

# Microwave-Assisted Synthesis of Hydroxyl-Terminated Polybutadiene Based Polyurethanes with Superior Properties

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## ABSTRACT

*This study focuses on the microwave-assisted synthesis of hydroxyl-terminated polybutadiene (HTPB) based polyurethanes. Driven by microwave irradiation, the synthetic rate of HTPB based polyurethanes is three times faster than the synthesis operated by traditional oil-bath heating. Though the synthesis time is significantly decreased, polyurethanes synthesized with microwave irradiation exhibit comparable mechanical performances to the similar polyurethanes obtained by traditional oil-bath heating. The tensile strength and Young's modulus of polyurethanes synthesized with microwave irradiation are also higher than conventional method. HTPB based polyurethanes also exhibit excellent thermal stability and hydrolysis resistance. Our research suggests a fast and interesting way to synthesize HTPB based polyurethanes.*

KEYWORDS: *Polyurethanes, HTPB, Mechanical properties, Microwave*

## INTRODUCTION

Polyurethanes, high strength, tear resistant, abrasion resistant polymer materials, are widely used in the civilian, industrial and medical fields<sup>[1,2]</sup>. The polyolsoligomer to synthesize polyurethanes mainly contains polyether, polyester and polyolefinpolyols. Compared to

polyether and polyester polyols, polyolefin polyols possess the lower polarity due to the absence of polar ether bonds and ester bonds. Thus, polyolefin polyurethanes exhibit excellent elasticity and good hydrolytic stability. As the most common polyolefin polyurethanes, hydroxyl-terminated polybutadiene (HTPB)

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based polyurethanes, are mainly used for adhesives, sealant, coating, membranes, etc.<sup>[3-8]</sup>.

Normally HTPB based polyurethanes were synthesized from HTPB, diisocyanates and chain extender under oil-bath heating, which required long reaction times. Microwave-assisted heating for chemical synthesis reduced the reaction time dramatically<sup>[9-13]</sup>. Furthermore, since microwave irradiation produces efficient internal heating by direct coupling of microwave energy with the polar molecules that are present in the reaction mixture<sup>[14,15]</sup>. The reactions under microwave irradiation require less energy than traditional processes, Microwave heating provides a uniform reaction environment<sup>[16, 17]</sup>, thus speeding up the steps of realizing large-scale industrial production of high-quality advanced materials. Due to all those advantages, microwave irradiation has been applied in many fields, such as organic and medicinal syntheses<sup>[18, 19]</sup>, polymer synthesis<sup>[20]</sup>, material sciences<sup>[21]</sup>, nanotechnology<sup>[22]</sup> and biochemical processes<sup>[23]</sup>. Biswas and coworkers had prepared polyurethanes from starch or maltodextrin and tolylene-2,4-diisocyanate with the assist of microwave irradiation<sup>[24]</sup>, and then they synthesized cyclodextrin polyurethanes under microwave irradiation<sup>[25]</sup>. In both study, they found that microwave heating saved energy, significantly reduced reaction time, and obtained similar or improved yield compared to traditional heating. Besides, Hiroki and coworker<sup>[26]</sup> have reported that microwave irradiation not only accelerated the polymerization of a fluorene unit-containing diol and diisocyanates, but also increased the molecular weights of

synthesized polyurethanes.

We would like to focus on the synthesis of several HTPB based polyurethanes from HTPB, various diisocyanates and 1, 4-butanediol by means of microwave-assisted method. The synthesis efficiency will be systemically exhibited in this study. Besides, the mechanical properties of HTPB based polyurethanes synthesized under microwave heating will be compared to those obtained under traditional oil-bath heating. The relationship between the structures and properties of HTPB based polyurethanes is also discussed.

## EXPERIMENTAL

### Materials

HTPB with number-average molecular weight of 1800g/mol was provided by Zibo Qilong Chemical Industry Co., Ltd. and dried under vacuum at 100°C over 2h for further use. DMF (N,N-dimethylformamide, >99.5%) and toluene (>99.5%) were obtained from Sinopharm Chemical Reagent Co., Ltd. and dried with molecular sieve. HMDI (4,4'-dicyclohexylmethane diisocyanate, > 90.0%) was supplied by TCI. IPDI (isophoronediiisocyanate, >99.0%), DBTDL (dibutyltin dilaurate, >95.0%) and 1,4-butanediol (>99.0%) were purchased from Aladdin Reagent. Phosphate buffered saline (PBS) was supplied from Sigma-Aldrich. All the other chemicals were in chemical grade and used without further purification.

### Synthesis of HTPB based polyurethane

HTPB based polyurethanes were synthesized following a two-step procedure (Scheme 1): reaction of HTPB with diisocyanate under 70°C to form NCO-terminated polyurethane prepolymer (the first step) with subsequent chain extension step by adding certain amount of 1,4-butanediol to the solution of polyurethane prepolymer under 80°C (the second step). The procedure was conducted in round bottom flask which was respectively heated by oil bath and a microwave reactor (M Wave-5000, Shanghai Xinyi) with a

frequency of  $2450 \pm 50$  MHz, output power from 0 to 1000 W and IR sensing temperature controller.

Instruments Q800 DMA operated in the tensile mode, at 1 Hz and from  $-100^\circ\text{C}$  to  $100^\circ\text{C}$  at  $3^\circ\text{C}\cdot\text{min}^{-1}$ .

#### Structural characterization

Fourier transform infrared (FTIR) analysis was performed using a Nicolet 6700 infrared spectrometer. The spectra ( $4000\text{--}400\text{cm}^{-1}$ ) were recorded with a resolution of  $0.9\text{cm}^{-1}$  and 32 scans per sample.

#### Mechanical properties

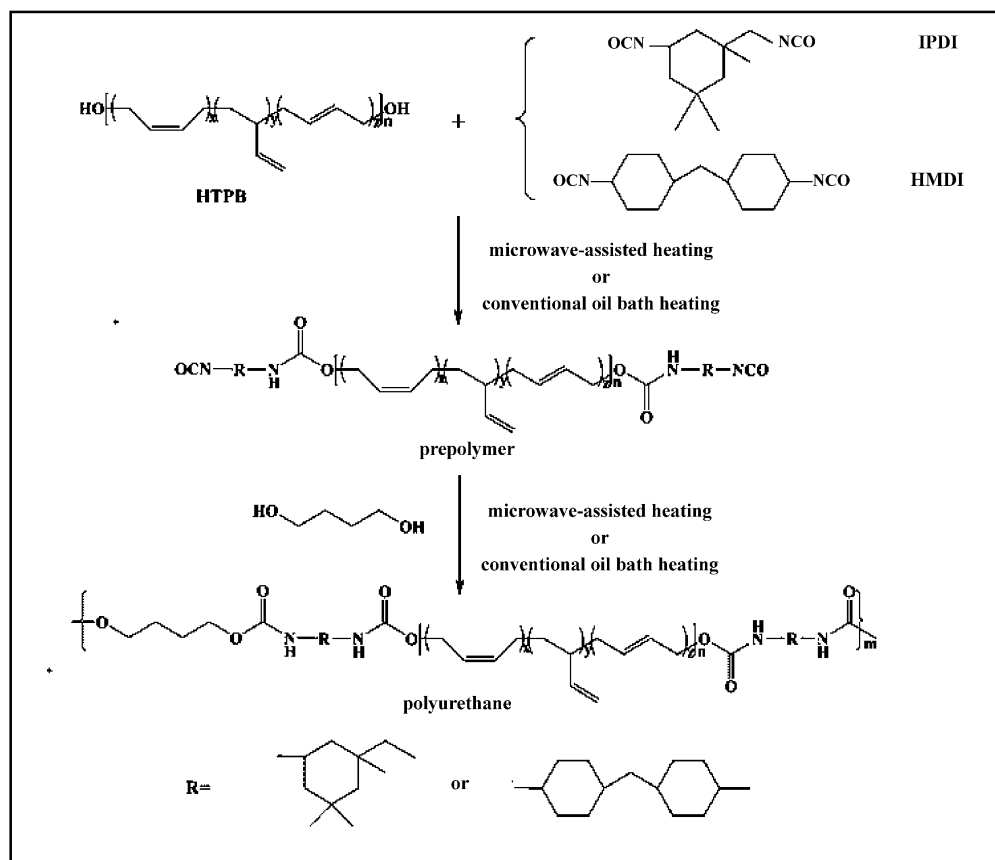
The tensile properties of polyurethanes before and after hydrolysis in PBS solution were measured using a Instron 5567 Universal Material Testing Machine with a crosshead speed of  $100\text{mm}\cdot\text{min}^{-1}$  at  $25^\circ\text{C}$ . Storage modulus ( $E$ ) and loss factor ( $\tan \delta$ ) values were determined with a TA

#### Thermal properties

Thermogravimetric analysis (TGA) was carried out in nitrogen atmosphere on a Mettler-Toledo TGA/DSC1 Thermogravimetric Analyzer. The samples in aluminum crucible were heated from  $50^\circ\text{C}$  to  $800^\circ\text{C}$  with a heating rate of  $20^\circ\text{C}\cdot\text{min}^{-1}$ .

#### Hydrolysis test

Tensile splines of polyurethane samples were immersed in phosphate buffered saline solution ( $\text{pH}=7.4$ ) at  $37^\circ\text{C}$ . After a certain time, tensile splines were taken out and then dried to constant weight.



Scheme 1. Synthetic route for polyurethanes.

## RESULTS AND DISCUSSION

### Synthesis of polyurethane

IPDI, HMDI are used as the diisocyanate to prepare polyurethanes. The mole ratios of HTPB/diisocyanate/1, 4-butanediol equals 1/4/3, 1/6/5 and 1/8/7, respectively. All polymerizations show a rather high yields about 90% and the molecular weights of all the polyurethanes are around  $1.6\text{--}1.9 \times 10^4$  g/mol. The corresponding amount of hard segment of synthesized polyurethanes are 39%, 42%, 50%, 53%, 57%, and 60%, respectively. The typical functional groups of polyurethanes are revealed by FTIR spectroscopy as shown in Figure 1. The N-H stretching vibration peaks and C=O stretching ones are clearly observed at around  $3330$  and  $1700$   $\text{cm}^{-1}$ , respectively. At the same time, no absorption band at  $2270$   $\text{cm}^{-1}$  is observed, which indicates that all the -NCO groups are

reacted with -OH groups. According to FTIR spectra between  $1670$  and  $1760$   $\text{cm}^{-1}$ , the hydrogen-bonding association (HBA) of carbonyl group, which can be used to characterize the microphase separation between hard and soft domains, can be calculated by resolving the overlapped peak into two independent spectral peaks<sup>[27,28]</sup>. FTIR peak-fit images and calculation results of HBA are shown in Figure 2 and Table 1.

### Comparison between microwave-assisted heating and traditional oil-bath heating

The reaction rates of the polymerization are characterized by the reaction time. As shown in Table 2, compared to traditional oil-bath heating method, microwave synthesis of both HMDI-42 and IPDI-39 are about three times faster. To further observe the difference in the process of polymerization, the conversion of HTPB in the first step and conversion of isocyanato in the

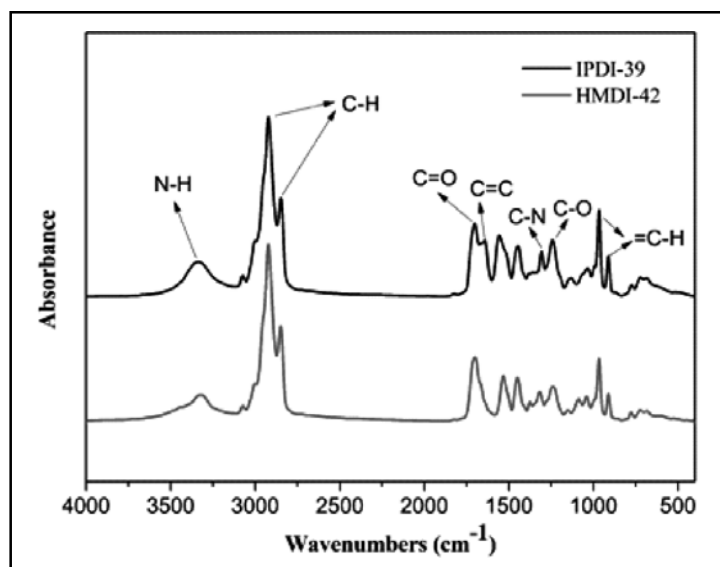


Figure 1. FTIR spectra of polyurethanes

second step at different reaction time under microwave-assisted heating or traditional oil-bath heating are determined. Conversion of HTPB is calculated by the NCO content in prepolymer which is determined by titration with di(*n*-butyl)amine. Conversion of isocyanato in the second step is determined by NCO peak which is located at  $2270\text{ cm}^{-1}$  on the Fourier transform infrared spectra (Figure 3), and the NCO peak area is normalized according to C=C peak (at  $1640\text{ cm}^{-1}$ ) area. The corresponded results are

showed in Figure 4. Compared with traditional oil-bath heating method, synthesis driven by microwave irradiation significantly promotes the rate of polymerization especially when the reaction is closed to completion. Further comparison with reported literatures<sup>[5,29]</sup> also demonstrates that microwave radiation speed up the polymerization process. As we all know, the effect of microwave irradiation on chemical processes is still debatable. Both non-thermal and thermal effects have been mentioned to

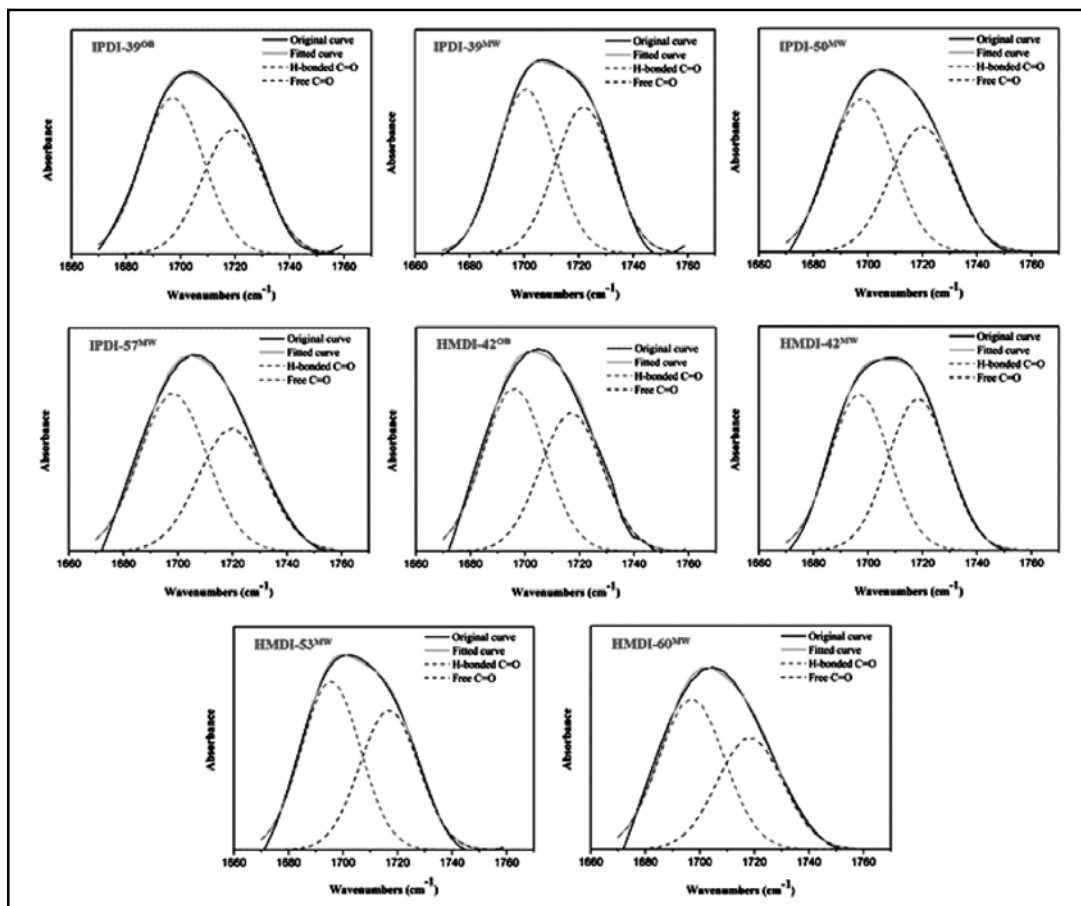


Figure 2. The absorbance spectra in the C=O stretching region of polyurethanes

TABLE 1. Composition and mechanical properties of polyurethanes.

Samples	NCO <sup>a</sup>	HS <sup>b</sup> (wt %)	HBA (%)	M <sub>n</sub> /10 <sup>4</sup> (g/mol)	$\sigma^c$ (MPa)	E <sup>d</sup> (MPa)	$\dot{\epsilon}^e$ (%)
IPDI-39 <sup>OB</sup>	IPDI	39	54.7	1.8	7.2 ± 0.2	18.3 ± 0.8	663.6 ± 31.9
IPDI-39 <sup>MW</sup>	IPDI	39	52.8	1.9	6.9 ± 0.3	19.8 ± 1.9	693.3 ± 25.6
IPDI-50 <sup>MW</sup>	IPDI	50	55.0	1.7	9.7 ± 0.2	148.7 ± 8.4	719.5 ± 10.1
IPDI-57 <sup>MW</sup>	IPDI	57	56.3	1.6	19.4 ± 0.1	303.6 ± 16.5	271.6 ± 15.3
HMDI-42 <sup>OB</sup>	HMDI	42	54.1	1.7	11.4 ± 0.3	56.3 ± 2.7	654.5 ± 30.2
HMDI-42 <sup>MW</sup>	HMDI	42	50.7	1.6	11.3 ± 0.3	43.4 ± 0.5	654.2 ± 15.8
HMDI-53 <sup>MW</sup>	HMDI	53	54.7	1.6	19.1 ± 1.2	226.4 ± 14.5	400.7 ± 19.8
HMDI-60 <sup>MW</sup>	HMDI	60	57.4	1.7	33.0 ± 1.6	380.6 ± 5.1	517.5 ± 22.4

<sup>a</sup>Diisocyanate. <sup>b</sup>Hard segment content. <sup>c</sup>Tensile strength. <sup>d</sup>Young's modulus.

<sup>e</sup>Elongation at break. MW: microwave-assisted heating. OB: oil bath heating.

TABLE 2. Reaction time of polymerization driven by microwave-assisted heating and oil-bath heating, respectively.

Samples	Reaction time (min)	
	First step	Second step
HMDI-42 <sup>OB</sup>	90	310
HMDI-42 <sup>MW</sup>	30	70
IPDI-39 <sup>OB</sup>	70	300
IPDI-39 <sup>MW</sup>	30	65

MW: microwave-assisted heating. OB: oil bath heating.

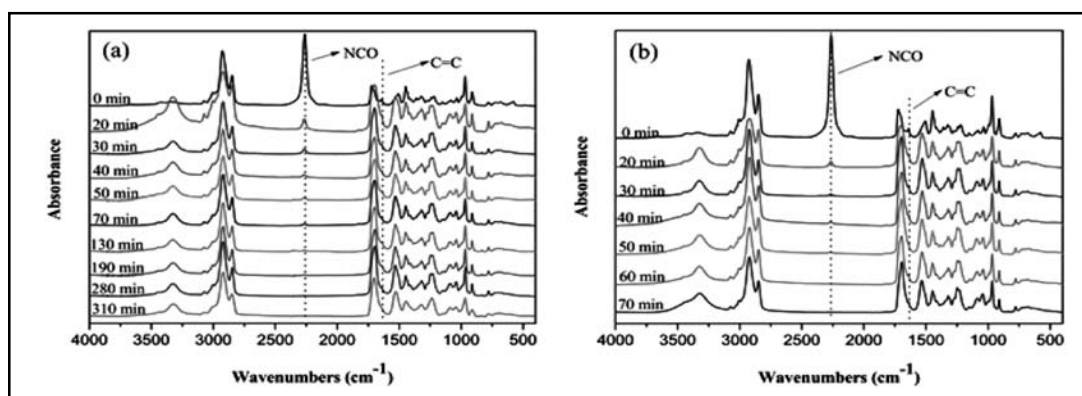


Figure 3. FTIR spectra of HMDI-42 polyurethanes under different reaction time in the second step: (a) oil bath heating, (b) microwave-assisted heating.

be existence<sup>[30]</sup>. Regardless, microwave energy has its own advantages which are still waiting to be fully understood and applied to chemical processes.

### Mechanical properties of polyurethanes

The typical tensile stress-strain curves of different heating method, compositions and hard segment contents of polyurethanes are

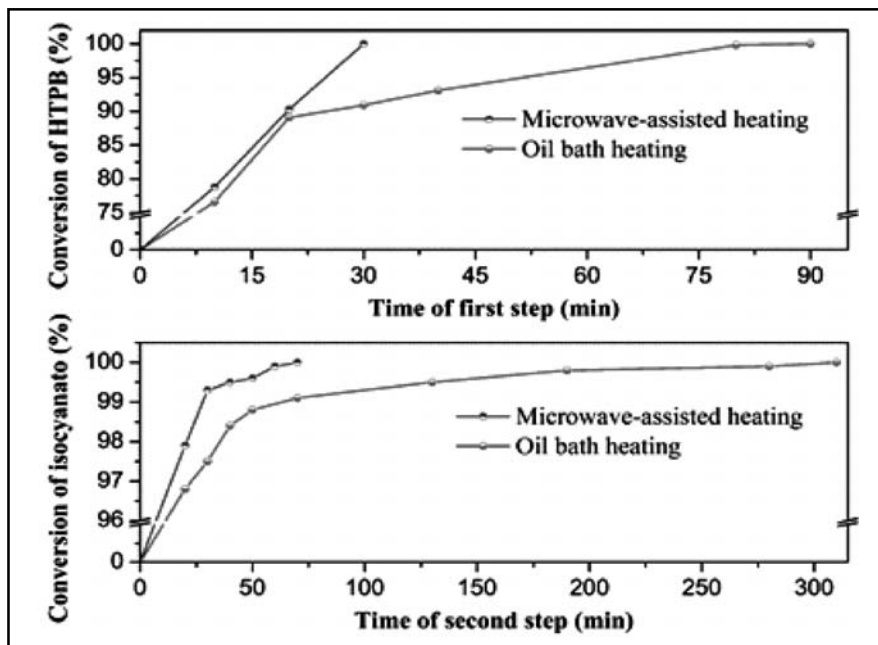


Figure 4. Conversion speed of HTPB in the first step and conversion of isocyanato in the second step, respectively.

shown in Figure 5, and the corresponding results are summarized in Table 1. Comparing the polyurethanes(HMDI-42<sup>MW</sup> and IPDI-39<sup>MW</sup>) synthesized by microwave-assisted heating with that (HMDI-42<sup>OB</sup> and IPDI-39<sup>OB</sup>) obtained under traditional oil-bath heating, the former show the similar and even better tensile properties, although the reaction time of them is greatly reduced. For the IPDI-based polyurethanes and HMDI-based polyurethanes, both Young's modulus estimates from initial slope of stress-strain curves and tensile

strength increase with the content of hard segment. However, their elongation shows different trends. For the IPDI-based polyurethanes, their elongation firstly increases and then decreases with the increase of hard segment. While for the HMDI-based polyurethanes, their elongation decreases first and then increases with the improved amount of hard segment. As shown in Table 1, the higher hard segment content is, the bigger hydrogen-bonding association is exhibited. In general, higher hydrogen-bonding association

of polyurethanes indicates higher intermolecular interactions between hard and hard segments which is responsible for the increase of Young's modulus and tensile strength. A larger elongation is often a sign of the greater extent of phase separation in segmented polyurethanes and the lower hard segment content<sup>[31,32]</sup>. Thus, when the influence of phase separation is more prominent than that of hard segment content, elongation increases with the content of hard segment, and vice versa.

### Thermal properties

The thermal stability of polyurethanes with different amount of hard segment synthesized under microwave radiation is presented in Figure 6. All polyurethanes demonstrate similar thermal decomposition behaviour. The first weight loss is the degradation of the hard segment due to the relatively low thermal stability of the urethane groups and then the second weight loss is associated to soft

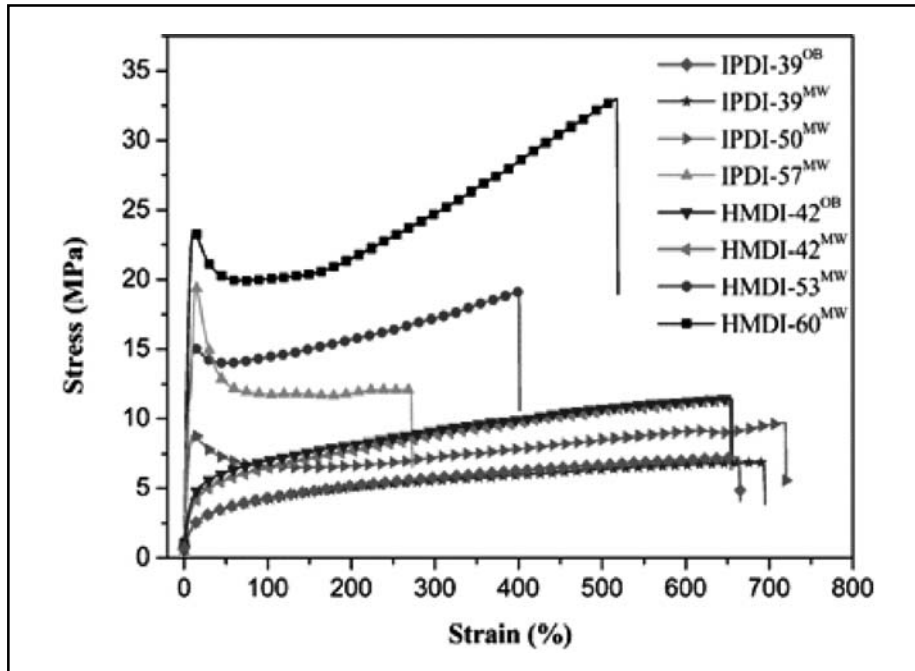


Figure 5. Stress-strain curves of polyurethanes

segment decomposition<sup>[33]</sup>. It can also be seen clearly from Table 3 that the decomposition temperature decreases as the amount of hard segment increases for IPDI-based and HMDI-based polyurethanes, respectively, which is due to the relative low stability of hard segment.

Figure 7 displays the temperature dependence of the  $E'$  and  $\tan \delta$  of polyurethanes synthesized under microwave radiation. The storage modulus shows an increase with increase of hard segment. Glass transition temperature ( $T_g$ ), determined as the peak of



$\tan \delta$ , are listed in Table 3. All polyurethanes show  $T_g$  of soft segment around 60°C and their  $T_g$  of hard segment vary greatly with hard segment contents. Specifically, the higher the content of hard segment, the higher  $T_g$  of hard segment is shown. This is attributed to stronger intermolecular interactions between hard and hard segments.

### Hydrolysis resistance

Due to the absence of polar ether bonds and ester bonds of HTPB, HTPB-based polyurethanes would possess higher hydrolytic stability. To estimate the hydrolysis resistance, tensile testing is performed on polyurethane samples after hydrolysis. Figure 8 presents the

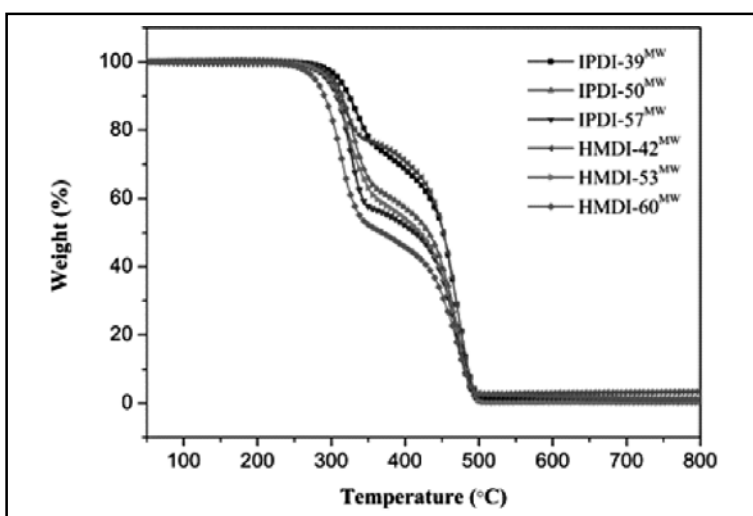


Figure 6. TGA curves of polyurethanes synthesized driven by microwave-assisted heating.

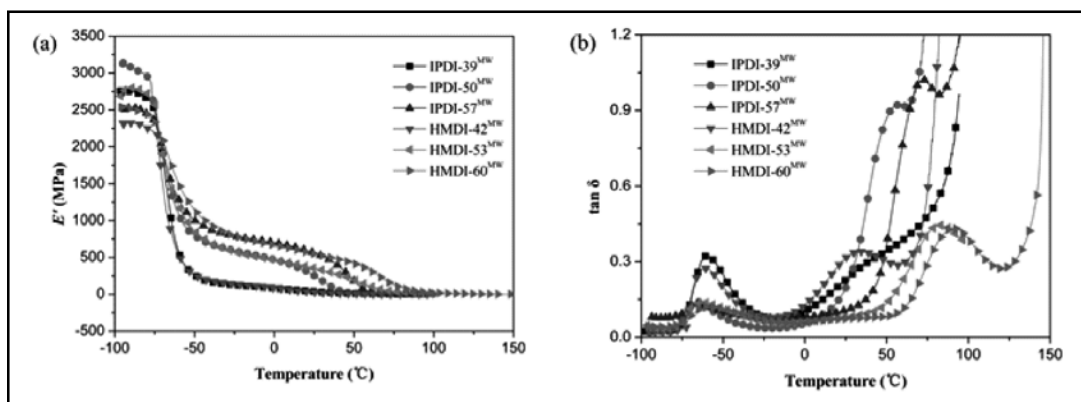


Figure 7. DMA curves of polyurethanes synthesized driven by microwave radiation: (a) storage modulus, (b) loss factor.

pictures of polyurethane splines before and after hydrolysis. The stress-strain curves and corresponding results are shown in Figure 9 and Table 4, respectively. With the increase of hydrolysis time, tensile strength of IPDI-39<sup>MW</sup>

polyurethane remains almost the same, while Young's modulus and elongation decrease slightly. Consequently, polyurethanes possess excellent hydrolysis resistance.

TABLE 3. Thermal properties of polyurethanes synthesized by microwave-assisted heating.

Samples	$T_{d5\%}^a$ (°C)	$T_g^b$ (°C)	$T_g^c$ (°C)
IPDI-39 <sup>MW</sup>	310.7	-59.5	34.4
IPDI-50 <sup>MW</sup>	302.7	-64.9	57.9
IPDI-57 <sup>MW</sup>	294.3	-65.7	72.9
HMDI-42 <sup>MW</sup>	297.3	-60.4	34.0
HMDI-53 <sup>MW</sup>	295.7	-61.1	82.9
HMDI-60 <sup>MW</sup>	277.7	-58.7	91.0

<sup>a</sup>Decomposition temperature: the degradation temperature for 5% weight loss.

<sup>b</sup>Glass transition temperature of soft segment. <sup>c</sup>Glass transition temperature of hard segment.

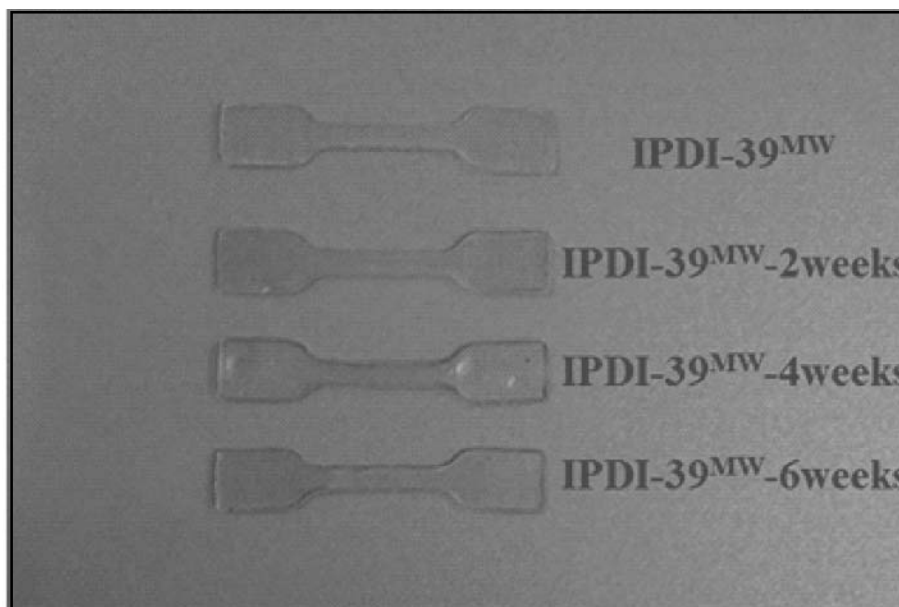


Figure 8. IPDI-39<sup>MW</sup> polyurethane splines before and after hydrolysis

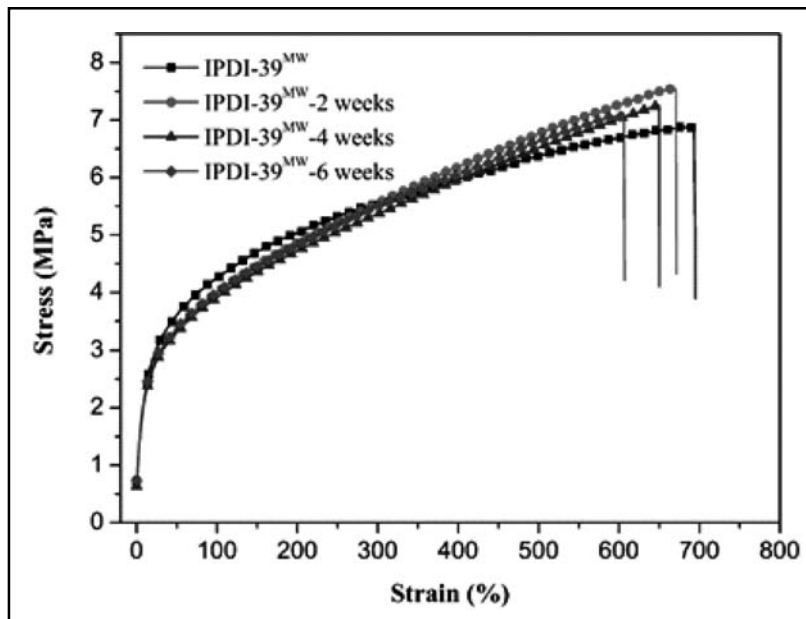


Figure 9. Stress-strain curves of IPDI-39<sup>MW</sup> polyurethanes before and after hydrolysis

TABLE 4. Tensile properties of IPDI-39<sup>MW</sup> polyurethanes before and after hydrolysis.

Sample	$\sigma$ (MPa)	$E$ (MPa)	$\epsilon$ (%)
IPDI-39 <sup>MW</sup>	6.9 ± 0.3	19.8 ± 1.9	693.3 ± 25.6
IPDI-39 <sup>MW</sup> -2 weeks <sup>a</sup>	7.5 ± 0.7	18.0 ± 1.4	670.8 ± 34.3
IPDI-39 <sup>MW</sup> -4 weeks	7.3 ± 0.6	18.6 ± 1.8	649.5 ± 26.5
IPDI-39 <sup>MW</sup> -6 weeks	7.1 ± 0.6	18.8 ± 1.1	605.9 ± 15.7

<sup>a</sup>The time of IPDI-39<sup>MW</sup> splines immersed in PBS solution (pH=7.4) at 37°C.

### CONCLUSION

In summary, HTPB based polyurethanes with excellent properties are successfully obtained with microwave-assisted heating. Because of the specific heating mechanisms of microwave radiation, the reaction rate is obviously enhanced to 3 times. More interestingly, the synthesized polyurethanes by microwave

reactions exhibit comparable mechanical performance to those obtained by traditional oil-bath heating, and the tensile strength and Young's modulus of them increase with the amount of hard segment. HTPB based polyurethanes also exhibit excellent thermal stability and hydrolysis resistance.

**NOTES**

The authors declare no competing financial interest.

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