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RESEARCH ARTICLE

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Poly(vinyl chloride) composite emulsion resins modified by polyurethane

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Abstract An ionomer-type of polyurethane (PU) emulsion was prepared from toluene diisocyanate (TDI), polypropylene glycol (PPG) and dimethylol propionic acid (DMPA) following a self-emulsification process. The modified poly(vinyl chloride) (PVC) emulsion resin was obtained by in situ emulsion copolymerization using the PU as seeds in an autoclave. The effects of PU molecular weight on the mechanical properties and thermal stability of the PU/PVC materials were investigated. The composite latex particles and composite materials were determined and characterized using a laser particle size analyzer, transmission electron microscopy or scanning electron microscopy. The study results showed that the PU/PVC hybrid emulsion particles possess a core/shell structure. When the general mechanical properties of the composite materials increase, the thermal stabilities decrease a little. The tough fractures on the surface of the PU/PVC composite sample following impact are quite obvious.

Keywords polyurethane, poly(vinyl chloride), emulsion resin, modifying

1 Introduction

Poly(vinyl chloride) (PVC) obtained generally by suspension and emulsion polymerization has been widely applied in many industries. PVC resin has disadvantages such as poor thermal stability, low-notched impact strength, and large melt viscosity. Therefore, there have been many studies on the modification of PVC. The methods of modified-PVC are classified into grafting copolymerization of chemical modification and blending physical modification; these mainly concentrate on modifications of elastomers and plasticizers [1,2]. Polyurethane (PU) elastomers are block copolymers composed of amorphous soft-sections and crystalline hard-sections. They not only have the properties of elasticity, abrasion resistance and oil resistance of rubbers, but also have the processability of plastics. PU with PVC can effectively maximize these advantages [3,4]. At present, studies of blending physical modification on PU and PVC are much more than chemical modifications. Polyether-typical and polyester-typical polyurethanes were prepared by Zhang et al. [5]. The compatibility, toughening effects and dynamic mechanical behaviors of the PU/PVC blends have been studied. Ha et al. [6] prepared the composites with different thermoplastic polyurethane elastomer (TPU) contents by melt blending plasticized PVC and TPU, then studied their mechanical properties and notched breaking features. The PVC/TPU blends were also prepared by Parnell et al. [7]. The reaction kinetics of thermoplastic polyurethane polymerization in situ with poly(vinyl chloride) was characterized through differential scanning calorimetry (DSC). Waterborne polyurethane keeps not only the virtues of PU, but also does not pollute the environment. In this paper, the authors combined waterborne PU with PVC and prepared PU/PVC composite emulsion resins using in situ emulsion copolymerization. The new synthetic process was developed, and the application range of the modified PVC materials was extended. There have been few reports about this aspect of related studies [8,9].

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2 Experimental

2.1 Materials

Commercial grade polyoxypropylene glycol (PPG) supplied by Tianjin Petrochemical Co. was dehydrated at 120°C

under reduced pressure. Chemically pure toluene-2,4-diisocyanate (TDI) was dried over 4 Å molecular sieves before use. Chemically pure dimethylol propionic acid (DMPA) purchased from the Huzhou Chang Sheng Chemical Plant was dried at 80°C under a vacuum for 2–4 h. Triethylamine(TEA), 1,4-butanediol, di-*n*-butyltindilaurate (DBTDL) bromcresol green, di-n-butylamine, hydrochloric acid, sodium dodecylsulfate (SDS) and sodium hydroxide are analytically pure. Potassium persulfate was recrystallized prior to use. Vinyl chloride, above 99.99 wt% purity, was supplied by the Cangzhou Cang Jing Chemical Co. (Hebei Province, China). Calcium stearate and stearyl alcohol, chemically pure, and Ca/Zn stabilizer, commercial grade, were supplied by the Tianjin Chemical Company.

2.2 Synthesis and preparation

2.2.1 Synthesis of waterborne PU

A polyaddition reaction was conducted in a four-necked flask equipped with a reflux condenser, a mechanical stirrer, a thermometer and a nitrogen gas inlet. 100.0 g of PPG was heated to a certain temperature. 37.3 g of TDI and a small catalyst were added to the mixture. DMPA then was added and reacted over a specific period. TEA was then added to neutralize the carboxy groups to obtain the PU prepolymer. The prepolymer and chain-extended agent were put into another beaker, then a calculated amount of deionized water was added following high-speed stirring. The PU dispersion with a semi-diaphanous blue gloss was obtained.

2.2.2 Preparation of PU/PVC hybrid emulsion resins

A 2-liter stainless steel autoclave was charged with a certain amount of deionized water, 3.7 g of $K_2S_2O_8$, 2.7 g of SDS and 95.09 of 25wt% concentration of the PU dispersion and mixed with agitation. A sodium hydroxide solution (100 mg/g) was utilized to adjust the pH of the reactive mixture (to 9–11). After closing, the nitrogen was charged, and the reaction vessel was evacuated. The operation was repeated thrice. 400 g of vinyl chloride (VC) monomer was introduced into the reactor gradually. The content of the reactor was then heated to 50°C. The copolymerization was maintained at (50 ± 0.5)°C until the pressure decreased to 0.30 MPa. The seeded emulsion copolymerization was terminated. After cooling, the un-reacted monomer was removed. The composite resin was isolated from the emulsion by freezing coagulation, followed by filtration, rinsed by deionized water, and dried under reduced pressure at 50°C. The PU/PVC emulsion resin powder was obtained.

2.2.3 Processing experiment

The synthesized composite resin was mixed with a determined quantity of additives. The processing recipe was 100 parts of composite resin, 2.5 parts of Ca/Zn stabilizer, 0.8 part of calcium stearate, and 0.8 part of stearyl alcohol. All components were first premixed in a KDF-260 type of multifunctional mixer at room temperature, then processed on a laboratory two-roll mill with 170°C of the former roll and 165°C of the latter roll for about 5 min. Two- or four-millimeter-thick plates were pressed and cooled under a cooling press. These samples were prepared for measurements of mechanical properties, transmission electron microscopy and scanning electron microscopy.

2.3 Characterization and measurements

2.3.1 Measurement of latex particle size

The particle sizes and particle size distributions of the PU and the PU/PVC composite latices were measured by dynamic light scattering method.

2.3.2 Transmission electron microscopy (TEM)

The morphology of the PU/PVC latex, which was diluted by deionized water and subjected to a supersonic wave for a determined period, was observed through an FEI TECNAIG^{2}20-type transmission electron microscope in conjunction with the RuO_4-staining method.

The material sample for TEM observation was ultramicrotomed to thin sections and stained with OsO_4 vapors. The ultrathin sample supported by a coppery mesh was examined using the above machine.

2.3.3 Scanning electron microscopy (SEM)

The morphology of fractured surfaces of the PU/PVC material samples was observed by SEM (Philips Electron Co., XL Series 30). The sample 3–4 millimeters in length beginning at the end of the fractured surface was cut. The fractured surface of the notched impact bar was coated with a thin layer of gold under a vacuum.

2.3.4 Thermogravimetric analysis (TGA)

The thermogravimetric analysis for the PU/PVC composite resin was conducted on a Model TA-2000B TGA Instrument supplied by DuPont Company. The heating rate was 20°C/min.

2.3.5 Tensile strength testing

Tensile strength testing was performed using an RGT-10A electronic universal testing machine with a computer controller system. The dumbbell-shaped samples for the tensile tests were cut from the two-millimeter-thick plates. The dumbbell specimens were measured after being set aside for 48 h.

2.3.6 Notched impact strength testing

Notched impact strength was measured on a ZBC-4 Charpy impact tester (Shenzhen New SANS Co. Ltd.). According to GB/T 1043-93, the samples with a size of 80 mm × 10 mm × 4 mm for the test were cut using a universal cutter.

2.3.7 Determination of the PU molecular weight

$$\text{PU molecular weight} = \frac{\text{Prepolymer weight (g)}}{\text{Prepolymer molar number(mol)}} = \frac{84}{w(\text{NCO})}\,(\text{g/mol})$$

Where w(NCO) – the weight percentage of NCO groups in the sample - can be acquired through chemical analysis.

2–3 g of the PU prepolymer-containing NCO group was put in a 250 mL-conical flask, dissolved in 20 mL anhydrous toluene. 15 mL of di-*n*-butylamine/toluene solution taken with a pipette was added. The mixture solution was shaken and set aside for 15–20 min. 50 mL of absolute alcohol and 2–3 drops of bromcresol green indicator were added. The mixture was titrated using hydrochloric acid solution until the blue color of the solution was converted into yellow. The control experiments were done. The calculation formula can be written as:

$$w(\text{NCO}) = \frac{(V_0 - V) \times N \times 42}{1000m} \times 100\%$$

Where V_0 is the volume of hydrochloric acid solution consumed in the control experiment, mL; V is the volume of hydrochloric acid solution consumed in titration of the sample, mL; N is the concentration of hydrochloric acid solution, mol/L; and m is the weight of the sample, g.

3 Results and discussion

3.1 Latex particle diameters and their distribution

The particle size distributions of the PU and PU/PVC composite latices are shown in Figs. 1(a) and 1(b). Their corresponding mean particle diameters (MPD) were determined to be 30.2 nm and 102 nm, respectively. Compared with that of the PU, the particles size of the PU/PVC emulsion increases remarkably, and the distribution of the composite latex becomes narrower. The result is attributed to the mechanical dispersion of the PU prepolymer used in this article, and the particles sizes are so inhomogeneous as to effect/enable wide distribution. In the course of grafting copolymerization, the small particles are swollen and their surface area is more covered. On the contrary, large particles are swollen and coated less. Therefore, from the PU to the PU/PVC, the distribution of the PU/PVC particles size narrows, and the PU/PVC particle sizes increase. The above result suggests that large numbers of vinyl chloride monomer have been polymerized and grow onto the PU seeds in grafting emulsion copolymerization, and particle diameters of the PU/PVC latex obviously became larger. This can be confirmed as shown in Fig. 2.

3.2 Morphology of composite latex particles

The TEM images of the PU/PVC composite latex particles with different magnifications are shown in Fig. 2 – a clearer morphology of the composite latex particles is displayed. The particle sizes are uniform at about 100 nm. The deep black portion in the particles is the rubbery polymer PU containing some PVC microparticles because of RuO_4-staining. The light-colored portion is the PVC composition [10]. When the PU was used as seeds in emulsion polymerization, the moiety of VC monomers was swollen in the PU latex particles and

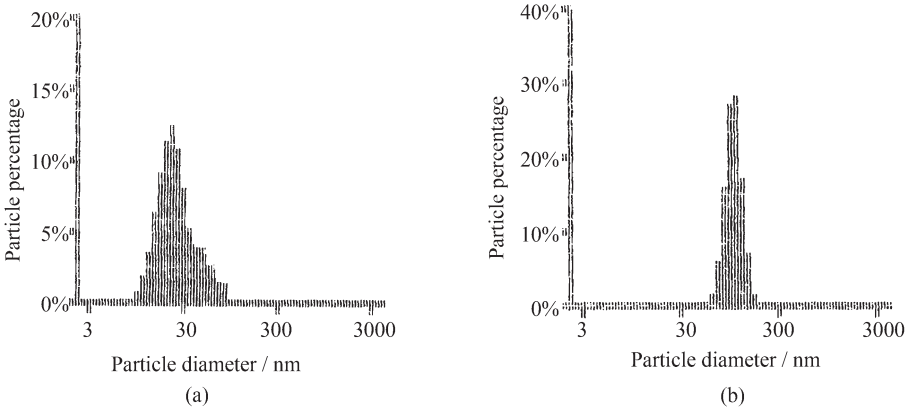

Fig. 1 Particle diameter distributions of the PU (a) and PU/PVC latices (b)

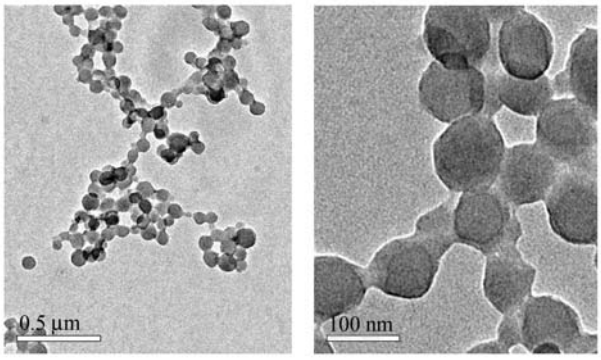

Fig. 2 TEM photographs of the PU/PVC composite latex particles

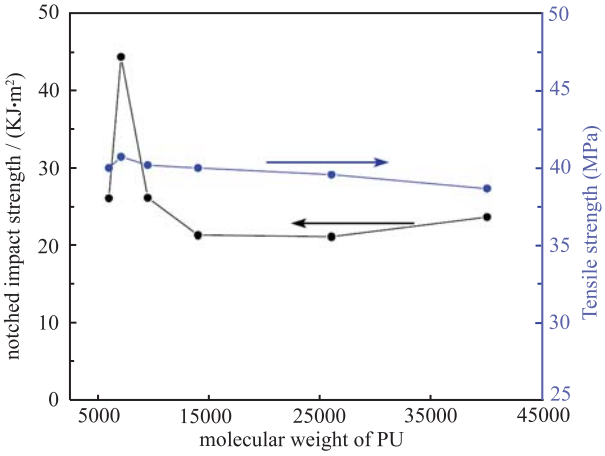

Fig. 3 Influence of the PU molecular weight on mechanical properties of materials

polymerized to form fine PVC particles dispersed in the PU rubber phase. It causes the bigger volume of the apparent rubber phase. At the same time, the graft-polymerized PVC particles gather onto surfaces of the rubbery particles [11].

3.3 Effect of PU molecular weight on mechanical property

Figure 3 presents the mechanical properties with varying PU molecular weight. As shown in Fig. 3, the notched impact strength of the PU/PVC composite resins increases with increasing PU molecular weight. When the PU molecular weight is about 8000, the composite emulsion resins have the best mechanical properties. However, the notched impact strength and tensile strength of the PU/PVC resins begin to weaken with continuously increasing PU molecular weight. The notched impact strength increases slightly when the PU molecular weight is above 26000. The result is possibly caused by cooperation between hydrogen bonds and molecular interaction in the PU structure. The PU molecular weight increase makes the relative content of the hard PU segments decrease, and the amount of hydrogen bonds also decrease. The tensile strength of the PU/PVC resins declines. At the same time, content of soft segments in the polyether system and the toughness of materials increase relatively. Therefore, the notched-impact strength of the PU/PVC composite resins has a rising trend.

3.4 TEM analysis

A TEM photograph of the composite sample in which the PU content had a 5.66 weight percentage is shown in Fig. 4. The black portion is the PU rubbery polymer stained by OsO_4 - the dispersion phase "island". The light-colored portion is the PVC macromolecules formed by polymerization of vinyl chloride and VC swollen in the PU phase, or the continuous phase "sea". The morphology of the composite sample shows a two-phase structure with micro-phase separation. Solubilization of the grafting transition layers obscures the interfaces between "sea" and "island". Since the PVC and the PU phases are interpenetrated to some extent, the effect of toughening the PVC is improved [12]. It can be seen that the composite resins will be influenced by external forces in the course of heating, shearing and pressing. The PU rubbery phase becomes soft, irregularly shaped and dispersed well in the PVC matrix as shown in Fig. 4, the PVC macromolecules were coated (or grafted) onto the surfaces of rubbery particles to form the composite particles. In processing, the PVC shell was melted to form the continuous phase. However, many the PU nano-particles with a strong adhesion did not agglomerate because of the coating of the PVC layer. Fig. 4 shows the blurry interface with good compatibility between the PVC matrix and the rubbery phase. It also shows the morphological features with rubbery particles dispersed in nano-sizes independently. All of these constituted the internal structure of phase state, which is helpful for enhancing notched impact strength and toughening efficiency of the PU/PVC composite resins.

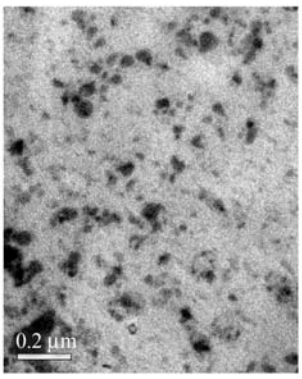

Fig. 4 TEM photo of composite sample

3.5 SEM analysis

Figure 5 presents an SEM image of the impact breaking surface of the PU/PVC composite sample in which the PU content had a 5.66 wt%. It appears as typical tough-fractured features. As seen from Fig. 5, the fractured surface of the PU/PVC material is rough. There are many yielding fibrils on the PU/PVC surface for high-speed impact action. Because the yielding of these fibrils absorbs a large area of external work and consumes impact energy in the break process of the bars, the PU/PVC bars exhibit toughness fracture. By checking the fractured surface of the sample, most of the fracture region shows stress-whitening. This behavior presents a type of tough-fractured characteristic for the impacted samples.

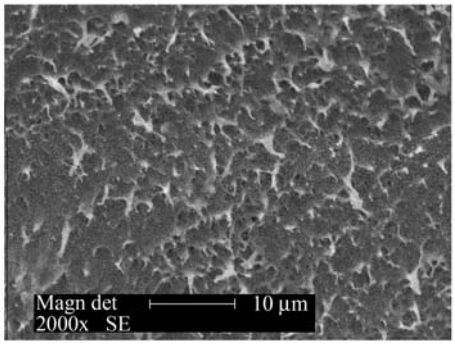

Fig. 5 SEM photograph of fractured surface for the PU/PVC composite sample

3.6 Thermogravimetric analysis

The weight-loss curves of pure emulsion PVC and the PU/PVC composite resins with different PU molecular weight are shown in Fig. 6. From the changing tendency of these curves, it can be seen that the PU/PVC composite emulsion resins have lower initial thermal decomposition temperature than that of pure PVC emulsion resin, and the rate of their weight loss is faster. The heat stability of the PU/PVC resins decreases; the bigger the PU molecular weight, the lower the heat stability. It can be considered that the carbamate groups of hard segments in PU components are greatly influenced by temperature. The larger the PU molecular weight, the harder the segment content and the greater the effect on thermal stability of the composite resins. Thermal stability of amine-ester bonds decreases with increasing substituent groups near oxygen atoms. Simultaneously, stability is reduced with increasing isocyanate reaction activity and the groups steric obstruction. In this research, TDI was used as the composition of the hard segment. The existence of a benzene ring decreases the thermal stability of the composite materials. On the other hand, when Ca/Zn composite stabilizer was used in the system, the association was poor. Other antioxidant agents are usually added to improve the synergistic actions [13]. In this article, we did not add other additives to ease investigation of the effects of the PU rubbery phase, which was used to modify PVC. Thus, thermal stability was not good.

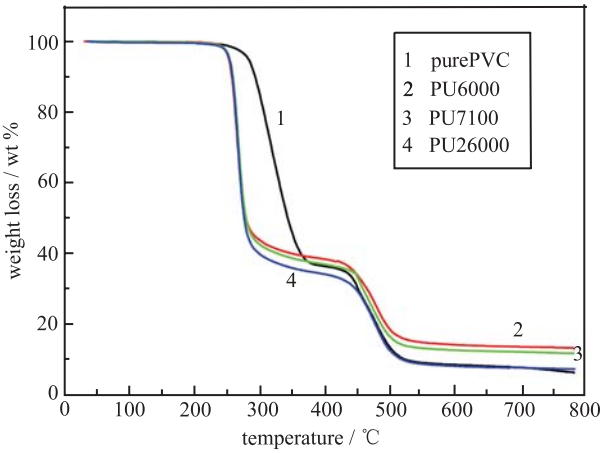

Fig. 6 Weight-loss curves of the PU/PVC composite resins

4 Conclusions

The PVC emulsion resin modified by the PU was obtained by in-situ emulsion copolymerization. The TEM study indicates that PU/PVC latex particles have a regular core-shell structure. The TEM study of the PU/PVC composite material shows that the nanometer-sized PU rubbery phase dispersed in the PVC matrix forms an ''island'' shape. There is some compatibility with each other. The mechanical properties of the PU/PVC resins were improved, but the thermal stabilities decreased slightly. The fracture of the PVC materials modified by the PU exhibits toughness characteristics. A new synthesis process of modifying PVC resins was developed, and the application field of modified PVC materials was extended.

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References

1. Pan M W, Zhang L C. Preparation and characterization of poly(butyl acrylate-co-2-ethylhexyl acrylate) grafting of vinyl chloride resin with good impact resistance. Journal of Applied Polymer Science, 2003, 90: 643–649
2. Wu G F, Zhao J F, Yang H D, Feng Z L, Zhang H X. Properties of AIM core-shell toughening agent/PVC resin

blending system. Acta Materiae Compositae Sinica, 2005, 22(3): 30–34 (in Chinese)
3. Ye C B, Zhang J. Research advances of thermoplastic polyurethane and poly(vinyl chloride) blends. China Plastics, 2003, 17(10): 1–6 (in Chinese)
4. Kim Y, Vho W J, Ha C S. Dynamic mechanical and morphological studies on the compatibility of plasticized PVC/thermoplastic polyurethane blends. Journal of Applied Polymer Science, 1999, 71(3): 415–422
5. Zhang B H, Qian H, Song M D, Hao G J, Zhang Y. Study on properties and morphological structure of PVC/PU blending system. Plastics Technology, 1998, 18(2): 6–10 (in Chinese)
6. Ha C S, Kim Y, Lee W K, Cho W J, Kim Y. Fracture toughness and properties of plasticized PVC and thermoplastic polyurethane blends. Polymer, 1998, 39(20): 4765–4772
7. Parnell S, Min K. Reaction kinetics of thermoplastic polyurethane polymerization in situ with poly(vinyl chloride). Polymer, 2005, 46: 3649–3660
8. Pan M W, Zhang X L, Yuan J F, Xing S N, Zhang L C. Polyvinyl chloride modified in situ by polyurethane and its composites and preparation method. China Patent: CN1743352A 2006-03-08 (in Chinese)
9. Zhang X L, Pan M W, Yuan J F, Xing S N, Zhang L C. Preparation and characterization of PUA/PVC composite emulsion resin. China Plastics, 2006, 20(3): 60–63 (in Chinese)
10. Pan M W, Zhang L C. Preparation and characterization of poly (butylacrylate-ethylhexyl acrylate)/polyvinyl chloride composite latex. Acta Polymerica Sinica, 2003, (4): 513–518 (in Chinese)
11. Pan M W, Zhang L C, Wan L Z, Guo R Q. Preparation and characterization of composite resin by vinyl chloride grafted onto poly(BA-EHA)/poly(MMA-St). Polymer, 2003, 44: 7121–7129
12. Zhu Y L, Xu X J. Toughening modification for polyvinyl chloride resin by graft copolymerization. Applied Chemical Industry, 2005, 34(4): 199–201, 208 (in Chinese)
13. Fang Y Q, Pan X S. Synthesis technology and applications of liquid calcium-zinc compound heat stabilizer for PVC. Plastics Additives, 2005, (2): 31–33, 53 (in Chinese)