

# Synthesis and Characterization of Soybean-Oil-Based Polyurethane Composites Containing Industrial and Agricultural Residual Wastes as Fillers

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**ABSTRACT:** Thermosetting composites were prepared from soybean-oil-based polyols (hydroxyl number = 190 mg of KOH/g,  $[\text{OH}]/[\text{NCO}]$  for 2,4-toluene diisocyanate = 0.9) and fillers (10 wt %) from industrial and agricultural residual wastes. Different types of inexpensive residual wastes were used: black rice husk ash, coconut husk ash, calcined retorted oil shale, and retorted oil shale. The fillers were characterized by thermogravimetric analysis and measurements of particle size distribution, specific surface area, and pore size distribution. The fillers were microporous materials with different chemical compositions, with average particle diameters varying from 5.6 to 76.6  $\mu\text{m}$ , specific surface areas varying between 6 and 165  $\text{m}^2/\text{g}$ , and thermal stability

at the polyurethane cure temperature (65°C). All composites were characterized by dynamic mechanical analysis, flexural tests, Shore A hardness tests, thermogravimetric analysis, and scanning electron microscopy analysis. Coconut husk ash, rice husk ash, and retorted oil shale presented better mechanical properties; nevertheless, coconut husk ash and rice husk ash had higher particle sizes, which caused bad dispersion of the filler in the matrix and resulted in nonhomogeneous composites. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 1370–1376, 2012

**Key words:** composites; fillers; mechanical properties; polyurethanes; structure

## INTRODUCTION

The utilization of renewable sources has received a lot of attention in the last few years because of the increasing demand for replacing petroleum-derived products.

Vegetable oils are triacylglycerols esters of fatty acids and are considered one important class of renewable sources. Soybean oil is one of the most common vegetable oils; it is an inexpensive, readily available, renewable resource, and it provides an excellent platform for polymeric materials. In its composition, there is a predominance of triacylglyceride molecules derived from unsaturated fatty acids, such as oleic acid (22%), linoleic acid (55%), and linolenic acid (7%). Triacylglyceride molecules possess double bonds, which are reactive sites; nevertheless, they need to be functionalized to prepare polymers.<sup>1</sup> Although their principal use is in the coating industry, in the last decade, triglyceride-

oil-based polymers have been investigated extensively by many groups.

Wool and coworkers<sup>2–5</sup> chemically modified oils, which could be polymerized with free-radical initiators into rigid composites, rubbers, and adhesives. Larock and coworkers<sup>6–9</sup> investigated polymers derived from soybean oils. Recently, they prepared thermosetting polymers by the cationic polymerization of fish oils, linseed oil, tung oil, and soybean oil with petroleum-based comonomers, such as styrene, divinylbenzene, and dicyclopentadiene, in the presence of boron trifluoride diethyl etherate as an initiator. John et al.<sup>10</sup> studied polyurethane (PU) foams derived from soybean oil; the sequence of the chemical reactions during the foaming process were monitored by Fourier transform infrared spectroscopy. The introduction of soybean oil caused an increase in the hydroxyl values and acid values. Petrovic and coworkers<sup>11–16</sup> developed methods for preparing soy polyols from soybean oil. The polyols were subsequently used to prepare PUs whose structures depended on the type of triglyceride used, the nature of the isocyanate group, and the degree of crosslinking.

There is growing interest in PUs for applications as composites because of their low viscosity, excellent bonding with different fillers, relatively low cost, and fast reaction time.<sup>15</sup>

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There are three main components in any composite: the matrix, the filler, and the so-called interfacial region. Fillers are used as reinforcing additives in the polymeric matrix to improve or modify its physical properties or processing characteristics and to reduce the product price.

To obtain a good final product, it is important that the filler and matrix interact strongly. This can be achieved when the filler has a high surface area, small particle size, and good chemical affinity with the matrix.

As with other polymers, the use of fillers in vegetable-oil-based PUs yields products with modified performance.<sup>17,18</sup> Calcium carbonate and glass fibers are the most commonly used fillers.<sup>15,19,20</sup> The former is primarily used to make cheaper formulations, and the latter is of great interest within reaction-injection-molding technology.

For several years, natural fibers have been used as reinforcing additives for polymers. Wood fibers have been commonly combined with thermoplastic<sup>21,22</sup> or thermoset<sup>23</sup> matrices to enhance mechanical properties, such as stiffness and impact strength. In recent years, annual crop fibers have increased in value through their incorporation into various polymers. Agricultural waste can come from different sources, such as sisal, jute, coconut, and flax, and it has significant potential as a source of low-cost reinforcements for polymers. The use of lignocellulosic materials as reinforcing components in vegetable-oil-based PU composites has several advantages, such as a lower density, higher deformability, and good adhesion to the matrix.<sup>24,25</sup>

The southernmost state of Brazil produces about 5.46 million tons of rice per year. The rice-milling industry generates a great amount of rice husk during the milling of the rice, which comes from the paddy fields. Husk is obtained as a byproduct of threshing rice. In fact, about 20% of the dry mass of harvested rice is husk. This agricultural waste represents a very big environmental problem. Rice husk is mostly used as a fuel in boilers for processing rice and is also used as a fuel for power generation. Rice husk ash (RHA) constitutes about 25 wt % of rice husk when it is burned in boilers, and it is a carbon-neutral green product. Many methods of disposing RHA are being considered, including the discovery of commercial uses for it. Depending on the combustion conditions, different structural forms of ashes are produced. The two most common are black RHA (14% organic material and 86% inorganic material) and white RHA (96% silica). The higher organic matter content of black RHA makes it a most suitable material for the preparation of composites with PU because the polar organic compounds possibly present in this organic material will improve interactions of the filler with the polymer matrix.

Coconut husk is a byproduct generated when the main products, coconut milk and edible coconut flesh, are extracted from the coconut. The utilization of coconut husk can be considered an environmental necessity because the husk is usually thrown into the garbage or left on the roads, and it takes more than 8 years to decompose. The husks and shells of coconuts can be used as fuel. The pyrolysis of coconut husk produces a material that mainly consists of carbon (~96%) and minerals (~4%) that can be used to prepare activated charcoal.<sup>26,27</sup> To a certain extent, husks are also used in handicrafts, floor polishers, and other minor applications. Coconut husk is mainly composed of cellulose (20–43%), hemicelluloses (3–12%), lignin (30–45%), and minerals (0.1–5%).<sup>28–30</sup> The analysis of coconut husk shows 77–81% volatile matter and moisture, 18–21% fixed carbon, and 0.1–3.6% ash.<sup>26–28,31</sup>

Retorted oil shale (ROS) is a solid residue of the thermal transformation of oil shale, which is a sedimentary rock containing an organic complex (kerogen) that decomposes when it is exposed to heat and produces oil and gas. Brazil has the second largest world reserve of oil shale and holds one international patent for a modern process in the commercial operation for the extraction of oil shale (Petrosix). During the process, ROS is produced in large amounts, and its disposal represents an environmental and economic problem. Most ROS is returned to the mine area; nevertheless, its mineralogical composition and lamellar structure shows great potential for the manufacture of ceramics,<sup>32</sup> composites,<sup>33</sup> or absorbent products.<sup>34,35</sup> ROS is approximately 84% inorganic minerals (mainly aluminum silicates) and 14% volatile organic compounds. When ROS is heated at higher temperatures in an oxidant atmosphere, most of the organic compounds are volatilized. The resulting material, called *calcined retorted oil shale* (CROS), has more than 97% inorganic compounds.<sup>34</sup>

The main objective of this study was to develop new types of inexpensive reinforced PU and to study the effects of fillers from industrial and agricultural residual waste on the mechanical properties of the materials developed. Different types of inexpensive residual waste were studied: two from agriculture [black RHA and coconut husk ash (CHA)] and two from industrial residues (CROS and ROS). The relationships between the filler nature, size, chemical composition, and morphological characteristics and the final mechanical properties of the composites were analyzed.

## EXPERIMENTAL

### Materials

2,4-Toluene diisocyanate (TDI; Bayer AG, Leverkusen, Germany) was purified before use by distillation

TABLE I  
Results of Fillers Characterization

Filler	Organic material (%) <sup>a</sup>	Residue (%) <sup>a</sup>	Average particle diameter (μm) <sup>b</sup>	Specific surface area (m <sup>2</sup> /g) <sup>c</sup>	Porous volume (cm <sup>3</sup> /g) <sup>d</sup>	Porous diameter (nm) <sup>d</sup>
CB	1.7	98.3	6.1	44	0.034	3.1
RHA	14.1	85.9	22.3	52	0.029	2.3
CHA	58.8	41.2	76.6	165	0.087	2.1
ROS	6.6	93.4	5.6	6	0.01	8.3
CROS	0.2	99.8	14.0	6	0.004	2.9

<sup>a</sup> Determined by TGA at 735°C.

<sup>b</sup> Determined by PSD.

<sup>c</sup> Determined with the Brunauer–Emmett–Teller method.

<sup>d</sup> Determined with the Barrett–Joyner–Halendar method.

under reduced pressure. The NCO index was determined according to ASTM D 5155-96.<sup>36</sup> Toluene (Merck, Darmstadt, Germany) was dried over sodium and distilled under a nitrogen atmosphere before use. ROS was supplied by TECPOL Solutions Provider (Porto Alegre, Brasil); RHA was supplied by Ingovel Indústria Riograndense de Óleos Vegetais, Ltda. (Pelotas, Brasil); coconut husk was provided by Artecola Indústrias Químicas, Ltda. (Campo Bom, Brasil); and carbon black (CB) was provided by Borrachas Tipler S.A. (São Leopoldo, Brasil) CHA and CROS were prepared by the calcination of coconut husk and ROS for 5 h at 600°C and were dried just before use for 2 h at 150°C. RHA underwent the same thermal treatment. ROS and CB were also dried before use under the same conditions.

### Soy-based polyol preparation

Soy-based polyols were prepared with a formic acid/hydrogen peroxide system and were characterized by our group as described in the literature.<sup>37</sup> Soybean oil (molecular weight = 868 g/mol, 4.5 mol of double bonds) was supplied by Oleoplan, Ltda. (Veranópolis, Brazil). The polyol sample had a hydroxyl number of

190 mg of KOH/g, which was determined according to the AOCS T1a-66 standard method.<sup>38</sup>

### Composite preparation

The soy-based polyol (hydroxyl number = 190 mg of KOH/g) and filler were manually mixed for 2–3 min. Fillers were added at 10% w/w. Afterward, TDI was added at an [OH]/[NCO] ratio of 0.9 under an inert atmosphere. After homogenization, the mixture was introduced into the mold and maintained for 24 h at 65°C in a vacuum oven.

### Characterization

The hardness was determined with a Shore A durometer (Barueri, Brasil) according to ASTM D 2240-97.<sup>39</sup> Measurements were made at 3, 15, and 30 s at six different points on the sample surface. The average value was taken as the hardness value.

Dynamic mechanical analysis was carried out on a TA Instruments Q800 dynamic mechanical analyzer (TA Instruments, USA) in the flexural strength mode. The storage modulus ( $E'$ ), loss modulus, and loss tangent ( $\tan \delta$ ) were determined from –60 to 100°C at a heating rate of 2°C/min and a frequency of 1 Hz.

Flexural tests were carried at room temperature out with an EMIC CL Trd 21 testing machine (São José dos Pinhais, Brasil) with a load cell capacity of 500 N. The tensile and flexural strength loads were measured at a

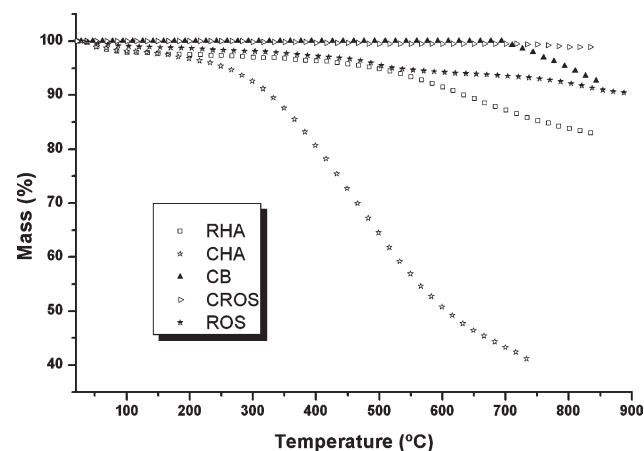


Figure 1 TGA curves of the fillers (10°C/min and N<sub>2</sub>).

TABLE II  
Chemical Composition of the Fillers

Filler	Carbon (%)	Oxygen (%)	Silicon (%)	Aluminum (%)	Iron (%)
CB	96 ± 0	4 ± 0	—	—	—
CROS	—	26 ± 2	37 ± 1	9 ± 0	24 ± 1
ROS	22 ± 5	20 ± 2	31 ± 0	7 ± 1	20 ± 0
RHA	43 ± 4	23 ± 1	32 ± 0	—	—
CHA	85 ± 1	13 ± 2	—	—	—

The values were determined by energy-dispersive spectroscopy.

TABLE III  
Mechanical Properties of Composites

PU/filler	$T_g$ (°C)	$E'$ (MPa) <sup>b</sup>	Flexural modulus (MPa)	Flexural deformation (mm <sup>2</sup> )	Hardness (Shore A)
PU <sup>a</sup>	83	0.974	16.0 ± 4.7	6.1 ± 1.8	71 ± 1
PU/10% CB	79	0.976	15.5 ± 2.1	6.1 ± 3.4	73 ± 0
PU/10% CHA	89	1.307	19.3 ± 3.1	3.0 ± 0.2	75 ± 1
PU/10% RHA	87	1.008	18.0 ± 3.8	2.8 ± ND	75 ± 1
PU/10% ROS	89	1.038	ND	ND	75 ± 1
PU/10% CROS	76	1.109	19.2 ± 4.9	4.6 ± 1.9	73 ± 1

ND = not determined.

<sup>a</sup> Soy-based polyol with a hydroxyl number of 190 mg of KOH/g ([OH]/[NCO] for TDI = 0.9).

<sup>b</sup> Determined at  $T_g + 40^\circ\text{C}$ .

50 mm/min strain rate with dimensions of  $10 \times 2 \times 40$  mm<sup>3</sup>. Each value obtained represented the average of three to five samples.

Thermogravimetric analysis (TGA) was performed with a Shimadzu TGA 50 instrument (Columbia, EUA) at a heating rate of 10°C/min in the temperature range 20–800°C under nitrogen gas.

The specific surface area was determined with the Brunauer–Emmett–Teller method, and the pore size distribution was determined with the Barrett–Joyner–Halendar method with equipment from Micrometrics (ASAP 2010, Norcross, EUA). The samples were previously degassed at 100°C *in vacuo* for 4 h.

The morphology of the cryogenically fractured samples was determined with a JEOL JSM 6060 scanning electron microscope (Tokyo, Japan) with an activation voltage of 15 kV. The samples were mounted on a sample holder and were sputter-coated with gold *in vacuo*.

The particle size distribution (PSD) was obtained by laser diffraction with CILAS 1180 equipment (New Orleans, EUA), with a measurement range from 0.04 to 2500  $\mu\text{m}$ , with a laser wavelength of 830 nm. The sample (0.1 to 5 g) was suspended in water at a concentration of 150 mmol/L and stirred at 200 rpm.

Energy-dispersive spectroscopy analysis was performed with a JEOL JSM 6060 apparatus with a Noran detector at 20 kV. The acquisition time was 100 s, and  $1000 \times$  magnification was used.

## RESULTS AND DISCUSSION

### Filler characterization

After the respective thermal treatment, the fillers were characterized with TGA, PSD, and specific surface area and pore size distribution measurements. Table I shows the results of the filler characterization. For comparison, commercial CB filler was also characterized and was used to prepare a composite.

The average particle diameter of the fillers varied from 5.6 to 76.6  $\mu\text{m}$ . CHA showed the largest average particle diameter. Through histograms (not shown), we observed that all of the fillers presented bimodal distribution.

The porous volume and porous diameter data for these materials showed that all fillers were microporous materials. The specific surface area varied between 6 and 165 m<sup>2</sup>/g, with CHA presenting the highest specific surface area.

Figure 1 shows the thermogravimetric curves of the fillers. All of the fillers started to decompose at temperatures higher than the cure temperature (65°C). Thus, they were considered suitable for preparing composites. The TGA curves also showed that the fillers had different amounts of volatile organic compounds. It is important to point out that as TGA was performed in an inert atmosphere, the residual components were fixed carbon and/or mineral materials. CHA started to decompose at the lowest temperature, 350°C, and up to 735°C, it lost almost 60% of its mass. This result shows that CHA still had volatile organic matter even after it underwent calcination. RHA, CROS, ROS, and CB lost

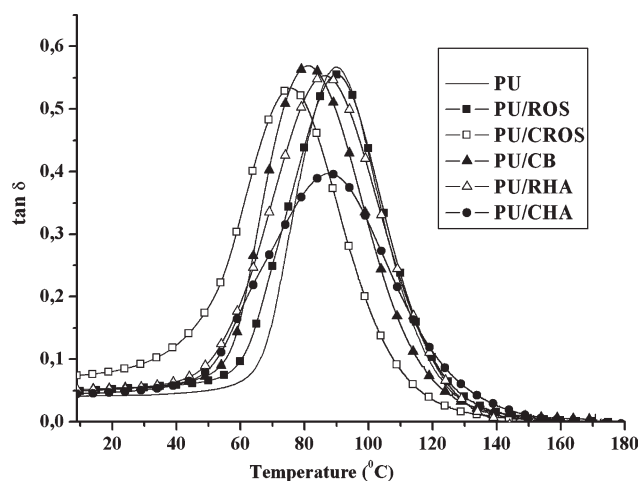
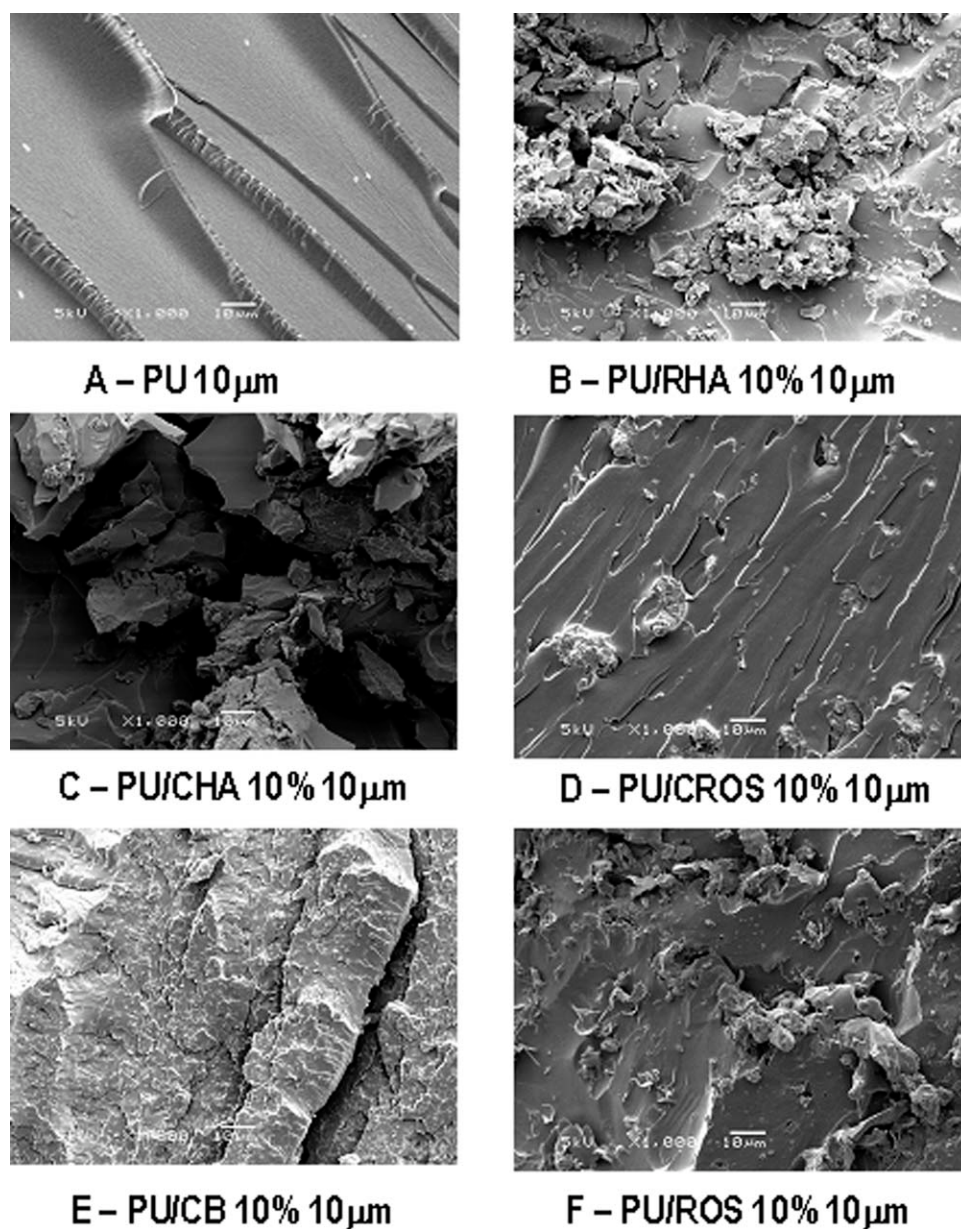


Figure 2 Tan  $\delta$  curves of PU and its composites (2°C/min and 1 Hz).



**Figure 3** SEM images (100 $\times$ ) of (A) PU and (B) PU/RHA, (C) PU/CHA, (D) PU/CROS, and (E) PU/CB, and (F) PU/ROS composites.

mass in lower extension, which was in accordance with their compositions. For RHA, CROS, and ROS, the high amounts of residue were attributed mainly to their high mineral contents. On the other hand, for CB, the high amount of residue was due to its high fixed carbon content ( $\sim 97\%$ ).

Table II shows the chemical composition of the fillers. The decrease in the carbon amount in CROS compared to ROS was expected because CROS was the product of ROS calcination. The higher amounts of silicon, aluminum, and iron present in ROS, CROS, and RHA were also expected because of their higher content of inorganic matter. Likewise, the CHA filler, which was mainly constituted of volatile organic compounds, had the highest carbon content. Finally, the higher amount

of elemental carbon founded for CB was in accordance with its composition; it was mainly constituted of amorphous and crystalline carbon substructures.

#### Composite properties

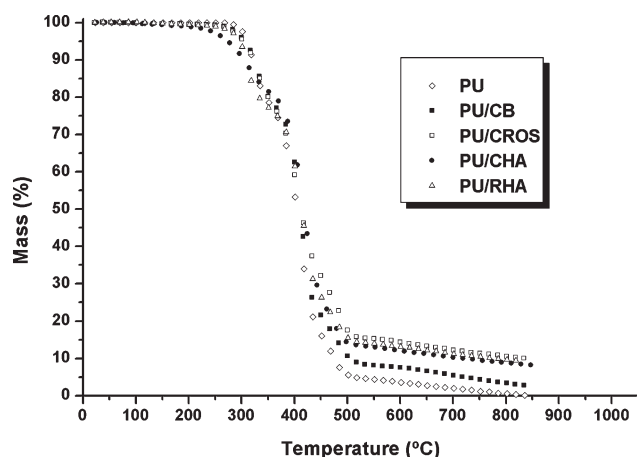
Table III shows the dynamic mechanical analysis, flexural, and hardness data for the composites. All of the composites showed only one glass transition in the  $\tan \delta$  curves, as shown in Figure 2. The data show that the composites prepared with CHA, RHA, and ROS presented higher glass-transition temperatures ( $T_g$ 's) and  $E'$  values than PU, whereas the composites prepared with CB and CROS showed lower  $T_g$  values than PU. The CHA, RHA, and CROS

composites presented higher resistance to deformation than PU, whereas in the CB composite, it was lower. These results could be attributed to the different chemical compositions of fillers. CHA and RHA presented lignocellulosic organic compounds, which were able to react with isocyanate and, thereby, increase the interaction between the matrix and filler. ROS was composed of approximately 7% volatile organic compounds; this could also increase the interaction between the matrix and filler. Additionally, we also expected a better compatibility between CROS/PU than CB/PU because of the chemical nature of these fillers and the polar PU matrix. The flexural values found for CROS (99% polar rigid inorganic matter) indicated that it acted as a reinforcing material; this led to a higher flexural modulus. On the other hand, the CB composite, which was composed of 96% nonpolar soft organic matter, presented similar  $E'$ , flexural modulus, and deformation values as PU.

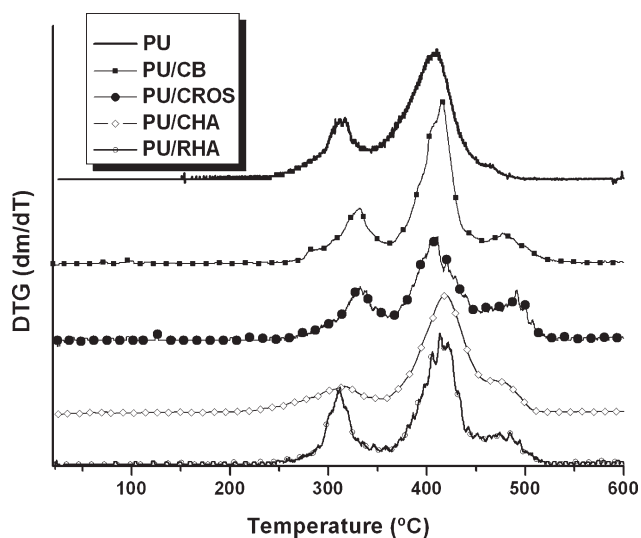
Another aspect that should be pointed out is the average particle size. The larger the particle size was, the worse the dispersion of the filler in the viscous soy-based polyol was. As the fillers were manually mixed with the polyol, a poor dispersion in the PU matrix was obtained; this resulted in a non-homogeneous composite. As observed in the  $\tan \delta$  curve (Fig. 2), the CHA composite showed a very broad glass transition ( $T_g$ ), which was associated with its larger particle size and broad PSD.

The average hardness values (Shore A) measured for the different composites were in the range 71–75 for an indentation time of 3 s (Table III). As expected, the hardness increased as the indentation time increased from 3 to 30 s. Nevertheless, we did not observe a significant variation of hardness values either when different fillers were used or when different amounts of filler were added, as is usually described in the literature.<sup>40,41</sup>

Figure 3 shows the scanning electron microscopy (SEM) images of pure PU and all of the composites



**Figure 4** TGA curves of PU and its composites prepared with the fillers CB, CROS, CHA, and RHA (10°C/min and N<sub>2</sub>).



**Figure 5** DTG curves of PU and its composites prepared with the fillers CB, CROS, CHA, and RHA.

examined in this study. The fracture image of PU [Fig. 3(A)] was smoother and more homogeneous than those of the composites. The SEM images of the RHA and CHA composites presented holes in their structures and were more irregular than those prepared with CROS and CB. These results indicate that the adhesion between PU and the fillers CHA or RHA was not good enough. This result could be explained by the filler's average particle diameter. CHA and RHA had higher particle sizes, which were responsible for the difficulty of dispersing the filler in the matrix and resulted in nonhomogeneous composites. On the basis of these results, we affirmed that the presence of the reactive groups in the fillers did not guarantee a better compatibility because the adhesion between the organic matter and inorganic components of the filler was not necessarily enhanced.

The TGA curves of the composites (Fig. 4) were similar to that of PU and showed no improvement in the thermal stability. No significant mass loss was observed until 200°C. Decomposition occurred in the range 250–500 °C. The amount of residue varied as a function of the filler. At 800°C, CB showed 3% residue, CHA showed 8% residue, CROS showed 10% residue, and RHA showed 9% residue; these values were in agreement with the amounts of mineral material in the fillers, as shown in Table II.

The differential thermogravimetry (DTG) curves obtained for PU and the composites are shown in Figure 5. Compared with the DTG curve of PU, the thermal degradation of the composites occurred in three stages. The first, from 210 to 350°C, corresponded to the urethane bond degradation;<sup>15,42</sup> the second, between 360 and 450°C, was related to the degradation of the polyol structure; and finally, the third was related to filler degradation.

## CONCLUSIONS

Soybean-oil-based PU composites containing industrial and agricultural residual wastes as fillers have great potential to replace nonrenewable petrochemical raw materials. The reaction of formiated soybean-based polyol with TDI gave rise to stiff elastomeric PU. The addition of the fillers (RHA, CHA, CROS, and ROS) resulted in materials with potential applications in the market.

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