

EVALUATION OF 1,3-PROPANEDIOL BASED POLYESTER AND POLYETHER POLYOLS IN POLYURETHANE WATER DISPERSIONS (PUDs) FOR TEXTILE COATING APPLICATIONS

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ABSTRACT

Two component polyurethane water dispersions (PUDs) based on 1,3-Propanediol polyester polyols (PDO Adipate 2000 and PDO Sebacate 2000) and polyether polyols (Velvetol H 2000, Allessa) were produced and applied on three uncoated fabric sources (cotton sateen, polyester duck, and textured nylon) to evaluate their performance and commercial viability. The commercial reference PUDs were based on BDO Adipate 2000 and poly(oxytetramethylene) glycol 2000 (PTMG 2000). The use of solvent-free waterborne urethane dispersions (PUDs) is widely discussed in literature and growing across various industries due to environmental factors.

The introduction of 1,3-Propanediol (1,3-PDO) as a bio-based component of chain diols in polyurethanes is accepted as shown by its use on commercial scale to produce polyester and polyether polyols for various applications. Solvent-free bio-based systems must offer all the same required properties of current commercial products with the added advantage of being eco-friendly and sustainably sourced. PUDs are a desirable coating for various textile application since they provide very good tensile strength, wear resistance, have good adhesion to various substrates, and can be formulated to be moisture resistant while maintaining vapor permeable (or breathable) properties. To obtain PUDs with good performance, the effects of varying the building block components (soft and hard segments) needs to be understood. The introduction of dimethyl propionic acid (DMPA) pendant ionic groups into hard segment block facilitates the formation of stable PUDs of acceptable solids loading by increasing hydrogen bond interactions. The bio-based coatings prepared in this investigation provided useful physio-mechanical properties, chemical resistance, and water resistance compared to reference commercial petroleum based two-component (2K-PUDs) and one-component (1K-PUD) waterborne polyurethanes.

INTRODUCTION

The use of waterborne urethane dispersions (PUDs) is growing due to the environmental factors. PUDs are used as coatings, adhesives and films in various industries such as wood, metal, textile, leather, footwear, inks, etc. 1,3-PDO is a 100% bio-based chain diol that is already used on a commercial scale to produce polyester polyols. Bio-based content of these polyols vary depending on the acid used as a co-reactant in the polyol synthesis and can go up to 100%. PUDs can be used in textile application as a protective top coat and as adhesives. There are many coating applications of PUDs in textile industry, including coated textile garment materials, protection for furniture fabrics, textile finishes with grain appearance, table cloths, sports footwear materials, protective clothing in the food industry and medical field, etc. PUDs are a desirable coating choice for various textile applications since they provide very good tensile strength, wear resistance, and have good adhesion to various substrates, all important factors for textile applications. PUDs can be formulated to be moisture resistant while maintaining breathable properties. Stain resistance of textile PUD coatings can be created either with composition of the polyol and/or with the addition of selected coating additives. PUDs based coatings preserve transparency and clarity when they are formulated with aliphatic isocyanates which resist yellowing. In general, PUDs can be linear (1K-PUD) or crosslinked two-

component reactive (2K-PUD). Since 2K-PUDs have better solvent, moisture resistance, and adhesion strength than linear 1K-PUDs, 2K-PUDs are more suitable, effective, and used for textile coating applications.

In this study, the following 1,3-PDO based polyols were evaluated in PUDs application: 1,3-PDO Adipate 2000 polyester polyol, 100% bio-based 1,3-PDO Sebacate 2000 polyester polyols and 100% bio-based PO3G 2000 polyether polyol (Velvetol H 2000, Allessa). BDO Adipate 2000 polyester polyol was used as the reference polyester polyols in preparation of PUDs and poly(oxytetramethylene) glycol 2000 (PTMG 2000) as a reference polyether polyol.

EXPERIMENTAL

The chemicals and materials used in this study are listed in Table 1. Aliphatic isocyanate IPDI and BAYHIDUR XP2655 were used as received from the supplier. The isocyanate content for each was checked by the di-n-butylamine method, ASTM D 5155. Moisture was removed from the polyols by continuous stirring under vacuum at ~3 mmHg at 70° to 80°C. The water content of the polyol used in the PUD synthesis was less than 0.06% and measured by Karl Fisher method, ASTM D 4672.

Preparation of 2K-PUDs

Two component crosslinked PUDs (2K-PUDs) were prepared by reaction of hydroxyl functional ionomer oligomer dispersed in water (HFO-4) with water-dispersible multifunctional aliphatic isocyanate (BAYHIDUR XP 2655).

The synthesis of hydroxyl functional ionomers (HFO-4) consists of the following steps (see Scheme 1):

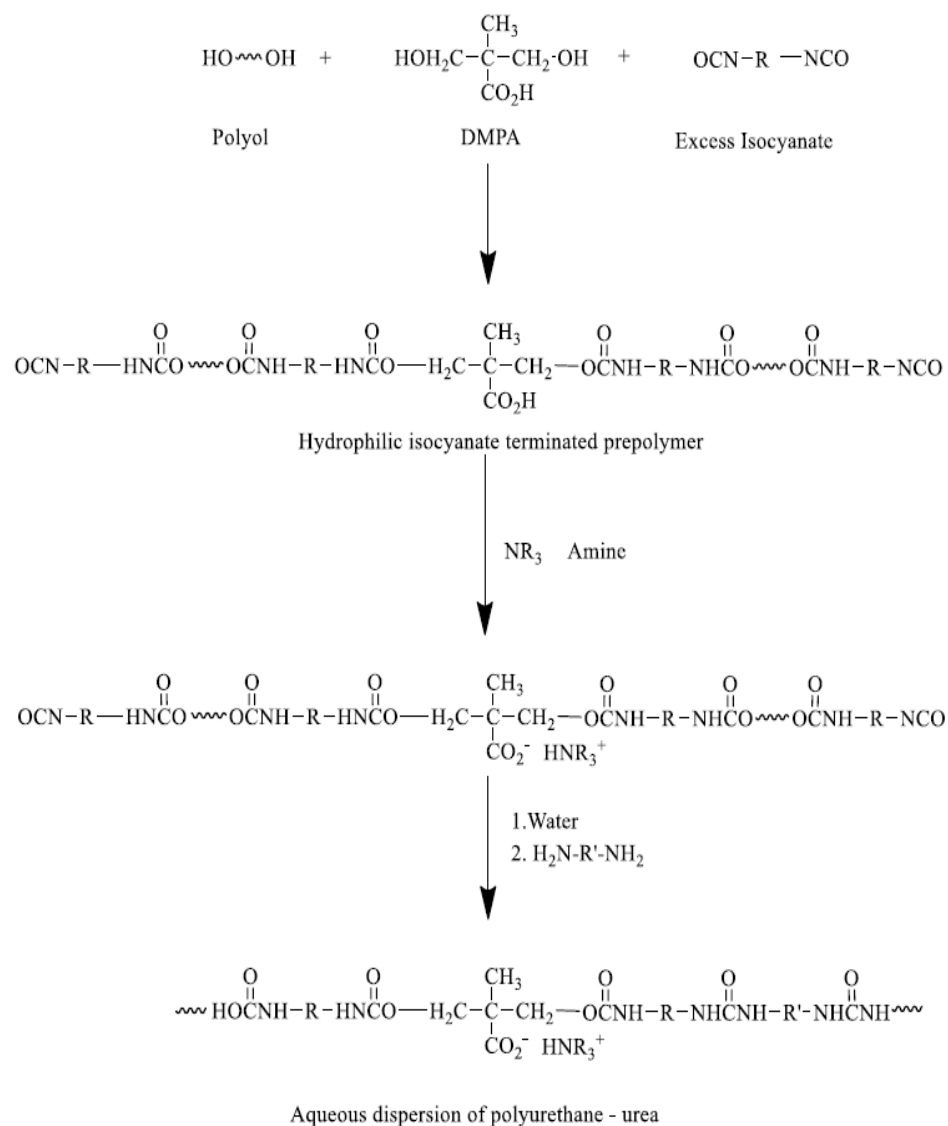
- Step 1:** NCO-terminated prepolymer was prepared by reacting aliphatic diisocyanate IPDI with a blend of polyol and chain extender DMPA (2,2-dimethylolpropionic acid) to introduce pendant carboxylic group into prepolymer backbone. The molar ratio of isocyanate: polyol: DMPA was 3.05:1:1.
- Step 2:** The carboxylic group is neutralized with tri-ethylamine, forming a salt ionomer group that enable dispersion of NCO-prepolymer in water.
- Step 3:** The NCO-prepolymer is dispersed in water.
- Step 4:** The NCO-prepolymer was reacted with the blend of end-capping diethanolamine and ethylene diamine at isocyanate index of 1.05. Therefore, 50% of isocyanate groups was reacted with R-NH group of DEA and 50% by R-NH₂ groups of EDA. The final oligomer (HFO-4) product was a hydroxyl-functional ionomer oligomer having 4 hydroxyl groups (two at each chain end). The solid contents of HFO-4 dispersions were about 30% (Table 3).

Table 1. Chemicals and Materials		
Designation	Description	Manufacturer/ Supplier
2,2'-Bis(hydroxymethyl) propionic acid	DPMA, 98%, chain extender	Aldrich
Desmodur I	IPDI - Isophorone diisocyanate	Covestro
BAYHIDUR XP 2655	Hydrophilic aliphatic polyisocyanate based on Hexamethylene diisocyanate	Covestro
Triethylamine	TEA	Sigma Aldrich
Ethylenediamine, 99%	Ethylenediamine	Alfa Aesar
Dabco T-12	Dibutyltin dilaurate catalyst	Air Products
Poly S 2000 PAR	PDO Adipate 2000 MW diol	ITWC, Inc.
Sb-PDO 2000	PDO Sebacate 2000 MW diol	Dupont Tate & Lyle Bio Products
Fomrez 44-56	BDO Adipate 2000 MW diol	Chemtura
Velvetol H 2000	PO3G 2000 MW polyether diol	Allessa
PTMG 2000	Poly(tetrahydrofuran) 2000 MW	Aldrich
Standard metal plate for coating, S-46	Steel plate, ground one side, (0.8 x 102 x 152 cm)	Q-Labs
Textured Nylon (Item No. 8596)	Textured Nylon 6.6 Stretch Fabric, Double Knit, Approximate Wt.: 7.66 oz./yd ²	TestFabrics, Inc.
Cotton Sateen (Item No. 12132)	Army Carded Cotton Sateen, Desized and Unbleached, Approximate Wt.: 6.6 oz./yd ²	TestFabrics, Inc.
Polyester Duck (Item No. 1411010)	Poly Duck, Approximate Wt.: 6.0 oz./yd ²	TestFabrics, Inc.

The syntheses of PUDs were carried out in a 1000 mL reactor equipped with nitrogen flow, heating mantle with temperature controller, and mechanical mixing. Liquid polyol (0.1 equivalent) and DMPA (0.1 equivalent) were charged into reactor and heated under mixing to 135°C (Table 3). At 135°C, DMPA was melted and homogenized with the polyol for 10 minutes. The mixture was cooled gradually while mixing to 80°C. Dabco T12 catalyst was added to the reactor followed by addition of IPDI (0.305 equivalents). The NCO-prepolymer synthesis was monitored via NCO% determination (ASTM D 5155). The synthesis of NCO-prepolymer was completed within 2 -3 hours depending on the formulation. After the NCO-prepolymer was formed, the temperature was cooled to down to 50°C. Triethylamine was added to react with the carboxylic group at equimolar ratio and mixed for 20 minutes. Subsequently, distilled water was added to the ionomer NCO-prepolymer under vigorous mixing to form milky stable dispersion. A calculated amount of diethanolamine (DEA) in 30mL water was added to NCO-prepolymer dispersion under stirring for 20 minutes. Afterwards, an equivalent amount of ethylene diamine (EDA) in 30mL of water was added to the prepolymer dispersion and mixed for 20 minutes to react with remaining terminal isocyanate groups forming hydroxyl-functional ionomer oligomer water dispersion (HFO-4). This process was optimized and summarized in Tables 2 and 4. HFO-4 water dispersions were prepared targeting 30 - 35% solid content.

HFO-4 water dispersions were mixed at room temperature with 100% sufficiency of multifunctional aliphatic isocyanate (Tables 2 and 3). The blended 2K-PUD was stirred at room temperature for 10 minutes and then kept unstirred for an additional 1 hour at room temperature prior to casting films and coatings. The polymerization of films prepared with 2K-PUDs was monitored via FTIR method to confirm isocyanate conversion and completion of polymerization.

Referent 1K- PUD based on PDO Adipate 2000 polyol was also prepared following the protocol presented in Scheme-1 (Steps 1 - 4). In Step 4, the ionomer NCO-prepolymer dispersed in water was chain extended with ethylene diamine forming poly(urethane –urea) water dispersion.



Scheme 1. Basic steps in preparation of anionic PUDs.

Testing of PUDs

A. PUD Liquid dispersions

- Viscosity at 25°C, (Brookfield), ASTM D 4878
- Solid content, %

B. PUD Films

Films were prepared by casting PUDs onto non-polar polyethylene substrate using Dr. Blade at 20 and 30 mils thickness. The films and coatings were tested after 3 days of aging at room conditions.

- Tensile strength and elongation (flexibility), ASTM D2370
- (The rate of Instron speed 4in./min.).
- Chemical characterization, FTIR.
- Glass transition temperature (T_g, Differential Scanning Calorimeter - DSC).
- Hydrolytic resistance (change of tensile properties prior and after humid aging at 50°C, 95% relative humidity for 3 days).

C. PUD Coatings on metal substrate

The coatings were prepared by casting PUDs onto standardized stainless-steel test coupons (S-46, Q-Panel) using Dr. Blade at 20 and 30 mils thickness.

- Hardness, Pencil hardness, ASTM D3363 (Table 4)
- Impact resistance, ASTM D2794 (Table 4)
- Adhesion – peel test, ASTM D3359 (Table 4)
- Solvent (IPA) resistance - Rub test, ASTM D5402
 - Change of film thickness of coatings on metal substrate after 200 double rubs was measured (Table 6).
- Solvent resistance – spot test
 - 10 drops of solvent were applied on the coating, covered with a watch glass for 10 minutes before scratching with metal spatula. The changes were visually observed and graded on a relative scale: (1) - No effect, (5) - Worst effect (Table 4).

D. Abrasion resistance of PUD coating

PUD films were coated with a brush onto octagonal solid ¼” wood substrate (POPLAR solid wood, 2618, Home Depot). The thickness of the PUD coating was ~0.1 mm.

- The abrasion resistance of PUDs was measured according to ASTM D4060 (test wheel CS-10, 1000 g weight on each side, 1000 cycles). The coating weight change was recorded (Table 5).

E. Fabrics coated with PUDs

Three types of standardized fabrics (cotton sateen, polyester duck and textured nylon) were coated with PUDs. PUDs were coated with Wire Coater size 15 (approximate wet film thickness 1.5 mils) and Wire Coater size 100 (approximate wet film thickness 10 mils). After coating, the fabrics were dried in the oven at 50°C for approximately 2 hours to remove water and cure the film.

F. Testing of fabrics coated with PUDs:

- Gloss of fabrics coated with PUDs was measured with ETB-0686 gloss meter (Table7).
- Humidity resistance method (Table 8)
 - PUD coated fabrics were placed in moisture chamber at 50°C and 70% relative humidity for 7 days.
 - Samples were dried in the oven at 50°C for 3 hours.
 - Adhesion peel test (ASTM D3359) and water resistance test were performed on fabrics.
- Stain Resistance & Cleaning (Table 8).
 - **Ink** was applied and cleaned first with IPA, then with 20% bleach and washed with water. The fabric was dried in the oven at 50°C for 1 hour.
 - **Coffee** stain was cleaned with a cheese cloth that was soaked in a dish liquid detergent/distilled water solution, and then rubbed over coffee stain.

- **Tomato Ketchup** was applied onto fabric and cleaned with a cheesecloth that was sprayed with non-abrasive cleaner, Formula 409, and slightly rubbed over the stained fabric. Cleaned area was rinsed with distilled water.
- **Lotion** (Jergens, soothing Aloe) was cleaned with a cheese cloth soaked in a dish liquid detergent/distilled water solution.
- Adhesion, peel test, ASTM D3359 (Unwashed samples)
- Washing method
 - **PUD coated fabrics** were washed by soaking 5 times at room temperature in laundry detergent (Spring Breeze Premium Laundry Detergent, Target) water solution (1.5 g/1500 ml, detergent/water) for 30 minutes, rinsed in water after each washing cycle, and dried at 50°C for 1 hour.
 - Adhesion peel test (ASTM D3359) was performed after completing 5 washing cycles
 - Water resistance test after 5 washing cycles: 2 drops of water was applied onto washed fabric and monitored for 5 minutes (Table 9).

RESULTS and DISCUSSION

PUD Synthesis and Formulations

The synthesis of PUDs was carried out using the procedure as outlined in Scheme 1. During the initial formulation screening, two types of hydroxyl-functional oligomer were prepared based on PDO Adipate 2000 (Table 2). In one case NCO-prepolymer was reacted first with DEA followed by EDA (HFO-4 Type A). HFO-4 Type B was prepared with reverse order of addition, EDA followed by DEA. The crosslinking of HFO-4 based on PDO Adipate 2000 polyol was carried out at 1.5/1 and 2.0/1 NCO/OH equivalent ratio (Table 2). These 2K-PUD films exhibited significantly different properties compared to the referent 1K-PUD. Furthermore, 2K-PUD films exhibited significantly higher tensile modulus and lower elongation at break as compared to 1K- PUDs, which can be attributed to crosslinking (Table 2). Based on this screening study, all 2K-PUDs were formulated at NCO/OH equivalent ratio of 2/1 and HFO-4 Type A.

2K-PUDs were prepared using 5 types of polyols: PDO Adipate 2000 polyester polyol, PDO Sebacate 2000 polyester polyol, PO3G polyether polyols, and for reference BDO Adipate 2000 polyester polyol and PTMG 2000. 1K-PUD based on PDO Adipate 2000 was also prepared according to Scheme 1. The formulations of hydroxyl-functional oligomers HFO-4 water dispersions are presented in Table 3. Hydroxyl-functional oligomer was prepared by preparing NCO-prepolymer based on IPDI, polyol and DMPA with a pendant ionomer group, which was dispersed in water. Subsequently, the water dispersed NCO- prepolymer was reacted with diethanolamine (DEA) and ethylene diamine (EDA), resulting in water dispersed hydroxyl-oligomer contained 4 terminal hydroxyl groups. Hydroxyl-functional HFO-4, Type A was crosslinked by reaction with water dispersible hydrophilic aliphatic isocyanate (BAYHIDUR XP 2655). The polymerization of cast films at room conditions was monitored via FTIR. The spectra indicated that absorption at 2230 cm^{-1} associated with unreacted -NCO groups decreased over time and disappeared after 22 hours (Figure 1). Other 2K-PUD films were mostly cured after 24 hours (Figures 2).

The solid content of HFO-4 dispersions was about 30%, and their viscosities were relatively low, ranging from 15 to 40 cps (Tables 2). HFO-4 water dispersions remained stable with low viscosity over prolonged storage at room conditions with exception to the HFO-4 based on PO3G 2000 which stratified with three days and thickened after seven days. With heating for 1 hour at 70°C, the viscosity of PO3G 2000 based HFO-4 dispersions was reduced, the emulsion became homogeneous again, and as such was used in coatings preparations.

Table 2. Effect of Hydroxyl - Oligomer type and amount of Isocyanate cross-linker on properties of PUD films				
PUD Type	1K - PUD PDO-A 2000	2K- PUD PDO-A 2000 (Type A)	2K- PUD PDO-A 2000 (Type A)	2K- PUD PDO-A 2000 (Type B)
Equivalent ratio: NCO/HFO-4	-	1.5	2.0	2.0
Properties				
Tensile stress at break, psi	5394±665	1940±392	2740±478	1975±175
Tensile strain at break, psi	795±93	232±39	200±40	217±22
Tensile stress at 50% extension, psi	442±46	708±117	945±74	893±74
Tensile stress at 100 extension, psi	524±50	952±187	1348±139	1124±131
Tensile stress at 200 % extension, psi	689±76	1544±310	2343±22	1729±27
Tensile stress at 300 %extension, psi	974±141	-	-	-

Table 3. Formulations of 1K-PUDs and 2K-PUDs (HFO-4)

PUD Type	1K- PUD PDO-A 2000	2K- PUD PDO-A 2000	2K- PUD PDO-Sb 2000	2K PUD BDO-A 2000	2K- PUD PO3G 2000	2K- PUD PTMG 2000
Formulations (pbw)						
PDO Adipate 2000	100.00	100.00	-	-	-	-
PDO Sebacate 2000	-	-	100.00	-	-	-
BDO Adipate 2000	-	-	-	98.42	-	-
PO3G 2000	-	-	-	-	100.00	-
PTMG 2000	-	-	-	-	-	101.95
DMPA, g	6.71	6.71	6.71	6.71	6.71	6.71
Desmodur I, g	35.01	35.01	35.01	35.01	35.01	35.01
Triethylamine, g	4.77	4.92	4.92	4.92	4.92	4.92
Dabco, T-12, g	4 drops	4 drops	4 drops	4 drops	4 drops	4 drops
H ₂ O, g	263.00	276.00	276.00	276.00	276.00	276.00
Ethylenediamine, g	3.41	1.71	1.57	1.57	1.57	1.57
DEA, g	0.00	6.83	6.26	6.26	6.26	6.26
Properties						
Solids, %	32.74	30.61	33.98	33.29	27.60	33.29
Viscosity @ 25°C, cps	20.46	31.98	14.76	16.68	34.08	15.70
Shelf stability, RT	Stable	Stable	Stable	Stable	Viscosity increased*	Stable
* Viscosity decreased after heating to 70°C						

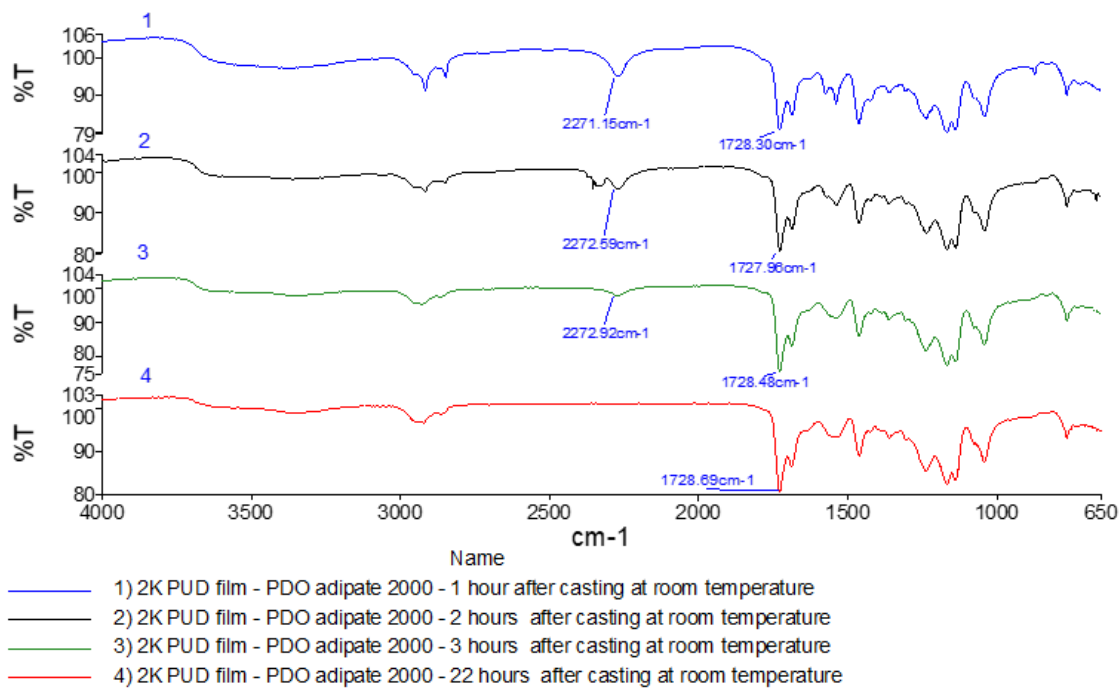


Figure 1. FTIR spectra of 2K-PUD based on PDO Adipate 2000 cured at various reaction times

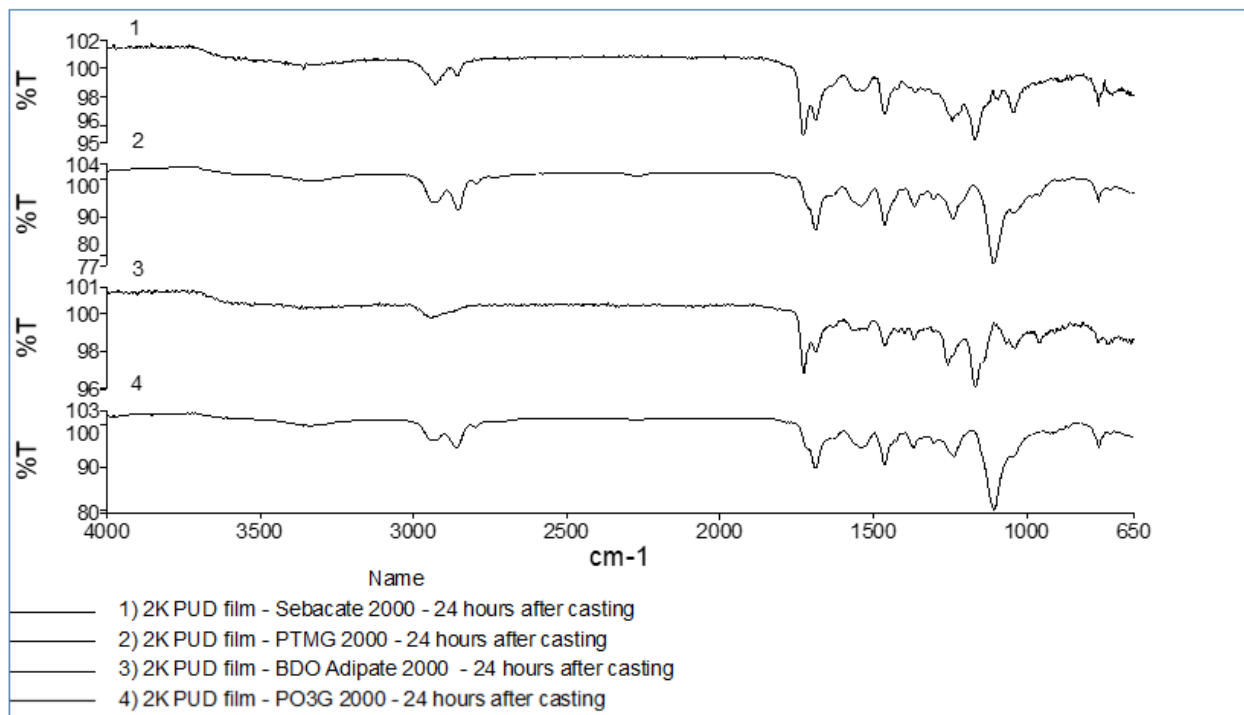


Figure 2. FTIR spectra of 2K-PUDs based on various polyols cured for 24 hours

Physico-Mechanical and Thermal Properties of PUD Films

All 2K-PUD films exhibited higher tensile modulus and lower elongation at break compared to 1K-PUD film, as could be expected due to the crosslinking (Table 4). The films based on PDO Adipate 2000 and PDO Sebacate 2000 polyols exhibited similar tensile properties. Stress-strain curve of 1K-PUD and 2K-PUD films based on PDO Adipate 2000 exhibited “S” shaped curve typical of elastomeric materials (Figure 3). 2K-PUD film based on PDO Sebacate 2000 exhibited weak yield in stress-strain curve (Figure 3). The film based on referent BDO Adipate 2000 polyol was brittle and exhibited a yield in stress-strain curve at low strain (~7%), (Figure 3 and Table 4). 2K-PUD film based on PO3G 2000 exhibited lower tensile modulus and higher elongation at break than the referent film based on PTMG 2000. This could be due to difference of -CH₂ sequence in backbone of two polyols (Table 4). The stress-strain curve of both polyether 2K-PUD films indicate elastomeric structure (Figure 3).

The glass transition temperature (T_g) of polyether based 2K-PUD films was lower than that of polyester films, which could be expected (Table 4, Figure 4). The T_g of 2K-PUD and 1K-PUD based on PDO Adipate 2000 polyols was very similar.

The hardness of 2K-PUD films was >9H (Pencil Hardness) with exception of the film based on PTMG 2000 which had hardness of 8H. All films had good impact resistance. Polyether polyol based 2K-PUD films coated on cardboard exhibited somewhat higher gloss than polyester polyols based PUD films (Table 4).

The weight loss of 2K-PUD films in the abrasion wear test was relatively low (Table 5). The weight loss of films based on polyether polyol 2K-PUDs was lower than that 2K-PUD based on polyester polyols which could be expected based on composition.

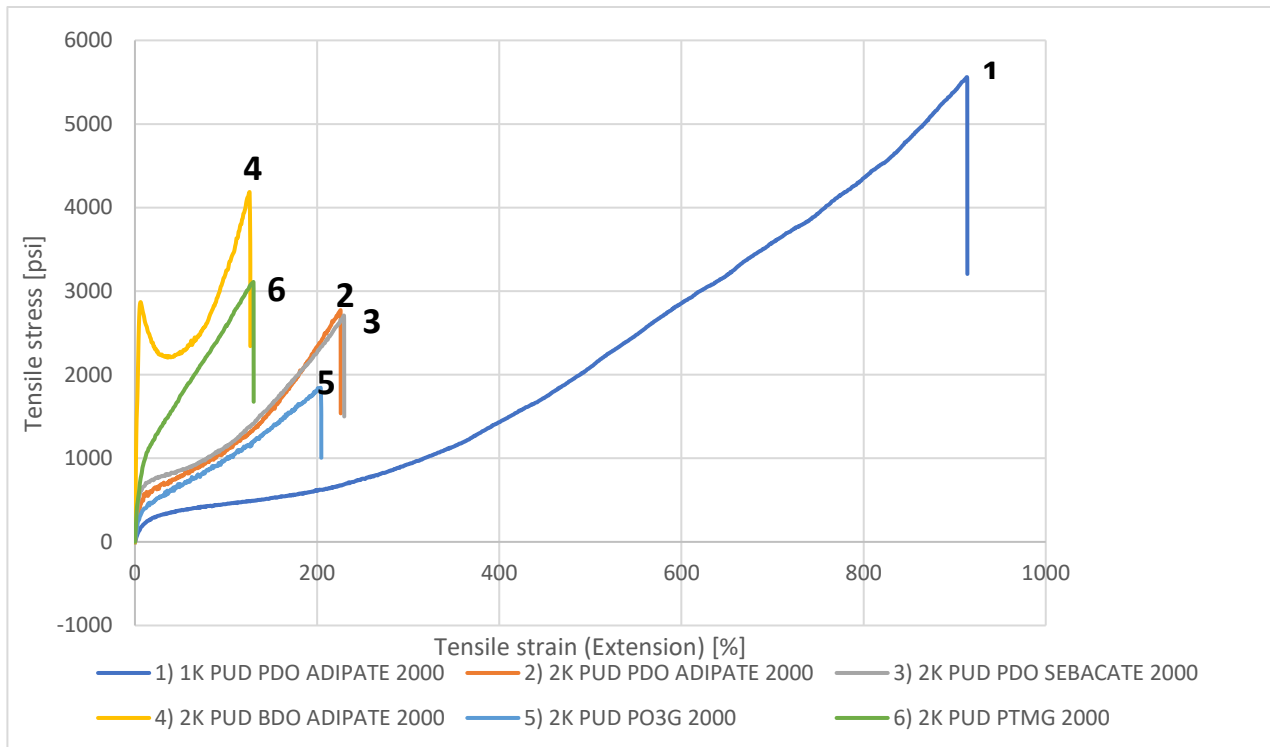


Figure 3. Stress-strain curve of PUD films based on various polyols.

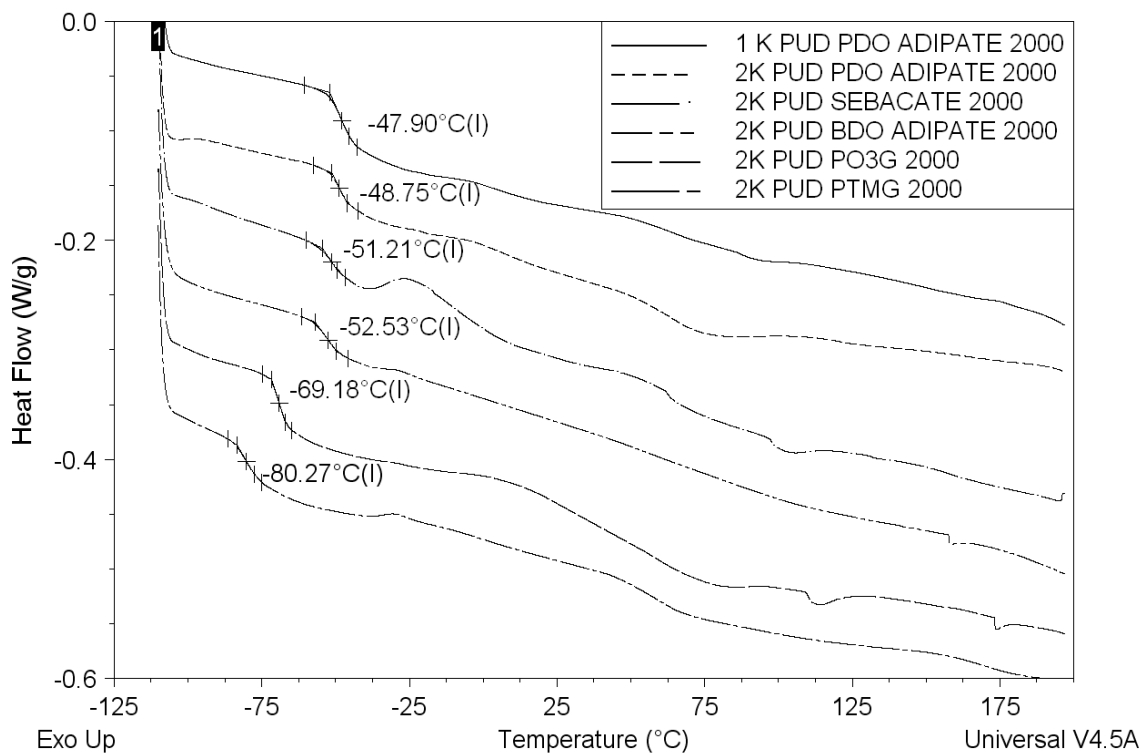


Figure 4. DSC graphs of PUD films based on various polyols.

Hydrolytic Resistance

Stress-strain properties of the films were measured after hydrolytic aging (Figure 5). 2K-PUD films based on PDO Adipate 2000, PDO Sebacate 2000, and PO3G 2000 retained most of tensile strength at break after hydrolytic age. In fact, PO3G 2000 based films retained 98.7% of its original tensile strength which was very impressive. The length of the acid group chain used to produce the polyester polyol proves to have a meaningful effect on hydrolytic resistance and can be defined as proportional to the ester group concentration and thus susceptible to hydrolysis; therefore, it would be expected that PDO Sebacate 2000 (C10 acid, 93% retention) would have greater hydrolytic resistance than PDO Adipate 2000 (C6 acid, 77.8% retention). Tensile strength of 2K-PUD film based on PTMG 2000 decreased significantly, especially in comparison to PO3G 2000. 2K-PUD film based on BDO Adipate 2000 changed from brittle to elastomeric, which is due to annealing with moisture absorption. 2K-PUD film based on PDO Adipate 2000 retained tensile strength better than the corresponding 1K-PUD, which can be attributed to crosslinking.

Solvent Resistance

Solvent resistance of the coatings was evaluated using a double rub test with IPA (Table 6). This test combines solvent resistance and abrasion resistance. All 2K-PUDs exhibited good resistance to IPA, which can be often found in cleaning/disinfecting solutions. The thickness of 1K-PUD film after 200 double rubs decreased significantly more (~44% reduction) compared to the films based on 2K-PUDs (7-18% reduction), which can be attributed to crosslinking (Table 6). 2K-PUD film based on PDO Sebacate 2000 exhibited a slight increase in film thickness which could be attributed to IPA absorption. The thickness loss of 2K-PUD films based on polyester groups (PDO Adipate 2000 and BDO Adipate 2000) loss appears to be proportional to the ester group concentration while in polyether polyol inversely proportional to the number of CH₂ groups.

For the solvent spot test, three different solvents (toluene, MEK and IPA) and water were applied onto PUD films coated onto metal substrate. The solvents were covered with a glass beaker and inspected and scratched with spatula 10 minutes after solvent was applied. 2K-PUD based on PDO Adipate 2000 performed better than referent 1K-PUD (Tables 4 and 7). 2K-PUD film based on PO3G performed the best in this test.

PUD Coated Fabrics

PUDs were coated on three types of test fabrics (cotton sateen, polyester duck, and textured nylon). The weight of the fabrics (6.0 – 7.66 ounces/yard²) were similar. PUDs were coated as one layer on one side of the fabric using Wire Coaters 15 and 100. After coating the fabric samples, the materials were dried and cured in the oven at 50°C for two hours. Overall, the gloss values of films coated on fabric were much lower than the gloss values observed on cardboard (Table 7 and Table 4). This is not unexpected as the porosity and material absorption of the fabric is much greater than cardboard.

Stain Test of Coated Fabrics

The stain resistance of 2K-PUD coated fabrics to ink, coffee, ketchup and lotion was evaluated. The stain was cleaned using a specific cleaning agent as described in the Experimental Section. The stain resistance was graded on relative scale by visual observation (Table 8). Overall 2K-PUD coated fabrics performed well in this stain resistance test.

Table 4. PUD Film Properties

PUD Type	1K- PUD PDO-A 2000	2K- PUD PDO-A 2000	2K- PUD PDO-Sb 2000	2K- PUD BDO-A 2000	2K- PUD PO3G 2000	2K- PUD PTMG 2000
Equivalent ratio: NCO/HFO-4	-	2.0	2.0	2.0	2.0	2.0
Properties						
Tensile stress at break, psi	5394±665	2739±478	2844±429	3518±1278 (break) 3097±348* (yield)	1822±25	3244±644
Tensile strain at break, %	795±93	199±39	239±48	106±39 (break) 7.4±1.4 (yield)	206±28	157±29
Tensile stress at 50% extension, psi	442±46	945±74	844±215	2313±508	628±65	1592±231
Tensile stress at 100% extension, psi	524±50	1347±139	1089±297	3085±208	946±103	2339±359
Tensile stress at 200% extension, psi	689±76	2342±22	2057±539	-	1707±175	-
Tensile stress at 300% extension, psi	974±141	-	2710±	-	-	-
Hardness, Pencil	> 9H	> 9H	> 9H	> 9H	> 9H	8H
Impact resistance (at max height)	No tear	No tear	No tear	No tear	No tear	No tear
Gloss of film, GU (cardboard)	87±8	69±7	76±8	79±4	89±4	99±10
Glass transition temp. (T _g), °C	-47.9	-48.7	-51.2	-52.63	-69.2	-80.24
Solvent resistance (spot test)						
Relative grade**						
Water	1	1	1	1	1	1
IPA	5	1	2	1	2	1
Toluene	3	2	4	4	2	4
MEK	5	4	4	1	2	4

* 4 of 15 tested specimens exhibited tensile strength at yield or tensile strength at break (reported). 11 specimens broke at yield with 5519 psi at ~ 7% strain.

** Relative scale of coating change: (1) = No effect, (5) = Worst effect.

Table 5. Abrasion Resistance of PUDs

PUD Type	1K- PUD PDO-A 2000	2K- PUD PDO-A 2000	2K- PUD PDO-Sb 2000	2K- PUD BDO-A 2000	2K- PUD PO3G 2000	2K- PUD PTMG 2000
Equivalent ratio: NCO/HFO-4	-	2.0	2.0	2.0	2.0	2.0
Taber abrasion test conditions: ASTM D4060: test wheel C-10, 1000g (on each side), 1000 cycles*						
Weight of test sample, g	1.490	1.178	1.330	1.301	1.121	1.543
Weight Loss, g/1000 cycles	0.020	0.035	0.022	0.014	0.005	0.008

* PUDs were coated on Poplar wood substrate (2618, Home Depot), 1/4" thickness. The PUD thickness was ~ 0.1mm.

Hydrolytic Aging Testing of Coated Fabrics

Hydrolytic aging was carried out on fabric coated with 2K-PUD and 1K-PUD films (Wire Coaters 15 and 100) at two wet application thicknesses, 1.5 mils and 10 mils, respectively. Water resistance of PUD coated fabrics prior and after hydrolytic aging was evaluated by measuring the time difference to hold water on top of the coating (Table 9). The samples were monitored up to 5 min. Water resistance of plain fabric was evaluated as a control. Plain fabrics absorbed water in less than 1 minute after application. Water resistance was found to depend on the thickness of coating, fabric substrate, and composition of PUD dispersion. The samples coated with Wire Coat 100 passed 5 minutes of water resistance with a few exceptions. The real time was significantly longer than 5 minutes. Water resistance of coated fabric with thinner films (Wire Coater 15) was lower as would be expected and re-emphasizes the film thickness dependence. 2K-PUD coating on cotton performed the best as all samples reached 5 minutes of water hold out. Polyester and Nylon followed in that order in terms of results. Nylon appears to be the most challenging fabric substrate tested.

These results indicate that the coating process needs to be optimized for each type of fabric. PUDs can be coated in one or two layers, on one or both sides. The thickness of coating is very important.

Washing of Coated Fabrics

PUD coated fabrics (Wire Coater 100) were washed by soaking each coated fabric five times at room temperature in a laundry detergent-water solution (Spring Breeze Premium Laundry Detergent, Target) for 30 minutes, rinsed in water after each washing cycle, and dried at 50°C for 1 hour. Coated fabrics that were washed exhibited no peeling of the coating. Water hold out testing was performed on the PUD coated fabrics and compared to data for water hold prior to washing/aging (Table 9 and Table 1). Coated cotton and polyester fabrics performed well after 5 washing cycles; however, coated nylon fabric did not resist water well after this washing testing (Table 10). These results indicate that coating process needs to be optimized for each type of fabric type.

Table 6. Solvent Resistance of PUD Coating to Isopropyl Alcohol (IPA), Rub Test

PUD Type	1K PUD PDO-A 2000	2K PUD PDO-A 2000	2K PUD PDO-Sb 2000	2K PUD BDO-A 2000	2K PUD PO3G 2000	2K PUD PTMG 2000
Equivalent ratio: NCO/HFO-4	-	2.0	2.0	2.0	2.0	2.0
Test Method: Double Rub Test, 200 rubs, Coated on Metal substrate						
Change in Film thickness after 50 double rubs, %	-13.33	-9.33	+10.22	-0.67	-10.68	-2.92
Change in Film thickness after 100 double rubs, %	-17.95	-13.17	+10.54	-3.7	-17.22	-7.34
Change in Film thickness after 150 double rubs, %	33.74	-11.03	-1.92	-7.02	-0.97	-8.05
Change in Film thickness after 200 double rubs, %	-43.97	-15.22	+8.31	-7.24	-17.41	-3.67
Relative Ranking	4	3	2	1	2	1

Table 7. Gloss of 2K-PUDs coated on various fabrics

PUD Type	1K PUD PDO-A 2000	2K PUD PDO-A 2000	2K PUD PDO-Sb 2000	2K PUD BDO-A 2000	2K PUD PO3G 2000	2K PUD PTMG 2000
Equivalent ratio: NCO/HFO-4	-	2.0	2.0	2.0	2.0	2.0
Gloss on Cotton Sateen	2.1±0.00	1.8±0.00	1.4±0.22	1.6±0.06	1.6±0.06	1.6±0.08
Gloss on Nylon		1.8±0.06	1.6±0.00	1.7±0.00	1.7±0.00	1.6±0.00
Gloss on Cotton Polyester Duck	1.6±0.14	1.5±0.05	1.2±0.05	1.4±0.08	1.4±0.08	1.5±0.00

* The Gloss was measured via ETB-0686 glossmeter. PUDs were coated with Wire Coat 100 (10 mil or 70 microns) on fabrics.

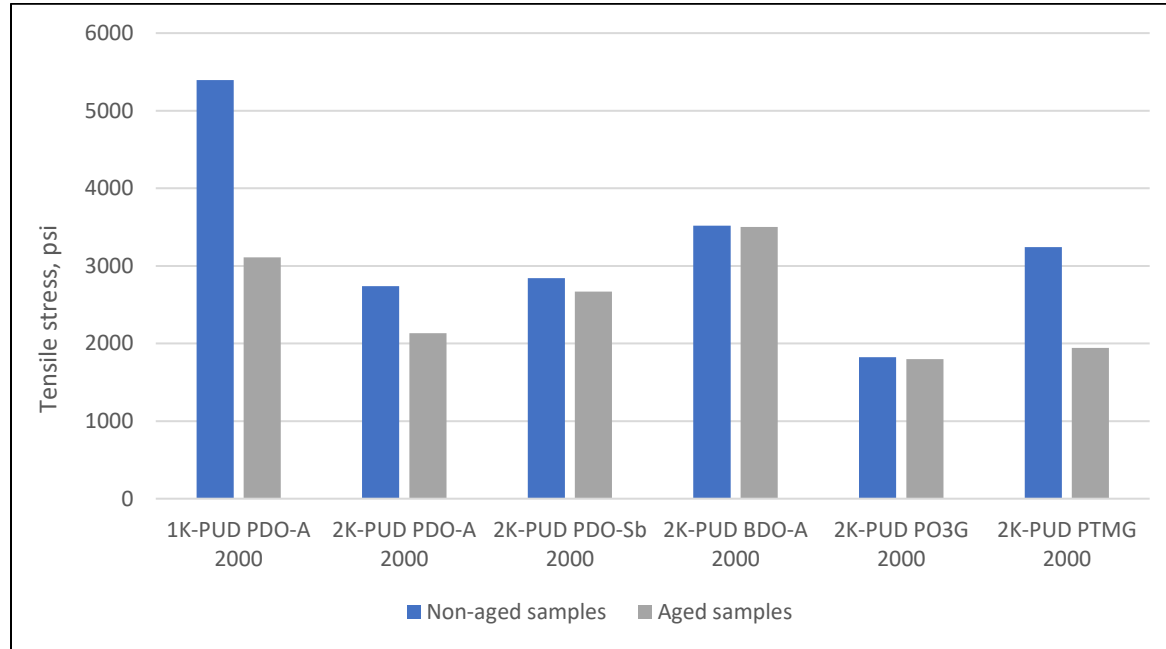


Figure 5. Effect of hydrolytic aging (50C, 95% relative humidity, 3 days) on tensile properties of PUD film

Tensile stress @ Break, psi	5394±665	2739±478	2844±429	3518±1278 (break) 3097±348* (yield)	1822±253	3244±644
Tensile strain@ Break, psi	795±93	199±39	239±48	106±39 (break) 7.4±1.4 (yield)	206±28	157±29
Hydrolytic Aging properties (50°C, 95% RH, 3 days)						
Tensile stress @ Break, psi	3111±335	2131±391	2670±402	3502±545	1799±192	1944±284
Tensile strain@ Break, psi	668±69	165±33	232±27	140±20	193±18	135±14
Retention of Tensile Strength, %	57.6	77.8	93	-	98.7	60.0

Table 8. Stain test of PUDs coated on fabrics (cotton, nylon, and polyester) *

Stain (cleaner)	Ink (20% bleach soln.)			Coffee (Liquid dish soap)			Ketchup (Formula 409)			Lotion (Liquid dish soap)			Total	Group#	Overall #
Fabric	Cotton	Nylon	Polyester	Cotton	Nylon	Polyester	Cotton	Nylon	Polyester	Cotton	Nylon	Polyester			
PUD Type															
1K- PUD PDO-A 2000	3	1	1	2	1	2	1	2	1	1	1	1	17	1	2
2K- PUD PDO-A 2000	3	1	2	3	1	2	1	2	2	1	1	1	20	4	5
2K- PUD PDO-Sb 2000	2	2	1	2	2	1	1	3	1	1	1	1	18	2	3
2K- PUD BDO-A 2000	3	1	2	2	1	1	1	3	1	1	1	1	18	2	3
2K- PUD PO3G 2000	1	2	1	3	1	2	1	2	1	1	1	1	16	1	1
2K- PUD PTMG 2000	2	3	3	3	1	3	1	3	1	1	1	1	23	2	6

* Relative scale: 1 - Best, 5 – Worst; # Polyether or polyester PUDs; Lower number is better. ## All PUDs

Table 9. Effect of hydrolytic aging (50°C, 70% RH, 7 days) on PUDs coated fabric.

Wire Coater No.	100 (non-aged fabric)			15 (aged fabric)			100 (aged fabric)			Total	Group*	Overall**
	Water drop holding (min)			Water drop holding (min)			Water drop holding (min)					
Coated Fabric	Cotton	Nylon	Polyester	Cotton	Nylon	Polyester	Cotton	Nylon	Polyester			
<u>Fabric only</u>	<u>< 1 min</u>	<u>< 1 min</u>	<u>< 1 min</u>									
PUD Type												
1K- PUD PDO-A 2000	> 5 min	2-3 min	> 5 min	> 5 min	> 5 min	< 30 sec	> 5 min	1-5 min	> 5 min	36.0	4	6
2K- PUD PDO-A 2000	> 5 min	> 5 min	> 5 min	> 5 min	< 1 min	< 2 min	> 5 min	> 5 min	> 5 min	38.0	3	4
2K- PUD PDO-Sb 2000	> 5 min	> 5 min	> 5 min	> 5 min	> 5 min	> 5 min	> 5 min	> 5 min	> 5 min	45.0	1	1
2K- PUD BDO-A 2000	> 5 min	> 5 min	> 5 min	> 5 min	< 2 min	4-5 min	> 5 min	> 5 min	> 5 min	41.5	2	2
2K-PUD PO3G 2000	> 5 min	1-2 min	> 5 min	> 5 min	> 5 min	> 5 min	> 5 min	1-2 min	> 5 min	38.0	2	4
2K-PUD PTMG-2000	> 5 min	> 5 min	4-5 min	> 5 min	> 5 min	< 2min	> 5 min	> 5 min	4-5 min	41.5	1	2

Sum of times, midpoint or maximum. * Polyether or polyester PUDs; Lower number is better. ** All PUDs.

Table 10. Effect of Washing on Water Resistance of PUDs coated fabrics.

Wire Coater	100 (non-aged fabric)			100 (fabric after washing)					
	Water drop holding (min)			Water drop holding (min)					
Coated fabric	Cotton	Nylon	Polyester	Cotton	Nylon	Polyester			
Fabric only	< 1 min	< 1 min	< 1min						
PUD Type							Total #	Group Ranking*	Overall Ranking**
1K-PUD PDO-A 2000	> 5 min	2-3 min	> 5 min	< 1 min	< 30 sec	4-5 min	18.50	4	6
2K-PUD PDO-A 2000	> 5 min	> 5 min	> 5 min	> 5 min	< 30 sec	> 5 min	25.50	3	3
2K-PUD PDO-Sb 2000	> 5 min	> 5 min	> 5 min	> 5 min	< 2 min	> 5 min	27.00	1	1
2K-PUD BDO- A 2000	> 5 min	> 5 min	> 5 min	> 5 min	30 sec – 1 min	> 5 min	25.75	2	2
2K-PUD PO3G 2000	> 5 min	1-2 min	> 5 min	> 5 min	< 30 sec	> 5 min	22.00	2	5
2K-PUD PTMG 2000	> 5 min	> 5 min	4-5 min	> 5 min	30 sec - 1 min	> 5 min	25.25	1	4

Sum of times, midpoint or maximum. * Polyether or polyester PUDs; Lower number is better. ** All PUDs.

CONCLUSIONS

Two component polyurethane water dispersions (PUDs) based on 1,3-Propanediol polyester polyols (PDO Adipate 2000 and PDO Sebacate 2000) and polyether polyols (Velvetol H 2000, Allessa) were produced and applied on three uncoated fabric sources (cotton sateen, polyester duck, and textured nylon) to evaluate their performance and commercial viability. The commercial reference PUDs were based on BDO Adipate 2000 and poly(oxytetramethylene) glycol 2000 (PTMG 2000).

The films and coatings explored in this study exhibited a good combination of properties including tensile strength, elongation, pencil hardness, abrasion resistance, impact resistance, and solvent resistance. Furthermore, the coatings demonstrated good hydrolytic aging resistance, adhesion and wash resistance on the three types of fabric. It is noted that nylon presents the most challenging fabric substrate and will need additional work to achieve the performance level of cotton or polyester. Overall, 2K-PUDs including those prepared with Bio-based Susterra® propanediol polyester and polyether polyols exhibited promising test results as compared to the referent materials in testing on coated fabrics and with additional optimization could become viable candidates as textile coatings.

ACKNOWLEDGEMENTS

DuPont Tate & Lyle Bio Products would like to thank Aisa Sendijarevic and Ibrahim Sendijarevic from Troy Polymers, Inc., for their dedication to this project and the ultimate preparation, syntheses and analyses.

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