

Effect of ethyleneglycol dimethacrylate crosslinker on the performance of core-double shell structure poly(vinyl acetate-butyl acrylate) emulsion

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ABSTRACT: Core-double shell structure poly(vinyl acetate-butyl acrylate) emulsion was prepared by semicontinuous emulsion polymerization, and the effects of ethyleneglycol dimethacrylate crosslinker (EGDMA) on the emulsion particle structure and film performance were studied systematically. The emulsion particles' structure was characterized by transmission electron microscopy and Fourier transform infrared spectroscopy, and the particle size and distribution were characterized by Zeta potential—particle analyzer, as well as analysis of the film mechanical properties, water resistance, thermal properties, and so on. The results show that, when 0.1 and 0.5% EGDMA were added to the inner-shell and outer-shell reaction stage under the core-double shell P(VAc-BA) emulsion preparation process, respectively, it led to a more clear core-double shell structure and a larger particle size (about 500–800 nm) of emulsion particles, and the comprehensive performance of the P(VAc-BA) emulsion showed better. This work provided some insight into modifying the surface properties of the emulsion particles, which may expand the application field of the emulsion. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 41899.

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INTRODUCTION

Polyvinyl acetate (PVAc) emulsion, commonly known as white latex, is one of the important emulsion adhesives. It is widely used in coatings, fire retardant coatings, adhesives, and so forth.^{1–3} The emulsion possesses poor stability, poor water resistance, bad cold resistance, low strength of film, and so on, which greatly affects its wide application. Therefore, when PVAc-series emulsion is prepared with new emulsifiers, initiators, protective colloids, and other ingredients, or copolymerization using VAc monomer and the butyl acrylate (BA) monomer, or modification emulsion by adding some acrylic acid (AA), acrylonitrile (AN), and other functional monomers, it is expected to improve the comprehensive performance of PVAc-series emulsion.^{4–9} However, most researchers focus on the performance of the emulsions, and rarely ponder the emulsion films' application study.

In this work, semicontinuous seed emulsion polymerization is used to prepare the core-shell structure P(VAc-BA) emulsion with the hydrophilic monomer vinyl acetate (VAc) and hydrophobic monomer BA as raw materials.¹⁰ Designing emulsion particles as “core-double shell” structure need three step emul-

sion polymerization.¹¹ The first step is the preparation for the core seed emulsion with hard monomer VAc as core-monomer to forming the seed homopolymer; the second step is inner shell copolymerization reaction with VAc/BA mixed monomers. Certain amount of crosslinking agent is added to increase the strength of the inner-shell; the third step is the PBA homopolymerization reaction of outer shell. Emulsion particle surface is modified by BA monomer to improve the water resistance, cold resistance and other properties.

The BA is regarded as the third monomer for the emulsion particles in the third reaction step. The third monomer possesses some special performance, such as water resistance, solvent resistance, low adhesion, and so forth. That is to say, the proper third monomer is chosen to modify the surface properties of the emulsion particles according to the requirement of indeed application. Then, adding some proper crosslinker can strengthen these properties in this reaction stage. The BA monomer is chosen as the third monomer in this study. Therefore, the dosage of crosslinker and the adding stage are the key factors for the preparation of the “core-double shell” structure emulsion particle and its properties.

Ethylene glycol dimethacrylate (EGDMA) is chosen as the cross-linking for the emulsion preparation. Its molecule contains two ester groups and two carbon-carbon double bond. The ester group is prone to hydrolysis reaction or double hydrolysis with other substances containing ester base, namely the transesterification.¹² The double ester groups are located at both ends of EGDMA molecule affecting by the strong electronegative effects of carbonyl, which leads to electron cloud density shifted and strong polarity exhibited. And it is easy to occur free radical polymerization with other conjugated functional groups. Therefore, EGDMA is mainly used in plastic and rubber industry, or used as a crosslinker for ethylene AA copolymer, PVC, ABS emulsion copolymerization, and so forth. Adding EGDMA in the copolymerization process could improve the performance of heat resistance, weather resistance, solvent resistance, and abrasion resistance of copolymer film. In this article, the effects of EGDMA on the emulsion particles' structure and film performance are studied systematically. It is an efficient method to improve the comprehensive performance of emulsion by adding proper a crosslinker in the emulsion preparation process.

EXPERIMENTAL

Materials

VAc and AA are provided by Damao Chemicals (Tian-jing, China). BA, poly (vinyl alcohol) (PVA-1788) and ethylene glycol methacrylate (EGDMA) are supplied by Xiya Chemicals (Chengdu, China). Polyoxyethylenealkylphenol ether is provided from Kelong Chemicals (Chengdu, China). Sodium dodecyl sulfate (SDS) and potassium persulfate (KPS) are obtained from Xilong Chemicals (Guang-dong, China). Sodium acetate ($\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$) and sodium hydroxide (NaOH) are purchased from Guanghua Chemicals (Guang-dong, China). All A.R are prepared with deionized water and all monomers are purified by distillation.

Emulsion Polymerization

(1) Core-PVAc homopolymerization reaction

The 500 mL five flask is placed in the water bath pot equipped with an electric stirrer, two dropping devices, a reflux condenser and a thermometer. Certain amount of deionized water (81 g in total), emulsifiers (SDS and OP-10 are 1.2 and 1.5 g, respectively), 1.22 g sodium acetate, 0.9 g AA and 30 g PVA (8 wt %) are added into the flask stirring at 65°C. Add about 24.0 g VAc core-monomer and emulsify 20 to 30 min. Then control the temperature at 70 to 75°C, and add a third of the total initiator KPS (0.2 wt % with respect to the total monomer). When the blue light of the emulsion is weak and the monomer returns slowly, the core-seeds emulsion is obtained.

(2) Inner-shell copolymerization reaction

Control the temperature at 75 to 80°C. Drip a monomer mixture of VAc/BA/EGDMA (84 g in total) and the rest of initiator in the seed emulsion. The reaction time is about 2.5 h.

(3) Outer-shell PBA homopolymerization reaction

Keep the temperature for 30 min when the inner-shell reaction is over. Then drip about 12 g of the shell monomer BA slowly, and strictly control the dripping speed.¹³ So that the BA homo-

polymerization reaction occurs on the emulsion particle surface with the "starvation state." Add a small amount of initiator at the same time. After monomer adding finished, keep the temperature for 15 min. Then heat the temperature up to 85°C, and cure for 1 h. Finally, naturally cool the emulsions to 40°C, adjust the pH value to 6.5–7.0 with 20 wt % NaOH solution. Then, the core-double shell structure P(VAc-BA) emulsion is obtained.

Film Preparation

A certain amount of the emulsion is diluted to a solid content of 30% with 120 mesh filter. Fifty grams filtrate is accurately weighed and uniformly spread on a clean glass on the flat table. The emulsion flows level at room temperature about 24 h for the natural film-forming.

After the film-forming, the film will be dried to transparent at a temperature of 75°C. Soak stripping and leach for 2 h in distilled water to wash the surface hydrophilic substances such as emulsifiers. Then the film is dried to transparent again by suspension method with hot air at a temperature of 105°C. Cool it in a desiccator.

Performance Test

Measurement of Emulsion Coagulation Rate. Precipitation rate refers to the precipitation produced by a percentage of total monomers during the emulsion polymerization process. The emulsion is prepared with 80 mesh stainless steel mesh filter plug, and then the filter residue is washed repeatedly with distilled water until no white latex particles remained. The filter residue is dried at 100°C in an oven until it is constant weight, which is condensate.

$$\text{Precipitation (\%)} = \frac{\text{Precipitation weight (g)}}{\text{Total Monomers weight (g)}} \times 100\% \quad (1)$$

Solid content is determined by weighing about 2.0 g wet emulsion, and spreading evenly on a glass plate. Dry it at 100°C until it is completely transparent, and then weigh it.

$$\text{Solid content (\%)} = \frac{\text{Dry film weight (g)}}{\text{Wet film weight (g)}} \times 100\% \quad (2)$$

Measurement of Emulsion Viscosity. Use the Spanish Fungilab falling ball viscometer method to determine the viscosity of emulsion. The test condition is at a room temperature.

Measurement of Emulsion Particle Size. Use the British MALVERN company's Zeta potential—particle size analyzer Nano-ZS MPT to measure particle size and particle size distribution of the emulsion particles. The sample concentration is 0.06%, the test temperature is 25°C, and deionized water is acted as a dispersing agent.

Measurement of the Water Absorption of Film. Water absorption rate: weigh about 4.0 g dry film and dry it to a constant weight. Immerse it in a constant temperature (28°C) of distilled water for 24 h. Remove the film, blot the water of film surface with the filter paper, and weigh it.

Table I. The Basic Properties of the P(VAc-BA) Emulsion

Crosslinker	Coagulation rate (%)	Solid content (%)	Conversion rate (%)	Viscosity (mPa s)
0%	1.8	37.4	97.5	501.2
0.6%	1.3	37.0	97.8	497.8
0.9%	0.9	36.4	95.8	1010.3
1.2%	5.6	34.7	96.0	1523.5
1.5%	7.4	31.7	96.7	-

“-” No test.

$$\text{Water absorption rate (\%)} = \frac{\text{Wet film weight (g)} - \text{Dry film weight (g)}}{\text{Dry film weight (g)}} \times 100\% \quad (3)$$

Contact Angle of film is measured by using JY-PHb contact angle measurement with hanging drop method.

Measurement of the Film Crosslinking Degree. The uncrosslinked P(VAc-BA) copolymer is easy to dissolve in the benzene, acetone, and other organic reagents. However, the crosslinked P(VAc-BA) copolymer only occurs swelling until the equilibrium. The residuum is the copolymer of equilibrium swelling after repeated dissolving, filtering and washing. Therefore, the crosslinking degree of film is measured by Soxhlet extraction method. Weigh accurately certain quality (W_1) film and pack up it with a constant weight (W_0) of the filter paper. Place it in a Soxhlet extractor, extract 20 h with acetone. Dry the filter bag for 12 h at 80°C, then cool and weigh it (W_2).

$$\text{Crosslinking degree} = \frac{W_2 - W_0}{W_1} \times 100\% \quad (4)$$

W_1 is the original weight of film; W_0 is the weight of filter paper; W_2 is the weight of filter paper, and the rest of film.

Measurement of the Mechanical Properties. Taiwan's U-CAN electronic tensile testing machine (UT-2080) is adopted to measure the mechanical properties of film with a tensile rate of 250 mm/min at a temperature of 25°C. It is in accordance with ISO 37:94 standards. The experiment repeats five times.

Analysis of Infrared Spectroscopy (FT-IR). American PERKIN ELMER company's Spectrum GX-1 Fourier transform infrared spectrophotometer is used to measure Fourier transform infrared spectroscopy (FTIR). The spectral resolution is 4 cm^{-1} , and the film is scanned eight times, and the wave number ranges from 4000 to 650 cm^{-1} .

Transmission Electron Microscopy. Japan Optical Electronics (JOEL)'s 200kV high-resolution transmission electron microscope (JEM 2100) is used to study the emulsion particle structures. The emulsion is diluted to turbidity slightly (about 150 times). Mold film with a special copper mesh and dry it, then stain with 2% phosphotungstic acid, and dry it again.

Scanning Electron Microscopy. Japan Hitachi Limited's scanning electron microscopy (SEM; S-4800) is used to observe the

surface roughness of films and the performance of film-forming.

Differential Scanning Calorimetry. U.S. TA Instrument's differential scanning calorimeter (DSC Q2000) is used to measure the glass transition temperature (T_g) of the film in the nitrogen atmosphere. The sample weight is about 6–8 mg, the heating rate keeps at 10°C/min, and the temperature ranges from -60 to 60°C.

Dynamic Thermal Analysis. German NETZSCH's dynamic mechanical thermal analyzer (DMA242C/1/G) is used to characterize the performance of film in nitrogen atmosphere with a scan frequency of 1 Hz. The heating rate keeps at 5 K/min, and the temperature ranges from -60 to 60°C.

Thermal Gravimetric Analysis. Germany NETZSCH's TG-DSC Analyzer (STA449) is used to measure the thermal stability of film. The high purity nitrogen is acted as protective gas at a rate of 25 mL/min and the ordinary nitrogen is acted as combustion gas at a rate of 50 mL/min. The measuring temperature ranges from 25 to 700°C and the heating rate is 10°C/min.

RESULTS AND DISCUSSION

The Basic Properties of the Emulsion

The solid content designed in this study is 40%. That the ratio of VAc/BA is 65/55 is chosen to study the effect of different amounts of EGDMA (0, 0.6, 0.9, 1.2, 1.5% of the total monomer mass) on the properties of P(VAc-BA) emulsion. The basic parameters of emulsion is shown in Table I.

Analysis of Zeta Potential-Particle

The particle size and distribution of synthetic emulsion reflect the structure of emulsion particles and uniformity, stability of the particle, respectively. It has great influence on the film-forming of emulsion and mechanical properties of film. The Zeta potential—particle size distribution curve of P (VAc-BA) emulsion is shown in Figure 1.

When the content of EGDMA are 0, 0.6, 0.9% of total monomer mass, the average size of emulsion particles are 1048.0d.nm, 754.3d.nm, 643.4d.nm, respectively. It means that the average size of emulsion particles decreased with the dosage

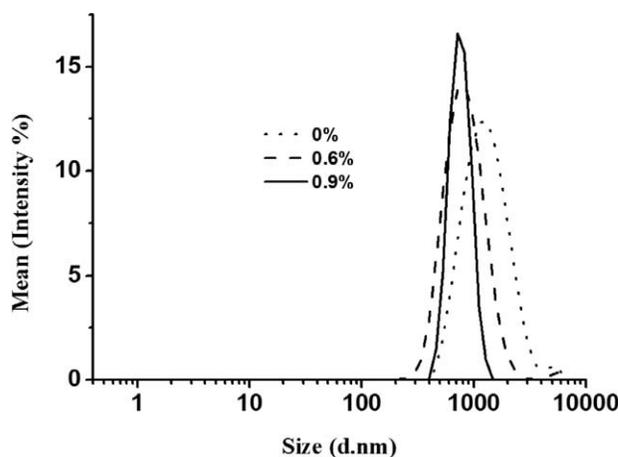


Figure 1. Zeta potential—particle size distribution curve.

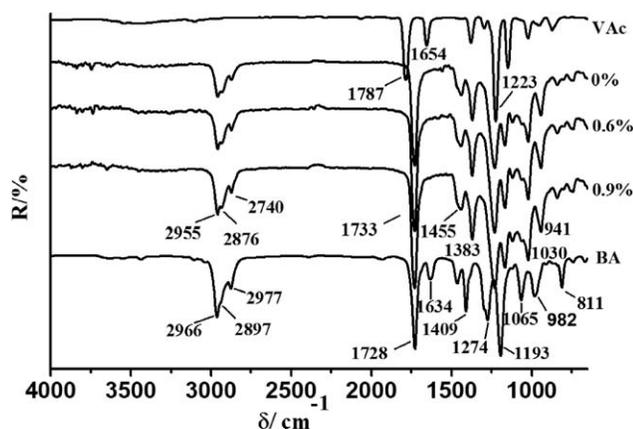


Figure 2. The FTIR analysis curve of films.

of crosslinking agent increased. As shown in Figure 1, the more dosages of crosslinking agent are added, the narrower the distribution of the particle size is, and the higher the distribution of the peak is. This could be because that the crosslinking density get larger and the exchange networks gain more with the dosage of crosslinking agent added. It leads to a great restriction of molecular chains' free stretch, and the size of emulsion particle become smaller. Besides, EGDMA is added in the preparation process. It involves in the composition of molecular structure, and it mainly forms the intramolecular crosslinking. The more

dosages of crosslinking agent are added, the larger the intramolecular crosslinking degree is, the smaller interaction between particles is and the narrower the distribution of particle size is.

Fourier Transform Infrared Spectroscopy Analysis

Figure 2 shows the FTIR curves of P(VAc-BA) films with different EGDMA dosage.

It can be found that those films have an identical FTIR figure when EGDMA is 0, 0.6, 0.9% of the total monomer mass, respectively. It illustrates that the crosslinking agent content has no evident effect on the infrared structures of emulsion particle molecular chains. The characteristic peaks of VAc and BA lie at 1223 and 1030 cm^{-1} in the FTIR figure of P(VAc-BA) films, respectively. The characteristic peaks of the two comonomers are all shown in the four FTIR figures. The C=C bond stretching vibration peaks of VAc and BA monomer which lie at 1654 and 1634 cm^{-1} disappear. It proves that the two monomers have a polymerization reaction, and there is no residual monomer.

Analysis of Transmission Electron Microscopy

Transmission electron microscopy (TEM) mainly characterizes the inner structure of particles. The PVAc homopolymer can be stained by phosphotungstic acid, while the PBA can not.¹⁴ This study designs PVAc homopolymer as the core of particle, P(VAc-BA) copolymer as the inner-shell, and PBA homopolymer as the outer-shell. So phosphotungstic acid is chosen to

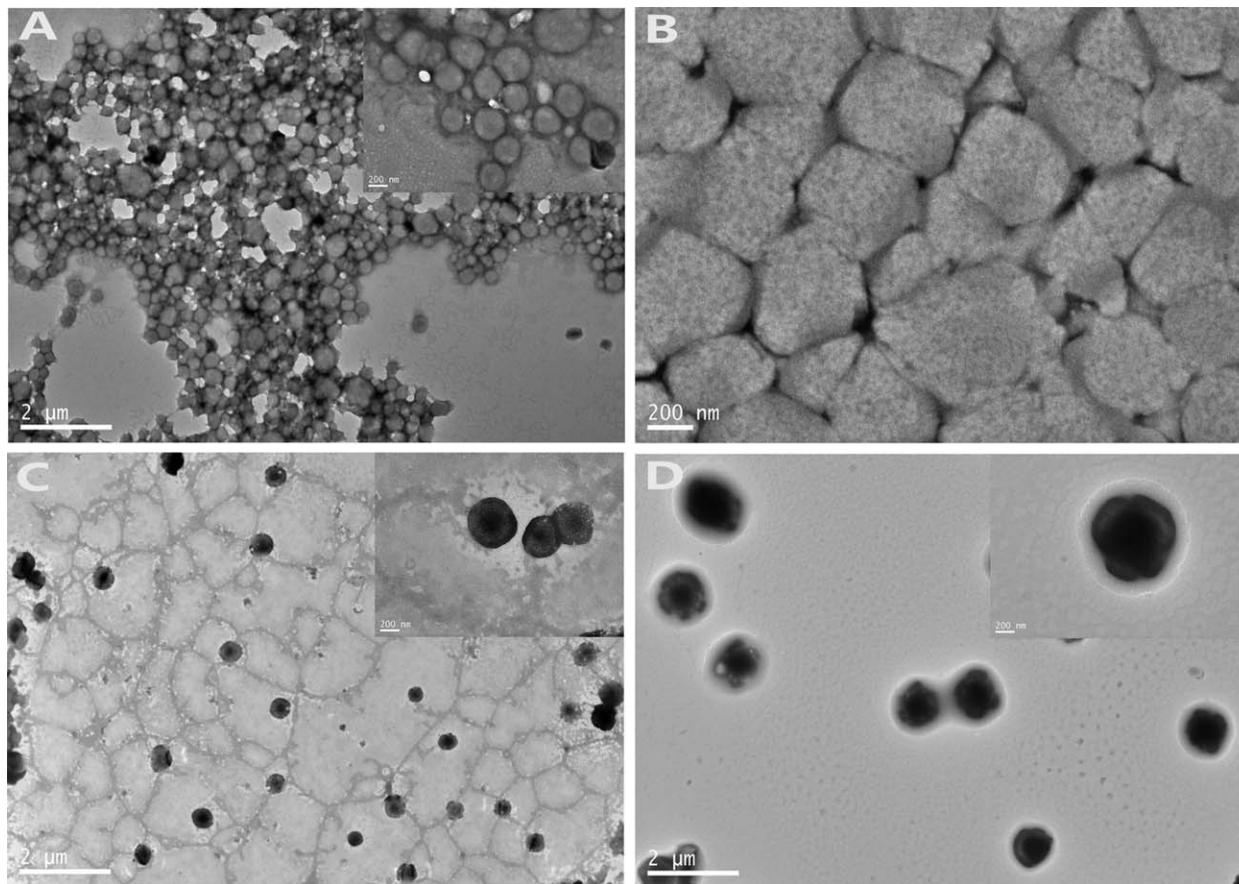


Figure 3. The TEM photographs of emulsion particles. 0, 0.6, 0.9, 1.5% EGDMA are A, B, C, D, respectively.

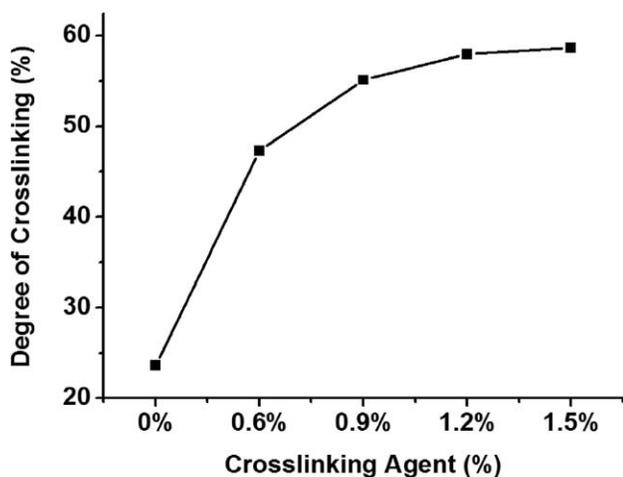


Figure 4. The degree of crosslinking curve of films.

stain the emulsion particles. In the TEM, the core is completely stained by phosphotungstic acid with the highest electron cloud density, so its color is the deepest. The color of inner-shell is shallow with low electron cloud density, but the outer-shell is almost not stained. Therefore, there will be a obvious level of light and shade, which distinguishes structure and morphology of the particles. Such as Figure 3.

As shown in Figure 3, when the dosage of EGDMA arrives at 0.9% of the total monomers, the emulsion particle shows a obvious core-shell structure in the TEM. Its color gets shallow from core to shell. Since the proper crosslinking agent is added into the inner-shell reaction stage, it could increase the crosslinking network structure of the inner-shell in emulsion particles and the crosslinking degree, strengthen the density of the molecular chains, decrease the behavior of migration of the cluster, and prevent the BA monomer or little molecular chain segments from entering into the core layer, which protects and isolates the core. Therefore, the emulsion particles form a stable core-shell structure. It can be found from A and B of Figure 3, it is difficult to form a core-shell structure when the dosage of EGDMA is less than 0.9%, and it is easy to cluster. The emulsion particle is spherical with 0% EGDMA, while cubic-shaped with 0.6% EGDMA. Particle shape changes greatly probably due to the molecular chains occurring "phase inversion" and "cluster migration."¹⁵ The molecular chains of PVAc, P(VAc-BA), and PBA occur migration and other reactions such as disorder crosslinking, grafting and blending, which leads to emulsion particles completely gray. According to Figure 1,

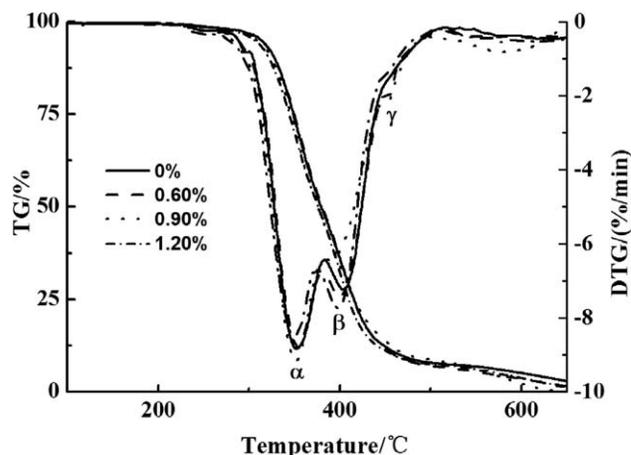


Figure 5. The TG-DTG curve of crosslinking agent films. EGDMA is 0, 0.6, 0.9, 1.5%, respectively.

there are some emulsion particle sizes more than $1\ \mu\text{m}$ even to $3\text{--}5\ \mu\text{m}$ in the Zeta potential-particle size distribution curve when the dosages of EGDMA are 0 and 0.6% respectively. Inferred from the TEM photos, the large particle may be caused by the emulsion particles cluster.

Analysis of the Mechanical Properties

P(VAc-BA) emulsion of different dosages of EGDMA is film-formed, and the indexes of mechanical properties are measured. The crosslinking degree is measured by Soxhlet extraction method. The results are shown in Table II and Figure 4.

As shown in Table II, the tensile strength of film increases with the dosage of EGDMA increased and tensile elongation increases first then decreases, which is mainly due to the crosslinking degree of molecular chain increased. When the molecular chain crosslinking degree increases to a certain extent, the flexibility of molecular chain decreases, and the free stretchability of molecular chain segments reduces, which leads to breaking elongation of film increases first and then decreases. However, the tear strength is less affected by the crosslinking degree, so further study is needed to find the specific reasons.

It can be found that the crosslinking degree's increase of molecular chain is limited in Figure 4. When EGDMA accounts for 1.5% of total monomer, the crosslinking degree will reach a constant extent. In addition, VAc and BA occur free radical polymerization to form the copolymer molecular chain with a water-soluble initiator KPS. Since both monomers exist esters,

Table II. The Mechanical Properties of Films

Crosslinker	Thickness (mm)	Tensile strength (MPa)	Tensile elongation (%)	Tear strength (kN/m)	Crosslinking degree (%)
0%	0.41	2.66	816.60	13.56	23.6
0.6%	0.50	2.65	940.28	14.65	47.3
0.9%	0.50	2.97	1178.38	13.63	55.1
1.2%	0.26	3.52	1268.84	14.09	58.0
1.5%	0.14	4.41	1070.98	-	58.7

"-" No test.

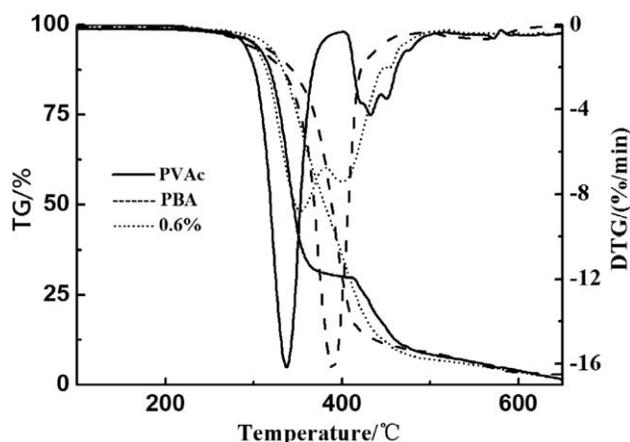


Figure 6. The TG-DTG curve of films for PVAc, PBA, 0.6% EGDMA.

and the ester group will occur hydrolysis reaction and the ester exchange reaction easily, it results in self-crosslinking reaction of molecular chain. Therefore, the crosslinking degree is still up to 23.6% without adding a crosslinking agent.

Thermal Gravimetric Analysis

In this study, a thermal gravimetric (TG) analysis is made for the dry films of the P(VAc-BA) emulsion, PVAc emulsion and PBA emulsion, in which the EGDMA accounts for 0, 0.6, 0.9, and 1.2% of the total monomer, respectively. Using the derivative thermogravimetric method and least squares to fit and analyze the reaction activation energy for different amount of crosslinking agent. The results are shown in Figures 5 and 6, Tables III and IV.

As seen from Figure 5, there are three degradation peaks in the DTG curves of the film which is the third degradation process of the P(VAc-BA) film, namely α , β , γ . While the thermal degradation of each film is basically the same, indicating that the dosage of crosslinking agent makes no significant effect on the thermal degradation mechanism of the P(VAc-BA) films. However, the initial degradation temperature (T_0), the maximum degradation rate temperature (T_p), and the terminated temperature (T_r) are obtained by double tangent method to deal with the TG curves. As shown in Table III, when the crosslinking agent accounts for 0.9%, the film has the highest T_p , which indicates that the amount of crosslinking agent is 0.9%. It will help to improve the thermal stability of the film.

Combined with the analysis of Figure 6, it can be found that the T_0 and T_r of PVAc, PBA and 0.6% EGDMA films are almost the same. But each of their thermal degradation process shows

Table III. The Thermal Degradation Temperature of Films

Crosslinker	First degradation temperature (°C)			Secondary degradation temperature (°C)		
	T_0	T_p	T_f	T_0'	T_p'	T_f'
0%	324.8	353.1	369.0	393.4	405.0	434.4
0.6%	327.8	354.3	365.0	380.2	401.2	424.1
0.9%	324.0	358.4	365.5	385.4	419.5	421.9
1.2%	322.4	352.3	361.9	373.3	391.1	421.9

a big difference. And the thermal stability of the PVAc is better than that of PBA. A phase separation occurs when the dosage of the crosslinking agent is 0.6%, resulting in two obvious degradation peaks, which is due to the “core-double shell” structure of P(VAc-BA) emulsion particles. PVAc, PBA and their copolymers display the thermal properties similar to the blend for the TG-DTG curve. What’s more, the two largest loss peaks of the film (the dosage of EGDMA is 0.6%) lie in the degradation process of PVAc and PBA. By inference, α is the overlapping peak which contains PVAc homopolymer and partial copolymer of the P(VAc-BA) and the degradation temperature is 320–369°C; β is the overlapping peak which contain partial copolymer of the P(VAc-BA) and PBA with partial additives of low thermal stability and the degradation temperature is 380–420°C; γ is the thermal degradation peak which contains a few additives with high thermal stability and the degradation temperature is 450–465°C.

According to the TG curve obtained by TG analysis and the corresponding weight loss rate of decomposition temperature obtained by the comprehensive quality variation analysis, the activation energy (E_a) of thermal degradation process can be calculated by the integral method of Coats–Redfern model.¹⁶ On the basis of reaction kinetics $dx/dt = K(1-x)^n$ and Arrhenius equation $K = Ae^{-E_a/RT}$, the variant equation $\ln\{[1-(1-x)^{1-n}]/[T^2(1-n)]\} = \ln[(1-2RT/E_a)AR/\beta Ea] - Ea/RT$ ($n \neq 1$) and $\ln[-\ln(1-x)/T^2] = \ln[(1-2RT/E_a)AR/\beta Ea] - Ea/RT$ ($n = 1$) can be obtained by mathematical treatment. Incidentally, n is the reaction order; x is the extent of reaction; T is the absolute temperature; β is the heating rate; E_a is the activation energy; R is the gas constant; A is the pre-exponential factor.¹⁷ When $n \neq 1$, make a straight line $\ln\{[1-(1-x)^{1-n}]/[T^2(1-n)]\}$ versus $1/T$, the slope is $-E_a/R$ and the intercept is $\ln[(1-2RT/E_a)AR/\beta Ea]$. By the least squares fit, it can obtain the maximum correlation coefficient (r^2) through assuming different values of n . When r^2 is the maximum, we can calculate

Table IV. The Thermal Degradation Temperature Mechanical Parameters of Films

Crosslinker	Decomposition rate (%)					E_a (kJ·mol ⁻¹)	n	A (10 ¹²)	r^2
	300°C	350°C	400°C	450°C	500°C				
0%	1.78	24.34	62.31	86.15	90.53	178.50	4.0	3.75	0.9896
0.6%	1.79	23.68	62.42	86.56	91.40	175.11	3.8	1.74	0.9921
0.9%	2.28	27.16	64.25	84.45	89.82	183.00	4.4	13.3	0.9949
1.2%	2.56	28.11	65.89	87.39	90.98	179.45	4.1	8.32	0.9870

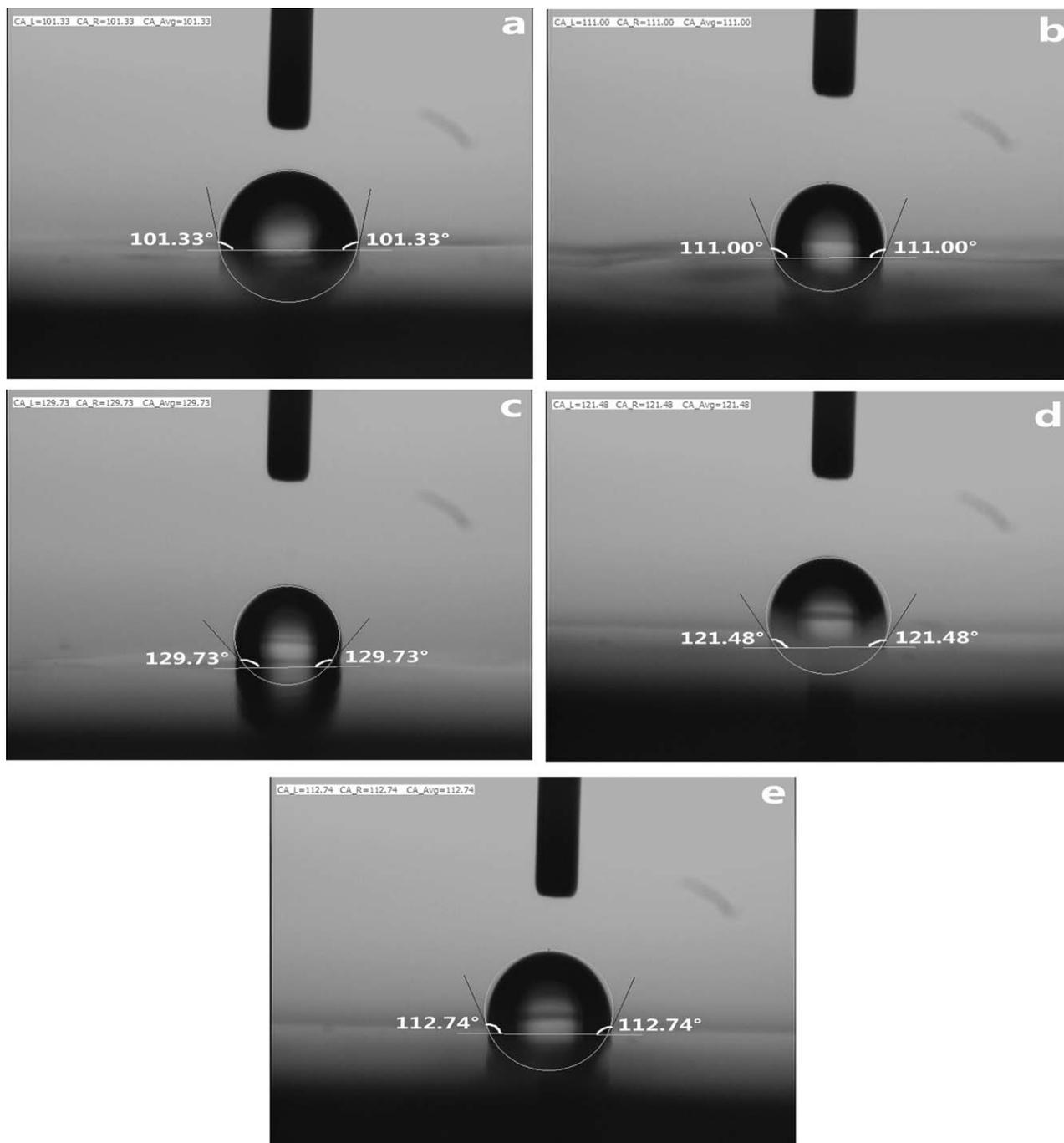


Figure 7. The contact angle photographs of films. 0, 0.6, 0.9, 1.2, 1.5% EGDMA are a, b, c, d, e, respectively.

reaction activation energy (E_a) according to the slope $-E_a/R$. The E_a can characterize the thermal stability and flexibility of polymer chains for a certain extent.¹⁸ The results are shown in Table IV.

As shown in Table IV, P(VAc-BA) film possess the largest E_a when the dosage of EGDMA is 0.9%, which indicates that the molecular chains possess a better thermal stability and flexibility. When the dosage of EGDMA is 1.2%, its E_a reduces a little. As seen from Table II and Figure 4, the crosslinking degree of molecular chains will arrive at a steady state value after the dos-

age of EGDMA arrives at 1.2%. Its tensile strength still increases, but elongation decreases. It is concluded that E_a of P(VAc-BA) film and the thermal stability and flexibility of the molecular chains will decrease when the dosage of EGDMA is more than 1.2%.

Analysis of the Resistance to Water

Contact Angle refers to the angle θ between a tangent and a line which is the boundary of solid and liquid, and the tangent is a line of gas-liquid interface made in the gas, liquid, solid three-phase intersection. It is a measure of the degree of

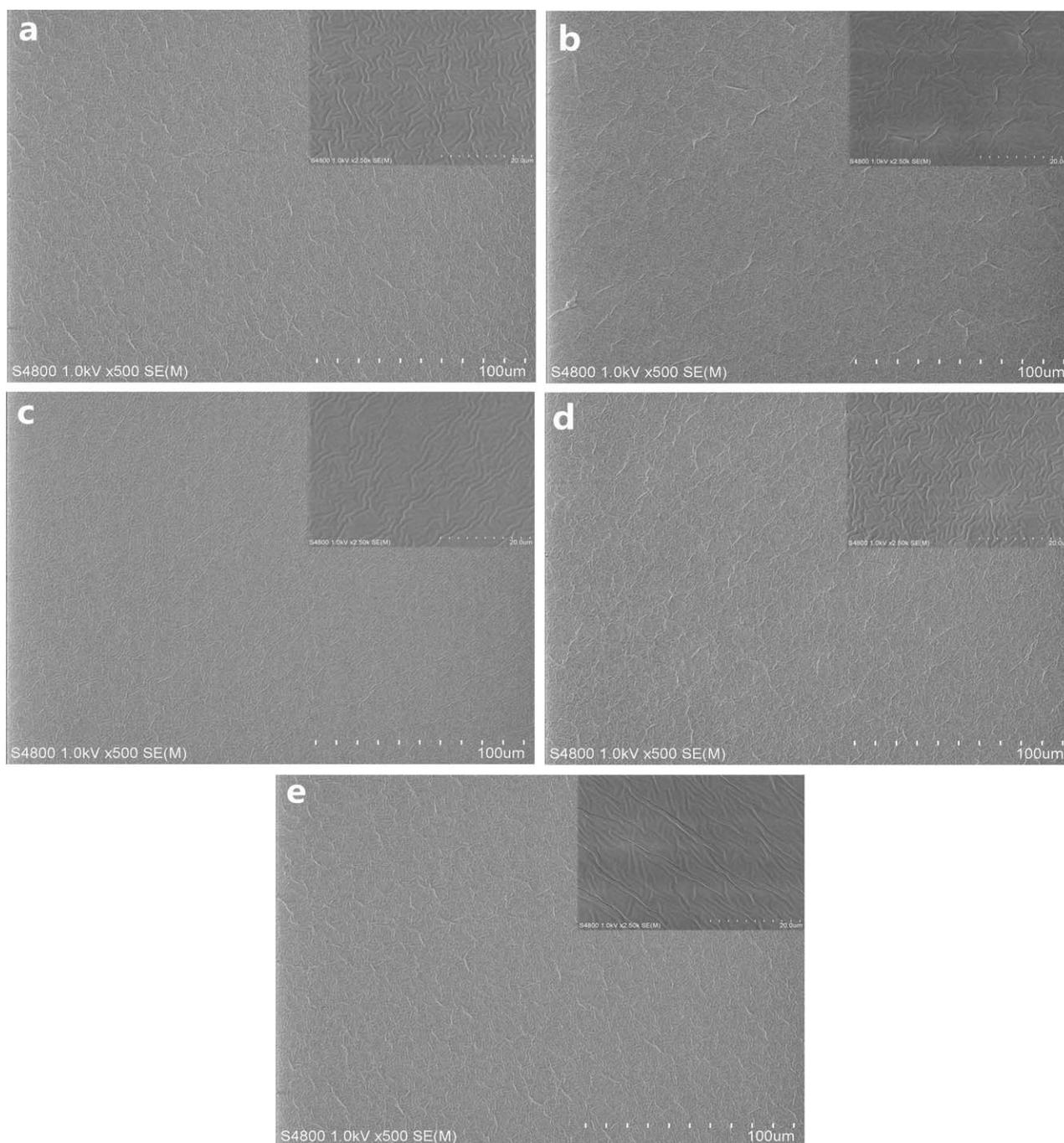


Figure 8. The SEM photographs of films. 0, 0.6, 0.9, 1.2, 1.5% EGDMA are a, b, c, d, e, respectively.

Table V. The Resistance to Water Analysis of Films

Crosslinker	Water absorption (%)	Contact angle (°)	Surface energy (J m^{-2})	Adhesion work (mJ m^{-2})
0%	34.6	101.93	21.87	57.75
0.6%	29.9	109.62	17.31	48.37
0.9%	20.0	125.61	8.91	30.53
1.2%	17.7	119.99	11.72	36.62
1.5%	14.1	113.97	14.94	43.40

wetting. Wetting process related to the interfacial tension of the system. If a drop of liquid falls on the level solid surface, when it reaches phase equilibrium, the correlativity between the contact angle and each of the interfacial tension conforms with the Young's equation ($\gamma_{s,g} = \gamma_{s,l} + \gamma_{g,l} \times \cos\theta$). The interfacial tension is closely related to the film itself particle structure, properties and film-forming properties. The film-forming process is seen from the surface roughness of film which is observed by SEM photograph. Water absorption directly reflects the water resistance of film. The related parameters of water absorption,

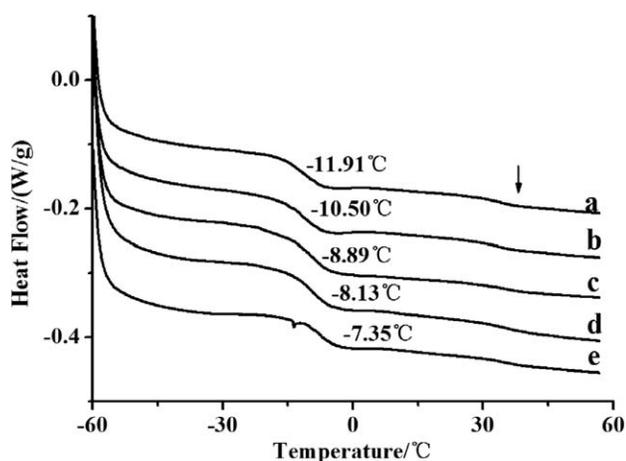


Figure 9. The DSC curve of films. 0, 0.6, 0.9, 1.2, 1.5% EGDMA are a, b, c, d, e, respectively.

contact angle of films and SEM photographs of films are shown in Table V, Figures 7 and 8.

As shown in Table V, the water absorption of films decreases with the increase of EGDMA dosage in the preparation of P(VAc-BA) emulsion. Immersed in the deionized water for 24 h, the water absorption mainly depends on the emulsion particle structure and the degree of entanglement of molecular chains. Figure 4 shows that the crosslinking degree of emulsion films is gradually increased with the increase of the amount of EGDMA, which indicates that the degree of entanglement of molecular chains is also gradually increased. Due to that EGDMA is mainly added into the inner-shell stage, the greater crosslinking degree of this stage is, the more complex entangled structure of the molecular chains and the greater density of the molecular chain mesh are. It results in the newly generated copolymer molecular chains and BA monomer of outer-shell inter into inner less. So that more PBA chains are generated on the surface of emulsion particles. Meanwhile, the hydrophobic of BA monomer is greater than VAc monomer so as to improve the water resistance of the film.¹⁰ Found from Figure 1, the greater the dosage of crosslinking is, the smaller the emulsion particle size is, which also proves that the free-movement of molecular chains is limited. That's to say, the water resistance of films is improved with the mesh of molecular chains increased.

Table V and Figure 7 show that, the contact angle θ of all the films are bigger than 90° and the solid surface is not wet by the liquid when $90^\circ < \theta < 180^\circ$, so it can be inferred that the film is hydrophobic and the denoized water does not wet the film.

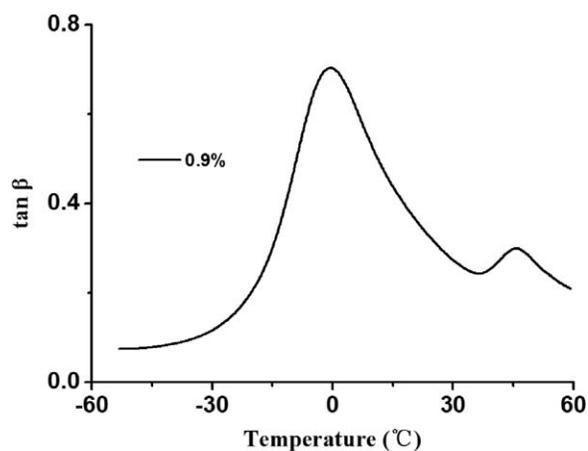


Figure 10. The DMA curve of films. EGDMA is 0.9%.

With the increase of EGDMA dosage, the contact angle does not increase but the maximum contact angle, the minimum surface energy and adhesion work occur when the dosage of EGDMA is 0.9%. DLVO theory think that colloidal stability depends on the potential energy of the interaction between the interface of particles. Expanding the theory, it can be found that the interactions of interface between the two components includes electrostatic force, van der Waals forces, hydrophobic attraction and hydration repulsion, which form free energy by forces each other.¹⁹ And the magnitude of various forces depends on film-forming properties. Therefore, there are two factors mainly affecting the contact angle. One is the distribution and properties of particles on the film surface, another is film-forming factors such as surface roughness, impurity content and crack crevice. Seen from Figure 8, the surface roughness of films looks quite close. If all these factors work together, and they concentrate expression for the total surface free energy (surface energy). The smaller the surface energy is, the smaller the contact angle will be, so the film surface hydrophobicity and film-forming properties are better. Table V shows that, there are minimum surface energy and adhesion work when the amount of EGDMA is 0.9%, which indicates the film-forming properties of P(VAc-BA) emulsion is the best. It is found that the film of 0.9% EGDMA is smooth and transparent in the film preparation process, but the film is obviously white and there are liquid flow traces when the EGDMA is 1.2 or 1.5%. Table I also shows, the two emulsions contain so much impurity content, and it is difficult to filter, which also leads to poor film-forming performance.

Table VI. The Performance Parameters of the Emulsion for the EGDMA Adding Technology

Sample	Viscosity (mPa s)	Crosslinking degree (%)	Tensile strength (MPa)	Tensile elongation (%)	Tear strength (kN m ⁻¹)	Water absorption (%)
S-1	224.20	46.2	8.9	617.4	27.5	26.4
S-2	273.11	55.7	12.4	577.5	30.8	18.2
S-3	257.22	52.3	10.5	483.1	30.4	20.5

Analysis of DSC and DMA

DSC and DMA can character the glass transition temperature (T_g) as a guide for practical applications. Meanwhile, they both reflect compatibility of the core-shell particles among each component. Figures 10 and 9 show the DSC and DMA curve of P(VAc-BA) films, respectively.

Figure 9 shows that the glass transition temperature (T_g) increase with the increase of the dosage of EGDMA gradually, and the arrow of each DSC curve is looming to occur at the second T_g inflection point. Two loss peaks, P(VAc-BA) copolymer peak and PVAc homopolymer peak, can be found obviously from Figure 10, respectively. Which indicates that there are at least two phase states in the film particles. It could be inferred that the emulsions have a core-shell structure. The emulsion particle is designed into three incompatible components, PVAc core, P(VAc-BA) inner-shell, and PBA outer-shell. But the free-radicals of BA monomer is more active than VAc monomer in the emulsion preparation process,²⁰ so that some BA monomer maybe involved into inner-shell copolymer reaction. And the BA monomer added in the outer-shell reaction is only 10% of the total monomers. So, fewer PBA molecular chains modify the outer-shell of emulsion particle. Therefore, it is difficult to detect the loss peak of PBA, or this loss peaks are merged by the copolymer peaks of P(VAc-BA). Found from the TEM photographs in Figure 3, some PBA molecular chains may enter inner-shell to involve copolymer reaction. In addition, the transition temperature of PVAc homopolymer is about 28°C, but a higher T_g which is above 30°C from the DMA loss peak is obviously found. In addition to instrument error, it only may be the effect of crosslinking agent. A larger crosslinking degree restricts the movement of the molecular segments, which leads to its flexibility lower and the transition temperature higher.

Effect of EGDMA Added Process on the Emulsion Properties

Above all the discussion, it can be found that adding EGDMA of the total monomers from 0.9 to 1.2% in the inner-shell reaction stage of emulsion preparation process, the P(VAc-BA) emulsion possesses the best comprehensive performance. Therefore, 1% EGDMA of the total monomers is chosen to add during the inner-shell reaction in the next study. 0.5% EGDMA will be added in the outer-shell reaction stage and heat preservation stages respectively in order to discuss the effect of addition process of the crosslinking agent on the emulsion properties. Meanwhile, the significance of emulsion performance study lies in its practical application, such as latex gloves. If P(VAc-BA) emulsion is expected to be applied to the thin film materials, it requires a certain strength. It is found from Table II, the mechanical properties of the films are lower when the value of VAc/BA is less than 80/40, which leads to a worse performance. So VAc/BA is designed as 85/35 and the differences of films among each performance will be more obvious. That the dosage of EGDMA is 1% of the total monomers in inner-shell reaction stage is named as S-1. 1% and 0.5% EGDMA in the inner-shell and outer-shell reaction stages is named as S-2. 1% and 0.5% EGDMA in the inner-shell reaction and heat preservation stage is named as S-3, respectively. Every P(VAc-BA) emulsion performance parameter measured is shown in Table VI.

It is found from Table VI, the comprehensive performance of sample S-2 is the best. The crosslinking degree of S-2 is the largest, and its viscosity, strength, tear strength, and water absorption are the largest consistent with the results discussed above. Compared with S-1, the tensile strength and water absorption increases 39.3 and 31.0%, respectively. Therefore, no matter which reaction process the 0.5% EGDMA is added in, the mechanical properties and water resistance of P(VAc-BA) film will increase with the dosage of crosslinking agent increased. And the properties of emulsion films about S-2 is a little better than that of S-3.

CONCLUSIONS

Through the analysis of EGDMA on the effect of the P(VAc-BA) emulsion performance, it could be concluded that a good comprehensive performance emulsion could be prepared by semicontinuous emulsion polymerization. On this condition, 1 and 0.5% crosslinking agent of the total monomers are added into the inner-shell and outer-shell reaction, respectively, in the core-double shell structure P(VAc-BA) emulsion preparation. When the core-double shell structure P(VAc-BA) emulsion is prepared as a ratio 85/35 of VAc/BA, the film made from it show a relatively better comprehensive performance. And the film is expected to be applied to the thin film products.

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