Characteristics of polyurethane adhesives with various uretonimine contents in isocyanate and average alcohol functionalities

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ABSTRACT: Polyurethane adhesives are found in a variety of applications. To ensure durability and functionality, a polyurethane adhesive is required to possess good adhesive properties and thermal stability. In this study, polyurethane adhesives were fabricated using isocyanate and polyols of various type and functionality (f_{av}). It was found that peel strength of an adhesive is strongly related to the f_{av} of a polyol and uretonimine content. At high uretonimine content, the probability of forming hydrogen bonded component increases and as a result the adhesive's peel strength increases. At high f_{av} and molecular weight of a polyol, an adhesive's wettability decreases so does its adhesion to a substrate. Therefore, designing for a functional adhesive, high uretonimine content and low f_{av} of polyol are desired. Thermal stability of a polyurethane adhesive also improves with uretonimine content. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43737.

INTRODUCTION

Polyurethane adhesive used for many products such as daily supplies attracts great attention due to its easiness of manufacturing process, and many researches on polyurethane adhesives for industrial applications are reported.[1–4] In particular, polyurethane adhesive fabricated by one-step polymerization is advantageous in terms of economics of operational budget in manufacturing system. Adhesive properties and thermal stability are important factors in industrial uses of polyurethane adhesives. First, adhesive properties are strongly related to mechanical, chemical, and physical properties of the adhesive materials. Especially, high wettability of materials on substrates is the key point on achieving good mechanical adhesive force,[5] and it is associated with mobility of polymer due to its anchoring effect. In addition, cohesive force is another important factor for adhesive property. If the adhesive does not have sufficient cohesive force, cohesive failure will happen.[6] Therefore, high wettability for strong adhesive force and high cohesive force of materials are very important parameters for good adhesive properties. In polyurethane chemistry, the cohesive force is strongly governed by the internal hydrogen bonding of polyurethane.[7] Second, thermal stability also affects polyurethane adhesive characteristics in long term usages or high temperature applications. Generally, polyurethane adhesives are used in various commercial products which are easily exposed to various thermal conditions such as sunlight and electrical heat sources. Therefore, polyurethane adhesives with robust thermal stability at elevated thermal conditions are promising in various commodity applications.

Generally, conventional polyurethane synthesis was mainly achieved by varying types of isocyanates, alcohols, ratio of isocyanate to hydroxyl groups, and chain extenders.[8–12] Amongst the ingredients, the molecule containing isocyanate groups is the most important component in formulating polyurethane because it provides not only urethane reactions with alcohols but also strong mechanical strength from the hard segments of the materials. Methyl diisocyanate (MDI) derivatives such as modified MDI containing carbodiimide groups, polymeric MDI, and toluene diisocyanate (TDI) are commonly used as a basic component in commercial polyurethane applications. In this study, modified MDI containing uretonimine linkages is used to improve adhesive property of polyurethanes. Only a few researches on polyurethane including uretonimine linkages have been reported.[13,14]

The purpose of this research is to improve adhesive property and thermal stability of polyurethane adhesives by varying the contents of uretonimine linkages and average functionalities (f_{av}) of alcohol. Both uretonimine structure and f_{av} have strong effects on the adhesive properties of polyurethane materials because molecular mobility and internal hydrogen bonding are highly related to the chemical structure of materials. Uretonimine contents and f_{av} were used as experimental parameters to investigate adhesive properties and thermal stability of
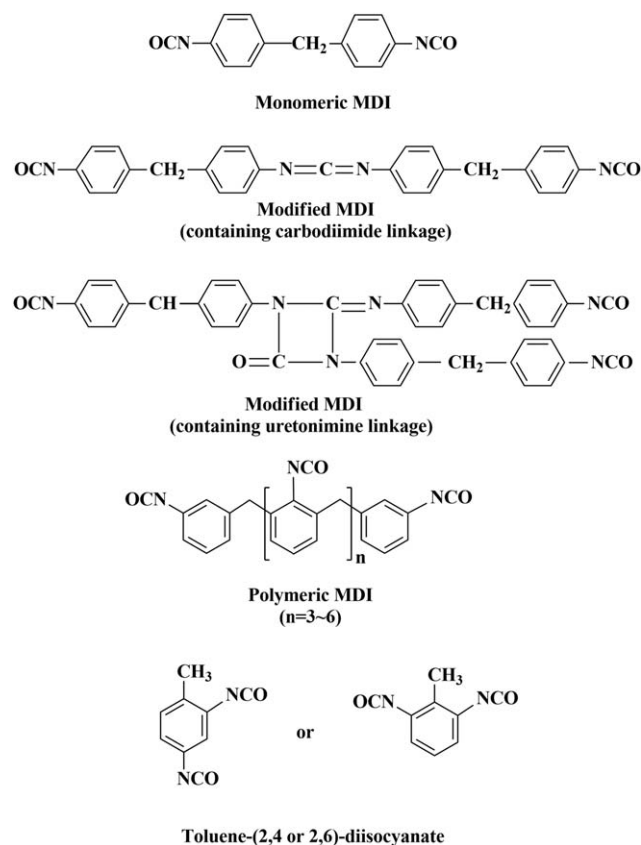
Figure 1. Molecular structure of the various types of MDI used for polyurethane synthesis.

polyurethane materials. Fourier transformed infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA), and 90 degree peel test were used for characterizations of materials and measurements of adhesive properties.

EXPERIMENTAL

Materials

In synthesis of polyurethane molecules, isocyanate and alcohol functionalities are the key components for reactions. Two types of methylenediphenyl diisocyanates (MDI) obtained from Kumho Mitsui chemical were used; COSMONATE LL (modified MDI containing carbodiimide linkage mixed with monomeric MDI, about 25% uretonimine linkage) and COSMONATE CG3701S(polymeric MDI mixed with monomeric MDI, about 25% TDI). Figure 1 shows the molecular structure of the monomeric, polymeric, and modified MDIs including carbodiimide and uretonimine linkages, and toluene diisocyanate (TDI). Three different molecular weights of polyether-based alcohols were also used; Polyol Y-3553 (SK Chemical), PP-1000, and PP-2000 (KPX Chemical). Materials characteristics of the isocyanates and alcohols are summarized in Table I. In addition, the chain extender (diethanolamine [DEOA], Sigma-Aldrich) and gelling catalyst (dibutyltin dilaurate [DBTDL], Sigma-Aldrich) were also used in manufacturing polyurethane adhesives. In preparation of the adhesive films, nondetachable corona-treated (50 μm, SKC) and detachable silicone-treated (23 μm, SKC) PET films were used.

Synthesis

Polyurethane adhesives were synthesized by one shot bulk polymerization without an intermediate step for the pre-polymer synthesis. First, the alcohol systems containing alcohol, chain extender, and gelling catalyst were weighed in a 400 mL paper cup. Secondly, pre-weighed isocyanate part for the calculated uretonimine contents was added to the alcohol systems and mixed for 10 s at 3000 rpm. Finally, the mixture was poured onto the bottom glass mold (30 cm × 30 cm) which has the detachable PET film and 1.0 mm thickness silicon rubber around the 1 cm edge of the mold. Then, the non-detachable PET film and the top glass mold are sequentially placed on the top of the mixture for manufacturing 1.0 mm adhesive films, and the mold was kept in a convection oven at 60 °C for complete polymerization for 1 h. Then, the mold was taken from the oven and remained in the room temperature condition for 24 h to form final adhesive films. The formulation details for the adhesive synthesis are shown in Table II.

FTIR Spectroscopy

Fourier transformed infrared spectroscopy (FTIR Frontier, PerkinElmer Inc.) with an attenuated total reflectance (ATR) accessory was used to qualitative analysis for the polyurethane reactions.[15] The FTIR spectra were obtained from 4 scans with a resolution of 4 cm^{-1}, and the conversion of polyurethane reaction was examined with the Time base software. For the conversion measurements, the final reaction mixtures were placed on the diamond crystal with a time interval of 10 s for 30 min. Using the spectra obtained from the samples, the NCO group conversion was calculated after the baseline corrections as the following eq. (1)[16];

$$\text{NCO conversion} = 1 - \frac{I_t}{I_0}, \qquad (1)$$

where I_0 and I_t are normalized peak heights for the NCO absorption band at the beginning of the reaction and time t. The free NCO stretching band at 2272 cm^{-1} was normalized by the intensity at 2970 cm^{-1} of an internal standard (C—H

Table I. Characteristics of Isocyanates and Alcohols

Material	Characteristics
COSMONATE LL	%NCO (wt %): 29.0 Equivalents weight: 112 Uretonimine: 25 wt %
COSMONATE CG3701S	%NCO (wt %): 37.5 Equivalents weight: 143
Polyol Y-3553	OH value (mg KOH/g): 33–37 $M_w \approx 5000$ $f_{av} = 3$
PP-1000	OH value (mg KOH/g): 108–116 $M_w \approx 1000$ $f_{av} = 2$
PP-2000	OH value (mg KOH/g): 54–58 $M_w \approx 2679$ $f_{av} = 2$

Table II. Chemical Composition of Polyurethane Adhesives

		System 1	System 2	System 3	System 4	System 5
f_{av} (−OH)		2.00	2.04	2.08	2.14	2.20
Polyol(g)	PP-1000	25.0	22.5	20.0	17.5	15.0
	PP-2000	25.0	22.5	20.0	17.5	15.0
						20.0
*Cosmonate LL (g)		1.29-7.75	0.00-8.59	0.00-11.64	4.40-11.01	4.15-10.38
Cosmonate CG3701S (g)		8.98-3.99	9.49-2.85	9.00-0.00	5.11-0.00	4.82-0.00
DEOA (g)		0.5	0.5	0.5	0.5	0.5
DBTDL (g)		0.4	0.4	0.4	0.4	0.4
Uretonimine contents ($\times 10^{-3}$ mol)		1, 3, 4, 5, 6, 8	0, 1, 2, 5, 7, 9	0, 1, 2, 3, 5, 7, 8, 9,10, 12	4, 7, 8, 9, 10, 11	4, 6, 7, 8, 9, 10

* NCO index: 1.0

stretching band), which shows invariable peak intensity during the polymerization.[17–20]

Thermogravimetric Analysis

Thermal decomposition behavior was also examined for the samples using a thermogravimetric analyzer (TGA, Pyris 1, PerkinElmer Inc.) with a heating rate of 20 °C min^{-1} for the temperature range from 50 °C to 700 °C, under nitrogen atmosphere. Mass loss rate was measured for samples with different amounts of uretonimine as a function of decomposition temperature.

Peel Strength

For sample preparation, the adhesive films were cut into 25 mm $\times$ 200 mm dimensions, and the detachable side of the films was stuck onto the stainless steel substrate under 2 kg gravitational force for 10 min. The sample was used to measure peel strengths of the adhesive films at a 90° angle by the universal test machine (LS1, Lloyd Instrument Ltd.) under crosshead speed of 300 mm per min.[21]

RESULTS AND DISCUSSION

FTIR Analysis

Using *in situ* FTIR-ATR spectroscopy measurements, the extent of conversion during polymerization can be monitored as a function of reaction time. As explained in the characterization section, the NCO conversion was measured as a guideline for the completion of urethane polymerization at various alcohol functionalities by monitoring the free NCO stretching band change at 2272 cm^{-1}. Figure 2 shows the NCO conversion for various average alcohol functionalities (f_{av}), and it reaches about 90% conversion after 1600 s ($\approx$30 min) reaction time for all the cases of alcohol functionalities. In addition, initial rate of the NCO conversion shown in the inset decreased with increasing f_{av}. Generally, reaction rate of step polymerization is higher for the high f_{av} than the low f_{av} case because of easy accessibility.[22] However, in this work, the f_{av} was increased by adding the high molecular weight triol to the low molecular weight diol mixture, and thus the sample with high f_{av} has lower mobility than the low f_{av} sample due to the molecular mobility. Regardless of

the different initial conversion rate depending on the f_{av} values, the NCO conversion of 90% after about 30 min reaction is safe enough for this study because the adhesive films were manufactured at 60 °C for 1 h and at room temperature for 24 h, as noted in the experimental section.

In addition to analyzing the NCO conversion in the urethane polymerization, chemical interactions between polyurethane molecules can also be analyzed using the FTIR spectroscopy. In polyurethane structure, the most intense stretching vibrations appears at the amide I mode (C=O and C−N) which is found in the range between 1600 cm^{-1} and 1780 cm^{-1}.[23–25] However, in this study, the amide I mode was overlapped with the major band position of the polyurethane adhesives including the uretonimine functional group at 1726 cm^{-1}.[13,14] Therefore, the amide II mode (mainly observed from in-plane N−H bending and C−N stretching vibrations) found in the range between 1510 cm^{-1} and 1580 cm^{-1} was utilized to examine the role of uretonimine functionality in polyurethane formations because there is no band overlapped with the uretonimine carbonyl peak in the amide II region.[26] In addition, the band position
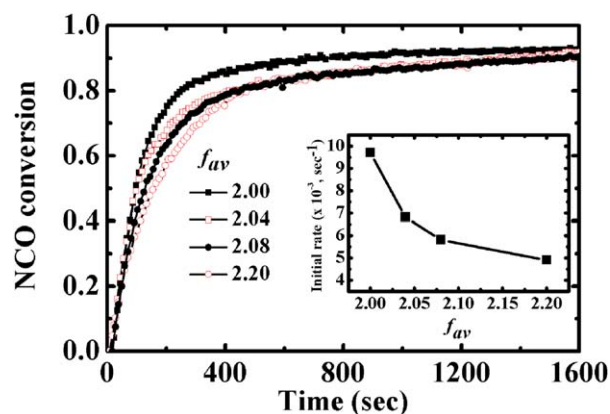
Figure 2. NCO conversion measured at 60 °C for various alcohol functionalities. The inset shows the initial conversion rate for various f_{av}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
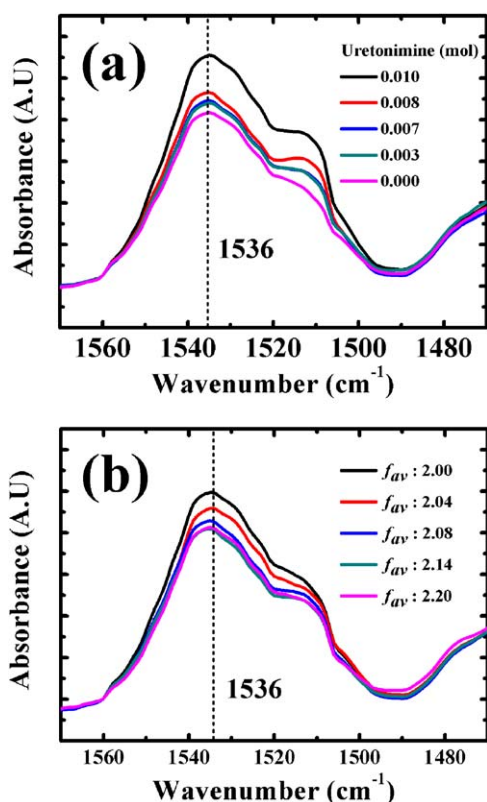
Figure 3. FTIR spectra showing the effect of hydrogen bonding for various uretonimine contents at f_{av} of 2.08 (a), and for various f_{av} at uretonimine content of 0.007 moles (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

for the hydrogen bonded urethanes in the amide II region are 1536 cm^{-1},[26] and this hydrogen bonding can be further used to understand the adhesive characteristics.

Figure 3(a) shows the FTIR absorbance spectra of the hydrogen bonded urethanes for the amide II region with various uretonimine contents. The peak absorbance increased with increasing the uretonimine content in the isocyanate composition, and it could be due to the additional nitrogen atoms included in the uretonimine structure. Furthermore, the uretonimine molecules can partially be thermal-decomposed during polymerization reactions to produce extra isocyanate functionalities,[13] and these can promote additional urethane linkages with the decomposed isocyanate groups for higher hydrogen bonding possibilities. In Figure 3(b), the FTIR absorbance spectra in amide II region with various f_{av} reveal that the increased f_{av} reduces the absorbance intensity of the hydrogen bonded urethane. It could also be due to the decreased mobility of polyurethane matrix from the high molecular triol. Therefore, these increased hydrogen bonds are expected to improve the cohesive forces of the polyurethane adhesive materials without cohesive failure.

Peel Strength

Peel strength is manifested from both the cohesive force of adhesive materials and the adhesive force between the substrate and adhesive material, and in this study it was measured with the 90° peel test method. Figure 4(a) shows the peel strength as a function

of uretonimine content for various f_{av}. For all f_{av} cases, the peel strength shows a gradual increasing tendency with increasing uretonimine content, and it can be attributed to the increased amount of hydrogen bond linkages at high uretonimine functionalities, as explained in FTIR section. Generally, high degree of hydrogen bonded urethane linkage makes polyurethane have high cohesive forces.[7] In addition, the low molecular weight of modified MDI including uretonimine linkages might lead to the higher wettability[27] with the substrates, and this increased wettability could further increase the final peel strength with increased adhesive forces. As a result, the increased amount of hydrogen bond linkages and wettability of polyurethane adhesives gave a synergistic effect on the final adhesive property.

Figure 4(b) also shows the peel strength as a function of f_{av} at the same amount of uretonimine content. In general, the peel strength is strongly dependent on wettability and cohesive forces (hard segment content, crosslinking density and hydrogen bonding). In addition to the wettability effect explained in Figure 4(a), the peel strength decreased with increasing f_{av} of alcohols, and it could be due to the decreases of hydrogen bonded urethanes and hard segment contents. As shown in FTIR analysis above, the high f_{av} and high molecular weight
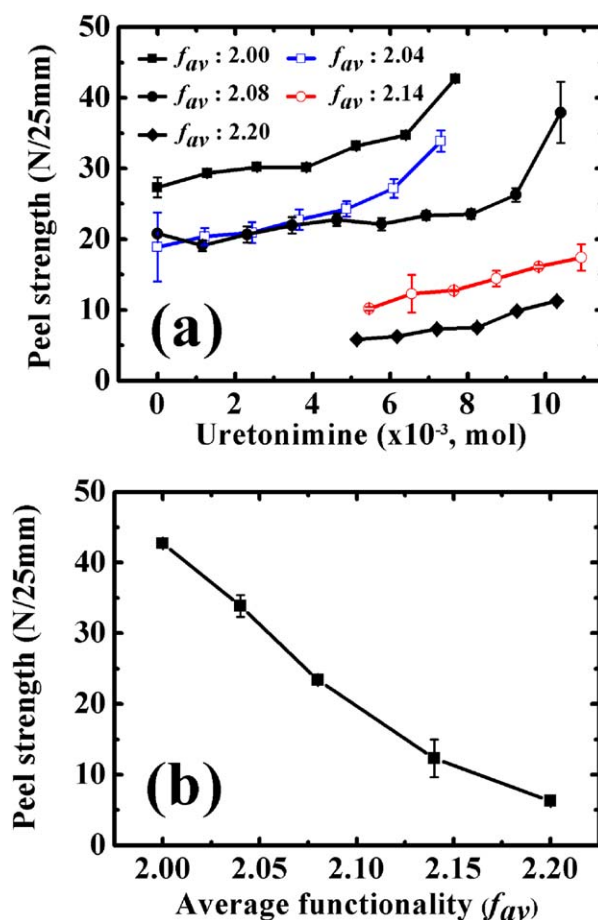

Figure 4. Peel strength as a function of uretonimine content for various f_{av}, (a), and as function of f_{av} at fixed uretonimine content (0.007 moles) (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
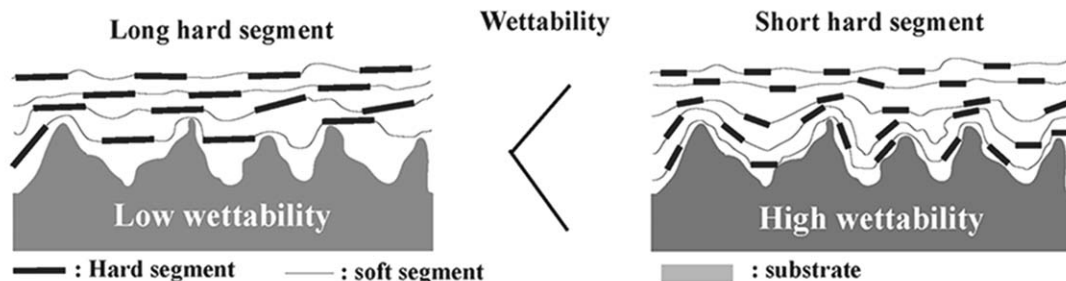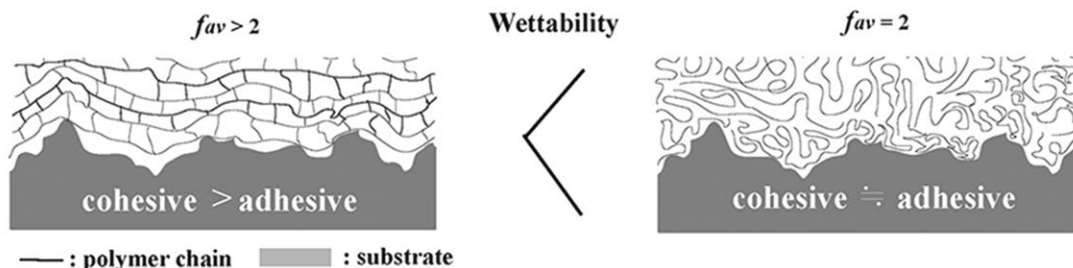
Figure 5. Scheme illustrations for high wettability depending on the length of hard segment in isocyanate (a) and f_{av} of alcohols (b).

alcohol reduce the possibility of hydrogen bonding, and it thus decreases the cohesive force of the polyurethane matrix materials. In addition, the polyol systems with high f_{av} (in Table II) include high amounts of PY3553, and thus they possess low OH values of alcohol. As a result, those polyol systems lead to the decrease of hard segment contents in the matrix at fixed NCO Index. Therefore, the peel strength of the materials including higher contents of PY3553 decreased at lower inclusions of the hard segments which can act as physical crosslinking sites in the matrix.

Schematic illustrations of adhesive forces depending on the molecular weight of isocyanates and f_{av} of alcohols are shown in Figure 5. As demonstrated in Figure 4, polyurethane synthesized with low molecular weight isocyanates containing uretonimine groups reveals higher wettability than the other case in Figure 5(a). As shown in Figure 5(b), higher f_{av} of alcohols leads to higher crosslinking units, and they increase cohesive force inside the adhesive materials. To the contrary, the increased crosslinking units reduce adhesive force between the adhesive material and the substrate surface. Therefore, isocyanates with short hard segments and low f_{av} of alcohols are strongly recommended in manufacturing polyurethane adhesive materials.

Thermal Degradation

Thermal stability of polyurethane adhesives is important in long term usages or high temperature applications. Figure 6 shows results of change of weight percentage and mass loss rate measured with differential thermal analysis for various uretonimine contents. The degradation of all polyurethane samples started at about 300 °C, but the 50% degradation and final degradation temperatures increase with increasing uretonimine contents. It

could be due to the additional hydrogen bonding arisen from the nitrogen atoms and carbonyl groups in the uretonimine functionalities. For example, Figure 6(a) shows the 50% degradation temperatures with no and 0.011 moles of uretonimine at 453 and 509 °C, respectively. Degradation plots for the mass loss rates in Figure 6(b) show additional peaks in cases of inclusions of uretonimine linkages, and these could be due to the second degradation steps of the uretonimine linkages. In addition, thermal stability of polyurethane chains is also related to the degree of internal hydrogen bonding.[28] Therefore, application of the uretonimine linkages in manufacturing polyurethane adhesives is advantageous for improving thermal stability of materials.

CONCLUSIONS

Polyurethane adhesive materials were fabricated using various types of isocyanates and various average functionalities of alcohols. The isocyanates consisted of monomeric MDI, modified MDI including carbodiimide or uretonimine linkage, polymeric MDI, and TDI. The alcohol functionalities were varied by mixing low molecular weight diols with high molecular weight triols. Polyurethane adhesive properties were strongly dependent on the f_{av} of alcohol and uretonimine contents in the isocyanate. As uretonimine contents increased, the chance of forming internal hydrogen bonding increased due to the carbonyl groups and nitrogen atoms in uretonimine linkages. Thus, the peel strength of the material increased with increasing cohesive forces of polyurethane adhesives. At high number of f_{av} of alcohols, high numbers of crosslinking units were introduced in the polyurethane chains, and this high crosslinking decreased wettability of material to the substrate. Therefore, high f_{av} of alcohols led to low peel strength of materials due to the reduced
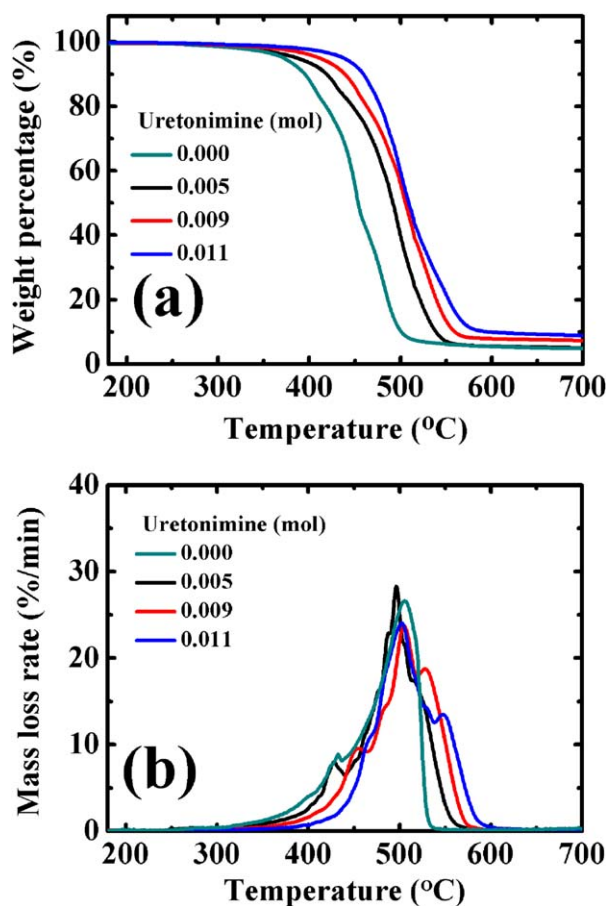
Figure 6. Change of weight percentage (a) and thermogravimetric mass loss rates (b) of polyurethane adhesives for various uretonimine contents. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

adhesiveness between the material and substrate surface. Finally, thermal stability of polyurethane adhesives was much improved with uretonimine linkages in isocyanates due to the additional hydrogen bonding.

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: Hard segment   : soft segment

$fav > 2$ $fav = 2$

: polymer chain   : substrate