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Design and cross-linking reaction of blend of reactive polymer latex particles

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In recent years, there has been growing interest in the reactive emulsion polymer, which has a vast of application in the field of coating and adhesive. The reactive groups in polymer chains can facilitate cross-linking reactions, thus enhances the physical and chemical integrity of coalesced latex films. These systems include functional latex particles containing, for example, epoxy groups [1], *N*-methylolacrylamide groups, *N*-(isobutoxymethy)-acrylamide [2], acetoacetate groups [3] and ketone carbonyl groups [4]. Latex film formation is a complicated and multistage phenomenon. In essence, utilization of physical coalescence and chemical reactivity represent a combination of thermoplastic and thermosetting processes, which involve water evaporation, latex particle packing, particle deformation, and coalescence with interparticle diffusion of polymer chains and cross-linking reactions [5]. Recent studies [6–8] show that in the thermosetting latex films polymer diffusion across the intercellular boundary must precede cross-linking or the film remain weak. If the kinetics of cross-linking reactions within individual latex particles exceeds particle interdiffusion across particle-particle boundaries, latex films may exhibit limited coalescence. Winnik *et al.* reported the relative rates of polymer diffusion and cross-linking in a latex film containing *N*-isobutoxymethylacrylamide as a cross-linking agent [2]. Park studied the effects of functional group density of reactive latexes on the reactive rates of interdiffusion and cross-linking reaction during film formation and annealing process [9]. Most of the literatures about reactive latex particles focused on the functional groups distributing on particle surfaces. However, few reports about the effect of reactive groups inside latex particles on polymer films cross-linking reaction and mechanical property can be found.

In this paper, reactive particles containing epoxy or carboxyl groups were synthesized to investigate the influence of epoxy inside latex particles on polymer diffusion and cross-linking reaction. Latexes were prepared by copolymerization of methyl methacrylate (MMA), *n*-butyl acrylate (nBA), glycidyl methacrylate (GMA) and acrylic methacrylate (AA) through seeded semicontinuous emulsion polymerization under monomer-starved conditions. Three types of latex particles were synthesized: epoxy groups were present on latex particles surfaces (*p*-(MMA/nBA)(core)/*p*-(GMA/MMA/nBA)(shell)) by adding reactive monomer GMA during the final stages of emulsion polymerization; epoxy groups were inside latex particles (*p*-(GMA/MMA/nBA)(core)/*p*-(MMA/nBA)(shell)) by adding GMA during the first stages of polymerization; carboxyl groups were present on latex particle surfaces (*p*-(MMA/nBA)(core)/*p*-(MMA/nBA/AA)(shell)) by adding reactive monomer AA during the final stages of emulsion polymerization. Two types of blend latex films shown in Fig. 1 were investigated, Blend A was obtained by mixing *p*-(GMA/MMA/nBA)(core)/*p*-(MMA/nBA)(shell) and *p*-(MMA/nBA)(core)/*p*-(MMA/nBA/AA) latexes in 1:1 w/w% ratio. Blend B was prepared in the same way, but *p*-(MMA/nBA)(core)/*p*-(GMA/MMA/nBA)(shell) and *p*-(MMA/nBA)(core)/*p*-(MMA/nBA/AA)(shell) latexes were used. The films used for gel content and tensile strength experiments were prepared as follows: a blend latexes which contains 2 wt.% of tetramethylammonium hydroxide (TMAH) was diluted to 22% w/w solids using distilled water and then poured in a poly(tetrafluoroethylene) mold and allowed to coalescence for 3 days at 25 °C, followed by annealing latexes films at 80 °C for 1 hr. A few drops of the latex dispersion were spread on a small glass plate. The film was allowed to dry at 25 °C for 5 hr and peeled off, followed by annealing at 80 °C for 1 hr. The film was used for FT-IR measurement.

In this study, we measured the degree of cross-linking by measuring films gel content. Tensile strength measurements were used as an indicator of the cohesive strength of a film.

A typical transmission electron microscope (TEM) image of the synthesized latex particles is shown in Fig. 2. It is seen that the latex particles have a broad size distribution and the larger particle size is ∼100 nm.

The cross-linking reaction between epoxy and carboxyl groups was confirmed by FT-IR examinations. Fig. 3 shows the FT-IR spectra of the blend A film, showing the characteristic absorption at 910 cm^{-1} for epoxy groups containing the latex particles before cross-linking reaction and missing one after cross-linking reaction. This indicates that epoxy groups reacted with carboxyl groups completely during the process of annealing to form a network structure.

Fig. 4 shows the gel content (wt.%) of blend latex films as a function of the concentration of GMA in

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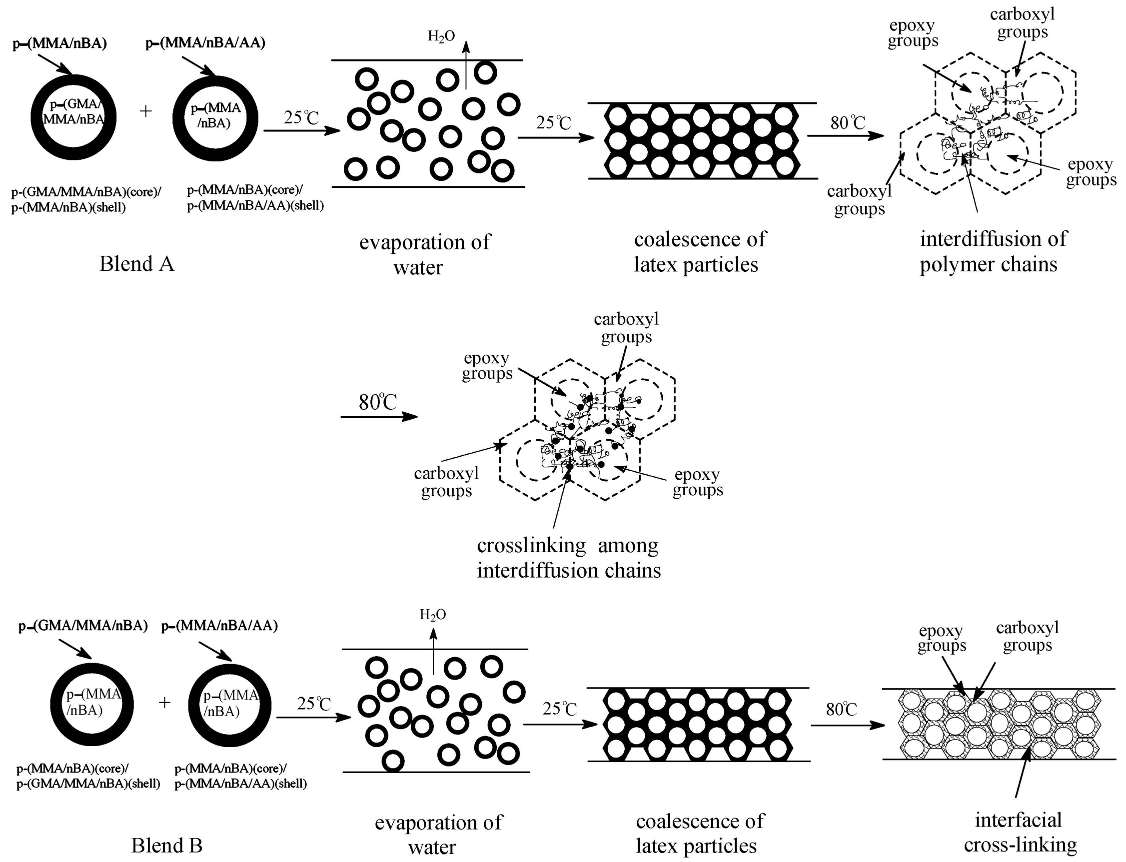

Figure 1 Schematic representation of interdiffusion and cross-linking of blend A and blend B films: blend A, 1:1 w/w% *p*-(GMA/MMA/nBA)(core)/*p*-(MMA/nBA)(shell) and *p*-(MMA/nBA)(core)/*p*-(MMA/nBA/AA) latexes; blend B, 1:1 w/w% *p*-(MMA/nBA)(core)/ *p*-(GMA/MMA/nBA)(shell) and *p*-(MMA/nBA)(core)/*p*-(MMA/nBA/AA)(shell) latexes.

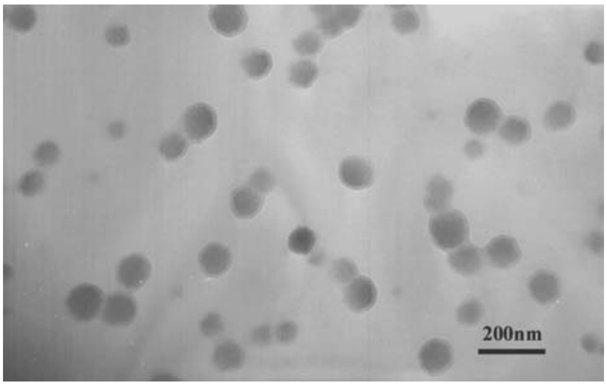

Figure 2 TEM micrographs of latex particles *p*-(GMA/MMA/nBA) (core)/*p*-(MMA/nBA)(shell).

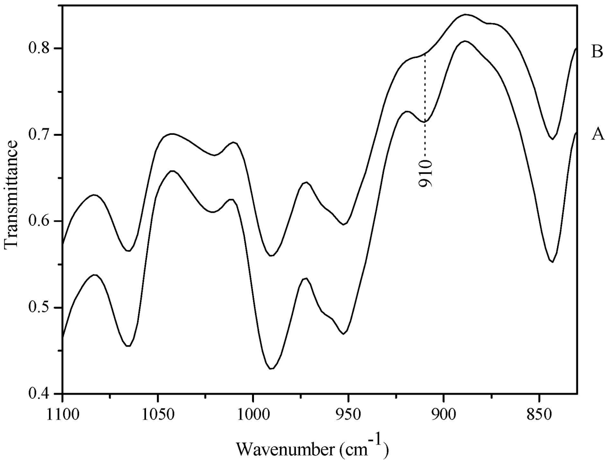

Figure 3 FT-IR spectra in the 1100–850 cm^{-1} region of blend A latex films: before (A) and after (B) cross-linking reaction.

feed of monomers (wt.%). It is seen that the gel content of blend A and B initially increases quickly with the increasing of GMA concentration, but subsequently increases slowly at GMA concentration greater than 5% for Blend A and decreases slowly at GMA concentration greater than 8% for blend B. In the case of blend B, the gel content decreases, which indicates the cross-linking reaction of polymer chain with reactive groups precede its interdiffusion across the particle boundaries. It is due to the epoxy and carboxyl groups on the shell layer of latex particles, respectively, and their cross-linking reaction would take place in the boundary of particles to form a cross-linking structure, as a result, the polymer chain interdiffusion across the particle boundaries and further reaction would be hindered. However, in the case of blend of A, the epoxy groups in the core layer of latex particles and the core layer is coated with a shell layer of inert copolymer, thus, polymer chains with reactive epoxy groups must diffuse across the inert polymer shell layer then contact and react with carboxyl groups on the surface of particles. This means the polymer chains diffusion precedes cross-linking reaction, which is important for improving the performance of latex films. As show in Fig. 5, the tensile strength always increases with increase of

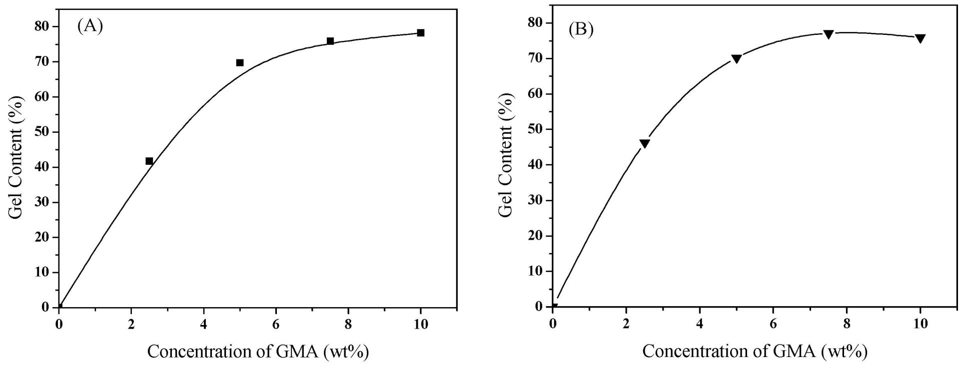

Figure 4 Plots of gel content (%) of blend latex films versus the concentration of GMA (wt%): (A) Blend A; (B) Blend B.

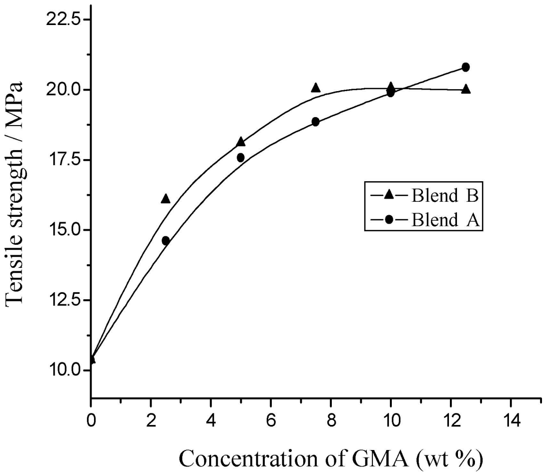

Figure 5 Tensile strength versus concentration of GMA for blend A and blend B latex films.

the GMA concentration for latex films of blend A, but not for the films of blend B.

In conclusion, the diffusion of polymer chains bearing reactive groups can precede the cross-linking reaction by designing the reactive groups in the core layer of the core-shell structured latex particles, resulting in the improvement of properties of latex films.

References

1. H. MOUAZIZ, A. LARSSON and D. C. SHERRINGTON, *Macromolecules* **37** (2004) 1319.
2. R. H. LIU and M. A. WINNIK, *Macromolecules* **34** (2001) 7306.
3. R. J. ESSER, J. E. DEVONA and D. E. SETZKE, *Prog. Org. Coat* **36** (1999) 45.
4. Y. NAKAYAMA, *Prog. Org. Coat.* **31** (1997) 105.
5. M. A. WINNIK, P. PINENQ, C. KRUGER, *et al.*, *J. Coat. Technol.* **71** (1999) 892
6. A. ZOSEL and G. LEY, *Macromolecules* **26** (1993) 2222.
7. H. H. PHAM and M. A. WINNIK, *Macromolecules* **32** (1999) 7692.
8. Y. Q. ZHAO and M. W. URBAN, *Macromolecules* **33** (2000) 8426.
9. Y. J. PARK and J. H. KIM, *Colloid. Surf. A* **153** (1999) 583.

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