

SOLVENT-FREE URETHANE-ACRYLIC HYBRID POLYMERS FOR COATINGS

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Abstract

Urethane-acrylic hybrid polymer dispersions (HPDs) can offer cost/performance advantages over common 1K coating materials such as polyurethane dispersions (PUDs), acrylic emulsions, and blends thereof. One disadvantage of both PUDs and HPDs is the inclusion of N-methylpyrrolidone (NMP) solvent, which is commonly a necessary processing solvent included at levels ranging from about 3 to 15%. Since NMP has recently been added to California's Proposition 65 list and has generally become objectionable for use in Europe, it has become desirable to eliminate NMP from these products. Consequently, solvent-free versions of HPDs have been developed that, despite the lack of NMP used in their preparation, have been found to perform favorably compared to analogous solvent-containing polymers (both hybrid and PUD). Like their solvent-containing counterparts, the outstanding properties of the new solvent-free versions are apparently due to their true hybrid nature, which is analogous to an interpenetrating network (IPN) as indicated by a broad glass transition temperature range. Although the NMP-free versions still require coalescing solvents for adequate film formation, they offer greater flexibility in choosing alternate solvents when formulating high performance coatings.

Introduction and Background

Thermoplastic polyurethanes are well known for their excellent balance of mechanical toughness and chemical resistance.¹⁻⁹ Unfortunately, the solvent-based versions require exceedingly high levels of VOC for application by conventional coating techniques. The waterborne versions (polyurethane dispersions or PUDs) require significantly lower VOC and are, therefore, becoming increasingly popular choices as binders for a variety of one-component coatings for wood (floors and furniture), plastic (business machine housings), leather, metal, and concrete. Their superior physical and chemical properties have been attributed to a combination of their molecular structure and hard/soft domain morphology.⁹⁻¹⁰

In general, PUDs are prepared by reacting an excess of diisocyanate with a polyol, dispersing the resulting prepolymer in water, and completing the reaction by adding a water-soluble diamine to consume the residual isocyanate and, thereby, chain-extend the prepolymer to an high molecular weight. The dispersed PUD particles are usually anionically stabilized, which is commonly accomplished by incorporating a carboxylic acid-functional polyol into the backbone of the

polyurethane and neutralizing the acid groups with a tertiary amine. Thus, in many cases, no external surfactants are present to contribute adversely to water sensitivity of PUD-based coatings.

PUDs are available in both aromatic and aliphatic varieties. Aromatic PUDs are not suitable for applications requiring low yellowing and, therefore, the aliphatic PUDs are required for such cases where exposure to direct or indirect sunlight occurs.

Unfortunately, one of the main disadvantages of the aliphatic PUDs is their relatively high cost. As a result, formulators have sought ways to reduce the cost of their coatings. The most popular strategy is to blend the PUD with an acrylic polymer emulsion that costs less than one-half that of a standard aliphatic PUD. Although the acrylics reduce the system cost, they also reduce the overall performance of the binder. The reduction in performance can be lower than what would be predicted from an arithmetic rule of mixtures.^{11,12} One possible reason for this behavior is that, on a molecular level, the acrylic polymers are not soluble in the polyurethane polymers. Therefore, the polymers remain phase-separated during film formation. Arguably, the resultant phase morphology is at least partly responsible for the diminished performance behavior noted above.

In order to take advantage of the potential cost reduction afforded by the acrylics and maintain a greater share of the advantageous PUD properties, so-called “hybrid” systems were developed. The hybrids incorporate both the urethane and the acrylic polymers into the same dispersion. As outlined in the simplified process flow diagram (*Figure 1*) below, there are generally 2 methods for preparing HPDs (Type 1 and Type 2). For Type 1 hybrids, a PUD is first prepared, acrylic monomers are added to the PUD, and the acrylic polymer is formed in the presence of the PUD.¹³ To prepare Type 2 hybrids, a polyurethane prepolymer is formed, the acrylic monomers are added to the prepolymer, the mixture is dispersed in water, and the urethane and acrylic polymerizations are completed concurrently.^{14,15}

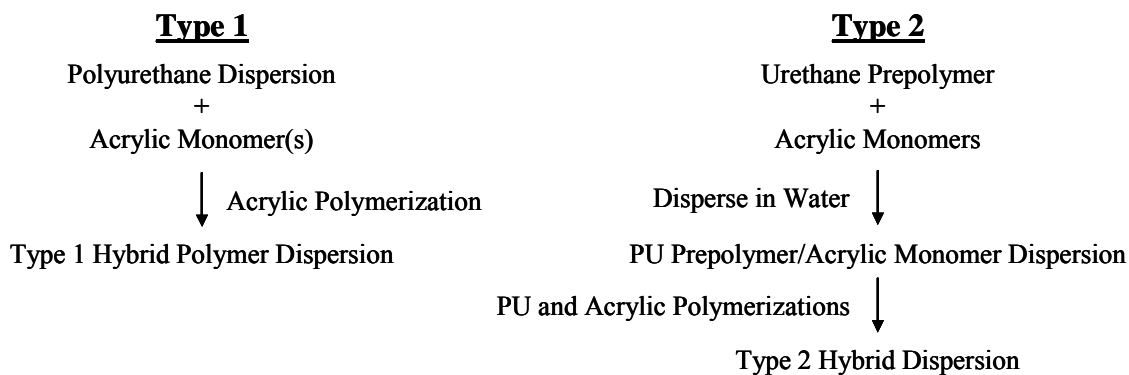


Figure 1. Simplified Process Flow Diagram for Preparation of Type 1 and Type 2 Hybrids.

The urethane and acrylic polymers in HPDs exhibit improved molecular compatibility versus simple blending. The improved compatibility is demonstrated by the dynamic mechanical analysis (DMA) data that are shown in *Figure 2*. The simple blend has 2 distinct tan delta ($\tan \delta$) peaks, which correspond to the glass transition temperatures (T_g) for the phase-separated urethane and acrylic polymers. The hybrid prepared from the first method described above also shows 2 T_g peaks, but the peaks have become somewhat broader, which is indicative of some limited molecular mixing. In contrast, a Type 2 hybrid, in which the urethane prepolymer and acrylic monomers are homogeneously

mixed prior to dispersion and subsequent polymerization, exhibits only a single, very broad $\tan \delta$ peak. The single peak, which spans the temperature range between the theoretical T_g s of the urethane and acrylic polymers, is strong evidence for a significant amount of polymer-polymer mixing, in which, presumably, the different polymer molecules are intertwined similar to that of an interpenetrating network (IPN). Presumably, the improved compatibility for the hybrids (especially Type 2) is at least partly the result of some molecular-level grafting of the two polymers.

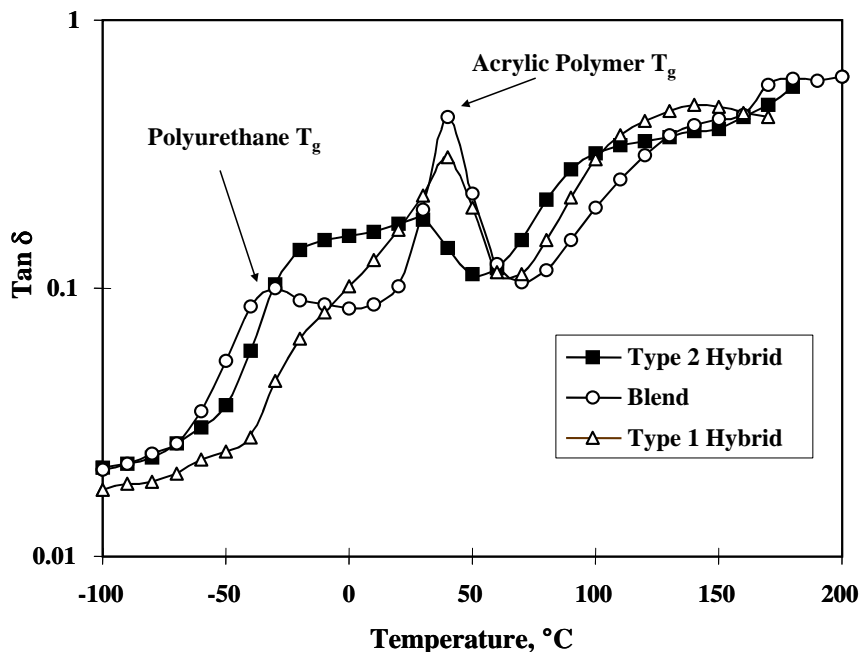


Figure 2. DMA Data Comparing a Simple Blend with HPDs.

As mentioned previously, the rationale for preparing the hybrids was to improve the performance relative to a simple blend. In *Figure 3*, the tensile strengths of films prepared from the individual

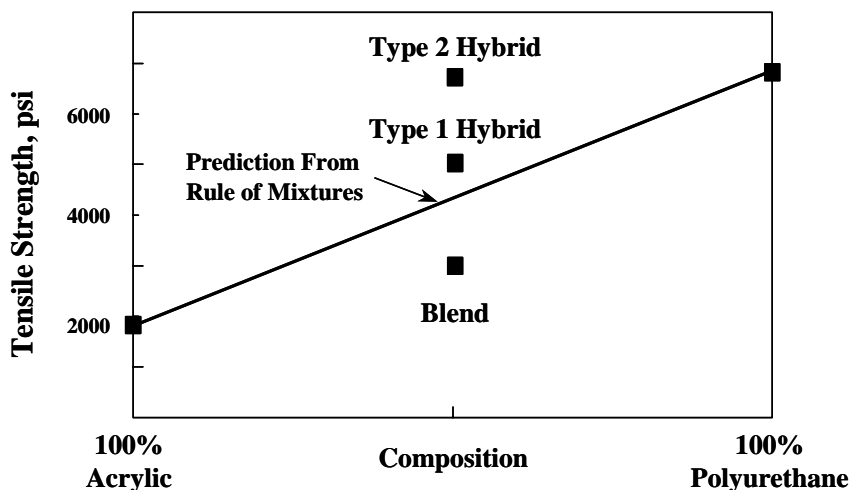


Figure 3. Tensile Strengths of Free Films Prepared from a Simple Blend and HPDs.^(11,12)

polymers (i. e., a blend) and the 2 hybrid types are compared to that predicted by a linear rule of mixtures. The blend and the hybrids contain equal amounts of the same urethane and acrylic polymers. As expected, the urethane polymer had a significantly higher tensile strength than the acrylic polymer. Interestingly, the tensile strength of the blend was found to be lower than that predicted by the simple averaging rule. On the other hand, the hybrid systems show higher tensile strengths than predicted. Remarkably, the Type 2 hybrid was found to have a tensile strength approximately equal to that of the polyurethane. Similar results for other properties have been reported as well.¹¹ One interpretation is that the phase morphology of an urethane/acrylic polymer system has a significant influence on the ultimate performance.

Typically, PUDs and HPDs are prepared using an aprotic solvent such as N-methylpyrrolidone (NMP). The NMP is required in the polyurethane prepolymer step to dissolve the dimethylolpropionic acid (DMPA), which is a crystalline carboxylic acid-polyol that is virtually insoluble in the polyol-diisocyanate mixture that reacts to form the urethane prepolymer. Being a relatively high boiling solvent, NMP cannot be readily removed from the process and, thus, remains in the final dispersion product. Although the amount of NMP can vary according to the product, typical NMP levels are 10% to 15% for PUDs and 3% to 8% for hybrids. In the final product, NMP is beneficial as a coalescing solvent for film formation. Conversely, NMP and high levels of residual acrylic monomers are undesired due to their odor and, in the case of NMP, its regulatory status (e. g., inclusion on California's Proposition 65). Therefore, there is a market need for NMP-free, low residual monomer HPDs that meet those requirements and still provide outstanding performance that is comparable to that of their NMP-containing counterparts.

In this paper, the properties and performance of new, NMP solvent-free, Type 2 urethane-acrylic HPDs will be discussed.

Experimental

Solvent-containing (Hybrids A and B) and solvent-free (Hybrids A_{SF} and B_{SF}) HPDs were prepared according to the procedures outlined previously.^{14,15} The letter designations (i. e., A or B) refer to the analogous polymer compositions, and the subscript "SF" indicates the solvent-free version. The typical properties of the HPDs used in this study are provided in *Table 1*. The composition of the urethane (aliphatic) portion was identical for all of the hybrid polymers. The acrylic polymer composition was kept the same for the Hybrid B variants, while the monomer ratios were varied within the A series. Nevertheless, the acrylic polymers had approximately the same theoretical T_g within a given series (either A or B). The amount of either urethane or acrylic was about 50% for each HPD. With the exception of dimethylethanolamine (DMEA) for Hybrid B_{SF}, the neutralizing amine used was triethylamine (TEA).

Coating formulations (Appendix A) were prepared using standard techniques. Coating properties were tested over cold-rolled steel with a zinc phosphate treatment (Bonderite 952), untreated cold-rolled steel, or on sealed-paper charts (Leneta Co.). The coatings were applied using a #60 wire-wound draw-down rod and were allowed to dry at 21 °C (70 °F) and 50% relative humidity for 7 days. Depending on the formulation, the dried film thickness ranged from 30 μm (1.2 mil) to 76 μm (3.0 mil).

The standard test methods listed in *Table 2* were used to evaluate coating performance. Spot tests were performed on clear coatings applied by drawdown on sealed-paper charts. The coatings were dried for 24 hours at room temperature (~25 °C), and the spots (2 - 3 cm wide) were rated after exposure to each reagent for 1 hour. The reagent spots were covered during the exposure to prevent evaporation. Prior to evaluating the coating, the reagent spots were removed by lightly patting with a clean paper towel.

Table 1. Typical Characteristics of the Type 2 Hybrid Polymer Dispersions Evaluated.

Property	Hybrid A ^a	Hybrid B ^b	Hybrid A _{SF} ^c	Hybrid B _{SF} ^d
Appearance	Opaque, Slight Milky	Opaque, Slight Milky	Opaque, Slight Milky	Opaque, Slight Milky
Viscosity, cP, 25 °C, Brookfield	50 - 150	50 - 150	50 - 150	50 - 150
Non-Volatiles, % by weight	39 - 41	39 - 41	39 - 41	39 - 41
Solvent Content, % by weight	6	6	<0.2	<0.1
Solvent	NMP	NMP	Acetone	Acetone
VOC, g/L (lbs/gal) ^e	160 (1.33)	164 (1.37)	30 (0.25)	24 (0.20)
Density, g/mL (lbs/gal)	1.03 (8.60)	1.04 (8.70)	1.05 (8.76)	1.07 (8.93)
pH	7.5 - 9.0	7.5 - 9.0	7.5 - 9.0	7.5 - 9.0
Acid Number, mg KOH/g ^f	14.5	14.5	16.0	14.5
T _g Range, °C ^g	-35 to 35	-35 to 100	-35 to 35	-35 to 100
Neutralizing Amine ^h	TEA	TEA	TEA	DMEA
Particle Diameter (Wt. Avg.), nm	75 - 85 ⁱ	75 - 85 ⁱ	75 - 85 ⁱ	75 - 85 ⁱ
Residual Acrylic Monomer, ppm	500 ⁱ	500 ⁱ	50 - 200 ⁱ	10 - 50 ⁱ
Particle Charge	Anionic	Anionic	Anionic	Anionic

^{a, b, c, d} Refer to Appendix C for material identification.
^e VOC includes contribution from the neutralizing amine (~1% by weight).
^f Calculated on a solids basis.
^g T_gs estimated from DMA measurements (breadth of tan δ peak) and polymer compositions.
^h TEA = triethylamine; DMEA = dimethylethanolamine. ⁱ Typical values.

Table 2. Test Methods Used to Evaluate the Performance Characteristics of the Coatings.

Property	ASTM Test Procedure
Adhesion, Dry and Wet Tape	D 3359
Dry Time	D 5895
Flexibility (Mandrel Bend)	D 1737
Gloss	D 523
Hardness (Persoz)	D 4366
Humidity Resistance (Cleveland)	D 2247
Immersion Resistance	D 870
Impact Resistance	D 2794
Solvent Resistance (Double Rubs)	D 4752
Tensile Properties	D 638
Minimum Film Formation Temperature	D 2354

DMA data was obtained on clear resin coatings (Appendix A) using a Rheometrics Solids Analyzer RSA II (Rheometric Scientific) in a tensile dynamic mode with a thin film fixture. The films were analyzed over the temperature range from $-150\text{ }^{\circ}\text{C}$ to $150\text{ }^{\circ}\text{C}$. The samples were not preconditioned with regard to humidity prior to data acquisition, but dry nitrogen was used as the atmosphere during the measurements. Data was acquired at intervals of $6\text{ }^{\circ}\text{C}$; a one-minute soak time was used at each measurement temperature to ensure isothermal equilibration. MFFT results were obtained using a Minimum Film Formation Temperature Bar Model MFFT-90 (Rhopoint Instrumentation Ltd.). Films were applied by drawdown to a wet film thickness of $152\text{ }\mu\text{m}$ (6 mils). Tensile data were obtained on clear films that had an average thickness of $\sim 152\text{ }\mu\text{m}$ (6 mils) and were dried at $21\text{ }^{\circ}\text{C}$ ($70\text{ }^{\circ}\text{F}$) and 50% relative humidity (RH) for 7 days. The crosshead speed used was 5.1 cm/min (2 in/min) and the temperature was $23\text{ }^{\circ}\text{C}$ ($73\text{ }^{\circ}\text{F}$) with 50% RH. Particle size determinations were made using an LA-910 Laser Scattering Particle Size Distribution Analyzer (Horiba).

Results and Discussion

Dispersion Properties

With the obvious exception of VOC and residual monomer levels, the physical property data as provided in *Table 1* are quite similar for all of the HPDs studied. Both the solvent-containing and the NMP-free versions exhibited similar viscosities at the same solids levels. Interestingly, the particle diameter distributions (*Figure 4*) and the respective means for the NMP-free dispersions were similar to those that contained NMP. All of the distributions were mono-modal with no particle diameters greater than 200 nm and weight-average particle diameters between 75 and 80 nm . The weight-average particle diameters (in nanometers) for the samples in *Figure 4* were 81 , 77 , 79 and 78 for Hybrids A, B, A_{SF} and B_{SF}, respectively. Since all of the hybrids have similar acid numbers and degrees of neutralization, the similarity in particle sizes suggests that, regardless of the NMP level (at least up to 6% by weight), the average particle diameter is determined by the zeta potential.¹⁶ In addition, the particle size distributions probably explains the similar viscosity-solids relation shown for these HPDs. Because of the lack of NMP and the low residual monomer levels, the NMP-free HPDs have very low odor compared to the solvent-containing versions.

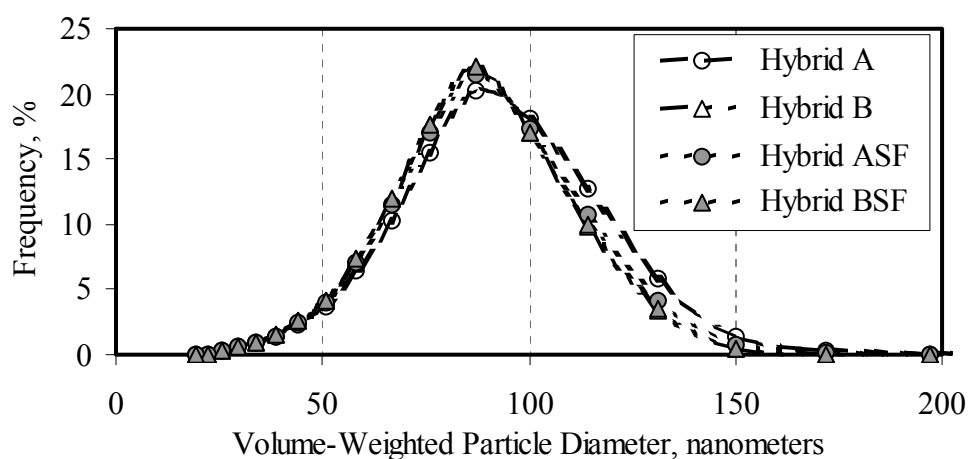


Figure 4. Particle Size Distributions for the Hybrid Polymer Dispersions.

Film Formation Characteristics

Film formation characteristics of Type 2 hybrid polymers has been reported previously for systems containing NMP solvent.¹⁷ Our experience with Hybrids A and B have shown that ultimate performance is impacted by particle coalescence which, of course, is greatly influenced by the type and amount of co-solvent used. Both Hybrids A and B, which contain NMP, formed clear films (from drawdowns) at room temperature (~25 °C). Hybrid A_{SF} formed a clear but non-continuous (cracked) film, whereas Hybrid B_{SF} formed a white, flaky film, which is indicative of poor coalescence. Films prepared using co-solvents (formulations in Appendix A) were clear and continuous.

In order to characterize and understand the effects of co-solvents and additives, minimum film-formation temperatures (MFFT) were determined for the NMP-free HPDs; the results are provided in *Table 3*. In line with the drawdown observations above, both of the neat solvent-containing products had MFFTs below 0 °C, whereas the NMP-free versions had, as expected, much higher MFFTs. In the case of Hybrid B_{SF}, the MFFT was 62.0 °C. The addition of co-solvents (6% by weight of either NMP or DMM - dipropylene glycol dimethyl ether) was found to significantly lower the MFFTs. Comparatively, NMP was shown to be somewhat more efficient (especially for Hybrid B_{SF}) for lowering the MFFT. Despite the addition of the co-solvents, the MFFTs for Hybrid B_{SF} were unexpectedly much higher than for Hybrid B. Perhaps, the order of addition has an effect on the coalescing efficiency of the co-solvent. Alternately, it may be that the formulations had not reached equilibrium prior to testing, although a sweat-in time of between 1 to 5 days after preparation was employed. Another possibility is that some fundamental differences between the polymers or polymer morphology exists, although the dynamic mechanical analysis (DMA) data to be discussed in the next sub-section does not seem to support this hypothesis.

Table 3. MFFT (°C) Data for the HPDs.

Additive (% Wt.)	Hybrid A	Hybrid B	Hybrid A _{SF}	Hybrid B _{SF}
None	< -4.6	< -4.6	19.1	62.0
NMP (6%)	*	*	< 0.0	18.3
DMM (6%)	*	*	-1.0	40.8
S-1 (2%) ^p	*	*	3.1	*
S-2 (2%) ^q	*	*	5.5	*
S-3 (2%) ^r	*	*	10.9	*
* Value was not determined.				
S-1, S-2 and S-3 are surfactants identified in Appendix C by superscript letter.				

Besides the co-solvents, several novel surfactants were tested in Hybrid A_{SF} as potentially ultra-low VOC coalescing agents. These surfactants are low volatility, alkyl ester-based products that are purported to have utility to reduce MFFTs. The results in *Table 3* show that these surfactants do indeed significantly reduce the MFFTs. At a level of 2% by weight (total emulsion basis), the MFFT was found to drop by the amount of 8 °C to 16 °C. Thus, the use of these surfactants may offer the potential to significantly lower VOCs in formulations developed from these materials.

Clear Film Mechanical Properties

The dynamic and static (tensile) mechanical properties of the hybrid polymers were determined. *Figures 5 and 6* compare the dynamic mechanical properties (storage modulus, E', and tan δ = E''/[loss modulus]/E') as a function of temperature. Below the T_g (~ -35 °C) of the urethane polymers (the

same composition for all 4 hybrids), both series (A and B) of hybrids had E' values between about 2 to 3×10^{10} dyn/cm². Above the urethane T_g , the E' values declined to about 10^9 dyn/cm² near the T_g of the individual acrylic polymers. Having the higher T_g acrylic polymers, the B-series did not reach an E' value of 10^9 dyn/cm² until > 100 °C versus about 50 °C for the A-series materials. The Hybrid A-series showed a pronounced rubbery plateau above the acrylic T_g s, whereas the B-series did not.

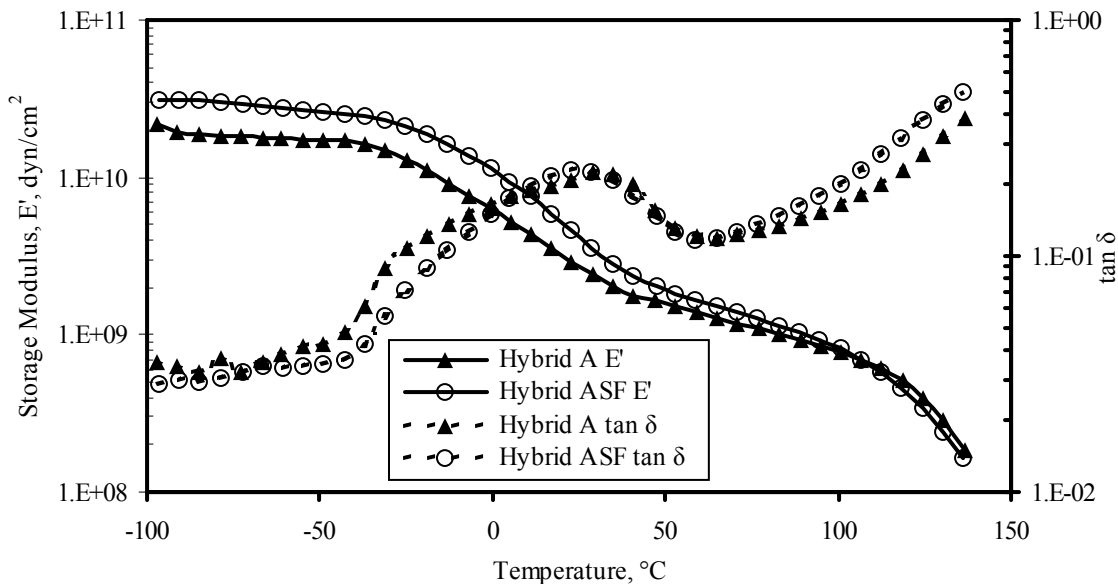


Figure 5. Comparison of the DMA Properties for Hybrids A and A_{SF} .

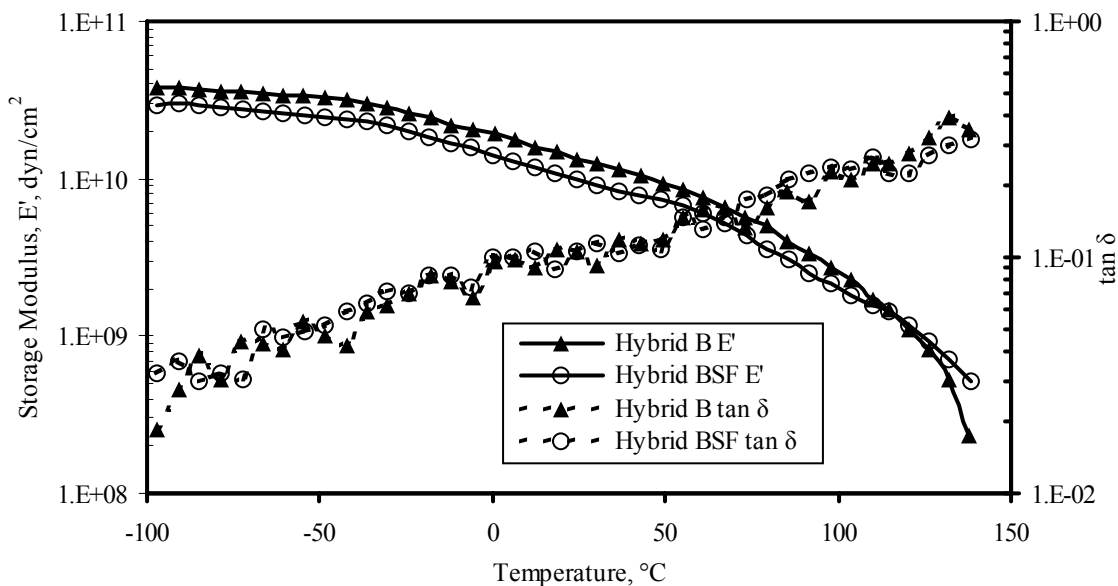


Figure 6. Comparison of the DMA Properties of Hybrids B and B_{SF} .

For the A-series polymers, the E' and $\tan \delta$ responses were similar, and both polymers showed very broad peaks in the $\tan \delta$ over the expected T_g ranges as listed in *Table 1*. Hybrid A_{SF} did have a

somewhat higher E' over most of the temperature range studied. The B-series polymers showed comparable E' and $\tan \delta$ behavior, although Hybrid B_{SF} did have a slightly higher E' over most of the temperature range examined. However, unlike that for the A-series, there was no apparent $\tan \delta$ peak over the anticipated T_g range. The $\tan \delta$ s did, however, show a steady increase with increasing temperature as the E' decreased. In general, both the solvent-containing and NMP-free versions displayed dynamic mechanical properties which would be expected if there were some molecular-level mixing of the urethane and acrylic polymers.

The room-temperature tensile mechanical properties of thin films of the hybrids are summarized in *Table 4*. Within a given series, the tensile properties were comparable. As expected the A-series, having the lower T_g acrylic polymers, had lower tensile strengths and moduli but higher tensile elongations. The A-series polymers showed a relatively good balance of properties with high elongations (> 230%) and moderate tensile strengths.

Table 4. Tensile Properties for the Hybrid Polymers.

Polymer	Strength, psi	Elongation, %	Modulus, 10 ³ psi
Hybrid A	2433 ± 458	236 ± 76	30 ± 11
Hybrid A _{SF}	2576 ± 650	245 ± 12	38 ± 11
Hybrid B	4552 ± 450	15 ± 8	115 ± 59
Hybrid B _{SF}	4407 ± 244	8 ± 0.4	155 ± 11

Coating Performance: B-Series Hybrids

The performance of Hybrids B and B_{SF} were evaluated and compared using chemical spot tests; the results of which are provided in *Table 5*. Both hybrids showed comparable performance, as the spot test resistance was relatively good for both systems. Of the chemicals studied, IPA showed the most effect on the coatings, and this could be a potential area for improvement.

Table 5. Chemical Spot Testing Results for Hybrids B and B_{SF}.

Chemical	Hybrid B	Hybrid B _{SF}
10% Wt. NH ₄ OH in water	10	10
Clorox (5.25% Wt. NaClO/water)	10	10
50% Wt. Ethanol in water	10	9
IPA	7	7
Commercial Cleaner 1	9	8
Commercial Cleaner 2	8	8
Commercial Cleaner 1 = Fantastik (S.C. Johnson); Commercial Cleaner 2 = Formula 409 (Clorox)		
Rating Key: 10 = no effect; 5 = moderate: swelling, softening and whitening; 0 = completely dissolved		

Coating Performance: A-Series Hybrids

In *Table 6*, the performance properties of the A-series hybrids in and pigmented coatings (Appendix B for 1 and 2) are compared and benchmarked versus commercial NMP-containing PUDs, an HPD, a PUD/acrylic blend, and an acrylic. Coating properties for the NMP-free Hybrid A_{SF} were similar to those of Hybrid A. Dry time, gloss, reverse impact resistance, MEK resistance, and UV resistance of

the NMP-free Hybrid A_{SF} compared favorably to Hybrid A and the benchmarked commercial materials. The IPA resistance was better for Hybrid A_{SF} than that for 3 of the other systems tested. Interestingly, the commercial paints had comparatively much lower impact resistance.

Table 6. Clear and Pigmented Coating Performance Property Comparison.

Property / Formulation	1	2	3 ^s	4 ^t	5 ^u	6 ^v	7 ^w	8 ^x
Dry-Hard Time, min	40	40	40	30	30	25	>60	60
60° Gloss	75-80	84	53	NA	NA	74	31	81
Reverse Impact, in-lb	160	160	160	160	160	28	4	72
IPA** Double Rubs	83	50	182	25	25	83	200	40
MEK** Double Rubs	>200	>200	200	25	25	90	115	<10
1000 Hrs. QUV-B, ΔE	<2	<2 *	<2	NA	NA	2	1	3.5

Key: 1 = Hybrid A; 2 = Hybrid A_{SF}; 3, 4, and 6 = PUDs; 5 = HPD; 7 = PUD/acrylic blend; 8 = acrylic. Formulation 3 was a pigmented white coating and 4 and 5 were clear coatings based on recommendations from the respective suppliers. Formulations 6, 7 and 8 were commercially available paints. See Appendix C for material identifications.
 * QUV-A.
 ** IPA = isopropyl alcohol; MEK = methyl ethyl ketone

Further study

A potential area for improvement of the NMP-free hybrids is their IPA resistance. Crosslinking of the HPDs through their carboxylic acid groups is a potential way to improve their resistance properties. Indeed, the resistance properties of acid-functional polymers have been found to be improved when crosslinked with an epoxy-silane crosslinker, β -(3,4-epoxycyclohexyl)ethyltriethoxysilane (a cycloaliphatic epoxy-silane).^{18,19} Shelf-stable (at least 6 months) formulations using Hybrid A have been formulated.²⁰ The use of epoxy-silane and other crosslinkers to improve the performance properties of NMP-free hybrids needs to be examined. Another market need is for lower cost formulations. Acrylics are often blended into PUDs for that purpose, and should be evaluated in the NMP-free HPDs.

Summary and Conclusions

Waterborne, high performance, urethane-acrylic HPDs have been developed to offer cost/performance advantages over standard 1K coating materials such as polyurethane dispersions (PUDs), acrylic emulsions, and blends thereof. These so-called Type 2 hybrid polymers provide many of the benefits (e. g., superior mechanical properties and chemical resistance) of PUDs but at a cost intermediate between PUDs and low-cost acrylics. The Type 2 hybrid has an IPN-like polymer structure which is characterized by a broad glass transition temperature range as measured by DMA. The IPN-like structure is the result of the chemical composition of the material and, particularly, the process by which the urethane and acrylic are polymerized together as a homogenous mixture that is dispersed as colloidal particles in water. The IPN-like morphology is apparently responsible for the hybrid's outstanding properties, which would not be predicted from a simple, arithmetic rule of mixtures. New NMP-free HPDs have been developed to meet the market needs for lower odor products that meet increasingly stringent regulations. The NMP-free HPDs have been shown to provide dispersion and coating properties comparable to their NMP-containing counterparts. Due to their lack of NMP and

low residual monomer contents, both NMP-free HPDs were observed to have reduced odor, which is obviously desirable from a health and safety perspective. In addition, the lack of NMP offers potential regulatory benefits (e. g., California Proposition 65). Because the performance of the HPD systems was found to compare favorably with other polymer systems (PUDs, HPD, and acrylic) evaluated, the possibility exists to replace or partially replace those types of polymers with HPDs.

Acknowledgments

Many people have contributed over the years to the development of HPD technology, and the authors extend their gratitude to all of them. Special mention and thanks must be made to Dick Derby who made significant contributions through the years. Many thanks to: Jeanine Snyder for formulating expertise; Bruce Gruber for his work in the field of hybrid synthesis; Chris Gunsser for synthesis support; Menas Vratsanos and Chris Walsh for their DMA work; Dennis Nagy and Gregg Meixell for particle size analyses; Steve Deppen and Jim Malloy for residual monomer analyses; Steve Robbins for the tensile measurements; Matt Marusiak for process support; Khalil Yacoub for surfactant advice; and Zay Risinger, Bob Stevens, Paula Mc Daniel, and Ellen O'Connell for supporting this work and the presentation of this paper.

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Appendix A. Clear Coating Formulations and Formulation Properties. (See Appendix C for list of materials and suppliers.)

Table A1. Clear Coating Formulation for Hybrid A.

Material	Weight %
Pre-Mix: <i>Mix a solution of the following.</i>	
Solvent ^e	5.98
Surfactant ^f	0.40
Defoamer ^g	0.21
Resin Blend: <i>Add to the following with agitation.</i>	
Hybrid A ^a	79.76
Letdown: <i>Dilute to brush and roll viscosity.</i>	
Water	13.65
Total	100.00

Table A2. Clear Coating Formulation for Hybrid B.

Material	Weight %
Pre-Mix: <i>Mix a solution of the following.</i>	
Solvent ^e	11.93
Surfactant ^f	0.40
Defoamer ^g	0.21
Resin Blend: <i>Add to the following with agitation.</i>	
Hybrid B ^b	79.51
Letdown: <i>Dilute to brush and roll viscosity.</i>	
Water	7.95
Total	100.00

Table A3. Clear Coating Formulation for Hybrid A_{SF}.

Material	Weight %
Pre-Mix: <i>Mix a solution of the following.</i>	
Solvent ^e	2.15
Solvent ^h	5.49
Solvent ⁱ	1.93
Surfactant ^f	0.05
Defoamer ^j	0.10
Resin Blend: <i>Add to the following with agitation.</i>	
Hybrid A _{SF} ^c	90.28
Total	100.00

Table A4. Clear Coating Formulation for Hybrid B_{SF}.

Material	Weight %
Pre-Mix: <i>Mix a solution of the following.</i>	
Solvent ^e	4.13
Solvent ^h	5.27
Solvent ⁱ	3.71
Surfactant ^f	0.05
Defoamer ^j	0.10
Resin Blend: <i>Add to the following with agitation.</i>	
Hybrid B _{SF} ^d	86.74
Total	100.00

Appendix B. Pigmented Coating Formulations and Formulation Properties. (See Appendix C for list of materials and suppliers.)

Table B1. Pigmented Coating Prepared from Hybrid A (Formulation 1 in *Table 6*).

Material	Gallons
Resin-Free Grind: <i>Mix the following under mild agitation until dissolved.</i>	
Water (Deionized)	2.31
Pigment Dispersant ^k	2.74
Defoamer ^o	0.06
<i>Continue agitation while adding the pigment below.</i>	
TiO ₂ Pigment ^l	22.85
<i>Increase speed to high and disperse to Hegman ≥ 7 grind. Do not exceed 140 °F.</i>	
<i>Reduce speed and add the following with medium agitation until blended.</i>	
Water (Deionized)	2.03
Blend: <i>Mix the following in a separate container until blended.</i>	
Hybrid A ^a	66.68
<i>Pre-blend the next 4 items before adding to the Hybrid A with strong agitation.</i>	
Surfactant ^f	0.13
Solvent ⁿ	1.67
Solvent ⁱ	1.50
Defoamer ^g	0.03
Final Blend: <i>Slowly add the resin-free grind to the blend and mix with mild agitation until homogeneous.</i>	
Total	100.00

Weight Solids, %	52.4	PVC, %	17.1
Volume Solids, %	41.2	VOC, lb/gal (g/l)	1.66 (199)
Viscosity, cP	500	Density, lb/gal (g/ml)	10.3 (1.23)

Note: Properties reported are based on theoretical calculations.

Table B2. Pigmented Coating Prepared from Hybrid A_{SF} (Formulation 2 in Table 6).

Material	Weight %
Resin-Free Grind: <i>Mix the following under mild agitation until dissolved.</i>	
Water (Deionized)	2.15
Pigment Dispersant ^k	2.55
Defoamer ^j	0.06
<i>Continue agitation while adding the pigment below.</i>	
TiO ₂ Pigment ^l	21.24
<i>Increase speed to high and disperse to Hegman ≥7 grind. Do not exceed 140 °F.</i>	
<i>Reduce speed and add the following with medium agitation until blended.</i>	
Water (Deionized)	1.89
Blend: <i>Mix the following in a separate container until blended.</i>	
Hybrid A _{SF} ^c	65.12
<i>Pre-blend the next 5 items before adding to the Hybrid A_{SF} with strong agitation.</i>	
Surfactant ^m	0.06
Solvent ^h	3.96
Solvent ⁿ	1.55
Solvent ⁱ	1.39
Defoamer ^j	0.04
Final Blend: <i>Slowly add the resin-free grind to the blend and mix with mild agitation until homogeneous.</i>	
Total	100.00

Weight Solids, %	48.5	VOC, lb/gal (g/l)	1.65 (184)
Volume Solids, %	36.9	Density, lb/gal (g/ml)	10.1 (1.21)
PVC, %	17.4		

Note: Properties reported are based on theoretical calculations.

Appendix C. List of Materials and Suppliers.

Superscript	Material	Supplier
a	HYBRIDUR [®] 570 Polymer Dispersion	Air Products
b	HYBRIDUR [®] 580 Polymer Dispersion	Air Products
c	HYBRIDUR [®] 870DEV Polymer Dispersion	Air Products
d	HYBRIDUR [®] 880DEV Polymer Dispersion	Air Products
e	ARCOSOLV [®] DPNB	Lyondell
f	BYK [®] -346	Byk-Chemie
g	SURFYNOL [®] DF-58 Defoamer	Air Products
h	PROGLYDE [®] DMM	Dow Chemical
i	TEXANOL [®] Ester Alcohol	Eastman
j	BYK [®] -024	Byk-Chemie
k	Disperbyk [®] -190	Byk-Chemie
l	TI-PURE [®] R706	DuPont
m	BYK [®] -333	Byk-Chemie
n	DOWANOL [®] DPnB	Dow Chemical
o	DEE FO [®] PI-4	Ultra Additives
p	EnviroGem [®] AE01	Air Products
q	EnviroGem [®] AE02	Air Products
r	EnviroGem [®] AE03	Air Products
s	NeoRez [®] R960	NeoResins
t	WITCOBOND [®] W-236	Uniroyal Chemical
u	Wilko White Industrial Coating	Wilko Paint
v	NeoPac [®] R9000	NeoResins
w	Polane [®] 700T	Sherwin Williams
x	Rust-o-Lastic Gloss Acrylic (DTM) Maintenance Finish	MAB Paints