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New Hybrid Latexes from a Soybean Oil-Based Waterborne Polyurethane and Acrylics via Emulsion Polymerization

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A series of new waterborne polyurethane (PU)/acrylic hybrid latexes have been successfully synthesized by the emulsion polymerization of acrylic monomers (butyl acrylate and methyl methacrylate) in the presence of a soybean oil-based waterborne PU dispersion using potassium persulfate as an initiator. The waterborne PU dispersion has been synthesized by a polyaddition reaction of toluene 2,4-diisocyanate and a soybean oil-based polyol (SOL). The resulting hybrid latexes, containing 15−60 wt % SOL as a renewable resource, are very stable and exhibit uniform particle sizes of 125 ± 20 nm as determined by transmittance electronic microscopy. The structure, thermal, and mechanical properties of the resulting hybrid latex films have been investigated by Fourier transform infrared spectroscopy, solid state ^{13}C NMR spectroscopy, dynamic mechanical analysis, extraction, and mechanical testing. Grafting copolymerization of the acrylic monomers onto the PU network occurs during the emulsion polymerization, leading to a significant increase in the thermal and mechanical properties of the resulting hybrid latexes. This work provides a new way of utilizing renewable resources to prepare environmentally friendly hybrid latexes with high performance for coating applications.

Introduction

Polyurethanes (PUs) ranging from high performance elastomers to tough thermoplastics are of great interest for applications in coatings, adhesives, medical devices, binders, sealants, and the textile industry.[1,2] Conventional PU products, such as coatings and adhesives, contain a significant amount of organic solvents and sometimes even free isocyanate monomers.[3] To meet the increasing concern for health, safety, and the environment, the solvent-based PUs have been gradually replaced by waterborne PUs. Waterborne PUs present many advantages relative to conventional solvent-borne PUs, including low viscosity at high molecular weight and good applicability,[4] and are now one of the most rapidly developing and active branches of PU chemistry and technology.[5]

Emulsion polymerization, a heterogeneous free radical polymerization process involving emulsification of one or more monomers in a continuous aqueous phase and stabilization of the droplets by a surfactant, is a unique chemical process widely used to produce waterborne resins with various colloidal and physicochemical properties.[6] The most advanced materials produced by emulsion polymerization are acrylic polymer latexes containing a combination of monomers, such as butyl acrylate, methyl methacrylate, and acrylic acid, etc.[7] Acrylic polymer latex films possess excellent weatherability, hardness, and water and alkali resistance due to the main polymer chain's carbon−carbon bonds, making them very useful for coatings, paper and textile finishes, cement additives, and other applications.[8] However, the elasticity and abrasion resistance of acrylic resins are inferior to those of urethane resins.[9] To improve the performance of acrylic polymers with respect to toughness, flexibility, abrasion resistance, and film-forming properties, considerable effort has been devoted to combining PUs and acrylics into hybrid latexes by blending,[10] seeded emulsion polymerization,[11,12] interpenetrating polymer networks (IPN),[13] and crosslinking[14] and graft copolymerization.[15,16]

Nowadays, the worldwide demands for replacing petroleum-derived raw materials with renewable, plant-based materials in the production of valuable polymeric materials are quite significant from both a social and an environmental viewpoint.[17] Vegetable oils, possessing a triglyceride structure with unsaturated fatty acid side chains, are considered to be an important renewable material for the production of bio-based polymers.[18−26] Polyols derived from vegetable oils have found utility in bio-based PU thermosets with excellent chemical and physical properties, including enhanced hydrolytic and thermal stability.[27−29] However, vegetable oil-based waterborne PU dispersions have not attracted much attention so far. One of us recently reported waterborne PU dispersions from the polyaddition reaction of isophorone diisocyanate and mixtures of dimethylol propanoic acid and a castor oil or rapeseed oil-based polyol.[30,31] The resulting dispersions are very stable and the resulting films exhibit excellent mechanical properties that can be varied by simply adjusting the composition of the reactants.

Soybean oil represents one of the cheapest and most abundant annually renewable natural resources available in large quantities. However, there have been no reports in the open literature of the preparation and properties of soybean oil-based waterborne PUs or hybrid latex materials with acrylic resins. The objective of this work is to explore the feasibility of developing a soybean oil-based waterborne PU dispersion and PU/acrylic hybrid latex materials with high performance. In this work, we report the synthesis of a soybean oil-based waterborne PU dispersion, and its use in the preparation of waterborne PU/acrylic hybrid latexes using emulsion polymerization. The structure, morphology, and properties of these novel hybrid latexes and films have been investigated by Fourier transform infrared spectroscopy, transmission electron microscopy, solid state ^{13}C NMR spectrometer, dynamic mechanical analysis, extraction, and mechanical testing.

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Experimental Section

Materials. Wesson soybean oil was purchased at the local supermarket and used directly without further purification. Toluene 2,4-diisocyanate (TDI), dimethylol propionic acid (DMPA), methyl methacrylate, and butyl acrylate were purchased from Aldrich Chemical Co. Sodium hydroxide, hydrochloride acid (37%), hydrogen peroxide (30%), formic acid (88%), sodium dodecyl sulfate (SDS), potassium persulfate (KPS), triethylamine (TEA), magnesium sulfate, methyl ethyl ketone (MEK), acetone, and ethyl acetate were purchased from Fisher Scientific Company. All materials were used as received without further purification.

Preparation of an Epoxidized Soybean Oil and a Soybean Oil-Based Polyol. An epoxidized soybean oil was prepared by reaction of the unsaturation sites of the soybean oil with a mixture of formic acid and hydrogen peroxide according to a literature procedure.[32] The soybean oil (100 g) was added to a 500 mL flask, and then hydrogen peroxide (64 g) was added, followed by formic acid (37 g) under vigorous stirring. The reaction was carried out at room temperature for 2.5 h. Then, 150 mL of ethyl acetate and 100 mL of distilled water were added, resulting in two layers. The organic layer was washed with aqueous sodium biocarbonate solution, until a slightly alkaline pH was obtained, and the organic layer was then dried over $MgSO_4$ and filtered. Finally, a clear viscous oil was obtained after removal of the organic solvent under vacuum. The soybean oil epoxide possesses an average of 2.5 epoxide groups per triglyceride as determined by ^{1}H NMR spectroscopy on a Varian Unity spectrometer (Varian Associates, Palo Alto, CA) at 400 MHz:[32] ^{1}H NMR ($CDCl_3$): δ 0.8−1.1 (CH_3 of fatty acids), 1.2−1.8 (CH_2 of fatty acids), 1.9−2.4 ($-CH_2C{=}O-$), 2.7 ($-C{=}C-CH_2-C{=}C-$), 2.8−3.2 ($-CH$ of the oxirane rings), 4.1−4.3 ($-CH_2-O-C{=}O$), 5.2−5.6 ($-CH{=}CH-$).

The soybean oil-based polyol (SOL) was prepared using the method reported by Guo et al.[26] Briefly, hydrochloric acid (40 g, 37%, 0.4 mol) and acetone (150 mL) were mixed in a flask equipped with a mechanical stirrer and dropping funnel. The resulting mixture was stirred vigorously, while the epoxidized soybean oil (100 g) was added dropwise. The reaction mixture was stirred for an additional 2 h at 40 °C. After purification using the same method used for the epoxidized soybean oil mentioned above, a clear, yellow, viscous polyol was obtained. The OH value of the resulting polyol is 130.9 mg KOH/g as determined by titration according to a literature procedure.[27] The molecular weight of the SOL was determined to be about 1×10^3 g/mol by a Waters Breeze GPC system (Milford, MA) using THF as a mobile phase.

Preparation of a Soybean Oil-Based PU Dispersion. The SOL (30 g, 0.0699 mol of OH groups), 11.6 g of TDI (0.0667 mol), and 4.2 g of DMPA (0.0313 mol) were added to a four-necked flask equipped with a mechanical stirrer, nitrogen inlet, condenser, and thermometer, and the reaction was carried out at 75 °C for 3 h under a dry nitrogen atmosphere. The reaction was then cooled to about 40 °C and 30 g of MEK was added to reduce the viscosity of the polymer, while the solution was stirred vigorously. This PU was then neutralized by the addition of TEA (3.4 g), followed by dispersion at high speed with distilled water (250 g) to produce a waterborne PU dispersion. The soybean oil-based PU dispersion with a solid content of about 20 wt % was finally obtained after removal of the MEK under vacuum.

Preparation of Waterborne PU/Acrylic Hybrid Latexes. SDS (3 g) and KPS (1 g) were dissolved in 414 g of distilled water. Mixtures totaling 100 g of a mixture of methyl methacrylate (MMA) and butyl acrylate (BA) in the weight ratio 60:40 were added to the above aqueous solution with vigorous stirring to obtain the pre-emulsions. The desired weight of the PU dispersion and the acrylate pre-emulsion was placed in a flask and stirred for 30 min at room temperature under an N_2 atmosphere and then brought to the polymerization temperature of 80 °C for 4 h to obtain the hybrid emulsion. During the polymerization, approximately 5 g portions of the emulsion were taken by a syringe at intervals and injected into a petri dish containing 0.5% hydroquinone solution in an ice bath. Monomer conversion was determined gravimetrically from these samples. By changing the weight ratio of between PU and acrylics from 100:0 to 90:10, 75:25, 65:35, 50:50, 25:75, and 0:100, a series of PU/acrylic hybrid latexes have been successfully prepared. Films were prepared by drying the emulsions at room temperature in a glass mold, except for the pure acrylic film, which was obtained by drying at a slightly higher temperature of 45 °C. The nomenclature used for the urethane/acrylic hybrid latex film is the following. PU and PA represent films from the polyurethane dispersion and polyacrylate latex, respectively. The hybrid latex films are identified as PUA-10, PUA-25, PUA-35, PUA-50, and PUA-75, where the number represents the weight percentage of acrylics in the latex. For the pure acrylate emulsion polymerization, the KPS content is 0.5 wt % based on acrylate monomers.

Characterizations. The FT-IR spectra of the films were recorded on a Nicolet 460 FT-IR spectrometer (Madison) using KBr pellets.

The ^{1}H NMR spectra were obtained on a Varian Unity spectrometer (Varian Associates, Palo Alto, CA) at 400 MHz using deuterated chloroform as the solvent. The solid state ^{13}C NMR spectra of the PU and hybrid latexes were recorded on a Bruker AVANCE-600 NMR (Karlsruhe, Germany).

Solvent extraction was performed in a Soxhlet extractor with approximately 1 g of dry latex film. The samples were first extracted with toluene for 24 h to remove the linear polyacrylates and then with *N*,*N*-dimethylformamide (DMF) for 24 h. The residual weight of the vacuum-dried samples was determined and used to calculate the incorporation of polyacrylates into the PU.

The morphology of the latex particles was observed on a transmission electron microscope (JEOL 1200EX). The emulsions prepared were diluted with deionized water to about 0.4 wt %. One drop of the diluted emulsion was placed on the coated side of a 200-mesh nickel grid in a petri dish. After drying, the samples were characterized.

The dynamic mechanical behavior of the specimens was determined using a dynamic mechanical analyzer (TA instrument DMA Q800) with tensile mode at 1 Hz and a heating rate of 5 °C/min in the temperature range from −60 to +100 °C. Specimens with a typical size of about 10 mm × 5 mm (length × width) were used.

A Perkin-Elmer Pyris-7 thermogravimeter was used to measure the weight loss of the latex films under an air atmosphere. The samples were heated from 50 to 650 °C at a heating rate of 20 °C/min. Generally, 10−15 mg samples were used for the thermogravimetric analysis.

The mechanical properties of the latex films were determined using an Instron universal testing machine (model-4502) with a crosshead speed of 100 mm/min. Rectangle specimens of 80 mm × 10 mm (length × width) were used. An average value of at least five replicates of each material was taken.

Results and Discussion

Monomer Conversion. The conversion-time profiles for the emulsion polymerization at 80 °C are shown in Figure 1. The emulsion polymerization of the pure acrylics is complete within about 30 min, and essentially all of the monomers are polymerized. However, when compared with the pure acrylics emulsion, the hybrid emulsions exhibit a lower rate of polymerization, which decreases with increasing PU content. Similar results have also been reported for other PU or alkyd resins used in hybrid latex systems.[33−35] The reason may be that some impurities in the resin inhibit polymerization or the resin itself reduces the polymerization rate by diluting the monomer concentration and by resin chain transfer that produces less active radicals.[33] Although a slightly lower rate of polymerization is observed for the hybrid emulsion, greater than 97% of the monomers have been polymerized after 2 h.

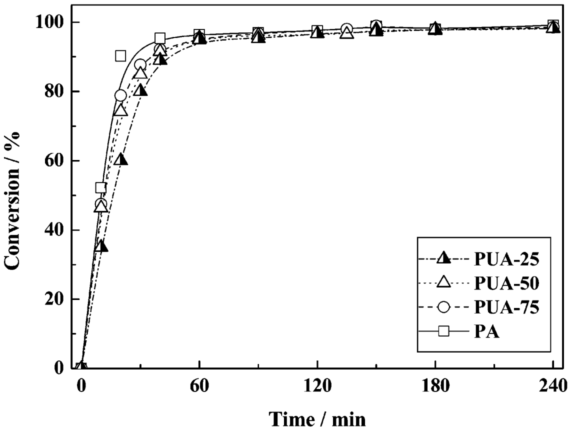


Figure 1. Total monomer conversion of the emulsion polymerization as a function of time for the latexes.

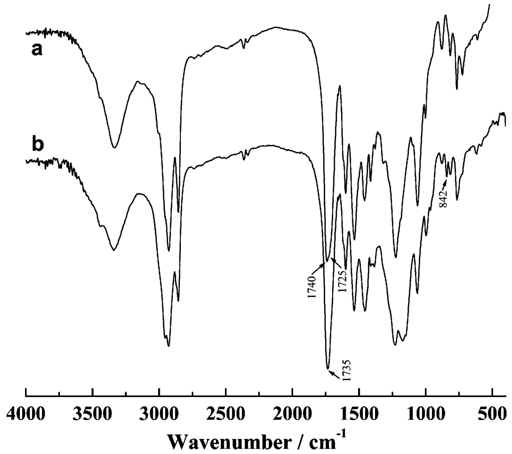


Figure 2. FT-IR spectra for PU (a) and PUA-50 (b).

Structure and Morphology of the Hybrid Latexes. The hybrid latexes, containing 15−60 wt % of the SOL as a renewable resource, are very stable at room temperature and show no precipitation even after 6 months. The hybrid latex films prepared by casting the hybrid emulsion are very tough and clear. The structure of the films derived from the PU and hybrid latex PUA-50 has been confirmed by FTIR as shown in Figure 2. The interactions between chemical groups on either the same or different molecules can cause a shift of the IR peak positions of the participating groups, which is commonly observed in macromolecular systems due to the existence of hydrogen bonds.[36] The spectrum of the PU exhibits absorption peaks of a typical PU at 3338 cm^{-1} (NH, hydrogen-bonded), 3445 cm^{-1} (NH, non-hydrogen-bonded), 1740 cm^{-1} (C═O, non-hydrogen-bonded), 1725 cm^{-1} (C═O, hydrogen-bonded), and 1536 cm^{-1} (CONH). The spectrum of the PUA-50 exhibits a typical absorption peak for the $-OC_4H_9$ group at 841 cm^{-1}, indicating the existence of the acrylics in the hybrid latex. However, the absorption of the free C═O groups is found to shift from 1740 to 1735 cm^{-1}, and the hydrogen-bonded C═O groups at 1725 cm^{-1} disappear in the hybrid latex. This implies that the intra- and intermolecular hydrogen bonds of the PU have been destroyed due to grafting of the acrylics and entanglement of the macromolecular chains between the PU and the PA, leading to good miscibility of the resulting hybrid latexes as shown later.

The functionality of the SOL used in this work is 2.3, so the resulting PU film is a thermosetting polymer, which does not totally dissolve in organic solvents, such as THF, DMF, DMAc, toluene, methylene chloride, etc. Figure 3 shows the extraction results for the PU and hybrid latexes as a function of PA content. A total of 49 wt % insoluble materials are observed after extraction of the PU film, indicating the network nature of this material. If no crosslinking or grafting were to occur between the PU and the PA, the hybrid latex should behave like a physical blend of PU and PA, and thus the insoluble percentage of the latex should decrease linearly with an increase in the PA content as shown in Figure 3. However, a significant increase in the percentage of insoluble materials, when compared with that from physical blends, is observed for the hybrid latexes. This means that grafting copolymerization or crosslinking reactions have occurred in the hybrid latex systems. Similar grafting or crosslinking reactions has been observed in petroleum-based PU/acrylic hybrid latex systems.[7,35] Soybean oil consists of triglyceride molecules with, on average, approximately 4.5 carbon−carbon double bonds per molecule in the fatty-acid side chains. The number of epoxide groups in the epoxidized soybean oil used for preparation of the SOL total about 2.5. So there are still approximately two carbon−carbon double bonds left in the fatty acid chains. During emulsion polymerization, grafting can occur by chain transfer from the propagating free radical to the PU resin[35,37] as shown in Scheme 1a. The free radical resulting from the fatty acid chain is much less reactive when compared with the acrylic radical, leading to a reduction in the hybrid emulsion polymerization rate, which has been confirmed by monomer conversion-time plots of the PU/acrylic hybrid latexes as shown in Figure 1. Another possible mechanism for grafting may involve copolymerization between the polymerizing radical and the double bonds in the soybean oil-based PU (Scheme 1b). Besides grafting polymerization, crosslinking can also take place between PU networks, which also makes the latex more insoluble.

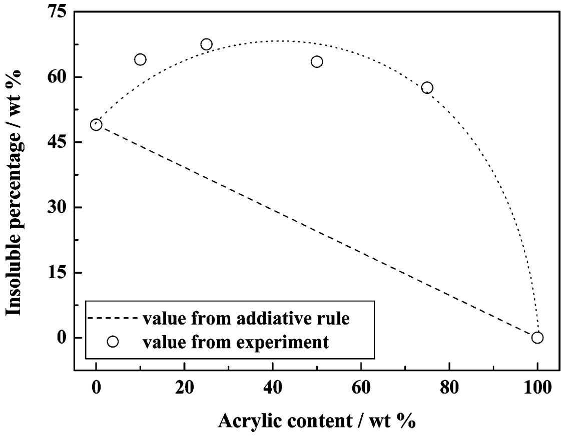
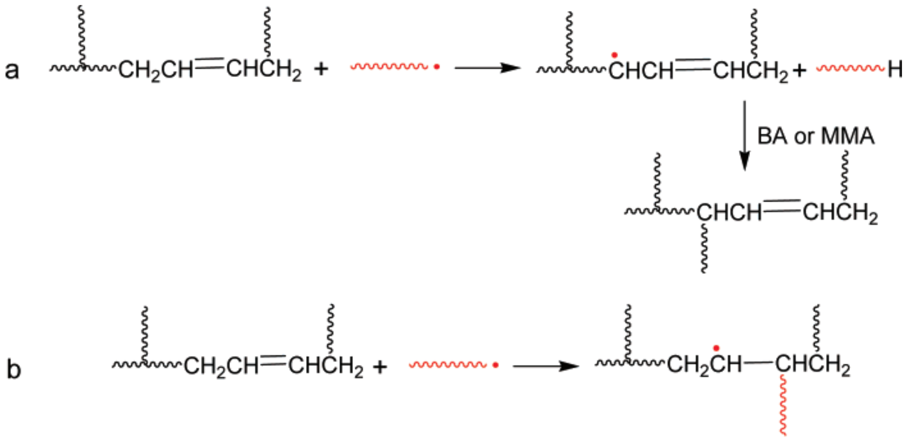


Figure 3. Insoluble percentage of hybrid latexes as a function of acrylic content.

In order to confirm the occurrence of graft copolymerization in the hybrid latex systems, solid-state ^{13}C NMR spectra for the PU and hybrid latex films were obtained (Figure 4). The PU spectrum exhibits characteristic peaks at 152 ppm and 126−133 ppm. The former peak is attributed to the carbon present in the urethane moiety, and the latter peak is mainly attributed to the carbon−carbon double bonds in the SOL.[35] The carbon in the urethane functionality can be used as an internal standard because its concentration is constant during hybrid polymerization. Thus, the ratio between the carbon in the urethane groups and the carbon of the carbon−carbon double bonds in the fatty acid can be used to determine the extent to which the carbon−carbon double bonds in the PU soft segment have polymerized. However, the sixth carbon present in the benzene ring of the 2,4-TDI has a chemical shift of 133 ppm, which also appears

Scheme 1. Proposed Reaction Mechanisms Occurring in the Hybrid Latexes



in the same region as the carbon−carbon double bonds.[38] Figure 4b−d shows the solid state ^{13}C NMR spectra of the PU and hybrid latexes in the region 120−160 ppm after subtraction of the contribution from the sixth carbon of the benzene ring. For pure PU, the ratio between the urethane carbons and the carbons of the carbon−carbon double bonds in the fatty acid is 0.89, which is consistent with the theoretical value of 0.899. However, with an increase in acrylics from 50 to 75 wt %, the ratios of these two carbons are 0.79 and 0.48, respectively, implying that some of the carbon−carbon double bonds in the fatty acid have been reacted and copolymerized with the acrylic monomers, which is in good agreement with the extraction results.

The TEM morphology of the PU dispersion and hybrid latexes is shown in Figure 5. The TEM confirms that the particle size of the PU and hybrid latexes is very uniform with an average diameter of 125 ± 20 nm. The particle diameter of the hybrid latexes hardly increases with an increase in the acrylics content. This indicates that this process is much different from the conventional seeded emulsion polymerization process, where the ratio of the urethane and acrylics substantially changes the particle size and size distribution of the resulting PU/acrylic hybrid latexes.[11] This maybe attributed to the fact that, when using the seeded emulsion polymerization process, the particle size of the hybrid emulsions is nearly the same as that of the PU dispersion, when a small amount of acrylic monomer is incorporated. However, further increasing the acrylic monomer content makes it difficult for the PU to envelop the acrylic polymer and form stable hybrid emulsion particles, resulting in larger hybrid emulsion particles.[9] Compared with seeded hybrid emulsion polymerization processes,[11] the emulsion process employed in this work, which mixes the PU dispersion with the acrylic monomer pre-emulsion, can sustain more dramatic changes in the composition between the PU and the acrylics without severely influencing the particle size of the final hybrid emulsion.

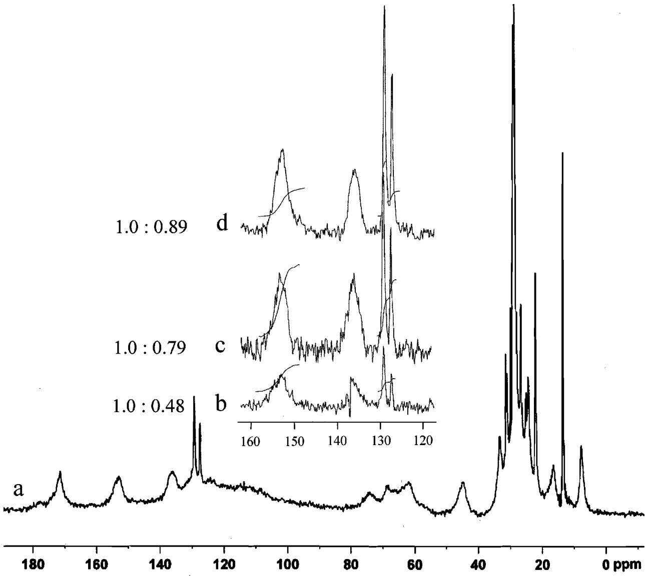


Figure 4. Solid state ^{13}C NMR spectra for PU (a and d), PUA-50 (c), and PUA-75 (b).

Thermal Properties of the Hybrid Latexes. The storage modulus (E') and loss factor (tan δ) of the latex films as a function of temperature are shown in Figure 6. The PU film exists in the glassy state at a very low temperature, and the modulus deceases slightly with increasing temperature. Then, a sharp decrease in the E' value is observed in the temperature range from 10 to 60 °C. This corresponds to the primary relaxation process (α) of the PU, where the tan δ goes through a maximum (T_α). Similar to the PU, all latex films exhibit a dramatic drop in the E' value in the temperature range from 20 to 80 °C. When compared with the PU, the E' values of the resulting latex films are significantly increased due to incorporation of the acrylics by hybrid emulsion polymerization. For instance, the E' values of the hybrid latex films at room temperature containing 10, 25, 50, and 75 wt % acrylics are approximately 2.0, 1.6, 2.9, and 5.7 times higher, respectively, than the PU itself, due to grafting and interpenetration between the acrylics and the PU networks.[16] The peak position (T_α) of tan δ relaxation for the PU and PA, defined as T_g in this work, are located at about 45 and 75 °C, respectively. These values are higher than the corresponding T_g values of 22 and 38 °C as determined by DSC (not shown). Such a difference is very common when comparing two methods. DSC measures the change in heat capacity going from the frozen to the unfrozen chain, whereas DMA measures the change in the mechanical response of these chains.[39] All hybrid latex films exhibit only one narrow loss factor peak in the temperature range 51−68 °C. This is intermediate between the loss factor peaks of the component polymers, indicating that phase separation is not occurring. This is supported by the perfect clarity of the hybrid latex films. It should be pointed out that, when compared with the hybrid latex films, the PU/PA blend latex films are translucent and brittle when the PA content is higher than 30 wt %, due to their poor miscibility. Considering the polymerization mechanism, the structure of the resulting hybrid latex can be taken as a mixture of graft-interpenetrating polymer networks (graft-IPN) and semi-interpenetrating polymer net-

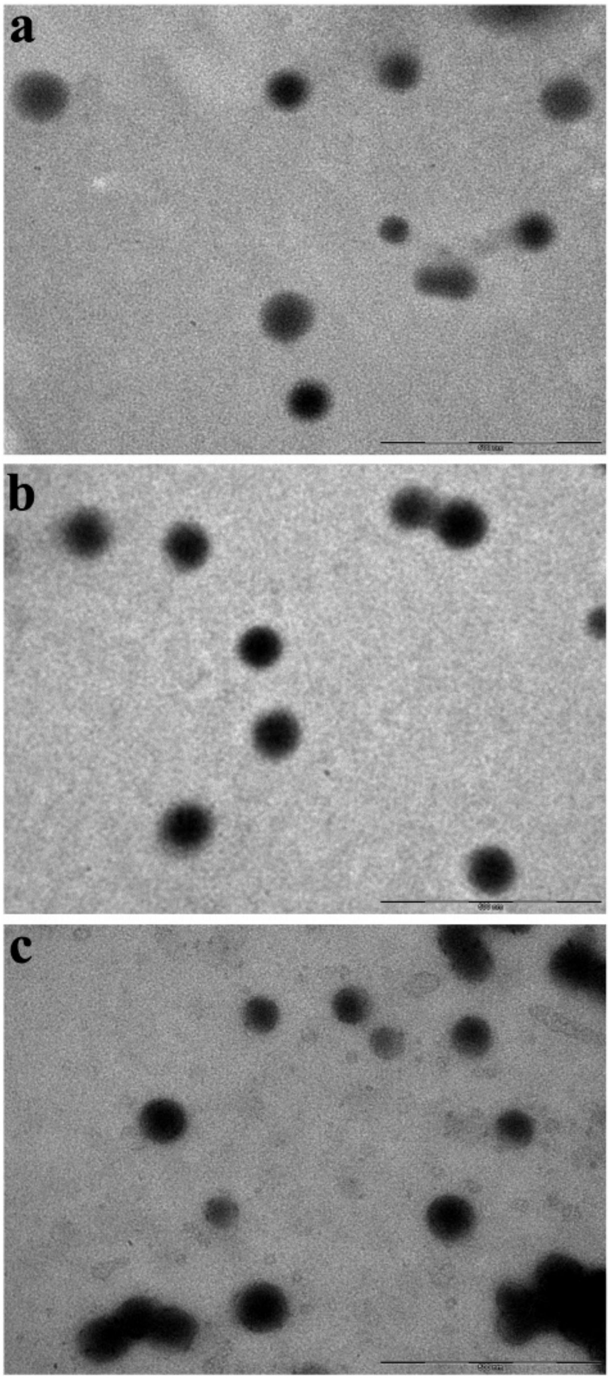


Figure 5. TEM microphotographs of particles from the PU dispersion (a) and hybrid latexes of PUA-25 (b) and PUA-50 (c). Scar bar = 500 nm.

works (semi-IPN), where the acrylics are grafted onto the PU to form a graft-IPN, whereas the linear ungrafted acrylic polymer can be interpenetrated into the PU network to form another semi-IPN. Thus, the most likely reason for the complete mutual solubility of these hybrid latexes is extensive grafting and interpenetration.[40,41] Generally, the predicted T_g value of a single phased IPN can be calculated from the Fox equation[41]

$$1/T_g = w_1/T_{g1} + w_2/T_{g2}$$

where w_1 (w_2) and T_{g1} (T_{g2}) are the weight fractions and glass transitions of the polymers 1 and 2, respectively. Figure 7 shows a comparison of the T_g values of the hybrid latexes obtained from DMA with that predicted from the Fox equation. The

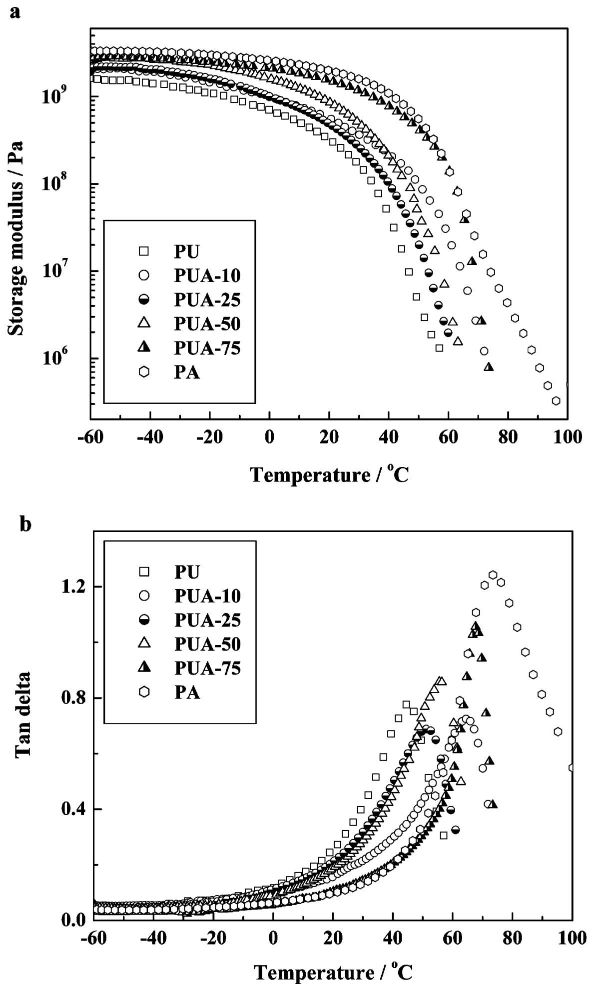


Figure 6. Storage modulus (a) and loss factor (tan δ, b) of latex films as a function of temperature.

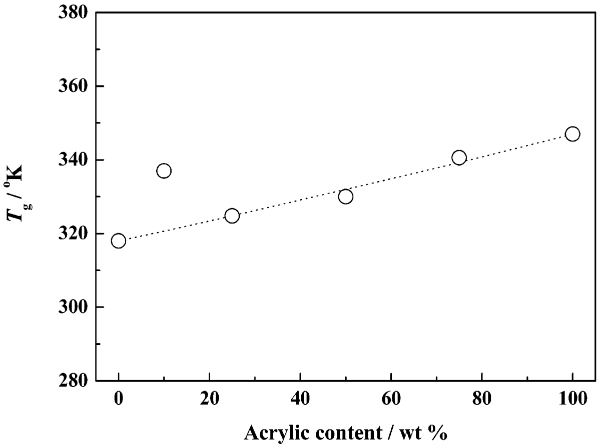


Figure 7. Plots of T_g obtained from DMA (○) as a function of acrylic content of the hybrid latexes. The curve is that predicted by the Fox equation.

experimental values increase with an increase in the acrylic content of the hybrid latexes and fit well with the predicted value, except for PUA-10. This is indicative of high miscibility between the PU and the acrylics due to extensive grafting and interpenetration. Similar results have also been observed for the solvent-borne poly(1,4-oxybutylene) glycol-based PU-polyacrylate IPNs[40] and for latex IPNs with crosslinked poly(butadiene-*stat*-styrene) as the seed latex interpenetrated with acrylics and bearing a poly(styrene-*stat*-acrylonitrile) shell layer.[42] PUA-10 exhibits a higher T_g than expected, which might be due to higher

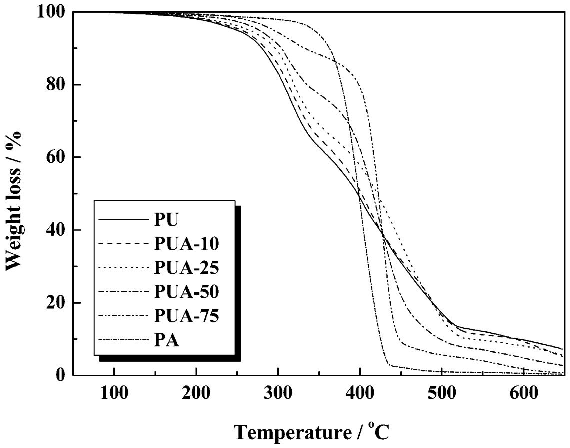


Figure 8. TGA curves for PU, PA and their hybrid latex films.

Table 1. TGA Data for the PU, PA, and Hybrid Latex Films

sample	T_5/°C	T_{50}/°C	T_{max}/°C	residue/%
PU	249.1	397.2	310/409/487	7.3
PUA-10	254.9	402.1	309/410/432	5.2
PUA-25	264.4	421.3	310/452/492	5.5
PUA-50	276.2	415.8	309/424	2.7
PUA-75	294.1	422.5	320/430	0.8
PA	343.1	398.6	402	0.4

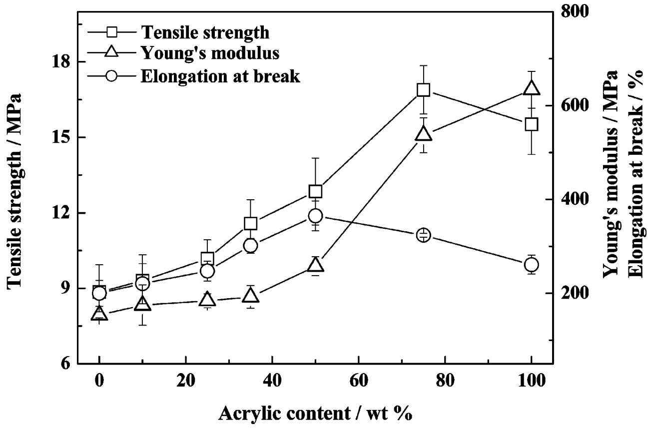


Figure 9. Mechanical properties of the hybrid latex films as a function of PA content.

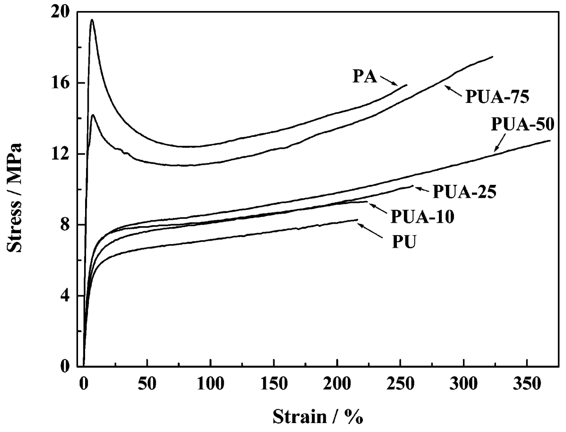


Figure 10. Stress−strain curves for the PU, PA and hybrid latex films.

crosslinking of the resulting hybrid latex. In this case, the addition of a small amount of acrylic monomers into a large amount of PU containing reactive carbon−carbon double bonds might favor crosslinking between PUs rather than grafting of the acrylic onto the PU networks.

The thermal stabilities of the PU, PA and hybrid latex films have been evaluated by TGA as shown in Figure 8 and the results are summarized in Table 1. Generally, PU exhibits a relatively poor thermal stability, due to dissociation of the urethane bond occurring around 200 °C.[26,43] PA exhibits a one-step thermal degradation, where the maximum degradation occurs at around 400 °C. This is in good agreement with the value reported by Wang et al.[44] As seen in Figure 8, the TGA curves of the hybrid latexes below 450 °C shift to a higher temperature when compared with the pure PU, indicating a higher thermal stability for the hybrid latexes. The interesting parameters for the thermal stability of the hybrid latexes have been taken from the onset of degradation, which is usually taken as the temperature at which 5% degradation occurs (T_5), the midpoint temperature of the degradation (T_{50}), the temperature of maximum weight loss rate (T_{max}) in each stage, and the nonvolatile residue, which remains at 650 °C, denoted as the char. The thermal degradation behavior of the hybrid latexes is largely influenced by the acrylic resin content. Increases in the T_5 value from 249 to 294 °C and the T_{50} value from 397 to 423 °C are observed for the hybrid latexes with an increase in the acrylic content from 0 to 75 wt %. It is worth noting that the hybrid latexes exhibit higher T_{50} values than the pure components. The PU shows three significant thermal degradation peaks at 310, 409, and 487 °C, respectively (T_{max} in Table 1). However, the corresponding T_{max} value of the hybrid latexes shifts to a higher temperature when compared with the pure components. These results indicate that the acrylics play an important role in enhancing the thermal stability of the PU/acrylic hybrid latexes. The improved thermal stability of the hybrid latexes can be explained by the occurrence of extensive grafting, crosslinking, and interpenetration. A similar enhancement in the thermal stability has also been reported for the IPNs from PU−polystyrene and PU−poly(methyl methacrylate) systems.[45,46] Increasing the acrylic content will increase the oxygen content in the hybrid latex system, thus more complete combustion takes place, leaving less residue (char content) in the resulting hybrid samples.[47]

Mechanical Properties of the Hybrid Latexes. The mechanical properties of the hybrid latexes as a function of the acrylic content are shown in Figure 9. The Young's modulus, tensile strength, and elongation at break of the PU film are 154 MPa, 8.8 MPa, and 200%, respectively. These values are very close to those of the waterborne PUs from castor oil- or rapeseed oil-based polyols.[30,31] For the hybrid latex films, both the Young's moduli and the tensile strengths are significantly increased respectively from 154 to 537 MPa and from 8.8 to 16.9 MPa with an increase in the acrylic content from 0 to 75 wt %. The elongation at break of the hybrid latex films first increases with increasing acrylic content and reaches a maximum of 365% at 50 wt % acrylic content. These improvements in the mechanical properties of the hybrid latex films can be attributed to extensive grafting and interpenetration between the PU and the acrylics, resulting in the highly miscible hybrid latexes. As mentioned earlier, due to the poor miscibility between component polymers, physically blended films from a PU dispersion and a PA emulsion are very brittle when the PA content is higher than 30 wt %. However, hybrid latex films with good mechanical properties can be prepared over the entire range of composition by hybrid emulsion polymerization technology. Moreover, the mechanical properties of this novel hybrid latex films containing 15−60 wt % of the renewable SOL are comparable to those of other PU/acrylic hybrid latexes with similar compositions, where the PU was prepared from petroleum-based polyols, such as polypropylene glycol (PPG).[7,48]

Figure 10 shows the stress−strain curves for the PU, PA, and hybrid latex films. The deformation feature of the hybrid latex films at room-temperature greatly depends on the acrylic content. When the acrylic content is less than 50 wt %, the latex films exhibit characteristics typical of soft and tough polymers that show uniform extension. However, the hybrid latex film containing 75 wt % acrylics displays behavior typical of rigid and tough plastics with a necking down across the width of the specimen, similar to the behavior of the PA copolymers.

Conclusions

A variety of new hybrid latexes prepared from a soybean oil-based waterborne PU and acrylic MMA/BA copolymers have been successfully synthesized by hybrid emulsion polymerization. The resulting PU/acrylic hybrid latexes, containing 15−60 wt % of the SOL as a renewable resource, are very stable and exhibit uniform particle size of 125 ± 20 nm. The particle size of the final hybrid latexes is not severely affected by the urethane/acrylic composition ratio, indicating that the emulsion process employed in this work has a different particle growth mechanism from seeded hybrid emulsion polymerization processes. The occurrence of extensive grafting of the acrylics onto the PU and interpenetration between the acrylics and the PU results in miscible hybrid latexes with enhanced thermal and mechanical properties. The mechanical properties of these novel hybrid latex films are comparable to those of polypropylene glycol-based PU/acrylic hybrid latex films. This work provides a new way of utilizing renewable resources to prepare environmentally friendly hybrid latexes with high performance for coating applications.

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