

Effect of Polyurethane Molecular Weight on the Properties of Polyurethane–Poly(butyl methacrylate) Hybrid Latex Prepared by Miniemulsion Polymerization

Cun Tian,^{1,2} Qing Zhou,² Li Cao,¹ Zhi-qiang Su,¹ Xiao-nong Chen³

¹Key Laboratory of Beijing City on Preparation and Processing of Novel Polymer Materials, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

²Beijing Research Institute of Yantai Wanhua Polyurethanes Co., Ltd, Beijing 102200, People's Republic of China

³Key Laboratory of carbon fiber and functional polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

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ABSTRACT: Polyurethane (PU) prepolymer was first prepared via introducing double bonds on-to the PU chains, and then polyurethane–poly (butyl methacrylate) (PU–PBMA) hybrid latex was prepared via miniemulsion polymerization. Transmission electron microscopy, Differential scanning calorimeter (DSC), Fourier transform infrared, and dynamic mechanical analysis were adopted to characterize the hybrid latex and its coating film. Both the coating property and the miscibility of PU–PBMA emulsion have been greatly improved through introducing double bonds into

PU prepolymer. With an increase in the molecule weight of PU (M_{PU}), the increase in the particle size of PU–PBMA emulsion was observed plus decreases in the stability of the hybrid latex and conversion of methacrylate. Besides, as M_{PU} increased, the final dried coating film of the hybrid latex showed decreased water resistance, weakened miscibility, and improved mechanical properties. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 5229–5235, 2012

Key words: PU; PBMA; miniemulsion; compatibility

INTRODUCTION

Polyurethane (PU) dispersions, with excellent toughness, flexibility, abrasion resistance, and film-forming properties, have been widely utilized in industrial coatings and adhesives.¹ To obtain better cost/performance benefits, a lot of efforts have been devoted to modify PU with different kinds of polymers, among which acrylic polymer is the most popular one² for it is mechanical strength favorable, anti-yellow, water resistant, and anti-aging. The combination of PU and polyacrylate (PA) leads to an improved hybrid system which incorporated the merits of both components. Researchers in this field have prepared polyurethane-polyacrylate (PUA) hybrid latices through a variety of methods, includ-

ing blending resin particles with acrylic latex,³ seed polymerization, cross-linking, core–shell emulsion polymerization,^{4,5} preparation of interpenetrating polymer networks,^{6,7} and grafting copolymerization of PU onto acrylic polymer chains,⁸ all of which may be processed via a conventional emulsion process or miniemulsion.

Sharma proposed a blend system of acrylic resin and polyester polymer, and superior properties were obtained compared with either of the system alone.³ A Slovenian team compared the hybrids prepared by seeded emulsion polymerization with that by mechanically blended, and it turned out with improvements in both chemical and mechanical properties, accompanying with a decrease in water resistance and oil resistance.⁵ Hegedus and Kloiber⁸ prepared hybrid system via miniemulsion in which the two monomer, acrylic and PU, grew independently and resulted in an interpenetrating network at the molecule scale.

Seeded emulsion polymerization has drawn much more attention than the other methods to prepare PUA core–shell structure due to relatively less phase separation, but the product is less water resistant and oil resistant. Besides, in the seeded emulsion polymerization, PA alone can nucleate, leading to a composition inconformity of the emulsion particles, which finally contributes to a phase separation of PU and PA and thus hindered its application in coatings.

Correspondence to: Z. Su (suzq@mail.buct.edu.cn) or X. Chen (chenxn@mail.buct.edu.cn).

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Conventional emulsion polymerization occurs in a micelle formed by surfactants and monomers have to pass into the micelle to be polymerized, thus mass transport comes, which slows down the polymerization process, typically for grafting polymerization, and the mass transport will lead to low grafting efficiency.³ However, in miniemulsion, the nucleus is formed mainly by monomer droplet,⁹ which avoids the diffusion of monomers to the micelle, hence there are little difference in the compositions among monomer droplets. Each droplet acts as an independent nanoreactor,^{10,11} compelling the two components to be tolerant with each other on the molecular scale. Besides, the monomer droplet in miniemulsion is about 50–500 nm,¹² in sharp contrast to that in a conventional emulsion process of 5–10 microns. The much smaller particles resulted in an increased surface energy which helps a lot to stabilize the dispersions and further application of the hybrid latex. In addition, there is no intrusion of ion group in the whole polymerization process, so a good water resistance was found in the product. As a result, a film of PUA hybrid latex with better water resistance and lower phase separation was prepared through miniemulsion and finally an optimization of the properties of PU and PA was achieved.

Meanwhile, studies have been carried out focusing on the factors which work on PUA hybrid latices during miniemulsion. Shork et al.¹³ has found that PU can stabilize the miniemulsion in a form of assistant emulsifiers. Wang et al.¹⁴ has reported the kinetics of polymerization, mechanical property, surface property,^{15,16} and the effect of PU with different end groups on the compound emulsion.¹⁷ However, little work has been reported concerning the influence of M_{PU} on the property of miniemulsion which actually imposes a major influence on the property of both the emulsion and the film. In this article, special attention has been paid to the effects of M_{PU} on the properties of polyurethane–poly (butyl methacrylate) (PU–PBMA) emulsion and its coating film, including emulsion stability, conversion of *n*-butyl methacrylate (BMA), compatibility of the two components, and water absorption of the paint film.

EXPERIMENTAL

Materials

Isophorone diisocyanate (IPDI), NCO = 37.0%, was purchased from Yantai Wanhua Polyurethane Co. Polypropylene glycol (PPG), $M_n = 2000$, was obtained from Dongda Polyurethane Co. and was dried at 105°C under reduced pressure for 4 h. BMA from Tianjin Jinke Fine Chemical Industry Research Institute was reagent grade and was used after distillation under reduced pressure. Hydroxyethyl meth-

acrylate (HEMA) of reagent grade was also purchased from Tianjin Jinke Fine Chemical Industry Research Institute and the water was removed with molecular sieve. Hexadecane (HD) and sodium lauryl sulfate (SLS) were both analytical grade and were obtained from Tianjin Jinke Fine Chemical Industry Research Institute. Dibutyltin dilaurate (DBTDL) produced by Tianjin Yongda Chemical Reagent Development Center was analytical reagent and was used without any further purification. Benzoyl peroxide (BPO) from Xilong Chemical Plant in Guangdong Province Shantou City was analytical reagent and was used as initiator. The water was deionized.

Polyurethane synthesis

The formulation for the preparation of PU is listed in Table I. The reaction was carried out in a nitrogen atmosphere at a constant temperature in oil bath. PPG and DBTDL (60 ppm) were first charged into the reactor and stirred for 5 min. IPDI was then added into the reactor. The whole reaction takes approximately 2 h at 60°C (the reaction end point was determined by the remained –NCO content). HEMA with a double bond in its structure was used, which first acts as a terminator agent and was charged into the prepolymer of PU and the reaction proceeded for another 1 h at 60°C, then in the following emulsion reaction, PU chain can be grafted onto the molecule of PBMA via the reaction of the double bond in HEMA, which improved the compatibility between PU and PBMA. Furthermore, since the reactivity of the two NCO groups in IPDI is different with one of which more reactive, therefore, the termination can be controlled to occur only at one end of the PU chain by regulating the temperature and controlling the dosage of HEMA. Finally, a small amount of ethyl alcohol was dripped into the reactor to further terminate the remained PU NCO groups. In conclusion, by changing the molar ratio of –NCO_(IPDI) to –OH_(PPG), the molecular weight of PU can be adjusted.¹⁸ The molecular weights of the samples were shown in Table I.

Miniemulsion polymerization

Before polymerization, PU, HD, and BPO were dissolved in BMA monomer. The oil mixture exhibited good shelf stability at room temperature and a lack of phase separation.² This indicates that PU can be dissolved in BMA monomer, and a homogeneous oil phase is obtained. At the same time, the surfactant (SLS) solution was prepared separately and then mixed with the oil mixture. The mixture was emulsified by mulser (FLUKO FA25, 10,000 rpm) for 10 min. Finally, the miniemulsion of the samples was completed by subjecting to a highly efficient sonifier

TABLE I
Recipe for the Preparation of PU with Different Molecular Weights

Sample	NCO _(IPDI) /OH _(PPG)	IPDI (g)	PPG (g)	HEMA (g)	Alcohol (g)	M_n	M_w/M_n
PU1	10/5	25	108.74	2.87	4.06	2814	1.66
PU2	10/6	25	129.35	2.87	3.04	4638	1.65
PU3	10/7	25	152.2	2.87	2.03	6062	1.82
PU4	10/8	25	171.48	2.87	1.01	11915	1.98

The amount of IPDI is constant, the mole ratio of $-\text{OH}_{(\text{HEMA})}/-\text{NCO}_{(\text{IPDI})}$ is 1/10, and $\text{NCO}_{(\text{IPDI})}/\text{OH}_{(\text{PPG})}$ refers to mole ratio of the two groups.

for 10 min at 80% output with NC ultrasonic cleaning KQ-500DB while being stirred by the magnetic bar. Stable BMA miniemulsion droplets containing urethane prepolymer were obtained by this process.

The hybrid miniemulsion was then transferred to a four-necked flask, equipped with a turbine stirrer, a thermometer, and a reflux condenser. The polymerization temperature was achieved at 80°C with gentle mechanical stirring, because the use of high-shearing mixers may destroy the stability of polymer particles during the polymerization. Before and after polymerization, the transformation of the droplet is showed in Scheme 1. Using PU1, PU2, PU3, and PU4 mixed with BMA, we have prepared PU1-PBMA, PU2-PBMA, PU3-PBMA, PU4-PBMA hybrid latices, and have studied the influence of molecule weight of PU prepolymer on emulsion stability, conversion of BMA, compatibility of the system, and water absorption of the paint film.

Polymer characterization

FTIR measurement

The PU formation was traced by Fourier transform infrared (FTIR) spectroscopy in the attenuated total reflection mode. The data of both the background and the samples were obtained at 4 cm^{-1} resolution, 32 scans, in a range from 500 to 4000 cm^{-1} wave number with a Thermo Nicolet-NEXUS. The mini-emulsion was baked to be a paint film before FTIR test.

Conversion of the monomer

Samples were collected at intervals of the reaction and the conversion of PBMA was calculated by gravimetric method.

Particle size and distribution

The particle size and particle size distribution of the hybrid latices were measured by dynamic light scattering (ZetaPALS, Brookhaven Instruments Co.) at 25°C. The latex was diluted with deionized water before measuring to adjust suitable light strength to the measurement conditions.

Dilute stability

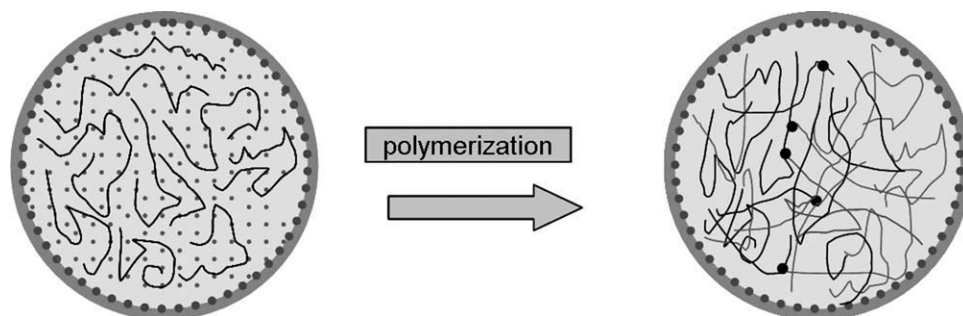
The hybrid latices were diluted by 10 times with deionized water and the diluted emulsion was placed for 72 h to observe whether any delamination happened.

Thermal stability

The hybrid latices of about 10.0 mL was collected in a tube and then placed in a thermostatic water bath of 60°C for 48 h. Thermo stability was determined by the delamination of the emulsion.

Differential scanning calorimeter

Tests of the glass transition temperature (T_g) of the paint film were performed with a METTLER TOL-EDO-822^e differential scanning calorimeter (DSC) at



Scheme 1 The transformation of the droplet before and after polymerization. “•” represents the grafting site formed by PU and PBMA.

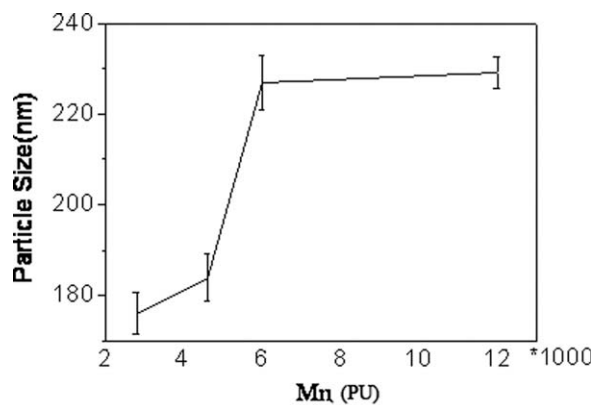


Figure 1 Influence of M_{PU} on the diameter of the particles.

a scan rate of $10^{\circ}\text{C}/\text{min}$ in a flowing nitrogen atmosphere, with a temperature range from -80 to 300°C . And the thermal history of the sample was erased by heating at 150°C for 5 min.

Transmission electron microscope measurements

The morphology of the hybrid latices particles were investigated by a H800 transmission electron microscope (TEM). The latices were diluted with deionized water by 400 folds. The emulsion was dripped on copper grids and dried for 24 h, dyed by RuO_4 for 15 min at last, and then the samples were ready to be tested.

Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) measurements were carried out with TA-Q800 at a fixed frequency (0.1Hz) from -80 to 150°C with a heating rate of $3^{\circ}\text{C}/\text{min}$. The ratio of loss modulus to storage modulus was measured.

Water-resistance test

The water-resistance property was determined as follows. A latex film was prepared by spreading the hybrid latices on a Petri dish, curing at 80°C for 24 h. The weighed latex film (W_0) was then immersed into distilled water at room temperature and kept for 24 h. After wiping off the surface water with a piece of filter paper, the determined weight was W_1 . The absorbed water ratio A of the film was calculated by the formula:

$$A = (W_1 - W_0)/W_0 \times 100\%$$

Stress-strain test

Stress-strain test was performed on Electronic Universal Tensile Stretm Tester (RGT-5, Reger Corp., Shenzhen) under the standard of GB/T528-1998, the samples were prepared by wide cut off knife as

dumbbell slice of 4 mm. The pulling rate was $200\text{ mm}/\text{min}$, scale distance 25 mm , and the temperature was $(23 \pm 2)^{\circ}\text{C}$.

RESULTS AND DISCUSSION

Effect of M_{PU} on particle size and stability of the obtained miniemulsion

When dispersing into emulsion, PU with different molecular weight contributes to different viscosity, which directly leads to the variety of particle size and system stability. Besides, the ratio of soft and hard segments which also contributes to change of particle size, will change with different PU molecule weight accordingly.

The particle size of PU1-PBMA hybrid latex showed in Figure 1 is about 178 nm , consistent with the TEM result in Figure 2. Obviously, the size of PU-PBMA hybrid particle increased rapidly as the PU molecule weight increased, and this can be explained by the fact that the lengthened molecule chains were tangled up and the systems became more sticky, which was not favorable for the dispersion into smaller droplets. When M_{PU} reached 6000 , the increasing trend slowed down. Kim¹⁹ reported the same phenomenon in ionic PU emulsion system. However, Ebrahimi²⁰ noticed a completely opposite phenomenon in aqueous polyether PU emulsion system, which was ascribed to the combined influence of both the structure of PU and the molecule weight on the particle size. In the polyether PU system, with the increase of M_{PU} , the percentage of rigid segments in PU decreased, leading to a loss in rigidity of molecule chains. In our work, the structure of PU varied little with different M_{PU} , so only the molecule weight is considered.

M_{PU} influences not only the particle size but also the stability of obtained emulsion. In Table II, when the M_{PU} was small, the emulsion exhibited perfect dilution,

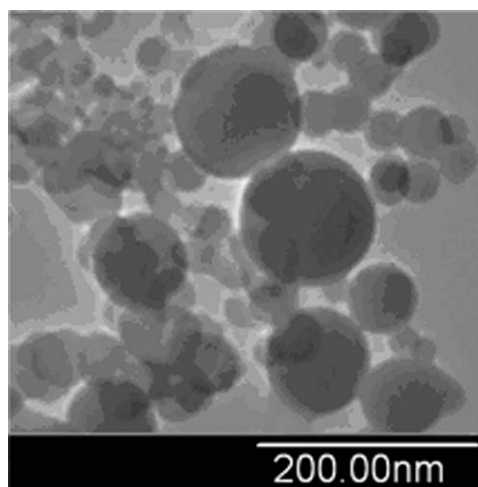


Figure 2 TEM image of PU1-PBMA emulsion particles.

TABLE II
Stability of PU Emulsion with Different Molecule Weight

Sample	Viscosity (Pa·s)	Dilution stability	Storage stability (day)	Thermo stability
PU1-PBMA	0.066	stable	<90	Stable
PU2-PBMA	0.072	stable	<90	Stable
PU3-PBMA	0.09	stable	<7	A little sediment
PU4-PBMA	0.192	stable	<7	A little sedimen

storage and thermal stability. When the M_{PU} exceeded 6000, the emulsion showed a weakened storage and thermal stability. It was accounted that with a smaller M_{PU} , the particle size is small, so the emulsifier and coemulsifier can easily wrap the surface of PU1-PBMA particles and overcome the Ostwald ripening²¹ effectively, which will keep the emulsion stable. As the M_{PU} reached a critical value, the particle size is too large that the gravity will exceed the Brownian motion. The emulsion will be no longer stable and become easier to form gel. Therefore, the molecule weight is a key factor for preparing stable PU-PBMA hybrid latices.

With the increase of M_{PU} , the viscosity of the hybrid latices also increased. For the first two stable systems in Table II, PU-PBMA exists mainly as the micelles, which curled into spherical forms and dispersed orderly into water, so the viscosity is low. However, when the system became unstable, molecule chains seem to be stretched, involved and circled with each other or even bonded with each other, which lead to a tight connection between or among molecules or particles. All these factors will result in an increase in the viscosity of the emulsion and the formation of gel.

Effect of M_{PU} on polymerization kinetics of BMA

For preparing PU-PBMA miniemulsion with high performance, a high conversion ratio of BMA is needed to guarantee the advantages of PBMA. Figure 3 showed the influence of M_{PU} on the conver-

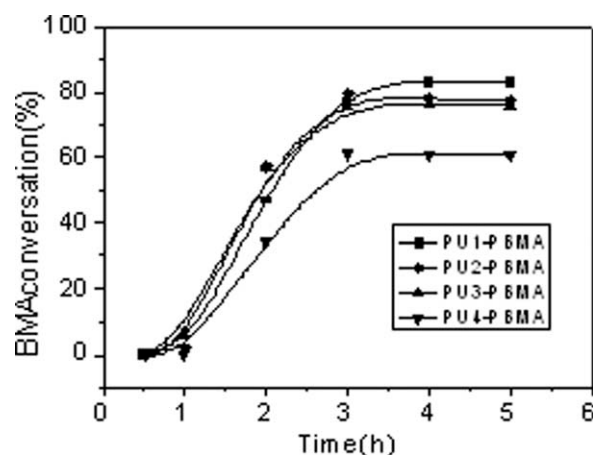


Figure 3 Conversion of BMA with elongation of time.

sion ratio of BMA. As the polymerization continued, the conversion ratio of BMA increased rapidly and reached a maximum at 3 h, and then stayed constant as time elongated. On the other hand, considering the M_{PU} , the conversion ratio of BMA declined successively as the M_{PU} increased, and reached about 60% when M_{PU} exceeded 10,000 (PU4-PBMA). It could be inferred that the grafting reaction occurs between PU and PBMA because of the introduction of the double bonds, and the reaction resulted in a decrease in the polymerization speed of BMA. Besides, with the increase of PU molecule weight, the viscosity of a single emulsion particle increased, and the conversion ratio of BMA decreased due to the "cage-closed effect" caused by PU network. Schork^{3,12} reported that in the synthesis of PUA miniemulsion with modified PU, the collision between methacrylate monomers was limited when PU was added and the convert ratio decreased. Wang²² reported a similar phenomenon when investigating the kinetics factors of the miniemulsion system.

Effect of M_{PU} on the compatibility between PU and PBMA

For the dramatic discrepancy in polarity, PU and PBMA are thermodynamically incompatible and easy to be separated. However, in the PU-PBMA miniemulsion, the particle sizes of hybrid latex were quite small, the component in each monomer droplet was the same, and each droplet nucleated by itself. All these factors forced PU and PBMA to be compatible on molecular level. The compatibility can be characterized by glass transition temperature (T_g).

Both PU and PBMA have their own typical T_g values. For a completely incompatible system, the two T_g s will not change for the reason of phase separation. Although for partially or perfectly compatible

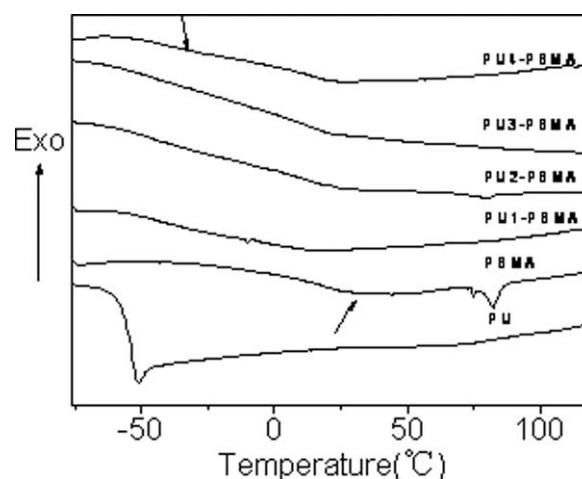


Figure 4 DSC diagram of PU-PBMA miniemulsion paint films.

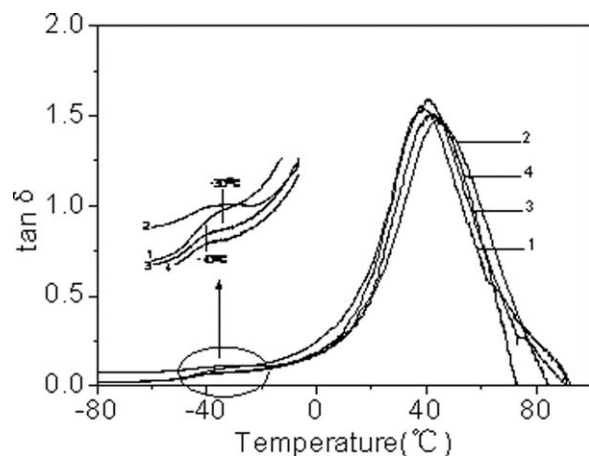


Figure 5 DMA diagram of PU-PBMA miniemulsion paint films. 1. PU1-PBMA, 2. PU2-PBMA, 3. PU3-PBMA, 4. PU4-PBMA.

system, the two T_g s will get close to each other or even merge into a new T_g with a value between the two original ones.

Figure 4 showed the DSC curves of PU-PBMA films. The T_g of the soft segments of pure PU and PBMA were -60°C and 35°C , respectively, and for PU-PBMA, there were two new T_g s between -40°C and 20°C , being obviously presented in the DMA curve in Figure 5, which meant that PU and PBMA were partially miscible. It can be explained that BMA monomers and PU were absolutely miscible before polymerization, so the PBMA was wrapped in the PU chain segments after polymerization, compelling the two components compatible on molecular level. Besides, the grafting sites between PU and PBMA molecules also enhanced the compatibility. When PU was absolutely separated from PBMA, there are two original T_g peaks in PU-PBMA DSC curve,²³ while only one T_g peak formed when cross-linking agents were added in the process of polymerization. In addition, the solubility coefficient of PU soft segments is similar to that of PBMA and there exists good compatibility between them, which can be a good explanation why the T_g of PU soft segments and PBMA get closer to each other in PU-PBMA film.

As the DMA curves (Fig. 5) show that the values of T_g for PU1-PBMA and PU2-PBMA at low temperature were -30°C , and -40°C for PU3-PBMA and PU4-PBMA, which indicates low M_{PU} helps to enhance the compatibility between PU and PBMA.

IR spectrum of PU and PU-PBMA film with different M_{PU} was presented in Figure 6. In the IR spectrum of PU, the C=O peaks for PU at 1718 and 1702 cm^{-1} shifted to low frequency,²⁴ demonstrating a short range disordered urea hydrogen bond. While in the IR spectrum of PU-PBMA, the intensity of C=O peak at 1728 cm^{-1} was strong and without

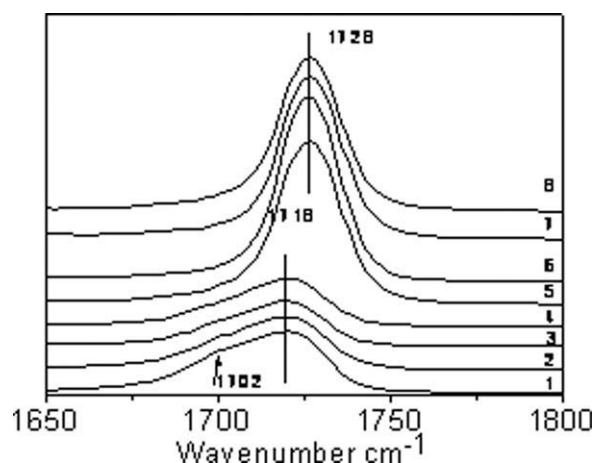


Figure 6 IR spectrum of PU-PBMA miniemulsion paint films. 1. PU1, 2. PU2, 3. PU3, 4. PU4, 5. PU1-PBMA, 6. PU2-PBMA, 7. PU3-PBMA, 8. PU4-PBMA 2.

any signal of hydrogen bond. This can be ascribed to the increasing content of C=O and the destroying of hydrogen bonds in PU when PBMA was introduced. At the same time, the C=O peak of PU (1718 cm^{-1}) shifted to higher wave number and merged with that of PBMA. Therefore, the original microstructure of PU was destroyed after introducing PBMA and the compatibility was enhanced, which is consistent with the results of both DSC and DMA analysis.

Effect of M_{PU} on mechanical properties and water absorption of PU-PBMA coating film

Mechanical properties and water absorptions of PU-PBMA film with different M_{PU} are listed in Table III. Conclusions can be drawn that with increasing M_{PU} , the tensile strength and the rigidity of the film increased and the elongation at break declined, tough deformation became difficult for there were more entangled structures and stronger intermolecular interactions when the polymer chain gets longer. However, when M_{PU} is too low, part of PU molecules act as plasticizer which reduced the mechanical property of the PU-PBMA film, all of which were confirmed by the stress-strain curves of PU-PBMA membranes in Figure 7.

TABLE III
Influence of PU Molecule Weight on the Properties of Paint Films

Sample	Tensile strength (Mpa)	Elongation at break (%)	Water absorption (%)
PU1-PBMA	2.21	495.7	3.3
PU2-PBMA	3.73	409.6	6.8
PU3-PBMA	4.25	390.7	8
PU4-PBMA	6.09	249.6	8.7

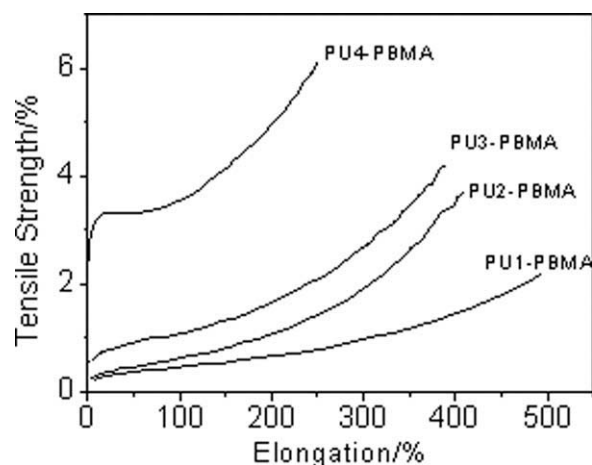


Figure 7 Stress-strain diagram of all PU-PBMA samples

In addition, with the increase of M_{PU} , water absorption of PU-PBMA film increased too. The reasons can be described as that, with the increase of M_{PU} , the conversion ratio of BMA decreased, the segment movement became difficult, the crystallization of PU rigid segment became hard, and the packing of molecules was loose. In fact, the water absorptions of all samples were not high, which means PU-PBMA hybrid system with good compatibility has done a good job in balancing the properties of PU and PBMA.

CONCLUSIONS

PU-PBMA hybrid latices with stable properties were successfully prepared via miniemulsion polymerization plus introducing double bonds into the PU. The procedure overcame the thermodynamical incompatibility of PU and PBMA and produced PU-PBMA paint film with an excellent compatibility. Further investigations about effects of PU molecule weight on the performance of the emulsion were carried out. The results showed that M_{PU} imposed a great influence on the particle size and stability of the emulsion. As the molecule weight increased, the particle grew bigger and the stability became weaker. When M_{PU} exceeded 6000, the emulsion was quite unstable and generated mass gel. More-

over, mechanical properties of the paint film improved with the increase of the molecule weight of PU, and water absorption went upward. When the M_{PU} was below 5000, water absorption was smaller than 6.7%. However, the conversion rate of BMA decreased when M_{PU} increased, when M_{PU} was about 12,000, the conversion rate was under 60%.

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