말단 수산화기를 가진 폴리락타이드와 이미다졸로 블록된 이소시아네이트를 이용한 폴리우레탄 바이오접착제의 합성 및 물성 평가

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Preparation and Characterization of Polyurethane Bioadhesive from Hydroxyl-terminated Polylactide and Imidazole-blocked Isocyanate

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Abstract: A series of novel imidazole-blocked diisocyanate bioadhesives (IBAs) were synthesized from reaction of toluene 2, 4-diisocyanate (TDI), isophorone diisocyanate (IPDI), hydroxyl-terminated polylactide (HO-PLA-OH), 1,1,1-trimethylolpropane (TMP), and imidazole. Synthesis of IBAs was confirmed by Fourier transform infrared spectroscopy (FTIR) and gel permeation chromatography (GPC). Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) revealed that the TDI-based IBA had lower thermal dissociation temperature and a faster deblocking rate than IBA based on IPDI. Hydroxyl-terminated polyurethane (HPU) was introduced to study the adhesive effect of the synthesized IBAs. Improvement on elastic modulus, tensile strength and water resistance of IBA-modified HPU in comparison with neat HPU suggested the good adhesive effect of IBA due to the strong chemical reaction between released NCO groups from IBA and hydroxyl groups from HPU.

Keywords: polyurethane adhesive, biodegradable, blocked isocyanate, hydroxyl-terminated polylactide.

Introduction

Polyurethanes have a wide range of applications such as coatings, adhesives, foams, textiles, membranes, elastomers, and so on.[1-5] Despite the possibility of tailoring their properties according to requirements, polyurethane suffers a serious disadvantage of poor mechanical strength, solvent and water resistance due to the linear structure. A solution to overcome these drawbacks is the use of reactive polyisocyanate.[6] A rapid reaction between a polyfunctional isocyanate and a hydroxyl-terminated oligomer leads to a urethane linkage.

Reactions of isocyanates are widely used to crosslink and extend chain length of polymers.[7,8] The main feature of isocyanate chemistry is their high reactivity toward nucleophiles,

e.g., reaction with alcohols to form urethanes readily occurs at room or slightly higher temperatures, and this is the basis of polyurethane technology.[9] However, in certain situations, this high reactivity, particularly toward water, can be a problem. As water is difunctional, chain extension or crosslinking results. The high reactivity and high toxicity of isocyanates do not allow their storage or use in the practical applications. These problems can be reduced by conversion to derivatives, known as blocked isocyanates.[10] They have a bright future in the field of powder coatings[11,12] and heat setting adhesives.[13-16]

Blocked isocyanate or polyisocyanate is an adduct containing a comparatively weak bond formed by the reaction of an isocyanate with a compound containing an active hydrogen atom. At elevated temperatures, this reaction tends to proceed in a way that leads to the regeneration of the isocyanate and the blocking agent. The regenerated isocyanate can react with a coreactant containing hydroxyl functional groups to form ure-

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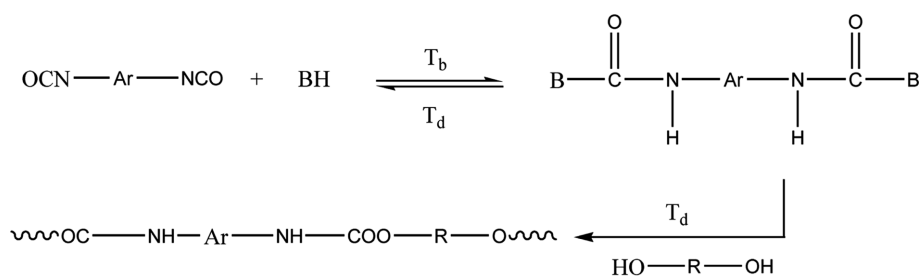
where BH= Blocking agent; T_b= Blocking temperature; T_d= Deblocking temperature.

Figure 1. Regeneration of isocyanate and its reaction with hydroxyl group.

thane, with its thermally more stable bonds. The overall reaction in a typical polyurethane heat-curable system is described as Figure 1.

Deblocking temperature of the blocked isocyanate is a crucial limiting factor in industrial applications. Generally 160 °C with 30 min duration or lower is preferable. This temperature is specific for a particular blocking agents. Commercial blocking agents include phenol, caprolactam, methyl ethyl ketoxime, amines, dimethyl pyrazoles, diethyl malonates, sodium bisulte and many others.[17-20] The rate and extent of deblocking reaction depend on many factors: the structure of isocyanate and blocking agent including substituents, solvents, catalysts, temperature and the thermal stability of the isocyanate-blocking agent bond.[21]

Recently, biodegradable polyurethane products are expected to be suited for applications requiring the use of a flexible elastic material such as soft tissue engineering such as skin and vasculature.[22-25] However, their mechanical properties including solvent, water, scratch, and abrasion resistance properties are poor due to the linear structure. All these drawbacks can be improved by crosslinking the polyurethane chains using isocyanate adhesive.

A novel bioadhesive from blocked diisocyanate has been described in this paper. Imidazole as the blocking agent and HO-PLA-OH as the degradable segment are introduced into the backbone of the prepared isocyanate bioadhesive. The blocking, deblocking and crosslinking reactions of released isocyanates of different structure and effect of the isocyanate structure on various properties of such kind of isocyanate bioadhesive were investigated and compared.

Experimental

Materials. The materials used to prepare bioadhesives from imidazole-blocked diisocyanate were given in Table 1. HPU

Table 1. List of Raw Materials Used in the Preparation of IBAs

Designation	Chemical description	Suppliers
TDI	Toluene 2,4-diisocyanate	Aldrich, USA
IPDI	Isophorone diisocyanate	Aldrich, USA
Imidazole	Imidazole	Fluka, Switzerland
HO-PLA-OH	Hydroxyl-terminated polylactide; M_n=2000 g/mol	NatureWorks, USA
TMP	1,1,1-Trimethylolpropane	Fluka, Switzerland
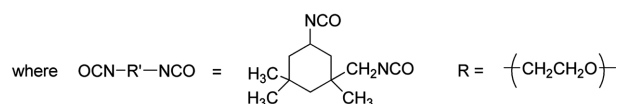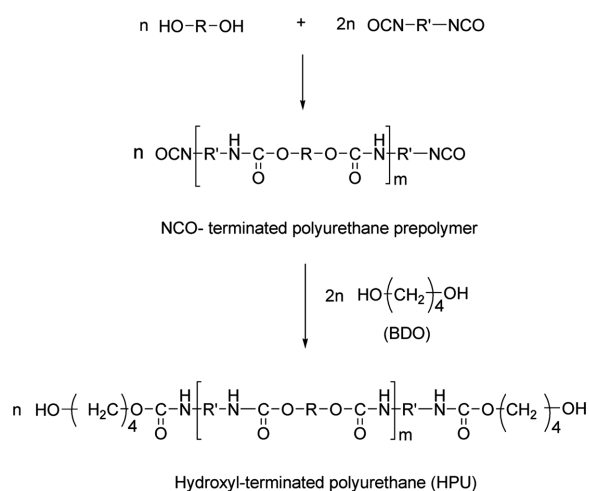
Scheme 1. Synthesis of hydroxyl-terminated polyurethane (HPU).

was synthesized in our lab and its structure is depicted in Scheme 1. All the materials were laboratory grade chemicals and were used as received without any further purification.

IBAs Preparation. The reaction scheme shown in Scheme 2 outlined the synthetic process used to prepare imidazole-blocked polyurethane bioadhesives. Diisocyanate (TDI and
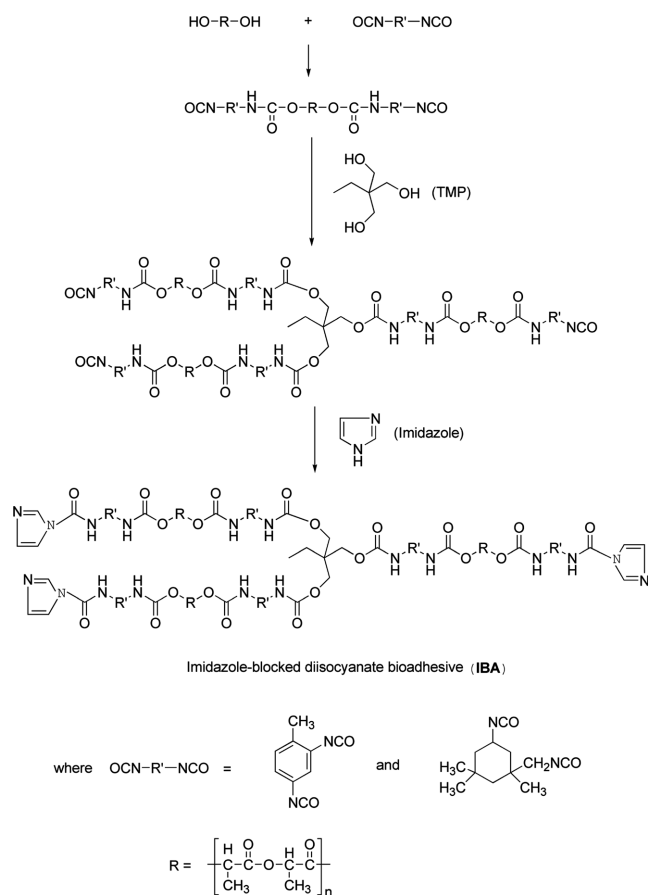
Scheme 2. Synthesis of imidazole-blocked diisocyanate bioadhesives (IBAs).

Table 2. Composition of Imidazole-blocked Diisocyanate Bioadhesives (Weight in Grams)

Adducts	TDI	IPDI	HO-PLA-OH	TMP	Imidazole
TDI-IBA	34.80	-	160	5.37	8.17
IPDI-IBA	-	22.23	80	2.68	4.09

IPDI) and HO-PLA-OH in acetone were firstly charged into the reaction kettle equipped with a mechanical stirrer, nitrogen inlet, and reflux condenser. The reaction mixture was heated to 75 °C for TDI-based prepolymer and 90 °C for IPDI based prepolymer in a constant temperature water bath and the reaction was carried out until theoretical NCO content was reached. The change in NCO content during reaction was determined using a standard di-n-butylamine back titration method.[26] Then, 1,1,1-trimethylolpropane (TMP) was added to the reaction mixture. During the reaction, the change in isocyanate content was determined by using the same method mentioned above until the theoretical end point was reached which was approximately about 3 h of reaction. Then the reaction mixture

was cooled down to 50 °C and the calculated amount of imidazole diluted with 50 mL of acetone, was slowly added. The reaction was further carried out under 85 °C until no NCO peak could be detected in the FTIR spectrum. The reaction product was obtained by vacuum drying of the final reaction mixture. All the experiments were carried out without catalyst to avoid side reaction. Recipe of each blocked adducts was given in Table 2.

HPU/IBA Films Formation and Curing. Films of pure HPU and HPU/IBA composite films by incorporating 1 wt% and 3 wt% TDI-IBA (named HPU-TA-1 and HPU-TA-3) and IPDI-IBA (named HPU-IA-1 and HPU-IA-3) were prepared using solution casting method. The composites were mixed and run in a Waring Blender for 5 min. The blender was used to thoroughly stir the two dispersions together. The formulations were then cast onto Petri dishes greased with silicone and left to evaporate at room temperature for 24 h. The samples were then dried in an air circulation oven at various deblocking temperatures (100, 120, and 140 °C). The temperature was fixed around the deblocking temperature to cause the reaction between HPU and IBA. After different curing time (15, 30, and 60 min) of baking, the films were removed from the air circulation oven and kept in vacuum oven at room temperature for 24 h before the test and characterization.

Measurements. FTIR spectra of samples were recorded using an RFX-65A IR analyzer in the range 400~4000 cm^{-1} using KBr disks at room temperature.

The weight-average molecular weight (M_w), number-average molecular weight (M_n), and polydispersity index (PDI; M_w/M_n) were determined by the gel permeation chromatography (GPC) using Waters 1515 Separation Module equipped with a 2414 Differential Refractive Index Detector. The operating temperature was 40 °C, the mobile phase was THF, and the flow rate was 1.0 mL/min. Calibration was performed using narrow molecular weight distribution polystyrene standards.

DSC (DSC Q200 TA instrument) measurements were conducted with a heating rate 10 °C/min and a dry nitrogen atmosphere over the range of -50 to 250 °C. TGA (TGA Pyris-1) was carried out with a Perkin Elmer Model TGA Pyris1 thermo-gravimetric analyzer. The sample weight was 8~10 mg. The experimental run was performed from 30 to 600 °C at a heating rate of 20 °C/min under nitrogen atmosphere with a gas flow rate of 30 mL/min.

Tensile properties of dispersion-cast films were measured using a universal testing machine (RGM-3030, Shenzhen

Reger Instrument) at a cross-head speed of 50 mm/min. Films containing IBAs were baked at various deblocking temperatures (100, 120 and 140 °C) for 30 min. Sample specimens were prepared from the films with a die of dimensions of 10 mm width and 50 mm length, the grip distance was set at 25 mm. The thickness of the film was 1.0~1.2 mm. For each sample, five specimens were tested and the average value was reported.

Water resistance of neat HPU and IBA modified HPU films were tested as follows: Pre-weighed dry slabs (50×10×1 mm in size) were immersed in deionized water for 1 week to study water resistance at room temperature. After immersing, the samples were blotted with a laboratory tissue and weighed. The water absorption was expressed as the weight percentage of water in the swollen sample:

$$\text{Water absorption } (\%) = (W_W - W_D)/W_D \times 100\%$$

Where, W_D is weight of the dry sample and W_W is the weight of the swollen sample.

Results and Discussion

Characterization. A series of novel IBAs with biodegradability as well as strong reactivity were synthesized with diisocyanate (TDI and IPDI), HO-PLA-OH, TMP, and imidazole by a general prepolymer process in an acetone solution. The IBAs were designed to be used as adhesive for hydroxyl functional polymers. Blocked polyisocyanates were introduced due to many technical and economic reasons such as marked reduction of moisture sensitivity and elimination of toxicity associated with the free isocyanates. In addition, their deblocking temperature could be tailored by choosing blocking agent type or use of catalysts. The blocking agent (imidazole) used in this study is highly reactive with isocyanate, so no catalyst was added to avoid any undesirable side reactions, such as dimerization or trimerization of isocyanate.

Characterizations of the synthesized IBAs were performed by FTIR and GPC. FTIR spectra of imidazole-blocked isocyanate adhesive were identical and showed no absorption in
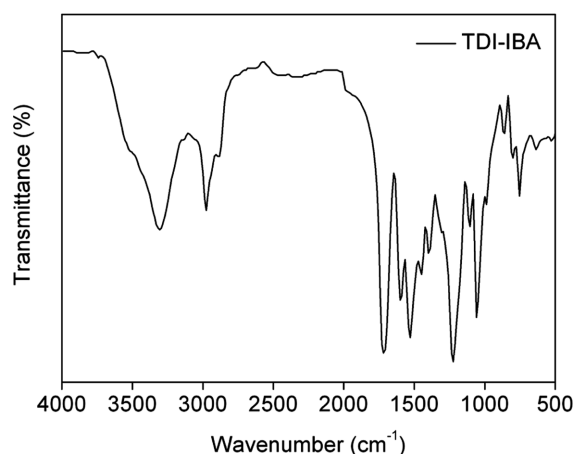
Figure 2. FTIR spectrum of imidazole-blocked bioadhesive (TDI-IBA).

the 2250-2270 cm^{-1} range, which indicated that the NCO groups of the diisocyanate molecules were completely blocked by imidazole. Strong absorptions at around 3325-3400 cm^{-1} (N-H stretching), 1700-1730 cm^{-1} (C=O stretching), 1530-1560 cm^{-1} (N-H bending), 1210-1240 cm^{-1} (the stretching vibration of C=O group of urea combined with the N-H group) confirmed the imidazole-blocked diisocyanate adhesive formation. A typical spectrum of imidazole-blocked diisocyanate adduct based on TDI was shown in Figure 2.

The molecular weight of the blocked polyisocyanates determined by GPC was given in Table 3. The data showed that the weight-average molecular weight (M_w) and number-average molecular weight (M_n) of TDI-IBA was higher than IPDI-IBA, which was due to the lower reactivity of IPDI (27). The low reactivity of IPDI was attributed to the presence of aliphatic group in the molecule, which increased the electron density on the nitrogen atom and decreased the electrophilicity of the central carbon atom of the isocyanate bond. In general, electron-withdrawing groups increase the reactivity of the isocyanate while electron donor groups decrease it. Polydispersity of IPDI-IBA slightly lower than TDI-IBA was also due to the high reactivity of TDI.

Deblocking Temperature. The onset of deblocking reaction has been determined by many analytical techniques.[27] It
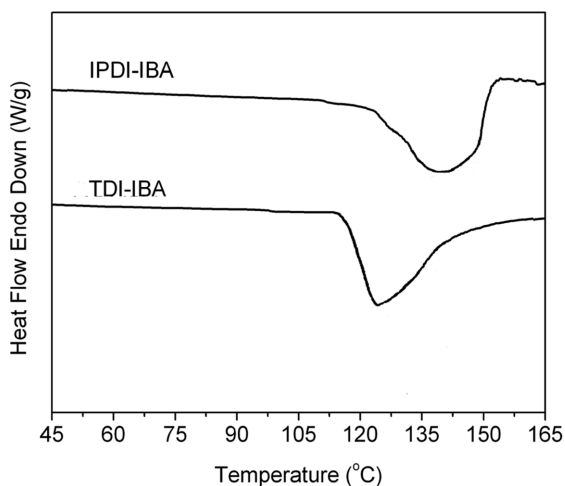
Table 3. Molecular Weight and Deblocking Temperature of TDI- and IPDI-IBA

Adducts	M_w (g/mol)	M_n (g/mol)	PDI	Deblocking temperature (°C)			
				DSC		TGA	
				T_{in}	T_{ma}	T_{in}	T_{ma}
TDI-IBA	15031	8896	1.69	110	125	100	155
IPDI-IBA	12048	7014	1.72	120	138	125	160

should be noted that different analytical techniques can give different deblocking temperatures for the same sample. In our study, DSC and TGA techniques were used to determine the deblocking temperature of the prepared imidazole-blocked diisocyanate adhesives.

DSC is one of the most common techniques for the determination of the deblocking temperature. The presence of an endothermic transition in DSC thermograms of the blocked isocyanate may be assigned to the deblocking reaction. DSC thermograms can appear an endothermic peak that is related to urethane scission taking place upon heating.[28] The deblocking temperature depends on the isocyanates and blocking agents.

Figure 3 showed the DSC results. It can be found that the DSC curves showed broad endotherm around 110-150 °C for TDI-IBA and 120-160 °C for IPDI-IBA. The obtained initial deblocking temperature (T_{in}) and maximum deblocking temperature (T_{ma}) of the imidazole-blocked diisocyanates by DSC measurement were given in Table 3. The broad deblocking temperature range may be due to slow and controlled release of imidazole. In addition, the melting of the short- and long-range order in hard segment domains of polyisocyanate might take place at these temperature ranges where deblocking might occur.[29] The deblocking temperature of imidazole-blocked diisocyanate adhesives determined by DSC was in the following order: IPDI-IBA > TDI-IBA. This suggested the fact that aromatic isocyanate deblocked at lower temperature than aliphatic isocyanate. Since the carbonyl carbon of the urethane group has a partial positive charge, the bond between the carbon and oxygen of the blocking agent will be more labile due to the reduction of the negative charge density of the carbonyl

carbon through resonance in the aromatic ring.

TGA is also a useful technique to find the deblocking temperature. The TGA/DTG curves of (a) TDI-IBA and (b) IPDI-IBA were depicted in Figure 4, respectively. TGA measured the changes in sample weight over a specified temperature range.[30] The detailed dissociation temperatures of the blocked TDI- and IPDI-IBA by TGA were listed in Table 3. As can be seen, the onset temperature of weight loss was in the following order, as same the results of DSC measurements: IPDI-IBA > TDI-IBA. We observed that weight loss of blocked IPDI-IBA started at higher temperature compared to blocked TDI-IBA which was related to higher electron density on nitrogen atoms in aromatic compounds. In addition, it was found that the deblocking temperature obtained by TGA is different from that measured by DSC. This was due to differences in sample pans and thermal effects in these two instruments.[7] Compared to the DSC results, the deblocking temperature measured by TGA is slight greater in our research.

Tensile Properties of HPU/IBA Films. Effects of the addition of IBAs on the tensile properties of the HPU dispersion cast films were evaluated and given in Table 4. Tensile prop-
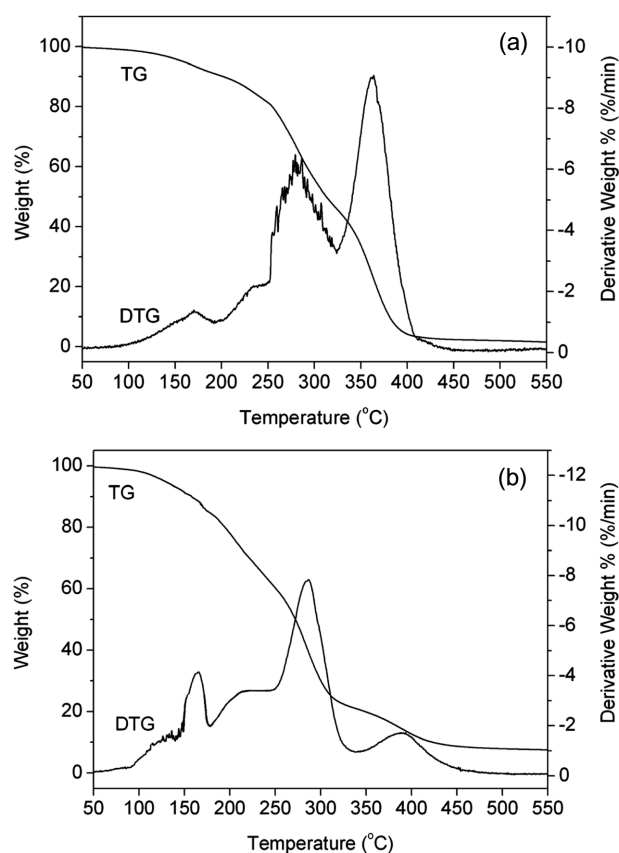
Figure 4. TGA/DTG curves of (a) TDI-IBA; (b) IPDI-IBA.

**Figure 3.** DSC curves of imidazole-blocked TDI and IPDI bioadhesive.

Table 4. Tensile Properties of Neat HPU and IBA Crosslinked HPU Films at Various Temperatures (100, 120, and 140 °C) at Different Times (15, 30, and 60 min)

Crosslinking temperature/Time	Tensile properties	Samples				
		HPU	HPU-TA-1	HPU-TA-3	HPU-IA-1	HPU-IA-3
Room temperature	EM(MPa)	2.71	-	-	-	-
	TS(MPa)	3.80	-	-	-	-
	EL(%)	>700	-	-	-	-
100 °C/30 min	EM(MPa)	-	5.44	8.50	3.33	6.75
	TS(MPa)	-	9.81	15.06	6.84	10.57
	EL(%)	-	>600	>500	>600	>500
120 °C/30 min	EM(MPa)	-	5.97	9.86	3.84	7.14
	TS(MPa)	-	12.67	18.45	7.76	13.69
	EL(%)	-	>500	428	>500	>500
140 °C/15 min	EM(MPa)	-	6.52	10.09	5.17	7.66
	TS(MPa)	-	12.78	19.16	8.66	15.65
	EL(%)	-	>500	402	>500	478
140 °C/30 min	EM(MPa)	-	7.18	11.50	5.32	9.45
	TS(MPa)	-	17.40	22.86	11.10	18.32
	EL(%)	-	456	350	>500	430
140 °C/60 min	EM(MPa)	-	6.98	11.42	5.31	9.20
	TS(MPa)	-	16.12	21.98	10.96	16.89
	EL(%)	-	448	348	487	480

erties such as elastic modulus (EM), tensile strength (TS), and elongation at break (EL) were tested and discussed. We found that HPU films containing IBA exhibited higher elastic modulus, tensile strength, and slight lower elongation than neat HPU. This is due to the strong interfacial adhesion of IBA modified HPU films, which is formed by the released NCO groups reacting with the hydroxyl groups of HPU around deblocking temperature. The variations in the tensile properties with diisocyanate (TDI and IPDI) were also studied in terms of the content of IBA, crosslinking temperature, and curing time.

Generally, elastic modulus and tensile strength increase with an increase in crosslinking density whereas elongation at break decreases. During the crosslinking reaction, the increased crosslinking density resulted in higher elastic modulus, tensile strength, and lower elongation at break. In addition, the elastic modulus, tensile strength, and elongation at break were affected by the changes in diisocyanate, crosslinking temperature, and curing time. It was found that TDI-IBA crosslinked HPU films showed higher elastic modulus, tensile strength in comparison with the ones crosslinked by IPDI-IBA.

Compared to the aliphatic structure of IPDI, the aromatic structure of TDI led to better polymer chain ordering and rigid structure favoring better tensile properties.[31] In addition, more ordered structure of the hydrogen bonds between the urethane groups in the hard segment of TDI-IBA resulted in better tensile properties, whereas, due to the aliphatic ring structure of IPDI, the hydrogen bonds were partly disrupted.[32] But the higher reactivity of TDI might result in increasing in rigidity of polymers, which subsequently reduced the value of elongation at break. Due to the electronic effect, blocked isocyanates based on aromatic isocyanates de-blocked at lower temperature, and thus the reactivity of the regenerated aromatic NCO group was higher than that of the aliphatic NCO group towards the hydroxyl groups. In the cases of crosslinking temperature and time, we observed that the samples under higher temperature displayed better tensile properties and 30 min was a proper curing time. This may be due to the crosslinking process related to the deblocking reaction, which could be increased by increasing the deblocking temperature. Higher curing temperature led to rapid de-blocking reaction and increased in the concentration of released NCO groups.
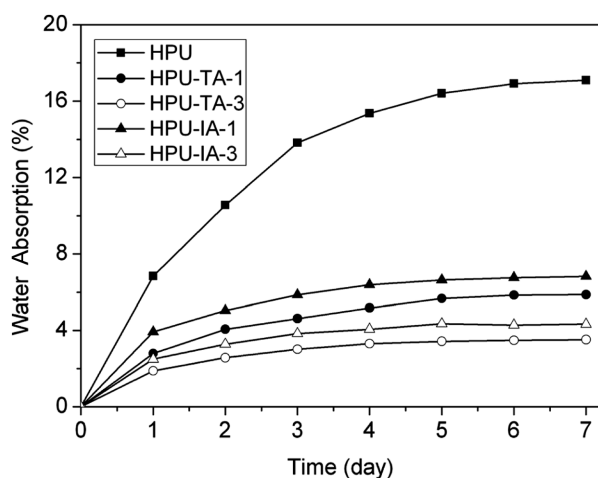
Figure 5. Effects of the addition of TDI-IBA and IPDI-IBA on water absorption of HPU films.

Water Resistance of HPU/IBA Films. Effects of the addition of IBAs on the water absorption of the HPU dispersion cast films were investigated and shown in Figure 5. All the used IBA modified HPU films for water absorption testing were the samples cured at 140 °C for 30 min. As can be seen, the water absorption for all specimens increased greatly during the first 4 days and then leveled-off. Compared to the samples with and without IBA, absorption amount and time to reach the plateau for all samples with IBA were smaller and shorter than the ones without IBA, which indicated that the addition of IBA resulted in the less hydrophilicity. This can be explained by the improvement of internal adhesion due to the crosslinking effect of IBA from the reaction of released NCO groups with the hydroxyl groups of HPU. In addition, it was also found that the water absorption amount of TDI-IBA crosslinked HPU samples showed less than the ones crosslinked by IPDI-IBA. This should be due to the higher reactive of TDI-IBA resulting in the faster crosslinking reaction and higher crosslinking density. This result is accordance with our tensile test in this study.

Conclusions

In this study, a series of novel imidazole-blocked diisocyanate bioadhesives based on diisocyanate (TDI and IPDI), HO-PLA-OH, and TMP were successfully synthesized and their relative properties were investigated and discussed. FTIR and GPC were used to characterize their chemical structures. Deblocking temperatures were determined by DSC and TGA techniques. The results showed that TDI-IBA had lower

deblocking temperature in comparison with IPDI-IBA and the deblocking temperatures determined by TGA were greater than those determined by DSC. However, deblocking temperatures obtained from DSC and TGA reflected the same trend. The adhesive properties of prepared IBAs were demonstrated by comparing with the tensile properties and water resistance of IBAs modified HPU films and neat HPU film. Better tensile properties and water resistance of IBA modified HPU films compared to neat HPU indirectly showed the good adhesive effect of prepared IBAs, which indicated that IBA as an adhesive indeed enhanced the interfacial adhesion by crosslinking reaction between released NCO groups from IBA and hydroxyl groups of HPU.

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