

Advances in the use of bio-based components in aqueous polyurethane dispersions for coating and adhesive applications

STEPHEN HURFF

*DuPont Tate & Lyle Bio Products Co., LLC
200 Powder Mill Road
Wilmington, DE 19803 USA*

AISA SENDIJAREVIC

*Troy Polymers
330 E. Maple Rd., Suite L
Troy, MI 48083 USA*

MICHAEL SHEN

*DuPont Tate & Lyle Bio Products Co., LLC
Bldg. 11, 399 Keyuan Road
Shanghai, 201203, China*

IBRAHIM SENDIJAREVIC

*Troy Polymers
330 E. Maple Rd., Suite L
Troy, MI 48083 USA*

ABSTRACT

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 is accepted as shown by its use on commercial scale to produce polyester and polyether polyols. 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. To obtain PUDs with good performance, the effects of varying the block components must be understood. The introduction of dimethylol propanoic acid (DMPA) pendant ionic groups into hard segment blocks facilitates the formation of stable PUDs of acceptable solids loading by increasing hydrogen bond interactions. The use of lower molecular weight bio-based polyester/polyether soft segments based on 1,3-PDO with increased hard segment blocks builds on our understanding of the structural relationships and properties in coatings and adhesives applications. The bio-based films prepared in this investigation provide an extended useful thermal range compared to reference commercial petroleum based PUDs as well as equivalent toughness and flexibility for these one-component 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 commercial scale to produce polyester polyols. Bio-based content of these polyols vary depending on the acid used as co-reactant in the polyol synthesis and can go up to 100%. In this study, the following 1,3-PDO based polyols were evaluated in PUDs application: 1,3-PDO adipate 1000 polyester polyol, 100% bio-based 1,3-PDO sebacate 1000 polyester polyols and 100% bio-based PO3G 1000 polyether polyol based (Velvetol H1000, Allessa). BDO adipate 1000 polyester polyol and polycaprolactone polyol 1000 were used as reference polyester polyols in preparation of PUDs and poly(oxytetramethylene) glycol 1000 (PTMG 1000) as a reference polyether polyol.

EXPERIMENTAL

The chemicals and materials used in this study are listed in Table 1 (next page). Aliphatic isocyanate IPDI was used as received from the supplier. The isocyanate content was checked by the dibutylamine method, ASTM D 5155. Moisture was removed from the polyols by 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%. Water content was measured via Karl Fisher method, ASTM D 4672. The following properties of polyols were tested with each test method indicated:

Polvol Property	Test method
Acid Value, mg KOH/g	ASTM D 4662
Hydroxyl Value, mg KOH/g	ASTM D 4274
Glass transition and melting temperature	Differential scanning analysis (DSC)

<i>Designation</i>	<i>Description</i>		<i>Manufacturer/Distributor</i>
2,2-Bis(hydroxymethyl) propionic acid	DMPA, 98%, chain extender		Aldrich
Desmodur I	IPDI – Isophorone diisocyanate		Bayer Material Science (now Covestro)
Triethylamine	TEA		Sigma Aldrich
Acetone	Reagent grade acetone		Chem Pure Brand Chemicals
Ethylenediamine, 99%	Ethylenediamine		Alfa Aesar
Dabco T-12	Dibutyltin dilaurate catalyst		Air Products
Poly S 1000 PAR	1,3-PDO adipate 1000 MW		ITWC, Inc.
Piothane 1000 PDO-SBA	1,3 PDO sebacate 1000 MW		Specialty Resins
Poly S 1000 BA	BDO adipate 1000 MW		ITWC, Inc
Capa 2100	Polycaprolactone polyol 1000 MW		Perstorp
Velvetol H 1000	PO3G 1000 polyol		Allessa
Terathane 1000	Poly(oxytetramethylene) glycol, 1000 MW		Invista
Standardized adhesion test plate, AR-14	Aluminum plates, Dimensions (1 x 4 x 0.063 inches)		Q-Lab
Metal plate for coating, S-46	Steel plate, ground one side, (0.8 x 102 x 152 cm)		Q-Lab

<i>Polyol</i>	<i>Poly S 1000 PAR</i>	<i>Piothane 1000 PDO-SBA</i>	<i>Poly S 1000 BA</i>	<i>Capa 2100</i>	<i>Velvetol H 1000</i>	<i>Terathane 1000</i>
<i>Polyol abbreviation</i>	PA	PSb	BA	PCL	PO3G	PTMG
OH Value, mg KOH/g	108.21	110.35	105.15	111.29	106.67	113.25
Acid Value, mg KOH/g	0.38	0.19	0.27	0.04	0.05	0.0
Tg, DSC (°C)	-68.86	ND	ND	-71.90	-77.41	ND
Melt transition, DSC (°C)	24.07	53.78	47.94	38.28	18.18	24.42

The DSC graphs used to determine the Tg and melt transition temperatures for the polyols listed in Table 2 are shown on the following pages. Note that for the PSb, BA and the PTMG there are no Tg temperatures detected. The DSC results for all the polyols tested were as expected based on previous work.

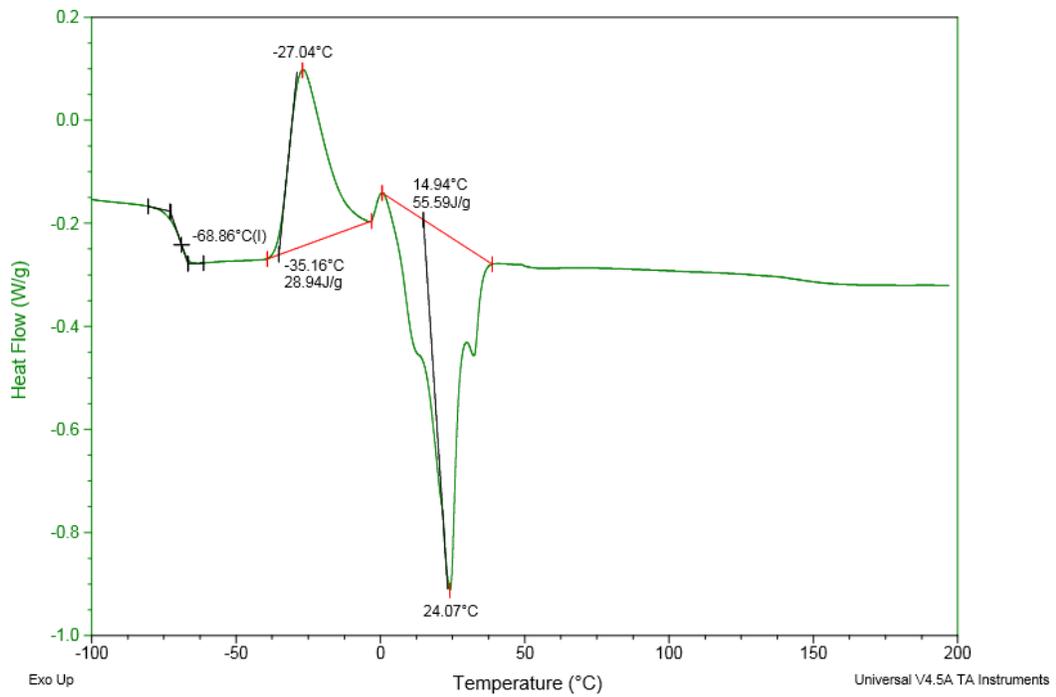


Figure 1. Differential scanning calorimetry graph of Poly S 1000 PAR polyol

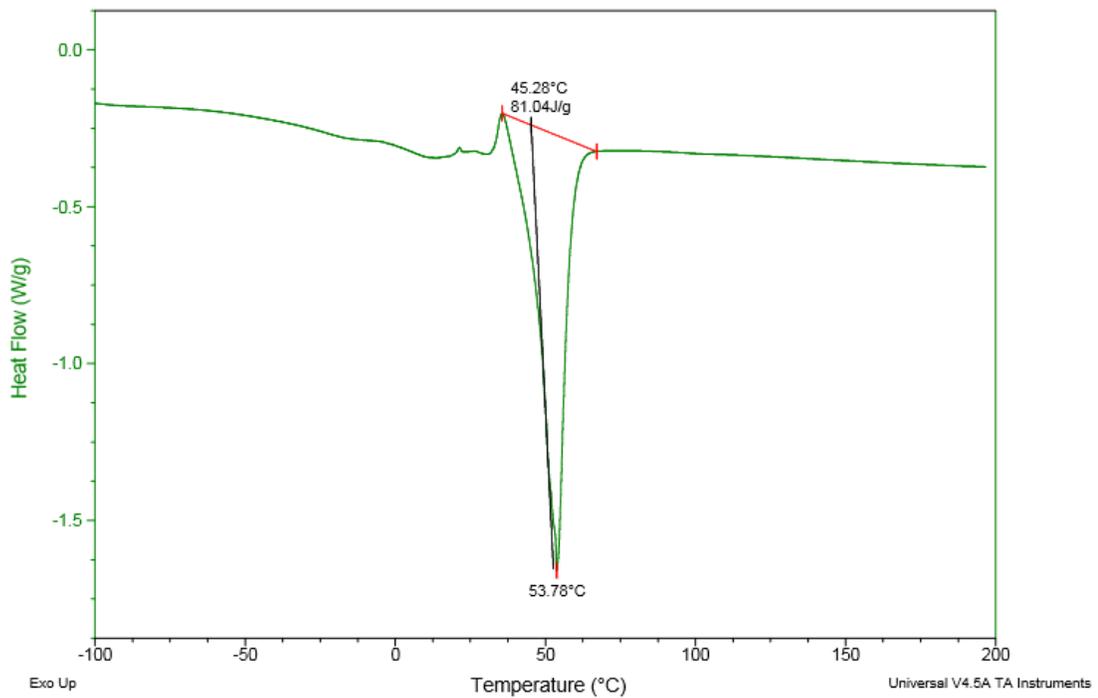


Figure 2. Differential scanning calorimetry graph of Piothane 1000 PDO-SBA polyol

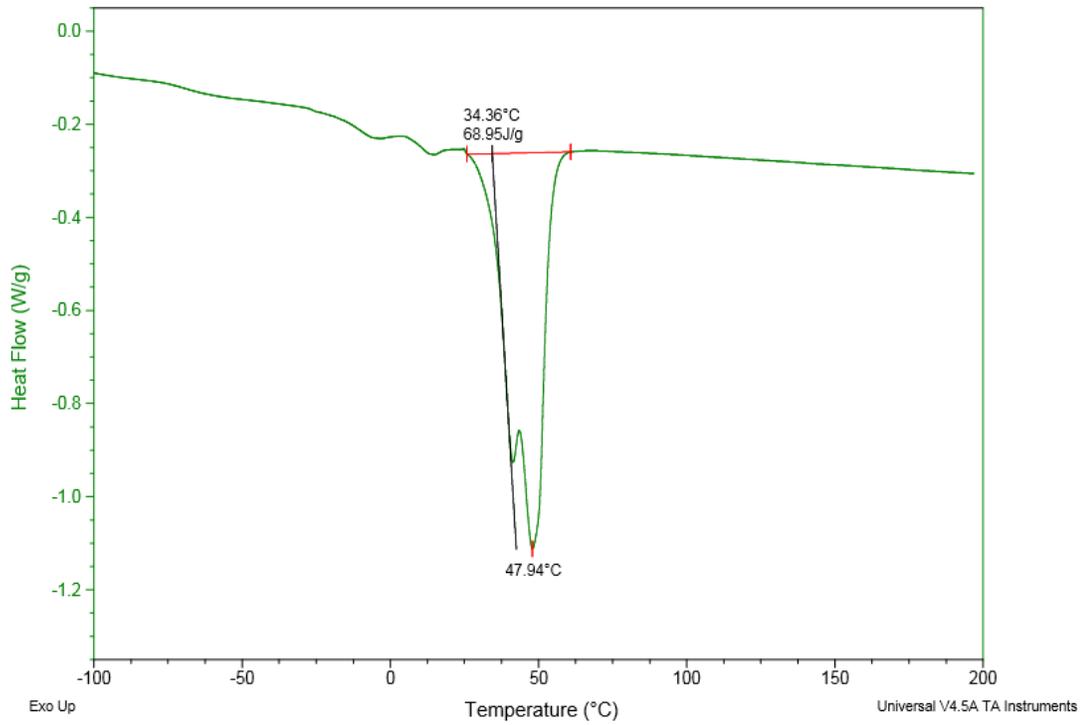


Figure 3. Differential scanning calorimetry graph of Poly S 1000 BA polyol

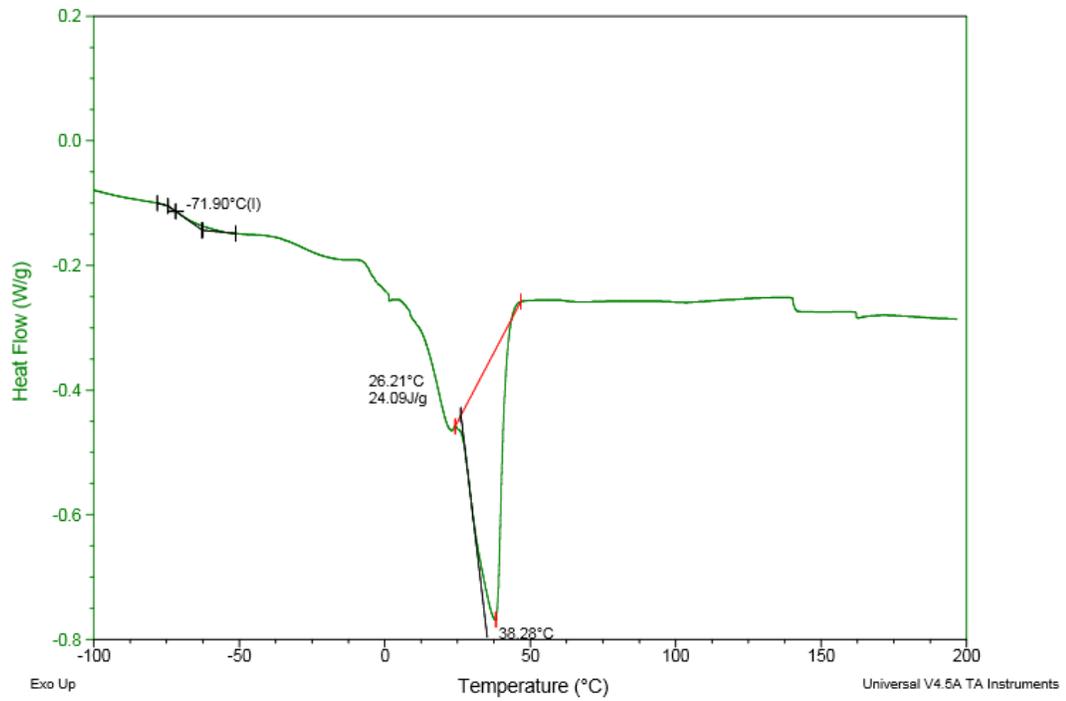


Figure 4. Differential scanning calorimetry graph of Capa 2100 polyol

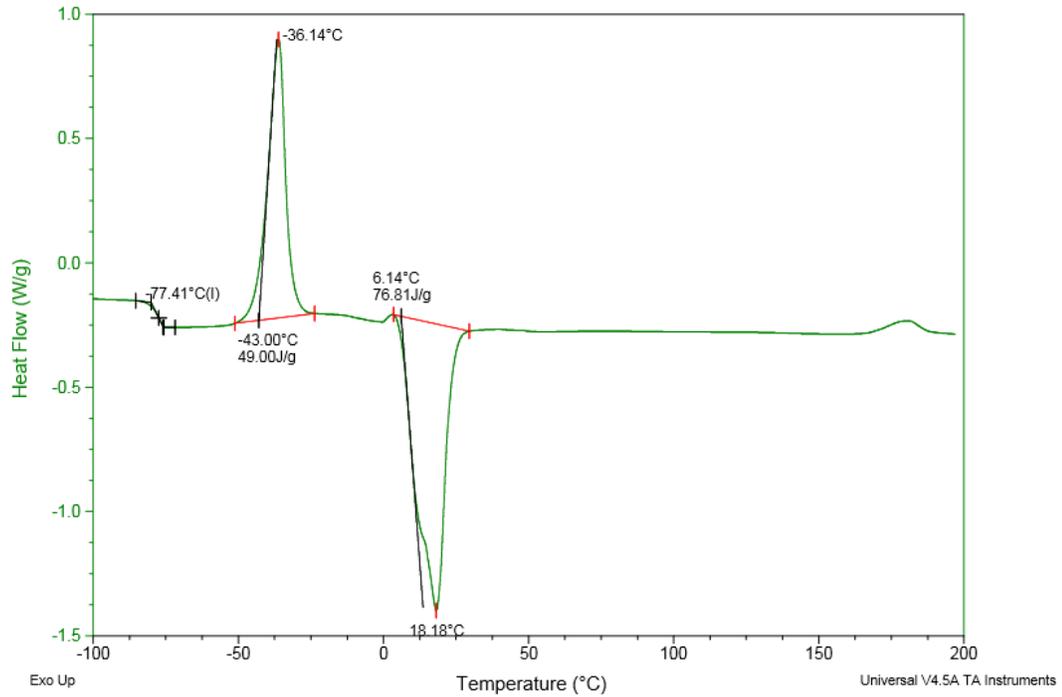


Figure 5. Differential scanning calorimetry graph of Velvetol H 1000 polyol

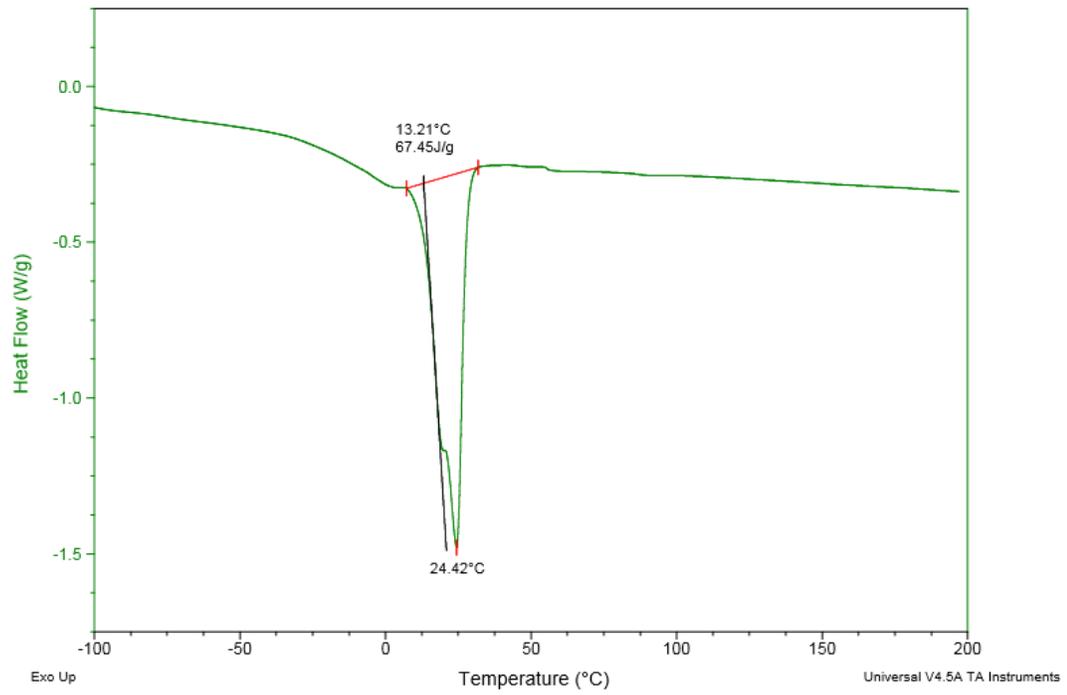


Figure 6. Differential scanning calorimetry graph of Terathane 1000

PUD formulation and synthesis

All PUDs were prepared at 1/1/3 molar ratio of polyol/DMPA/isocyanate and 50% hard segment concentration (Tables 3 and 4).

In this study, anionic type PUDs were prepared as presented in Scheme I. The synthesis for these types of PUDs consist of the following steps:

Step 1: NCO-terminated prepolymer is prepared by reacting aliphatic diisocyanate with a blend of polyol and chain extender DMPA (2,2-dimethylolpropionic acid) to introduce the pendant carboxylic group into the prepolymer backbone.

Step 2: The carboxylic group is neutralized with triethylamine (TEA), forming a salt group that helps with dispersion of NCO-prepolymer in water.

Step 3: The NCO-prepolymer is dispersed in water.

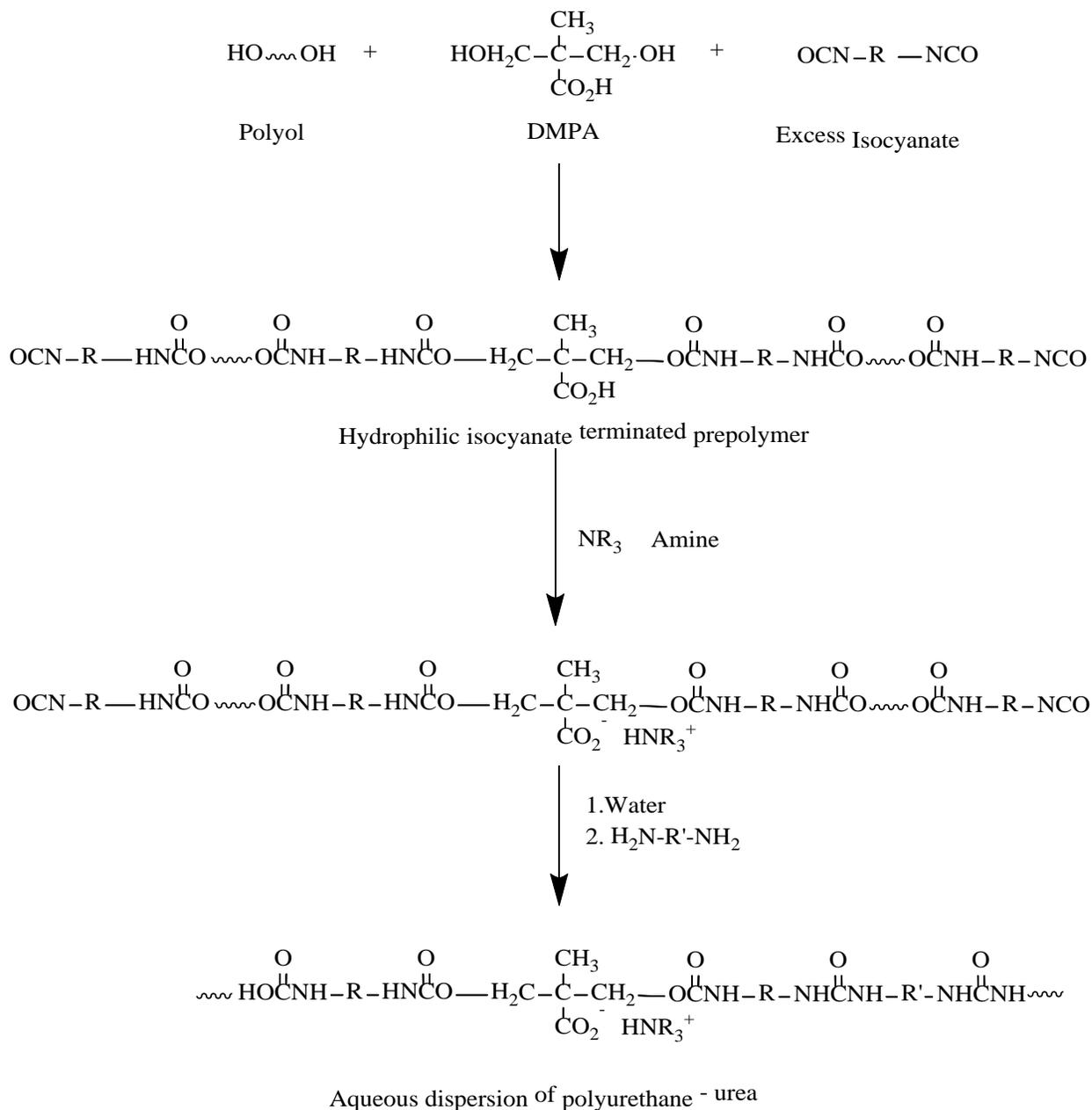
Step 4: The NCO-prepolymer is chain extended with diamine to form poly(urethane-urea) water dispersion.

Initially, PUDs based on the PTMG 1000 polyol were prepared using this “bulk” procedure at 40% solid content (Table 3, Column 2); however, gelling occurred in Step-4 of the reaction. The synthesis was repeated **using the acetone process** in which the product of the Step-2 reaction is dissolved in acetone instead water (Table 3, Column 3). The acetone solution of Step-2 product is dispersed in water (phase inversion) under vigorous mixing followed by Step-4 reaction.

Table 3. Properties of PUDs vs. Synthesis Conditions		
PUD Designation	PUD/ PTMG_1	PUD/ PTMG_2
Protocol	Bulk	Acetone
Formulations:		
Poly S 1000 PAR, g		-
Terathane 1000, g	200	200
DMPA, g	26.82	26.82
Desmodur I – IPDI, g	140.05	140.05
Triethylamine, g	20.24	20.24
Dabco T-12, g	0.069	0.069
Acetone, g	-	144.25
H ₂ O, g	598+48	598+48
Ethylenediamine, g	12.57	12.57
Hard segment, %	50	50
Solid content, %	40% (gel)	40% (paste) (when acetone removed from paste)
Solid content, %	NA	32.1*
Stability of dispersion over time (visual observation)	NA	Stable
Viscosity (25°C), cps	NA	86

*PUD of 32.1% solid content was prepared by adding additional amount of acetone and water to PUD/PTMG-2 of 40% solid content and subsequently removing acetone.

The synthesis of PUDs was carried out in 1000 ml reactor, equipped with nitrogen flow, heating mantle (with temperature controller) and mechanical mixing. Liquid polyol and DMPA were charged into the reactor and heated under mixing to 135°C. At that temperature DMPA was melted and homogenized with the polyol for 10 minutes. The mixture was cooled gradually under mixing to 80°C. Dabco T12 catalyst was added to the reactor followed by addition of IPDI. The NCO-prepolymer synthesis was monitored via NCO% determination (ASTM D 5155). After NCO-prepolymer was formed, the temperature was reduced to 50°C. Triethylamine was added to react with carboxylic group and mixed for 20 minutes with the NCO-prepolymer. The heating mantle was detached from the reaction kettle and then acetone was added to NCO-prepolymer and homogenized. Distilled water was added to the acetone solution of ionomer-prepolymer via syringe under vigorous mixing forming a fine dispersion. Ethylene diamine (EDA) mixed with 25 grams of water was added to the prepolymer dispersion and mixed for 20 minutes to react with terminal isocyanate groups to form the polyurethane/urea polymer. Acetone was removed from the PUD dispersion via Rota-evaporator under vacuum of about 100 mmHg and with a water bath temperature of 45°C.



Scheme 1. Basic steps in preparation of anionic PUDs

Testing of PUDs

a. PUD liquid dispersions:

- Viscosity of water polyurethane dispersions (25°C, ASTM D 4878 (Brookfield viscometer))
- Stability of dispersion over time (visual observation)
- pH value
- Solid content, %
- Density

Solid content was measured by the weight change after drying PUD dispersions four hours at 105°C.

b. PUD-based films and coatings:

Coatings were prepared by coating PUD dispersion via Dr. Blade at 30 mils thickness onto steel panels (Type S-46, Q-Lab Corporation) and films by coatings dispersion onto polypropylene substrate. The films and coatings were left to dry for 24 hours at room temperature and conditioned for additional two days prior to testing. The following properties of films and coatings were measured:

PUD films:

- Tensile strength, modulus and elongation at break (flexibility) ASTM D2370 (ten specimens tested)
- Gloss (Gloss-meter)
- Thermal properties (Glass transition temperature, T_g), DSC analysis
- FTIR analysis

PUD coatings:

- Hardness, Pencil hardness, ASTM D3363
- Impact resistance, ASTM D2794
- Adhesion, Tape test, ASTM D3359

Humid aging properties:

- Stress-strain properties of PUD-based films were measured upon hydrolytic aging in a moisture chamber at 95% relative humidity, 50°C for 3 days
- The hardness and adhesion of coatings cast on metal substrate was measured after hydrolytic aging in a moisture chamber 3 days, 38°C and 95% relative humidity ASTM D 2247

Solvent resistance properties:

- Solvent rub test, ASTM D5402 (change of film thickness of coatings after 25 double rubs)
- The spreading of various liquids (water, alkaline and acid water solution, toluene and MEK) upon application onto surface of films

c. PUD-Adhesives:

The adhesive strength of PUDs in bonding aluminum substrate was measured according to ASTM D1002 (Lap-shear test). Standardized aluminum plates 1 x 4 x 0.063 inches (AR-14, Q-Lab) were used a substrate in adhesive testing. 0.2 g of water dispersion was spread over ½ x 1 inch bond area of standardized adhesion test plate. Two plates were clamped together over bond area and let to dry at 50°C for three days before testing.

RESULTS and DISCUSSION

PUD synthesis and properties

Initially, the synthesis of PUDs was carried out using the procedure as outlined in Scheme 1 (Table 3, PUD/PTMG_1). The gelling that occurred in Step-4 of the reaction is most probably due to high hard segment concentration and viscosity of the pre-polymer, thus limiting its solubility in water. The synthesis was repeated using *the acetone process* in which the product of Step-2 reaction is dissolved in acetone instead water (Table 3, Column 4). The acetone solution of Step-2 product is dispersed in water (phase inversion) under vigorous mixing followed by the Step-4 reaction. This dispersion (40% solid content) was paste like. The solid content was reduced to ~30% by addition of

acetone and water resulting in significantly lower viscosity. Acetone was removed from dispersion via Rota-evaporator under vacuum 100 -150 psi.

The solid content, as well as the ratio of acetone to water had an effect of the viscosity of dispersions, which is most probably related to the particle size of the PUDs (Table 3, PUD/PA_1 and PUD/PA_2).

Table 4. Formulation and properties of PUDs prepared via acetone procedure							
PUD Designation	PUD/PA_1	PUD/PA_2	PUD/PSb	PUD/BA	PUD/PCL	PUD/PO3G	PUD/PTMG
A. Formulation:							
<i>Poly S 1000 PAR, g</i>	100	100	-	-	-	-	-
<i>Piothane 1000 PDO-SBA, g</i>	-	-	100	-	-	-	-
<i>Poly S 1000 BA, g</i>	-	-	-	100	-	-	-
<i>Capa 2100, g</i>	-	-	-	-	100	-	-
<i>Velvetol H 1000, g</i>	-	-	-	-	-	100	-
<i>Terathane 1000, g</i>	-	-	-	-	-	-	100
<i>DMPA, g</i>	13.41	13.41	13.41	13.41	13.41	13.41	13.41
<i>Desmodur I – IPDI, g</i>	70.02	70.02	70.02	70.02	70.02	70.02	70.02
<i>Triethylamine, g</i>	10.12	10.01	9.61	9.61	9.72	9.46	9.61
<i>Dabco T-12, g</i>	0.0345	0.069	0.069	0.0345	0.069	0.0345	0.069
<i>Reaction time in the synthesis of prepolymer, (Step-I, Scheme 1) hrs</i>	1:30	2:00	3:15	3:00	2:50	4:00	2:30
<i>Acetone, g</i>	200	100	100	100	100	100	200
<i>H₂O, g</i>	298	450	400	348.19	440	430	400
<i>Ethylenediamine, g</i>	5.33	7.26	6.88	7.21	6.99	7.07	6.81
B. Hard segment, %	49.7	50.2	50.0	50.1	50.0	50.0	50.0
C. Properties of dispersions							
<i>pH</i>	8	8.5	8.5	8.5	9	9	9
<i>Stability of dispersion over time (visual observation)</i>	Stable	Stable	Stable	Stable	Stable	Stable	Stable
<i>Solids, %</i>	28.2	29.86	30.6	34.5	28.78	29.4	31.3
<i>Viscosity (25°C), cps</i>	734	23.1	27	59	24.6	43.2	37.5
<i>Density, g/ml</i>	1.04	1.06	1.05	1.06	1.05	1.04	1.04

It should be noted that the acetone process is a common industrial procedure for PUD synthesis.

The PUDs were anionic and thus slightly alkaline with a pH range from 8 to 9 (Scheme 1, Table 4).

The solid content of PUDs ranged from 28% to 35% and the viscosity was relatively low, typically 23 to 60 cps (Table 4). Polyurethane water dispersions were stable over time.

PUD films and coating - formulations and properties

PUDs in this study were formulated at 50% hard segment concentration to obtain coatings of high hardness (Tables 4 and 7). Most of the polyols used in PUDs synthesis exhibited melt transition in the temperature range from ~18°C to 50°C (DSC), depending on the type of polyol (Table 2, Figures 1 - 6)). However, PUD-based films did not show polyol melt transitions (Figures 7 - 12). The glass transition temperature (T_g) of PUD films was found to depend on the polyol type (Table 9). The absence of soft segment crystallinity is important for clarity of coatings. All coatings and films based on PUDs were transparent and clear. The gloss values for the coatings were relatively high (Table 8).

Table 5. The effect of drying on tensile properties of PUD based films						
<i>Sample designation</i>	PUD/ PA-2	PUD/* PA_2 Dried	PUD/ BA	PUD/* BA Dried	PUD/ PO3G	PUD/* PO3G Dried
<i>Properties</i>						
Appearance	Clear	Clear	Clear	Clear	Clear	Clear
Tensile Strength, psi	6244.96 ± 303.17	5500.71 ± 230.24	6417.14 ± 735.41	5132.36 ± 373.74	6059.21 ± 277.42	6101.67 ± 668.66
Elongation at break, %	522.12 ± 102.89	436.14 ± 24.66	494.06 ± 26.33	380.50 ± 32.43	672.10 ± 32.19	648.35 ± 73.74
Tensile stress at extension 50% , psi	998.90 ± 170.88	1103.96 ± 72.97	925.64 ± 281.94	1158.08 ± 217.09	1085.80 ± 268.73	1080.13 ± 883.59
Tensile stress at extension 100%, psi	1219.89 ± 222.16	1332.67 ± 58.24	1118.72 ± 271.27	1368.00 ± 271.10	1297.75 ± 263.46	1290.28 ± 1032.82
Tensile stress at extension 200%, psi	1842.53 ± 371.82	2111.49 ± 165.81	1903.37 ± 262.48	2203.26 ± 446.11	1725.84 ± 234.50	1712.07 ± 1114.66
Tensile stress at extension 300%, psi	2932.78 ± 632.84	3236.15 ± 188.52	3146.59 ± 485.50	3666.91 ± 453.24	2273.11 ± 173.62	2280.66 ± 1156.27
Toughness, psi	13027.4 ± 1028.0	10481.5 ± 560.4	13304.1 ± 2508.8	8698.0 ± 675.2	19725.5 ± 1315.4	16994.1 ± 1782.1

*The films dried at 50°C for two hours.

DSC Spectra

The DSC Spectra results are shown in Figures 7 through 12 below and were utilized to extract the Tg (flexible segment transition) and the hard segment transition temperatures as summarized in Table 9.

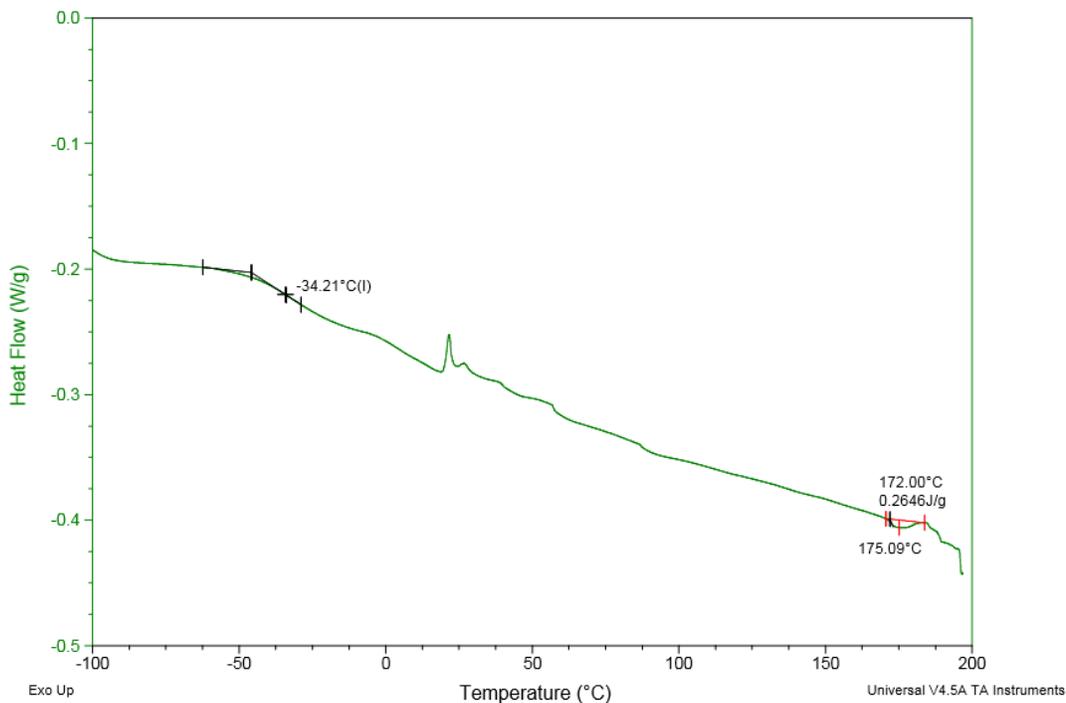


Figure 7. Differential scanning calorimetry graph of film PUD/PA (Table 6)

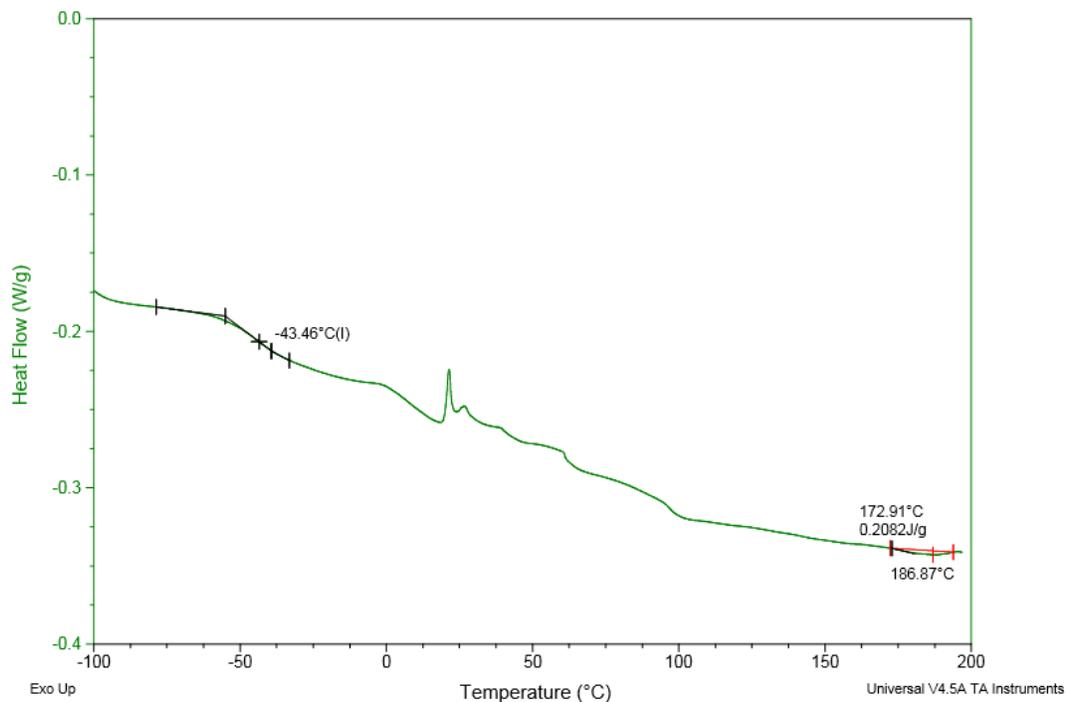


Figure 8. Differential scanning calorimetry graph of film PUD/PSb (Table 6)

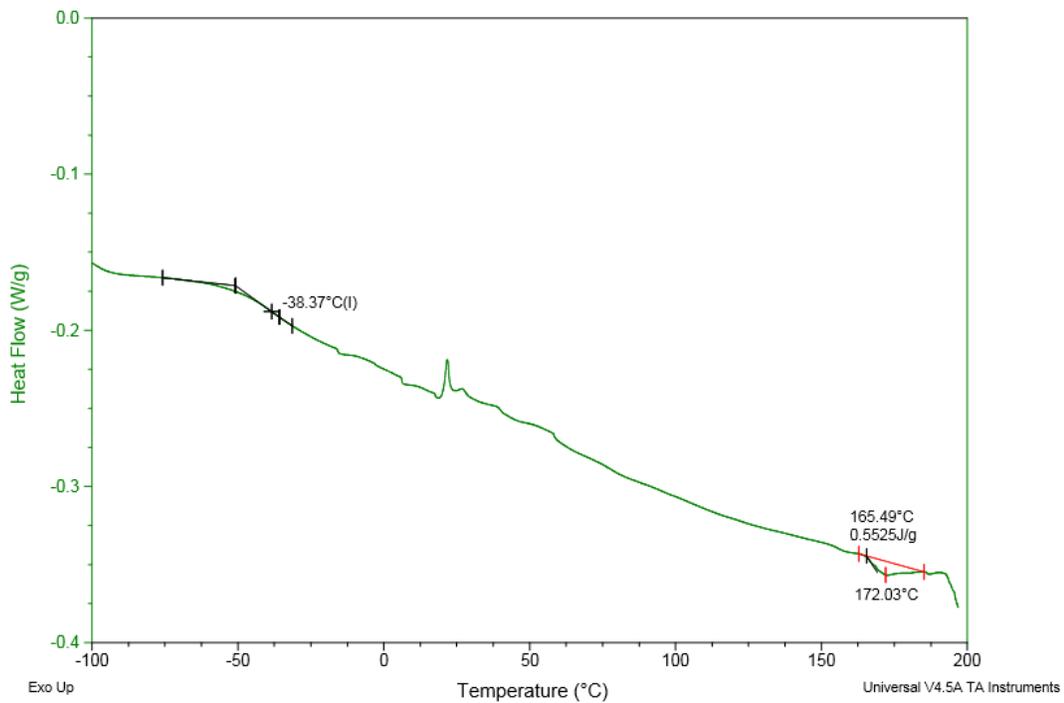


Figure 9. Differential scanning calorimetry graph of film PUD/BA (Table 6)

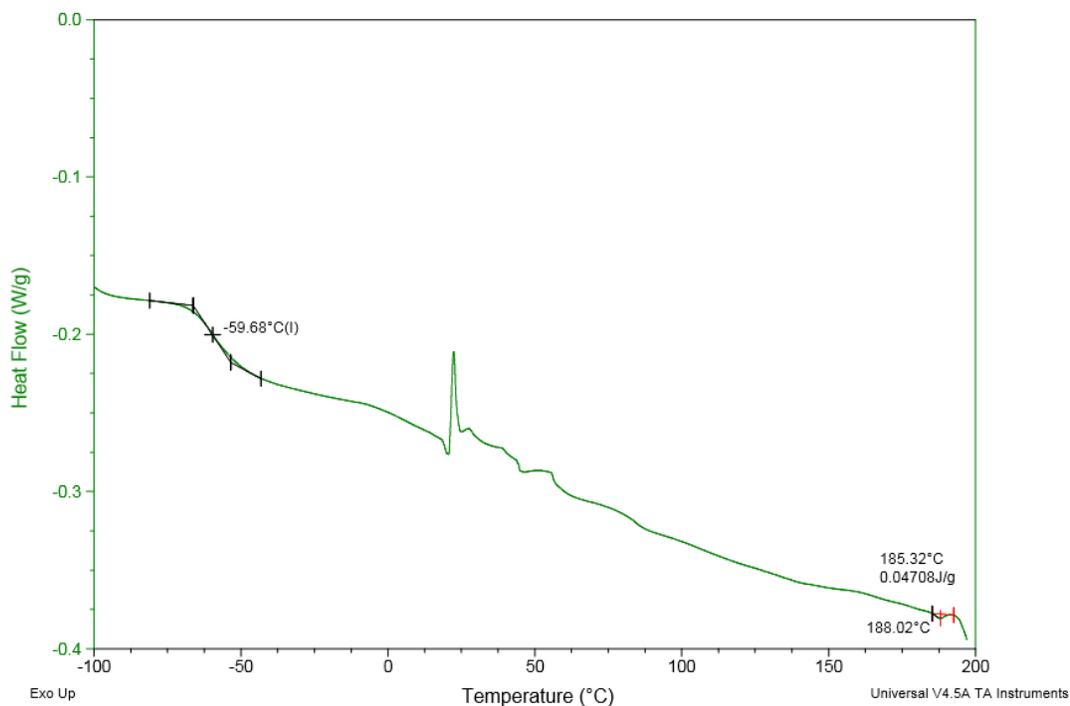


Figure 10. Differential scanning calorimetry graph of film PUD/PO3G (Table 6)

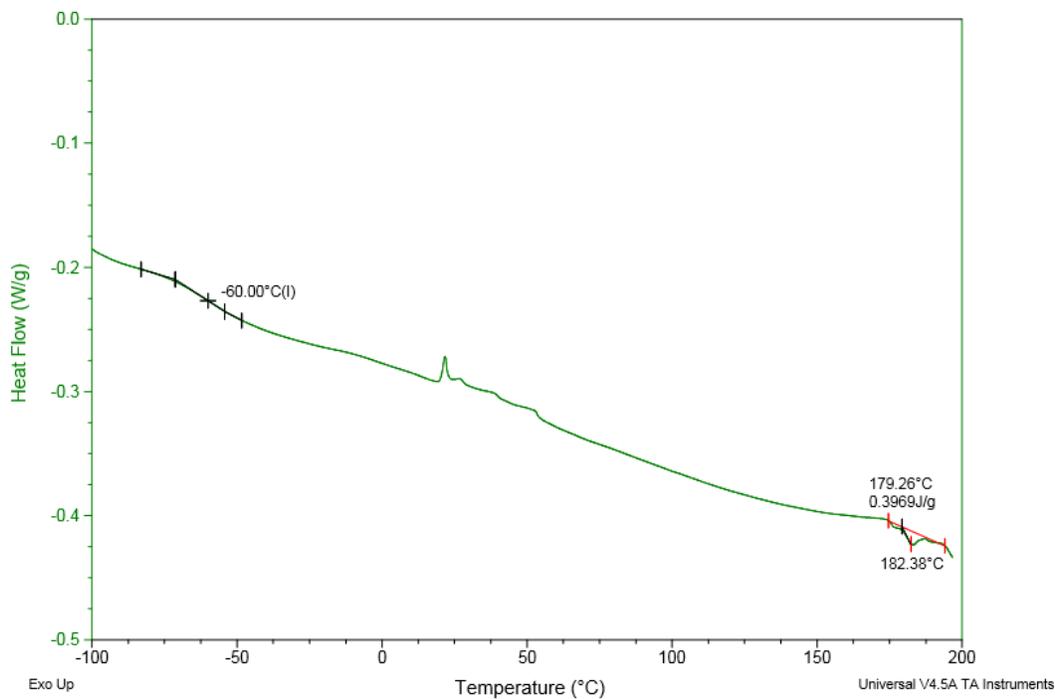


Figure 11. Differential scanning calorimetry graph of film PUD/PTMG (Table 6)

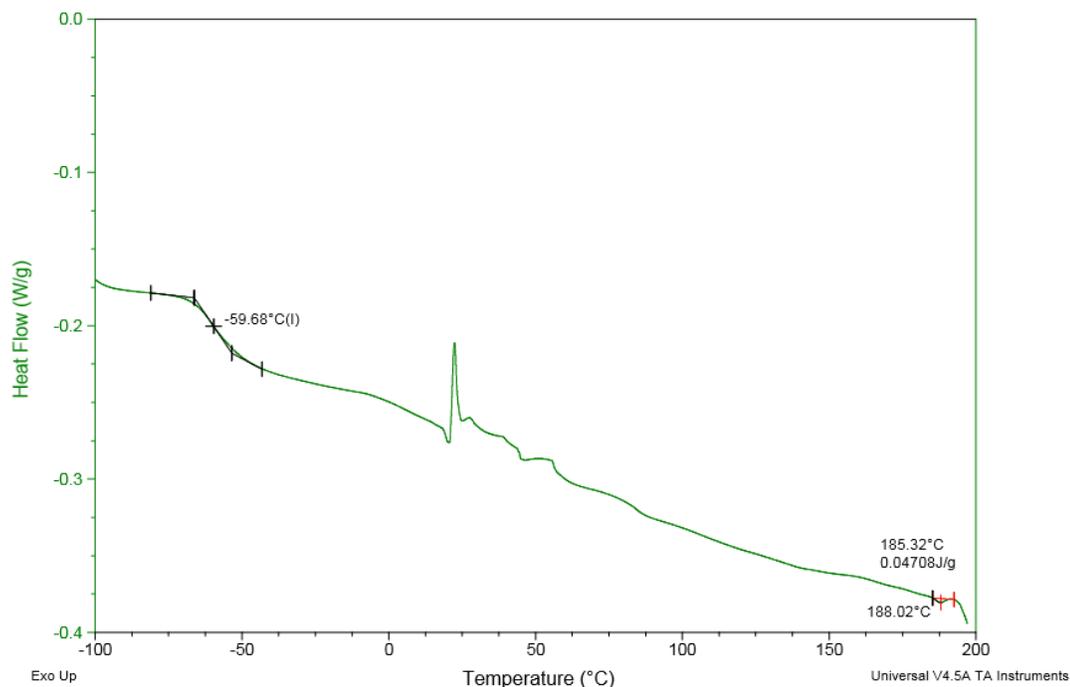


Figure 12. Differential scanning calorimetry graph of film PUD/PCL (Table 6)

FTIR Spectra

The FTIR spectra of PUD-based films exhibited no absorption at 2230 cm^{-1} which would be indicative of NCO - functional groups, thus indicating polymerization was complete (Figures 13 -18).

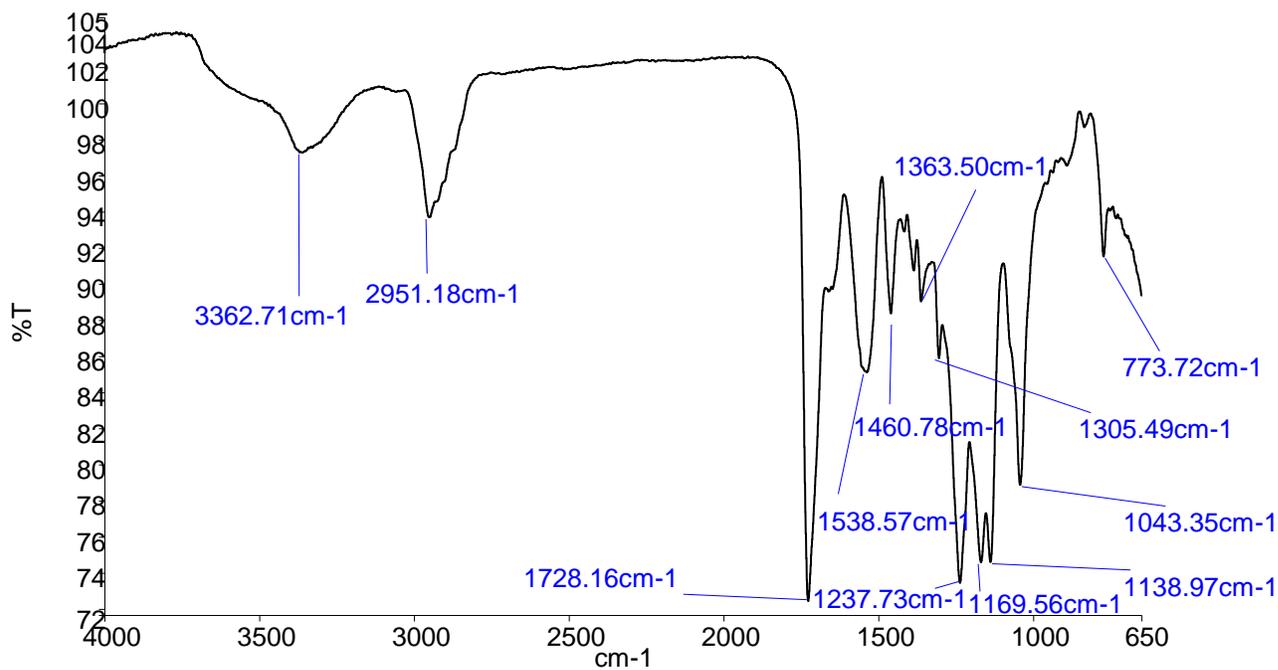


Figure 13. FTIR spectra of film based on PUD/PA dispersion (Table 6)

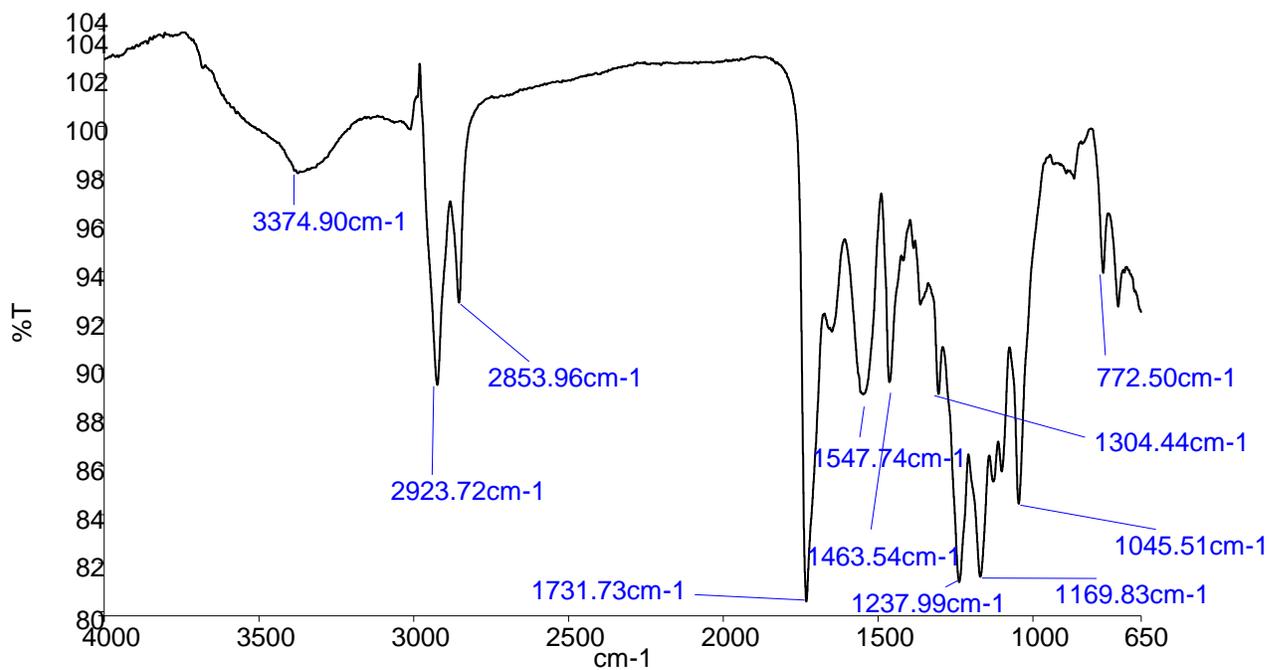


Figure 14. FTIR spectra of film based on PUD/PSb dispersion (Table 6)

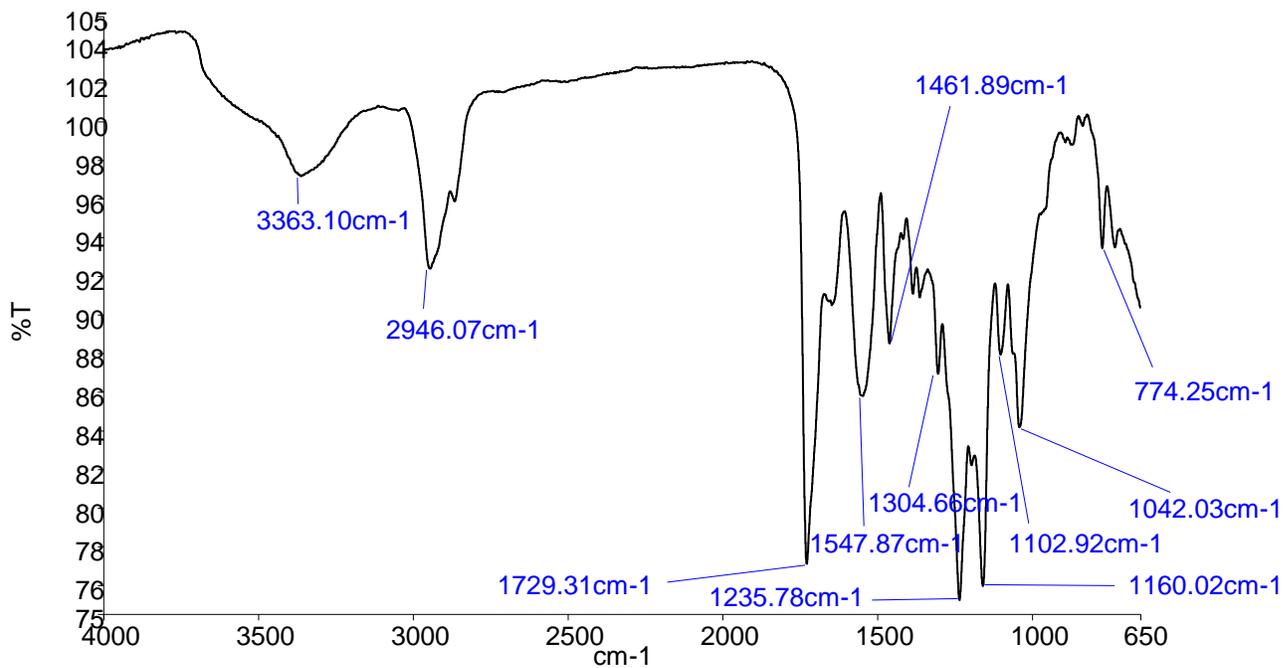


Figure 15. FTIR spectra of film based on PUD/BA (Table 6)

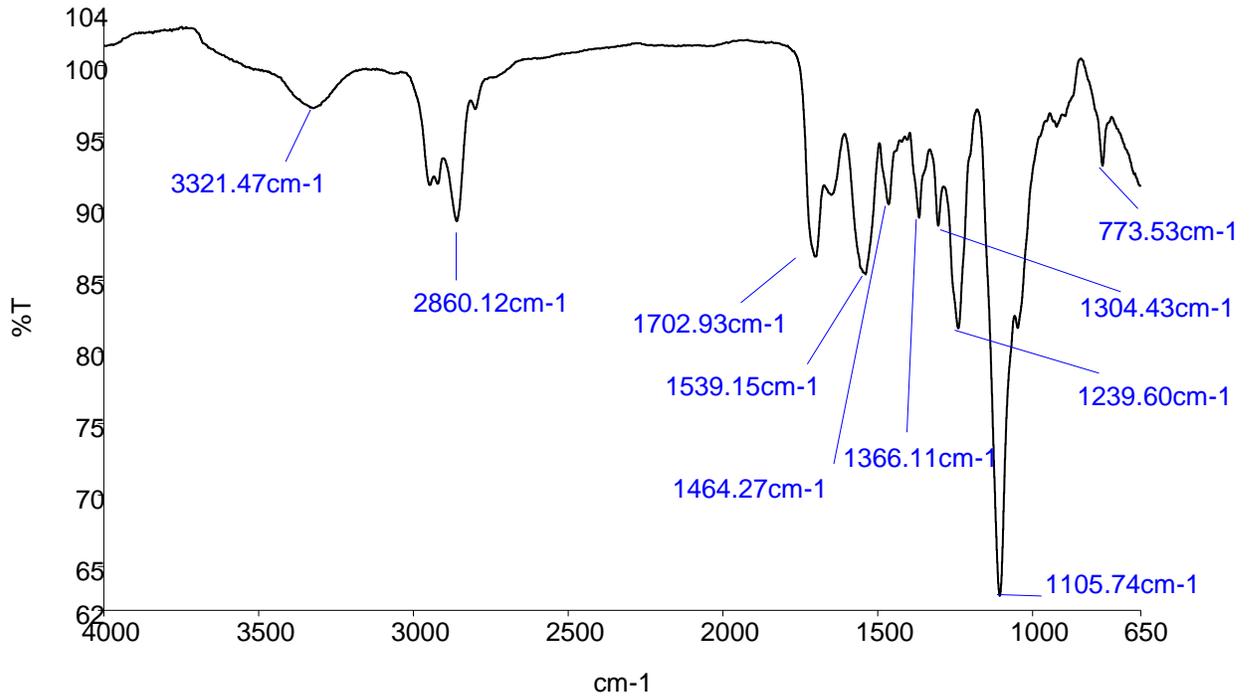


Figure 16. FTIR spectra of film based on PUD/PCI dispersion (Table 6)

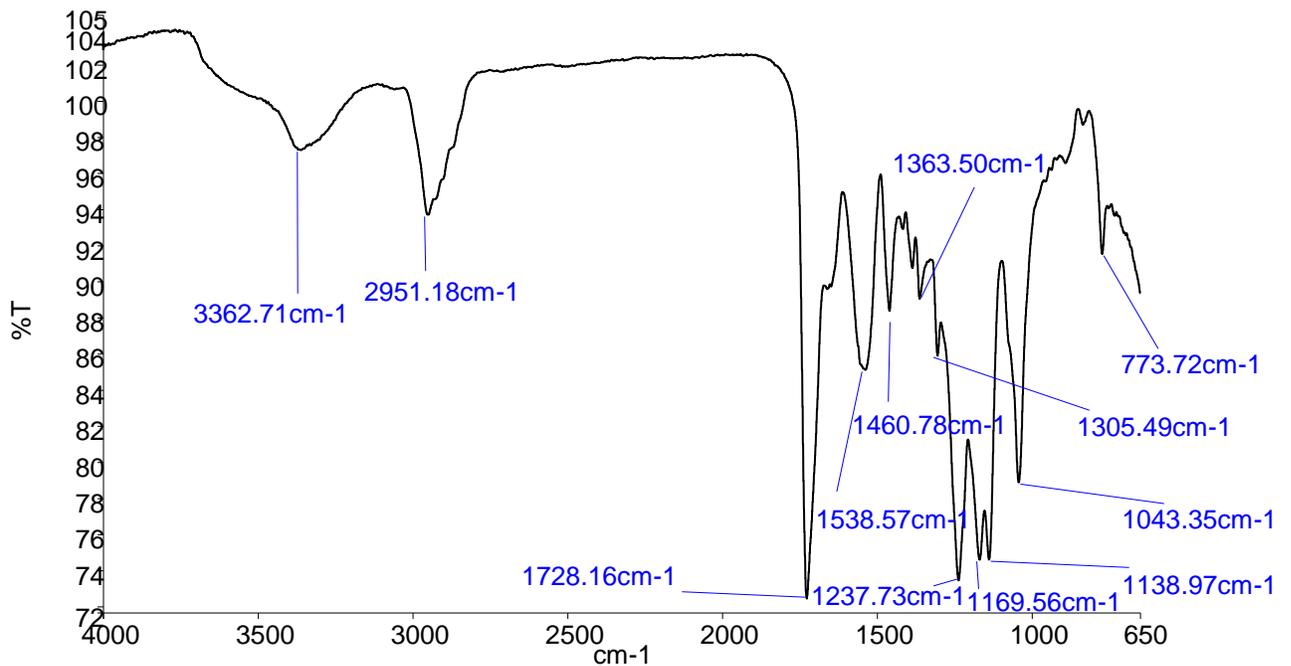


Figure 17. FTIR spectra of film based on PUD/POG dispersion (Table 6)

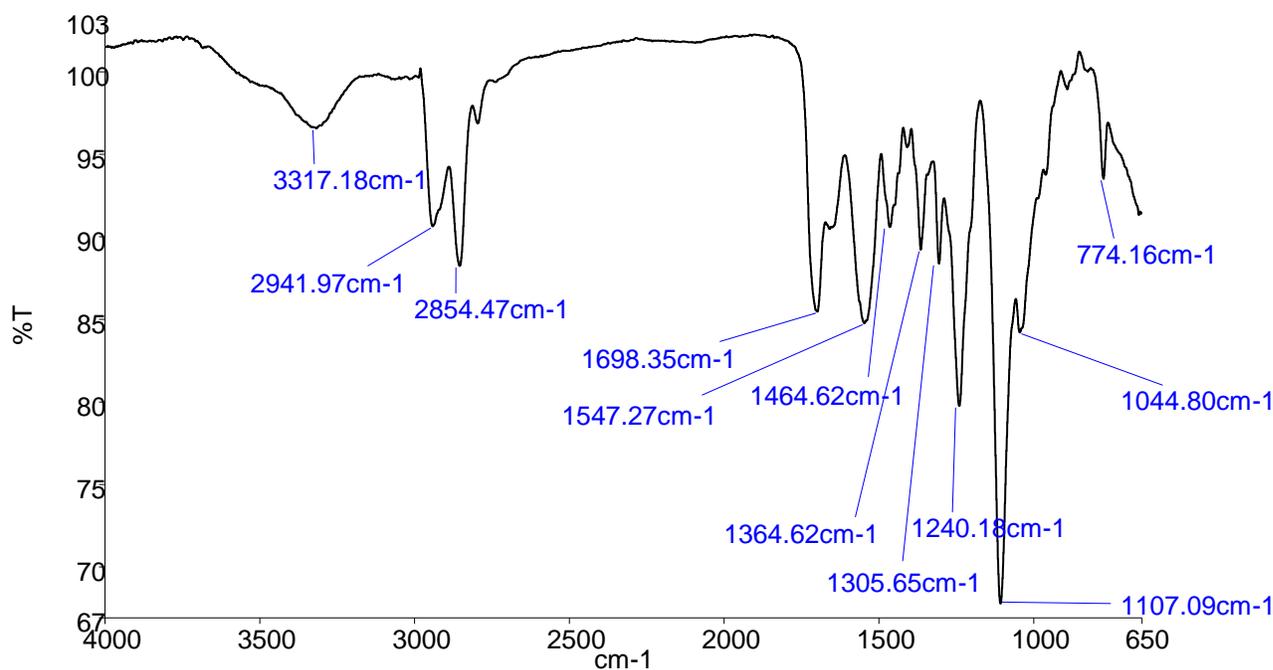


Figure 18. FTIR spectra of film based on PUD/PTMG dispersion (Table 6)

All PUD-based films exhibited good tensile strength and good elasticity (elongation at break) (Table 6). The hardness of all coatings cast on the metal substrate was consistent at 4H Pencil hardness for all samples (Table 7). The tensile strength of PUD films based on PDO adipate 1000 was comparable to referent films based on BDO adipate 1000 and polycaprolactone 1000. The tensile strength of PUD films based on PDO sebacate 1000 was lower than PDO adipate 1000 based PUD films (Table 6). The tensile strength and toughness of film-based PUDs prepared with PO3G 1000 polyol was excellent (Table 6, Figure 19). Their toughness, due to higher elasticity, was higher than films based on PTMG 1000 polyol (Table 6, Figure 19).

Table 6. Properties of various PUD-based films							
Sample designation	PUD/ PA_2	PUD/ PA_3	PUD/ PSb	PUD/ BA	PUD/ PCL	PUD/ PO3G	PUD/ PTMG
Appearance	Clear						
Tensile Strength, psi	6244.96 ± 303.17	5096.38 ± 163.05	4383.56 ± 205.97	6417.14 ± 735.41	5434.06 ± 134.07	6059.21 ± 277.42	5225.45 ± 107.08
Elongation at break, %	522.12 ± 102.89	452.44 ± 33.32	353.45 ± 18.85	494.06 ± 26.33	393.42 ± 28.82	672.10 ± 32.19	451.79 ± 15.79
Tensile stress at extension 50%, psi	998.90 ± 170.88	899.96 ± 175.35	733.75 ± 97.95	925.64 ± 281.94	841.97 ± 114.50	1085.80 ± 268.73	875.62 ± 146.02
Tensile stress at extension 100%, psi	1219.89 ± 222.16	1103.88 ± 194.25	929.10 ± 110.63	1118.72 ± 271.27	1133.03 ± 107.71	1297.75 ± 263.46	1070.10 ± 140.84
Tensile stress at extension 200% psi	1842.53 ± 371.82	1812.34 ± 269.76	1904.97 ± 381.94	1903.37 ± 262.48	2278.21 ± 287.75	1725.84 ± 234.50	1708.06 ± 104.99
Tensile stress at extension 300%, psi	2932.78 ± 632.84	2934.53 ± 373.16	3315.72 ± 279.59	3146.59 ± 485.50	3720.90 ± 410.70	2273.11 ± 173.62	2776.66 ± 200.21
Area under curve, psi	13027.4 ± 1028.0	10537.3 ± 947.9	6613.6 ± 446.9	13304.1 ± 2508.8	9585.2 ± 507.8	19725.5 ± 1315.4	10208.6 ± 415.4

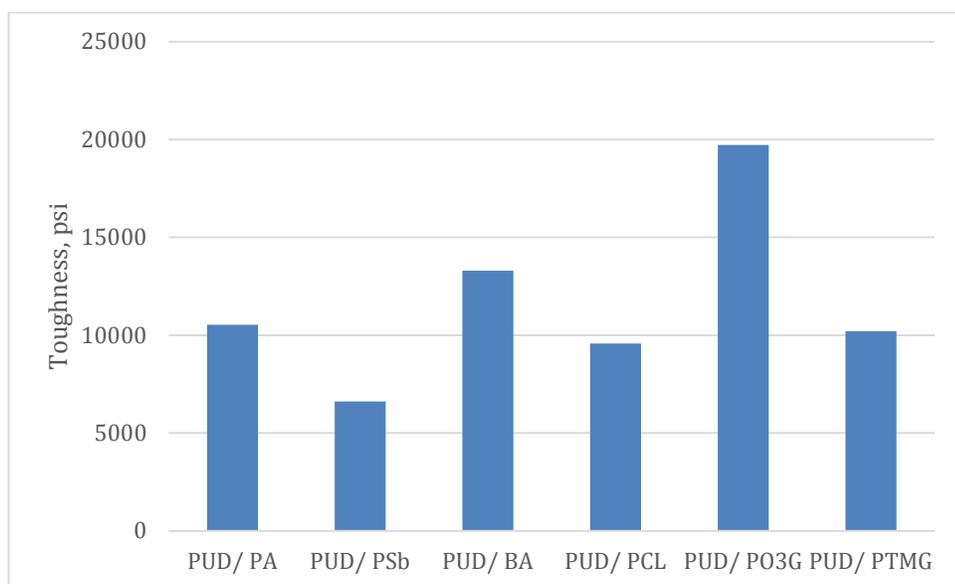


Figure 19. The effect of film based PUD composition on film toughness (Table 6)

Some films were first dried at room temperature and subsequently exposed to 50 °C for 2 hours for additional drying. Their tensile properties slightly changed as compared to those dried at room temperature (Table 5).

The impact resistance of PUD coatings was good, which is due to good elasticity of coatings (Table 7). The adhesion of coatings to the metal substrate, as evaluated according ASTM 3359 (Adhesion tape test) was very good (Table 7).

Sample designation	PUD/PA_3	PUD/PSb	PUD/BA	PUD/PCL	PUD/PCL	PUD/PO3G	PUD/PTMG
Hardness, Pencil hardness, (STM D3363)	4H						
Adhesion Tape test, (ASTM D3359)	5A						
Impact resistance, (ASTM D2794)	No rupture from maximum height						

Sample designation	PUD PA6	PUD PSb1	PUD BA1	PUD PCL3	PUD PO3G1	PUD PTMG2
Gloss	77	90	100	96	81	91

*The films were placed onto card-board, Gloss 2.

Sample designation	PUD/ PA	PUD/ PSb	PUD/ BA	PUD/ PO3G	PUD/ PTMG	PUD/ PCL
Flexible segment transition, T _g , °C	-34.21	-43.46	-38.37	-59.68	-60.00	-59.7
Hard segment transition via, °C	175.09	186.87	172.03	188.02	182.38	188

* Thermal transitions were measured using differential scanning calorimetry (DSC)

Overall, the films and coatings exhibited a good combination of properties - high hardness combined with good toughness and impact resistance.

PUD-based adhesives

PUDs as one component adhesives have applications in textiles, footwear and automotive among other industries. The adhesive properties of PUDs were tested using aluminum as a substrate and a Lap-shear test method ASTM D 1002 (Table 10). All PUDs exhibited cohesive bonding. The adhesive strength of PUDs based on PDO sebacate 1000 and BDO adipate 1000 were similar and higher than that of other PUDs, including that based on PDO adipate 1000 (Table 10, Figure 21). PUDs based on polyether polyols PO3G 1000 and PTMG 1000 exhibited similar adhesive strength, 568 psi and 589 psi, respectively.

Sample designation	PUD/ PA	PUD/ PSb	PUD/ BA	PUD/ PCL	PUD/ PO3G	PUD/ PTMG
Load at failure, psi	443.8 ± 77.52	917.5 ± 183.52	951.6 ± 151.10	377.5 ± 71.03	568.4 ± 97.83	588.6 ± 110.05
Strain at Break, %	6.05 ± 0.68	6.15 ± 0.54	6.26 ± 0.65	5.68 ± 0.67	6.79 ± 1.03	8.13 ± 1.53
Area under curve, (J)	0.3776 ± 0.11	0.6803 ± 0.17	0.7253 ± 0.17	0.2543 ± 0.05	0.5005 ± 0.13	0.5427 ± 0.17
Adhesive vs. cohesive	10/10 cohesive	10/10 cohesive	10/10 cohesive	10/10 cohesive	10/10 cohesive	10/10 cohesive

*The adhesion properties were measured using ASTM D1002 (Apparent Shear Strength of Single-Lap-Joint Adhesively Bonded Metal Specimens by Tension Loading)

Hydrolytic resistance of PUD-based films and coatings

The tensile strength of all PUD-based films changed somewhat upon hydrolytic aging test at 50 °C and 95% relative humidity for three days, which is expected due to water absorption and temperature (Table 11, Figure 20). PUD based on PO3G exhibited the highest toughness after hydrolytic aging (Figure 20). The toughness of PUD films based on PTMG 1000 and PDO Sebacate 1000 slightly increased upon hydrolytic aging which could due to annealing process (Figure 20). PUD based on PDO sebacate 1000 performed better in hydrolytic aging testing than other types of polyester polyols based PUDs, which is due to hydrophobicity of C10 - sebacic acid.

PUD-based coatings performed very well in the hydrolytic aging testing. There was no change in hardness and adhesion in coatings which were aged 50 °C and 95% relative humidity for three days (Table 12).

<i>Sample designation</i>	PUD/ PA	PUD/ PSb	PUD/ BA	PUD/ PCL	PUD/ PO3G	PUD/ PTMG
Tensile strength, psi	2768.31 ± 133.92	5334.25 ± 176.50	3140.89 ± 200.53	3559.26 ± 171.35	4714.98 ± 275.94	7329.50 ± 211.38
Elongation at break, %	482.15 ± 22.33	360.82 ± 22.54	448.04 ± 25.75	447.38 ± 38.34	662.65 ± 40.84	429.74 ± 22.12
Tensile stress at extension 50%, psi	612.28 ± 50.16	657.48 ± 52.00	650.93 ± 87.78	728.75 ± 82.07	873.85 ± 63.56	897.19 ± 202.77
Tensile stress at extension 100%, psi	718.96 ± 52.48	900.59 ± 65.77	777.94 ± 74.32	868.53 ± 97.00	992.02 ± 90.86	1196.66 ± 221.28
Tensile stress at extension 200%, psi	1099.08 ± 83.70	1938.73 ± 325.57	1180.94 ± 73.12	1390.60 ± 172.44	1331.30 ± 181.74	2215.15 ± 369.84
Tensile stress at extension 300%, psi	1674.58 ± 144.44	3904.40 ± 554.49	1858.57 ± 120.15	2208.06 ± 290.07	1798.80 ± 264.06	3920.12 ± 282.49
Toughness, psi	6782.3 ± 609.3	7548.0 ± 387.1	6633.0 ± 739.9	6083.6 ± 3234.3	15084.4 ± 1108.4	12523.3 ± 879.3

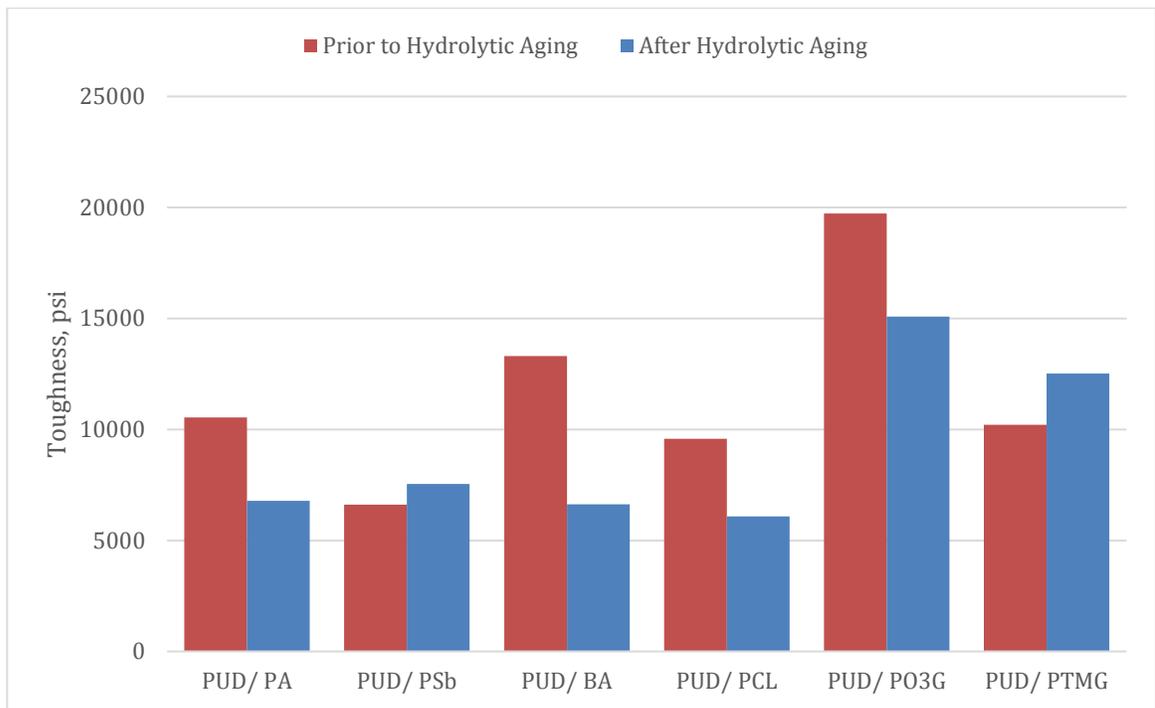


Figure 20. The effect of hydrolytic aging on properties of PUD-based films (Table 11)

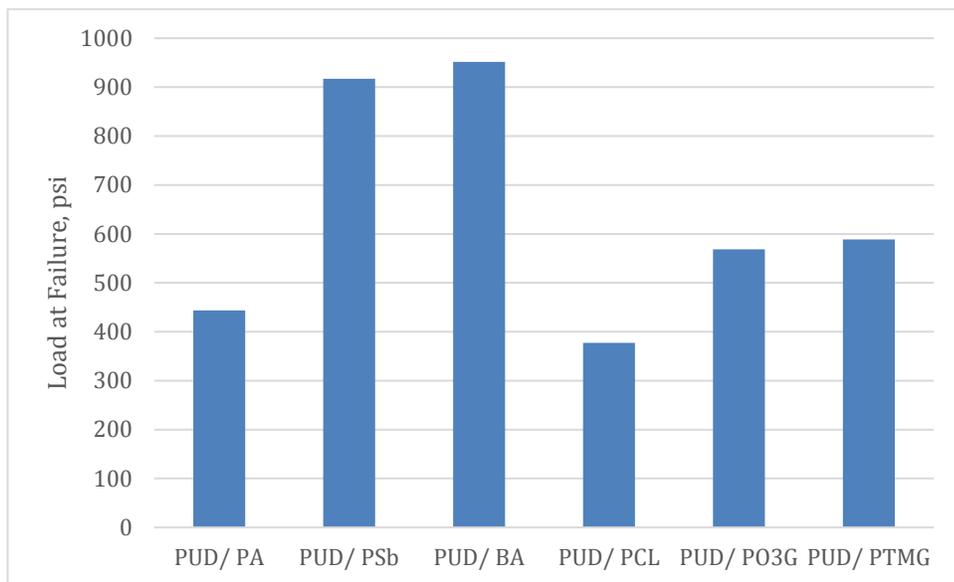


Figure 21. The adhesive strength of various PUDs (Table 10)

Table 12. Properties of PUD-based coatings on metal substrate after hydrolytic aging (3 days, 38 °C and 95% relative humidity)						
<i>Tested 5 minutes after humid aging completed</i>						
<i>Sample Designation</i>	PUD/PA	PUD/PSb	PUD/BA	PUD/PCL	PUD/PO3G	PUD/PTMG
Hardness, Pencil hardness, ASTM D3363	4H	4H	4H	4H	4H	4H
Tape test, ASTM D3359	5A	5A	5A	5A	5A	5A
Appearance	No apparent color change					
<i>Tested 24-hours after humid aging completed</i>						
Hardness, Pencil hardness, ASTM D3363	4H	4H	4H	4H	4H	4H
Tape test, ASTM D3359	5A	5A	5A	5A	5A	5A
Appearance	No apparent color change					

Solvent resistance of PUD based films and coatings

The solvent resistance of coatings on metal substrate were evaluated using solvent rub test (ASTM D 5402). There was no change of coating hardness after 25 double rubs with IPA and toluene as a solvent (Table 13). There was slight change of coating thickness for most of coatings. PUD based on polycaprolactone 1000 polyols exhibited significant change in thickness when exposed to toluene (Table 13).

In another solvent resistance test, a drop of various liquids (water, water acid solution, water alkaline solution, MEK and toluene) were applied onto PUD-based films. The diameter of the liquid drop was measured 15 minutes after

application onto surface of the films (Figures 22 and 23). The diameter of the liquid spot varied slightly, depending on their composition and type of liquid (solvent). Overall, films based on polyether polyols PO3G and PTMG 1000 performed somewhat better than films based on polyester polyols, that could be expected. PUD films based on PDO sebacate 1000 and BDO adipate 1000 were similar in this test and performed slightly better in contact with some solvents than films based on PDO adipate 1000 and polycaprolactone 1000 polyol (Figures 22 and 23).

Table 13. Solvent resistance properties of PUD-based coatings on metal substrate using solvent rubs, ASTM D5402						
<i>Sample designation</i>	PUD/PA	PUD/PSb	PUD/BA	PUD/PCL	PUD/PO3G	PUD/PTMG
Solvent: IPA						
Film thickness prior to testing, μm	269	256	342	37.8	209	248
Film thickness, μm (tested after 25 double rubs)	249	234	327	18.6	201	228
Loss of film thickness, %	7.43	8.59	4.39	50.79	3.83	8.06
Hardness, Pencil hardness	4H	4H	4H	4H	4H	4H
Solvent: Toluene						
Film thickness prior to testing, μm	151	233	371	29.3	182	264
Film thickness, μm (tested after 25 double rubs)	146	223	364	26.9	178	264
Loss of film thickness, % (tested after 25 double rubs)	3.31	4.29	1.89	8.19	2.20	0
Hardness, Pencil hardness, (tested after 25 double rubs)	4H	4H	4H	4H	4H	4H

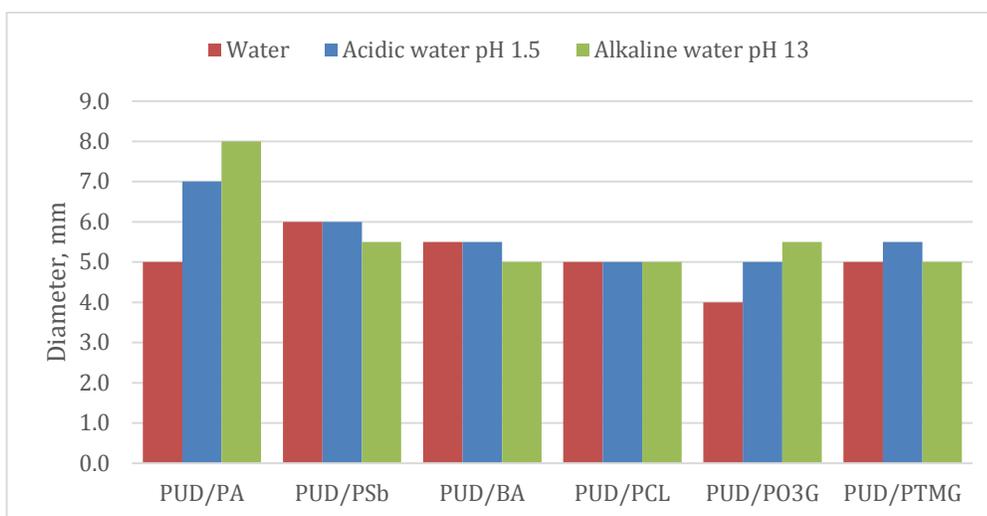


Figure 22. The effect of various solvents on PUD films
(The diameter of a liquid spot: 15 minutes after 1 drop of solvent applied on the film surface)

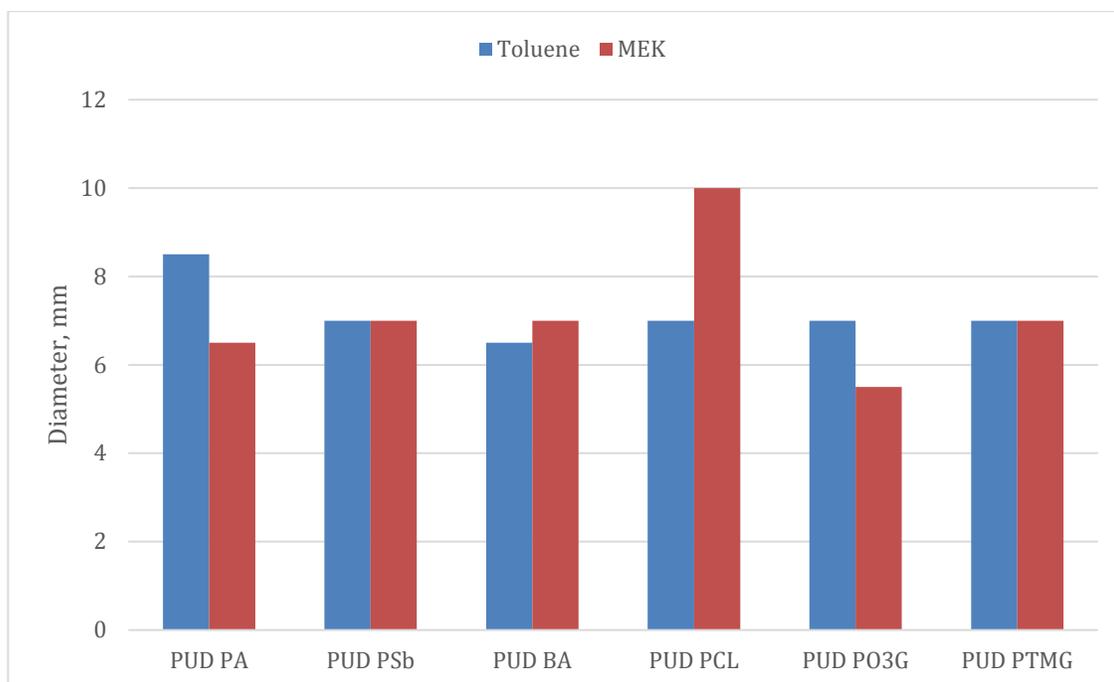


Figure 23. The effect of various solvents on PUD films

(The diameter of a liquid spot 15 minutes after 1 drop of solvent applied on the surface of film.)

CONCLUSION

Six types of waterborne PUDs were synthesized from a range of different polyol chemistries. To produce these waterborne polyurethanes dispersions (PUDs), dimethylolpropionic acid (DMPA) neutralized with triethylamine (TEA) was used as the ionic hydrophilic segment and incorporated into the polymer backbone. The effects of different soft segments on the stability of waterborne PUDs, as well as the physical, mechanical, thermal and chemical resistance properties of the resultant PUDs as films and coatings were investigated.

DSC results indicated that polyether-based waterborne polyurethane (WPU) films have better flexibility and cold resistance than polyester-based WPU films from PA, BA and PSb based polyol. Moreover, mechanical testing showed that PUD films based on PDO adipate 1000 was comparable to referent films based on BDO adipate 1000 and polycaprolactone 1000 and higher than films based on PDO sebacate 1000. The toughness measurement results illustrated that PUD/PO3G films have the best elastic behavior with good strength when compared to PUD/PTMG films and all other polyester-based PUD films evaluated in this study. This finding is attributed to the odd number of carbon atoms and higher density of ether groups in the repeating unit of the PO3G soft-segment.

Overall, the films and coatings explored in this study exhibited a good combination of properties including high hardness combined with good toughness and impact resistance. The solvent resistance and aging test performance for the six types of PUDs evaluated in this study demonstrated that the PUD coatings from PDO-based polyols performed very well. There was no change in hardness and adhesion in coatings which were aged for three days at 50 °C and 95% relative humidity.

ACKNOWLEDGEMENT

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

REFERENCES

1. H.X. Xiao, K.C.Frisch, ed.: Advances in Urethane Ionomers., Inc. Technomic Publishing Company Inc., Lancaster, Pennsylvania, USA; 1995
2. D. Dietrich, Progress in Organic Coatings. Vol. 9 (1981) 298.
3. Z. W.Wicks, Jr., D.A.Wicks, J.W. Rosthauser, Progress in Organic Coatings, Vol.44 (2002) 161-183.
4. B.K.Kim, J.C Lee., J. Polymer. Sci., Polym. Chem. Ed, Vol. 34 (1996), 1095-1104.
5. J. W. Rosthauser, K. Nachtkamp, Adv. Urethane Sci. Technol., Vol. 10 (1987) 121.
6. R. Miller (DuPont Tate & Lyle Bio Products), R. Janssen and L. Theunissen (Reverdia), "Evaluating the Properties and Performance of Susterra 1,3-Propanediol and Biosuccinim Sustainable Succinic Acid in TPU Application", CPI Polyurethanes 2012 Technical Conference, September 2012, Atlanta, Georgia.
7. ASTM D3794: Standard Guide for Testing Coil Coatings.

BIOGRAPHIES



Stephen Hurff

Steve is the Vice President of Marketing & Sales for DuPont Tate and Lyle Bio Products Company and has served as the commercial officer since 2007. He has held various positions at DuPont during his 35-year career including roles in management, technical, manufacturing, marketing and sales. Steve is a graduate from the University of Delaware holding a MBA, a Bachelor of Chemical Engineering and a BS in Chemistry.



Michael T. Shen

Michael is the Technical Marketing Manager for DuPont Tate and Lyle Bio Products Company since 2013. Michael previously worked in the polyurethane industry with a focus on footwear. Michael is a graduate from the Fudan University holding a Master of Polymer Science degree. He is responsible globally for customer technical support and new business development related to the Bio-PDO™ product for all market segments and end-use applications.



Aisa Sendijarevic

Dr. Aisa Sendijarevic is a Research Director at Troy Polymers, Inc., a consulting and contract R&D laboratory specializing in polyurethanes. She has authored over 80 technical articles (papers, book chapters, and conference proceedings) and 14 US patents. She has over 30 years of research experience in isocyanate-based polymers and polyurethanes. Her research experience includes development of novel materials for medical, space, automotive, transportation and other industries. Specific interests include syntheses of isocyanate-based polymers and co-polymers of defined chemical structure and properties; morphology and structure property relationships in polyurethane elastomers, coatings and adhesives; polyurethanes based on renewable components.



Ibrahim Sendijarevic

Ibrahim Sendijarevic is Business Development Director at Troy Polymers, Inc. He is responsible for commercial development of new technologies ranging from development and marketing of sustainable raw materials to development of variety of polyurethane end-use applications. From 2009 to 2013 he served as President of InfiChem Polymers, where he led the team in implementation on novel recycling technology for production of polyols. He holds a Ph.D. in Chemical Engineering from University of Illinois.

This paper may contain copyrighted material, the use of which has not always been specifically authorized by the copyright owner. In accordance with Title 17 U.S.C. Section 107, the material in this paper is being used for nonprofit educational purposes and will not be made available for distribution. ACC believes this constitutes a 'fair use' of any such copyrighted material as provided for in section 107 of the US Copyright Law. For more information, go to: <http://www.copyright.gov/title17/92chap1.html#107>. If copyrighted material from this paper is further used for purposes that go beyond "fair use," permission from the copyright owner must be obtained.