Natural Oil Polyols for Waterborne Polyurethane Dispersions

by
John Argyropoulos,
Bedri Erdem,
Debkumar Bhattacharjee,
Paul Foley, and
Kumar Nanjundiah
The Dow Chemical Company*

Natural oil polyols (NOPs) can be prepared from fatty acid methyl esters derived from seed oils utilizing a novel hydroformylation technology. The NOPs are saturated aliphatic polyester polyols and are water-white clear liquids, with very low viscosities at room temperature. These new polyols are renewable raw materials useful for the preparation of waterborne polyurethane dispersions (PUDs) with low volatile organic compound content. NOP-based PUDs, not containing N-methylpyrrolidinone (NMP free), provide coatings with superior physical properties (good hardness and abrasion resistance), excellent mechanical properties, and exceptional hydrolytic and acid resistance.

INTRODUCTION

In recent decades, aqueous polymeric dispersions have emerged to replace solvent-based products in many applications such as coatings, foams, sealants, and adhesives. Not only do these systems result in the preparation of products with mitigated environmental health and safety (EH&S) issues (solvents, monomers, etc.), but the products have improved properties and performance.

Aqueous polyurethane dispersions (PUDs) are an important class of polymeric dispersions and are often produced by the emulsification of an isocyanate-terminated polyurethane prepolymer in water via the use of vigorous shear and mixing. The type and amount of shear and surface active agents employed are very critical in obtaining PUDs with submicron particle size and colloidal stability. The batch process, which is the most commonly utilized process to produce PUDs, relies heavily on the incorporation of ionic molecules such as carboxylates, sulfonates, or tertiary ammonium salts into the polymer backbone.[1] These groups impart water dispersibility to the resin upon neutralization and help minimize the requirement of shear in a

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*1714 Building, Midland, MI 48674.

batch process.[7] Dimethylolpropionic acid (DMPA) is the most commonly used internal stabilizer for the preparation of aqueous PUDs. Solvents such as acetone, N-methyl pyrrolidinone (NMP), and methyl ethyl ketone (MEK) are commonly used in the preparation of PUDs. NMP, which is the most common solvent, is preferred since it readily dissolves DMPA, reduces the viscosity of the prepolymer, and helps in subsequent film formation. Increasing EH&S regulations have created an opportunity for NMP free PUDs.

Isocyanates and polyols are important building blocks of the polyurethane dispersions from both synthesis and application perspectives. Aliphatic isocyanates are commonly used for coating applications because of weatherability requirements. Various types of polyols such as polyether, polyester, and polycarbonate polyols are commonly used for construction of polyurethane dispersions. The PUDs produced using these conventional polyols have not always been able to respond to increasing performance requirements in coating applications. Water resistance (especially during the early stages of drying) and superior mechanical properties are some key requirements for PUDs in coating applications. There is also a desire in the coatings market to produce PUDs from renewable feedstocks. In particular, the preparation of polyols from renewable raw materials is highly desirable in order to reduce the dependency on petroleum-based raw materials and provide sustainable and green solutions to the coatings industry. Polyester polyols based on seed oils have been developed for the coatings industry[3-5] but have found limited use due to a combination of reasons, such as higher cost, lower reactivity (secondary hydroxyl groups), poor control of functionality (presence of higher molecular weight oligomers), and color (from unsaturation).

A new composition of natural oil polyester polyols (NOPs) has been developed based on a unique process technology.[6] The novel polyols have good reactivity (primary hydroxyl groups), controlled functionality, and are water-white clear liquids with very low viscosities at room temperature. They provide environmentally friendly (green) coating formulations that are low in volatile organic compound (VOC) emissions, which lead to coatings with superior properties, such as exceptional hydrolytic resistance and mechanical properties.

EXPERIMENTAL

Prepolymer Preparation Procedure

Preparation of prepolymers was carried out in a 500-mL, 4-neck round-bottom flask equipped with an addition device, water-cooled condenser, mechanical stirrer, thermometer, and nitrogen inlet/outlet tubes. Nitrogen purge and an agitation rate of 500 rpm were applied throughout the course of the reaction. An oil bath was used as the heating source to maintain reaction temperature. As in a typical prepolymer preparation, polyester polyols and dimethylolpropionic acid were added into the reaction flask, followed by the addition of isocyanate. The polyols, which were added either individually or as a blend, were initially heated to a temperature of 15-20°C below the desired reaction temperature. Upon completion of the polyol and solvent additions, the reaction mixture was heated to the desired temperature (80–90°C) with agitation (200 rpm). Once the theoretical %NCO was reached, the final product was transferred to sample containers under a nitrogen blanket and used for the dispersion. The PUD recipe utilized in this study is summarized in *Table* 1. Suitable solvents for the prepolymer include acetone, methyl ethyl ketone, and the dimethyl ether of dipropylene glycol.

PUD Synthesis

PUDs were prepared in a small scale (500 ml) batch process where the prepolymer was neutralized using a tertiary amine (e.g., triethyl amine, TEA) at 95–110% stoichiometric amount (moles) of the acid used in the prepolymer. Predetermined amount of water was slowly added to the prepolymer as it was vigorously mixed using a special mixer generating high shear (50,000–100,000 sec^{-1}). Water was continuously added as the dispersion viscosity dropped below ~3000 cP (Brookfield Spindle #4, 50 rpm). The dispersion was then fully chain extended with an amine (e.g., ethylene diamine). The final dispersions had a solids content ~35 wt% and number average particle size ~100 nm.

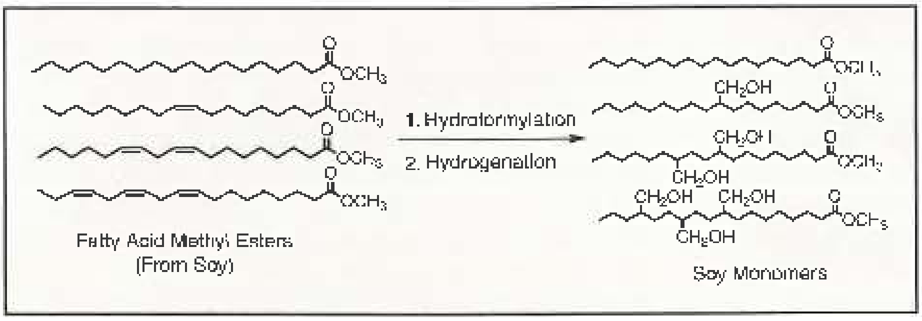
Contact Angle Measurements

Contact angle measurements were performed at 23°C utilizing a Kruss DSA 100 Surface Free Energy Station. The instrument had a movable sample stage and an eight-needle selector. The Kruss software controlled operation of the instrument and performed the data analysis. The measurements were performed in static mode. Each substrate, containing four coating samples, was placed on a sample stage and four meas-

Table 1—General Ranges of the Recipes Used in PU Dispersion Synthesis

Ratio	Moles
NCO/OH	1.4 1.75
COOH/OH	0.3–0.5
COOH/ TEA	0.95–1.10
Free NCO/ethylene diamine	0.9–1.05

Figure 1—Soy monomer chemistry.



urement templates with predefined drop positions were run, one for each of the four coatings. Drop volumes were 5 μL and all measurements were made two seconds after drop placement. Once the drop was imaged and the baseline was determined, left and right contact angles were computed by the software. The reported contact angle is the arithmetic mean of left and right contact angles.

Coatings Test Methods

Pencil hardness of the coating was measured according to ASTM D 3363. Pendulum hardness of the coating was measured according to ASTM D 4366 and reported in Konig units. Impact resistance of the coating was measured according to ASTM D 2794. Abrasion resistance of the coating was determined using a Taber abrader (CS-10 wheels, 1000 g weight, 1000 cycles). Gloss measurements were performed according to ASTM D 523.

Water resistance of the coating was determined by placing a large drop of deionized water on the coatings surface and covering the drop and observing the visual effect on the film after 24 hr (rating of 5 = no change to coating surface, rating of 3 = whitening of the coatings surface, rating of 1 = blistering of the coatings surface).

Acid etch resistance of the coating was measured by placing 50 μL drops of a 10% H_2SO_4 solution along the length of the panel. The acid drops were left uncovered on the coating for 5 hr (rating of 5 = no change to coating surface, rating of 3 = whitening of the coatings surface, rating of 1 = blistering of the coatings surface).

Dynamic Mechanical Analysis

The mechanical properties of the PUDs were analyzed using RSA III Dynamic Mechanical Analyzer from TA Instruments. The tests were carried out in tension geometry. The films for the test were cast and dried for seven days before measurement. The films were die cut to a width of 0.5 in. The thickness of the films was between 0.4–0.6 mm. The dynamic experiments were done at a frequency of 1 Hz with varying percent strain from 0.01–0.5%, based on temperature. Experiments with varying percent strain were used to determine the range showing linear behavior. The temperature scan was done by choosing strain amplitude in the linear region. The temperature was increased in steps of three degrees and allowed to equilibrate for a period of one minute before each measurement.

Atomic Force Microscopy

The morphology of the dried PUD films was probed using an atomic force microscopy (AFM). The tapping mode AFM images were obtained on a Digital Instruments MultiMode, using a Nanoscope IV controller. Silicon cantilevers and tips were used with a tip resonance frequency of 178 kHz. The tip to surface interaction was repulsive. Both height and phase images were collected. An area of 0.5 μm x 0.5 μm was probed. The sample was prepared by placing a drop of the PUD on freshly cleaved mica and drying the sample for a day before measurement.

Water Uptake Measurements

The PUD films after drying were tested for hydrolytic stability as well as for the extent of water absorption. To measure the extent of water uptake, a piece of the film was immersed in deionized water and the weight of the film was recorded before immersion and at regular intervals (daily). The percent increase in weight was recorded as a measure of water absorption. Optical images were collected to study the effect of water uptake on the transparency of the clear PUD films.

Differential Scanning Calorimetry

The thermal physical properties of the polyols were characterized using a TA Instruments DSC 2910 Modulated DSC. Samples of 10 mg were cooled to −100°C and warmed at 10°C/min to 100°C.

RESULTS AND DISCUSSION

Polyol Chemistry

The natural oil polyols (NOPs) are prepared in three reaction steps from the fatty acid methyl esters (FAMES) derived from soy oil. The FAMES are first hydroformylated to the aldehyde intermediates and then hydrogenated in the second step to the soy monomers,

Table 2—Physical Properties of Seed Oil and Comparative Polyols

Polyol	Hydroxyl EW	Diol Component	Brookfield Viscosity @ 50°C (cps)	T_g (°C)	Mp (°C)
Soy	521	Unoxol™ Diol	448	58	—
Caprolactone	415	Diethylene glycol	208	—	44.4
Adipate	500	1,4-Butanediol	520	-68	5.2

as shown in *Figure* 1. The average hydroxyl functionality of the soy monomers is approximately 1.0.

The resulting monomers are then transesterified with a suitable glycol. In this process, polyol molecular weight advances both by condensation of the monomers with the glycol initiator and self-condensation of the monomers. By controlling average functionality of the monomers and their ratio to the glycol initiator, both polyol molecular weight and average functionality can be systematically controlled. Furthermore, the structure of the initiator can be adjusted to enable desired performance characteristics or compatibility. Preferred glycol initiators contain reactive primary hydroxyl groups, such as 1,6-hexanediol and Unoxol™ Diol.* Unoxol Diol is a liquid cycloaliphatic diol that is an approximately 50:50 mixture of 1,3-cyclohexanedimethanol and 1,4-cyclohexanedimethanol.[7] As a result of this chemistry, the polyols contain primary hydroxyl groups and no unsaturation. The unique chemistry enables polyol structure design to be tuned to meet the diverse application requirements of the coatings industry.

Polyol Physical Properties

The physical properties of the polyols used for the preparation of the PUDs in this study are shown in *Table* 2. Soy polyol is a transparent colorless liquid that can be easily poured at room temperature. A caprolactone polyol with an equivalent weight of 415 was used as one of the controls. The polyol is a diethylene glycol (DEG) initiated caprolactone based polyester that is a solid at room temperature and forms a transparent colorless liquid on melting. The caprolactone polyol has no distinct T_g as determined by differential scanning calorimetry (DSC), and only a number of possible minor transitions from -73°C to its melting point, 44.4°C, were observed. An adipate polyol with an equivalent weight of 500 was also used as a control. This adipate polyol is a transparent colorless liquid at room temperature that can be easily poured. All the polyols had similar equivalent weights so that property differences observed between the PUDs were due to polyol molecular structure differences rather than from PUD formulation differences. The caprolactone and adipate polyols are diols, while the soy polyol possesses a distribution of OH containing species with an average functionality of 1.98. At 50°C, the caprolactone polyol showed the lowest viscosity followed by the soy polyol and the adipate polyol had the highest viscosity. A commercially available PUD, based on a polyester polyol, was also used as a control for the studies.

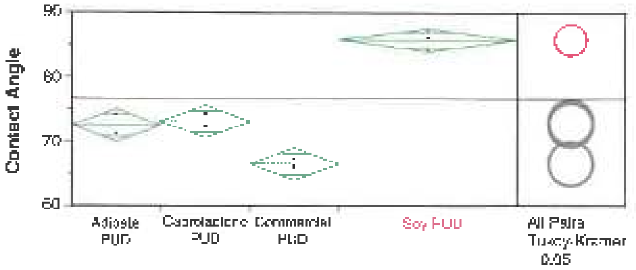
Contact Angle Results

Contact angle measurements using water were carried out to compare the film properties of polyurethane dispersions based on conventional polyester polyols to a soy-based polyol. The results of the study are summarized in *Figure* 2. PU dispersions based on conventional polyester polyols gave coatings that had contact angles for water ranging from 67 to 73 degrees. The soy-based PUD coatings had a significantly higher (95% confidence interval) contact angle for water of 85 degrees. This data indicates that soy polyol can significantly increase the hydrophobicity and lower the surface energy of PUD coatings relative to conventional polyester polyols. The 85 degree contact angle is similar to the value observed for ethylene-propylene (EPR) copolymers.[8] The higher hydrophobicity and lower surface energy of soy-based PUDs are expected to improve the water resistance and dirt pick-up resistance of the resulting coatings.

DMA Results

Figure 3 shows the DMA results for PUDs made with different polyols. The left axis represents the elastic modulus E′ and the right axis shows the tan δ values. Considering the elastic modulus, below 0°C all PUDs show a similar trend with modulus in gigapascals associated with solid-like behavior. However, close to 50°C, the commercial PUD, caprolactone PUD, as well as the adipate PUD, show a drop in modulus associated with

Figure 2—Contact angles of PUD films.



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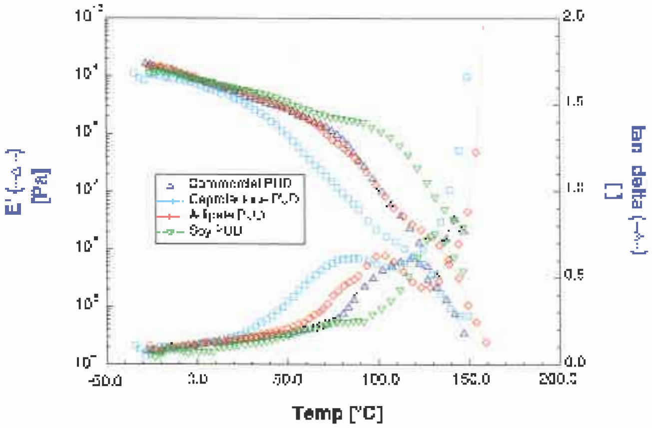
*Unoxol™ Diol is a registered trademark of the Dow Chemical Company.

Figure 3—DMA test results for PUD films.



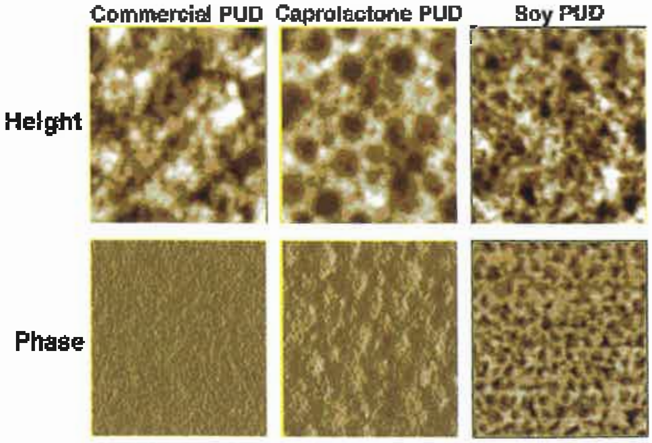
softening. The tan δ curves reflect a similar trend with tan δ increasing beyond 50°C. The peaks seen in the tan δ are broad, suggesting extensive phase mixing in these PUDs. In comparison, the elastic modulus remains high, up to 100°C, for the PUD made with soy polyol. The tan δ shows a small shoulder and the main peak is seen close to 130°C, which can be attributed to the hard segment undergoing glass transition. This result points to a phase-separated morphology for the soy PUD with microphase-separated domains, which may result from immiscibility of soft and hard blocks, which leads to favorable property profiles.

AFM Results

To further probe the morphology, AFM images of the PUD film surfaces were collected.

Figure 4 shows the AFM images of the surface of PUD films. Both height and phase images were taken over an area of 0.25 μm² in tapping mode in air. The depression in height is only on the order of 1 nm, suggesting a relatively smooth surface. However, the phase images show morphology that is consistent with the DMA data. The commercial PUD as well as the PUD made from the caprolactone polyol show considerable phase mixing, whereas the PUD from soy polyol shows discrete domains. Analysis of the dominant length scale in the image gives a value of 42 nm, suggesting well segregated hard and soft blocks in a honey comb like structure. This morphology is known to give enhanced mechanical properties as well as durability.[9]

Figure 4—AFM images of PUDs displaying height (top) and phase (bottom).



Water Absorption Results

Figure 5 shows the results of water absorption studies measured in terms of the increase in film weight over time. The images to the left depict the initial state of the films before they are immersed in water. It can be seen that all the films are initially clear. The images to the right show the state of the films after immersion for a period of 10 days. The commercial PUD film and the PUD film based on caprolactone polyol became opaque due to absorption of water. The soy polyol PUD, on the other hand, retained its clarity. The caprolactone polyol PUD film absorbs water readily, doubling in weight over the 10-day period. The soy polyol PUD film, because of its inherent hydrophobic nature, absorbs less than 10% of its weight in water. The film clarity, low water uptake, and enhanced mechanical properties allow the soy-based PUDs to be excellent candidates for many coating applications.

General Coating Properties

The properties of coatings prepared from the various PU dispersions are compared in *Table* 3. With the exception of the commercial PUD, all the dispersions

Figure 5—Water absorption studies for PUD films.

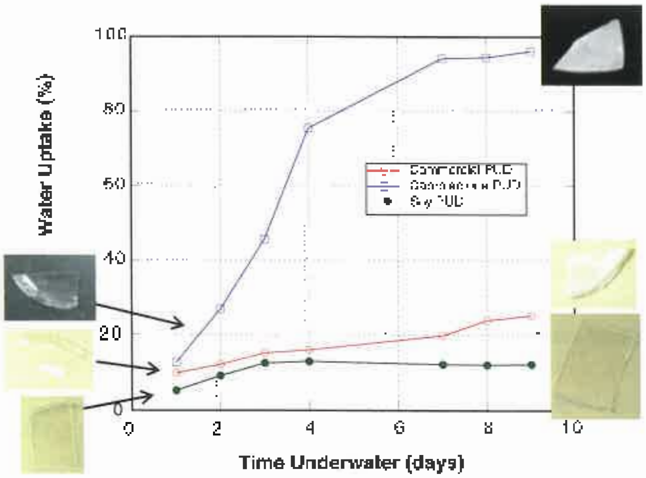


Table 3—Coatings Properties of the Soy PUD vs Conventional PUDs

PUD Properties	Soy PUD	Caprolactone PUD	Adipate PUD	Commercial PUD
Pendulum hardness (Konig, sec) After 1 day dry	133	97	89	49
Pencil hardness (gouge/scratch) After 1 day dry	HB/5B	2H/3B	F/5B	2H/5B
Gloss (20°/60°)	80.2/93.8	68.3/93.6	61.5/92.1	89.6/97.1
Taber abrasion resistance Weight loss (mg) after 1000 cycles	13.9	3.1	2.4	0.5
Impact resistance (direct/reverse) (in./lb)	160/160	160/160	160/160	160/160
Acid Resistance (after 7 days dry time) *10% H_2SO_4, 5 hours (uncovered)* (5 = no effect, 3 = blushing, 1 = blistering)	5	1	3	1
Water resistance (after 1 day dry time) Water, 1 day (covered) (5 = no effect, 3 = blushing, 1 = blistering)	5	3	1	1

were NMP-free. The soy-based PUD had exceptional water and acid resistance compared to the PUDs based on conventional polyester polyols.

The soy-based coating developed excellent water resistance after a dry time of only one day. The appearance (gloss) and flexibility (impact resistance) of all the coatings were good. The soy-based coating gave the best hardness based on Pendulum hardness measurement, but had lower pencil hardness. The abrasion resistance of all the coatings was good, with the soy coating having slightly lower abrasion resistance. Based on these results, the soy PUD based on the NOP technology can provide excellent coating properties for wood, cement, and plastic substrates.

CONCLUSIONS

Clear, low viscosity aliphatic polyester polyols from renewable natural oil-based monomers provide coatings with differentiated performance. Waterborne polyurethane dispersions with excellent stability were prepared from a soy based polyester polyol and its performance was compared with an adipate-based PUD, a caprolactone-based PUD, and a common commercial PUD. The contact angle data support the increased hydrophobicity of the soy PUD coating. Fundamental material science and microscopy results clearly demonstrate phase-separated morphology with micro-phase separated domains resulting from immiscibility of soft and hard blocks in the soy PUD, while considerable phase mixing was observed in the conventional PUDs. The soy PUD gave coatings with good hardness while maintaining good impact resistance. In addition, the soy PUD led to significantly improved water and acid etch resistance compared to the conventional PUDs.

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