Investigation of the Hydrolytic Stability of Polyurethane Applied to Vehicle Suspension Components

Mateus Rigotti[*], Eveline Bischoff and Douglas Simon

Instituto Federal do Rio Grande do Sul, campus Farroupilha, 785 São Vicente, Farroupilha, Rio Grande do Sul, Brazil

Abstract: Process parameters such as temperature and humidity, as well as formulation are the key factors in the manufacture of a polymeric component through a polyurethane prepolymer. These define the reaction kinetics, bonding and the resulting chemical interactions which determine the final characteristics of the material. One of the expected skills of polyurethane, when applied to components used in contact with water, is hydrolysis resistance. Consequently this research focused on exposure of a polymerized TDI (toluene diisocyanate) polyether polyurethane to different proportions of the curing agent, MOCA (4,4'-methylene-bis), in an environment susceptible to reactions with water at 70 °C. In this case, this material is applied in the manufacture of coil spring solid axle with trailing arms and Panhard rod suspension bushings. Mechanical tests and DSC (differential scanning calorimetry), TGA (thermogravimetry) and FT-IR (Fourier transform infrared) evaluations of the samples and prepolymer are conducted for the characterization of the different formulations, showing the negative relationship of the curing agent proportion parameters with the hydrolysis resistance. Here depolymerization of urethane and ether groups, as well as lower retention of yield stress are verified. These findings can subsidize developing predictive models for performance and lifetime of polyurethanes.

Keywords: Polyurethane, prepolymer, MOCA, hydrolysis, bushing, suspension.

I. INTRODUCTION

Polyurethanes are chemically and morphologically highly adaptable, covering a broad spectrum of properties. They also have a wide field of application in paints, foams and the rigid products such as roller tires, skateboards, shoes and hammers [1-4]. Moreover, polyurethanes are used in the medical industry [5-7], except for the polymers synthesized with TDI (toluene diisocyanate) or MDI (diphenylmethane diisocyanate) due to their harmful effects on humans [6]. Yet, studies of biocompatibility are a key factor and can be used to deliver treatments where degradation is required but should be controlled [8, 9].

In the automotive industry, polyurethanes are mainly applied as elastomers in suspension components. Coil spring solid axle with trailing arms and Panhard rod suspension are employed where the working travel needs to be high due to off-road application. Military vehicles are generally designed this way in order to be adaptable, among other characteristics, in the wet environments. Polyurethane bushings, applied to trailing arms and Panhard rods, have the function of dissipating energy. Moreover, if it is in poor condition, it will affect the vehicle's handling and stability, as well as transmit noise to the occupants, therefore knowledge of the degradation mechanisms is required along with the

process control and formulation (e.g. isocyanate content). These are crucial in order to achieve the required properties, once the basic components, formulation and process parameters have been properly selected.

Polyurethane elastomers are block copolymers comprising hard and soft segments. The former are usually formed by short chains of diol and diisocyanates that affect hardness and shear strength. The interactions between these segments occur by dipole dipole and hydrogen bonds. Soft chains are mainly composed of long chains of polyester or polyether and provide flexibility and resistance at low temperatures [2, 3, 10]. Hydrolysis in hard segments is smaller compared to soft segments [2, 6].

The main reaction in the production of rigid polyurethanes has as reactants a diisocyanate, available in aliphatic or aromatic forms, a polyol and a chain extender [2, 3, 11], which have the combination of excellent mechanical properties. High abrasion resistance and chemical resistance, as well as the possibility of fabrication with different structures through variations of parameters in the manufacturing process [10] are the chief properties exhibited. The reactions cited above are shown in Figure **1** [11] in case the polyurethane is formed by a prepolymer.

For the preparation of an ideal polyurethane the reactions of formation of urea, allophanate, biuret and NCO (functional group formed by nitrogen, carbon and oxygen) with water (humidity) must be controlled. Urea

*Address correspondence to this author at the Instituto Federal do Rio Grande do Sul, campus Farroupilha, 785 São Vicente, Farroupilha, Rio Grande do Sul, Brazil; Tel/Fax: +55 54 3260 2400; E-mail: matrigotti@hotmail.com

formation may occur due to the reaction of NCO with water, just as formation of allophanate and biuret may occur at low temperatures with excess isocyanate [10]. The removal of atmospheric moisture is a crucial factor in the process to avoid formation of amines [8, 12, 13].

Figure 1: Chemical reactions for polyurethane production.

Polyurethanes can be depolymerized by eight different mechanisms, photolysis and pyrolysis, hydrolysis being among them, which results in reduced molecular weight and loss of physical and chemical properties [3, 14]. In thermoset polymers, the final molecular structure depends on the conditions of the curing reactions during the manufacturing process [2, 3]. Polyurethanes made from prepolymers are less susceptible to these circumstances because they do not have different reactions to the hydroxyls [2, 10]. However, for prepolymers, different reaction rates for NCO may affect the distribution of hard segments by differences in activation energies [2, 10, 14, 15]. Still, studies are conducted to investigate the post cure conditions and their impacts on the properties of polyurethane, naming this phenomenon as maturation [12, 13].

Figure **2** [3] shows the urethane group and its hydrolysis reactions [1, 17, 18]. Carbamic acid formed during hydrolysis is unstable, decomposing into amines upon release of CO_2. These amines react with isocyanate to form urea [3, 18, 20]. Under high temperatures urethane can depolymerize to form isocyanate and hydroxyl, thus amine formation and CO_2 release can occur by combining water with NCO

[2, 8]. For soft segments, it is accepted that depolymerization occurs by breaking the radical chain between the C-C and C-O bonds [21].

Figure 2: Chemical reactions in polyurethane hydrolysis.

However, the phase separation for polyether-based polyurethanes is higher when compared to their polyester equivalent, that is, the phase mixture is higher in polyesters than polyethers [10] and less susceptible to hydrolysis [2, 3, 22]. This is due to the strong hydrogen bonds formed between the hard and soft segments due to the high polarity of the ester group [23].

In this context, this research aims to verify the hydrolytic stability of polyurethane used in the manufacture of bushings used in the automotive industry as part of the coil spring solid axle with trailing arms and Panhard rod suspension. The Figures **3** and

Figure 3: Bushing example.

Figure 4: Schematic drawing of a coil spring solid axle with trailing arms and Panhard rod suspension, the applied bushings are highlighted in red.

4 show an example of an applied bushing and a schematic drawing of this type of suspension, respectively.

II. MATERIALS AND METHODS

Materials

For this research, the material used was thermofixed polyurethane (PU), polyether base, TDI with 90-95 Shore A hardness, and cured with 4,4'-methylene-bis, known as MOCA, which has 6.1% free NCO.

Preparation

Three different formulations were tested which varied the relationship between MOCA: prepolymer. The 1:1 ratio refers to the ratio indicated in the data sheet and 0.85:1 and 1.2:1 refers to the smaller and higher proportion of curing agent, respectively. The other process conditions were conducted according to the manufacturer's guidelines as follows: temperature of ADIPRENE LF-950A 66 °C, MOCA 116 °C and 100 °C mold as well as pot lifetime 7 min, cure 25 min at 100 °C and post cure 16 min at 100 °C.

The preparation of the specimens, dimensions according to ASTM D638, was through the homogenization of the components (prepolymer and curing agent, MOCA) by manual shaking and subsequent casting. Figure **5** is the mold used (steel SAE1020), which was placed in a glass base for the casting of the material.
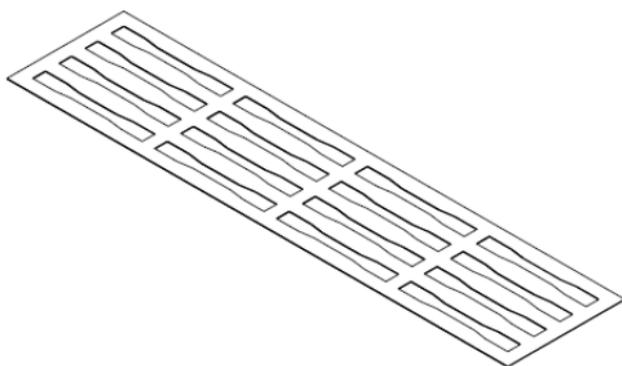
Figure 5: Mold used for sample manufacture.

The nomenclature for the prepared samples is presented in Table **1**, which identifies the MOCA: prepolymer ratio and the letters p and h, which indicate the samples kept in the natural environment and those subjected to hydrolysis, respectively.

Table 1:   Samples Evaluated

Sample identification	
PUp1	PUh1
PUp0.85	PUh0.85
PUp1.2	PUh1.2

Description

Fourier Transform Infrared (FT-IR) analyzes, 400–4000 cm^{-1}, were conducted to observe changes in chemical bonding [20, 24, 25] on a PerkinElmer FT-IR Spectrometer Frontier device. For comparative evaluation of the peak intensities evaluated they are compared with the peak intensity of aliphatic CH_2 stretching vibration (2920 to 2850 cm^{-1}) according to Equation 1. Then, this ratio of areas, for each band studied, is compared with their respective pair, i.e. the material of the same chemical composition preserved and hydrolyzed.

$$\%R = \frac{I_S - I_{ref}}{I_{ref}} \times 100\% \tag{1}$$

Where:

%R is the areas ratio

I_S is the integral of the peak area for the evaluated sample

I_{ref} is the integral of the peak area for CH_2 of the evaluated sample

The bands evaluated are shown in Table **2**.

Table 2:   Rating Bands

Component	Vibration group	Frequency band (cm^{-1})
Isocyanate	NCO	2250-2270
Urethane	C=O	1650-1765
Ether	C-O-C	1100

The samples were immersed in water at 70 ºC for 168h (1 week) and subsequently submitted to desorption in an oven at 50 ºC. During the desorption process the sample masses were periodically recorded until they reached constant mass as defined in Equation 2:

$$m = \frac{m_t - m_o}{m_o} \times 100\% \tag{2}$$

Where:

m_t is the mass in the given time

m_o is the initial mass

The thermal stability of the samples were analyzed by thermogravimetry (TGA) on a PerkinElmer TGA4000 equipment. The samples were heated from 30 to 900 ºC at a rate of 10 °C/min under a nitrogen atmosphere. In addition, the respective derivatives of TGA curves for decomposition temperature evaluation are calculated, thus obtaining the DTG (differential thermogravimetry) curves.

In addition, DSC (differential scanning calorimetry) analysis was conducted to determine phase transformation and glass transition temperatures using a PerkinElmer DSC6000 device. The samples were heated from 30 to 400 ºC (isotherm for 10 minutes) and cooled to -70 °C with a heating and cooling rate of 20 °C/min under a nitrogen atmosphere. The measurements were performed in the first cooling and in the second heating cycle.

Hardness (ASTM D2240) and tensile (ASTM D638) tests were conducted to characterize the mechanical properties. The latter test was performed with EMIC DL2000 equipment, which is the most suitable to correlate hydrolysis resistance with different samples [16, 23, 27, 28]. Also, analysis of variation in yield stress results, conducted through the ANOVA (Analysis of Variance) method, were performed to verify the causes of variation and interaction between them.

III. RESULTS

After the hydrolysis and drying process (17h at 50 ºC) the samples reached constant mass, with approximate reduction of 0.8% by mass, as can be seen in Figure **6**.
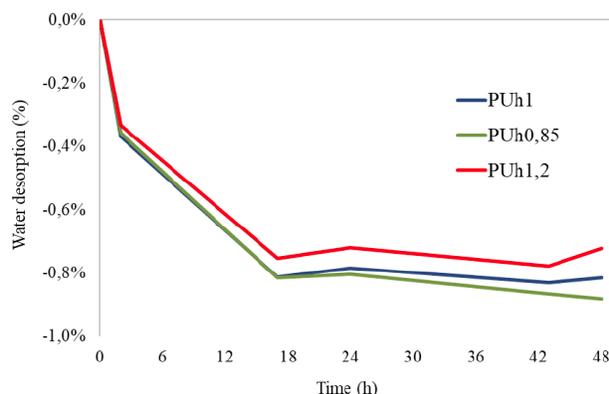
Figure 6: Water desorption.

However, the process was monitored for 48h to evaluate the stability of the result. It can be observed that PUh1.2 samples show a slightly smaller reduction and slightly larger PUh0.85 when compared to the reference. This assessment indicates the presence of higher water desorption points for higher prepolymer concentrations.

Hydrolysis assays performed at 70 °C are suitable to avoid interference by biological degradation - found at room temperature, and because the samples are immersed, it prevents oxidation [28, 29]. However, high temperatures, such as 100 and 120 °C, are severe conditions for polyurethanes to deteriorate, both polyester and polyether based [17, 24, 25, 30]. Also, tests conducted at 50 to 100 ºC correlate the life span of polyurethane with samples immersed in the sea at temperatures of 9 to 20 ºC [17]. In this case, the authors also compare the mechanical properties with and without the water desorption process.

All excess NCO was consumed [23]. Also, there was no depolymerization of the samples in NCO after hydrolysis. The pre-polymer and sample spectrometries (Figure **7**) demonstrate the existence of NCO by the presence of the peak at 2270 cm^{-1} [2, 11, 12] and no residue of this range in the final polyurethanes, respectively. Therefore, it is not necessary in this case to assess the ratio of areas by integration.
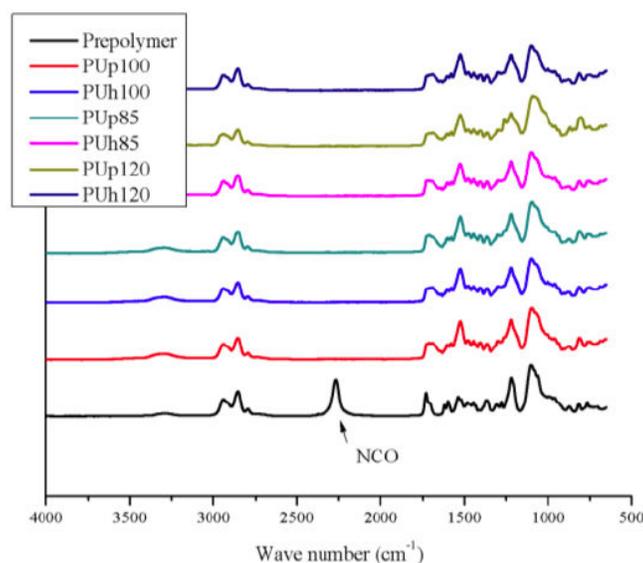
**Figure 7:** FT-IR all samples and prepolymer.

Figure **8** shows that the spectrum in the C-O region of elongated vibrations, peak intensity of 1100 cm^{-1}, attributed to ether group (C-O-C) vibrations, was

drastically reduced, regardless of the proportion used. In addition, there was a reduction in the 1080 cm^{-1} peak, attributed to the stretching of urethane group [5], also for hydrolyzed samples. The ether bond is very resistant to hydrolysis, occurring only under special conditions, and under normal conditions the dominant hydrolytic degradation is the rupture of the urethane group [29].
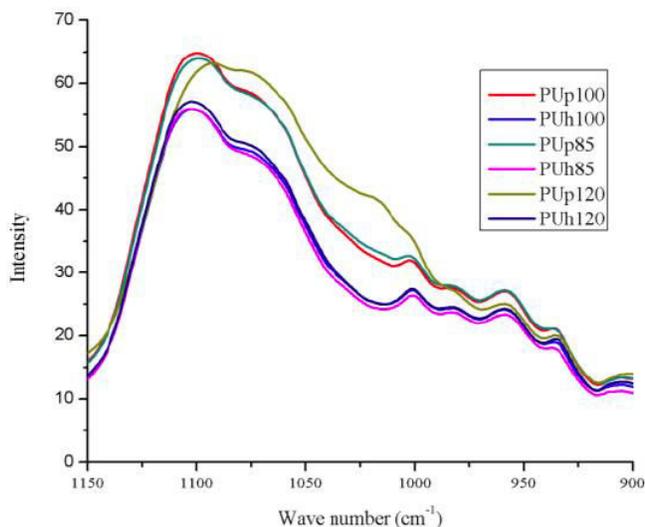
Figure 8: FT-IR, Ether band 1100cm^{-1} and Urethane group 1080cm^{-1}.

In the spectrum of the three hydrolyzed groups, when compared to the base material, PUp1, and the respective preserved materials, there is a reduction in the peaks of C = O, 1700-1730 cm^{-1}, as shown in Figure **9**.
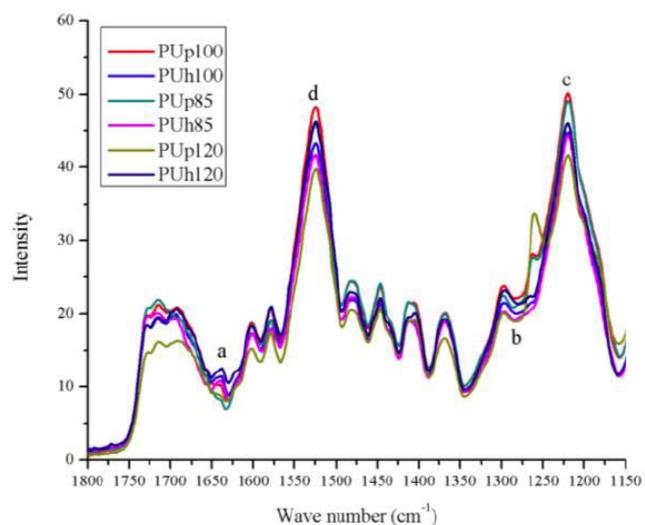
Figure 9: FT-IR, 1150 a 1800cm^{-1}.

In addition, there is a peak at 1638 cm^{-1} (a) indicating amine formation (1580-1650 cm^{-1}) [3] or formation of urea groups, C=O bonds, 1640-1710 cm^{-1} [2, 13, 31]. There was also a significant reduction in the 1265 cm^{-1} range (b), characterized by the C-O bond in the carbonyl group, 1210-1320 cm^{-1}, as well as the reduction in the 1220 cm^{-1} (c), amide III, and 1530 cm^{-1} (d), amide II [2, 25].

In addition, from Figure **10**, some changes in the N-H, 3310-3340 cm^{-1}, urethane group bonds can be observed [2, 13, 31].
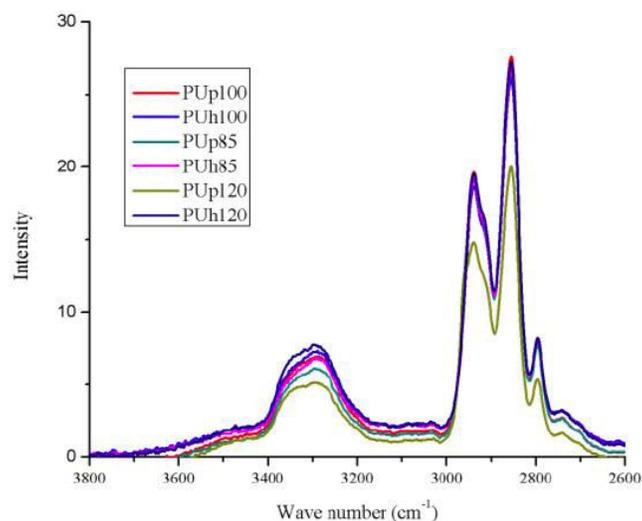
Figure 10: FT-IR, 2600 a 3800cm^{-1}.

Table **3** shows the relationship of areas in the ranges mentioned in Table **2** by comparing PUh with PUp for each formulation. All samples show a reduction in the urethane and ether group ranges, but the 1:1 formulation is the most stable, which is directly related to the retention of mechanical properties.

**Table 3:   List of Areas in the Assessment Peaks**

Vibration group	PUp 100	PUh 100	PUp 85	PUh 85	PUp 120	PUh 120
C=O	-12%		-50%		-60%	
C-O-C	-19%		-28%		-92%	

Regarding the hardness, it can be seen, according to Figure **11**, that the material with 1:1 ratio, PU1, besides reaching the desired parameter, 95 Shore A hardness, presents identical stability and averages, even after being subjected to the cited conditions. PU1.2 has the same hardness average, around 88.4 Shore A, in preserved and hydrolyzed samples. On the other hand, PU0.85 samples increased from 88.0 to 94.2 Shore A after dipping and drying.
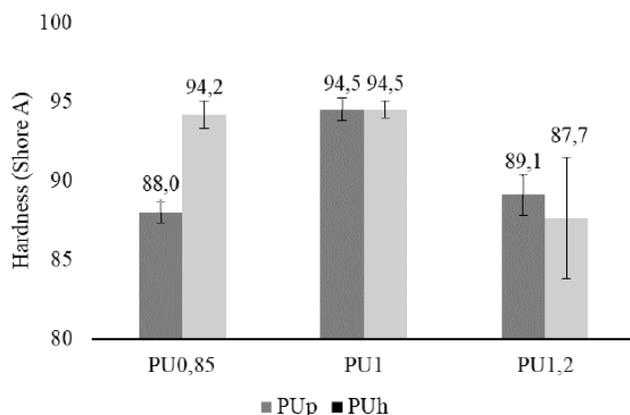
Figure 11: Hardness (Shore A).

Regarding the tensile test, regarding the yield stress, it is verified that the reference material, sample PUp1:1, had a small reduction in the yield stress (Figure **12**), however, the two averages can be considered statistically equal, however, for the other two situations the reduction in this resistance property is observed, showing changes in its chemical bonds, due to the hydrolysis process. Thus, a retention of 91% of the yield stress for the PU1 samples after hydrolysis and only 81 and 75% for the PU0.85 and PU1.2 samples, respectively.
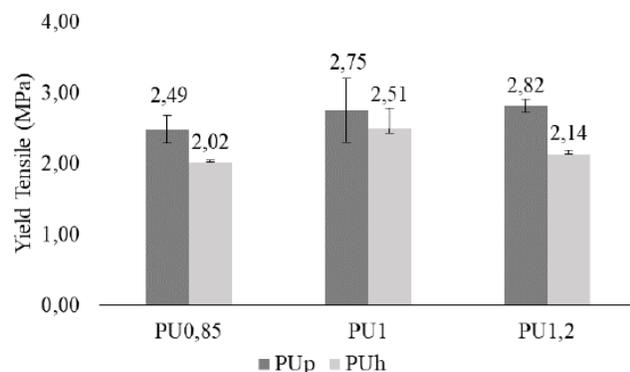
Figure 12: Yield stress (MPa) a 0,5%.

As reported in the literature, the post cure process can be very intense in the presence of excess NCO and also be influenced by the presence of atmospheric moisture. Such conditions may lead to increased cure time, as well as the formation of groups of urea and allophanate, and, consequently, lead to adverse effects on mechanical properties, as shown for the polyurethanes studied [23]. Corroborating with the above, it can have the plasticizing effect [8, 20, 29] which reflects in the fall of the rupture stress and the increase of the elongation, however, in tests conducted for comparison of three different polyurethanes (polyether base) exposed to the marine environment, it

was found that the tensile strength and elongation parameters were maintained [26].

With a 95% confidence interval, the analysis of variation (ANOVA) shows that the curing agent: prepolymer ratio and hydrolysis process influence the yield strength, with p-values of 0.043 and 0.004, respectively, but have no interaction between these variables, resulting in a p-value of 0.327 for the interaction.

The thermal stability of the samples was analyzed by thermogravimetry. The characteristic temperatures of $T_{10\%}$, $\%m_{450°C}$, T_1, T_2 and T_f, which correspond respectively to the temperatures in which 10% mass decomposition occurs, mass remaining at 450 °C, hard segment degradation temperature, soft segment degradation temperature and final degradation temperature. These results are presented in Table **4**.

Studies show that 10% mass loss for the evaluated polyurethanes occurs from approximately 297 to 334 °C, and these differences are attributed to the different polyols used [32]. However, a lower temperature is observed at the beginning of the process for PUp1.2, and a smaller thermal degradation process occurs with PUp1 samples, resulting in a higher mass percentage at 450°C than the other samples, as shown in Table **4**, column $\%m_{450\ °C}$.

In relation to $T_{10\%}$, the thermal stability was reduced for samples prepared with different MOCA proportions, being 10 and 15 °C for PUp0.85 and PUp1.2 proportions, respectively. This reduction may be associated with a lower proportion of polymer in the sample.

The initial temperature of thermal degradation is attributed to the amount of existing soft segments, i.e. polyurethanes with higher concentration of these segments demonstrate a lower initial mass loss and a higher onset temperature. As shown, the initial temperature can be as low as 100 °C for 100% hard segmented polyurethane and range from 220 to 280 °C, depending on the concentration of the soft segments and their length [33].

It can also be seen from Table **4** that PU1 loses mass after degradation at 450 °C, while PU0.85 and PU1.2 gain, showing that hydrolysis significantly affects chemical bonds when the ratio is not optimum. In addition, the thermal stability at 10% ($T_{10\%}$) is lower for PU1.2 than PU0.85.

Table 4: TGA Results

Samples	$T_{10\%}$	$\%m_{450°C}$	T_1	T_2	T_f
PUp1	307.8	15.6	306.0	377.1	416.0
PUh1	304.5	10.5	315.0	382.0	419.2
PUp0.85	298.0	8.1	310.5	386.2	410.6
PUh0.85	298.5	12.3	312.4	387.0	415.8
PUp1.2	293.5	8.6	304.6	380.3	416.0
PUh1.2	297.9	11.0	301.2	371.5	404.6

$T_{10\%}$(°C): temperature with 10% mass loss, $\%m_{450°C}$: mass remaining at 450 °C, T_1(°C): degradation temperature of hard segments, T_2(°C): degradation temperature of soft segments and T_f(°C): final degradation temperature.

Analyzing the TGA and DTG curves, Figures **13** and **14**, respectively, show that the thermal decomposition follows the same degradation pattern (3 stages) for all evaluated situations: samples with different process variations and hydrolyzed or preserved.
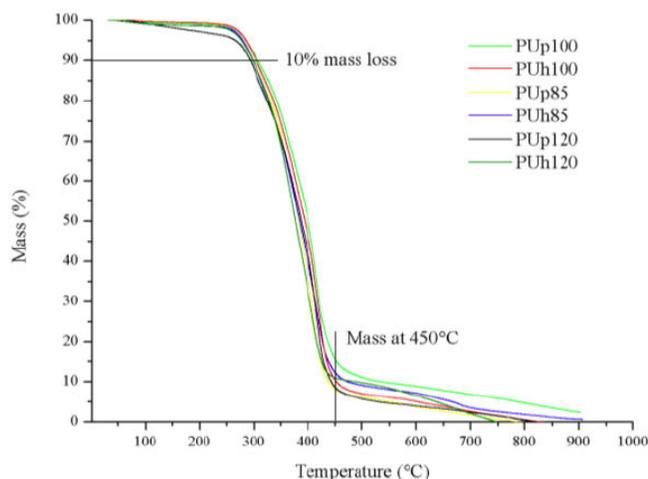
Figure 13: Thermogravimetry.
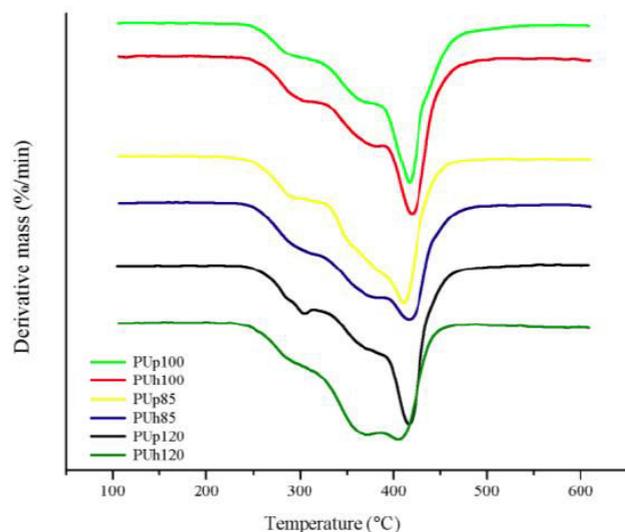
Figure 14: Derivative mass.

The degradation range of 330 °C is related to the degradation of hard segments, such as urethane. The degradation range of 390 °C is attributed to the decomposition of ether bonds, according to research carried out on polyurethane foams [34]. According to TGA studies, segmented polyurethanes usually have two degradation stages, plus the final stage, with increasing temperature [32, 33]. The former usually occurs above 250 °C due to thermolysis of urethane bonds, hard segments [23]. And the second stage of degradation is due to the decomposition of macrodiol components [22]. According to tests carried out with various polyurethanes from prepolymers, two characteristic peaks in the DTG curves can be found, between 260 and 420 °C and between 360 and 440 °C, additionally DTA (differential thermal analysis) results demonstrate that both are considered endothermic reactions. The maximum temperature for the first reaction is due to the destruction of the urethane group, while the second is probably caused by the destruction of the ether bonds [35].

Ratifying the above, FT-IR evaluations were performed on different samples of polyurethanes degraded at 300 °C, demonstrating the reduction of absorbance in the characteristic urethane peaks. They also showed, through the DTA peaks, that the process is endothermic, initially attributed to the diol and diamine volatilization, which are produced in the decomposition of the urethane group. The study further demonstrates that a higher thermal stability correlates with a higher degree of phase separation, however, in case of a degradation in nitrogen atmosphere, a higher phase mixture favors the thermal stability at high temperatures after the dissociation of the hydrogen bonding in urethane [32].

Finally, we have the DSC analysis for the three preserved and hydrolyzed PU1, PU0.85 and PU1.2 sample sets. Table **5** shows the comparison of

materials PU1, PU0.85 and PU1.2 with regard to glass transition temperatures (Tg), as well as the melting temperatures of hard segments (Tf_1) and soft segments (Tf_2).

Table 5:　DSC Results

Samples	Tg	Tf_1	Tf_2
PUp1	-56.0	208.7	294.6
PUh1	-56.4	209.0	294.3
PUp0.85	-50.3	207.1	315.3
PUh0.85	-55.3	206.4	304.3
PUp1.2	-50.0	218.1	319.9
PUh1.2	-42.4	213.1	305.3

Tg (°C): glass transition temperature, Tf_1 (°C): melting temperature 1 and Tf_2 (°C): melting temperature 2.

Evaluating the PU1 material it is observed that the glass transition temperatures of the two samples are identical, as well as the temperatures of the two endothermic processes Tf_1 and Tf_2, approximately 209 and 294 °C, respectively. This result indicates that the hydrolysis process is not favoring the formation of new chemical bonds between the two segments. According to the observed values for $\%m_{450°C}$ (Table **4**), the hydrolysis process presented mass loss for only this sample.

Glass transition temperatures (Tg) between -65 and -48 °C are reported in the literature as the glass transition temperatures of the soft segments of the evaluated polyurethanes, where lower temperatures are attributed to the higher polyol molar masses due to the strengthening of the end of the polyol chain in the soft segment by chemical bonding to the hard urethane blocks [35]. Also, the authors attribute the decrease in Tg with the increase in the length of the urethane segment, verified in polyurethanes produced from prepolymers. Additionally, temperatures between -41 and 35 °C are attributed to the amorphous phase relaxation, this glass transition temperature is usually accompanied by an endothermic peak related to the relaxation of the crystalline part. However, this phenomenon was not observed in this research, just as only a few of the polymers studied by the authors demonstrated a third glass transition temperature, which is attributed to the hard segments [35].

Polyurethane transition temperatures are directly related to the degree of segregation between the hard and soft segments. The short soft segments may dissolve in the soft micro phase if their length is less than the critical length for the separation of the micro phase. This dissolution process increases the glass transition temperature of the soft micro phase and decreases the material's response to low temperatures [23].

For PU0.85 samples, there is an increase in the second stage degradation temperature (Tf_2), especially in the preserved sample which is 315.3 °C, however, the first stage degradation temperature (Tf_1) is on the same level as compared to PU1 samples. Glass transition temperatures differ from -50.3 to -55.3 °C for preserved and hydrolyzed samples, respectively.

For PU1.2 samples the glass transition temperatures are changed in relation to PU1 samples, especially for the hydrolyzed material, -42.4 °C, as well as the two melting temperatures that are higher when compared to the other studied materials, mainly in relation to the preserved material PU1.2 that reaches levels of 218 and 320 °C for both degradations.

IV. CONCLUSION

The change in the proportion of MOCA has a direct influence on the material's resistance to hydrolysis, which can be verified by the reduction of the yield stress, however, even before the material is submitted to the medium (immersion in water for 168h at 70 °C), the mechanical properties are different. From this, it is proposed that hydrolysis occurs in the hard segments, urethane group, by the chemical changes observed through FT-IR analysis and in the soft segments by the reduction of yield stress and by the changes in chemical bonds.

In the case of PU1.2 material, it is understood that excess diamine catalyzing hydrolysis and, in the case of PU0.85, excess NCO are the main causes of reduction of yield stress when samples are hydrolyzed. The possible depolymerization of the urethane group, when surrounded by soft segments in NCO and hydroxyl, by the reaction of NCO with water and formation of secondary bonds, was not observed in this research.

Therefore, for all cases, even with PU1 material, hydrolysis occurs, as demonstrated by FT-IR analyzes, mainly in the ether structure and, to a lesser extent, in urethane structures, however, PU1 samples are the only ones that maintained mechanical and thermal properties of the material analyzed.

Finally, the alterations of the indicated proportions are detrimental to the application of the evaluated material under the defined boundary conditions, being demonstrated by the reduction of the yield stresses.

ACKNOWLEDGMENTS

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