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Application of TGA/FTIR to the study of the thermal degradation mechanism of silanized poly(ether-urethanes)

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ABSTRACT

TGA/FTIR was employed to investigate the thermal degradation mechanism of two types of self-curable Polyurethanes obtained from isophorone diisocyanate (IPDI), Poly(propyleneglycol) (PPG), and (trimethoxysilyl) propyl isocyanate and N-butyl 3-trimethoxysilyl propyl amine respectively. The TGA/FTIR results for isocyanatesilane based systems showed that the degradation behavior differed between the cured and non-cured samples in relation to the evolution of isocyanate moieties in the first case and CO_2 in the second one.

Aminosilane based systems, both non-cured and cured samples released isocyanate containing volatile compounds.

1. Introduction

Polyurethane/silica hybrids have broadened the application window of polyurethanes as the presence of silica can enhance particular characteristics such as modulus, strength, fire performance and heat resistance [1–3]. Alkoxysilane-capped low molecular weight polyethers (SPUR) are proving to be adhesives of great commercial interest as they can be applied to heat sensitive substrates [4,5]. This property is due to the presence of sylanol groups along the polymer chains capable of reacting with ambience humidity and, as a consequence, generating silica network.

Polyurethanes have traditionally been synthesized using aromatic diisocyanates such as 4,4′-diphenylmethane diisocyanate (MDI) and toluene-2,4-diisocyanate (TDI), although they are being substituted by aliphatic ones, mainly because of the toxicity shown by their degradation compounds [6–9]. One of the candidates for the synthesis of polyurethanes is isophorone diisocyanate (IPDI), whose properties are considered to be similar to those of aromatic isocyanates.

In this article the results concerning the thermal degradation of one of these types of systems are presented. Polyurethane degradation has been extensively studied through different instrumental techniques and various mechanisms have been proposed to explain their degradation behavior. These include the dissociation to isocyanate and alcohol, the formation of primary amines and olefins, the generation of secondary amines and transesterification [10,11]. Among the different results reported in literature, it should be highlighted on the one hand, those of Cervantes-Uc et al. [12] who support a degradation mechanism through the urethane decarboxylation and the formation of primary amines and olefin moieties. On the other hand, Zhang et al. [13] establish that the degradation of IPDI based polyurethanes takes place mainly by means of a depolymerization process, giving rise to isocyanate and hydroxyl functional groups.

In a previous work [14] we attempted to characterize the degradation process of these hybrid systems by means of a conventional thermogravimetric analysis (TGA). But due to the existing controversy and with the aim of determining the thermal degradation products, here we present a TGA/FTIR combined study, which enables us to establish the more plausible degradation mechanism [15–17].

2. Experimental

2.1. Materials

Poly(propylene glycol) (PPG) of M_w = 3550, 2000 and 1000, isophorone diisocyanate (IPDI) and dibutyl tin diacetate (DBTDA) were purchased from Aldrich. 3-(trimethoxysilyl) propyl isocyanate (ISM) and N-butyl-3-(trimethoxysilyl) propyl amine (ASM) were

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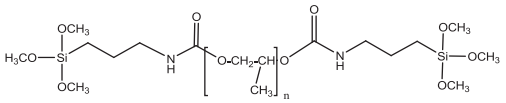
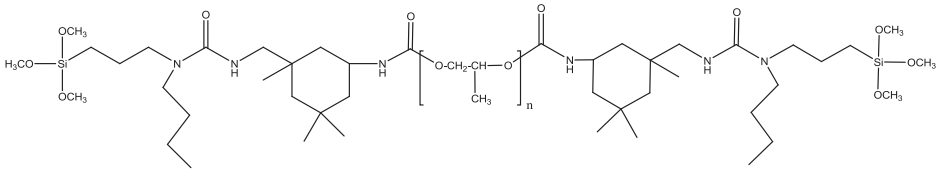
Table 1
Nomenclature and structure of the synthesized polymers.

Name	Structure
3550ISM 2000ISM 1000ISM	
3550ASM 2000ASM 1000ASM	

purchased from Osy/Crompt and Degussa respectively. All products were used as received.

2.2. Synthesis of silanized poly (ether-urethane) (SPUR) systems

Two different types of SPUR were synthesized by reacting PPG hydroxyl groups with organosilane compounds as described in our previous work [18]. A description of the systems is shown in Table 1.

2.3. Curing process

Alkoxysilane groups can react with moisture generating silanol and alcohol groups. Silanol groups can then condense to form siloxane groups with elimination of water [18,19]. These reactions are shown in Scheme 1.

In this study the samples were cured at room temperature for 15 days using 0.5% of DBTDA (w/w) as catalyst.

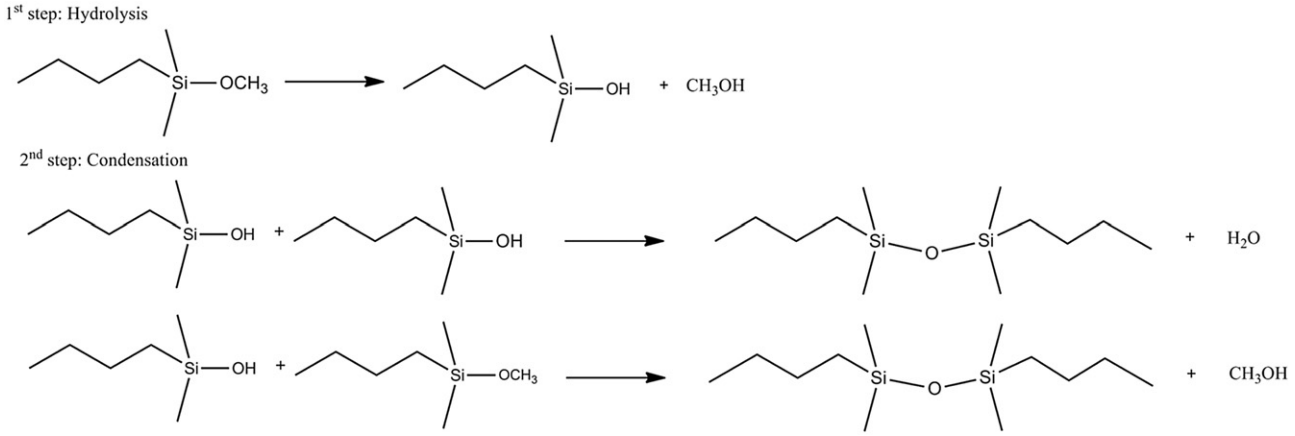
2.4. Thermal degradation studies

TGA/FTIR experiments were carried out in a TGA Q 500 (TA Instruments) (with an EGA furnace) thermobalance coupled to a Thermo Nicolet 6700 FTIR spectrometer. Sample masses ranging from 20 to 25 mg were heated from 50 to 600 °C using a HiRes™ 4 heating method under dry nitrogen atmosphere. In the HiRes™ method the heating rate is not constant along the experiment, but depends on the degradation behavior of the sample [20,21]. The flow rate of nitrogen in the cell for TGA/FTIR experiments was 90 mL/min. Both the IR cell and the transferring line evolved gases from the TGA to the FTIR were maintained at 225 °C. IR spectra were recorded in the spectral range of 4000–500 cm^{-1}. From the interferogram at each time the Gram-Schmidt (GS) representation was built. This representation corresponds to the total infrared absorbance as a function of time, and enables us to correlate the chemical nature of the evolving products, from their infrared spectra, with the different degradation steps resolved in the TGA measurements as a function of temperature.

3. Results and discussion

3.1. ISM systems

Fig. 1A and B show the TG and DTG of the non-cured ISM systems. As can be observed, all of them degrade in two main steps in the temperature regions between 150–275 °C and 300–450 °C respectively, although this second step displays a small shoulder at higher temperatures. According to the relative mass loss it seems to be a direct correlation between the extension of the degradation steps and the molecular weight of the soft segment of the polymer. Thus, the mass loss of the first step decreases as PPG molecular weight increases, indicating that the polymer chain ends do participate in this degradation step. The mass loss observed in the temperature region between 300 and 450 °C responds to the



Scheme 1. Condensation reactions of alkoxysilane groups.