Early Development of a Biodegradable Energetic Elastomer

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ABSTRACT: The expected depletion of oil resources and a greater awareness for the environmental impact of plastic products have created a strong interest toward energetic polymers that are not only biodegradable but also obtainable from renewable resources. In this work, a copoly(ester/ether) was synthesized from polyepichlorohydrin and sebacoyl chloride using pyridine as a Lewis-base catalyst. The chlorinated polymer was azidified with NaN_3 in dimethyl sulfoxide solutions. The success of the reaction was confirmed by ^{1}H-NMR, ^{13}C-NMR, and Fourier-transform infrared spectroscopy. Two types of polyurethane networks were synthesized from the nonenergetic and the energetic copolymers, adding polycaprolactone triol and using L-lysine diisocyanate as a nontoxic curing agent. The two resulting polyurethanes were soft thermoset elastomers. The polyurethanes were chemically and mechanically characterized, and their biodegradability was evaluated in compost at 55°C. The nonenergetic and the energetic polyurethanes showed a glass-transition temperature of −14°C, and −23°C, respectively. The weight loss of the polyurethanes during the composting experiments was monitored. It increased almost linearly with time for both materials. After 20 days, the nonenergetic samples lost about 50% of their mass because of the biodegradation mechanism. Instead, the energetic elastomers lost only about 25% of their initial mass after 25 days. The experimental results revealed that the azide pendant group in the soft segment (the polyether segments) is the main factor that controls the physical, mechanical, and degradation properties of these polyurethane networks. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 3645–3657, 2011

Key words: energetic polymer; thermoset elastomers; biodegradability; polycondensation; processability

INTRODUCTION

Over the last few decades, plastics have become the materials of choice for the fabrication of an increasingly large number of products found in a spectrum of applications that ranges from biomedical to military uses.[1–3] However, the expected depletion of oil resources and a greater awareness for the environmental impact of plastic products have created a strong interest toward polymers that are not only biodegradable but also obtainable from renewable resources. Various natural and synthetic biodegradable elastomers have been developed by means of a cross-linked network to satisfy specific mechanical and physical requirements and to improve the product properties.[4]

The current trend toward the development of biodegradable materials was recently extended to less-traditional areas, such as energetic materials. Because a large fraction of the ordnances used by a country's armed forces are often fired on its own homeland for training purposes, the interest of using propellants and explosives that are less harmful for the environment becomes evident. In this perspective, biodegradable polymers are an interesting option and more so because of recent advances in their production at the industrial scale. Among them, aliphatic polyesters like poly(ε-caprolactone) and poly(L-lactide) are well known for their biodegradability,[5] but they show relatively weak physical and mechanical properties. To scale up the reaction, aliphatic synthetic copoly(ester/ethers) for polyurethane formulations were studied.

Contemporary plastic-bonded energetic materials often rely on a polyurethane binder to ensure the structural integrity of formulations that may contain up to 80% in solids. Biodegradable polyurethanes based on lysine derivatives have been reported in the literature to decompose into nontoxic products.[6] L-Lysine diisocyanates (LDIs) are synthesized by phosgenation of amine-terminated lysine esters, and they have a lower vapor pressure than other aliphatic diisocyanates (e.g., hexamethylene diisocyanate).[7] Considering the inhalation toxicity of many diisocyanates, the low vapor pressure of LDI is a key advantage for its handling and processing. However, the production of biodegradable elastomeric polyurethane networks from lysine diisocyanate has so far mainly only been investigated for biomedical applications.[8]

In contemporary energetic materials formulations, perchlorate-based oxidizers that decompose to chloric acid during combustion tend to be replaced by greener but less-powerful oxidizers such as ammonium nitrate. To compensate the energy loss from the change in the oxidizer, the polymeric binder found in these materials can be substituted by novel energetic polymers. These so-called energetic binders carry the double advantage of improved performance and lower vulnerability. The energy released during their thermal decomposition is due to the presence of an azide, amino, or nitro group on the side chain. In the propellant industry, there is a progressive substitution of inert binders such as hydroxyl-terminated polybutadiene by energetic polymers such as glycidyl azide polymer (GAP). In fact, GAP materials are at the core of the development of most of these novel energetic binder systems. A biodegradable energetic binder could be either thermoplastic or thermoset elastomers. The latter offers the advantage of a lower viscosity and a lower processing temperature. The general reaction of a polyol with a diisocyanate to form a thermoset elastomer is given by:

$$R_1 - N = C = O + R_1 - OH \longrightarrow R_1 - NH - CO - O - R_2 \tag{1}$$
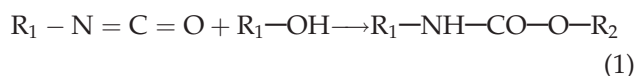
Therefore, a polyester polyurethane thermoset elastomer could be an attractive material for the preparation of composite solid propellants in which the elastomer is an intimately mixed rubbery phase, used as a binder for dispersed solids such as ammonium perchlorate and other oxidizers, as well as metallic fuels such as aluminum particles. Azido plasticizers can also be used to add energy to the binders because of the presence of N_3 group providing 85 kcal/mol of energy to the system. The generic formula for GAP is:

$$HO - (CH_2 - CH(CH_2N_3) - O)_n H \quad 7 \leq n \leq 30 \tag{2}$$
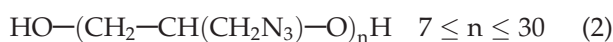
The chemical precursor for GAP is polyepichlorohydrin (PECH). The Cl atom in its repeating units can easily be exchanged with a N_3 by S_{N2} reaction (bimolecular nucleophilic substitution) following Frankel's method.[9] However, other halogenated oligomers such as bromine containing polyether can also be used.[10] In general, the GAP polymer is cured by the reaction of its hydroxyl groups with diisocyanates such as toluene diisocyanate, isophorone diisocyanate, or triisocyanate to yield cross-linked polyurethane network.[11]

One drawback of PECH-based energetic materials is that they are nonbiodegradable. To increase the biodegradability of PECH-based energetic materials, a possible solution could be the insertion of some specific chemical linkages, such as ester bonds, which are known to promote biodegradability. This type of polymer can be produced by a step-growth polycondensation reaction between carboxylic acids (or derivatives such as chloride, esters, or anhydrides) and diols (or polyols) or by ester interchange or alcoholysis. The polycondensation reaction itself proceeds by a slow increase in the molecular weight of the polymer. To increase the yield of the polymerization, several methods can be applied: using nonstoichiometric conditions with an excess of one of the reactants, removing the by-product formed during the reaction to shift the equilibrium toward the products, or activating the dicarboxylic acids. Carothers[12] elaborated a standard method to prepare polyesters at a laboratory scale or in larger quantities with the acid-catalyzed direct polycondensation of a diol with a free dicarboxylic acid. In acid-catalyzed reactions, the acid catalyst forms a complex with the alcohol: the oxygen atom of the end group is electrophilic and able to accept the nucleophilic carbon of the dicarboxylic acid. Kricheldorf et al.[13] conducted a remarkable research work to compare basic methods of producing polyesters to find a synthetic method leading to better yield. They succeeded to produce an aliphatic polyester using a pyridine-catalyzed polycondensation method between butyne-1,4-diol and several aliphatic dicarboxylic acid dichlorides at room temperature. In this way, the activated acid reacts with an alcohol in relatively mild conditions according to the Schotten–Baumann mechanism where pyridine acts as a catalyst, shifting the equilibrium toward the products. Nevertheless, the achievement of this reaction is rather delicate. Using a GAP precursor such as PECH, the prepolymer polymerization would depend on the reactivity of PECH itself. To use the final product in a thermoset energetic materials formulation, it must be purified from any traces of HCl, and its viscosity must be low enough to allow for a cast-cure process.

The objective of this work was to design a biodegradable and energetic copoly(ether/ester-urethane) network from PECH and sebacoyl chloride (SC) derivatives able to release only nontoxic degradation products and compatible with contemporary ingredients found in propellants and gas generators. The choice of thermoset polyurethane elastomers for this task was motivated by the fact that they can present excellent mechanical properties over a large range of temperature. At this early stage of development, the biodegradability of the synthesized products is evaluated using standardized composting experiments, but the bio/ecotoxicity of the decomposition products is not assessed.

EXPERIMENTAL

Materials

PECH, 625 g/mol (relative to polystyrene standards), was supplied from 3M™ and was treated

with activated charcoal to absorb impurities and contaminants before its use. Sebacic acid (SA), 228 g/mol, and its dichloride, SC, 234 g/mol, were purchased from Sigma-Aldrich Ltd. (Oakville, ON, Canada) and used as received. Dichloromethane and toluene were both purchased from Laboratoire Mat Inc., (Quebec, QC, Canada), and the dichloromethane was dried using a molecular sieve. Triethylamine, pyridinium hydrochloride, pyridine, p-toluene sulfonic acid (PTSA), and activated charcoal were purchased from Sigma-Aldrich, and sulphuric acid from Laboratoire Mat, and used as received.

For the polyurethane formulation, polycaprolactone (PCL) triol, 300 g/mol, was purchased from Sigma-Aldrich. Dibutyl tin dilaurate (DBTL), 631.56 g/mol, was also purchased from Sigma-Aldrich, and used as 0.01M, 0.1M, and 1M solutions in dichloromethane. L-Lysine diisocyanate, 226.23 g/mol, was purchased from Shanghai Infine Chemicals Co., Ltd. (Shanghai, China). The stabilized compost used as a substrate for the biodegradation tests was purchased from a composting company (Fafard, Saint-Bonaventure, QC, Canada). It contained composted manure, sphagnum peat moss, shellfish flour, and seaweed and had the following characteristics: pH = 6.89, water retention = 4.29%, and initial humidity = 1.62%. Before being used, the compost was homogenized, cleaned from all inert material (rocks, metals, and wood), homogenized using a mortar, and finally sieved.

Synthesis of the copoly(ester/ether)

A copoly(ester/ether) of PECH and aliphatic dicarboxylic acids was prepared in two different ways: by direct polycondensation between a dialcohol and a dicarboxylic acid (Fig. 1, R=OH) and polycondensation between a dialcohol and a diacyl dicarboxylic acids (Fig. 1, R=Cl).

Direct polycondensation

A 500-mL three-necked flask equipped with a mechanical stirrer and a Dean-Stark water trap was charged with an equimolar solution of PECH and SA in toluene. During this polycondensation reaction, water is produced as a by-product. Hence, its removal using a Dean Stark apparatus in combination with a reflux condenser is an essential step for the completion of the reaction. The reaction was carried out under reflux in toluene, which is less dense than water, immiscible with it, and forming an azeotrope. The apparatus allows the water to be separated from the condensed azeotrope, preventing it from returning to the reaction mixture. The reaction vessel was placed in an oil bath preheated to a temperature that ranged 100–160°C. The reaction was
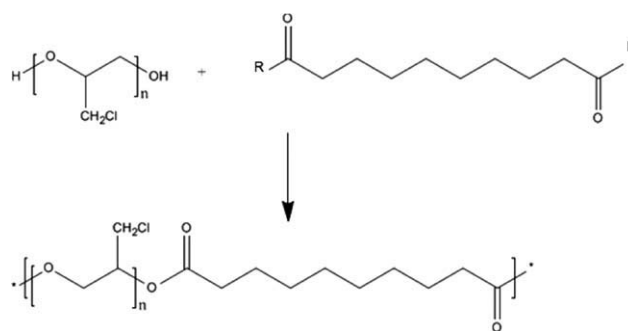

Figure 1 Polycondensation between PECH and SA (R=OH) and PECH and SC (R=Cl).

allowed to proceed for at least 8 h but, in some instances, for up to a 24-h period of time. Different catalysts were tested. At the end of the reaction, the now viscous solution was cooled down and washed with brine and extracted with toluene, then dried over Na$_2$SO$_4$, and filtered. The solvent was evaporated off in a rotary evaporator and dried overnight in an oven under vacuum at 80°C.

Polycondensation with diacid dichlorides

PECH and SC in equimolar ratio were dissolved in dichloromethane into a three-necked glass flask, equipped with gas-inlet and gas-outlet tubes and a mechanical stirrer, and cooled to −5°C. Pyridine (240 mmol) was added drop-wise under cooling conditions. After a complete addition of the pyridine, the reaction mixture was stirred at room temperature for 24 to 48 h and afterward poured into cold methanol. The precipitated polyester/polyether copolymer was washed several times with brine or water, dried over Na$_2$SO$_4$, and filtered. The solvent was evaporated off in rotary evaporator equipment and dried overnight in an oven under vacuum at 80°C.

Azidation of the copoly(ester/ether)

To produce an energetic copoly(ester/ether), 40 g of a synthesized low-molecular-weight copoly(ester/ether) obtained using previously described experimental conditions were dissolved in 500 mL of dimethyl sulfoxide and put in a 1-L Buchi glass reactor (Buchi laboratory autoclave BEP 280, Uster, Switzerland) equipped with nitrogen inlet and outlet. The jacketed reactor was heated by an external oil bath circulator and mixing was provided by a top-mounted magnetic drive impeller.

After 15 min, an excess of NaN$_3$, also dissolved in dimethyl sulfoxide, was added, and the temperature was slowly increased to 85°C, and the reaction was continued for 24 h. Subsequently, the product was washed with water, and the organic phase was

extracted using methylene chloride. The organic phase was dried over $MgSO_4$ to remove all traces of water, filtered, and finally the solvent was evaporated under vacuum. An energetic polymer was obtained with $\sim$ 95% yield.

Characterization of the copoly(ester/ether)

The ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance DRX 500 MHz NMR spectrometer using 5 mm (outer diameter) sample tubes. $CDCl_3$ containing tetramethylsilane as reference served as the solvent. Gel permeation chromatography (GPC) was performed using a system equipped with a refractive index (RI detector Waters 2414). A combination of two columns HSP gel^{TM} HR MB-M (6.0 × 150 mm) was used with tetrahydrofuran (THF; high-performance liquid chromatography grade) as the mobile phase at a flow rate of 0.5 mL/min. Commercial polystyrene standards were used for calibration. Sample concentrations were approximately 1.8 mg/mL in THF, with an injection volume of 1 μL. Fourier-transform infrared (FTIR) spectroscopy was performed using an FTIR Instrument (Bio-Rad instrument, model 3000 Excalibur). Absorbance measurements were carried out using calibrated 0.5 mm KBr and BaF_2 cells. The spectrometer was operated during a scan time of 32 min on the full frequency range, with a resolution of 4 cm^{-1}. For these experiments, the copoly(ester/ether) was dried overnight in the oven at 60°C under vacuum for 2 days, and the solvent as well dried with molecular sieve. In this way, THF and the samples were dried and oxygen-freed.[14]

The number of hydroxyl groups (-OH) was evaluated according to a standard procedure that consisted of an esterification reaction of the hydroxyl end groups with acetic anhydride in pyridine, followed by a titration of the excess acid reagent by an equimolar amount of potassium hydroxide in solution (ASTM D-4662-93).[15] The hydroxyl number is expressed as milligrams of potassium hydroxide equivalent for 1 g of the sample (mg KOH/g). The results of this titration method were compared with FTIR analysis. In the latter, the hydroxyl concentration or OH equivalent weight was evaluated from the comparison between the FTIR absorption bands of THF-associated hydroxyl groups of the copoly(ester/ether) near 3500 cm^{-1}. The calibration curve was obtained using the OH/THF-associated absorption of PECH as a reference plotted against the concentration of PECH. The OH number was evaluated in such conditions that all the OH groups were associated to the solvent and the presence of free or self-associated OH was negligible. Differential scanning calorimetry (DSC) tests were performed with TA

Instruments (Q1000) at a scan rate 5°C/min, varying the temperature from 30°C to 300°C.

Synthesis of thermoset polyurethane elastomers

The synthesis procedure for an LDI-based thermoset polyurethane was as follows: in the first step, the energetic and nonenergetic copolymers were mixed with PCL triol (0.26% mol) and heated at 60°C under vacuum to form a reactive liquid mixture in the presence of DBTL in a methylene chloride solution (0.1M or 1M, and 0.015% mol of catalyst). In the second step, LDI was added to achieve a molar ratio of NCO groups to the OH groups of 1.33. The desired ratio satisfied the following equation:

$$\frac{NGO}{OH} = \frac{W_{LDI}/EW_{LDI}}{W_{polyol}/EW_{polyol}} \qquad (3)$$

The equivalent weight (EW) for LDI was provided by the supplier and was EW_{LDI} = 113.15 g/mol. The mixtures were casted in an open mold to form a solid material at 60°C under vacuum for 6–12 h and then left for curing at ambient pressure and 75°C for 24 h.

Characterization of the thermoset polyurethane elastomers

Rectangular samples of 61 × 13 × 3 mm were analyzed by dynamic mechanical analysis (DMA). DMA was used to determine the viscoelastic properties of the polyurethane elastomers. The measurements were performed on a dynamic thermoanalyzer (TA Instruments DMA-2980) using a dual cantilever geometry in the linear viscoelastic regime at a frequency of 1 Hz and an oscillation amplitude of 25 μm over a temperature range of −50°C to 20°C. The scanning rate was varied between 2°C/min and 5°C/min.

Water absorption of the samples was measured according to ASTM test method D-570. The samples were weighed and placed in a container of distilled water, and the equilibrium weight value was determined after 24 h of soaking in water at room temperature. The results are expressed in percentage of water absorbed relative to the dry samples.

Biodegradation analysis

According to the standard protocols ASTM D 5988-03 and ASTM D5338-98(2003), the samples were put in boxes filled with compost and incubated for a period of time that varied between 10 and 20 days. The water content was regularly checked to guarantee 60% humidity. The temperature was set at 55°C as an average recommended temperature from the

literature surveyed.[16,17] Every 10 days, systematic sampling and Soxhlet extraction were performed to evaluate the evolution of the soluble fraction of the polyurethane. From the extraction results, it was possible to report the extent of the degradation process using a conversion defined as:

$$\alpha = \frac{(W_o - W)}{W_o} \qquad (4)$$

where W_0 is the initial weight of insoluble elastomer before composting and W is the actual weight of insoluble elastomer after Soxhlet extraction.

The chemical composition of the degraded binder was monitored through FTIR measurements performed using a Digilab FTS6000 FTIR spectrometer equipped with a Photoacoustic cell (MTEC Model 300 Detector; from the company MTEC Photoacoustics, Inc., Ames, IA) filled with helium gas. In general, the signal-to-noise ratio was high enough for all the measurements, and all the samples were tested in the same conditions at room temperature. Each sample was scanned 64 times with a resolution setting of 8 cm^{-1} using the rapid scan mode at the lowest mirror frequency (2.5 kHz) to maximize the signal and to probe the deepest layers possible into the samples. Photoacoustic spectroscopy (PAS) was also carried out to detect alterations in the surface because of degradation, because it directly measures infrared (IR) absorption by sensing absorption-induced heating of the sample. To obtain quantitative data, it was necessary to use an internal normalization for the peaks of interest. The aliphatic β-C-H$_2$ stretch band peak was chosen as an internal reference because of the stability of these chemical links, and their strong absorption in IR. The decrease in specific chemical bonds was estimated based on the average area for nondegraded polyurethane and the area of the peak of interest of the degraded samples.[18]

$$\%\text{change} = 100 * \frac{(A_i - A_f)}{A_f} \qquad (5)$$

where A_i is the area under the peak of nondegraded sample and A_f is the area under of degraded samples at different composting times. Because of the extent of degradation, DMA analysis could not be performed on the degraded samples after only 10 days of composting.

RESULTS AND DISCUSSION

Synthesis of the copoly(ester/ether)

In this work, the synthesis of the copoly(ester/ether) from PECH was carried out in chemically different conditions and at various temperatures. SA was first used along with PECH in toluene and different catalysts. The temperature was varied from 120°C to 145°C. Pyridinium hydrochloride at 5–10 wt %, H$_2$SO$_4$ at 10% or PTSA at 1% were used as catalyst. The extent of the polycondensation was evaluated by GPC measurements. The direct polycondensation between PECH and SA did not yield a high-molecular-weight copolymer. Even with 4-h reactions at 165°C, molecular weight of less than 700 g/mol was obtained. The highest molecular weight ($M_n \approx 1500$ g/mol) was obtained using PTSA in toluene. It is known that polyesterification reactions are very sensitive to elevated temperature, and side reactions, such as hydrolysis because of the presence of residue of water, or dimerization of the chains can lead to a low yield, to low-molecular-weight polymers and a loss of functionality.

Another method to produce the copoly(ester/ethers) is the reaction with dicarboxylic dichlorides using pyridine as catalyst as well as HCl acceptor. This kind of reaction still remains somewhat unattractive because of the cost of the dicarboxylic chlorides and the required dry operating conditions. However, it has the advantages of being carried out at lower temperature because of the enhanced reactivity of the chloride compared with the acid. We conducted these reactions at a SC/PECH molar ratio of 1 : 1 in methylene chloride at 25°C. The GPC characterization of a sample from a 24-h synthesis showed a M_n value of 5857 Da, relative to a polystyrene standard, and a polydispersity index of 1.50. A similar polymerization conducted for 48 h gave a polymer with an M_n of 25,000 Da with a polydispersity of 1.41. These results were obtained in perfect stoichiometric conditions of the reactants, and using an excess of pyridine (catalyst). It has been reported, however, that the molecular weight based on polystyrene standards can overestimate the real molecular weight by about 50–70%[19]; hence, the reported values may be larger than in reality.

The OH equivalents of the synthesized polymers were evaluated with FTIR and also using the acetylation/titration technique. An equivalent weight of 1990 g/eq was evaluated for the low-molecular-weight copolymer using the FTIR technique, whereas the titration technique gave a value of 2000 g/eq. Therefore, within the limits of experimental error, both techniques provided similar values, confirming their reliability.

The polycondensation of PECH with SC proved to be easy to control, and polymers of higher molecular weight were also produced. However, they were not transformed to energetic polymers in light of their high viscosity that rendered them impractical for the preparation of polyurethane elastomers using a cast-cured process. In a following step, only the 6000 g/
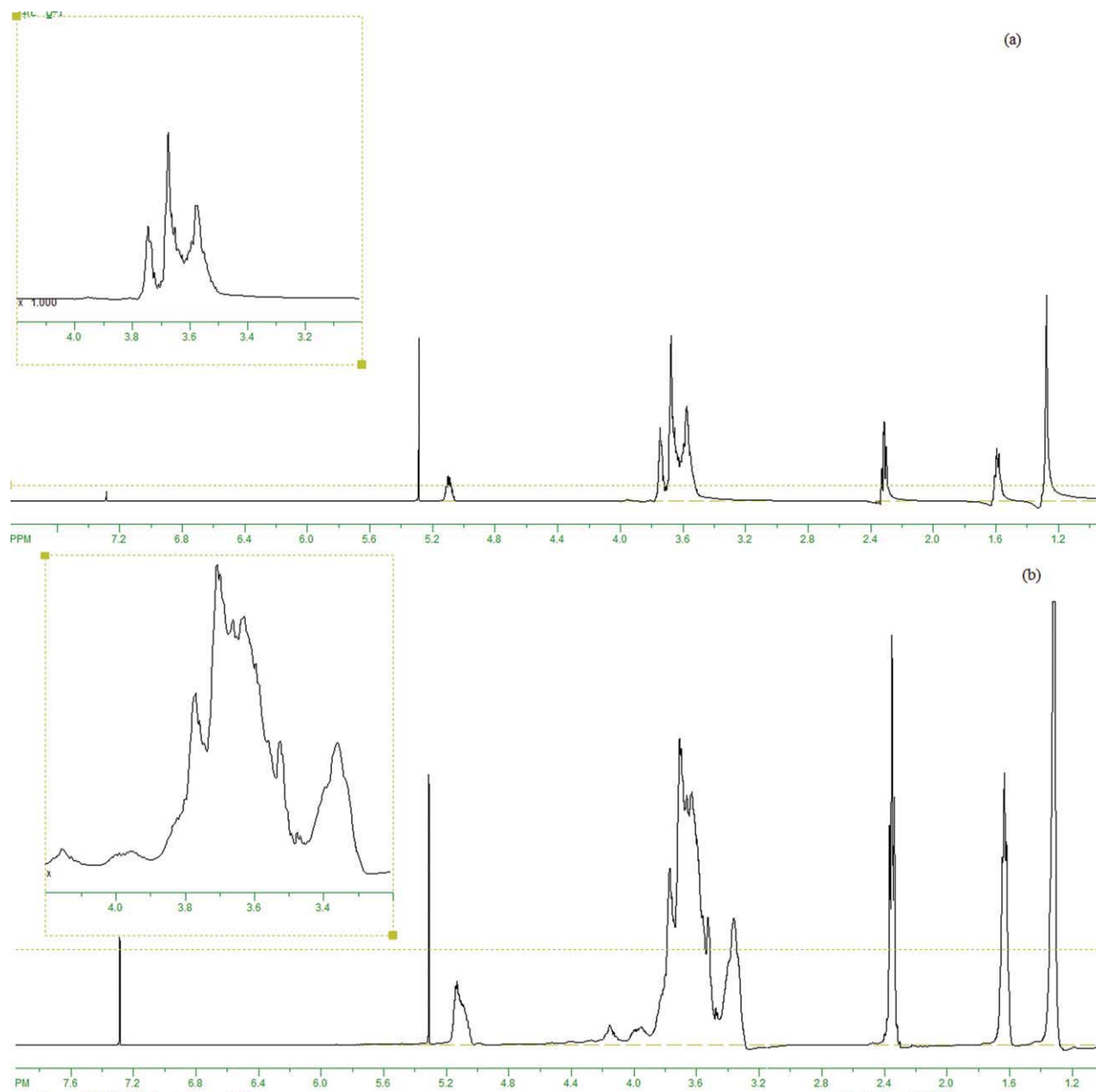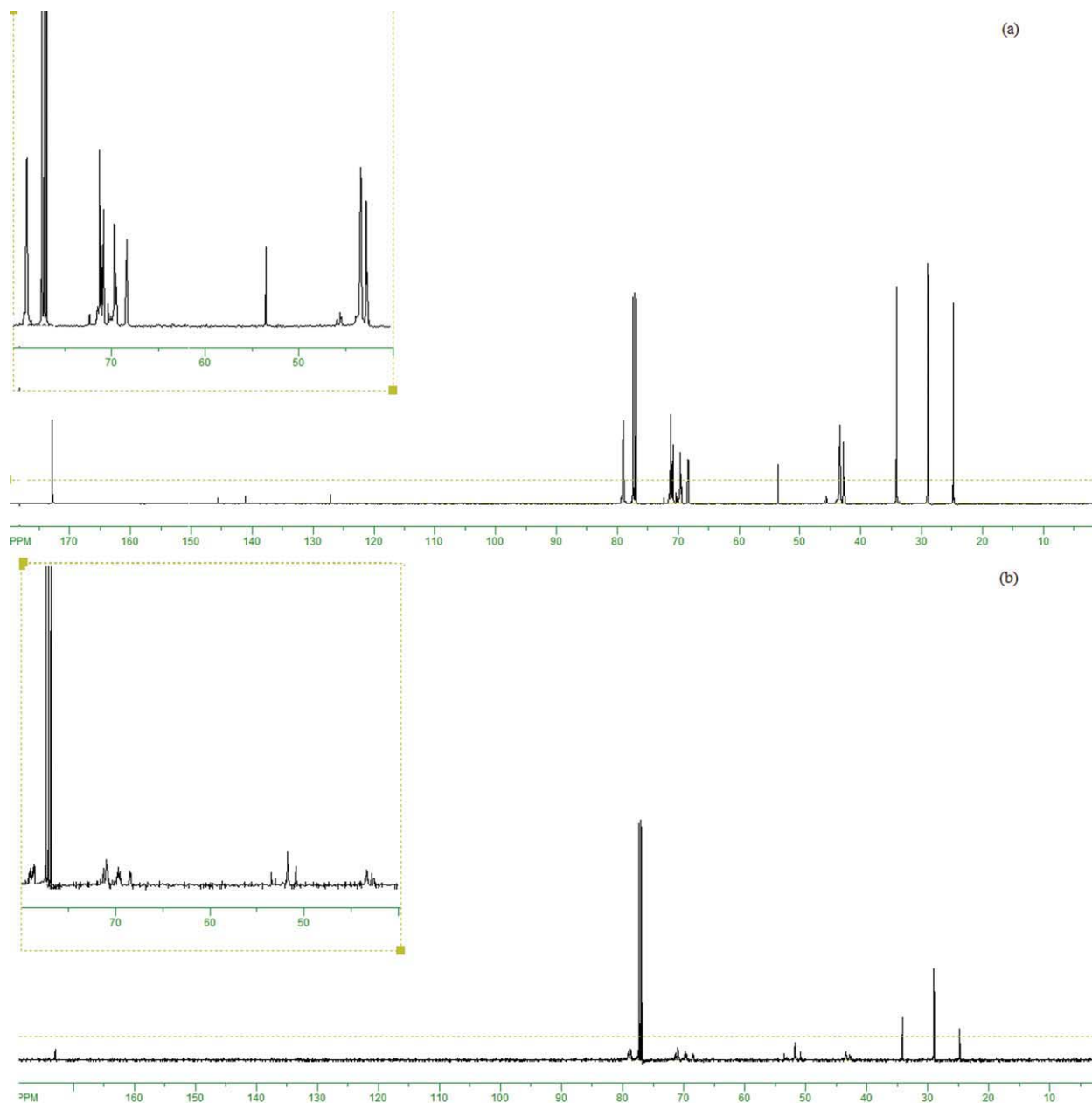
Figure 2 Comparison of ^{1}H-NMR of the copolymer (a) and the energetic copolymer (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mol copolymer was azidified to give an oily yellow product with a molecular weight of about 6500 g/mol relative to polystyrene standards and an equivalent weight of about 2230 g/eq. The energetic copolymer showed monomodal distribution in GPC analysis (polydispersity $\approx$ 1.8). During the azidation reaction, the molecular weight could drop because of the degradation of the polymer backbone itself.[20] However, in this work, our GPC results confirmed that both the ether and ester links were conserved, showing a slight increase in the molecular weight because of the substitution of the Cl atom (35 Da) by the N_3 group (42 Da) on each repeating unit.

The success of the reaction was confirmed by ^{13}C-NMR, ^{1}H-NMR, and FTIR. Figure 2 shows the comparison of ^{1}H-NMR for the nonenergetic and energetic copolymers. On comparing the ^{1}H-NMR spectra of the nonenergetic copolymer [Fig. 2(a)] and of the energetic copolymer [Fig. 2(b)], it is possible to notice the changes in the polymeric chains. The nonenergetic copolymer showed peaks between 3.5 and 3.8 ppm because of the presence of -CH_2Cl, -O-CH_2, and -O-CH. On the other hand, the presence of resonance signals around 3.4 ppm corresponding to -CH_2N_3 protons of the energetic copolymer has confirmed the conversion of -CH_2Cl into -CH_2N_3.

Figure 3 Comparison of ^{13}C-NMR of the copolymer (a) and the energetic copolymer (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The ^{13}C-NMR spectra of the nonenergetic [Fig. 3(a)] and energetic copolymers [Fig. 3(b)] confirm the information provided by the ^{1}H-NMR spectra. The peaks observed between 65 and 80 ppm in both spectra correspond to methylene carbons along both copolymer chains, either attached to hydroxyl or ether oxygen. The dual chloro-methyl peaks of the PECH units of the nonenergetic copolymer were found between 43 and 46 ppm. The energetic copolymer showed the azidomethyl carbon resonance peak at 54 ppm along with a quasi total absence of resonance signals at 43–46 ppm corresponding to chloro-methyl protons.

Moreover, FTIR spectra of the copolymers also reveal the completion of the azidation reaction because the energetic copolymer showed the appearance of the -C-N$_3$ characteristic peak at 2100 cm^{-1}, proving the conversion of -C-Cl into -C-N$_3$ (Fig. 4). For both copolymers, the broad band close to 3500 cm^{-1} is attributed to the hydroxyl groups in the polymeric chains.

DSC experiments were carried out on the energetic copolymer and on the nonenergetic one to better understand the structure–property relationships and thermal stability of these copolymers. As shown in Figure 5, no endothermic peak is found for either
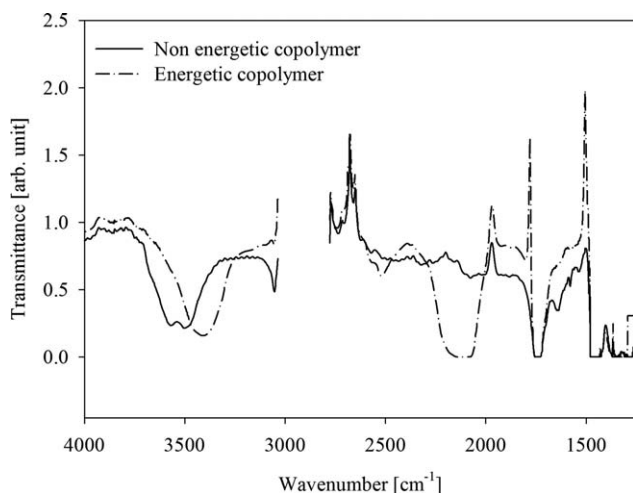
Figure 4 FTIR of the copolymer and of the energetic copolymer.

products, and, hence, they are supposed to be completely amorphous. The DSC traces show only a single exothermic peak at 176°C in the energetic copolymer, which is associated with the decomposition temperature, for a heat flow of 7000 mW/g. This is mainly attributed to the elimination of nitrogen because of the cleavage of the azide bonds from the pendant azide group. In the literature, a decomposition temperature (T_{mcd}) of about 220–250°C has been reported for GAP.[21,22] The addition of N_3 on the polymer chains has the expected effect on the thermal stability of the copolymer itself, but the alternating pattern of ether/ester groups on the polymeric backbone has lowered the temperature of decomposition. It is assumed that the linear moieties increase the mobility of the polymeric main chain during the decomposition of the azide pendant groups, reducing the decomposition temperature.
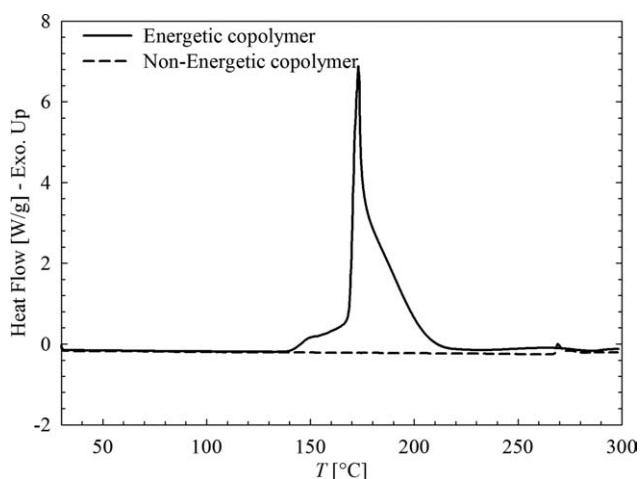

Figure 5 Comparison of DSC curves of the energetic copolymer and the nonenergetic copolymer.

Synthesis of thermoset polyurethane elastomers

Several methods have been investigated for the synthesis of the thermoset polyurethane elastomers starting from the copolymers described in the previous section. Two copoly(ester/ethers-urethane) networks were formed based on the low-molecular-weight nonenergetic copolymer (NE) and the energetic copolymer (E). The most effective preparation method for both copolymers was the two-stage approach. Before the addition of the diisocyanate (LDI), which provides the hard segment of the elastomeric network and also enhances the biodegradability of the material itself, the polyol and the PCL were carefully hand mixed, using a 70/30 wt % ratio, with a 0.01M solution of DBTL catalyst, used at a 0.15% w/w concentration. Both polyurethane formulations, mixed at a NCO/OH ratio of 1.33, were degassed under vacuum at 60°C for a few minutes and then allowed to cure at 75°C for 24 h. The reaction time and the temperature reflected the appropriate conditions to prepare polyurethane with complete consumption of the polyols and the diisocyanates.

DMA gave further insight on the mechanical properties and viscoelastic behavior of the two elastomers. Figure 6 shows the storage modulus and tan δ as a function of temperature. Both tan δ curves displayed broad peaks, which are attributed to the glass transition of the copoly(ester/ether) soft blocks of the elastomers. According to the literature,[23] the glass-transition temperature, T_g, values can be evaluated at the peak of the tan δ curve as a function of temperature. According to this criteria, the T_g of the polyurethanes are nearly 10°C apart, with −23°C and −14°C for the E and NE elastomers, respectively.

Also shown in Figure 6 is the storage modulus, presented in a semilogarithmic plot to clarify the transition region. The storage modulus G' represents the elastic and nondissipative component of the
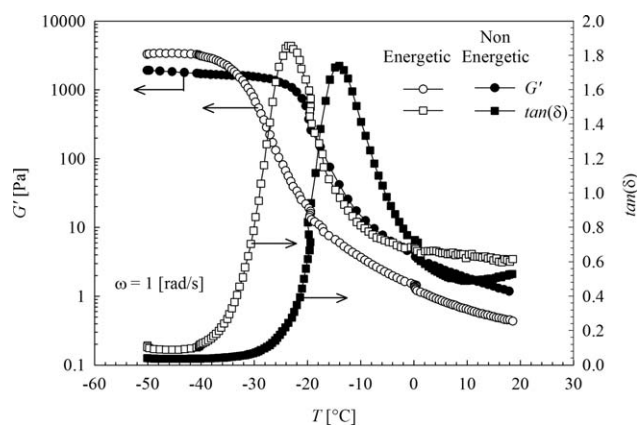

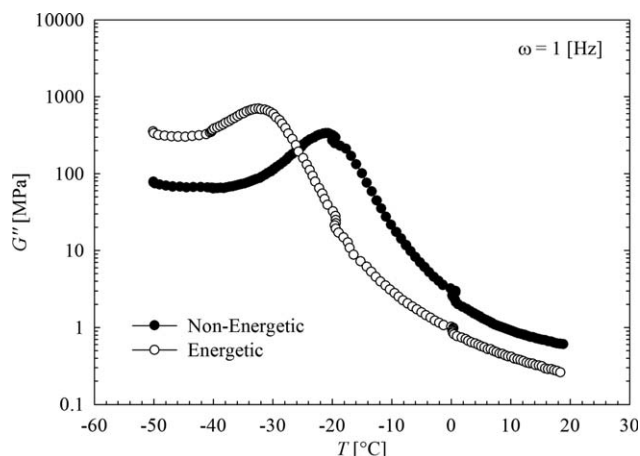**Figure 6** DMA of the polyurethane binders.

Figure 7 DMA of elastomers: loss modulus vs. temperature

elastomers and, hence, is related to the energy stored in the samples. At low temperature, below −34°C, the E polyurethane presents a storage modulus of about 3300 MPa, compared with 1800 MPa for the NE polyurethane. At these low temperatures, i.e., below the T_g, the storage modulus is often affected by the polymer structure,[23] e.g., by the molecular weight and chemical structure of the prepolymer, with larger molecular weight resulting in larger storage modulus. Although the E polyurethane presents a higher modulus at low temperature, the molecular weight of the energetic prepolymer (6500 g/mol) is essentially the same compared with the nonenergetic one (6000 g/mol). Consequently, the difference comes from the chemical structures of the respective polyether and polyether/polyester chains. Starting from approximately −41°C and −31°C for the E and NE elastomers, respectively, the storage modulus decreases progressively with temperature because of the increase in thermal energy and molecular chain motions.

The decrease of the storage modulus in the glass-transition region occurs at lower temperature and more sharply for the energetic elastomer than for the nonenergetic one. Taking into account the correspondence between time and temperature, the kinetics of relaxation affects the temperature range necessary for the rearrangement of the molecules.[24] Thus, these different behaviors can be explained based on molecular hindrance of the two polymeric chains. The energetic polymer backbone differs from the nonenergetic one, where the former carries three nitrogen atoms at each repeating unit instead of only a chlorine atom in the latter case. As a result, for the E elastomer only a small portion of the total volume is occupied by the backbone of the polymeric chain, easing molecular motion and resulting in a faster relaxation process, or considerable relaxation over a lower temperature range. In addition, because these

are cross-linked materials, the storage modulus should eventually approach a rubbery plateau at elevated temperatures. At room temperature (20°C) the storage modulus is quite small, 0.26 Pa for the E elastomer and 0.45 Pa for the NE one, indicating that these materials do not have tremendous mechanical properties. In addition, the rubbery plateau is not completely reached at room temperature because the G' curves are still decreasing slightly.

In Figure 7 the loss modulus G'' of both polyurethanes is presented. The loss modulus, related to the energy dissipation, shows a peak at −32°C for the E elastomer, and at −21°C for the NE elastomer. The T_g can also be evaluated from the peak of the loss modulus curve as a function of temperature. These values are reported in Table I, along with the ones corresponding to the maximum peak of tan δ. There is approximately a 10°C difference between the T_g values evaluated from both methods, with the ones from the loss modulus being lower. These lower values seem more representative of the elastic modulus behavior in Figure 6. Nevertheless, the T_g's reported in Table I are in the neighborhood of the glass-transition temperature of PECH-based elastomers (−20°C to −25°C).[20] The addition of ester bonds to PECH reduces the flexibility of the polymeric chains and, consequently, slightly increases the T_g of the nonenergetic polyurethane. In a polymer with nonsymmetrical chains, an additional restriction to rotation is imposed by steric effects, increasing T_g as seen for the NE elastomer.[23] In addition to the effects related to the polymeric backbone, the presence, polarity, size, and flexibility of pendant groups can also affect the viscoelastic properties of the materials. Generally, polar pendant groups such as CH_2-Cl tend to increase the T_g rather than nonpolar ones such as CH_2-N_3. Thus, although the further substitution of a Cl atom by a larger size azide group on the polymeric backbone increases the steric hindrance and reduces the flexibility of the polymeric chain. At the same time, it results in an increase in the free volume required for molecular motions.[25] Consequently, the created additional free volume and the nonpolar nature of the azide groups can possibly explain the lower T_g values of the energetic elastomer (Table I). Finally, the E elastomer is observed to be less viscous and less elastic at room temperature (Figs. 7 and 6, respectively). This can be

TABLE I
Comparison of the Polyurethane Networks

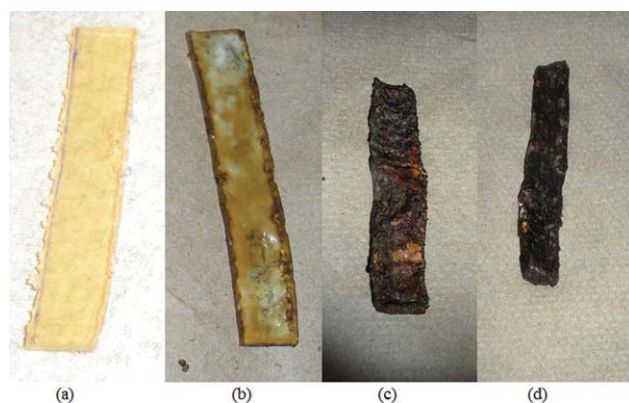| Polyurethane network	Water uptake (%)	T_g (°C)
NE	7.1	−14
E	2.3	−23

NE, non energetic; E, energetic.

Figure 8 Evolution of the degradation of the E elastomers at different times; (a) $t = 0$, (b) $t = 10$, (c) $t = 20$, and (d) $t = 25$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 10 Weight loss of the E and NE elastomers.

interpreted in terms of neighboring molecules and their effects on G' and G'', i.e., lower local frictional forces between short and long segments of the polymeric chains.[24] This explanation is valid not only for low-molecular-weight materials, which is the case here if we consider the prepolymers, but also with the final elastomers, where the loss modulus is clearly correlated to the internal frictions factors of the polymer chains.

Biodegradation in the compost of the energetic and nonenergetic polyurethane binders

In Figure 8, the evolution of the degradation of the E polyurethane is shown. It can be seen that even after only 10 days in the compost, the degradation process was already in progress. At this point, the elastomers retained their original shape but were no longer transparent. The degradation was initiated at the surface of the samples, as expected. After 25 days,
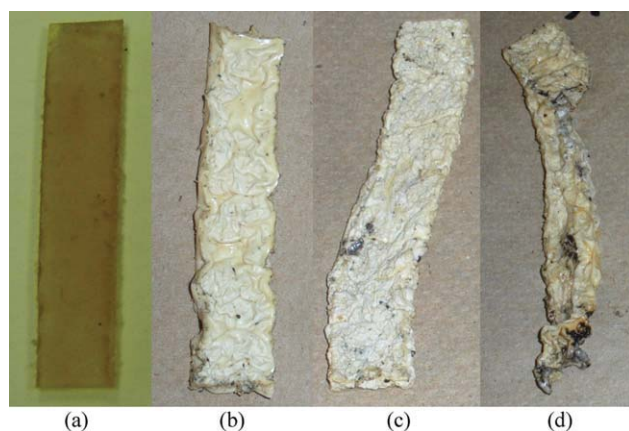
the bacterial attack became stronger, penetrating deeper inside the samples and creating holes all through them. The surface roughness increased, and the samples lost their original shape and dimensions. The degradation of the NE polyurethanes is depicted in Figure 9 for comparison purposes. In this case, after 10 days, the degradation is already more advanced (showing signs of hydrolytic and bacterial attack on the surface of the samples) and causing a color change from transparent amber yellow to white opaque. After 15 days, the samples were more and more degraded, and a width reduction of about 50% was observed. The samples extracted after 20 days showed a severe degradation, and they lost their original shape.

On comparing Figures 8 and 9, it is possible to notice how the degradation proceeded in each material: slower for the energetic polyurethanes and faster for the nonenergetic ones. The degradation mechanism depends on the chemical structure and

Figure 9 Evolution of the degradation of the NE elastomers at different times; (a) $t = 0$, (b) $t = 10$, (c) $t = 15$, and (d) $t = 20$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
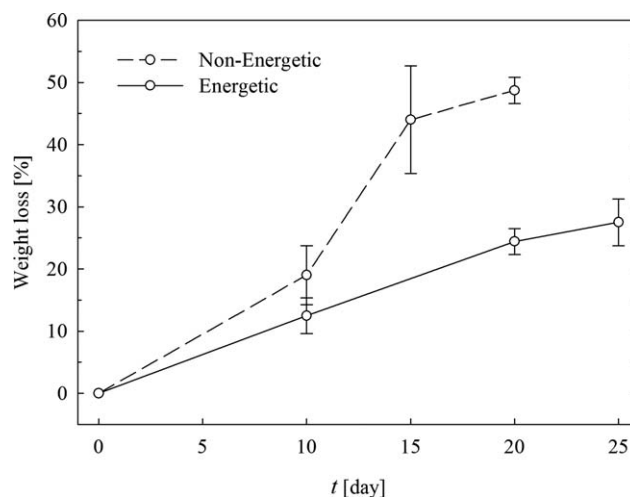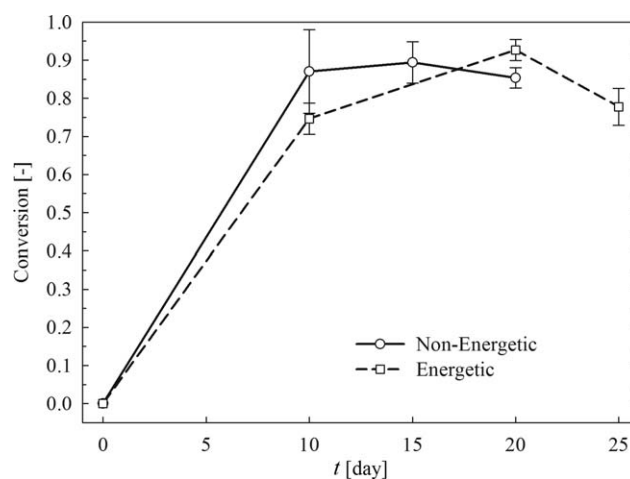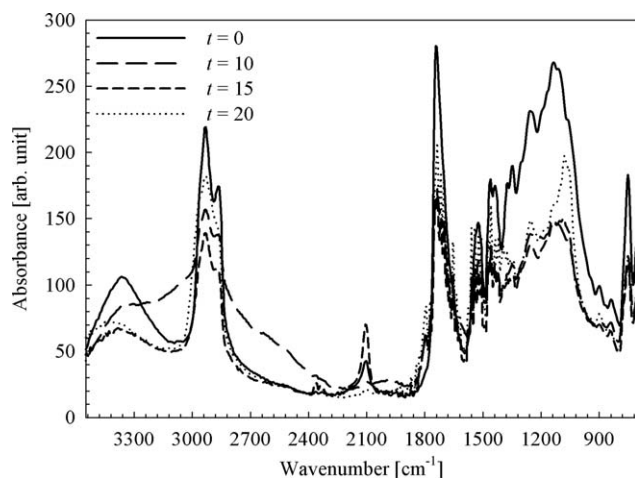

Figure 11 Soxhlet extraction.
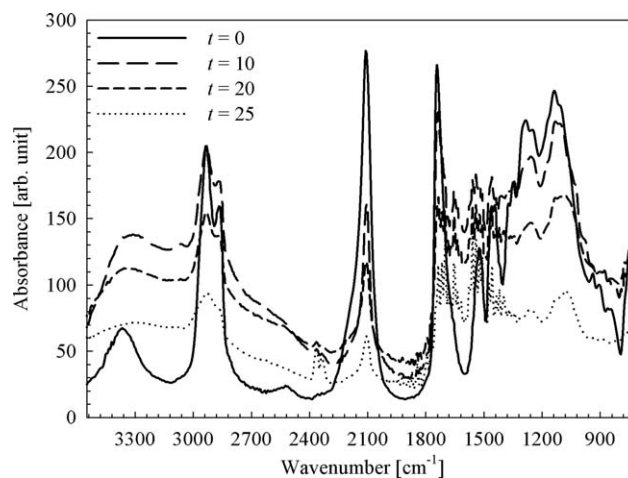
Figure 12 FTIR PAS of NE elastomer.

Figure 13 FTIR PAS of E elastomer.

configuration of the polymeric chains. One can, therefore, affirm that the energetic copoly(ester/ ether) segments are more stable and resistant to degradation than the nonenergetic ones. Figure 10 shows the weight loss of both polyurethane binders versus degradation time at 55°C. The weight loss increases almost linearly with time for both materials, but it is more pronounced for the nonenergetic binder: after 20 days, the samples lost about 50% of the mass because of the biodegradation mechanism. Instead, the energetic elastomers lost only about 25% of their initial mass after 25 days.

The network integrity of the degraded samples was evaluated by Soxhlet extraction in dichloromethane and FTIR-PAS analysis. From the Soxhlet extraction results (Fig. 11), it seems that the solubility of the polyurethane networks in the solvent increases with time in the compost. After 10 days, both polyurethanes binders show a conversion [eq. (4)] larger than 0.7, which slowly continues to increase with time. Accordingly, the spontaneous cleavage of the polyurethane network during the composting process resulted in low-molecular-weight by-products soluble in organic solvents.

FTIR spectroscopy has already been used extensively to investigate chemical changes in degraded polymers.[26–28] FTIR-PAS spectroscopy was used to investigate the structural difference in the degraded samples compared with the nondegraded ones. Figures 12 and 13 present the FTIR-PAS spectra of nonenergetic and energetic binders, respectively; while the proposed peaks assignation is reported in Table II. According to the literature,[26] N-H stretching is detected near 3300 cm^{-1}, the carbonyl urethane stretching near 1730 and 1700 cm^{-1}, the N-H bending and C-N stretching near 1535 cm^{-1}, the C-N stretching near 1222 cm^{-1}, and the ester absorbance near 1110 cm^{-1}. In this study, two more peaks were detected: C-N$_3$ antisymmetric stretching near 2100 cm^{-1} and CH$_2$-Cl near 750 cm^{-1}. At the first glance, it is possible to notice in both Figures 12 and 13 the decrease in the magnitude of the absorption bands relative to the mentioned functional groups with the composting time.

Generally speaking, the absorbance in a FTIR-PAS spectra depends on the heat transport properties in the sample. Given the significant changes in the polyurethane binders during the composting

TABLE II
Proposed Assignments of FTIR PAS Absorbance Peaks for NE and E Elastomers

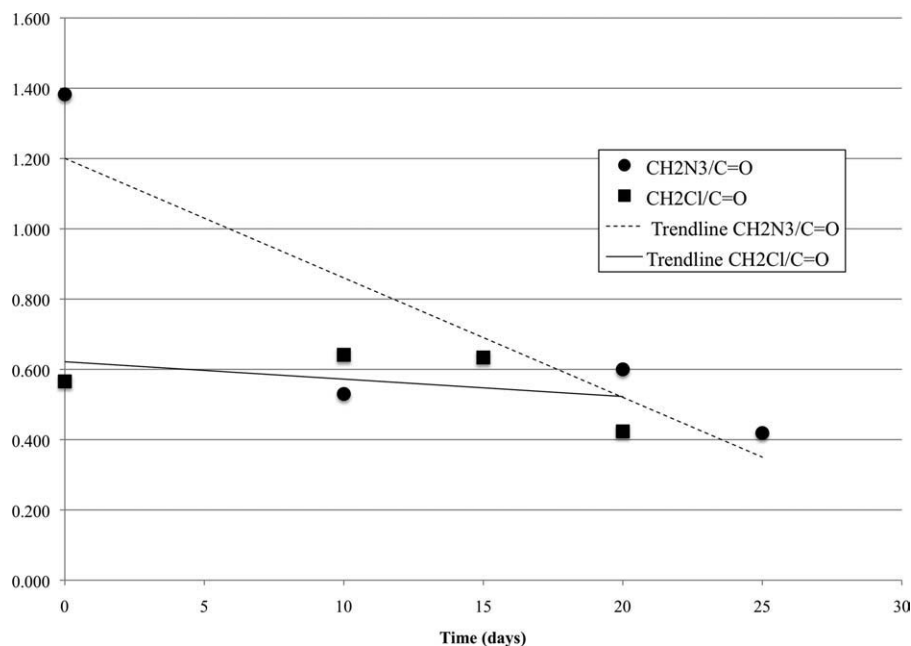| NE elastomers	E elastomers	Assignments
3370 cm^{-1}	3381 cm^{-1}	N-H stretching (hydrogen bonded to carbonyl)
2943 cm^{-1}	2940 cm^{-1}	Aliphatic antisymmetric β-CH$_2$ stretching
2869 cm^{-1}	2862 cm^{-1}	Aliphatic antisymmetric α-CH$_2$ stretching + symmetric β-CH$_2$ stretching
	2100 cm^{-1}	C-N$_3$ stretching
1753 cm^{-1}	1764 cm^{-1}	Non-hydrogen bonded urethane C=O stretching
1476 cm^{-1}	1463 cm^{-1}	Aliphatic CH$_2$ bending
1243 cm^{-1}	1242 cm^{-1}	CH$_2$ wagging
1133 cm^{-1}	1132 cm^{-1}	Aliphatic asymmetric C-O-C stretching (ether)
1056 cm^{-1}	1103 cm^{-1}	Urethane C-O-C stretch and aliphatic symmetric C-O-C stretching
756 cm^{-1}		C-Cl$_2$ stretching

Figure 14 Evolution of normalized azide and chlorine to carbonyl peaks ratio of NE and E elastomers.

experiments, it is not possible to compare the spectra from samples taken at different times on an absolute basis. Nevertheless, it was desired to highlight, if any, the differences in the degradation process of each type of polymer. Therefore, the absorbance intensity for the few peaks of interest was normalized by the intensity of the peak corresponding to aliphatic antisymmetric β-CH$_2$ stretching (2940 and 2943 cm^{-1}), which was used as an internal reference seen as more stable than other links in the polymer molecules. Figure 14 presents the evolution in the ratio of the normalized area of the CH$_2$-N$_3$ or CH$_2$-Cl peak to carbonyl C=O signal at different stages of degradation. As can be observed, because of the limited set of data, it was difficult to make definitive conclusions, but clearly, the degradation process proceed differently for each type of elastomers. For NE elastomers, the ratio remains more or less constant whereas it decreases for the energetic elastomer. Considering that the weight loss over time is more pronounced in the NE polyurethanes, this would indicate that in the latter case the fraction in polyether segments in the network decreases more rapidly than the polyester parts.

Ester bonds play a fundamental role during the degradation process because they can undergo hydrolytic scission more easily than other chemical bonds. The urethane and urea linkages are less sensitive to hydrolysis than the ester bonds.[29] An initially homogeneous sample undergoes hydrolysis, with consequent cleavage of the ester bonds confirmed by a decrease in the mass. On the FTIR spectra shown in Figures 12 and 13, a very broad absorbance band develops in the 3300–3000 cm^{-1} area

during the first half of the composting experiment. This can probably be associated to the presence of carboxylic acid groups resulting from hydrolytic chain scissions. The velocity of the hydrolysis is determined by the "concentration" of reaction partners, water, and labile bonds.[30] From water uptake tests NE elastomers resulted to be more hydrophilic (7.1%) than the E elastomers (2.3%), and, after 10 days, the absorption peaks of ester bonds substantially decreased. This is in accordance with the larger weight loss occurred to nonenergetic binders. The inherent more hydrolytic resistance of the energetic polyurethane must be attributed to the presence of the azide group in the backbone chains. The final hydrolysis products of the polyesters will be degraded by microorganisms to smaller end products after they are released in a natural environment. But, at this stage of the work, no ecotoxicity tests were conducted. In summary, FTIR-PAS spectra have shown that the combination of the hydrolytic and bacterial attack in the compost was more efficient in the case of nonenergetic binders.

CONCLUSIONS

This work aimed to produce an energetic biodegradable polyurethane elastomer. The first step was devoted to the production of a low-molecular-weight prepolymer. The synthesized azide polyol was suitable for being modified by an azidation reaction and being included in polyurethane elastomer formulation. Copoly(ester/ethers) of PECH and SA were prepared by two standard polycondensation

methods to evaluate the appropriate operation conditions. First, direct polycondensation of PECH with SA was conducted in toluene using a Dean Stark apparatus. Even if different reaction conditions and catalysts were tried, a copolymer of satisfactory molecular weight was not produced. On the other hand, pyridine-promoted polycondensation of PECH with SC resulted in producing copolymers of higher molecular weight (6000–25,000 g/mol, relative to polystyrene standard). Biodegradable cross-linked energetic and nonenergetic polyurethanes (binders) were prepared from PCL and copolymers of PECH and SC as soft segments and LDI as hard segments. The cross-linked elastomers showed good biodegradability in the compost. The rate of weight loss was significantly higher for the nonenergetic binders with respect to energetic ones. This was due to the presence of the chlorine group in the molecular chains on nonenergetic binder. The ether/ester bonds of the energetic polyurethane were found to be less susceptible to hydrolysis, probably because the azide group affecting the steric hindrance reduced the possibility of cleavage of the molecular chains. These biodegradable binders with elastomeric properties may be used in military applications where more environmentally acceptable products are sought. Future work includes the optimization of the mechanical properties of these novel materials.

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