EVALUATION OF TG DATA OF HTPB-BASED POLYURETHANES

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Abstract

Thermogravimetry (TG) was used to provide some new information on some polybutadiene-based polyurethanes. The results showed two main mass decomposition stages, from 230 to 564°C. The first mass loss stages were used to quantify the hard segments of the polymers. The results correlated well with the ASTM methodology. In addition, two 2^3 factorial design studies were applied to evaluate the importance of some selected factors on the TG results of the polyurethanes.

Keywords: chemometrics, factorial design, HTPB-based polyurethanes, quantitative thermogravimetry, thermal properties of polymers

Introduction

The segmented polyurethanes (PUs), because of their high tensile strength, chemical resistance, good processability and mechanical properties, are being used in many technological studies [1–7]. These polymers have the general structure $(A–B)_n$, where A is the hard segment and B is the soft segment, usually formed from a polyester-kind of molecular mass less than 2000. Their thermal stability can be improved by modification with specific molecules or polymers, forming soft-hard semi-interpenetrating polymer networks (SIPNs) [8–10] in order to obtain properties with specific needs.

In this paper we describe results on the TG analysis of PUs, obtained from hydroxyl-terminated polybutadiene (HTPB) and tolylene diisocyanate (TDI), forming the soft segment, and 1,3-propanediol (PDO), 1,4-butanediol (BDO) and 1,6-hexanediol (HDO), forming the hard segments, in a two-step, bulk polymerization process. The TG results are also evaluated using factorial designs, a relatively unexplored tool in this polymer field, in order to supply information on the importance of some experimental factors on the thermal behavior of the soft-hard PUs.

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Experimental

All chemicals were reagent grade and were purified as described earlier [11]. The poly-urethanes were prepared and characterized as described earlier [3, 11]. In brief, a prepolymer (PP) was synthesized by adding of HTPB and TDI in order to obtain the de-sired value for the free NCO content, which varied from 2 to 9%. In a second step the required amount of chain extender (PDO, BDO and HDO) was added in order to set the overall NCO/OH ratios from 1.13 to 1.27. The cure was completed after 24 h at 100°C.

Thermogravimetry (TG) measurements were carried out using a TA Instruments thermobalance, in a nitrogen flow rate at 150 mL min^{-1}. The amount of sample used was in the range 8–10 mg.

Results and discussion

TG has extensively been used to supply important information on the thermal stability of several polyurethane samples [1, 4, 7, 8, 12]. The manner of the preparation of the polymers, the composition of the chains and the presence of substances used to im-prove chemical and mechanical properties also affect, the profiles of the TG curves. Since the TG plots are very similar in shape, Fig. 1 shows the thermogravimetric curves of the PP-PDO, as examples. The separation of the first and the second mass loss pla-
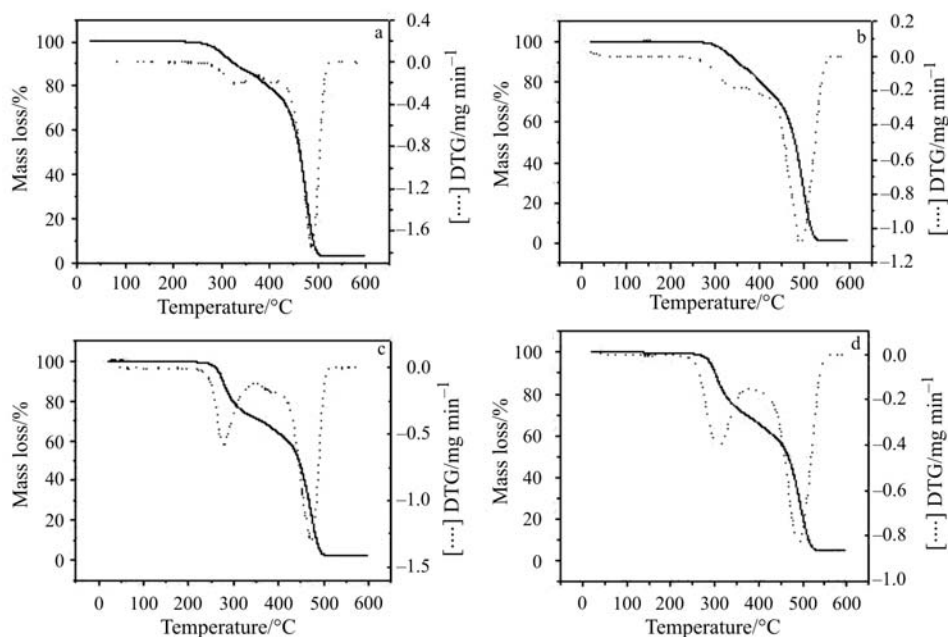
Fig. 1 TG and DTG curves of the polyurethanes: a – PP-2% free NCO+PDO (10°C min^{-1}), b – PP-2% free NCO+PDO (30°C min^{-1}), c – PP-9% free NCO+PDO (10°C min^{-1}) and d – PP-9% free NCO+PDO (30°C min^{-1})

teaus were roughly observed. This behavior is related to a greater cross-linking degree and hydrogen bonding interactions for this kind of polymer. From Fig. 1, the typical sigmoidal forms of the TG curves of PU can be noted [4, 7]. The data from the TG curves are found in Table 1, where T_1–T_2 and T_3–T_4 (°C) are the temperatures ranges, for the first and second plateaus, respectively and $P_{1–2}$ and $P_{3–4}$ (%) are the respective mass losses. The first stages of degradation of the PP-BDO and PP-HDO polymers were between 221–250 and 240–261°C, for heating rates of 10 and 20°C min^{-1}, respectively. For PP-PDO this temperatures were between 221–270 and 240–260°C, at 10 and 30°C min^{-1}, respectively.

Table 1 TG results of the polyurethanes, where T_1–T_2 and T_3–T_4 (°C) are the temperature ranges, for the first and second plateaus, respectively; $P_{1–2}$ and $P_{3–4}$ (%) are the respective mass losses, and X is the hard segment content (ASTM)[a]

Polymer	β/°C min^{-1}	T_1/°C	T_2/°C	T_3/°C	T_4/°C	$P_{1–2}$/%	$P_{3–4}$/%	X^a/%
PP-BDO-2	10	222.0	369.1	430.5	510.0	14.3	83.9	13.2
PP-BDO-9	10	251.0	335.9	414.7	509.4	33.2	64.9	31.4
PP-PDO-2	10	229.4	358.0	401.0	527.0	15.0	81.7	12.9
PP-PDO-9	10	206.8	350.4	397.7	527.0	28.5	69.5	27.6
PP-HDO-2	10	247.6	347.9	420.9	510.6	14.0	84.6	13.8
PP-HDO-9	10	233.4	344.6	420.0	508.9	33.0	75.8	33.2

[a]X=Hard segment content=$[(M_{TDI}+M_{chain\ extender})/M_{total}]\times100$; M=mass and $M_{total}=M_{TDI}+M_{chain\ extender}+M_{PBLH}$ [9, 11]

It was observed that polymers with similar free residual NCO groups in the PP structure presented very similar mass losses contents in a determined temperature range, as it can be observed in Table 1. This behavior seems to suggest that the two mass loss steps for all polymers studied can be attributed to the thermal degradation of the hard and soft segments of the polymers, as defined in the introduction section.

However, in general, there is a good correlation between the first-step mass loss values ($P_{1–2}$) with the hard segment contents (X, %), provided by the ASTM methodology, which are calculated as shown in the footnote of Table 1 [11, 13]. In this sense, the first-step mass loss values seem to be a new manner to found a good estimative of the reactivity of the soft and hard segments of the PUs polymers.

On the other hand, factorial design data have improved the knowledge of many processes, which are dependent on the experimental conditions, such as the interaction of metals and dyes on solid supports, biocatalysis, as well as on the synthesis of new materials for use on traditional and new technological applications [14–17]. Table 2 shows the factors and levels used in the factorial designs. All effects were calculated from the results presented in Table 3, based on the initial mass loss amount, $P_{1–2}$ (%), as observed in Table 1.

Table 2 Factors and levels used in the TG factorial designs

Factors	Level	
	(–)	(+)
Factorial design 1		
1. Extensor of the PP chain	BDO	HDO
2. Free residual NCO/% in PP	2	9
3. Heating rate, β/°C min^{-1}	10	20
Factorial design 2		
1. Extensor of the PP chain	PDO	BDO
2. Free residual NCO/% in PP	2	9
3. Heating rate, β/°C min^{-1}	10	30

Table 3 Factorial design results. P_{1-2} (1) and P_{1-2} (2) represent average first mass loss values for the first (1) and second (2) factorial design, respectively

Experimental number	Execution order	Factor 1 PP-extensor	Factor 2 Free NCO	Factor 3 β/°C min^{-1}	P_{1-2} (1)/ %	P_{1-2} (2)/ %
1	4	–	–	–	14.3	16.5
2	8	+	–	–	14.0	15.0
3	3	–	+	–	25.2	33.2
4	2	+	+	–	23.0	28.5
5	7	–	–	+	15.2	14.2
6	1	+	–	+	14.2	10.6
7	5	–	+	+	28.2	34.2
8	6	+	+	+	14.8	31.5

The success of a factorial design depends, in part, on the range of the factors investigated. One must choose differences in levels that are large enough to give changes in the response larger than experimental error. However, these differences should not be larger than quadratic or higher order effects, due to the individual factors, which might invalidate the factorial model [18]. The results of preliminary univariate studies for the thermal decomposition of the polymers were used in order to identify the most relevant factors, which were used in factorial design scheme, as shown in Table 1.

The principal and interactive effects of the factors were calculated using Eq. (1), based on the first mass loss amount, P_{1-2}, as observed in Table 1, since this amount seems to be strongly related to the extensor chain of the polymers [13].

$$\text{Effect} = \overline{R}_{+} - \overline{R}_{-} \tag{1}$$

$\overline{R}_{+}$ and $\overline{R}_{-}$ parameters are average values of the P_1 mass loss (%) for the high and low levels of each of the three factors, $i=1-3$. In general, high order interactions are calculated using the above equation by applying signs obtained by multiplying those

for the factors involved, (+) for high and (−) for low levels [14–18]. Since independent duplicate experiments were performed, standard error for principal and interactive effect values (E) can be calculated as follows in Eq. (2) [18]:

$$E = [\Sigma(d_i)^2/8N]^{1/2} \qquad (2)$$

where d_i is the difference between each duplicate run and N is the number of distinct experiments performed (eight for the 2^3 design used here). Table 4 shows the results of principal and interactive effects for the factorial designs.

Table 4 Principal and interaction effect values calculated for the factorial 1 (A_1) and 2 (A_2)

Calculated effects	A_1/%±3.00	A_2/%±3.00
Principal		
1. Extensor of the PP chain	−4.24	−3.11
2. Free residual NCO/%	8.40	17.80
3. Heating rate, β/°C min^{-1}	−1.02	−0.70
Interactions		
1–2	−3.59	−0.57
1–3	−2.95	−0.01
2–3	−1.57	2.67
1–2–3	−2.64	1.04

From the inspection of Table 4, the calculated errors presented very similar values in comparison with the interactions effects. In this manner, only the principal effects were significant for the first-step mass loss processes [14–18]. The negative value of the $A_{1,1}$ effect for the variable 1 (chain extensor) indicate that the mass loss for the first plateau (P_1) was lower for the polymer PP-HDO in relation to the polymer PP-BDO.

It was observed that the presences of high-length extensor chains provoke difficulties in the thermal decomposition of the hard segment of polyurethanes.

On the other hand, the values for the mechanical properties of the polymers, such as tensile strength, shore hardness, and elastic modulus, increased with decreasing number of carbon atoms in the chain extender, that is PDO>BDO>HDO [13]. This finding disagrees with previous results, which showed an inverse order, i.e., HDO>BDO>PDO [18] being correlated with the sequence of thermal stability found in this work.

Regarding variable 2, the positive A_1 and A_2 values reveal that the presence of high amounts of free residual NCO (9%) increases significantly the thermal degradation of the polymers. This behavior can be explained in terms of the number of hydrogen bonds, since with decreasing the number of diol (chain extender) a decrease of both the hard segment and hydrogen bond contents is presumed.

Variable 3 (heating rate) and all interactions of the variables, in general, were insignificant, since their numerical values were very close to the errors calculated [19]. These results indicate that all TG measurements, in order to find the mass loss amounts, can be made using the highest heating rate, 30°C min^{-1}.

Conclusions

In this study, TG results of soft-hard segments of polyurethanes were evaluated. The first-step mass loss values correlated well with the hard segment contents, using the usual ASTM methodology. However, the confirmation of this correlation and the quantitative separation of the soft and hard segments in the TG curves, require further studies and detailed investigations.

The factorial designs allowed us to find some new information on the importance of the factors related to the thermal behavior of the PUs studied (variables 1 and 2). Using classical univariate experiments, the clear visualization of the importance of the selected TG variables is difficult, since the effects of variables, frequently, could not be separated [19].

Other studies concerning the thermal properties of the PUs, using other thermal techniques, as DSC, correlated with appropriate factorial designs, are in progress in our laboratory.

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