Study on effective parameters on adhesion in segmented Polyurethanes
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Study on effective parameters on adhesion in segmented polyurethanes

M. Amrollahi ,[a] G. Mir Mohamad Sadeghi, [a] * M. Haghshenas [b]

a Department of Polymer Engineering, Amirkabir University of Technology, 15875/4413 Tehran, Iran
b Engineering Research Institute(ERI) , Ministry y of Agriculture, 16th km. Karaj Road, Tehran, Iran

1. Abstract
Phase separation in segmented polyurethanes is an important phenomenon, which affects on characteristic properties of polyurethanes. Morphology, formation and distribution of micro-domains (hard segments and soft segments) are effective parameters on interfacial interaction and adhesion of polyurethane system. In this work segmented polyurethanes based on 4,4 -diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BDO) were synthesized and the effect of hard segment content and some additives on lap shear strength and tack of synthesized polyurethanes well defined.

2. Introduction
Segmented polyurethanes that consist of alternating soft and hard segments offer unique possibilities of tailor-made polymers by varying block length and composition [1]. Thermodynamic immiscibility between hard and soft segments induces phase separation and generates a two-phase morphology in these segmented block copolymers. There are some reports on evaluation of structure-properties in these segmented polyurethanes [2-4]. Microstructural parameters such as hard segment content, chemical nature and molecular weight of soft segments as well as additives has important role in final adhesion properties of polyurethane [5]. In the present study the effect of hard segment content as well as some additives on lap shear strength and tack of synthesized polyurethanes has been studied.

3. Experimental

Materials
Hydroxyl terminated polybutadiene were prepared locally [6] with low vinyl microstructures and Mn being about 2500 gr/mol. Polybutadiene-ol was degassed at 50°C for 24 hr before use. MDI (4,4-diphenylmethane diisocyanate), BDO (1,4-butanediol) from Merck were used after drying at 50 °C and 800 mm-Hg vacuum for 8 hr. Poly functional (PFA); with average functionality about 3 were synthesized locally [6]. Aluminum and glass sheets were chosen as substrate to determine lap shear strength of polyurethanes.

Analytical techniques

A VPO Knauer apparatus was used to determine Mn of HTPB. Toluene as solvent at 90° C and benzyl was used for calibration. A Shimadzu spectrometer was used for FTIR analysis of prepared films. MTS Tensile machine was used to measure lap shear strength of adhesives. Lap shear strength and tack of polyurethane were measured according to ASTM D-3221 and ASTM D-1002 respectively.

Synthesize of adhesives and preparation method

To evaluate the effect of hard segment, samples were prepared through one-shot method using theoretical amount of MDI, BDO and hydroxyl-terminated polybutadiene. Polyurethanes were synthesized in three molar ratios. Hard segment contents of synthesized polyurethanes were 15%, 25% and 40% named PU-HS 15%, PU-HS 25% and PU-HS 40% respectively. Steel fixtures were used to hold and compress adhesive between two substrates. Aluminum to Aluminum (Al-Al) and Aluminum to Glass (Al-Gl) were chosen as adherents. Assemblies were hold in an 85ºC oven for 3 days.

To evaluate addition of poly-functional agent three samples were synthesized based on 40% HS polyurethanes, which contain various weight percent of poly-functional agent (PFA). The procedure was as follows: HTPB, MDI and BD were mixed vigorously for a few minutes. The calculated amounts of MDI were mixed with pre weighed HTPB/BDO mixture in a suitable vessel. Three various amount of poly functional agent were used as shown in Table 1(5%, 10% and 15% of total weight of HTPB named PU-PFA 5%, PU-PFA 10% and PU-PFA 15% respectively) and the amount of MDI and BDO were constant. The above mixtures were coated on substrates .Steel fixtures were used to hold and compress adhesive between two substrates during 24 hr after processing. Assemblies wee kept in desiccators until testing. Hard segment content of polyurethanes were determined by this formula:

$$(\%wt) = \frac{(\frac{af+2}{2})M_{iso} + aM_{Diol}}{\overline{M}_n + (\frac{af+2}{2})M_{iso} + aM_{Diol}}$$

f = functionality of chain extender
a = molar ratio of diol to HTPB
M_{iso}=Molecular weight of isocyanate

Results and Discussions

Effect of hard segment content

Figure 1 shows FTIR spectrums of 25% HS and 40% HS polyurethanes respectively. Polyurethane N-H groups consist of, hydrogen bonded at 3330 Cm^{-1} and non-hydrogen bonded groups at 3400 Cm^{-1}. Furthermore C=C bond at 1640 Cm^{-1} is chosen as reference peak. It is also mentioned in the literature that there is no interference of peaks in HTPB based polyurethanes [7]. N-H hydrogen bonded group divided by C=C absorbance intensity for 25% HS, 40% HS results in 35 and 51

respectively. It is seen that as hard segment content increases, hydrogen bonding increases.
Figure 2 shows lap shear strength of PU-HS. As shown in Figure 2, increasing of hard segment content increases from 25% to 40%, the shear strengths (N/mm) of Al-Al samples relatively doesn't change but for Al-Gl samples increases.

Effect of addition of poly functional agent

Reactions between -OH groups of poly functional agent (f~3) or H_2O in moisture of air with –NCO groups caused curing of adhesives. As shown in Figure 1, characteristic bonds at about 1500 Cm^{-1} and 1700 Cm^{-1}, are due to formation of urethane linkages in the spectrum of synthesized polyurethane. Figures 3 shows measured tack of adhesives (L) versus time for synthesized adhesives which contains 5, 10 and 15% poly functional agent. As shown in Figure 3, tack decreases with time for all three samples which contain of 5%, 10% and 15% poly functional agent. Figure 4 shows lap shear strength of adhesives applied on Al-Al substrates contains 5, 10, and 15% poly functional agent.

Also it is seen that the tack decreases exponentially versus time: $y = 36\ e^{-0.01x}$ for PU-10% PFA and $y= 45\ e^{-0.02x}$ for PU-PFA 15 %. Therefore dependence of tack to time for sample 15 % is higher than sample 10% poly functional agent.
A shown in figure 4 lap shear strength increases for Al-Al and Al-glass bonding but decreases for glass-glass bonding as the content of poly functional agent increases.

Conclusions

Experiments showed that hard segment content of polyurethanes as well as addition of flame retardant affect on mechanical and adhesion properties of polyurethanes. As hard segment content increases, storage modulus of polyurethane increases but damping decreases. Moreover in HTPB, low temperature damping of network increases. Peel strength of ester-type polyurethane is higher than two others.
Results showed that with increasing the functionality of the HTPB, lap shear strength increased for Al-Al and Al-glass bonding but decreased for glass-glass bonding. Tack varies exponentially versus time for samples which contains different amounts of poly functional agent. Comparison of adhesion strength (lap shear strength) in metal-metal and metal-glass bonding shows that this method is a novel method, has high efficiency and could be scaled up to be used in industrial applications

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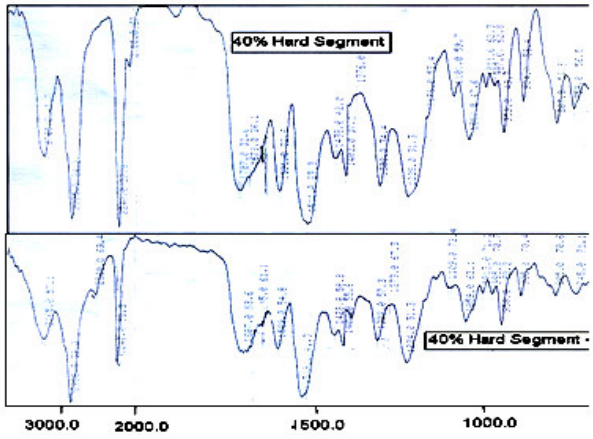

Figure 1 – FTIR spectrums of PU-HS 25% and PU-HS 40%

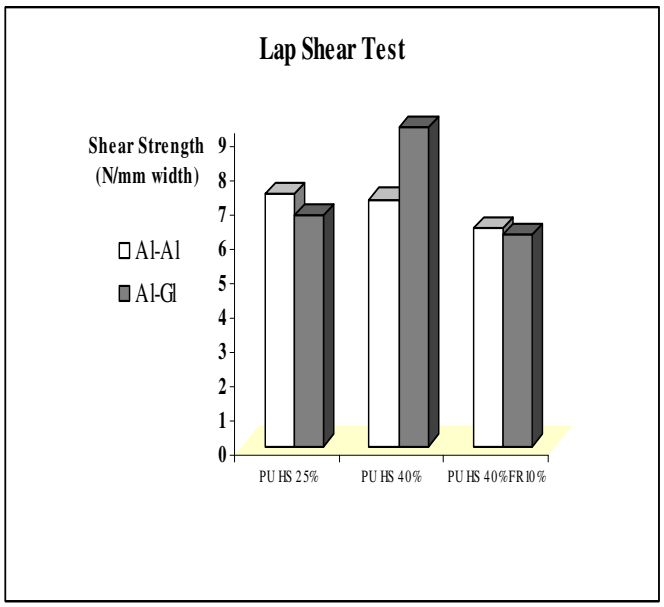

Figure 2 – Effect of hard segment content on lap shear strength of Polyurethanes

Table 1: Conditions for Preparing of Samples and obtained Lap Shear Strength

Sample	Substrate	PFA (gr)	Lap Shear Strength (Kg/Cm2)
PU-5 PFA1	Al-Al	5	60
PU-5 PFA2	Gl- Al	5	36
PU-5 PFA3	Gl- Gl	5	42
PU-10 PFA1	Al-Al	10	45
PU-10 PFA2	Gl- Al	10	82
PU-10 PFA3	Gl- Gl	10	67
PU-15 PFA1	Al-Al	15	115
PU-15 PFA2	Gl- Al	15	87

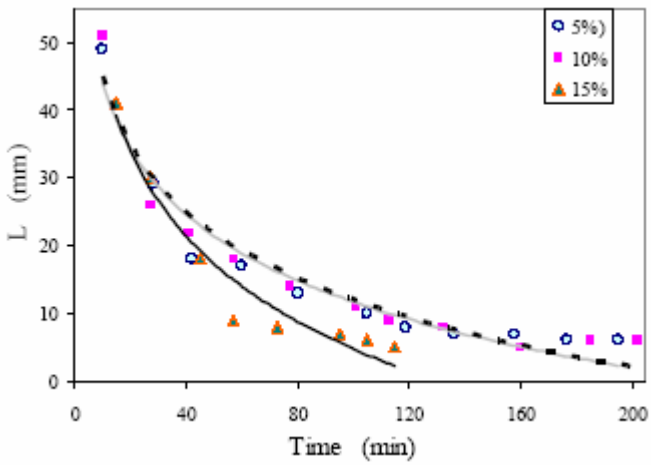

Figure 3: tack of adhesives (L: mm) versus time

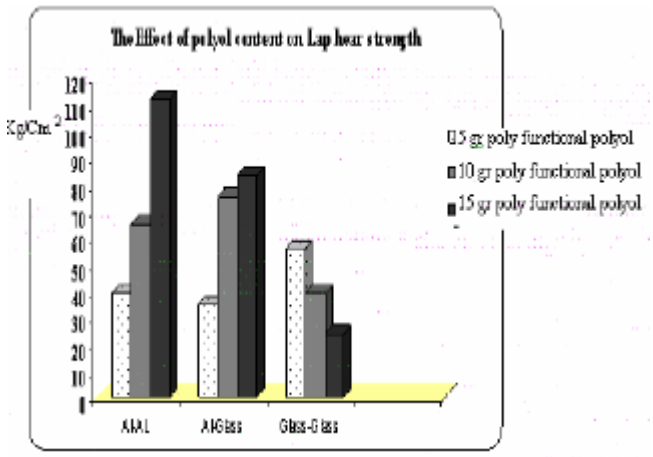

Figure 4-*:* Lap shear strength of the samples A to I