

# Evaluation of Adhesion Strength, Flammability, and Degradation of HBCD-Containing Polyurethane Adhesives

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**ABSTRACT:** In this work, moisture curable flame retardant HTPB-based polyurethane adhesives were synthesized. The influence of HBCD (Hexabromocyclododecane) as flame retardant on adhesion, degradation and change in flammability of synthesized HTPB-based polyurethane has been studied. Relationship between phase separation in hard and soft domains and adhesion has also been investigated. FTIR analysis was used to determine phase separation in synthesized adhesives. Lap shear test was used to determine adhesion properties of adhesives applied on aluminum and glass substrates. Thermal

Gravimetry analysis and Limited Oxygen Index (LOI) tests were carried out on flame retardant adhesives to evaluate effect of HBCD on degradation and flammability. Addition of HBCD to adhesives leads to reduction of thermal stability and lap shear strength for all substrates, in spite of flame retardant adhesives show higher LOI value. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3538–3543, 2008

**Key words:** polyurethane; adhesive; flame retardant; TGA; adhesion strength; FTIR

## INTRODUCTION

Polyurethanes are widely used in the field of coatings and adhesives due to their high reactivity and high flexibility in formulation, application technologies, mechanical, and adhesion properties and weathering resistance. In particular, polyurethanes are commonly used as adhesives to join different materials in the footwear, automotive industries and so on.<sup>1</sup> Segmented polyurethanes that consist of alternating soft and hard segments offer unique possibilities of tailor-made polymers by varying block length and composition. Thermodynamic immiscibility between hard and soft segments induces phase separation and generates a two-phase morphology in these segmented block copolymers. Polyurethane elastomers containing diene groups such as HTPB appear to be completely phase-separated, due to nonpolar polyol. The degree of phase separation and final bulk mechanical properties is depended on to polymerization conditions and additives such as reactants and flame retardant.<sup>2</sup> Phase separation depends on existence of hard domain and related hydrogen bonding is responsible for phase separation.

Hydroxyl terminated polybutadiene (HTPB)-a low viscosity colorless liquid with number average molecular weight of 1500–10,000 g/mol is used in production of adhesives, foams, and unsaturated polyesters as well as a polymer additive. Polyurethanes, which are prepared based on HTPB, exhibit excellent properties such as high abrasion resistance, high hydrolytic stability, and high low-temperature flexibility being used as special purpose polyurethane elastomers.

Using of additives can decrease the flammability of many materials. Thus, development of flame-retardants would allow a greater degree of safety in some applications like elastomeric compounds, adhesives, coatings, fibers, and cellular materials. Generally, polyurethanes do not exhibit sufficient flame retardancy and are easily burned. Therefore, studies emphasizing the development of technologies to promote flame retardancy and create flame retardant materials have increased.

There are two common approaches for improvement of flame retardancy in polyurethanes.

The first approach is due to addition of flame retardant to polyurethane through *in situ* polymerization such as polyphosphazene<sup>3</sup> or during processing as additive flame retardant, such as incorporating mica and ATH or ammonium polyphosphate in to polyurethane.<sup>4,5</sup>

The second approach is using reactive flame-retardants that covalently incorporated into the polyurethane backbone. There are some reports in the

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second approach: segmented MDI/HMDI-based Polyurethanes with lowered flammability using halogenated chain extender such as 3-chloro-1, 2-propanediol in the main chain,<sup>6</sup> Polyurethanes that contain (aliphatic phosphate) with various phosphorus contents were prepared from 4-diethoxyphosphoryloxyphenoxy(4-hydroxyphenoxy) cyclotriphosphazene (EPPZ).<sup>7</sup> Poly amide-imides containing phosphine oxide.<sup>8</sup> Aromatic phosphate and cyclotriphosphazene-containing polyurethanes as an effective flame retardant covalently incorporated into the polyurethane backbone.<sup>9</sup> In fact, halogenated or phosphorus groups in main backbones of polymer chains caused to change in thermal and mechanical properties.

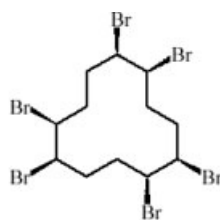
In present study, first approach is chosen in which flame retardant is incorporated to polyurethane through *in situ* polymerization. Polyurethane adhesives using hydroxyl-terminated polybutadiene/MDI/1,4-butanediol and Hexa bromocyclododecane (HBCD) as flame retardant were synthesized through one-shot method and effect of HBCD on adhesion behavior, degradation and flammability has been studied.

## EXPERIMENTAL

### Materials

Materials which were used to synthesis of polyurethanes were hydroxyl terminated polybutadiene [ $f \sim 2.1$ ,  $M_n$  about 2600 (gr/mol)] which synthesized and provided locally,<sup>10,11</sup> phenyl methane diisocyanate (MDI), butanediol (BDO) from Merck and Hexa-Bromo-cyclododecane (HBCD) from Great lakes.

Hexa bromocyclododecane is a highly brominated cycloaliphatic flame retardant. It is a white powder with 74.7% bromine content and melting temperature about 190°C.



Hexa-Bromo-cyclododecane (HBCD)

### Synthesize of polyurethanes

Samples were prepared through one-shot method using theoretical amount of MDI, BDO, hydroxyl-terminated polybutadiene (HTPB) and desired amounts of HBCD. Polyurethanes were synthesized based on stoichiometry amounts of reactants to obtain products with various hard segment contents according to Table I.

TABLE I  
Composition and Excess Molar Ratio Used to Synthesize of Samples

Sample	MDI (gr)	HTPB (gr)	BDO (gr)	I
HS25	6.12	22.63	1.35	1.014
HS40	3.06	6.088	0.873	1.006
HS55	12.6	13.83	4.02	1.005
HS40FR2	4.57	9.13	1.31	1.002
HS40FR6	4.57	9.13	1.31	1.002
HS40FR10	4.57	9.13	1.31	1.002

Excess ratio of the samples was determined by formula 1:

$$I = \frac{\left[ \frac{m_{\text{used}}}{M_m} \right]_{\text{disocyanate}} \times f_1}{\left( \left[ \frac{m_{\text{used}}}{M_n} \right]_{\text{polyol}} \times f_2 + \left[ \frac{m_{\text{used}}}{M_m} \right]_{\text{chain extender}} \times f_3 \right)}$$

where,  $I$  = excess molar ratio,  $m_{\text{used}}$  = amount of used materials,  $M_n$  = number average molecular weight of HTPB,  $M_m$  = molecular weight,  $f_i$  = functionality.

Synthesized polyurethanes with hard segment contents of 25, 40, and 55% named HS 25, HS40, and HS55 respectively. Hard segment content of polyurethanes was determined by formula 2<sup>12</sup>:

$$(\% \text{ wt}) = \frac{\left( \frac{af+2}{2} \right) M_{\text{iso}} + aM_{\text{Diol}}}{M_n + \left( \frac{af+2}{2} \right) M_{\text{iso}} + aM_{\text{Diol}}}$$

$f$  = functionality of chain extender,  $a$  = molar ratio of diol to HTPB,  $M_{\text{iso}}$  = Molecular weight of isocyanate.

Flame retardant polyurethane samples were synthesized based on 40% hard segment and amounts of 2, 6, and 10% HBCD named HS40FR2, HS40FR6, and HS40FR10, respectively.

To synthesize samples, HTPB and BDO were degassed in vacuum at 600 mmHg and 50°C for 8 h. Reaction was carried out under  $N_2$  at 70°C by one-shot method. At first HBCD was mixed to HTPB and BDO in a 270 rpm mixer. Then MDI was added to mixture and mixed vigorously. The above mixture as a polyurethane adhesive was applied directly on Aluminum to Aluminum (Al-Al), Aluminum to Glass (Al-Gl) and Glass to Glass (Gl-Gl) which were used as adherents. Steel fixtures were used to hold and compress adhesive between two substrates. Assemblies were hold in an 85°C oven for 3 days.<sup>13</sup> After processing, assemblies were kept in desiccators by the test time. Specimens used in ignitibility and LOI tests were prepared using the above mixture after keeping in 80°C oven for 3 days.

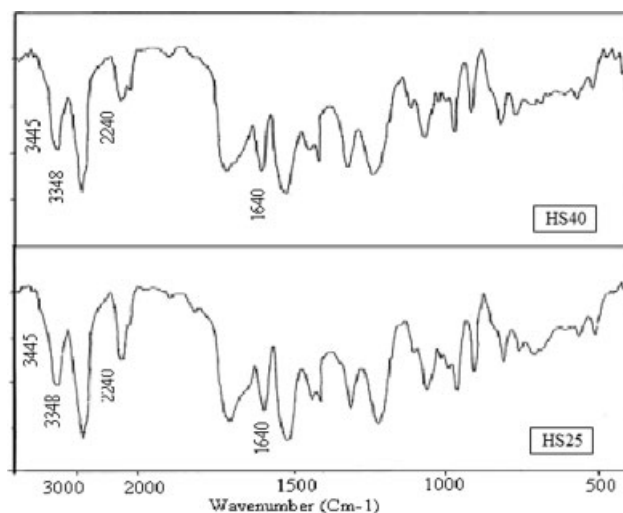


Figure 1 FTIR Spectrums of HS25 and HS40 samples.

### Experimental techniques

To compare hydrogen bonding in various polyurethanes, a Shimadzu spectrometer was used for FTIR analysis on prepared films. Lap shear strengths of HS25, HS40, HS55, and HS40FR10 measured according to ASTM D 1002 test method using a Gal-dabini tensile tester. Thermal properties and flame retardant behavior of the polyurethanes were investigated using thermal gravimetric analysis (TGA and DTG) and limited Oxygen index (LOI) tests. Thermogravimetry Analysis was carried out using TG 951-Dupont. Tests were carried out in Nitrogen atmosphere and heating rate was 10 °C/min. The LOI values were used to evaluate the flammability of the polyurethane samples according to ASTM-D2863 using (Stanton Redfort-FTA Flammability Unit). To measure-burning times of various samples,  $40 \times 10 \times 2 \text{ mm}^3$  bars were prepared and burning time to 2 cm-mark lines was measured according to Clause 6.2.5 of DIN 4102 standard (ignitibility test).

## RESULTS AND DISCUSSION

### Degree of phase separation

It is possible to calculate the degree of phase separation (DPS) and the degree of phase mixing (DPM) in

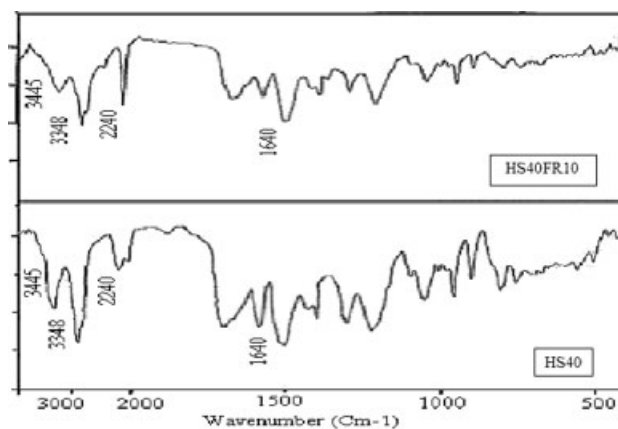


Figure 2 FTIR Spectrums of HS40 and HS40FR10 samples.

the polyurethanes. DPS and DPM can be readily obtained respectively, according to formula 3<sup>14</sup>:

$$DPS = \frac{NH_{\text{bonded}}}{NH_{\text{bonded}} + NH_{\text{free}}}$$

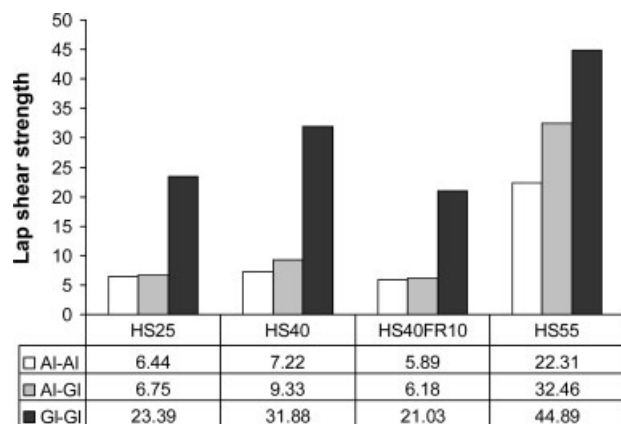
$$DPM = 1 - DPS$$

Polyurethane N—H groups consist of hydrogen bonded at  $3348 \text{ cm}^{-1}$  and Nonhydrogen (free) bonded groups at  $3445 \text{ cm}^{-1}$  in FTIR spectroscopy. Furthermore C=C bond at  $1640 \text{ cm}^{-1}$  is chosen as reference peak, it is also mentioned in the literature that there is no interference of peak in HTPB based polyurethanes.

FTIR results for HS25 and HS40 and HS40FR10 are shown in Figures 1 and 2 respectively. The ratio of  $(A_{3348}/A_{1640})$  shows amount of hydrogen bonding in samples. These calculations are shown in Table II. As shown in Table II, since the concentration of NHCOO groups in unit volume of polyurethane (Total hard and soft domains) increase, hard segment content and hydrogen bonding increased. Degree of phase separation in sample with 55% hard segment is lower than HS40; it seems that there isn't enough time to arrange hard and soft domains due to using one-shot method.

TABLE II  
FTIR Characterization and Calculation of DPS

Sample	Absorbance ( $1640 \text{ cm}^{-1}$ )	Absorbanc ( $3348 \text{ cm}^{-1}$ )	Absorbance ( $3445 \text{ cm}^{-1}$ )	$N_1 \left( \frac{A_{3348}}{A_{1640}} \right)$	$N_2 \left( \frac{A_{3445}}{A_{1640}} \right)$	DPS
HS25	0.372	0.228	0.121	0.612	0.324	0.654
HS40	0.304	0.311	0.093	1.021	0.305	0.769
HS55	0.250	0.199	0.104	0.796	0.416	0.658
HS40FR10	0.155	0.077	0.044	0.500	0.285	0.637



**Figure 3** Lap shear strength of HS25, HS40, HS55, and HS40FR10.

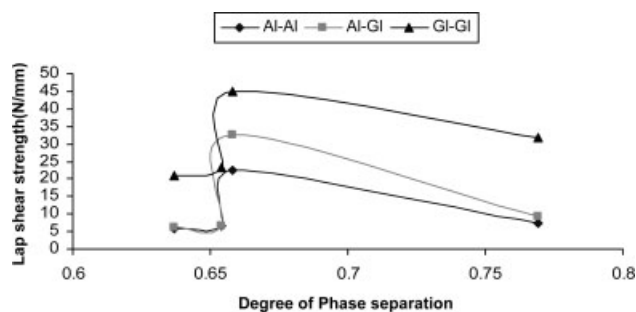
### Adhesion strength

As shown in Figure 3, increasing of hard segment content caused to increase lap shear strength (N/mm) of adhesives, because of increasing of hydrogen bonding in unit volume of hard domains. Hard domains in polyurethanes act as physical crosslinking to improve tensile strength and elastic modulus.<sup>15,16</sup> But presence of flame retardant in polyurethane matrix leads to reducing of phase separation and increasing of stress concentration and also caused to disordering in domain formation, therefore lap shear strength decreases.

As shown in Figure 4, results confirm relation between strength of adhesives and their microstructures (degree of phase separation). This phenomenon is observed for Al-Al, Al-GI, and GI-GI substrates. However DPS in sample HS55 is lower than HS40, this sample shows the highest lap shear strength. The reason of this event is mentioned above in "Degree of phase separation" section.

### The effect of HBCD

As shown in Table III, increase in hard segment content caused to increasing of resistance to fire and flame retardancy. Increasing in hard segment con-



**Figure 4** Lap Shear strength values as a function of DPS.

**TABLE III**  
Effect of Composition on Flammability (Ignitibility Test)

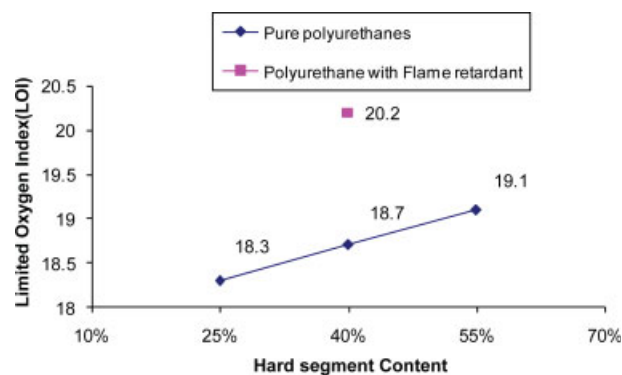
Sample	Burning time (Second)
HS25	71
HS40	112
HS55	107
HS40FR2	110
HS40FR6	143
HS40FR10	Self extinguish

tent leads to increase in hydrogen bonding. In addition, lower heat release value in hard segments compared to the soft segments is responsible for higher heat resistance. Also, addition of only 6% HBCD results in about 30% slow in burning rate and addition of 10% HBCD caused to self-extinguishing.

LOI test results are shown in Figure 5, confirm results of ignitibility tests. In fact, increasing in hard segment content increases LOI values, Furthermore addition of 10% HBCD to HS40 caused to 8% improvement in LOI value while increasing 15% hard segment leads to 2% improvement in LOI value.

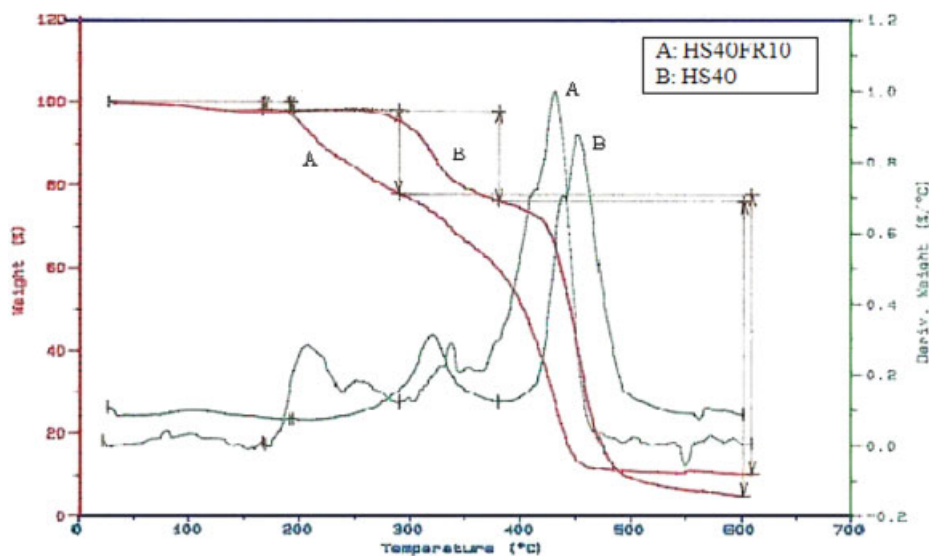
Thermal Gravimetry was used to evaluate thermal stability of synthesized polyurethanes. Figure 6 shows TGA and DTG curves for samples HS40FR10 and HS40. As shown in Figure 6, addition of HBCD as flame retardant to PU causes to shift initiation of degradation to lower temperatures. However, char formation is higher in HS40FR10 rather than HS40. Table IV is shown first to third weight loss temperatures and other TGA test results. According to Table IV, polyurethanes HS40 and HS40FR10 exhibit third weight loss as 67 and 71% respectively. It seems addition of HBCD caused to decreasing in thermal stability.

Saunders and Frisch<sup>17</sup> summarized thermal degradation mechanisms in four types of reactions that may take place in the thermal degradation of



**Figure 5** Limited Oxygen Index of Samples HS25, HS40, HS55, and HS40FR10DPS. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com)]





**Figure 6** TGA diagrams of HS40 and HS40FR10. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com)]

polyurethanes. Reactions are: Dissociation to isocyanate and alcohol; Formation of primary amino and olefin; Formation of secondary amine; Transesterification type bimolecular displacement. Because of the complex structure of polyurethane segmented elastomers, the degradation results in a complicated mixture of products that is often difficult to relate precisely to the above degradation mechanisms. The mechanism of the thermal degradation of polyurethanes depends upon the type of the substituents on the N and O atoms in the urethane groups.

It is well-known that the principal mechanism of thermal degradation of polyurethanes represents the reaction in which they are formed and thus yield diisocyanate and dialcohol or their secondary degradation products. A number of authors claimed that the thermal degradation is primarily a depolycondensation process (The first mechanism).<sup>18</sup> Since polybutadiene starts liberating volatile components only above 310°C, the weight loss in the first degradation step occurs mainly due to the depolycondensation of urethane groups.<sup>19</sup> It is seen that HTPB-based polyurethanes show crosslinking and cyclization of HTPB over the chain scission during degradation.<sup>20</sup>

On the other hand, HBCD has weight loss about 90% during thermal degradation and produces some different materials such as HBr in gas phase, nonbrominated C8–C24 and also bromine-substituted compounds in condensable phase and residual char.<sup>21</sup>

Regarding to above researches we suggest that during degradation of samples containing flame retardant, HBCD has been decomposed. Produced HBr, Bromine radicals and also cycloaliphatic radicals could be reacted with double bonds of HTPB leads to formation of complicated compounds in residual char. Comparison of samples A: HS40FR10 and B: HS40 in the Figure 6 shows char residual equal to 10.3 and 5.2% respectively. It could be concluded that higher char is result of formation of reacting of radicals and complicated compounds based with the PU polymer backbone to create crosslink sites which would lead to higher amounts of char formation.

The LOI value of Estane-58244; polyether-type thermoplastic polyurethane, a nonhalogenated flame retardant compound is 28 whereas, halogenated flame retardant polyurethanes show higher LOI up to 30. As it has been expected, LOI values of synthesized adhesives are lower than commercial ones.

**TABLE IV**  
Decomposition Steps and Limited Oxygen Index

Sample code	First degradation temperature (°C)	First weight loss (%)	Second degradation temperature (°C)	Second weight loss (%)	Third weight loss (%)	Char residue (%)	LOI
HS40	185	2.01	360	21.76	71.02	5.21	18.7
HS40FR10	170	1.87	276	20.19	67.03	10.31	20.2

## CONCLUSION

We investigated the adhesion strength of typical polyurethane adhesives coated on different substrates, to evaluate their performance and the influence of flame retardant on lap shear properties and flammability. It is observed that reduction of hydrogen bonding in hard segments and phase separation due to addition of HBCD to HTPB-based polyurethane adhesives finally leads to decrease of lap shear strength of adhesives containing HBCD. Furthermore, TGA results show increasing in degradation for adhesives containing HBCD and degradation shifts to lower temperatures. Increasing of hard segment content caused to thermal stability and higher LOI values. Addition of HBCD to HTPB-based adhesives leads to reduction of thermal stability because of formation of HBr during decomposition process, in spite of self-extinguishing in flammability test and higher LOI value.

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