Preparation and Physico-Mechanical, Thermal and Acoustic Properties of Flexible Polyurethane Foams Based on Hydroxytelechelic Natural Rubber

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ABSTRACT: Novel flexible polyurethane foams were successfully prepared from a renewable source, hydroxytelechelic natural rubber (HTNR) having different molecular weights (1000–3400 g mol^{-1}) and variation of epoxide contents (EHTNR, 0–35% epoxidation) by a one-shot technique. The chemical and cell structures as well as physico-mechanical, thermal, and acoustic properties were characterized and compared with commercial polyol analogs. The obtained HTNR based foams are open cell structures with cell dimensions between 0.38 and 0.47 mm. The HTNR1000 based foam exhibits better mechanical properties but lower elongation at break than those of commercial polyol analog. However, the HTNR3400 based foam shows the best elastic properties. In a series of EHTNR based foams, the tensile and compressive strengths show a tendency to increase with increasing epoxide content and amount of 1,4-butanediol (BD). The HTNR based foams demonstrate better low temperature flexibility than that of the foam based on commercial polyol. Moreover, the HTNR based polyurethane foams was found to be an excellent absorber of acoustics. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 828–837, 2010

Key words: polyurethane foams; Physico-mechanical properties; acoustic properties; telechelic; natural rubber

INTRODUCTION

Polyurethane foams were discovered in the 1940s and have been an ongoing subject of research since. These foams are used for various applications ranging from shipbuilding and construction to footwear and mattresses.[1] Among the various different types of polyols from products of petroleum oil used to synthesize polyurethane foams, polyether or polyester backbones are most commonly used because of their thermal,[2,3] chemical[4,5] biological,[6,7] and mechanical properties.[8–10] A few hydroxyl telechelic polydienes such as hydroxyl telechelic polybutadienes[11,12] and hydroxyl telechelic butylene-isoprene[13] have attracted particular interest from both industries and public researches.

Concerns about the levels of natural resources and the environment have led researchers to focus on the development of new polyurethane foams from renewable sources such as soybean oil,[14–18] palm oil,[19–22] starch,[9] cellulose,[23] rape seed oil,[24] and biopitch.[12]

Natural rubber is one of the most promising choices because of its mechanical and physical properties. In addition, it can be chemically modified in either latex phase, solvent phase, biphasic systems, or solid phase[25] owing to the double bonds on the polymeric backbone. Chemically modified natural rubber would increase the potential number of applications in particular for polyurethane foams based on natural rubber.

In the past few years, our laboratory has reported a preparation of well-defined telechelic polyisoprene with selective controlled molecular weight, microstructures and functionalities[26–30] through a degradation of an original high molecular weight cis-1,4-polyisoprene. The physico-mechanical and biological
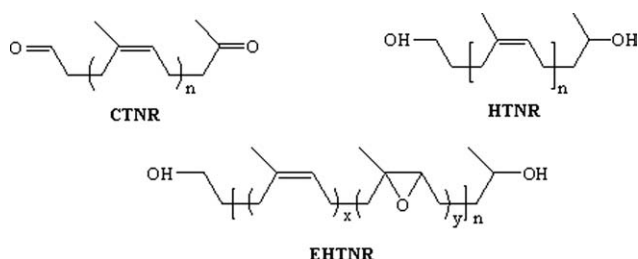
Figure 1 Chemical structure of the different telechelic oligomers from natural rubber.

properties of the obtained polyisoprene based polyurethane materials[26,31] were also studied. However, the preparation and properties of polyurethane foams based on telechelic natural rubber have never been reported.

The objective of this work was therefore focused on the preparation of polyurethane foams from hydroxytelechelic natural rubber as polyols, which was prepared from a carefully controlled degradation and modification of natural rubber, according to a methodology described in our previous work.[32] The physico-mechanical, thermal, acoustic properties, and cell morphology were also investigated and compared with those of commercial polyol based analogs.

EXPERIMENTAL

Materials

Dabco T-12 (dibutyl tin dilaurate) was purchased from Huntsman. Sodium borohydride and 1,4-butanediol were purchased from Acros Organic. Polymethylene polyphenylpolyisocyanate (P-MDI, 31.5% free NCO content, $\overline{fn}$ = 2.7) and Dabco 33LV (33% triethylenediamine in propylene glycol) were purchased by

BASF and Air products, respectively. Silicone surfactant was obtained from Goldchmidt. The commercial polyether polyols with different molecular weights were supplied by TPI polyol, Thailand (Raypol 1010 with $\overline{Mn}$ = 1000 g mol^{-1}, OH value, = 117 and Raypol1020 with $\overline{Mn}$ = 2000 g mol^{-1}, OH value = 56.4). Dichloromethane was distilled before use.

Synthesis

Synthesis of hydroxytelechelic natural rubber

The hydroxytelechelic natural rubbers (HTNR) with different molecular weights (1000, 2000, 3400 g mol^{-1}) and different ratios of epoxidation (approximately 10, 20, and 30% epoxidation) were prepared from carbonyl telechelic natural rubber (Fig. 1), according to a methodology described in our previous work.[26,30,32]

Synthesis of polyurethane foams

Polyurethane foams were prepared by a one-shot method. All ingredients as listed in Table I were mixed together in a 250 mL beaker by homogenizer at a speed of 11,000 rpm until the whitening of the liquid was observed. The mixture was then poured into molds and kept in an oven at 40°C for curing for 48 h before being tested.

Characterization of polyurethane foams

FTIR analysis

IR spectra were recorded on a FTIR Perkin–Elmer spectrophotometer, equipped with a diamond ATR (attenuated total reflection) device, and recorded over a wavenumber range of between 4000–500 cm^{-1}.

TABLE I
Polyurethane Foams Formulations

Ingredients	Weight (g)									
	PUF1	PUF2	PUF3	PUF4	PUF6	PUF7	PUF8	PUF9	PUF11	PUF12
HTNR1000	40	–	–	–	–	–	–	–	40	40
HTNR2000	–	40	–	–	–	–	–	–	–	–
HTNR3400	–	–	40	–	–	–	–	–	–	–
9%EHTNR2000	–	–	–	–	40	–	–	–	–	–
23%EHTNR2000	–	–	–	–	–	40	–	–	–	–
35%EHTNR2000	–	–	–	–	–	–	40	–	–	–
Raypol 1010	–	–	–	40	–	–	–	–	–	–
Raypol 1020	–	–	–	–	–	–	–	40	–	–
B 8110	0.34	0.70	0.70	0.34	0.70	0.70	0.70	0.34	0.34	0.34
Water	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60	1.60
1,4-Butanediol	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.38	0.76
Dabco 33-LV	0.06	0.30	0.30	0.06	0.30	0.30	0.30	0.06	0.06	0.06
Dabco T-12	0.04	0.20	0.20	0.04	0.20	0.20	0.20	0.04	0.04	0.04
CH_2Cl_2	10	10	10	10	10	10	10	10	10	10
P-MDI	36.8	29.3	27.9	35.5	29.3	30.1	30.4	29.6	36.6	37.7

Each formulations used an isocyanate index = 100.

Cell morphology

The cell dimensions of the polyurethane foams were determined according to BS 4443-Part I: 1988. The cell count is defined as the number of cell per centimeter of sample length. Cell size is defined as the average value of the cell dimensions. The samples were magnified to 22 times and photographed by Optical microscope (Olympus model SZ-PT, Japan).

Physico-mechanical properties

Density. The densities of the polyurethane foams were measured according to ASTM D 3574 Test A. Three specimens were cut to have a dimension of 10 mm × 10 mm × 10 mm. After that, these specimens were precisely weighed. The result of the weight (M) divided by volume (V) of the specimens was a density in a unit of kg.m^{-3}.

Compression force deflection test (compressive strength). The compressive strengths of the polyurethane foams were investigated according to ASTM D 3574 Test C by using a universal tensile testing machine in compression testing mode. The dimension of specimens was 50 mm × 50 mm × 25 mm. The specimens were compressed to 50% of their thickness at a speed of 50 mm min^{-1}. Three specimens per sample were tested. The compressive strength was obtained from the average value of three specimens and reported in a unit of kilopascal (kPa).

Constant deflection compression set. The compression set is the percentage change of the original thickness after the specimens have been constantly deflected under a specific condition of temperature and time according to ASTM D 3574 Test D. The dimension of the specimens was 50 mm × 50 mm × 25 mm. The original thickness of these specimens were measured deflected to 50% of their original thickness by compression device. They were kept under 70°C for 22 h, then removed from the apparatus, left at room temperature for 30 min and finally measured a thickness of the specimens.

Tensile properties. The tensile strength and elongation at break of polyurethane foams were measured with a crosshead speed of 500 mm min^{-1} according to ASTM D 3574 Test E by using a universal tensile testing machine in tensile testing mode. Five dumbbell shaped specimens were cut using die type A. The tensile strength was calculated by dividing the maximum breaking force by the original cross-sectional area of the specimen and reported in a unit of kilopascal (kPa).

The ultimate elongation was also calculated by subtracting the original distance between the bench marks from the total distance between the bench marks at the time of rupture and expressed the difference as a percentage of the original distance.
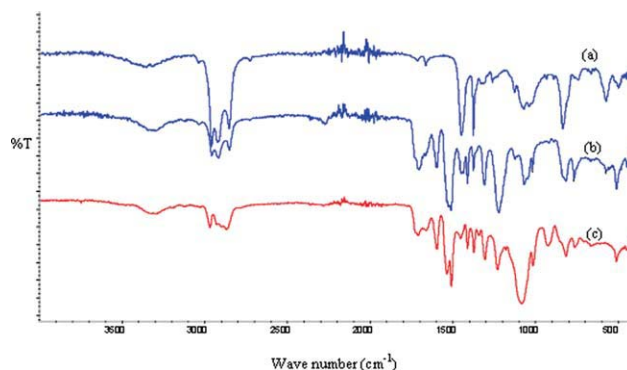
Figure 2 FTIR spectra of HTNR (a), polyurethane foams based on HTNR (b), and commercial precursor (c). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Thermal properties

Differential scanning calorimetry (DSC). Differential scanning calorimetry (DSC) characterization was performed using a TA instruments (DSC Q 100) at a temperature range of −80 to 200°C with a heating rate of 10°C min^{-1} under nitrogen atmosphere. The sample weight was about 5 mg. Calibration was performed using indium as a reference material.

Thermogravimetric analysis (TGA). Polymer thermal stabilities were characterized by Thermo-Gravimetric Analysis (TGA Q 100) in a temperature range of room temperature to 600°C, at a heating rate of 10°C min^{-1} under nitrogen atmosphere using approximately 10 mg of sample. For each sample weight loss and the maximum rate of degradation (T_{max}) were determined.

Acoustic properties

The acoustic properties were studied in term of the acoustic absorption coefficient according to ASTM E 1050 using Kundt's tube comprising of an impedance tube, two microphones, and frequency analyzer. The acoustic absorption coefficient (α) is defined as the ratio of the acoustic energy absorbed by the foam ($I_{incident} - I_{reflected}$) to the incident acoustic energy ($I_{incident}$) on the surface, and is dependent on frequency. The acoustic coefficient was calculated from cylindrical samples were cut off each formulation foams 29 mm in diameter and 13 mm thick over the frequency range from 400 to 6400 Hz.

RESULTS AND DISCUSSIONS

Polyurethane foams structure analysis

The chemical structures of all the polyurethanes were confirmed by the existence of absorption bands at around 3300 and 1700 cm^{-1} in FTIR analysis which correspond to N—H and C=O stretching vibrations
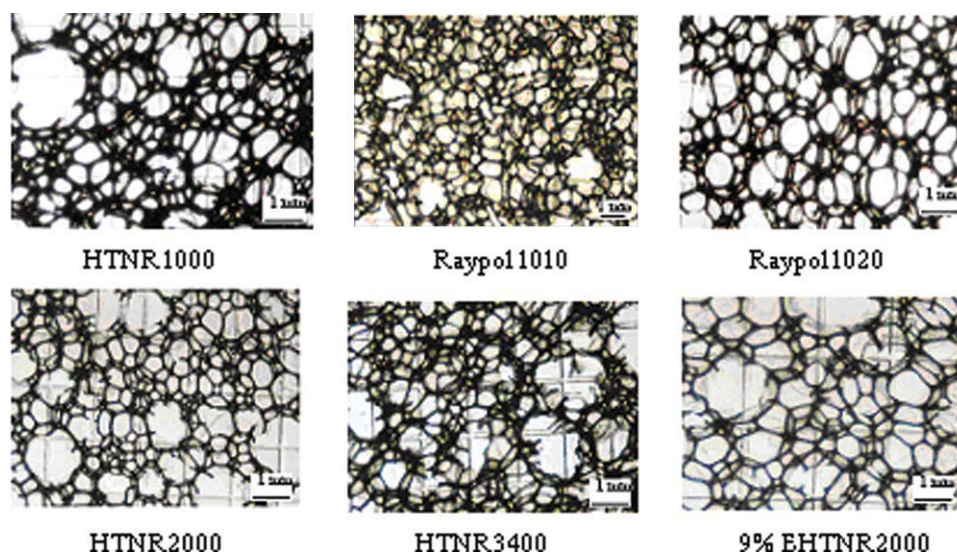
Figure 3 Optical micrographs of cross-sectioned polyurethane foams (×22).

of urethane functional group, respectively. Polyurethane foams prepared from commercial precursor (polyether polyols) show the strong absorption peak at 1100 cm^{-1} of C—O stretching, whereas this peak was not observed in HTNR based polyurethane foams. The disappearance of absorption peak at 2270 cm^{-1} confirms that there was no residual NCO in the HTNR based foams, shown in the overlaid FTIR spectra of the polyurethane foams, Figure 2.

Physico-mechanical properties of polyurethane foams

Cell morphology

The cell of foams based on HTNR and commercial polyols had no significant difference in size and showed a spherical shape, as well as regular size distribution shown in Figure 3 and Table II. Cell sizes range between 0.38 and 0.47 mm. Moreover, the obtained HTNR based foams exhibit open cell structure, as illustrated in Figure 3.

Effect of molecular weight of precursors

The effect of molecular weight of HTNR precursors on the physico-mechanical properties of polyurethane foams were studied in comparison with those of foams based on commercial polyol (Raypol1010). The molecular weights were varied at 1000, 2000, and 3400 g mol^{-1}. The results are shown in Table III.

The densities of the polyurethane foams based on HTNR range between 20 and 28 kg m^{-3}, while the densities of commercial polyol based polyurethane foams were varied from 28 to 34 kg m^{-3}.

The physico-mechanical properties of HTNR based polyurethane foams (PUF1, PUF2 and PUF3) with various precursor molecular weights (1000, 2000, and 3,400 g mol^{-1}) were compared with those of the commercial analogs as shown in Table III. It was found that PUF1 gives the highest tensile and compressive strengths when compared with other HTNR based polyurethane foams (PUF2 and PUF3). These results were influenced by the molecular weight of the precursor HTNR1000, which evidently

TABLE II
Appearance and Cell Morphology of Polyurethane Foams

Samples	Precursors	Appearance of foam	Cell count (cells)	Cell size (mm)
PUF1	HTNR1000	L-y, F	24 ± 1.8	0.42
PUF2	HTNR2000	L-y, F	23 ± 0.7	0.42
PUF3	HTNR3400	L-y, F	26 ± 0.6	0.38
PUF4	Raypol1010	L-y, F	24 ± 1.1	0.42
PUF6	9%EHTNR2000	L-y, F	26 ± 1.2	0.38
PUF7	23%EHTNR2000	L-y, F	23 ± 1.9	0.43
PUF8	35%EHTNR2000	L-y, F	26 ± 2.0	0.38
PUF9	Raypol1020	L-y, F	22 ± 17	0.46
PUF11	HTNR1000 (2BD)	L-y, S-f	21 ± 1.9	0.47
PUF12	HTNR1000 (4BD)	L-y, S-f	22 ± 0.6	0.45

L-y = light yellow, F = Flexible, S-f: semi-flexible.

TABLE III
Effect of Molecular Weight of Precursors on Physico-Mechanical Properties of Polyurethane Foams

Samples	Precursors	Hard segment (%)	Density (kg/m³)	Tensile strength (kPa)	Elongation at break (%)	Compressive strength (kPa)	Compression set (%)
PUF1	HTNR1000	48.6	28.7 ± 4.3	99.0 ± 9.8	28.6 ± 6.9	32.5 ± 1.3	46.0 ± 0.8
PUF2	HTNR2000	43.7	20.0 ± 3.7	52.6 ± 2.5	46.8 ± 8.4	7.4 ± 1.6	36.5 ± 1.8
PUF3	HTNR3400	42.6	24.5 ± 2.6	41.6 ± 9.0	77.8 ± 5.3	3.4 ± 1.0	9.5 ± 0.7
PUF4	Raypol1010	48.2	28.7 ± 3.1	87.0 ± 3.3	68.9 ± 4.7	13.1 ± 4.0	45.9 ± 0.4

Hard segment (%) = [(wt. of P-MDI)/(wt. of P-MDI+wt. of Poly + wt. of water + wt of chain extender)] × 100.

has a shorter length between two hydroxyl end groups resulting in an increase of percentage of hard segment in the polyurethane foams. The results are in agreement with the previous work which studied polyisobutylene isoprene triol,[13] in which the mechanical properties (tensile and compressive strengths) of polyurethane based elastomers were increased with decreasing molecular weight of triol. In the same manner, increasing the amount of hard segments in hydroxyl polybutadienes and hydroxyl terminated natural rubber based polyurethane leads to an increase of tensile and compressive strengths properties.[33,34] Thus it is possible to obtain higher tensile and compressive strengths when using a lower molecular weight HTNR. On the contrary, the flexibility of foams decreases with decreasing molecular weight. The elongation at break and compression set of PUF1 are poorer than those of PUF2 and PUF3, respectively.

The physico-mechanical properties are markedly dependent on foam density. Generally, tensile and compressive strengths increase with increasing density. Although it is very difficult to compare the influence of microstructure of precursors on properties of foams, fortunately, the densities of both HTNR1000 and commercial polyol (Raypol1010) based polyurethane foams are similar, i.e., approximately 28 kg m⁻³. Therefore, the mechanical properties of both polyurethane foams based on HTNR1000 and commercial polyols (Raypol1010) can be compared without the influence of density.

Table III shows the compressive and tensile strength of polyurethane foams. It was found that the polyurethane foams based on HTNR1000 has higher tensile and compressive strengths than that of the foam based on commercial polyols because of the different structure of the precursors. The HTNR has an isoprenic structure which has a stronger tensile strength than that of ether structure of commercial polyols. Therefore, the compressive and tensile strengths of PUF1 were higher but elongation at break was lower. This is in agreement with the results of Ako and Kennedy,[13] who reported the preparation of polyurethane foams based on polyisobutylene-isoprene (PIB) triol comparing with those based on polyether triol in the same range of molecular weight at isocyanate index 105. The results revealed that the mechanical properties of polyurethane foams based on PIB triol were superior to those of polyether triol based polyurethane foams.

The compression set test was performed by deflecting the foam specimen to 50% of initial thickness, exposing it to 70°C for 22 h and finally measuring the change in the thickness of specimen after recovery at room temperature for 30 min. A low compression set indicates that the foam is more flexible or has a high elasticity, i.e., it can recover better to its original shape after deformation. It was found that both of the foam types (HTNR based (PUF1) and commercial polyol based polyurethane foams (PUF4)) have poor thickness recovery. The inferior compression set of PUF1 and PUF4 foams is attributed to the effect of high amount of hard segment.[10] On the contrary, PUF3 based on HTNR3400 with longer soft segment has excellent flexibility or elastic behavior.

Effect of epoxide content

The effect of epoxide content on the physico-mechanical properties of polyurethane foams was studied using various epoxide ratios; 0, 9, 23, and 35%,

TABLE IV
Effect of Epoxide Content on Physico-Mechanical Properties of Polyurethane Foams

Samples	Precursors	Hard segment (%)	Density (kg/m³)	Tensile strength (kPa)	Elongation at break (%)	Compressive strength (kPa)	Compression set (%)
PUF2	HTNR2000	43.7	20.0 ± 3.7	52.6 ± 2.5	46.8 ± 8.4	7.4 ± 1.6	36.5 ± 1.8
PUF6	9%EHTNR	43.7	18.6 ± 1.7	50.2 ± 2.2	44.0 ± 4.2	8.0 ± 2.1	42.9 ± 2.0
PUF7	23%EHTNR	44.3	23.5 ± 2.6	67.4 ± 6.4	34.8 ± 5.0	14.8 ± 3.2	46.6 ± 0.8
PUF8	35%EHTNR	44.6	22.8 ± 2.9	79.7 ± 6.7	33.2 ± 2.2	16.4 ± 2.7	47.0 ± 1.8
PUF9	Raypol1020	44.0	33.9 ± 2.8	70.2 ± 4.4	52.1 ± 7.4	9.4 ± 2.0	40.1 ± 1.2

TABLE V
Effect of Amount of 1,4-butanediol on physico-mechanical Properties of Polyurethane foams

Samples	Precursors	Hard segment (%)	Density (kg/m³)	Tensile strength (kPa)	Elongation at break (%)	Compressive strength (kPa)	Compression set (%)
PUF1	HTNR(BD)	48.6	28.7 ± 4.3	99.0 ± 9.8	28.6 ± 6.9	32.5 ± 1.3	46.0 ± 0.8
PUF11	HTNR(2BD)	49.0	32.6 ± 5.0	120.9 ± 8.8	30.7 ± 5.2	39.1 ± 4.8	47.0 ± 0.5
PUF12	HTNR(4BD)	49.7	38.8 ± 2.0	144.3 ± 7.5	21.5 ± 4.9	64.1 ± 9.0	47.0 ± 0.7

to prepare HTNR2000 based PUF2, PUF6, PUF7 and PUF8, respectively. The commercial polyol (Raypol1020 based foam, PUF9) was also prepared for comparison. The formulations are shown in Table I.

The physico-mechanical properties of HTNR2000 based polyurethane foams with various epoxide contents (PUF6, 9%; PUF7, 23% and PUF8, 35%) and those of commercial precursors based foam (PUF9, Raypol1020) are shown in Table IV. It is clear that tensile and compressive strengths of PU based on HTNR are better but elongation at break and compression set are worse with an increasing amount of epoxide on precursors. It is possible that the cell wall and struts in polyurethane foams become more rigid and damage under compression leading to poor recovery after testing. Tu et al.[35] reported a similar effect of epoxidized precursor on properties of flexible polyurethane foams, reporting that the replacement up to 20% of polyether polyol by epoxidized soybean oil in flexible foams led to better compressive strength, but inferior compression set.

The influence of microstructure on the mechanical properties of PUF2 (HTNR2000) and PUF9 (Raypol1020) was difficult to analyze because of their difference in densities (about 20 and 34 kg m⁻³). However, the lower density PUF7 and PUF8 (23% and 35% EHTNR2000 based polyurethane foams) have better mechanical properties i.e., higher tensile and compressive strengths than PUF9 based on Raypol1020.

Effect of amount of chain extender

The effect of amount of 1,4-butanediol (PUF1, 0.19g; PUF11, 0.38 g and PUF12, 0.78 g in Table I) on physico-mechanical properties of polyurethane foams based on HTNR1000 was also studied. These results are shown in Table V.

The amount of 1,4-butanediol in polyurethane foams based on HTNR1000 had more influence on the mechanical properties of foam than the type of chain extender. It is clearly shown that the tensile and compressive strengths of foams increase with increasing amount of 1,4-butanediol in foams with isocyanate index equal to 100. PUF12 has the highest tensile and compressive strengths. The increase of these mechanical properties is probably the result of both increased density and increased hard segment content. However, PUF12 shows no difference in elongation at break and compression set properties of foams.

Thermal analysis

DSC

The T_g of the different polyurethane foams were evaluated from the second heating thermograms at a heating rate of 10°C min⁻¹ under nitrogen atmosphere and the results are summarized in Table VI. All polyurethane foams showed only one glass transition temperature (T_g) of soft segment, which is

TABLE VI
#### Thermal Properties of Polyurethane Foams

| Samples	Precursors	T_g (°C)	Thermal degradation steps			
			1st step		2nd step	
			T_{max} (°C)	weight loss (%)	T_{max} (°C)	weight loss (%)
PUF1	HTNR1000	−50	306	43.8	372	48.7
PUF2	HTNR2000	−57	301	32.1	378	52.0
PUF3	HTNR3400	−61	293	14.2	380	76.5
PUF4	Raypol1010	−21	309	36.0	375	54.4
PUF6	9%EHTNR2000	−52	290	25.7	375	65.4
PUF7	23%EHTNR2000	−45	302	27.4	381	66.9
PUF8	35%EHTNR2000	−34	297	28.5	393	67.2
PUF9	Raypol1020	−48	298	26.0	376	64.4
PUF11	HTNR1000 (2BD)	−44	302	41.6	371	51.0
PUF12	HTNR1000 (4BD)	−45	307	41.9	375	49.7
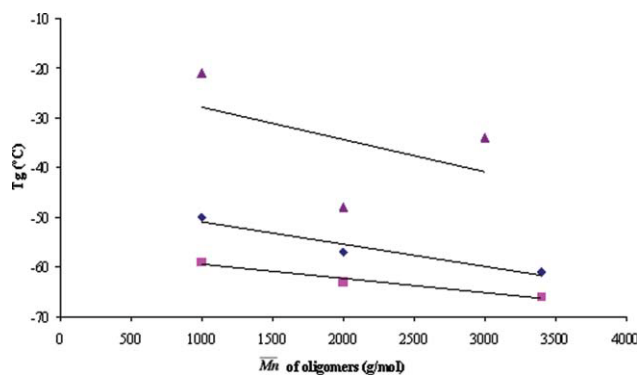
Figure 4 T_g (°C) versus $\overline{\text{Mn}}$ of oligomers (g mol^{-1}) (■ HTNR, ◆ HTNR based PUF, ▲ commercial oligomers based PUF). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

either HTNR or commercial precursors indicating that each phase (hard segment and soft segment) is not completely separated. It is possible to explain that their synthesis polyurethane foams were one-shot technique. That technique had more an opportunity to form in random structure than block structure. The reference that can be support our opinion is Kebir et al.[27] They synthesized polyurethane solids by prepolymer technique using HTPI, hydroxytelechelic polyisoprene as staring material. The phase separation of them was clearly observed.

Figure 4 shows the influence of molecular weight of soft segment on T_g of all polyurethane foams examined. It was found that the observed T_g of the foams based on both HTNR and commercial precursors decreased with increasing length of soft segments due to an increase of the molecular chain flexibility in foams. In addition, the HTNRs based foams (PUF1, PUF2 and PUF3) exhibited lower T_g (between −50 and −61 °C) than those of commercial precursors based foams (PUF4 and PUF9) (−48 and −21°C). It indicates that the HTNR based foams
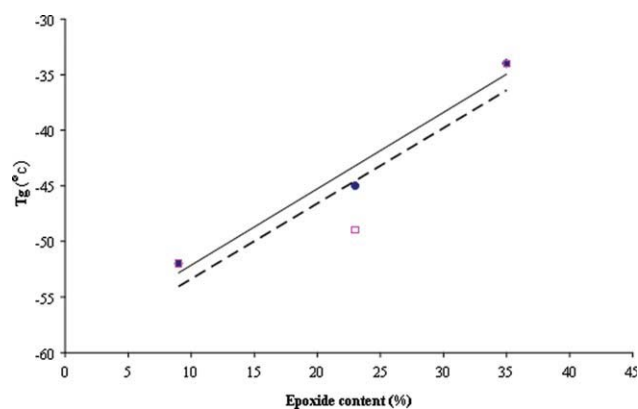
Figure 5 T_g (°C) versus epoxide content (%) (□---□ EHTNR oligomers, ●—● EHTNRs based PUF). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
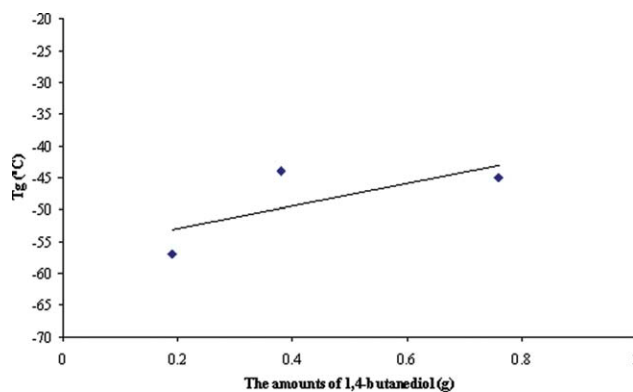
Figure 6 T_g (°C) versus the amounts of 1,4-butanediol (g). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

show excellent low temperature flexibility. This can be explained by interactions of the ether groups of the commercial polyols with urethane or urea linkages that reduce flexibility of polyurethane chains and therefore T_g of commercial polyols based foams are higher when compared with T_g of HTNR based foams.

The effect of the epoxide content on T_g of both oligomers and foams was also considered and it was shown that T_g increased with increasing epoxide content because of higher backbone rigidity and higher chain interactions. This effect clearly caused an increase in the tensile and compressive strengths of polyurethane foams with increasing of T_g, and a linear relationship between epoxide content and T_g is established in Figure 5.

In addition, the influence of the chain extender (1,4-butanediol) content on T_g of foams was studied. The amounts of 1,4-butanediol was varied at 1,2, and 4 times of 1,4-butanediol in the formulations (PUF1, PUF11, PUF12 in Table I). It can be seen that the T_g increases with increasing amounts of chain extender because of higher backbone rigidity (urethane segments) and because of interactions between chains (Fig. 6).
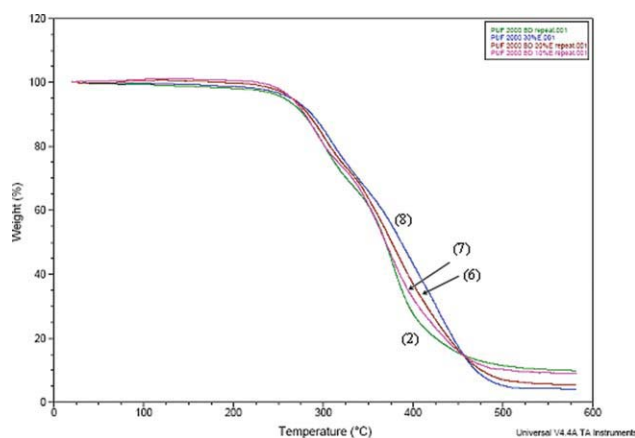
TGA

A two-step thermal degradation was observed[26,27,36] for all polyurethane foams tested. Weight losses and characteristic temperatures determined from the maximum of the derived curve ($T_{\max}$) were analyzed. The first stage degradation at 290–309°C corresponds to urethane bond breakage, while the second stage at 371–393°C corresponds to a decomposition of precursors (soft segment). All the foams have approximately the same degradation temperatures (Table VI and Figs. 7–9).

We observed that the increased hard segment contents by varying both $\overline{\text{Mn}}$ of oligomer and the
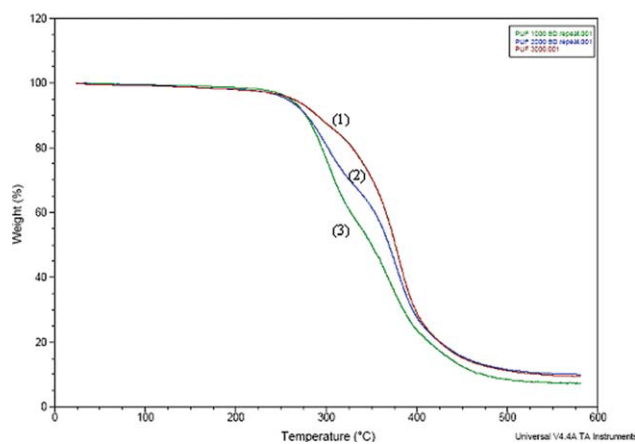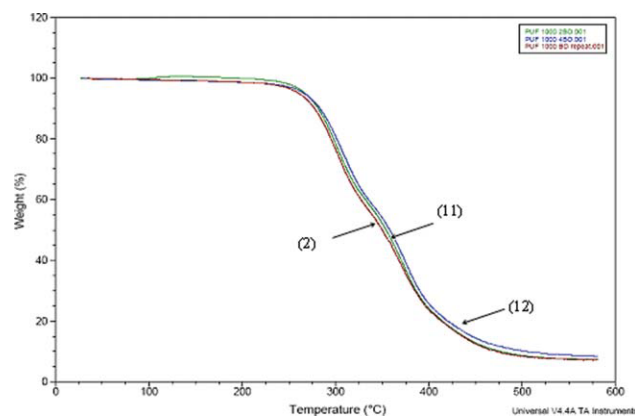
Figure 7 TGA curves of polyurethane foams based on HTNR: (1) (PUF1, 1000), (2) (PUF2, 2000), and (3) (PUF3, 3400). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
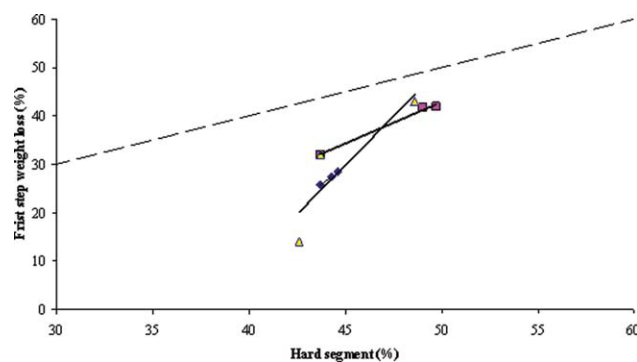

Figure 9 TGA curves of polyurethane foams based on HTNR1000 with different in the amount of 1,4-butanediol: (1) (PUF2, 0.19g) (11) (PUF11, 0.38 g) and (12) (PUF12, 078 g). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

amount of 1,4-butanediol lead to an increase of first step weight loss. This means that increasing of hard segment leads to a decrease of thermal stability in term of weight loss (Fig. 10). Theoretically, the degradation of urethane functional group in the first step should display a linear relationship between theoretical weight loss (%) and hard segment (%). As shown in Figure 10, the first step weight losses increase linearly with increasing hard segment contents by varying oligomer molecular weight, epoxide content and the amount of 1,4-butanediol, but the values measured are lower than the theoretical values. This result can be explained by a higher stability of urethane linkage that occurs from an influence of aromatic isocyanate structures of P-MDI and some crosslinks in the foam because of a functionality of NCO, which is equal to 2.7.

Acoustic properties

Figure 11 shows the experimental results for the acoustic absorption coefficient of the samples as a function of frequency. The HTNR (PUF2, PUF3 and PUF7) and commercial polyol (PUF9) based polyurethane foams show clear absorption peaks over a range of 2000–5000 Hz. At higher frequencies, the absorption coefficient consistently increases a behavior characteristic of open cell foams. However, the observed shift of the absorption peak toward higher frequencies may be related to the increase in density.[37]

Sound waves are absorbed by two main mechanisms; (1) when the sound waves reach the open cell foam structures, the sound energy is converted to heat energy within the porous structures as the vibration of the air molecules produces friction upon

Figure 8 TGA curves of polyurethane foams based on EHTNR2000: (2) (PUF2, 0%), (6) (PUF6, 9%) (7) (PUF7, 23%) and (8) (PUF8, 35%). [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

Figure 10 Weight loss in first step (%) versus hard segment (%) in polyurethane foams (▲ varying of $\overline{Mn}$ of oligomers, ◆ varying of the epoxide content on oligomers molecule, ■ varying of the amount of 1,4-butanediol, ---- theoretical curve). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley. com.]
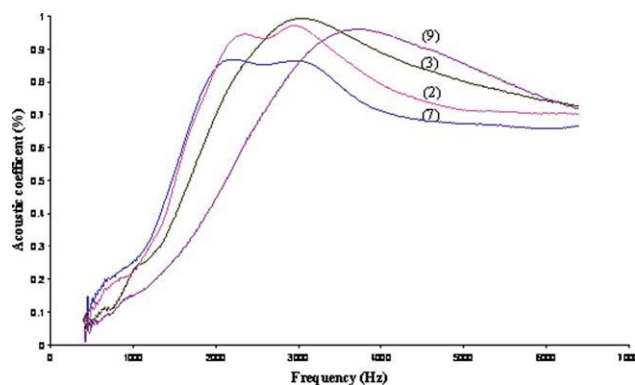
Figure 11 Acoustic coefficient of polyurethane foams: (2) (PUF2, HTNR2000) (3) (PUF3, HTNR3400), (7) (PUF7, 23%HTNR2000) (9) (PUF9, Raypol1020). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

contact with the open cell foams and (2) the dissipation of sound energy in the form of heat energy due to the molecular chain damping effect of the polymer.[37,38]

The absorption peaks of HTNR based polyurethane foams show dramatically high acoustic coefficient of more than 80%, indicating that these foams exhibit excellent acoustic properties of a similar level as polyurethane foams based on commercial precursor (PUF9). However, polyurethane foams based on HTNR3400 (PUF3) and HTNR2000 (PUF2) showed a better acoustic coefficient than that based on 23%EHTNR (PUF7). It is possible that the flexibility of polyol chain has been improved upon the sound absorption coefficient of foam.[38,39]

CONCLUSIONS

Flexible polyurethane foams were successfully prepared by one-shot method based on HTNR with different molecular weights (1000, 2000, and 3400 g mol^{-1}), epoxide levels (0–35%), and amount of 1,4-butanediol (0.19, 0.38, and 0.78 g), then compared with commercial polyol analogs. An isocyanate index for each formulation was equal to 100. The HTNR based foams exhibited open cell structure and their cell sizes were between 0.38 and 0.47 mm. The comparison between the HTNR1000 and Raypol1010 based polyurethane foams which have the same density reveals that the tensile and compressive strengths of polyurethane foams based on HTNR1000 were higher, but the elongation at break was lower than those of commercial polyol analogs. However, HTNR3400 based polyurethane shows the best elastic property, i.e., elongation at break and compression set. In the series of EHTNR based PUF, the mechanical properties were improved but the elastic property was decreased with increasing epoxidation levels. In addition, the same results were

observed with the increasing amount of 1,4-butanediol. However, T_g was found to increase with increasing of degree of epoxidation and amount of chain extender. The HTNR based foams display the lower flexibility temperature when compared with the commercial analogs. Moreover, the HTNR based polyurethane foams exhibit an excellent acoustic absorption characteristic.

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