Preparation and Properties of Thermo-sensitive Latex Films

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Abstract

Polymer particles with hydrophobic core and hydrophilic shell were prepared via a three-step method. First, poly (butyl methacrylate –co- methyl methacrylate) (p-(BMA-MMA)) latex was prepared through emulsion polymerization. Then, using the p-(BMA-MMA) latex as seed, a uniform shell of poly(glycidyl methacrylate) (p-GMA) was formed by using a redox initiation system under kinetically controlled conditions. The contents of the shell were in the range of 5-15 wt. %. Finally, the epoxy groups existing in the shell were converted into the ionic species through the reaction with triethanolamine hydrochlorid in aqueous phase, resulting in a charged hydrophilic shell. The solid particles could be re-dispersed in water to afford a stable emulsion. Latex films were prepared by spin-casting the aqueous mixture of the latex made from the solid latex particles and poly (vinyl alcohol) (PVA) onto an aluminum substrate and then dried at room temperature. The contact angles between the core-shell latex films and water were in the range of 16.1^o-27.5^o at 25 ^{o}C, but would turn to be larger than 87^o after the films were baked at 150 ^{o}C for a short period of time. This indicated that the films were completely switched from hydrophilicity to hydrophobicity by the action of heat. Additionally, the latex films before baking could be easily washed away from the substrate with neutral water, but could no longer be removed after baking. When an IR dye (with maximal absorption at 830nm) was incorporated into the film, the film became sensitive to LD lasers emitting at 830 nm and negative images were obtained after exposed by LD laser and developed by neutral water.

Keywords: core-shell particle; latex film; thermo-sensitive

Introduction

Core-shell particles have attracted much attention due to their unique structure and properties. [1-3]. The main reason is that these particles have found wide applications in various fields such as catalysis and coatings, nonlinear optics, optical and magnetic data storage, chemical and biochemical sensors, diagnostic testing, bioseparations, controlled release of drugs and gene therapy, etc. [4, 5] The properties of core-shell particles largely depend on the shell polymer and especially the morphological feature of the particles. For example, surface properties (such as surface energy or affinity) of the film formed by core-shell particles are mainly determined by the shell polymer despite that the shell is only a small fraction of the core [6]. Furthermore, the surface properties may undergo great changes when the core-shell particles are physically or chemically destructed, e.g., melted by heat. Thus, it is possible to design an imaging media which is made up of polymer particles with large hydrophobic core and a thin hydrophilic shell and, it should undergo affinity change from hydrophilic state to hydrophobic one when exposed to thermal laser radiations. In this paper, we mainly focused on the synthesis of a kind of core-shell particle and its potential use in building a new negative working thermo-sensitive imaging media, which could be processed with neutral water.

Experimental

Preparation of Core-shell Latex Particles Containing Epoxy Groups in the Shell (CS-1)

A mixture of 700 ml of deionized water, 150.0 g of MMA, 150.0 g of BMA and 1.5 g of SDS were added into a four-necked flask and mechanically stirred for 2 h at room temperature under a nitrogen atmosphere to allow for pre-emulsification. Then, the temperature was raised to 60 ^{o}C and 100 ml of $K_2S_2O_8$ solution (5 wt.%) was added. The polymerization was allowed to proceed at 70 ^{o}C for 5 h and at 80 ^{o}C for 2 h, yielding a stable latex with the particle size of 56 nm (Figure 1a), which was used as seed latex in the next stage. For the preparation of core-shell latex, *t*-BHP + $VOSO_4$ aqueous solution was added to the above emulsion under continuous nitrogen flow and mechanic stirring at 25 ^{o}C in 15 min. LAA aqueous solution and pre-emulsion of GMA / SDS were fed alternately by separate peristaltic pumps at different predetermined intervals. The feeding rate was carefully adjusted to allow the addition of the pre-emulsion to be completed 15-20 minutes earlier than that of the LAA solution. The core-shell latex in this stage was denoted as CS-1. The relative content of the shell polymer was controlled by the amount of the GMA pre-emulsion added in the second stage polymerization. In this work, the weight fractions of GMA relative to that of the core were 5.0 wt.% (CS-1-5), 10 wt.% (CS-1-10) and 15 wt.% (CS-1-15), respectively. The recipes are also listed in Table 1.

Surface Modification of CS-1 (Preparation of CS-2)

At ambient temperature and with constant stirring, calculated amount of aqueous triethanolamine hydrochlorid was added dropwise into the CS-1 latex. Then, the temperature was slowly raised to 70 ^{o}C and kept for 6 h. The resulting modified core-shell latex derived from CS-1-5, CS-1-10 and CS-1-15 were denoted as CS-2-5, CS-2-10 and CS-2-15, respectively. Solid colloidal particles were obtained with the emulsions by precipitation in aqueous methanol (75 wt.%), centrifugation, washing with fresh aqueous methanol (75 wt.%) and dried at 40 ^{o}C.

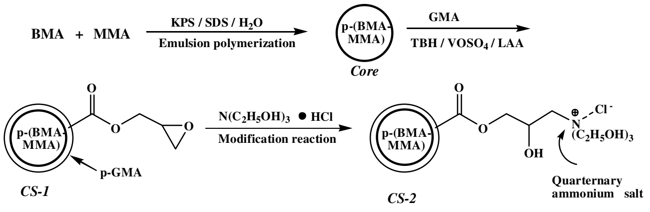
Preparation of Latex Films

In a typical experiment, CS-2-5 solid particles (2.00 g) and PVA1788 (0.15 g) were added into 20 ml of water and the suspension was agitated with a magnetic stirrer for 2 h, followed by ultrasonic emulsification for 10 min to obtain a stable latex. CS-2-5 latex film was prepared by spreading the above latex directly on a cleaned aluminium plate and allowed to dry at 40 ^{o}C in a vacuum oven. The CS-2-10 and CS-2-15 latex films were prepared according to the same procedure as CS-2-5.

Results and Discussion

Preparation of Core-shell Particles

The synthetic route of the core-shell particles was depicted in Scheme 1. First, p-(MMA-BMA) core latex was prepared by batch emulsion polymerization and subsequently used as seed for the semi-continuous polymerization of GMA in the same reactor. GMA was pre-emulsified with SDS and fed at a sufficiently low rate to avoid possible formation of new particles. Since the epoxy group is very active, it is necessary that the polymerization be conducted at relatively low temperatures. A redox initiation system, TBH/LAA/$VOSO_4$, was employed to prepare the p-GMA shell around the core. Because TBH was polymer-affinic, it was more likely adsorbed onto the surface of the core particles where in situ polymerization of GMA was started.



Scheme 1. *Synthesis of core-shell particles containing quaternary ammonium salts in the shell.*

Epoxy values of the prepared particles were measured according to the reported procedure and compared with the theoretic values to evaluate the efficiency [7]. As seen in Table 1, the actual epoxy values were about 82-88% of the calculated ones. The differences might be due to the hydrolysis of some epoxy groups in the shell. The shell polymer (p-GMA) of CS-1 was reacted with triethanolamine hydrochloride, giving the target product of CS-2 which possessed a hydrophobic core and a highly charged hydrophilic shell. The conversion rates of the epoxy group were found fixed in the range of 66-74% (Table 1) even if excess triethanolamine hydrochloride was used. About 26-34 percent of the epoxy groups still remained unchanged. With the progress of the modification, epoxy groups at the shell surface were all converted into the corresponding quarternary ammonium salts, creating a highly charged shelter which might prevent triethanolamine hydrochloride molecules from diffusing into the shell layer.

The latex particles were found narrowly distributed in size according to TEM. The results were also listed in Table 1. It could be found that there was little change in particle size for CS-1-5 and CS-1-10 relative to the core latex particle (56 nm). For CS-1-15, there was a slight increase (about 5%) in particle size after the incorporation of an epoxy containing shell. This net increase in size was reasonably attributed to and also a direct evidence of successful growth and attachment of the shell. In order to obtain sharp and contrasted images, latex samples were diluted and stained in 2.0 wt.% aqueous solution of phosphotungstic acid. The color of CS-2 (Figure 1c) was much darker than those of the core and CS-1 particles. The modified core-shell particle (CS-2) had an ionic shell which was more attractive to the phosphotungstic acid molecule. In other words, it was easier for the staining agent to be adsorbed on the surface of the CS-2 particles compared with that of the core and the CS-1 particles.

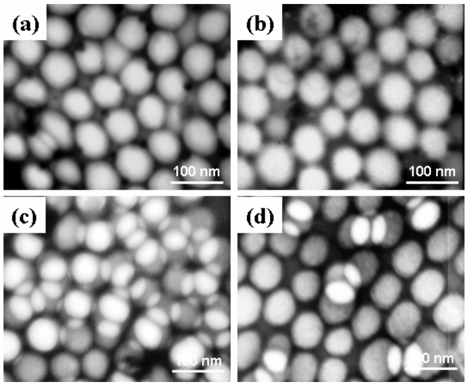


Figure 1. *TEM photographs of latex particles: (a) p-(BMA-MMA) core latex; (b) CS-1-15 latex; (c) CS-2-15 latex; (d) CS-2-15 solid particles redispersed in water. All the latex particles are stained with phosphotungstic acid. The scale bars stand for 100 nm.*

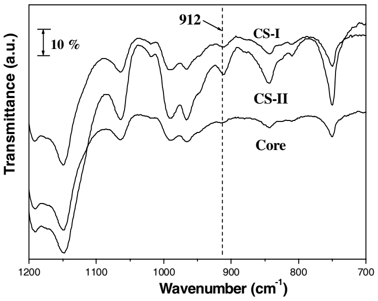


Figure 2. *FT-IR curves in the 700-1200 cm^{-1} region of the core, CS-1-15 and CS-2-15 latex particles.*

Table 1: Recipe and characteristics of the core-shell particles

	CS-1-5 (CS-2-5)	CS-1-10 (CS-2-10)	CS-1-15 (CS-2-15)
p-(BMA-MMA) core latex (27.1 wt.%) (g)	50.00 (0)	50.00 (0)	50.00 (0)
GMA(g)	0.68 (0)	1.36 (0)	2.04 (0)
GMA / core (wt:wt)	5:100(0)	10:100 (0)	15:100 (0)
TBH / $VOSO_4$ (mg)	40/1 (0)	80/2 (0)	120/3 (0)
LAA (mg)	55 (0)	110 (0)	165 (0)
Triethanolamine hydrochloride (g)	0 (3.56)	0 (7.11)	0 (10.67)
Particle size (nm)	56(56)	58(58)	59 (58)
Calculated epoxy value ($\times 10^{-2}$ mol/100g)	3.36 (0.00)	6.42 (0.00)	9.21 (0.00)
Measured epoxy value ($\times 10^{-2}$ mol/100g)	2.97 (0.78)	5.55 (1.69)	7.62 (2.52)
Conversion of epoxy group (%)	0 (73.73)	0 (69.55)	0 (66.93)

FTIR spectra were also recorded to monitor the presence of epoxy group (Figure 2). As seen, a new band at 912 cm-1 arising from the terminal epoxy group was detected after GMA polymerized over the p-(MMA-BMA) seed. As expected, a decrease of the 912 cm-1 absorption band was found in the spectrum of CS-2, indicating that some of the epoxy groups had been consumed after the reaction.

Thermal Behaviors of the Latex Particles

The thermal behaviors of the latex particles were monitored by TGA (Figure 3). As revealed by the figure, they exhibited different thermal decomposition behaviors. There was little weight loss (less than 1%) detected for the core particle until the temperature was raised to 250 °C, and the onset decomposition temperature was around 300 °C. However, two-staged decompositions were observed for the core-shell particles (CS-1-15 and CS-2-15). The first-stage decomposition started at 170 °C and the second-stage decomposition began at about 240 °C for both CS-1-15 and CS-2-15. The two-stage decomposition behavior might be explained by the presence of weakly bonded substituents such as epoxy or (and) quarternary ammonium moieties in the shell. It should be noted that there were much large weight losses observed for the core-shell particles when the temperature reached 300 °C, about 56% for CS-1-15 and 30% for CS-2-15. However, the weight loss for the core particles was around 10%. The big differences in weight loss were thought to be the result of the different epoxy contents of the core-shell particles according to the fact that the weight loss was in direct proportion to the epoxy content. Maybe the epoxy moieties could release active oxygen atoms or radicals, which greatly facilitated thermolysis of the polymers at high temperatures. Further investigation was needed to determine the mechanism. Moreover, the residual weight retentions at 400 °C were 8.7%, 23.7% and 28.5% for the core, CS-1-15 and CS-2-15 solid particles, respectively. Although at temperatures below 240 °C, the thermal stability decreased in the following order: the core polymer > CS-1-15 > CS-2-15, but when the temperature was increased above 380 °C, the core-shell particles of CS-1-15 and CS-2-15 showed better heat resistance than the core particles. It was likely that some cross-linking reactions occurred with the decomposition of epoxy groups (or quarternary ammonium salts) in the core-shell particles in the heating process, resulting in the formation of extra cross-linked polymers which should be more thermally stable than their linear counterparts.

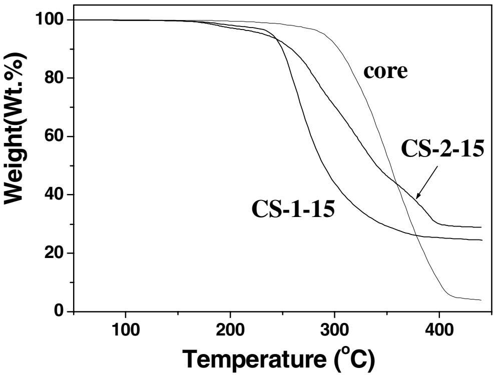


Figure 3. *TGA curves of the core, CS-1-15 and CS-2-15 latex particles (in nitrogen, heating rate: 10 °C min^{-1}).*

Properties of CS-2

One of the unique properties of CS-2 was that the solid colloidal particles could be redispersed in water very easily under the action of supersonic agitation, and the resulted suspension was very stable without the assistance of surfactants and other dispersant agents. This effect was believed to have been brought about by the ionic polymers of the shell surrounding the core, which acted as a very strong emulsifier or stabilizer and prevented the dispersed particles from aggregation. This assertion was supported by the micrographs of the redispersed solution of CS-2-5 particles (Figure 1d), and no apparent aggregations were found.

Latex films were made with the dilute latexes mediated by a water-soluble polymer of PVA1788, which acted as the binder polymer to facilitate the film forming. Contact angles of the latex films with water were taken as a criterion for evaluating the affinity of the film surface. The contact angles with water were 16.1 °, 22.4 ° and 27.5 ° for the CS-2-5, CS-2-10 and CS-2-15 latex films, respectively. This water loving property of the latex films presumably came from the ionic polymers present in the surface of the core-shell particles. However, after the films were treated at 150 °C for 1 min, their contact angles with water changed to 95.5 °, 92.4 ° and 87.6 °, respectively. This indicated that the hydrophilic surface was completely switched to the hydrophobic one. The well-defined core-shell structure must be destroyed at high temperatures. As a result, the original individually separated particles in the films would join together into a mass. Because the hydrophilic shell constitutes only a small fraction of the whole particle (less than 15 wt.%) and the binder polymer (PVA1788) only accounted for a very limited fraction of the films (about 7.0 wt.% relative to the latex particles), the surface properties of the CS-2 latex films after heat treatment should be determined by the core polymer. Considering that the quaternary ammonium moieties were stable below 170 °C, the wettability change should be mainly attributed to the phase inversion of the latex films. Generally, all the CS-2 latex films before heat treatment could be easily washed out from the substrate with neutral water, but could no longer be removed after heat treatment.

IR Laser-induced Imaging Performance of CS-2 Latex Films

The thermal-imaging latex film typically consists of the following three main components: CS-2 latex particles, PVA1788 (the binder polymer) and CTP-2 (an IR-absorbing dye). Investigation of laser-induced thermo-imaging was carried out according to the procedure described in the experimental section. Figure 4 depicts the laser imaging process. Once the sample was exposed to IR laser beam, the temperature of the exposed area increased sharply (typically above 250 °C). By the action of heat, the latex particles would melt and their original core-shell geometry would be broken to combine into a unified whole. Considering the hydrophobic core constituted the majority (about 90 %) of the latex particles, the exposed area couldn't be removed from the substrate any longer. However, the unexposed area of the latex film could be easily washed away by water because the core-shell particles remain intact and still possessed a highly hydrophilic shell. Figure 5 is a typical micrograph after exposure and development procedures. The exposure dose was 400 mJ/cm^2. The grey areas represented the surface of the aluminum substrate or the unexposed areas, and the black strips (about 50 µm wide) were the remained polymer matrix or the exposed areas. The photograph showed clearly that the latex film of the unexposed area was completely removed with water, while that of the exposed area survived and remained on the substrate. Negative image was obtained successfully.

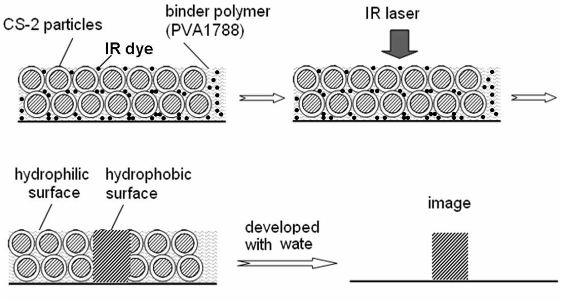


Figure 4. *Schematic diagram of laser imaging process.*

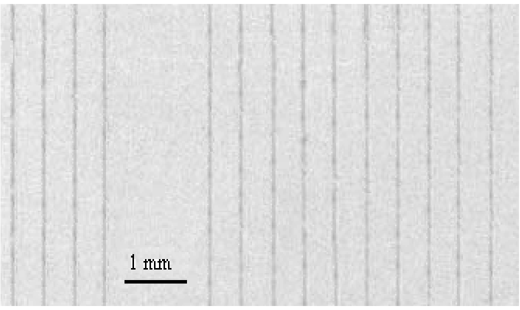


Figure 5. *SEM image of the surface of a latex film (CS-2-15) after exposed by IR laser and developed in neutral water.*

Conclusion

Well-defined core-shell particles with hydrophobic core and hydrophilic shell were prepared and characterized. The core-shell latex films exhibited thermo-induced irreversible affinity change. A negative working and neutral water processable laser thermal imaging material was built through the combination of the prepared core-shell latex particle, a binder polymer and an IR absorbing dye. This kind of material could give satisfactory images, indicating that it might be used in thermal-imaging applications.

References

[1] E. P. Pedraza, M. D. Soucek. Effect of functional monomer on the stability and film properties of thermosetting core–shell latexes. Polymer, 46(24), 11174 (2005).

[2] R. K. O'Reilly, M. J. Joralemon, et al. Facile syntheses of surface-functionalized micelles and shell cross-linked nanoparticles J Polym Sci Part A: Polym Chem, 44, 5203 (2006).

[3] N. Jungmann, M. Schmidt, M. Maskos. Synthesis of amphiphilic poly(organosiloxane) nanospheres with different core-shell architectures. Macromolecules, 35(18), 6851 (2002).

[4] C. Chen, C. H. Yu, et al. Preparation and characterization of biodegradable nanoparticles based on amphiphilic poly(3-hydroxybutyrate)-poly(ethylene glycol)-poly(3-hydroxybutyrate) triblock copolymer. Eur Polym J, 42, 2211 (2006).

[5] T. Morinaga, K. Ohno, Y. Tsujii, T. Fukuda. Two-dimensional ordered arrays of monodisperse silica particles grafted with concentrated polymer brushes. Eur Polym J, 43, 243 (2007).

[6] J. W. Ha, I. J. Park, et al. Preparation and characterization of core-shell particles containing perfluoroalkyl acrylate in the shell. Macromolecules, 35(18), 6811 (2002).

[7] D.H. Wang, L. Jiang, editors. Theory and applications of ultraviolet curing materials (Beijing: Science Press, 2001), pg. 326.

Acknowledgment

This work was supported by Beijing Municipal Education Commission (NO. KZ200510015011).

Author Biography

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