Recycling Waste Tires: Generation of Functional Oligomers and Description of Their Use in the Synthesis of Polyurethane Foams

Thi Kieu Nhung Tran, Jean-François Pilard, Pamela Pasetto

LUNAM Université, Institut des Molécules et des Matériaux du Mans, Equipe Méthodologie et Synthèse des Polymères, UMR CNRS 6283, Université du Maine, Avenue Olivier Messiaen, 72085 Le Mans Cedex 9, France
Correspondence to: P. Pasetto (E-mail: pamela.pasetto@univ-lemans.fr)

ABSTRACT: The accumulation of waste tires is a big environmental issue and different approaches have been proposed to eliminate or recycle this material in the end of its life. However, each approach presents drawbacks and the need for a real valorization of the tire components is still of interest. In a previous work by our group, it was demonstrated that an oxidative cleavage of the polyisoprene and polybutadiene chains contained in the tires led to the synthesis of telechelic oligomers with a ketone and an aldehyde at the chains ends. In this work, the process to obtain these carbonyl oligomers has been improved, with a particular concern for the elimination of the maximum amount of carbon black. The carbonyl oligomers can be easily reduced to hydroxyl oligomers and, in order to show the benefit of the recycling process, an application of these hydroxyl oligomers is reported: they have been used as building blocks (polyol precursors) in the preparation of polyurethane (PU) foams. The morphology of the resulting foams was observed by scanning electron microscopy technique: the images showed an almost open-cell structure and a homogeneous distribution of cell size. Mechanical (tensile and compressive strength) and thermal properties of PU foams synthesized from "recycled" oligomers from waste tires were compared to those of PU foams synthesized from analogue oligomers derived from natural rubber. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41326.

INTRODUCTION

In this "Plastic Age," the disposal of waste tires has caused some serious environmental and social challenges. The European tire production[1] was estimated 4.8 million tons in 2011. This paramount annual production will become waste tire, sooner or later. Initially, the waste tires were discarded as landfill. Nevertheless, this discard caused environmental problems such as soil pollution due to the leaching of small molecular additives, and mosquitoes spreading, not to mention the air pollution and the public danger provoked by accidental fires. That is why in the Directive 1999,[2] the European Commission has banned the discard of waste tires as landfill. The worn tires have also been burnt in boilers in cement kilns or electricity generation plants. A study[3] compared different ways of employing the used tires and it came out that fuel substitution in cement production is the one with the minor environmental impact, in the sense that it does not involve the use of conventional fuels which are required in the grinding process. However, this fuel source creates air pollution and represents also a low value recovery process of waste rubber. As consequence,

the reclaiming of waste tire is the most desirable approach to solve the disposal problem and also to save some precious petroleum. The reclaiming of waste tires can be categorized in three groups: physical reclaiming processes, chemical reclaiming processes, microbial treatments. There are many types of physical processes: mechanical,[4,5] thermomechanical,[6] cryomechanical,[7] microwave,[8] and ultrasound.[9] The chemical reclaiming processes by organic disulfides and mercaptans,[10] by inorganic compounds,[11] by miscellaneous chemicals,[12] by pyrolysis[13] have also been attempted. The possibility of using microorganisms to degrade the vulcanized rubber has been considered and "biological" treatments have been investigated using chemoautotrophic, acidophilic, and sulfur-oxidizing bacteria to degrade the crosslinked material.[14,15] All these processes are aimed to devulcanize the crosslinking network of rubber. However, compared to virgin rubber, this reclaimed rubber loses some important physical–mechanical properties.

We have focused our attention on the chemical reclaiming related to the polyisoprene/polybutadiene main-chain scission

Additional Supporting Information may be found in the online version of this article.

by inorganic compounds. Some attempts have been already reported but these processes were carried out at an high temperature[16] or with systems[11] that could not control the molecular weight or the functionality of the smaller molecules obtained. Sadaka et al.[17,18] reported the controlled degradation of waste tire by an oxidative cleavage with periodic acid at low temperature (30°C). By this cleavage, telechelic carbonyl oligomers were obtained.

In the present work, hydroxyl telechelic oligomers (HTOs) have been synthesized from two sources: natural rubber (NR) and waste tire crumbs. They were used as Polyols in the reaction with polyisocyanates and the different properties of the polyurethane (PU) foams synthesized from these precursors were investigated and compared.

PU foams are one of the largest segments of PU industry because of their omnipresence in our everyday life. Flexible foams are used in bedding (mattresses, pillows), furniture, noise abatement, automotive comfort, or even filtration, whereas the rigid foams are mostly used in the construction industry as thermal insulation material. The PU is generally synthesized from a polyol (polyethers, polyesters) and an isocyanate (toluene diisocyanate; poly[(phenyl isocyanate)-co-formaldehyde]; 4,4′methylenebis[phenyl isocyanate]).[19] These precursors are produced from petrol chemistry, therefore, due to limited resource fossil feedstock, the production of polyurethane foams (PUFs) from renewable sources is an ongoing area of research. So far vegetable oils,[20] cellulose,[21] biopitch,[22] and starch[23] have been used as precursors. Recently, three main competitive products have been launched into the market: BASF product Lupranol® Balance 50[24] from castor oil; Cargill BiOH® polyols[25] from triglycerides; Dow Chemical Company Renuva™ polyols[26] from biodiesel. Foam producers such as Foamex, Recticel, Carpenter, and Sanko Espuma are adopting the manufacture of foams based on renewable polyols for mattresses and furniture.[27] In conclusion, the production of PU foams from renewable polyols is a promising subject in both academic and industrial research.

In previous work of our team, flexible PU foams were successfully synthesized using NR.[28] Hence, the objective of the present work was to prepare PU foams from waste tires, which contain approximately 40% of synthetic or NR[29] and compare their properties to the ones of the foams from NR. This work concerned not only the recycling of waste tires, but also an application of the derived products to show the potential valorization of this waste to obtain a new material.

EXPERIMENTAL

Materials and Methods

$NaHCO_3$ technical reagent grade, dried $MgSO_4$ laboratory reagent grade, $Na_2S_2O_3 \cdot 5H_2O$, and NaCl general purpose grade were purchased from Fisher. Celite® 545 (particle size 0.02–0.1 mm) was from Merck. Poly[(phenyl isocyanate)-co-formaldehyde] (PMDI, 31.5% free NCO content, $\bar{f}_n = 2.7$), triethylenediamine (DABCO-33LV), dibutyl tin dilaurate (DABCO-T12), 1,4-butanediol (BDO), periodic acid, $NaBH_4$ were purchased from Sigma-Aldrich and used without any further purification.

Silicone surfactant (B8110) was obtained from Goldschmidt. NR was 5CV. Tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were purchased from Fisher and were used as received. Waste tires crumbs were donated by Delta Gom.

¹H-NMR and Matrix-Assisted Laser Desorption/Ionization Time-of-Flight Analysis

¹H spectra were recorded on a Bruker 400 Fourier transform spectrometer at 400.13 MHz. The samples were dissolved in $CDCl_3$, using tetramethylsilane as an internal standard.

The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) spectrum was registered on a Bruker Biflex III spectrometer equipped with a nitrogen laser ($\lambda = 337$ nm). The spectrograms were obtained in linear mode with an acceleration tension of 19 kV. The irradiated sample was dissolved in chloroform. The DIT (dithranol) and AgTFA (silver trifluoroacetate) were employed as matrix and cationizing agent, respectively.

Size Exclusion Chromatography

The number-averaged molecular weight ($\bar{M}_n$) and molecular weight distribution [Đ, dispersity[30]] were measured at 35°C on a ThermoFinnigan SEC instrument (equipped with a Spectra SYSTEM AS1000 autosampler, a SpectraSYSTEM UV2000 and a SpectraSYSTEM RI150 detectors), using a polymer laboratories gel 5 mm MIXED-D columns, calibrated with a series of standard polystyrenes (580–483 $\times$ 10^3 g mol^{-1}). THF (1.0 mL min^{-1}) was used as eluent and the polymeric solutions injected had a concentration of 5 mg/mL.

Themogravimetric Analysis

Thermogravimetric analysis (TGA) was performed on a TA Instrument (Hi-Res-Dynamic TGA Q 500) with an initial heating rate 50°C/min, under nitrogen or oxygen, in the range 25–1000°C. The sample weight was 10 mg.

TGA coupled with mass spectrometry was performed on a Netzsch STA 449 F3 Jupiter® coupled with a Netzsch QMS 403 C Aëolos. The heating rate was 5°C/min and the flow was 60 mL/min air 20 mL/min argon.

Characterization of Mechanical Properties

The density of PU foams was measured according to ASTM-D3574-test A. This test concerns the determination of the density of foams by calculation from the mass and the volume of the specimen. The density value thus obtained applies only to the immediate area from which the specimen has been taken. It does not necessarily relate to the bulk density of the entire molded pad. A representative specimen of regular shape, circular, or square without skins or densification lines, not less than 1000 mm^3 in volume, was cut from a portion free of voids and defects and as near as possible to the foam section of which the tension and tear specimens were taken. Three specimens were tested. The calculation of the density (kg/m^3) comes from the formula: density $= M/V \times 10^6$, where $M =$ mass of specimen (g) and $V =$ volume of specimen (mm^3).

The viscosity measurements were carried out on AR2000 viscometer (TA instrument), using a plate-plate geometry (diameter of 40 mm and gap of 700 μm). Peltier system was used to
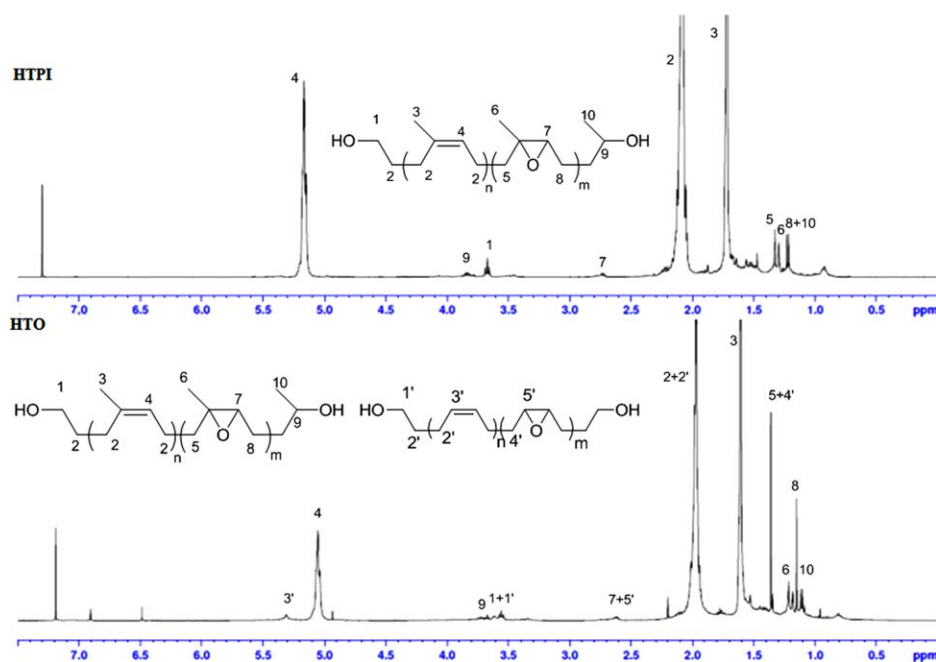
Figure 1. ^{1}H-NMR spectra of oligomers HTPI from natural rubber and HTO from waste tires. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

control the temperature. The viscosity of hydroxyl telechelic *cis*-1,4-polyisoprene (HTPI) was studied at 20°C, 50°C and 100°C.

Compression force deflection test and tensile strength test were carried out according to ASTM-D3574-test C and ASTM-D3574-Test E, respectively.

Scanning Electron Microscopy

The samples were analyzed without metallization on a JEOL JSM-6510LV scanning electron microscopy (SEM) at a voltage of 10 kV and low vacuum (30 Pa). The same instrument was used to perform EDX (energy-dispersive X-ray spectroscopy) analyses. The program JEOL Scanning Electron Microscope allowed the calculation of cell sizes. The PU foams were scanned on a surface of 48 mm^2. The diameter of each cell in this surface was measured and the mean of the diameters gave the average cell size.

Elemental Analysis

Elemental analysis was performed by the Service Central d'Analyses du Centre National de Recherche Scientifique, Gif-sur-Yvette (France).

Synthesis of CTPI From NR

The synthesis is described in Scheme S1(a) of Supporting Information.

A NR block was cut in small pieces (163.12 g) and then it was dissolved in 4 L of THF in a jacketed reaction flask (capacity 5 L) equipped with a mechanical stirrer, for one night, at room temperature. A solution of periodic acid (37.2 g) in THF (0.4 g/mol) was added dropwise into the suspension of NR. After this addition, the solution was vigorously stirred for 24 h at 30°C. At the end of the reaction, the solution was filtered to eliminate the solid residues and evaporated with a rotary evaporator.

A sticky product was obtained, which was then dissolved in CH$_2$Cl$_2$. This solution was washed once with a saturated NaHCO$_3$ solution, then, once with a 20% weight Na$_2$S$_2$O$_3$ solution, and finally once with a saturated NaCl solution. Then, the organic phase was dried over MgSO$_4$ overnight. A yellowish viscous liquid was obtained after filtration and evaporation of CH$_2$Cl$_2$ (145 g; yield: 89%). Carbonyl Telechelic *cis*-1,4-polyisoprene (CTPI) structure and chemical shifts are shown in Figure S6 of Supporting Information.

^{1}H-NMR (CDCl$_3$) δ (ppm): 9.77(s, 1H, CH$_2$C*H*O), 5.10(s, 1 nH, C=C*H*), 2.49 (m, 2H, C*H*$_2$CHO), 2.43 (t, 2H, CH$_3$COC*H*$_2$CH$_2$), 2.34 (m, 2H, C*H*$_2$CH$_2$CHO), 2.25 (m, 2H, CH$_3$COCH$_2$C*H*$_2$), 2.13 (s, 3H, C*H*$_3$COCH$_2$), 2.05(s, 4nH, C*H*$_2$CC*H*$_3$CHC*H*$_2$), 1.65 (s, 3nH, CH2CC*H*3CHCH2). $\overline{M}_{n,\text{GPC}}$= 4400(g/mol); Đ = 1.86

Synthesis of HTPI From CTPI

The synthesis is described in Scheme S1(b) of Supporting Information.

A suspension of CTPI (145 g) and NaBH$_4$ (15 g, 65.82 mmol) in THF (2.250 L) was introduced in a jacketed reaction flask (5 L). After stirring overnight at 60°C, the solution was cooled at room temperature, then hydrolyzed by adding 300 g of ice. This reaction mixture was transferred in a separating funnel and washed two times with a saturated NaCl solution. It was dried over MgSO$_4$ overnight the filtered. The final product was obtained after THF evaporation, as a viscous, yellowish liquid. (130 g; yield: 89.7%). Viscosity (4.6 Pa s, 50°C). HTPI structure and relative chemical shift values are shown in Figure 1.

^{1}H-NMR (CDCl$_3$) δ (ppm): 5.15(s, 1nH, C=C*H*), 3.80 (m, 1H, C*H*OH), 3.65 (t, 2H, C*H*$_2$OH), 2.1(s, 4 nH, C*H*$_2$CCH$_3$CHC*H*$_2$),
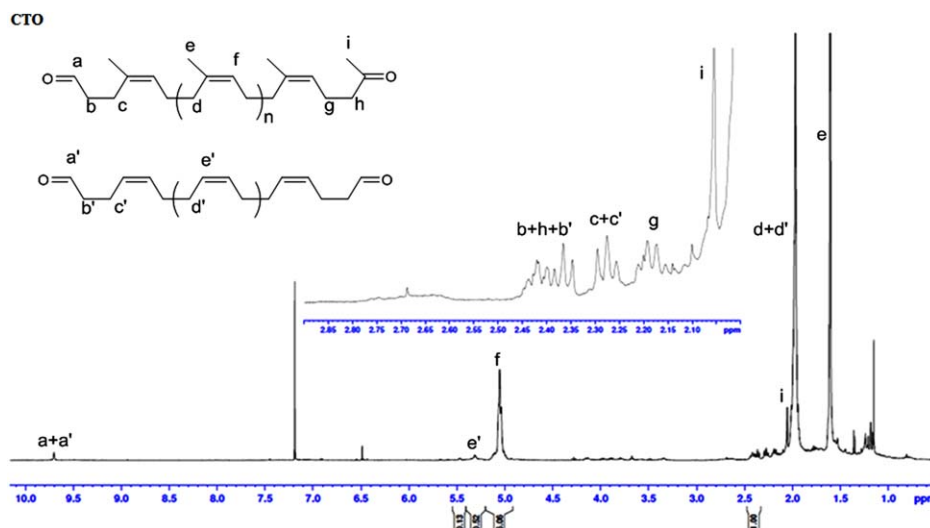
Figure 2. ^{1}H-NMR spectrum of Carbonyl Telechelic Oligomer (CTO) from waste tires. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

1.7 (s, 3 nH, CH$_2$CCH_3CHCH$_2$). $\overline{M}_{n,\text{GPC}}$=4400 (g/mol), Đ = 1.72.

Synthesis of CTO From Waste Tires

The synthesis is described in Scheme S2(a) of Supporting Information.

Particle sizes of tire crumbs were detailed in the work of Sadaka et al.,[17] 55% of powders waste have a size range between 0.63 mm and 1 mm.

170 g of waste tire crumbs were extracted for 24 h in a Soxhlet system with THF. Then, they were swollen in clean THF (1.7 L) in a jacketed reaction flask (5 L) equipped with a mechanical stirrer, on reflux overnight. A solution of periodic acid (45 g) in 493 mL of THF was then added dropwise. The temperature was maintained at 30°C during 24 h. At the end of the reaction, a solid fraction containing a small amount of partially dissolved tire crumbs was separated from the carbonyl telechelic oligomer (CTO) solution, which was washed 2 times with a mixture of Na$_2$S$_2$O$_3$ solution (250 mL, 20% weight) and of saturated NaHCO$_3$ solution (250 mL). These washing steps allowed the partial elimination of carbon black (CB), which went into the aqueous phase. The organic phase was filtered through a sintered glass funnel containing a layer of Celite powder (5 cm height) and then washed with 500 mL of saturated NaCl solution. This phase was dried over MgSO$_4$ overnight, filtered, and evaporated under reduced pressure. A brownish viscous product was obtained. (45 g, yield = $m_{\text{CTO}}/(m_{\text{tyre crumbs}} \times 0.6) = 60\%$). CTO structure and relative chemical shift values are shown in Figure 2.

^{1}H-NMR (CDCl$_3$) δ (ppm): 9.7(s, 1H, CH$_2$CHO), 5.05(s, 1 nH, C=CH), 2.43 (m, 2H, CH_2CHO), 2.36 (t, 2H, CH$_3$COCH$_2$CH_2), 2.26 (m, 2H, CH_2CH$_2$CHO), 2.20 (m, 2H, CH$_3$COCH$_2$CH_2), 2.09 (s, 3H, CH_3COCH$_2$), 1.95(s, 4 nH, CH$_2$CCH_3CHCH_2), 1.6(s, 3 nH, CH$_2$CCH_3CHCH$_2$). $\overline{M}_{n,GPC}$= 4300 (g/mol), Đ = 2.3.

Synthesis of HTOs From Waste Tires

The synthesis is described in Scheme S2(b) of Supporting Information.

In a two necked flask (1 L) equipped with a mechanical stirrer and a reflux system, CTOs (30 g) and NaBH$_4$ (5.31 g, 0.15 mol) were dissolved in THF (375 mL). The reaction occurred at 60°C for 12 h. After this time, the flask was cooled to room temperature, and then 100 g of ice were added to the reaction medium. The reaction solution was transferred in a separating funnel and washed twice with a saturated NaCl solution (250 mL). The organic phase was dried over MgSO$_4$ overnight, filtered and then evaporated in a rotary evaporator. The final product had a brownish color. (27.9 g, yield: 92.8%). HTO structure and relative chemical shift values are shown in Figure 1.

^{1}H-NMR (CDCl$_3$) δ (ppm): 5.05(s, 1 nH, C=CH), 3.82 (m, 1H, CHOH), 3.66 (t, 2H, CH_2OH), 2.1(s, 4 nH, CH_2CCH$_3$ CHCH_2), 1.7(s, 3 nH, CH$_2$CCH_3CHCH$_2$)

Viscosity (50 Pa s, 50°C). Elemental analysis results: C (72.8%), H(10.2%), O(13.2%), S(2.5%). $\overline{M}_{n,GPC}$=4200(g/mol), Đ = 1.97.

Synthesis of PU Foams From Polyols (HTPI or HTO)

In the first step, reagents were added into a beaker (100 mL) in the following order: water, catalysts (T-12 and 33-LV), surfactant (B8110), chain extender (BDO), Polyols, dichloromethane (relative percentages in weight are reported in Table I). These compounds were mixed using a homogenizer at a speed of 11,000 rpm for 60 s (Figure S5 of Supporting Information). Then P-MDI was rapidly added into the beaker, this mixture was homogenized for 30 s, and it was then poured into a mold and kept at 60°C in oven for 24 h. For the foam formulation the chosen NCO index was 105. Three kinds of PU foams were prepared: the HTPI foam from NR oligomers (HTPI foam), the HTO foam from recycled tire oligomers, and the mixed foam from a mixture of HTPI/HTO oligomers, with a proportion 1 : 1 in weight.

Table I. Typical Formulation of PU Foams

Components	Water	T-12	33-LV	B8110	BDO	Polyols	DCM	PMDI
(% in weight)	1.92	0.34	0.34	0.84	0.23	47.98	14.39	33.95

RESULTS AND DISCUSSION

Synthesis of Oligomers (HTPI, HTO)

In the present study, the process of recycling waste tires into new useful materials began by cutting some of the carbon–carbon double bonds in the polyisoprene and polybutadiene backbone using an inorganic chemical, the periodic acid, in order to obtain building blocks for successive applications. This procedure was inspired from the one previously optimized in our group[28] to perform the selective degradation of NR chains. Being the procedure an oxidative cleavage of C–C double bonds, it was imagined that it could work also for synthetic rubbers containing double bonds in the main chain (the reactions involved have been reported in Schemes S1 and S2 in the Supporting Information). In this way, functional telechelic oligomers are obtained, which possess a ketone and an aldehyde group at their chain ends, with a reasonably low dispersity (size exclusion chromatograms of HTPI and HTO are reported in Figure S3 of Supporting Information). These carbonyl chain ends can be successively transformed into many different chemical groups. In this project, we aimed to synthesize hydroxyl oligomers from waste tires and to use them as polyol precursors in the PUFs fabrication. The HTPI synthesis has already been described[31] and the preliminary work about the synthesis of CTO has already been published[17]; however, the first reported synthesis of HTO needed to be improved in terms of elucidation of the molecular structure and CB elimination.

Oligomers were first synthesized from NR and characterized by ^{1}H-NMR and SEC, for comparison. The polymer chain degradation was carried out in a one-pot method by adding a solution of periodic acid to the NR dissolved in THF. In the first method described by Kebir et al.,[32] the cleavage was realized in two steps; a first epoxidation by *m*-chloroperbenzoic acid, followed by the addition of periodic acid, after a purification step. In the present work, it was found out that increasing the amount of periodic acid added directly to the NR leads to the same results of the two steps process, so the first step was eliminated in order to save time, energy, chemicals consumption, and improve the overall yield in view of the future scale-up of the reaction. However, in the carbonyl products (CTPI, CTO), some epoxy cycles, which were not opened by periodic acid, remained. The percentage of epoxidation of HTPI [$\tau_{\text{epox-HTPI}}$, eq. (1), corresponding to the percentage of double bonds transformed in epoxy groups on the total number of double bonds] and HTO [$\tau_{\text{epox-OB}}$ for oligobutadiene, eq. (3) and $\tau_{\text{epox-OI}}$ for oligoisoprene, eq. (4)] were determined from the ^{1}H-NMR spectra (*I* stands for the value of the integration of the relative protons, Figure 1). In the case of HTO, the calculation was more complicated because of the presence of two type of oligomers: 1,4-oligoisoprene (OI) and oligobutadiene (OB). Thus, the ratio $\tau_{\text{OB/OI}}$ (oligobutadiene/oligoisoprene) had to be

first calculated from the ratio of the integration values of the characteristic peaks of protons H_3, and H_4 [eq. (2)].

$$\tau_{\text{epox-HTPI}} = \frac{I_7}{I_7 + I_4} \tag{1}$$

$$\tau_{\text{OB/OI}} = \frac{I_{3'}}{I_{3'} + 2I_4} \tag{2}$$

$$\tau_{\text{epox-OB}} = \frac{\tau_{\text{OB/OI}} \times (I_7 + I_{5'})}{\tau_{\text{OB/OI}} \times (I_7 + I_{5'}) + I_{3'}} \tag{3}$$

$$\tau_{\text{epox-OI}} = \frac{(1 - \tau_{\text{OB/OI}}) \times (I_7 + I_{5'})}{(1 - \tau_{\text{OB/OI}}) \times (I_7 + I_{5'}) + I_4} \tag{4}$$

$$\overline{M}_{n,\text{NMR-HTPI}} = \frac{2I_4}{I_1} \times 68.12 + 104 \tag{5}$$

$$\overline{M}_{n,\text{NMR-HTO-OB}} = \frac{2I_{e'}}{I_{b,h,b'} \times \tau_{\text{OB/OI}} \times (1 - \tau_{\text{epox-OB}})} \times 54.09 + 86 \tag{6}$$

$$\overline{M}_{n,\text{NMR-HTO-OI}} = \frac{4I_f}{I_{b,h,b'} \times (1 - \tau_{\text{OB/OI}})(1 - \tau_{\text{epox-OI}})} \times 68.12 + 128 \tag{7}$$

The molecular weights of oligomers (HTPI, HTO) have been determined by ^{1}H-NMR (Table II). The molecular weight of HTPI (2380 g/mol) was calculated from eq. (5) from the intensity of protons H_1, H_4 (Figure 1). The molecular weight of HTO was determined from the ^{1}H-NMR spectrum of CTO (Figure 2). As said before, there are two types of oligomers in CTO: oligobutadiene and oligoisoprenes; using eqs. (6) and (7), the masses for the oligobutadiene of 860 g/mol and for the oligoisoprene of 2020 g/mol were obtained. These molecular masses are similar to the ones obtained from size exclusion chromatography, multiplying the values from the chromatograms by 0.67, the Benoit factor for polyisoprene.[33] For the application in the foam synthesis, we had targeted a molecular weight of 2000 g/mol and the oligomers (HTPI, HTO) obtained were in this range, with a dispersity close to 2.

To confirm the presence of hydroxyl groups at each extremity, the MALDI spectrum of HTPI was performed and it is reported in Figure 3. Two series of peaks could be easily identified: the first series of peaks at $m/z = 1234.93$ (calculated value = 1233.83) represents HTPI ionized with Ag^+ ions. The second one at $m/z = 1931.82$ (calculated value = 1931.02) is attributed to epoxidized HTPI chains ionized by Ag^+. The shift

Table II. Molecular Weight and Epoxy Ratio of Oligomers

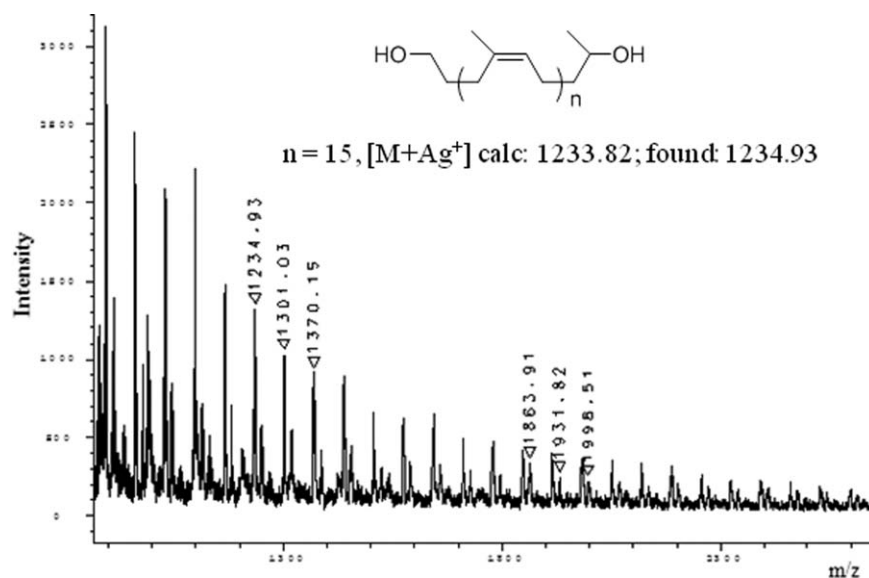| Oligomer	OB ratio (%)	Epoxy ratio (%)	Mn, NMR (g/mol)
HTPI	0	0.8	2380
HTO	7.5	OB : 2.9	860
		OI : 5.7	2020

Figure 3. MALDI-TOF spectrum of HTPI. Matrix: DIT+AgTFA.

of around 16 m/z between the two series corresponds to the oxygen atom of the epoxy cycle, confirming the presence of some epoxidized units that was also found in ^{1}H-NMR spectra.

Sulfur and Carbon Black Residues in HTO Precursors

The oligomers obtained from the selective degradation of NR using periodic acid are generally honey-like viscous liquids, with a viscosity that depends on the average molecular weight and on the nature of the chain ends. The oligomers obtained from waste tires were considerably more viscous (50 Pa·s) than the analogue with the same average molecular weight obtained from NR (4.6 Pa·s). These viscosity values were determined from Newtonian plateau and are reported in Figure 4(a). Having roughly the same molecular weight but a big difference in viscosity means that the structure of the oligomers from NR and waste tires is different; the first hypothesis is that linear chains are obtained from NR while branched structures are obtained from tires. Therefore, an in-depth characterization of the HTO oligomers was carried out to elucidate their structure.

When an EDX analysis of a HTO foam was performed, a peak corresponding to sulfur was present [Figure S1(b) in Supporting Information], while it was absent in the foam from NR [Figure S1(a) in Supporting Information]. The issue of devulcanization was not addressed in the first work[17]; therefore, this was the first indication that sulfur was still present in the foam precursors. In order to determine the amount of sulfur, the elemental analysis of a sample of HTO was carried out and it revealed the presence of 2.5% sulfur. This means that the treatment with periodic acid did not break the carbon–sulfur bonds so that crosslinks or branches still exist in the oligomers and they could be mainly responsible of the high viscosity. A literature research supported this hypothesis: it was found[34] that the reaction of periodic acid with a glycoprotein led to the formation of cysteic acid and methonine sulfone from the aminoacid residues cysteine and methionine. Periodic acid did not break the carbon–sulfur bond but it broke the sulfur–sulfur bond, oxidizing the sulfur atom to $-SO_2R$ or $-SO_2OH$ groups.
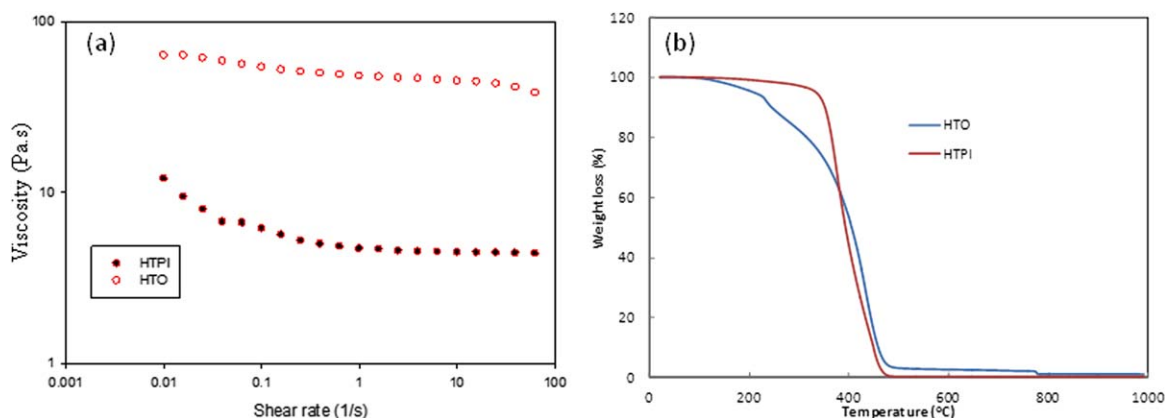

Figure 4. a) Viscosity of HTPI and HTO oligomers b) TGA curves of HTPI and HTO oligomers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

A TGA coupled with mass spectroscopy was carried out of both HTPI and HTO samples (Figure S2 in Supporting Information): no signal was registered for the release of SO (48.06 g/mol) and SO_2 (64.06 g/mol) when HTPI was heated up to 900°C, but five signals were displayed when HTO was heated up to 900°C (at 210°C, 260°C, 300°C, 370°C, 500°C, and 610°C). These data confirmed that different carbon–sulfur and sulfur–sulfur bonds still exist in the HTO and that they have different strength because they are broken at different temperatures (Figure S2 in Supporting Information).

Another relevant issue in comparing the oligomers from waste tires and NR is their color: the HTPI precursor has a yellowish color typical of NR derivatives, while the HTO precursor has a brownish color, which is caused by the presence of CB. The residue of CB in HTO was determined by TGA using a special procedure. The first heating was carried out between 30°C and 800°C, to observe the decomposition of the oligomers (OB or OI), which takes place in a N_2 flow; the second heating scan was carried out between 800°C and 1000°C, to burn out the residues of CB in oxygen flow. By thermal analysis [Figure 4(b)], the conclusion was drawn that there is still about 1.5% of CB in HTO. Another experiment was carried out to visualize the presence of CB in the oligomers; the same masses of CTPI and of CTO were put in a pan and heated up to 700°C and pictures have been taken of each pan after heating in the TGA oven (Figure S4 in Supporting Information). It could be clearly seen that for CTO a layer of a black powder remained after heating and this was not present for the CTPI.

Although the CB remaining in the final product was a really small amount, it could be in part responsible for the higher viscosity. Many efforts and different techniques like filtration, centrifugation, and washings were applied to eliminate the CB from the oligomers but the small size of the remaining CB particles made it difficult to have completely free-CB samples. However, it was later demonstrated that the presence of this very small amount of CB is not affecting the potential applications of the HTO oligomers because it was possible to synthesize foams with promising properties.

Another factor that could also explain the higher viscosity of HTO in comparison to HTPI is the higher number of epoxy groups that it contains, which was confirmed by thermal analyses of the oligomers. The TGA curves indicated the presence of epoxidized double bonds in the oligomers: in the HTO curve, the first step (100–270°C) corresponds to the degradation of epoxy cycles and the second one (270–500°C) is relative to the decomposition of oligoisoprene and oligobutadiene. In the case of HTPI, because of the little epoxidation ratio, it was not possible to observe the epoxy decomposition step.

In conclusion, the oligomers from waste tires have a branched structure because the carbon–sulfur bonds are not cleaved by periodic acid, nevertheless they have carbonyl chain ends and these could be turned into hydroxyl groups in order to use them as polyols.

Synthesis and Characterization of PUFs

After the optimization of the synthesis of the hydroxyl oligomers from waste tires crumbs, the objective was to demonstrate

that they could be used to make new useful materials. In our group there was a previous experience in the synthesis of NR-based foams[28]; therefore, we imagined that we could adapt the procedure and use the HTO instead of the HTPI (which had been used before), and that we could compare the properties of the two different types of foams. The characterization of the HTPI oligomers by MALDI-TOF revealed that their functionality was $\bar{f} = 2$. The molecular weight of Polyols was obtained from ^{1}H-NMR. Therefore, the number of moles of hydroxyl groups was calculated dividing the grams of polyol ($m_{Polyols}$) by the average molecular weight of the chains ($M_{n,NMR,Polyols}$, choosing the value obtained from ^{1}H-NMR). The proportion of water, chain extender and hydroxyl oligomers were taken from the previous formulation, and the grams of PMDI (m_{NCO}) to add for a given amount (g) of polyols, of butanediol (m_{BDO}), and of water (m_{H2O}) were calculated using the following formula (using an isocyanate index $I_{NCO} = 105$):

$$m_{NCO} = 1.05 \frac{\overline{M}_{n,NCO}}{\overline{f}_{n,NCO}} \left(\frac{f_{H2O} \cdot m_{H2O}}{M_{H2O}} + \frac{f_{BDO} \cdot m_{BDO}}{M_{BDO}} + \frac{\overline{f}_{n,Polyols} \cdot m_{Polyols}}{\overline{M}_{n,NMR,Polyols}} \right)$$

$$\overline{M}_{n,NCO} = 340 (g/mol); \overline{f}_{n,NCO} = 2.7$$

$$\overline{f}_{H2O} = \overline{f}_{BDO} = \overline{f}_{n,Polyols} = 2$$

The volume expansion ratio was roughly 8; for example from 16 g of ingredients in the foam formulation (~16 cm^3), a foam of dimensions 10.5 cm × 8.5 cm × 1.5 cm was obtained.

Foams have been synthesized using 100% HTPI, 100% HTO and a mixture of 50% in weight of each as polyol in order to compare their properties (Figure 5).

Morphology and Density

The PU foams were realized in different sizes and shapes depending on the application needed. The observation of different samples showed that both HTO and HTPI derived foams have a homogeneous pores distribution (Figure 6) and the brownish color of HTO is a consequence of the brown color of the corresponding oligomer.

The scanning electron micrographs (Figure 6) revealed that all PU foams have a morphology at an intermediate step between open-cell and closed cell; some of the cells' windows are still closed, regardless the initial sources used (HTPI, HTO, or mixture of HTPI/HTO). In the follow up of the project, the nature and amount of surfactant will be changed in order to have completely open or closed cells, to adapt the formulation to a targeted application. The mean cell size of all foams was measured from SEM pictures and it is listed in Table III.

Given the difference in the structure and composition of the oligomers from NR and waste tires, is was not surprising that the density of these foams was different; it varied from 41 kg/m^3 for HTPI to 56 kg/m^3 for HTO, giving an intermediate value for the mixed foam (47 kg/m^3).

EDX analysis of HTO and HTPI derived foams were performed (Figure S1 in Supporting Information) to ensure that no free chloride ions remained after the washing of the oligomers with

Figure 5. PU foams synthesized from HTPI (left) and from HTO (right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

sodium chloride solutions during the purification steps. No peak was detected for chlorine; therefore, we concluded that the urethane bond formation is not affected by the presence of remaining chloride ions.

Mechanical and Thermal Properties

Although the three types of foams showed a quite different density to compare their properties, tests were carried out to complete their characterization and to determine the tensile strength, the elongation at break, and the compressive strength.

All parameters of mechanical properties are summarized in Table IV. As it can be seen [Figure 7(a)], the compressive stress–strain curves consist of three different regions, initial stress increase, a plateau region and final stress increase. This behavior is similar to that reported by Saha et al.[35] Deformation during the plateau region is the deformation of the cell
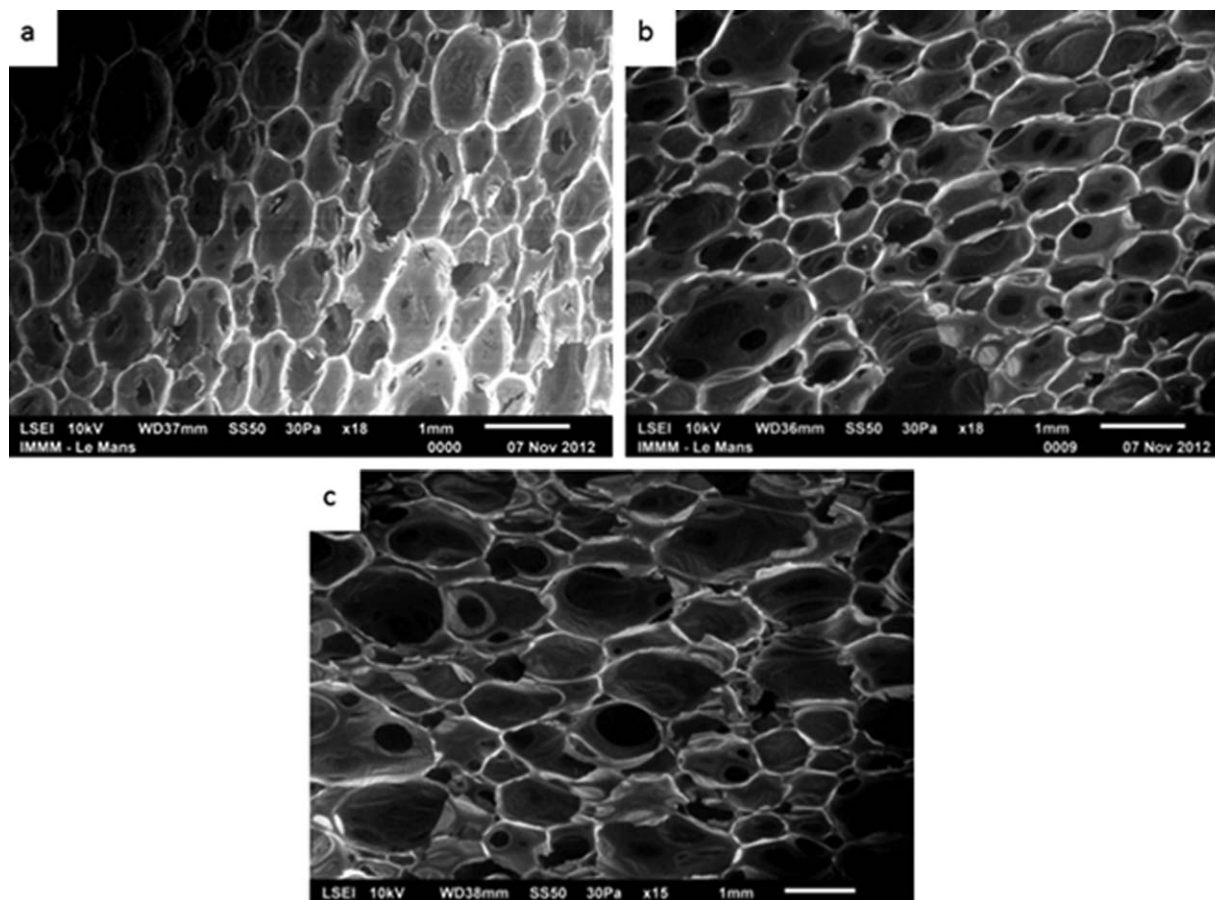

Figure 6. a) Scanning electron micrographs of HTPI foam, b) HTO foam, c) mix foam.

Table III. Cell Size and Density of PU Foams

PU foam	Mean cellular size (mm)	Density (kg/m^3)
HTPI	1.1 ± 0.1	41.6 ± 0.6
HTO	1.2 ± 0.3	56.5 ± 0.3
Mix	1.4 ± 0.3	47 ± 4

Table IV. Mechanical Properties of HTPI Foam, HTO Foam, and Mix Foam

PU foams	Tensile strength (kPa)	Elongation at break	Compressive strength (kPa)[a]
HTPI	78 ± 6	60 ± 5	20 ± 1
HT)	220 ± 11	22 ± 4	188 ± 5
Mix[b]	148 ± 2	41 ± 4	23 ± 1

[a] Compressive deflection at 50%.
[b] HTPI/HTO (1 : 1 in weight).

structure, and at the end of this region the cells are totally collapsed. The final stress increase shows the bulk properties of the foam where the cellular structure has collapsed. The compressive strengths were measured at 50% of deflection of foams. As observed, the PU foam synthesized from HTO has a very important compressive strength (188 kPa) compared to HTPI foam (20 kPa) and mixed foam (23 kPa). A significant rigidity of HTO foam has been remarked at the end of curing. This rigidity can be explained by the different nature of the oligomers. HTPI is composed of polyisoprene chains with average molecular weight around 2380 g mol^{-1}; HTO instead is composed by polyisoprene chains with average molecular weight 2020 g mol^{-1} and by smaller oligobutadiene chains, only 860 g mol^{-1}. It has already been found[36] that reducing the polyol molecular weight results in higher tensile and compressive strengths, and therefore, it is not surprising that the presence of the shorter butadiene chains in HTO makes the relative foam less flexible that the ones made from oligoisoprene only.

The discussion about the partial devulcanization should also be taken into account: it is likely that some of the HTO oligomers have branches or crosslinks because of unbroken carbon–sulfur, sulfur–sulfur bonds, and this branched structure would impact the mechanical properties increasing the rigidity of the three-dimensional structure.

A third difference is that in HTO there is still about 1.5% of CB that was not eliminated during all the purification steps; these particles are a known reinforcement agent which improves the physico-mechanical properties of the tire. Saha et al.[35] included 1 wt % of different nanoparticles (platelet nanoclays, TiO$_2$ spherical particles, and carbon nanotubes) into the PU precursors and obtained foams with enhanced mechanical properties.
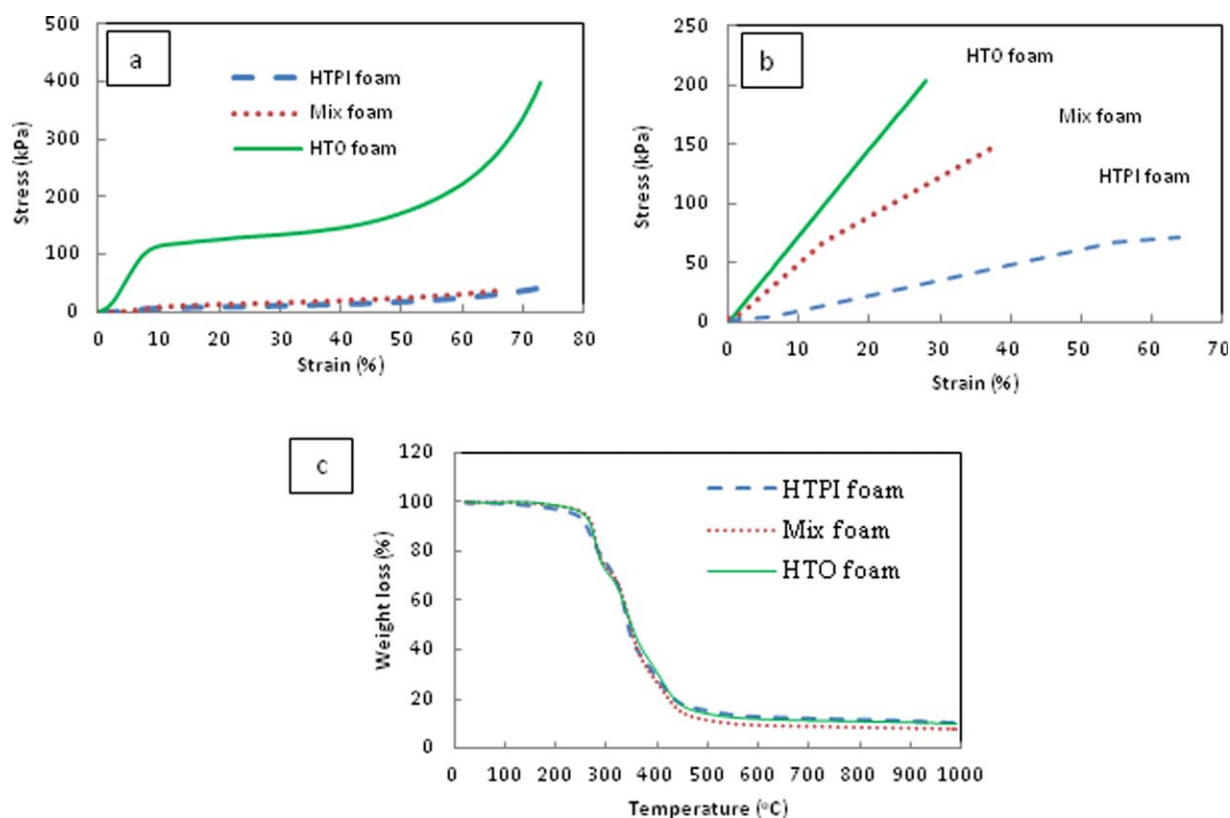

Figure 7. Mechanical and thermal properties of the three types of foams: a) compressive test; b) tensile test; c) thermograms. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Based on these results, it is possible that in our case the presence of CB nanoparticles, even if in a so small percentage, may be in part responsible of the increase in modulus and compressive strength of the HTO foams.

On the other hand, NMR spectra showed the presence of a significant proportion of epoxide groups in the oligomers, which could be responsible for the decrease in the flexibility of the chains, as it has already been found by Saetung et al.,[28] in his study of the influence of the epoxide percentage on the mechanical properties of NR-derived foams. The polyisoprene oligomer is the soft segment in PU foams thus the decrease in the flexibility of the soft segment could make the PU foam less flexible.

In the tensile strength test [Figure 7(b)], the more rigid HTO foam showed the highest strength (about 200 kPa), whereas it was around 78 kPa for HTPI foam, and the mix foam had an intermediate value between HTPI and HTO ones. Concerning the elongations at break, the values are linear with the tensile strength.

Thermo gravimetric analysis was performed for the three types of foams in order to gather information about their structure and detect the changes occurring raising the temperature, in view of future applications. By analyzing the TGA curves [Figure 7(c)], the same behavior of the different types of foams versus heating was observed. The degradation of the PU foams takes place in the range 300–450°C in two steps; the first between 300°C and 350°C corresponds to the urethane decomposition; the second one (350–450°C) correspond to the degradation of NR-based polyols and polyurea.

CONCLUSIONS

A methodology has been developed to recycle waste tires into PUFs. In the first step, waste tire crumbs were submitted to an oxidative cleavage of some of the polyisoprene and polybutadiene double bonds to obtain telechelic carbonyl oligomers; these ones were then reduced to hydroxyl oligomers (HTO), which were afterward employed as Polyols in the synthesis of PUFs. The properties of these foams from recycled tires were studied and compared to those of foams prepared from HTOs (HTPI), obtained with the same procedure but directly from NR. A third kind of foam was synthesized mixing HTO and HTPI to have a material with intermediate properties. The SEM observation showed that the foams had a morphology intermediate between completely open or completely closed cells. The three types of foams had similar thermal properties. However, their physicomechanical properties were different because of the presence of branching in the HTO oligomers (due to the remaining carbon–sulfur, sulfur–sulfur bonds from the vulcanized rubber), because of a small residue of CB in HTO and of a high ratio of epoxidized double bonds. The HTO foam was more rigid than the HTPI foam or the mixed foam; hence, the former had a higher tensile and compressive strength. This rigidity of HTO foam could be decreased by adding the telechelic oligomers synthesized from NR in the formulation, thus allowing the possibility of tuning the mechanical properties of the final material, by adjusting the percentage of the different kinds of oligomers. The reported results are related to a first attempt to synthesize PUFs from HTO to demonstrate that the process of converting waste tires into new useful materials is viable. Further studies are in progress to elucidate the oligomers structure and to optimize the foams mechanical properties.

REFERENCES

1. ETRMA report (European Tire and Rubber Manufacturers' Association), European Tire and Rubber Industry, Statistics, Edition 2012. Available at: http://www.etrma.org/statistics-2. Published on 15 October 2012.

2. Landfill of waste directive. Brussels, Belgium: European Commission. Council Directive 1999/31/EC, 1999.

3. Corti, A.; Lombardi, L. *Energy* 2004, 29, 2089.

4. Barton, N. R.; Koutsky, J. A. *Chem. Eng. News* 1974, 52, 21.

5. Phadke, A. A.; Bhattacharya, A. K.; Chakraborty, S. K.; De, S. K. *Rub. Chem. Tech.* 1983, 56, 726.

6. Harshaft, A. A. *Env. Sci. Tech.* 1972, 6, 412.

7. Leyden, J. J. *Rubber World* 1991, 203, 28.

8. Novotny, D. S.; Marsh, R. L.; Masters, F. C.; Tally, D. N. US Pat. 4,104,205, 1978.

9. Isayev, A.; Yushanov, S. P.; Kim, S. H.; Levin, V. Y. *Rheol. Acta* 1996, 35, 616.

10. Lawrence, T. E. US Pat. 2,471,866, 1949.

11. Kawabata, N.; Okuyama, B.; Yamashita, S. *J. Appl. Polym. Sci.* 1981, 26, 1417.

12. Nicholas, P. P. US Pat. 4,161,464, 1979.

13. Schulman, B. L.; White, P. A. Progress Report, ACS Symposium Series No. 76, Washington, DC, 1978.

14. Park, J. W.; Roh, H. S.; Kim, J. K.; Joe, Y. I. *Komu Hakhoechi* 1997, 32, 325.

15. Holst, O.; Stenberg, B.; Christiansson, M. *Biodegradation* 1998, 9, 301.

16. Myers, R. D.; Nicholson, P.; MacLeod, J. B.; Moir, M. E. US Pat. 5,602,186, 1997.

17. Sadaka, F.; Campistron, I.; Laguerre, A.; Pilard, J.-F. *Polym. Degrad. Stab.* 2012, 97, 816.

18. Sadaka, F.; Campistron, I.; Laguerre, A.; Pilard, J.-F. *Polym. Degrad. Stab.* 2013, 98, 736.

19. Ashida, K. Polyurethane and Related Foams: Chemistry and Technology; CRC/Taylor & Francis: Boca Raton, FL, 2006.

20. Guo, A.; Zhang, W.; Petrovic, Z. S. *J. Mater. Sci.* 2006, 41, 4914.

21. Rivera-Armenta, J. L.; Heinze, T.; Mendoza-Martínez, A. M. *Eur. Polym. J.* 2004, 40, 2803.

22. Araújo, R. C. S.; Pasa, V. M. D.; Melo, B. N. *Eur. Polym. J.* 2005, 41, 1420.

23. Kwon, O. J.; Yang, S. R.; Kim, D. H.; Park, J. S. *J. Appl. Polym. Sci.* **2007**, *103*, 1544.

24. BASF http://www.polyurethanes.basf.de/pu/solutions/en/content/productbrand/lupranol.

25. Cargill http://www.cargill.com/company/businesses/bioh-polyols/index.jsp.

26. Dow http://www.dow.com/polyurethane/news/2008/20081120a.htm.

27. Babb, D. A. In Synthetic Biodegradable Polymers; Springer-Verlag Berlin: Berlin, **2012**; Vol. *245*, p 315.

28. Saetung, A.; Rungvichaniwat, A.; Campistron, I.; Klinpituksa, P.; Laguerre, A.; Phinyocheep, P.; Doutres, O.; Pilard, J.-F. *J. Appl. Polym. Sci.* **2010**, *117*, 828.

29. Lievana, E. PhD Thesis, Technical University of Kaiserslautern, Kaiserslautern, Germany, **2005**.

30. Stepto, R. F. T. *Pure Appl. Chem.* **2009**, *81*, 351.

31. Kébir, N.; Morandi, G.; Campistron, I.; Laguerre, A.; Pilard, J.-F. *Polymer* **2005**, *46*, 6844.

32. Kébir N.; Campistron, I.; Laguerre A.; Pilard J.-F.; Bunel C.; Couvercelle J.-P.; Gondard C. *Polymer* **2005**, *46*, 6869.

33. Busnel, J. P. *Polymer* **1982**, *23*, 137.

34. Krotoski, W. A.; Weimer, H. E. *Arch. Biochem. Biophys.* **1966**, *115*, 337.

35. Saha, M. C.; Kabir, M. E.; Jeelani, S. *Mater. Sci. Eng. A* **2008**, *479*, 213.

36. Huang, S.-L.; Lai, J.-Y. *Eur. Polym. J.* **1997**, *33*, 1563.