Water-Based Radiation-Curable Latexes

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SYNOPSIS

Film-forming polystyrene/poly(n-butyl acrylate-co-glycidyl methacrylate) [PS/P(BA-co-GMA)] core-shell latex particles were prepared via a two-stage emulsion polymerization procedure using a polystyrene latex seed. Delayed addition of GMA was used in order to locate functional epoxy groups close to the particle surfaces. It was found that a temperature of 25°C at the second-stage polymerization, in combination with a redox initiator system, was essential for the formation of a uniform shell of BA-GMA copolymer around the PS core. The latex particle morphology was investigated by transmission electron microscopy (TEM). Reactive double bonds were introduced into the particle shells in order to produce a film-forming latex system that could be cured by ultraviolet (UV)-radiation without any need to use reactive multifunctional monomers or oligomers as crosslinkers. The surface-bound epoxy groups were used as grafting sites for amine or carboxyl functional unsaturated monomers, respectively. The grafting was demonstrated by Fourier transform infrared (FTIR) spectroscopy. Films prepared from modified and unmodified latexes were exposed to UV radiation in the presence of a photoinitiator. Crosslinking was tested by thermal mechanical analysis (TMA) and by determination of swelling and gel content of exposed films. It was demonstrated that films from the modified latexes after irradiation had significantly higher stiffness and gel content and showed lower swelling than unmodified ones. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The mechanical properties of a coating material can be improved by crosslinking the binder after film formation, e.g., by radiation curing. The simplified mechanism for radiation curing involves formation of free radicals, which react with double bonds present in the film to form propagating species. If more than one double bond is present per molecule, a cross-linked network develops.

A conventional radiation-curing coating system generally consists of a liquid reactive prepolymer, different monomers, a photoinitiator (UV-curing systems), pigments, and various additives.[1] In a water-based coating system, the reactive polymeric binder may be dissolved or dispersed in water. In the latter case, the binder may be prepared by emulsion polymerization.

As compared to organic-based coating systems, water-based systems have the advantage of low emission of organic compounds to the atmosphere.[2-4] Different radiation-curing water-borne coatings have been reported, e.g., water-soluble,[5] water-thinnable,[6] water-dispersible,[7] and latex-based[8] systems. Some of these systems contain multifunctional acrylates. The main disadvantage of water-based UV curable coatings are essentially the same as for conventional water-borne coatings, i.e., the need to evaporate water before UV curing.[9]

Reduction of the amount of polluting solvents and monomers in radiation curable coatings may be achieved by incorporating the functionality needed for radiation curing into the film-forming latex particles. Therefore, the objectives of our work were to investigate methods for the preparation of radiation curable latexes suitable for coating applications.

Emulsion polymerization is a well-known technique for producing dispersions of polymer particles.[10] The latex is film-forming, provided the poly-

mer particles have a T_g below the application temperature. However, for coating applications, a low film-forming temperature and a high modulus of the film is desirable, which can be achieved by using heterogeneous latex particles.[11,12] Such particles can be prepared by a two-stage seeded polymerization in which one monomer is polymerized onto particles prepared from another monomer (seed). The morphology of the heterogeneous particles depends on many parameters, for example, the relative polarity of the monomers, the mode of monomer addition, and the temperature.[13] Particles having a core-shell morphology are film-forming if the shell is film-forming at the application temperature. The properties of a film prepared from heterogeneous latex particles depend on the mechanical properties of each phase as well as on the morphology of the latex particles and the film.[14]

In the present work, we preferred to use film-forming core-shell particles rather than homogeneous particles as carriers of the UV reactivity because of more suitable mechanical properties and presumably higher efficiency of the post-polymerization modification reactions. This work is aimed at the preparation of latex particles having a hard PS core surrounded by a soft, film-forming shell of P(BA-co-GMA) and modification of the particles by epoxide reactions in order to create UV reactivity.

The epoxide function is known for its ability to undergo ring-opening reactions with active-hydrogen compounds such as carboxylic acids, phenols, and amines to give hydroxy esters, hydroxy ethers, and hydroxy amines, respectively.[15] Kjellquist et al.[16,17] have shown previously that modification of epoxy functional latexes can be performed by surface grafting in the water phase. The surface of the particles was modified by introducing an acetal functionality, suitable for acid catalyzed curing processes. A reverse procedure was reported in a study by Wolfsberger et al.[18] in which latex particles having an acid functionality were esterified with GMA in order to introduce reactive double bonds into the particle surface.

The system used in the present study, i.e., an epoxy functional latex reacting with an amine or carboxyl functional unsaturated compound, has certain advantages as compared to the one used by Wolfsberger et al. Firstly, by having GMA bound to the particles in the polymerization step rather than using it as a post-polymerization reagent, the adverse health effects connected to low molecular weight epoxy compounds can be avoided. Secondly, latex particles having surface-bound epoxy groups are po-

tentially useful for a number of different applications.

In the present investigation, the preparation of epoxy-reactive core shell particles and their subsequent reaction with amine and carboxyl functional unsaturated monomers are described. It may be noted that at film formation, the soft shell forms a continuous matrix surrounding the cores; i.e., the seed particle residues. In order to obtain high UV cross-linking efficiency, a high concentration of unsaturated groups should be available in the soft matrix, and the groups should have high mobility. The mobility should increase by the introduction of spacer groups, i.e., inert chains of different lengths separating the functional groups from the high polymer backbone.[19] In a further study, the effects of such groups on the grafting and the cross-linking efficiency will be investigated.

EXPERIMENTAL

Reagents

Styrene (ST, Merck), n-butylacrylate (BA, Merck) and glycidyl methacrylate (GMA, Lancaster, UK), were purified from inhibitors by passing the monomers through a column filled with active basic aluminium oxide (Merck). The purified monomers were kept at 8°C before use. Acrylic acid (Aldrich), allyl amine (Aldrich), sodium hydroxide (NaOH, Merck), sodium dodecyl sulfate (SDS, BDH), potassium persulfate (KPS, Merck), tert-butyl hydroperoxide (t-BHP, Janssen Chimica), anhydrous sodium carbonate (Merck), vanadium(IV)-oxide sulfate (Merck), and ascorbic acid (Merck) were of analytical grade and used as supplied. Water used was deionized and distilled.

Preparation of Polystyrene Seed

The PS seed latex was prepared batchwise in a 2 L glass reactor by emulsion polymerization at 70°C, using KPS as the initiator and SDS as the surfactant. The reactor was charged with an emulsion containing ST (320 g), water (1500 mL), SDS (4.5 g), and sodium carbonate (2.25 g). The reactor was repeatedly degassed and purged with N_2. The reactor content was heated to 70°C, and 1.2 g of KPS dissolved in 30 mL water was added. The polymerization was allowed to proceed until completion. In order to eliminate monomers and excess of the initiator, the PS seed latex was dialysed against an aqueous solution of SDS (2 g/L) using dialysis tub-

ing (Spectrum®, molecular cut 6000–8000). The aqueous solution of SDS was changed daily for 14 days. The solids content of the dialysed latex was 20 wt %.

Preparation of Core–Shell Particles

To produce core-shell particles, a second-stage polymerization at 25°C was carried out in a 200 mL calorimetric reactor (C151 Reaction Monitor, ChemiSens, Sweden), which allowed close monitoring of the polymerization rate.[20] PS seed latex (50 mL), water (50 mL), ascorbic acid (0.6 g), and vanadium(IV)oxide sulfate (5 mg) were charged to the reactor. The reactor was repeatedly degassed and purged with N_2. Ascorbic acid and vanadium(IV)oxide sulfate were components of the redox initiator system. The initiator solution was prepared by dissolving 1.0 g of tert-butyl hydroperoxide (t-BHP) in 100 mL of water. BA (7.2 g), GMA (3.3 g), and initiator solution were fed continuously through separate valves to the reactor under so-called starvation conditions. Approximately 75% of the BA was first continuously pumped into the reactor at a constant feed rate of 6.0 mL/h and with a initiator feed rate of 3.0 mL/h (6×10^{-6} mol/min). The remaining BA was then copolymerized at a constant feed rate of 3 mL/h with approximately 60% of the GMA at a constant feed rate of 3 mL/h and with an initiator feed rate of 3.6 mL/h (6.7×10^{-6} mol/min). Finally, the remaining GMA was then pumped into the reactor at a constant feed rate of 6 mL/h and with an initiator feed rate of 3.0 mL/h. The polymerization was allowed to proceed until completion.

The pH of the final latex was adjusted with NaOH to neutral condition in order to avoid hydrolysis of the epoxy groups.

Surface Modification

Core-shell latex (25 mL) was charged into a 100 mL vessel and heated to 75°C. An aqueous solution (2% w/w) of allyl amine or sodium acrylate, respectively, was added dropwise to the reactor for 30 min, and the reaction was allowed to proceed for 8 h at 75°C under stirring. A 10% stoichiometric excess of the reagents was used relative to the epoxy groups. The reaction scheme is shown in Figure 1(a) and 1(b).

In order to eliminate grafting chemicals and other impurities, the reactive core-shell particles were dialysed against an aqueous solution of SDS (2 g/L), using dialysis tubing (Spectrum®, molecular cut
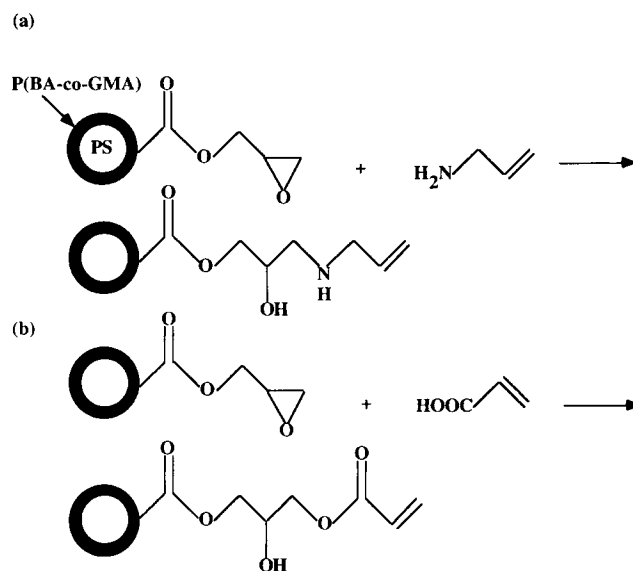
Figure 1 (a) Surface modification using an amine functional monomer (allyl amine). (b) Surface modification using an carboxyl functional monomer (acrylic acid).

6000–8000). The aqueous solution of SDS was changed daily for 14 days.

Quasielastic Light Scattering (QELS)

Particle sizes for all latexes were measured using a Coulter Model N4MD submicron particle analyzer at 20°C and at a scattering angle of 90 degrees. The latexes were diluted with an aqueous SDS solution (3 g/L) before analysis.

Transmission Electron Microscopy (TEM)

The latexes were stained with ruthenium tetroxide (RuO_4), and the particle morphologies were examined by TEM (JEOL 100U).[21] The staining with RuO_4 vapor was carried out as follows. A drop of the latex was placed on a Cu microscope grid. The Cu microscope grids were mounted on the edge of a glass slide and suspended above an aqueous solution of RuO_4 in a closed container. The exposure to the RuO_4 vapors was 10 min at room temperature. In the TEM micrographs, the PS cores appear dark and the P(BA-co-GMA) shells bright.

UV Curing

A photoinitiator (Darocur 1173, Ciba) was added to the core-shell latexes (2% w/w calculated on solids content). The mixture was allowed to stand overnight. Films were prepared from the latexes by cast-

ing onto clean glass plates and air-drying at room temperature for 3 days. The films were then dried at room temperature under vacuum in a desiccator for 2 days. Curing of the films was performed at room temperature by exposure to UV light from a I.S.T. Giardina curing unit. The unit contained two medium pressure mercury lamps operating at 80 watts/cm. Exposure time was 32 s for all samples.

Fourier Transform Infrared Spectra (FTIR)

The grafting reactions were demonstrated by FTIR spectroscopy. Dried latex films were dissolved in chloroform, and thin films were prepared by casting the solutions onto potassium bromide pellets. The FTIR spectra were recorded using a Bruker IFS 66 instrument. All spectra were recorded in the mid-infrared range ($4000-500$ cm^{-1}) with a resolution of 2 cm^{-1}.

Determination of Free Acrylic Acid

Unreacted acrylic acid was determined by GC analysis after allowing the free acrylic acid to react with methanol under acidic conditions to give methyl acrylate.[22] Latex (2.0 g), methanol (0.2 g), and toluene (0.1%) as an internal reference were mixed at room temperature. The mixture was analysed for acrylic acid and methyl acrylate by GC after 1, 3, 6, and 24 h. One drop of 4N H_2SO_4 was then added, and the mixture stirred at room temperature. The mixture was reanalyzed for methyl acrylate by GC after 5 min and after 24 h. After 48 h, one drop of concentrated H_2SO_4 was added to the same mixture and analyzed after 15 min. The procedure was controlled by analyzing a mixture of acrylic acid (0.03 g), methanol (2 g), and toluene (0.1%) with and without the addition of H_2SO_4.

Thermal Mechanical Analysis (TMA)

Latex films were examined by TMA using a Mettler TMA 40 measuring cell with a Mettler TA 4000 Processor. Cured and uncured film samples (7×7 mm, thickness $110-190$ μm) were analyzed between $-40°C$ and $70°C$ at a constant temperature rate of $5°C$/min, using a load of $0.05N$ and a dynamic load of $\pm0.025N$. The frequency used was $\frac{1}{12}$ Hz.

Degree of Swelling and Gel Content

Swelling in butanol and determination of gel content of cured and uncured film samples was performed according to Pepper et al.[23] Swelling index was de-

termined by eq. (1) and the Gel content was determined by eq. (2).[24]

Approximately 0.1 g of dry latex film was weighed into a tube containing a sintered glass filter disk. The tube containing the sample was immersed in 1-butanol at room temperature for 24 h. The amount of 1-butanol taken up by the film was determined by first weighing the glass filter tube after removing excess 1-butanol by centrifugation for 20 min at 3500 rpm and then by reweighing after drying at 50°C for 24 h.

Swelling Index

$$= \frac{\text{weight of wet gel} - \text{weight of dry gel}}{\text{weight of dry gel}} \quad (1)$$

$$\text{Gel content } (\%) = \frac{\text{weight of dry gel} \times 100}{\text{weight of dry latex film}} \quad (2)$$

RESULTS AND DISCUSSION

The objective of the present investigation was the preparation of a latex binder system that was UV curable without the use of any crosslinking monomers. A heterogeneous film-forming latex system consisting of particles having a high T_g PS core and a low T_g shell of poly(BA-co-GMA) was prepared as a model system. The latex particles were modified by post-polymerization reactions of the pendant epoxy groups with allyl amine and sodium acrylate, respectively.

Preparation and Modification of Core–Shell Particles

A PS seed latex was prepared by batch emulsion polymerization of styrene at 70°C under the influence of potassium persulphate (KPS). The latex particles were shown to have a narrow size distribution with an average diameter of 108 ± 19 nm (Table I), according to quasielastic light scattering (QELS). After dialysis, which was carried out in

Table I QELS Measurements of Seed Latex and Modified and Unmodified Core–Shell Latex Particles

Particles	Diameter (nm)
PS seed	108 ± 19
PS/P(BA-co-GMA) unmodified	123 ± 26
PS/P(BA-co-GMA) modified	126 ± 26

order to eliminate the excess of the initiator, the latex was used as a seed for a semicontinuous polymerization of BA and GMA. The monomers were continuously fed to the reactor under starvation conditions; i.e., the monomers were added at a sufficiently low rate in order not to create a pool of liquid monomer in the reactor. Under such conditions, formation of new particles in the second stage polymerization is avoided. The polymerization was carried out in a calorimetric reactor using a vanadium (IV)/ascorbic acid redox initiation system, which permitted close control of the polymerization rate.

The GMA monomer was added late in the second-stage polymerization in order to locate the epoxy groups near the surface of the particles.[25] Because of their high reactivity, some of the epoxy groups may enter into crosslinking side reactions or become hydrolysed by water.[26] Hydrolysis was minimized by adjusting the pH of the final latex.

Particle morphology is controlled by many factors, including the hydrophilicity of the monomers and polymers; the internal particle viscosity; the molecular weight of the polymers; the degree of grafting between the two polymer phases; the temperature; and the rate of transport of monomers, radicals, and oligomers.[13] Cavaillé et al.[27] have investigated the preparation of PS/PBA heterogeneous particles, and they reported that PBA formed domains that did not surround the PS seed particles. The second-stage polymerization was conducted at 70°C. In the present work, however, the second stage was carried out at a much lower temperature (25°C) under redox initiation. Under these conditions, particles having a uniform shell of the BA-GMA copolymer around the PS core were produced. Higher temperatures resulted in the formation of large domains of P(BA-co-GMA) on the PS-particles instead of a true core-shell morphology. The morphology development presumably is a consequence of the higher molecular mobility of the polymer phases at the higher temperature, and the increased rates of diffusion of the monomers.[28]

The TEM micrograph in Figure 2(a) shows the unmodified core shell particles. Because of the RuO₄ staining, the core appears dark and the shell bright in the micrographs. It is evident that although the PS core is not perfectly centered in the heterogeneous particle, it is completely covered by the soft poly(BA-co-GMA) phase. No inclusions of the soft phase could be observed. The average particle diameter of the core-shell particles was 123 ± 26 nm, according to QELS measurements (Table I).

As mentioned above, allyl amine and the sodium salt of acrylic acid, respectively, were used as nucleophiles for the pendant epoxy groups in the core-shell particles for the introduction of UV-reactive double bonds into the shell. A reaction scheme is given in Figure 1. Since the carboxylate group is a weaker nucleophile than the amino group, longer reaction times had to be used for the sodium acrylate in order to accomplish the reaction. For comparative reasons, however, the same reaction time was used for both reagents (8 h). Increasing the reaction rates by increasing the concentration of the grafting chemicals was found to destabilize the latex, unless high concentrations of the surfactant (SDS) were used. High SDS concentrations had to be avoided, however, because of the adverse effects on the film formation.

## Characterization of Modified Core–Shell Particles

The grafting reactions gave rise only to a very limited increase of the average particle diameters, according to QELS measurements (Table I). This observation indicates that no agglomeration occurred during the grafting process. However, the morphology of the PS/P(BA-co-GMA) core shell particles showed some changes, according to the TEM micrographs given in Figure 2(b) and (c). The RuO₄ staining used in the preparation of the TEM samples is known to be more selective for polymers containing C — C double bonds and aromatic groups than for the BA/GMA polymers. A comparison of the original core–shell particles and the allyl amine modified ones in Figure 2(a) and (b), respectively, indicates that the grafting reaction has produced unsaturated domains at the particle surfaces. The formation of these domains also changed the cross section of the particles, which became more irregular in shape. A similar morphology change was also visible for the acrylate grafted particles [Fig. 2(c)], although, in this case, the domains seemed to be smaller and more evenly distributed over the particle surface.

The incorporation of allyl amine and sodium acrylate, respectively, into the particles was demonstrated by FTIR analysis of films prepared from the modified and unmodified latexes, after removal of the excess of the grafting chemicals by dialysis. The absorbance band connected to the out-of-plane phenyl ring vibration of PS at 700 cm⁻¹ was used as an internal reference to account for variations in sample thickness and instrument recording.[29,30]

The FTIR spectra given in Figure 3(a) show characteristic changes attributable to the reaction of epoxy groups with allyl amine [see Fig. 1(a)]. As
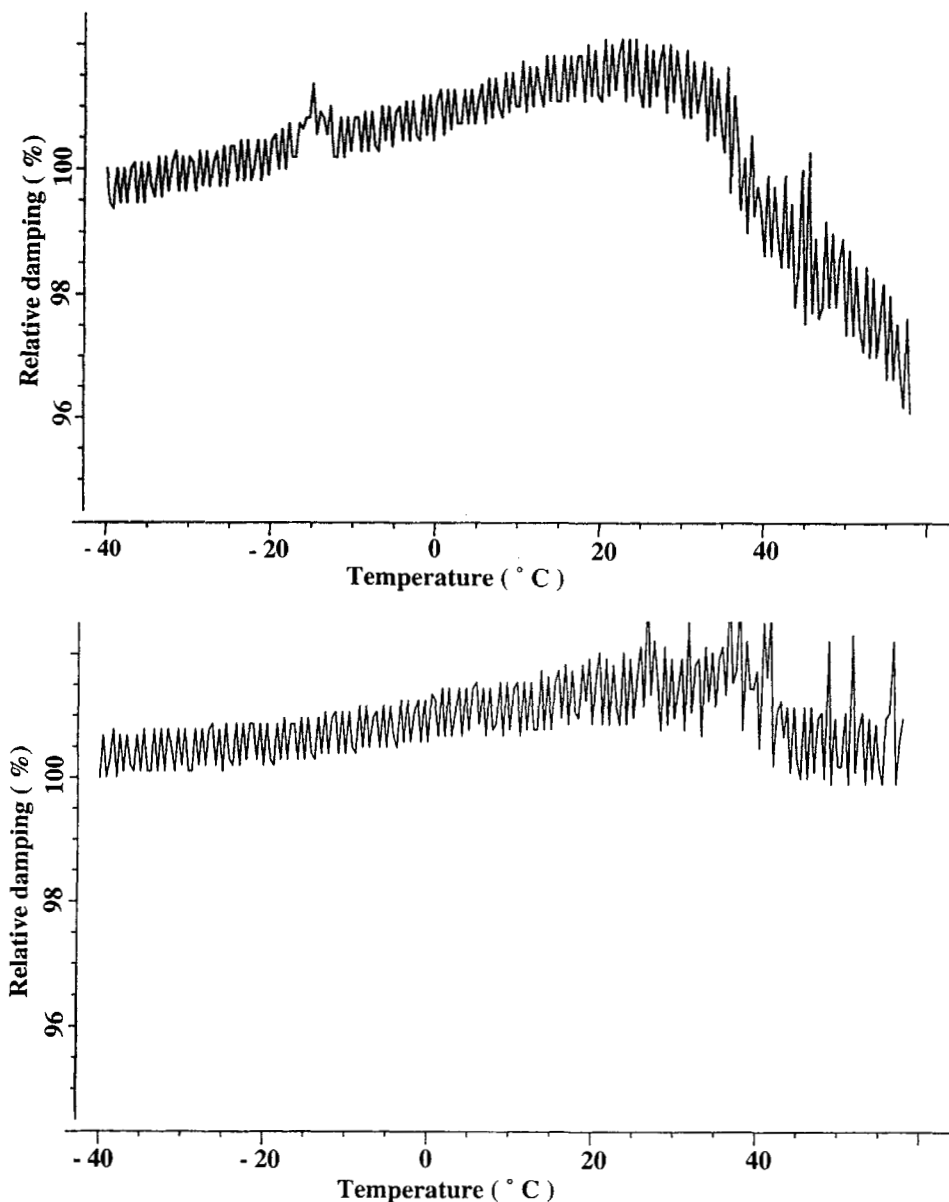
(a)

(b)

(c)
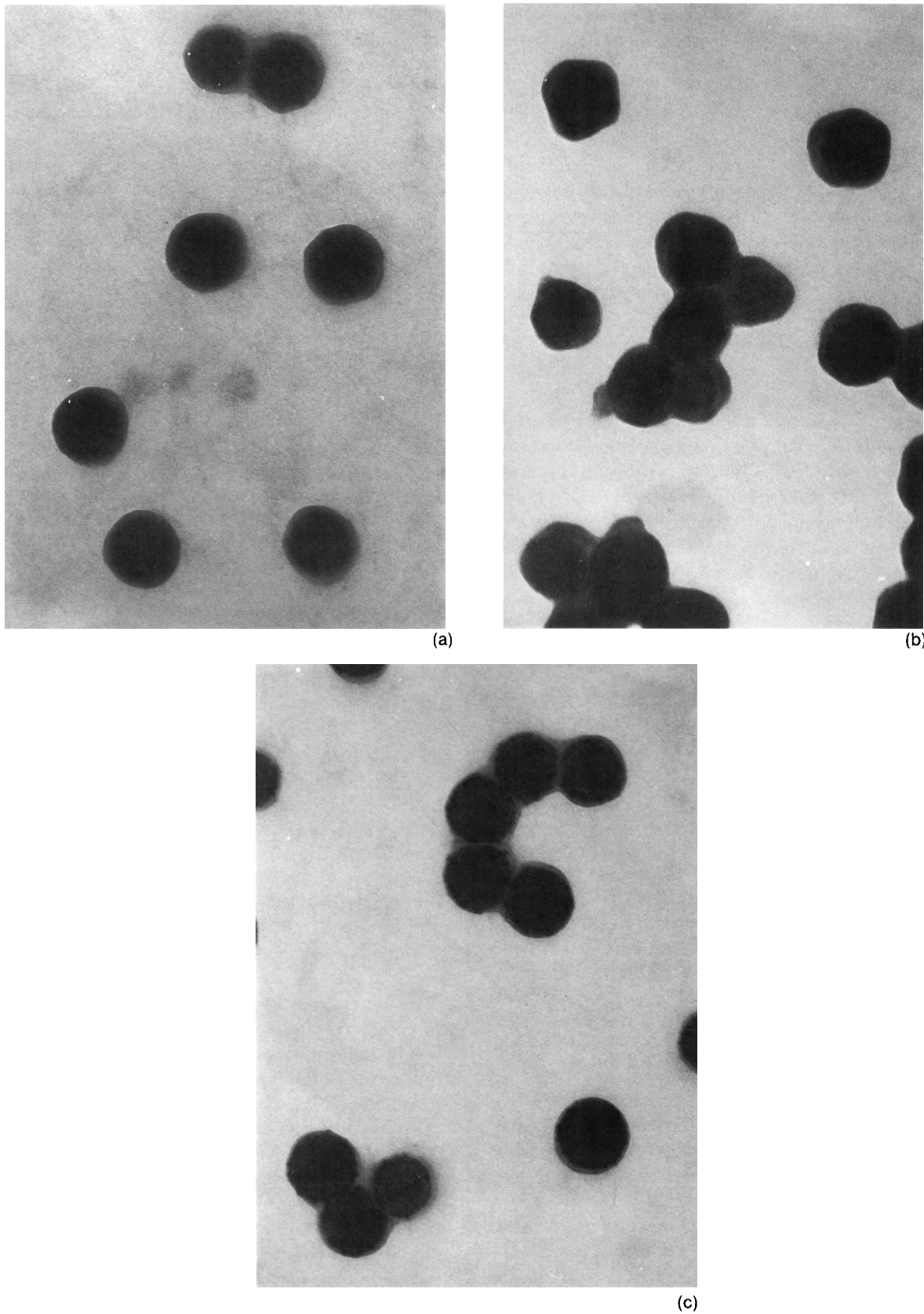
Figure 2 (a) TEM micrograph of unmodified PS/P(BA-*co*-GMA) core shell particles. (b) TEM micrograph of allyl amine modified PS/P(BA-*co*-GMA) core shell particles. (c) TEM micrograph of sodium acrylate modified PS/P(BA-*co*-GMA) core shell particles.
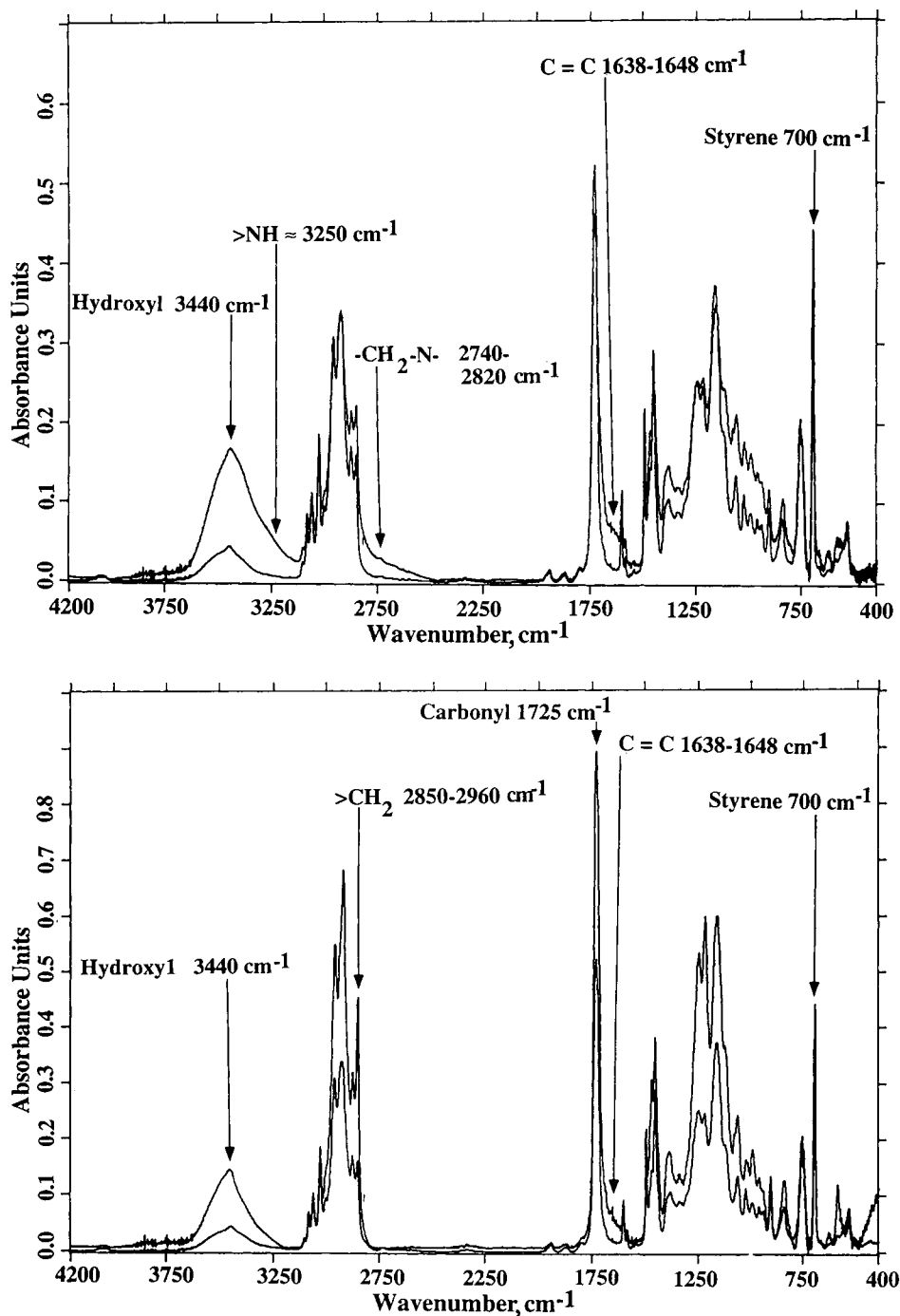
Figure 3   (a) FTIR spectra showing unmodified PS/P(BA-*co*-GMA) core shell latex (lower curve) and allyl amine modified latex (upper curve). (b) FTIR spectra showing unmodified PS/P(BA-*co*-GMA) core shell latex (lower curve) and sodium acrylate modified latex (upper curve).

compared to the spectrum of the unmodified latex [Fig. 3(a), lower curve], the modified one shows changes in the hydroxyl content, and new absorbance peaks assigned to $\diagdown$NH, $-CH_2-N-$, and

$C=C$ [Fig. 3(a), upper curve]. Similarly, the spectra in Figure 3(b) show characteristics depending on the reaction of epoxy groups with sodium acrylate [Fig. 1(b)], i.e., an increase of the content of hydroxyl and carbonyl groups and a new absorbance band that may

Figure 4 (a) TMA diagram of unmodified PS/P(BA-*co*-GMA) core shell particles before UV radiation. (b) TMA diagram of unmodified PS/P(BA-*co*-GMA) core shell particles after 32 s of UV radiation. (c) TMA diagram of sodium acrylate modified PS/P(BA-*co*-GMA) core shell particles before UV radiation. (d) TMA diagram of sodium acrylate modified PS/P(BA-*co*-GMA) core shell particles after 32 s of UV radiation.

be assigned to C═C double bonds (modified latex, upper curve; unmodified latex, lower curve). The FTIR analyses thus supports the view that allyl amine and sodium acrylate, respectively, have reacted with epoxy groups of the GMA residues in the shell polymer.

UV Curing

When exposed to UV radiation, films prepared from the modified core-shell latexes should display greater changes in their physical and mechanical properties than films prepared from the unmodified latexes. For testing of the UV reactivity, film specimens were prepared from the latexes after addition of an acetophenone photoinitiator, Darocure 1173. Acetophenone derivatives form initiating radicals under UV radiation either by hydrogen abstraction or by homolytic scission.[1] Since Darocure 1173 is resin-soluble rather than water-soluble, it was necessary to allow the mixture of the latex and the photoini-
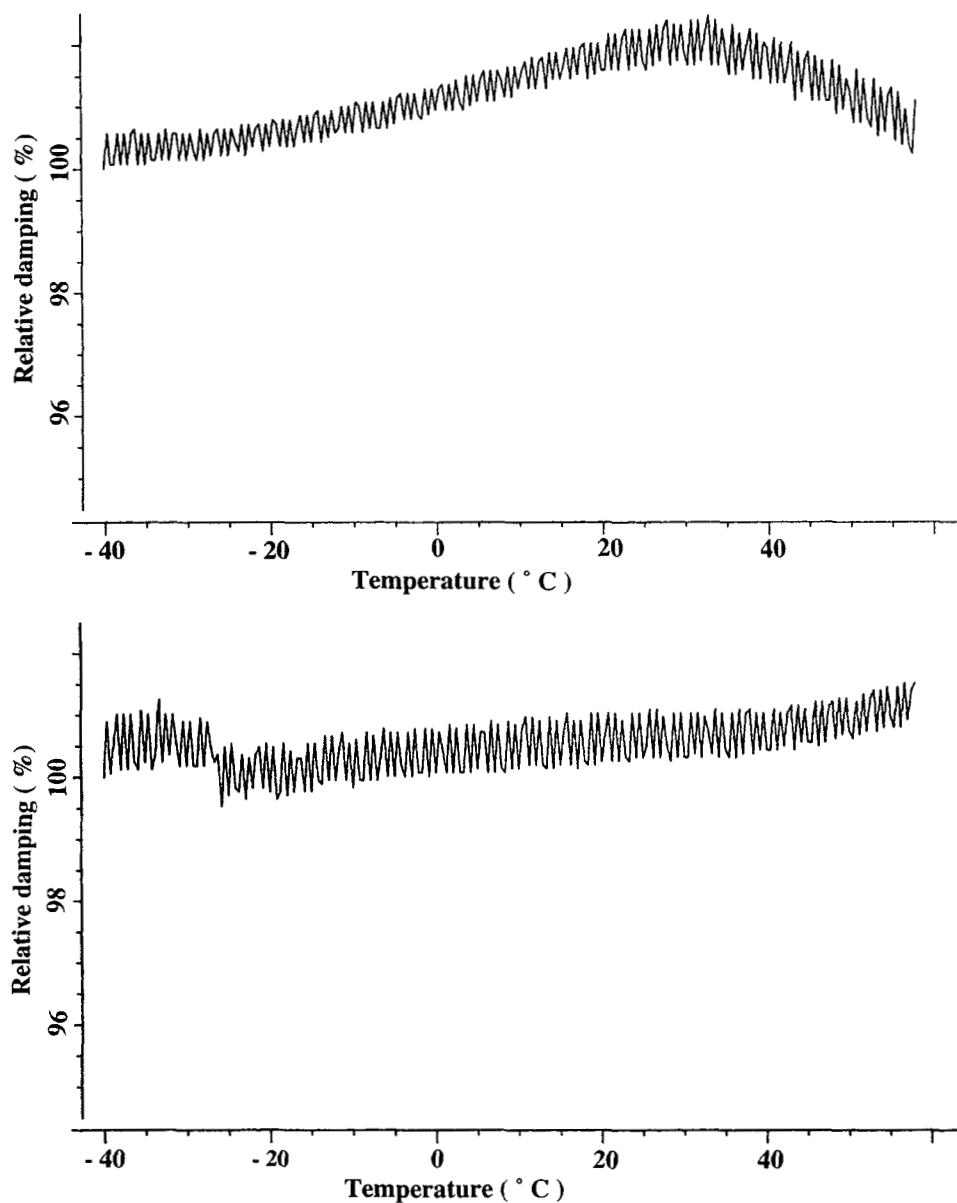
Figure 4   (*Continued from the previous page*)

Table II   Gel Content and Swelling in 1-Butanol for Cured and Uncured Latex Film Samples

Sample	Swelling Index	% Gel
PS/P(BA-GMA) ungrafted[a]	1.16	89
PS/P(BA-GMA) ungrafted[b]	0.72	90
PS/P(BA-GMA) allyl amine grafted[a]	0.67	89
PS/P(BA-GMA) allyl amine grafted[b]	0.38	94
PS/P(BA-GMA) acrylic acid grafted[a]	1.11	88
PS/P(BA-GMA) acrylic acid grafted[b]	0.53	94

[a] No UV-Radiation.
[b] 32 seconds of UV-Radiation.

tiator to stand overnight before film preparation in order to incorporate the photoinitiator into the particles.

Upon UV irradiation, a decrease of the carbon–carbon double bond absorbance at 1638–1648 cm^{-1} in the FTIR spectrum was expected to take place. However, because of a substantial broadening of the carbonyl peak at 1725 cm^{-1}, quantitative determinations of such changes were prevented.

The mechanical properties of exposed and unexposed films were tested by TMA analysis. The TMA diagrams given in Figure 4(a)–(d) show the differences between ungrafted core shell particles before and after radiation and the acrylic acid grafted core shell particles before and after radiation, respectively. The diagrams indicate that exposed film derived from the ungrafted particles shows an increase in the softening temperature, as compared to the unexposed film. In the presence of a photoinitiator and at the level of UV radiation used in the present case, some crosslinking is likely to occur through chain transfer reactions, even though no unsaturation is present. However, if comparing films prepared from the acrylic acid grafted particles before and after radiation, a large increase of the softening temperature can be noted, as well as a decrease of the flexibility. These effects can be explained by the acrylic double bonds taking part in the crosslinking reaction. The effects of the unsaturation in the acrylic acid grafted material are also evident when comparing irradiated films prepared from ungrafted particles and acrylic acid grafted particles, respectively. A significant increase of softening temperature and stiffness can be noted.

It is clear from the TMA measurements that the core shell particles grafted with acrylic acid gave a more thoroughly cured film than the ungrafted core shell particles. The films derived from allyl amine grafted particles gave, after irradiation, films too brittle to be analyzed by TMA.

Swelling of a crosslinked material in a solvent is indicative of the degree of crosslinking. In order to further evaluate the UV curing of the latex films prepared, they were treated with 1-butanol for 24 h, and the swelling and the fraction of nonsoluble material (gel content) was determined. The results from the swelling experiments are summarized in Table II. It is obvious that all the film samples exposed to UV radiation, including those derived from the unmodified particles, showed a lower swelling ability and an increased gel content, as compared to the unexposed ones. These results demonstrate that a certain degree of crosslinking was obtained even if no unsaturation was present in the films, as

noted above. The films prepared from latex particles modified with allyl amine or acrylic acid, respectively, showed after UV irradiation a higher gel content and a lower degree of swelling, as compared to the unmodified latex film. It seems highly probable that the change in properties is a result of crosslinking via the carbon–carbon double bonds. The results from the swelling experiments are in good agreement with the results obtained from TMA analysis.

CONCLUSIONS

PS/P(BA-co-GMA) core-shell latex particles can be prepared via a two-stage emulsion polymerization procedure. Morphological characterization of the particles by TEM showed that the second stage polymerization had to be performed at a low temperature, (25°C) in order to produce a uniform P(BA-co-GMA) shell around the PS core.

The epoxy groups derived from the GMA comonomer can be utilized for the introduction of UV reactive unsaturated groups at the particle surfaces. Allyl amine and sodium acrylate, respectively, were shown to be active as nucleophilic reactants in this reaction.

The core shell particles carrying unsaturated groups were film-forming at room temperature. These films can be cross-linked by UV radiation, as shown by increased stiffness and gel content and decreased swelling in 1-butanol.

REFERENCES

1. R. Holman and P. Oldring, *U. V. and E.B. Curing Formulation for Printing Inks, Coatings and Paints.* Selective Industrial Training Associates Ltd., London, 1991, Chap 1.
2. J-M. Loutz, W. Demarteau, and P.-Y. Herze, *Polym. Paint Colour J.,* **178**(4219), 571–580 (1988).
3. P. G. Garratt and K. F. Klimesch, *Polym. Paint Colour J.,* **184**(4343), 30–32 (1994).
4. P. H. Stenson, *Radtech Rept.,* **7**(1), 18–23 (1993).

5. F. J. Kosnik, *Mod. Paint Coatings J.*, 42–44 (June 1989).
6. M. Philips, J. M. Loutz, S. Peeters, R. Destexhe, and L. Lindekens, *Radtech '92 Conf. Proc.*, 157–161 (1992).
7. P. H. Stenson, *Radtech '90 Conf. Proc.*, 697–702 (1990).
8. V. D. McGinnes, R. J. Seidewand, and J. R. Erickson, U.S. Pat. 4,107,013, (1978).
9. E. P. Zahora, S. C. Lapin, G. K. Noren, and E. Wehman, *Radtech '94 Conf. Proc.*, 120–124 (1994).
10. W-D. Hergeth, K. Schmutzler, and S. Wartewig, *Makromol. Chem., Macromol. Symp.*, **31**, 123–142 (1984).
11. S. Lee and A. Rudin, *J. Polym. Sci., Polym. Chem.*, **30**, 865–871 (1992).
12. J-E. Jönsson, PhD Thesis, Lund Institute of Technology, Sweden, 1994.
13. J-E. L. Jönsson, H. Hassander, L. H. Jansson, and B. Törnell, *Macromol.*, **24**, 126–131 (1991).
14. M. Hidalgo, J. Y. Cavaillé, J. Guillot, A. Guyot, J. Perez, and R. Vassoille, *J. Polym. Sci., Polym. Phys.*, **33**, 1559–1572 (1995).
15. R. H. Yocum and E. B. Nyquist, Eds., *Functional Monomers. Their Preparation, Polymerization, and Application.* Vol. 2, Marcel Dekker, New York, 1974, Chap. 1.
16. K. Kjellquist, J. Rassing, and B. Wesslén, *J. Appl. Polym. Sci.*, **51**, 1063–1070 (1994).
17. K. Kjellquist, J. Rassing, and B. Wesslén, *J. Appl. Polym. Sci.*, **57**, 1381–1390 (1995).
18. M. Wolfsberger, F. J. Schindler, R. S. Beckley, and R. W. Novak, U.S. Patent 5,306,744A, (1994).
19. O. Vogl, Y. Okahata, D. A. Bansleben, J. Muggee, and M. Purgett, *J. Macromol., Sci. Chem.*, **A21**, 1217–1235 (1984).
20. H. Nilsson, C. Silvergren, and B. Törnell, *Chem. Scr.*, **19**, 164 (1982).
21. J. S. Trent, J. I. Scheinbeim, and P. R. Couchman, *J. Polym. Sci., Polym. Lett. Ed.*, **19**, 315–319 (1981).
22. A. Streitwieser and C. H. Heathcock, *Introduction to Organic Chemistry*, 3rd ed., Macmillan, New York, 1985, Chap. 28.
23. K. W. Pepper, D. Reichenberg, and D. K. Hale, *J. Chem. Soc.*, **4**, 3129–3136 (1952).
24. R. T. Klun, *Fundamentals of Latex Technology,* Tappi 1988 Coating Binders Seminar, 5–15 (1988).
25. S. Magnet, J. Guillot, A. Guyot, and C. Pichot, *Prog. Org. Coat.*, **20**, 73–80 (1992).
26. J. A. Kling and H. J. Ploehn, *J. Polym. Sci., Polym. Chem.*, **33**, 1107–1118 (1995).
27. J. Y. Cavaillé, R. Vassoille, G. Thollet, L. Rios, and C. Pichot, *Colloid Polym. Sci.*, **269**(3), 248–258 (1991).
28. S. Lee and A. Rudin, *J. Polym. Sci., Polym. Chem.*, **30**, 2211–2216 (1992).
29. D. H. Williams and I. Fleming, *Spectroscopic Methods in Organic Chemistry*, 4th ed., McGraw-Hill, London, 1989, Chap. 2.
30. C. Lowe and P. K. T. Oldring, *Test Methods for UV and EB Curable Systems*, SITA Technology, London, 1994, Chap. 9.