

## Vegetable Oil Based Fatty Amide as Hydrophobes in Associative Thickener

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**ABSTRACT:** A vegetable oil based high performance associative thickener has been designed and synthesized from a hydroxyl functional soybean oil derivative (hydroxyl value 159 mg KOH/g). An isocyanate-terminated prepolymer was synthesized from polyethylene glycol (PEG) and isophorone diisocyanate (IPDI), and end-capped with the hydroxyl functional soybean oil derivative to prepare a hydrophobically modified ethoxylated polyurethane (HEUR) thickener. The synthesis was monitored by infrared spectroscopy via the isocyanate peak at 2258–2270  $\text{cm}^{-1}$ . Thickener efficiency was tested with a commercial styrene–acrylic latex UCAR<sup>TM</sup> 443, an acrylic latex Acronal<sup>®</sup> Optive 130 and an alkyd emulsion WorléeSol<sup>®</sup> E 150W. High thickening efficiency was noted in the low shear region, e.g., 0.5 wt % HEUR loading with UCAR 443 increased viscosity from 0.66 P to 3.06 P at a shear rate of 1333  $\text{s}^{-1}$ . The effect of soybean oil fatty amide based rheology modifier as additive in coating was evaluated in terms of gloss, viscosity, sag resistance, and flow and leveling properties. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 1530–1538, 2013

**KEYWORDS:** biodegradable; coatings; polyurethanes; rheology; synthesis and processing

Received 15 January 2013; accepted 10 March 2013; Published online 30 April 2013

**DOI:** 10.1002/app.39284

### INTRODUCTION

Associative thickeners, part of the class of rheology modifiers, are critical additives for latex coating formulations where they are employed to control the viscosity, improve storage stability, facilitate pigment suspension, and favor application characteristics.<sup>1–5</sup> Clays, cellulose derivatives, acrylics, and urethanes are used as thickeners in latex paints.<sup>1</sup> Associative thickeners employed in waterborne coatings include cellulose derivatives, hydrophobically modified alkali soluble emulsions (HASE), and hydrophobically modified ethoxylated urethanes (HEURs). Hydrophobically modified cellulosics,<sup>1,6</sup> acrylics,<sup>1,7,8</sup> and urethanes<sup>1,7,9–11</sup> constitute the building block materials for such associative thickeners. The associative thickening mechanism is primarily due to interactions between the hydrophobic portions of thickener and latex particles, but is also influenced by surfactants, coalescing solvents, and pigments. The resulting network of polymer chains with pseudo crosslinks yields a pseudoplastic rheological profile with anti-sag and anti-settling properties. HEURs are gaining commercial value due to their characteristic thickening efficiency even at very low levels of loading, improved aqueous medium compatibility and robustness in ionic environments. HEURs consist of polyethylene oxide (PEO) blocks linked via urethane moieties and end-capped with

long alkyl chains such that the PEO blocks act as hydrophilic segments and the long alkyl chains function as flexible hydrophobes.<sup>9–12</sup> Commercial HEUR rheology modifiers are currently based on petroleum derivatives. In this study, vegetable oil derivatives were synthesized to function as hydrophobes in the bio-based HEURs.

Vegetable oils are of increasing interest as renewable, environmentally friendly, non-toxic, and biodegradable resources as they can be modified in several different ways.<sup>13,14</sup> Epoxidation of unsaturated vegetable oils yields commercially viable products.<sup>15,16</sup> The triglyceride ester moieties are amenable to modification via transesterification, amidation, and alcoholysis.<sup>17–20</sup> Conversion of vegetable oils to vegetable oil macromonomers (VOMMs) yields bio-based comonomers for synthesizing auto-oxidizable latexes.<sup>21</sup> Castor oil and lesquerella oil contain ~89% ricinoleic acid and ~69% lesquerolic acid, respectively, both of which possess a secondary hydroxyl group that offers an additional avenue for modification.<sup>22–25</sup> HEURs based on either castor oil or lesquerella oil will result in a combination of unreactive and reactive triglycerides. A soybean oil-based fatty amide containing a hydroxyl group was synthesized earlier to develop bio-based ultraviolet (UV) inhibitors.<sup>20</sup> The same fatty amide was employed to synthesize a bio-based HEUR for

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**Table I.** Commercial Latexes Evaluated

Latex	Type of latex	Solid content	Particle size (nm)
UCAR 443	Styrene-acrylic	41%	184 ± 5
Acronal Optive 130	All acrylic	50%	145 ± 4
WorléeSol E 150 W	Alkyd dispersion	40%	70 ± 2

evaluation as rheology modifier in waterborne architectural coatings. An added advantage of this bio-based thickener is that its unsaturated fatty acid content enables auto-oxidative cross-linking to occur upon application. There is no report in the current literature regarding vegetable oil-based HEUR thickeners. In this article, we report on the synthesis and characterization of HEURs synthesized with soybean oil derived hydrophobes.

## MATERIALS AND METHODS

### Materials

Soybean oil was purchased from Alnor Oil Company. *N*-methyl ethanolamine, sodium methoxide, and polyethylene glycol (PEG) of molecular weight 6000 were procured from Acros Organics. Anhydrous magnesium sulfate, methanol, and toluene were purchased from Fischer Scientific. PEGs were refluxed in toluene using a Dean–Stark trap to remove moisture prior to polyurethane synthesis. The soybean oil derivative was synthesized in our laboratory. Isophorone diisocyanate (IPDI) was procured from Bayer (trade name Desmodur® I). Dibutyltin dilaurate (DBTDL), and diethylene glycol monobutyl ether were purchased from Aldrich. UCAR 443 was procured from Dow Chemical Company. Acronal Optive 130 was obtained from BASF Chemical Company. WorléeSol E 150 W was procured from Worlée-Chemie GmbH. A high shear commercial thickener, Aquaflow™ NHS 300 (hydrophobically modified polyether) and a low shear commercial thickener, Drewthix 864 (hydrophobically modified urethane) were obtained from Aqualon (Hercules, Inc.) and Drew Industrial Specialty Additives, respectively.

### Synthesis of Hydrophobically Modified Ethoxylated Polyurethane (HEUR)

The soybean oil precursor synthesis has been reported previously.<sup>20</sup> In a 1000 mL round bottom flask, 500 g soybean oil was heated to 60°C, and sodium methoxide (50 g, 25% solution in methanol) and *N*-methyl ethanolamine (125.46 g) were added to the flask. The reaction was monitored via FTIR spectroscopy by following the disappearance of the ester peak (1746 cm<sup>-1</sup>) and appearance of the amide peak (1627 cm<sup>-1</sup>). The reaction product (soyamide) was washed with brine solution to remove glycerol and excess *N*-methyl ethanolamine. The soyamide was dried with magnesium sulfate and filtered (product yield 90%). The hydroxyl functional soyamide was characterized via FTIR and NMR spectroscopy and its hydroxyl value was determined via ASTM D 4274 - 94, Test method C to be 159 mg KOH/g.

In a 1000 mL three-neck round bottom flask, 150 g of PEG 6000 and 400 mL toluene were refluxed at 112°C under nitrogen purge using a Dean–Stark trap to remove water. After 18 h of reflux, the temperature was reduced to 80°C, and the catalyst, DBTDL, was added to the flask. Part of the required IPDI was added to the flask while maintaining the NCO:OH at 0.85. After the reaction had proceeded for an hour, the remaining IPDI was added to raise the NCO:OH to be 1.60 and generate a *N*-NCO terminated prepolymer. The hydroxyl functional soybean oil derivative was then added in slight excess (NCO:OH = 0.89) to ensure complete consumption of the isocyanate groups. The reaction was continued till no more isocyanate peaks were visible in the IR spectrum of the product.

### Preparation of HEUR Dispersions and Latex Blends

The soyamide-based HEUR was dispersed in deionized water with 15 wt % diethylene glycol monobutyl ether to yield a dispersion of 25 wt % solids. For performance evaluation, the HEUR was blended with each commercial latex using a mechanical stirrer at 1000 rpm. Characteristic parameters of the commercial latexes are summarized in Table I.

### Characterization Methods

FTIR spectra were recorded with a Digilab FTIR spectrometer over a frequency range of 600–4000 cm<sup>-1</sup>. Samples were analyzed as thin films over sodium chloride discs. <sup>1</sup>H and <sup>13</sup>C NMR spectra of soybean oil and soyamide were obtained using a Varian Mercury NMR spectrometer operating at a frequency of 300.13 and 75.5 MHz for <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, respectively. Typical <sup>1</sup>H NMR acquisition parameters were as follows: recycle delay of 1 s, 7.1 μs pulse width corresponding to a 45° flip angle, and acquisition time of 2 s. <sup>13</sup>C NMR acquisition parameters were: 1 s recycle delay, 7.8 μs pulse width corresponding to 45° flip angle, and acquisition time of 1.8 s. All chemical shifts (indicated as δ ppm) were referenced either automatically by the software (VNMR 6.1C) or manually using the resonance frequency of the deuterated solvent (DMSO-*d*<sub>6</sub> or CDCl<sub>3</sub>). Individual NMR spectra of *N*-methyl ethanolamine, soybean oil, soyamide, and IPDI were obtained in CDCl<sub>3</sub>, while HEUR was analyzed in DMSO-*d*<sub>6</sub>. NMR spectral data for the starting point chemicals and the respective products are summarized as follows.

*N*-Methyl ethanolamine (<sup>1</sup>H CDCl<sub>3</sub>, δ ppm): 7.26 (CDCl<sub>3</sub>), 3.47 (*t*, 2H, –N–CH<sub>2</sub>–CH<sub>2</sub>–OH), 2.50 (*t*, 2H, –N–CH<sub>2</sub>–CH<sub>2</sub>–OH), and 2.25 (*s*, 3H, H<sub>3</sub>C–N–CH<sub>2</sub>–CH<sub>2</sub>–OH); (<sup>13</sup>C CDCl<sub>3</sub>, δ ppm): 77.22 (CDCl<sub>3</sub>), 58.94 (–N–CH<sub>2</sub>–CH<sub>2</sub>–OH), 52.75 (–N–CH<sub>2</sub>–CH<sub>2</sub>–OH), and 34.94 (H<sub>3</sub>C–N–CH<sub>2</sub>–CH<sub>2</sub>–OH).

Soybean oil (<sup>1</sup>H CDCl<sub>3</sub>, δ ppm): 7.26 (CDCl<sub>3</sub>, δ ppm), 5.35 (*m*, –CH=CH–), 5.27 (*m*, –CO–O–CH<sub>2</sub>–CH(O–CO–)–CH<sub>2</sub>(O–CO–)), 4.35–4.08 (*m*, –CO–O–CH<sub>2</sub>–CH(O–CO–)–CH<sub>2</sub>(O–CO–)), 2.77 (*m*, –CH=CH–CH<sub>2</sub>–CH=CH–), 2.32 (*t*, –O–CO–CH<sub>2</sub>–), 2.04 (*m*, –CH=CH–CH<sub>2</sub>–), 1.61 (*m*, –O–CO–CH<sub>2</sub>–CH<sub>2</sub>–), 1.28 (*m*, –CH<sub>2</sub>–), 0.97 (*t*, –CH=CH–CH<sub>2</sub>–CH<sub>3</sub>), and 0.88 (*m*, –CH<sub>2</sub>–CH<sub>3</sub>); (<sup>13</sup>C CDCl<sub>3</sub>, δ ppm): 172.51 (–O–CO–CH<sub>2</sub>–), 131.58–126.97 (–CH=CH–), 77.22 (CDCl<sub>3</sub>), 68.83 (–CO–O–CH<sub>2</sub>–CH(O–CO–)–CH<sub>2</sub>(O–CO–)), 61.89 (–CO–O–CH<sub>2</sub>–CH(O–CO–)–CH<sub>2</sub>(O–CO–)), 33.80 (–O–CO–CH<sub>2</sub>–), 31.85 (ω<sub>3</sub>–CH<sub>2</sub>–), 31.42 (ω<sub>3</sub>–CH<sub>2</sub>–), 29.76–28.50 (CH=CH–CH<sub>2</sub>–, –CH<sub>2</sub>–), 27.06

(-CH=CH-CH<sub>2</sub>-CH=CH-), 25.64–24.33 (-O-CO-CH<sub>2</sub>-CH<sub>2</sub>-), 22.47 ( $\omega$ 2 -CH<sub>2</sub>-), 14.13 ( $\omega$ 1-CH<sub>3</sub>), and 13.97 ( $\omega$ 1 -CH<sub>3</sub>).

Soyamide (<sup>1</sup>H CDCl<sub>3</sub>,  $\delta$  ppm): 7.26 (CDCl<sub>3</sub>), 5.35 (*m*, -CH=CH-), 3.75 (*t*, 2H, -N-CH<sub>2</sub>-CH<sub>2</sub>-OH), 3.58–3.40 (*d t*, 2H, -N-CH<sub>2</sub>-CH<sub>2</sub>-OH), 3.13–2.89 (*d s*, 3H, -N-CH<sub>3</sub>), 2.77 (*m*, -CH=CH-CH<sub>2</sub>-CH=CH-), 2.35 (*m*, -N-CO-CH<sub>2</sub>-), 2.04 (*m*, -CH=CH-CH<sub>2</sub>-), 1.61 (*m*, -N-CO-CH<sub>2</sub>-CH<sub>2</sub>-), 1.28 (*m*, -CH<sub>2</sub>-), 0.97 (*t*, -CH=CH-CH<sub>2</sub>-CH<sub>3</sub>), and 0.88 (*m*, 3H, -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>); (<sup>13</sup>C CDCl<sub>3</sub>,  $\delta$  ppm): 174.55 (-N-CO-CH<sub>2</sub>-), 174.0 (-N-CO-CH<sub>2</sub>-), 131.58–126.97 (-CH=CH-), 77.22 (CDCl<sub>3</sub>), 60.61 (-N-CH<sub>2</sub>-CH<sub>2</sub>-OH), 59.39 (-N-CH<sub>2</sub>-CH<sub>2</sub>-OH), 52.06 (-N-CH<sub>2</sub>-CH<sub>2</sub>-OH), 50.77 (-N-CH<sub>2</sub>-CH<sub>2</sub>-OH), 36.67 (-N-CH<sub>3</sub>), 33.82–32.82 (-N-CO-CH<sub>2</sub>-), 31.85 ( $\omega$ 3 -CH<sub>2</sub>-), 31.42 ( $\omega$ 3 -CH<sub>2</sub>-), 29.76–28.50 (CH=CH-CH<sub>2</sub>-, -CH<sub>2</sub>-), 27.06 (-CH=CH-CH<sub>2</sub>-CH=CH-), 25.70–24.77 (-N-CO-CH<sub>2</sub>-CH<sub>2</sub>-), 22.47 ( $\omega$ 2 -CH<sub>2</sub>-), 14.13 ( $\omega$ 1 -CH<sub>3</sub>), and 13.97 ( $\omega$ 1 -CH<sub>3</sub>).

Isophorone diisocyanate (<sup>13</sup>C CDCl<sub>3</sub>,  $\delta$  ppm): 122.80–121.96 (-N=C=O), 77.22 (CDCl<sub>3</sub>), 56.60–50.51 (-H<sub>2</sub>C-N=C=O, H<sub>2</sub>C-CH(CH<sub>2</sub>)-N=C=O), 48.44–47.60 (O=C=N-CH(CH<sub>2</sub>-)(CH<sub>2</sub>-C(CH<sub>3</sub>)<sub>2</sub>-), 45.98–45.65 (O=C=N-CH<sub>2</sub>-C(CH<sub>3</sub>)<sub>2</sub>-)(-CH<sub>2</sub>-C(CH<sub>3</sub>)<sub>2</sub>-), 43.53–43.08 (O=C=N-CH(-CH<sub>2</sub>-)-CH<sub>2</sub>-C(CH<sub>3</sub>)<sub>2</sub>-)(-CH<sub>2</sub>-N=C=O), 36.43–36.21 (O=C=N-CH<sub>2</sub>-C(CH<sub>3</sub>)<sub>2</sub>-)(-CH<sub>2</sub>-), 34.47 (-CH<sub>2</sub>-C(CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>-), 31.62 (-CH<sub>2</sub>-C(CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>-), 29.56 (O=C=N-CH<sub>2</sub>-C(CH<sub>3</sub>)<sub>2</sub>-)(-CH<sub>2</sub>-), 27.27–26.71 (CH<sub>2</sub>-C(CH<sub>3</sub>)<sub>2</sub>-(-CH<sub>2</sub>-)), 22.96 (O=C=N-CH<sub>2</sub>-C(CH<sub>3</sub>)<sub>2</sub>-(-CH<sub>2</sub>-)).

HEUR (<sup>13</sup>C DMSO-*d*<sub>6</sub>,  $\delta$  ppm): 172.28 (-N-CO-CH<sub>2</sub>-), 156.99–156.53 (-O-CH<sub>2</sub>-CH<sub>2</sub>-O-C(O)-NH-, -CH<sub>2</sub>-C(O)-N(CH<sub>3</sub>)-CH<sub>2</sub>-CH<sub>2</sub>-O-C(O)-NH-), 129.72–128.07 (-CH=CH-), 72.00–65.00 (-O-CH<sub>2</sub>-CH<sub>2</sub>-O-, -O-CH<sub>2</sub>-CH<sub>2</sub>-O-C(O)-NH-), 63.00–60.00 (-CH<sub>2</sub>-C(O)-N(CH<sub>3</sub>)-CH<sub>2</sub>-CH<sub>2</sub>-O-C(O)-NH-), 54.37 (-H<sub>2</sub>C-NH-C(O)-O-CH<sub>2</sub>-CH<sub>2</sub>-N(CH<sub>3</sub>)-CO-CH<sub>2</sub>-, H<sub>2</sub>C-CH(CH<sub>2</sub>)-NH-C(O)-O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 51.33 (-H<sub>2</sub>C-NH-C(O)-O-CH<sub>2</sub>-CH<sub>2</sub>-N(CH<sub>3</sub>)-CO-CH<sub>2</sub>-), 48.38 (-O-(O)C-NH-CH(-CH<sub>2</sub>-)(-CH<sub>2</sub>-C(CH<sub>3</sub>)<sub>2</sub>-), 46.61–45.51 (-O-(O)C-NH-CH<sub>2</sub>-C(CH<sub>3</sub>)<sub>2</sub>-)(-CH<sub>2</sub>-C(CH<sub>3</sub>)<sub>2</sub>-), 43.91 (-O-(O)C-NH-CH(-CH<sub>2</sub>-)-CH<sub>2</sub>-C(CH<sub>3</sub>)<sub>2</sub>-)(-CH<sub>2</sub>-NH-C(O)-O-), 39.33 (DMSO), 36.25–35.83 (-N-CH<sub>3</sub>-, -O-(O)C-NH-CH<sub>2</sub>-C(CH<sub>3</sub>)<sub>2</sub>-), 34.95 (-CH<sub>2</sub>-C(CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>-), 33.50–32.58 (-N-CO-CH<sub>2</sub>-), 31.89–31.33 ( $\omega$ 3 -CH<sub>2</sub>-,  $\omega$ 3 -CH<sub>2</sub>-, -CH<sub>2</sub>-C(CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>-), 29.85–28.87 (CH=CH-CH<sub>2</sub>-, -CH<sub>2</sub>-, -O-(O)C-NH-CH<sub>2</sub>-C(CH<sub>3</sub>)<sub>2</sub>-)(-CH<sub>2</sub>-), 27.44–26.58 (-CH=CH-CH<sub>2</sub>-CH=CH-, CH<sub>2</sub>-C(CH<sub>3</sub>)<sub>2</sub>-(-CH<sub>2</sub>-)), 25.50–24.01 (-N-CO-CH<sub>2</sub>-CH<sub>2</sub>-), 23.10 (-O-(O)C-NH-CH<sub>2</sub>-C(CH<sub>3</sub>)<sub>2</sub>-)(-CH<sub>2</sub>-), 22.10 ( $\omega$ 2 -CH<sub>2</sub>-), 13.86 ( $\omega$ 1-CH<sub>3</sub>).

Molecular weight of fatty amide based HEUR was determined by gel permeation chromatography (GPC). GPC was conducted on a Varian PL GPC-50 equipped with dual angle light scattering, differential pressure, and refractive index detectors. Tetrahydrofuran (THF) was employed as the eluent at a flow rate of 0.5 mL/min at 40°C and series of three Polymer Laboratory columns (Polypore®, Oligopore®, and one 50 Å PLGel® column) and a guard column (Polypore®). Mass recovery was assumed to be 100% for analysis.

DSC analysis of fatty amide based HEUR was conducted on a DSC Q 2000 from TA Instruments and the data was processed

via Universal Analysis 2000 software. ~5.5 mg of sample was weighed into an aluminum pan and DSC was conducted in a temperature range of -90 to 150°C at a heating rate of 10°C/min and cooling rate of 5°C/min under N<sub>2</sub> environment.

The particle size distribution of commercial latexes was measured using a Microtrac UPA 250 dynamic light scattering analyzer. The viscosity of latex and thickener blends was measured at ambient temperature using Brookfield, Cap 2000 + Viscometer equipped with a cone and plate geometry (cone angle 0.45°, cone radius 1.511 cm). A Rheometric Scientific SR 5000 with bob-cup geometry (inside cup diameter 24.6047 mm, outside cup diameter 31.9960 mm, inside bob diameter 27.0899 mm, outside bob diameter 29.0863 mm, and bob length 44.2656 mm) was used to measure low shear rheology of the blends. The same instrument with cone and plate geometry (cone diameter 25 mm, cone angle 0.0999 radian, cone and plate gap 0.01 mm) was also used to test the dynamic rheology of the samples, and measurements were performed in a linear viscoelastic region.

Specular gloss of coatings was tested at 20° and 60°. Coating consistency was evaluated by determining the Stormer viscosity via ASTM D562-01 and high shear viscosity via ASTM D 4287-00 method. Sag resistance was tested using a multi-notch applicator via ASTM D 4400-99. Flow and leveling properties were evaluated according to ASTM D4062-99.

## RESULTS AND DISCUSSION

### Soyamide Synthesis

Figure 1 displays the Fourier transform infrared (FTIR) spectra of *N*-methyl ethanolamine, soybean oil, and its amide derivative. *N*-Methyl ethanolamine showed its characteristics bands at 3500–3200, 2934–2870, 1540, 1482, 1387, 1301, 1258, 1045, and 820 cm<sup>-1</sup> due to the presence of OH and N-H stretchings, C-H asymmetric, and symmetric stretchings of CH<sub>2</sub> and CH<sub>3</sub>, N-H deformation of secondary amine, CH<sub>2</sub> scissoring, CH<sub>3</sub> bending, CH<sub>2</sub> twisting, CH<sub>2</sub> wagging, C-N and C-O stretchings, and N-H wagging respectively.<sup>26</sup> Absorption bands at 3009, 2926, 2854, 1744, 1464, 1377, 1238, 1164, 1099 and 725 cm<sup>-1</sup> due to C-H stretching of CH=CH, C-H asymmetric stretching of CH<sub>2</sub>, C-H symmetric stretching of CH<sub>2</sub>, C=O stretching of ester (glyceride), CH<sub>2</sub> scissoring, CH<sub>3</sub> bending, CH<sub>2</sub> twisting, O-C-C stretching of ester, C-O stretching, and CH<sub>2</sub> rocking, respectively, were observed in the spectrum of soybean oil.<sup>13</sup> In the spectrum of reaction product from soybean oil and *N*-methyl ethanolamine, new bands at 3399 and 1627 cm<sup>-1</sup> attributed to OH (H-bonded) stretching, and C=O stretching of amide, respectively, were observed. Additionally, glyceride ester carbonyl (C=O) and O-C-C bands at 1744 and 1164 cm<sup>-1</sup>, respectively, were not noticed in the product spectrum. The appearance of peaks at 3399 and 1627 cm<sup>-1</sup> and disappearance of peaks at 1746 and 1164 cm<sup>-1</sup> confirmed the formation of fatty amide from the co-reaction with soybean oil.

In the <sup>1</sup>H NMR spectrum of soybean oil, the glycerol methine proton at  $\delta$  5.27 ppm and glycerol methylene protons at  $\delta$  4.35–4.08 ppm were observed (Figure 2).<sup>13</sup> Proton signals at  $\delta$  3.47, 2.50, and 2.25 in the spectrum of *N*-methyl ethanolamine

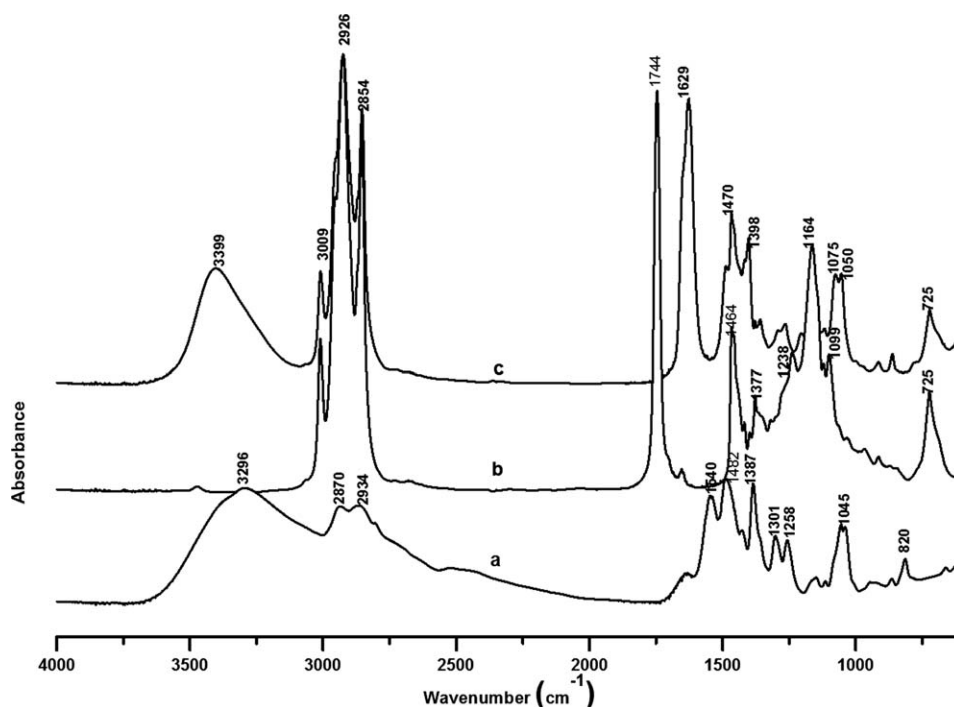


Figure 1. FTIR spectra of (a) *N*-methyl ethanolamine, (b) soybean oil and (c) soyamide.

were observed due to methylene protons adjacent to OH, methylene protons attached to nitrogen of  $-N-CH_2-CH_2-OH$ , and methyl protons of  $H_3C-N-$  respectively. Glycerol methine and methylene proton signals were not observed in the product spectrum. Additionally, methylene protons adjacent to the  $-OH$  group of  $-N-CH_2-CH_2-OH$ , methylene protons adjacent to nitrogen of  $-N-CH_2-CH_2-OH$ , and methyl protons of  $-N-CH_3$  of *N*-methyl ethanolamine were noted with a shifting at higher  $\delta$  3.75, 3.58–3.40, and 3.13–2.89 ppm in the spectrum of product as expected. These indeed verified soyamide synthesis from soybean oil and

*N*-methyl ethanolamine. The integration on  $^1H$  NMR spectrum resulted in the ratio, 0.67 of protons  $-N-CH_2-CH_2-OH$  to terminal protons  $-CH_2-CH_3$ , which was very close to expected value 0.66 and 1.03 of protons  $N-CH_3$  to terminal protons  $-CH_2-CH_3$ .

Soyamide synthesis was further confirmed by  $^{13}C$  NMR spectrum of *N*-methyl ethanolamine, soybean oil and soyamide in  $CDCl_3$  (Figure 3). Glycerol methine and methylene carbons in soybean oil were observed at  $\delta$  68.84 and 61.97 ppm, respectively. Those signals were no longer noticed in the  $^{13}C$  NMR

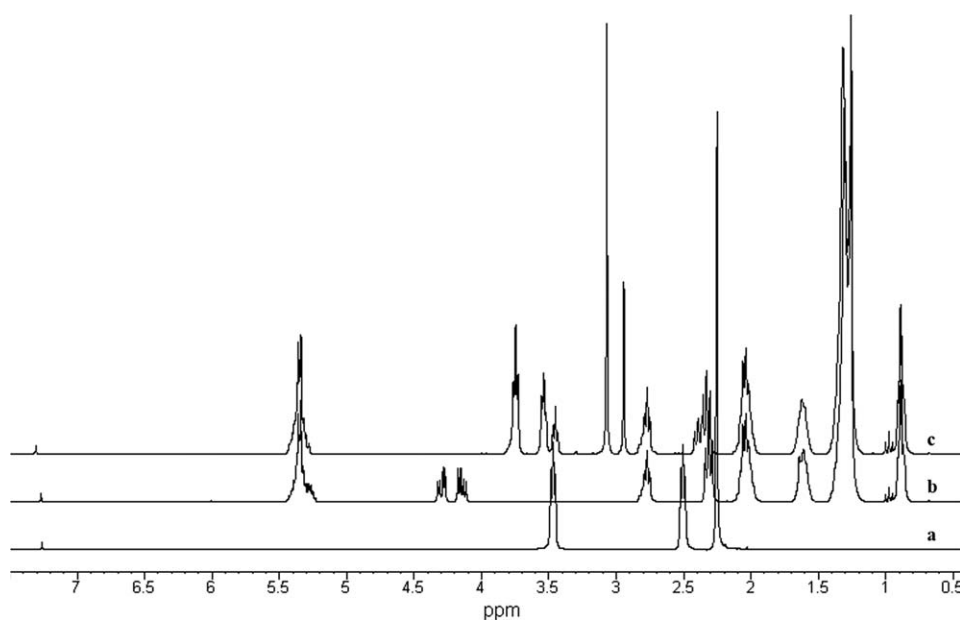
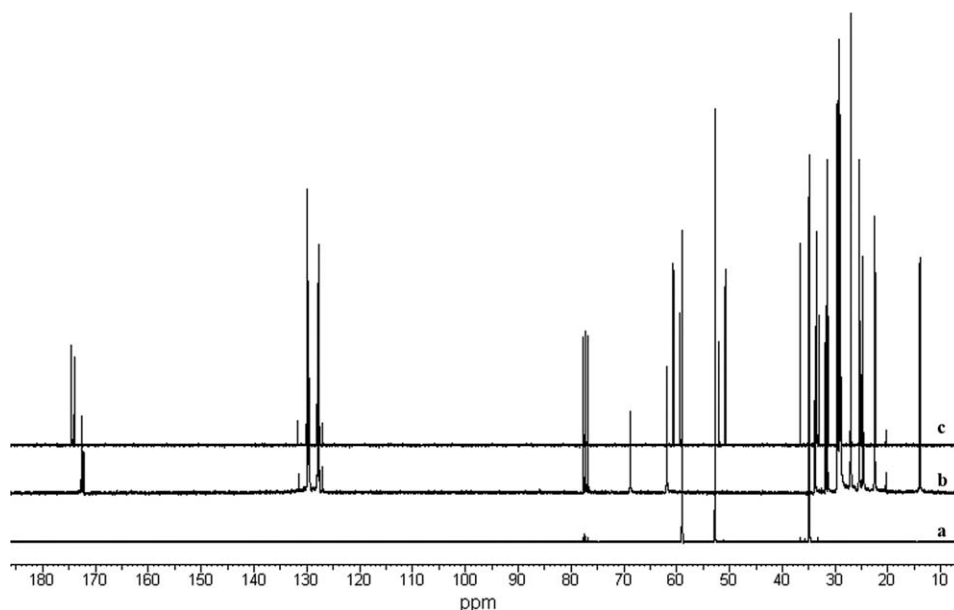


Figure 2.  $^1H$  NMR spectra of (a) *N*-methyl ethanolamine, (b) soybean oil and (c) soyamide.



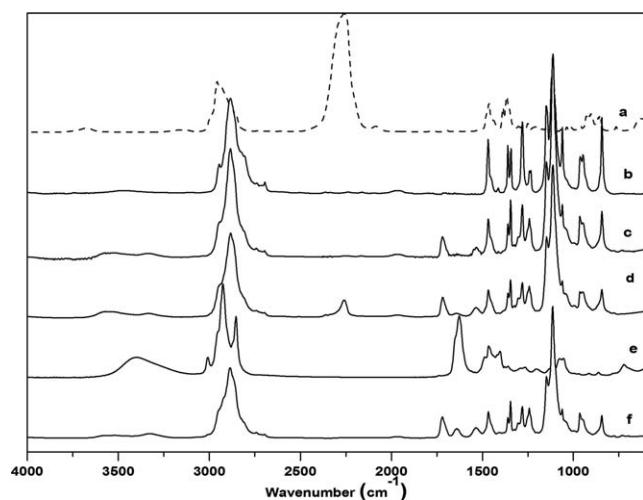


**Figure 3.**  $^{13}\text{C}$  NMR spectra of a) *N*-methyl ethanolamine, b) soybean oil and c) soyamide.

spectrum of soyamide. New signals in spectrum of amide derivative were noted at  $\delta$  60.61–59.39 ppm for methylene carbon attached to OH of  $-\text{N}-\text{CH}_2-\text{CH}_2-\text{OH}$ , at  $\delta$  52.06–50.77 ppm for methylene carbon attached to nitrogen of  $-\text{N}-\text{CH}_2-\text{CH}_2-\text{OH}$ , and at  $\delta$  36.67 ppm for methyl carbon of  $-\text{N}-\text{CH}_3$ .

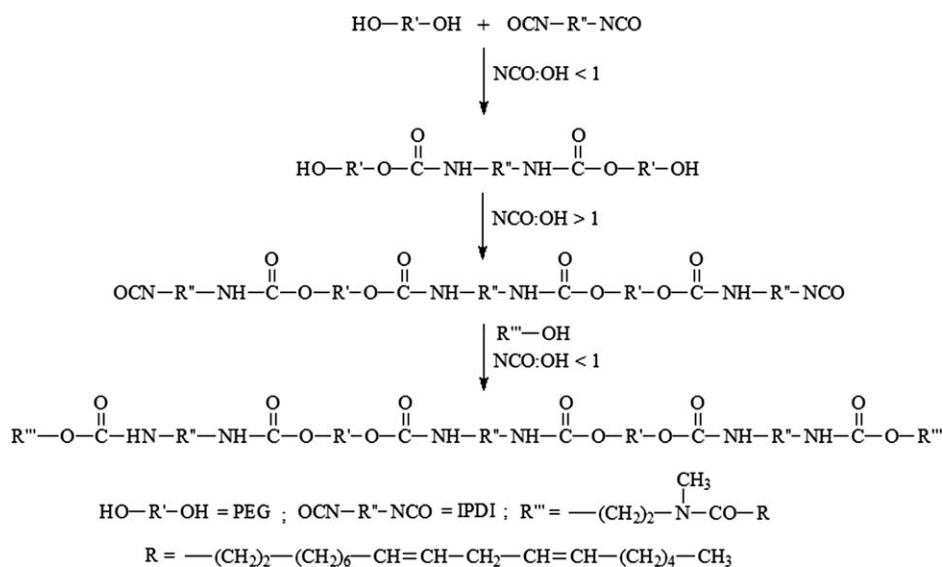
#### Soyamide HEUR Synthesis

Figure 4 summarizes the FTIR spectra of IPDI, PEG, reaction product of PEG, and IPDI ( $\text{NCO}:\text{OH} < 1$ ), isocyanate terminated pre-polymer ( $\text{NCO}:\text{OH} > 1$ ), soybean oil derivative, and reaction product of isocyanate terminated prepolymer and soybean oil derivative. In the FTIR spectrum of IPDI, characteristic bands at about 2960–2845 (overlapping), 2264, 1463, 1386,



**Figure 4.** FTIR spectra of a) IPDI, b) PEG 6000, c) reaction product of IPDI and PEG 6000 ( $\text{NCO}:\text{OH} < 1$ ), d) reaction product of (c) and IPDI ( $\text{NCO}:\text{OH} > 1$ ) and e) soyamide and f) reaction product of (d) and soyamide.

1365, 1251, 927–865  $\text{cm}^{-1}$  were observed for  $\text{CH}_2$  asymmetric and symmetric stretching of  $\text{CH}_2$  and  $\text{CH}_3$ ,  $-\text{N}=\text{C}=\text{O}$  stretching,  $\text{CH}_2$  bending,  $\text{CH}_3$  (gem-dimethyl) bending,  $\text{CH}_3$  (gem-dimethyl) bending,  $\text{CH}_2$  bending (out of plane), and cyclohexyl ring stretching and ring breathing motions, respectively.<sup>27–29</sup> Characteristics bands of PEG were noticed at about 3608–3371, 2949–2833, 1467–1242, 1118, and 1060  $\text{cm}^{-1}$  due to the presence of O–H (H bonded) stretching,  $\text{CH}_2$  asymmetric and symmetric stretching,  $\text{CH}_2$  bending, C–O–C stretching, and C–O stretching, respectively.<sup>28–30</sup> Synthesis of this soyamide-based HEUR is depicted in Scheme 1. In the IR spectrum of reaction product of PEG and IPDI ( $\text{NCO}:\text{OH} < 1$ ) shown in Figure 4(c), bands at about 3591–3332, 1720, 1535, and 1301  $\text{cm}^{-1}$  were observed because of the presence of N–H and O–H stretching, C=O stretching of (amide I region), C–N stretching and N–H bending (amide II), and C–N stretching of (C=O)–NH, respectively, resulting in the formation of urethane.<sup>28,29</sup> The NCO band at about 2264  $\text{cm}^{-1}$  was found to be absent because of complete consumption of IPDI by PEG ( $\text{NCO}:\text{OH} < 1$ ). NCO band was reappeared in the IR spectrum of reaction product with  $\text{NCO}:\text{OH} > 1$  shown in Figure 4(d); which implied the formation of isocyanate terminated prepolymer urethane. In the case of the reaction product of isocyanate terminated prepolymer and soybean oil derivative ( $\text{NCO}:\text{OH} < 1$ ), bands at about 3591–3332, 1720, 1627, 1535, and 1301  $\text{cm}^{-1}$  were noticed and at the same time, band at 2264  $\text{cm}^{-1}$  for NCO was disappeared shown in Figure 4(f) because of complete consumption of NCO groups by OH groups of soybean oil derivative. These indicated that isocyanate terminated prepolymer was successfully reacted by soybean oil derivative, which in turn infers the formation of hydrophobically modified ethoxylated urethane (HEUR). HEUR synthesis was further confirmed by  $^{13}\text{C}$  NMR spectrum displayed in Figure 5 where carbon signals at  $\delta$  156.99–156.53 ppm was observed for carbonyl carbon of urethane group. Other signals in HEUR spectrum

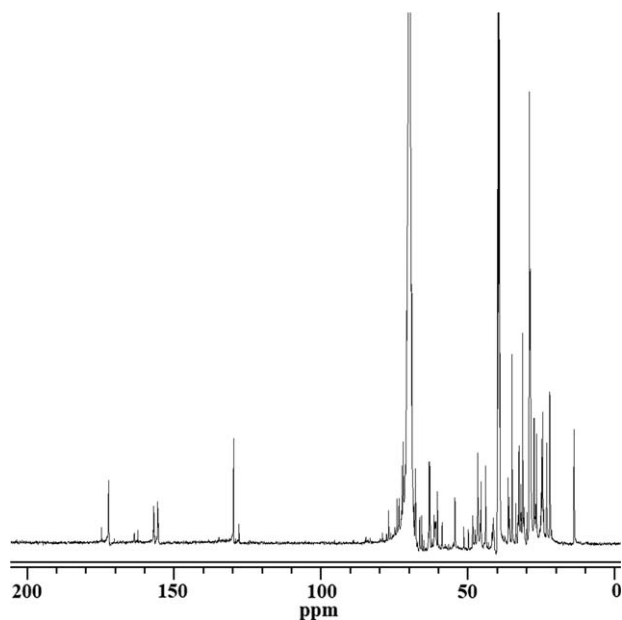


**Scheme 1.** Synthesis of biobased hydrophobically modified ethoxylated polyurethane.

were observed as well at  $\delta$  172.28, 129.72–128.07, and 72.00–65.00 for amide carbonyl carbon, unsaturated carbon, carbon in  $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$ , and  $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{C}(\text{O})-\text{NH}$ , respectively.<sup>31,32</sup> Molecular weight of the soyamide-based HEUR was analyzed by gel permeation chromatography.  $M_n$  and  $M_w$  values of the soyamide-based HEUR were 28,415 and 45,209, respectively (Figure 6). This HEUR exhibited a crystalline melting with peak temperature of 50.29°C and crystallization with peak at 35.04°C (Supporting Information Figure S1).

### Rheological Performance of Soyamide-Based HEUR

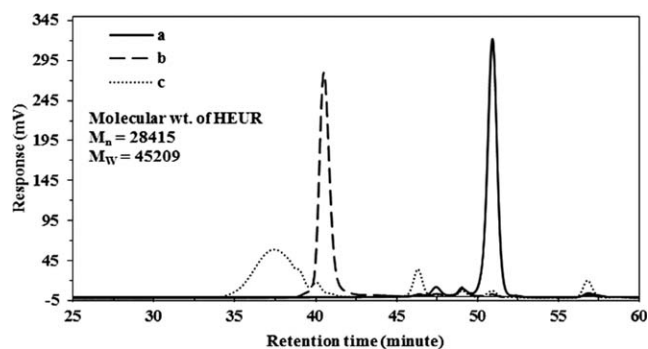
The effects of the soyamide-based associative thickeners on the rheological properties of its blends with commercial latexes were measured at low and high shear as is typical for



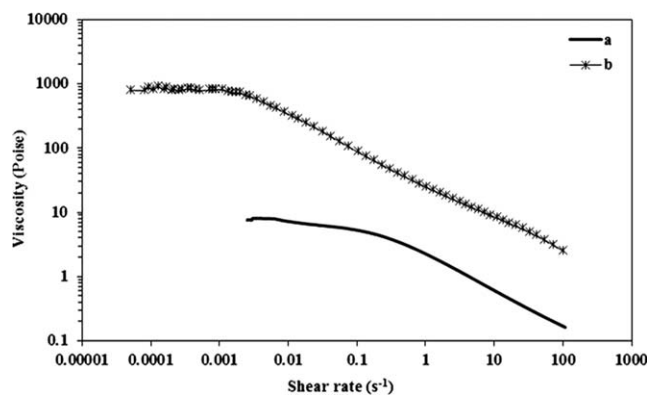
**Figure 5.** <sup>13</sup>C NMR of soybean oil derivative based HEUR.

architectural and light industrial latex-based coatings. Low shear rheological properties of commercial latex and its blend with the soyamide-based HEUR are shown in Figure 7. Non-Newtonian flow behavior was observed for UCAR 443 latex and its thickener blend. Soyamide-based HEUR blend had higher viscosity than the UCAR 443 latex over the full shear rate range.

The high shear rheology of UCAR 443, Acronal Optive 130, WorléeSol E 150 W latexes, and their individual blends with soyamide-based HEUR are displayed in Figure 8. Expectedly, the soyamide-based HEUR showed an increase in viscosity throughout the high shear range studied. The soyamide-based HEUR resulted in a viscosity increase factor of 10.62 and 3.64 for Acronal Optive 130 and UCAR 443, respectively, at 1333 s<sup>-1</sup> shear rate. The data supports that the soyamide-based HEUR resulted in comparatively higher thickening efficiency when blended with Acronal Optive 130. Several authors have shown that thickener efficiency is a function of several parameters such as latex structure, latex particle size, and surfactant concentration.<sup>33–36</sup> Variations in thickening efficiency are to be expected when a rheology modifier is blended individually with latexes that differ in composition, particle size, and solids. The higher



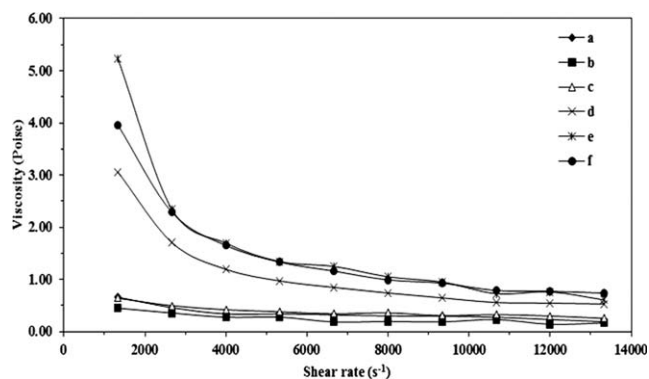
**Figure 6.** GPC traces of a) soyamide, b) polyethylene glycol, and c) soyamide-based HEUR.



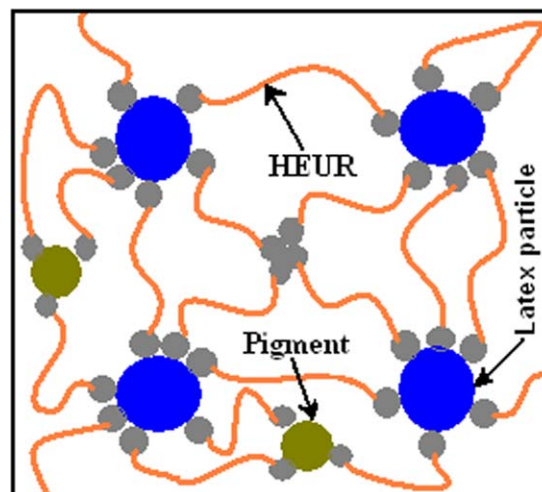
**Figure 7.** Low shear rheology profile: change in viscosity as a function of shear rate of a) UCAR 443 latex, b) blend of UCAR 443 latex with 0.5 wt% soyamide-based HEUR.

viscosity noted with Acronal Optive 130 latex is attributed at least in part to its particle size distribution, which translates directly to greater particle surface area at the same solids content. The smaller particle size of Acronal Optive 130 compared to UCAR 443 results in greater surface area, and strengthens the junctions between hydrophobes in HEUR and latex particles as greater numbers of hydrophobic segments are adsorbed. The blend of WorléeSol E 150 W with soyamide-based HEUR also exhibited higher viscosity than WorléeSol E 150 W at high shear rate. These results firmly establish that the bio-based HEUR is capable of thickening a variety of latexes and alkyd dispersions.

Additionally, it was observed that soyamide-based HEUR thickener has comparable thickening efficiency with commercial waterborne rheology modifiers as experienced from rheology profiles (Supporting Information Figures S2–S5) of individual blends of UCAR 443, Acronal optive 130, and WorléeSol E 150 W latexes with polyurethane (low shear rheology modifier, Drewthix 864) based and polyether (high shear rheology modifier, Aquaflo NHS 300). The higher viscosity is attributed to the formation of a transient or associated physical network structure that can fall apart in a shear field and then reform over time through the re-association of hydrophobic segments



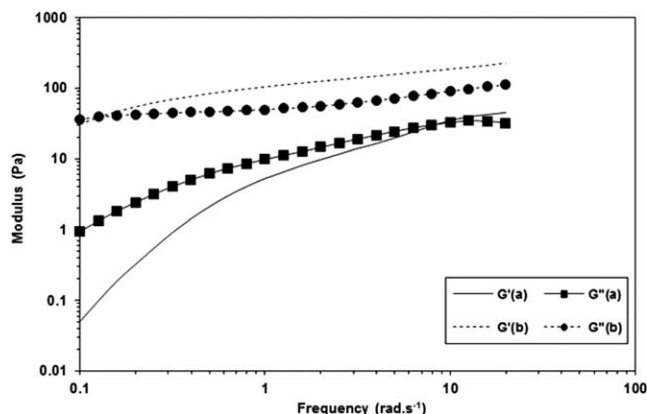
**Figure 8.** High shear rheology of a) UCAR 443 latex, b) Acronal Optive 130, c) WorléeSol E 150 W, d) blend of UCAR 443 with 0.5 wt% HEUR, e) blend of Acronal Optive 130 with 0.5 wt% HEUR, and f) blend of WorléeSol E 150 W with 0.5 wt% HEUR.



**Figure 9.** Schematic presentation of thickening mechanism of associative thickener in the presence of latex particles as well as pigment particles. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

of HEURs with latex particles.<sup>37</sup> A schematic presentation of thickening mechanism based on hydrophobic association of HEUR with latex and coatings is shown in Figure 9.

Dynamic rheology studies were conducted in the linear viscoelastic region (LVR). A stress sweep was adopted to select LVR (Supporting Information Figure S6). Dynamic rheological properties of UCAR 443 and its blend with HEUR are displayed in Figure 10 which describes the variation of modulus ( $G'$ ) and loss modulus ( $G''$ ) as a function of frequency. UCAR 443 showed a cross-over point at 1.27 Hz at which  $G' = G''$ , and below which  $G''$  had higher value than  $G'$  over the whole lower frequency range. This indicated that below the 1.27 Hz frequency, viscous component of the complex modulus dominates over the elastic component. The soyamide-based HEUR–UCAR 443 blend showed a cross-over point at 0.023 Hz; above which  $G'$  curve runs above the  $G''$  curve. Thus, the soybean oil-based HEUR thickened UCAR 443 latex is believed to exhibit dominating elastic behavior under dynamic condition.



**Figure 10.** Dynamic rheology: change in  $G'$  and  $G''$  as a function of frequency a) UCAR 443 latex, b) blend of UCAR 443 with 0.5 wt% HEUR.

**Table II.** Coating Performance of Soyamide-Based HEUR

Sample	Thickener	20° gloss	60° gloss	Stormer viscosity (KU)	ICI viscosity (poise)	pH	Sag resistance	Flow and leveling
Coating 1	Urethane based commercial	22.2	66.4	119	0.68	7.85	24	7
Coating 2	Urethane based commercial + polyether based commercial	19.0	63.5	114	0.62	7.78	24	9
Coating 3	Soyamide HEUR	20.5	66.0	116	0.72	7.79	20	9
Coating 4	Soyamide HEUR + polyether based commercial	22.2	66.7	135	1.89	7.88	24	7

### Coating Performance

Coating performance of soyamide-based HEUR was evaluated in a semi-gloss formulation at 22% pigment volume concentration (PVC) with WorléeSol E 150 W. Coating testing and characterization were conducted with the individual HEUR thickener as well as blends, i.e., blend of urethane based commercial thickener and polyether based commercial thickener, and blend of soybean oil-based HEUR with polyether based commercial thickener. Coating viscosities were tested at 12,000 s<sup>-1</sup> shear rates (ICI viscosity). Solid content was maintained constant across all coating formulations. In the case of thickener blend formulations, the thickener proportion was three parts of polyether based commercial thickener to one part of urethane based commercial thickener or soyamide-based HEUR (on coating formulation). Coating performance was evaluated in terms of gloss, viscosity, sag resistance, and flow and leveling properties (Table II).

The coating containing the soybean oil-based HEUR had a Stormer viscosity of 116 KU which was very close to the coating containing urethane based commercial thickener (119 KU). However, the coating with blend of urethane based commercial thickener and polyether based commercial thickener resulted in a slightly lower viscosity (114 KU) than the blend of HEUR with polyether based commercial thickener (135 KU). The coating formulated with the soyamide-based HEUR and polyether based commercial thickener displayed much higher viscosity than coatings formulated with commercial thickeners. These data indicate the rheological efficiency of the soyamide-based HEUR thickener. Coatings formulated with the soybean oil-based HEUR displayed comparable sag resistance to the coatings containing commercial thickeners and offered marginally better flow and leveling properties. Gloss, sag resistance, and flow and leveling properties of the coating formulated with the soyamide-based HEUR matched the best of the commercial thickeners evaluated individually. The goal to synthesize and characterize a natural product containing thickener and to evaluate its performance capabilities against similar commercial materials was thereby achieved.

### CONCLUSIONS

Bio-based hydrophobically modified ethoxylated urethanes (HEUR) were synthesized successfully. Rheological data of different blends showed that low levels of soyamide-based HEUR

with commercial latexes can impart significant thickening; the extent of thickening is dependent on the latex particle size. Coatings formulated with the soyamide-based HEUR were performed creditably with respect to gloss, viscosity, sag resistance, and flow and leveling when compared to commercial thickeners. These results infer that the soyamide-based associative thickener has excellent potential as a biobased HEUR thickener.

### ACKNOWLEDGMENTS

The authors thank the Cooperative State Research, Education, and Extension Service, US Department of Agriculture, for their financial support under Agreement Nos. 2006-38202-16954 and 2007-38202-18599.

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