# Formulation/Property Relationships in Radiation-Cured Poly(urethane methacrylate) Pressure-Sensitive Adhesives. I. Incorporation of Hydrophilic Polyols

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**ABSTRACT:** Electron beam-curable urethane methacrylate oligomers were prepared which, when cured, produce pressure-sensitive adhesives. The effect of replacing hydrophobic blocks with more hydrophilic polyols in the prepolymer, in order to increase the moisture vapor transmission rates (MVTRs), was investigated. Subsequent effects on the resulting adhesive properties were also monitored. The MVTRs of the adhesives were found to increase upon incorporation of poly(ethylene glycol) but with a detrimental effect on the adhesive properties. The nature of the change in properties was related to the distribution of ethylene oxide units in the prepolymer. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2313–2318, 1999

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# INTRODUCTION

The field of radiation-curable pressure-sensitive adhesives (PSAs) has grown considerably in recent years with environmental factors demanding reduced solvent emissions and energy requirements.<sup>1-3</sup> Previous work on electron beam (eb)curable PSAs suitable for medical applications has involved the preparation of poly(urethane methacrylate)s and the properties of the crosslinked adhesives.<sup>4</sup> These oligomeric polyurethanes were prepared from aliphatic diisocyanates, ethanediol, and difunctional polyglycols. The isocyanate functional oligomers were then end-capped with hydroxyethyl (meth)acrylate and a tackifier to produce viscous liquids which formed PSAs upon eb irradiation. These materials are in the class "urethane (meth)acrylates" and offer the possibility of wide performance modification as a result of the flexibility of formulation. The aim of this article was to investigate the substitution of hydrophobic poly(propylene glycol) blocks with more hydrophilic polyols in the adhesive prepolymer in order to improve the moisture vapor transmission rates (MVTRs). The subsequent effects on the adhesive properties of the resultant cured adhesives were determined.

## **EXPERIMENTAL**

#### **Oligomer Synthesis**

The same general procedure was used in the synthesis of all urethane methacrylate oligomers. Water contents and hydroxyl values were obtained for all hydroxy functional reactants and were used in the calculation of reaction quantities (Tables I–IV). All starting materials were used as received: PPG 2025 [ $\alpha,\omega$ -dihydroxy-terminated poly(propylene glycol) of number average molecular weight 2025 (BP Chemicals)], PEG 1500 and

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Sample	Hydrophobic Polyglycol (mol, g)	Hydrophilic Polyglycol (mol, g)	Diisocyanate (mol, g)	Chain Extender (mol, g)	Acrylic Terminator (mol, g)	Chain Terminator (mol, g)
S1	PPG 2025 (1.00, 69.05)	_	DW (2.07, 18.27)	Ethanediol (0.40, 0.84)	2-HEMA (0.30, 1.32)	Abitol (0.90, 10.53)

 Table I
 Standard Formulation for Radiation-curable Oligomers

600 [ $\alpha, \omega$ -dihydroxy-terminated poly(ethylene glycol) of number average molecular weight 1500 and 600, respectively (BP Chemicals)], Breox 75W270 [ $\alpha, \omega$ -dihydroxy-terminated ethylene oxide/propylene oxide random copolymer, 75%EO/ 25%PO of number average molecular weight 2600 (BP Chemicals)], Synperonic PE/L64 and L35 [dihydroxy-terminated PEG-PPG-PEG triblock copolymer containing 40 and 50% PEG, respectively (ICI)], ethanediol (Aldrich Chemical Co.), Desmodur W [4,4'-dicyclohexylmethane diisocyanate (Bayer AG)], Abitol [hydroabietyl alcohol (Hercules Ltd.)], 2-hydroxyethyl methacrylate [2-HEMA (Aldrich Chemical Co.)], Metatin 812ES [dioctyl tin dilaurate (Acima Chemicals)], and *p*-methoxy phenol [MEHQ (Aldrich Chemical Co.)].

The synthesis of the urethane methacrylate was a two-stage process (Fig. 1). In stage 1, the polyglycol, ethanediol, and diisocyanate were mixed at 90°C until homogeneous in a 700-mL flange flask fitted with an air-driven stirrer, under a blanket of nitrogen. The Metatin 812ES catalyst was added and the reaction continued for 1 h to give an isocyanate-terminated oligomer. For the second stage of the synthesis, the reaction was cooled to 60°C prior to the addition of 2-HEMA (in which 200 ppm

Table II	Formulation	Details for	PEG-containing	Oligomers
I able II	rormulation	Details for	FEG-containing	Ungomers

Sample	Hydrophobic Polyglycol (mol, g)	Hydrophilic Polyglycol (mol, g)	Diisocyanate (mol, g)	Chain Extender (mol, g)	Acrylic Terminator (mol, g)	Chain Terminator (mol, g)
HP1	PPG 2025	PEG 600	DW	Ethanediol	2-HEMA	Abitol
	(0.85, 253.06)	(0.15, 13.60)	(4.13, 78.68)	(0.40, 3.61)	(0.30, 5.67)	(0.90, 45.39)
HP2	PPG 2025	PEG 600	DW	Ethanediol	2-HEMA	Abitol
	(0.77, 239.16)	(0.23, 21.75)	(4.13, 82.04)	(0.40, 3.76)	(0.30, 5.92)	(0.90, 47.35)
HP3	PPG 2025	PEG 600	DW	Ethanediol	2-HEMA	Abitol
	(0.71, 227.95)	(0.29, 28.35)	(4.13, 84.76)	(0.40, 3.89)	(0.30, 6.12)	(0.90, 48.95)
HP4	PPG 2025	PEG 600	DW	Ethanediol	2-HEMA	Abitol
	(0.68, 222.02)	(0.32, 31.81)	(4.13, 86.20)	(0.40, 3.95)	(0.30, 6.22)	(0.90, 49.78)
HP5	PPG 2025	PEG 600	DW	Ethanediol	2-HEMA	Abitol
	(0.50, 182.83)	(0.50, 55.67)	(4.13, 94.36)	(0.40, 4.43)	(0.30, 6.97)	(0.90, 55.75)
HP6	PPG 2025	PEG 600	DW	Ethanediol	2-HEMA	Abitol
	(0.40, 156.21)	(0.60, 71.35)	(4.12, 100.72)	(0.40, 4.73)	(0.30, 7.44)	(0.90, 59.54)
HP7	PPG 2025	PEG 1500	DW	Ethanediol	2-HEMA	Abitol
	(0.90, 253.24)	(0.10, 20.67)	(4.14, 74.44)	(0.40, 3.41)	(0.30, 5.36)	(0.90, 42.90)
HP8	PPG 2025	PEG 1500	DW	Ethanediol	2-HEMA	Abitiol
	(0.80, 229.36)	(0.20, 42.12)	(4.14, 75.88)	(0.40, 3.47)	(0.30, 5.46)	(0.90, 43.71)
HP9	PPG 2025	PEG 1500	DW	Ethanediol	2-HEMA	Abitol
	(0.70, 204.56)	(0.30, 64.40)	(4.14, 77.36)	(0.40, 3.54)	(0.30, 5.57)	(0.90, 44.55)

Sample	Hydrophobic Polyglycol (mol, g)	Hydrophilic Polyglycol (mol, g)	Diisocyanate (mol, g)	Chain Extender (mol, g)	Acrylic Terminator (mol, g)	Chain Terminator (mol, g)
BP1	PPG 2025 —	Synperonic PE/L62 (1.00, 178.62)	DW (4.46, 42.53)	Ethanediol (0.40, 1.75)	2-HEMA (0.30, 2.84)	Abitol (0.90, 24.25)
BP2	PPG 2025 —	Synperonic PE/L64 (1.00, 186.95)	DW (5.16, 39.75)	Ethanediol (0.40, 1.41)	2-HEMA (0.30, 2.29)	Abitol (0.90, 19.58)
BP3	PPG 2025 —	Synperonic PE/L35 (1.00, 168.72)	DW (4.44, 48.35)	Ethanediol (0.40, 2.00)	2-HEMA (0.30, 3.24)	Abitol (0.90, 27.68)
BP4	PPG 2025 (0.60, 103.30)	Synperonic PE/L35 (0.40, 67.75)	DW (4.20, 45.90)	Ethanediol (0.40, 2.01)	2-HEMA (0.30, 3.26)	Abitol (0.90, 27.79)
BP5	PPG 2025 (0.60, 88.59)	Synperonic PE/L64 (0.40, 91.02)	DW (4.49, 42.05)	Ethanediol (0.40, 1.72)	2-HEMA (0.30, 2.79)	Abitol (0.90, 23.83)

Table III Formulation Details for Block PEG-containing Oligomers

MEHQ had been dissolved) and Abitol and reacted for 1 h. The formulations investigated in this work are shown in Tables I–IV. Note that all the weights take into account both the water and isocyanate contents of the respective reagents.

# **Oligomer Curing**

All the oligomers were cured using an eb generator (Pilot ESI S.O. 7834). The oligomers were first heated to approximately 70°C to enable the films

Table IV	Formulation	<b>Details for</b>	Random	<b>PEG-containing</b>	Oligomers
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Sample	Hydrophobic Polyglycol (mol, g)	Hydrophilic Polyglycol (mol, g)	Diisocyanate (g)	Chain Extender (mol, g)	Acrylic Terminator (mol, g)	Chain Terminator (mol, g)
RBI	PPG 2025 (0.50, 29.76)	Breox 75W270 (0.50, 41.37)	DW (16.64)	Ethanediol (0.40, 0.76)	2-HEMA (0.30, 1.20)	Abitol (0.90, 10.26)
RP2	PPG 2025 (0.60, 36.56)	Breox 75W270 (0.40, 33.88)	DW (17.04)	Ethanediol (0.40, 0.78)	2-HEMA (0.30, 1.23)	Abitol (0.90, 10.50)
RP3	PPG 2025 (0.70, 43.69)	Breox 75W270 (0.30, 26.03)	DW (17.47)	Ethanediol (0.40, 0.80)	2-HEMA (0.30, 1.26)	Abitol (0.90, 10.76)
RP4	PPG 2025 (0.80, 51.16)	Breox 75W270 (0.20, 17.78)	DW (17.92)	Ethanediol (0.40, 0.82)	2-HEMA (0.30, 1.29)	Abitol (0.90, 11.02)
RP5	PPG 2025 (0.90, 59.03)	Breox 75W270 (0.10, 9.12)	DW (18.38)	Ethanediol (0.40, 0.84)	2-HEMA (0.30, 1.32)	Abitol (0.90, 11.31)



#### Vinyl / Hydroabietyl terminated radiation curable product

Polyglycol	Structure
Polypropylene glycol (PPG 2025)	HO(CH <sub>2</sub> CHO) <sub>h</sub> H CH <sub>3</sub>
Polyethylene glycol (PEG 600 and 1500)	HO(CH <sub>2</sub> CH <sub>2</sub> O) <sub>n</sub> H
Synperonic PE/L64 and PE/L35 block copolymer	HO[(CH <sub>2</sub> CH <sub>2</sub> O) <sub>n</sub> (CH <sub>2</sub> CHO) <sub>n</sub> (CH <sub>2</sub> CH <sub>2</sub> O) <sub>n</sub> ]H CH <sub>3</sub>
Breox 75W270 random copolymer	HO[(CH <sub>2</sub> CH <sub>2</sub> O) <sub>n</sub> (CH <sub>2</sub> CHO) <sub>n</sub> ]H CH <sub>3</sub>

Figure 1 Reaction schme of oligomer synthesis.

to be spread at a thickness of 35  $(\pm 5)$  g<sup>-2</sup> onto either 36  $\mu$ m Melinex (polyester), Estane 5714 (polyurethane), or HPU 25 (hydrophilic polyure-

than eelastomer with water content of 25% at full hydration) film. Samples were then passed under an eb generator in a nitrogen atmosphere (<200

Table V	Physical	Properties	of PEG-containing	Adhesives
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Sample	Mean Peel Strength (N/m)	Shear Time to Fail (min)	$\begin{array}{l} MVTR \ Upright \\ (g \ m^{-2} \ 24 \ h^{-1}) \end{array}$	$\begin{array}{c} MVTR\\ Inverted\\ (g\ m^{-2}\ 24\ h^{-1}) \end{array}$	Equilibrium Water Content (%)
HP1	878 (Bloom)	114 (AF/Bloom)	1205	1411	1.7
HP2	959 (Bloom)	206 (AF/Bloom)	1152	1404	2.0
HP3	929 (Bloom)	127 (Bloom)	1127	1264	_
HP4	972 (AF)	204 (AF/Bloom)	1122	1403	2.5
HP5	662 (Bloom)	82 (Bloom)	1227	1560	_
HP6	592 (Bloom)	56 (Bloom)	1200	1860	_
HP7	673 (Bloom)	82 (Bloom)	1319	1519	_
HP8	444 (Bloom)	158 (Bloom)	1283	2011	_
HP9	486 (Bloom)	385 (Bloom)	1426	4357	—

Sample	Mean Peel Strength (N/m)	Shear Time to Fail (min)	$\begin{array}{l} MVTR \ Upright \\ (g \ m^{-2} \ 24 \ h^{-1}) \end{array}$	$\begin{array}{c} MVTR\\ Inverted \; (g\\ m^{-2} \; 24 \; h^{-1}) \end{array}$	Equilibrium Water Content (%)
S1	988 (AF)	71 (Bloom)	1181	1132	

Table VI Physical Properties of Adhesive Derived from Standard Formulation

ppm oxygen) and cured at a total dose of 3 MRad with an accelerating voltage of 175 keV and a web speed of 20 ft min<sup>-1</sup>.

#### **Physical Characterization**

MVTRs were determined on adhesive films cured on either HPU 25 or Estane film by a cup method (upright and inverted) based on ASTM E96-92 at 37°C and 10% relative humidity. Upright values indicated the transmission rate of the adhesive to water vapor, while inverted ones gave the transmission rate in contact with the liquid. Water contents were measured at full hydration on samples that had been immersed in distilled water for at least 24 h. The water content was then calculated using the following equation:

Water content =

$$\frac{\text{hydrated weight} - \text{dry weight}}{\text{hydrated weight}} \times 100$$

Peel strength was determined using adhesive films cured on Melinex from a standard stainlesssteel surface at a peel angle of 180° and a machine crosshead speed of 300 mm min<sup>-1</sup>. Shear strength was determined using glass plates at 20°C and a  $15 \times 15 \text{ mm}^2$  lap joint with a 1-kg load. Peeling results were also assessed for the mode of failure: adhesive failure (AF) being when the adhesive peeled cleanly from the substrate leaving no residue, cohesive failure (CF) arising when the failure occurred within the adhesive, and bloom indicating a nonadhesive residue on the steel plate after peeling.

## **RESULTS AND DISCUSSION**

Increasing the PEG 600 content, at the expense of PPG 2025, up to 0.32 mol (HP1–HP4 in Table V) did not significantly affect the peel strengths of the adhesives with respect to the standard formu-

lation S1 (Table VI). The upright MVTRs of these adhesives did not change even though the EO content was increased. However, the inverted MVTR figures for the aforementioned PEG containing PSAs showed an increase relative to the standard S1. It was notable that the inverted MVTR for S1 was lower than the upright one. This result, although unexpected, has been shown to be reproducible.

At higher PEG 600 concentrations (HP5 and HP6), the peel strengths decrease, indicating a hardening of the adhesives. A slight increase was seen in the MVTR data of the adhesives with PEG 600 contents greater than 0.32 mol, particularly for the inverted test. Equilibrium water contents increased with EO concentration as expected. Due to the crosslinked nature of these adhesives, the shear failure times were not true indications of shear strengths and were therefore not discussed for any of the formulations in this article.

The changes in the physical properties of the PEG 1500-containing adhesives were more noticeable compared to S1, even at low concentration. As the PEG 1500 content was increased from 0.1 to 0.3 mol (HP7–HP9), the peel strengths tended to decrease, indicating an increase in the hardness of the adhesive. The MVTR data showed that the transmission rates increased significantly as the concentration of PEG 1500 was increased. Therefore, although an MVTR of greater

Table VIIPhysical Properties of Block PEG-<br/>containing Adhesives

Sample	Mean Peel Strength (N/m)	Shear Time to Fail (min)
BP1 <sup>a</sup> BP2 <sup>a</sup> BP3 BP4 BP5	 715 (Bloom) 894 (Bloom) 642 (AF/Bloom)	43 (CF/Bloom) 60 (CF/Bloom) 75 (Bloom)

<sup>a</sup> Oligomers too viscous to spread.

Sample	Mean Peel Strength (N/m)	Shear Time to Fail (min)	$\begin{array}{l} \text{MVTR Upright} \\ (\text{g m}^{-2} \ 24 \ h^{-1}) \end{array}$	$\begin{array}{c} MVTR\\ Inverted \ (g\\ m^{-2} \ 24 \ h^{-1}) \end{array}$	Equilibrium Water Content (%)
RP1	412 (CF)	_	2008	3064	66.2
RP2		_	1915	2902	57.1
RP3	_	_	1720	2672	48.6
RP4	595 (AF)	194 (Bloom)	1613	2028	37.8
RP5	451 (AF)	164 (Bloom)	1345	1323	9.1

Table VIII Physical Properties of Random PEG-containing Adhesives

than 4000 g m<sup>-2</sup> 24 h<sup>-1</sup>was achieved with HP9, a favorable result compared to typical acrylic PSAs used in medical applications,<sup>5,6</sup> the adhesive properties with respect to peel strength had been compromised.

Another method of introducing hydrophilic blocks into PSA formulations was by the incorporation of PEG–PPG–PEG triblock copolymers (Table VII). The partial replacement of PPG 2025 in the standard formulation (S1) with 0.4 mol of the PEG-containing copolymer (BP4 using Synperonic PE/L35 with 50% PEG and BP5 using Synperonic PE/L64 with 40% PEG) resulted in a reduction in peel strength and hardening of the adhesive. The total replacement of PPG 2025 with Synperonic PE/L35 (BP3) caused further hardening of the adhesive and subsequent reduction in the peel strength.

As a comparison to the adhesives containing blocks of EO previously discussed, a series of PSAs were formed utilizing the Breox 75W270 random PPG/PEG copolymer. From the peel strength data in Table VIII, it can be seen that as the concentration of Breox was increased the adhesives become softer with increased tack, which initially resulted in an increase in peel strength (RP5 and RP4) until the mode of failure on peeling changed to cohesive.

MVTRs of Breox-containing PSAs showed a significant improvement over the standard formulation, with an increase in the transmission rate being seen with increasing Breox content. The equilibrium water content showed the expected increase as the EO concentration was increased, particularly from 0.1 to 0.2 mol of Breox (RP5 to RP4).

## CONCLUSIONS

This article has shown that the substitution of PPG with more hydrophilic polyols produced radiation-curable PSAs with increased MVTRs. The MVTR was seen to be related to the distribution of the hydrophilic EO units, with larger, higher molecular weight blocks having a greater influence than smaller blocks. However, the incorporation of PEG blocks tended to harden the adhesives (HP and BP samples), resulting in lower peel strengths. The inclusion of PEG into the adhesive formulations in the form of random copolymers (RP samples) also increased the MVTRs; however, in this case, a softening of the adhesives was observed with a subsequent increase in peel strengths within this series.

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