

Novel Hydrophobic Polyols Yield Durable, High Performance Elastomers

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ABSTRACT

The development of polyurethanes capable of maintaining excellent performance properties upon exposure to aqueous environments and chemical agents continues to be a challenge for polyurethane formulators. For polyurethanes to perform in such an environment, they must possess the ability to prevent the ingress of water or other liquid media into the polymer matrix. Hydrophobic polyols based on hydrocarbon backbones are available in the market to meet the need for moisture resistant polyurethanes. However, these polyols are often incompatible with other polyols and formulation additives due, in part, to their non-polar nature. Polyurethanes derived from popular hydrophobic polyols such as castor oil and polybutadiene often fail to provide the same level of mechanical performance that is observed with polyether and polyester polyols.

The Dow Chemical Company has developed a novel class of hydrophobic polyether polyols. The performance properties of urethane elastomers produced using these hydrophobic polyols are presented and compared against commercially available polyether polyols and a hydrophobic polybutadiene polyol. It was found that elastomers derived from these novel polyols maintain the exceptional physical and mechanical performance typically observed for polyether polyols while also exhibiting reduced water absorption and retention of mechanical properties upon long-term exposure to humid environments. Such elastomers were also found to provide superior resistance to chemical degradation and resistance to UV exposure when compared to polybutadiene-based elastomers.

INTRODUCTION

Polyurethanes are highly versatile materials with respect to the range of properties and applications in which they can be employed. Nowhere is this versatility more evident than in coating, adhesive, sealant and elastomer (CASE) applications. However, the application space addressable with PU technology remains limited due to the sensitivity of the urethane linkage to hydrolysis under aqueous conditions. For those applications involving temporary or permanent exposure to a moisture rich environment, degradation of urethane properties can be reduced by careful polyol selection. For example, polyether polyols are preferred over polyester polyols in many applications due to the greater hydrolytic stability of the ether linkage versus the ester linkage. When stability in harsh aqueous environments is required, formulators utilize “hydrophobic polyols” to control the ingress of water into the polyurethane. Commonly employed hydrophobic polyols include polybutadiene polyols and castor oil. However, the resultant polyurethanes provide neither the physical properties nor the mechanical properties achievable using either polyether or polyester polyols.

Seeking to meet the demand for high-performance and moisture-resistant polyurethanes, The Dow Chemical Company has developed a novel class of hydrophobic polyether polyols. These polyols are low viscosity, clear liquids that can be designed to a wide range of molecular weight and functionality. This paper presents the physical and mechanical properties of polyurethanes derived from these new polyols in cast elastomer formulations. Key properties such as tensile strength, hydrolytic stability, chemical resistance, and UV stability are compared to a polybutadiene polyol and a polyether polyol VORANOL(TM) 220-056.

EXPERIMENTAL DETAILS

Name	Description	Eq. Wt.	Functionality	Source
VORANOL™ 220-056	Polyether polyol	1000	2	The Dow Chemical Company
VORANOL™ CP 450	Polyether polyol	145	3	The Dow Chemical Company
VORAPEL™ D3201	Hydrophobic polyol	1000	2	The Dow Chemical Company
VORAPEL™ T5001	Hydrophobic polyol	200	3	The Dow Chemical Company
Polybutadiene polyol	Hydrocarbon polyol	1160	2.4	Cray Valley USA
ISONATE™ 143L	Modified 4,4'-MDI	144	2.1	The Dow Chemical Company
PAPI™ 27	Polymeric MDI	134	2.7	The Dow Chemical Company
2-EHD	2-Ethyl hexane diol	73	2	Aldrich
1,4 BDO	1,4 Butane Diol	45	2	Aldrich
T-12	Dibutyltin dilaurate			Air Products

Plaque Preparation

Cast elastomers were prepared utilizing a two-step procedure. In the first step, a NCO-terminated prepolymer was prepared by reacting polyol with 4,4' methylene bis(phenyl isocyanate) (MDI) at 80 °C in a round bottom flask under nitrogen for 3 h. The prepolymer was combined with the curative comprised of either 1,4-butane diol or 2-ethyl hexane diol, and T-12 catalyst. Bubble-free plaques were cast in an open mold preheated to 80 °C. The plaques were demolded after 5 min and post cured at 100 °C for 16 h. All plaques were equilibrated under ASTM conditions for at least 24 h prior to analysis.

Analysis

Hardness was measured following ASTM standard test D2240; ASTM standard test D-1708 was utilized to measure tensile strength and elongation at break. Tear strength (Die C) was measured according to ASTM standard test D624. Rebound resilience was evaluated according to ASTM standard test D3574. DMTA analysis was used to determine the glass transition temperature.

Hydrolytic stability was measured by immersing 2x2 inch coupons (3 mm thick) in water for 2 weeks at 70 °C. After immersion, samples were patted dry, weighed and stored in a plastic bag prior to tensile analysis to prevent evaporation of water. Chemical resistance was measured according to ASTM standard test D534-95 by immersing 2x2 inch coupons in the desired media for 7 days at 25 °C. Samples were then washed with water, patted dry and stored in plastic bags prior to tensile analysis. UV stability was measured by exposing the samples to UV radiation (313 nm) for 300 hrs at 60 °C.

RESULTS AND DISCUSSION

The physical and mechanical properties of cast elastomers based on hydrophobic polyol VORAPEL D3201 were evaluated and compared to those of a typical polyether diol, VORANOL™ 220-056, and a hydrophobic polybutadiene polyol. The performance properties of cast elastomers prepared at 75 Shore A and 90 Shore A are shown Table 2. For each polyol examined, the % NCO level of the prepolymer was adjusted to achieve the desired hardness. 1,4-BDO was used as the chain extender for the polyether-based elastomers. A more hydrophobic chain extender, 2-EHD, was used to produce elastomers based on polybutadiene polyols due to known compatibility issues with more polar chain extenders such as 1,4-BDO. Ninety Shore A elastomers based on hydrophobic diol VORAPEL D3201 exhibited tensile properties (tensile strength, elongation, tear strength) comparable to those observed for a typical hydrophilic polyether diol. On the other hand, polybutadiene-based elastomers exhibited lower tensile properties. For example, tensile strength of 23 MPa was observed for VORAPEL D3201 based elastomers compared to a tensile strength of only 15 MPa for the polybutadiene-based elastomer. When the hard segment content was reduced to yield elastomers of approximately 75 Shore A, the performance gap between the new hydrophobic VORAPEL D3201 polyol and the polybutadiene polyol became even larger. The tensile properties of VORAPEL D3201 were nearly double the values observed for the polybutadiene elastomers. The glass transition temperature, T_g , of VORAPEL D3201 based elastomers occurs at -20 °C while polybutadiene-based elastomers exhibit a soft segment transition at -64 °C. Based on the available data, elastomers based on VORAPEL D3201 should provide significant improvement in low-temperature flexibility over commercial polyether polyol VORANOL™ 220-056 ($T_g = -10$ °C).

Table 2. Performance Properties of Cast Elastomers						
Polyol	VORANOL 220-056		VORAPEL D3201		Polybutadiene	
Formulation						
Hard Segment Concentration (%)	48	38	44	40	43	29
Prepolymer % NCO	14.8	8.6	12.3	10	8.1	4.1
Prepolymer viscosity (Pa·s) at 25 °C	7	13	5	7	50	125
Prepolymer used (g)	100	100	100	100	100	100
1,4-BDO (g)	15.05	8.74	12.50	10.27	---	---
2-EHD (g)	---	---	---	---	13.36	6.76
T-12 (drop)	1	1	1	1	1	1
Isocyanate Index	105	105	105	105	105	105
Pot Life (sec)	90	90	90	90	90	90
Elastomer Properties						
Hardness (Shore A)	91	76	89	78	91	74
T _g (°C) by DTMA	-46	-48	-51	-51	-73	-73
Ultimate Tensile Strength (MPa)	0	0	0	0	0	0
Ultimate Tensile Strength (psi)	3485	2945	3328	2190	2226	935
Elongation at Break (%)	485	644	483	534	228	213
Die C Tear Strength (pli)	575	347	472	380	315	175
Ball Rebound (%)	36	27	31	27	60	54

Hydrolytic Stability of Elastomers

The ability of a polyurethane to prevent the ingress of water is a major determinant of stability in a humid environment. In many cases, a direct correlation is observed between mass change and reduction of physical properties of polyurethanes. To assess the overall hydrolytic stability of our new hydrophobic polyols, samples were fully immersed in de-ionized water at 70 °C for 14 days. Under these conditions, an increase in mass of 2–2.5 % is observed for the commercial polyether diol VORANOL™ 220-056 (Figure 1). The hydrophobic nature of VORAPEL D3201 significantly reduces the ingress of water, and only a change in mass of 1% is observed. Polybutadiene polyols are capable of further reducing water absorption to less than 1% change in mass after exposure. Data shown in Figure 2 demonstrate the effect of hydrolytic aging on elastomer hardness. Elastomers comprised of VORAPEL D3201 exhibited nearly complete retention of hardness, while those of a commercial polyether underwent a hardness change of approximately 4 points after the 14 day exposure period. The small increase in hardness is observed for polybutadiene derived elastomers likely the result of additional moisture curing of the urethane during the exposure period.

The effect of hydrolytic aging on the elastomer samples was further evaluated by measuring changes in tensile strength and ultimate elongation after exposure. The role of water as a plasticizer versus degradation of the polymer network via urethane bond hydrolysis was evaluated by allowing aged samples to dry at ambient temperature for 4 days prior to mechanical analysis. As shown in Figure 3, commercial polyether-based elastomers undergo a reduction in tensile strength of nearly 30% after exposure. Due to their hydrophobic nature, elastomers based on VORAPEL D3201 experience only small tensile strength reduction (< 10%). When VORAPEL D3201 elastomers were dried, 110% of the initial tensile strength was recovered, this suggests that water serves primarily as a plasticizer in the soft segment of the elastomer and no significant network degradation occurs during the exposure period. For, elastomers based on polybutadiene, no reduction of tensile properties was observed. Ultimate elongation for both the commercial polyether polyol and VORAPEL D3201 are reduced by approximately 10% after aging, while no change is observed for the polybutadiene-based elastomer (Figure 4).

Figure 1. Effect of Hydrolytic Aging on Mass Increase

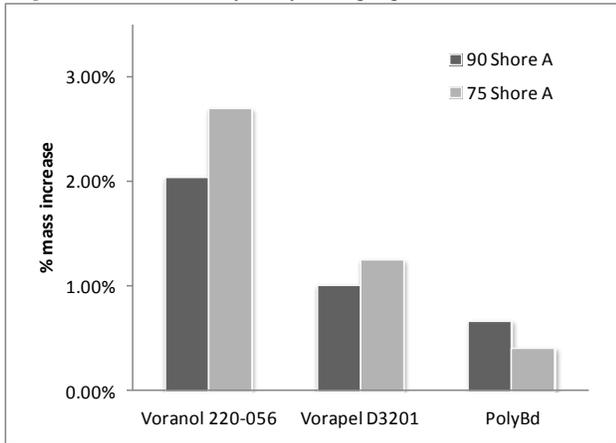


Figure 2. Effect of Hydrolytic Aging on Hardness

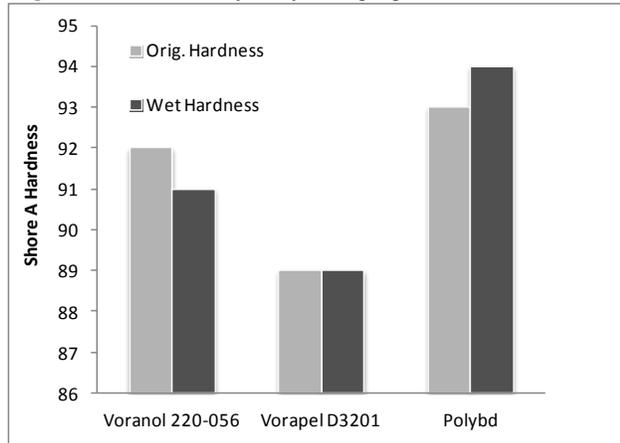


Figure 3. Effect of Hydrolytic Aging on Tensile Strength

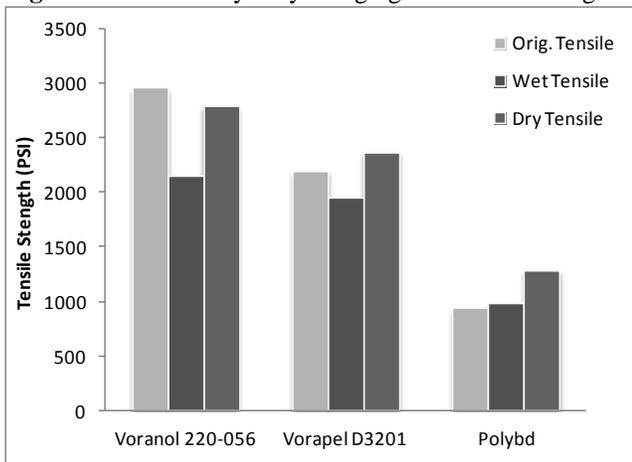


Figure 4. Effect of Hydrolytic Aging on Elongation

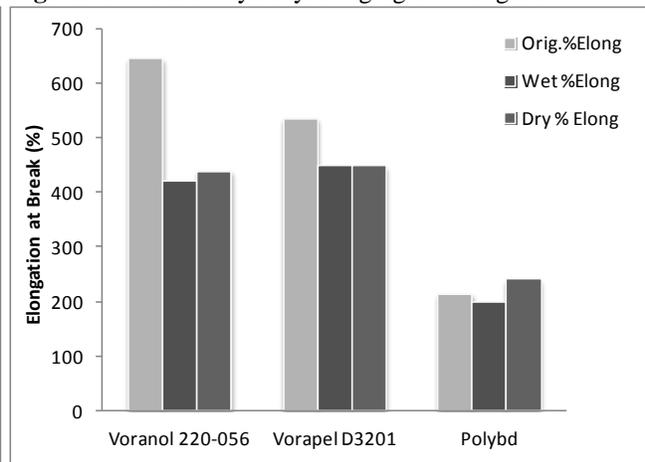


Figure 5. Effect of Chemical Exposure on Tensile Strength

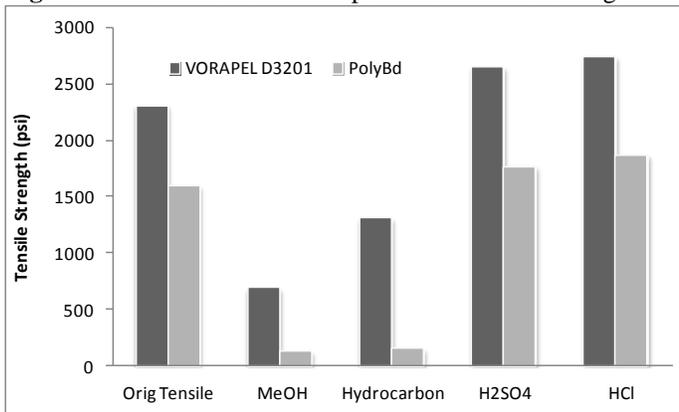


Figure 6. Effect of Chemical Exposure on Elongation

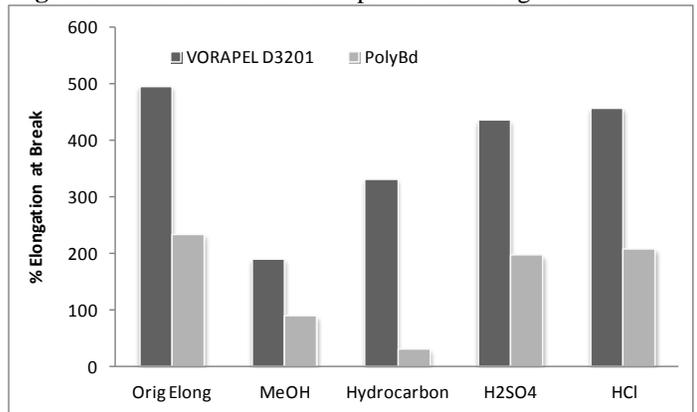
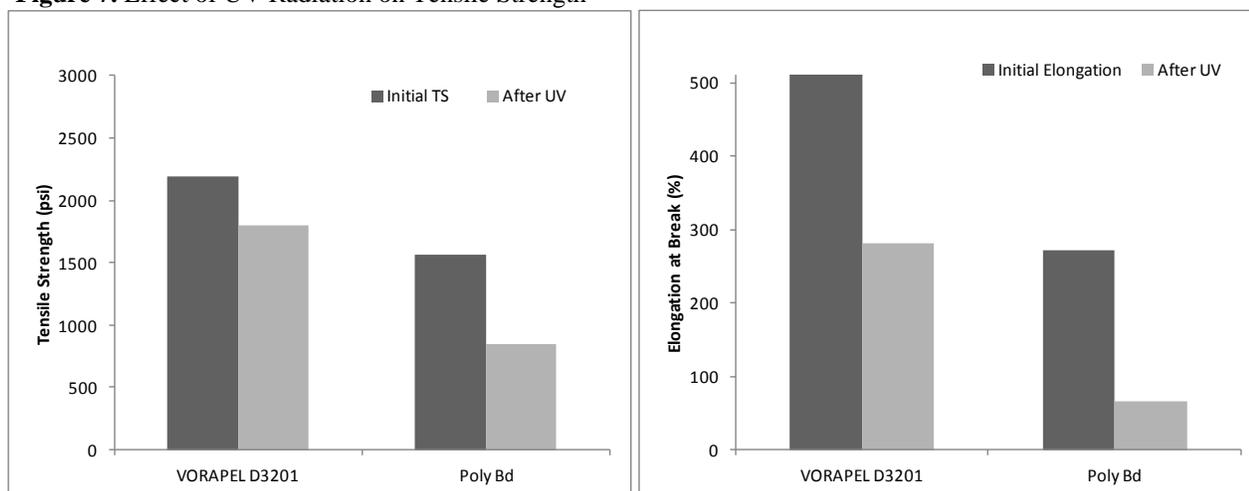


Figure 7. Effect of UV Radiation on Tensile Strength



Chemical Resistance of Urethane Elastomers

The lack of resistance to chemical exposure poses significant limitations on the use of polyurethanes for many applications. Elastomers based on polybutadiene polyols are well regarded for their improved chemical resistance to aqueous acids compared to other polyurethanes. Incorporation of a hydrocarbon backbone generally provides polyurethanes with improved resistance to aqueous media including both acidic and caustic materials. However, the use of a hydrocarbon based polyol renders these materials more susceptible to degradation and swelling in the presence of organics and hydrocarbons. The chemical resistance of VORAPEL D3201 based urethanes was measured against polybutadiene-based elastomers to determine if a hydrophobic polyether based urethane could yield materials which demonstrate resistance to both aqueous media and organic media. Samples were immersed in either methanol, hydrocarbon (Diesel), H₂SO₄ (30%), or HCl (10%) for 7 days prior to measurement of mechanical properties. Figure 5 shows the effect of chemical exposure on tensile strength. Hydrophobic polyol VORAPEL D3201 exhibits excellent retention of tensile properties in the presence aqueous acidic media. More significantly, this elastomer also exhibits far superior resistance to methanol and hydrocarbon in comparison to those derived from polybutadiene. Temporary resistance to hydrocarbons and organics is a critical design feature for applications in which such chemicals are present at only contaminant levels. Elastomers based on VORAPEL

D3201 were also found to maintain high levels of flexibility, nearly twice that of a polybutadiene-based elastomer, even after chemical exposure.

UV Stability of Urethane Elastomers

The degradation of polyurethanes in the presence of ultra violet (UV) radiation is a critical design feature of urethane elastomers designed for outdoor use. As shown in Figure 7, elastomers based on VORAPEL D3201 provide excellent resistance to UV radiation when measure by change in tensile strength. After 300 hours of exposure, elastomers based on polybutadiene polyols loose more than 50% of their tensile strength.

Performance of Cured Polyurethanes

The physical and mechanical properties of polyurethanes derived from a low molecular weight hydrophobic triol, XWT 5001, were also evaluated. In this case the data were compared to a commercially available polyether triol VORANOL™ CP450. As shown in Table 3, the performance properties of XWT 5001 derived urethanes are comparable to those obtained using a standard polyether triol. However, the use of XWT 5001 yields urethanes with significantly longer open times (30% longer) when compared to a typical polyether polyol of similar functionality. As shown in Figure 8, the hydrophobic character of XWT 5001 yields urethanes with greater resistance to the ingress of water vs. VORANOL™ CP 450. The barrier properties of thin films derived from XWT 5001 were also evaluated. As shown in Figure 9, urethanes based on the more hydrophobic polyol exhibited a significant decrease in the transmission of water vapor through the polyurethane film. Urethanes which exhibit such a unique combination of mechanical integrity, extended pot life, and moisture resistance should find many uses in challenging adhesive, coating and composites applications.

CONCLUSIONS

In summary, polyurethane elastomers based on a two new hydrophobic polyether polyols, VORAPEL D3201 and XWT 5001, provide end users with the excellent physical and mechanical properties typical for polyether based polyurethanes, while exhibiting moisture resistance similar to polyurethanes based on polybutadiene polyols. Prepolymers based on the new polyol also have low viscosity that may aid processing. Due to their polyether backbone structure, these polyols yield elastomers with excellent resistance to attack by aqueous and organic media as well as superior resistance to UV induced degradation. Urethane with these advantageous properties should find many uses in challenging applications within the CASE market.

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Table 3. Performance Properties of Cured Urethanes		
Polyol	VORANOL CP 450	XWD 5001
Formulation		
Polyol (g)	46	55
PAPI 27 (g)	54	45
Isocyanate Index	100	100
Urethane Properties		
Hardness (Shore D)	70	74
Tg (°C) by DTMA	80	61
Pot Life at 80 °C (min)	22	28
Ultimate Tensile Strength (psi)	10150	7685
Ultimate Tensile Strength (MPa)	70	53
Elongation at Break (%)	9	6
Modulus (Mpa)	1379	1234

Figure 8. Effect of Hydrolytic Aging on Mass Increase

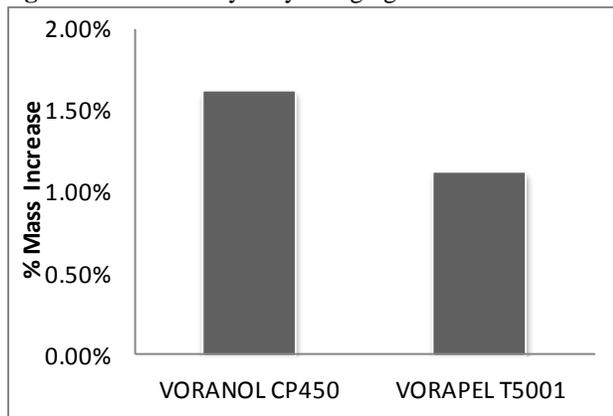
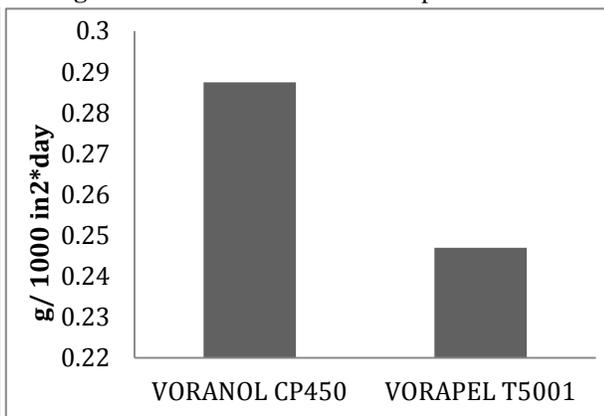


Figure 9. Urethane Film Water Vapor Transmission Rates



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