Characterization of Polyurethane Resins by FTIR, TGA, and XRD

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ABSTRACT: Fourier Transformed Infrared Spectroscopy, Thermogravimetric Analysis, and X-ray Diffractometry have been used to investigate the rigid, semi rigid, and soft polyurethane (PU) forms, which were developed by the Group of Analytic Chemistry and Technology of Polymers - USP - São Carlos. The –NCO/–OH ratios were 0.6, 0.5, and 0.3% for rigid, semi rigid, and soft PUs, respectively, showing that different ratios cause differences in thermal behaviors and crystalline structures of the synthesized PU resins. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 263–268, 2010

Key words: polyurethane; thermal analysis; x-ray diffraction

INTRODUCTION

Otto Bayer and co-workers discovered in the late 1930s the synthesis of polyurethanes (PU) materials, which have found an increasingly outstanding position among the most important organic polymers for intensive technological applications,[1] biomaterials in implants,[2] materials for engineering,[3] electronic, and coating industries.[4] This broad spectrum of applications is closely linked to the plethora of physical forms that these materials can assume: elastomers,[5,6] rigid and flexible forms,[7,8] adherent films and powders.[9]

Castor oil, which derivates from the seeds of the tropical "castor oil plant" (*Ricinus communis*),[10] occupies a unique position in the field of natural fatty and oils. Although, like other common oils, it is a glyceride, it is unusual in that the acid components of the glyceride are primarily hydroxyl compounds. No other common natural fat or oil contains an appreciable quantity of combined hydroxyl acids. This acid in castor oil has been named ricinoleic acid, and its amount in the mixes acids from castor oil has been subject to a number of analytical investigations.[11] Approximately, 90% of fatty acids in castor oil is ricinoleic acid. Ricinoleic acid, a monounsaturated, 18-carbon fatty acid, has a hydroxylfunctional group at the 12th carbon; this is a very uncommon property for a biological fatty acid and is the main driving point for the direct use of this oil as a hydroxyl containing trifunctional monomer.[12] In the field of biodegradable polymers, PU based on castor oil have been suggested as potentially interesting materials. The high concentration of triglycerides in castor oil makes it almost a pure chemical, allowing it to be treated as a natural poliol.[13]

The synthesized resins consist of polymerized urethane, which is a product of chemical reaction between an isocyanate and a hydroxyl group, as showed in Figure 1.[13] In this polymerization, a compound containing two or more isocyanate groups per molecule reacts with a polyol or a polyfunctional alcohol. Despite the apparent simplicity of this synthesis, any alterations in the polyol and pre-polymer ratio (–NCO/–OH) cause substantial morphological changes in the resin chains, leading to modifications in mechanical properties of the material.[14,15] The degree of crosslinking is controlled by isocyanate group (–NCO) of the pre-polymer and by the hydroxyl group of the polyol.

The research reported on here investigated three different sorts of resins, which were prepared by the direct reaction of the two components (–NCO/–OH) in mass proportions of 1/1, 1/1.5, and 1/2.5. Thus, this study concerns the correlation between these ratios using Fourier Transformed Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), and X-ray Diffractometry (XRD).

EXPERIMENTAL

Materials

Castor oil-based PU resins employed in this work were developed by the Group of Analytic Chemistry

and Technology of Polymers - USP - São Carlos – Brazil. The resin consists of two components, pre-polymer and polyol. Currently, the components of resin, pre-polymer, and polyol, are produced by Cequil® Industry. The pre-polymer used was 249, which is based on the diphenylmethanodiisocyanate (MDI) with percentage of free isocyanate equal 23%. Polyols are polyesters derivate from the castor oil with different amount of the functional hydroxyl. The hydroxyl index resulted were 300 and 150 mg KOH/g. These values were provided by Cequil® Industry and more information about chemical structure is industry confidential. The pre-polymer was synthesized from diphenylmethanediisocyanate (MDI) and prepolymerized with polyols, also derived from castor oil, keeping a percentage of free isocyanate for later reaction. Three different samples of PU (rigid, semi rigid, and soft) were studied in this work, which are a product of pre-polymer and polyols polymerization. There is one part of pre-polymer (249) and one part of polyol (1640) in rigid sample with stoichiometric relation (1/1). In the semi rigid sample, the ratio between prepolymer (249) and polyol (1640) was 1/1.5, whereas in soft sample, the ratio was 1/2.5 for pre-polymer (249) and polyol (160), respectively. In addition, the semi rigid and soft samples are out of stoichiometric relation.

Mechanical property

The hardness of the PU samples was determined using Shore-A and Shore-D durometer, Wultest Model MP-2, according to ASTM-D2240.

FTIR analysis

Infrared spectra were measured with a BOMEM MB-Series Hartmann & Braun spectrophotometer in the wavenumber range 400–2000 cm^{-1} and 16 scans. The samples were prepared by grinding (powdery) with KBr powder with ratio of 1 : 100, and then pressing the mixtures into tablets.

TGA analysis

The TGA was carried out in an alumina crucible with 5 mg mass sample for each polymer, using the simultaneous Thermal Analysis Modulus, SDT Q600 (TA Instruments) controlled by Advantage for Q Series software. The experiment was carried out under N_2 atmosphere (flow of 100mL/min) from 24 to 700°C at 10°C/min and heating rate.

XRD analysis and peaks decomposition

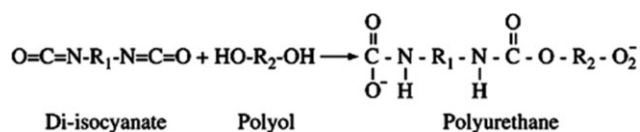Wide-angle X-ray diffraction was used to study the interplanar distances (d-spacing) in the PU crystal-

Figure 1 Polymerization of Urethane.

line samples. X-ray diffraction patterns were collected with a Rigaku RotaFlex operating with CuKα radiation, 50 kV, 100 mA, and equipped with a graphite monochromator. The data collection was recorded in the range of $2\theta = 5$–$60°$ with a step of $0.02°$ and 2 seconds/step. The d-spacings corresponding to the large peak(s) in the respective curves were calculated from Bragg's equation:

$$\lambda = 2(d-\text{spacing}) \sin \theta$$

where 2θ is the X-ray scattering angle.

A commercial Peak Fitting Module (PFM) inbuilt in Microcal Origin 7.5 software[16] was used for decomposition of single peak data from PU samples peak clusters. The PFM was operated through a wizard interface and a Gaussian function was used as a fitting function for symmetrical peaks. The determination of the amorphous to crystalline percentage was obtained from peak area ratios.

RESULTS AND DISCUSSION

Mechanical property

The hardness of the PU samples with prepolymer (249) and polyol (1640) mass proportion 1/1 was 74 ± 1 Shore D. However, the hardness of the PU samples with prepolymer (249) and polyols (1640/160) mass proportions 1/1.5, and 1/2.5 were 86 ± 1 and 30 ± 1 Shore A, respectively. As a result, three different samples of polymers were categorized according to its hardness degree and classified as rigid (1/1), semi rigid (1/1.5), and soft (1/2.5).

FTIR analysis

FTIR analysis performed in polyol and pre-polymer are shown in Figure 2. Characteristic bands of the hydroxyl and carbonyl groups were obtained in the 3373 and 1726 cm^{-1} regions. The two bands observed between 2938 and 2845 cm^{-1} were attributed to symmetric and non symmetric stretching of the C—H bond with carbonyl. In the pre-polymer are observed band features of the isocyanates at 2312 cm^{-1} and polymerized urethanes in 1736, 1608, 1570, and 1520 cm^{-1}. These bands are typical of the stretching C=O and N—H bonds.
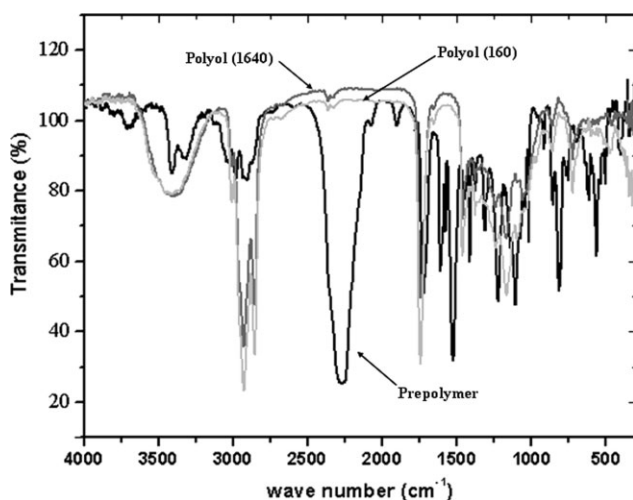
Figure 2 FTIR spectra for polyol and pre-polymer samples.

Figure 3 shows FTIR spectra of the rigid, semi rigid, and soft PUs. The weak band found at 2312 cm^{-1} is assigned to isocyanates region. In the rigid and semi rigid PUs, the infrared shows less intense bands than soft PU, which means that there is no excess of OH in rigid and semi rigid samples and in all isocyanates present in the pre-polymer reactants. The excess of trifunctional OH favors cross-linking yielding of the rigid PU. In the semi rigid and soft PU samples, the trifunctional hydroxyl molecules have only one free group reactioning in two points, decreasing the cross-linking degrees. Thus, a large amount of free hydroxyl favors a more flexible polymer structure with variable degree of branching and, consequently, different physical properties.

TGA analysis

The thermal stabilities of polyols, pre-polymer, and PU were analyzed by TGA/DTG as it can be seen in Figures 4–7. It is evident from TGA/DTG curves
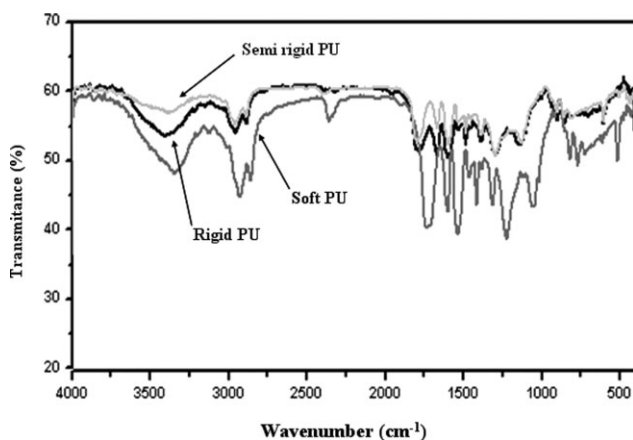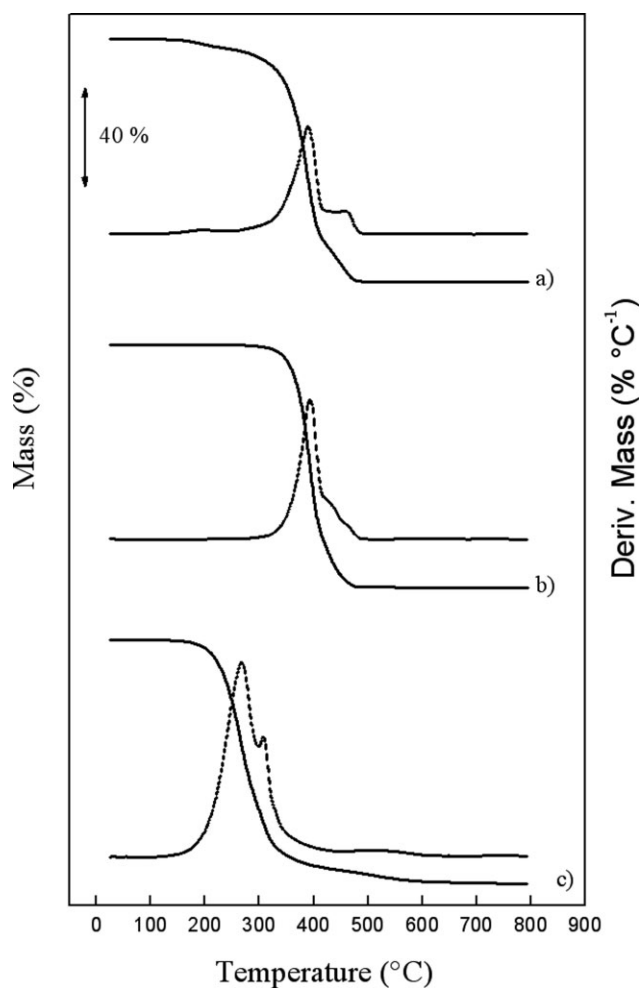

Figure 4 TG/DTG curves of a) polyol 1640; b) polyol 160, and c) prepolymer 249 under N_2 atmosphere.

(Fig. 4) that pre-polymer and polyols decompositions occur at different temperature ranges, showing two steps of mass loss. These steps were attributed to decomposition MDI present in pre-polymer and ester groups present in polyols (Table I).[14]
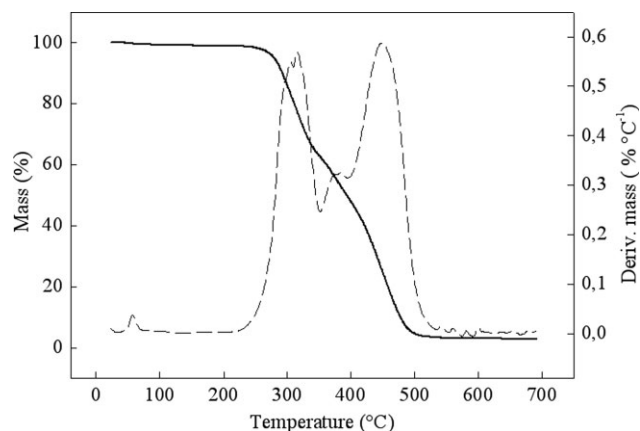

Figure 3 Infrared Spectra of the rigid, semi rigid, and soft PUs.

Figure 5 TG/DTG curve of rigid PU under N2 atmosphere.

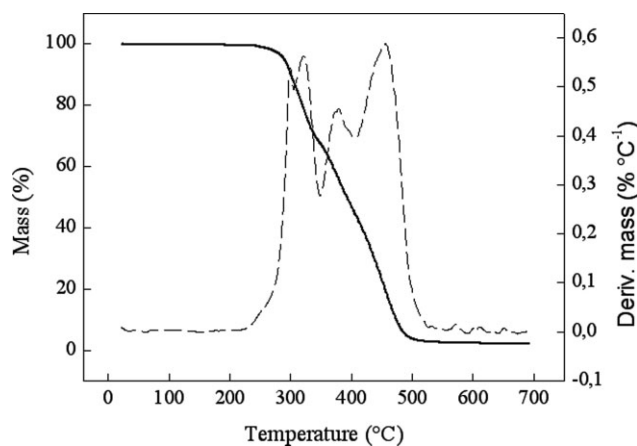**Figure 6** TG/DTG curve of semi rigid PU under N$_2$ atmosphere.

Figure 7 TG/DTG curve of soft PU under N$_2$ atmosphere.

In PU analysis, the TGA/DTG (Figs. 5–7) curves show mass loss for the groups of interest, in this case, decomposition of MDI with break of urethane bonds and later ester decomposition. The curves show three steps, the first step was attributed to decomposition of urethane bonds; the second and third were considered consecutive and related to the decomposition of ester groups.[14,17] The percentage ratios of urethane and ester present in PU samples and their thermal decomposition are summarized in Table II.

The largest value of the (%urethane/%ester) ratio in rigid PU can be justified by large quantity of the urethane crosslinking formed during the polymerization. On the other hand, the smaller (%urethane/%ester) ratio in soft and semi rigid PU were attributed to excess polyol or larger quantity of free hidroxyl.[17]

According to the TG curve (Fig. 5) two steps of the thermal decomposition were observed for the rigid PU sample: in the first step 36% mass loss occurs between 200 and 350°C and in the second step 62% of mass loss between 350 and 535°C. For the semi rigid PU sample (Fig. 6), which has the same composition of the polyol and prepolymer as rigid PU, but with different mass proportion, the temperature range observed in the first step was between 200 and 350°C with 32% mass loss and in
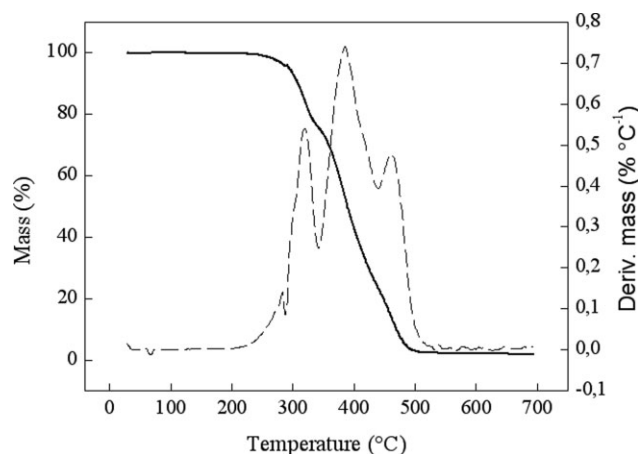
the second step temperature range was 350–525°C, 67% mass loss. The TG curve for soft PU (Fig. 7) showed also two steps of thermal decomposition: in the first step, the 24% of mass loss between 200 and 340°C, and in the second step, 75% of mass loss occurs between 340 and 525°C.

Although the PUs have shown the same behavior (two step of decomposition), it was observed a significant difference in the mass loss in NCO/OH ratios. These ratios were 0.6, 0.5, and 0.3% for rigid, semi rigid, and soft PUs, respectively. Thus, the increased degree crystallinity of PUs were greatly influenced by the urethane crosslinking.

XRD analysis

X-ray diffraction techniques examine the long-range order produced as a consequence of very short-range interactions. Figure 8 shows the X-ray diffraction patterns of the rigid, semi rigid, and soft PU. The powder diffractograms exhibits broad peaks at 2θ angles around 8, 11, 19, and 43°, indicating some degree of crystallinity. These peaks are assigned to the scattering from PU chains with regular interplanar spacing.[18] The degree of order in these materials was established in relation of the pre polymer and polyols mass proportions (–NCO/–OH) of 1/1,

TABLE I
Thermal Decomposition of Pre-Polymer, Polyols, and PUs

Samples	First step		Second step	
	Range temp. (°C)	Loss mass (%)	Range temp. (°C)	Loss mass (%)
Pré-polymer 249	200–293	62	293–343	21
Polyol 1640	331–419	76	419–516	17
Polyol 160	319–420	80	420–537	19
Rigid PU	202–351	36	351–535	62
Semi rigid PU	200–349	32	349–526	67
Soft PU	201–343	24	343–526	75

TABLE II
Ratios of Urethane and Ester Present in PU Samples

Samples	% Urethane	% Ester	% Urethane/ %Ester
Rigid PU	36	62	0.6
Semi rigid PU	32	67	0.5
Soft PU	24	75	0.3

TABLE III
Summary of Wide-Angle X-Ray Scattering (WAXS) peaks, *hkl* Indices and Corresponding *d-spacing* for Rigid, Semi Rigid and Soft PU

2θ	hkl	d (nm)
8	(0 0 4)	11.05
11	(0 0 6)	7.82
19	(−1 1 1)	4.69
43	(2 0 4)	2.10

1/1.5, and 1/2.5 showing that any alteration causes morphological changes in the resin chains.

The decrease of crystallinity of the PU samples is evidenced mainly by the disappearance of the peak located at 11° 2θ. The rigid PU, which has pre polymer and polyol mass proportion of 1/1 is more crystalline, with the most intense peaks located at 11 and 19° 2θ. In this case, PU has complete trifunctional active sites, which increase the degree of crystallinity in the structure. With the change in the proportion of pre polymer and polyol to 1/1.5, the peak located at 11° 2θ became smaller, showing a decrease of crystallinity of the sample, and it disappears completely in the sample of soft PU, which has pre polymer and polyol mass proportion of 1/2.5. These results show that the degree of crystallinity is controlled by the ratio between pre polymer and polyol. The change of crystallinity can be explained by the degree of crosslinking of the samples, which is controlled by the hydroxyl group existing in the polyol. Thus, increasing the mass proportion of polyol is decreased the proportions of urethane crosslinking in the samples, the polymer becoming less rigid or less crystalline. The Bragg diffraction peaks found in PU samples, its crystallographic planes[19] and *d*-spacing as shown in Table III.

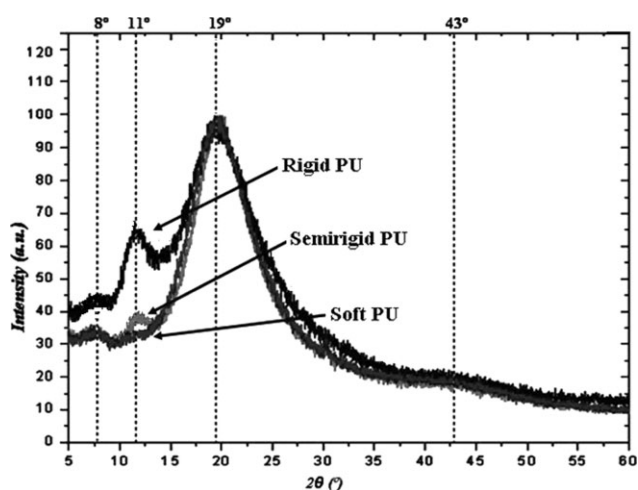The degree of crystallinity of the samples was determined from de XRD patterns using the PFM

Figure 8 XRD patterns of rigid, semi rigid and soft PUs.

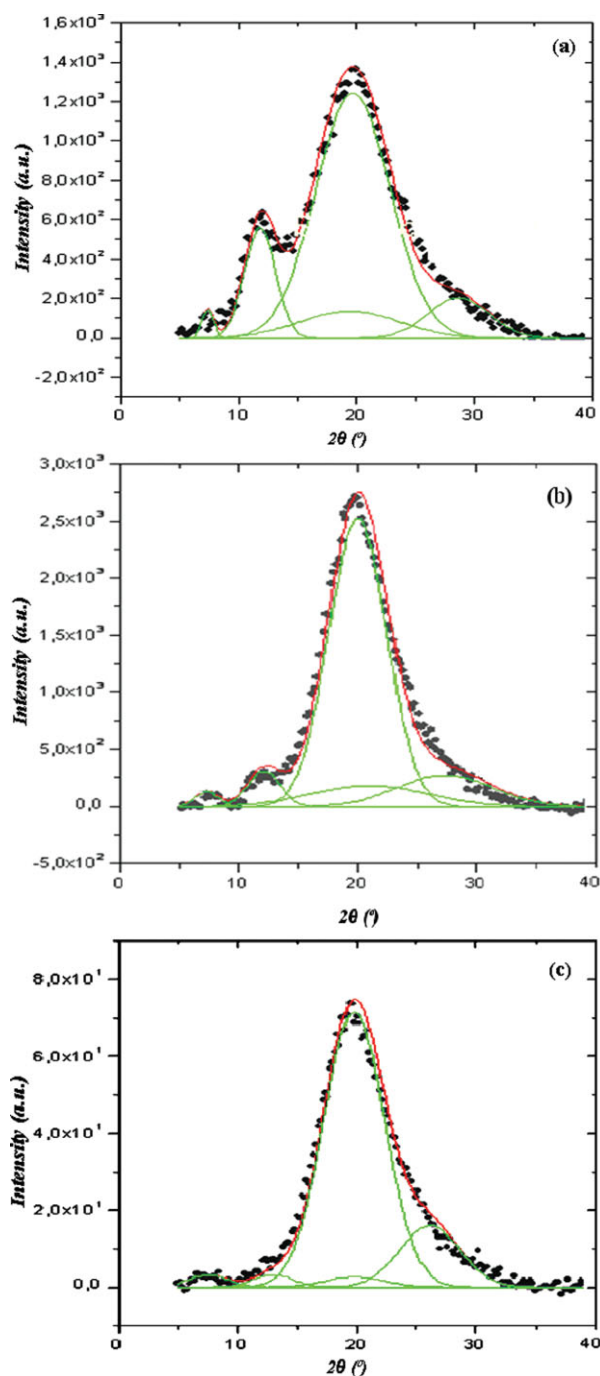**Figure 9** XRD patterns of rigid, semi rigid, and soft PUs decomposition of the peaks in the range of 5–40° 2θ. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

program.[16] The 2θ scan range was 5–40°, because all the intense crystalline peaks were found in this range. Figure 9 shows the peak decompositions of the diffractograms for rigid, semi rigid, and soft PU. It was determined that the rigid PU has 37% of crystallinity, whereas semi rigid and soft PU are less crystalline, with 29 and 24% of crystallinity, respectively.

CONCLUSIONS

FTIR spectra showed the characteristic absorptions of each material, and TG/DTG curves suggest that the three different ratios of urethane/ester had great influence in rigidity of the materials, agreeing with the results obtained in XRD analysis and mechanical properties. We report a systematic observation of crystallinity, showing that rigid, semi rigid, and soft PU differs in their crystal structures.

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