Adhesive Behavior of Polyurethane-Based Materials

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ABSTRACT: The role of prepolymer on the interfacial strength of polyurethane-based assemblies is examined for two hydroxyl-terminated (telechelic) polybutadienes, R45M and R45HT. Although it is known that both prepolymers lead to very different adhesive behavior, the reasons that explain this are not understood. In this study, we show that two main effects have to be considered: the length of the free chains, which can diffuse across the interface during the formation of the joint and the relative reactivity of the various hydroxyl groups of the chains and chain extenders with the isocyanate. The R45M chains are more efficient connectors than the R45HT chains. Migration of chain extenders and isocyanate over large distances creates a thick interphase where physical crosslinks appear. This interphase is thicker for R45M-based polyurethane showing the role of the chain reactivity. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 665–671, 2000

Key words: adhesion; telechelic polybutadiene; polyurethane; interface/phase; migration

INTRODUCTION

Polymer interfaces are of special interest because they directly influence the properties of multicomponent materials. Adhesive performance of these materials is strongly related to different mechanisms such as adsorption phenomena, chemical bonding, and interdiffusion of polymer chains through the interface. Moreover, macroscopic interphases can be formed due to migration of crosslinking agents or other additives.

Here we are interested in polyurethane (PU) interfaces based on hydroxyterminated polybutadiene (HTPB). HTPB is widely used as solid propellant binder to get improved mechanical properties.[1] A liner, often of the same nature as the binder, is deposited on the internal insulation to ensure a high level of adhesion between the propellant and the insulation, which in turn guarantees optimum burning of the propellant.[2] The role of this thin layer has often been neglected, although many faulty behaviors have been attributed to the bad adhesion of the propellant on the case.

PUs based on HTPB have been studied extensively as they can be efficiently used as adhesives.[3,4] In a well known review, Ajaz[5] defines the following criteria for HTPB to be a useful binder for highly filled materials: molecular weight in the range of 2500–3000 g/mol; narrow molecular weight distribution; low 1,2-vinyl content and hence low viscosity; low glass transition temperature; and functionality very near to 2.0.

It has been shown that the adhesive as well as the mechanical performance[6] is strongly dependent on the prepolymer used.

The interfaces studied here are representative of the propellant/liner interface. To better understand the interfacial mechanisms between the highly filled PU and the adhesive-based PU, we

Table I Main Characteristics of the Two HTPB

	R45M			R45HT	
M_n (g/mol)	3300			3000	
M_p (g/mol)	5400			5100	
F_i (OH/kg)	M_i (g/mol)	% Weight	F_i (OH/kg)	M_i (g/mol)	% Weight
< 2	< 800	0.9	< 2	< 700	2.5
$2 \leq F_i \leq 3$	800–8000	81.3	$2 \leq F_i \leq 3$	700–5000	56.5
$3 < F_i \leq 4.5$	8000–16,000	17.8	$3 < F_i \leq 6.5$	5000–12,000	41
G (%)	14.3			14.4	
H (%)	49.0			45.8	
V (%)	36.7			39.8	

have compared the adhesive behavior of liners in which two HTPB (R45M and R45HT), known in practice for their distinct behavior, are used.

EXPERIMENTAL

Both materials, liner and model propellant, are based on HTPB chains and the same isocyanate and may be reinforced by some chain extenders or short-chain diols (SD) together with a variety of fillers. The formation of filler-free simple networks containing the two HTPB (R45M and R45HT) were first studied. They are both obtained by free radical polymerization. Their main characteristics are given in Table I. It was shown that the molecular weight as well as the functionality distribution can vary not only from manufacturer to manufacturer but also from batch to batch.[7] The average functionality of the prepolymers used is about 2.5. The formation of the three-dimensional network with a diisocyanate is possible mostly because of a higher (>2) mean functionality of the HTPB chains.[8] The R45HT prepolymer contains a higher amount of chains with higher functionality compared to R45M (Table I). This feature is in agreement with Inagaki et al.[9] High functionality is generally accompanied by high molecular weight fractions.[10] R45HT contains more highly functionalized but smaller chains than R45M.

Three main hydroxyl groups can be defined, as seen in Figure 1. It was shown that the concentrations in different hydroxyl functions are almost identical for both polymers, especially that of geraniol (G) type,[11–14] which contribute to the formation of crosslinking points. The distribution

of the hydroxyl groups (Table I) are in agreement with the results published by Pham[15] within the error bars, because of batch variations.

All blends used in this study are prepared by the one-shot method.[16] During the polymerization/curing reactions, the hydroxyl functional groups of the SDs compete with the ones from the long polymer chains to form the urethane bond with the isocyanate function. The formation of the network is then even more complex when one considers unequal reactivity of the different hydroxyl functions [hexene (H), vinyl (V), and G] of the macromolecular chains.[17]

The control of the density of crosslinking of the unfilled networks is performed by swelling measurements in toluene. Sol fraction and swelling ratio are determined. The molecular weight between crosslinks M_c is calculated from the Flory–Rhener relation

$$M_c = \frac{V_1 \rho \left(V_2^{1/3} - \dfrac{V_2}{2} \right)}{-\left[\ln(1 - V_2) + V_2 + \chi V_2^2 \right]}$$

where V_1 is the molar volume of the solvent (106.3 cm³/mol), χ is the polymer/solvent interaction parameter (0.355 for HTPB/toluene),[18,13] ρ is the density of the polymer (0.9g/cm³), and V_2 the vol-
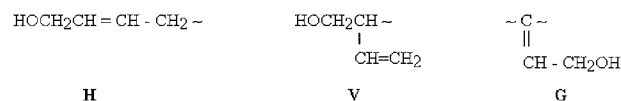

Figure 1 Various hydroxyl groups on HTPB chains [hexene (H), vinyl (V), and geraniol (G)].

Table II Dispersive γ_L^D and Nondispersive γ_L^{ND} Components of the Surface Energy of the Liquids; $\gamma_{L/water}$ Measured Interfacial Energy with Water

Liquid	Viscosity (cSt)	γ_L^D (mJ/m^2)	γ_L^{ND} (mJ/m^2)	$\gamma_{L/water}$ (mJ/m^2)
Ethanol	1.5	17	5.8	/
PDMS-S	45–85	17.6	2.8	12
PDMS-T	50	17.6	2.6	34

ume fraction of the polymer in the swollen specimen at equilibrium.

The studied joints are constituted on the one hand by a highly filled material and on the other hand by the adhesive material. The highly filled material representative of the propellant is mainly based on HTPB polymer, diisocyanate, and 80% of nonreinforcing, nonactive fillers (aluminum and potassium chloride). This material is slightly undercured; the equivalent ratio [NCO]/[OH] is equal to 0.8. This material will be hereafter referred as PU$_P$. Only R45HT polymer is used. The adhesive material representative of the liner is also based on HTPB prepolymer, the same diisocyanate, but chain extenders are added together with carbon black (20%). The equivalent ratio [NCO]/[OH] is slightly higher than the stoichiometric ratio (1.05). The ratio between the SDs (OH$_s$) and the polymer chain diols (OH$_l$) is equal to 2 leading to about 30% of hard segments. The two HTPB prepolymers (R45HT and R45M) are introduced for the adhesive compounding leading to materials PUHT and PUM, respectively.

To prevent damage of the adhesive during PU$_P$ casting, the adhesive must be strengthened by a precuring step at 60°C. The degree of crosslinking of the adhesive can be modified by changing the time of precuring before the PU$_P$ casting. Once the two materials are put into contact, the curing of the assembly is performed for up to the optimum time of curing (14 days at 50°C). The final

bulk properties of the materials are identical whatever the precuring time.

A 90° peel test serves to evaluate the adhesive strength at room temperature. Various peel rates ranging from 0.1 to 100 mm/min are used. The adhesive after mixing is poured on a backing before the precuring step so that the extension of the peeled parts can be neglected. The peel test is performed in air and liquid media. The liquids are chosen so that they act on physical bonds at the crack tip without affecting the bulk properties by swelling or dissolution. It is possible to evaluate qualitatively the importance of these bonds in the failure region.[19] Liquids with different polar components of the surface energy [ethanol, silanol-terminated polydimethylsiloxane (PDMS-S), and trimethylsiloxy terminated polydimethylsiloxane (PDMS-T)] are used as shown in Table II together with the interfacial energy with water. The expected interfacial energy PDMS/water is equal to 30 mJ/m^2. The measured value for PDMS-S indicates the preferential orientation of the hydroxyl groups at the water/PDMS interface to minimize interfacial energy.

RESULTS AND DISCUSSION

Preliminary Study of Simple Networks

The evolution of filler-free simple networks is followed as a function of time of curing at 60°C. Swelling measurements are performed for compositions with and without SD according to compositions given in Table III. It should be noted that the soft segments swell in toluene, whereas hydrogen-bonded hard segments remain unaffected. The cure reaction of these simple networks is carried out with slight and constant excess of isocyanate with a [NCO]/[OH] equivalent ratio of 1.05.

The evolution of the two networks (R45M- and R45HT-based) show many differences. A gel is

Table III Constituents of the Blends Used to Study the Network Formation

HTPB (R45HT)	HTPB (R45M)	Diisocyanate	Short Diols	[OH$_s$]/[OH$_l$]	Network
×		×		0	HT+Di
	×	×		0	M+Di
×		×	×	2	HT+Di+SD
	×	×	×	2	M+Di+SD
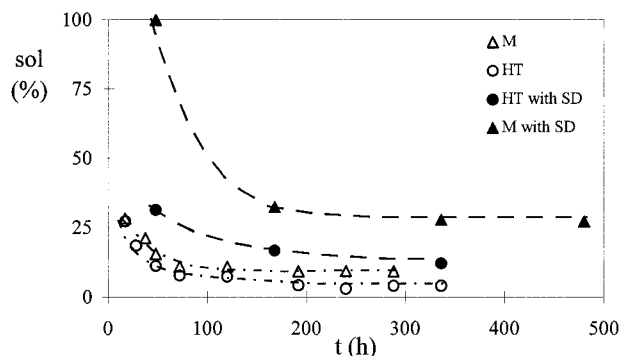
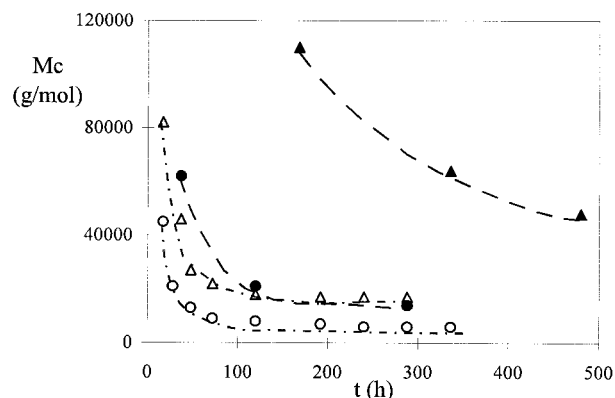**Figure 2** Evolution of the sol fraction as a function of time of curing for the different blends.

Figure 3 Evolution of the molecular weight between crosslinks as a function of the time of curing (symbols are the same as those used in Fig. 2).

formed in all cases but its formation is slower when SDs are introduced in the blends, especially for R45M (Fig. 2). This effect is more clearly seen for R45M and is a consequence of the amount of chains with functionality of >3 (30% for R45HT compared to 14% for R45M). However, it can be seen on this figure that the sol fraction remains high even after 300 h of curing, implying that many chains remain free and are not integrated into the network. This effect is more pronounced when chain extenders are added. Moreover, it has been checked by GPC (Table IV) that, at optimum curing, the free chains are longer and are only affected by the type of HTPB and not by the presence of chain extenders.

Descheres et al.[12] and Panicker and Ninan[13] have shown that the G-type hydroxyl functions are more reactive than the H and V types. Also, the distribution of the molecular weight of the chains remaining in the sol fraction after complete curing of the blends based on R45HT (with and without chain extenders) remains about the same as in the initial one. For the R45M-based blends, chain extension seems to be more efficient, M_n and M_w increase significantly in the sol fraction together with the molecular weight between crosslinks in the gel (Fig. 3). However, in-

frared spectroscopy analysis of the urethane bonds (the peak located around 1725 cm^{-1} compared to the C=C peak which is constant in all cases) indicates that more urethane bonds are detected when the blend is based on R45HT. This means that chain extension occurs with shorter chains which are globally less functionalized, whereas longer chains are involved in the reaction with R45M. The formation of these urethane linkages and hard segments in the case of the blends containing chain extenders leads to phase separation and pseudo-or physical-crosslinking points because of hydrogen bonding.

In summary, the sol fraction generated when using R45HT compared to R45M is less important, is richer in rigid segments, has a lower average molecular weight, and the network is tighter.

Study of the Formulations

The glass transition temperature of the soft segments is slightly higher (4–5°C) in the adhesive material than in the corresponding HTPB, implying complete phase segregation.[20] No clear tran-

Table IV   Some Characteristics of the Sol Fraction After Optimum Curing

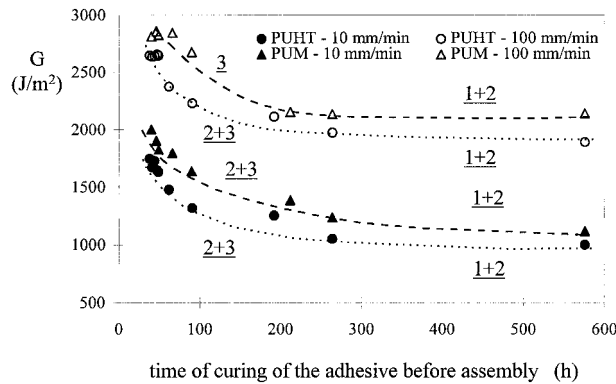|	Sol w/w (%)	M_n (PS equivalent)	M_w (PS equivalent)
R45M and R45HT	—	5600	13,000
M	9	17,000	32,000
HT	4	6000	13,000
M with SD	27	17,000	42,000
HT with SD	12	7000	15,000

Figure 4 Peel strength as a function of the degree of crosslinking of the adhesive before assembly.

sition at high temperature characteristic of the hard segments domain due to hydrogen bonds disruption is observed by DSC analysis. The concentration of hard segments is not sufficient to create large spherullites. At room temperature, the modulii (static and dynamic) are higher for PUHT. A broad peak appears in the evolution of loss tang δ peak as a function of temperature; the maximum is found for PUHT at 57°C, 16°C below that for PUM. This indicates that the miscibility of hard and soft segments in PUHT is slightly improved compared to that in PUM.

Influence of the State of Cure of the Adhesive on the Joint Formation

The influence of the precuring step of the adhesive on the peel strength is given in Figure 4 for two peel rates (10 and 100 mm/min) and both adhesive materials. The effect of peel rate is detailed for a 48 h precured sample on Figure 5. The peel strength decreases as the time of curing (or degree of curing) increases up to 100–200 h as a result of the network formation. Then it remains about constant. The failure always occurs in PU_P phase. It occurs closer to the interface when the degree of crosslinking before the joint formation is higher. The distance at which the failure occurs is also indicated according to code numbers shown in Table V. Although the failure is systematically cohesive in PU_P, the exact locus of failure depends on the rate of peeling and the HTPB used: lower peel rates and use of R45HT in the adhesive formulation lead to thinner layers of PU_P left on the adhesive side. The expected increase of peel energy G with peel rate due to viscoelastic dissipation effects is observed. Even at very low peel rate (0.1 mm/min), the failure remains cohesive in

PU_P and is always deeper for R45M-based material. This means that the interpenetration of the chains from PU_P into the adhesive layer is reduced but still possible whatever the degree of curing of the adhesive.

The facts that the distance of failure increases with peel rate and that the peel strength depends on the HTPB used to compound the adhesive suggest the formation of a gradient of mechanical properties in PU_P related to the chemistry involved in the formation of the networks and the HTPB characteristics. Interdiffusion of molecules (macromolecules, SD, and diisocyanate) is possible, which may lead to various proportions of hydrogen-bonded hard segments. Moreover, it is noticed that no separation by swelling of the two materials after peeling was observed even after long times (several weeks). Therefore, covalent bonds are most likely to have been formed at the interface during the formation of the PU_P network whatever the degree of cure of the adhesive material and the prepolymer used. We used the peel test in air and liquid media to get a better understanding of the influence of the HTPB on the adhesive behavior.

Peel tests in the various liquids discriminate the adhesive behavior of precured (48 h) PU_P based on PUM and PUHT. Figures 6 and 7 respectively, show the measured peel energy at different peel rates in air and in the presence of the liquids at the peel front for PUHT/PU_P and PUM/PU_P joints. When the liquid is no longer present at the crack tip, the peel energy has the same value as in air.[21] The rate of peeling at which this
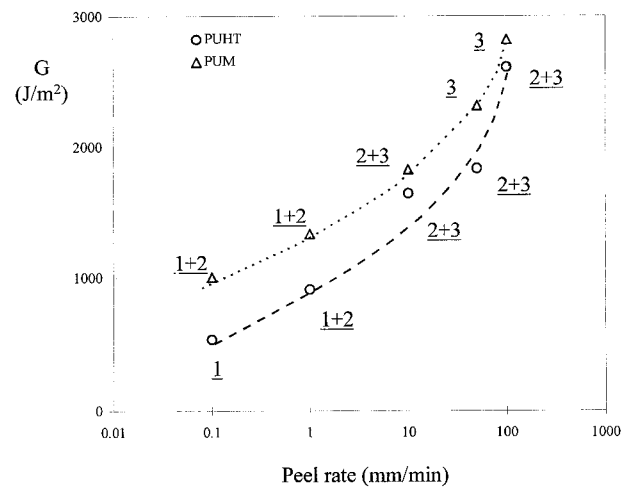

Figure 5 Peel strength as a function of peel rate for PUHT/PU_P and PUM/PU_P joints.

Table V Failure Code Numbers

0	Interfacial Failure	
1		0–20 μm from the interface
2	Cohesive failure in PU_P	20–50 μm from the interface
3		> 50 μm from the interface
4	Cohesive in PUHT or PUM	

happens depends on crack opening, viscosity, and surface energy of the liquid, liquid/solid interactions. The peel rate in ethanol has a much stronger influence for PUM-based joints compared to PUHT-based joints.

PDMS-S has a low surface energy and is nonpolar (Table II). No effect on the peel energy is observed. The influence of the silanol end groups of PDMS-T indicates that, in the zone where the failure occurs, hydrogen bonds are affected by the presence of the functional groups of the liquid. This effect is more significant for peeling in ethanol environment. Moreover, particularly with ethanol, the locus of failure is closer to the interface. Physical and chemical interactions are playing a role at the polymer/polymer interface. It is noted that interdigitated chains have the same effect as chemical bonds when they are broken and nonextracted at a finite peel rate. The comparison of the behavior of PUHT/PU_P and PUM/PU_P joints (Figs. 6 and 7) indicates that the effect is greater in the second ones at low peel rate. Therefore, the hydrogen bonds are more important. However, such bonds are very weak in PU_P because no chain extenders are added and few hydrogen-bonded carbonyl groups should be

present. The assumption is then that the migration of short segments constituted by SDs and diisocyanate migrate from the adhesive layer toward PU_P. This leads to an interphase enriched in hard segment in the highly filled material. This can be related to the sol fraction which is higher for the adhesive based on PUM (Fig. 2).

Influence of SDs

To check the influence of the SDs on the formation of the interphase, the adhesive behavior of adhesive materials based on both HTPB but containing no SDs is considered. It is clear that the quantitative comparison of the peel energies is not possible due to the differences in bulk properties and the consequence on dissipated energy. In absence of chain extenders, the isocyanate functionalities diminish more quickly. Therefore, the conditions of preparation of the assemblies are based on the amount of residual functional groups (15% for PUM and 20% for PUHT). The precuring time is only 20 h instead of 48 h in presence of chain extenders. The results shown in Figure 8 indicate that the absence of chain extenders decreases the
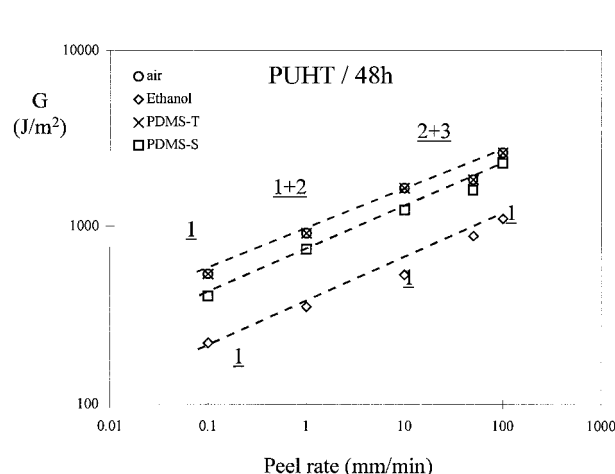

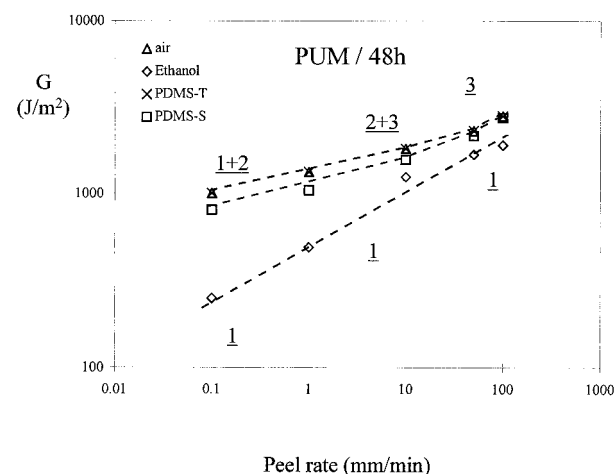**Figure 6** Peel test in air and liquid media for PUHT/PU_P for which the precure time is 48 h.

Figure 7 Peel test in air and liquid media for PUM/PU_P for which the precure time is 48 h.
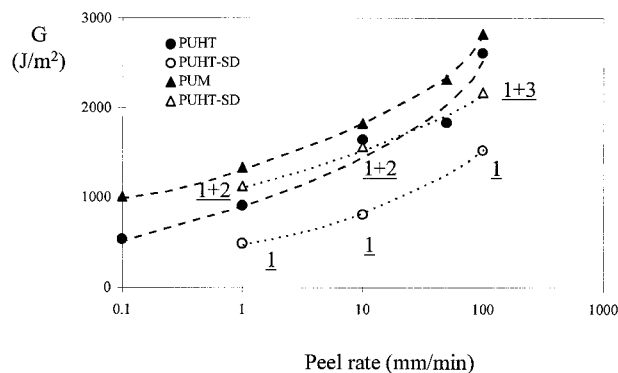
Figure 8 Influence of short chain diols on the peel energy.

adhesive peel strength of PUM/PU$_P$ joints, whereas the interface becomes very weak when the adhesive is based on R45HT. Moreover, failure still occurs in PU$_P$ but nearer to the interface and always deeper with the R45M-based adhesive. In this case, we can expect migration of diisocyanate and interdiffusion of macromolecular chains only. This will lead to cocrosslinking between HTPB chains originating from both sides of the interface. However, less hydrogen-bonded segments are formed. This can be checked by the peel test in air and liquid media as before.

By peeling the assemblies in ethanol, it is found that there is only a weak variation of the peel energy compared to that observed in the presence of SDs. This confirms the failure in a zone of the highly filled PU enriched in hard segments associated by hydrogen bonding. The reactivity of the hydroxyl groups of the HTPB chains used in the adhesive formulation and the role of the covalent bonds in the interfacial region appear clearly.

CONCLUSION

The formation of the polymer/polymer interface described here is a rather complex mechanism. The interdiffusion phenomena of long chains and their cocrosslinking play the most important role although it is very difficult to get direct evidence. More free chains are present in R45M-based adhesive and as they are longer, their role as connectors is enhanced. The stress transfer depends on the interfacial and intrinsic strength which is higher for these assemblies. However, the observed failure is the result of the combination of the interfacial strength and the mechanical properties near the interface; the failure occurs at a distance that depends on the peel rate and the gradient properties (modulus and ultimate properties) in the interphase. The role of the physical crosslinks in this zone was shown by the peel test in different liquids. The reactivity of the various hydroxyl groups carried by the chains R45M and R45HT explains the difference of the size of the interphase thickness on the PU-based assemblies studied here. Future work includes the characterization of these thick interfaces by various techniques.

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