Bio-based waterborne polyurethane dispersion evaluation for synthetic leather applications

Waterborne polyurethane dispersions (PUDs) are used to prepare polyurethane coatings and adhesives containing very low volatile organic compounds for textiles and synthetic leathers used in furniture and automobile applications. PUDs provide the performance of polyurethanes with additional advantages such as the lack of harmful monomers and absence of toxic volatile organic compounds. Polyurethane synthetic leathers are normally produced in a multi-stage process which involves removing toxic dimethyl formamide (DMF) from a solventborne layer, then applying a solventborne wear layer. Solvent-free waterborne PUDs with a very high solids content and excellent performance have now been produced for this application and industry trends have shown that waterborne PUDs are replacing traditional solvent-based systems. These new waterborne systems must offer all of the same required properties of comparable solvent-based systems with the added advantage of being eco-friendly in nature. Waterborne systems are clearly a step in the right direction from an environmental standpoint however most of the polyurethanes used today in these PUD systems are still petroleum-based. This study evaluates the effect of bio-based polyols and petroleum-based polyols on the stability of waterborne PUDs and the physical, mechanical and thermal properties of the resultant films and coatings.

1 Introduction

Many commercial polyurethane (PU) adhesives and coatings are known to contain a significant amount of organic solvents. Some systems also contain volatile isocyanate which under certain exposure limits is harmful to human health as well as the environment. Increasing concern on this issue has pressured the polyurethane industry to move towards water-based systems [1 – 3]. However, water cannot be used directly as a solvent or a diluent, since PUs are water insoluble and one of the main raw materials,

isocyanate, is highly moisture sensitive. PUs can be dispersed in water by using external emulsifiers or by incorporating emulsifying groups into the PU backbone. The latter is preferred, since it leads to films with excellent mechanical properties. The emulsifying groups can be non-ionic polyether segments or ionic groups [4, 5]. PU modified with ionic groups give rise to dispersions of high stability and improved properties compared to their non-ionic analogues. Generally, aliphatic diisocyanates, i.e., isophorone diisocyanate (IPDI) are preferred because of their low reactivity with water as compared to aromatic isocyanates, such as 4,4'-di-p-phenylmethane diisocyanate (MDI) and toluene diisocyanate (TDI).

Currently, most waterborne PUDs are derived from petroleum-based polyols, such as

poly(tetramethylene ether)glycol (PTMG), poly(propylene oxide)glycol (PPG), polycaprolactone polyol (PCL) and polyesters based on adipate polyols, which are all non-renewable. As consumers are becoming more aware of environmental issues, they are changing their preferences toward bio-based products [6 – 10]. Susterra® 1,3-propanediol (PDO), a 100 % bio-based diol, continues to be used successfully as a building block in a variety of polyurethane applications globally [11 – 14]. The successful evaluation of PDO as an alternative to 1,4-butanediol (BDO) has been reported at CPI Technical Conferences, PMA Technical Conference and literature [15]. Poly(trimethylene ether)glycol (PO3G), a high performance polyether polyol, is produced by the process of self-condensation polymerization of Susterra PDO [16]. PO3G bio-based polyols based on

Michael Shen

michael.t.shen@dupont.com

Global Technical Specialist

Dupont Tate & Lyle Bio Products Company, LLC,

Loudon, TX, USA

www.susterra-performs.com

Xianglian Niu,

Guiyou Wang

School of Materials Science and Engineering,

East China University of Science and Technology,

Shanghai, China

www.ecust.edu.cn/_t41/main.htm

All figures and tables, unless otherwise stated, have been kindly provided by the authors.
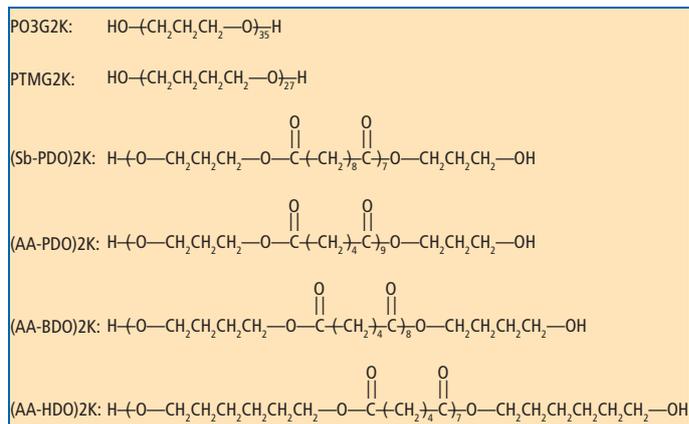

Fig. 1:
Chemical structures of different polyols

PDO can be good candidates for waterborne polyurethane applications due to their flexibility, softness and unique mechanical performance at low temperature.

The purpose of this study was to investigate the effect of bio-based polyols and petroleum-based polyols on the stability of the waterborne PUDs and the physical, mechanical and thermal properties of waterborne polyurethane (WPU) films. To prepare these waterborne polyurethanes, dimethylolpropionic acid (DMPA) neutralized with triethylamine (TEA) as the ionic hydrophilic segment was incorporated into the polymer backbone. The particle size and size distribution of waterborne polyurethane emulsions were measured by dynamic light scattering (DLS). Thermal properties and glass transition temperature of waterborne polyurethane films were determined by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). Dynamic mechanical properties and tensile performance of the films were investigated by dynamic mechanical analysis (DMA) and mechanical measurements.

2 Experimental section

2.1 Materials

Isophorone diisocyanate (IPDI) was obtained from Covestro. The following diols with an average molecular weight (M_n) of 2,000 g/mol were used:

- PO3G Velvetol, poly(trimethylene ether) diol or poly-1,3-propanediol with (PO3G-2000) was provided by Allessa GmbH.
- PolyTHF®2000, poly(tetramethylene ether)diol (PTMG-2000) was purchased from BASF.
- Poly(1,3-propylene sebacate)diol (Sb/PDO-2000) and poly(1,3-propylene adipate)diol (AA/PDO-2000) were synthesized in the lab.
- Commercial poly(1,4-butylene adipate)diol (AA/BDO-2000) and poly(1,6-hexamethylene adipate)diol (AA/HDO-2000) were kindly provided by Xuchuan Chemical Co., Ltd., China and used as references.

Dimethylolpropionic acid (DMPA) was purchased from Perstrop. Other materials were standard laboratory reagents and were used as received, except that N-methylpyrrolidone (NMP), triethylamine (TEA) and ethylenediamine (EDA) were treated with 4-Å molecular sieves for over 1 week before use. **Figure 1** shows the chemical structures of the different polyols.

2.2 Synthesis of WPU dispersions

The preparation process of the waterborne PUDs was divided into three steps, illustrated in **figure 2**:

(1) Formation of isocyanate-terminated prepolymer,
(2) Neutralization of the NCO-terminated prepolymer, and
(3) Emulsification for particle formation and chain extension for higher molecular weight.

The isocyanate-terminated PU prepolymer was prepared in a 500 ml round bottom, three-necked flask equipped with a mechanical stirrer, a thermometer, and a nitrogen inlet. First, diol (200 g; 0.1 mol), DMPA (11.8 g; 0.088 mol), and NMP (17.7 g) were charged into the flask, and dehydrated at 85 °C for 2 h under vacuum. Then the mixture was cooled to 50 °C. IPDI (67.3 g; 0.303 mol) and dibutyltin dilaurate (DBTDL, 0.01 wt% based on the total reaction mass) were added as catalysts.

The viscous isocyanate-terminated PU prepolymer was obtained by keeping the reaction at 80 °C under nitrogen atmosphere until the isocyanate content reached its theoretical value (the isocyanate content was determined according to ASTM D2572-97).

The reaction mixture was cooled to 60 °C. TEA (8.89 g; 0.088 mol) was added to neutralize the carboxylic acid for 30 min. After that, the obtained mixture was dispersed into deionized water at 40 °C with a stirring speed of 600 min⁻¹. Finally, EDA (4.9 g; 0.082 mol) was slowly added into the dispersion, and the dispersion continued to react for another 30 min to obtain the waterborne PUDs. Six types of waterborne

Fig. 2: The synthetic route for waterborne polyurethane dispersions
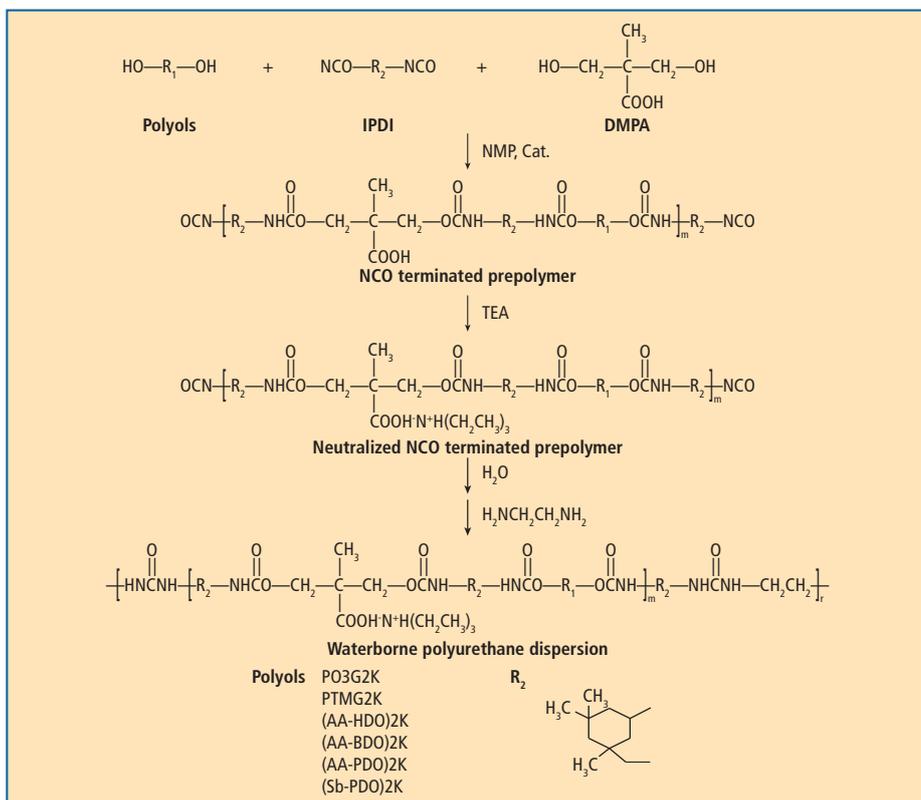
PUDs from different diols were prepared and the solid content and DMPA content for all waterborne PUDs were 40 % and 4 %, respectively.

2.3 Preparation of WPU films

The WPU films were prepared by casting of the waterborne PUDs into a mould that was then dried at room temperature for 1 week. Then, the films were dried at 60 °C for 24 h, at 80 °C for another 24 h until a constant weight was obtained. The WPU films with 0.6 – 1.0 mm thickness were stored at room temperature for further studies.

2.4 Characterizations

Viscosities of the waterborne PUDs were measured at 23 °C by a rotational Brookfield viscometer with a number 21 rotor at a rate of 200 min⁻¹. The pH values of the waterborne PUDs were measured at 25 °C in a pH meter. The mean particle size and distribution of the waterborne PUDs were determined using a Malvern Zetasizer Nano ZS instrument equipped with a He-Ne laser (λ = 633 nm) and at a scattering angle of 173°. Thermal transitions of the samples were measured on a DSC2910 (TA Instruments). Samples (8 – 10 mg) were put into aluminium pans and heated from -100 °C to +200 °C at a heating rate of 10 °C/min under a nitrogen atmosphere with a flow rate of 40 ml/min. The dynamic mechanical analysis (DMA) properties of the WPU films (30 mm × 5 mm × 1.0 mm) were measured on a Q800 (TA Instruments) at a heating rate of 3 °C/min from -100 °C to +100 °C in three-point bending mode with 1 Hz. Tensile tests were performed on a SANS tester with a crosshead speed of 100 mm/min at room temperature. The dumbbell specimens with a 40 mm × 4 mm × 1 mm neck were used according to ASTM D638-2010 and the values reported reflected an average from five tests. Hydrolysis resistance of the WPU films was evaluated as follows: WPU films were aged at 70 °C and 95 % relative humidity, and the tensile strength of WPU films were measured after aging for different times.

3 Results and Discussion

3.1 Physical properties of polyols

The physical properties of different polyols are listed in **table 1.** The acid values (A_v) of all polyols were below 0.5 mg KOH/g, and the hydroxyl values (OH_v) were about 56 mg KOH/g. These results from chemical titration indicate that the molecular weights (M_n) of all polyols were about 2,000 g/mol, which was confirmed by gel permeation chromatography (GPC) measurements. **Figure 3** displays the DSC curves of all polyols, and the DSC scan results are also listed in **table 1.** The melting points (T_m) of polyester diols were higher than that of polyether diols (i.e. PO3G-2000 and PTMG-2000) leading to higher viscosities at 70 °C for the polyester diols.

This is due to the ether groups having more flexibility and lower polarity than the ester groups. However, although there is one more

carbon atom in the repeating unit of Sb/PDO-2000 than in that of AA/HDO-2000, the T_m value of the Sb/PDO-2000 sample is a bit lower than that of the AA/HDO-2000 sample. This result could be due to the fact that there is an odd number of carbons in the repeating unit of the Sb/PDO-2000 sample. Thus, it is important that for both the polyester and polyether samples, the melting points and viscosities are higher if the total number of methylene groups in the repeating unit is even, as this permits achievement of the most suitable conformations and improved packing of the chains in the crystals [16]. Furthermore, there is an exothermic peak at -36.2 °C for the PO3G-2000 sample **(fig. 3; dark blue curve)**, which corresponds to the cold-crystallization of the PO3G-2000 sample.

3.2 Physical properties of waterborne PUDs

The physical properties of waterborne PUDs are presented in **table 2.** It can be seen that

Tab. 1:
Physics properties of polyester and polyether diols

Sample	A_v	OH_v	Viscosity at 70 °C	M_n*	M_n**	T_g***	T_m***	ΔH***
	in mg KOH/g		in mPa·s	in g/mol		in °C		in J/g
PO3G	0.42	56.4	350	1,974	2,032	-75.0	18.8	89.3
PTMG	0.27	56.1	460	1,900	1,911	/	32.9	107.2
AA-PDO	0.37	57.1	470	1,952	2,027	-59.8	41.1	60.4
Sb-PDO	0.45	56.2	1,120	1,980	2,146	/	54.5	79.2
AA-BDO	0.25	57.3	660	1,949	2,086	-58.9	53.7	64.7
AA-HDO	0.40	56.8	1,850	1,961	2,127	/	60.3	77.9

▶ * $M_n = 2 \times \dfrac{56.1 \times 10^3}{OH_v + A_v}$, where OH_v and A_v are obtained from chemical titration
** determined by GPC
*** measured by DSC

▼ **Fig. 3:** *DSC curves of different polyols*
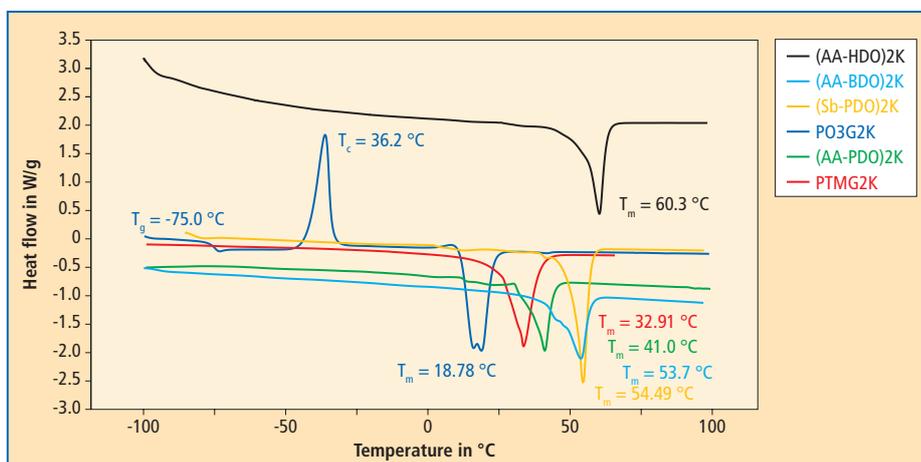
the solid contents of all waterborne PUDs were about 40 %, the particle sizes ranged from 65.6 nm to 76.8 nm with a polydispersity of 0.04 – 0.10, and the pH values were a bit higher than 7. It is worth noting that small particle sizes favour the storage stability (>6 months) of dispersions. It is also interesting to note that the viscosity of the PO3G waterborne PUD sample was lowest among all of the waterborne PUD samples due to its high particle size.

3.3 Morphology and properties of WPU films

3.3.1 DSC analysis

Figure 4 shows DSC curves of the WPU films. Glass transition temperature (T_g), melting point (T_m) and melting enthalpy (ΔH) of the WPU films are listed in **table 3**. The DSC curves show that for polyether-based WPU films, the T_g value of the PTMG-WPU film (-70.8 °C) was lower than that of the PO3G-WPU film (-65.7 °C). However, the T_g values (<-60 °C) of these two polyether-based WPU films were both lower than all of the polyester-based WPU films.

This indicates that the flexibility and cold resistance performance of the polyether-based WPU films should be improved when compared to the polyester-based WPU films. The T_g values for the polyester-based WPU films are also decreased a bit when the total numbers of carbon atoms in the repeating unit is increased. Furthermore, the Sb/PDO-WPU film and the AA/HDO-WPU film have melting peaks at about 48 °C, indicating that the polyester soft phases formed into crystalline structures. The T_m and ΔH values of the Sb/PDO-WPU film sample were lower than those of the AA/HDO-WPU film sample, but the lower T_g from the Sb/PDO-WPU film sample agrees with the trend found for pure polyester samples in the DSC results.

3.3.2 Mechanical properties

Table 4 lists the mechanical properties of the WPU films. When comparing the PO3G-WPU film sample with the PTMG-WPU film sample, tensile strength, stress at 100 % and 300 % strain, and tear strength were lower, but elongation at break was higher. The results show that the PO3G-WPU film sample has more flexibility and lower

strength when compared to the PTMG-WPU film sample, which is attributed to the odd number of carbon atoms in the repeating unit of the PO3G soft segments. The tensile strength and tear strength of the polyether-based WPU films were much lower than those of the polyester-based WPU films. This is because the cohesive energy density of ester groups in the polyester soft segments is higher than that of ether groups in polyethers.

The tensile strength of the polyester WPU films also increased due to the increasing numbers of carbon atoms in the repeating units. The stress at 100 % and 300 % strain, and tear strength of the AA/BDO-WPU film sample was highest among the six samples, because there are even numbers of carbon atoms and a high ester group concentration in the repeating unit of the AA/BDO polyester soft segment. The Sb/PDO-WPU sample showed the strongest properties in terms of tensile strength.
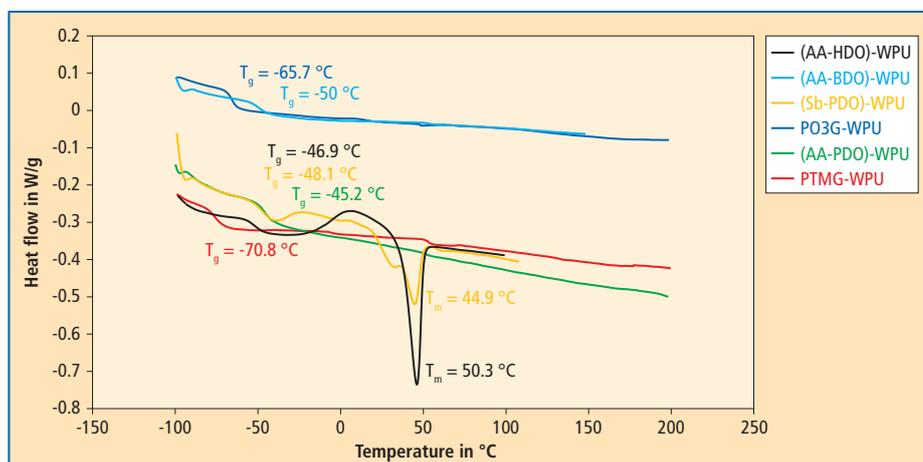
3.3.3 Dynamic mechanical analysis

DMA experiments have been used to understand the micro-phase separation of the WPU films. The storage modulus (E') and loss factor (tan δ) as a function of temperature for all of the WPU films are shown in **figure 5**. **Table 5** summarizes some results from the DMA test. E' values of the WPU films decreased with the increase of temperature, due to the transition from a glassy state into a rubbery state **(fig. 5a)**. The T_g can be readily determined from inspection of the tan δ versus temperature curve **(fig. 5b)**. It is noticeable that the T_g values (from DMA) of the polyether-based WPU films were lower than those of the polyester-based WPU films, and the PTMG-

Sample	Polyol	Solid content in %	pH	Viscosity in mPa·s	Particle size in nm	PDI
PO3G-WPU	PO3G-2000	38.9	7.36	18.0	76.8	0.081
PTMG-WPU	PTMG-2000	39.7	7.11	46.5	72.3	0.081
(AA-PDO)-WPU	AA/PDO-2000	40.6	7.23	34.3	74.8	0.099
(Sb-PDO)-WPU	Sb/PDO-2000	40.7	7.34	76.3	68.2	0.095
(AA-BDO)-WPU	AA/BDO-2000	40.6	7.15	29.3	65.6	0.073
(AA-HDO)-WPU	AA/HDO-2000	40.1	7.44	41.3	73.9	0.046

◄ **Tab. 2:** Physical properties of waterborne PUDs

▼ **Fig. 4:** DSC curves of WPU films

Sample	T_g in °C	T_m in °C	ΔH in J/g
PO3G-WPU	-65.7	/	/
PTMG-WPU	-70.8	/	/
AA/PDO-WPU	-45.2	/	/
Sb/PDO-WPU	-48.1	44.9	16.2
AA/BDO-WPU	-50.0	/	/
AA/HDO-WPU	-46.9	50.3	22.9

▼ **Tab. 3:** DSC results of WPU films

WPU film had the lowest T_g value among the six samples. This agrees with the trend found in the DSC experiments.

The E' value of the PO3G-WPU sample was lower than the PTMG-WPU sample, when temperatures were T_g, T_g+30 °C and 23 °C, respectively. This indicates that the PO3G-WPU sample had better flexibility than the PTMG-WPU sample and may bring excellent softness to the final PU-based coating.

At the rubbery plateau, comparing the Sb/PDO-WPU and AA/PDO-WPU samples, it can be observed that the E' values of the AA/BDO-WPU and the AA/HDO-WPU samples were much higher because of the odd-even carbon effect. Moreover, the E' values of the AA/BDO-WPU samples at T_g, T_g+30 °C and 23 °C were the highest among the set of six samples.

3.3.4 Hydrolysis resistance test

Hydrolysis resistance tests were made to evaluate the durability of the WPU films. The test temperature was 70 °C and the humidity was kept at 95 %. **Table 6** and **figures 6 and 7** display the hydrolysis resistance test results of the WPU films. The PO3G-WPU and PTMG-WPU samples had similar hydrolysis behaviour because the ether groups have excellent hydrolysis resistance. After the 4 weeks hydrolysis test, the strength reten-

tion of the PO3G-WPU and the PTMG-WPU films were about 80 %. The Sb/PDO-WPU film had the best hydrolysis resistance compared to the other three kinds of polyester-based WPU films. After 4 weeks hydrolysis test, the strength retention of the Sb/PDO-WPU sample was more than 70 %, which was close to the behaviour of PO3G-WPU and PTMG-WPU samples. With the longer carbon chain in the repeating unit and lower concentration of ester groups, the Sb/PDO polyol can provide improved hydrolysis resistance to PU dispersion and its end-use PU products.

3.3.5 PU leather test

The six types of waterborne PUDs were used to synthesize the PU solution for synthetic leather samples for further evaluation. The hard segment of PU solution was setup as 30 %. The PU solutions were applied on the surface of textile by a dry process. The properties of chemical resistance to MEK, low temperature flexibility (-20 °C; 100,000 cycles) and abrasion resistance were evaluated for these six types of leather samples. The test results **(tab. 7)** show that the synthetic leather sample based on the PO3G PU solu-

▼ **Tab. 4:** Mechanical properties of WPU films

Sample	Tensile strength in MPa	Elongation at break in %	Stress (100 % strain) in MPa	Stress (300 % strain) in MPa	Tear strength in kN/m
PO3G-WPU	23.7	1,035	2.74	3.62	43.4
PTMG-WPU	33.5	870	3.93	7.88	47.3
AA/PDO-WPU	45.5	814	3.20	6.75	64.5
Sb/PDO-WPU	62.8	765	3.56	10.3	87.1
AA/BDO-WPU	53.9	644	7.67	23.3	119.4
AA/HDO-WPU	57.2	673	4.68	15.4	71.8

Tab. 5:
DMA results of WPU films ▶

Sample	T_g (DMA) in °C	Modulud E' in MPa at different temperatures		
		at T_g	at T_g+30 °C	at 23 °C
PO3G-WPU	-52.8	501	81	8
PTMG-WPU	-62.9	504	99	24
AA/PDO-WPU	-35.9	422	44	10
Sb/PDO-WPU	-39.2	690	282	92
AA/BDO-WPU	-34.6	1,898	1,149	721
AA/HDO-WPU	-41.4	1,314	659	291

▼ **Fig. 5:** (a) Storage modulus and (b) tan δ versus temperature for WPU films
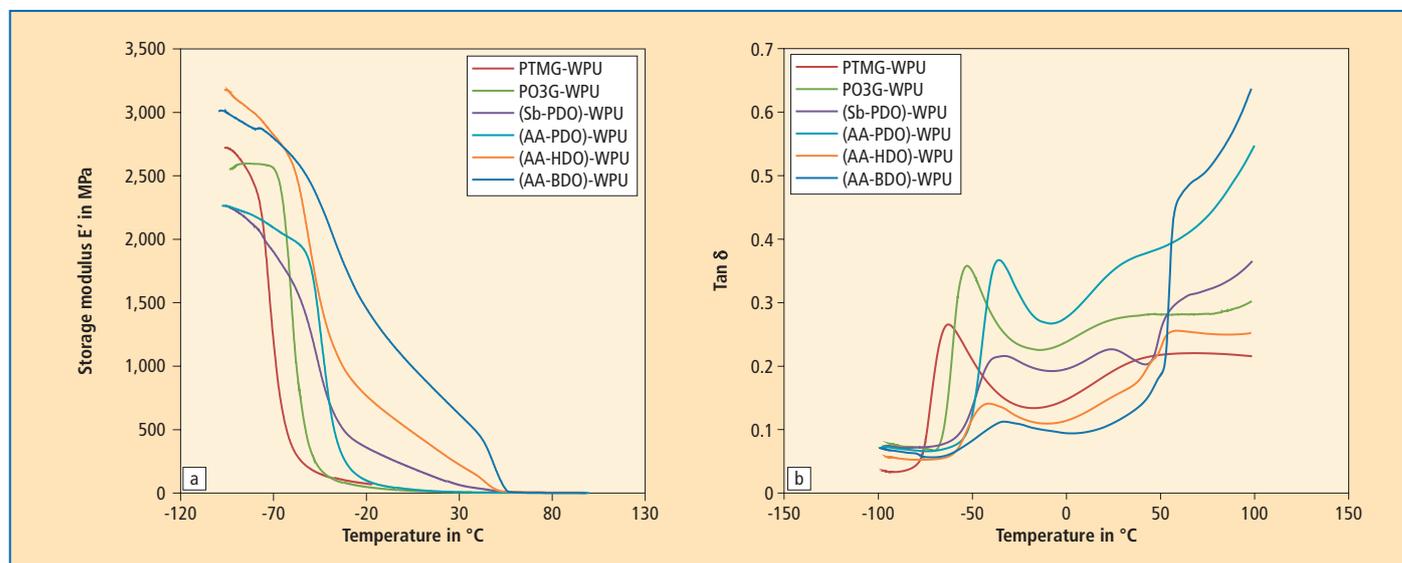
tion had best combined abrasion resistance and low temperature flexibility when compared to the other five types of PU leather samples. This agrees with the previous DMA results.

4 Conclusion

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

DSC results indicate that polyether-based WPU films have better flexibility and cold resistance than polyester-based WPU films. Moreover, the T_g values of the polyester-based WPU films decreased a bit with increasing total numbers of carbon atoms in the repeating unit indicating that these films are stiffer.

The mechanical measurement results illustrate that PO3G-WPU films have better flexibility but lower strength when compared to PTMG-WPU films which is attributed to the odd number of carbon atoms in the repeating unit of the PO3G soft segment. However, the polyester WPU films were both stronger than the polyether WPU films and were shown to increase in strength with increasing numbers of carbon atoms in the repeating unit.

DMA results display that at the rubbery plateau the E' value of the PO3G-WPU sample was lower than the PTMG-WPU sample, when temperatures were T_g, T_g+30 °C and 23 °C, respectively. This indicates that the PO3G-WPU sample had better flexibility than the PTMG-WPU sample and may bring excellent softness to the final PU-based coating. When comparing the polyesters, the Sb/PDO-WPU and AA/PDO-WPU samples were observed to be more flexible than the AA/BDO-WPU and the AA/HDO-WPU samples because of the odd-even carbon effect.

The hydrolysis resistance results illustrate that polyether-based WPU films have excellent hydrolysis performance. In general, ether groups have better hydrolysis resistance than ester groups. There was one new finding in this experiment and that is that the polyester Sb/PDO polyol provided a similar hydrolysis resistance to the ether based-polyols. Since the Sb/PDO-based WPU film has similar hydrolysis resistance to polyether WPU films but better mechanical strength it can be a potential raw material for the tie coat layer for PU synthetic leather.

▼ **Tab. 6:** Hydrolysis resistance test results of WPU samples

| Sample	After 2 weeks hydrolysis			After 4 weeks hydrolysis		
	Tensile strength in MPa	Elongation at break in %	Tear strength in kN/m	Tensile strength in MPa	Elongation at break in %	Tear strength in kN/m
PO3G-WPU	21.7	951	39.5	18.8	798	33.6
PTMG-WPU	30.1	792	45.0	28.1	776	40.2
AA/PDO-WPU	15.5	214	34.5	0	0	0
Sb/PDO-WPU	52.7	669	77.7	46.2	613	67.5
AA/BDO-WPU	43.9	464	58.4	20.7	231	32.1
AA/HDO-WPU	34.1	551	50.0	25.7	452	41.3

▼ **Tab. 7:** Physical test results of WPU leather samples

PU solution	Polyol	MEK (30 min)	-20 °C 100,000 cycles	Taber abrasion (H22 1 kg) cycles
PO3G-WPU	PO3G-2000	Pass	Pass	10,000
PTMG-WPU	PTMG-2000	Pass	Pass	7,500
(AA-PDO)-WPU	AA/PDO-2000	Pass	Slight damage	850
(Sb-PDO)-WPU	Sb/PDO-2000	Pass	Pass	2,100
(AA-BDO)-WPU	AA/BDO-2000	Pass	Crack	700
(AA-HDO)-WPU	AA/HDO-2000	Pass	Pass	1,700

▼ **Fig. 6:** Change of tensile strength versus time for WPU films
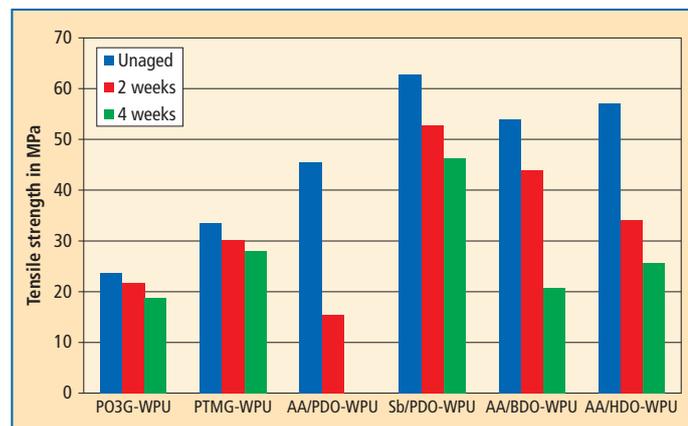
▼ **Fig. 7:** Change of tear strength versus time for WPU films
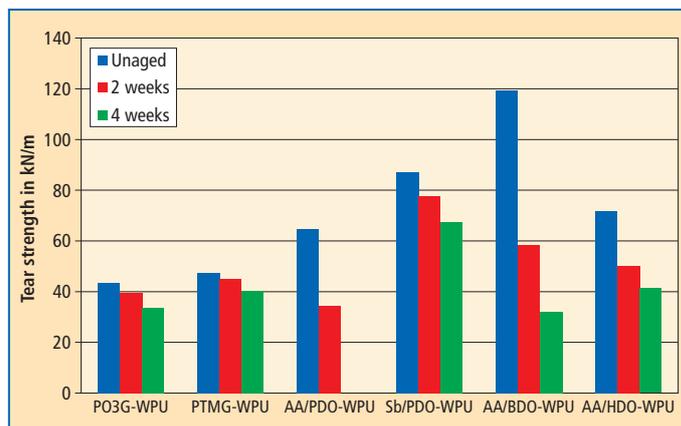
The PU leather tests demonstrate that the synthetic leather sample coated with a PO3G-based PU solution had the best combined abrasion resistance and low temperature flex performance when compared to the other five types of PU coatings. This indicates that PO3G-based PU coating solutions offer enhanced abrasion resistance and low temperature performance as well as excellent elasticity and a soft hand versus traditional polyols. PO3G-based PU coatings can be used as a key raw material to top-coat PU synthetic leather.

5 References

[1] A. Santamaria-Echart, L. Ugarte, C. Garcia-Astrain, A. Arbelaiz, M. A. Corcuera, A. Eceiza; Carbohydrate Polymers, 2016, 151, 1203-1209

[2] C. Q. Fang, X. Zhou, Q. Yu, S. L. Liu, D. G. Guo, R. E. Yu, J. B. Hu; Progress in Organic Coatings, 2014, 77, 61-71

[3] H. Y. Mao, S. Y. Qiang, F. Yang, C. Y. Zhao, C. X .Wang, Y. J. Yin; Journal of Applied Polymer Science, 2015, 132, 42780-42789

[4] R. Q. Chen, C. Q. Zhang, M. R. Kessler; RSC Advances, 2014, 4, 35476-35483

[5] S. K. Gaddam, A. Palanisamy; Colloid and Polymer Science, 2016, 294, 347-355

[6] C. Q. Fu, Z. T. Zheng, Z. Yang, Y. W. Chen, L. Shen; Progress in Organic Coatings, 2014, 77, 53-60

[7] S. Gogoi, N. Karak; ACS Sustainable Chemistry & Engineering, 2014, 2, 2730-2738

[8] T. Travinskaya, Y. Savelyev, E. Mishchuk; Polymer Degradation and Stability, 2014, 101, 102-108

[9] M. E. V. Hormaiztegui, V. L. Mucci, A. Santamaria-Echart, M. A. Corcuera, A. Eceiza, M. I. Aranguren; Journal of Applied Polymer Science, 2016, 133, 44207-44219

[10] L. Poussard, J. Lazko, J. Mariage, J. M. Raquez, P. Dubois; Progress in Organic Coatings, 2016, 97, 175-183

[11] B. J. Rashmi, D. Rusu, K. Prashantha, M. F. Lacrampe, P. Krawczak; Journal of Applied Polymer Science, 2013, 128, 292-303

[12] J. Datta, E. Głowinska; Industrial Crops and Products, 2014, 61, 84-91

[13] L. Ugarte, A. Saralegi, R. Fernández, L. Martín, M. A. Corcuera, A. Eceiza; Industrial Crops and Products, 2014, 62, 545-551

[14] Y. Niu, P. Zhang, J. J. Zhang, L. P. Xiao, K. K. Yang, Y. Z. Wang; Polymer Chemistry, 2012, 3, 2508-2516

[15] M. A. Corcuera, L. Rueda, B. Fernandez d'Arlas, A. Arbelaiz, C. Marieta, I. Mondragon, A. Eceiza; Polymer Degradation and Stability, 2010, 95, 2175-2184

[16] D. N. Bikiaris, G. Z. Papageorgiou, D. J. Giliopoulos, C. A. Stergiou; Macromolecular Bioscience, 2008, 8, 728-740

■