

Synthesis and Properties of Grafted Latices from a Soybean Oil-Based Waterborne Polyurethane and Acrylics

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ABSTRACT: A novel soybean oil-based vinyl-containing waterborne polyurethane (VPU) dispersion has been successfully synthesized from toluene 2,4-diisocyanate, dimethylol propionic acid and a 90 : 10 mixture of chlorinated soybean oil-based polyol and acrylated epoxidized soybean oil (AESO). Then, a series of VPU/acrylic grafted latices have been prepared by emulsion graft copolymerization of acrylic monomers (40 wt % butyl acrylate and 60 wt % methyl methacrylate) in the presence of the VPU dispersion, using potassium persulfate as an initiator. The structure, morphology, and thermal and mechanical properties of the resulting latices, containing 15–60 wt % soybean oil-based polyols as a renewable resource, have been investigated by Fourier transform infrared spectroscopy,

solid state ^{13}C NMR spectroscopy, transmission electron microscopy, thermogravimetric analysis, dynamic mechanical analysis, and mechanical testing. The results indicate that graft copolymerization of the acrylic monomers onto the VPU network occurs during emulsion polymerization, leading to a significant increase in the thermal stability and mechanical properties of the resulting miscible grafted latices. This work provides new environmentally-friendly latices from a renewable resource with high performance for coating applications. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 3305–3314, 2011

Key words: waterborne polyurethane; latex; soybean oil; emulsion polymerization

INTRODUCTION

Polyurethanes (PUs) are the most versatile of all polymers; their applications include diverse types of foams, coatings, adhesives, sealants, and elastomers.¹ Conventional PU resins usually contain a high proportion of volatile organic solvent and sometimes even free isocyanate monomers. To meet increasing concerns regarding health, safety, the environment, and the economy, waterborne PU dispersions have been gaining increasing importance in a wide range of applications, including inks, adhesives, and various protective or decorative coatings.² Waterborne PUs feature exceptional performance properties, such as adhesion to various substrates, abrasion resistance, flexibility and toughness, and superior low-temperature impact properties, but suffer from hardness and alkali resistance.^{3,4} To upgrade the performance of waterborne PU films with regard to weatherability, hardness, and water and alkali resistance, waterborne PU/acrylic blend emulsions are a simple and popular approach.⁵ However, the physical blending of acrylic emulsions and PU dispersions have their inherent limitations because of the incom-

patibility between the PU dispersions and acrylic emulsions, which result in phase-separated materials with relatively poor properties.⁶ Therefore, many efforts have been made to combine urethane and acrylic polymers in a single component hybrid system through emulsion polymerization. This is expected to result in a superior balance of properties when compared with their physical blends,^{5–7} because totally different particle and film morphologies can be obtained in a sequentially polymerized system, as both polymers can exist in the same particle.³ Thus far, hybrid latices have been synthesized by seeded emulsion polymerization,^{5,8,9} forming interpenetrating polymer networks (IPN),¹⁰ cross-linking,¹⁰ and graft copolymerization^{11,12} between PU and acrylic polymers.

Nowadays, there is increasing interest in replacing petroleum-derived raw materials with renewable, plant-based materials for the production of valuable polymeric materials.¹³ Vegetable oils, possessing a triglyceride structure with highly unsaturated fatty acid side chains, are considered to be among the most important classes of renewable materials for the production of bio-based polymers,^{14–22} because of their low toxicity, high purity, low cost, and ready availability. Vegetable oil-based polyols are relatively new raw materials from renewable resources and are increasingly used for the preparation of bio-based PU products with excellent chemical and physical properties, including enhanced hydrolytic

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and thermal stability.^{23–28} However, research and development of vegetable oil-based waterborne PU dispersions have not attracted much attention so far. One of us recently reported waterborne PU dispersions from the reaction of isophorone diisocyanate and mixtures of dimethylol propanoic acid (DMPA) and a castor oil or rapeseed oil-based polyol.^{21,22} In our previous work,²⁹ a soybean oil-based waterborne PU dispersion has also been successfully synthesized from the reaction of toluene 2,4-diisocyanate, DMPA, and a soybean oil-based polyol. The resulting vegetable oil-based waterborne PU films exhibit the mechanical properties that can be comparable with that of the petroleum-based waterborne PUs.^{21,22,29}

It has been reported that graft copolymerization between vinyl-containing polyurethane (VPU) macromonomers and vinyl monomers, such as styrene,^{30,31} and acrylics,^{12,31–33} can significantly increase the thermal stability, tensile strength, hardness, and water-resistance of the resulting materials, because of the covalent linkage between the two components. Generally, the synthesis of a grafted VPU-vinyl copolymer is carried out in a two-stage reaction. First, excess isocyanate is allowed to react with the polyol to obtain a VPU prepolymer, followed by addition of 2-hydroxyethyl acrylate (HEA) or 2-hydroxyethyl methacrylate (HEMA) as an end-capping monomer. Then, the vinyl monomers are added to the VPU for graft copolymerization, leading to grafted urethane-vinyl copolymers with high performance. Acrylated epoxidized soybean oil (AESO), another renewable resource-based product containing both vinyl and hydroxyl groups, is readily synthesized from acrylic acid and epoxidized soybean oil. It has been extensively used in surface coatings,³⁴ ink,³⁵ polymer resins,²⁰ and composites.³⁶ The objective of this work is to explore the feasibility of developing a novel soybean oil-based VPU dispersion by replacing petroleum-based polyols and end-capping monomers in the VPU with chlorinated soybean oil-based polyol (SOL) and AESO, and to prepare grafted latices with acrylics through emulsion copolymerization. A soybean oil-based VPU dispersion, its grafted latices, and the resulting latex films have been successfully prepared and their structure, morphology, and properties have been extensively investigated by Fourier transform infrared spectroscopy (FTIR), solid state ¹³C NMR spectroscopy, transmission electron microscopy, differential scanning calorimetry (DSC), dynamic mechanical analysis (DMTA), and mechanical testing.

EXPERIMENTAL

Materials

Wesson soybean oil was purchased at the local supermarket and used directly without further puri-

fication. Acrylated epoxidized soybean oil (AESO) was obtained from UCB Radcure under the brand name Ebecryl 860 (~ 3.4 acrylates per triglyceride, $M_w = 1200$ g/mol). SOL (OH number = 130 mg KOH/g, $M_w = 1000$ g/mol) was synthesized using a published procedure.³⁷ Toluene 2,4-diisocyanate (TDI), dimethylol propionic acid (DMPA), dibutyltin dilaurate (DBTDL), methyl methacrylate (MMA), and butyl acrylate (BA) were purchased from Aldrich Chemical Company. Sodium hydroxide, hydrochloric acid (37%), hydrogen peroxide (30%), formic acid (88%), sodium dodecyl sulfate (SDS), potassium persulfate (KPS), magnesium sulfate, methyl ethyl ketone (MEK), triethylamine (TEA), and ethyl acetate were purchased from Fisher Scientific Company. All materials were used as received without further purification.

Synthesis of a soybean oil-based VPU dispersion

The soybean oil-based VPU dispersion was prepared using one-step method as follows. The SOL (27.0 g, 0.0629 mol of OH groups), 3.0 g of AESO (0.0085 mol of OH groups), 11.8 g of TDI (0.0678 mol), 4.4 g of DMPA (0.0328 mol), and 0.15 g of DBTDL were added to a three-necked flask equipped with a mechanical stirrer, nitrogen inlet, and thermometer, and the reaction was carried out at 75°C under a dry nitrogen atmosphere. After 2 h, the reaction was cooled to about 40°C, and 30.0 g of MEK was added to reduce the viscosity of the system while the solution was stirred vigorously. Then, TEA (3.5 g) was added to neutralize the acid groups, followed by dispersion at high speed with 200 g of distilled water to produce the soybean oil-based VPU dispersion. After removal of the MEK under vacuum, a final VPU dispersion with a solid content of about 20 wt % was obtained. For comparison, the soybean oil-based waterborne polyurethane dispersion without vinyl groups, henceforth known as PU, has also been synthesized from SOL, TDI, and DMPA using the same NCO/OH ratio as that of the VPU dispersion.

Synthesis of VPU/acrylics grafted latices

SDS (3.0 g) and KPS (1.0 g) were dissolved in about 414 g of distilled water. One hundred gram 60 : 40 mixtures of MMA and BA were added to the above aqueous solution with vigorous stirring to obtain the pre-emulsions for hybrid emulsion copolymerization.

The desired weight of the VPU dispersion and the acrylic pre-emulsion were placed in a flask and stirred for 30 min at room temperature under an N₂ atmosphere, and then, brought to the polymerization temperature of 80°C for 4 h to obtain the grafted

emulsion. During polymerization, ~ 5 g samples of the emulsion were taken intermittently by a syringe and injected into a petri dish containing a 0.5% hydroquinone solution in an ice bath. Monomer conversion was determined gravimetrically from these samples. By changing the weight ratio of VPU dispersion to the acrylics pre-emulsion from 90 : 10 to 75 : 25, 65 : 35, 50 : 50, and 25 : 75, a series of grafted latices have been successfully prepared and recorded as VPU-10, VPU-25, VPU-35, VPU-50, and VPU-75, respectively, where the number represents the weight percentage of acrylics in the grafted latex. For comparison, the hybrid latex from the PU dispersion and acrylics pre-emulsion has also been synthesized, and nomenclature similar to that used for the VPU-based grafted latices has been used. For example, hybrid latex PU-50 represents 50 wt % of the acrylics in the soybean oil-based waterborne PU dispersion without vinyl groups. The dispersions or latices were dried at room temperature in a glass mold to obtain films, except for the pure acrylics emulsion (PA), which was dried at a slightly higher temperature of 45°C.

Characterizations

FTIR spectra of the vacuum-dried extracted films were recorded on a Nicolet 460 FTIR spectrometer (Madison, USA) using KBr pellets.

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

Solvent extraction was performed in a Soxhlet extractor with ~ 1 g of dry latex films. The samples were first extracted with toluene for 24 h to remove the linear polyacrylate, 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 extent of incorporation of the acrylics into the VPU. An average value of three replications of each material was taken.

The morphology of the grafted latex particles was observed on a transmission electron microscope (JEOL-2100). The emulsions prepared were diluted with deionized water, and 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 with a dynamic mechanical analyzer (TA instrument DMA Q800-USA) 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 \times 5 mm (length \times width) were used.

A Perkin-Elmer Pyris-7 thermogravimeter was used to measure the weight loss of the latex film samples under an air atmosphere. The samples were heated from 100 to 650°C at a heating rate of 20°C/min. Generally, 10–15 mg samples were used for the thermogravimetric analysis.

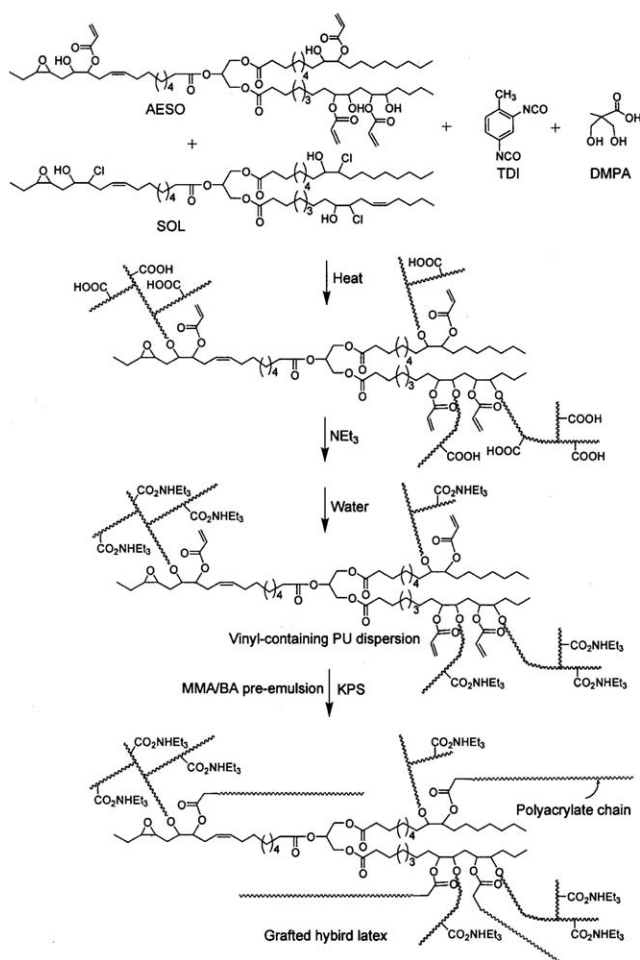
The mechanical properties of the latex films were determined with an Instron universal testing machine (model-4502) at a crosshead speed of 100 mm/min. Rectangular specimens of 80 mm \times 10 mm (length \times width) with thickness of about 0.6 mm were dried for 3 h at 95°C and then used for testing. An average value of at least five replications of each material was taken.

RESULTS AND DISCUSSION

Structure and morphology

The average OH functionality of the SOL and AESO used in this work is 2.3 and 3.4, respectively. Therefore, a thermosetting polyurethane with vinyl pendant groups will be obtained when the SOL and AESO are used as soft segments to react with the TDI. During emulsion polymerization, grafting can occur by chain transfer from the propagating free radical to the vinyl groups of the polyurethane or by copolymerization between the polymerizing radical and the vinyl groups of the polyurethane to form soybean oil-based VPU/acrylics grafted latices as shown in Scheme 1. The conversion of acrylic monomers in these grafted latices as determined gravimetrically can reach as high as 97% after 2 h of reaction. Considering the possible reactions that can occur in the current system, the components of the resulting latices are polyacrylics and urethane-acrylics grafted copolymers with small amounts of crosslinking fractions of VPU as well. The occurrence of grafting will enhance the miscibility of the latex components, which in turn will improve the physical properties of the films formed from the latices.³⁸

To test the occurrence of grafting between the acrylics and the VPU, Soxhlet extraction with toluene and DMF as solvents has been carried out for the films of VPU and latices. Figure 1 shows the gel fraction for the latices as a function of acrylics content. Approximately, 76 wt % insoluble materials are observed for the VPU film after extraction, indicating the crosslinked nature of this material. If no reaction were to occur between the VPU and the PA, the resulting grafted latices should behave like a physical blend of VPU and PA, and thus, the gel fraction of the latices should decrease linearly with an increase in the PA content as predicted by the additive rule illustrated in Figure 1. However, a



Scheme 1 Synthesis of soybean oil-based urethane-acrylics grafted latices.

significant increase in the gel fraction percentage is observed for the grafted latices when compared with that from physical blends. This indicates that graft copolymerization or crosslinking reactions have occurred in the latex systems. Similar reactions have also been observed in other urethane-acrylic hybrid latex systems.^{7,38}

The FTIR spectra of the VPU film and the extracted latex film VPU-50 with toluene and DMF have been measured and are shown in Figure 2. Peaks due to NH stretching of the VPU are observed in the range of 3300–3500 cm^{-1} . In this region, the major peak centered at 3300–3350 and the small shoulder peak at 3450 cm^{-1} are attributed to the NH groups hydrogen-bonded with carbonyl groups and free NH groups, respectively.^{39,40} Thus, most of the NH groups in the VPU are hydrogen-bonded with carbonyl oxygen. Bands due to carbonyl stretching in the VPU are observed at 1724 and 1738 cm^{-1} , which can be assigned to stretching of the hydrogen-bonded carbonyl and free carbonyl groups, respectively.⁴⁰ For the extracted grafted latex VPU-50, the absorption peaks at 1167, 1147, and 841 cm^{-1}

are assigned to OCH_3 and OC_4H_9 groups in the acrylics. The intensity of the band at 1414 cm^{-1} corresponding to the deformation vibration of the double bonds in the VPU appears to be significantly decreased in the spectrum of VPU-50, which indicates that grafting has taken place on the crosslinked soybean oil-based PU through the double bonds,⁴¹ leading to good miscibility of the resulting latices as shown later.

Solid-state ^{13}C NMR spectroscopy has been used to determine that grafting polymerization has occurred in the urethane-acrylic hybrid latices.^{29,38} Generally, the VPU exhibits characteristic peaks at 154 ppm and 126–133 ppm, which are attributed to the carbons present in the urethane moiety and the carbon-carbon double bonds in the soft segment of the VPU.³⁸ Thus, the carbon in the urethane moieties can be used as an internal standard, because its concentration is constant during emulsion polymerization. The ratio between the carbon in the urethane moieties and the carbon of the carbon-carbon double bonds present in the VPU can, therefore, be used to determine the extent to which the carbon-carbon double bonds in the polyurethane have polymerized. However, for the polyurethanes synthesized from 2,4-TDI, the sixth carbon in the benzene ring also has a chemical shift of about 133 ppm, which appears in the same region as the carbon-carbon double bonds of SOL or acrylate groups.²⁹ To eliminate the peak area due to the sixth carbon of the benzene rings, the soybean oil-based VPU and latices resulting from grafting with acrylics have also been synthesized from isophorone diisocyanate (IPDI), instead of TDI, with the same stoichiometry as the VPU, VPU-25, and VPU-50, respectively. Figure 3(a–c) shows the solid state ^{13}C NMR spectra of the VPU from IPDI and its grafted latices with

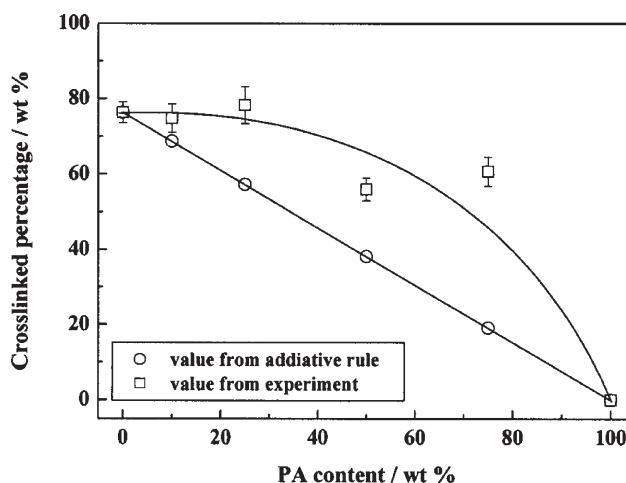


Figure 1 Gel fraction of grafted latices as a function of acrylics content.

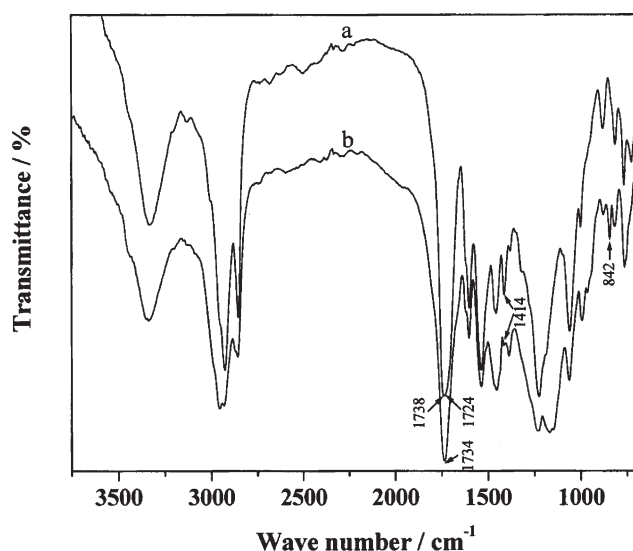


Figure 2 FTIR spectra of VPU (a) and extracted grafted latex VPU-50 (b).

25 wt % and 50 wt % acrylics. All samples exhibit absorption peaks of a typical vinyl-containing polyurethane at 154 ppm and 126–130 ppm. For the VPU film from IPDI, the ratio between the urethane carbons and the carbons of the carbon–carbon double bonds is 0.91, which is consistent with the theoretical value of 0.92. However, the ratio of these two carbons decreases from 0.91 to 0.75 when the acrylics content increases from 0 to 50 wt %, which indicates that some of the carbon–carbon double bonds in the polyurethane have reacted, resulting in a grafted latex. This is in good agreement with the extraction results shown in Figure 1.

The TEM images of the VPU dispersion and the grafted latices are shown in Figure 4. The TEM confirms that the particle size of the VPU is relatively uniform with an average diameter of 75 ± 15 nm, which is smaller than that of the soybean oil-based waterborne PU dispersion (125 ± 20 nm) without AESO as reported earlier.²⁹ The smaller particle size can be attributed to incorporation of the AESO that causes relatively higher crosslinking in the VPU dispersion.¹⁰ For the grafted latices, the particle diameter hardly increases with an increase in the acrylics content. This indicates that the process in this work is much different from the conventional seeded or core-shell emulsion polymerization in which the ratio of the urethane and acrylics substantially changes the particle size and size distribution of the resulting latices.^{10,42} This may be attributed to the fact that, when using the seeded or core-shell 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. Further increasing the acrylic mono-

mer content makes it difficult for the PU to envelop the acrylic polymers and form stable hybrid emulsion particles, resulting in larger hybrid emulsion particles.⁹ However, during the synthesis of VPU/acrylics grafted latices, the VPU dispersion present in the system does not serve as a real core or seed. In the meanwhile, the pre-emulsified acrylic monomers are polymerized in micelles, rather than in the particles of the PU dispersion. As the grafted latex particles grow, the hydrophilic VPU is attracted to the acrylic latex particles as stabilizers, resulting in an indirect connection in particle size between the VPU dispersion and the grafted latices.³ Therefore, the emulsion process employed in this work, which mixes the VPU dispersion with the acrylic monomer pre-emulsion, can sustain more dramatic changes in the composition between the VPU and the acrylics without severely influencing the particle size of the final grafted latices.

Thermal properties

Figure 5 shows the storage modulus (E') and loss tangent ($\tan \delta$) of the films from VPU, PA, and their grafted latices. An enhancement in moduli in various temperature ranges is observed for the grafted latices when compared with those of the VPU.

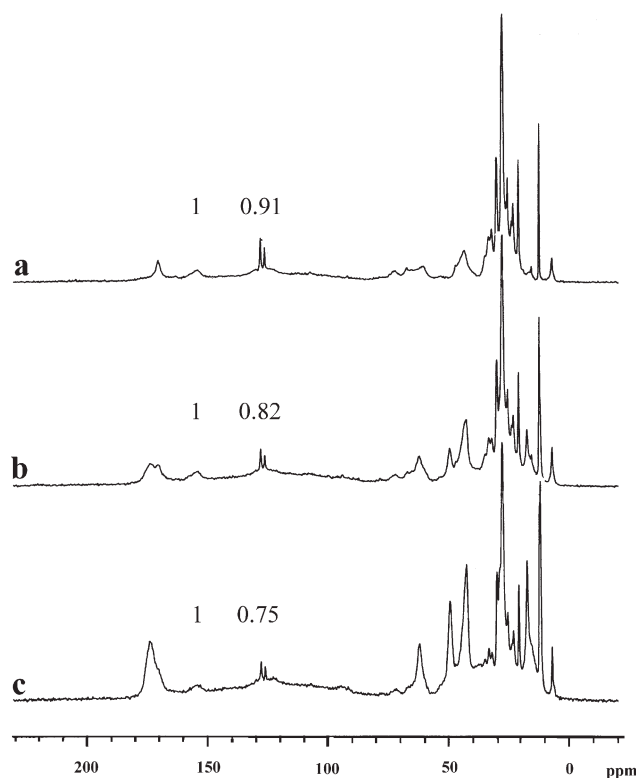


Figure 3 Solid state ^{13}C NMR spectra of soybean oil-based polyurethane from IPDI (a) with the same stoichiometry as the VPU, and its grafted latices with 25 wt % (b) and 75 wt % (c) acrylics.

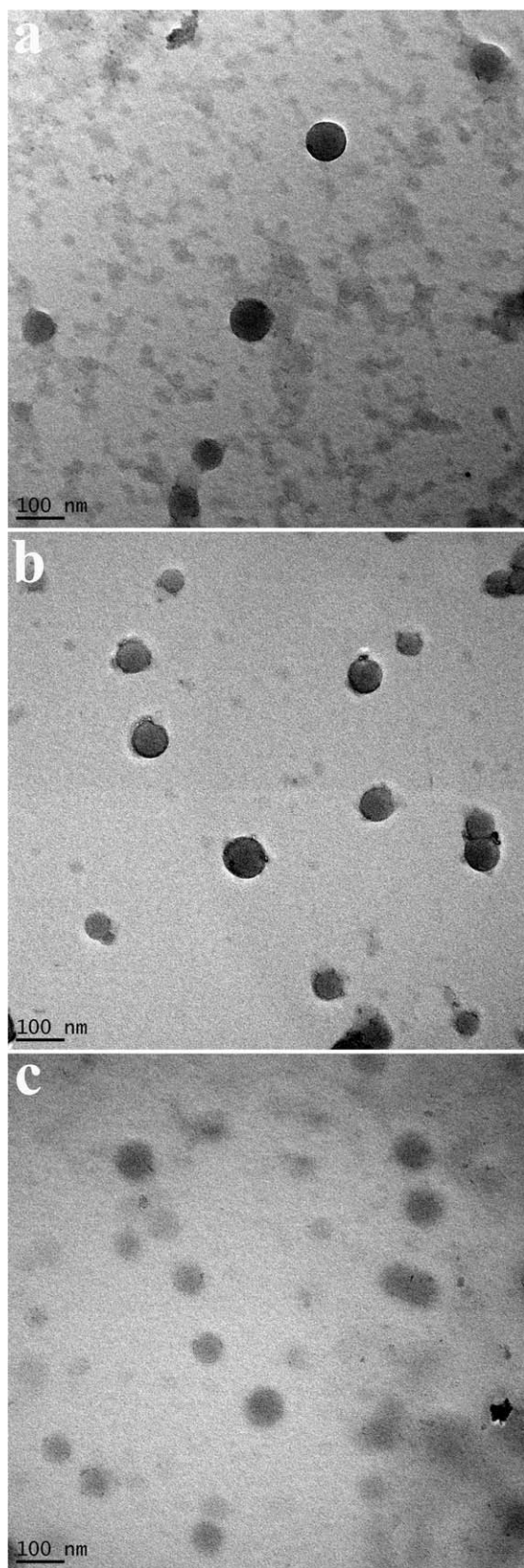


Figure 4 TEM microphotographs of particles from the VPU dispersion (a) and grafted latices of VPU-25 (b) and VPU-50 (c).

Below the T_g , the storage modulus of the grafted latices increases with the acrylics content, which is similar to the Young's modulus results from tensile testing as shown in Figure 7, but this sharply changes in the T_g region. For example, at room temperature, the increases in E' are 82% for VPU-10, 143% for VPU-25, 187% for VPU-50, and 252% for VPU-75 when compared to the corresponding values of the VPU. Above the T_g , the three grafted latices VPU-10, VPU-25, and VPU-50 exhibit higher E' values compared to those of either the VPU or PA. This is due to a synergistic effect between the VPU and PA through graft copolymerization and crosslinking. The $\tan \delta$ -temperature curves display loss peaks associated with the glass transition temperature and damping capacity of the resulting materials. The VPU exhibits one prominent damping peak centered at 59°C, associated with the T_g of soft segments. Above 70°C, this material became too soft for measurement. For the grafted latices, only one T_g is observed, indicating the presence of miscible hybrid latices due to extensive grafting. This is supported by the perfect clarity of the resulting latex films. It should be pointed out that when compared with the films from the grafted latices, the films of physical blends from the VPU dispersion and the PA latex are translucent, weak, and brittle when the PA content is higher than 25 wt %, due to their poor miscibility. Surprisingly, the highest T_g of about 80°C is seen with VPU-10 and VPU-25. This might be attributed to higher crosslinking present in the resulting latices, in which the addition of a small amount of acrylic monomers into a large amount of vinyl-containing polyurethane might favor crosslinking among VPUs, rather than grafting of the acrylic onto the VPUs, which leads to a latex with an interpenetrating polymer network structure.¹⁰ A similar trend in T_g variation of the grafted latex films is observed

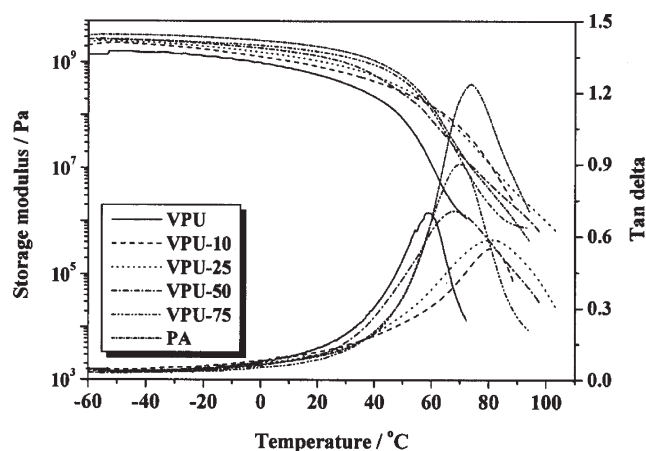


Figure 5 The storage modulus and loss factor ($\tan \delta$) of VPU, PA, and their grafted latex films as a function of temperature.

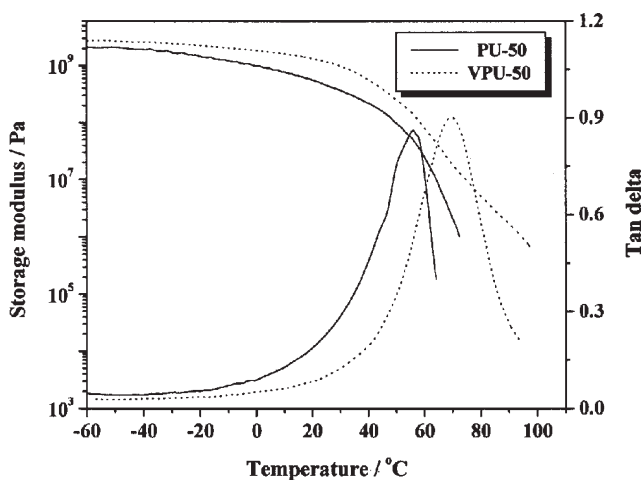


Figure 6 The storage modulus and loss factor ($\tan \delta$) of PU, PA, and their grafted latex films as a function of temperature.

in the DSC curves (not shown), in which the T_g s are in the range of 20–50°C. The difference in T_g values from the two methods might be caused by a frequency and temperature lag in the thick samples used for the DMA tests.²⁶ The sharpness and height of the damping peaks give information about the degree of order and the freedom of motion of molecules in the soft domains.⁴³ Compared with the VPU, the grafted latices VPU-10 and VPU-25 exhibit a clearly broader transition peak with a significant decrease in the transition height, because of reduced chain segment mobility, due to the relatively high crosslinking in these materials.⁴³

To evaluate the effect of the AESO on the thermo-mechanical properties of the resulting latices, the dynamic mechanical behavior of the grafted latex

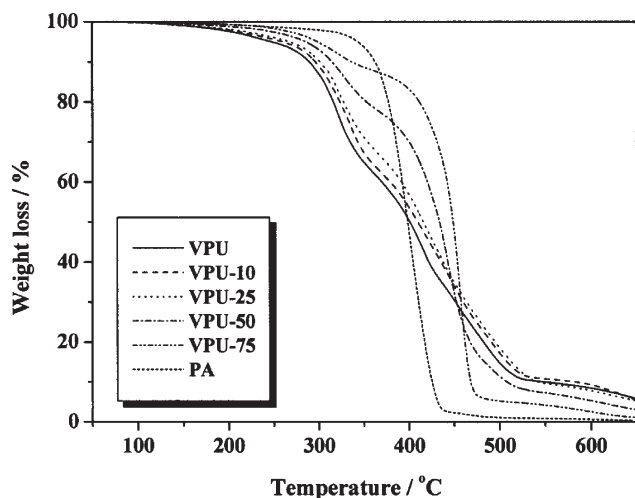


Figure 7 TGA curves of VPU, PA, and their grafted latex films.

film VPU-50 with AESO and hybrid latex film PU-50 without AESO have been examined, along with the corresponding storage modulus and $\tan \delta$ values as a function of the temperature as shown in Figure 6. The addition of 10 wt % AESO to polyurethane soft segments causes an increase of E' over the entire temperature range. The E' of the grafted latex VPU-50 at 25°C is nearly 2.6 times higher than that of the PU-50. At the same time, the T_g is increased markedly from 56°C for PU-50 to 70°C for VPU-50 due to the effective and extensive grafting that has occurred in the VPU-based grafted latices.⁴⁴

The thermal stabilities of the VPU, PA, and their grafted latex films have been evaluated by TGA and the results are illustrated in Figure 7 and Table I. The thermal stability of the PU is poor. The onset of urethane bond dissociation is somewhere between 150 and 220°C depending upon the isocyanate and polyol employed. In this study, the VPU undergoes more than one thermal degradation process. The degradations observed in the range of 200–350°C can be attributed to decomposition of the urethane bonds, which takes place through dissociation to isocyanate and alcohol, the formation of primary amines and olefins, or the formation of secondary amines.²³ The degradation process occurring at temperatures between 350 and 500°C is attributed to soybean oil chain scission. Similar degradation behavior has been reported previously for polyurethanes derived from vegetable oils and fatty acids.^{23,26} Compared with the VPU, the TGA curves of the grafted latices shift to a higher temperature, indicating a higher thermal stability for the grafted latices. The most interesting parameters for the thermal stability of the grafted latices appear at the onset of degradation, which is usually taken as the temperature at which 5% degradation occurs (T_5), the mid-point 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. Increases in the T_5 value from 247 to 298°C and the T_{50} value

TABLE I
Thermal Properties of the Grafted Latices

Samples	T_g (DMA) (°C)	TGA			Residue (%)
		T_5 (°C)	T_{50} (°C)	T_{max} (°C)	
VPU	59	247	400	315/414/453/474	5.9
VPU-10	81	259	409	326/418/447/481	5.5
VPU-25	80	267	416	327/440	5.3
VPU-50	68	286	434	323/458	3.1
PU-50	57	276	416	309/424	2.7
VPU-75	70	298	449	320/430	1.1
PA	75	343	399	402	0.4

from 400 to 445°C are observed for the grafted latices with an increase in the acrylics content from 0 to 75 wt %. Four maximum thermal degradation peaks at 315, 414, 453, and 474°C have been observed for the VPU as shown in Table I. However, when compared with the VPU and PA, the T_{\max} value of the grafted latices shifts to a higher temperature, indicating that the acrylics play an important role in enhancing the thermal stability of the resulting grafted latices. A similar enhancement in the thermal stability has also been reported for the IPNs from PU-polystyrene⁴⁵ and PU-poly(methyl methacrylate)⁴⁶ systems. The residual weight of the latices at 650°C decreases with increasing acrylics content. This can be explained by the fact that more complete combustion takes place in the grafted latices with a higher oxygen content due to incorporation of acrylics.⁴⁷

The TGA curves of VPU-50 with AESO and PU-50 without AESO are shown in Figure 8, and the corresponding results are summarized in Table I. No difference is observed in the degradation process below 300°C for the two latices. However, above 300°C, the TGA curve for VPU-50 shifts to higher temperatures when compared with that of PU-50, indicating a higher thermal stability for the grafted latex. The improved thermal stability of the grafted latices can be attributed to the occurrence of extensive grafting between the acrylics and the VPU in the grafted latex due to incorporation of the AESO.

Mechanical properties

The mechanical properties of the grafted latices, including Young's modulus, tensile strength, and elongation at break are summarized in Table II. The

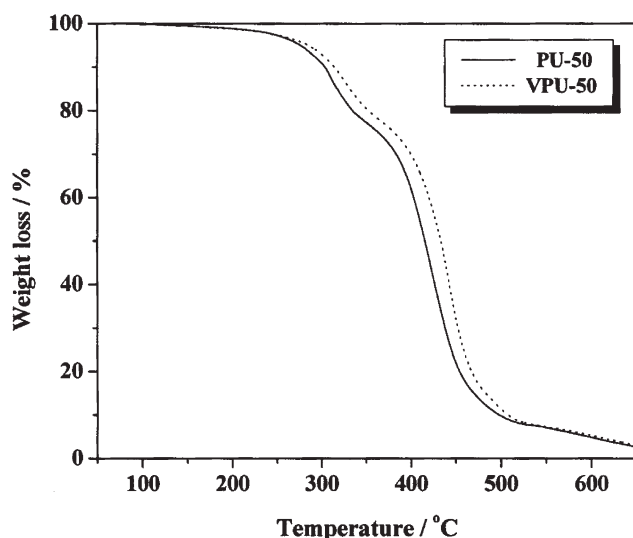


Figure 8 TGA curves of PU-50 and VPU-50 latex films.

TABLE II
Mechanical Properties (E , Young's modulus; σ_b , tensile strength; ϵ_b , elongation at break) of the Soybean Oil-Based Polyurethane, Grafted Latices and PA Films

Samples	E (MPa)	σ_b (MPa)	ϵ_b (%)
VPU	245 ± 19	11.9 ± 0.3	175 ± 26
VPU-10	275 ± 20	14.7 ± 1.5	126 ± 23
VPU-25	367 ± 27	15.9 ± 0.9	108 ± 26
VPU-50	469 ± 22	17.4 ± 1.8	149 ± 14
PU-50	258 ± 20	12.9 ± 1.3	365 ± 32
VPU-75	556 ± 17	15.7 ± 1.4	162 ± 19
PA	633 ± 15	15.5 ± 0.4	261 ± 21

Young's modulus, tensile strength, and elongation at break of the VPU film are 245 MPa, 12 MPa, and 175%, respectively. For the grafted latex films, the Young's moduli are significantly increased from 245 to 551 MPa with an increase in the acrylics content from 0 to 75 wt %. The tensile strength of the grafted latex films first increases with increasing acrylics content, and reaches a maximum of 17.4 MPa for the grafted latex film VPU-50, then slightly decreases. Compared with the hybrid latex PU-50 without AESO, the grafted latex VPU-50 exhibits much higher values of Young's modulus and tensile strength. These improvements in the mechanical properties of the grafted latex films can be attributed to extensive grafting that occurs between the VPU and the acrylics, resulting in the highly miscible latices. The elongation at break of the grafted latices decreases at first with increasing acrylics content from 0 to 25 wt %, due to the relatively high cross-linking which occurs in these cases, and then increases from 108 to 162%. It is worth noting that

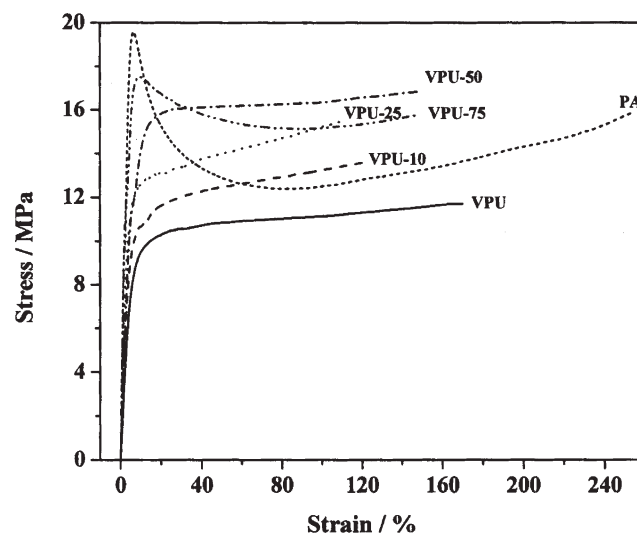


Figure 9 Stress-strain curves of grafted latices with different acrylics content.

the mechanical properties of these novel grafted latex films, containing 15–60 wt % of biorenewables, are comparable to or even better than those of petroleum-based polyurethane/acrylics hybrid latices.^{7,47}

Figure 9 shows the stress–strain curves for films from the VPU, PA, and their grafted latices. The deformation feature of the grafted latex films at room temperature greatly depends on the acrylics content. The grafted latex films exhibit characteristics typical of soft and tough polymers that show uniform extension when the acrylics content is less than 50 wt %. However, behavior typical of rigid and tough plastics is observed for the grafted latex VPU-75, indicating the rigid nature of this latex, which is similar to that of PA.

CONCLUSIONS

A novel bio-based vinyl-containing waterborne polyurethane (VPU) dispersion has been successfully synthesized from the reaction of TDI, DMPA and a mixture of chlorinated soybean oil-based polyol and acrylated epoxidized soybean oil. By polymerization of acrylic monomers of MMA and BA in the presence of the VPU dispersion, a variety of VPU-acrylics grafted latices with a relatively uniform particle diameter of 75 ± 15 nm have been prepared using emulsion polymerization. The resulting grafted latices, containing 15–60 wt % of the SOL and AESO as renewable resources, exhibit enhanced thermal stability and mechanical properties because of the occurrence of graft copolymerization between the acrylics and the VPU. Depending on the ratio of components, the grafted latex films exhibit characteristics typical of soft and tough polymers or rigid and tough plastics, whose mechanical properties are comparable to or better than those of petroleum-based urethane-acrylic hybrid latex films. Compared with a hybrid latex prepared from soybean oil-based PU without AESO, the grafted latex from the VPU exhibits a substantial improvement in thermal stability and mechanical properties, due to extensive grafting, which has occurred in the grafted latices. This work provides promising new environmentally-friendly latices with high performance for coating applications, which are prepared from a biorenewable resource.

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