. A sample weight of  $5 \pm 2$  mg was used in each experiment.

The glass transition temperature of the copolymer was calculated using Fox equation<sup>13</sup> as follows:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} + \frac{W_3}{T_{g3}} + \dots$$

### Morphological characterization

Morphological characterization was done using transmission electron microscopy (TEM, Morgagni 268D FEI, Netherland). The latex samples diluted with aqueous solution (2%) of phosphotungstic acid (PTA, Merck), (negative staining) were placed on copper grids covered with formvar and dried using UV lamps.

### Adhesive performance testing

**Preparation of laminates.** The laminate preparation for the adhesive performance testing was done in accordance with ASTM D1876.<sup>14</sup> The emulsion was coated on a substrate [poly(ethylene terephthalate)] of 12  $\mu\text{m}$  thickness having low surface energy by a bar coater. The coated film was dried by hot air. The dry film thickness was 2.0–3.0  $\mu\text{m}$ . After drying, the film coated in this way was rolled up together with the corona-treated surface of the second substrate (polyethylene of 20  $\mu\text{m}$ ) and subsequently passed through a heat sealer with only top bar heated at 65°C for 2 s. Then the laminates were conditioned for 24 h at room temperature before testing. The test panels, thus prepared (6 in. wide and 12 in. long) were bonded only over 9 in. in length.

**T-peel strength.** For peel strength, the laminates prepared above were used and tested in accordance with ASTM D1876. Peel strength of the laminates was determined by debonding the laminates ( $\sim 1$  in. width) on an Instron (USA) using a T-peel test. At least five strips were tested for each adhesive, and the average bond strength was reported in g/in. width. The dry coat weight of the adhesive was 2–3 g/m<sup>2</sup>. It is generally desirable to have a high bond strength at low coat weight with failure occurring as film tear.

**Water and chemical resistance.** For water resistance studies, known weight of laminates were immersed in water at room temperature for 72 h. After 72 h of immersion, the samples were taken out; surface water was wiped using the filter paper and kept at room temperature to dry. Then the bond strength of the laminates was measured using the same procedure as reported above.

In the same way, the laminates were dipped in 5% solution of acid (HCl) and alkali (NaOH) to study the acid and alkali resistance.

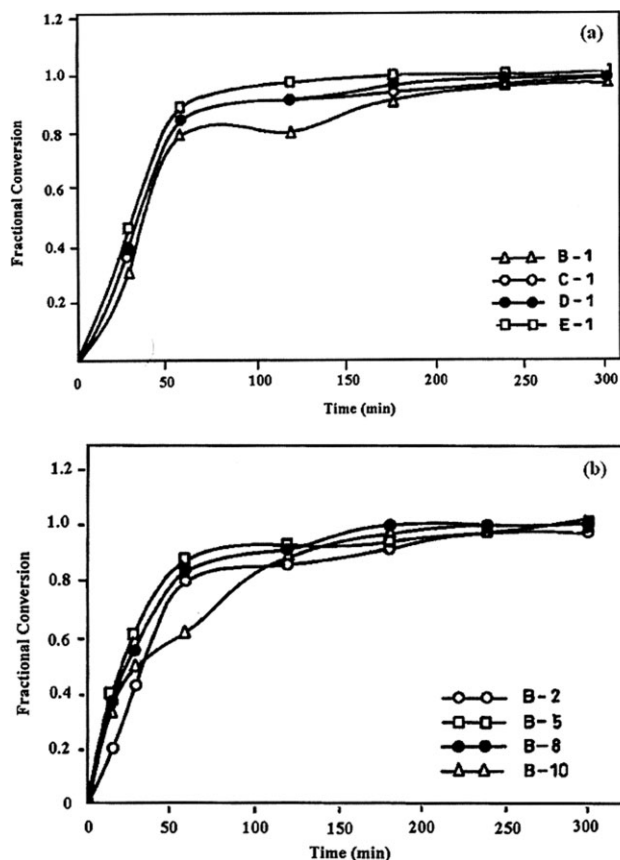
## RESULTS AND DISCUSSION

### Monomer conversion

Figure 1(a) shows the evolution of fractional conversion in the experiments with varied weight ratio of BA : MMA keeping GMA amount constant. The effect of third monomer i.e. GMA on the copolymerization of BA : MMA (3 : 1) was also investigated. Figure 1(b) shows the effect of GMA content on the rate of monomer conversion. In all these polymerizations, 99% conversion was obtained in about 5 h. The polymerization rate was unaffected by BA/MMA ratio whereas it slightly decreased with the increasing amount of GMA in the copolymerization.

### FTIR spectroscopy

Figure 2 shows the FTIR spectra of the copolymers prepared with GMA content as 2, 5, 8, and 10% (w/w). The absence of absorption band at 1600 cm<sup>-1</sup> indicates the absence of monomer impurities in the polymer. The band due to >C=O group of all the acrylate comonomers appears to have overlapped at 1735 cm<sup>-1</sup>. So it was not possible to determine the copolymer composition. The presence of small peak



**Figure 1** Plot of fractional monomer conversion vs. time for BA/MMA/GMA system; (a) effect of BA : MMA ratio and (b) effect of GMA content.

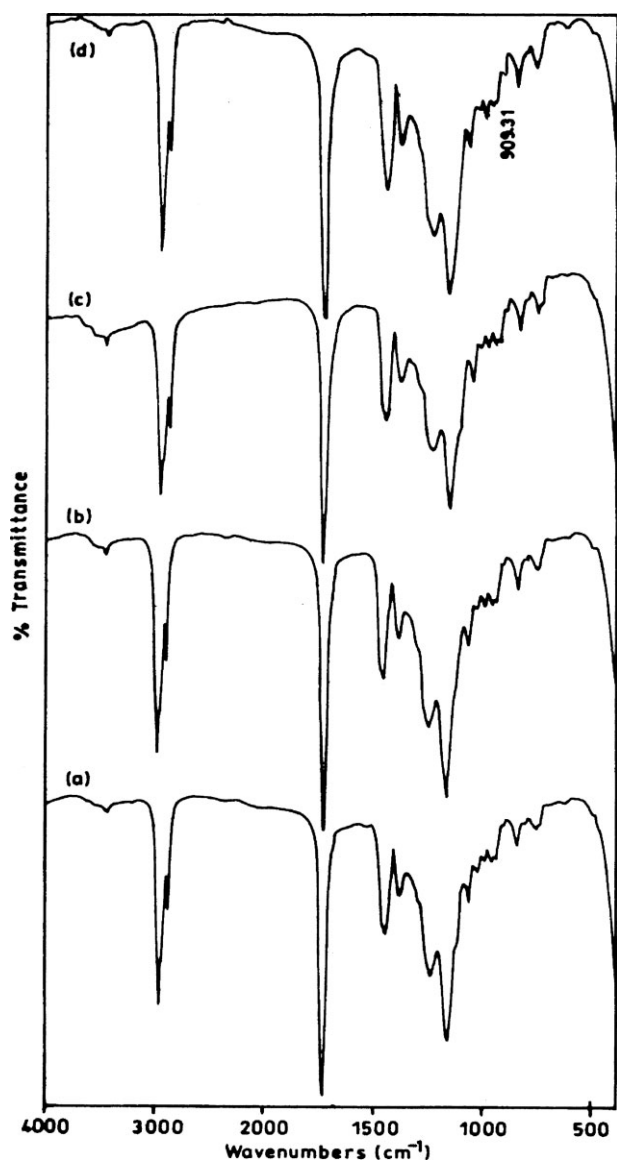


Figure 2 FTIR spectra of BA/MMA/GMA copolymers; (a) B-2, (b) B-5, (c) B-8, and (d) B-10.

at  $909\text{ cm}^{-1}$  in B-8 and B-10 showed the presence of GMA in the copolymers.

#### Chemical composition by NMR

Figure 3 shows the  $^1\text{H-NMR}$  spectra of copolymers recorded in  $\text{CDCl}_3$  using TMS as the internal standard. Absence of signal in the region of 5–6 ppm in  $^1\text{H-NMR}$  spectra of all the copolymers confirms the absence of free monomer.

The peaks at  $\delta\ 3.8\text{--}\delta\ 4.15$  are due to  $-\text{OCH}_2$  groups of both BA and GMA and the peaks at  $\delta\ 3.5$  ppm due to  $-\text{OCH}_3$  groups of MMA, respectively. At higher concentration of GMA (B-8, B-10), two small peaks were observed at  $\delta\ 2.8$  and  $\delta\ 2.6$  ppm due to  $-\text{CH}_2$  protons of epoxy group. The ratio of signal intensities has been used to determine the

copolymer composition by several authors.<sup>15-17</sup> In the present work, the ratio of intensities of  $-\text{OCH}_2$ : $-\text{OCH}_3$  derived from  $^1\text{H-NMR}$  spectra was used to calculate the copolymer composition and the results are given in Table III. There was good agreement between the theoretical and experimental values

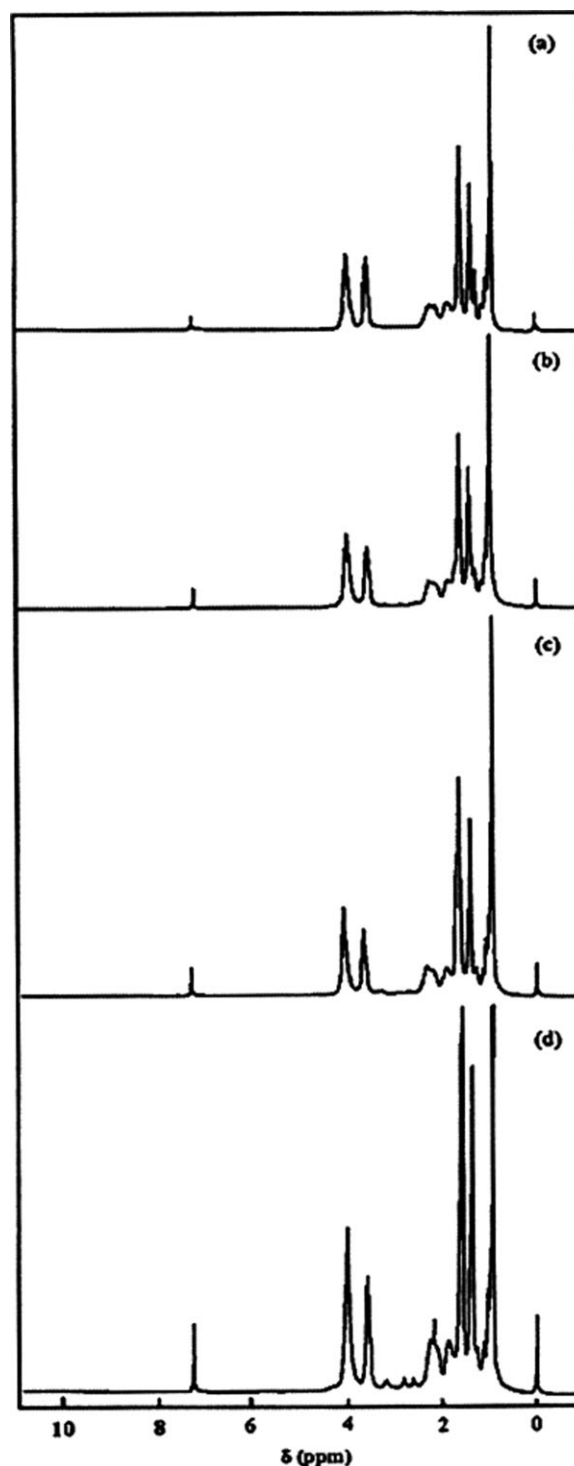


Figure 3  $^1\text{H-NMR}$  spectra of BA/MMA/GMA copolymers in  $\text{CDCl}_3$  at different ratio of GMA in  $\text{CDCl}_3$ ; (a) B-2, (b) B-5, (c) B-8, and (d) B-10.

**TABLE III**  
Copolymer Composition from  $^1\text{H-NMR}$  Analysis and Glass  
Transition Temperature of Copolymer

Sample code	Conversion (%)	Amount of MMA % (w/w)		$T_g$ ( $^{\circ}\text{C}$ )	
		In feed	In copolymer <sup>a</sup>	Experimental	Calculated (Fox equation)
B-1	99.5	24	25	-27	-27.3
D-1	99.2	35	26	-	-
B-2	99.3	24	23	-27.4	-27.7
C-2	99.3	29.5	23	-23	-22
D-2	97.1	34.5	31	-15	-15
B-3	98.8	23.5	29	-	-
B-5	99.3	23	19	-27	-26.1
C-5	99.6	28.5	27	-22	-20
B-8	99.1	22	23	-	-
B-10	99.5	22	29	-	-

<sup>a</sup> Calculated from  $^1\text{H-NMR}$ .

(calculated using NMR). Similarly in the  $^{13}\text{C-NMR}$  spectra of samples (Figure not shown) small peak due to the epoxy group of GMA was observed at 40– $\delta$  45 ppm. The other characteristic signals i.e. ( $>\text{C}=\text{O}$ ) group of esters ( $\delta = 170\text{--}180$  ppm),  $-\text{OCH}_2$  group of both BA and GMA ( $\delta 60\text{--}\delta 65$  ppm) and  $-\text{OCH}_3$  group of MMA ( $\delta 50\text{--}\delta 55$  ppm) were also observed.

### Molecular weight

The results of molecular weight ( $M_n$  and  $M_w$ ) and molecular weight distribution as determined by GPC using polystyrene as calibration standards are given in Table IV. All the samples had molecular weight with  $M_n$  values ranging from 1.01 to  $3.06 \times 10^4$  and  $M_w$  values in the range of  $1.15 - 3.06 \times 10^5$ . PDI val-

ues were very high, ranging from 7 to 12. The results of molecular weight (both in  $M_n$  and  $M_w$ ) did not show any definite trend as a function of monomer feed composition. The weight average molecular weight ( $M_w$ ) and polydispersity index was highest in case of sample D-2.

The Brookfield viscosity of the latexes determined using spindle No. 1 was in the range of 45–60 cps. This low viscosity show good film-forming behavior and adhesive property as it facilitates the flow of the latex in both the substrates during lamination.

### Gel content

A higher amount of gel content was observed in samples C-1, B-2, and C-2 (Table IV). However, no definite trend was observed as a function of monomer

**TABLE IV**  
Molecular Weight, Gel Content, Particle Diameter, and Peel Strength Data of BA/MMA/GMA Latexes

Sample no.	$M_n \times 10^{-4}$	$M_w \times 10^{-5}$	Polydispersity	Gel content (%)	Particle diameter (nm)	Peel strength (g/in.)
B-1	1.79	2.02	11.2	32.8	322.0	228.8
C-1	3.06	2.59	8.43	62.6	358.5	215.2
D-1	1.88	3.06	16.2	38.3	295.8	274.6
E-1	1.55	1.63	10.5	41.7	-	210.0
B-2	1.72	1.54	8.98	69.7	-	245.8
C-2	2.77	1.97	7.11	55.6	-	288.1
D-2	1.01	1.19	11.7	42.7	-	218.6
E-2	2.25	1.46	6.49	43.4	304.8	208.3
B-3	2.87	1.70	5.94	33.0	315.9	262.7
C-3	2.78	1.89	6.81	36.5	-	371.1
D-3	1.86	1.32	7.08	35.7	221.3	286.1
E-3	1.43	1.28	8.97	32.3	-	172.0
B-5	1.95	1.65	8.49	38.5	268.0	271.2
C-5	2.79	1.62	5.81	43.0	358.5	426.3
D-5	1.29	1.15	8.91	39.2	-	158.0
E-5	2.06	1.53	7.46	31.0	348.9	167.6
B-8	-	-	-	-	223	356.2
B-10	-	-	-	-	207	385.3

composition. The major contributor to the gel content in this system is likely to be the BA monomer and high BA content can lead to "back biting" or chain transfer to polymer, resulting in the formation of double bonds that can further polymerize and form branches.<sup>18</sup> The monomer starved conditions also favored chain transfer to polymer leading to the formation of highly branched polymer structures and microgels inside the latex.<sup>19</sup> On the other hand, an increase of MMA content in the copolymer reduces the gel content significantly (Table IV).

### Particle size distribution

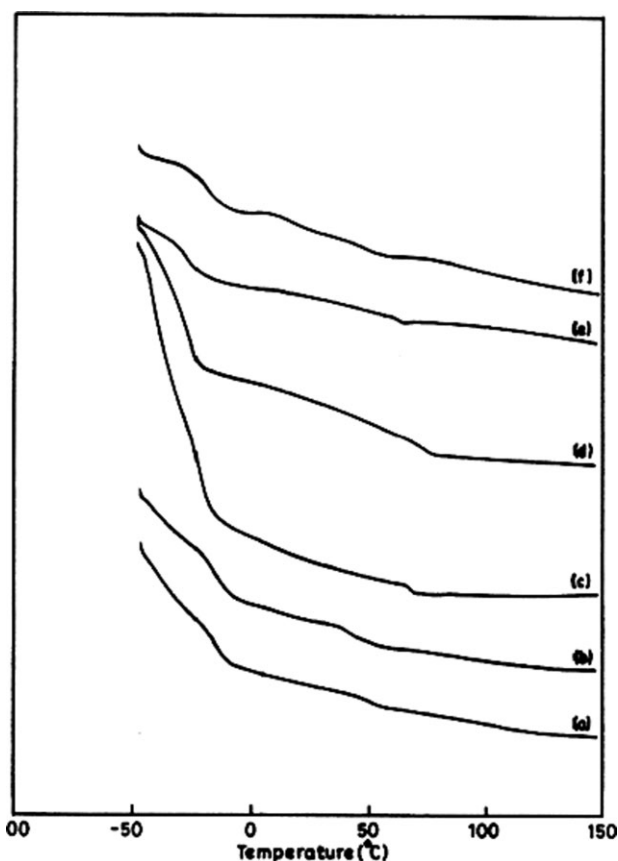
The results of particle size as determined by dynamic light scattering are given in Table IV. Particle size, as expected, remains unaffected by the effect of monomer composition. The samples C-1, C-3, and B-5 show lower particle diameter and a broader particle size distribution which might be due to the secondary particle generation. A broad particle size distribution with small particle diameter was also observed with increase in GMA content (B-8, B-10).

In all the experiments, a bimodal volume-average particle size distribution was observed which shows the generation of secondary particles during the reaction. In some cases a small peak around 25–30 nm was seen. This might be due to the polymerization of hydrophilic monomer in aqueous phase as their concentration on the surface of the polymer particle was more. Similar behavior has been reported by Xu et al.<sup>20</sup> The lower viscosity of the emulsion observed at a solid content of 56% could be due to the multimodal PSD.

In adhesive application, low viscosity latex is required for better spreading of the latex on substrate. Since the peel strength and gloss of adhesives mostly depends upon the structure of latex, particle diameter is an important parameter. Because of the small particle size, the latex film cast on the glass plate is clear and transparent. It is assumed that smaller particles could pack more tightly and coalesce during the drying process, thus increasing the area of contact between the adhesive and the substrate

### Glass transition temperature

The glass transition temperature ( $T_g$ ) was determined by recording DSC scans. Figure 4 shows the DSC scans of samples having varying amounts of GMA. A shift in the base line corresponding to  $T_g$  was observed in all the samples.  $T_g$  was noted as mid-point inflection and the results are given in Table III. There was good agreement between the  $T_g$  values calculated theoretically and determined using



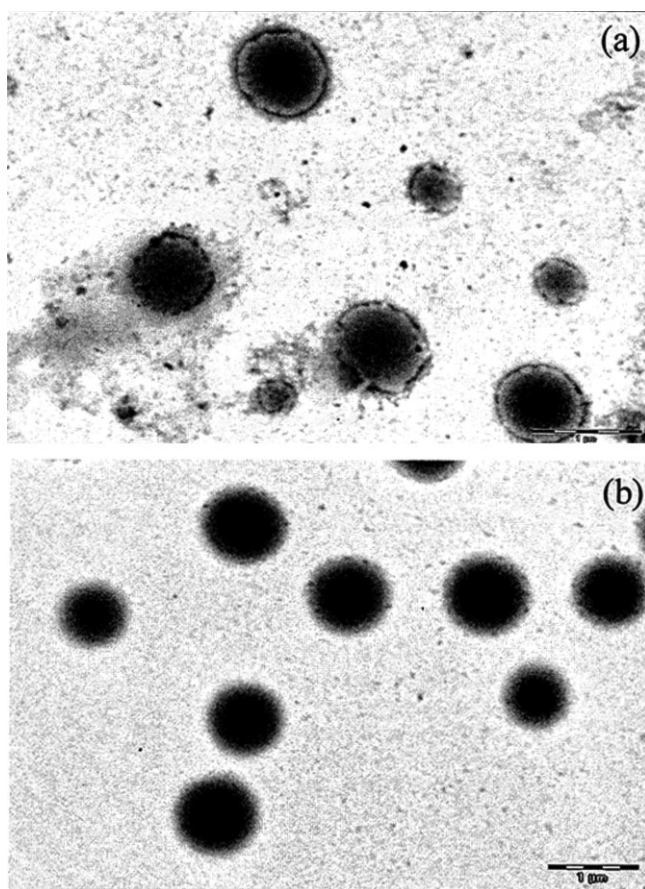
**Figure 4** DSC scans of polymers at different concentrations of GMA; (a) B-1, (b) B-2, (c) B-3, (d) B-5, (e) B-8, and (f) B-10.

DSC. In all samples, shift in base line corresponding to  $T_g$  of BA was observed below 0°C in the temperature range from -27 to -15°C. Homopolymer of BA has a  $T_g$  of -54°C and MMA has a  $T_g$  of 105°C. As expected,  $T_g$  of the copolymer increased with increasing amount of hard monomer MMA and GMA.

A second transition in the temperature range of 60–70°C was also observed in the DSC scans. This may be due to copolymer formed when a mixture of MMA and GMA was fed at the end of the polymerization.  $T_g$  was also calculated using the Fox equation, and the results are summarized in Table III. There was good agreement between the calculated and observed values of  $T_g$ .

### Morphology

Figure 5 shows the transmission electron micrographs of samples having 5% and 10% of GMA i.e. samples B-5 and B-10. As expected, a perfect core-shell structure was obtained in both the cases. In the latex with 10% GMA (B-10), a distinct shell layer (light gray) was present around the core (darker region). Because of chemical similarity between the



**Figure 5** TEM micrographs of samples (a) B-5 and (b) B-10.

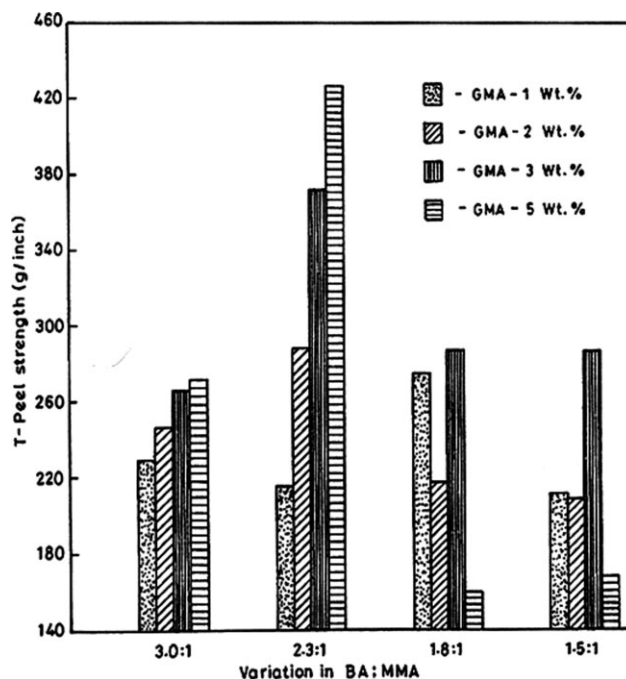
core and shell polymer, phase separation was not distinct. The small shell thickness is due to the presence of hydrophilic and functional group at the surface of the particle. MMA and GMA, being more hydrophilic as compared to BA, might migrate to the surface of the shell thus forming a hard shell.<sup>6</sup> But with increase in GMA content, the particles were more uniform and shell was more distinct as shown in Figure 5(b). The polymerization conditions such as surfactant, initiator, monomer and seed polymer which affect the interfacial tension was kept constant during the polymerization.<sup>21</sup>

### T-Peel strength

The results of T-peel strength for polyester /polyethylene laminates with latexes of varying copolymer composition are given in Table IV. T-peel strength depends both on cohesive and adhesive strength. Figure 6 showed the effect of BA : MMA ratio as well as the GMA content in the copolymer. In series B (i.e. BA : MMA = 3 : 1) and series C (i.e. BA : MMA = 2.3 : 1), peel strength increased with increasing amount of GMA content. However the comparison of samples at equal weight percentage of GMA i.e. B-1 and C-1, B-2 and C-2, B-3 and C-3,

and B-4 and C-4, peel strength was higher in C series as compared to B series. In case of series D (i.e. BA : MMA = 1.8 : 1) and series E (i.e. BA : MMA = 1.5 : 1), it did not show any definite trend with increasing GMA content. All the samples prepared using BA : MMA in the ratio of 1.8 – 1.5 : 1 showed poor T-peel strength at all levels of GMA content. Unexpectedly samples with higher amount of GMA showed poor peel strength. The results revealed that T-peel strength of polymer depend on both BA/MMA ratio and the functional monomer (GMA) concentration. Increase in peel strength with increase in GMA content at higher BA : MMA ratio could be due to the interaction between epoxy group of GMA and –COOH or –OH group on the surface of substrate generated after corona treatment as well as due to higher BA content which enhances the tack and film-forming characteristics.

The bond strength mainly depends on the adhesive and cohesive strength of the adhesive systems which mainly depend upon the monomer composition in the final latex. The adhesive strength increases with increase in BA concentration. BA being soft and tacky in nature provides the required cohesive strength to the system. With increases in its concentration in the copolymer, cohesive strength increases and hence the adhesive strength drops down. But the presence of MMA increases the hardness of copolymer thus increasing the adhesive strength. On further increase of MMA concentration, the cohesive strength crosses the optimal level because of increasing hardness, thus adversely



**Figure 6** T – Peel strength of laminates at different mono-mer ratio.



affecting the adhesive strength. The bond strength also depends on the concentration of functional monomer GMA. At a constant ratio of BA/ MMA, the bond strength increases with increase in GMA content in series B and C. It was assumed that the pendant epoxy group of GMA hydrolyzed to hydroxyl amine upon curing with  $\text{NH}_3$  which is responsible for the increase of bond strength.<sup>2</sup>

The glass transition temperatures of the above latexes lie in the range of PSA. So the surface tack of all the emulsions was measured by a loop tester (Model: LT 100, Cheminstruments, USA) by casting a film on the PET film. The loop tack was almost negligible in all the latexes. The experiments having BA amount greater than 72–74%, shows the loop tack of 0.06 to 0.15 which is negligible in comparison to that of PSA. The other compositions have loop tack less than 0.03. On the other hand, samples having BA amount more than 75% showed a loop tack of more than 1.5 and behaved like PSA.

Adhesive strength was also determined after immersion of samples in water at 25°C for 72 h. About 20% loss in the bond strength was observed after immersion in water. To evaluate the resistance in alkali and/or acid, the samples were immersed in 5% of aqueous solution of NaOH and HCl solution and the strength was measured. After immersion for 72 h, T-peel strength decreased by  $\sim 10\%$ .

### CONCLUSION

From these studies it can be concluded that the optimum ratio of BA : MMA (2.3 : 1) at 5% GMA content showed highest adhesive strength. In case of series B (BA : MMA ratio of 3 : 1), adhesive strength increased with increasing amounts of GMA up to 10%. The latexes with molecular weight ( $M_w$ ) in the

range of  $1.5\text{--}2.0 \times 10^5$  and  $T_g$  in the range of  $-22$  to  $-20^\circ\text{C}$  showed good adhesive strength.

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