실리콘 수식 비닐아세테이트-아크릴 공중합체 수지의 방수성 및 열적 성질

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Water Resistance and Thermal Properties of Resin Based on Silane-modified Vinyl Acetate-Acrylic Emulsion Copolymers

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Abstract: Triphenylvinylsilane (TPVS) containing vinyl acetate (VAc), butyl acrylate (BA), and *N*−methylolacrylamide (NMA) copolymers were prepared by emulsion polymerization. The polymerization was performed at 80 ℃ in the presence of auxiliary agents and ammonium peroxodisulfate (APS) as the initiator. Sodium dodecyl sulphate (SDS) and Arkupal N−300 were used as anionic and nonionic emulsifiers, respectively. The resulting copolymers were characterized by using Fourier transform infrared spectroscopy (FTIR), gel permeation chromatography (GPC), and dynamic light scattering (DLS). Thermal properties of the copolymers were studied by using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The morphology of copolymers was also investigated by scanning electron microscopy (SEM) and then the effects of silicone concentrations on the properties of the TPVS−containing VAc−acrylic emulsion copolymers were discussed. The obtained copolymers have high solid content (50%) and can be used in weather resistant emulsion paints as a binder.

Keywords: emulsion polymerization, triphenylvinylsilane, vinyl acetate, butyl acrylate, *N*−methylol−acrylamide.

Introduction

Polyacrylate latexes have been widely applied in many industries based on their special properties such as good film−forming, cohesiveness and mechanical properties.[1] On the other hand, polyacrylates have poor water−repellency owing to their hydrophilicity. Their mechanical properties are often temperature−dependent. In contrast, polysiloxanes usually have low surface tension, low glass transition temperature, high hydrophobicity and good heat resistance. In the past decades there has been more interest in the combination of polyacrylates with polysiloxanes in order to obtain stable polymer latexes and polymer materials with improved performance.[1,2]

On the other hand it is inevitable for a coated film to undergo deterioration with exposure. Weatherability is a property that resists deterioration caused by several environmental factors, such as radiation, temperature, moisture, substrate, and chemicals.[3−5] Since the film of a weatherable coating is densely crosslinked and exhibits high hardness, it stands well against the factors causing deterioration of the film. Therefore, there is a growing need for weatherable coatings in various architectural industries. Since weatherable coatings require special film properties, it has been difficult to meet the needs with common synthetic resins. Since the 1980s, coatings containing fluorine resin which are copolymerized by fluoroethylene and alkyl vinyl ether have been used as weatherable coatings.[6] However; coatings containing fluorine resin have some disadvantages, such as being expensive, environmentally pollutive, poor hardness, and bad workability. Recently, coatings containing silicone modified acrylic resins have gained recognition as weatherable coatings. Since the coatings containing these resins are a composite of organic and inorganic polymeric materials, it is easy to control the film hardness and to apply them to various substrates. There are two types of coatings containing silicone modified acrylic resins: tem−

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perature-cured and moisture-cured at room temperature. Of these two, the type of hardening by moisture at room temperature will be spotlighted because of its good workability and weatherability. There have been some reports on the coatings containing silicone modified acrylic resins. Rao and Babu[7] synthesized a copolymer of vinyltriacetoxysilane and bromomethacrylate and investigated its thermal behavior. Witucki[8] prepared a silicone modified acrylic resins by cold blending an alkoxy silane and acrylic emulsion through the following two step processes. The first step was hydrolysis of an alkoxy functional group, and the second step was the formation of silicone polymer. He reported that the existence of 10% silicone increases gloss retention and decreases chalk phenomenon and color difference. There have been some patents similar to this work. Kanegafuchi Kagaku Kogyo Co. holds two patents [9,10] on weather resistant coatings, in which curing catalysts are used. DuPont Co. also holds a patent[11] on weather resistant coating that consists of hydroxyl group-containing acrylic polymer/hydroxyl or alkoxy group-containing siloxane. The coatings are not the moisture-curing type, but the two component reactive type. PPG Co.[12] also patented weather resistant coatings that use a cure-accelerating catalyst. However, there have been few papers reporting on the synthesis of the silicone modified acrylic resin that is cured by moisture at room temperature and its application to weather resistant coatings.

In the current work, a silicone modified acrylic resin, was prepared by the copolymerization of vinyl acetate, butyl acrylate, N-methylolacrylamide and triphenylvinylsilane. The morphology of the latex particles was observed by using scanning electron microscopy (SEM), while the polymerization reactions between the triphenylvinylsilane, vinyl acetate and acrylates were confirmed by Fourier-transform infrared (FTIR) spectroscopy. Thermal properties of the copolymers were studied by using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The molecular weights and particle sizes of copolymers were determined by gel permeation chromatography (GPC) and dynamic light scattering (DLS), respectively. The obtained results show that the increase in the content of silicone increases the thermal stability and decreases the water absorption ratio of the latex films.

Experimental

Materials. Reagent grade VAc (Fisher Scientific Co) was further purified by distillation in a rotary evaporator at a reduced pressure of 30 mmHg to remove inhibitor. BA (Aldrich), were freed from the inhibitor by shaking with

10% aqueous NaOH, washing with water and drying over Na_2SO_4. TPVS (Aldrich), NMA and $NaHCO_3$ (Merck) were analytical grades and used directly without further purification. SDS and Arkupal N-300 were purchased from Henkel, Germany and initiator APS (Fisons), were used as received. Water was deionized.

Polymerization Procedure. Semi-continuous emulsion copolymerization was carried out using a 500 mL five-necked round-bottom flask equipped with a reflux condenser, stainless-steel stirrer, sampling device, and two separate feed streams. The first feed stream was a solution of VAc, BA, NMA, TPVS and anionic surfactant. The other feed was the initiator solution of 7.6 mM. Before emulsion polymerization start-up, the reaction vessel was first charged with a solution of $NaHCO_3$, 0.25 g, nonionic emulsifier: Arkupal N-300, 6.66 g, water, 68 g, anionic emulsifier: sodium dodecyl sulphate, 1.35 g, and a little amount of antifoam which prepared under stirring at 60 ℃. After 5 min 10 w% of the total amount of the monomer mixture and 0.10 g initiator (initial charge) were added to the flask in a period of 20 min for preparation of a pre-emulsion. During polymerization, the reaction mixture was stirred at a rate of 60 rpm, and the temperature was maintained at 60 ℃. After finish of 20 min, the temperature was kept at 80 ℃ until the end of polymerization (4 h). The polymerization was performed with a feeding rate of 1.0 mL/min under nitrogen atmosphere to investigate the effect of TPVS concentration on monomer conversion. A typical recipe for the preparation of a 50% solids product is given in Table 1. In order to determine the conversion percent during the polymerization process, it was necessary to withdraw samples at various intervals from the reaction vessel. These samples are relatively small so that the overall composition in the reactor is not seriously affected; once a sample is removed and put in a watch glass, polymerization is terminated by the addition of 7 ppm hydroquinone. Then two drops of ethanol is added to the sample

Table 1. Polymerization Recipe at 80 ℃

Compound	Initial charge	Feed	Total
VAc (g)	10	89	99
n-BA (g)	1	8	9
NMA (g)	1	8	9
TPVS (g)	10 w%	90 w%	Variable (0-1)
Buffer: $NaHCO_3$ (g)	0.25	–	0.25
Initiator: $(NH_4)_2S_2O_8$ (g)	0.10	0.34	0.44
Demineralized water (g)	68	57	125
Nonionic emulsifier: Arkupal N-300 (g)	6.66	2.82	9.48
Anionic emulsifier: Sodium dodecyl sulphate (SDS) (g)	1.35	0.15	1.50

Table 2. Physical Properties of Vinyl Acetate-Acrylic Resin with and without TPVS

No.	TPVS (molar)	T_g (℃)	Water absorption ratio(%)	Coagulum (wt%)	Particle size(μm)	Appearance
1	0.00	22.50	1.78	0.00	0.95	Milky
2	0.10	–	1.58	0.02	1.20	Milky
3	0.20	17.00	–	0.50	1.42	Milky
4	0.30	–	–	0.50	1.66	Milky
5	0.40	–	1.40	0.70	1.85	Yellowish
6	0.50	14.00	1.35	1.00	1.90	Yellowish
7	0.60	–	–	1.30	1.95	Yellowish
8	0.70	–	–	1.50	1.97	Yellowish
9	0.80	–	–	2.30	2.00	Yellowish
10	0.90	–	–	3.00	2.00	Yellowish
11	1.00	10.00	1.30	3.50	2.30	Yellowish

Figure 1. FTIR spectra of (a) VAc/BA; (b) VAc/BA/NMA; (c) VAc/BA/NMA/TPVS copolymers. $[M]_0 = 5.0$ M, $[TPVS] = 0.10$ M, $T = 80$ ℃, $[I]_0 = 7.6$ mM.

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 percent was determined gravimetrically. The 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. Some physical properties of these resins have been shown in Table 2. 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 four measurements and the deviation between four runs was always less than 3 %.

Polymer Characterization. DSC thermograms were taken on a Mettler TA 4000 Model apparatus at a heating rate of 10 ℃/min. The glass transition temperature (T_g) was taken 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 ℃/min. FTIR spectra of the copolymers were taken using a Nicolet Impact 400 D Model spectrophotometer. Scanning electron micrographs were taken on a JEOL−JXA 840 A SEM (JEOL, Boston, USA). The specimens were prepared for SEM by freeze−fracturing in liquid nitrogen and the application of a gold coating of approximately 300 A° with an Edwards S 150 B sputter coater. The copolymer latexes were dried on a glass plate at room temperature and then these films were fractioned with tetrahydrofuran (THF) to determine the M_n and M_w values of latexes by gel permeation chromatography (GPC). GPC was Waters model using an 1100 type instrument with a refractive index detector and calibrated with polystyrene standards consisting of three Waters styragel colums (HR 4, HR 3, and HR 2). THF was diluent solvent
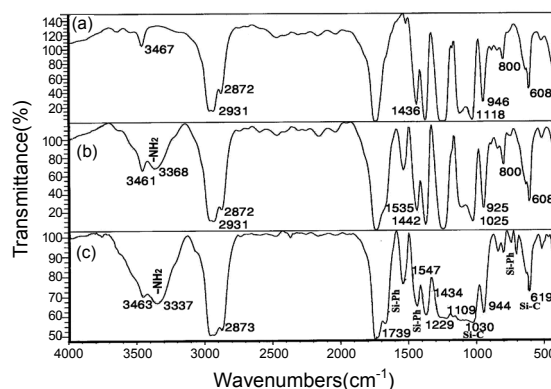
at a flow rate of 0.3 mL/min at 30 ℃. Average particle size and particle size distributions of the latexes were determined by applying a dynamic light scattering (DLS) method using a Zetasizer NanoZS model instrument, which analyzed with HeNe light source with a wavelength of 632.8 nm at 0.1−10000 nm particle size distribution. Saturated water ab−sorption (A_w) of the films was measured as the following method: a certain weight (about 2 g) of film was put in water for 14 days at 20 ℃, and then it was dried again. By com−paring the weight of the film before drying (W_1) and after drying (W_2), the absorption ratio can be calculated by: A_w (%) = (($W_1 - W_2$)/W_2) × 100.

FTIR Analysis. The 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, then removing the film from the glass. Figure 1 shows the FTIR spectra of (a) VAc−co−BA, (b) VAc−co−BA−co−NMA and (c) VAc−co−BA−co−NMA−co−TPVS latexes, respectively. The comparison of A spectra with B and C shows two peak at 3368 and 3337 cm^{-1} which demonstrate the amine groups of NMA in the copolymers. Silicone could be characterized by Si–C symmetric deformation, stretching vibration at 650 and 1000 cm^{-1}, respectively; and Si–Ph asymmetric stretching at 740, 1430, and 1595 cm^{-1}. From these spectra, it is clear that silicone was successfully copolymerized to poly(VAc−co−BA−co−NMA).

Results and Discussion

Effect of TPVS Concentration on Reaction Rate. Addition of silane compounds in acrylic emulsion provides beneficial effects by improving various mechanical properties, such as water, weather ability, good acid, and alkali resistance.[13−18] In addition to this, the incorporation of silicone plays the
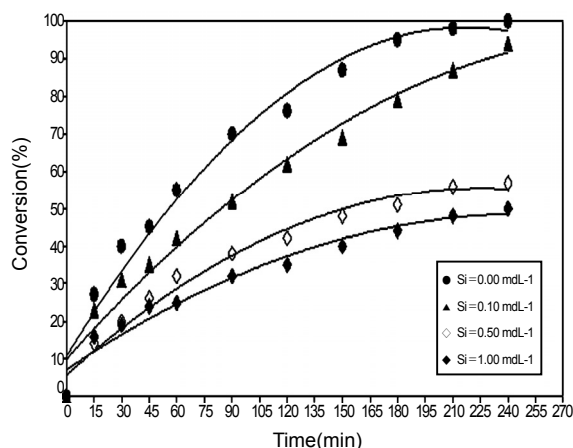
Figure 2. The effect of initial TPVS concentration on monomer conversion vs. time at (●) 0.00; (▲) 0.10; (◇) 0.50; (◆) 1.0 M. $[M]_0=5.0$ M, $[TPVS]=0.10$ M, $T=80$ °C, $[I]_0=7.6$ mM.
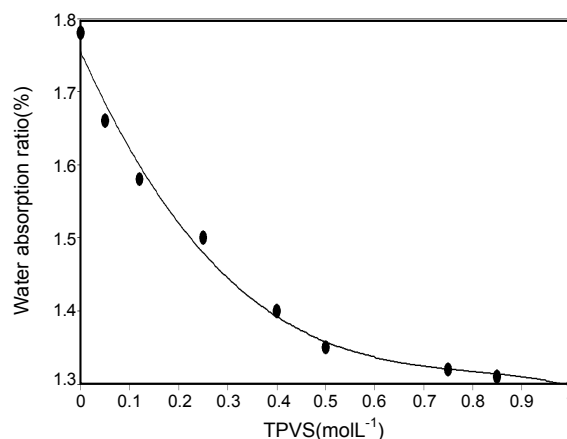

Figure 3. Effects of the TPVS content seed latex to water absorption ratio of the latex films. $[M]_0=5.0$ M, $T=80$ °C, $[I]_0=7.6$ mM.

(a)

(b)

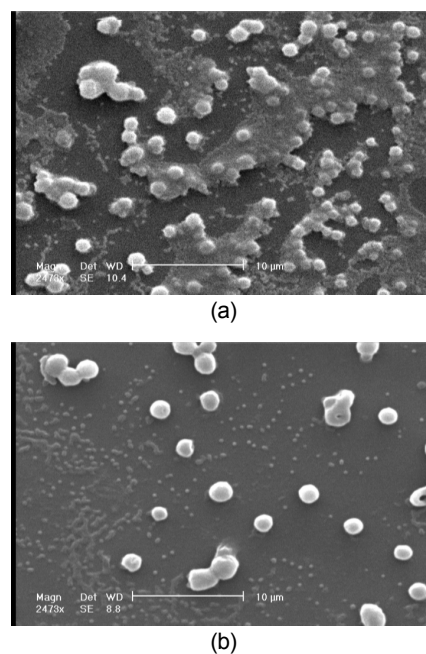**Figure 4.** Scanning electron microscope pictures of (a) VAc/BA/NMA copolymer; (b) with 1.00 M TPVS. $[M]_0=5.0$ M, $T=80$ °C, $[I]_0=7.6$ mM.

roles of coupling agent and softener[19] and it is enriched on surface of the film.[20] On the other hand You *et al.*[21] demonstrated that silanes can be bonded with hydroxyl groups on the surface of substrate to increase the adhesion and also FTIR analysis indicated that organic functional silanes can be polymerized with other monomers. Although copolymerization of VAc−*co*−BA has been well established,[22−28] their copolymerization in the presence of TPVS has not been reported. Therefore, the role of this monomer is not perfectly clear. It is possible that during of copolymerization process this monomer will make part of the copolymer chain. However, the extent of its incorporation in the polymer chain was not measured. Figure 2 shows the effect of TPVS concentration on the monomer conversion versus time where the initial initiator and total monomer concentrations were fixed at $[I]_0=7.6$ mM and $[M]_0=5.0$ M, respectively. It can be observed that the rate of reaction decreased with increasing TPVS concentration. It is known that the rates of propagation and consequently copolymerization in a radical copolymerization reaction are inversely related to the termination rate constant.[14,17] As the amount of TPVS increased, it acted as a chain transfer agent and the rate of polymerization decreased. Although chain transfer generally does not decrease polymerization rate, this matter has been observed by the authors for many times and it can be justified as follow. The radicals obtained from TPVS are more stable in comparison with other radicals which exist in the TPVS modified emulsion copolymers. This stability is due to the π bonds and resonance effects of double bonds, consequently a reduction in the reaction rate was observed.

Water Absorption Ratio of the Latex Films. The poly(VAc−*co*−BA−*co*−NMA), 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 characterization of the hydrophobicity. As shown in Figure 3 the absorption ratio was greatly influenced by the content of the silicone. With the increase of the silicone concentration, the water absorption ratio of the latex films decreased, which can be contributed to the excellent hydrophobicity of silicone. We could make a conclusion that higher silicone content would give better water resistance.
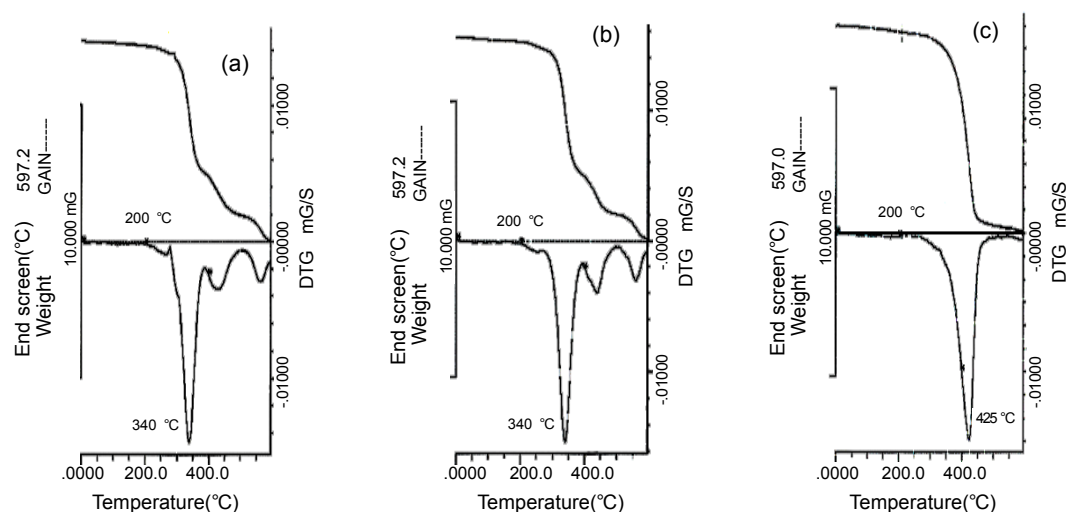
Figure 5. TGA/DTG thermograms of (a) VAc/BA/NMA copolymer; (b) with 0.50; (c) with 1.00 M TPVS in N$_2$ atmosphere. [M]$_0$= 5.0 M, T=80 ℃, [I]$_0$=7.6 mM.
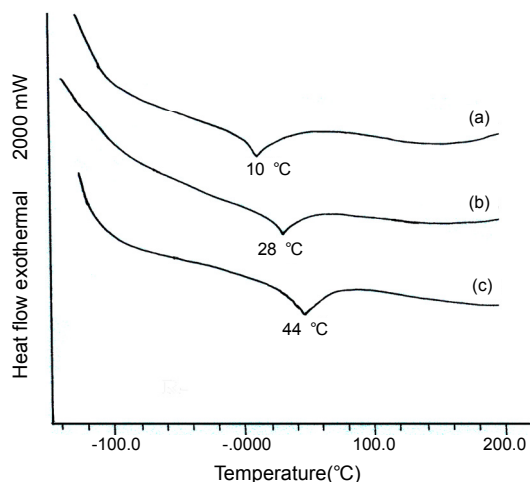

Figure 6. DSC thermograms of (a) VAc/BA/NMA with 1.00 M TPVS; (b) VAc/BA; (c) VAc/BA/NMA copolymer. [M]$_0$=5.0 M, T=80 ℃, [I]$_0$=7.6 mM.

Morphologies of Latex Particles at Different TPVS Concentrations. The particle morphologies of the TPVS modified VAc−acrylic copolymers were examined by scanning electron microscope. Figure 4(a) and (b) are micrograph of the latex particles of sample that containing 0.00 and 1.00 M TPVS. According to these micrographs the VAc−acrylic copolymers have very small particle size compared to TPVS modified samples and by increasing the TPVS concentration the particle size will become larger. The results suggest that VAc, BA, and NMA monomers were completely polymerized in the presence of TPVS.

Thermal Properties. The thermal properties of VAc−co−BA, VAc−co−BA−co−NMA and VAc−co−BA−co−NMA−co−TPVS latexes were evaluated by means of TGA/DTG

and DSC under nitrogen atmosphere and are shown in Figures 5 and 6. The VAc−co−BA emulsion (Figure 5(a)) and VAc−co−BA−co−NMA (Figure 5(b)) show a stable situation up to 200 ℃. The chemical decomposition will start after this temperature and the maximum decomposition is around 340 ℃. On the other hand, the VAc−co−BA−co−NMA−co−TPVS copolymers exhibited thermal decomposition similar to the above mentioned, but the maximum decomposition is around 425 ℃ which contains 1.00 M TPVS. According to these results it can be concluded that the existence of TPVS 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 6(a) for VAc−co−BA−co−NMA−co−TPVS, 6(b) VAc−co−BA−co−NMA, and 6(c) VAc−co−BA, respectively. Figure 6(a) reveals an endothermic shift around 10 ℃ which corresponds to T_g with 1.00 M TPVS and the T_g is around 28 ℃ for (b), and 44 ℃ for (c) thermograms, respectively. According to the above data it should be mentioned that presence of TPVS moiety causes the change in thermal behavior and particularly affects on T_g.

Molecular Weights of Copolymers. The M_w and M_n values of the poly(VAc−co−BA−co−NMA−co−TPVS) were determined by GPC. In Figure 7, it is seen that M_n and M_w values regularly change with increasing TPVS concentration of the copolymer composition. The M_n and M_w results give some information about reaction kinetics, so it can be determined that copolymerization takes place under control and progresses at a steady low rate. Due to high concentration of TPVS in the copolymerization low M_n values of
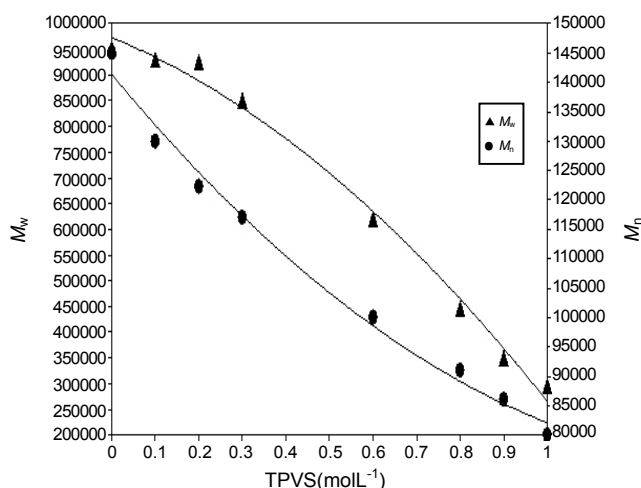
Figure 7. The M_w and M_n values of copolymer latexes versus TPVS concentration in the copolymer composition. $[M]_0 = 5.0$ M, $T = 80$ ℃, $[I]_0 = 7.6$ mM.
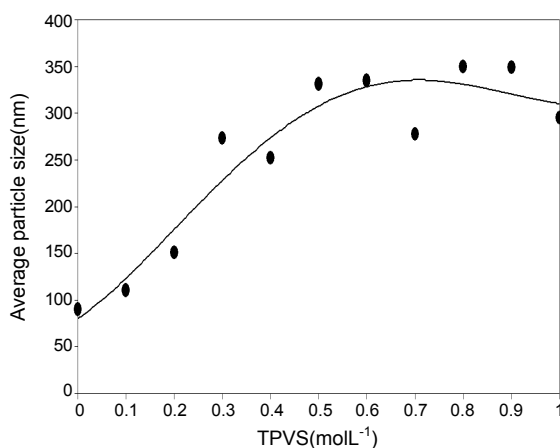

Figure 8. Particle size of copolymer latexes versus TPVS concentration in the copolymer composition. $[M]_0 = 5.0$ M, $T = 80$ ℃, $[I]_0 = 7.6$ mM.

the latexes but high M_w values of the latexes were found. The emulsion copolymerization of (VAc−co−BA) system is characterized by large differences in reactivity ratios (rVAc=0.05 and rBA=5.5), water solubilities (2.3 wt% for VAc and 0.04 wt% for BA). Due to these significantly different monomer properties and copolymerization ingredients, latexes having a wide range of molecular properties can be obtained by varying monomer ratios, thus influencing the viscosity and molecular weight of the latex paints. Either M_n or M_w values of copolymers increased with the increasing TPVS concentration in the copolymer mixture.

The Size of Particles. Particle sizes of copolymer latexes are given in Figure 8 for copolymers depending on TPVS concentration in the copolymerization. Particle nucleation is assumed to take place predominantly in the aqueous phase

for semi−continuous emulsions. Thus the particles are formed over the entire period of the polymerization process, and the particle growth occurs by coalescence of smaller size particles or low molecular weight oligomers with larger size particles. When the monomer mixture is rich in the relatively more hydrophobic BA monomer, adsorption of emulsifier onto the particle surface results in small size latex particles. When the average particle size decreases for constant solid contents of latexes the total surface area of polymer particles increases. This means that the increase in the latex viscosity corresponds to an increase in the total surface area, and because emulsifier concentration is proportional to the total surface area, an increase in the latex viscosity with an increase in the emulsifier concentration is reasonable. The abundance of particle size is the reason that small particles enter larger particles, which leads to a compartmentalization effect. Because of this effect there is an increase is an in latex fluidity and a decreases in the latex viscosity.

Effects of the TPVS on Stability of Latex. The effect of TPVS on stability of latex was investigated and the results were presented in Table 2. The coagulum increased gradually as the content of TPVS increased and resulted in instability of the emulsion in the course of polymerization as the content of TPVS reached 8%. Moreover, the emulsion would be demulsified in 37 days.

Conclusions

Continuous emulsion copolymerization of TPVS−modified VAc−acrylic emulsions, initiated by $(NH_4)_2S_2O_8$ was evaluated. The properties and the structure of the resulting copolymers were investigated using FTIR, GPC, DLS, TGA, DSC and SEM measurements. The particle sizes of the produced latexes are in the range of 90−400 nm and the sized of polymer latexes are spherical and are very uniform with nearly monodisperse distributions. The FTIR spectra indicate the reaction between polymerizable silane monomer and VAc or BA copolymers. From the thermogravimetric study, it can be concluded that, the introduction of TPVS into VAc or BA copolymers increase the heat stability. The incorporation of siloxane moiety further decreases the T_g values of latexes due to the presence of flexible and free rotation of Si–C linkage. Among the latexes, the silicone (1.0 M) modified VAc−BA copolymers exhibit better water repellency and higher thermal stability due to its Si–C and Si−Ph linkages and can be used as thermal barrier coatings for industrial and marine structures. Further work on these copolymers will be reported later.

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