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Characterization of silanized poly(ether-urethane) hybrid systems using thermogravimetric analysis (TG)

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Abstract The thermal behaviour of a new kind of hybrid system based on silanized poly(ether-urethanes) (SPURs) has been analyzed by thermogravimetric analysis (TG). The influence of the chemical nature of employed alkoxysilanes, polyether diol molecular weight and the physical state of the obtained hybrids (cured and non-cured) has been studied. The results show that in the non-cured state, aminosilane-based systems present a higher stability compared with those based on isocyanatesilane. However, in the cured state, both types of hybrids present a similar thermal stability, but much higher than their corresponding partners before the curing process. The presence of the inorganic silica network improves the thermal stability of all the systems studied.

Keywords Organic–inorganic hybrid · Thermal properties · Thermogravimetric analysis (TG)

Introduction

In the last few years, alkoxysilane-capped low-molecular weight polyethers (SPURs) have been experiencing great development because they have excellent adhesive properties [1, 2]. In fact, sealants based on SPURs are now commercially available [3, 4]. These types of sealants are low-molecular weight polymers capped with alkoxysilane end groups. Alkoxysilane groups can react with moisture, generating silanol and alcohol groups. Silanol groups can then condense to form siloxane groups with the elimination of water. These reactions are shown in Scheme 1.

As a consequence of these reactions, after moisture curing, a silicon dioxide network is generated, which is strictly interconnected with the polymer matrix.

Due to this hybrid character, sealants and adhesives based on SPURs show better adhesive properties and weathering resistance than traditional polyurethane adhesives. However, until 6–7 years ago, the synthesis of these systems was under patent, and as a consequence, the number of published articles in the literature is limited [5].

In previous works [6, 7], we reported on the curing process and the weathering resistance of these types of sealants, and in this article, we present some thermogravimetric results obtained for the same systems that can be generally used in order to characterize them.

Experimental

Materials

Poly(propylene glycol) (PPG) of Mw = 3550, 2000, 1000 and 425, isophorone diisocyanate (IPDI) and dibutyl tin diacetate (DBTDA) were purchased from Aldrich. 3-(Trimethoxysilyl) propyl isocyanate (TMSPI) and 3-(triethoxysilyl) propyl isocyanate were purchased from Osy/Crompton, and N-butyl-3-(trimethoxysilyl) propyl amine

$$\equiv\mathrm{Si{-}O{-}R} + \mathrm{H_2O} \longrightarrow \equiv\mathrm{Si{-}OH} + \mathrm{R{-}OH} \qquad (1)$$

$$\equiv\mathrm{Si{-}OH} + \equiv\mathrm{Si{-}OH} \longrightarrow \equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{H_2O} \qquad (2)$$

$$\equiv\mathrm{Si{-}OH} + \equiv\mathrm{Si{-}O{-}R} \longrightarrow \equiv\mathrm{Si{-}O{-}Si}\equiv + \mathrm{R{-}OH} \qquad (3)$$

Scheme 1 Alkoxysilane moisture-curing process

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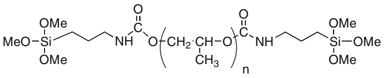
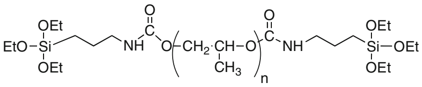
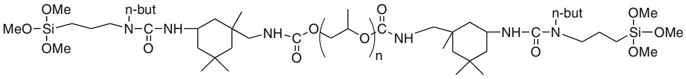
Table 1 Nomenclature and structure of the synthesized polymers

Name[a]	Structure
PPG3550ISM PPG2000ISM PPG1000ISM PPG425ISM	
PPG3550ISE PPG2000ISE PPG1000ISE PPG425ISE	
PPG2000ASM PPG1000ASM	

[a] The number after PPG indicates its molecular weight

ISE reaction with triethoxyisocyanatesilane, *ISM* reaction with trimethoxyisocyanatesilane, *ASM* reaction with trimethoxyaminosilane

(TMSPA) was purchased from Degussa. All products were used as received.

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

Three different types of SPUR were synthesized by reacting PPG hydroxyl groups with organosilane compounds as described in our previous work [6]. A description of the systems is shown in Table 1.

Thermogravimetric analysis

Thermogravimetric analysis (TG) was conducted using a high resolution thermobalance (TA instruments, model TG-Q500) under nitrogen flow (75 cm^3 min^{-1}) with a heating rate of 10 °C min^{-1}. Sample mass was about 5 mg. The scanned temperature range was from 50 to 800 °C.

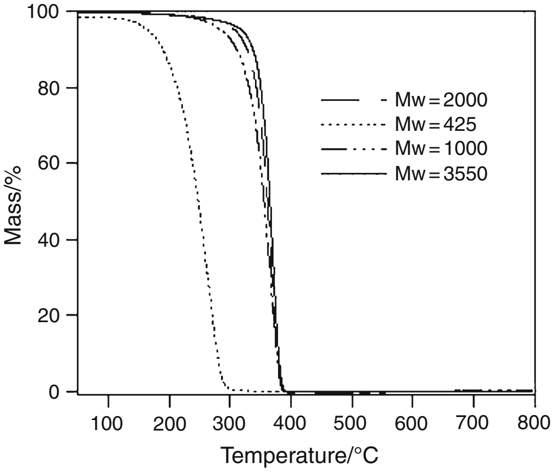


Fig. 1 TG thermograms of different molecular weight polyols

Results and discussion

Figure 1 shows the TG curves obtained for the different molecular weight poly(propylene glycols).

As seen in Fig. 1, regardless of the polyol molecular weight, pure polyol samples degrade in one single step, without leaving any remaining residue at the end of the process. This result is in accordance with literature data [8] where it is mentioned that the thermal degradation of poly(propylene oxide) proceeds by random homolytic chain scissions of C–O and C–C bonds.

Another point that can be addressed from Fig. 1 is that the lower molecular weight polyol (PPG425) starts loosing mass at a very low temperature compared with the other polyols. This result suggests that for this system (PPG425), the first chain scissions generate fragments of such a low molecular weight that they can easily evaporate under the experimental conditions.

Figure 2 shows the mass loss (TG) and differential mass loss (DTG) curves for sample PPG1000 ISM before curing. The TG curve displays four distinct regions of mass loss that are reflected in four peaks in the DTG curve. The first step, with a gradual mass loss from room temperature up to 140 °C, could be attributed to the evaporation of methanol, as a consequence of a previous slight condensation of the alkoxysilane end groups. Apart from this step, the decomposition of SPUR takes place in three main stages: the first one with a gradual mass loss between 150 and

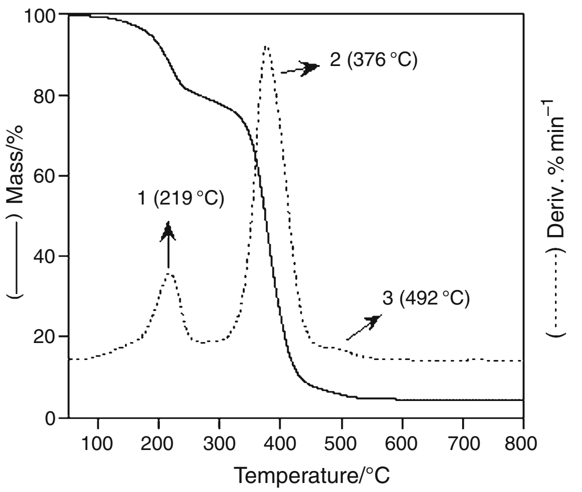


Fig. 2 Mass loss (TG) and differential mass loss (DTG) curves for sample PPG1000 ISM before curing

250 °C, the second one between 300 and 420 °C and the last one between 420 and 500 °C. The sample leaves a residue of about 4%.

Comparing this result with the thermogravimetric behaviour of pure polyols (Fig. 1), it is clear that the mass loss of the second step is related to the degradation of the ether soft segments. The other two steps and the residue obtained correspond, therefore, to the decomposition of urethane and methoxysilane groups present in the silanized polyurethane.

In order to determine the influence of the polyol molecular weight, the thermograms of all the samples obtained using 3-(trimethoxysilyl) propyl isocyanate, before curing, were registered, and the results are shown in Fig. 3. As can be seen, the decomposition profile for all the samples is very similar, showing three main degradation steps. However, their relative contributions depend on the molecular weight of the polyol. The relative percentage of all these processes has been calculated as a function of polyether molecular weight, and the results are shown in Fig. 4.

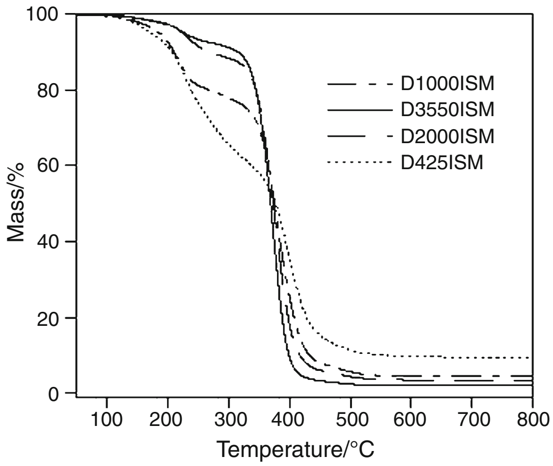


Fig. 3 TG thermograms for systems based on trimethoxysilyl propylisocyanate before curing

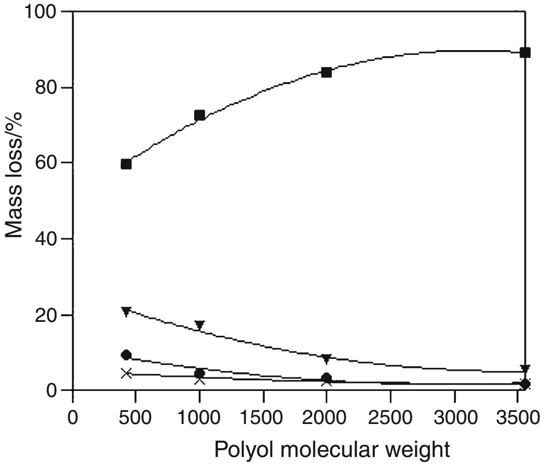
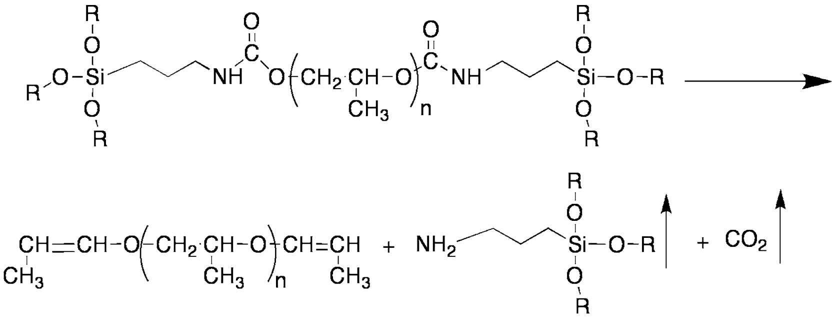


Fig. 4 Mass loss of the different steps and remaining residue for samples obtained using 3-(trimethoxysilyl) propyl isocyanate, before curing as a function of polyol molecular weight: 1. step (*filled inverted triangle*), 2. step (*filled square*), 3. step (*times*), residue (*filled circle*)

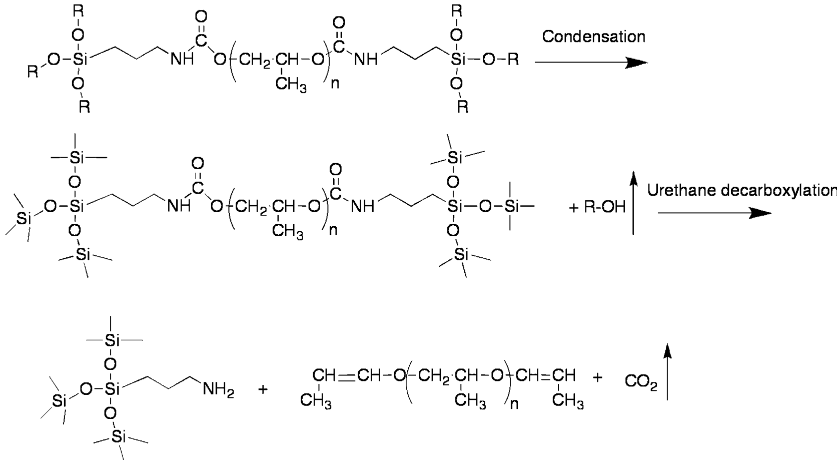
The mass loss detected in the second stage increases with polyether molecular weight, whereas the mass loss experienced in the other steps decreases. As the systems of lower molecular weight polyethers have in their composition higher contents of urethane and alkoxysilane end groups, these results confirm that the second mass loss stage is due to the polyether degradation process.

It is well known [9, 10] that the thermal degradation of poly(ether-urethanes) initiates through the decomposition of the hard segment, at about 210 °C. This fact suggests that this process can be responsible for the first stage observed in our systems. This process involves the dissociation of urethane groups giving rise to the original polyol and isocyanate functional groups, which in turn form a primary amine, an alkene and carbon dioxide. In the case of silanized polyurethanes, the urethane group is located near the alkoxysilane end groups and, therefore, if urethane decarboxylation takes place as the initial step of the thermal degradation, the generated alkoxysilane-based fragments will be of a low enough molecular weight to evaporate, as shown in Scheme 2. The reaction process shown in Scheme 2 was designated as process (1). However, if the degradation proceeded exclusively by the mechanism shown in Scheme 2, at the end of the process no residue would remain, yet, all the samples leave a residue whose percentage is inversely proportional to polyol molecular weight (Figs. 3, 4). In order to explain this behaviour, it must be taken into account that the alkoxysilane end groups can condense at a temperature close to

Scheme 2 Thermal decomposition of SPUR (process 1)



Scheme 3 Thermal decomposition of SPUR (process 2)



that of the urethane group decarboxylation [11]. If the condensation process takes place before urethane decarboxylation, the alkoxysilane cannot volatilize as it forms a silicon dioxide network. This process is shown in Scheme 3. The reaction process shown in Scheme 3 was designated as process (2).

The two proposed processes for SPURs thermal decomposition (Schemes 2, 3) would give rise to different mass loss percentages of the first step and final residue. These values can be theoretically calculated taking into account the stoichiometry of the proposed reactions. The values obtained compared with the experimental ones are shown in Figs. 5 and 6. As can be seen in both figures, the experimental values are in all cases closer to the values obtained assuming that the samples degrade by the process denominated 2 (Scheme 3) and, therefore, in this case when the urethane decarboxylation takes place, the majority of the alkoxysilane groups are already condensed. In addition, the relative contribution of both processes does not depend on polyol molecular weight.

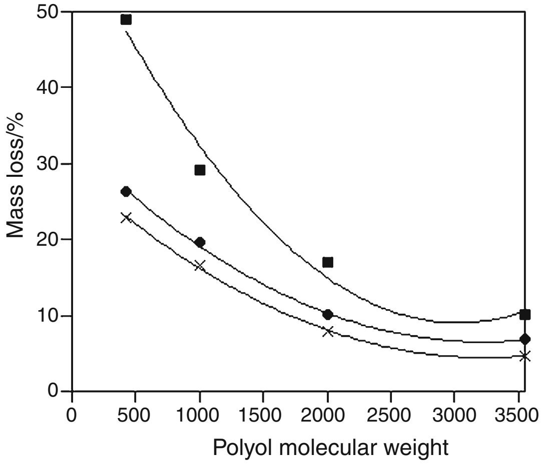


Fig. 5 Mass loss of the first step for samples obtained using 3-(trimethoxysilyl) propyl isocyanate. Experimental (*filled circle*), theoretical [following process 1 (*filled square*), following process 2 (*times*)]

Figure 7 shows the thermograms obtained for samples containing triethoxy silane (ISE) end groups, before curing. It can be observed that the thermogravimetric behaviour of these samples is very similar to the one observed using trimethoxysilane end groups. However, for samples of the same molecular weight, the percentage of the first step is higher in the system that contains ethoxy end groups (ISE systems). This result clearly confirms that the condensation of the final ethoxy groups contributes to the mass loss registered in this step.

As in the case of methoxysilane end capped polyols, the mass loss of the first stage and the remaining residues were compared with that of the theoretically predicted using the

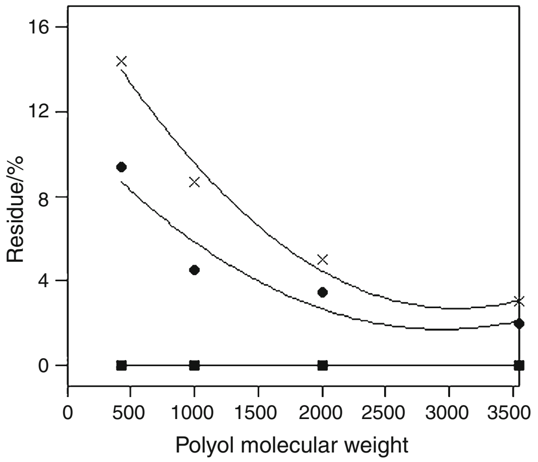


Fig. 6 Experimental (*filled circle*) and theoretical residue for samples obtained using 3-(trimethoxysilyl) propyl isocyanate [processes 1 (*filled square*) and 2 (*times*)]

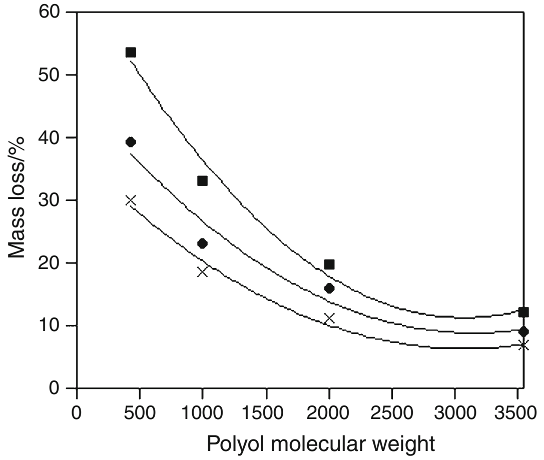


Fig. 8 Experimental (*filled circle*) and theoretical mass loss of the first stage for samples obtained using triethoxysilane [processes 1 (*filled square*) and 2 (*times*)]

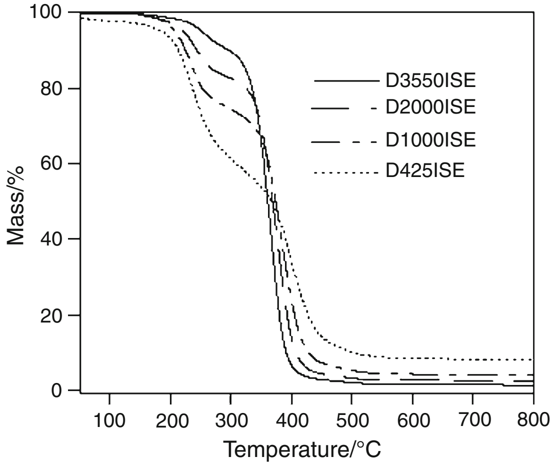


Fig. 7 TG thermograms for PPG3550ISE, PPG2000ISE, PPG1000ISE and PPG425ISE, before curing

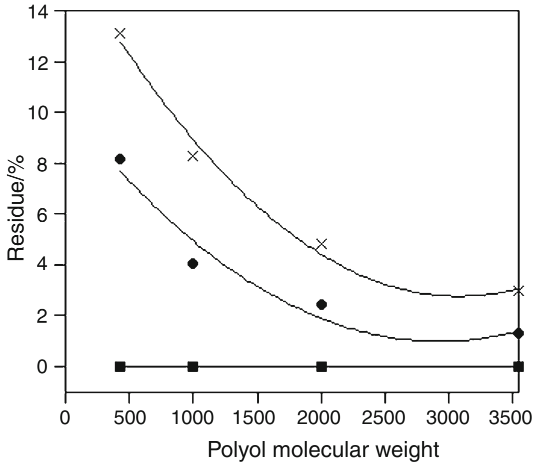


Fig. 9 Experimental (*filled circle*) and theoretical residue obtained using triethoxysilane [processes 1 (*filled square*) and 2 (*times*)]

two proposed processes. Both types of values are shown in Figs. 8 and 9. It can be observed that the experimental values of the first stage mass loss as well as the residue are between the values calculated, assuming the previously mentioned processes. This fact confirms that the thermal degradation of these systems proceeds by a combination of the processes shown in Schemes 2 and 3. However, comparing these results with those of methoxysilane-based systems, the experimental data are closer to the data calculated assuming the mechanism numbered 1. Accordingly, the condensation of ethoxysilane end groups takes place at a higher temperature than that of methoxysilane ones.

The results shown, up to now, correspond to non-cured samples. Nevertheless, the final use of these types of systems is in their cured form. Samples were moisture cured for 14 days, and afterwards the TG curves were registered. Figure 10 shows the mass loss curve (TG) for samples PPG1000ISM and PPG1000ISE obtained after curing. TG curves obtained for both samples after curing are very similar. This fact can be explained taking into account that during the curing process the alkoxy end groups are lost, and therefore, after curing the chemical structure of both systems is the same. Consequently, and in order to simplify Fig. 10, we have only shown the derivative of one of the samples.

The TG curves for the cured samples are also characterized by showing three distinct regions of mass loss. Nevertheless, the temperature of the first process is clearly higher in the cured samples (compare Figs. 2, 10). This result indicates that the thermal stability of the systems greatly improves after curing. This enhanced thermal

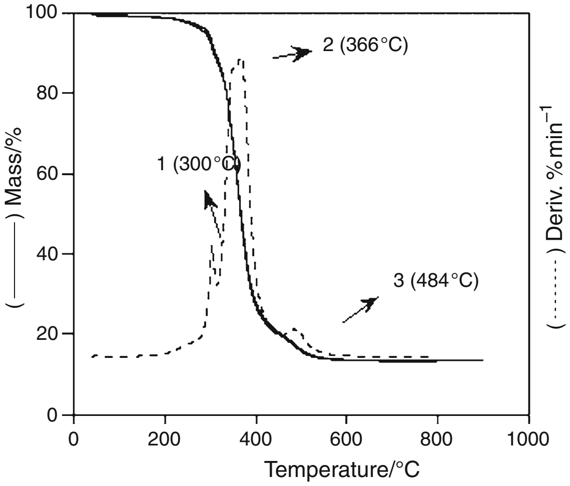


Fig. 10 Mass loss (TG) and differential mass loss (DTG) curves for samples PPG1000 ISM and PPG1000ISE after curing

stability has also been reported in literature [12, 13] where the first decomposition step increased over 45 °C with the introduction of the siloxane network. According to Yeh et al. [14], the cured systems may have an interpenetrated network that limits the segmental movement of SPUR, leading to the increase in thermal stability. According to other authors [15], the thermal resistance is enhanced due probably to the thermal insulation effect of nanosilica.

All the cured systems show a similar behaviour to that displayed in Fig. 10. As alkoxysilane groups have already condensed during the curing process, the first stage is related to the urethane group decarboxylation. This fact has been confirmed comparing the mass loss registered in this stage with the one obtained theoretically (Table 2). As can be seen, except for the lower molecular weight polyol, the experimental mass loss of the first stage matches the theoretical one. The higher value obtained in PPG425-based systems can be attributed to the volatilization of this polyol at the analysis temperature. Nevertheless, the experimental residual content at 800 °C (Table 2) is considerably higher than the silica content in all the systems. This result has also been referred to in literature [16], and it has been attributed to the entrapping of some organic part in the silica phase.

Finally, the results obtained with aminosilane systems are presented. Figure 11 shows TG and DTG curves for the system PPG1000ASM, obtained before curing. As seen, the thermogram basically shows two stages with maxima at 263 and 398 °C, respectively. Compared with the data obtained with isocyanatesilane-based systems, the mass loss maximum rate temperature of the first step is clearly higher in the aminosilane-based ones. In the former, the first stage has been assigned to the urethane group decarboxylation, alkoxysilane condensation, and evaporation. Taking this into account, we can assume that in the aminosilane-based systems, the origin of this mass loss is related to the same process. Nevertheless, it is important to realize that, in addition, aminosilane-based systems contain urea groups (see Table 1). At first glance, it would seem that urea groups impart stability to the aminosilane-based systems.

There is a great deal of controversy in literature about the thermal stability of systems containing urea groups. According to some authors [6, 17], the increased thermal stability of urea linkages is due to the greater hydrogen bonding capacity compared with that of urethane, whereas others believe that the relatively low thermal stability of urea groups is explained with reference to the electrophilic characteristics of the urea carbonyl groups [9].

According to our results, the influence of the presence of urea groups in the thermal stability of the systems studied clearly depends on their physical state. Thus, as shown in Fig. 12, the temperature of maximum rate of mass loss for the first stage (302 °C) matches that of the cured systems not containing urea groups (300 °C). This fact means that the higher stability observed in the urea containing systems before curing has no effect once the systems are cured.

The higher stability of urea containing systems before curing can be explained upon the basis of a higher viscosity compared with that of the same molecular weight isocyanate silane system (η_0 PPG1000ISM = 0.79 Pa s, η_0 PPG1000ASM = 79 Pa s). The higher viscosity could retard the liberation of volatiles and therefore could be responsible for the higher temperature of maximum decomposition rate observed in the aminosilane-based SPUR before curing [17].

Table 2 Experimental and theoretical mass loss for isocyanate silane-based cured systems

Sample	1st step experimental mass loss/%	1st step calculated mass loss/%	Experimental residue/%	Calculated residue/%
PPG425ISM/ISE	20.4	12.0	22.2	17.2
PPG1000ISM/ISE	8.7	6.7	13.4	9.4
PPG2000ISM/ISE	3.1	3.8	8.5	5.3
PPG3550ISM/ISE	2.5	2.3	5.1	3.1

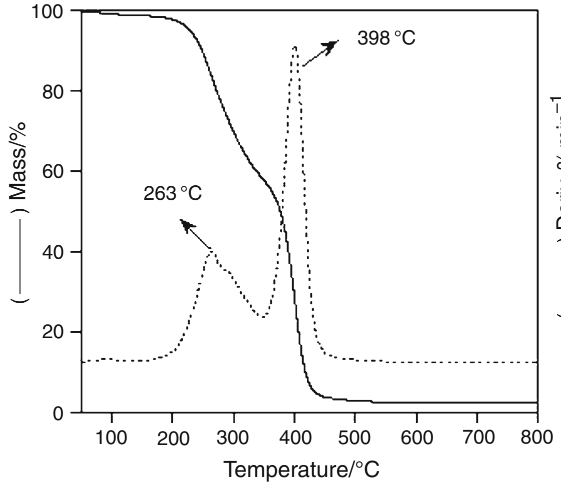


Fig. 11 Mass loss (TG) and differential mass loss (DTG) curves for sample PPG1000ASM before curing

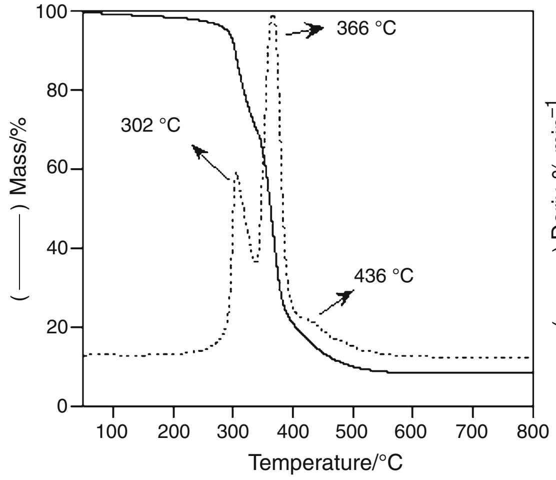


Fig. 12 Mass loss (TG) and differential mass loss (DTG) curves for sample PPG1000ASM after curing

Another alternative could be the higher molecular weight of the fragments originated in the initial decomposition step, not able to volatilize under the experimental conditions.

Conclusions

The thermogravimetric behaviour of several silanized polyether urethane systems before and after curing has been studied.

The results show that the ability of methoxysilane end groups to condense is higher than in ethoxysilane ones. However, polyetherdiol molecular weight has no effect in this condensation process.

For non-cured urea containing systems, the DTG maximum of the first step shifts to higher values compared with that shown by non-cured isocyanate silane-based systems. After curing, the stability of both types of systems is very similar, although much higher than the stability of the same systems before curing.

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References

1. United States Patent No. 3,971,751. Vulcanizable silylether terminated polymer; 1976.
2. United States Patent No. 4,444,974. Room temperature curing composition; 1984.
3. United States Patent No. 4,507,469. Curable composition comprising polyether having silyl group; 1985.
4. Chef MYL. Curing characteristics and elastic recovery of sealants. Build Environ. 2001;36:925–9.
5. Ni H, Sailer RA, Skaja AD, Soucek MD. Moisture-curing alkoxysilane functionalized isocyanurate coatings. Macromol Chem Phys. 2000;201(6):722–32.
6. Rekondo A, Fernández-Berridi MJ, Irusta L. Synthesis of silanized polyether urethane hybrid systems. Study of the curing process through hydrogen bonding interactions. Eur Polym J. 2006;42:2069–80.
7. Rekondo A, Fernández-Berridi MJ, Irusta L. Photooxidation and stabilization of silanised poly(ether-urethane) hybrid systems. Polym Degrad Stab. 2007;92:2173–80.
8. Costa L, Camino G, Luda MP, Camaron GG, Quereshi MY. The thermal degradation of poly(propylene oxide) and its complexes with LiBr and LiI. Polym Deg Stab. 1995;48:315–471.
9. Chuang FS, Tsen WC, Shu YC. The effect of different siloxane chain extenders on the thermal degradation and stability of segmented polyurethanes. Polym Degrad Stab. 2004;84:69–77.
10. Zhang Y, Xia Z, Huang H, Chen H. Thermal degradation of polyurethane based on IPDI. J Anal Appl Pyrolysis. 2009;84:89–94.
11. Eklund T, Britcher L, Backman J, Rosenholm JB. Thermogravimetric analysis of γ amino propyl-trimethoxysilane adsorbed on silica support. J Therm Anal Calorim. 1999;58:67–76.
12. Jiang H, Zheng Z, Song W, Li Z, Wang X. Alkoxysilane functionalized polyurehane/polysiloxane copolymers: synthesis and the effect of end-capping agent. Polym Bull. 2007;59:53–63.
13. Baudrit JV, Ballestero MS, Vázquez P, Torregosa-Maciá R, Martín Martinez JM. Properties of thermoplastic polyurethane adhesives containing nanosilica with different specific surface and silanol content. Int J Adhes Adhes. 2007;27:469–79.
14. Yeh JM, Yao CT, Hsieh CF, Yang HC, Wu CP. Preparation and properties of amino terminated anionic waterborne polyurethane silica hybrid materials through a sol–gel process in the absence of an external catalyst. Eur Polym J. 2008;44:2777–83.
15. Jeon HT, Jang MK, Kim BK, Kim KH. Synthesis and characterization of waterborne polyurethane-nanosilica hybrids using sol–gel process. Colloids Surf A. 2007;302:559–67.
16. Chen YC, Zhou SX, Yang HH, Wu LM. Interaction and microstructure of polyurethane/silica hybrid films prepared by sol–gel process. J Sol-Gel Sci Technol. 2006;37:39–47.
17. Chattopadhyay DK, Sreeddhar B, Raju KVJN. Thermal stability of chemically crosslinked moisture-cured polyurethane coatings. J Appl Polym Sci. 2005;95:1509–18.