Kinetic study and thermal decomposition behaviour of viscoelastic memory foam

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Abstract

A systematic investigation of the thermal decomposition of viscoelastic memory foam (VMF) was performed using thermogravimetric analysis (TGA) to obtain the kinetic parameters, and thermogravimetric analysis coupled to Fourier Transformed Infrared Spectrometry (TGA-FTIR) and thermogravimetric analysis coupled to Mass Spectrometry (TGA-MS) to obtain detailed information of evolved products on pyrolysis and oxidative degradations. Two consecutive nth-order reactions were employed to correlate the experimental data from dynamic and isothermal runs performed at three different heating rates (5, 10 and 20 K/min) under an inert atmosphere. On the other hand, for the kinetic study of the oxidative decomposition, the data from combustion (synthetic air) and poor oxygen combustion ($N_2:O_2=9:1$) runs, at three heating rates and under dynamic and isothermal conditions, were correlated simultaneously. A kinetic model consisting of three consecutive reactions presented a really good correlation in all runs.

TGA-FTIR analysis showed that the main gases released during the pyrolysis of VMF were determined as ether and aliphatic hydrocarbons, whereas in combustion apart from the previous gases, aldehydes, amines and CO₂ have also been detected as the main gases. These results were confirmed by the TGA-MS.

Keywords: Viscoelastic; Kinetics; Pyrolysis; Combustion; Thermogravimetric

30 Nomenclature table

α_i	Conversion degree in the reaction i
DTG	Derivative Thermogravimetric curve
E_i	Activation energy for the reaction i
FPUF	Flexible Polyurethane Foam
HDPE	High density polyethylene
k_i	Kinetic constant for the reaction i
K_i^*	Compatible kinetic constant for the reaction i
k_{i0}	Pre-exponential factor of the Arrhenius equation for the reaction i
k'_{i0}	Pre-exponential factor of the Arrhenius equation corrected with the effect of the oxygen for the reaction i
MSW	Municipal solid waste
NCV	Net calorific value
n_i	Reaction order for the reaction i
N	Total number of experimental data employed in the optimisation
P	Number of optimised parameters
PE	Polyethylene
P_{O_2}	Partial pressure of oxygen in the atmosphere
PUF	Polyurethane foam
PVC	Polyvinyl chloride
R	Gas constant ($J\ mol^{-1}\ K^{-1}$)
TDI	Toluene Diisocyanate
TGA	Thermogravimetric analysis
TGA-FTIR	Thermogravimetric analysis- Fourier Transformed Infrared Spectrometry
TGA-MS	Thermogravimetric analysis-Mass Spectrometry
T_{max}	Temperature around the maximum decomposition rate
VC (%)	Variation coefficient

$v_{i\infty}$	Mass fraction of volatiles that can be obtained at infinity time from the reaction i
V_i	Mass fraction of volatiles at any time in the reaction i
VMF	Viscoelastic memory foam
w_{exp}	Average of the experimental values of mass fraction

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1. Introduction

Polyurethanes are a wide range of materials that are characterized by the presence of the urethane linkage ($-\text{NH}-\text{C}(=\text{O})-\text{O}-$) in their structure which came from the reaction between diols and diisocyanates. Depending of the type of diisocyanate and diol employed and the manufacture process, it is possible to find products on the market such as rigid and flexible polyurethane foams, adhesives, coating and elastomers among others.

In the field of flexible polyurethane foams (FPUF), the viscoelastic memory foams (VMF) are mainly employed in the manufacture of high quality mattresses due to their ability to distribute the body weight over the surface.

Every year, 60% of discarded mattresses thrown out in the European Union are sent to landfill and the rest 40% are incinerated [1]. Due to their low density, mattresses are not desirable material for landfilling and recycling and although this is a possible method to manage these wastes, it has shown important economic disadvantages [2]. The increase in the demand for energy due to economic growth and the decrease in landfill space in almost all developed countries, make pyrolysis and combustion processes optimal routes for upgrading from waste [3], allowing the production of fuels, gases and/or energy [4].

With a concern of the usage of waste as fuel or as raw material for gases, it is essential to have the knowledge of its thermal decomposition and reaction kinetics during the combustion and pyrolysis in order to design the systems and optimize their operation conditions [5]. Thermogravimetric analysis (TGA) is said to be a useful tool to study the solid-phase thermal degradation behavior and to determinate the most common kinetic parameters [6, 7] such as the pre-exponential factor (k_0), activation energy (E), reaction order (n) and the mass fraction of volatiles evolved at infinity time (v_{inf}) [8].

Different authors have recently employed TGA to characterize really different types of waste such as Municipal Solid Waste (MSW)[9-11], orange waste (pulp) [12], printed

circuit boards [13, 14], sewage sludge [15] and even, tobacco waste [16]. Also, in recent years the number of studies related with co-pyrolysis or co-combustion of two or more types of waste (including plastic waste) have increased considerably [7, 17-19].

In addition to characterizing the waste, the most useful application of TGA is perhaps to suggest a kinetic model to design an adequate reactor. One of the most practical studies found in this respect has recently been developed by Chandrasekaran et al. [20]. These authors employed TGA to study the pyrolysis of waste plastics such as polypropylene based bottles, high density polyethylene (HDPE), landfill liners (PE), packing materials (Polystyrene) and polyurethane foams (PUF), with and without catalysts in order to study the activation energy variation for each material. After this study, they used the optimized parameters to perform the experiments in a batch reactor analyzing the gasoline, diesel and vacuum gas oil fractions from the distillation of the crude oils obtained.

Thermogravimetric analysis (TGA) coupled with Fourier transform infrared (FTIR) analysis is a useful method to extract information regarding the evolved species during thermal degradation in real-time and with a high sensitivity. In fact, different authors used this technology to characterize wastes such as pine sawdust [21], flame retardant polyurethane foams materials [22] or mixtures of polyethylene (PE), polystyrene (PS) and polyvinyl chloride (PVC) [23]. Not only the infrared equipment can be connected with the TGA analyzer but: a Mass Spectrometer (MS) analyzer is also usually coupled with TGA to analyze the evolution of some ions with the time. For example, six representative components of municipal solid waste (lignin, printing paper, cotton, rubber polyvinyl chloride and cabbage) were extensively studied by Zhang et al.[24] with a TG-MS analyzer focusing on the evolution of gases such as H_2 , CH_4 , CO and CO_2 . In the same way Garrido et al. [8] conducted a thermo-analytical and kinetics study of flexible polyurethane foam by TGA under various atmospheres (N_2 , $N_2:O_2=4:1$ and $N_2:O_2=9:1$)

performing dynamic and isothermal experiments at three different heating rates (5, 10 and 20 K/min). The proposed model for pyrolytic degradation consisted of two consecutive reactions, whereas for the oxidative degradation it was necessary to employ three consecutive reactions to correlate the experimental data. In addition, TGA-FTIR and TGA-MS analysis were carried out under inert and oxidative atmospheres comparing the effect of the presence of oxygen in the evolved gases.

Regardless of the great number of studies on synthetic polymer pyrolysis and combustion kinetics, no research has been found in literature for the thermal behavior of viscoelastic memory foam. Therefore, the aim of the present work is to provide an analysis of thermal degradation kinetics under different atmospheres and operating conditions, along with evolved products for each step of the process.

2. Materials and methods

2.1. Raw material

The viscoelastic memory foam (VMF) was collected from mattresses disposed of in a landfill in Alicante (Spain). The sample was dried in a furnace at 105°C until constant mass in order to determine the moisture, which was 1.3%.

The density was determined following the ISO 845:2006 [25] for the apparent density in plastic and cellular rubbers, the value obtained being 43 kg/m³. This data is in the middle of the range (32-96 kg/m³) proposed by the Polyurethane Foam Association [26] and is really similar to those measured by Shoaib et al. [27].

Net Calorific Value (NCV) was determined in a calorimetric bomb model AC-350 from Leco Instruments. To determine the ash content and the volatile matter, the sample was calcined in a muffle furnace at 550°C and 950°C, respectively. The ultimate elemental

analysis (C, H, N and S), was performed in a CHNS analyzer (FlashEA 1112 Series, ThermoFinnigan). The results of these analyses are shown in **Table 1**.

Table 1. VMF characterization (dried sample).

NCV (MJ/kg)	27.13
Volatile matter (%)	99.73
Ash (%)	0.11
C(%)	61.26
N(%)	3.34
H(%)	8.45
S(%)	0.16
O by difference (%)	26.68

The semi-quantitative analysis of the remaining elements was performed by X-ray Fluorescence with an automatic sequential spectrometer (TW 1480, Philips MagixPro, Philips Co., Ltd) finding that the Calcium (Ca), Silicon (Si) and Magnesium (Mg) were the most abundant elements presented in the sample.

An Attenuated Total Reflection-Fourier Transform Infrared spectrometer (ATR-FTIR) from Bruker model IFS 66S was employed to obtain information about the functional chemical groups of the sample. The spectrum was recorded from 600 cm^{-1} to 4500 cm^{-1} with a resolution of 1 cm^{-1} and is shown in **Figure 1**. The spectrum obtained is similar to that published by Shoaib et al. [27] in their study of viscoelastic foam with blowing agent. The peak at 3344 cm^{-1} is characteristic from the N-H stretch amide and peak at 2867 cm^{-1} is the C-H₂ symmetric stretch of aliphatic alkanes [28]. The next peak, 1706 cm^{-1} , belongs to the C=O bond vibration from the carboxylic acid. Meanwhile those detected at 1596, 1510 and 1409 cm^{-1} show the presence of C-C bonds from benzene rings. The peak at 1537 cm^{-1} is common from the nitro compounds (N-O) and the peak at 1452 cm^{-1} is characteristic from the CH₃ group in the toluene diisocyanate employed to make the foam. The presence of amines is confirmed with the peak at 1375 cm^{-1} and the aromatic ethers from the polyether polyols are detected in the peak at 1305 cm^{-1} . The most intensive

peak at 1067 cm^{-1} is C-O-C asymmetric stretching in urethane bonded (-O-CO-NH). The rest of the peaks are characteristic from the C-H bond in alkenes (946 cm^{-1}) and aromatic rings (833 and 759 cm^{-1}) [27].

Figure 1. ATR-FTIR spectra of VMF.

2.2. Thermogravimetric analysis (TGA)

Viscoelastic memory foam (VMF) was subjected to thermogravimetric analysis (TGA) to characterize the thermal degradation in a wide range of conditions. To achieve this purpose, a Perkin Elmer thermobalance (model STA6000) with a vertical furnace was used to carry out a series of analysis at three different atmospheres: pyrolysis (N_2), combustion (synthetic air) and poor oxygen combustion ($\text{N}_2:\text{O}_2=9:1$) with a flow rate of 100 mL/min . Dynamic runs were carried out at three different heating rates (5 , 10 and 20 K/min) between 300 K and 1000 K . Additionally, three isothermal experiments for each atmosphere were performed starting with a constant heating rate until the selected temperature was reached, and then, this final temperature was maintained for 120 min . The study of dynamic and isothermal runs ensures that an intensive range of decomposition conditions is covered.

In order to check the good performance of the thermobalance, and before the runs with VMF, an experiment was carried out with Avicel PH-105 micro-crystalline cellulose at 5 K min⁻¹ in nitrogen. From the results, the corresponding kinetic constants were calculated and compared with those published by Grønli et al. [29] in their round-robin study of cellulose pyrolysis kinetics by thermogravimetry, obtaining good agreement.

Prior to the main study, tests of the effect of the initial sample mass were done. **Figure 2** presents the curves obtained employing 5, 7.5 and 10 mg of VMF confirming that the initial mass had a very small effect in the degradation process. For the rest of the runs, the sample mass used was approximately 7 mg.

Figure 2. Study of initial mass effect in the VMF thermal degradation under N₂ atmosphere and working at constant heating rate of 10 K/min.

To ensure the system errors were corrected, blank runs were performed under the same conditions but with the crucible empty and the weight values recorded for each experimental time were subtracted from the values obtained in the runs with sample. **Figure 3** shows two TG curves obtained under the same degradation conditions (employing around 7 mg of sample) in order to check the reproducibility of the equipment. The synthetic air atmosphere was selected to perform this analysis due to its

most reactive atmosphere. Furthermore, a heating rate of 20 K/min was selected because heat transfer limitations could appear when working at a high heating rate due to the fact that higher heating rate decreases the heat distribution in solid molecules, as has been reported recently [30, 31]. However, really good reproducibility was obtained for the degradation of this waste.

Figure 3. Weight loss curves of VMF performed under synthetic air atmosphere at 20 K/min.

2.3. *TG-FTIR analysis*

To characterize the volatile compounds evolved during the thermal degradation, a Thermogravimetric-Fourier Transform Infrared (TGA-FTIR) analysis was performed using the same thermobalance coupled to a Nicolet 6700 FT-IR spectrometer. Nitrogen and synthetic air were employed as carrier gases with a flow rate of 100 mL/min heating up to 1100 K at 10 K/min and with 7 mg mass sample of VMF. The absorbance was measured between 4000 and 600 cm^{-1} .

2.4. *TG-MS analysis*

Thermogravimetric-Mass Spectrometry analysis (TGA-MS) provides additional identification information that the FTIR may not provide because some diatomic molecules do not have a permanent dipole moment. Runs were carried out in a Mettler

Toledo thermobalance (model TGA/SDTA851e/LF/1600) coupled to a Pfeiffer Vacuum mass spectrometer (model Thermostar GSD301T) operating in SIR mode and with an ionization of 70 eV . Two different atmospheres were studied, He (pyrolysis) and He:O₂=4:1 (combustion runs), both with a flow rate of 100 mL/min. Approximately 5 mg of sample was heated with a constant heating rate of 30 K/min from room temperature to 1100 K.

3. Result and discussion.

3.1. Thermal degradation

In order to study the thermal degradation of the viscoelastic memory foam (VMF) in a wide range of conditions, six pyrolysis (N₂), six poor oxygen combustion (N₂:O₂=9:1) and six combustion (synthetic air) runs were carried out in dynamic and isothermal modes. **Figure 4A, Figure 5A and Figure 6A** present the experimental weight loss variation with the temperature in dynamic experiments performed at three different heating rates (5, 10 and 20 K/min) for each of the atmospheres employed. In all TG figures, w represents the mass fraction of the solid, defined as the ratio between the solid mass at any time (m) and the initial solid mass (m_0). The solid mass at any time includes the non-reacted initial solid and the residue formed during the degradation.

In addition, **Figure 4B to Figure 6B** also show the derivative thermogravimetric curves (DTG) versus temperature for the same conditions in order to know the number of decomposition processes in each experiment.

Figure 4. Experimental data from the pyrolysis of VMF. A) TG curves at 5, 10 and 20 K/min. B) DTG curves at 5, 10 and 20 K/min.

Figure 5. Experimental data from the combustion (synthetic air) of VMF. A) TG curves at 5, 10 and 20 K/min. B) DTG curves at 5, 10 and 20 K/min.

Figure 6. Experimental data from the poor oxygen combustion ($N_2:O_2=9:1$) of VMF. A) TG loss curves at 5, 10 and 20 K/min. B) DTG curves at 5, 10 and 20 K/min.

In the previous graphs, it can be appreciated that regardless of the atmosphere employed, when the heating rate increases the weight loss curves move to the right (higher

temperatures), as expected. In spite of the shift observed in TG curves with heating rate, the pattern of thermal decomposition does not change, obtaining the same final residue at any heating rate under the inert atmosphere (**Figure 4A**), around 10%. This fact can also be also appreciated in **Figure 5A** and **Figure 6A** (combustion and poor oxygen combustion) where the amount of final solid residue decreases significantly and presents a value of ca. 0.1%, which agrees with the ash content reported in **Table 1**.

Analyzing the pyrolytic decomposition of VMF (**Figure 4A** and **Figure 4B**), it can be observed that in the three experiments performed at different heating rates, there is a large peak located around 645-685 K preceded by a small band or wide peak (from 550 to 611 K for 5 K/min and from 550 to 640 K for 20 K/min), which means that the proposed kinetic model should consider at least two degradation steps.

Figure 5A shows the TG curve from the thermal decomposition of VMF under the most oxidative atmosphere studied (synthetic air) where two different steps can be clearly distinguished, the first with a weight loss of ca. 80% and the second with a soft slope around 800 K which is usually is associated with the oxidation of char. However, the DTG curve from the run performed at 20 K/min (**Figure 5B**) shows that in the first step considered there are two different steps: one wide peak from 555 to 623 K followed by a peak located at 680 K. The oxidative degradation of VMF takes place in three different steps, the last of them being the char oxidation, which means that at least three different steps should be considered in the kinetic model.

Figure 6A and **Figure 6B** show the experimental results for dynamic poor oxygen combustion runs ($N_2:O_2=9:1$), with really similar behavior to that explained for combustion runs.

In order to highlight the effect of the atmosphere in the process, **Figure 7** shows the weight loss curves at 20 K/min for the three atmospheres, where it is clear that the weight

loss process starts at approximately the same temperature, and that the presence of oxygen in the furnace involves an acceleration in the decomposition of VMF, as has also been obtained in other materials [21, 32].

Figure 7. TGA curves at 20 K/min under an atmosphere of N₂, Synthetic air and N₂:O₂=9:1.

3.2. Species identification and discussions from TGA-FTIR

In order to analyze more deeply the evolution of volatiles, **Figure 8** shows the TG-DTG curves from the pyrolysis and combustion of VMF at 10 K/min together with the characteristic spectrum obtained at temperatures where the sample presents the major thermal events. Moreover, the absorption bands of the gaseous species detected at the main degradation steps the in pyrolysis and combustion of VMF are summarized in **Table 2**.

Under a nitrogen atmosphere (**Figure 8A**), the sample is thermally degraded in two steps, the first is slightly visible around 598 K and the second, more striking, at 673 K. The spectra obtained at maximum degradation temperatures (**Figure 8C**) are really different and more gaseous species are evolved at 673 than at 598 K, which was the expected trend observing the DTG curve (**Figure 8A**).

The pyrolytic degradation of VMF starts breaking the urethane bonds as can be confirmed by the detected compounds detected such as cyanates (-NCO) and amines (-NH-). However, at 598 K the most intensive peaks belong to carbon dioxide (CO_2) that can be an unexpected product under an N_2 atmosphere but that has also been observed previously by other authors [33, 34] and which comes from the breaking of the urethane bond (-NH-C(=O)-O-). The presence of CO_2 and the rest of peaks mentioned previously, and the high intensity of CO_2 peaks, confirms the widely accepted thermal degradation mechanism for based polyurethane materials under an inert atmosphere which consist of two main steps, the first one being the breaking of hard segments producing the emission compounds such as cyanates, primary and secondary amines and carbon dioxide [34] and the formation of a condensable phase.

The second step, observed in this study at 673 K, involves the thermal destruction of the condensable phase obtained previously producing a great amount of gaseous products, as can be seen in the FTIR spectrum (**Figure 8C**), and an important weight loss (**Figure 8A**). The main gases evolved detected at 673 K were aliphatic hydrocarbons, high polarity ethers and aromatic hydrocarbons, as was expected bearing in mind that toluene diisocyanate (TDI) (two most important isomers 2,4- and 2,6-TDI) and polyether polyols are the common raw materials in the production of based polyurethane materials. Also, CO_2 has been detected at this temperature, but with lower intensity than was obtained at 598 K. Finally, water vapor was evolved not only at 673 K but also at 598 K (peaks in range $3600\text{-}3900\text{ cm}^{-1}$) [35].

Figure 8. TG and DTG curves of VMF pyrolysis (A) and Combustion (B). FTIR spectrum obtained at maximum decomposition rates in pyrolysis (C) and combustion (D) of VMF.

Regarding the thermal decomposition under an oxidative atmosphere, in **Figure 8B** it can be seen that this consists of three steps, the first around 629 K, the second at 654 K and the last at 796 K. In the FTIR analysis, no difference has been detected in the spectrum at 629 K and 654 K, so **Figure 8D** only shows the evolved gases at the highest temperature of 654 K. Analyzing the spectra from the VMF combustion, it can be seen that the amount of evolved products evolved at 654 K is higher than that obtained at 796 K, which is confirmed in the weight loss and DTG curves **Figure 8B**. This means that under an oxidative atmosphere, the decomposition is shifted through the lower temperature compared to the maximum degradation temperature detected in pyrolysis (673 K). The exhaust stream gas at 654 K (**Figure 8D**) contains most of the groups detected in the

pyrolysis, as can be seen in **Table 2** . Apart from these groups, aldehydes and carbon monoxide (CO) have also been detected which mean that under an oxidative atmosphere the virgin VMF is degraded at lower temperature than in pyrolytic conditions to produce, CO₂, CO, isocyanates, alcohols and aldehydes and a carbonaceous residue which will be oxidized in the next step (796 K) [32]. In the spectrum at 796 K (**Figure 8D**) it can be seen that some of the compounds detected in the previous step are not present in this step whereas for CO₂ there is an increase in the peak intensity and CO presents a light decrease, which means that the carbonaceous residue formed previously is oxidized in this step as has mentioned previously. However, in this step the presence of -NH- groups (1518 and 3363 cm⁻¹), methyl and methylene (~2862 cm⁻¹) and a new peak at 1599 cm⁻¹ from the aromatic rings, involves that a part from carbonaceous residue, in this last step other compounds are degraded. More concretely, the shapes of the combustion and poor oxygen combustion curves observed in **Figure 7** suggest that at the second step (673 K) oxidized compounds are formed obtaining, at the end of this step, an increase in the sample weight, compared with that detected under pyrolytic conditions. Therefore, the thermal decomposition of these oxidized products in the last step, could be responsible for the -NH- groups, methyl and methylene groups and aromatic rings mentioned previously.

Table 2. FTIR results of evolved gases during the main steps of pyrolysis and combustion of VMF.

Chemical bond	Vibration	Evolved gaseous products	Wavenumber (cm ⁻¹)				References
			Pyrolysis		Combustion		
			598 K	673 K	629 and 654 K	796 K	
C=O	Bending	CO ₂	670	671	667	669	[33, 34, 36]
C-O-C	Streching	Ethers	-	1113	1115	1113	[8, 37]
C-H	Bending	Aliphatic hydrocarbons	-	1200-1452	1228-1450	1227-1450	[6, 34]
N-H	Bending	Amines	1512	1512	1512	1518	[38]
C=C	Streching	Aromatic hydrocarbons	1606	1620	1608	1599	[12]
C=O	Streching	Aldehydes	-	-	1714	1707	[8, 12, 35]
C-O	Streching	CO	-	-	2110, 2183	2110, 2183	[12, 21, 22, 33, 34, 39]
-NCO	Streching	Cyanates	2291	-	-	-	[22]
C=O	Streching	CO ₂	2330, 2357	2330, 2357	2328, 2362	2328, 2362	[33, 34, 36]
C-H	Streching	Aliphatic hydrocarbons	-	2870-2970	~2866	~2862	[6, 34]
N-H	Streching	Amines	3390	3373	3375	3363	[38]
O-H	Streching	Water vapor	3600-3900	3600-3900	3600-3900	-	[35]

Summarizing, it could be said that under an N₂ atmosphere the most important weight loss occurs at 673 K producing mainly ethers and aliphatic hydrocarbons, whereas in combustion the principal degradation is at lower temperature (654 K) obtaining more compounds like aldehydes, CO₂, amines, ethers and aliphatic hydrocarbons. The last step in the oxidative degradation involves the decomposition of the carbonaceous residue formed producing CO, CO₂ and compounds with -NH-, methyl and methylene groups and aromatic rings.

3.3. Species identification and discussions from TGA-MS

Different TGA-MS runs were carried out to analyze the characteristic fragment ion intensity of the volatiles according to their respective mass to char ratios (m/z) at two different atmospheres (He and He:O₂=4:1) with a heating rate of 30 K/min.

Figure 9A shows the weight loss curve for VMF under pyrolytic (He) conditions together with the ion current curves for $m/z=16$, $m/z=17$ and $m/z=18$ whereas **Figure 9B** presents the same curves but for oxidative conditions (He:O₂=4:1). On the other hand, responses of products evolved with m/z equal to 27, 28, 30 and 44 and the weight loss curves are also shown in **Figure 9C** and **Figure 9D** for the runs carried out under an He and He:O₂=4:1 atmosphere, respectively. As can be seen, it is confirmed that the pyrolytic degradation of VMF (**Figure 9A** and **Figure 9B**) takes place in two main steps (583 and 669 K) whereas the decomposition under an oxidative atmosphere (**Figure 9C** and **Figure 9D**) occurs in three steps (615, 645 and 783 K). The $m/z=18$ is characteristic from water (H₂O) which shows the highest intensity in both atmospheres (**Figure 9A** and **Figure 9C**) and is only detected in the second step in pyrolysis and at the first and the second step in oxidative decomposition. Also methane (CH₄) with $m/z=16$ is emitted not only in pyrolysis (around 669 K) but also in combustion where no clear difference can be seen between the first and the second step (615 and 645 K). Another product evolved, common from the thermal degradation of high content nitrogen material like VMF, is ammonia (NH₃) with $m/z=17$ that has been detected at 669 K in pyrolysis run with a higher intensity than those obtained in the two first steps of oxidative decomposition due to the oxidation of NH₃ to produce NO [40, 41].

Figure 9. TG-MS of viscoelastic memory foam at heating rate of 30 K/min. Ion profiles monitored for $m/z=16$, 17 and 18 under He (A) and He:O₂=4:1 (C) atmospheres. Ion profiles for $m/z=27$, 28, 30 and 44 under He (B) and He:O₂=4:1 (D) atmospheres.

Hydrogen cyanide (HCN) has a mass to char equal to 27 and is a common product from the decomposition of based polyurethane materials which has been detected previously by other authors [8, 39, 42] following a similar trend to that obtained in this study. Under an He atmosphere (**Figure 9B**), this compound is detected only in the second step with a really high intensity whereas in combustion (**Figure 9D**) the emission of this product decreases significantly as a consequence of oxidation. The $m/z=28$ is associated not only with carbon monoxide (CO) but also with ethylene (C₂H₄) [43] which mean that both

compounds contribute to the peaks shown in **Figure 9B** and **Figure 9D**. For this reason, the bands detected in the second step of TG-FTIR analysis under N₂ atmosphere in the range 2870-2970 cm⁻¹ (**Figure 8C**) which are characteristic from methylene (=CH₂) groups could be responsible for the peak for m/z=28 obtained in He (**Figure 9B**) at the second degradation step. On the other hand, the presence of ion 28 in the three decomposition steps under the He:O₂=4:1 atmosphere (**Figure 9D**) agrees with the results from the TG-FTIR analysis for combustion degradation (**Figure 8D**) where not only methylene groups but also CO were detected at 629, 654 and 796 K. Finally, CO₂ (m/z=44) is the only product that is also detected at first degradation step in pyrolysis (**Figure 9B**), as has been obtained previously in the TG-FTIR analysis (**Figure 8C**) whereas under oxidative atmosphere (**Figure 9D**), this gas product presents the highest intensity, which also agrees with the results obtained in the TG-FTIR analysis (**Figure 8D**).

It is important to note that TG-MS and TG-FTIR analyses can be useful in the qualitative analysis of products evolved from the thermal degradation under different atmospheres, giving valuable complementary information from both [39].

3.4. Kinetic model

Due to the great differences in the pyrolytic and oxidative decomposition commented previously (**Figure 7**), two different models have been developed: one for pyrolysis and another for combustion, being this latter common for both oxidative atmospheres (synthetic air and N₂:O₂=9:1) but includes the effect of different partial pressures of oxygen.

3.4.1. Pyrolysis Model

A two-step kinetic model has been proposed to simulate the pyrolysis degradation of viscoelastic memory foam (**Scheme 1**). This model consists of two consecutive reactions where the initial foam is degraded in the first reaction and the products obtained are decomposed in the second one, according to TG-MS and TG-FTIR analyses. The first step could be interpreted as the break of urethane linkage producing the emission of carbon dioxide (**Figure 8C** and **Figure 9C**) and the formation of isocyanate monomers and polyol segments which are degraded at the second step [44] emitting a wide variety of gases and volatiles (**Figure 8C**).

Scheme 1. Reaction scheme for pyrolysis.

In the previous **Scheme 1**, Solid_1 is the initial solid, Volatiles_1 and Volatiles_2 are the gases and condensable volatiles evolved in the corresponding reaction and Residue_1 and Residue_2 are the solid residues formed in the decomposition. On the other hand, $v_{i\infty}$ ($i = 1, 2$) represents the yield coefficient for Volatiles_i or, in other words, the maximum kg of Volatiles_i obtained from reaction i with respect to the kg of the initial solid Solid_1 . At this point it is important to point out that, the maximum value of the yield coefficient for Volatiles in reaction 1 can range between 0 and 1. Nevertheless, in the next reaction the yield coefficient can go from 0 to the highest possible yield i.e., in this case the maximum value for $v_{2\infty}$ is $(1 - v_{1\infty})$.

The mathematical procedure followed for optimizing the kinetic constants is similar to that employed in a previous paper [8], where the concept of conversion degree for each reaction was also used. This parameter is defined as the ratio between the mass fraction

of volatiles obtained at any time during the reaction v_i and the corresponding coefficient yield $v_{i\infty}$:

$$\alpha_1 = \frac{v_1}{v_{1\infty}} \quad (1)$$

$$\alpha_2 = \frac{v_2}{v_{2\infty}} \quad (2)$$

Employing the kinetic law for solid decomposition proposed elsewhere [45], the kinetic expression for Reactions 1 and 2 can be expressed as follow:

$$\frac{d(v_1/v_{1\infty})}{dt} = \frac{d\alpha_1}{dt} = k_1(1 - \alpha_1)^{n_1} \quad (3)$$

$$\frac{d(v_2/v_{2\infty})}{dt} = \frac{d\alpha_2}{dt} = k_2(\alpha_1 - \alpha_2)^{n_2} \quad (4)$$

where k_1 and k_2 are the kinetic constants for the corresponding reaction and n_1 and n_2 are the reaction orders for reactions 1 and 2, respectively. These kinetic constants follow the Arrhenius equation, which has been widely applied to reactions involving solids [46-49]:

$$k_i = k_{i0} \exp\left(\frac{-E_i}{RT}\right) \quad i = 1, 2 \quad (5)$$

k_{i0} and E_i being the pre-exponential factor (s^{-1}) and the apparent activation energy (kJ/mol) for reaction i , respectively. The Euler method was employed to integrate the previous equations to calculate the α_i at each experimental time (also mass fraction and temperature are known for each time from the TGA analyzer) assuming 8 parameters (n_i , k_{i0} , E_i and $v_{i\infty}$ for each of two reactions). From these data, it is possible to calculate the mass fraction at each time applying equation (6).

$$w_{cal} = 1 - V_{tot} = 1 - V_1 - V_2 = 1 - \alpha_1 v_{1\infty} - \alpha_2 v_{2\infty} \quad (6)$$

All the experimental data obtained at different heating rates in both dynamic and isothermal conditions have been simultaneously correlated with the same 8 optimized

parameters minimizing the objective function, employing the optimization method of Solver function in Excel program:

$$O.F. = \sum_{m=1}^M \sum_{j=1}^J [w_{exp_{m,j}} - w_{cal_{m,j}}]^2 \quad (7)$$

M being the number of runs (3 dynamic and 3 isothermal) and J the number of points in each run (approximately 600).

The variation coefficient (VC (%)) has been calculated in order to validate the model following equation 8:

$$VC = \frac{\sqrt{\frac{O.F.}{(N-P)}}}{\overline{w_{exp}}} \times 100 \quad (8)$$

where N is the number of data, P is the number of parameters fitted and $\overline{w_{exp}}$ is the average of experimental values of mass fraction.

It is known that a great interrelation exists between the pre-exponential factor, activation energy and reaction order, so in order to decrease this fact a parameter K_i^* has been employed as suggested by Martin-Gullón et al. [50]. They proposed the optimization of this “compatible kinetic constant” K_i^* (defined in equation 9) instead of optimizing the pre-exponential factor (k_{i0}). As can be seen in equation 9, this parameter is calculated at a temperature close to that where the maximum weight loss occurs (T_{max}) and from the K_i^* , E_i and n_i optimized, the k_{i0} is calculated.

$$K_i^* = k_i (0.64)^{n_i} = \left(k_{i0} \exp\left(\frac{-E_i}{RT_{max}}\right) \right) (0.64)^{n_i} \quad (9)$$

The optimized values obtained are presented in **Table 3**. As can be seen, the pre-exponential factor and activation energy corresponding to the second reaction are higher than those obtained in the first reaction, which agrees with the trend observed by other authors from the pyrolysis of different types of polyurethane materials [8, 51, 52] but with

different values as a consequence of the great interrelation between E , k_0 and n commented previously and the type of experiments employed for the kinetic study (dynamic and isothermal in this study).

Table 3. Kinetic parameters obtained for pyrolysis model for $n_i \neq 1$ and $n_i = 1$.

	Reaction 1	Reaction 2	Reaction 1	Reaction 2
$k_{i0} (s^{-1})$	1.37×10^9	3.02×10^{14}	1.06×10^5	2.53×10^{16}
$E_i (kJ/mol)$	131.3	213.2	87.5	237.2
n_i	2.26	0.62	1.00	1.00
$v_{i\infty}$	0.284	0.635	0.284	0.635
VC (%)	0.96		1.5	

The experimental and calculated data are presented in **Figure 10A-C**. As expected, overlapping in most cases curves overlap and the small value of the variation coefficient obtained (0.96% or 1.5%) can be observed.

Figure 10A and Figure 10B show the experimental and calculated weight loss curves for the dynamic and isothermal experiments with a really good agreement in all runs. In order to understand better the kinetic model proposed, **Figure 10C** shows the contribution of each reaction in the global decomposition process. More concretely, in **Figure 10C** the experimental and calculated dV/dt curves are represented and the kinetic evolution of both reactions considered (dV_1/dt and dV_2/dt). Analyzing this Figure, can be seen that the first step starts around 530 K evolving gases and condensable volatiles from reaction 1, reaching the maximum value at 616 K. From this, the second reaction starts to degrade the residue formed in the previous step and reaches the maximum volatiles production at 688 K

Figure 10. Results from the pyrolytic model. A) Experimental and calculated data for dynamic runs at three different heating rates. B) Isothermal TG curves (experimental and calculated) at different heating rates. C) Experimental and calculated dV/dt curves together with the kinetic evolution of each consecutive reactions considered at 20 K/min (dV_i/dt).

Many authors consider that the pyrolysis of synthetic polymers follows first-order reactions [6, 20] and some of them even postulate that an n^{th} order reaction model would produce a deviation of Arrhenius parameters from the real ones [4]. In order to test this, the rest of parameters (keeping the reaction order equal to 1) have been optimized for the

two reactions. The results also show good agreement but in this case the variation coefficient reaches a value of 1.5%.

3.4.2. Combustion model

As has previously been indicated and due to the differences between the degradation under inert and oxidative atmosphere (**Figure 7**), a new model has been proposed to explain the behavior obtained at two different oxidative atmospheres. **Scheme 2** presents the model, that accounts for three consecutive reactions considering the graphs shown in **Figure 5** and **Figure 6**.

Scheme 2. Reaction scheme for combustion

The procedure followed is similar to that presented previously, but includes a new conversion factor for reaction 3 which is defined as:

$$\alpha_3 = \frac{v_3}{v_{3\infty}} \quad (10)$$

The kinetic expressions for these three oxidative reactions are defined as:

$$\frac{d(v_1/v_{1\infty})}{dt} = \frac{d\alpha_1}{dt} = k'_1(1 - \alpha_1)^{n_1} \quad (11)$$

$$\frac{d(v_i/v_{i\infty})}{dt} = \frac{d\alpha_i}{dt} = k'_i(\alpha_{i-1} - \alpha_i)^{n_i} \quad i = 2, 3 \quad (12)$$

Note that in the previous equation the kinetic constants have been defined as k'_i instead of k_i because the effect of oxygen has been included in the reaction. The pre-exponential factor has therefore been considered to consist of two terms: one Arrhenius pre-

exponential factor (k_i) and, the second, the partial pressure of oxygen raised to the power of the reaction order for oxygen (b_i):

$$k'_{oi} = k_{oi}(P_{O_2})^{b_i} \quad i = 1 \text{ to } 3 \quad (13)$$

where the partial pressure of oxygen is, approximately, 0.10 atm and 0.21 atm for atmospheres N₂:O₂=9:1 and synthetic air, respectively.

The mass fraction at any time in this case is calculated following equation 14:

$$w_{cal} = 1 - v_{tot} = 1 - \sum_i \alpha_i v_{i\infty} \quad i = 1 \text{ to } 3 \quad (14)$$

Employing the same objective function as in the pyrolysis, 15 kinetic parameters have been optimized ($3 \times n_i$, $3 \times k'_{i(N_2:O_2=9:1)}$, $3 \times k'_{i(synthetic\ air)}$, $3 \times E_i$ and $3 \times v_{i\infty}$) from the correlation of dynamic and isothermal runs at three different heating rates (12 runs). The results obtained are given in **Table 4**, and the experimental and calculated data are shown in **Figure 11** and **Figure 12**.

Table 4. Kinetic parameters obtained for combustion model.

	Reaction 1	Reaction 2	Reaction 3
$k_{i0} (s^{-1} atm^{-b_i})$	7.81×10^5	4.64×10^{10}	7.26×10^6
$E_i (kJ/mol)$	91.3	152.1	137.4
n_i	1.08	1.15	1.48
$v_{i\infty}$	0.232	0.576	0.180
b_i	0.320	0.645	0.347
VC (%)		2.3	

The second reaction presents the highest values for all kinetic parameters which was the expected trend bearing in mind that in this step is where the viscoelastic memory foam undergoes the most important degradation, losing a great amount of weight. On the other hand, the apparent activation energy for reaction 1 (E_1) obtained in the combustion model is lower than that proposed for the pyrolytic model which confirms that the presence of

oxygen in the atmosphere involves an acceleration in the decomposition as commented previously during the analysis of **Figure 7**.

Figure 11 and Figure 12 show the total agreement between the experimental and calculated curves. Both curves overlap in most cases, which is confirmed observing the variation coefficient obtained (2.3 %) that is a value relatively small taking into account that twelve different runs have been correlated with the same set of parameters.

Figure 11. Results under $N_2:O_2=9:1$ atmosphere. A) Experimental and calculated data for dynamic at different heating rates. B) Isothermal TG curves (experimental and calculated) at different heating rates. C) Experimental and calculated dV/dt curves and kinetic evolution of four consecutive reactions considered at 20 K/min (dVi/dt).

Figure 12. Results under synthetic air atmosphere. A) Experimental and calculated data for dynamic runs at different heating rates. B) Isothermal TG curves (experimental and calculated) at different heating rates. C) Experimental and calculated dV/dt curves and kinetic evolution of four consecutive reactions considered at 20 K/min (dV_i/dt).

Figure 11C and Figure 12C also show the evolution of the decomposition of the three reactions considered in the kinetic model. It can be seen that really good agreement has been obtained under both atmospheres and in both cases the degradation starts around 510 K forming Volatiles1 that reach the highest value about 615 K. The second reaction, which involves the major gases and volatiles production, starts around 580 and the

maximum peak is obtained at 670 K. Finally, at 690 K the 3rd reaction decomposes the residues obtained in the previous steps presenting a maximum around 820 K.

4. Conclusions

A thermogravimetric study on the degradation of viscoelastic memory foam has been done under several different operating conditions, such as heating rates, dynamic and isothermal experiments and atmospheres and obtaining satisfactory models were obtained to reproduce the experimental results. The products evolved during some of this runs have been analyzed by TGA-MS and TGA-FTIR obtaining similar and complementary results from both techniques.

The pyrolytic degradation consist of two main steps, the first being the break of urethane bond and the second the decomposition of the condensable phase formed in the first step producing the emission of ethers, aliphatic and aromatic hydrocarbons. On the other hand, the combustion of VMF involves at least three steps where the highest amount of products evolved was detected at a lower temperature than in pyrolytic degradation which involves an advance in the decomposition. The presence of compounds with -NH-, methyl and methylene groups or aromatic rings emitted in the last step, suggests the formation of oxidized compounds in the second step which produces a slight increase in the sample weight at the end of this step.

Different kinetic models for the pyrolysis and the oxidative degradation have been proposed to correlate the experimental data from 6 and 12 runs, respectively, obtaining an acceptable correlation for dynamic and isothermal runs performed at different heating rates. The pyrolytic model assumes that degradation of VMF consist of two consecutive

566 reactions whereas to explain the combustion and the poor oxygen combustion, three
567 consecutive reaction have been employed to accurately correlated the experimental data.

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