

Polyurethane foams from oligomers derived from waste tire crumbs and polycaprolactone diols

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ABSTRACT: This work was an initial study on the synthesis of polyurethane foams (PUF) by using diols obtained from the controlled degradation of waste tire crumbs and from polycaprolactone (PCL) followed by examination of their biodegradability. Natural rubber (NR, *cis*-1,4 polyisoprene) and butadiene rubber (BR) chains contained in waste tire crumbs were chemically modified into carbonyl telechelic (CTWT) and successively into hydroxyl telechelic oligomers (HTWT). Four types of PUF were prepared with different molar ratios between the HTWT and the PCL diols. CTWT and HTWT were analyzed by ¹H-NMR, SEC, and FT-IR to confirm their chemical structure. Formation of the urethane bond was demonstrated by FT-IR spectra. The addition of the PCL diol increased the thermal degradation temperature of the PUF based on thermogravimetric analysis. According to scanning electron microscopy, polyhedral closed cells were obtained. The molar ratio of HTWT/PCL diols strongly affected the kinetic rate of foam formation and foam morphology. A low kinetic rate provided PUF with a high density, small cell size, and a broad cell size distribution. In order to assess biodegradation of PUF, the modified Sturm test was carried out for 60 days at ambient temperature (27–30 °C). The biodegradation of PUF containing only HTWT was 31.2% and 51.3% at 28 days and 60 days of testing, respectively whereas the PUF containing 1/0.5 HTWT/PCL diols (by mole) showed a higher biodegradation: 39.1% and 64.3% at 28 days and 60 days of testing respectively.

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INTRODUCTION

Waste tires are a major concern as they cause environmental problems. Although some recycling methods of used tires do exist, they are not sufficient to consume all the amount of accumulated ones. The dispersion of tires in the natural environment is the cause of a huge pollution phenomenon as the materials that constitute a tire are not biodegradable and produce toxic smokes when incinerated. Therefore, new methods of reusing waste tires are needed, especially if they aim at transforming this waste into a cheap resource. There are many methods to manage waste tires such as reclamation, recycling, devulcanization, high pressure and high temperature sintering, burning for energy recovery or use as fuel, pyrolysis to produce carbon black and others.^{1,2} With regard to generating an environmental friendly and economical aspect, one of the preferred methods is recycling by grinding followed by use of the rubber crumbs as raw materials.^{1–3} However, although rubber is the major component of tires (41–48%), there are other components to consider: carbon black, metal, textiles, curing agents,

and other additives but the rubber recovered from waste tires is the main target of this recycling. The recovered rubber can be classified into four types according to its composition, shape, density, and size: shredded tires, tire chips, ground rubber, and waste tire crumbs. Waste tire crumbs can be produced by two major technologies: ambient mechanical grinding and cryogenic grinding. There are several grades of waste tire crumbs depending on the quality and granule size. Generally the granule size is ≤6.35 mm. The quality is determined from impurity due to the metal component in the waste tire such as guaranteed metal free grade and magnetically separated grade. Waste tire crumbs contain natural rubber (NR, *cis*-1,4-polyisoprene) and butadiene rubber (BR); therefore, they can be chemically modified in a similar way to pure NR or BR. Carbonyl telechelic oligomers from the waste tire crumbs have been synthesized and first characterized by Sadaka *et al.*,⁴ and recently by Tran *et al.*⁵ They have been turned into hydroxyl telechelic oligomers, which have been used to prepare polyurethane foams (PUF) by reaction with commercial polyisocyanate.

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There have been several studies related to the synthesis of bio-based polyurethane using HTNR as a soft segment.^{5–18} Considering the biodegradation of the final material, the HTNR-based PU are not easily biodegraded due to the chemical structure that has no ester linkage and very few bacteria strains and fungi are known to attack polyisoprene backbone. Therefore, our group has synthesized polyurethane films using hydroxyl telechelic natural rubber (HTNR) and polycaprolactone (PCL) diols as soft segments^{19–22} and synthesized polyurethane foam (PUF) using HTNR and PCL diols as soft segments.^{23,24} We assumed that the PCL diols would enhance the biodegradation of PU and PUF because PCL is a biodegradable polymer. Our most recent study on the biodegradation of PUF prepared from HTNR oligomers and PCL diols showed a promising result in that the biodegradation of PUF was increased when PCL diols were added in the prepolymerization mixture. Consequently, it should be of interest that PUF synthesized from waste tire oligomers (HTWT) and PCL diols could show similar or different characteristics compared to PUF synthesized from HTNR and PCL diols, as this may be more susceptible to biodegradation.

The objective of the present study was to investigate the influence of the molar ratio between HTWT and PCL diols on foam formation and the physical and thermal properties of this novel bio-based PUF. The biodegradation of PUF according to the Sturm test was also studied and this is an initial work on the biodegradation of PUF synthesized from waste tire crumbs with and without PCL diols.

EXPERIMENTAL

Materials

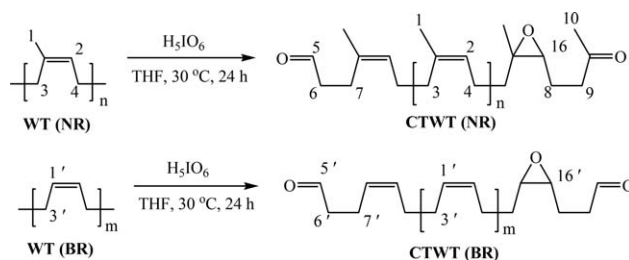
Waste tire crumbs were donated by Delta Gom. PCL diol was purchased from Sigma-Aldrich (number-average molecular weight of 2000 g/mol). Poly[(phenyl isocyanate)-*co*-formaldehyde], PMDI (Lupranate[®]M20S) was obtained from BASF, and consisted of 31.5% of free NCO content and a functionality (fn) of 2.7. Triethylenediamine (DABCO-33LV), dibutyl tin dilaurate (DABCOT12), 1,4-butanediol (BDO), sodium bicarbonate (NaHCO₃), periodic acid, and Celite[®]545 (particle size 0.02–0.1 mm) were from Sigma-Aldrich and used without any further purification. Sodium borohydride (NaBH₄) and silicone surfactant (B8110) were from Acros Organics and Evonik Industries, respectively. Tetrahydrofuran (THF), hydrochloric acid (HCl), and dichloromethane (CH₂Cl₂) were from RCI labscan and used as received. Magnesium sulfate (MgSO₄), sodium thiosulfate pentahydrate (Na₂S₂O₃·5H₂O), and sodium chloride (NaCl) were from Fisher Scientific. Barium hydroxide octahydrate (Ba(OH)₂·8H₂O) was from Quality Reagent Chemicals.

Determination of Waste Tire Crumbs Composition

Thermogravimetric analysis (TGA) was used to quantify the compositions of the waste tire crumbs.^{4,5} It was executed on a TA Instrument (Hi-Tes-Dynamic TGA Q500) with a heating rate of 10 °C/min in a nitrogen atmosphere. The sample weight for analysis was 10 mg.

Synthesis of Telechelic Oligomers from Waste Tire Crumbs

Waste tire crumbs used in the present study were obtained from the same source as those studied by Sadaka *et al.*⁴ and Tran *et al.*⁵



Scheme 1. Synthesis routes of carbonyl oligomers from waste tire crumbs (CTWT).

and it has been reported that the bigger size of these waste tire crumb powders (55%) was in a range of 0.63 to 1 mm. Purification of the waste tire crumbs was performed by Soxhlet extraction in THF for 24 h.⁵ Synthetic methods to obtain the telechelic oligomers were carried out according to Tran *et al.*⁵

Carbonyl Telechelic Oligomers from Waste Tire Crumbs

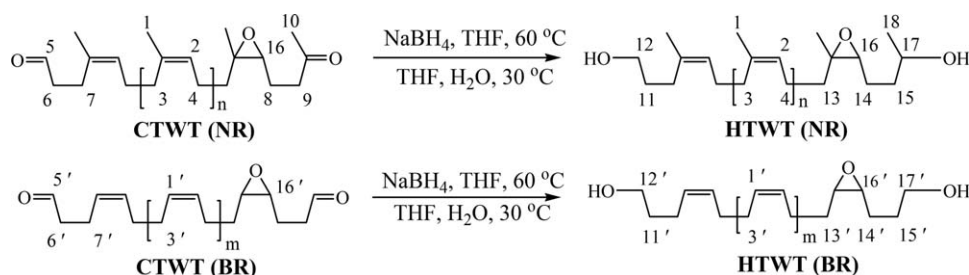
(CTWT). The purified waste tire crumbs (200 g) were suspended in THF (2 L) in a jacketed reaction flask equipped with a mechanical stirrer for 24 h, at room temperature. H₅IO₆ (106 g) was suspended in THF (1.178 L) and was added dropwise to the suspension of the waste tire crumbs. The reaction took place at 30 °C for 24 h. The solid fraction was separated from the CTWT solution by filtration and the solution was washed twice with a mixture of saturated NaHCO₃ solution and a 20 w/v % of Na₂S₂O₃ solution. The obtained organic solution was filtered again through a glass funnel containing a layer of Celite[®] powder in order to remove carbon black residues. The purified solution was washed with saturated NaCl, dried over MgSO₄ overnight, filtered, and evaporated under reduced pressure. The sample was analyzed by ¹H-NMR, FT-IR, and SEC. The schematic reactions of the NR and BR fractions in the waste tire crumbs are shown in Scheme 1.

Hydroxyl Telechelic Oligomers from Waste Tire Crumbs

(HTWT). The transformation of the NR-based and BR-based CTWT into HTWT is shown in Scheme 2. NaBH₄ (10 g) was dissolved in THF (900 mL) in a reaction flask equipped with a magnetic stirrer. A solution of CTWT (30 g) in THF (390 mL) was added dropwise to the solution of NaBH₄. The reaction temperature and time was 60 °C and 24 h, respectively. The solution was cooled to room temperature and a mixture of THF (70 mL) and ice (200 g) was slowly added. The solution was washed twice with a saturated NaCl solution and dried with MgSO₄. After filtration the solvent was evaporated by using a rotary evaporator and the polymer was dried in a vacuum oven. The sample was analyzed by ¹H-NMR, FT-IR, and SEC.

Synthesis of PUF

PUF was prepared by the one-shot technique in which all ingredients were mixed together at once and allowed to cure. Polyol (HTWT and PCL), water, surfactant (B8110), chain extender (BDO), catalyst (DABCO-33LV and DABCO-T12), and CH₂Cl₂ were mixed in a homogenizer with vigorous stirring (11,000 rpm), followed by addition of PMDI with continuous stirring until the liquid became whitened and this was referred to as the creaming time.^{5,12} Then the mixture was poured into a plastic mold, and the rising and tack free time were measured. These times were



Scheme 2. Synthesis routes of hydroxyl oligomers from waste tire crumbs (HTWT).

measured with a digital stopwatch timer device during the PUF preparation. The value of the tack free time included the creaming and rising time. The curing reaction was operated in an oven at 60 °C for 24 h. The foam formulations are listed in Table I and the NCO index was 100. The creaming time, rising time and tack free time were used to calculate the kinetic rate (rate of foam formation).

Characterization

The molecular weight and chemical structure of the telechelic oligomers were determined by $^1\text{H-NMR}$ (BRUKER[®] 400). The Fourier transform-infrared spectroscopy (BRUKER[®] EQUINOX 55) was used to investigate the functional groups in the telechelic oligomers and PUF. The average molecular weight (\bar{M}_n and \bar{M}_w) and dispersity (\bar{D}) of CTWT and HTWT were determined by using a size exclusion chromatography (ThermoFinnigan[®] SEC) instrument. The given values of \bar{M}_n and \bar{M}_w have been obtained after considering the Benoit factor for polyisoprene ($\bar{M}_n = \bar{M}_{n\text{SEC}} \times 0.67$).

The foam density was measured according to ASTM D 3574 Test A. Five specimens were cut to have dimensions of 10 mm \times 10 mm \times 10 mm. The cell dimensions and morphology of the PUF were determined using a JEOL[®] JSM-6510LV scanning electron microscope (SEM). The thermal degradation stability of PUF was investigated on a TA Instrument[®] TGA Q 100 with a heating rate of 10 °C/min in a nitrogen atmosphere.

Table I. Formulation of PUF

Samples	PUF1	PUF2	PUF3	PUF4
Ratio of HTWT and PCL by mole	1/0	1/0.5	1/1	0.5/1
Ingredients	Weight (g)			
HTWT-1270	4	2.21	1.53	0.95
PCL-2000	0	1.79	2.47	3.06
Dichloromethane	1	1	1	1
1,4-Butanediol	0.02	0.02	0.02	0.02
Dabco 33-LV	0.03	0.03	0.03	0.03
Dabco T-12	0.02	0.02	0.02	0.02
B8110	0.07	0.07	0.07	0.07
Water	0.16	0.16	0.16	0.16
PMDI	3.33	3.18	3.13	3.08

Biodegradation Test

PUF1-PUF4 were cut into cubes and the LDPE sample was cut from a LDPE bottle. The weight of PUF and LDPE samples were approximately 24 and 10 mg, respectively. The present study employed the modified Sturm test (OECD 301 B) in which the CO_2 evolution after incubation was measured. In theory, the aerobic microorganisms consume carbon from the foams and CO_2 is the byproduct. Sewage from a natural latex factory (Top Glove Technology (Thailand) Co., Ltd.) was used as a source of microorganisms in the present study. The experiment was carried out at ambient temperature, 27 to 30 °C. The concentration of microorganisms in the culture medium was 30 mg solid/L. Liquid culture medium for biodegradation experiments for the foam was prepared according to OECD 301. Sodium benzoate and low density polyethylene (LDPE) were used as a positive and negative control sample, respectively, and the blank sample was the liquid culture medium. The test was monitored every 2 days for 60 days. The CO_2 was trapped by 100 mL of a 0.02M $\text{Ba}(\text{OH})_2$ solution and consequently precipitated as BaCO_3 . The CO_2 concentration was evaluated by titration of the remaining $\text{Ba}(\text{OH})_2$ from each trap with 0.2M HCl to the phenolphthalein end-point. The total CO_2 concentration was calculated by reference to the blank control flask. The percentage of biodegradation (%biodegradation) of the sample was calculated according to eq. (1)²⁵:

$$\% \text{ Biodegradation} = \left[\frac{(\text{CO}_2)_t - (\text{CO}_2)_b}{\text{ThCO}_2} \right] \times 100 \quad (1)$$

where $(\text{CO}_2)_t$ was the cumulative amount of CO_2 evolved in each test flask containing the sample material, and $(\text{CO}_2)_b$ was the cumulative amount of CO_2 evolved in the blank flask, in grams per flask. The theoretical amount of CO_2 (ThCO_2), in grams per flask, was calculated according to eq. (2)²⁵:

$$\text{ThCO}_2 = M_{\text{TOT}} \times C_{\text{TOT}} \times \frac{44}{12} \quad (2)$$

where ThCO_2 was the theoretical amount of CO_2 that can be produced by the sample, in grams per test flasks; M_{TOT} was the total dry solids in grams, in the sample added into the test flasks at the start of the test; C_{TOT} was the proportion of total organic carbon in the total dry solids in the sample, in grams per gram; 44 and 12 were the molecular mass of CO_2 and atomic mass of carbon, respectively.

Determination of Colony Numbers of Bacteria

Monitoring colony numbers of bacteria was conducted on the first day and last day of the biodegradation test to support the evidence of biodegradability of the samples. 30 mg of the

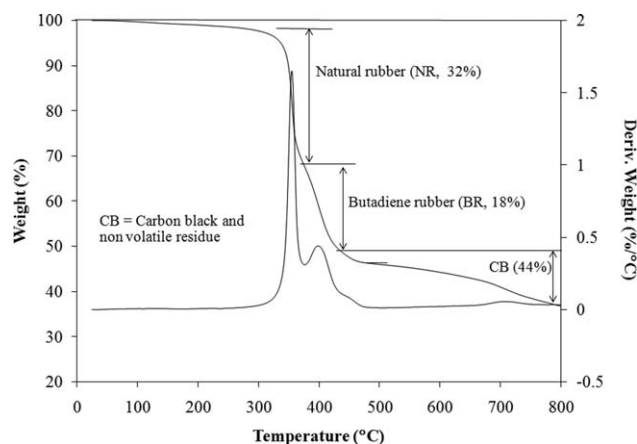


Figure 1. TGA and DTG curves of waste tire crumbs.

sewage water from the sample of the biodegradation test was mixed with 1 L of liquid culture medium. 1 mL of this solution was diluted with saline solution (0.85% NaCl aqueous solution) in order to obtain the concentration of 1:1000. Then, 0.1 mL of this diluted solution was dropped onto a Petri dish containing Plate Count Agar. The Petri dish was kept at 30 °C for 3 days and the colony growth was observed visually and counted according to Jurconi *et al.*²⁶ and Ghazali *et al.*²⁷

RESULTS AND DISCUSSION

Composition of WT

The waste tire crumbs used in the present study came from the same source as that used by Sadaka *et al.*⁴ and Tran *et al.*⁵ in the previous study they have been fully characterized. Therefore, in the present study only the thermogravimetric analysis was executed again to verify the rubber composition. Sadaka *et al.*⁴ reported that processing oil or any other low boiling point components degraded between 200 and 300 °C, and NR and BR degraded with a maximum rate at 350 °C and 410 °C, respectively. The residue at 410 to 560 °C was attributed to carbon black and the residue at the higher temperature was assigned to the inorganic fillers. The result obtained in the present study (Figure 1) agreed with that reported by Sadaka *et al.*⁴ The waste tire crumbs consisted of approximately 32% NR and 18% BR.

Synthesis of CTWT and HTWT

The originality of the approach of this research work is that the polyisoprene and polybutadiene chains in the waste tire crumbs are reduced and functionalized to small oligomers that have reactive chain ends and that can consequently be used as building blocks in the synthesis of polyurethane. Using the same procedure previously applied to polyisoprene chains from pure NR, some of the carbon-carbon double bonds in the NR and BR backbones in the waste tire crumbs were chemically cleaved by the action of periodic acid to obtain carbonyl telechelic oligomers (CTWT). The ketone and aldehyde end-groups of these oligomers were reduced to hydroxyl end-groups (HTWT) by using NaBH₄. As the NR and BR were both present in the tires; therefore, CTWT and HTWT consisted of CTNR/CTBR and HTNR/HTBR, respectively. The ¹H-NMR spectra of the NR and CTWT are shown in Figure 2. The chemical shift (δ) at 5.10

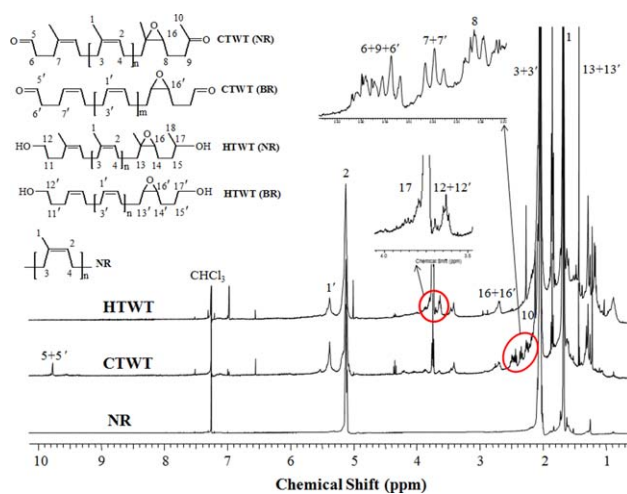


Figure 2. ¹H-NMR spectra of NR, CTWT, and HTWT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ppm (=CH), 2.05 ppm (CH₂) and 1.70 ppm (CH₃) due to the isoprene unit in NR appeared also in CTWT and HTWT. The appearance of new signals at 2.10, 2.15 to 2.60, and 9.80 ppm was observed in the CTWT. These signals were assigned to the protons adjacent to the carbonyl functional groups: 2.49 ppm (H₆, -CH₂CHO), 2.43 ppm (H₉, CH₃COCH₂CH₂-), 2.34 ppm (H₇, -CH₂CH₂CHO), 2.25 ppm (H₈, CH₃COCH₂CH₂-), 2.10 ppm (H₁₀, CH₃COCH₂CH₂-), and 9.80 ppm (H₅, -CH₂CHO). The protons adjacent to the carbonyl functional groups in the BR component included 2.49 ppm (H₆, -CH₂CHO), 2.34 ppm (H₇, -CH₂CH₂CHO), and 9.80 ppm (H₅, -CH₂CHO). The results confirmed the presence of ketone and aldehyde groups at the chain ends of CTWT. Epoxidation is always obtained in the first step of the reaction between the periodic acid and carbon-carbon double bonds of rubbers. Most of the epoxide rings were opened and formed carbonyl groups in the next reaction. CTWT showed the signal at 2.70 ppm for a proton linked to the carbon of the epoxide ring that indicated the presence of epoxy groups and allowed counting their number per chain. The FT-IR spectrum of CTWT is shown in Figure 3. The characteristic peaks in NR were the

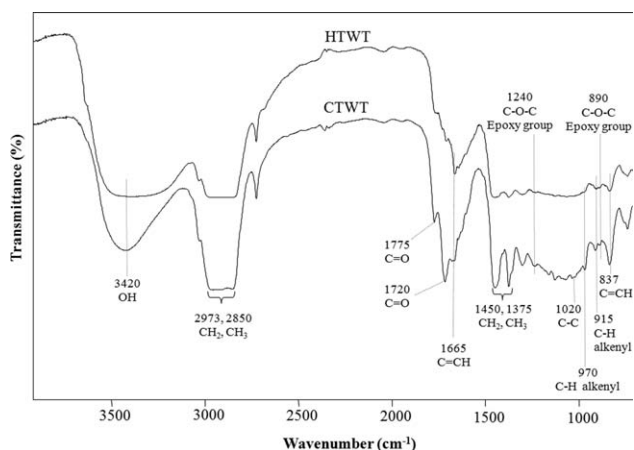


Figure 3. FT-IR spectra of CTWT and HTWT.

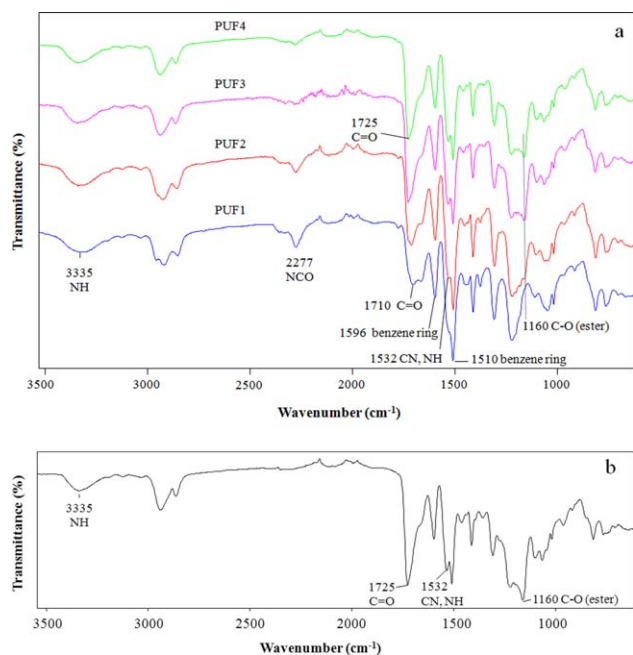


Figure 4. FT-IR spectra of PUF: (a) PUF1–PUF4, and (b) PCL foam. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

band at 1665 cm^{-1} that represented symmetric —C=CH stretching, and the band at 837 cm^{-1} that was attributed to —C=CH bending. The peaks of the CH_2 and CH_3 stretching appeared at 2973 and 2850 cm^{-1} , respectively. The bands at 1450 and 1377 cm^{-1} were assigned to the C—H bending of CH_2 and CH_3 , respectively. The characteristic peaks of BR were found at 915 and 970 cm^{-1} that corresponded to the C—H bending of alkenyl²⁸ and at 1020 cm^{-1} that corresponded to the C—C stretching.²⁹ The C=C stretching of BR was overlapped with that of NR. Very strong absorption bands of the carbonyl group (C=O stretching) were observed at 1720 and 1775 cm^{-1} . Based on SEC analysis, \bar{M}_w , \bar{M}_n , and \bar{D} of CTWT were 1000 g/mol , 3100 g/mol , and 3.1 , respectively. The \bar{M}_n of CTNR and CTBR in the CTWT calculated from the $^1\text{H-NMR}$ spectrum of CTWT were 1200 and 900 g/mol , respectively.

The $^1\text{H-NMR}$ spectrum of the HTWT (Figure 2) did not show the signal at 9.80 ppm for the aldehyde group but the signal of the CH_2 and CH proton in the α position of the hydroxyl end group appeared at 3.65 and 3.80 ppm , respectively. The signal at 2.70 ppm was assigned to the epoxide ring (H_{16} and $\text{H}_{16'}$ proton in HTWT). The percentage of epoxidation of the NR and BR portions in the HTWT was determined from the $^1\text{H-NMR}$ spectrum of HTWT.⁵ The epoxide content in the NR and BR portions (HTNR and HTBR) were 5.3% and 10% , respectively. The FT-IR spectrum of HTWT showed a peak at 3420 cm^{-1} , which was assigned to the O—H stretching of the hydroxyl group, while the absorption band of the carbonyl group at 1720 cm^{-1} was not found (Figure 3). This result substantiated that the carbonyl group in the CTWT was changed to the hydroxyl group in the HTWT. The molecular weight, \bar{M}_w , of HTWT was also calculated by the $^1\text{H-NMR}$.⁵ The \bar{M}_n calculated from the $^1\text{H-NMR}$ spectrum of HTNR and HTBR

were 1400 and 1000 g/mol , respectively. \bar{M}_w , \bar{M}_n , and \bar{D} of the HTWT as determined from the SEC were 1600 g/mol , 3619 g/mol , and 2.3 , respectively.

Synthesis of PUF

Bio-based PUF were prepared in earlier projects using oligoisoprene diols obtained from pure NR. Successively the oligoisoprene diols were obtained from waste tire crumbs and used to prepare PUF with similar properties as those generated from pure NR. In this project, the oligomer diols obtained from waste tire crumbs were used in a combination with commercial PCL diols to synthesize potentially biodegradable PUF. Therefore, the formulation was optimized from previous syntheses.

In order to verify foam structure, the FT-IR spectra were recorded with an attenuated total reflection (ATR) mode and they are shown in Figure 4(a). PUF2, PUF3, and PUF4 were synthesized from a mixture of HTWT and PCL diols and their FT-IR spectra looked similar to that of PUF1. The broad absorption band at 3335 cm^{-1} represents the stretching vibration of hydrogen bonded N—H urethane. The bands at 1532 cm^{-1} was attributed to the bending vibration of N—H and the stretching vibration of C—N which confirmed that urethane linkages were formed between —OH in the HTWT and —NCO . The band at 1710 to 1725 cm^{-1} which was observed in PUF1–PUF4 was assigned to the carbonyl stretching of C=O that was hydrogen bonded with the N-H group of polyurethane.^{20–22,30,31} The bands at 1510 and 1596 cm^{-1} were derived from the aromatic rings of PMDI.³² The PCL-based PUF [Figure 4(b)] also showed similar main characteristics, except there was no peak at 2277 cm^{-1} that belonged to the free —NCO . This result indicated that the reaction between —NCO and —OH in this foam was complete. The carbonyl stretching of PCL-based PUF appeared at 1725 cm^{-1} which overlapped to the carbonyl stretching of PCL.³³

The rate of foam formation or the kinetic rate of PUF involved a creaming time, rising time, and tack free time.^{34–36} The creaming time started at the mixing step until the foam began to rise. The time at which the foam reached its maximum height was referred to as the rising time, and the tack free time was the time at which the outer surface of the foam lost its stickiness. Generally the tack free time included times for creaming and foam rising as well. The creaming, rising and tack free time of PUF are listed in Table II. The addition of PCL diols decreased the kinetic rate of foam formation because PUF2–PUF4 showed a significant increase in the tack free time. Regarding to PUF2–PUF4, PUF2 showed the longest tack free time whereas PUF4 showed the shortest time. The tack free time depended on the molar ratio of HTWT/PCL diol. A highest HTWT content provided the highest tack free time. This result agreed with the preliminary study²³ in that the PUF from the PCL diols showed a higher rate of foam formation than that from HTNR. This indicated that the hydroxyl groups from PCL were more reactive than those from the HTWT. The influence of the molar ratio of HTWT/PCL diols not only affected the tack free time but also affected the creaming and rising time with the same trend. Viscosity of the mixture might be another parameter that should be of concern in the formation of the foam. Unfortunately, we could not measure the viscosity of the

Table II. Rate of Foam Formation and Physical Properties of PUF

Code	HTWT/PCL	Creaming time (s)	Rising time (s)	Tack free time (s)	Density (kg/m ³)	Cell size (mm)
PUF1	1/0	25	113	145	32.04 ± 2.09	0.36 ± 0.08
PUF2	1/0.5	27	127	300	61.16 ± 6.62	0.26 ± 0.10
PUF3	1/1	24	106	267	70.11 ± 4.64	0.29 ± 0.12
PUF4	0.5/1	18	98	223	38.10 ± 1.08	0.52 ± 0.21

mixture during mixing and foam formation. However, by virtual observation it was found that the two-component system (HTWT and PCL diol) in the PUF2-PUF4 had higher viscosity than the single component system of PUF1.

Morphology of PUF

The cellular structure of the PUF as observed by the SEM is shown in Figure 5. Polyhedral, closed cells appeared in all the PUF and some semi-closed cells were also observed. A higher distribution of cell size was observed in the PUF2 and PUF3.

The addition of the PCL diols provided more irregular shaped cells. The density and cell size of the PUF1-PUF4 were in the range of 32 to 70 kg/m³ and 0.26 to 0.52 mm, respectively (Table II). The two-component system (HTWT and PCL diols) of PUF2-PUF4 showed a higher density and a larger cell size than the single component system (HTWT) of PUF1. The high density of PUF2 and PUF3 seemed to correlate with their small cell size and tack free time. PUF2 and PUF3 showed more sluggish foaming than PUF1 as these formulations were characterized with a longer tack free time and resulted in a higher

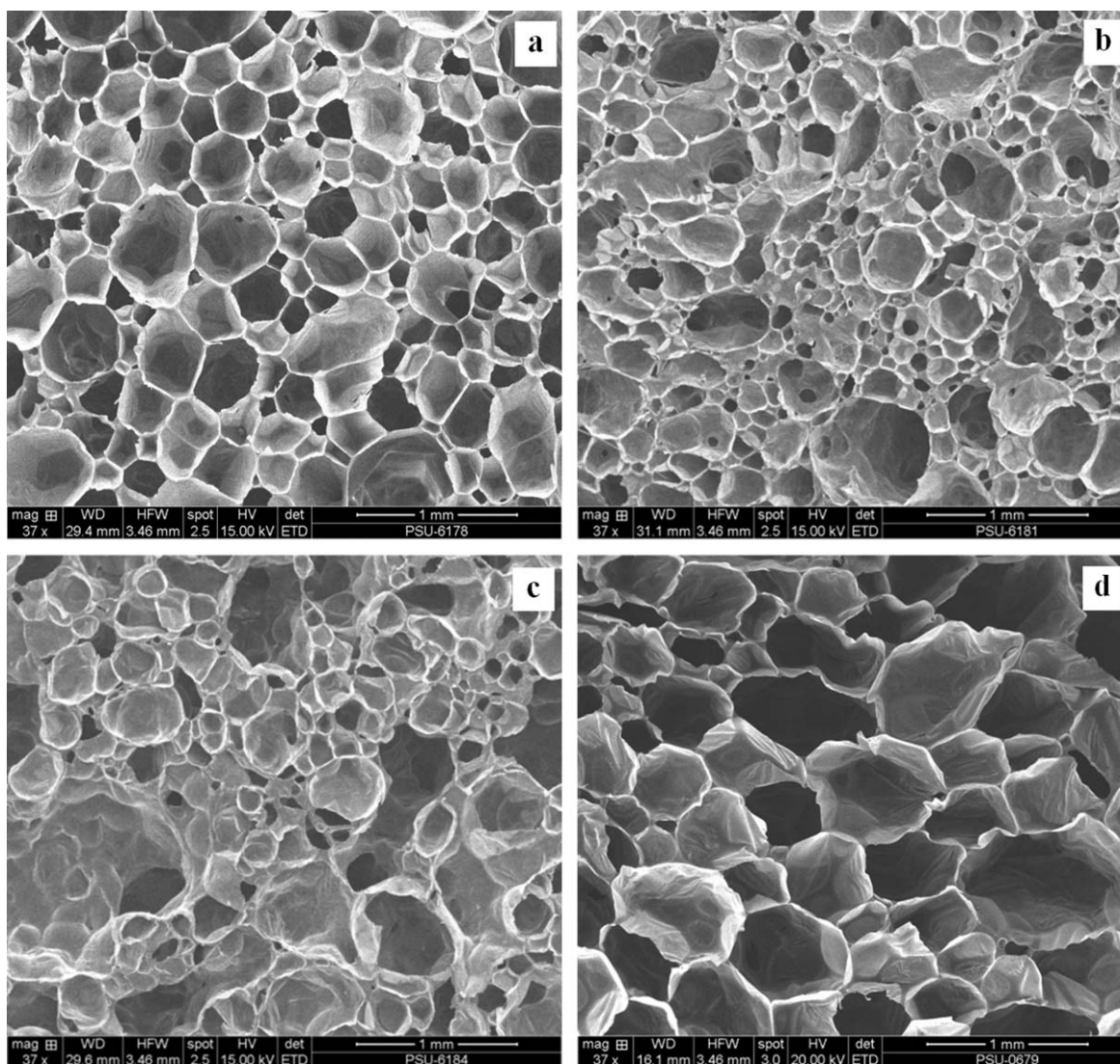


Figure 5. SEM micrographs of PUF: (a) PUF1, (b) PUF2, (c) PUF3, and (d) PUF4.

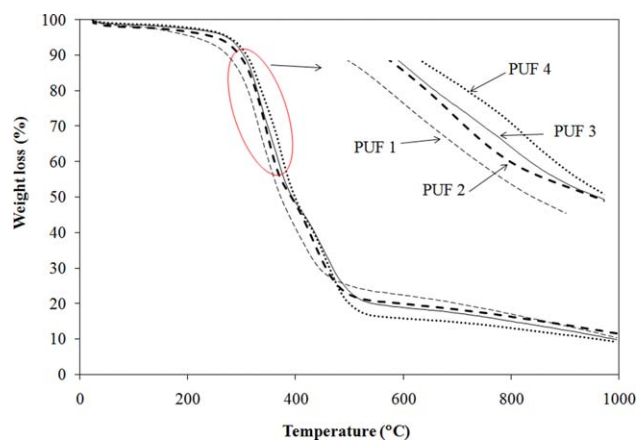


Figure 6. TGA curves of PUF1–PUF4. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

density foam with a smaller average cell size. As stated earlier both the molar ratio of the HTWT/PCL diols and the viscosity of the mixture played an important role on foam formation, they also had an effect on the density and cell size of the foam. This indicated that based on the density of the obtained PUF these molar ratios (1/0.5 and 1/1) were not suitable for the preparation of PUF and a higher molar ratio of the PCL diol (0.5/1) was required. If the system had a relatively high viscosity, a higher concentration of the more reactive diols was essential.

Thermal Stability of PUF

The thermal stability of PUF was investigated performing the thermogravimetric analyses that included both the analysis of the weight loss and the derivative of the weight loss curves. The TGA and DTG curves are shown in Figures 6 and 7. The degradation temperature (T_d) was expressed in terms of the temperature at which the sample weight loss of 5%, 10% and 50% referred to T_{d5} , T_{d10} , and T_{d50} , respectively, as shown in Table III. It was found that the PCL diols increased the thermal stability of PUF. The weight loss of PUF at T_{d5} , T_{d10} , and T_{d50} rose with the increasing PCL content. The highest thermal stability was found in PUF4, for which T_{d5} , T_{d10} , and T_{d50} were higher than those of the PUF1 of approximately 63, 36, and 27 °C, respectively. The presence of the PCL diols in the PUF also resulted in a change of the thermal decomposition route of the PUF. The DTG curves of PUF1 presented a two-step thermal decomposition and PUF2–PUF4 presented a three-step thermal decomposition. A characteristic temperature was determined from the maximum of the derivative curve (T_{max}) and is listed in Table III. The first stage of degradation at 330 to 346 °C

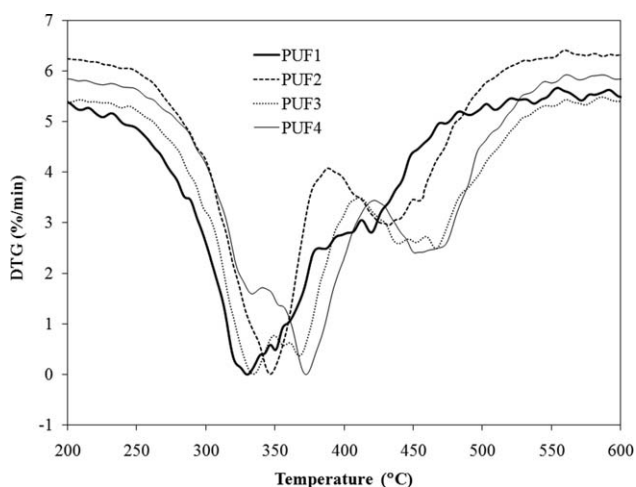


Figure 7. TGA derivative curves of PUF1–PUF4.

corresponded to breakage of the urethane bond. The second stage at 367 to 432 °C corresponded to the decomposition of the HTWT,^{5,11,12} and the third stage at 451 to 466 °C corresponded to the decomposition of the PCL diols.^{31,37}

Biodegradation of PUF

The Sturm test is one of the most well-known biodegradability tests due to its simplicity. This test is generally used for a preliminary study of new potentially biodegradable materials. The theory assumes that the CO_2 generated in the system is related to the biodegradation of a sample, whereby the microorganisms consume carbon from the sample as a nutrient and CO_2 is one of the main byproducts of their metabolisms. Higher metabolic processes will release higher amount of CO_2 and is an indication of higher biodegradation of the sample. This type of test is strongly dependent on the type of microorganisms chosen and their metabolisms. There have been many research efforts on seeking the most promising microorganisms for biodegradation of plastics but very few bacteria strains able to decompose plastics have been isolated from wastes. In order to increase the probability of biodegradation, often sludge from waste water plants are used because they are “cocktails” of numerous strains of bacteria. Therefore, in this study the waste water from a sewage system from the concentrated latex factory was used as a source of microorganisms. We believed that some microorganisms in this waste water could consume NR as their carbon source and some could consume the PCL, which is already known as a biodegradable polymer.

The Sturm test was adapted to the present study and the experimental results are shown in Figure 8. Generally the Sturm test was

Table III. Thermal Degradation Stability of PUF

	Degradation temperature (°C)			T_{max} (°C) from TGA curves at		
	T_{d5}	T_{d10}	T_{d50}	First step	Second step	Third step
PUF1	213	273	372	330	419	—
PUF2	251	295	392	346	432	451
PUF3	272	304	394	334	367	466
PUF4	276	309	399	333	372	451

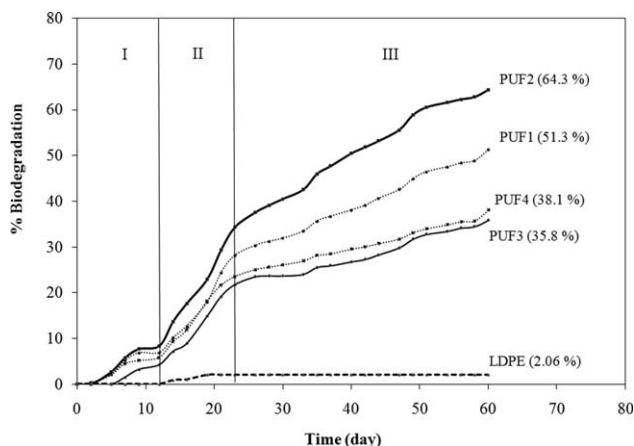


Figure 8. %Biodegradation of PUF and LDPE.

performed for 28 days and the data reported as %Biodegradation versus time, based on eqs. (1) and (2) (see Biodegradation Test section). The results showed that after 28 days the percentage of biodegradation of samples could be ranked in the following order: PUF2 (39.1%) > PUF1 (31.2%) > PUF4 (25.5%) > PUF3 (23.7%). These results were very interesting because they showed a triple increase in the percentage of biodegradation compared to the PUF having a similar composition but constituted by the hydroxyl telechelic oligomers (HTNR) from the pure NR (STR CV60 grade) and PCL diols (these data have been obtained from our previous experiments) as shown in Table IV. The test was continued and at the end (60 days), the rank of %Biodegradation did not change and a high percentage of biodegradation was obtained for all samples. These values were also higher than those of the PUF prepared from the pure NR and they also showed the same ranking of %Biodegradation (Table IV).

The addition of the PCL diols increased biodegradability of the HTWT-based PUF and a low PCL diol content was more favorable. As this is the first study of the biodegradation of polyurethane foams obtained from waste tire crumb diols and PCL diols, we do not have any data in literature to which compare our results; therefore, we looked at other biodegradation studies involving NR-based materials. It has been reported that the %Biodegradation of the NR latex gloves was 10% when using *Streptomyces coelicolor* CH13 for 30 days³⁸ whereas the %Biodegradation of PUF1 was 31.2% at 28 days. The much higher biodegradation in the present study may arise from the difference in bacteria strain and the molecular architecture

Table IV. %Biodegradation of PUF Prepared from HTWT and HTNR

Sample	Percentage of biodegradation (%) at testing of			
	HTWT-based PUF		HTNR-based PUF	
	28 days	60 days	28 days	60 days
PUF1	31.2	51.3	8.4	31.9
PUF2	39.1	64.3	11.3	45.6
PUF3	23.7	35.8	N/A	N/A
PUF4	25.5	28.1	7.5	35.5

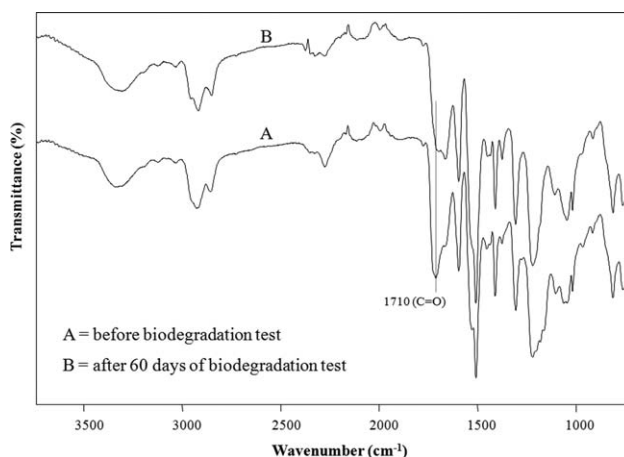


Figure 9. FT-IR spectra of PUF2 before and after biodegradation test.

(morphology) of the sample. *Streptomyces coelicolor* CH13 was extracted from soil while the bacteria used in the present study were from waste water and contained many types of strains that were not identified because it was not in the scope of this study. The latex glove sample was a dense solid sample; in contrast, the PUF1 was a foam sample. Some open cells in the foam may have allowed bacteria deposited inside the foam sample while it was more difficult for the bacteria to penetrate into the dense sample. Another significant difference was the molecular weight of NR. NR in the latex glove had a very high molecular weight, e.g., >100,000 g/mol, but the molecular weight of HTWT was very low, e.g., 1600 g/mol. Compared to our previous study that used HTNR prepared from pure NR mentioned earlier, this HTNR had a similar molecular weight to the HTWT but the PUF prepared from HTWT showed a higher %Biodegradation. There were two significant differences between HTNR and HTWT. First, HTWT is composed by a second polymer, BR. Secondly, the structure of the HTWT and HTNR oligomers is not the same, because sulfur is still present in the HTWT oligomers, which means they still have branches from the incomplete devulcanization. We cannot exclude that some bacteria strains can break the carbon-sulfur bonds left after the action of periodic acid during the oligomers synthesis (in fact periodic acid can break sulfur-sulfur bonds but not carbon-sulfur).

The biodegradation rate was derived from the slope of the curves in Figure 8. All samples, except LDPE, showed a similar behavior that could be classified into three periods based on the biodegradation rate that was derived from a slope of the curve. The first period (I), of approximately 12 days, was an induction period in which the %Biodegradation was less than 10%. After the induction period the biodegradation rate increased remarkably. After 23 days, the biodegradation rate decreased and biodegradation continued at a constant rate. The biodegradation rate for all the periods was in the following order: PUF2 > PUF1 > PUF4 > PUF3. We expected that the addition of PCL diols should increase the biodegradation of PUF because PCL is a biodegradable polymer and PCL diols would increase the hydrophilicity of PUF. The water contact angle of NR and PCL is 106 and 77°, respectively.^{39,40} However, this assumption

was verified only for PUF2, which showed higher %Biodegradation than PUF1.

PUF2 was characterized by FT-IR before and after testing for biodegradation to examine any changes in the functional groups. A decrease at wavelength 1710 cm^{-1} was observed (Figure 9), which could correspond to a cleavage of the ester bonds of the urethane groups ($\text{H}_2\text{N-CO-OR}$) by the action of microbial esterases.⁴¹ The colony numbers of PUF2 increased from 8×10^4 CFU/mL at the beginning of the biodegradation test to 31×10^4 CFU/mL at 60 days. These results indicated that there were effective bacteria in the waste water that could live and grow by using PUF as a carbon source.

CONCLUSIONS

Rubber crumbs from waste tires were used as a starting material for the synthesis of hydroxyl telechelic oligomers (HTWT), which have been used as diols in the polyurethane foam preparation (PUF). HTWT consisted of oligoisoprene chains from natural rubber (NR) and oligobutadiene chains from butadiene rubber (BR) in a ratio that depended on the composition of the waste tire crumbs. HTWT were successfully synthesized via carbonyl telechelic oligomers from the purified waste tire crumbs (CTWT). Four PUF types were prepared with different molar ratios between the HTWT and polycaprolactone (PCL) diols. ¹H-NMR and FT-IR were performed on the obtained CTWT, HTWT, and PUF to confirm molecular structure. The kinetic rate of foam formation and foam morphology depended on the molar ratio between HTWT and PCL diol. The presence of the PCL diols decreased the kinetic rate by increasing the tack free time, which might be due to the higher viscosity of the mixture. The longer tack free time produced higher density foams with a smaller cell size. All foams showed a closed cell structure with a polyhedral shape. Addition of the PCL diols increased the thermal degradation stability of PUF. The biodegradation test showed a promising result that all PUF samples were subject to partial biodegradation. PUF2 having 1/0.5 HTWT/PCL diols showed the maximum percentage of biodegradation at 39.1% and 64.3% after 28 days and 60 days of testing, respectively.

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