

Study on thermal degradation of segmented polyurethanes based on HMDI using TGA/FTIR and TGA/MS

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1. Abstract

Thermogravimetry coupled with Fourier Transform Infrared Spectroscopy (TGA/FTIR) and Thermogravimetry coupled with Mass Spectrometry (TGA/MS) were used to investigate the thermal degradation behavior of segmented polyurethanes based on HMDI (4,4'-methylenebis cyclohexyl isocyanate), PTMG (polytetramethyleneglycol) and BD (1,4-butanediol). The results showed that the thermal degradation of SPU's occurred in two stages being the first due to degradation of hard segments and the second due to the degradation of soft segments. Spectrum obtained during the first gas emission was completely different to that obtained in the second stage. The former showed mainly bands attributed to carbon dioxide and peaks related to C-H stretching vibrations. In contrast, the spectrum obtained during the second stage showed bands related to methylene and methyl groups, a carbonyl band at 1743 cm⁻¹ and a band at 1112 cm⁻¹ related to C-O vibration of the ether group. Also, the release of carbon dioxide during the first degradation stage was confirmed by a fragment at m/z = 44. It was also observed the release of fragments based on C_xH_y with m/z values of 50-57 during second degradation stage. These fragments were attributed to short hydrocarbon chains with 4 carbon atoms, possibly from PTMG. In addition, it was observed peaks related to water (m/z=18) and other compounds (m/z=30-31, 36-38, 68-72).

2. Introduction

Thermal degradation of both polyurethanes and segmented polyurethanes has been extensively investigated by numerous research groups. In these studies, the type of diisocyanate (aliphatic or aromatic), polyol (polyester or polyether) and the chain extender were the main interest. For polyurethanes various mechanisms have been proposed to explain their degradation including dissociation to isocyanate and alcohol, formation of primary amine and olefins, formation of secondary amine and transesterification [1-2]. In this work, Thermogravimetry coupled with Fourier Transform Infrared Spectroscopy (TGA/FTIR) and Thermogravimetry coupled with Mass Spectrometry (TGA/MS) were used to investigate the thermal degradation behavior of segmented polyurethanes based on HMDI (4,4'-methylenebis cyclohexyl isocyanate), PTMG (polytetramethyleneglycol) and BD (1,4-butanediol).

3. Experimental

3.1 Materials

4,4'-methylen-bis(cyclohexyl isocyanate), (HMDI), 1,4-butanediol (BD) and dimethyl formamide (DMF) were purchased from Aldrich Co. and used without further purification. Poly(tetramethylene ether) glycol was obtained from Lyondell (PTMG, Mn=2000 g/mol). Stannous octoate was supplied by Polysciences and used as catalyst.

3.1.1 Synthesis of segmented polyurethanes

Segmented polyurethanes (SPU) with a molar ratio of 2.05:1:1 (HMDI:BD:PTMG) were prepared in DMF solution by a two steps procedure. In the first stage, PTMG was mixed with a slight excess of HMDI in the presence of 0.15 wt% stannous octoate in order to

TGN-P

form the soft segment. In the second stage, BD was used as chain extender to form the hard segments. The reaction was conducted in a glass reactor under nitrogen atmosphere. The reaction time for the pre-polymer formation (first step) was 2 h at 60°C while the second stage lasted 2 h. After this time, the polymer was precipitated and washed with distilled water and then dried at 60°C. The chemical structure of SPU is displayed in Figure 1.

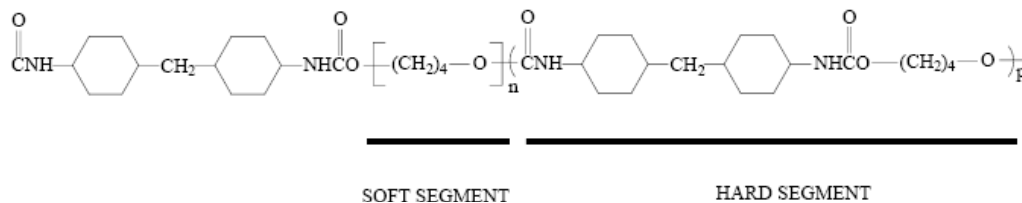


Figure 1. Chemical structure of the synthesized SPU.

3.1.2 Thermal degradation studies

TGA/FTIR experiments were carried out on a TGA Pyris 1 coupled to a Spectrum GX FT-IR system (Perkin Elmer). Sample masses ranging from 15 to 20 mg were heated from 50 to 600 °C at a rate of 10 °C/min. in a dry nitrogen atmosphere. The flow rate of nitrogen into the cell for TGA/IR experiments was approximately 60 ml/min. Both the IR cell and the heated line transferring evolved gases from the TGA to the FTIR were maintained at 250 °C. IR spectra were recorded in the spectral range of 4000-650 cm⁻¹ with a 4 cm⁻¹ resolution and 8 scans.

4. Results y discussion.

4.1. TGA

Figure 2a shows the TGA curve and its corresponding derivative weight loss curve (DTGA) for segmented polyurethanes (SPU). As it can be seen, the sample exhibited two degradation stages located ca. 292 and 380°C. The weight losses for the first and second stages were 17 and 83 % w/w, respectively. In this sense, it has been reported that the first weight loss during thermal degradation of SPU's is due to the degradation of the hard segment whereas the second weight loss has been associated to soft segment decomposition [3]. Furthermore, it has been suggested that the amount of weight loss at each degradation stage may be used as a quantitative measurement of the hard and soft content in the SPU's [4]. Thus, using this approximation the amount of the hard segment in SPU's prepared in this study was ca. 17 wt% which is close to the 24 wt% calculated by stoichiometry.

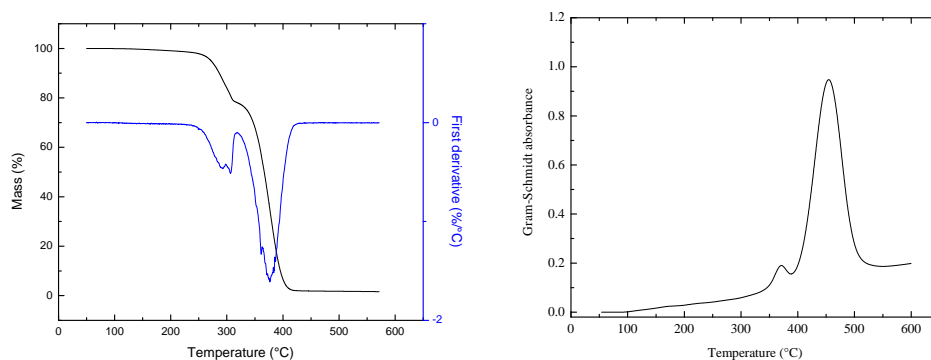


Figure 2. TGA and DTGA curves (a) and Gram-Schmidt plot (b) for SPU.

4.2. Gram-Schmidt plot

Figure 2b shows the Gram-Schmidt plot for SPU where it is clearly seen that the sample exhibit two evolved gases regions which can be related to the weight losses recorded in the DTGA curve. It can be noted that the peaks in the GS plots are shifted to higher temperatures than their corresponding DTGA curve. This is due to the existence of a delay time between the gas generation and its detection in the FTIR equipment. The first peak observed in the Gram-Schmidt was small, suggesting that the amount of the evolved gases in this stage was low and with low infrared extinction coefficients. In contrast, the second degradation stage seems to be composed by a considerable amount of evolved gases with high infrared extinction coefficients.

4.3. Degradations of SPU's

Stack plot of FTIR spectra obtained during thermal decomposition of segmented polyurethanes are shown in Figure 3a, whereas FTIR spectra obtained at the maximum evolution rate for each decomposition step are shown in Figure 3b. As it can be noticed, spectrum obtained during the first gas emission is completely different to that obtained in the second stage. The former showed mainly bands at 2357 and 2310 cm^{-1} (attributed to carbon dioxide), and peaks at 2926 and 2859 cm^{-1} (related to C-H stretching vibrations), indicating that the most of evolved gases at this stage are hydrocarbons (probably derived from cyclohexyl group) and CO_2 . If one considers the proposed mechanism by Petrovic et al. [3] for thermal decomposition of segmented polyurethanes, then it is reasonable to assume that the presence of CO_2 is due to the decomposition of urethane groups, while the presence of C-H stretching vibrations is related to methylene groups from both cyclohexyl and butanediol. Spectrum also showed a small band at 1092 cm^{-1} which would be attributed to C-O stretching vibration of an ether group and another small broad band in the $4000\text{--}3500\text{ cm}^{-1}$ range, which could be related to O-H stretching vibrations from either water or hydroxyl-terminated compounds, and N-H stretching vibrations from either urethane or amine groups.

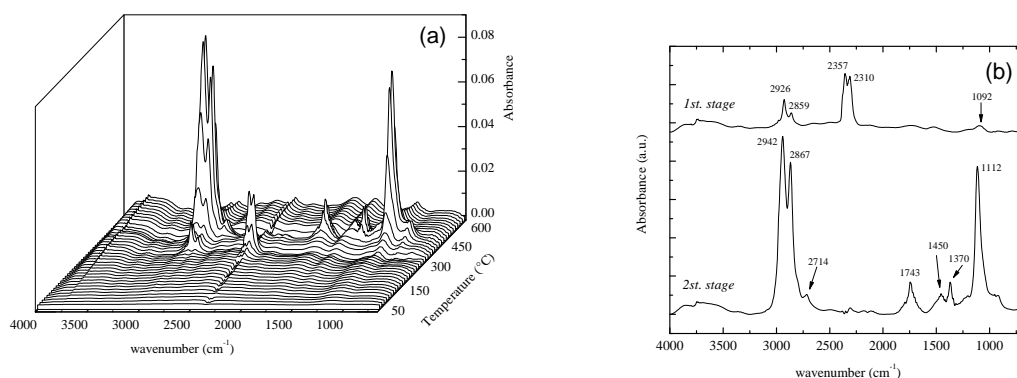


Figure 3. Stack plot of FTIR (a); FTIR spectra obtained at the maximum evolution rate for each decomposition step (b) for SPU.

In agreement with this observation, similar compounds have been detected by several authors [1,5-6] during thermal decomposition of polyurethanes. It should be mentioned that the presence of amines should also imply the presence of unsaturated compounds in the evolved gases, however, in this work there was no evidence of this chemical group. In contrast, the spectrum obtained during the second stage showed bands at 2942 and 2867 cm^{-1} which are related to C-H stretching vibrations for methylene and methyl groups from

thermal degradation of PTMG; the existence of these groups was confirmed by the presence of bands at 1450 and 1370 cm^{-1} . A carbonyl band at 1743 cm^{-1} and a band at 1112 cm^{-1} related to C-O vibration of the ether group from PTMG were also observed. Herrera et al. [7] reported similar absorption bands during the second degradation stage of thermoplastic polyurethanes based on MDI. They claimed (with exception of carbonyl band) that the absorption bands obtained are typical absorptions of butyl ether. Orzeszko et al. [5] studied the thermal degradation of polyurethanes using polyethylene glycol as model compound for soft segments and found aldehydes in the thermal decomposition products of this compound. In this line of thought, the thermal degradation of PTMG could also generate aldehydes (butanal) which would explain the carbonyl band at 1743 cm^{-1} . The presence of this type of compounds was confirmed by a small band ca. 2714 cm^{-1} .

The exact composition of the SPU degradation products was determined by Thermogravimetry coupled to a Mass Spectrometer (TGA-MS). These experiments were conducted on TA Instruments Q500 TGA interfaced to a Pfeiffer Vacuum ThermoStar mass spectrometer. Figure 4 shows some MS results of the evolved products from SPU. As it can be seen, the release of carbon dioxide during the first degradation stage was confirmed by a fragment at $m/z = 44$; this signal was also observed in the second degradation stage. This result was unexpected as the FTIR spectrum obtained at the second stage (see Figure 3b) did not show bands related to CO_2 . The peak of $m/z = 44$ can also be attributed to the presence of the fragment C_3H_8 which have associated an additional mass number (m/z) at 41, 42 and 43 as show in the same figure. It was also observed the release of fragments based on C_xH_y with m/z values of 50-57 during second degradation stage. These fragments were attributed to short hydrocarbon chains with 4 carbon atoms, possibly from PTMG. In addition, it was observed peaks related to water ($m/z=18$) and other compounds ($m/z=30-31$, 36-38, 68-72).

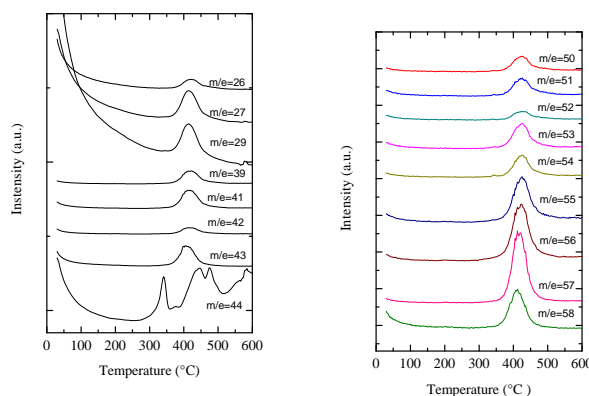


Figure 4. MS results of the evolved products from thermal degradation of SPU.

5. Conclusions.

A SPU were successfully prepared from HMDI, BD and PTMG. The results showed that the thermal degradation of the SPU occurred in two stages being the first due to degradation of hard segments and the second due to the degradation of soft segments.

6. References

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