

Preparation and Colloidal Properties of an Aqueous Acetic Acid Lignin Containing Polyurethane Surfactant

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ABSTRACT: Aqueous acetic acid lignin containing polyurethane (ALPU) surfactants were prepared by the replacement of some hydrophobic poly(caprolactone diol) with different concentrations of multifunctional acetic acid lignin (AL), and with dimethylol propionic acid as the hydrophilic segment. The infrared spectra, together with thermogravimetric analysis, demonstrated the presence of AL in the polyurethane (PU) chains. In addition, the effects of the AL concentration on the particle size, morphology, rheological behavior, and surface activity of the dispersions were investigated. The ALPU particles displayed a spherical morphology. With increasing AL concentration from 0 to 10 wt %, the particle size increased from 36 to 260 nm, and the unimodal distribution was detected for ALPU₁₀ with a 10 wt % AL addition. The viscosity and shear-thinning behavior of the ALPU dispersions decreased, and the lowest surface tension and critical micelle concentration (cmc) were detected for ALPU₁₀. However, when the AL concentration was 15 wt % (ALPU₁₅), the surface tension and cmc increased. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 1855–1862, 2013

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INTRODUCTION

The utilization of renewable resources in polymers has received increased attention because of their potential for the substitution of petrochemical derivatives.^{1,2} Acetic acid lignin (AL), as a nontoxic, low-cost, and renewable resource, possesses numerous active hydroxyl groups and has been considered a promising candidate as a biopolymer. The acetic acid acidolysis method^{3–5} has been shown to be an efficient method for extracting lignin, with a better yield than that gained by conventional acidolysis and with a much lower content of impurities. In addition, conventional hydrolysis modifies the structure of the lignin polymer and causes the cleavage of some aryl–ether linkages, whereas the acetic acid method is less damaging.³

The high reactivity associated with lignin polyols makes them ideal for the synthesis of polyurethane (PU). Heretofore, lignin has been adopted as a polyol for preparing hydrogels,⁶ foams,⁷ films,⁸ and composites.⁹ However, several reports are available on acetic acid lignin containing polyurethane (ALPU) materials. Peng and Chen⁶ obtained AL-based PU hydrogels through a chemical crosslinking reaction between AL and isocyanate-group-terminated PU. The thermal stability of the hydrogels could be improved by the introduction of AL, and the hydrogels were simultaneously endowed with pH sensitivity. Li et al.¹⁰ investigated the thermal decomposition of the ALPU foam with

different AL concentrations. Ma et al.¹¹ developed a new PU composite prepared by the treatment of the original and secondary fibers with ALPU, and the strength and water resistance were investigated. The effects of annealing on the tensile strength and thermal stability of AL-based lignin films were also investigated.¹² In our previous study,¹³ we investigated the thermooxidative stability and kinetics of ALPU membranes crosslinked with 1-aminopropyltriethoxy silane and/or trimethylolpropane. Moreover, we found that AL could be converted to an amphiphilic polymer through derivatization with poly(ethylene glycol diglycidyl ether),¹⁴ and the surface activity was further improved by modification with monoepoxides.¹⁵ To the best of our knowledge, the utilization of AL in the preparation of an aqueous PU surfactant has never been reported.

The interest in polymeric surfactants for emulsion polymerization has increased in recent years.¹⁶ Polymeric surfactants are promising alternatives to traditional low-molecular-weight surfactants. With respect to emulsions stabilized with low-molecular-weight surfactants, hydrophilic domains are formed during film formation. Low-molecular-weight surfactants tend to migrate to the polymer interface, and this results in decreased water resistance and enhanced delamination.¹⁶ However, the possibility for polymeric surfactants to migrate is limited because of their lower diffusion rate. PU has been demonstrated

to be an interesting class for designing tailor-made polymeric surfactants.¹⁶ The structure of PU can be varied in a wide range by a change in the building blocks. PU surfactants have been demonstrated to exhibit excellent surface-active properties, such as the surface tension, wetting tendency, and formation of stable emulsions.¹⁷

In this article, a feasible and economically route for the preparation of a series of aqueous ALPU surfactants is reported. The structure of the ALPU surfactant was characterized by Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA)–differential thermogravimetry (DTG). The steady rheological properties, particle size, and morphology of dispersions were studied with rheometry, dynamic light scattering, and transmission electron microscopy (TEM), as were the surface tension of the PU and ALPU dispersions.

EXPERIMENTAL

Materials

Toluene diisocyanate (TDI) was purchased from Xinhui Leather Chemical Co., Ltd. (Guangdong, China). Poly(ϵ -caprolactone diol), with a number-average molecular weight of 1000 (PCL₁₀₀₀), was purchased from Shengfang Chemical Co., Ltd. (Guangdong, China). Dimethylol propionic acid (DMPA) was purchased from Hongdu Chemical Co., Ltd. (Jiangxi, China). Triethyl amine (TEA) was purchased from Zhiyuan Chemical Reagent Co., Ltd. (Tianjin, China), and distilled before use. 1-Methyl-2-pyrrolidone (NMP), acetic acid, HCl, dioxane, and diethyl ether were purchased from Zhiyuan Chemical Reagent Co. Acetic AL was prepared in our laboratory. Deionized water was used for all of the experiments.

Preparation of Acetic AL

White pine wood chips were submitted to treatment with 90% acetic acid solutions (500 mL) catalyzed by a small amount (0.6%) of HCl (8.3 g). The mixture was refluxed with a liquor/wood ratio equal to 5 g/g for 3 h. Lignin was dissolved in the spent liquor and was then separated by filtration; it was subsequently concentrated in a rotary vacuum evaporator at 60°C. The AL was then obtained by the dilution of the previously obtained concentrated filtrate with distilled water (a dilution factor of 9) and filtered. The procedure and subsequent purification processes were given in an earlier article.¹³

Preparation of the ALPU Dispersions

The synthesis of aqueous ALPU was performed as follows. The mixture of AL and PCL₁₀₀₀ (38 wt %, on the basis of the total mass of monomers; the following was the same) was homogeneously dissolved in NMP under mechanical stirring. Then 27 wt % TDI was added dropwise, and the reaction was kept at 70°C for 2 h under an N₂ atmosphere. Afterward, 16 wt % DMPA was added and allowed to react for another 1.5 h. After the reaction mixture was cooled to 40°C, the –COOH of DMPA in the PU chains was neutralized by 19 wt % TEA. Emulsification was subsequently carried out by the addition of distilled water under vigorous shear (1200 rpm) for 20 min to produce an ALPU dispersion with a solid content of 25 wt %. Through the adjustment of the AL concentration (on the basis of the total mass of PCL₁₀₀₀) over a range of 0, 5, 10, and

15 wt %, PU and a series of ALPU dispersions were obtained and were coded as PU, ALPU₅, ALPU₁₀, and ALPU₁₅, respectively. The experimental scheme for the preparation of the PU and ALPU dispersions are depicted in Figure 1.

Film Preparation

The aqueous dispersions were cast on leveled tetrafluoroethylene plates to allow them to dry at room temperature for 5 days and then at 60°C for 12 h. After demolding, the films were kept in a desiccator to avoid moisture.

FTIR Analysis

The infrared spectra of PU and ALPU were obtained on a Bruker Vector-22 spectrophotometer (Bruker, Germany) at a resolution of 4 cm⁻¹, with scanning from 4000 to 400 cm⁻¹.

TGA-DTG

TGA-DTG was performed in a TGA-Q500 Instrument (TA Instruments). Film samples of about 5 mg were placed in a platinum sample pan and heated from 30 to 600°C under an N₂ atmosphere at a heating rate of 10°C/min.

Rheology Measurement

The rheological properties of the dispersions were analyzed in a TA Instrument AR2000ex rheometer. All tests were carried out at 25°C with a DIN concentric cylinders geometry. The diameters of the rotating rod and static cylinder were 28 and 30 mm, respectively. All of the samples were loaded into the rheometer measurement cup and allowed to equilibrate at 25°C for 5 min, and then, the samples underwent a constant shearing treatment (1 s⁻¹ for 10 min) before analysis to remove history effects.

Particle Size and Micromorphology Measurement

The particle size and ζ potential (ZP) of the PU and ALPU dispersions were analyzed by Nano-ZS dynamic light scattering (Malvern, United Kingdom). Its morphology was observed by Hitachi (H-600) TEM instrument. The concentration used for dynamic light scattering and TEM measurements was 10 g/L. All of the samples were dispersed by a sonicator before the analysis.

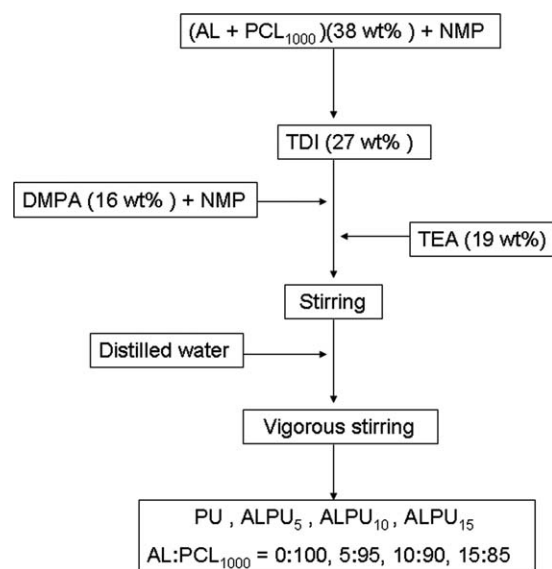


Figure 1. Experimental scheme for the preparation of the PU and ALPU dispersions.

Surface Tension Measurement

The measurement of the surface tension was performed in an automatic surface tensiometer (Chengde Jinjian tensiometer XJZ-200) at 25°C through the Du Nouy ring method. Different surfactant concentrations from 6.05×10^{-7} to 0.1 g/L were adopted for the measurement. Three measurements were taken, and the mean value was used for further analysis.

RESULTS AND DISCUSSION

Structural Characteristics

The structures of AL, PU, and ALPU₁₀ were characterized by FTIR spectroscopy. As shown in Figure 2, several features indicated the occurrence of interactions between AL and PU.

1. The broad absorption from 3000 to 3632 cm^{-1} , with the peak at 3463 cm^{-1} from the AL spectrum, characterized the stretching vibration of —OH groups in the AL structure. At the same time, the peaks at 1600, 1500, 1456, and 850 cm^{-1} characterized the aromatic structure in AL. The characteristic peaks of the aromatic structure were also observed in the FTIR spectra of ALPU₁₀; this suggested the successful incorporation of AL into the PU chains.
2. The peak at 1210 cm^{-1} , with a shoulder at 1140 cm^{-1} in the PU spectrum, was ascribed to the stretching vibration of the C—O of ester in PU.¹⁸ However, the peak was split into two peaks at 1232 and 1105 cm^{-1} for ALPU₁₀. The increased intensity of the peak at 1105 cm^{-1} could be assigned to the ester groups formed between —OH in AL and —NCO. This further confirmed the reaction between AL and PU.
3. As shown in the PU spectrum, the peak at 3290 cm^{-1} , with a shoulder at 3490 cm^{-1} , could be ascribed to the stretching vibration of hydrogen-bonded —NH and free —NH, respectively.^{19–21} In addition, the bending vibration absorption peaks of the —NH group at 1525 cm^{-1} and the stretching

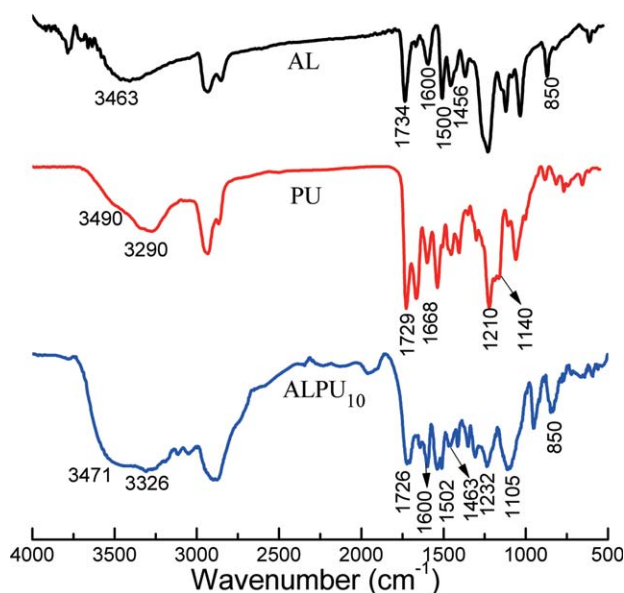


Figure 2. FTIR spectra of AL, PU, and ALPU₁₀. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

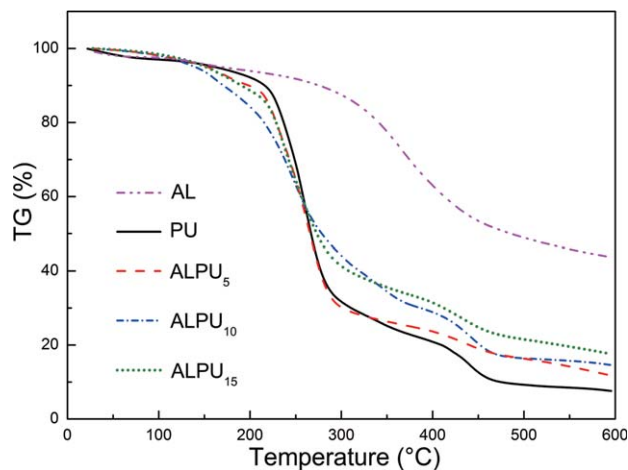


Figure 3. TGA curves of the AL, PU, and ALPU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

vibration absorption peaks of the free C=O at 1729 cm^{-1} and hydrogen-bonded C=O at 1668 cm^{-1} were also detected in the PU spectrum.

With the introduction of AL (ALPU₁₀), the intensities of the hydrogen-bonded —NH peak and hydrogen-bonded C=O peak were greatly reduced. We also observed from the ALPU₁₀ spectrum that the —NH peak shifted to a higher wave number at 3409 cm^{-1} . This indicated that the original hydrogen bonding in the PU chains was weakened with the incorporation of AL, and the aggregation of hard segments in PU was destroyed to some extent.

Thermal Properties

Figures 3 and 4 shows the TGA and DTG curves of the AL, PU, and ALPU. The decomposition temperatures at various mass loss percentages and the char residues are summarized in Table I. We observed that the AL decomposed in two stages, peaking around 145.1 and 367.2°C, respectively. The first stage, from 95.4 to 194.2°C, was attributed to the breaking of α - and β -aryl-alkyl-ether linkages, dehydration, and decarboxylation reactions; the second stage, from 203.8 to 526.0°C, was mainly attributed to the cleavage of C—C linkages in the AL structure.^{8,13,22}

We also observed that PU decomposed in two distinct stages. The first stage (200.1–306.3°C, with a peak at 260.2°C) was ascribed to the breaking of urethane bonds. The second stage (404.5–465.9°C, with a peak at 440.1°C) was assigned to the degradation of the soft segment PCL₁₀₀₀ in PU chains.^{22,23}

For the ALPU, a new decomposition stage around 150.0°C was observed. This stage was related to the first decomposition stage in AL.^{13,22} The second stage was attributed to the breaking of the urethane group formed between isocyanate and hydroxyl groups of AL, whereas the last stage was due to PCL₁₀₀₀.^{8,13,22,24} At the same time, we also found that the AL concentration played an important role in the high-temperature thermal stability; the decomposition temperature at 50% mass loss increased from 248.6 to 273.2°C when the AL concentration was increased from 0 to 15 wt %. A similar phenomenon was

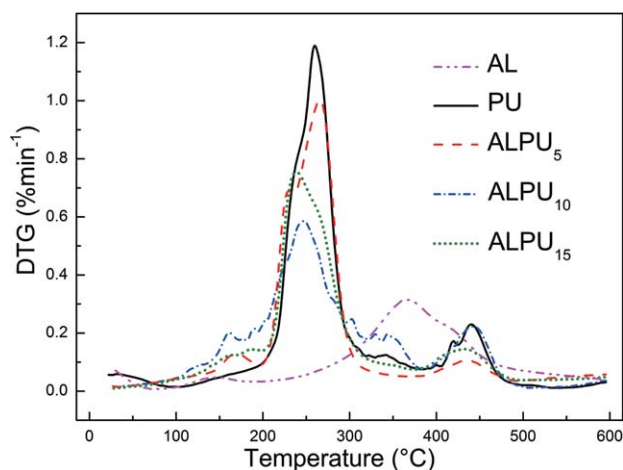


Figure 4. DTG curves of the AL, PU, and ALPU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

detected for the decomposition temperature at an 80% mass loss. In addition, the residues increased from 7.6 to 17.57% with the increase in the AL concentration. The aromatic ring content and crosslinking degree increased with increasing AL concentration; this thereby inhibited the degradation of the polymer and improved the ALPU thermal stability.²⁵ We could explain such behavior by taking into account the presence of highly active reactions between TDI, PCL₁₀₀₀, and AL.¹³

Particle Size and Morphology

The effects of the AL concentration on the particle size and dispersivity index (DPI) of the dispersions were analyzed by dynamic light scattering. As shown in Figure 5, the Z-average particle size of the dispersions increased from 36 to 260 nm with increasing AL concentration. In this research, part of PCL₁₀₀₀ was replaced by the ALPU surfactant. In contrast to bifunctional PCL₁₀₀₀, AL is a type of multifunctional polyol with a higher DPI, which has more reactive hydroxyl groups.^{26–28} It was reported that a starlike network with a lignin core was formed when nitrolignin was used to prepare waterborne PU.²⁹ Therefore, AL could act as crosslinking points for the PU chains and result in the transition from a linear structure to a three-dimensional network structure; this thereby increased the particle size of the aqueous ALPU dispersion. The model structure of ALPU is illustrated in Figure 6.

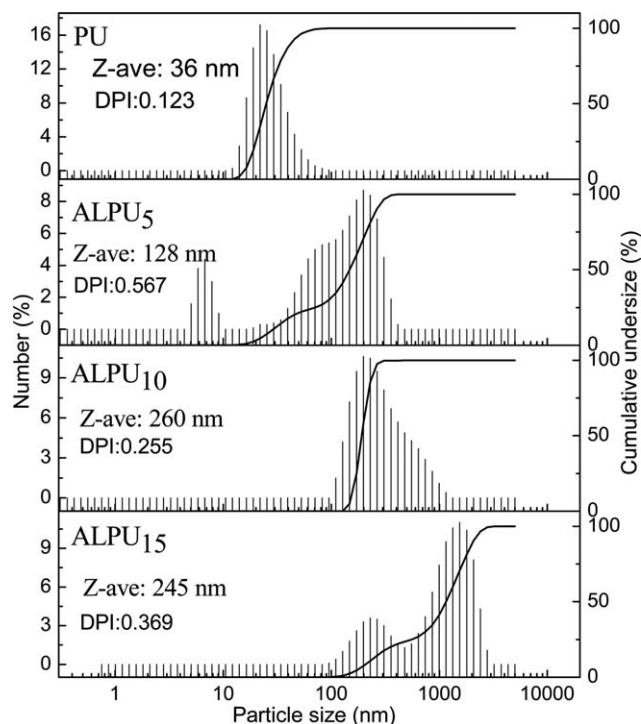


Figure 5. Particle sizes and distributions of the PU and ALPU dispersions with different AL concentrations.

Also, the ALPU₅ and ALPU₁₅ dispersions had bimodal distributions with DPI values of 0.567 and 0.369, respectively. When the AL content was 5 wt % (ALPU₅), the amount of AL was not enough for the crosslinking of all of the PU chains. There existed two kinds of colloidal particles in the ALPU₅ system, that is, pure PU colloidal particles corresponding to the smaller particle size peak and ALPU colloidal particles corresponding to the bigger particle size peak. When the AL content was 15 wt % (ALPU₁₅), the amount of AL may have been excessive for the PU system, aggregation among AL took place,⁸ and the amount of AL aggregates in each ALPU colloidal may have been different; this led to the bimodal distribution. On the basis of the previously mentioned results, the micellar structure of the PU and ALPU colloidal particles are shown in Figure 6.

At the same time, the structures of the PU, ALPU₅, ALPU₁₀, and ALPU₁₅ colloidal particles are shown in Figure 7. To

Table I. Results from the TGA and DTG of AL, PU, and ALPU

Sample	TGA (°C)				DTG	
	$D_{0.05}$	$D_{0.1}$	$D_{0.5}$	$D_{0.8}$	T_{max} (°C)	Residue (%)
AL	168.5	275.6	485.4	—	145.1, 367.2	43.93
PU	161.5	216.3	248.6	409.6	260.2, 440.1	7.6
ALPU ₅	153.5	198.5	265.8	440.2	167.5, 267.5, 435.6	11.73
ALPU ₁₀	140.0	170.6	278.8	451.9	162.0, 246.0, 440.8	14.58
ALPU ₁₅	151.6	190.5	273.2	539.1	238.6, 431.9	17.57

$D_{0.05}$, degradation temperature at 5% mass loss (the number 0.05 represents the mass loss, and the other D values are named in a similar manner); T_{max} , temperature at the maximum rate of mass loss.

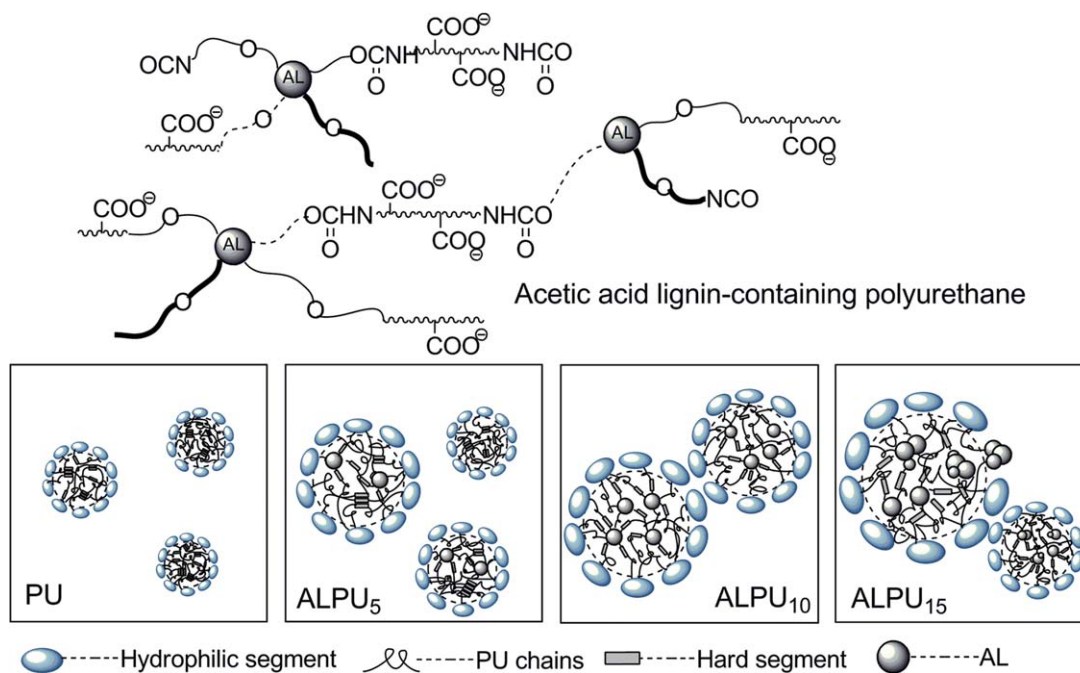


Figure 6. Models and micellar structures of the PU and ALPU colloidal particles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

enhance the contrast behavior of the particles, they were dyed with phosphotungstic acid. The TEM morphology confirmed that the surfactants aggregated spontaneously to form spherical

particles at a concentration of 10 g/L. Similar results were observed by Zheng et al.³⁰ for PU surfactants, and it was found that the size of the PU micelles increased several times when the

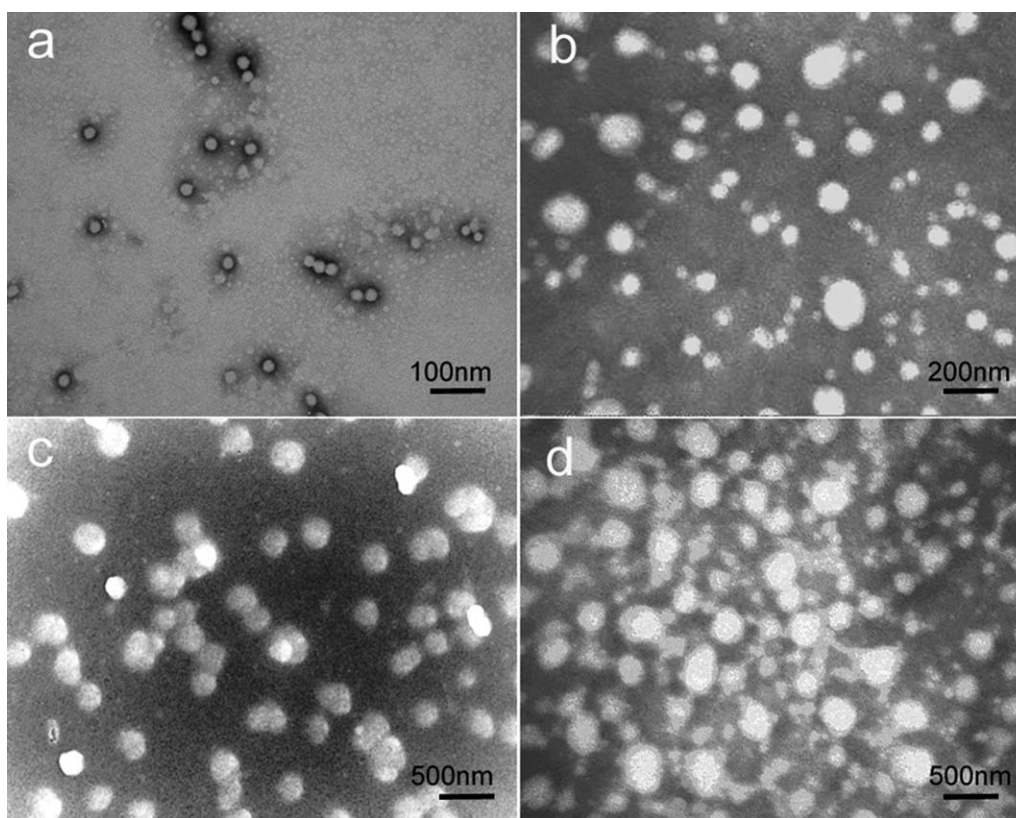


Figure 7. Structures of the PU and ALPU colloidal particles observed by TEM at a 10 g/L concentration: (a) PU, (b) ALPU₅, (c) ALPU₁₀, and (d) ALPU₁₅.

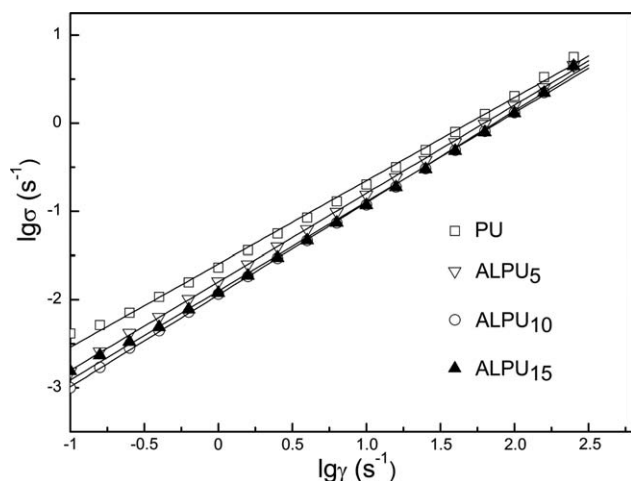


Figure 8. Linear relationship between $\log \sigma$ and $\log \gamma$ fitted by the Ostwald–de Wale Power law equation.

surfactant concentration was increased from 0.1 to 10 g/L. As shown in Figure 7, the ALPU₁₀ particles displayed a spherical morphology with a relative uniform particle size distribution, although for the ALPU₅ and ALPU₁₅ dispersions, particles with a heterogeneous distribution were observed. The results are in agreement with the particle size results obtained by the light-scattering technique.

Steady Rheological Behavior

In this study, the rheological behavior of the polymer dispersions could be well described by the Ostwald–de Wale Power law equation:³¹

$$\sigma = K\gamma^n \quad (1)$$

On both sides of the equation for logarithm

$$\log \sigma = \log K + n \log \gamma \quad (2)$$

where σ is the shear stress, γ is the shear rate, K is the consistency coefficient [if the K value is higher, the apparent viscosity (η_a) is higher], and n is the flow index ($n = 1$ is a Newtonian fluid, $n < 1$ is a pseudoplastic fluid, and the n value decreases with the enhancement of the pseudoplasticity). Here, the n and K values were calculated by linear regression analysis for the $\log \sigma$ versus $\log \gamma$ curves. Figure 8 illustrates the linear regression curves of the PU and ALPU dispersions with different AL concentrations, and the fitting parameters are displayed Table II. It was found that the n values of all of the dispersions were less than 1; this suggested that the PU and ALPU dispersions presented as pseudoplastic fluids. However, the n value increased and the K value decreased with increasing AL concentration to 10 wt %. This phenomena suggested the reduced pseudoplastic behavior and viscosity with increasing AL concentration.

Table II. n and K Values for the PU and ALPU Dispersions

Sample	n	K
PU	0.915	0.0086
ALPU ₅	0.993	0.0050
ALPU ₁₀	0.997	0.0034
ALPU ₁₅	0.980	0.0039

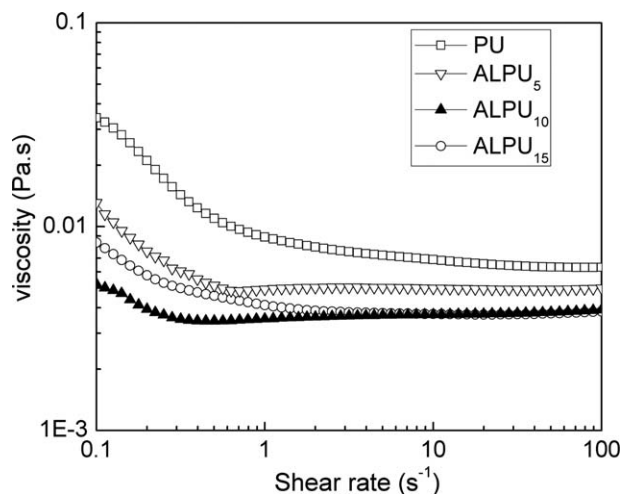


Figure 9. Viscosity versus γ curves of the PU and ALPU dispersions with different AL concentrations.

η_a as a function of γ for the PU and ALPU dispersions with different AL concentrations is shown in Figure 9. As shown in Figure 9, the PU dispersion displayed the highest viscosity and the most remarkable shear-thinning behavior, that is, the strongest pseudoplastic behavior; this was consistent with the results from the n and K values. In general, the viscosity arose from interactions among the particles in the dispersion. Therefore, we considered that there were many factors, such as the molecular architecture, molecular weight, solid content, and dispersion medium, which affected the rheology of the dispersions.³² The higher viscosity of the PU dispersion indicated stronger interactions between the PU colloidal particles at low γ , and the interactions could be destroyed with an increase in γ . A milder shear thinning at a low γ followed by a plateau region was observed for ALPU₅ and ALPU₁₀. η_a decreased with increasing AL concentration. With increasing AL concentration, the particle size increased, and this resulted in weakened hydrodynamic interactions, which were beneficial to the motion of the molecular chains and thereby decreased η_a .^{33,34} In addition, the introduction of AL destroyed the original hydrogen bonding in PU; therefore, the local entanglement PU network was disrupted, and the entanglement density of molecular chains was reduced; this resulted in a lower viscosity. On the other hand, the linear structure of the PU molecules was changed to a ramose structure with the introduction of AL. It was reported that ramose prepolymers in solvent had a lower viscosity, and the viscosity of a frizzer coil was lower than that of linear ones; this was more convenient than preparing a stable dispersion with a low viscosity.³⁵ Therefore, the decrease in the viscosity with increasing AL concentration could also be explained by the fact that relatively compact and globular structure could be formed when AL with multifunctional groups was incorporated into the PU chain. Asif et al.³² also reported that the viscosity of waterborne rein with a linear structure was higher than those resins, which had less entanglement in branched structure.

However, the viscosity of ALPU₁₅ increased at lower γ when the AL concentration was 15%; that is, there was more apparent shear thinning behavior at lower γ . This could be attributed to

the aggregation formed among AL, which was caused by the excessive AL concentration.

SURFACE ACTIVITY

The objective of this study was to prepare aqueous ALPU dispersions as polymeric surfactants, which could have extensive applications in the field of emulsion polymerization. Therefore, it was necessary to check whether the ALPU surfactants had the ability to reduce the surface tension with increasing surfactant concentration. It was reported by Homma et al.¹⁵ that lignosulfonate, a commercial lignin surfactant, showed 46 mN/m of surface tension at a critical micelle concentration (cmc) of 19.7 g/L. However, no depression of surface tension was observed with the addition of AL because of its insoluble properties in water. AL could be converted to an amphiphile by modification with hydrophilic monomer.^{14,15} Aqueous PU surfactants have been demonstrated to have amphiphilic structures similar to traditional surfactants. The polyol building blocks such as polyester diol formed the hydrophobic segments, whereas the hydrophilic centers were introduced via DMPA.¹⁶ In this research, part of PCL₁₀₀₀ was replaced by hydrophobic AL to prepare ALPU surfactants. The dependence of the surface tension on the PU and ALPU dispersion concentration is shown in Figure 10. We found that the surface tension decreased with increasing surfactant concentration and then leveled off. The inflection points, which corresponded to the cmc, were observed for all of the surfactants. The characteristic parameter of the surface activity and ZP for PU and ALPU are summarized in Table III. As expected, the cmc of the PU dispersion (6.81×10^{-3} g/L) was greater than ALPU₅ (1.86×10^{-3} g/L), ALPU₁₀ (1.06×10^{-3} g/L), and ALPU₁₅ (2.77×10^{-3} g/L). The cmc values were found to be much smaller than lignosulfonate, and it was also noteworthy that the ALPU surfactant with a higher AL concentration reduced the surface tension even at very low concentration levels. This could have been due to the high-molecular-weight and larger hydrophobic segment of the

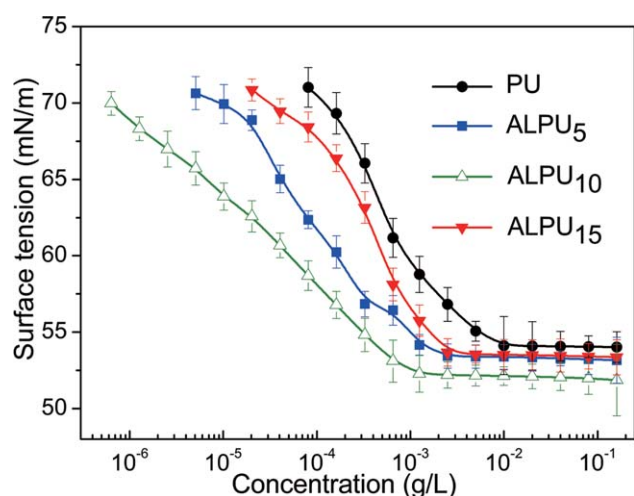


Figure 10. Surface tensions as a function of the concentration for PU, ALPU₅, ALPU₁₀, and ALPU₁₅ at 25°C, and the cmc was obtained by the tangent method for the inflection point. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

Table III. Surface-Active Parameters and ZP of the PU and ALPU Surfactants

Sample	cmc $\times 10^3$ (g/L)	γ_{cmc} (mN/m)	ZP (mV)
PU	6.81	54.64	-24.4
ALPU ₅	1.86	53.56	-28.6
ALPU ₁₀	1.06	52.41	-34.9
ALPU ₁₅	2.77	53.66	-26.4

γ_{cmc} , surface tension at critical micelle concentration.

aqueous ALPU surfactants.¹⁷ More crosslinking points were introduced in the ALPU system when PCL₁₀₀₀ was replaced by multifunctional AL (as shown in Figure 6); these were responsible for the increased hydrophobic segments. In addition, the tendency for micelle formation was strengthened at lower concentrations with increasing hydrophobic content; this led to an increase in the solubilization capacity of the PU surfactants.³⁶ The ability to reduce the surface tension increased with increasing AL concentration to 10 wt %. This also stemmed from the increasing ratio of the hydrophobic segment because more hydrophobic chains were oriented on the surface with their hydrophilic segments dissolved in the aqueous solution; this consequently reduced the surface tension.³⁶⁻³⁹ On the other hand, as demonstrated by the FTIR results, the aggregation of hard segments in PU was destroyed to some extent with the addition of 10 wt % AL, and a starlike network was formed;⁴⁰ this may have been beneficial for the uniform and denser distribution of hydrophilic segments on the surface of the micelles and thereby reduced the surface tension.⁴¹ This was confirmed by the increased ZP for ALPU with higher AL concentrations.

However, the surface tension increased when the AL concentration was further increased to 15 wt %. This indicated that a moderate content of hydrophobic segments was beneficial for decreasing the surface tension, but an excessive hydrophobic content increased the surface tension. Thereby, it is important to control the hydrophilic/hydrophobic ratio and the polymer structure when designing a surfactant. In addition, with regard to ALPU₁₅, the formed AL aggregation may have inhibited the local motion of molecular motion; therefore, the structure of the uniformly distributed hydrophilic segment was destroyed to some extent, and the surface tension was increased.

CONCLUSIONS

Aqueous ALPU surfactants were successfully synthesized with PCL₁₀₀₀ and multifunctional acetic AL as a hydrophobic segment and DMPA as a hydrophilic segment. FTIR spectroscopy and TGA-DTG demonstrated the presence of AL in the ALPU chains. This also indicated that the original hydrogen bonding in the PU chains was weakened with the incorporation of AL, and the aggregation of hard segments in PU was destroyed to some extent. TEM morphology confirmed that the surfactants aggregated spontaneously to form spherical micelles at a concentration of 10 g/L. The Z-average particle size of the dispersions increased from 36 to 260 nm with increasing AL concentration. Unimodal distribution was detected for ALPU₁₀, whereas the ALPU₅ and ALPU₁₅ dispersions had a bimodal distribution with higher DPI

values of 0.567 and 0.369. This was ascribed to the heterogeneous crosslinking between AL and PU at lower and higher AL concentrations, and a moderate amount of AL was important for the preparation of an ALPU surfactant with uniformly distributed particles. The steady rheological behavior suggested that the PU and ALPU dispersions presented as pseudoplastic fluids. The shear-thinning behavior was weakened, and the viscosity was decreased with increasing AL concentration to 10 wt %. However, the viscosity of ALPU₁₅ increased at lower γ when the AL concentration was 15%; that is, there was more apparent shear-thinning behavior at lower γ . This could be assigned to the aggregation formed among AL, which was caused by excessive AL concentration. With 10 wt % AL addition, cmc decreased from 6.81×10^{-3} to 1.06×10^{-3} g/L, and the surface tension decreased. The presence of AL in the PU chains enhanced the hydrophobic segment and thereby improved the surface activity. However, the surface tension increased when the AL concentration was further increased to 15 wt %. This indicated that moderate content of hydrophobic segment was beneficial for decreasing the surface tension, but an excessive hydrophobic content increased the surface tension. Thereby, it is important to control the hydrophilic/hydrophobic ratio when designing a surfactant.

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