Selection of coalescing solvents for coatings derived from polyurethane dispersions utilizing high throughput research methods

Jung Kwon Oh*
Department of Chemistry and Biochemistry, Concordia University, 7141 Sherbrooke St. W., Montreal, Quebec, Canada H4B 1R6
Tel: 1-514-848-2424 ext 5306, email: joh@alcor.concordia.ca

Jeff Anderson, Bedri Erdem, Ray Drumright, and Greg Meyers
The Dow Chemical Company, Advanced Materials Division, Dow Coating Materials, Midland, MI 48674, USA

Abstract

Reduction of volatile organic compounds (VOCs) in coatings is being driven by regulation and consumer preference. Development of binders that are capable of delivering expected performance at low VOC is a major thrust of coatings research and development. Toward this end, polyurethane dispersions (PUDs) from natural oil polyols (NOPs) have been developed. These hydrophobic NOP-based PUD coatings exhibit exceptional early water resistance and hydrolytic stability, excellent acid resistance, and good toughness & abrasion resistance. Most high performance PUDs require large amounts of solvent to form crack-free films with good properties. However, with the right choice of process and solvent parameters, PUDs have been shown to require reduced amounts of coalescing solvents to yield the desirable array of end-user properties with ambient temperature drying. High-Throughput Research (HTR) was used as a means to accelerate formulation and product development of PUDs. Rapid formulation and testing allows for probing of interactions between variables in greater depth and breadth than conventional formulation techniques, leading to rapid development of robust products and formulations. The HTR methods for coatings applications include the use of specially designed experiments, robotic formulation, coating, and characterization tools as well as informatics for data visualization, extraction, and modeling. This paper details the use of HTR capability to explore the effect of cosolvents on end-use properties of NOP based PUD coatings as well as proposed mechanisms of film formation in NOP-PUDs. The results provide a basis for guidelines for selection of cosolvents for PUD coatings with high performance and low VOC (<100 g/L VOC).

1. Introduction

Waterborne polyurethane dispersions (PUDs) are a rapidly growing segment of the polyurethane coating market. Such rapid growth is primarily driven by environmental regulations to reduce volatile organic compounds (VOC) and technological advances resulting in improved properties and performance. Due to their attributes, PUDs have become effective substitutes for solvent-based counterparts in various coating applications including wood and concrete coatings.[1,2] PUDs derived from natural oil polyester polyols (NOPs) have been developed. Coatings made from the NOP-based PUDs have good toughness, abrasion resistance, hydrolytic stability, and acid resistance. They also exhibit superior water uptake (less) relative to competitive PUDs, due to the hydrophobic nature of NOPs.[3,4,5]

Water-based solvents are often used in preparation and formulation of PUDs. In the “prepolymer mixing process”, isocyanate-inert, water-miscible, high boiling point solvents are used to facilitate prepolymer synthesis.[6] The solvents include N-methylpyrrolidone (NMP) as well as PROGLYDE™ DMM (DMM) and N-ethylpyrrolidone.[7] These solvents remain in the PUDs, enhancing film formation as coalescing aids, but contribute to VOCs (>15%, corresponding to >200 g/L VOC). Furthermore, the presence of NMP or DMM in PUDs limits the formulators’ options in balancing VOC level and coating properties. NMP and DMM are excellent solvents for synthesis of PU prepolymer, but there are better coalescing solvents.

VOC regulations calling for <100 g/L limit for industrial coatings, such as the South Coast Air Quality Management District (SCAQMD) exert a continuous pressure on coatings manufacturers. To meet the requirements, PUD producers are utilizing acetone and methyl ethyl ketone (MEK) for prepolymer synthesis, followed by solvent stripping in order to provide solvent-free PUDs (USP 4,820,762). The recent availability of solvent-free PUDs including solvent-free versions of NOP based PUDs presents an opportunity for new options in the selection of cosolvent in order to minimize total

VOC while achieving good film formation and coating properties. Better understanding of cosolvents versus end-user properties will lead to the selection of the best cosolvents for development and commercialization of high performance NOP-PUDs with low VOC.

Today's coatings market exerts multiple pressures to successfully develop and introduce new coating products. Improving the environmental profile of these new products is a major driver that often requires significantly different formulation strategies. These complex coating formulations offer an excellent opportunity to use the strengths of High-Throughput Research (HTR) to understand how interactions between coating components affect final properties.[8,9,10] Not only in the area of coatings and formulations, but also in a broad variety of areas including catalysis, materials, genomics, protein assay, pharmacology, and pathology, HTR approach has been utilized for screening and development of new materials.[11,12,13] Compared to conventional bench-top research, such broad appeal to the establishment of HTR is attributed to the fact that HTR offers multiple and timely solutions by rapid screening of broad range of materials and parameters using robot-driven automation and software-based models.

This paper describes the effect of cosolvents on end-use properties of NOP-PUD coatings using HTR methods. The central idea of the project is to select cosolvents that can reduce VOC level as well as improve end-use properties. In order to explore resulting coating properties, zero-VOC NOP-PUDs (formed using an MEK process followed by solvent stripping) were formulated with glycol solvents as well as NMP as a control. The resulting coatings were tested for minimum film formation temperature (MFFT), early water resistance, impact resistance, and pendulum hardness. In addition, the results from combined bench-top experiments and analytical methods allowed for better understanding of potential mechanisms of film formation and coalescence in terms of the distribution of hard domains in soft matrix in NOP-PUDs.

1.1. HTR capabilities for development of coating formulations.

HTR is an integrated set of advanced capabilities in hardware and software that allow many more experimental variables to be explored and understood than could be achieved with traditional approaches. Hardware includes material handing robots as well as automated stations for measuring key properties of intermediates and final products to provide the key information for identifying promising products. Software includes HT experimental design, robotic control, data collection, processing, storage, visualization, analysis, and modeling.

In coatings, the basic steps are to formulate the materials, make the coatings, and test the dried films. The formulation capabilities cover most coating materials including solids and liquids over a broad range of viscosities. Each coating is coated on various substrates including Leneta paper, steel, aluminum, and wood that are placed in a substrate holder and tracked based on a unique experimental ID attached to the substrate holder via a barcode. The dried films are tested using automated HTR tools, including color, gloss, thickness, tack, friction, scrub resistance, stain resistance, block resistance, and low temperature coalescence. In addition, wet formulations are tested for pH, colloidal stability, freeze-thaw stability, viscosity, and rheology.

1.2. PUDs derived from bio-renewable NOPs

NOPs are prepared from chemically modified fatty acid methyl esters (FAMEs) derived from soy oil. The FAMEs are hydroformylated to the corresponding aldehyde intermediates and subsequently hydrogenated to the primary hydroxyls. The soy monomers are transesterified with a suitable glycol to increase molecular weight and generate the NOPs. The NOPs used in this study possess an average hydroxy functionality of two.

PUDs derived from NOPs are prepared by polycondensation reactions of polyisocyanates and polyols. Figure 1 illustrates the structure of NOP-PUDs. Polyols include NOPs, acid-containing diols such as 2,2-bis(hydroxymethyl)propionic acid (DMPA), and optionally short chain diols (SCDs) to enhance the hard segments. To facilitate PU prepolymer synthesis, high boiling point solvents such as

DMM and NMP or low boiling point solvents such as ketones are often used. They can reduce the viscosity of PU prepolymers and dissolve solid DMPA in reaction mixtures. Sequential steps including neutralization, dispersion, and chain extension yield stable NOP-PUDs with a diameter of 50 – 150 nm.

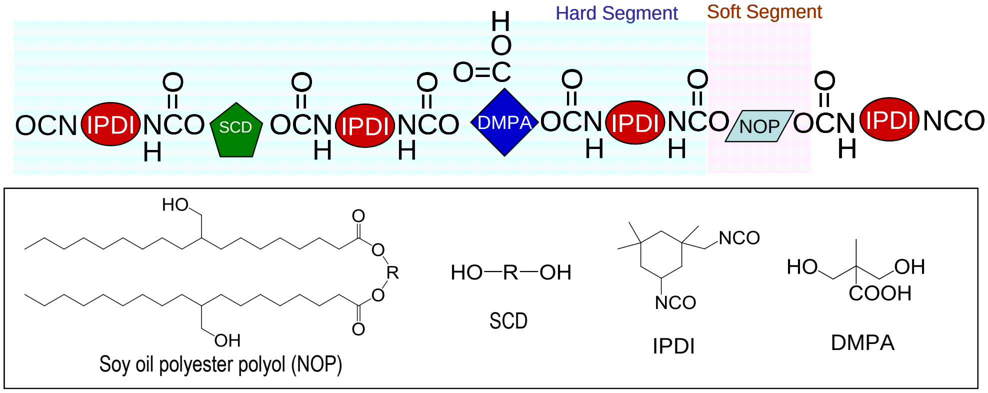

Figure 1. Schematic illustration of structure of NOP-PUDs.

2. Experimental Section

2.1. Solvent-free NOP-PUDs (SF-NOP-PUDs) using MEK process

SF-NOP-PUDs were prepared by the MEK process. Briefly, NOP-based PU prepolymers were first synthesized from polyols including NOPs, DMPA, optionally SCDs, and MEK charged in a round-bottom flask under nitrogen. The mixture was immersed in an oil-bath preset at 70 °C. When the reaction temperature reached 55 – 60 °C, polyisocyanates were slowly added using a dropping funnel. The mixture was then stirred for 4-5 hrs. Samples were taken periodically to measure %NCO and COOH level. When the target values were reached, triethylamine (TEA) was added to neutralize COOH groups of PU prepolymers. The resulting PU prepolymers were dispersed in water under high shear, yielding a stable dispersion of PU prepolymers. Chain extender was added and then MEK was stripped off under vacuum at 50 – 55 °C.

2.2. Glycol solvents and NMP

Table 1 summarizes glycol solvents whose structures are classified into three groups; ethylene glycols (EG), propylene glycols (PG), and EGs and PGs of diether (PEGR). For comparison, NMP is included as a control.

Table 1. Characteristics of glycol solvents and NMP

Structure	Glycol Solvent a)		bp (°C)	Evaporation rate (n-BuAc = 1)	Solubility in water (wt%)	Hansen dispersion parameter	Hansen polar parameter	Hansen Hydrogen bonding parameter
EG	Butyl CELLOSOLVE™ Solvent	BCs	171	0.079	∞	16	7.6	12.3
	Methyl CARBITOL™ Solvent	MCb	194	0.019	∞	16.2	7.8	12.6
	CARBITOL™ Solvent	Cb	202	0.01	∞	16.1	9.2	12.2
	Butyl CARBITOL™	BCb	230	0.004	∞	16	7	10.6
PG	DOWANOL™ DPM Glycol Ether	DPM	190	0.035	∞	15.5	4	10.3
	DOWANOL™ DPnP Glycol Ether	DPnP	213	0.014	19.6	15	2.9	9.2
	DOWANOL™ DPnB Glycol Ether	DPnB	230	0.006	4.5	14.8	2.5	8.7
	DOWANOL™ TPnB Glycol Ether	TPnB	274	0.0004	4.5	14.8	1.7	7.9
PEGR	PROGLYDE™ DMM Glycol Ether	DMM	175	0.13	35	14.9	2.1	3.8
	DOWANOL™ DPMA Glycol Ether	DPMA	209	0.015	16	16.3	4.9	8
	NMP		202					

a) BCs: butyl cellosolve; MCb, BCb: methyl, butyl carbitol; Cb: carbitol, DPM, DPnP, DPnB: dipropylene glycol methyl, n-propyl, n-butyl ether; TPnB: tripropylene glycol n-butyl ether; DMM:

dipropylene glycol dimethyl ether; DPMA: dipropylene glycol methyl ether acetate. All are trademark of The Dow Chemical Company. NMP: N-methyl pyrrolidone.

2.3. HTR workflow including formulation, coating, and testing properties

Figure 2 illustrates the HTR workflow for PUD wood coatings used in the experiment. This workflow leverages HTR capabilities developed for waterborne architectural coatings and is augmented with manual-type ASTM test methods. The workflow includes the use of the HT Hamilton robot and a conventional shaker for the formulation of PUD coatings. The Hamilton Robot was first calibrated for dispensing of all coating components. The different components exhibited a linear relationship of actual vs target amount with R^2 values higher than 0.99. The resulting calibration file defines detailed aspiration/dispensing conditions, tip used, and calibration results including dispensed/requested weights for each liquid. A weighing robot was also used to determine the actual amount of components to be dispensed in the Hamilton.

Various coatings on steel panels were applied on either the Symyx Automated Coating Station using a doctor blade or manually applied using a drawdown bar. The films were tested for thickness using the HTR Color-Gloss-Thickness tool, universal hardness using HTR microindenter, pendulum hardness using Gardner pendulum hardness tester (ASTM D4366), and impact resistance using Gardner impact tester with falling weight (ASTM D1709). Early water resistance using water drop method at 60% humidity was tested after 1 day drying. Early water resistance was evaluated on the following scale (5: no effect, 4: slight trace of water, 3: blister, wrinkling, and bubble, 2: corrosion, and 1: coating failure).

2.4. Characterization of NOP-PUDs

Minimum film formation temperature (MFFT) of SF-PUD-A with and without post-added cosolvents ranging from 32 to 100 ºF was measured according to ASTM D2354 using a house-built MFFT instrument. Atomic force microscopy (AFM) was used to characterize morphology of surface for SF-PUD-A. Aliquots of SF-PUD-A was mixed with various solvents and the resulting mixtures were cast on mica and dried for 1 day. Images were obtained on a MultiMode AFM (Veeco, Inc., Santa Barbara, CA. S/N MMAFM-2) using a Nanoscope IV controller (S/N NS4-143) equipped with a "J" scanner and running software version 6.13. The microscope was operated in the Tapping Mode™ (trademark of Veeco Instruments, Inc.) where the lever is oscillated at resonance and the feedback control adjusts for constant tapping amplitude. In Tapping Mode AFM (TMAFM), phase imaging is sensitive to local elastic, viscoelastic, and adhesive material properties and also enhances nanostructural features. Therefore, the contrast observed in phase images can represent compositional maps of the scanned surfaces or exhibit enhanced contrast of nanostructures. Scanning was carried out in air using commercially available silicon cantilevers and tips with nominal force constants of 5 N/m (HiRes-C probes, MikroMasch). The scanning was operated in either light Tapping (Ao ~ 1V, Asp ~ 0.9V) or moderate tapping (Ao ~3V, Asp ~ 2V). Digital images are 512x512 pixels. Gas chromatography (GC) was used to determine residual solvents remaining in dried films. Mixtures consisting of SF-PUD-A with 10% cosolvents was cast on glass using a drawdown bar, and dried at RT for 7 days. Pieces of dried film were taken as a function of time over 7 days, and dissolved in MeOH to extract residual solvents. The MeOH solution was analyzed by GC. The GC was also used to determine partitioning coefficient of cosolvents between the aqueous phase and particles. Mixtures consisting of SF-PUD-A with 10% cosolvents were centrifuged using a tube with a filter with pore diameter of <40 nm. The clear and transparent serum (~ 1 mL) separated from particles was used for GC. Solubility parameters of polymers were determined using a solvent swelling method. Aliquots of polymer (1 g) dried for 7 days were mixed with a series of 16 solvents with different solubility parameters. After 7 days, swelling behavior of the polymer was recorded to calculate the solubility parameter of polymer.

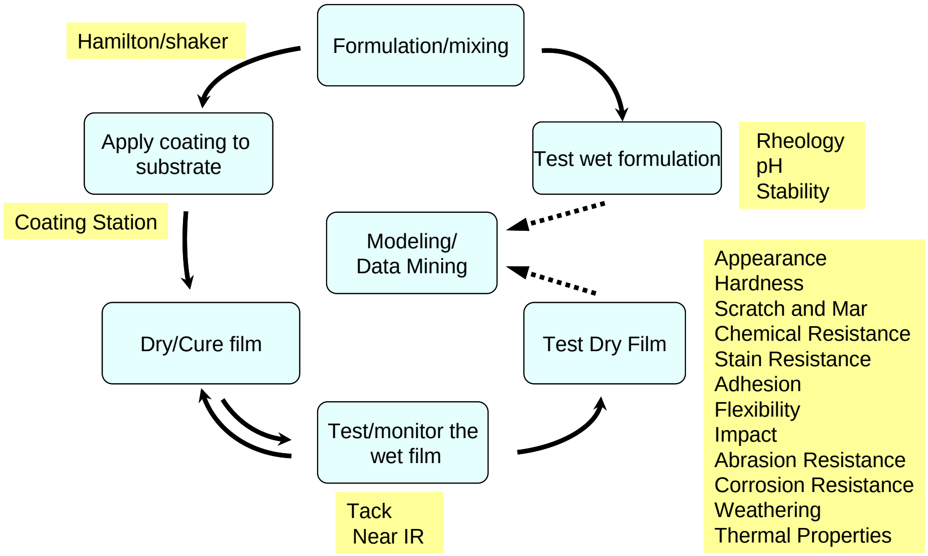

Figure 2. HTR workflow used in the experiment

3. Results and Discussion

3.1. Effect of post-added cosolvents on properties of PUD coatings

MFFT - solvent plasticization efficiency constant. MFFT of SF-PUD-A was measured to be 38 °C. Upon post-addition of cosolvents, its MFFT decreased to below 0 °C. The extent of decreasing MFFT was not the same for all cosolvents at similar levels. Overall, EG such as BCb and BCs and PG such as DPnB were better than PEGR including DMM and NMP to lower MFFT of SF-PUD-A. In addition, when <9% DMM was post-added, cracked-films were formed at RT. The plasticization efficiency of cosolvents are defined as plasticization efficiency constant (K_{PL}, °C/wt% solvent). The K_{PL} value means the extent of decrease in MFFT of polymers upon addition of 1wt% cosolvent. The higher the K_{PL} value, the more efficient the solvent is at reducing MFFT. In the experiments, MFFT change (Δ_{MFFT}) of SF-PUD-A was calculated by subtracting the MFFT without cosolvents (38 °C) from that with different amounts of cosolvents. From the plot of MFFT changes that occur for SF-PUD-A as a function of wt% cosolvents of PU solids, plasticization efficiency constants (K_{PL}) of cosolvents were calculated. Linear fitting of the data yielded K_{PL} values of cosolvents on a wt% basis. As seen in Table

2, the K_{PL} value ranged from 1.3 – 2.2 for NMP, DMM, MCb, and Cb; 2.9 – 3.0 for DPnP and TPnB; and 3.5 – 3.9 for BCs, BCb, and DPnB. The KPL value means how much MFFT decreases upon addition of every 1% cosolvent. These results suggest that the order of plasticization efficiency of cosolvents based on K_{PL} values is BCb ≈ BCs ≈ DPnB > DPnP ≈ TPnB >> DMM ≈ NMP.

Table 2. Plasticization efficiency constants (K_{PL}) of cosolvents for solvent-free SF-PUD-A.

Cosolvents			Plasticization constant (K_{PL})
EG	Butyl CELLOSOLVE Solvent	BCs	3.8
	Metyl CARBITOL Solvent	MCb	1.3
	CARBITOL™ Solvent	Cb	2
	Butyl CARBITOL Solvent	BCb	3.9
PG	DOWANOL DPnP Glycol Ether	DPnP	3
	DOWANOL DPnB Glycol Ether	DPnB	3.6
	DOWANOL TPnB Glycol Ether	TPnB	3
PEGR	PROGLYDE* DMM Glycol Ether	DMM	2.2
	NMP		2

* Trademark of The Dow Chemical Company

Impact resistance. Figure 3 shows impact resistance of SF-PUD-A mixed with glycols and NMP ranging from 8 to 25% of PU solids. Impact resistance varied with glycol structures. It was higher with OH-bearing glycols including EGs and PGs than non-OH-bearing glycols such as DMM (diether). In addition, EGs were better than PGs except for TPnB. NMP was similar to EGs. Overall, the order of cosolvents to enhance impact resistance was EGs ≈ NMP > PGs > PEGRs. Another important observation is that impact resistance increased with an increasing amount of cosolvents. For EGs, approximately 15% was required to achieve 160 lb-in of impact resistance (maximum level for current test method), while >20% was required for other solvents.

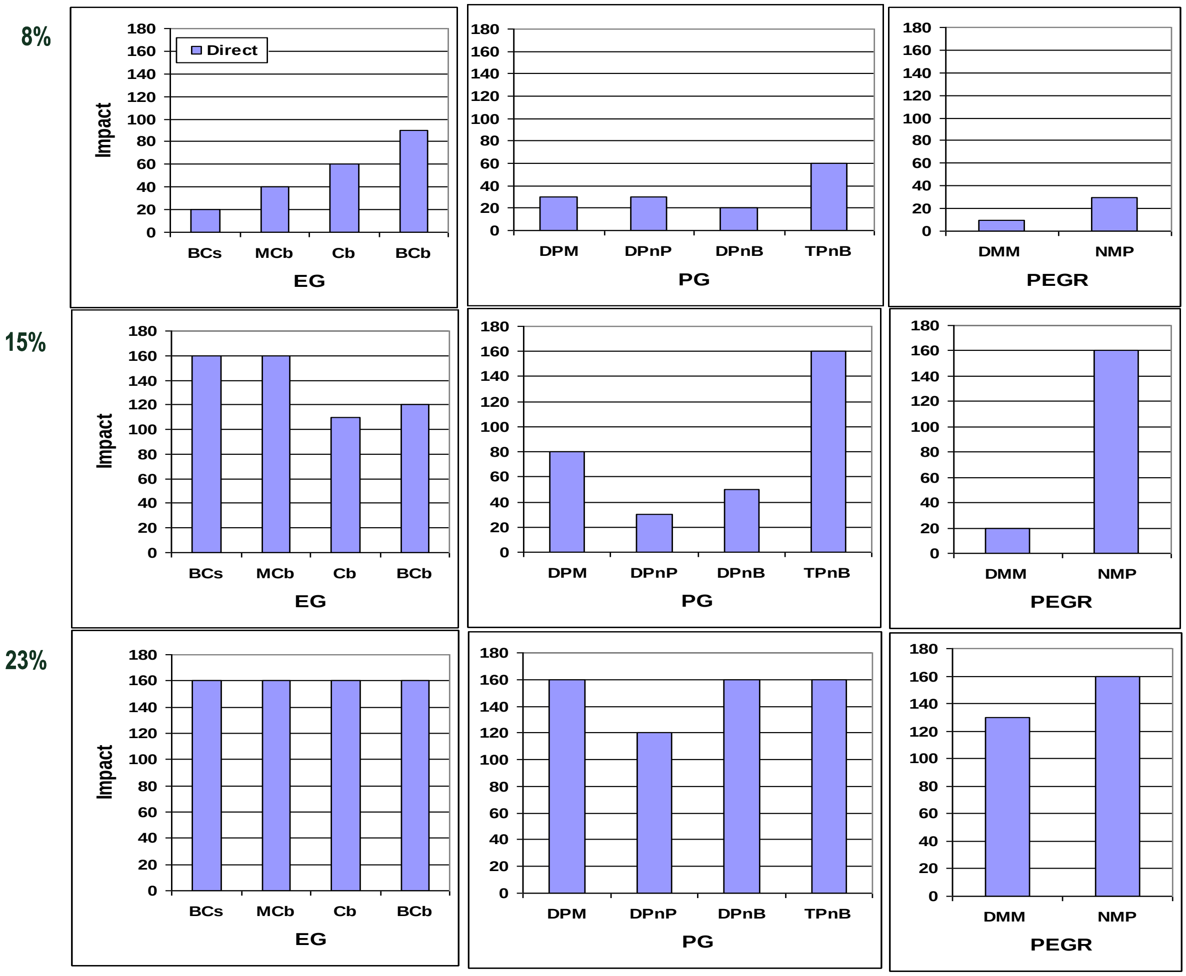

Figure 3. Direct impact resistance (lb-in) of SF-PUD-A mixed with cosolvents ranging from 8 to 23% of PU solids.

Hardness. Konig hardness of SF-PUD-A mixed with different amounts of cosolvents ranged from 150 to 175, indicating no significant effect of cosolvents on hardness. For TPnB, however, increasing amounts (5 to 28%) led to a pendulum hardness decrease from 140 to 100, while direct impact resistance increased from 30 to 160. Such decrease in pendulum hardness is presumably due to residual TPnB remaining in dried films, acting as a plasticizer. In fact, TPnB has a relatively high boiling point (275 °C) and low evaporation rate (0.0006, where n-BuAc = 1).

Development of early pendulum hardness. Figure 4 shows the evolution of hardness of SF-PUD-A in the presence of 10% of glycol cosolvents with different boiling point and evaporation rate. It was found that early hardness development correlated strongly to evaporation rate; DMM>BCs>DPnB>BCb. After 24 h, pendulum hardness of all films increased to 120 – 140. Upon further drying, it increased further to 157 after 8 days. The results are important in the selection of cosolvents for solvent-free NOP-PUD-based wood coatings. For applications that require fast development of hardness such as factory-applied furniture and floor, BCs with high evaporation rate can be recommended. However, BCb with low evaporation rate can be recommended for DIY applications that require extended open times to improve workability and reduce lap marking. DIY coatings are generally applied by inexperienced applicators who often overwork coatings during application. If the coating dries too fast, overworking imprints a pattern in the partially dried under layer, from a brush or roller, causing the successive coats to mimic this pattern. The result is lap marks or poor flow characteristics that produce an unattractive finish.

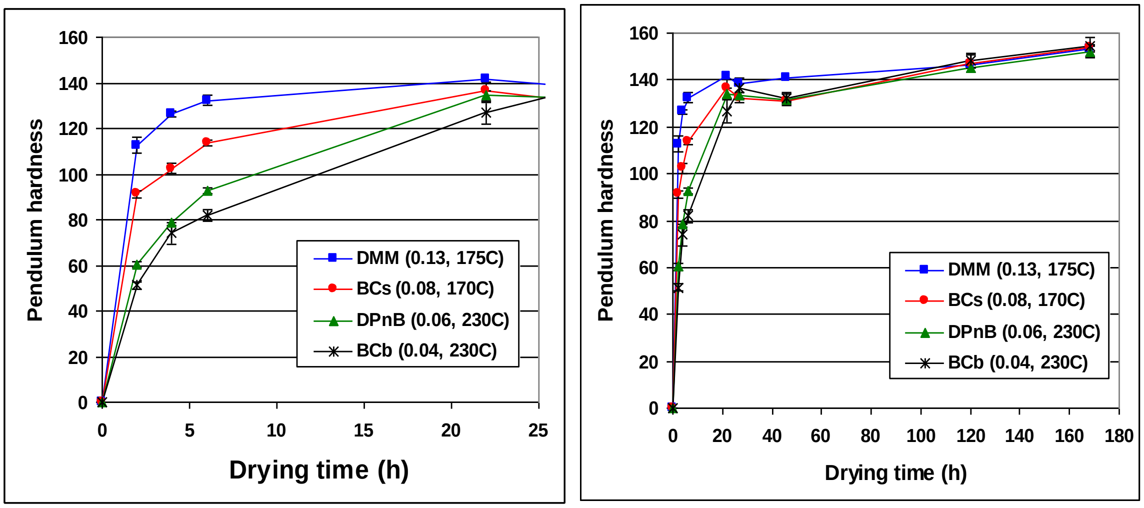

Figure 4. Evolution of Konig hardness of SF-PUD-A in the presence of 10% of glycol cosolvents with different boiling point and evaporation rate.

Early water resistance. Early water-spot resistance of SF-PUD-A was tested with DMM and BCb. Figure 5 shows that good early water-spot resistance was observed when >9% DMM and >4% BCb was post-added. With <9% DMM, and >24% BCb, dried films exhibited poor water-resistance. These results indicate the importance of coalescence in dried films during film formation. When the amount of post-added cosolvents is not enough for coalescence of NOP-PUDs, cracked films are formed at RT, leading to poor water-spot resistance. In addition, poor results are also observed when excess solvent is added. This is presumably due to residual solvent remaining in films.

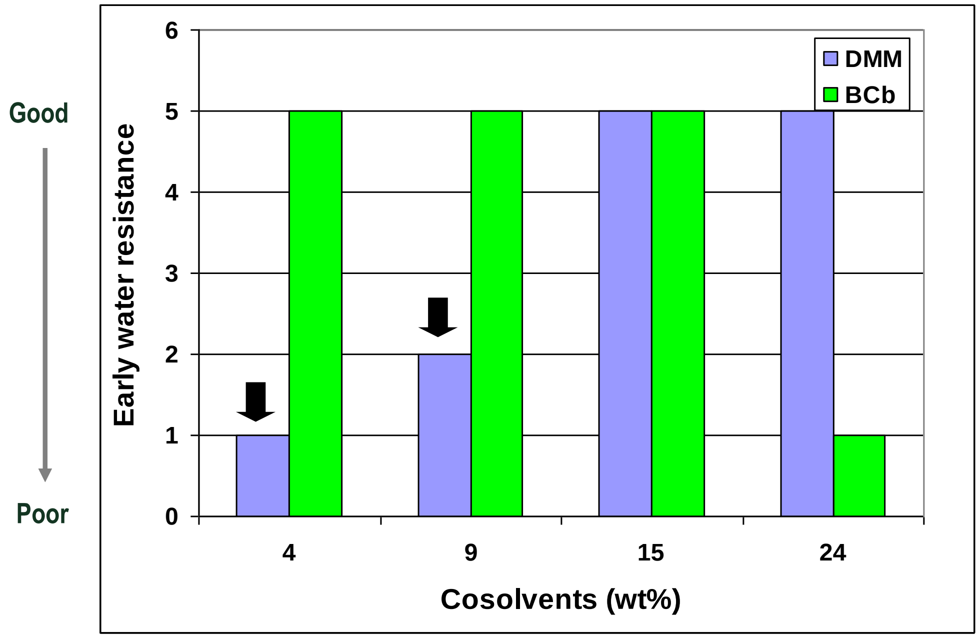

Figure 5. Early water-spot resistance of SF-PUD-A mixed with different amounts of DMM and BCb after dried for 1 day. Arrows indicate crack-forming films.

3.2. Understanding coalescence and morphology change of NOP-PUDs during film formation

In the previous sections, the post-addition of solvents to NOP-PUDs enabled the enhancement of their end-use properties including MFFT, early water resistance, and impact resistance. A lower amount of good solvent such BCb and BCs, compared to a higher amount of poor solvents like DMM were required to obtain enhanced end-use properties. This section describes the results that can address the above learning with respect to coalescence and morphology change during film formation at RT.

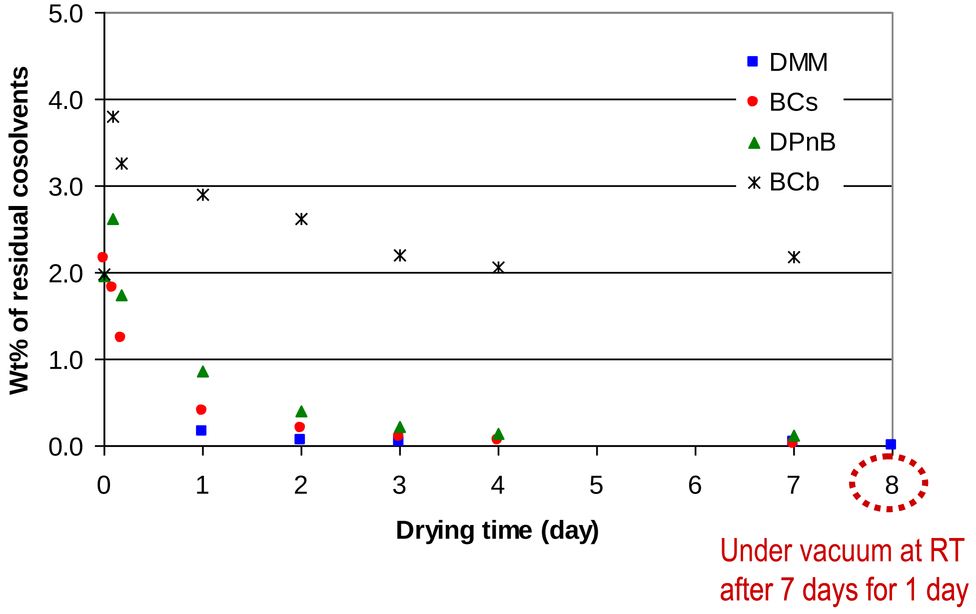

Figure 6. Determination of residual cosolvents remaining in SF-PUD-A films as a function of drying time using GC/MeOH extraction method. After dried for 7 days at RT, the films were treated with vacuum for 1 day at RT. Solvent content (wt %) of y-axis is based on PU solids.

a) Plasticization by residual solvents remaining in dried films. GC measurements were explored to determine the amount of residual solvents in dried films consisting of SF-PUD-A separately mixed with 10% DMM, BCs, DPnB, and BCb. As seen in Figure 6, after 2 h, it was 1.8% for BCs, 2.6% for DPnB, and 3.8% for BCb, indicating that significant amounts (>75%) of DMM and BCs with high evaporation rates were evaporated out of films. After 1 day, it reduced to 0.16% for DMM, 0.34% for BCs, 0.9% for DPnB, and 2.9% for BCb. As films were further dried, the amount of residual solvents further decreased to 0.03% for DMM and BCs, 0.12% for DPnB, and 2.2% for BCb after 7 days. Such difference in the amount of residual solvents could be related to the evaporation rates of solvent at RT. When films dried for 7 days at RT were treated with vacuum for 1 day at RT, the amount of residual solvent decreased to none.

In order to explore whether the enhancement of impact resistance is due to residual solvents remaining in films, impact resistance of SF-PUD-A mixed with 25% of cosolvents was tested before and after vacuum treatment. Impact resistance of most dried films at RT for 8 days was 160. After vacuum treatment, it did not change from 160. Since values are all at test maximum it is not possible to determine if there was a real change. However, any change is of practical insignificance.

b) Partitioning of cosolvents between water and particles. A centrifugation/GC method was utilized to determine partitioning coefficient (C_{PA}) of solvents to particles. The C_{PA} value was calculated from the wt ratio of solvent in particles to total solvent (10%). It was determined to be 0.41 for DMM, 0.38 for BCb, and 0.71 for DPnB. That the C_{PA} of DPnB was higher is due to its hydrophobicity (or low water solubility). Interestingly, the values of C_{PA} for DMM and BCb were similar. However, the partitioning coefficients of co-solvents did not appear to correlate to end-use properties such as impact resistance of SF-PUD-A. Recall that the order of impact resistance was BCb >> DPnB>DMM at 10%, while the order of partitioning coefficient to particles was DPnB >> DMM ~ BCb.

c) Solubility parameter of NOP-PUDs. Solvent swelling method was used to determined Hansen solubility parameters of SF-PUD-A to be 18.7 for dispersion, 11.4 for polar, and 9.5 [√(J/cc)] for hydrogen-bonding parameter as well as its solubility sphere radius (interaction radius, Ro) = 10.5 [√(J/cc)]. The Ro value determines the radius of the sphere in Hansen space for the substance being dissolved in solvent. The distance (Ra) in Hansen space is calculated by square root of sums of difference in Hansen parameters. Since the relative energy distance (RED) is calculated by the ratio of Ra/Ro, the RED value indicates solubility of polymer in solvent. For example, polymers will dissolve when RED < 1; they will partially dissolve when RED = 1 and will not dissolve with RED > 1. For SF-PUD-A, the RED value of glycol and other solvents was calculated to be 0.27 for NMP, 0.67 for BCb, 0.69 for BCs, 0.96 for DPM, and 1.26 for DMM. These results suggest that NMP, BCb, and BCs are better solvents than DMM to dissolve hard and soft segments of NOP-PUD polymer.

d) Morphology change of hard domains during film formation. PUD polymer chains consist of hard segments including hydrogen bonds and soft segments (NOPs). It is known that most PU films, particularly PU-based thermoplastic elastomers, are phase-separated with hard domains surrounded with soft matrix due to thermodynamic immiscibility of hard and soft segments.[14,15,16] It can be assumed that good solvents can soften hard segments to be mobile with soft segments, forming smaller hard domains well-distributed in soft phase, enhancing impact resistance. Figure 7 shows the AFM images for surfaces of SF-PUD-A mixed with DMM, DPnB, and TPnB. Note that light color indicates high density species (hard segments), while dark color indicates low density species (soft segments). Coarse structures of hard domains were observed for films with DMM, while fine or intermediate structure of hard domains are observed with DPnB and TPnB. Impact resistance was higher for films coalesced with DPnB and TPnB as good solvents than for films coalesced with DMM as a poor solvent. Similar observation was made for AFM images for internal structures of the samples.

In dispersion, cosolvents are partitioned in both PUD particles and water phase. The above results suggest that DPnB is more partitioned in particles, compared to DMM. During film formation, water evaporates and particles come in contact; high boiling point DPnB and TPnB slowly evaporate and thus the concentration of these glycols became higher to be enough to soften hard segments to be mobile, leading to fine microstructure of hard segments, and thus eventually enhancement of properties of dried films. However, DMM which is poor cosolvent evaporates too fast to touch hard segments in drying films, leading to coarse microstructure of hard domains.

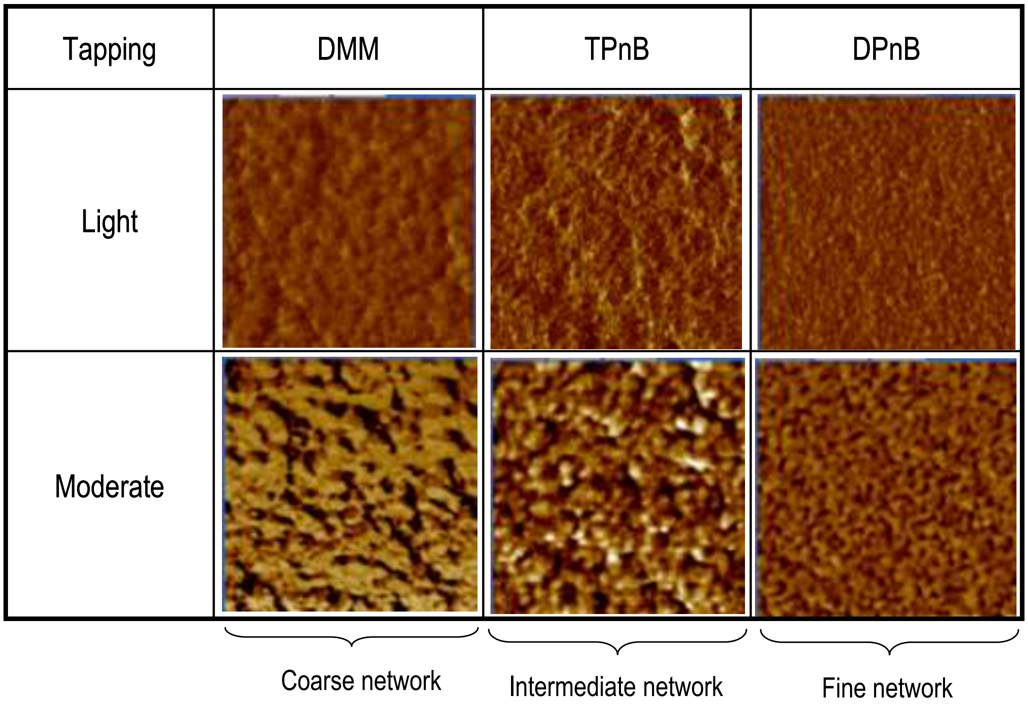

Figure 7. AFM images for surfaces of SF-PUD-A containing post-added DMM, DPnB, and TPnB. The size of images is 500 nm x 500 nm.

4. Conclusions

An HTR workflow developed for PUD wood coatings was leveraged to explore the effect of cosolvents on end-use properties of NOP-based PUD coatings. The post-addition of solvents to SF-PUD-A enabled the enhancement of the properties including MFFT, early water resistance, and impact resistance. The selection of solvent enabled reduction of VOC level as well as improvement of end-use properties. In order to obtain good properties, lower amounts of good solvents such BCb and BCs are required, relative to poorer solvents like DMM. The combined results from bench-top experiments and analytical methods suggest that good coalescence as well as a fine morphology of hard domains are main factors that enhance properties such as impact resistance and early water resistance. In addition, development of the properties in early drying stage (within 2 h) is very solvent dependent. Good cosolvents soften (or plasticize) hard segments to be mobile for polymer diffusion, yielding mechanically coherent films enhancing impact resistance.

5. Acknowledgments

The authors thank Dr. Kumar Nanjundiah, Dr. Charles Diehl, Dr. John Argyropoulos, and Suresh Subramonian for their fruitful discussions, Felipe Donate and Ellen Hock for solubility parameter calculation, as well as Jamie Sullivan, Evelyn Wilson, Cory Peitsch for their tremendous supports in synthesis of PUDs and test of PUD coatings at Dow Chemical Company. The authors also thank Dow Chemical Company for support and permission for this publication.

6. References

---

[1] Tyre, et al., Utilization of PU acrylic blends in 1K wood floor coatings. Proceedings of 2008 Wood Coatings & Substrates Conference, UNC Greensboro, September. 2008.

[2] Schriven et al. US Patent 4066591; Coogan et al. US Patent 4801644; Reiff et al. US Patent 4108814.

[3] Argyropoulos, J. et al. Natural oil polyols for waterborne polyurethane dispersions. *JCT CoatingsTech*. **2009**, *6*, 44.

[4] Erdem, B. et al. Aqueous polyurethane dispersions and their applications: From biomedical and industrial applications. Prague, Czech Republic, July **2008**.

[5] Erdem, B. et al. Ahead of the field (Part 2). Natural oil polyols redesigned to give high performance PUDs. *Eur. Coat. J.* **2009**. 36.

[6] Dou, Z. et al. Low VOC Polyol alkyd dispersion and polyurethane dispersions. WO02/31021 A1.

[7] Ott, K. et al. Novel solvent for producing polyurethane dispersions. US2007/0197720 A1 (BASF)

[8] Johnson, M. et al. High-Throughput methods for developing water-borne coating formulations. New Orleans, *Proceedings of International Waterborne, High-Solids, and Powder Coatings Symposium.* **2009**.

[9] Oh, J. K. et al. High-Throughput methods for developing low VOC waterborne coatings derived from polyurethane dispersions based on natural oil polyols. *Proceedings of International Waterborne, High-Solids, and Powder Coatings Symposium.* **2010**, *37*, 83.

[10] Oh, J. K. et al. Development of Low VOC Waterborne Coatings Derived from Polyurethane Dispersions based on Natural Oil Polyols using High Throughput Methods. *JCT CoatingsTech*. **2010**, *7*, 30.

[11] Chrisman, R. W. High throughput research. *Micro Instrum.* **2007**, 67.

[12] Peil, K. P. et al. Applications of high throughput research at the Dow Chemical Company. *Macromol. Rapid Commun.* **2004,** *25*, 119.

[13] Takahashi, N. et al. Functional multineuron calcium imaging for systems pharmacology. *Anal. Bioanal. Chem.* **2010**, *398*, 211.

[14] Shi, H. et al. Thermosensitive polyurethane film and finished leather with controllable water vapor permeability. *J. Appl. Polym. Sci.* **2010**, *117*, 1820.

[15] Schoen, P. et al. Quantitative mapping of elastic moduli at the nanoscale in phase separated polyurethanes by AFM. *Eur. Polym. J.* **2011,** *47*, 692.

[16] Sanchez-Adsuar, M. S. et al. Properties of polyurethane elastomers with different hard/soft segment ratio. *J. Adhes.* **1998**, *67*, 327.