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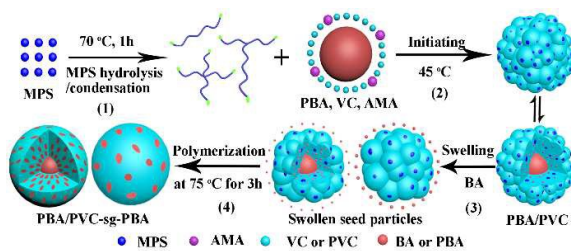
Polyacrylate plasticized PVC composite particles without toxicity and migration were synthesized via multistage seeded emulsion polymerization of BA swelling nonspherical PBA/PVC latex particles with a flowerlike shell.

Journal Name

ARTICLE

Morphology and Film Performance of Phthalate-free Plasticized Poly(vinyl chloride) Composite Particles via Graft Copolymerization of Acrylate Swelling Flowerlike Latex Particles

Yanning Chang,[a] Mingwang Pan,*[a] Jinfeng Yuan,[a] Ying Liu,[a] Xiaomei Wang,[a] Peizhao Jiang,[a] Yaling Wang,[a] Gan-Ji Zhong*[b] and Zhong-Ming Li[b]

This paper reports on an intriguing preparation of a nontoxic and phthalate-free polyacrylate/poly(vinyl chloride)-swollen then grafted-polyacrylate (PBA/PVC-sg-PBA) for the production of flexible PVC by means of multistage emulsion polymerization. Flower-like PBA/PVC composite particles with rich hydrophilic groups and functional end groups were first synthesized through seeded emulsion polymerization of poly(butyl acrylate) (PBA), vinyl chloride (VC), 3-(trimethoxysilyl) propyl methacrylate (MPS), and allyl methacrylate (AMA), then the anisotropic PBA/PVC composite particles were used as seeds to prepare PBA/PVC-sg-PBA composite particles. And PBA is biologically safe without producing an acute toxicity response. This formation process was studied in detail, and the effects of BA/(PBA/PVC) feed weight ratio on PBA/PVC-sg-PBA composite particle morphology and mechanical properties of the prepared film materials were investigated. Scanning electron microscopy (SEM) observation indicated that the content of MPS in the PBA/PVC seeds was crucial to control the morphologies of flower-like PBA/PVC composite particles. Transmission electron microscope (TEM) study illustrated that the PBA was uniformly dispersed in the PBA/PVC particles to form an interpenetrating network layer. Dynamic mechanical analysis (DMA) study revealed that the compatibility between PBA and PVC was well improved with an increasing PBA content. The flexibility of phthalate-free PBA/PVC-sg-PBA was comparable to the corresponding performance of commercial PVC/DOP mixture, and its stretchability was superior to the PVC/DOP system.

1. Introduction

Poly(vinyl chloride) (PVC) resin has become one of major polymers in the world because of its relatively low cost, low flammability, high mechanical strength, and good corrosion resistance.[1] In particular, flexible PVC is widely used for the medical field such as blood or urine bags, transfusion tubing, etc., and is further used for toys, infant care products, and food packaging.[2] In order to achieve the desired durability and flexibility, large amounts of low molecular weight liquid plasticizers have been commonly used in PVC formulations. According to the desired properties of the flexible PVC material, the plasticizer content is varied usually between 15 and 60 wt%[1], and in some cases can be as high as 70 wt%.[3] Most of them are phthalates which account for more than 80 % of the plasticizer industry, such as di(2-ethylhexyl) phthalate (DOP), di(isodecyl) phthalate (DIDP) and di(2-ethylhexyl) adipate (DEHA). DOP is by far the most commonly used plasticizer for PVC.[1]

Phthalate molecules interact with PVC through van der waals forces but not chemically bound. Thus, the plasticizers, when not grafted or copolymerized, may be separated from the PVC matrix and migrate into adjacent media.[4] Phthalates migration out of the PVC matrix leads to a loss of its initial properties. And when flexible PVC products are used for medical field or children toys, phthalates migrating onto the products' surface can contaminate biological fluids like blood, and poison the lungs, kidneys, liver, heart, and other organs, which implies serious environmental and health problems.[5,6] Therefore, the flexible PVC materials without phthalate and toxicity and with good mechanical properties are urgently needed.

To solve these problems, several approaches have been tested. Surface modifications involving surface treatment and crosslinking have been shown to successfully inhibit plasticizer migration.[7] For example, peroxides, azides,[8-10] sulfides,[11] or acrylates have been used to modify the surface of flexible PVC materials. But the physicochemical properties of PVC materials will decline.[11] Polymeric plasticizers and oligomers have a great advantage in their inherent low volatility and are now being studied as replacements to substitute traditional plasticizers.[12] However, polymeric plasticizers are usually expensive and have lower plasticizing efficiency than most of

traditional plasticizers. And some researchers have investigated the approach of replacing phthalates and low molecular weight plasticizers with non-toxic and analogous compatible polymeric plasticizers.[13] Slightly branched poly(butyl acrylate) (PBA) was found to exhibit better plasticizing efficiency and migration resistance[14,15] than plasticizers typically used in PVC-based films.[16-18] And PBA is biologically safe without producing an acute toxicity response. For allylic chlorines and tertiary chlorines at branching points are considered to be labile chlorines, then the BA and 2-ethyl hexyl acrylate (EHA) could germinate from sites of the labile chlorines of PVC.[19,20] Bicak and his collaborators[21] grafted BA and EHA with the PVC by copper-mediated atom transfer radical polymerization (CM-ATRP) and high grafting and self-plasticized PVC was attained in 7.5 h. The drawback of this procedure is greenish graft products, a common problem in CM-ATRP.

Our group has been focusing on the study of use polyacrylate-grafted PVC for a long time.[22-27] We synthesized P(BA-EHA)-core/PVC-shell, and used it as a modifying agent of PVC,[25] also *in situ* grafted PVC onto the core P(BA-EHA)/shell P(MMA-St) (poly(methyl methacrylate-co-styrene)) composite latex particles by multistage emulsion polymerization.[24] By these ways, the compatibility between the polyacrylate core and PVC shell has been well improved, and the composite sample exhibited good toughness. The aim of those researches is to prepare a new kind of core-shell PVC emulsion resin with an improved impact resistance. But by preparing core-shell PBA/PVC composite resin, we haven't still obtained a desired PVC soft material. For a flexible intertwined mixture of both PVC and PBA, interpenetrating polymer network method is considered as an ideal method.[27] The research interest mainly comes from their capacity of achieving the forced compatibilization of immiscible polymers without using any compatilizers.[28,29] In the present study, to achieve a phthalate-free and nontoxic flexible PVC and minimize the property deterioration, we first synthesize the crosslinked PBA as seed latex. Next, large amounts of flowerlike PBA/PVC nonspherical particles containing hydrophilic groups and functional end groups on their surface are prepared by the copolymerization of vinyl chloride (VC), 3-(trimethoxysilyl) propyl methacrylate (MPS), allyl methacrylate (AMA) and PBA seeds. Then BA monomer is precedently swollen into the flowerlike core-shell PBA/PVC composite particles and graft-copolymerized onto the particles to form PBA/PVC-sg-PBA composite particles with both grafting transition layer and interpenetrating network layer.

2. Experimental Section

2.1 Materials

The monomer, *n*-butyl acrylate (BA, above 99.5%, industrial product, Beijing Dongfang Chemical Plant, China) was purified by distillation under reduced pressure before using. The crosslinking agent, 1,4-butylene glycol diacrylate (BDDA, chemically pure, Tianjin Tianjiao Chemical Co. Ltd.), allyl methacrylate (AMA, chemically pure, Tianjin Tianjiao Chemical Co. Ltd.), 3-(trimethoxysilyl) propyl methacrylate (MPS, chemically pure, J&K Chemical Reagent Co.) were stored in a refrigerator prior to use. Sodium dodecylsulfate (SDS, chemically pure, Tianjin Guangfu Fine Chemical Research Institute), was used as an emulsifier. The initiators, potassium persulfate (K$_2$S$_2$O$_8$, chemically pure, China Medicine Group Chemical Reagent), and sodium bisulfite (NaHSO$_3$,

chemically pure, Tianjin Wendaxigui Chemical Reagent), were used without further purification. Sodium hydroxide (NaOH, chemically pure, Tianjin Fengchuan Chemical Co. Ltd.), was the pH modifying agent. Vinyl chloride (VC, above 99.99 wt% purity) was furnished by Tianjin Chemical Plant. The commercial PVC resin MP-1700G was kindly provided by the Tianjin Botian Chemical Co. Ltd. Di(2-ethylhexyl) phthalate (DOP) was obtained from Xian Changsheng Chemical Co. Ltd. The thermal stabilizer (organic tin 8831 type, commercially) was supplied by Beijing Sananhua Chemical Co. Ltd. All of the water used was deionized.

2.2 Synthesis

2.2.1 Synthesis of PBA latex (stage one)

PBA latex was prepared by seeded emulsion polymerization at 75 ºC in a 500 mL four necked round-bottom flask equipped with a mechanical stirrer, a condenser, a nitrogen inlet and a thermometer. In brief, 200 g of deionized water and 0.50 g of SDS were introduced into the glass flask and heated. After the temperature of the reactor was up to 45 ºC, 18.50 g of BA and 0.20 g of BDDA mixture were added. When the temperature was enhanced till 65 ºC, 0.19 g of K$_2$S$_2$O$_8$ dissolved in 25 g of deionized water was added. Then the mixture was heated to 75 ºC for 50 min. Next, 74.00 g of BA and 0.80g of BDDA were premixed and began to be added dropwise over one hour period. At 10min before the instillment finished, 0.37 g of K$_2$S$_2$O$_8$ dissolved in 80 g of deionized water was added. After the instillment finished, the reaction was maintained for another 2 h.

2.2.2 Synthesis of PBA/PVC composite latex (stage two)

Typically, 1.60g of MPS and 500 g of deionized water were first mixed in a 1000 mL four neck round-bottom flask equipped with a mechanical stirrer, a condenser, a nitrogen inlet and a thermometer. One weight percent of aqueous sodium hydroxide solution was used to adjust the pH value of the mixture between 10 and 11 and then stirred with 300 rpm at 70 ºC for 1 h, for the pre-hydrolysis and condensation of MPS. Then the MPS solution, 274g of deionized water, 41.11g of PBA latex, 1.33g of AMA, and 1.20 g of NaHSO$_3$, 0.80 g of KPS were introduced into a 2 liter-stainless steel autoclave. Sodium hydroxide solution was still used to regulate the pH value of the reactive mixture between 8 and 9. Then, the autoclave was vacuumed and charged with nitrogen repeatedly for three times to remove O$_2$. After homogenizing the mixture at a stirring speed of 250 rpm, 150g of the VC monomer were charged into the autoclave. The resultant mixture was further stirred for mixing the VC, AMA, PBA and MPS, followed by heating up to 45 ºC. Then the reaction was maintained at 45±0.5 ºC. When the pressure in the autoclave decreased to 0.25 MPa, the content was cooled down to room temperature and then the system was vacuumed to remove the unreacted VC monomer from PBA/PVC latex. The obtained PBA/PVC latex was sampled for the measurement of solid content and morphology observation.

2.2.3 Synthesis of PBA/PVC-sg-PBA composite latex(stage three)

The PBA/PVC-sg-PBA composite latexes were synthesized by multi-step emulsion polymerization. First, 100 g of PBA/PVC latex with a solid content of 22 wt% were added into a 250 mL four necked round-bottom flask equipped with a mechanical stirrer, a condenser, a nitrogen inlet and a thermometer at room temperature. Then 12.8 g (or 10.1 g, 7.7 g, 5.7 g, 3.9 g) of BA were added into the flask. The mixture was stirred for 1 h to let the BA monomer penetrate inside the PBA/PVC colloidal particles at room temperature. Then the content was heated to

75 °C, 0.08 g of $K_2S_2O_8$ (i.e., 0.6 wt% of the BA monomer) dissolved in 8 g of deionized water was supplemented into the mixture, and the polymerization was kept at 75 °C for 3 h until the conversion of BA monomer reached above 90 wt%.

2.2.4 Sample preparation

The flexible PVC samples were fabricated with 100 g of PBA/PVC-sg-PBA latexes mixed with 2.5 wt% (based on PBA/PVC-sg-PBA solid weight) of the thermal stabilizer, and the commercial PVC resin was mixed with the thermal stabilizer in the following proportion: 6 g of commercial PVC emulsion resin, 4 g of DOP and 0.15 g of the thermal stabilizer. All the mixing operation was carried out under reduced pressure in order to avoid the presence of air bubbles in the final product. Then the PBA/PVC-sg-PBA latexes were plasticized at 165 °C in a flat mould within 10 min, and PVC sheets with 0.6 mm (or 2 mm, 3 mm) of thickness were obtained by compression moulding of the above polymer.

2.3 Characterization

The particle size distributions of PBA latex, PBA/PVC and PBA/PVC-sg-PBA composite latex in aqueous dispersions were analyzed by Zeta-Sizer 90 type of dynamic laser scattering particle size analyzer (DLS, Malvern, England). The contact angle of water on the polymer film was measured on a DSA30S instrument (KRÜSS Co., Germany) at room temperature. The preparation of polymer particle films followed the procedure that a certain amount of latex was cast onto a glass slide and then dried at room temperature for 12 h. Shore D hardness test was carried out using a XHS hardness tester. The sheets at 3 mm of thickness were used for hardness measurements. The carbon, chlorine and silicon content on the surface of the PBA/PVC-sg-PBA composite particles were confirmed by X-ray photoelectron spectroscopy (XPS, K-Aepna ThemoFisher, America).

2.3.1 Morphology observation of composite particles

The morphologies of PBA latex particles, PBA/PVC and PBA/PVC-sg-PBA composite particles were observed by scanning electron microscopy (SEM, Nano 450, FEI, America). A few drops of PBA, PBA/PVC or PBA/PVC-sg-PBA latex were diluted with deionized water to obtain a translucent solution and ultrasonicated for 30 min. Then a drop of the suspension was cast onto a conductive silicon wafer and was dried at room temperature. Further, the sample was sputtered with Au by sputter coater (SC7620, Quorum, England) for 15s to improve the quality of the images.

The morphology of PBA/PVC-sg-PBA composite particles was studied by transmission electron microscope (TEM, H-7650B at 80 kV, Hitachi, Japan). Few composite particles were embedded in melted epoxy resin, which was solidified in 60 °C for two days. The particles were sectioned in the ultramicrotome according to the procedure often used in electron microscopy and the thickness of sections was about 70 nm. The ultrathin samples were stained by osmium tetraoxide (OsO$_4$) vapor for 2 h.

2.3.2 Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis was performed by a Tritec 2000B DMA type of dynamic mechanical analyzer. The measuring frequency was 1 Hz, the heating rate was 3 K/min. And tanδ was measured in temperature range from -150 to +150 °C. The size of the samples for the DMA test was 40×7×2 (height × width ×thickness) mm^3.

2.3.3 Determination of mechanical properties

Tensile strength testing was performed by an RGT-10A electronic tensile tester with a computer controlling system. The size of the dumbbell samples for the testing was 25 mm long with a cross-section of 6×0.6 (width × thickness) mm^2. The samples were exposed at 23 °C for 48 h before being tested. Tests were conducted at an extension rate of 10 mm/min at 23 °C and 50 % relative humidity.

3. Results and discussion

3.1 Synthesis of PBA seeds

Figure 1 shows the size distribution and particle morphology of PBA latex particles obtained by particle size analysis and SEM observation, respectively. The number-average particle size (APS) was determined to be 180 nm and the polydispersity index (PDI) was 0.003 (Figure 1A). As shown in Figure 1B, it is clear that the PBA latex particles are spherical and monodispersed for the containment of SDS concentration.
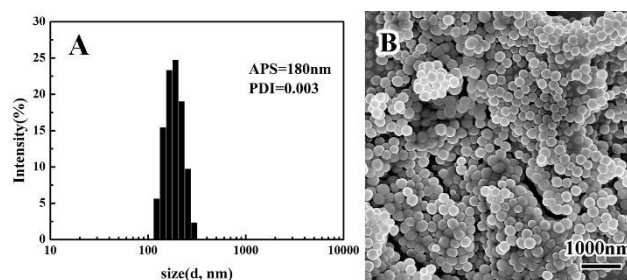

Figure 1. (A) Size distribution histogram and (B) SEM micrograph of the PBA latex particles.

### 3.2 Morphology and structure study of PBA/PVC composite particles

To prepare the PBA/PVC-sg-PBA composite particles without toxicity and phthalate migration, the flowerlike core-shell PBA/PVC (6.5 wt/93.5 wt) composite particles containing hydrophilic groups and functional end groups on their surface were prepared. Here, the silane coupling agent MPS could improve the hydrophilicity of the particles because it was predominantly located on the surface after the copolymerization with VC, and the AMA is an efficient cross-linker for the PVC and subsequent graft reagent of BA (stage three), since it has two different activities of end groups (CH$_2$=CCH$_3$-COO- and CH$_2$=CH-CH$_2$-).[30]

Flower-like particles have concavo-convex shapes where those bulges or concavities have the sizes at nanometer scale to allow for high surface roughness, larger surface area in comparison with the smooth surface analogue.[31,32] The silane coupling agent MPS is critically important for the structure formation of flower-like particles. MPS contains a trialkoxysilane, which can be hydrolyzed for coupling with each other (see Scheme 1), and an acrylate group that can copolymerize with VC. Therefore the hydrolyzed MPS can be also used as a cross-linking agent to copolymerize with VC. To investigate the influence of the content of MPS on morphology of the PBA/PVC composite latex particles, we fixed the content of MPS as 0 wt%, 0.5 wt%, 0.8 wt%, 1.0 wt%, 1.2 wt%, or 1.5 wt% (all based on VC monomer). Figure 2 shows SEM micrographs of the as-obtained PBA/PVC composite particles as a function of the initial amount of MPS. Without MPS, the as-obtained PBA/PVC composite particles (Figure 2A) were

monodispersed with APS of 410 nm and PDI of 0.003, and had smooth surface. When 0.5 wt% of MPS was added, the particles had smooth surface but not monodispersed, and some newly generated tiny particles appeared. When the content of MPS was increased to 0.8 wt%, the PBA/PVC composite particles became irregular and unstable, and partially aggregated particles with a mean size of around 878 nm were produced, following a little new formation of small particles (Figure 2C). However, when continuing to increase MPS content to 1.0 wt%, some lobes were anchored on the surface of the composite particles, forming a flower-like structure. The APS of the composite particles was 416 nm and the PDI was 0.065 (Figure 2D). When up to 1.2 wt% MPS was added, flower-like particles could also be obtained, and the APS was 417 nm with PDI being 0.032 (Figure 2E), but the emulsion was more stable. When the content of MPS was continuously enhanced to 1.5 wt%, we still obtained the flower-like particles (Figure 2F). After considering the stability of PBA/PVC composite latex, the content of MPS was limited to 1.2 wt% (based on VC monomer).

In this study, MPS was pre-hydrolyzed for 1 h with sodium hydroxide aqueous solution (in this case, the pH value of the system was adjusted between 10 and 11), so the $(CH_3O)_3$-Si- groups of MPS molecules hydrolyzed into metastable Si-OH groups, and some of them self-condensed further into polyfunctional oligomers with two or more acrylate groups via the sol-gel process,[31,33,34] as seen in Scheme1. These oligomers were more hydrophilic than MPS monomers. Once the reaction occurred, these oligomers could undergo homopolymerization and/or copolymerization with VC monomers. Based on the thermodynamic criterion, the final morphology of the particles should minimize Gibb's interfacial free energy of the system, so the hydrophilic oligomers were mainly distributed on the surface of the particles.[35] And due to the MPS oligomers contacted with water, the MPS-enriched segments produced on the surface of the composite particles. And then these MPS-enriched segments were unevenly distributed on the surface. On the other hand, because of the limitation of the cross-linking networks, some MPS-enriched segments were be kept in the inner region of the swollen PBA/PVC composite particles, and

produced an osmotic pressure, which forced some water to permeate into the inner region of the PBA/PVC composite particles.[36] Then the flower-like PBA/PVC composite particles with water in the inner were produced (see Scheme 2 (2)). The more MPS used, the more MPS oligomers would distribute on the surface of the particles. Obviously, the hydrophilicity and stabilization of the PBA/PVC could be enhanced by increasing the MPS content. The functionalized latexes were stabilized by the negative ionic charges formed on their surface, and particles aggregation was prevented.
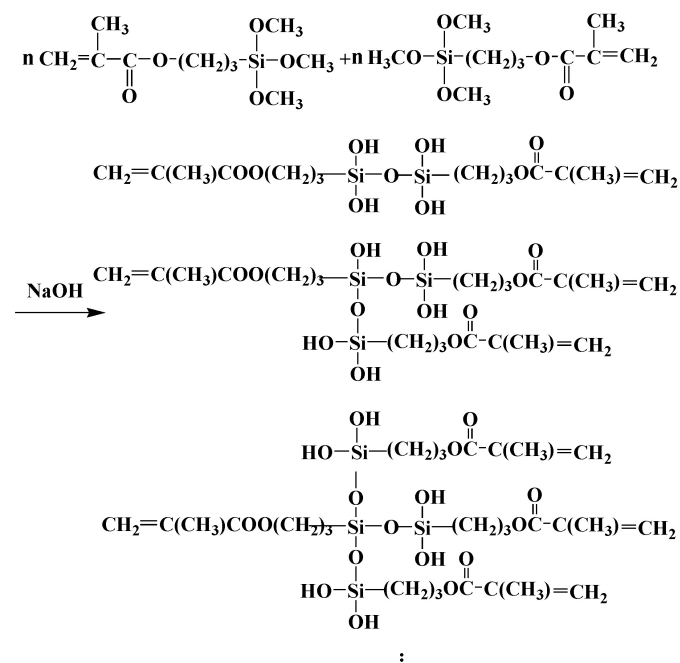
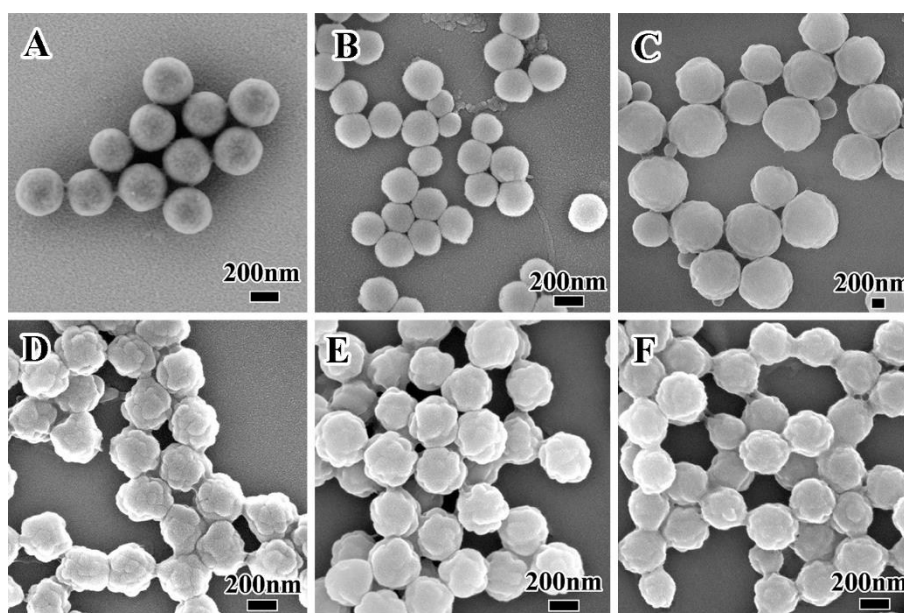**Scheme 1.** Hydrolytic Reaction of MPS

Figure 2. SEM micrographs of the as-obtained PBA/PVC composite latex particles prepared using different contents of MPS, the MPS content was (A) 0 wt%; (B) 0.5 wt%; (C) 0.8 wt%; (D) 1.0 wt%; (E) 1.2 wt%; (F) 1.5 wt% (all based on VC monomer).
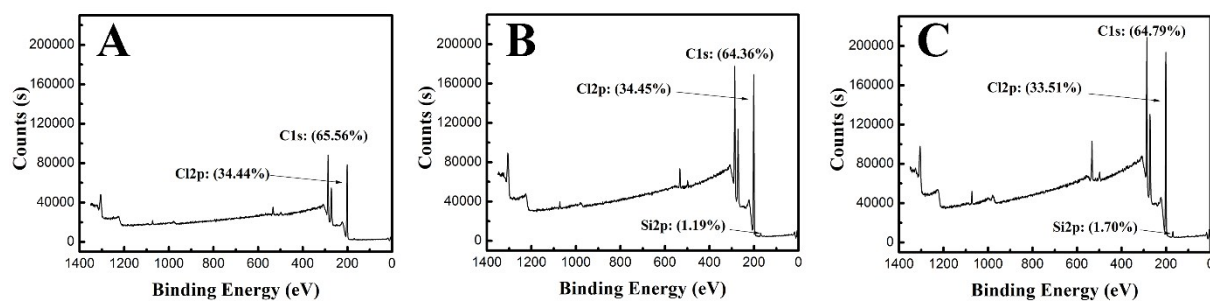
Figure 3. XPS spectra of the as-obtained PBA/PVC composite latex particles prepared using different contents of MPS, the MPS content was (A) 0 wt%; (B) 1.0 wt%; (C) 1.2 wt% (all based on VC monomer).

In order to confirm that the hydrophilic oligomers were mainly located on the surface, the XPS spectra of the surfaces of the PBA/PVC composite particles with different MPS contents were recorded. From Figure 3, the Cl2p signal of PVC in the surface of the PBA/PVC composite particles was clearly detected. As shown in Figure 3A, in the absence of MPS, the atomic ratio of C1s:Cl2p in the surface of the PBA/PVC composite particles was 65.56:34.44, which was consistent with the calculated atomic ratio in the particles. When the MPS content was 1.0 wt% (based on VC monomer), the detected atomic ratio of Cl2p:Si2p in the particles surface was 34.45:1.19 (Figure 3B), which was much higher than the whole calculated atomic ratio (Cl: Si= 99.75: 0.25) in the PBA/PVC composite particles. When the MPS content was 1.2 wt% (based on VC monomer), the detected atomic ratio of Cl2p:Si2p in the particles surface was 33.51:1.70 (Figure 3C), but the entire calculated atomic ratio of Cl:Si in the PBA/PVC composite particles was only 99.70:0.30. The above analysis results indicate that the MPS-enriched segments were distributed on the surface, that is to say, the hydrophilic oligomers were mainly located on the surface of the PBA/PVC composite particles.

3.3. Formation process of PBA/PVC-sg-PBA composite particles

To achieve the desired PBA/PVC-sg-PBA composite particles, the PBA/PVC composite particles were first swollen for 1 h to let the BA monomer penetrate inside the PBA/PVC colloidal particles at room temperature. The morphological evolution of the PBA/PVC composite particles during swelling was studied by sampling aliquots at different time intervals and characterized using the SEM technique. Here, we fixed the BA/(PBA/PVC) weight ratio as 12.8 g/ 22.0 g. As shown in Figure 4, it is clear that these bulges on the flowerlike PBA/PVC composite particles gradually reduce with swelling time. And it should be noted that the sizes of PBA/PVC composite particles decrease with swelling time (shown in Figure 6).[37] As we know, the prepared PBA/PVC composite particles had the external layers with rich hydrophilic groups, consequently permeated by water in the inner region, which derived from the hydrophilic groups embedded therein. Also, these particles had an oleophilic PBA core, the swelling BA monomer could diffuse into the PBA/PVC seed through the hydrophilic external layer to substitute the space of PBA/PVC-hydrated H_2O molecules, thus the particles shrunk (see dash line region in Figure 6). In the swelling process, BA droplets could exist in two possible forms: one part of BA permeated into the PBA/PVC seeds and uniformly dispersed in the particles, another part was distributed around the seeds.
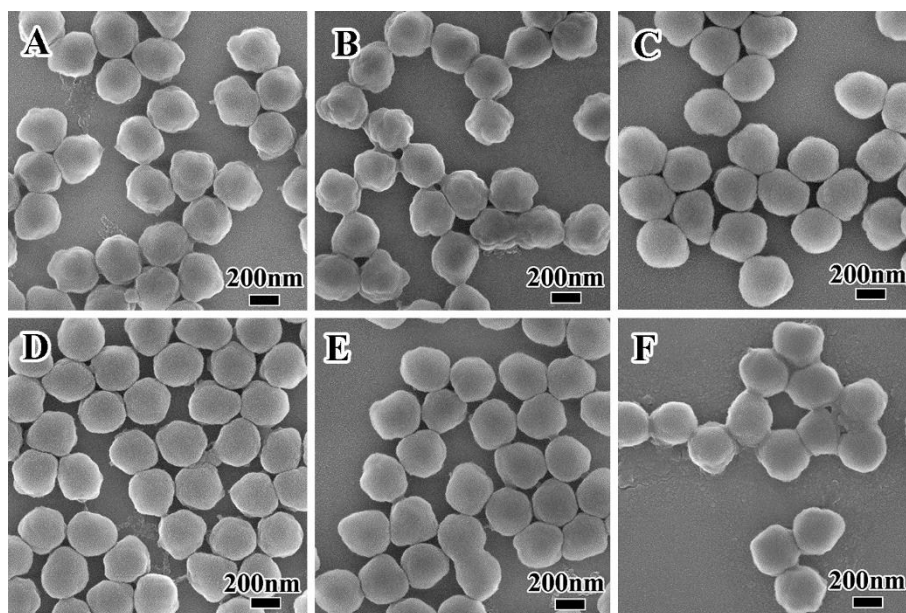

Figure 4. SEM micrographs of the PBA/PVC seed particles swollen by BA for (A) 10min; (B) 20min; (C) 30min; (D) 40min; (E) 50min; (F) 60min when the BA/(PBA/PVC) feed ratio being 12.8 g/ 22 g. The polymerization temperature was 75 °C.
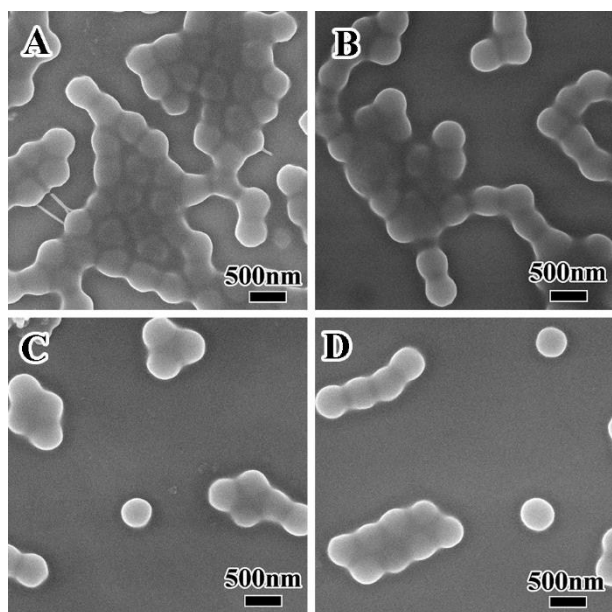
Figure 5. SEM micrographs of the PBA/PVC-sg-PBA composite particles with different reaction time: (A) 0.5h; (B) 1h; (C) 2h; (D) 3h when the BA/(PBA/PVC) feed ratio being 12.8 g/ 22 g. The polymerization temperature was 75 ºC.
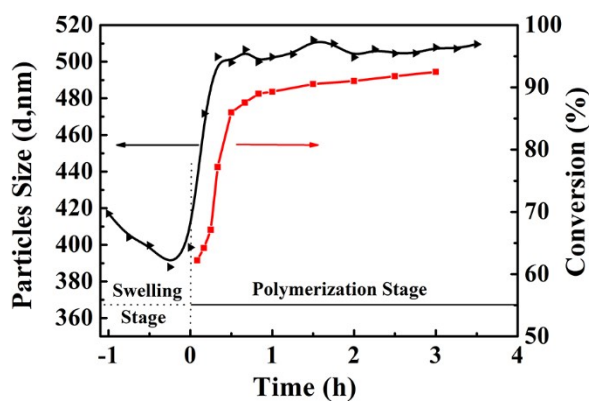

Figure 6. Change of average particle size of PBA/PVC-sg-PBA particles and BA conversion (%) during the swelling and polymerization at 75 ºC with a fixed BA/(PBA/PVC) feed ratio of 12.8 g/22.0 g.

Subsequently, the water-soluble initiator KPS was added and thermally decomposed to produce free radicals. The free radicals mostly migrated into the seed to initiate the BA monomer. For the adding of the AMA which contains two different active groups during the synthesis of the PBA/PVC composite particles, consequently a fraction of functional allyl groups remained on the PVC chains, which could further react with BA monomer. Then the PBA chain was grafted to the PBA/PVC composite particles to form interpenetrating network structure. To elucidate the formation process, morphological evolution of the PBA/PVC-sg-PBA composite particles during polymerization was also characterized by SEM technique. The results are shown in Figure 5, with the polymerization going forward, the morphology of the obtained polymer particles changed from nonmonodisperse and nonspherical particles (Figure 5A) to spherical and monodisperse particles (Figure 5D)

and the diameter of the obtained particles increased with the conversion improving (see Figure 6). At the same time, in Figure 5, we notice that some PBA/PVC-sg-PBA composite particles conglutinated each other and the SEM image was fuzzy, which was attributed to the oligomers formed at the beginning stage of BA polymerization shielded part of electron beam. At the beginning, some BA monomer swollen in the PBA/PVC seed was initiated rapidly and the size of the particles increased quickly, the composite particles became larger than the PBA/PVC, but the fuzzy protrusions of the PBA/PVC-sg-PBA composite particles could also be observed. With the polymerization performed, the new PBA phase domain grew through the absorption of the BA monomers from the seed phase domain and around the seeds, because a lower free energy of mixing in the new domain than in the seed phase was the driving force for the transport of monomer.[38-40] When the polymerization time reached 1 h, the composite particles were nearly spherical (Figure 5B) with the monomer conversion reaching nearly 88 wt%. With continuance of the polymerization time to 3 h, the spherical and monodispersed PBA/PVC-sg-PBA composite particles (at APS of 507 nm with PDI of 0.01 by DLS) could be obtained with the BA conversion of 93 wt%. After this, the conversion was not further increased with the polymerization time (as shown in Figure 6). Therefore, we limited the maximum polymerization time at 3 h.

The influence of the BA/(PBA/PVC) feed ratio on morphology of PBA/PVC-sg-PBA composite particles was also investigated, we tested the feed weight ratio of BA/(PBA/PVC) to be 3.9 g/22.0 g, 5.7 g/22.0 g, 7.7 g/22.0 g, 10.1 g/22.0 g or 12.8 g/22.0 g, respectively. All the PBA/PVC-sg-PBA composite particles were synthesized at the same reaction time of 3 h. As shown in Figure 7B, it could be noticed that the PBA/PVC-sg-PBA composite particles with lower PBA content had the flower-like morphology. With the increase of the feed weight ratio, the more BA monomer diffused into the PBA/PVC seeds, and the composite particles became spherical (Figure 7F). As such the spherical and monodispersed PBA/PVC-sg-PBA composite particles were obtained. This is because there was more monomer existed in the inside of the PBA/PVC seed particles after swelling, and initiated therein. Further, with an increment of the BA/(PBA/PVC) feed ratio, the more PBA chains would be formed in the PBA/PVC seed particles, and grafted to the PVC chains, resulting in a grafting transition layer and interpenetrating network structure.

To prove that most of BA monomer existed in the inside of the PBA/PVC composite particles after swelling and initiated in the particles, the influence of the BA/(PBA/PVC) feed ratio on the contact angles of PBA/PVC-sg-PBA composite particles was also investigated by DSA30S instrument. The measurement result is presented in Figure 8. As we know, PBA is more hydrophilic than PVC because of its -COOR group. Here, the contact angle of PBA was measured to be 68º (picture not shown). Figure 8B illustrates that when the BA/(PBA/PVC) feed ratio was 3.9 g/22.0 g, the most of BA was polymerized in the inner of the PBA/PVC seed particle, so the contact angle of PBA/PVC-sg-PBA composite particle was close to that of the PBA/PVC seed (104 º). With the increase of the BA feed ratio, the contact angles of the composite particles gradually decreased, as seen from Figure 8. This is probably because the swelling of BA monomer in the PBA/PVC seed was saturated, and then part of PBA phase was gradually formed onto the surface layer of the seeds. Consequently the hydrophilicity of PBA/PVC-sg-PBA composite particles increased. From the

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above data of contact angles, it is suggested that in the beginning, most of BA monomer was swollen into the PBA/PVC seed and initiated in the seed particles, with continuance of the polymerization, some new PBA phase

domains gradually came out of the surface of the seed and grew on through adsorbing the BA monomer from the circumference and/or interior of the seeds.
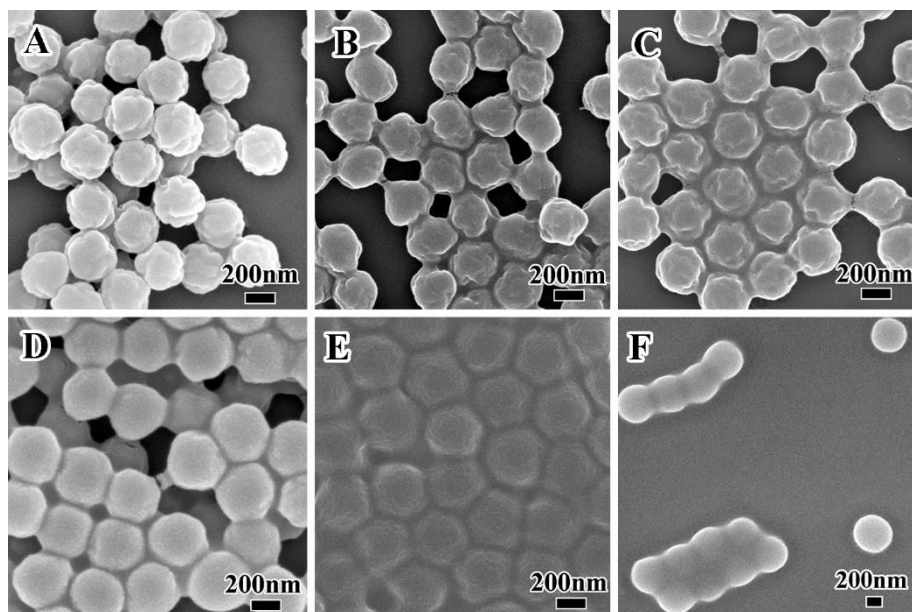

Figure 7. SEM micrographs of the PBA/PVC seed particles (A) and PBA/PVC-sg-PBA composite particles at the polymerization time of 3 h when the BA/(PBA/PVC) feed weight ratio being (B) 3.9 g/ 22.0 g; (C) 5.7 g/ 22.0 g; (D) 7.7 g/ 22.0 g; (E) 10.1 g/ 22.0 g; (F) 12.8 g/ 22.0 g, respectively. The polymerization temperature was 75 ºC.
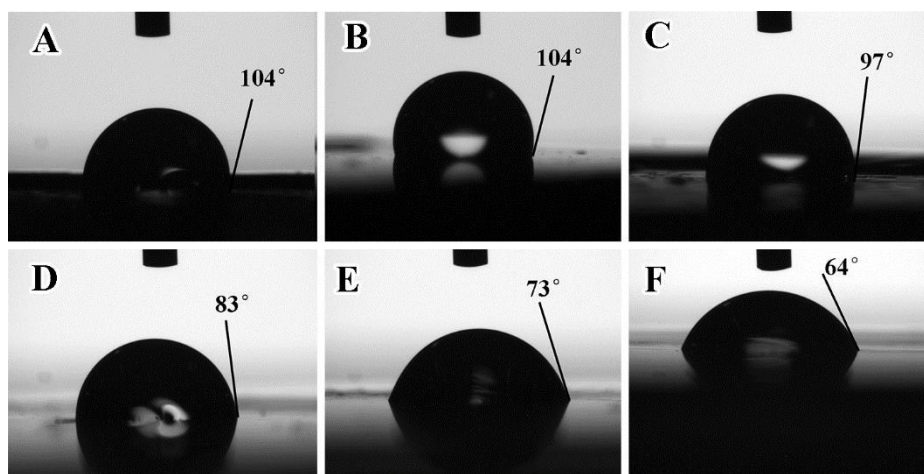

Figure 8. Contact angles of water droplets on the polymer particle films. The corresponding sample: (A) PBA/PVC seed particles; PBA/PVC-sg-PBA composite particles prepared with different BA/(PBA/PVC) feed weight ratios of (B) 3.9 g/22.0 g; (C) 5.7 g/22.0 g; (D) 7.7 g/22.0 g; (E) 10.1 g/22.0 g; (F) 12.8 g/22.0 g. The polymerization time was 3 h and the polymerization temperature was 75 ºC.

To further investigate the microstructure and formation mechanism of the obtained PBA/PVC-sg-PBA composite particles, they were cut with an ultramicrotome and then stained with OsO$_4$ vapor for 2 h. In general, the PBA phase is more easily stained than the PVC phase. As shown in Figure 9, the darker area in the cross-sections of the composite particles was the PBA phase, and the light-colored ultrathin shell was PVC phase. It must be mentioned that the cross-sections of PBA/PVC-sg-PBA composite particles showed more complicated morphologies with different sizes of black and white domains in Figure 9. This is because in the

ultramicrotome-assisted cutting process, the cross-sections obtained from different cutting directions allowed for different morphological views. The schematic cutting model of these morphologies is given in the left inset of Figure 9. We noted that on the particle surface was mostly PVC phase, the PVC phase height on the surface ranged from 7 nm to 35 nm (see the right inset). But if the PBA/PVC-sg-PBA composite particle was an ideal PBA/PVC core-shell structure for the same total PBA/PVC weight ratio, the shell thickness of PVC phase would be 78 nm by theoretical calculation. In addition, for the compatibility between PBA and PVC in the PBA/PVC-sg-PBA

composite particles, the boundaries between PVC and PBA were much fuzzy. On the basis of the above mentioned results, we can conclud that the BA monomer diffused into the PBA/PVC seed particles and polymerized inside the PBA/PVC seed particles, and then grafted to the PBA/PVC particles to form interpenetrating network structure.
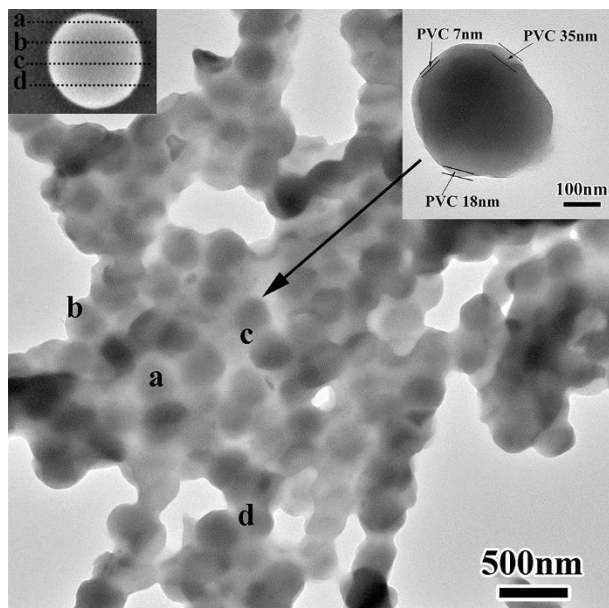

Figure 9. TEM photographs of ultrathin cross sections of the PBA/PVC-sg-PBA composite particle. The PBA/PVC weight ratio was 7.7 g/22.0 g. The polymerization time was 3 h and the polymerization temperature was 75 °C.

Based on above research results, we propose a possible formation mechanism of the flower-like PBA/PVC core-shell particle and the PBA/PVC-sg-PBA composite particle, as shown in Scheme 2. We use dark blue droplets to represent the MPS monomer, purple droplets to represent the AMA monomer, light blue droplets to represent the VC monomer or PVC and red droplets to represent the BA monomer or PBA. At 70 °C, when MPS was dispersed in water (adjusting pH=10-11), the MPS molecules underwent hydrolysis reactions, two or more MPS molecules can be coupled to form low-molecular-weight linear or branched hydrophilic oligomers with many Si-OH groups[41] (Path 1, also see Scheme 1). Therefore, the hydrolyzed MPS can be used as a cross-linking agent, which may copolymerize with VC. Then the MPS_dispersion was mixed with the PBA latex, VC monomers and AMA graft reagent, the reaction was initiated by $NaHSO_3$ and KPS coinitiator (Path 2). The hydrophilic oligomers were mainly distributed unevenly on the surface of the composite particles to form the flowerlike final morphology for minimizing the interfacial free energy of this system.[39, 40] And for the adding of AMA containing two different activities of double bonds during the synthesis of PBA/PVC, consequently the flower-like PBA/PVC composite particles embodied a fraction of functional allyl groups on the PVC chains.

To achieve the unique structure of PBA/PVC-sg-PBA composite particles but different from typical PBA/PVC/PBA multilayered core-shell particles, the flowerlike PBA/PVC composite particles were first swollen for 1 h to let the BA monomer penetrate inside the seed particles at room temperature (Path 3). During the monomer swelling stage, the BA monomer diffused into the PBA/PVC seed to occupy the

space of PBA/PVC-hydrated H_2O molecules derived from the embedded hydrophilic oligomers in the seeds, and then the particles shrunk moderately. We guess that the BA droplets existed in two possible forms: one part of BA permeated into the PBA/PVC seed and uniformly dispersed there, another part was distributed around the seeds, as schematically illustrated in Scheme 2. Then KPS was added and the polymerization was initiated (Path 4). The free radicals mostly migrated into the seed to initiate the BA monomer since the specific surface area of seed particles was much larger than that of the BA monomer droplets. Then the PBA chain was grafted to the PBA/PVC composite particles due to the existence of above AMA molecules. With the polymerization performed, the new PBA phase domain grew by absorption of the BA monomers from the seed phase and around the seeds. This reason is a lower free energy of mixing in the new domain than in the seeds or other domains is the driving force for the transport of monomer.[38, 39] Still, a part of new PBA phase domains emerged from the seed surface because of continuous growth of the new domains. As a result, the PBA/PVC-sg-PBA composite particles with the grafting transition and interpenetrating network of shell layers were produced, avoiding the formation of layer by layer PBA/PVC/PBA core-shell particles which was difficult to form a soft smooth film due to the viscous character of PBA polymer. Generally, the preparation procedure for the PBA/PVC-sg-PBA composite particles combined character of the PBA/PVC flowerlike core-shell structure with advantage of typical interpenetrating network conformation (PBA penetrating into PVC shell), allowing for internal plasticization of the PVC. From design thought of complex particle morphology, the flexile PVC without a low molecular plasticizer was available through multistage seeded emulsion polymerization associated with various swelling, grafting and toughening techniques.
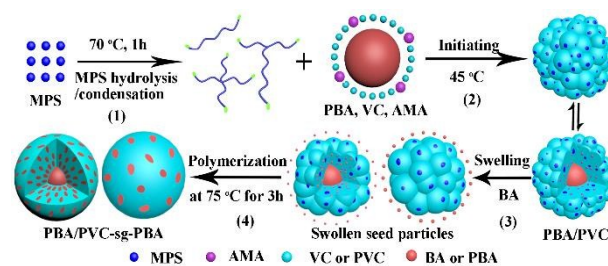
Scheme 2. Schematic illustration of synthesis of PBA/PVC-sg-PBA composite particles via multistage seeded emulsion polymerization

3.4 Dynamic mechanical analysis (DMA) and mechanical properties

Dynamic mechanical analysis is a sensitive method to study polymer miscibility. If the polymer pair is miscible, forming one phase, then one sharp glass transition will be observed. When two incompatible polymers are mixed, the individual phase domains retain the glass transitions of their respective parent homopolymers. So the two glass transition temperatures (T_gs) will be closer when the molecular mixing takes place.

In order to examine the compatibility of PBA with PVC, DMA for the PBA/PVC-sg-PBA samples with different PBA contents and without MPS, and the sample composed of commercial PVC resin mixed with DOP for comparison were performed. The specifications of the samples are listed in Table 1. Typical results from this analysis are presented in Figure 10, and the corresponding T_gs of the samples are summarized in

Table 2. For every curve, there are two distinct spectral peaks. As seen from Figure 10 (1) to (4), the intensity of mechanical loss peak (tan δ) in the low-temperature range of -25 °C to 20 °C is markedly enhanced with the increment of PBA content. Furthermore, with the PBA content increasing, the T_{g1} in low-temperature range for the PBA/PVC-sg-PBA samples gradually shifted a little toward higher temperature, while the T_{g2} in high-temperature gradually shifted to lower temperature. Here, T_g is considered as a peak temperature of tan δ. In low-temperature range, T_{g1} for PBA/PVC-sg-PBA was much higher than the T_g of pure PBA (T_g, ca. -55 °C) in the literature. And when the total PBA/PVC was 40/60 (wt%/wt%), the T_{g2} (53.3 °C) was so lower. This is related to the diffusion of BA monomer into the PBA/PVC particles to form grafting transition layer and interpenetrating network layer. And with the increase of the PBA content, the compatibility of PBA with PVC greatly improved, thus the glass transition temperatures (T_gs) was more closer.

Table 1. Specifications of the samples

Sample no.	1	2	3	4	5[c]	6[d]
BA/(PBA/PVC[a]) feed ratio (wt/wt)[b]	5.7/22.0	7.7/22.0	10.1/22.0	12.8/22.0	12.8/22.0	-
Total PBA/PVC (wt%/ wt%)[e]	25/75	30/70	35/65	40/60	40/60	-

[a] The weight ratio of PBA/PVC was 6.5/93.5 (wt%/wt%) and fixed in these reactions.
[b] BA/(PBA/PVC) feed weight ratio at the third stage of preparing PBA/PVC-sg-PBA composite particles.
[c] PBA/PVC-sg-PBA sample was made when using the PBA/PVC seed without MPS.
[d] Sample of commercial PVC mixing with DOP when the DOP/PVC weight ratio was 40/60 (wt%/wt%) for comparison.
[e] The total proportion of PBA/PVC in the PBA/PVC-sg-PBA samples corresponding to the BA/(PBA/PVC) feed weight.
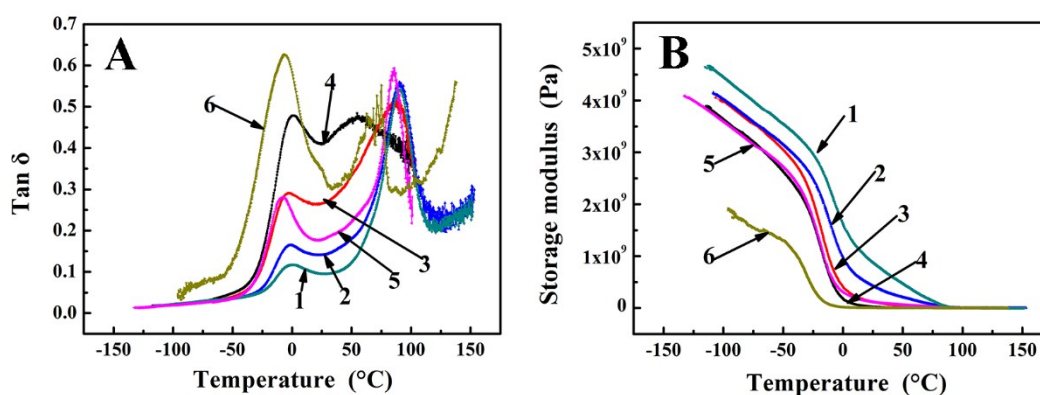

Figure 10. DMA spectra of PBA/PVC-sg-PBA samples with the total PBA/PVC weight ratio being (1) 25/75; (2) 30/70; (3) 35/65; (4) 40/60, respectively, when the MPS being 1.2 wt% (based on VC monomer), (5) sample without MPS when the PBA/PVC weight ratio being 40/60, and (6) commercial flexible PVC sample when the DOP/PVC weight ratio being 40/60 at 1.000 Hz of measuring frequency.

Table 2. Glass transition temperatures for the samples

Sample no.	PBA/PVC (wt%/wt%)	T_{g1} (°C)	T_{g2} (°C)	$T_{g2} - T_{g1}$ (°C)
1	25/75	-3.6	88.8	92.4
2	30/70	-3.5	88.6	92.1
3	35/65	-3.9	85.8	89.7
4	40/60	0.4	53.7	53.3
5	40/60	-10.4	84.1	94.5
6	DOP/PVC=40/60	-8.7	71.8	80.5

In this study, to confirm that the composite structure established by the present method can significantly affect the properties, we also had synthesized the PBA/PVC-sg-PBA (without MPS) with the same total PBA/PVC ratio being 40/60 (wt%/ wt%). As seen from Figure 10 (4) and (5), the sample without MPS have a lower T_{g1} (-10.4 °C) and a higher T_{g2} (84.1 °C). This indicated an obvious two phase separation. Without MPS, there was no hydrophilic MPS-enriched segments on the seed surface and in the inner region of the PBA/PVC composite particles, so we could not obtain the flowerlike PBA/PVC composite particles with water molecules in the inner (Figure 2A). When the BA added, the core-shell PBA/PVC composite particles should be obtained but not the PBA/PVC-sg-PBA particles with interpenetrating network structure.[22-26] By adding MPS, the flowerlike PBA/PVC particles with water in the inner region were obtained, then BA could diffuse into the PBA/PVC to form interpenetrating network structure, and the compatibility between the PBA and the PVC was enhanced to a great extent.

Figure 10 (4) and (6) curves show dynamic mechanical spectra of the PBA/PVC-sg-PBA composite sample and commercial flexible PVC with DOP. Compared with the PVC/DOP system, for the BA monomer diffused into the PBA/PVC particles, the PBA chains would be grafted to the PBA/PVC particles to form an interpenetrating network structure. The PBA could be compatible with PVC at a molecular level. Then in low-temperature range, T_{g1} for PBA/PVC-sg-PBA was much higher than the T_{g1} of commercial flexible PVC, and oppositely the T_{g2} (53.3 °C) was lower. Herein, it is noted that the PBA polymer plasticization sharply decreased the T_{g2} of PVC, even beyond the same amount of low molecule plasticizer, making the fabrication of flexible PVC material probably realizing.

From Figure 10 (B), with the increase of the PBA content, the storage modulus decreased gradually. This resultant trend is

expected, as more PBA particles incorporated into the PBA/PVC-sg-PBA composite particles, the elasticity or flexibility of the polymer chain was increased. The PBA that reduced the modulus of composite should also reduce the

hardness of the thermoplastic elastomer.[42] This statement is supported with the results shown in Table 3.

Table 3. Mechanical properties of compounds

Sample no.	PBA/PVC (wt%/wt%)	Tensile strength (TS, MPa)	Standard deviation (S_{TS})	Elongation at break (EB, %)	Standard deviation (S_{EB})	Shore D hardness
1	25/75	5.41	3.35	8.8	0.7	68
2	30/70	8.79	0.48	17.1	2.4	58
3	35/65	4.65	0.21	50.0	10.4	46
4	40/60	2.81	0.28	353.0	17.2	32
5	40/60	0.22	0.02	207.3	64.9	46
6	DOP/PVC=40/60	0.66	0.12	225.5	60.7	24

The tensile strength (TS) and elongation at break (EB) of PBA/PVC-sg-PBA films are very important for the end use. As shown in Table 3, the EB of the materials markedly improved with an increasing PBA content, while the TS of the materials gradually decreased. And the PBA/PVC-sg-PBA material displayed a higher TS and a greater EB value compared to the PBA/PVC-sg-PBA material without MPS and the commercial flexible PVC with DOP. For the adding of the MPS, the PBA/PVC-sg-PBA interpenetrating network structure was formed, the molecular mixing took place and the EB of PBA/PVC-sg-PBA material was enhanced. These indicated that the phthalate-free and nontoxic flexible PVC can be achieved by using PBA replacing phthalates, and the properties were much greater than those of the flexible PVC plasticized by DOP, whereas the Shore hardness value of both materials was near, upon comparing sample 4 with sample 6 (see Table 3).

4. Conclusions

A new and effective process for fabricating novel flower-like PBA/PVC polymer particles by seeded emulsion polymerization using PBA, VC, MPS and AMA has been developed. The morphology of the flower-like PBA/PVC composite particles can be easily controlled by adjusting the adding amount of MPS. The formation mechanism of flower-like structure is mainly attributed to the further reaction of hydrophilic species derived from base-catalyzed pre-hydrolyzed MPS molecules on the PBA core surface. These resulting colloidal particles, which have controllable flower-like structures, are good candidates for the construction of functional colloidal films and complex colloidal architectures.[36,43] By using the PBA/PVC as seeds, we further synthesized the flexible PBA/PVC-sg-PBA without toxicity and phthalate migration through multistage emulsion graft copolymerization, in which associated with swelling, interpenetrating, grafting and toughening diversified techniques. Morphology studies proved that the BA monomer uniformly dispersed in the PBA/PVC particles to form grafting transition layer and interpenetrating networks. As revealed by the DMA spectra, there were two distinct transition peaks for each sample. The maximum value of the loss peaks in the low temperature region gradually shifted to a higher temperature with an increasing PBA content. Then, the two loss-peaks for every composite sample became closer. Thereby the compatibility between PBA and PVC got improved greatly. The EB of the materials greatly increased with an increasing PBA content,

whereas the TS of the materials decreased a little. Furthermore, the stretch ability of the PBA/PVC-sg-PBA material (for sample 4) was superior to the commercial use PVC/DOP system.

In summary, derived from the tailored morphology of nonspherical seed particles, a novel preparation method was invented for the PBA/PVC-sg-PBA composite particles. This clever structure combined character of the flowerlike PBA/PVC core-shell structure with advantage of the interpenetrating network conformation, by this way taking in the inner core toughening and exterior shell plasticized synergistic action. As a specific application example of the anisotropic particles, the developed polymer-plasticized flexible PVC material is expected to realize industrialization and widely applied in the medical fields without the migration and toxicity worry in the future.

Acknowledgements

Notes and references

[a] Institute of Polymer Science and Engineering, Hebei University of Technology, Tianjin 300130(P. R. China). Tel: +86-22-60202054. E-mail: mwpan@126.com

[b] College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, Sichuan, People's Republic of China. E-mail: ganji.zhong@scu.edu.cn

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