Progress in Natural Science: Materials International 2012;22(1):71–78

Chinese Materials Research Society

Progress in Natural Science: Materials International

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ORIGINAL RESEARCH

Synthesis of core–shell acrylic–polyurethane hybrid latex as binder of aqueous pigment inks for digital inkjet printing

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Received 15 October 2011; accepted 30 November 2011
Available online 16 February 2012

KEYWORDS

Core–shell structure;
PUA hybrid emulsion;
Latex ink binder;
Rheological properties

Abstract Acrylic–polyurethane (PUA) hybrid aqueous emulsion with core–shell structure was prepared via semibatch emulsion copolymerization of the acrylate monomers (AC) in the presence of a commercial polyurethane dispersion as seeds. The core–shell structure of the emulsion was observed by TEM. The particle size and distribution of the emulsion was found to vary drastically with the core–shell ratio. The thermal response properties of emulsion films were measured by DSC, and the results indicated the good compatibility between PA and PU moieties in PUA hybrids. The chemical structures of emulsion films were studied by FTIR, and the surface properties were tested by contact angle measurement. The results supported the idea that the surface of the cast films was rich in polyurethane component. The water resistance of the cast films became better by increasing the AC fraction. The rheological properties of the latex and its utilization as a binder for aqueous pigment inks of digital inkjet printing were thoroughly investigated, indicating that the prepared hybrid emulsion could be used safely for aqueous pigment inks of digital ink jet printing.

1. Introduction

The application of digital ink-jet printing in the textile field increased recently because this technique offers benefits such as speed, flexibility, creativity, cleanliness, competitiveness and eco-friendliness [1–3]. Inks for digital textile printing are usually classified into two categories, dye and pigment inks. Pigment inks show more environmental advantages and have shorter processes than dye inks because the final products printed can be achieved by simple curing of the printed textile instead of steaming and washing [4]. With improvement in the digital textile printing technology and increasing environmental pressure on dye-based

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Peer review under responsibility of Chinese Materials Research Society.
doi:10.1016/j.pnsc.2011.12.012

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textile printing systems requiring a washing off stage, pigment-based digital textile printing is perhaps the most commonly and extensively used technique for printing textile. The prediction from a recent study by BASF is that pigment textile printing will increase from 11 billion square meters in 2002 to 15 billion meters in 2012 [5].

However, pigment textile printing has a few problems, such as relatively high temperature curing, stiff hand feeling and poor crock fastness of printed textile. Formaldehyde emissions and clogging on the screens during the actual printing process must also be taken into account [6]. These disadvantages are related to the binders used. Therefore, reconsideration of the overall properties of the binders is necessary to improve the quality of the pigment printed goods.

Water-borne polyacrylic (PA) and polyurethane (PU) resins have been applied widely as binders for paints and inks [7–9]. In general, PA resins show excellent properties in terms of hardness, weather ability, chemical resistance, gloss and affinity to pigments, but they show poor performance such as toughness, mar-resistance, elongation, adhesion properties and softness, which are peculiar to PU resins. So, a better binder could be achieved if it provides the complementary advantages of both PA and PU resins. Physical blending of PA and PU emulsion dispersion results in films with properties of lower quality than those predicted by the “rule of mixtures”, because of the limited compatibility between PA and PU [10]. An alternative approach to the physical mixing of PA and PU emulsion dispersion is the emulsion copolymerization of acrylic monomers in the presence of PU emulsion dispersion, which is called “hybrid process”. It was reported that the acrylic monomers swelled into the particles of PU dispersion and increased the ability of mixing of these two kinds of polymers via the hybrid process [11]. In order to obtain water-borne emulsion with superior performances, different hybrid emulsion polymerization techniques, such as seeded emulsion polymerization or interpenetrating network formation, were developed and utilized. Emulsion containing both PA and PU phase in each emulsion particle are expected to exhibit excellent properties, which are hard to attain by emulsion with a homogeneous phase [12–14]. It is of great interest to produce emulsion in which each particle is composed of PA and PU from the viewpoint of practical application as binders for aqueous inks and coatings. There are some patents and references concerning acrylic–polyurethane hybrid emulsion [6–8], but there are few reports on their application performances and rheological properties when they were used as the binder for aqueous pigment inks for digital textile printing.

The rheological properties of latex systems are of both practical importance and theoretical interest. Most practical uses of latexes in processing and in various coatings applications require the control of viscosity. Some latex may exhibit Newtonian behavior with constant viscosity, independent of shear stress or shear rate. However, the viscosity of many liquids and latex depends on shear rate (non-Newtonian). The pseudoplastic or shears thinning emulsion show decrease of viscosity with increasing shear rate. Many kinds of dispersion, including latex systems, may exhibit complex viscoelastic rheological properties [15]. It is known that the rheological properties of the latex used in the digital textile printing ink are essential to avoid deflections in printer head, and play a critical role in drop-on demand (DOD) drop formation characteristics, jet straightness, sustainability and productivity. One of the most important properties of the latex is shear viscosity. The shear viscosity of latex inkjet ink has to be less than 5 $\mathrm{mPa \cdot s}$ for Epson print heads. However, inkjet ink may exhibit various non-Newtonian behaviors with a high volume fraction of suspended or soluble functional materials [16].

The purposes of this study are as follows: (1) preparation of aqueous PUA hybrid nano-emulsion with core–shell structures via semibatch emulsion copolymerization of acrylic monomers in the presence of commercial PU emulsion dispersion as the seeds. (2) Application of the prepared latex as the binder of aqueous pigment inks for digital textile printing. (3) Investigation on the rheological properties of the latex and latex ink.

2. Experimental

2.1. Materials

Butyl acrylate (BA), Methyl methacrylate (MMA) and acrylic acid (AA) were supplied by Shanghai Sinopharm Chemical Reagent Co. Ltd., China. The anionic emulsifier, sodium dodecyl sulfate (SDS), was supplied by Sangjing chemical Co. Ltd., Shanghai. Sodium bicarbonate ($NaHCO_3$) was used as a buffer, and potassium persulfate (KPS) was used as a water-soluble initiator. The chemicals were all of analytically pure grade and no further purification was carried out. Phosphotungstic acid hydrate (PTA) was analytically pure grade and was supplied by Shanghai Sinopharm Chemical Reagent Co. Ltd., China. The commercial available PU emulsion dispersion, N-methyl-2-pyrrolidone (NMP) and TEGO-Wet (KL-245) were supplied by Zhongfang chemical Co. Ltd., China. CAB-O-JET$^{®}$ 480V (PV 19RS) pigment dispersion was purchased from Cabot Corporation, USA.

2.2. Synthesis of PUA hybrid emulsion

PUA hybrid emulsion PA/PU ratio of 20/80 was synthesized by semibatch emulsion polymerization in a 250 ml four-neck glass flask, equipped with a reflux condenser, a mechanical stirrer, a digital thermometer and a nitrogen gas inlet.

Pre-emulsion was prepared by dissolving SDS (2.0 g per 100 g of acrylic and PU content) in water. Then the mixture of 5.0 g MMA, 5.0 g BA and 0.015 g AA (0.15 wt% based on the total MMA and BA weight) was slowly added to the emulsifier solution under stirring. Finally, the emulsion was stirred for additional 0.5 h.

The reactor vessel was first charged with 111.3 g PU emulsion dispersion and 10% of the monomers, heated to 80 °C under stirring. After that, 10% of the initiator solution (0.4 g of KPS per 100 g acrylic monomers) was slowly introduced, which was continued for 0.5 h. The residual monomer pre-emulsion and initiator solution were fed into the flask at a constant flow-rate during 4 h. Then the temperature was increased additional 5 °C and the contents were held at 85 °C for 0.5 h. Finally, the emulsion was cooled to room temperature while stirring. The pH value was maintained in the desired range with addition of $NaHCO_3$. Samples with the different PA/PU ratios in Table 1 were prepared in the same method.

Table 1 Recipes for preparation of PUA hybrid emulsion.

Samples	PUA0	PUA20	PUA40	PUA60	PUA80	PUA100
Total polyacrylic fraction (wt%)	0	20	40	60	80	100
PU dispersion (g)	200	111.3	83.5	74.2	41.7	0
MMA (g)	0	5.0	10.0	20.0	30.0	50.0
BA (g)	0	5.0	10.0	20.0	30.0	50.0
AA (g)	0	0.015	0.03	0.06	0.09	0.15
Solid content of final emulsion (wt%)	36.0	36.4	37.2	36.8	37.4	36.5

2.3. *Preparation of digital textile printing inks*

Inks used in the samples were made according to standard procedures in the inkjet art. Each ingredient fraction was in weight percentage of the final ink. First, the ink vehicle was prepared with the composition of 11 wt% glycol, 12 wt% NMP, 5 wt% glycerol, 0.5 wt% TEGO Wet (KL-245) and 38.5 wt% deionized water. Then the aqueous dispersion of PUA40 hybrid latex binder (15 wt% of the final ink) was added to the ink vehicle with stirring. After stirring until a good dispersion was obtained, the magenta pigment dispersion (CAB-O-JET® 480V, PV 19RS, 18 wt%) was then added to the mixture and stirred for another 3 h, or until a good ink dispersion was obtained. The pH value and surface tension of the inkjet ink as prepared were 7.0 and 28.67 m N/cm, respectively.

2.4. *Characterization*

Microstructure of the latex particles was observed by a Hitachi H-800 transmission electron microscope (Hitachi, Japan) after staining with 1–2 wt% PTA in water solution, which was adjusted exactly to pH 6.4 with 0.1 mol/L NaOH aqueous solution.

The particle size and distribution of the synthesized emulsion was determined by Nano ZS Particle Size and Zeta Potential Analyzer (Malvern Instruments Company, UK). The samples of the emulsion were diluted with deionized water.

Fourier transform infrared (FTIR) spectra were recorded on a Spectrum BXII FT-IR spectrometer (Perkin Elmer, USA). A total of 32 scans for each sample were taken with a resolution of 2 cm^{-1}. Potassium bromide (KBr) powder was used as the reference to produce a background spectrum.

Differential scanning calorimetry (DSC) was performed in order to characterize the thermal response properties of the cast films prepared from the PUA hybrid emulsion. The measurement was performed on a 204F1 Differential Scanning Calorimeter (DSC, NETZSCH, Germany), with nitrogen purging the cell at the heating rate of 20 °C min^{-1} from −80 °C to 200 °C.

Shear viscosity of the latex and latex ink was measured by a R/S-Plus Rheometer (BROOKFIELD, USA) under different temperatures.

Flow properties of the latex and latex ink were carried out on an Advanced Rheology Expanded Systems (ARES-RFS rheometer, TA Instruments Company, USA) at 25 °C. The rheological properties were studied under small and large deformation with different measuring procedures: stress and frequency sweeps. The steady shear tests were carried out in the range of shear rate from 0.1 to 10^3 s^{-1}. The stress sweep was test under 200% strain amplitude and angular frequency of the frequency sweep was from 0.1 to 100 s^{-1}.

Contact angles (CA) of droplets of water on the cast films were measured using OCA20 contact angle goniometer (Datephysics, Germany). The contact angles were calculated according to the equation, $\theta = 2\tan^{-1}(2h/r)$ (where h is equal to the height of a droplet and r is the width of a droplet on the substrate film).

Water absorption of the cast films was assessed according to the standard method. Dry films cast from emulsion (30×30 mm^2; original weight designated as w_1) were immersed in water for 24 h at 25 °C. After the residual water was wiped from the films using filter paper, the weight (w_2) was measured immediately. Water absorption was calculated by the equation, $W\ (\%) = (w_2 - w_1)/w_1 \times 100\%$.

Mechanical properties were examined by measuring tensile strength and elongation at break of the cast films on a WDT-10 Tinius Olsen tensile tester (Toyo Baldwin Company, Japan) at a constant drawing rate of 50 mm/min at room temperature. The samples with the thickness of 60 μm were stored at ambient condition for 7 day, and then were placed in a vacuum until constant weight was obtained.

3. Results and discussion

3.1. *Core–shell structure of PUA hybrid emulsion*

Fig. 1 showed the TEM images of the PUA hybrid emulsion with different polyacrylic/polyurethane ratios of 40/60 (PUA40), 60/40 (PUA60) and 80/20 (PUA80). The three kinds of hybrid emulsion were of core–shell spherical microstructures. In these core–shell particles, the darker regions of the outer layers were PU domains, and the relatively lighter regions in the cores were PA domains [8]. Electronic cloud density around the PU chains was higher than that around PA chains because PU chains had greater polarity in comparison with that of the PA chains, which was in good agreement with the results reported previously [6–8]. More hydrophilic PU chains in the PUA hybrid system were selectively located in the shell region, and thus the hydrophobic PA chains were concentrated in the core region of the emulsion particles in the course of the phase-inversion process.

In addition, the average particle size of the PUA40 emulsion obtained from Fig. 1(a) was 54 ± 12 nm, which was in good agreement with the results obtained from the Nano ZS Particle Size and Zeta Potential Analyzer. By comparison, fusion and coagulation of particles could be recognized in Fig. 1(b) and (c). Therefore, coalescence of the particles occurred when the PA/PU ratio increased to 60/40 and 80/20, and larger particles formed due to the particle coalescence. Considering the emulsion stability and application requirements, the PA/PU ratio must be kept in a certain range.

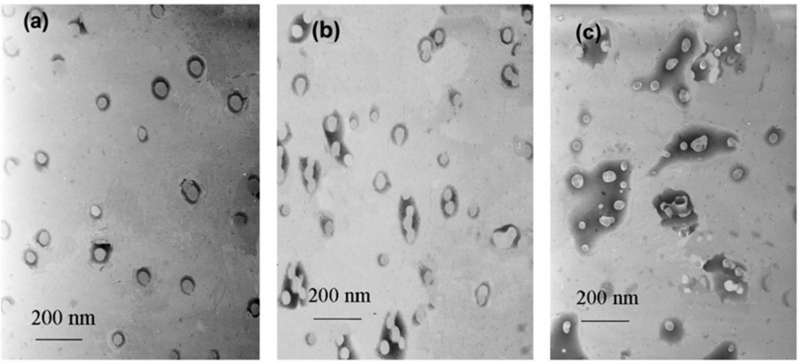

Fig. 1 TEM images of PUA hybrid emulsion with polyacrylic/polyurethane ratios of (a) 40/60 (PUA40), (b) 60/40 (PUA60) and (c) 80/20 (PUA80).

3.2. *Particle size and distribution*

In order to figure out the influence of the ratio of PA/PU on the particle size and distribution of the PUA hybrid emulsion, particle size and distribution was further characterized via light scattering.

The particle sizes and distribution of the PUA hybrid emulsion were depicted in Fig. 2. In Fig. 2(a), the number-average particle size of the PUA0 dispersion was 38 nm, and the particle size distribution (PSD) was relatively narrow. The PSD of the PUA20 sample had similar particle size and distribution as the PUA0 dispersion, although it shifted slightly to higher number-average diameter. For the samples of PUA40 and PUA60, the PSD was relatively broader. However, the PUA80 dispersion showed a wide PSD due to particle coalescence.

The number-average particle size of the PUA hybrid emulsion derived from Fig. 2(a) was shown in Fig. 2(b). The number-average particle size of the PUA emulsion increased with the PA/PU ratio from ~40 to ~170 nm. When the ratio increased from 0 to 20/80, the number average particle size of the hybrid emulsion increased from 38.4 nm to 45.7 nm. However, further introduction of the acrylic moiety resulted in drastic increase of the number-average particle size due to the inclusion of the acrylic monomers into the PU particles to form inverted core–shell morphology with polyacrylic as the core, PU as the shell. The mechanism of particle growth was suggested by Hirose et al. [6] and Chai and Jin [8]. They explained that when the amount of the acrylic moiety was small, the acrylic monomers could easily swell into the PU particles to conduct the copolymerization and form the core of the hybrid particles. However, further introduction of acrylic monomers made it difficult for the PU micelles to contain the acrylic moiety and form the stable hybrid emulsion particles. Consequently, larger particles were formed presumably by the fusion of several particles. When more acrylic moiety was introduced, the fusion of particles further proceeded to form much larger particles, which was verified by the TEM analysis.

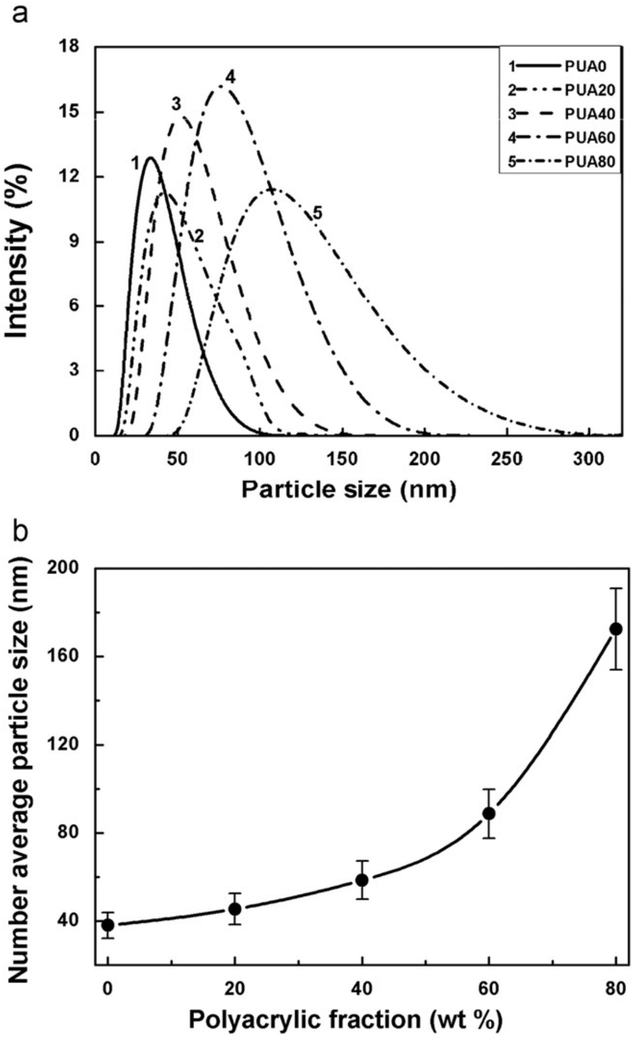

Fig. 2 Particle size and distribution of PUA hybrid emulsion with different PA/PU ratios, (a) particle size distribution and (b) number average particle size derived from (a).

The practical application of the hybrid emulsion is used as the binder for inkjet ink. So several important factors must be taken into account in order to meet the requirements of inkjet printing. The most important factor is the particle size. The particles must be sufficiently small to permit free flow of the ink through the inkjet printing heads, especially the ejecting nozzles. Nevertheless, the particle size also affects dramatically the dispersion stability and flow behavior of the ink, which is critical during the life time of ink. The emulsion with small particle size and homogeneous particle size distribution is desired as the binder to achieve jettable inkjet ink. So PUA40 seemed to be a good choice.

3.3. *FTIR analysis*

The chemical structures of PUA were tested by FTIR. The absorption peaks of typical polyurethane at 3470 cm^{-1} [ν (NH)], 2855–2955 cm^{-1} [ν (CH$_2$) and ν (CH$_3$)], 1720–1780 cm^{-1} [ν (C=O)], 1540 cm^{-1} [δ (N–CO)] and 1110 cm^{-1} [ν (C–O–C)] were presented in Fig. 3(a) and (b). Compared with the PUA0 sample (no PA), the absorption peaks of typical acrylic polymer at 1169 cm^{-1} [ν (C=O)], 852 cm^{-1} [ν (CH$_3$)], 631 cm^{-1} [ν (C–O–C)] could be clearly detected in Fig. 3(b), indicating that acrylic component had been successfully introduced into the polyurethane. In Fig. 3(b), the absorption peak at 1640 cm^{-1} for C=C stretching vibration was not distinguished, indicating that most acrylic monomers had been involved in the copolymerization.

3.4. *Glass transition temperature (T_g)*

The glass transition temperature T_g of the emulsion was determined by DSC (Fig. 4). T_g was used to illustrate the compatibility between PA and PU moieties in the PUA hybrids. It was found that pure acrylic polymer exhibited a glass transition at 0 °C, and pure PU possessed one glass transition at 42.5 °C, respectively. The PUA40 hybrid emulsion with the core–shell microstructure exhibited two glass transitions, one for PA moiety at 12 °C and one for PU moiety at 39 °C. The shifts of T_g from 0 to 12 °C at the lower temperature, and 42.5 to 39 °C at the upper temperature were attributed to the partial compatibility and interdiffusion of the PA and PU moieties.

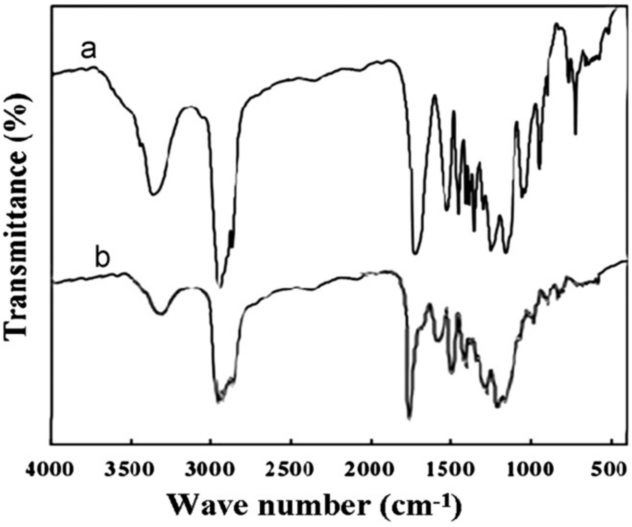

Fig. 3 FTIR spectra of cast films of (a) PUA0 and (b) PUA40.

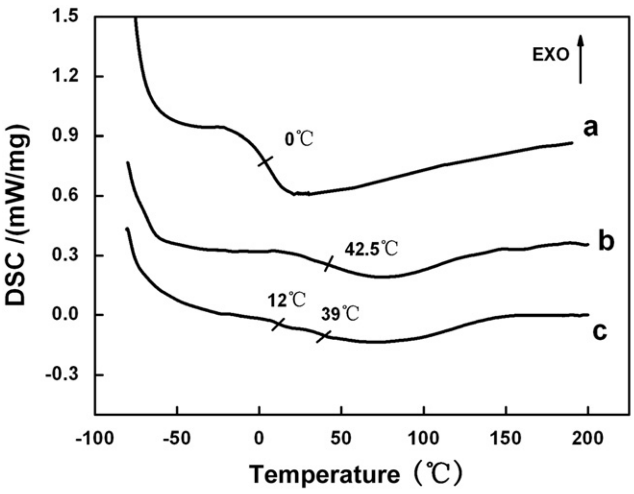

Fig. 4 DSC curves of (a) PUA100, (b) PUA0 and (c) PUA40.

3.5. *Rheological properties*

Low shear rates (less than 1000 s^{-1}) were generally employed to characterize the rheological properties of inkjet inks in both the inkjet industry and academia [16]. However, for the measurement of the shear viscosity of the latex, the maximal shear rate of 5000 s^{-1} was utilized to simulate the flow behaviors in inkjet printers due to the limitation of the rheometer, although very high shear rates (~10^5 s^{-1}) were involved during the ejection process in inkjet printing.

Fig. 5 described the dependence of shear viscosity η of the latex dispersion on shear rate $\dot{\gamma}$ under different temperatures. The results revealed that all the latex samples exhibited provisional shear-thinning behaviors at the initial stage of the shear process, followed by Newtonian behaviors above a certain critical shear rate $\dot{\gamma} \approx 1000\,\mathrm{s}^{-1}$, which indicated that the latex dispersion was a Newtonian liquid and there was no significant interaction among the suspended particles. Moreover, similar rheological behaviors were observed under the temperature higher than 50 °C, which demonstrated that the good thermal stability of the latex. However, it was also noted that the influence of temperature on the shear viscosity of the latex was obvious. The shear viscosity decreased with the temperature, indicating that the temperature was also an important factor of flow properties. The temperature-dependent shear viscosity for the latex was of a practical significance to guide the ink jet printing.

Fig. 6 showed the shear viscosity of the aqueous violet pigmented inkjet ink. It was found that the latex ink also exhibited Newtonian behaviors under high shear rates, and the shear viscosity of the latex ink was low enough to meet the requirements of the ink jet printing.

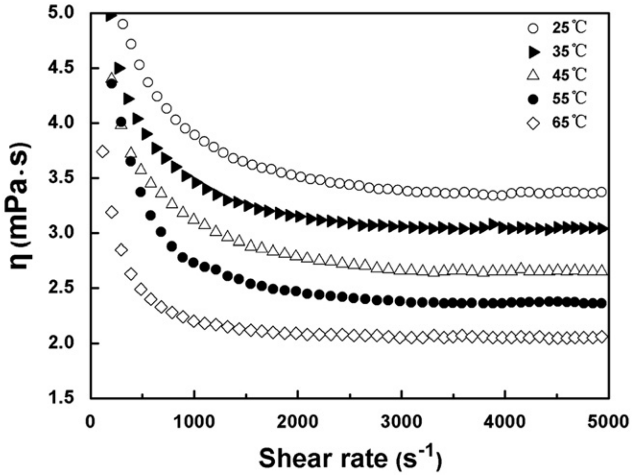

Fig. 5 Shear viscosity for PUA40 hybrid emulsion (15 wt%) under different temperatures.

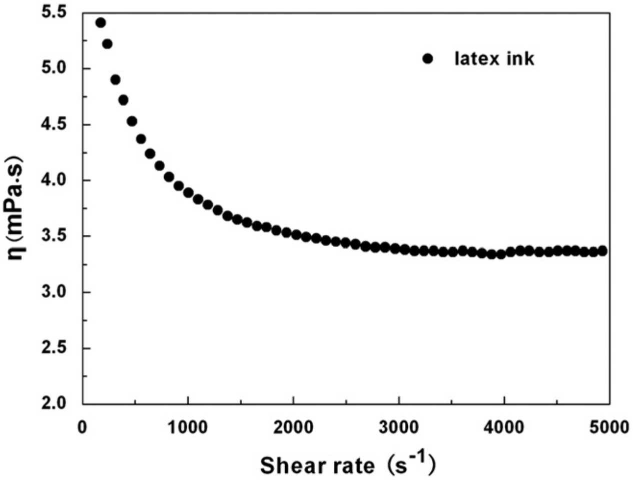

Fig. 6 Shear viscosity η of latex ink with 15 wt% PUA40 latex (25 °C).

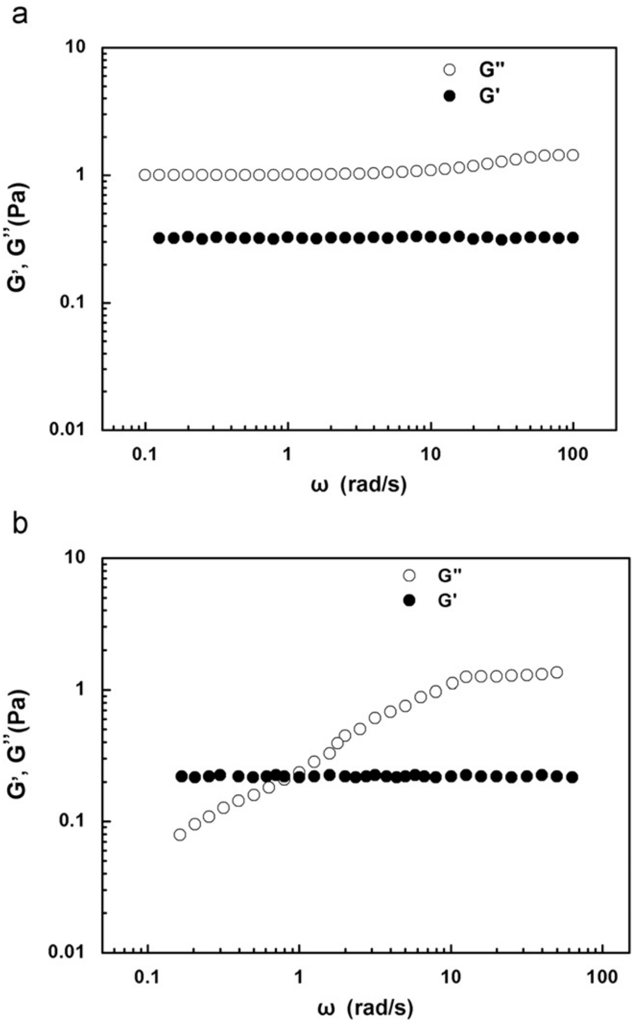

Fig. 7 (a) Dynamic moduli (G' and G'') of PUA40 latex (10 wt%) and (b) its latex ink.

Fig. 7(a) and (b) depicted the storage modulus (G') and the loss modulus (G'') versus the angular frequency (ω) under a constant amplitude strain in the linear viscoelastic range of the samples. In Fig. 7(a), both of dynamic moduli of the latex were independent of the angular frequency over the entire angular frequency range investigated. Moreover, the loss modulus G'' was higher than the storage modulus G', which meant that the latex was dominated by the viscous behavior.

From Fig. 7(b) it could be understood that the loss moduli G'' of the latex ink depended on the angular frequency, while the storage moduli G' was frequency independent. At critical frequency $\omega \approx 0.2$ rad s^{-1}, there was an obvious intersection between the G' and G'', which meant that networks were formed inevitably due to some interaction among the latex and pigment particles in the latex ink. However, the loss modulus G'' became higher than the storage modulus G' with the increase of frequency, indicating that the latex ink was also dominated by viscous behaviors.

3.6. *Water response of cast films from latex emulsion*

3.6.1. *Contact angle*

To confirm the surface structure of the dry film from the PUA40 hybrid emulsion, the determination of the surface properties by contact angle measurements was carried out. In Fig. 8, the contact angle of the cast film from the PUA40 hybrid emulsion was provided in comparison with those of dry films from both pure PU and PA.

Based on the contact angles of the water droplets in Fig. 8, hydrophilicity was in the order of PU (shell) > PUA40 > PA (core). The surface of the PUA hybrid emulsion film was similarly hydrophilic as the shell part. Therefore, the hydrophilic character, which was common in the PUA hybrid emulsion and the shell part was related to the contribution of the PU moiety, which also indicated that the surface of the hybrid type emulsion was rich in the polyurethane component.

3.6.2. *Water absorption of cast films from PUA hybrid emulsion*

Aqueous ink jet inks generally have pigment dispersed in water. Ink jet images printed with these inks have limited image fastness when exposed to humid conditions or water and usually results in significant loss of information, which can render the image useless. In order to obtain water-resistance for images, the images usually need to be sprayed with a lacquer material or laminated with another material. Water absorption is determined by the binder used for digital textile printing ink.

Water absorption of the emulsion prepared from physical blends of PUA0 to PUA100 with the same ratios of the hybrid emulsion was also used to illustrate water response of the images. Fig. 9 showed that the water absorption of the cast films varied with the composition of the hybrid emulsion and physical blends. By comparison, it was found that the hybrid emulsion films were of lower water absorption than the corresponding blends, indicating that these hybrid polymers exhibited good compatibility between the PA and PU moieties. However, water absorption decreased with the polyacrylic fraction. The results were consistent with those obtained by contact angle measurement in Fig. 8.

3.7. *Mechanical properties*

Mechanical properties of the cast films from the emulsion are of great significance, which must be taken into consideration

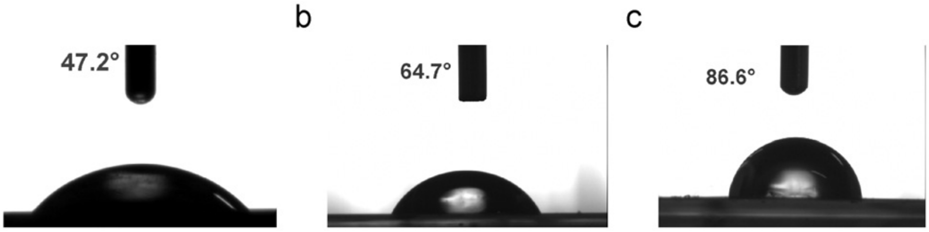

Fig. 8 Contact angles of cast films form (a) PUA0, (b) PUA40 and (c) PUA100.

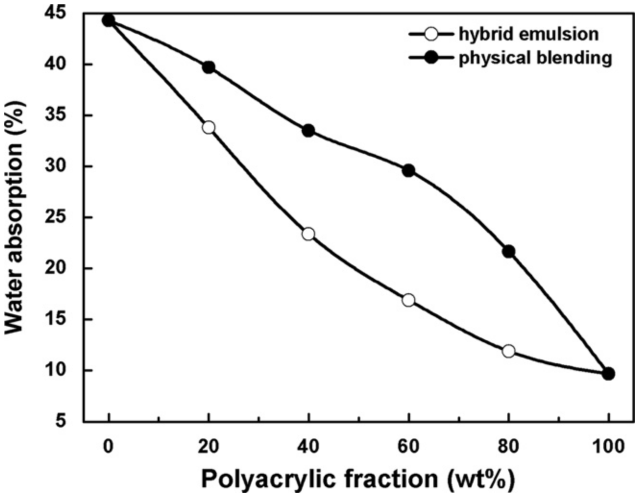

Fig. 9 Dependence of water absorption of cast films on emulsion composition (●—physical blending latex, ○—PUA hybrid latex).

when the emulsion is used as binder for the pigment ink. The reason is that the color fastness and handling of the printing goods are strongly influenced by the mechanical properties of the binder film, especially the elongation at break and the tensile strength.

The mechanical properties were shown in Fig. 10. The elongation at break of the cast films decreased with the polyacrylic fraction, as shown in Fig. 10(a). But Fig. 10(b) indicated that the tensile strength increases with the polyacrylic fraction. The reason might be that PA was harder than PU, which improved the rigidity and strength and reduced the toughness of the hybrid emulsion films.

Comparing the results of mechanical properties between the hybrids and physical blends, a remarkable advantage for the hybrid emulsion could be observed. The improved mechanical properties of the hybrid emulsion were derived from the particle–particle or interfacial contacts, and molecular interdiffusion of the polymer chains between the latex particles during the coalescence phase in the film formation process.

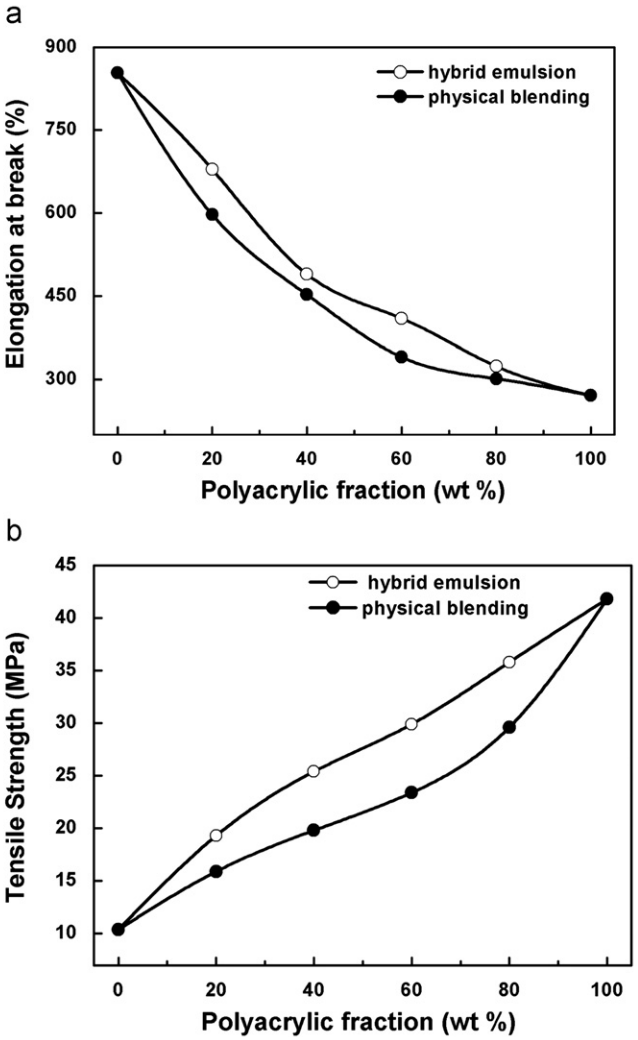

Fig. 10 Mechanical properties as a function of composition of hybrid emulsion and physical blends: (a) elongation at break and (b) tensile strength.

4. Conclusions

The PUA hybrid emulsion containing the polyacrylic and polyurethane moieties were prepared by semibatch emulsion polymerization in the presence of polyurethane dispersion. The particle size analysis indicated that the sizes of emulsion particles varied with the PA/PU ratios. Considering the emulsion stability and the application requirements, the PA/PU ratio must be limited within a certain range.

The shifts of T_g together with the enhanced water absorption and mechanical properties of hybrid emulsion indicated the good compatibility between the PA and PU moieties in the PUA hybrids. The surface layer of the cast film from the hybrid emulsion was rich in the PU component, but the water response of the hybrid emulsion also exhibited the pronounced characteristics of the polyacrylate emulsion.

The latex and latex inks exhibited viscosity plateau of Newtonian fluid behaviors, and viscous behaviors dominated in the latex and latex inks. However, there was some interaction among the latex and pigment particles. Furthermore, the prepared binder latex could be used safely for aqueous pigment inks of digital ink jet printing.

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