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Shelf Stability of Isocyanate-Functionalized Vinyl Acrylic Latexes

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Summary: Copolymerization of vinyl acetate (VA) with butyl acrylate (BA) and dimethyl meta-isopropenyl benzyl isocyanate (TMI) was carried out at 40 °C in emulsions stabilized with sodium dodecyl sulfate (SDS) or sodium dodecyl benzene sulfonate (SDBS). Regardless of the type of surfactant employed, latexes were very unstable during storage. Moreover, the hydrolysis of TMI and undesirable premature crosslinking of the polymeric chains did occur at room temperature during latexes storage.

Keywords: crosslinking; emulsion polymerization; shelf stability; TMI; vinyl acrylic

Introduction

TMI is a bifunctional monomer that contains a tertiary aliphatic isocyanate group and a reactive double bond. The double bond readily undergoes free radical emulsion polymerization with vinyl monomers like BA, methyl methacrylate and styrene, to yield copolymers with pendant isocyanate functionality that can be maintained intact for moisture curing systems.[1–3] Moisture curing of latexes containing TMI has been shown to improve tensile strength and scrub resistance of the resulting films.[2,4] The stability of the isocyanate (—NCO) groups in the TMI latexes is dependent upon a number of factors, the two most critical being the presence or absence of carboxylic acid containing monomers, and the location of the —NCO groups in the latex particle.[1,4–7]

Isocyanates are highly reactive toward a large number of active hydrogen compounds. Therefore, more than one reaction may occur in a system at a given time. Nevertheless, Lovell et al. have reported that hydrolysis of —NCO groups followed by urea formation may be a dominant crosslinking mechanism for TMI latexes. The —NCO group undergoes hydrolysis by acid catalysis forming an unstable carbamic acid intermediate that spontaneously decarboxylates into the corresponding amine and carbon dioxide. The resultant amine reacts with another —NCO group to produce urea crosslinked network. Furthermore, the authors found that acetic acid catalyzed the TMI-water reaction.[7]

Another interesting study by Guo et al. has demonstrated that TMI grafted polypropylene (TMI-PP) greatly improved the interfacial interaction between wood-flour (WF) and PP. Apparently, the —NCO groups of TMI react with free superficial —OH groups on the surface of WF to form chemical bonds, resulting in an improved interfacial adhesion.[8]

The purpose of this work is to produce isocyanate functionalized vinyl-acrylic latexes by batch emulsion copolymerization using two of the most common commercial surfactants (SDS and SDBS) in order to evaluate their efficiency on the shelf stability of the latexes. These latexes have been prepared in view of future work involving the improvement of adhesion and moisture resistance of wood adhesives.

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Experimental Part

All chemicals used were from Aldrich. SDS and SDBS, both with a purity > 98%, were used as received. TMI was > 95% pure and also used as received. VA and BA were distilled under reduced pressure and stored at 4 °C. Potassium persulfate (KPS) and potassium metabisulfite (KMBS) were 99.99 and 98% pure, respectively, and they were used as received. Distilled-deionized water was used in all experiments. Nitrogen sparging was used to remove oxygen from the reaction mixture and from the reactor.

Polymerizations were carried out at 40 °C in a 100 mL jacketed glass reactor equipped with a reflux condenser and inlets for argon, monomer feed, sampling and mechanical agitation. A 45° pitched down flow four-bladed impeller was used with a stirrer speed of 450 rpm. Polymerization recipes are shown in Table 1. The typical procedure for polymerization started with the preparation of the initial charge. For this, the surfactant (SDS or SDBS) and most of the water were charged in the reactor; then they were bubbled with argon for 2 h and heated to 40 °C. A redox initiator system was employed. Separate aqueous solutions of the oxidant (KPS) and the reductant (KMBS) were prepared and 33% of each solution was added to the reactor in order to start the reaction. The rest of initiator solutions was dosed dropwise over a period of 90 min using a Cole-Parmer double syringe pump. Samples were withdrawn during the whole polymerization to follow conversion gravimetrically and for measuring particle sizes. Polymerization reactions were performed at least three times to ensure reproducibility. Particle size was measured at 25 °C in an angle of 90° in a Malvern 4700 quasielastic light scattering (QLS) apparatus equipped with an Argon laser ($\lambda = 514$ nm). Latex samples were diluted with water up to 100 times. The average particle diameter (Dp) used throughout was the intensity-weighted average diameter. Intensity correlation data were analyzed by the method of cumulants. Number density of particles (Np) was calculated from the polymer content and Dp. All latexes obtained were stored at room temperature and their colloidal stability was monitored by Dp measurements. Gel polymer fraction for the films cast from latexes was determined from the weight ratios of the insoluble polymer in anhydrous chloroform and the film samples before the solvent extraction. Gel and soluble polymer fractions were analyzed by FTIR infrared spectroscopy using a Nicolet FT magna 550 spectrophotometer in the 4000-400 cm^{-1} range.

Results and Discussion

Conversion vs. time curves for the polymerization at 40 °C of VA/BA/TMI using SDS or SDBS as surfactant are represented in Figure 1. An inhibition period at the beginning of the polymerization is always present for the reactions when SDS is used. This effect could be only attributed to the

Table 1.
Recipes for batch emulsion copolymerization at 40 °C.

Component	Latex I	Latex II
	Amount (g)	Amount (g)
Vinyl acetate	15.68	15.68
Butyl acrylate	15.68	15.68
TMI	0.64	0.64
Sodium dodecyl sulfate	0.25[a)]	—
Sodium dodecyl benzene sulfonate	—	0.30[a)]
Potassium persufate	0.16	0.16
Potassium metabisulfite	0.16	0.16
Water	48.00	48.00

[a)] 18 mmol based on water.

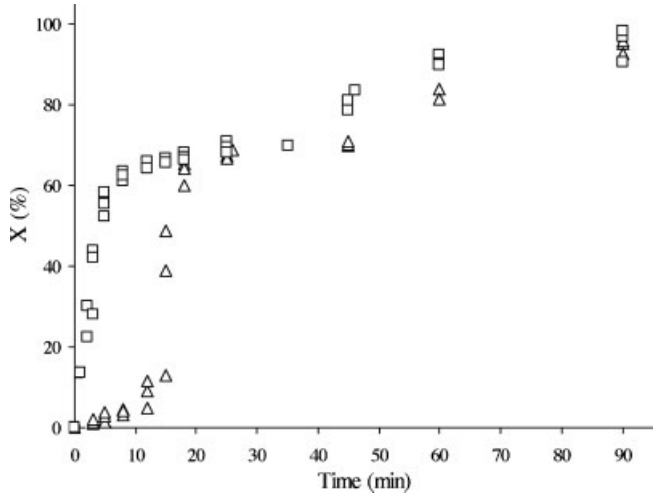

Figure 1.
Conversion vs. time for the copolymerization at 40 °C of VA/BA/TMI (49/49/2 wt. %) in emulsions stabilized with SDS (Δ) and SDBS (□).

polar head of SDS since all the other parameters are identical. The reason for this behavior is not clear and requires further study.

In both cases, the presence of a two-step reaction is noticeable. This kinetic behavior has already been reported for the copolymerization of VA with BA.[9,10] Due to the large difference in the reactivity ratios, VA is polymerized in two stages: the first corresponds to effective copolymerization and the second corresponds to VA homopolymerization. During the reaction, polymerization rate decreases as BA concentration decreases, reaching a minimum when this most reactive monomer is totally consumed at the end of the first stage. Moreover, batch emulsion copolymerization of these two monomers results in particles with core-shell morphology because of the great differences in reactivity ratios and water solubilities between VA and BA.[11] Another important fact to be considered is that TMI is converted at a faster rate than BA in bulk copolymerization[12] and emulsion copolymerization.[3] In agreement with this we can suppose for the batch emulsion copolymerization studied in this work, the formation of a terpolymer rich in TMI and BA up to about 70% conversion followed by the formation of a VA homopolymer. The more hydrophobic VA/BA/TMI terpolymer would be predominantly located in the core of the particles surrounded by the more hydrophilic VA homopolymer.

Figure 2 shows the evolution of Dp as a function of conversion. At the end of the polymerization, all latexes have Dp values between 110 and 120 nm. With the assumptions that particles are spherical and all of them have the same size, Np was estimated from Dp. The observed Np drop after 40% conversion (Figure 3), regardless of the type of surfactant, suggests a coalescence process. In fact, coalescence has been reported for the batch emulsion copolymerization of VA with BA. The shell rich in the more hydrophilic VA, would become less stable against coalescence due to ''poor'' emulsifier packing on the particle surface.[13] Nevertheless, latexes of VA/BA/TMI obtained in this work were relatively stable during polymerization and coagulum formation was not observed.

Figure 4 shows the evolution of Dp/Dpo (where Dpo is the particle size at the end of the polymerization) during storage at room temperature of latexes stabilized with SDS or SDBS. Both latexes had poor colloidal

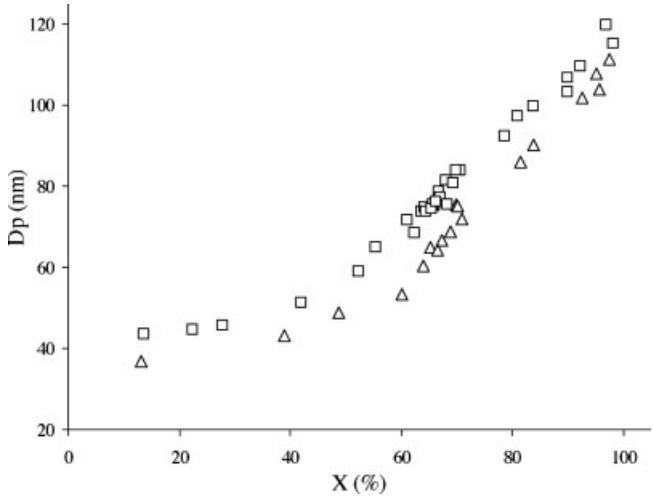

Figure 2.
Particle size as a function of conversion for the copolymerization at 40 °C of VA/BA/TMI (49/49/2 wt. %) in emulsions stabilized with SDS (Δ) and SDBS (□).

stability. The Dp values become progressively larger after polymerization and triple in original size after 180 days of storage. This type of instability also was observed by Edelhauser et al.[14] when they studied the effect of solubilization of latex polymer in various anionic surfactant solutions. The authors found that anionic surfactants like SDS and SDBS can penetrate into PVA latex particles. The surfactant penetration is accompanied by water imbibition, causing swelling and hydrolysis of PVA. Due to this reaction, the polymer became more hydrophilic and more capable of imbibing additional water and surfactant, and so forth. The loss of surfactant molecules at the particle surface leads to unstable latex.

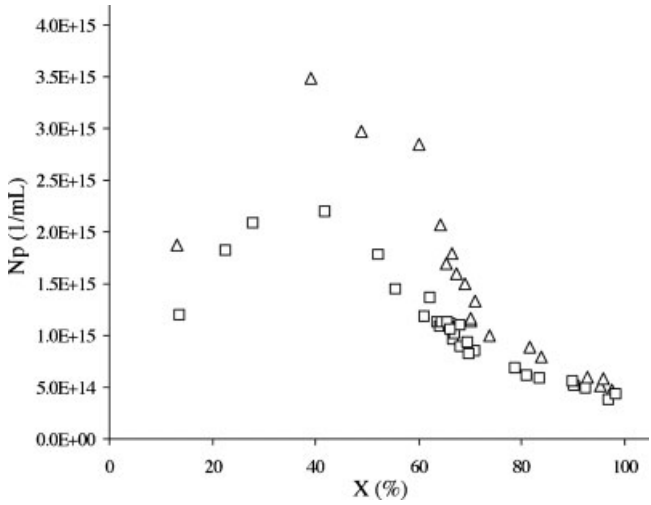

Figure 3.
Number density of particles vs. conversion for the copolymerization at 40 °C of VA/BA/TMI (49/49/2 wt. %) in emulsions stabilized with SDS (Δ) and SDBS (□).

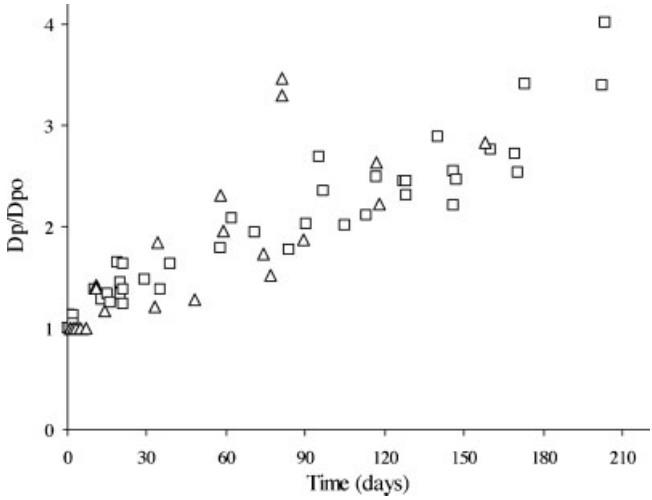

Figure 4.
Evolution of particle size, during storage at room temperature, with reference to particle size at the end of the polymerization of latexes stabilized with SDS (Δ) and SDBS (□).

As a result of water diffusion through the PVA shell, the hydrolysis of BA and —NCO groups of TMI could be expected to occur. The hydrolysis of VA results in the formation of —OH groups and acetic acid while the hydrolysis of BA results in the formation of carboxylic acid groups (—COOH) and butanol.[15] All of these conditions favor the hydrolysis of —NCO groups.[7]

Films prepared from samples of latexes taken at different storage times were immersed in anhydrous chloroform for 25 h. Then, gel contents of the films were determined after the soluble polymer was separated. Gel fraction in each film increases with the storage time and peaks at about 70% after storage for 180 days (Figure 5). Soluble fraction of these last films was analyzed by FT-IR and it was

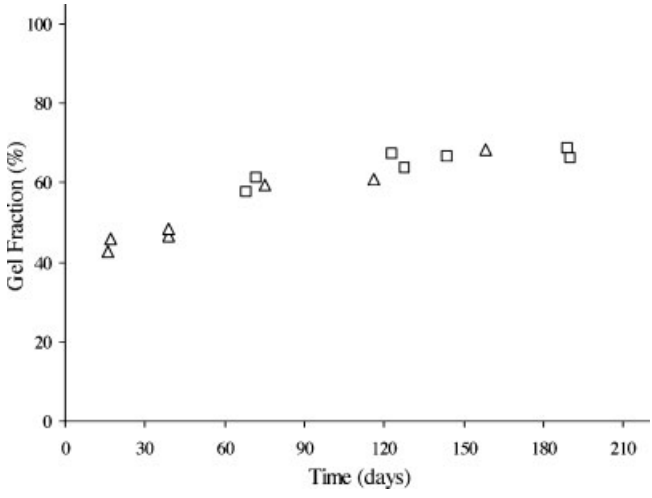

Figure 5.
Gel fractions as a funtion of storage time of the films cast from latexes stabilized with SDS (Δ) and SDBS (□).

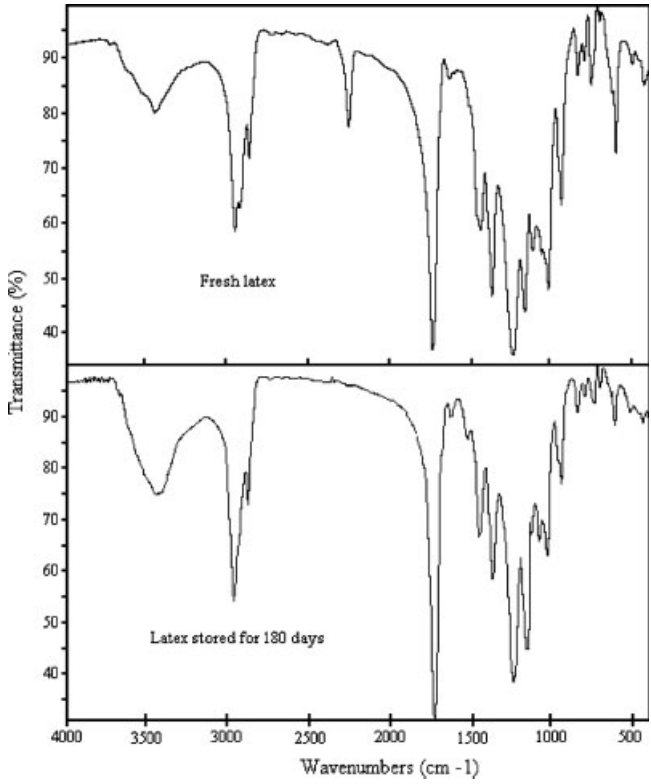

Figure 6.
IR spectrum of the films cast from fresh and stored latexes stabilized with SDBS.

determined that corresponds to VA homopolymer. This supports the hypothesis about the formation of a terpolymer rich in TMI and BA up to about 70% conversion followed by the formation of a VA homopolymer. The crosslinked fraction would be the VA/BA/TMI terpolymer.

The IR spectra in KBr (Figure 6) of the dried and pulverized gels of a film cast from fresh and stored latexes stabilized with SDBS, showed the disappearance of the absorption band at 2260 cm^{-1} (characteristic of the —NCO function) confirming the hydrolysis of —NCO groups and the subsequent crosslinking reactions. Same result was obtained for SDS also.

Conclusions

The batch emulsion copolymerization of VA with BA and TMI leads to highly heterogeneous polymer. There was no significant effect of the type of surfactant employed, SDS or SDBS, on final particle size of both latexes obtained. Regardless of the type of surfactant employed, the latexes were very unstable during storage at room temperature. Moreover, the hydrolysis of TMI and crosslinking of the polymeric chains did occur during latex storage.

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