

EVALUATION OF MOISTURE RESISTANCE PROPERTIES IN POLYURETHANE ELASTOMERS

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ABSTRACT

Moisture resistance is a key property requirement for polyurethanes used in a variety of applications such as adhesives, sealants, electrical potting compounds and general purpose elastomers. A fundamental study was conducted on the relationship of physical properties including moisture resistance to polymer structure of several types of polyurethanes.

Solid polyurethanes were prepared from MDI-based prepolymers derived from polypropylene oxide (PolyPO) polyols, polybutylene oxide (PolyBO) polyols, polytetramethylene glycol (PTMEG) polyols and hydroxyl-terminated polybutadiene (PolyBD) polyols. These polyurethanes were tested for moisture resistance properties such as Moisture Vapor Transmission Rate (MVTR). Retention of physical properties was also measured by evaluation before and after an extended water soak cycle. Susceptibility of these polymers to UV degradation was also examined.

In general, polymers with PolyBD moieties showed the highest level of moisture resistance properties followed by those with PolyBO, PTMEG and PolyPO backbones respectively. Some of these advantages seen with PolyBD were counteracted by the relatively high viscosities of PolyBD-based prepolymers and by their relatively poor resistance to UV degradation.

INTRODUCTION

The structural integrity of polyurethane polymers is influenced in large part by their resistance to moisture incursion. While polyurethanes are known for their dry physical properties, they can be susceptible to the encroachment of moisture and the subsequent loss of strength and adhesion. Polyurethane elastomers because of their flexible nature have a relatively high polyol content and subsequently their properties are significantly impacted by the nature of their polyol moieties. Hydrophobicity is also a property that is substantially influenced by polyol structure. A number of so-called "hydrophobic" polyols have been commercially available for many years, however, a good basis for judging comparative performance and physical properties has been lacking. In this paper, a study was conducted on the relationship of polymer structure to moisture resistance for several polyol classes commonly used in the manufacture of polyurethane adhesives, sealants and castable elastomers.

The author is aware of several studies that have addressed moisture resistance as a function of structure in polyurethanes (1,2). However, it was felt that insufficient comparative moisture resistance data existed on the various commercial products widely used in the polyurethane elastomers industry .

In the interests of direct comparability, it was attempted to keep all other factors save the polyol constant. Process conditions as well as other formulation components were maintained as uniformly as possible. It was expected therefore that the observed differences in moisture resistance would be polyol related. A general scheme of the procedures used follows.

Isocyanate prepolymers were made from four different polyols: polypropylene oxide (PolyPO), polybutylene oxide (PolyBO), polytetramethylene ether glycol (PTMEG) and polybutadiene polyol (PolyBD). MDI was used as the isocyanate in all cases. 1,4 Butanediol was used as a common chain extender. Polypropylene oxide and polybutylene oxide based polyols are available from The Dow Chemical Company under the VORANOL* polyether polyol tradename. The basic chemical structures of these polyols are shown in Figure 1.

These prepolymers were either cured with chain extenders to form elastomer plaques for property retention and UV stability tests or else were moisture cured to form thin films for MVTR tests. Details on specific procedures used to produce and test polymers are given in the Experimental section.

EXPERIMENTAL

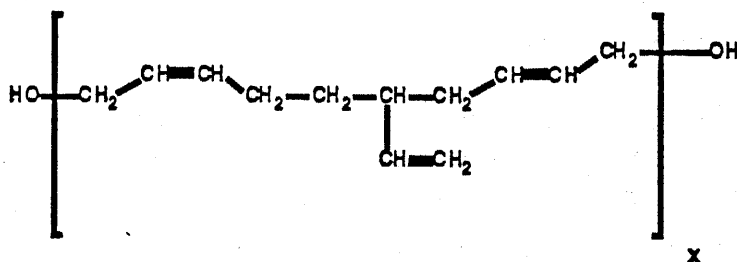
A flow diagram of procedures used to generate data is shown in Figure 2.

Prepolymers were made using each of the 4 polyols. Pure MDI was used as the isocyanate and heated to 80 C in a reaction kettle under dry nitrogen. A listing of chemicals used in this study is given in Table I. Polyol was vacuum dried at 90 C overnight and added in a single step and the prepolymer cooked at 80 C for 4-6 hours. Target % NCO for all cases was 9 %. Actual % NCO's ranged between 8.7 and 9.4 %. Final % NCO was checked using a standard dibutylamine titration analysis

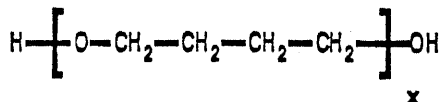
Polyurethane elastomers were made from each prepolymer using the following procedure. Samples of prepolymer were degassed in a vacuum oven at a temperature of 45 C for up to 4 hours depending on viscosity. 1,4 butanediol was

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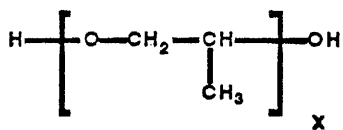
Figure I: Polyol Chemical Structures (repeat units)



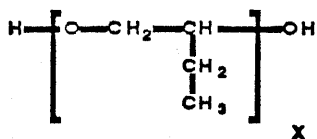
**Polybutadiene polyol
(PolyBD)**



**Poly (tetramethylene ether) glycol
(PTMEG)**



**Poly (propylene oxide) glycol
(PolyPO)**



**Poly (butylene oxide) glycol
(PolyBO)**

Figure 2: Sample Preparation

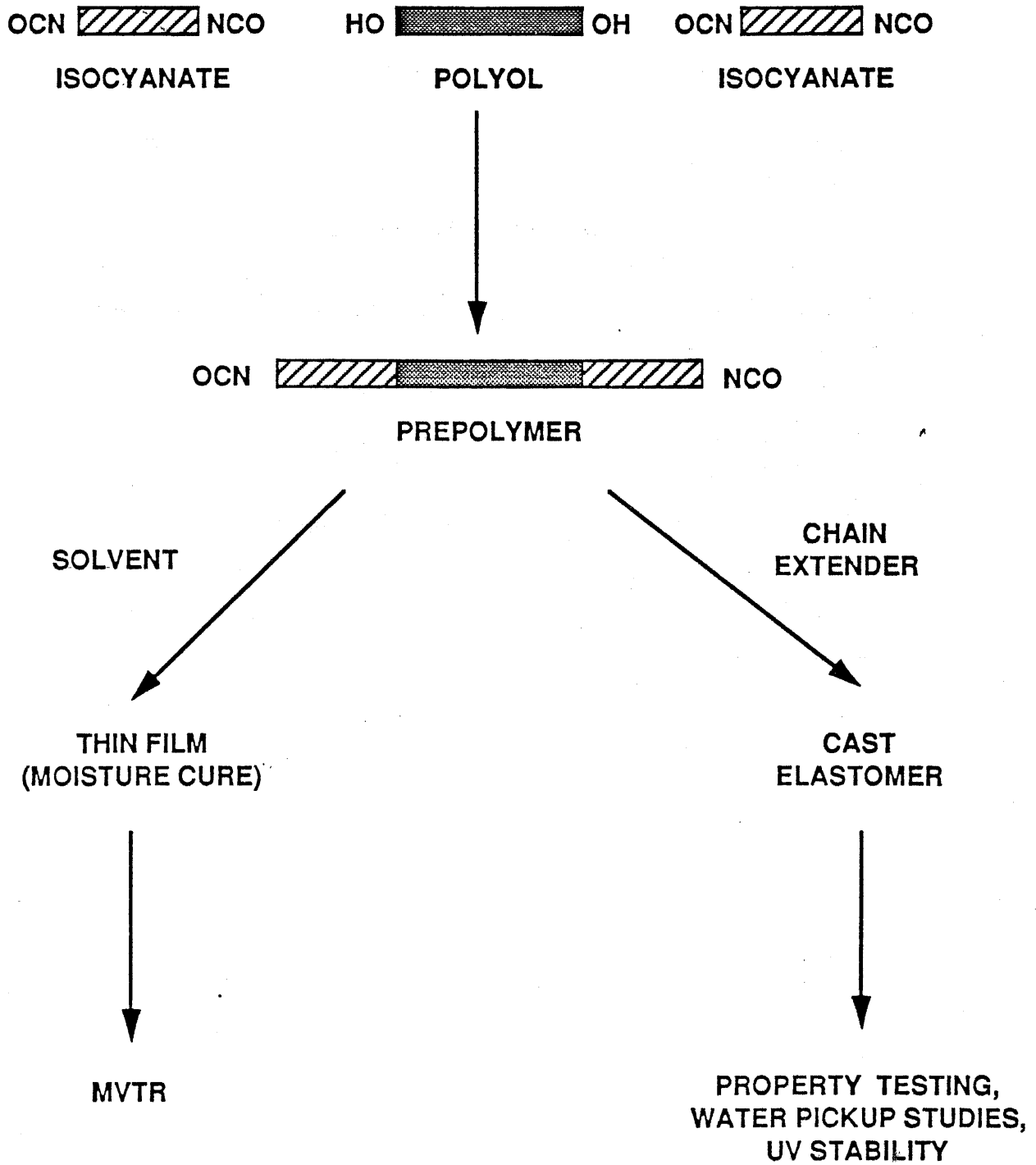


Table I: Chemicals List

• Poly bD R45-HT (polybutadiene polyol)	Atochem Corporation
• TERATHANE 2000 (PTMEG polyol)	E.I. Dupont deNemours Corp.
• XAS 10961.00 Experimental Polyol (polyoxybutylene diol)	The Dow Chemical Company
• VORANOL 220-056N (polyoxypropylene diol)	The Dow Chemical Company
• 1,4 Butanediol	E.I. Dupont de Nemours Corp.
• ISONATE 2125M (MDI isocyanate)	The Dow Chemical Company
• COCURE 44 organomercuric catalyst	Cosan Company
• AROMATIC 100 Petroleum solvent	Exxon Chemical Company

used as the common chain extender as was an organomercuric catalyst . Small handcasts were made with varying catalyst amounts to determine concentration needed for a 5 minute pot life. Chain extender and catalyst, mixed separately from the prepolymer, were then added to the prepolymer and mixed together at low speed (< 200 rpm) using a drill press mixer for roughly 20 seconds. Minimal air entrainment was afforded by careful mixing and by maintaining blades well under liquid surface.

Mixed liquids were poured into a heated 1/8" clamshell plaque mold and maintained under pressure with the clamps for 1 hour until fully cured. Samples were allowed to cool overnight and then postcured for 16 hours at 100 C. Samples were allowed to cool for at least seven days before physical testing was performed.

Small samples (roughly 1 inch squares) were cut out for water weight gain studies. Samples were initially weighed and then immersed in 70 C water for 14 days. Weight gains were measured at 3, 7 and 14 days. Other plaques (8 X 8 X 0.125 inch) were placed in a water bath heated also to 70 C and maintained for 14 days. After 14 days these samples were removed from the water bath, wrapped in aluminum foil and ZIPLOC* freezer bags to maintain moisture saturation. Parts were not tested until 7 days after removal from the water bath to allow room temperature equilibration.

Standard property tests were performed using the following ASTM methods:

Ultimate Tensile Strength	ASTM D-412
Ultimate Elongation	ASTM D-412
Shore A Hardness	ASTM D-2240
Split Tear Strength	ASTM D-1938
Die C Tear Strength	ASTM D-624
Rebound	ASTM D-2632

Thin films of polymer were cast and used for the moisture rate transmission studies using the following procedure. A solution of prepolymer and AROMATIC[^] 100 solvent was made at an 80% solids level. Organotin catalyst was added to the solution at a level of 100 ppm and also mixed in. Films were made using a 25 mil draw-down bar on clean plate glass. After drawing down, glass and film were placed in a vacuum oven at full vacuum for 5-7 minutes to pull out entrained bubbles. Atmospheric pressure was then restored and films were allowed to self level and cure. Films were cured in an oven at 65 C for 12 hours to drive off solvent and then

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[^] Trademark of Exxon Chemical Company

further allowed to moisture cure at ambient temperature for 3 days. Glass plates were then placed in a water bath to strip off the films from the plates, which usually occurred overnight. Films were further allowed to moisture cure for at least 7 days in water before use. Film thicknesses were measured for use in calculations.

MVTR data was obtained using a PERMATHAN V1[^] permeability measurement device. A 5 mil MYLAR^{*} film is normally used as a reference for this equipment. Due to the much higher moisture permeabilities of polyurethanes, thicker films were used and the area available for transport was reduced by application of a non-conducting aluminum foil overlay. A small hole in the overlay markedly decreased the potential transport area. Using these techniques, measurement of the transport rates of various urethane films was possible.

Films were conditioned prior to measurement by placing in a sealed desiccator with an open dish of water for periods of 3-5 days prior to testing. Depending on the desired test temperature, desiccators could be placed in pre-set ovens to allow conditioning to take place at that temperature. In this study only one temperature, 37 C, and 100% relative humidity was used.

Once placed in the test device, pre-conditioned films reached an equilibrium state within 4 hours, roughly corresponding to the manufacturers' instructions on films of comparable thickness. For consistency, a 4 hour measurement period was adapted for all samples. Final permeabilities were obtained by correcting for transport area and film thickness.

UV stability was measured using a UV accelerated weathering tester. Plaque strips of roughly 1" X 4" of each polymer type were adhered to a flat steel panel. Samples were exposed to alternating cycles of 40 C water spray (6 hours) and 60 C UV light (4 hours). Samples were removed and measured for discoloration after 3 days. Strips were measured for discoloration using a ColorQuest100⁺⁺ tester in comparison to samples not subjected to the UV test. The tester uses the Hunter Color scale to measure deviations in light/dark (L) , red/green (a) and yellow/blue (b) from a chosen standard.

[^] Trademark of Mocon Control Company

^{*} Trademark of E.I. Dupont deNemours Company

⁺ Trademark of Hunter Labs

RESULTS AND DISCUSSION

Three main categories of data are presented: standard physical property retention upon moisture exposure for each of main elastomer types, polymer hydrophobicity and stability as measured by water uptake, and moisture barrier measurement by MVTR determination. Additional data on resistance to UV degradation is also presented

Tables II and III present differences in polyol and prepolymer bulk properties. The relatively low viscosities of both PolyPO and PolyBO resulted in prepolymers with fairly low viscosities also. PTMEG, a solid at ambient temperatures, formed a prepolymer with roughly a four fold increase in viscosity over these materials. Prepolymers of PolyBD, a viscous liquid at ambient temperature, were roughly 6 times higher in viscosity.

Water uptake data is presented in Figure 3 . Data is presented in the Appendix. Test conditions are total immersion at 70 C. In all four cases, It can be seen that equilibrium was reached within the 14 day period.

Polymers made with PolyBD polyol had lower water weight gains than those made with other polyols. Water weight gain is perhaps the most simple measurement of hydrophobicity and on the basis of this test, PolyBD polyols appear to be the most hydrophobic followed by PolyBO, PTMEG and PolyPO respectively.

This conclusion is perhaps not surprising if one considers the chemical structures shown in Figure 1. The chemical structure of PolyBD is pure hydrocarbon with the exception of the terminal hydroxyl groups. The structures of the other chemicals have ether linkages which introduce some polarity and hence hydrophilicity into the polyol structure.

If one calculates the percentage of oxygen (-O-) in a polyol repeat unit, the results can be shown as in Table IV.

While the polyol portions of a PolyBD elastomer (soft segment) are essentially hydrophobic, the hard segment or isocyanate-glycol chain extender portions of the polymer are not. These hard segments are relatively polar in comparison to the polyol soft segment and will aggregate together to form hydrophilic islands in the polymer matrix. It seems clear that a significant portion of the water pick up of the PolyBD polymers is due to these hard segments, while the water pick up of the other polymers is the sum of contributions of their hard and soft segments.

Table II: Polyol Bulk Properties

	<u>OH No.</u>	<u>Functionality</u>	<u>Viscosity^o</u>
PolyBD polyol	45.5	2.3-2.5	7200
PTMEG 2000	54.5	2.0	solid
PolyBO 2000	57.3	2.0	500
PolyPO 2000	56.0	2.0	500

^o cps @ 25 C

**Table III: Prepolymer Bulk Properties
and Processing Conditions**

Polyol	PTMEG	PolyBD	PolyPO	PolyBO
Isocyanate	MDI	"	"	"
% NCO	8.7	9.3	9.4	8.7
Viscosity (cps) ^a	15,200	23,400	3,500	3,800
Chain Extender ^b	1,4 BD	"	"	"
Catalyst (%)	0.04	0.01	0.04	0.03
Mold Temp. (C)	70	"	"	"
Demold (hr)	1	"	"	"
Post Cure (hr) ^c	16	"	"	"

^a @ 25 C

^b @ 1.05 Index

^c @ 100 C

Figure 3: Water Uptake Data

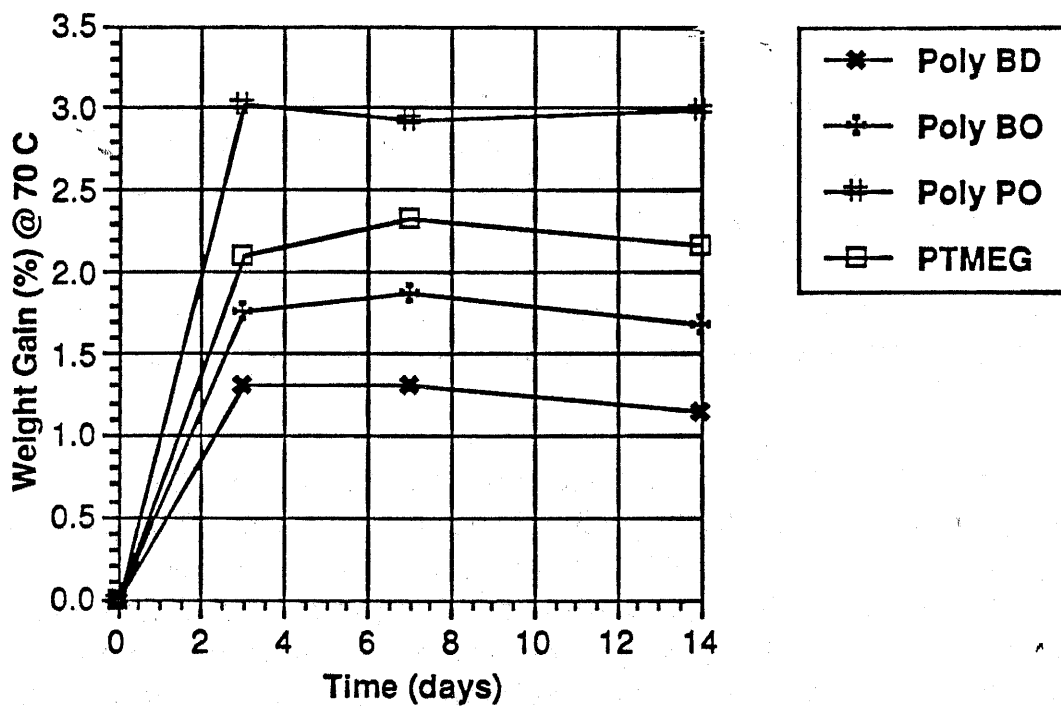


Table IV : Calculation of Oxygen Content In Polyol Repeat Unit

PolyPO	27.8 %
PolyBO	22.2 %
PTMEG	22.2 %
PolyBD	0

Property retention tests were conducted on standard plaques of 1/8 inch thickness. One set of samples was tested after complete cure. The second set was tested after a 14 day water exposure at 70 C. Data from both sets of plaques is shown in Table V.

In general terms, both PolyBD and PolyBO retained roughly the same high proportion of original properties after the extended water soak cycle. PTMEG retained a much smaller portion. PolyPO polymers experienced severe deterioration during water soak. In most instances, PolyPO polymers could not be tested because of their loss of structural integrity.

The conditions chosen for this test were admittedly severe and were only meant to accelerate any moisture-related deterioration rather than to represent any real-world conditions.

A comparison of PolyBD and PolyBO retention data shows that while both materials are quite moisture resistant, the PolyBO polymer has a considerably higher level of physical properties than the PolyBD polymer particularly in the areas of tear strength and elongation. Both of these properties are of importance in the formulation of good elastomers. It would appear that the higher functionality of PolyBD (~ 2.4) imparts a level of cross-linking that can significantly reduce elastomer properties.

MVTR data is displayed in Table VI. Here also the same general data trends are evident: PolyBD possesses the lowest MVTR followed by PolyBO then PTMEG and PolyPO respectively. Thin film vapor transmission may be thought of as a sequence of several processes: dissolution of water vapor on one side of the polymer, transport through the film and de-sorption on the opposite side. Figure 3 shows that water is not very soluble in PolyBD, in comparison to the other polymers. Hence its subsequent low transport rates are of little surprise.

UV Stability data for the four polymers is given in Table VII. As previously mentioned, the Hunter Color scale expresses color change as a sum of three separate variables (L,a,b). In this data set, differences in light intensity (L) were most significant and are listed in the table. Changes noted were all negative, in other words, all samples darkened upon exposure relative to standard coupons of the same polymer which were not tested. In this case, the PolyBD coupons darkened more than the other polymers relative to its standard. Changes in the yellow/blue and red/green components were not significant in comparison to this intensity change. The full data set (L,a,b) is given in the Appendix. It is noted that PolyBD coupons were more discolored than the others at the start and that they continued to discolor during testing and finished the test more discolored than the others. The initial discoloration of PolyBD polymers resulted from the heated post-cure of

Table V: Physical Property Retention Data^{oo}

	<u>POLY BD</u>	<u>POLY BO</u>	<u>PTMEG</u>	<u>POLY PO</u>
<u>HARDNESS (Sh. A)</u>				
Original	72	81	81	79
After water soak	75	79	82	60
<u>TENSILE (psi)</u>				
Original	1535	2075	3306	1850
After water soak	1381	1915	1842	°
% retention	90	92	56	°
<u>ELONGATION (%)</u>				
Original	159	307	325	395
After water soak	136	227	221	°
% retention	85	74	68	°
<u>SPLIT TEAR (pli)</u>				
Original	75	85	79	101
After water soak	52	68	55	°
% retention	69	80	70	°
<u>DIE C TEAR (pli)</u>				
Original	157	400	367	356
After water soak	107	312	272	°
% retention	68	78	74	°
<u>REBOUND (%)</u>				
Original	54	56	55	55
After water soak	53	57	35	32

° Sample could not be tested. °°Water soak conditions are 14 days @ 70 C

Averaged values are stated. Retention data is based on average values

Table VI: MVTR Data

	<u>Thickness (mil)</u>	<u>MVTR (37 C)</u>
PolyBD	10.1	116
PolyBO	10.5	208
PTMEG	10.5	392
PolyPO	10.7	560

MVTR Units are (gm. water-mil / 100in²-day)

Table VII: UV Stability Data

	<u>L(Intensity)^o</u>
PolyBO	-18.1
PolyPO	-17.9
PTMEG	-18.1
PolyBD	-28.1

^o HunterColor Scale; see Appendix for further data

Values reported are deviations from control sample of same polymer

plaques and suggests at least qualitatively that these polymers have lower thermo-oxidative resistance. Differences in both UV and thermal stability are likely attributable to the unsaturation present in the polybutadiene chain and the potential for these linkages to be involved in oxidative or free radical types of degradation reactions.

CONCLUSIONS

In general terms, the following trends in hydrophobicity were observed:

PolyBD > PolyBO > PTMEG >> PolyPO

These findings were confirmed in both water pick-up and MVTR studies. These results are most easily explained by the fact that the polyol structure of PolyBD is virtually all hydrocarbon whereas the other polyols contain ether linkages which are somewhat polar and serve to increase water compatibility. In all cases, however, the polymer hard segment (reaction product of MDI and the chain extender) would behave in a relatively hydrophilic manner and would promote some water solubility. As hard segment content was increased in a polymer, the observed differences in water solubility between these polymers would be expected to narrow. This observation would argue that the hydrophobic properties of PolyBD are best maximized in making very soft and extensible polymers, ie, ones with minimal hard segment content.

Both PolyBD- and PolyBO-based polymers showed roughly the same level of property retention after water soak. PTMEG and PolyPO polymers retained considerably lower levels. However, the absolute level of properties seen with PolyBD polymers was much lower than with those of other polymers, particularly in the areas of elongation and tear strengths. It is likely that the higher functionality of PolyBD (~ 2.4 versus 2.0 for the other polyols) develops additional crosslinking that is responsible for this reduction in elastomeric properties.

As has been noted already, the stability of PolyBD polymers was observed to be poorer than the other polymers from a thermo-oxidative and a UV resistance standpoint. This effect is best attributed to the presence of unsaturation groups in the PolyBD backbone being more susceptible to attack than the ether backbones of the other polymers.

In summary, it was determined that PolyBD based polymers show the highest level of hydrophobicity among the group of polymers tested. PolyBO, PTMEG and PolyPO

ranked behind in this order. PolyBD and PolyBO showed roughly the same level of physical property retention after an extended water soak, but the more crosslinked PolyBD polymer had a lower absolute level of elastomeric properties than the other polymers. The unsaturation groups in PolyBD were found to be more susceptible to thermal and UV degradation than the ether groups in the other polymers. This result may have implications for the use of PolyBD polymers in exterior applications which involve a significant heat history. In terms of processing variables, the viscosities of PolyPO and PolyBO polyols and prepolymers were significantly lower than PTMEG and PolyBD polyols and prepolymers.

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Appendix
Table VIII: UV Stability Data

Hunter Scale

	<u>L</u>	<u>a</u>	<u>b</u>
PolyBO	-18.1	-2.2	28.4
PolyPO	-17.9	3.7	30.8
PTMEG	-18.1	1.7	30.3
PolyBD	-28.1	10.6	28.4

Values reported are deviations from control sample of same polymer

L= light/dark intensity

a= red/green intensity

b= yellow/blue intensity

Appendix Moisture Pickup Study Data

	A	B	C	D	E	F	G
1		POLY BB(1)	POLY BB (2)	AVG.	POLY BB(1)	POLY BB(2)	AVG.
2	INITIAL	1.9751	2.029		2.0324	2.3148	
3	3 DAYS	2.0802	2.0542		2.0845	2.3303	
4	%WT GAIN	1.27%	1.34%	1.31%	1.98%	1.53%	1.76%
5	7 DAYS	1.9986	2.0578		2.6937	2.3479	
6	% WT. GAIN	1.19%	1.42%	1.30%	2.33%	1.43%	1.88%
7	14 DAYS	1.9969	2.0327		2.6822	2.3487	
8	% WT. GAIN	1.18%	1.17%	1.14%	1.89%	1.46%	1.68%
9							
10							
11		POLY PB(1)	POLY PB(2)	AVG.	PTMB(1)	PTMB(2)	AVG.
12	INITIAL	1.9995	2.1014		1.9347	1.742	
13	3 DAYS	2.0585	2.2491		1.9746	1.7792	
14	%WT GAIN	2.95%	3.18%	3.03%	2.06%	2.14%	2.10%
15	7 DAYS	2.0682	2.243		1.9819	1.7803	
16	% WT. GAIN	3.04%	2.92%	2.93%	2.44%	2.20%	2.32%
17	14 DAYS	2.0597	2.248		1.9773	1.7791	
18	% WT. GAIN	3.01%	2.96%	2.99%	2.20%	2.13%	2.17%