

Preparation and Properties of Triethoxyvinylsilane-Modified Styrene - Butyl Acrylate Emulsion Copolymers

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The copolymers of triethoxyvinylsilane (TEVS) with styrene (St), butyl acrylate (BA), and methacrylic acid (MAA) were prepared by emulsion polymerization. The copolymerization was carried out by using auxiliary agents at 90 °C in the presence of potassium peroxydisulfate (KPS) as the initiator. Nonylphenol ethylene oxide – 40 units (NP-40) and sodium lauryl sulfoacetate (SLSA) were used as nonionic and anionic emulsifiers, respectively. The resulting copolymers were characterized by Fourier transform infrared spectroscopy (FTIR). Thermal properties of the copolymers were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The morphology of copolymers was also investigated by optical microscopy (OM) and then the effects of temperature, agitation speed, initiator and silicone concentrations on the properties of the silicone-containing St/BA/MAA emulsion copolymers were discussed. The obtained copolymers have high solid content (50%) and can be used in emulsion paints as a binder.

The monomer conversion and monomer conversion versus time histories indicate that by increasing the TEVS concentration the polymerization rate decreases.

Key Words: Triethoxyvinylsilane, emulsion copolymerization, poly (styrene-co- butylacrylate).

Introduction

Copolymers of acrylics and styrene have many specific features such as good film-forming, gloss, transparency, and mechanical properties, and their corresponding products have been widely used as coatings, paints, and adhesives. However, the poor ultraviolet light resistance and low (or high) temperature resistance limit their applications. In contrast, silicone compounds have many excellent properties such as high flexibility and hydrophobicity, low surface tension, low glass transition temperature (T_g), weather resistance, and excellent thermal stability, but the low tensile strength and relatively high costs limit their applications.

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Thus, the combination of polyacrylates or poly (acrylates-co-styrene) with silicone has been of importance and interest during the past few decades.^{1–21} Since waterborne paint is environmentally friendly, latices have been the most popular products for coatings etc. Modification of polyacrylates or poly (acrylates-co-styrene) latices by silicone is a convenient and effective way of improving their properties. That is why there is abundant literature about this subject, and due to the strong commercial interest many studies have appeared as patents.^{1–6,10–16} Among these works, 3 methods were widely used: (a) core-shell (polysiloxane-other polymers) composite latex particles were generally prepared by multistage emulsion polymerization typically involving, first, forming the polysiloxane seed particle and, second, polymerizing the second monomers into the polysiloxane seed;^{1–9} (b) copolymerization of vinyl monomers with vinyl silanes or polymerizable polysiloxanes was also investigated;^{10–18} and (c) in recent years, novel core/shell latex particles with polyacrylates or polystyrene as a core and with polysiloxane as a shell were successfully synthesized through a special seeded emulsion polymerization, and properties of the latices and latex films were also studied.^{19–22}

In the present study, polymer latexes were successfully prepared by the emulsion copolymerization of styrene (St), butyl acrylate (BA), and methacrylic acid (MAA) monomers with triethoxyvinylsilane (TEVS) catalyzed by nonylphenol ethylene oxide – 40 units (NP-40) and sodium lauryl sulfoacetate (SLSA). By changing the silicone concentration and surfactant kinds, a series of latexes with different TEVS contents were obtained. The morphology of the latexes was investigated by optical microscopy. The copolymerization between St, BA and MAA monomers and TEVS was confirmed by FT-IR. The heat stability, the glass transition temperature T_g , and water absorption ratio were also studied.

Experimental

Materials

The monomers, St (Aldrich) and BA (Aldrich), were freed from the inhibitor by shaking with 10% aqueous NaOH, washing with water, and drying over Na₂SO₄. They were then distilled under reduced pressure before use and stored at –20 °C to avoid thermal polymerization. The MAA (Merck) was distilled directly under vacuum and stored at 0 °C. TEVS (Merck) was analytically graded and used directly without further purification. The initiator, KPS (Merck), and buffer, tetra-sodium pyrophosphate anhydrous (TSPP) (Fluka), were used as received. The emulsifiers, SLSA and sodium dodecyl sulfate (SDS), were purchased from Hoechst AG, Germany. Sodium dodecyl benzene sulfonate (SDBS) was provided by Henkel KGaA, Germany, sodium lauryl ether sulfate (SLES) and sodium cocoil isotionate (SCI) were kindly supplied by Akzo Chemicals BV, Netherlands, and nonylphenol ethylene oxide-40 units (NP, Iconol NP-40, BASF), Germany, also were used as received. Water was distilled and deionized.

Polymerization procedure

Semi-continuous emulsion copolymerization was carried out using a 500-mL 5-necked round-bottom flask equipped with a reflux condenser, stainless steel stirrer, sampling device, and 2 separate feed streams. The first feed stream was a solution of BA, St, MAA, TEVS, and anionic surfactant. The other feed was the initiator solution 7.8×10^{-3} mol L⁻¹. Before emulsion copolymerization start-up, the reaction vessel was first charged with the desired amounts of water, emulsifier, TSPP, and initiator solution, in that order. During

polymerization, the reaction mixture was stirred at a rate of 50 rpm and the temperature was maintained at 80 °C. After 5 min, 10% of the total amount of the monomer mixture was added to the flask over 13 min. Then the temperature was kept at 90 °C until the end of polymerization. The polymerization was performed with a feeding rate of 1.0 mL/min under air atmosphere to investigate the effect of temperature, agitation speed, initiator and silicone concentration on monomer conversion. A typical recipe for the preparation of a 50% solid product is given in the Table. In order to determine the conversion percentage during the polymerization process, it was necessary to withdraw samples at various intervals from the reaction vessel. These samples were relatively small so that the overall composition in the reactor was not seriously affected; once a sample was removed and put in a watch glass, polymerization was terminated by the addition of 7 ppm hydroquinone. Then 2 drops of ethanol were added to the sample as a coagulant and the contents of the watch glass were evaporated at room temperature and then dried to a constant weight in a vacuum oven. The conversion % was determined gravimetrically. The purification and precipitation of the polymer were done using Grassie's method.²³ However, the produced copolymers have low solubility in various solvents such as toluene, benzene, acetic acid, xylene, *N, N'* dimethylformamide (DMF), dimethylsulfoxide (DMSO), *N*-methylpyrrolidone (NMP), acetone, and dichloroethane, which makes their characterization difficult by GPC or NMR. Their morphology as well as thermal properties gave important information about their structure and property relation. The appearance properties of the products such as adhesiveness, transparency of the film, and elasticity are excellent and indicate the formation of copolymers. The reproducibility of the monomer conversion was checked by repeating the experiments and each monomer conversion considered in this paper is an average of at least 4 measurements. The deviation between 4 runs was always less than 3%.

Table. Polymerization recipe at 90 °C.

| Compound | Initial charge | Feed | Total |
|--|----------------|-------|-----------------|
| St (g) | 6 | 44 | 50 |
| n-BA (g) | 7 | 45 | 52 |
| MAA (g) | 0.05 | 0.45 | 0.50 |
| TEVS (g) | 10% w | 90% w | Variable (0-12) |
| Buffer: sodium pyrophosphate (g) | 0.30 | - | 0.30 |
| Initiator: KPS (g) | 0.06 | 0.34 | 0.40 |
| Deminerlized water(g) | 54 | 42 | 96 |
| Nonionic emulsifier: Nonylphenol ethylene oxide – 40 units (NP-40) (g) | 2.80 | 0.60 | 3.40 |
| Anionic emulsifier: sodium lauryl sulfoacetate (SLSA) (g) | - | 3.0 | 3.0 |

Polymer characterization

DSC thermograms were obtained on a Mettler TA 4000 Model apparatus at a heating rate of 10 °C/min. The glass transition temperature (T_g), was measured at the onset of the corresponding heat capacity jump. TGA measurements of copolymers were carried out by a Dupont TGA 951 under nitrogen atmosphere at a heating rate of 10 °C/min. FT-IR spectra of the copolymers were obtained using a Nicolet Impact 400 D Model spectrophotometer and saturated water absorption (A_w) of the films was measured as described below: a certain weight (about 2 g) of film was put into water for 14 days at 20 °C, and then it was dried again. Comparing the weight of the film before drying ($W1$) and after drying ($W2$), the absorption ratio A_w (%) = $(W1 - W2)/W2 \times 100$.

Results and Discussion

Agitation effect on polymerization rate

In heterogeneous reaction systems, mass transfer is an important factor affecting the polymerization rate. To investigate the mass transfer effect on the polymerization rate, experiments were carried out under conditions of different impeller speeds.²⁴

Experimental results are presented in Figures 1 and 2, where the conversions of monomer to polymer are plotted against reaction time at different agitation speeds. In these experiments, initiator concentration, I_0 , was $7.8 \times 10^{-3} \text{ mol L}^{-1}$ in H_2O , and the concentration of total monomer added per unit volume of aqueous phase, M_0 , was 4.60 mol L^{-1} in H_2O . In Figure 1, agitation speeds show the highest polymerization rate at 50 rpm and lowest polymerization rate at 300 rpm. Figure 2 confirms a decrease in the polymerization rate with increasing agitation speed. However, a reduction in impeller speed to 50 rpm leads to earlier attainment of acceleration in the polymerization. Accordingly, the reaction time required to attain high conversion is shorter at 50 rpm than at the other impeller speeds. According to Arai et al.,²⁵ a similar tendency was observed for emulsion polymerization in the absence of a solid phase and was explained by considering a monomer mass transfer from monomer droplets to the polymer particles formed in the aqueous phase. Air atmosphere is also very effective. Oxygen prolongs inhibition and so an increase in the agitation speed causes the arrival of a lot of oxygen in the polymerization, and consequently the polymerization rate decreases.

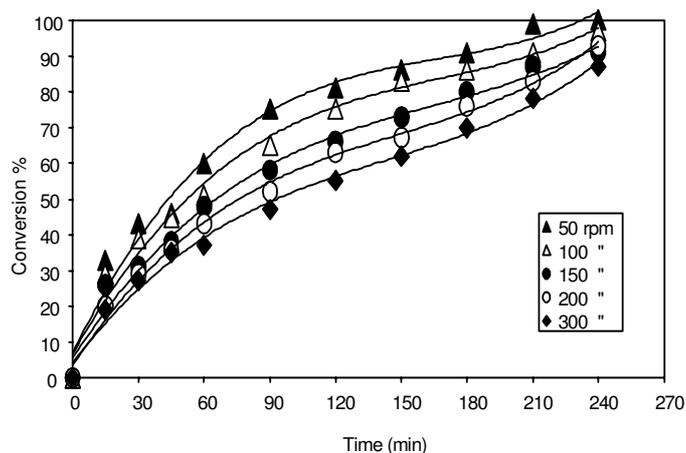


Figure 1. The effect of agitation speed on monomer conversion vs. polymerization time at (▲) 50; (△) 100; (●) 150; (○) 200; and (◆) 300 rpm. $[M]_0 = 4.60 \text{ mol L}^{-1}$, $[\text{TEVS}] = 0.30 \text{ mol L}^{-1}$, $T = 90 \text{ }^\circ\text{C}$, 50 rpm, $[I]_0 = 7.8 \times 10^{-3} \text{ mol L}^{-1}$.

Effect of initiator concentration

Figure 3 shows the variation in conversion with time at 4 initiator levels. As expected,^{26–28} the polymerization rate increases with increasing initiator concentration. This behavior can be explained as follows. First, the higher the initiator concentration, the higher the number of adsorbed fixed radicals on the particle surface and therefore the lower the retardation of polymerization due to the seed particles. Secondly, by increasing initiator concentrations the proportion of usual emulsion polymerization increases in the aqueous phase, and, at very high initiator concentrations, the proportion of surface layer polymerization will be

negligible. This difference also may be attributed to the homogeneous nucleation of particles that is typical in styrene emulsion polymerization. Analyzing the above results, it is difficult to decide what the main effect is.

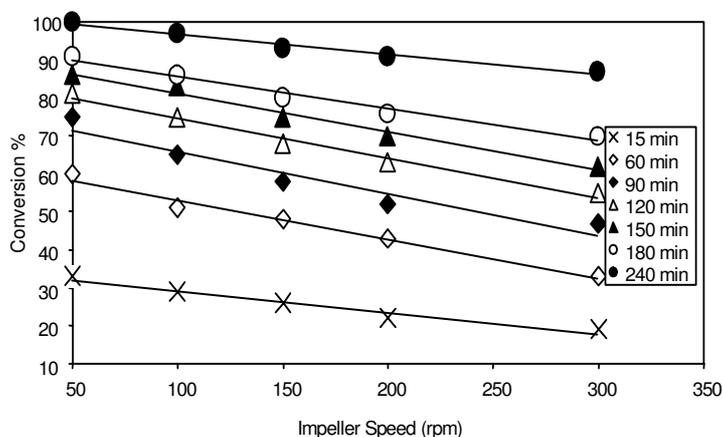


Figure 2. The effect of agitation speed on monomer conversion vs. impeller speed at (x) 15; (◇) 60; and (◆) 90; (△) 120; (▲) 150; (○) 180; and (●) 240 min. $[M]_0 = 4.60 \text{ mol L}^{-1}$, $[\text{TEVS}] = 0.30 \text{ mol L}^{-1}$, $T = 90 \text{ }^\circ\text{C}$, 50 rpm, $[I]_0 = 7.8 \times 10^{-3} \text{ mol L}^{-1}$.

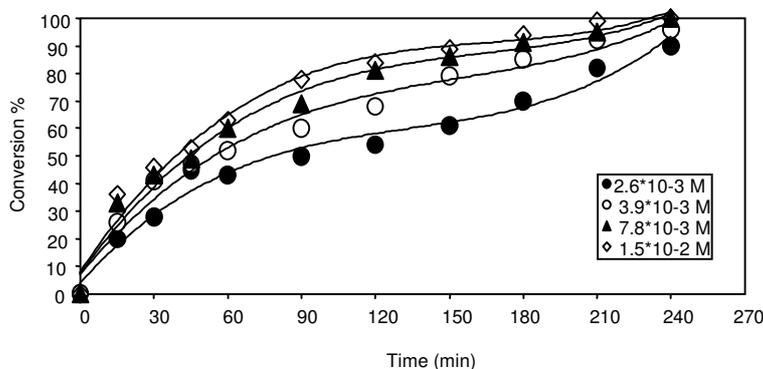


Figure 3. The effect of initial initiator concentration on monomer conversion vs. time at $[\text{k}_2\text{S}_2\text{O}_8] = (\bullet) 2.6 \times 10^{-3}$; (○) 3.9×10^{-3} ; (▲) 7.8×10^{-3} ; and (◇) $1.5 \times 10^{-2} \text{ mol L}^{-1}$, $[M]_0 = 4.60 \text{ mol L}^{-1}$, $[\text{TEVS}] = 0.30 \text{ mol L}^{-1}$, $T = 90 \text{ }^\circ\text{C}$, 50 rpm.

Effect of temperature

The effect of temperature of maximum conversion and initial rate of emulsion copolymerization of TEVS containing St, BA, and MAA is presented in Figure 4. The temperature range studied at fixed concentration of monomers and initiator was between 70 and 90 °C. It was observed that both the initial rate of polymerization and maximum conversion increased with increasing temperature.

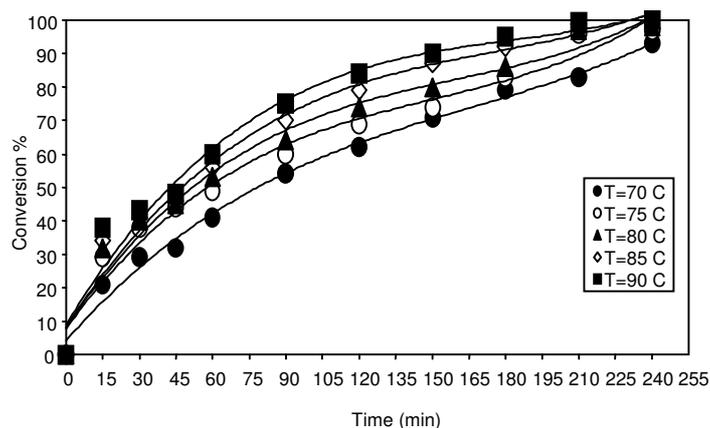


Figure 4. The effect of reaction temperature on monomer conversion vs. time at (●) 70; (○) 75; (▲) 80; (◇) 85 and (■) 90 °C. $[M]_0 = 4.60 \text{ mol L}^{-1}$, $[\text{TEVS}] = 0.30 \text{ mol L}^{-1}$, $T = 90 \text{ °C}$, 50 rpm, $[I]_0 = 7.8 \times 10^{-3} \text{ mol L}^{-1}$.

Effects of TEVS concentration

Addition of silane compounds in acrylic emulsion provides beneficial effects by improving various mechanical properties such as water and weather ability and good acid and alkali resistance.^{29–31} In addition, the silicone incorporated plays the roles of coupling agent and softener³² and it is enriched on the surface of the film.³³ On the other hand, You et al.³⁴ demonstrated that silanes can be bonded with hydroxyl groups on the surface of substrate to increase the adhesion, and FTIR analysis indicated that organic functional silanes can be polymerized with other monomers.

Although the copolymerization of St, BA, and MAA has been well established,³⁵ their copolymerization in the presence of TEVS has not been reported. Therefore, the role of this monomer is not perfectly clear. It is possible that during the copolymerization process this monomer will make part of the copolymer chain. However, the extent of its incorporation in the polymer chain was not measured. Figures 5 and 6 show the effect of TEVS concentration on the monomer conversion versus time and monomer conversion versus silicone percentage, respectively, where the initial initiator and total monomer concentrations were fixed at $I_0 = 7.8 \times 10^{-3} \text{ mol L}^{-1}$ and $[M]_0 = 4.60 \text{ mol L}^{-1}$. It can be observed that the rate of reaction decreased with increasing amounts of TEVS in both figures. It is known that the rates of propagation and consequently copolymerization in a radical copolymerization reaction are inversely related to the termination rate constant. As the amount of TEVS increased, it acted as a chain transfer agent and the rate of polymerization decreased. Although chain transfer generally does not decrease the polymerization rate, this matter has been observed by the authors many times and it can be justified as follows. The radicals obtained from TEVS are more stable in comparison with other radicals that exist in the TEVS containing emulsion copolymers. This stability is due to the π bonds and resonance effects of double bonds, and consequently a reduction in the reaction rate was observed.

Effect of surfactant kinds on the rate of copolymerization

The effects of different types of surfactants on the monomer conversion are shown in Figure 7. These surfactants, which were used in the copolymerization of St/BA/MAA/TEVS, are NP-40/SCI, NP-40/SDBS, NP-40/SLES, NP-40/SDS, and NP-40/SLSA. It can be seen from this figure that the rate of the copolymerization reaction varies with changes in the kind of surfactant system. Moreover, in Figure 7 kinds of

surfactant show that the highest copolymerization rate belongs to the curve of surfactant NP-40/SLSA and the lowest copolymerization rate belongs to the curve of NP-40/SCI. Therefore, this is the logical reason for choosing the NP-40/SLSA emulsifier system for the whole copolymerization process.

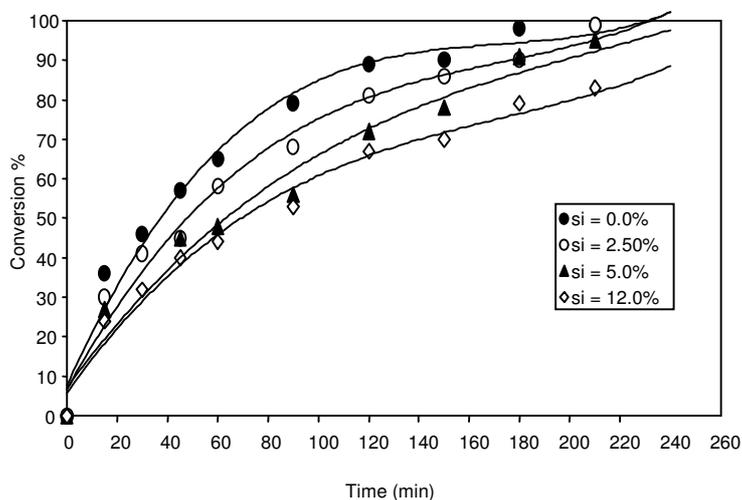


Figure 5. The effect of initial TEVS concentration on monomer conversion vs. time at (●) 0.0%; (○) 2.50%; (▲) 5.0%; and (◇) 12%. $[M]_0 = 4.60 \text{ mol L}^{-1}$, $[\text{TEVS}] = 0.30 \text{ mol L}^{-1}$, $T = 90 \text{ }^\circ\text{C}$, 50 rpm, $[I]_0 = 7.8 \times 10^{-3} \text{ mol L}^{-1}$.

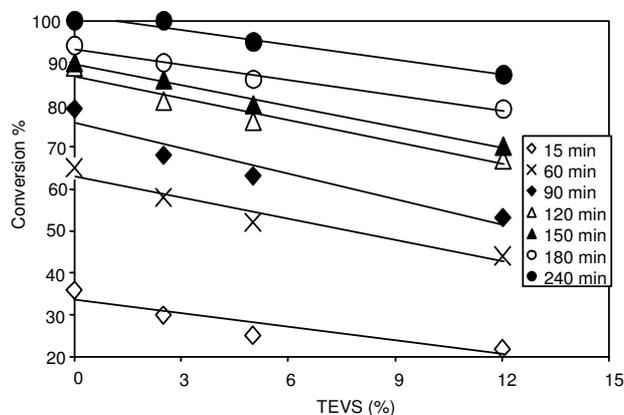


Figure 6. The effect of initial TEVS concentration on monomer conversion vs. silicone percentage at (◇) 15; (×) 60; (◆) 90; (△) 120; (▲) 150; (○) 180; and (●) 240 min. $[M]_0 = 4.60 \text{ mol L}^{-1}$, $[\text{TEVS}] = 0.30 \text{ mol L}^{-1}$, $T = 90 \text{ }^\circ\text{C}$, 50 rpm, $[I]_0 = 7.8 \times 10^{-3} \text{ mol L}^{-1}$.

It is interesting to mention that the sodium cocoyl isethionate (SCI) is a derivative of the acyl isethionates, which are fairly strong acids and they will be hydrolyzed in aqueous solutions spontaneously. On the other hand, it is an unknown fact that the effects of acyl isethionates are milder in comparison with those of the sulfuric acid and alkyl sulfonates. For this reason, the SCI does not show the properties of a suitable surfactant.

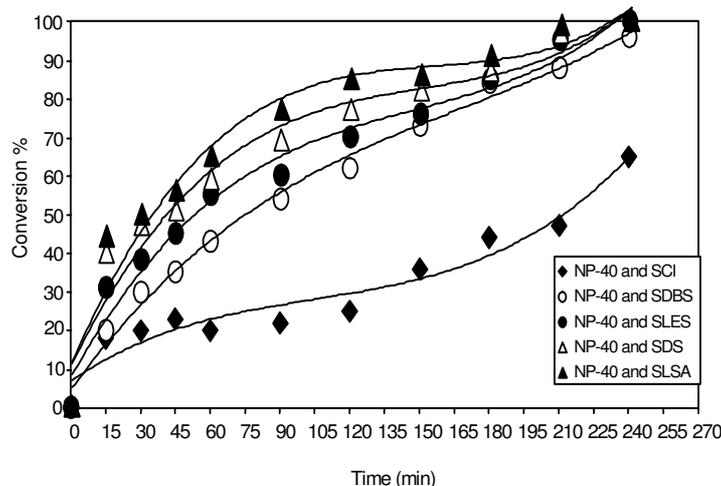


Figure 7. The effect of surfactant kinds on monomer conversion vs. time at (♦) NP-40 and SCI; (○) NP-40 and SDBS; (●) NP-40 and SLES; (△) NP-40 and SDS and (▲) NP-40 and SLSA. $[M]_0 = 4.60 \text{ mol L}^{-1}$, $[\text{TEVS}] = 0.30 \text{ mol L}^{-1}$, $T = 90 \text{ }^\circ\text{C}$, 50 rpm, $[I]_0 = 7.8 \times 10^{-3} \text{ mol L}^{-1}$.

Water absorption ratio of the latex films

The poly (St/BA) latex was one of the basic formulation components of the waterborne coatings, and the water resistance of the waterborne coatings was mostly determined by the latex polymer hydrophobicity. The water absorption ratio of the latex films is an important parameter for the characterization of hydrophobicity. As shown in Figure 8, the absorption ratio was greatly influenced by the content of silicone. With the increase in silicone content, the water absorption ratio of the latex films decreased, which can contribute to the excellent hydrophobicity of silicone. Therefore, it can be concluded that higher silicone content would give better water resistance.

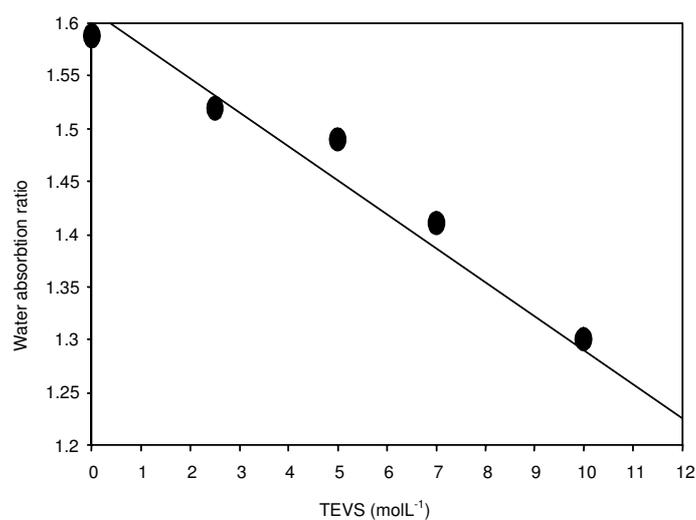


Figure 8. Effects of the TEVS content seed latex to water absorption ratio of the latex films.

Solubility and FTIR analysis

The emulsion copolymers basically have low solubility or do not have any solubility in organic solvents at all. These copolymers, which have been synthesized from St, BA, and MAA with or without TEVS, are not exceptions. They are not soluble even in aprotic polar solvents such as NMP, DMSO, DMF, or dimethyl acetamide (DMAc). This insolubility could be due to conversion of the polymer samples to gelation immediately during drying under air atmosphere or vacuum. Different procedures for the preparation, purification, and drying of the polymer samples were carried out. For example, the product was isolated by filtration after precipitation with a large amount of methanol and dried under vacuum at 60 °C. After 48 h it was observed that it is insoluble in all of the above-mentioned solvents. It is worth mentioning that the obtained copolymers will turn to gel with the addition of 2 drops of ethanol after dissolving in the DMF, DMSO, THF, toluene, and benzene, respectively. The characterization of these copolymers is very difficult due to their solubility. For example, NMR study of these copolymers is nearly impossible to perform, but FTIR spectra in the region from 4000 to 500 cm^{-1} were recorded with a sample prepared by making a film of the latex on the surface of a glass and drying it, and then removing the film from the glass. Figure 9 shows the typical FTIR spectra of (A) polystyrene, (B) poly (St-co-BA), and (C) poly (St-co-BA-co-TEVS) copolymers, respectively. The peaks at 3070, 1733, and 1600 cm^{-1} were associated with C–H of Ph, C=O, and C=C of Ph stretch of the poly (St-co-BA), respectively. Silicone could be characterized by Si–CH₃ symmetric deformation, stretching vibration at 1260 and 801 cm^{-1} , respectively; and Si–O–Si asymmetric stretching in the range 1100–1000 cm^{-1} . From these spectra, it is clear that silicone was successfully copolymerized to poly (St-co-BA).

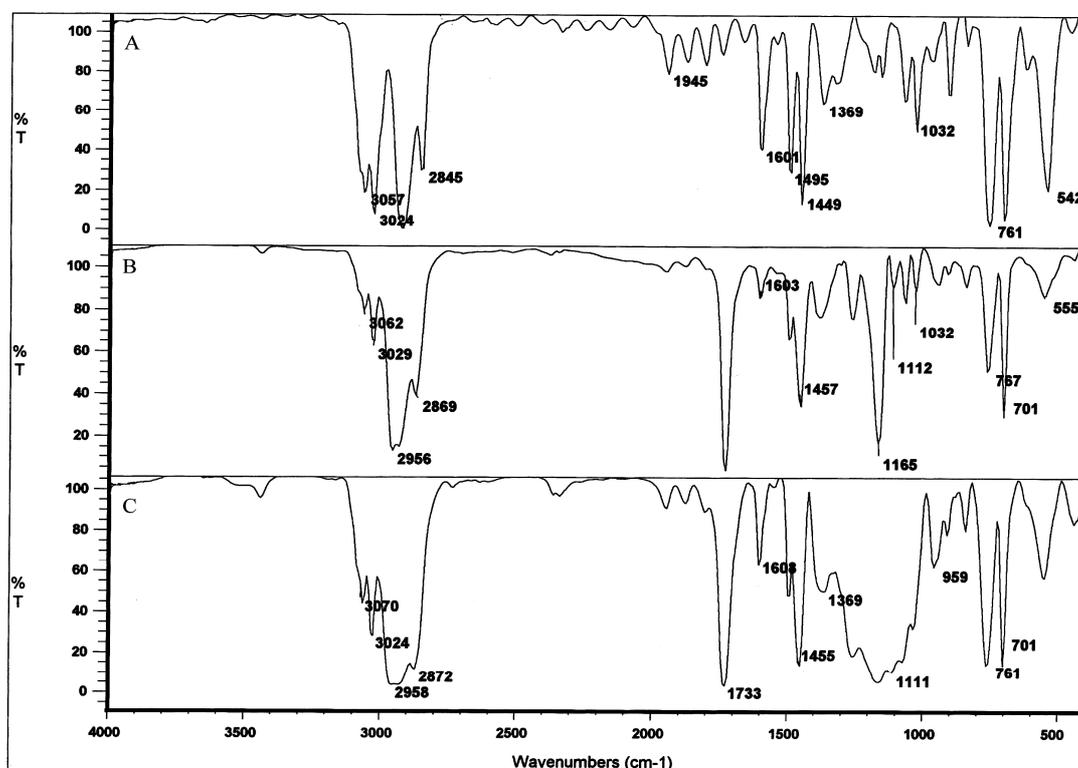


Figure 9. FTIR spectra of (A) poly (St), (B) (St/BA) and (C) (St/BA/TEVS) copolymers. $[M]_0 = 4.60 \text{ mol L}^{-1}$, $[\text{TEVS}] = 0.30 \text{ mol L}^{-1}$, $T = 90 \text{ }^\circ\text{C}$, 50 rpm, $[I]_0 = 7.8 \times 10^{-3} \text{ mol L}^{-1}$.

Morphologies of latex particles at different TEVS concentrations

The particle morphologies of the TEVS containing St/BA copolymers were examined by optical microscopy. Figure 10 is a micrograph of the latex particles of samples that contain 0.00%, 2.50%, 5.00%, and 12.00% TEVS. According to these micrographs, the St/BA copolymers have a very low particle size compared to TEVS modified samples, and by increasing the TEVS concentration the particle size increases and their size distributions become narrower. It is worth mentioning that the St/BA copolymers have considerable porosity on their surfaces compared to TEVS modified sample, and by increasing the TEVS concentration the porosity decreased and reached the minimum, and the surfaces of polymer films were soft and smooth. On the other hand, there are some tiny cracks on the surface of micrograph A in comparison with the others. These results suggest that St/BA and MAA monomers were completely polymerized in the presence of TEVS.

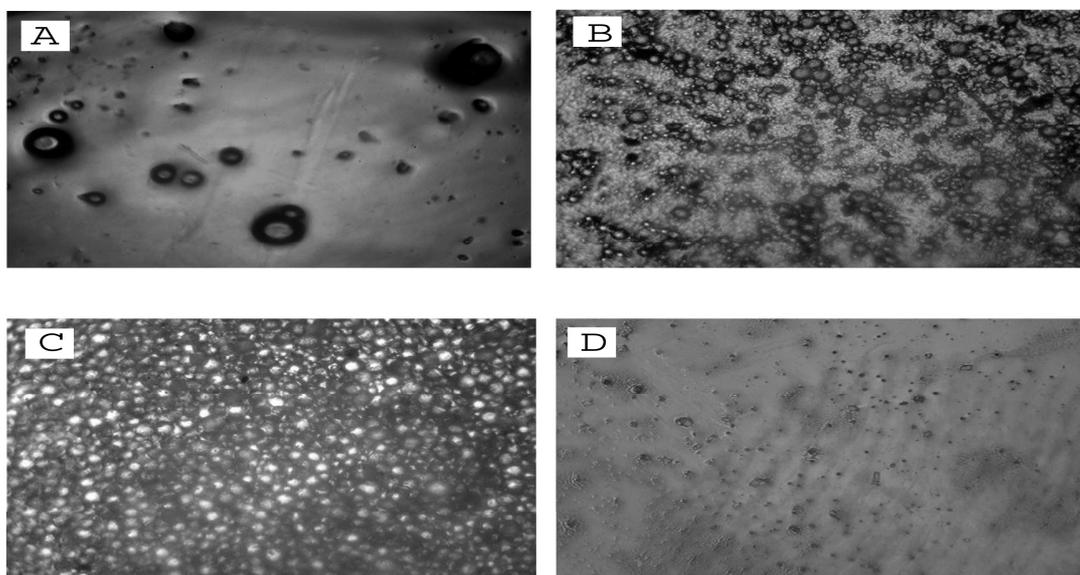


Figure 10. Optical microscopy pictures of (A) St/BA copolymer (B) with 2.50%, (C) with 5.00%, and (D) with 12.00% TEVS, $[M]_0 = 4.60 \text{ mol L}^{-1}$, $[\text{TEVS}] = 0.30 \text{ mol L}^{-1}$, $T = 90 \text{ }^\circ\text{C}$, 50 rpm, $[I]_0 = 7.8 \times 10^{-3} \text{ mol L}^{-1}$.

Thermal properties

The thermal properties of St/BA and TEVS containing St/BA copolymers were evaluated by means of TGA/DTG and DSC under nitrogen atmosphere and are shown in Figures 11 and 12. The St/BA emulsion (Figure 11A) shows a stable situation up to 200 °C. The chemical decomposition will start after this temperature and the maximum decomposition is at around 380 °C. On the other hand, the silicone modified St/BA copolymers exhibited thermal decomposition similar to the above, but the maximum decomposition was around 390, 400, and 425 °C for B, C, and D thermograms, which contain 2.50%, 5.00%, and 12% TEVS, respectively. Based on these results, it is concluded that the existence of TEVS moiety in the copolymers causes some thermal stability, and by increasing the amount of silicone thermal stability increases. The DSC curve of the copolymers is shown in Figure 12A-D for 0.00%, 2.50%, 5.00%, and 12.00% TEVS, respectively. Figure 12A reveals an endothermic shift around -20 °C, which corresponds to T_g without TEVS, and the

T_g is around 0.00 °C for B, and 3 and 5 °C for C and D thermograms, respectively. From these data it is very interesting that without TEVS the resulting copolymer is thermoplastic, while by adding TEVS the copolymer will have a drastic effect on lowering its T_g and shift to the elastomeric materials while its T_m remain unchanged. According to these results, it is found that the presence of TEVS moiety causes the change in thermal behavior and particularly affects T_g.

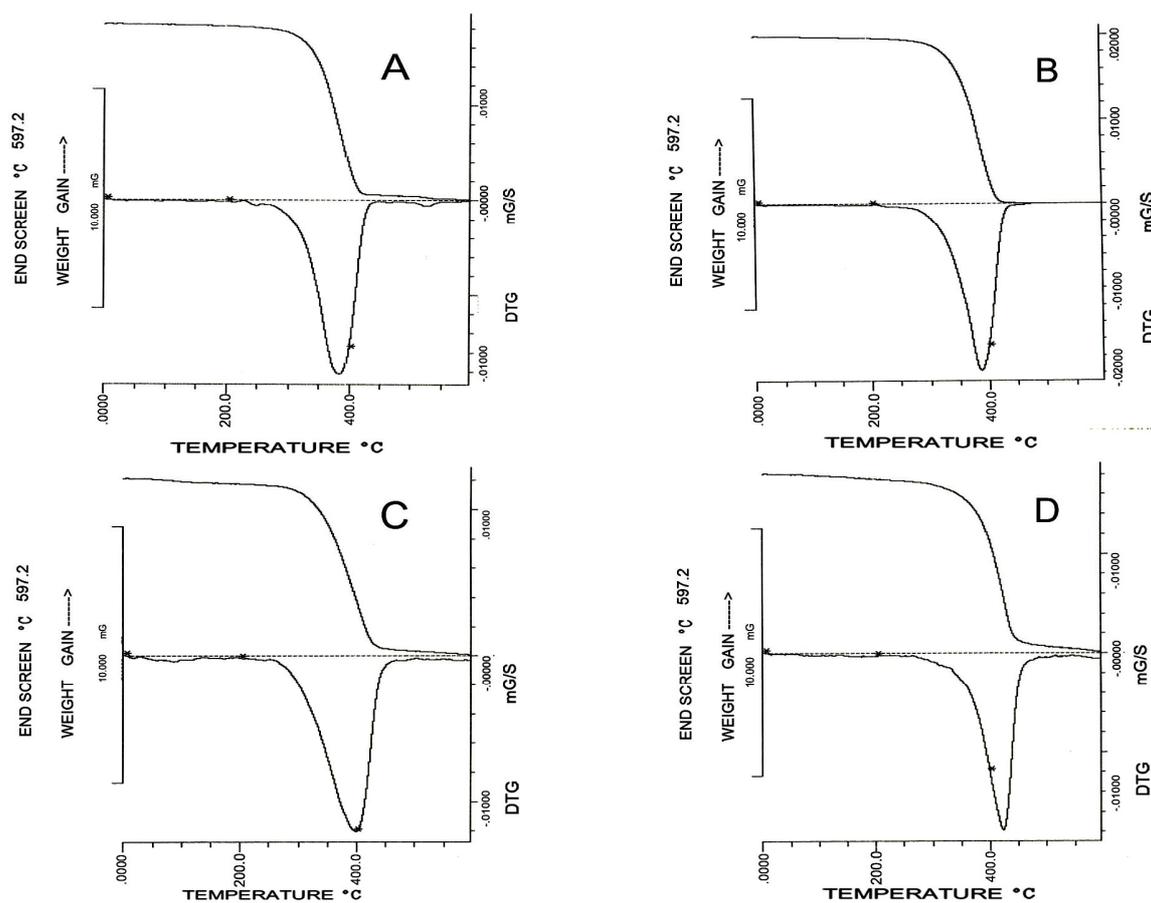


Figure 11. TGA/ DTG thermograms of (A) St/BA copolymer (B) with 2.50, (C) with 5.00 and (D) with 12.00% TEVS in N₂ atmosphere, $[M]_0 = 4.60 \text{ mol L}^{-1}$, $[\text{TEVS}] = 0.30 \text{ mol L}^{-1}$, $T = 90 \text{ }^\circ\text{C}$, 50 rpm, $[I]_0 = 7.8 \times 10^{-3} \text{ mol L}^{-1}$.

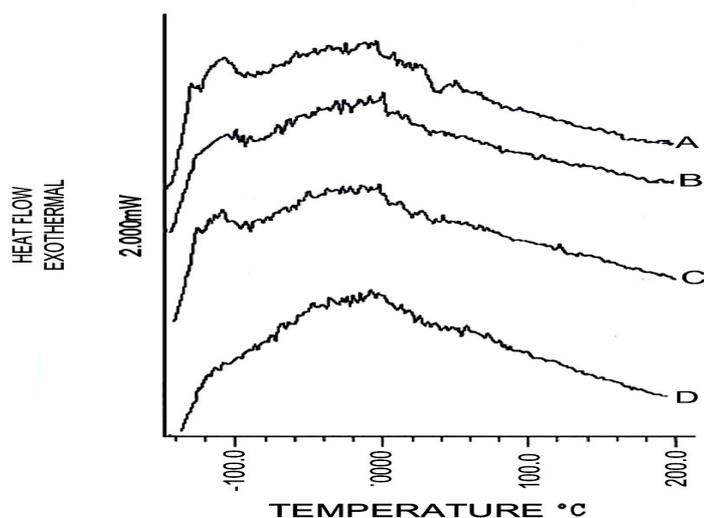


Figure 12. DSC thermograms of (A) St/BA copolymer (B) with 2.50%, (C) with 5.00%, and (D) with 12.00% TEVS, $[M]_0 = 4.60 \text{ mol L}^{-1}$, $[\text{TEVS}] = 0.30 \text{ mol L}^{-1}$, $T = 90 \text{ }^\circ\text{C}$, 50 rpm, $[I]_0 = 7.8 \times 10^{-3} \text{ mol L}^{-1}$.

Conclusions

Continuous emulsion copolymerization of TEVS-modified St/BA emulsions initiated by potassium peroxydisulfate (KPS) was evaluated. Experimental conditions of impeller speed, initiator and TEVS concentrations, surfactant kinds, and temperature were varied. The following results were obtained.

1. An increase in TEVS concentration caused an increase in heat stability, while the T_g and polymerization rate decreased.
2. An increase in initiator concentration caused an obvious increase in polymerization rate.
3. In the region of relatively low impeller speed, a reduction in impeller speed shortened the reaction time required to attain high conversion.
4. Both the initial rate of polymerization and maximum conversion increased with increases in temperature.
5. The presence of TEVS moiety in the copolymers caused the thermoplastic structure to become elastomeric.
6. The obtained copolymers had good storage stability.
7. The reaction between polymerizable TEVS and styrene or butyl acrylate was confirmed by FT-IR spectra.
8. The water absorption ratio of the latex films was minimum at a seed latex content of 10%.
9. The transparency of the films fell as the TEVS concentration increased.

References

1. I. Sasaki, A. Yanagase, Y. Kawaachi, T. Mayuzumi, T. Oba and F. Okada, **US Pat. 4, 690, 986** (1987).
2. C. Lindner, L. Morbitzer and D. Rempel, **Eur. Pat. Appl. 3891905** (1990).
3. N. Yamamoto, A. Yanagase, T. Iwasak and K. Ito, **Jpn. Pat. 06-49313** (1994).
4. A. Yanagase, A. Nakad and A. Koshirai, **Jpn. Pat. 07-207148** (1995).
5. N. Niessner and W. Fischer, **Eur. Pat. Appl. 657480** (1995).
6. M. Matsumoto, T. Urabe, M. Kato and K. Tamori, **Jpn. Pat. 09-208642** (1997).
7. W.D. He, C.T. Cao and C.Y. Pan, **J. Appl. Polym. Sci. 61**, 383-388 (1996).
8. W.D. He, C.T. Cao and C.Y. Pan, **Polym. Int. 39**, 31-36 (1996).
9. C.Y. Kan, D.S. Liu and X.Z. Kong, **J. Appl. Polym. Sci. 82**, 3194-3200 (2001).
10. K.G. Olson, M.E. Hartman, S.K. Das and R. Dowbenko, **Eur. Pat. Appl. 053600** (1985).
11. A.C. Lavoie, **Eur. Pat. 0350240/A2** (1990).
12. W. Shimozawa and T. Koshio, **Jpn. Pat. 03227312** (1991).
13. D.T. Liles and D.L. Murray, **Eur. Pat. Appl. 771826/A2** (1997).
14. E. Yamada, M. Hasegawa and T. Hattori, **Jpn. Pat. 10-152507/A2** (1998).
15. I. Lee, **US. Pat. 5,712,346A** (1998).
16. M. Yamatani, M. Furuya, H. Kasaki and A. Yamamoto, **Jpn. Pat. 11-255846** (1999).
17. C.Y. Kan, Q. Yuan, M.C. Wang and X.Z. Kong, **Polym. Adv. Technol. 7**, 95-97 (1996).
18. C.Y. Kan, X.L. Zhu, Q. Yuan and X.Z. Kong, **Polym. Adv. Technol. 8**, 631-633 (1997).
19. S.Q. Huang, Z.S. Xu, H. Peng and S.Y. Cheng, **J. Appl. Polym. Sci. 71**, 2209-2217 (1999).
20. X.Z. Kong, C.Y. Kan and Q. Yuan, **Polym. Adv. Technol. 7**, 888-890 (1996).
21. C.Y. Kan, X.Z. Kong, Q. Yuan and D.S. Liu, **J. Appl. Polym. Sci. 80**, 2251-2258 (2001).
22. M.X. Zou and Z.C. Zhang, **Polym. Int. 53**, 1033-1039 (2004).
23. N. Grassie, **Trans. Faraday. Soc. 48**, 379 (1952).
24. M. Konno, K. Shimizu, K. Arai and S. Saito, **J. Polym. Sci. Part A: Polym. Chem. 25**, 223-230 (1987).
25. K. Arai, M. Arai, S. Iwasaki and S. Saito, **J. Polym. Sci. Polym. Chem. 20**, 1203-1209 (1982).
26. H. Javaherian Naghash, S. Mallakpour and N. Kayhan, **Iranian Polym. J. 14** 211-222 (2005).
27. D.H. Wolf, S. Peter and S.W. Klaus, **Polymer, 29**, 1328-1335 (1988).
28. H. Javaherian Naghash, S. Mallakpour and N. Mokhtarian, **Progress In Organic Coatings, 55**, 375-381 (2006).
29. O. Maeda, H. Kobayashi and K. Kageishi, **Jap. Pat. 26**, 691 (2000).
30. H. Javaherian Naghash, A.R. Momeni, H. Alian, A.R. Massah and S. Ataei, **Polym. Int. 54**, 1564-1571 (2005).
31. Z. Sun, W. Ding, J. Liu and J. Li, **Shanghai Tuliao, 4**, 201-204 (1998).
32. K. Kumar and K.S. Rana, **Iranian Polym. J. 11**, 287-293 (2002).
33. Y. Qiao, J. Yu, D. Song, D. Wang and Z. Hou, **Tuliao Gongye, 31**, 3-6 (2001).
34. B. You, X. Chen, D. Li, Q. Feng and L. Wu, **Zhanjie, 21**, 21-23 (2000).
35. Z. Mingxuan, W. Shijie, Z. Zhicheng and G. Xuewu, **Eur. Polym. J. 41**, 2602- 2613 (2005).