

Manuscript Details

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Title	Study of waterborne polyurethane materials under aging treatments. Effect of the soft segment length
Short title	Waterborne polyurethane aging vs. polyol segment
Article type	Research Paper

Abstract

Coatings made of waterborne polyurethane dispersions are a promising alternative to solvent-borne ones but their mechanical and thermal properties under harsh outdoor conditions such as high temperature and humidity are somewhat limited. In this work saturated polyesters (PBA) with different molecular weights (800-2600 g/mol) were synthesized by reacting adipic acid with 1,4 butanediol. These polyols, an internal emulsifier, and an aliphatic diisocyanate were used as raw materials to synthesize polyurethane (PU) aqueous dispersions with solids contents of 29-38 wt.%. The increase of the molecular weight of the polyol decreased the mean particle size of the PU dispersions from 308 to 78 nm. Polyurethane (PU) films were obtained by water evaporation of the PU dispersions and they were annealed at 80 °C for 2 hours. Accelerated aging studies were performed by submerging the PU films in the water at 80 °C for 2 hours. The PU films synthesized with the polyols with lower molecular weight exhibited enhanced phase miscibility, giving place to storage and loss moduli of similar magnitudes in a wide temperature range and they were less susceptible to hydrolytic degradation. Microphase miscibility was favored when larger polyols are used. Contact angle measurement and cross-hatch adhesion test on PU coatings placed on stainless steel plate, before and after annealing and water aging were carried out. All PU coatings retained the adhesion to the substrate after aging, the PU coatings synthesized with shorter polyols exhibited enhanced adhesion.

Keywords	Polyurethane-urea dispersion; saturated polyester polyols; molecular weight; microphase miscibility; accelerated aging; cross-hatch adhesion;
Corresponding Author	Víctor H Orozco
Corresponding Author's Institution	Universidad de Antioquia
Order of Authors	Anny Catalina Ospina, Víctor H Orozco, Luis Fernando Giraldo, Jose Miguel Martin-Martinez, Mónica Fuensanta Soriano, Noemi Mateo-Oliveras
Suggested reviewers	Haley Hagg, Veronika Kozlovskaya, Thein Kyu

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August 2019

Editorial Department of Progress in Organic Coatings

Dear Editor of Progress in Organic Coatings,

I am submitting this manuscript for consideration of publication in Progress in Organic Coatings. The manuscript is entitled “*Study of waterborne polyurethane materials under aging treatments. Effect of the soft segment length*”.

It has not been published elsewhere and it has not been submitted simultaneously for publication elsewhere.

In this work, saturated polyesters with different molecular weights were synthesized and were included in a polyurethane chain dispersed in water. It was found that the larger polyol influences the decreasing of the mean particle size of the dispersions.

Polyurethane films with different soft segment lengths were obtained from dispersions and their behavior after submerging the films in the water at 80 °C were reported by first time in this work.

Microphase miscibility was favored when shorter polyols were used. They presented a wide temperature range in which the material exposed a gel behavior and they were less susceptible to hydrolytic degradation.

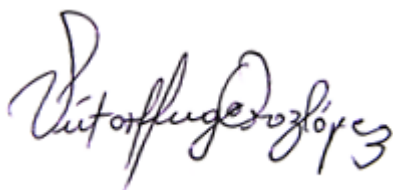
Additionally, the adhesive behavior of the materials was tested, it was founded that all PU based coatings retained the adhesion to the substrate after aging.

The more segmented materials, which were synthesized with the largest polyols, showed strong hydrolysis of the soft segments when they were submitted to water aging treatments, but they withstood heat treatment in an improved way than polyurethanes obtained from shorter length polyols which showed less microphase segmentation.

According to the results obtained in this study, the polyurethane dispersions obtained with short polyols are highly promising coatings for metallic surfaces under high humidity conditions.

Thank you very much for your consideration.

Yours Sincerely,



Prof. Víctor Hugo Orozco
Universidad de Antioquia
Laboratorio de Investigación en Polímeros
Bloque 2, Laboratorio 2-303
Tel.: +57 3174370257
E-mail: hugo.orozco@udea.edu.co,

Authors:

Anny C. Ospina¹

Víctor H. Orozco^{1*}

Luis F. Giraldo¹,

José Miguel Martín-Martínez²

¹ *Laboratorio de Investigación en Polímeros, Instituto de Química, Universidad de Antioquia, 050010 Medellín, Colombia*

² *Adhesion and Adhesives Laboratory, University of Alicante, 03080 Alicante, Spain*

Highlights

- By using polyester with high molecular weight induces crystallization of the polyurethane films.
- By using shorter polyols, improved resistance to aging conditions was found.
- All polyurethane coatings retained the adhesion to the substrate after aging.
- The studied systems are promising coatings for metallic surfaces under high humidity conditions.

Corresponding author:

Víctor Hugo Orozco: Laboratorio de Investigación en Polímeros, Instituto de Química, Universidad de Antioquia, 050010 Medellín, Colombia – Phone no. +57 3174370257; e-mail: hugo.orozco@udea.edu.co

Keywords: Polyurethane-urea dispersion, saturated polyester polyols, molecular weight, microphase miscibility, accelerated aging, cross-hatch adhesion.

September, 2019

Editorial Department of Progress in Organic Coatings

Dear Editor of Progress in Organic Coatings,

I am submitting the reviewed version by Anny C. Ospina, Luis F. Giraldo Mónica Fuensanta, José Miguel Martín-Martínez, Noemi Mateo-Oliveras and myself of the entitled manuscript “*Study of waterborne polyurethane materials under aging treatments. Effect of the soft segment length*”.

In this corrected version we have checked the reference format of the journal as the reviewer suggested.

Reference [1] and [26] were updated according to the citation format, there were not included pages number because the whole books were information sources for the preparation of the manuscript, we did not use specific sections.

In addition, we have taken advance of the revision in order to strengthen the discussion of the rheologic behavior in the temperature sweep. In page 14 we have written from line 6 to 27:

- “*Briefly, there is a crossover point ($G'=G''$) where the viscoelastic behavior changes from a mainly solid, liquid-like ($G'>G''$) to an elastic liquid-like behavior ($G''>G'$). This crossover point represents the melting temperature of the crystalline domains, or their crystallization temperature [26,27]. The temperature and moduli at which this crossover occurs are similar in all the samples, hence the rheological properties of the melt polyurethane films are not significantly affected by the differences in the molecular weight of the used polyol, in the worked range. In addition, these temperatures are similar to the melting temperatures of the polyols obtained by DSC presented in **Error! Reference source not found.***

*It is worth to mention that the PU made with the shortest polyol presents their crystallization temperature in a wider range (30-60°C), where their storage and loss moduli have similar magnitude, as it can be seen in **Error! Reference source not found.** Since the soft segments are related to the viscous moduli and the hard segments to the elastic moduli, it is an indication that the sample with the shortest molecular weight presents lower ordered crystalline segments, in smaller proportion and more dispersed, that is, it has a greater miscibility of phases compared to the materials obtained with longer soft segments.*

This characteristic can lead to gel-like behaviors with tacky properties because it has values of $\tan \delta$ close to the unit in a considerable range at room temperature, which can be very useful when you want to design materials with potential use as pressure-sensitive adhesives.[27]

instead of:

- *“Briefly, there is a crossover point ($G'=G''$) where the viscoelastic behavior changes from a mainly viscous, liquid-like ($G''>G'$) to an elastic solid-like behavior ($G'>G''$). This crossover point is also called the gel point [26,27]. The temperature and moduli at which this crossover occurs are similar in all the samples, hence the rheological properties of the melt polyurethane films are not significantly affected by the differences in the molecular weight of the used polyol, in the worked range. It is worth to mention that the PU made with the shortest polyol has a gel range instead of gel point, it means, both moduli crosses in a temperature range, as it can be seen in **Error! Reference source not found.**, i.e. the storage modulus has similar magnitude than the loss modulus from 30 to 60 °C. Since the soft segments are related to the viscous moduli and the hard segments to the elastic moduli, it is an indication that the sample with the shortest molecular weight presents the highest miscibility between hard and soft segments. It would be useful for designing materials as pressure-sensitive adhesives since they would present gel behavior in a wide range of temperatures[27]*

Besides, in the conclusions section it was added:

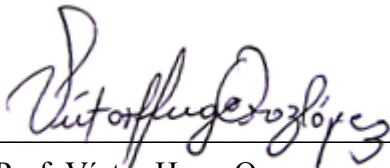
- *“In addition, the poorly segmented polyurethane exposes a wide temperature range in which the material presents its melting.”*

instead of

“In addition, the poorly segmented polyurethane exposes a wide temperature range in which the material exposes gel behavior”

Thank you very much for your consideration.

Yours Sincerely,



Prof. Víctor Hugo Orozco

Universidad de Antioquia

Laboratorio de Investigación en Polímeros

Bloque 2, Laboratorio 2-303

Tel.: +57 3174370257

E-mail: hugo.orozco@udea.edu.co,

Authors:

Anny C. Ospina¹

Víctor H. Orozco^{1*}

Luis F. Giraldo¹

José Miguel Martín-Martínez²

¹ *Laboratorio de Investigación en Polímeros, Instituto de Química, Universidad de Antioquia, 050010 Medellín, Colombia*

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- By using polyester with high molecular weight induces crystallization of the polyurethane films.
- By using shorter polyols, improved resistance to aging conditions was found.
- All polyurethane coatings retained the adhesion to the substrate after aging.
- The studied systems are promising coatings for metallic surfaces under high humidity conditions.

Corresponding author:

Víctor Hugo Orozco: Laboratorio de Investigación en Polímeros, Instituto de Química, Universidad de Antioquia, 050010 Medellín, Colombia – Phone no. +57 3174370257; e-mail: hugo.orozco@udea.edu.co

Keywords: Polyurethane-urea dispersion, saturated polyester polyols, molecular weight, microphase miscibility, accelerated aging, cross-hatch adhesion.

1 **Study of waterborne polyurethane materials under aging**
2 **treatments. Effect of the soft segment length.**

3
4
5 **ABSTRACT**

6
7 Coatings made of waterborne polyurethane dispersions are a promising alternative
8 to solvent-borne ones but their mechanical and thermal properties under harsh
9 outdoor conditions such as high temperature and humidity are somewhat limited. In
10 this work saturated polyesters (PBA) with different molecular weights (800-2600
11 g/mol) were synthesized by reacting adipic acid with 1,4 butanediol. These polyols,
12 an internal emulsifier, and an aliphatic diisocyanate were used as raw materials to
13 synthesize polyurethane (PU) aqueous dispersions with solids contents of 29-38 wt%.
14 The increase of the molecular weight of the polyol decreased the mean particle size
15 of the PU dispersions from 308 to 78 nm.

16
17 Polyurethane (PU) films were obtained by water evaporation of the PU dispersions
18 and they were annealed at 80 °C for 2 hours. Accelerated aging studies were
19 performed by submerging the PU films in the water at 80 °C for 2 hours. The PU films
20 synthesized with the polyols with lower molecular weight exhibited enhanced phase
21 miscibility, giving place to storage and loss moduli of similar magnitudes in a wide
22 temperature range and they were less susceptible to hydrolytic degradation.
23 Microphase miscibility was favored when shorter polyols are used. Contact angle
24 measurement and cross-hatch adhesion test on PU coatings placed on stainless steel
25 plate, before and after annealing and water aging were carried out. All PU coatings
26 retained the adhesion to the substrate after aging, the PU coatings synthesized with
27 shorter polyols exhibited enhanced adhesion.

28
29 **Keywords.** Polyurethane-urea dispersion, saturated polyester polyols, molecular
30 weight, microphase miscibility, accelerated aging, cross-hatch adhesion.

31
32 **INTRODUCTION**

33
34 Polyurethanes (PUs) are versatile polymers because of their wide range of physical,
35 chemical, and mechanical properties, and their suitable performance and durability.
36 The PUs are widely used in furniture, construction, packaging, footwear, bedding,
37 paints, sealants, coatings and adhesives industries, among others [1]. In most of these
38 applications, good adhesion of the PUs is an essential property, particularly for
39 coatings in which high abrasion resistance, good hardness, elastomeric properties
40 and high flexibility at low temperature are important [2].

1
2 Waterborne polyurethane dispersions are emerging in the adhesives and coatings
3 industry because of the need of replacing the solvent-borne polyurethanes that
4 contain volatile organic compounds (VOC's), owing to the currently stricter
5 environmental legislation. In fact, the European Parliament has demanded the
6 compulsory reduction in the use of VOCs (Directive 2004/42/CE) especially in paints,
7 varnishes, and adhesives [3,4]. One way to fulfill this requirement is the use of
8 waterborne dispersions as raw materials for adhesives and coatings formulation.
9 Furthermore, it has been demonstrated that the performance of waterborne
10 dispersions as coatings or adhesives is similar or even better than the one of the
11 solvent-borne formulations [5–7].

12
13 PUs exhibit structure-property relationship and therefore, their properties, including
14 adhesion, can be designed and modulated by selecting the adequate composition
15 and method of synthesis. The properties of the waterborne polyurethane dispersions
16 are determined by the method and conditions of synthesis [4] but mainly by the
17 nature and molecular weight of the raw materials (polyol, isocyanate, chain extender,
18 etc), the amount and distribution of hard to soft segments [8,9], and the pendant
19 group in the internal emulsifier, among other. On the other hand, the glass transition
20 temperature (T_g) and phase miscibility of the polyurethanes are affected by the
21 molecular weight and the hard segment content of the polyurethane [10,11].

22
23 Resistance against environmental agents such as humidity and high temperature is
24 important in coatings because their degradation may cause unwanted alterations in
25 adhesion and mechanical properties. The water absorption on to polymer bulk
26 affects the glass transition temperature in certain polymers [12,13] leading to
27 plasticization [14]. Furthermore, the formation of hydrogen bonding between
28 absorbed water and soft or hard segment domain in PUs may contribute to
29 deterioration and aging [15], these also depend on the hard to soft segments ratio,
30 and the shape, size and distribution of the crystalline domains. The influence of the
31 percentage of amorphous domains, and the intramolecular and intermolecular
32 hydrogen bonds on the thermal and mechanical properties, on the aging resistance
33 and the extent of retained water, and on shape memory functionality of PUs have
34 been studied elsewhere [8], [14]. The increase of the amorphous domains promotes
35 water sorption due to easier penetration into the internal structure of the polymeric
36 chains, i.e., the hard segment domains act as a tortuous path for the diffusion of
37 water into the PU bulk. On the other hand, it has been demonstrated [15] that the
38 hydrolytic degradation shortens the soft segment chains, reduce the molecular
39 weight, and affect the hydrogen bond interactions in the PUs, all of which cause a
40 deterioration of their properties [15].

1
2 Pretsch et al. [14] have proposed a degradation model for poly (ester urethane) aged
3 in hot water for 21 days. Initially, there is an induction step (0-2 days) in which the
4 water diffuses into the hard and soft segments, the latter one seems to be hydrolyzed
5 in a reversible way but the hard segments are not affected; the induction step lead
6 to reduced moduli but the elongation at yield and the shape memory functionality
7 remain unaffected. On the other hand, the extent of hydrolytic degradation increased
8 by increasing the water sorption and when less crystalline was the polyurethane
9 backbone [14]. Furthermore, the solid PU coatings obtained from waterborne
10 polyurethane dispersions may contain some retained water into the structure owing
11 to the residual water or humidity of the environment, PUs made with polyester polyol
12 can absorb water in the bulk which accumulates between the interstices of the
13 polymeric chains.

14
15 A current challenge in the industry is to develop coatings and adhesives with
16 excellent stability to high relative humidity and temperature while their VOC contents
17 are reduced. Changing the hard to soft segment ratio is possible to understand the
18 characteristics that improve the aging resistance of the films. Therefore, in this study,
19 aqueous polyurethane dispersions were obtained by using DMPA internal emulsifier,
20 IPDI diisocyanate and poly (1,4 butylene adipate) - PBA- polyols of different
21 molecular weights. Their structure and adhesion properties before and after
22 accelerated aging by immersion in water at 80 °C for 2 hours have been studied.

23

24

EXPERIMENTAL

Materials

Adipic acid of 99.8% purity (BASF, Bogotá, Colombia), 1,4 butanediol of 99% purity (Sigma Aldrich, Bogotá, Colombia), and butyl stannic acid of 95% purity (FASCAT 4100, Arkema, Colombes, France) were used for the synthesis of the new polyester polyols.

Dimethylolpropionic acid of 98% purity -DMPA- was kindly supplied by GEO Specialty Chemicals (Pennsylvania, USA), isophorone diisocyanate (IPDI) of 98% purity (Evonik, Medellín, Colombia), butyl stannic acid (FASCAT 4100, Arkema, Colombes, France), and N-methyl pyrrolidone of 99 % purity (NMP, Merck, Bogotá, Colombia) were used for the synthesis of the waterborne polyurethane dispersions.

Synthesis of the polyester polyols (PBAs)

Poly(1,4 butylene adipate) polyols -PBA- (Figure 1) of different molecular weights (800-2600 g/mol) were synthesized by reacting 1,4 butanediol and adipic acid in the presence of 0.09% m/m butyl stannic acid catalyst. The general reaction to obtain the polyester is shown in Figure 1. The 1,4 butanediol to the adipic acid molar ratio (OH/COOH) was set to 1.05 for having controlled excess of 5% of hydroxyl groups during synthesis to ensure that the polyester chains contain OH groups at the head and the tail.

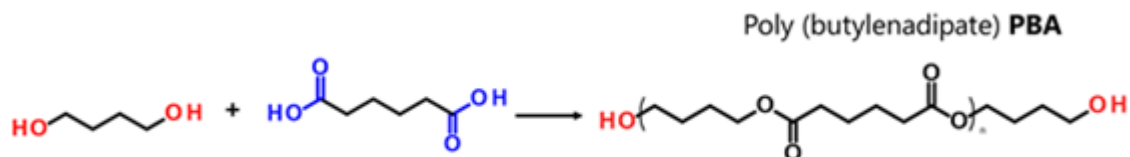


Figure 1. Scheme of reaction to obtain poly(butylenadipate)

The monomers and the catalyst were loaded in a 100 mL three-neck round bottom flask under a continuous nitrogen flow of 10 mL/min and under magnetic stirring at 450 rpm. The reactor was heated from room temperature up to 180 °C (heating rate: 2.4 °C/min) and this temperature was maintained during the reaction. The kinetics of the polymerization was monitored by quantifying the amounts of acid groups during the course of the synthesis according to ASTM D4274-05 standard [16]. The polyesters were cooled down to 60 °C and poured into a clean 60 mL glass container. The polyesters were solid at room temperature and were heated at 90 °C for 1 hour before using to remove residual water. The polyesters were characterized by infrared spectroscopy, proton nuclear magnetic resonance (¹H-NMR), gas permeation chromatography (GPC) and differential scanning calorimetry (DSC).

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Synthesis of waterborne polyurethane dispersions (PUDs)

The PUDs were synthesized with PBA polyester polyol, 4 wt% DMPA (with respect to the total mass of all monomers) internal emulsifier, IPDI aliphatic diisocyanate, and five drops of a solution at 10%wt of dibutyltin dilaurate in xylol. An NCO/OH ratio of 1.7 was used. Due to the low solubility of DMPA in the reactants, a small amount of N-methyl pyrrolidone - DMPA/NMP=1:3 (wt/wt) - was added.

The catalyst was pre-dissolved in NMP and together with the polyester polyol and DMPA were poured into a 100 mL three-neck reactor under nitrogen atmosphere (10 mL/min) at the constant mechanical stirring of 400 rpm. The reactants were heated up to 90 °C, and once the temperature was reached, IPDI was added. The reaction progress was monitored by collecting small amounts of the reactants mixture at different times and determining the NCO content by n-dibutyl amine titration according to ASTM D2572-97 standard [17]. Depending on the molecular weight of the polyol, about 40 to 120 minutes of the reaction was needed for reaching constant free NCO groups content, i.e., all hydroxyl groups of the polyester were consumed. Afterward, the temperature was lowered to 60 °C and the acid groups of DMPA were neutralized with triethylamine at 600 rpm for 30 minutes. Then, the temperature was decreased to 30 °C and the dispersion of the polyurethane in water was carried out by increasing rapidly the stirring speed to 2400 rpm and maintaining the stirring at 30 °C for one hour; the amount of added water was the needed to get a dispersion with a solids content of 30 wt%.

Some properties of the polyurethanes were measured in PU films that were obtained by drying the dispersions at 50°C, over polytetrafluoroethylene plates during 20 h.

Experimental techniques

ζ potential and particle size distribution analysis. The zeta-potential values and the particle size distributions of the waterborne polyurethane dispersions were carried out in Micromeritics Nanoplus 3 dynamic light scattering equipment (Norcross, Georgia, USA). Dispersions were diluted in ultrapure water in a 1:20 (vol/vol) ratio. The pH of the dispersions was near to 8. For obtaining the particle size distributions of the dispersions 30 scans for each measurement and three replicates for each dispersion were obtained and averaged.

Surface tension. The surface tension of the waterborne polyurethane dispersions was measured at 23 °C by using the Du Nouy’s ring method in Cole-Parmer surface tension 20 tensiometer (Vernon Hills, Illinois, USA) equipped with a metal ring of 19.8 mm diameter. The dispersion was poured into a beaker of 50 mL and the ring was

1 placed on the dispersion surface, determining the force (F) necessary to separate the
2 ring. The surface tension (γ) was calculated by using Eq. 1

$$\gamma = \frac{F}{4\pi r} \quad \text{Eq. 1}$$

3
4
5
6 where r is the radius of the ring.

7
8 **Solids content and drying rate.** The solids contents of the PUDs were determined
9 in a DBS 60-3 thermobalance (Kern, Balingen, Germany). About 1 g of PUD was
10 spread on aluminum foil plate with 9 cm diameter. The solids content was measured
11 in two steps; first, the PUD was heated at 105 °C for 15 minutes and then heated at
12 120 °C until a constant mass was obtained. Three replicates were carried out and
13 averaged.

14
15 **Gel permeation chromatography (GPC).** The molecular weights of the polyesters
16 were determined by gel permeation chromatography (GPC) in Agilent 1100 liquid
17 chromatography (San Francisco, California, USA) provided with a differential
18 refractometer detector. Two columns in serial configuration Agilent PLgel MIXED-C
19 were used and tetrahydrofuran was employed as the mobile phase. The molecular
20 weights were calculated by using the calibration curve obtained with polystyrene
21 standards in tetrahydrofuran at 30 °C.

22
23 **Free isocyanate groups content.** The content of free NCO groups during
24 polymerization reaction was quantified by titration with dibutyl amine according to
25 ASTM D2572-97 standard [7,17]. The excess of dibutyl amine was titrated with HCl
26 0.1 M using bromophenol blue as the indicator.

27
28 **Attenuated total reflectance infrared (ATR-FTIR) spectroscopy.** The ATR-IR
29 spectra of the PU films before and after accelerated aging were obtained in a Tensor
30 27 FT-IR spectrometer (Bruker Optik GmbH, Ettlinger, Germany) by using a Golden
31 Gate single reflection diamond ATR accessory. 64 scans with a resolution of 4 cm^{-1}
32 were recorded and averaged in the wavenumber range of 400-4000 cm^{-1} . The
33 incidence angle of the IR beam was 45°.

34
35 **Differential scanning calorimetry (DSC).** The glass transition temperature (T_g) of
36 the PU films was determined by differential scanning calorimetry in a DSC Q100
37 instrument (TA Instruments, New Castle, DE, USA). 10 mg of PU films were placed in
38 an aluminum pan hermetically closed and were heated from -80 to 100 °C at a
39 heating rate of 10 °C min^{-1} under nitrogen atmosphere (flow rate: 50 mL/min). Then,
40 the PU films were cooled to -80 °C and one-second heating run from -80 to 150 °C

1 at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere (flow rate: 50 mL/ min)
2 was carried out. The glass transition temperatures (T_g) of the PU films were obtained
3 from the DSC thermograms of the second heating run.

4
5 **Plate-plate rheology.** The viscoelastic properties of the PU films were measured in
6 a DHR-2 rheometer (TA Instruments, New Castle, DE, USA) using parallel plates
7 (upper plate diameter = 20 mm). One piece of PU film was placed on the bottom
8 plate heated at 150 °C and, once softened, the upper plate was lowered onto the
9 bottom plate to set a gap of 1 mm. Then, the temperature was increased to 200 °C
10 and the excess PU film dough was carefully trimmed off by using a spatula.
11 Experiments were performed in the region of linear viscoelasticity by decreasing the
12 temperature from 200 to 30 °C in a Peltier system by using a cooling rate of 5 °C/min.
13 A frequency of 1 Hz and a strain amplitude of 0.05% was used.

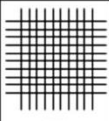
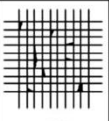
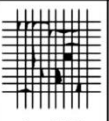
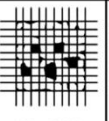

14
15 **Thermogravimetric Analysis (TGA).** The thermal stability of the PU films before
16 and after accelerated aging was studied in TGA Q500 equipment (TA Instruments,
17 New Castle, DE, USA) under nitrogen atmosphere (flow rate: 50 mL/min). 10-15 mg
18 of PU film was placed in a platinum crucible and heated from 25 to 800 °C at a
19 heating rate of 10 °C/min.

20
21 **Adhesion properties of the PU coatings (cross-cut tests):** The adhesion of the PU
22 coatings on stainless steel 304 before and after accelerated aging were obtained by
23 cross-cut tests according to ASTM D3359-02 standard [18]. The cross-cut test
24 determines the percentage of 1x1 mm squares of a polymeric coating on a substrate
25 removed by means of standard adhesive tape.

26 The coatings were prepared by pouring 4 mL of PUD over stainless steel 304 plates,
27 leaving a wet film of 20 µm thick by means of RDS8 Meyer rod (about 10 µm thick
28 solid film). Then, the water was removed in an oven at 50 °C overnight. A multi-blade
29 cutting device 0302001 (Neurtek Instruments S.A., Eibar, Spain) was used for making
30 6 parallel cuts on the coating surface in perpendicular direction; afterward, standard
31 Tesa[®] adhesive tape was applied on the coating squares and the tape was pulled out
32 accounting for the number of removed coating squares. Three replicates were carried
33 out and averaged.

34
35 The cross-cut adhesion values were ranked according to the scale given in ASTM
36 D3359 standard [18] that is summarized in Figure 2. A cross-cut adhesion value of
37 5B means excellent adhesion, i.e. all coating squares remain on the coated stainless-
38 steel plate -, and a cross-cut value of 0B means poor adhesion, i.e. the most coating
39 squares are detached from the stainless steel plate.

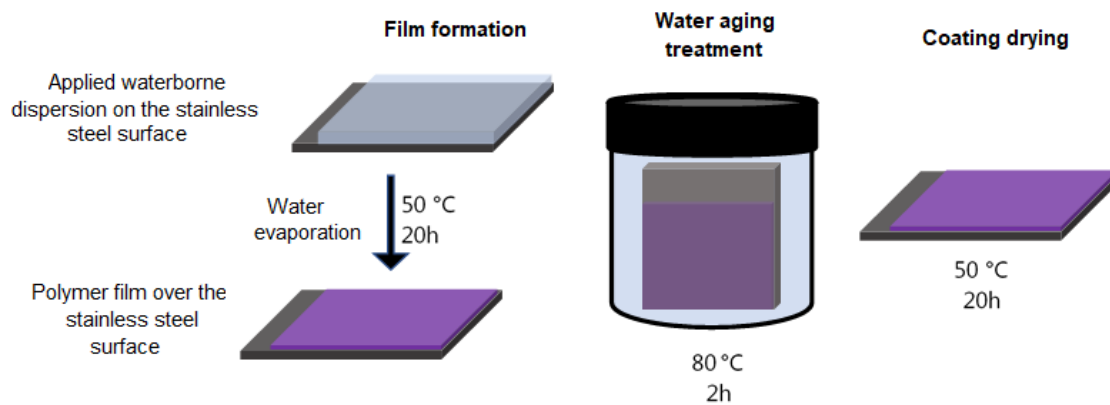
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Example for adhesion range by percent						65%~
Classification	5B	4B	3B	2B	1B	0B

2 **Figure 2.** Cross-cut adhesion scale for coatings according to ASTM D3359 standard
 3 [13].

4 **Accelerated aging.** The aging resistance of the PU films and PU coatings on stainless
 5 steel 304 was tested by immersion in water at 80 °C for 2 hours. The scheme of the
 6 procedure used to develop the accelerated aging treatment is shown in **Figure 3**.
 7 After water immersion, the films were dried at 50 °C for two hours.

8



9

10 **Figure 3.** Scheme of film formation and aging treatment for the coatings

11

RESULTS AND DISCUSSION

Characterization of the polyester polyols

The number average molecular weight of the polyester polyols (PBAs) was varied between 780 and 2610 g/mol, for changing the soft segment content of the polyurethanes. The polydispersity of PBAs was near 2 irrespective of the molecular weight, and the acid number of the PBAs decreases because of the increase of the chain length (Table 1). On the other hand, as it is expected, the increase of the molecular weight increases the glass transition temperature (T_g), and the melting (T_m) and crystallization (T_c) temperatures also increase because of the interactions between polyester groups are more numerous, this restricts the mobility of the chains.

Table 1. Some properties of the polyester polyols.

Polyol	\bar{M}_n (g/mol)	\bar{M}_w (g/mol)	PDI	Acid number (mg KOH/g polyester polyol)	T_g^* (°C)	T_m^* (°C)	T_c^* (°C)
PBA800	780	1750	2.2	82	-24	45	14
PBA2000	1980	3960	2.0	49	6	53	24
PBA2600	2610	5640	2.2	32	6	54	25

*Values obtained from the second run of DSC thermograms.

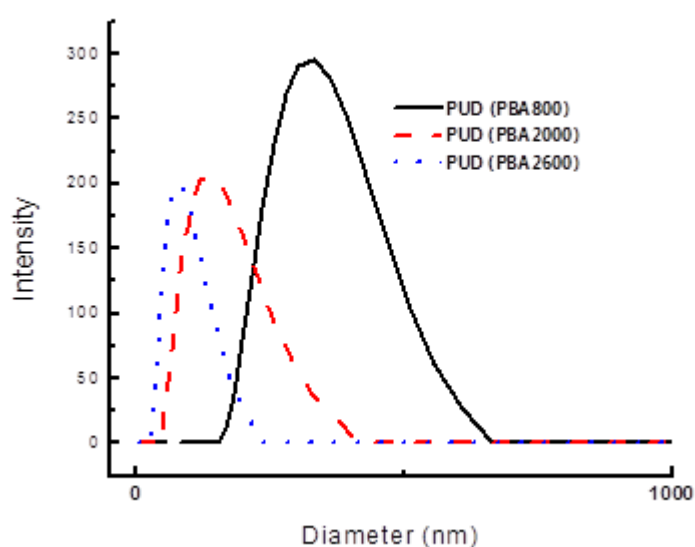
Characterization of waterborne polyurethane dispersions

The synthesis conditions and the colloidal properties of the samples are shown in Table 2. The hard segment content was calculated considering the mass fraction of short reactants (IPDI, DMPA, EDA) related to the total mass of the reactants (IPDI, DMPA, EDA, PBA). The dispersions were stable at least 4 months after preparation.

Table 2. Some properties of the PUDs synthesized with PBAs of different molecular weight.

PUD	Hard segments (%)	Mean particle size (nm)	Surface tension (mN/m)	pH	ζ Potential (mV)	Solids content (wt%)
PUD (PBA800)	41	308	47±1	8.5±0.1	-46,4	29.4± 1.0
PUD (PBA2000)	31	92	48±1	8.2±0.1	-48,3	37.3 ± 0.4
PUD (PBA2600)	28	78	53±1	7.8±0.1	-47,8	36.7 ± 0.8

1 In Figure 4 is shown the particle size distribution for the polyurethane dispersions
2 obtained with the different synthesized polyols, it can be seen that at a higher
3 molecular weight of the used polyol decrease the mean particle size, this behavior is
4 due the increased the flexibility of the chains, which allows the fragmentation of the
5 prepolymer to primary particles of the dispersed phase to smaller and more
6 homogeneous particles.
7 At higher proportions of hard segments, it is more difficult to fragment those primary
8 particles and could appear some hindrance of soft segments to have an effective
9 packaging, so that bigger particle size are obtained, similar results were previously
10 reported [19]



11 **Figure 4.** Particle size distributions of PUDs synthesized with different molecular
12 weights.

13 In Table 3 is possible to observe that increasing the length of the soft segments
14 decrease the pH, due the improving diffusion of the triethylamine between the
15 chains increases the proportion of neutralized DMPA, which favors the ionic
16 interactions that promote cohesion, giving place to increased surface tension.

17 **Characterization of the polyurethane films before aging**

18
19 The ATR-IR spectra of the PU samples are shown in **Figure 5**. There, it is possible to
20 identify the N-H stretching band of urethane and urea and the -CH₂ symmetric and
21 asymmetric stretching of soft segments at ≈ 3300 and ≈ 3000 - 2800 cm⁻¹ respectively,
22 in the zone between 1725 and 1600 cm⁻¹ it is possible to find the carbonyl stretching
23 signals of urethane, ester and urea carbonyls [20].

1 The shoulder at 1645 cm^{-1} corresponds to the stretching of the hydrogen-bonded
2 carbonyl. It is generally accepted that the bonded carbonyls are mainly located in
3 the hard domain and the free carbonyls come from the soft and hard segments
4 dispersed, so the bigger proportion of bonded carbonyls for PUD(PBA800) indicates
5 a lower degree of microphase separation between the hard and soft segments [9].
6 The signal about 1543 cm^{-1} corresponds to N-C stretching. The several bands at
7 $1237\text{-}1138\text{ cm}^{-1}$ correspond to the stretching of C-O-C bonds in the soft segment.

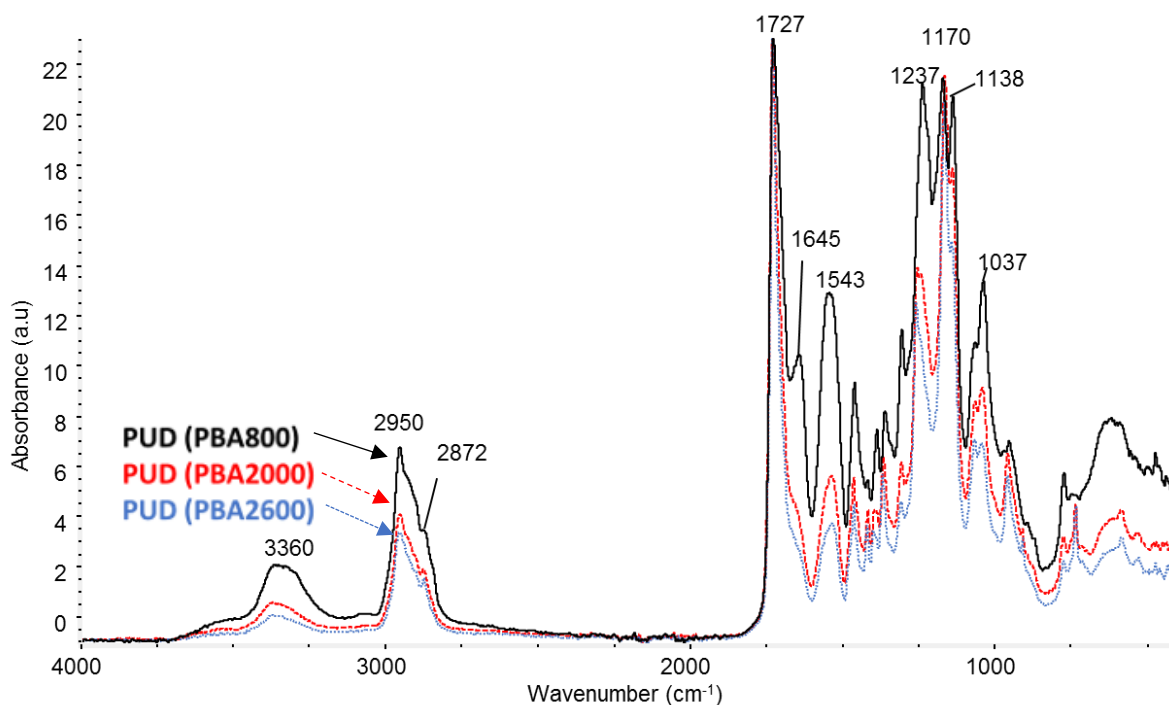


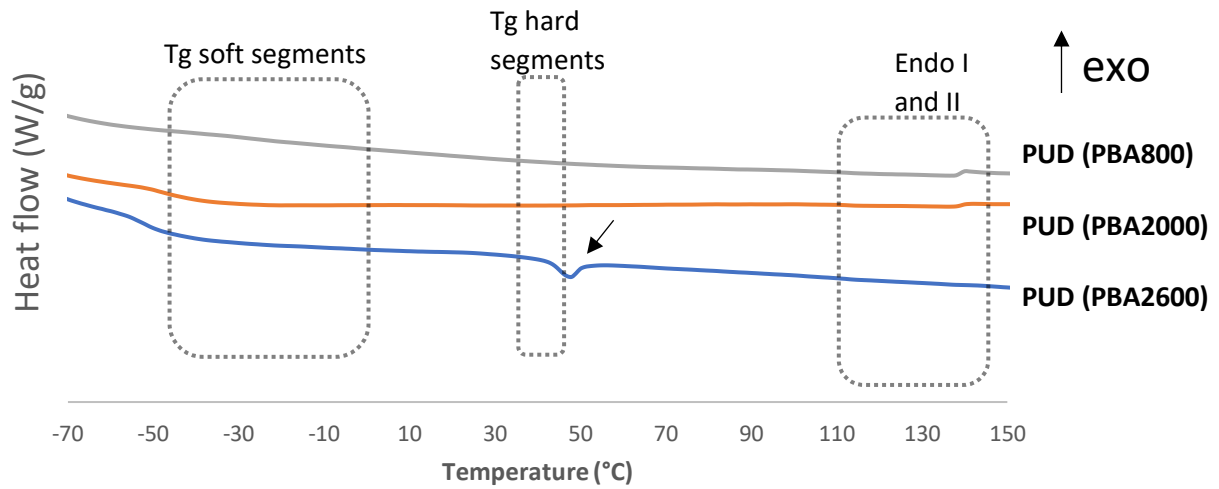
Figure 5. ATR-IR spectra of PU films synthesized with polyols of different molecular weight

8 In Figure 6 is shown the DSC thermograms of the PU film made with different
9 molecular weight polyols, the thermal changes for all polyols are registered in Table
10 3. The first glass transition temperature (T_{gS}) can be attributed to the beginning of
11 the mobility of the soft segments, it is noticed from Table 1 and Table 3, that the
12 incorporation of the soft segments on the PU elastomeric chain restricts the mobility
13 of the polyols, decreasing the T_g values [21,22]. The second glass transition (T_{gH})
14 corresponds to the mobility of hard segments in the PU matrix, due to the similar
15 composition and proportion of hard segment fraction, the T_g doesn't show important
16 differences [23].

17
18 The absence of melting peaks in the samples is evidence of its amorphousness, the
19 slightly melting peak observed on PUD(PBA2600) corresponds to the melting of
20 crystalline domain that coincides with the melting temperature of the pristine polyol,

1 evidencing that the soft segments fractions are isolated, which is an indicative that
 2 using longer polyol chains, the materials show greater phase separation degree [24].

3
 4 Small endotherms changes **I** and **II** have been ascribed to the break-up of short-
 5 range and long-range ordered hard segment domain interactions respectively [10],
 6 it can be seen that for more segmented materials, the energy necessary to break the
 7 short-range ordered domains interactions increase due to the more isolated and
 8 organized domains.



21 **Figure 6.** DSC thermograms of PU films synthesized with polyols of different molecular
 22 weightl. Second heating run.

23
 24 **Table 3.** Some thermal properties of PU films made with polyols of different
 25 molecular weights. DSC experiments.

PU	T _{gs} (°C)	T _{gh} (°C)	Endo I (°C)	Endo II (°C)
PU (PBA800)	-27	26	113	138
PU (PBA2000)	-48	22	113	137
PU (PBA2600)	-53	27	120	-

27
 28 The thermograms are represented in Figure 7 and relevant data of decomposition
 29 are summarized in

1 **Table 4.** The first weigh loss could be attributed to free or bonded (ionic or hydrogen
2 bonds) water, because of incomplete drying and DMPA decomposition.

3

4 The thermal stability of hard segments is represented by the second and third loss
5 corresponding to the degradation of urethane and urea linkages. [25]

6 For all the samples, the remaining weight was 2%, they present a similar
7 decomposition rate, except the PUD based on PBA800, which decomposes earlier
8 than the others, at 160°C this sample has lost 5% of his weight, while for the others
9 more than 200°C are needed. This could be due to the higher content of hard
10 segments and the proximity of urethane and urea groups that have a lower thermal
11 resistance.

12

13 The thermal stability of the soft segments is represented by the maximum
14 decomposition peak at 350 °C. It is possible that when the hard and soft segments
15 are well distributed, more energy would be needed to reach and break the soft
16 segment chains, as can be seen in the higher value of temperature at maximum
17 decomposition for the most homogenous (less segregated) film -PUD(PBA800)-, it
18 could suggest that the miscibility of the phases protects the soft segments against
19 thermal degradation.

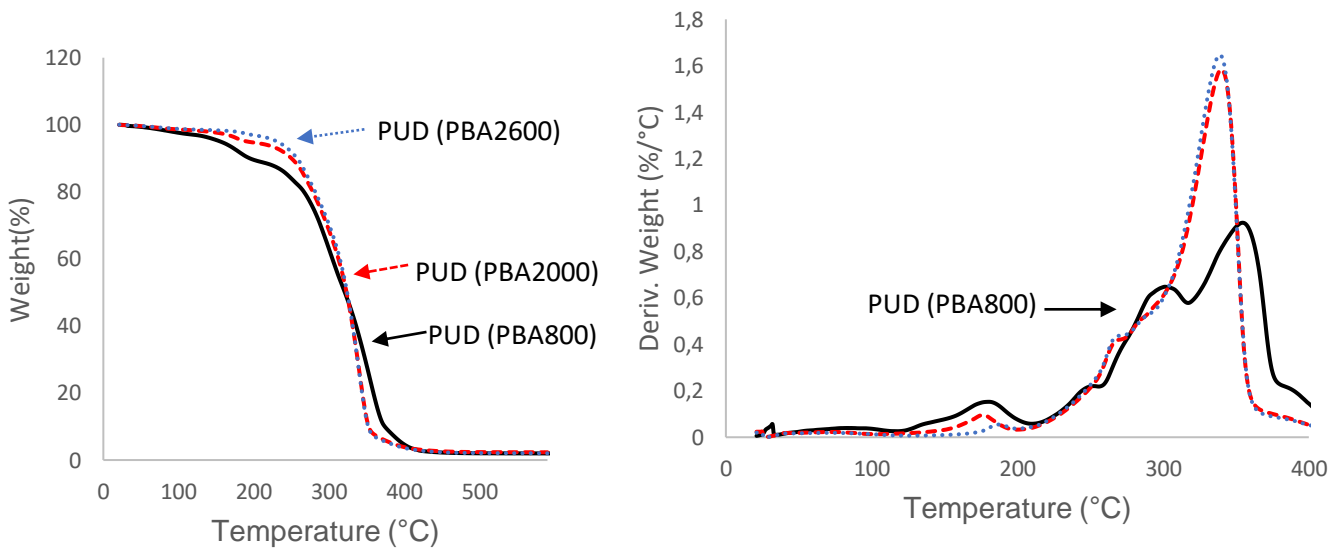


Figure 7. a) Thermogram and **(b)** Weight derivative of PU with different molecular weights

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22

1 **Table 4.** Data extracted from TGA analysis

2

Sample	Loss at 5% T (°C)	Loss at 50% T (°C)	Max. Decomp. T (°C)
PUD(PBA800)	157	323	358
PUD(PBA2000)	202	333	350
PUD(PBA2600)	240	334	349

3
4 The storage and loss modulus and $\tan \delta$ of each sample with temperature were
5 recorded. The values in the crossover point for modulus and temperature are in
6 **Table 5.** Briefly, there is a crossover point ($G' = G''$) where the viscoelastic behavior
7 changes from a mainly solid, liquid-like ($G' > G''$) to an elastic liquid-like behavior
8 ($G'' > G'$). This crossover point represents the melting temperature of the crystalline
9 domains, or their crystallization temperature [26,27]. The temperature and moduli at
10 which this crossover occurs are similar in all the samples, hence the rheological
11 properties of the melt polyurethane films are not significantly affected by the
12 differences in the molecular weight of the used polyol, in the worked range. In
13 addition, these temperatures are similar to the melting temperatures of the polyols
14 obtained by DSC presented in **Table 1.**

15
16 It is worth to mention that the PU made with the shortest polyol presents their
17 crystallization temperature in a wider range (30-60°C), where their storage and loss
18 moduli have similar magnitude, as it can be seen in **Figure 8.** Since the soft segments
19 are related to the viscous moduli and the hard segments to the elastic moduli, it is
20 an indication that the sample with the shortest molecular weight presents lower
21 ordered crystalline segments, in smaller proportion and more dispersed, that is, it
22 has a greater miscibility of phases compared to the materials obtained with longer
23 soft segments.

24 This characteristic can lead to gel-like behaviors with tacky properties because it has
25 values of $\tan \delta$ close to the unit in a considerable range at room temperature, which
26 can be very useful when you want to design materials with potential use as pressure-
27 sensitive adhesives.[27]

28
29 **Table 5.** Temperature and modulus at the cross-over between the storage and loss
30 moduli of the polyurethane films.

31

Sample	Modulus at the cross-over (Pa)	Temperature at the cross-over (°C)
PUD (PBA800)	161000	30-60

PUD (PBA2000)	119000	56
PUD (PBA2600)	115000	56

1

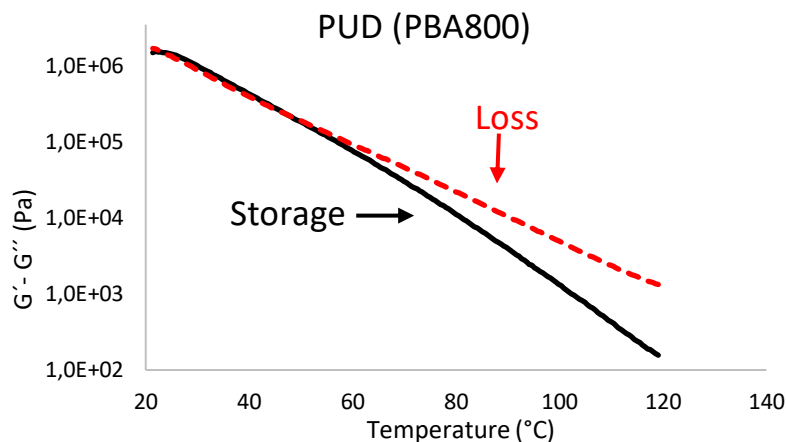


Figure 8. Rheological analysis of temperature sweep experiments of PU (PBA800) film.

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Characterization of PU films after severe accelerated aging

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In **Table 6** it can be seen that the sample synthesized by using the lower molecular weight polyol shows the best resistance to the accelerated aging in water, due to the high content of hard segments and the close proximity between them, the films swell but there is not visible degradation compared to the other films which dissolve in some proportion, as it can be seen in the pictures in the milky appearance of the aqueous phase

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In ATR-FTIR experiments, the band near at 1453 cm^{-1} can be ascribed to the stretching of OC-O⁻ groups from carboxylic acid, which is a product of the hydrolysis of ester groups of polyesters polyol, previously described in the literature[11]. Focusing the attention on this signal, it is possible to compare the degradation rate of each sample, the comparative spectra of each pristine sample and after their aging experiments are shown in Figure 9.

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19

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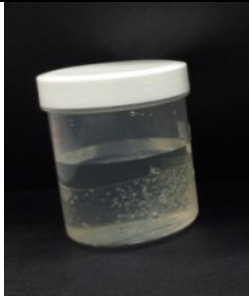
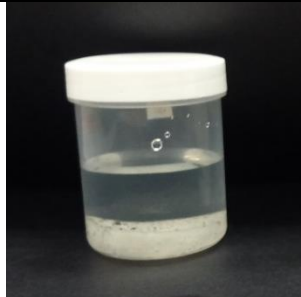
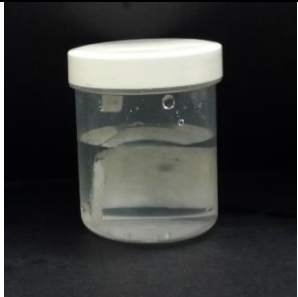
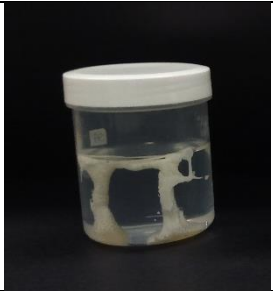
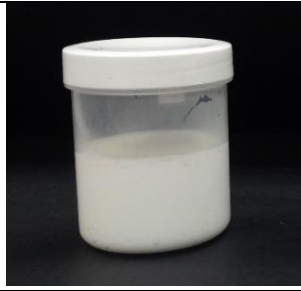
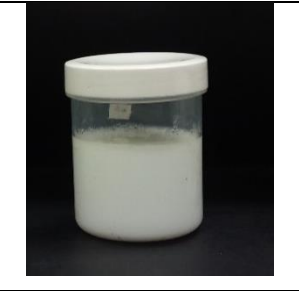
After annealing treatment, as it can be seen in Figure 10(a), the most affected sample is the one synthesized with the shortest molecular weight polyol, it is due to the closeness of the thermally unstable urethane groups, which when broken can expose easily the soft segments to the degradation.

23

1 Figure 10 (b) presents the ATR-IR spectra of the samples thermally aged on water, it
 2 is possible to notice that the increase in the molecular weight promotes the
 3 degradation of the soft segments by hydrolysis, due the increasing proportion of
 4 hydrolyzable ester groups in the chain.

5

6 **Table 6.** PU films before and after immersion in water at 80 °C

	PUD (PBA800)	PUD (PBA2000)	PUD (PBA2600)
Immersed films before water heating			
After water immersion (80°C, 2h)			

7

8

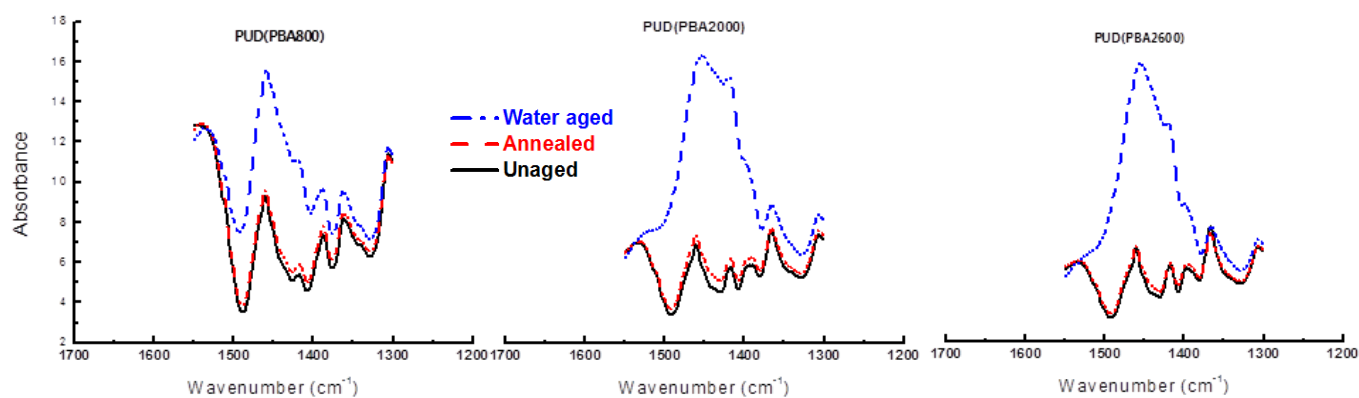


Figure 9. 1600-1300 cm^{-1} zone of ATR-FTIR spectra

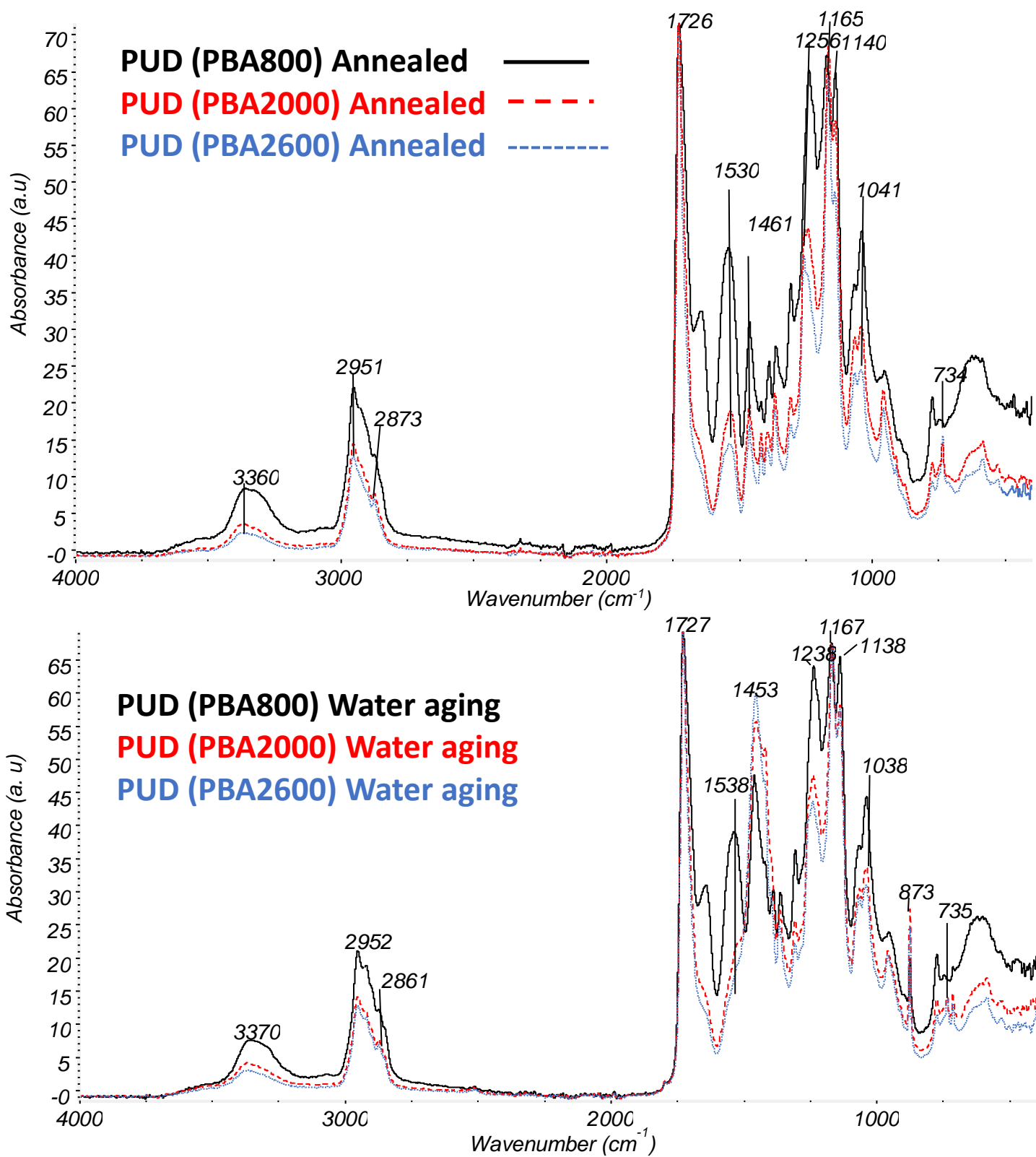


Figure 10. ATR-IR spectra of aged films. (a) After annealing treatment (b) After water immersion

1 The effect on DSC thermograms, of the films after the aging treatment, is shown in
 2 **Table 7**. The T_g of hard and soft segments didn't change in a significant way, so the
 3 miscibility of the hard and soft segments phases was not affected by aging
 4 treatments.

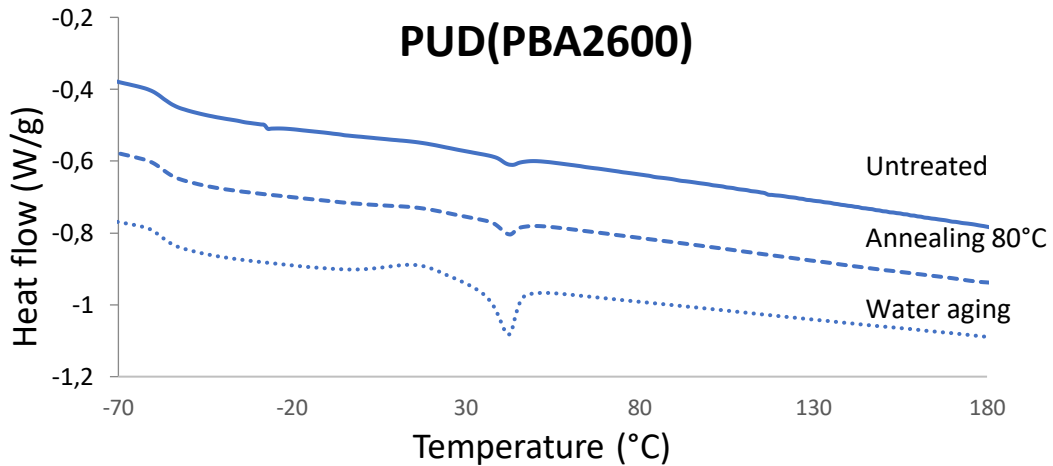
5
 6 The values of endotherm **I** indicate that for PU's synthesized with shorter polyols, the
 7 annealing treatment increases the thermal resistance of the short-range ordered
 8 hard segment domains.

9
 10 In **Figure 11**, where **UA** refers to unaged, **AN** to annealed or thermal aged and **WA**
 11 to water aged samples, it can be seen that aging under hot water increases the
 12 melting enthalpy in the most segmented material -PUD(PBA2600)-, due the polarity
 13 of the largest polyol chain and the ionic nature of the PU, more water can be
 14 absorbed in the material through Van der Waals interactions, which favors
 15 secondary bonds between chains, increasing crystallinity and the need of more
 16 energy to melt the soft segments as it has been reported before[14].

17
 18 **Table 7.** Thermal transitions of PU films made with different molecular weights

Sample	$T_g(1)$ (°C)			$T_g(2)$ (°C)			Endo I (°C)		
	UA	AN	WA	UA	AN	WA	UA	AN	WA
PUD (PBA800)	-39	-37	-33	26	26	25	113	123	116
PUD (PBA2000)	-51	-51	-49	26	26	26	113	125	116
PUD (PBA2600)	-53	-53	-53	27	29	covered	120	111	117

19
 20



21
 22 **Figure 11.** Accelerated aging effect on DSC thermogram of PU made with PBA2600

1 In Table 8 the maximum decomposition temperature of the samples before and after
2 aging treatment according to TGA experiments it is shown, it can be seen that when
3 higher molecular weight polyols are used, the temperature at which the
4 decomposition rate is maximum decreases due to the decrease in the content of the
5 hard segments and the increase of soft segments content, which facilitates a greater
6 diffusion of radical species that promote the thermal decomposition in the polymer.

7

8 **Table 8.** Maximum decomposition temperature according to TGA experiments

Sample	Temperature of maximum decomposition velocity (°C)		
	UA	AN	WA
PUD (PBA800)	358	356	347
PUD (PBA2000)	350	340	342
PUD (PBA2600)	349	346	340

9

Aging effect of coatings on a stainless-steel plate

10

11

PU coatings on stainless-steel sheets

12

13

14 The water contact angle before aging treatment is summarized in Table 10, it can be
15 seen that there are not important differences, so that the reviewed changes in the
16 molecular weight of the polyols don't affect the contact angle.

17

18 The result of the cross-hatch analysis before aging treatment is in Figure 11, where
19 it can be seen how the only place where the coating is detached is in the grids. In
20 general, as it can be seen from these results by using polyols of lower molecular
21 weights, improves the adhesion. The higher content of hard segments and the
22 shorter soft segments can improve the cohesion of the films, avoiding the detaching
23 from the surface.

24

25 In Table 9, it can be seen how the hot water affects the coating applied over stainless
26 steel sheets which are not evidenced in the unaged samples. On the surface of the
27 polymeric coating appears some pinhole like empty bubbles, maybe due to hot
28 points caused by water evaporation. According to the count of degradation points,
29 is visible that PU's based on the longer polyols are more susceptible to water
30 degradation due to the higher content of soft segments which have the lower
31 melting temperature.

32

1 As can be seen in Table 10, the water contact angle of the samples increases after
 2 the annealing treatment which promotes the segmentation in of the films allowing
 3 the migration of the less polar fraction to the surface.



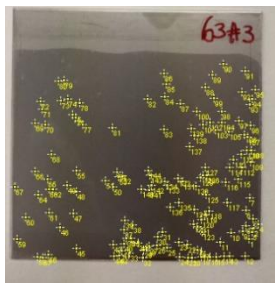
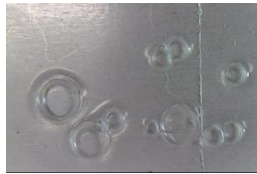
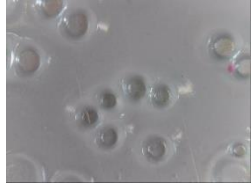
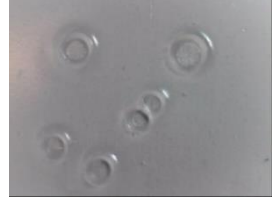
4

5 After water aging experiments the contact angle over the coating is reduced due to
 6 the incorporation of water onto the bulk, it is more evident as increase the molecular
 7 weight of the used polyol due to the more hydrophilic character of the long soft
 8 segments.

9

10 Despite the bubbles over the surface, the behavior of the coatings as the adhesive
 11 is not affected in a significative way, as is shown in Table 11. In general, the
 12 samples of aging experiments maintain the same adhesion properties.

13 **Table 9.** Degradation of coatings after water immersion




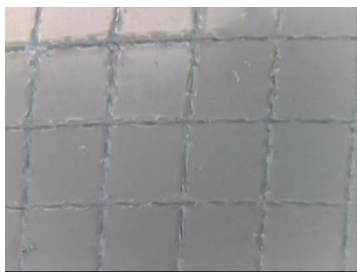
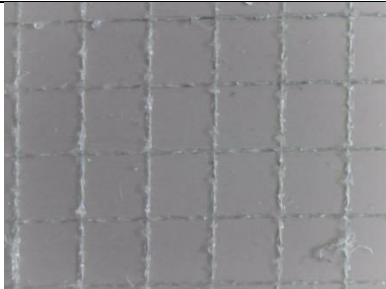
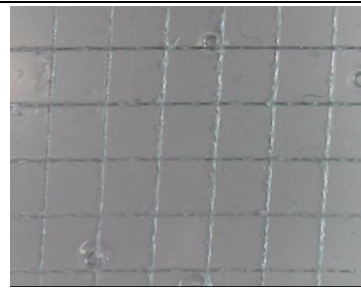

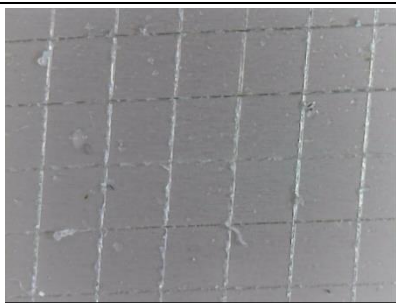
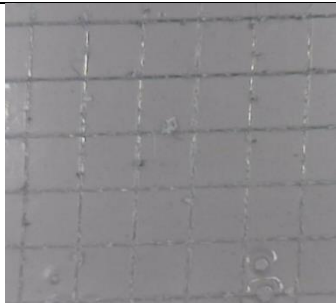
Degradation points after aging in water 80°C-2h			
Sample	PUD (PBA800)	PUD (PBA2000)	PUD (PBA 3000)
	111	160	144
Counting			
Detail			

14

15 **Table 10.** Effect of aging treatments on water contact angle

Sample	Unaged (°)	Annealing 80°C 2h (°)	Water aging¹⁶ 80°C, 2h (°)
PUD (PBA800)	73 ± 1	79 ± 3	75 ± 2
PUD (PBA2000)	75 ± 1	76 ± 2	70 ± 2
PUD (PBA2600)	71 ± 1	73 ± 1	60 ± 1

1 **Table 11.** Crosshatch analysis after aging treatment

Coating	Unaged	Annealed	Water aged
PUD (PBA800)			
Thickness	47		
Classification ASTM D 3359 – 02	4B	4B	4B
PUD (PBA2000)			
Thickness	118		
Classification ASTM D 3359 – 02	4B	4B	4B
PUD (PBA2600)			
Thickness	97		
Classification ASTM D 3359 – 02	4B	4B	4B

2

3

4

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 6 and to CODI for the economic and time support on the project 785 registered in the
 7 act 2018-19331.

8

9

Acknowledgments

Conclusions

In this work, it was demonstrated that increasing the molecular weight of the polyol included in the PU chains and decreasing the hard segment content allows the fragmentation of the dispersed phase in smaller and more homogeneous particles. The inclusion of the polyols on the polyurethane chains restricts the mobility of them, decreasing the T_g of the soft segments once they are incorporated in the elastomeric PU.

According to the rheology, the ATR-IR and the DSC experiments, it was found that the shortest polyols give place to enhanced miscibility between hard and soft segments and using longer polyols promotes the phase segmentation.

The sample with improved miscibility presents a higher maximum decomposition temperature of soft segments in TGA experiments due the closeness of the thermally unstable urethane groups, which can expose easily the soft segments to degradation, this hypothesis is supported by the ATR-IR experiments where the hydrolysis of soft segments by annealing is enhanced compared with more segmented materials.

In addition, the poorly segmented polyurethane exposes a wide temperature range in which the material presents its melting.

The more segmented materials, which were synthesized with the largest polyols, show strong hydrolysis of the soft segments when they are submitted to water aging treatments, but they withstand heat treatment in a better way than polyurethanes that show more segmentation.

The enhanced phase segmentation promotes the absorption of water, increasing the crystallinity of the materials trough Van der Waals interaction between water and the PU chains.

Despite the bubbles over the surface, the adhesive behavior of the coatings over the stainless steel is not affected in a significant way.

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Highlights

- By using polyester with high molecular weight induces crystallization of the polyurethane films.
- By using shorter polyols, improved resistance to aging conditions was found.
- All polyurethane coatings retained the adhesion to the substrate after aging.
- The studied systems are promising coatings for metallic surfaces under high humidity conditions.

1 **Keywords.** Polyurethane-urea dispersion, saturated polyester polyols, molecular
2 weight, microphase miscibility, accelerated aging, cross-hatch adhesion.

3 4 **INTRODUCTION**

5
6 Polyurethanes (PUs) are versatile polymers because of their wide range of physical,
7 chemical, and mechanical properties, and their suitable performance and durability.
8 The PUs are widely used in furniture, construction, packaging, footwear, bedding,
9 paints, sealants, coatings and adhesives industries, among others [1]. In most of these
10 applications, good adhesion of the PUs is an essential property, particularly for
11 coatings in which high abrasion resistance, good hardness, elastomeric properties
12 and high flexibility at low temperature are important [2].

13
14 Waterborne polyurethane dispersions are emerging in the adhesives and coatings
15 industry because of the need of replacing the solvent-borne polyurethanes that
16 contain volatile organic compounds (VOC's), owing to the currently stricter
17 environmental legislation. In fact, the European Parliament has demanded the
18 compulsory reduction in the use of VOCs (Directive 2004/42/CE) especially in paints,
19 varnishes, and adhesives [3,4]. One way to fulfill this requirement is the use of
20 waterborne dispersions as raw materials for adhesives and coatings formulation.
21 Furthermore, it has been demonstrated that the performance of waterborne
22 dispersions as coatings or adhesives is similar or even better than the one of the
23 solvent-borne formulations [5–7].

24
25 PUs exhibit structure-property relationship and therefore, their properties, including
26 adhesion, can be designed and modulated by selecting the adequate composition
27 and method of synthesis. The properties of the waterborne polyurethane dispersions
28 are determined by the method and conditions of synthesis [4] but mainly by the
29 nature and molecular weight of the raw materials (polyol, isocyanate, chain extender,
30 etc), the amount and distribution of hard to soft segments [8,9], and the pendant
31 group in the internal emulsifier, among other. On the other hand, the glass transition
32 temperature (T_g) and phase miscibility of the polyurethanes are affected by the
33 molecular weight and the hard segment content of the polyurethane [10,11].

34
35 Resistance against environmental agents such as humidity and high temperature is
36 important in coatings because their degradation may cause unwanted alterations in
37 adhesion and mechanical properties. The water absorption on to polymer bulk
38 affects the glass transition temperature in certain polymers [12,13] leading to
39 plasticization [14]. Furthermore, the formation of hydrogen bonding between
40 absorbed water and soft or hard segment domain in PUs may contribute to

1 deterioration and aging [15], these also depend on the hard to soft segments ratio,
2 and the shape, size and distribution of the crystalline domains. The influence of the
3 percentage of amorphous domains, and the intramolecular and intermolecular
4 hydrogen bonds on the thermal and mechanical properties, on the aging resistance
5 and the extent of retained water, and on shape memory functionality of PUs have
6 been studied elsewhere [8], [14]. The increase of the amorphous domains promotes
7 water sorption due to easier penetration into the internal structure of the polymeric
8 chains, i.e., the hard segment domains act as a tortuous path for the diffusion of
9 water into the PU bulk. On the other hand, it has been demonstrated [15] that the
10 hydrolytic degradation shortens the soft segment chains, reduce the molecular
11 weight, and affect the hydrogen bond interactions in the PUs, all of which cause a
12 deterioration of their properties [15].

13
14 Pretsch et al. [14] have proposed a degradation model for poly (ester urethane) aged
15 in hot water for 21 days. Initially, there is an induction step (0-2 days) in which the
16 water diffuses into the hard and soft segments, the latter one seems to be hydrolyzed
17 in a reversible way but the hard segments are not affected; the induction step lead
18 to reduced moduli but the elongation at yield and the shape memory functionality
19 remain unaffected. On the other hand, the extent of hydrolytic degradation increased
20 by increasing the water sorption and when less crystalline was the polyurethane
21 backbone [14]. Furthermore, the solid PU coatings obtained from waterborne
22 polyurethane dispersions may contain some retained water into the structure owing
23 to the residual water or humidity of the environment, PUs made with polyester polyol
24 can absorb water in the bulk which accumulates between the interstices of the
25 polymeric chains.

26
27 A current challenge in the industry is to develop coatings and adhesives with
28 excellent stability to high relative humidity and temperature while their VOC contents
29 are reduced. Changing the hard to soft segment ratio is possible to understand the
30 characteristics that improve the aging resistance of the films. Therefore, in this study,
31 aqueous polyurethane dispersions were obtained by using DMPA internal emulsifier,
32 IPDI diisocyanate and poly (1,4 butylene adipate) - PBA- polyols of different
33 molecular weights. Their structure and adhesion properties before and after
34 accelerated aging by immersion in water at 80 °C for 2 hours have been studied.

35

36

EXPERIMENTAL

Materials

Adipic acid of 99.8% purity (BASF, Bogotá, Colombia), 1,4 butanediol of 99% purity (Sigma Aldrich, Bogotá, Colombia), and butyl stannic acid of 95% purity (FASCAT 4100, Arkema, Colombes, France) were used for the synthesis of the new polyester polyols.

Dimethylolpropionic acid of 98% purity -DMPA- was kindly supplied by GEO Specialty Chemicals (Pennsylvania, USA), isophorone diisocyanate (IPDI) of 98% purity (Evonik, Medellín, Colombia), butyl stannic acid (FASCAT 4100, Arkema, Colombes, France), and N-methyl pyrrolidone of 99 % purity (NMP, Merck, Bogotá, Colombia) were used for the synthesis of the waterborne polyurethane dispersions.

Synthesis of the polyester polyols (PBAs)

Poly(1,4 butylene adipate) polyols -PBA- (Figure 1) of different molecular weights (800-2600 g/mol) were synthesized by reacting 1,4 butanediol and adipic acid in the presence of 0.09% m/m butyl stannic acid catalyst. The general reaction to obtain the polyester is shown in Figure 1. The 1,4 butanediol to the adipic acid molar ratio (OH/COOH) was set to 1.05 for having controlled excess of 5% of hydroxyl groups during synthesis to ensure that the polyester chains contain OH groups at the head and the tail.

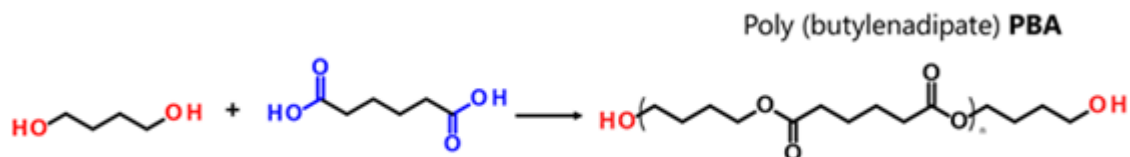


Figure 1. Scheme of reaction to obtain poly(butylenadipate)

The monomers and the catalyst were loaded in a 100 mL three-neck round bottom flask under a continuous nitrogen flow of 10 mL/min and under magnetic stirring at 450 rpm. The reactor was heated from room temperature up to 180 °C (heating rate: 2.4 °C/min) and this temperature was maintained during the reaction. The kinetics of the polymerization was monitored by quantifying the amounts of acid groups during the course of the synthesis according to ASTM D4274-05 standard [16]. The polyesters were cooled down to 60 °C and poured into a clean 60 mL glass container. The polyesters were solid at room temperature and were heated at 90 °C for 1 hour before using to remove residual water. The polyesters were characterized by infrared spectroscopy, proton nuclear magnetic resonance (¹H-NMR), gas permeation chromatography (GPC) and differential scanning calorimetry (DSC).

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Synthesis of waterborne polyurethane dispersions (PUDs)

The PUDs were synthesized with PBA polyester polyol, 4 wt% DMPA (with respect to the total mass of all monomers) internal emulsifier, IPDI aliphatic diisocyanate, and five drops of a solution at 10%wt of dibutyltin dilaurate in xylol. An NCO/OH ratio of 1.7 was used. Due to the low solubility of DMPA in the reactants, a small amount of N-methyl pyrrolidone - DMPA/NMP=1:3 (wt/wt) - was added.

The catalyst was pre-dissolved in NMP and together with the polyester polyol and DMPA were poured into a 100 mL three-neck reactor under nitrogen atmosphere (10 mL/min) at the constant mechanical stirring of 400 rpm. The reactants were heated up to 90 °C, and once the temperature was reached, IPDI was added. The reaction progress was monitored by collecting small amounts of the reactants mixture at different times and determining the NCO content by n-dibutyl amine titration according to ASTM D2572-97 standard [17]. Depending on the molecular weight of the polyol, about 40 to 120 minutes of the reaction was needed for reaching constant free NCO groups content, i.e., all hydroxyl groups of the polyester were consumed. Afterward, the temperature was lowered to 60 °C and the acid groups of DMPA were neutralized with triethylamine at 600 rpm for 30 minutes. Then, the temperature was decreased to 30 °C and the dispersion of the polyurethane in water was carried out by increasing rapidly the stirring speed to 2400 rpm and maintaining the stirring at 30 °C for one hour; the amount of added water was the needed to get a dispersion with a solids content of 30 wt%.

Some properties of the polyurethanes were measured in PU films that were obtained by drying the dispersions at 50°C, over polytetrafluoroethylene plates during 20 h.

Experimental techniques

ζ potential and particle size distribution analysis. The zeta-potential values and the particle size distributions of the waterborne polyurethane dispersions were carried out in Micromeritics Nanoplus 3 dynamic light scattering equipment (Norcross, Georgia, USA). Dispersions were diluted in ultrapure water in a 1:20 (vol/vol) ratio. The pH of the dispersions was near to 8. For obtaining the particle size distributions of the dispersions 30 scans for each measurement and three replicates for each dispersion were obtained and averaged.

Surface tension. The surface tension of the waterborne polyurethane dispersions was measured at 23 °C by using the Du Nouy’s ring method in Cole-Parmer surface tension 20 tensiometer (Vernon Hills, Illinois, USA) equipped with a metal ring of 19.8 mm diameter. The dispersion was poured into a beaker of 50 mL and the ring was

1 placed on the dispersion surface, determining the force (F) necessary to separate the
2 ring. The surface tension (γ) was calculated by using Eq. 1

$$\gamma = \frac{F}{4\pi r} \quad \text{Eq. 1}$$

3
4
5
6 where r is the radius of the ring.

7
8 **Solids content and drying rate.** The solids contents of the PUDs were determined
9 in a DBS 60-3 thermobalance (Kern, Balingen, Germany). About 1 g of PUD was
10 spread on aluminum foil plate with 9 cm diameter. The solids content was measured
11 in two steps; first, the PUD was heated at 105 °C for 15 minutes and then heated at
12 120 °C until a constant mass was obtained. Three replicates were carried out and
13 averaged.

14
15 **Gel permeation chromatography (GPC).** The molecular weights of the polyesters
16 were determined by gel permeation chromatography (GPC) in Agilent 1100 liquid
17 chromatography (San Francisco, California, USA) provided with a differential
18 refractometer detector. Two columns in serial configuration Agilent PLgel MIXED-C
19 were used and tetrahydrofuran was employed as the mobile phase. The molecular
20 weights were calculated by using the calibration curve obtained with polystyrene
21 standards in tetrahydrofuran at 30 °C.

22
23 **Free isocyanate groups content.** The content of free NCO groups during
24 polymerization reaction was quantified by titration with dibutyl amine according to
25 ASTM D2572-97 standard [7,17]. The excess of dibutyl amine was titrated with HCl
26 0.1 M using bromophenol blue as the indicator.

27
28 **Attenuated total reflectance infrared (ATR-FTIR) spectroscopy.** The ATR-IR
29 spectra of the PU films before and after accelerated aging were obtained in a Tensor
30 27 FT-IR spectrometer (Bruker Optik GmbH, Ettlinger, Germany) by using a Golden
31 Gate single reflection diamond ATR accessory. 64 scans with a resolution of 4 cm^{-1}
32 were recorded and averaged in the wavenumber range of 400-4000 cm^{-1} . The
33 incidence angle of the IR beam was 45°.

34
35 **Differential scanning calorimetry (DSC).** The glass transition temperature (T_g) of
36 the PU films was determined by differential scanning calorimetry in a DSC Q100
37 instrument (TA Instruments, New Castle, DE, USA). 10 mg of PU films were placed in
38 an aluminum pan hermetically closed and were heated from -80 to 100 °C at a
39 heating rate of 10 °C min^{-1} under nitrogen atmosphere (flow rate: 50 mL/min). Then,
40 the PU films were cooled to -80 °C and one-second heating run from -80 to 150 °C

1 at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere (flow rate: 50 mL/ min)
2 was carried out. The glass transition temperatures (T_g) of the PU films were obtained
3 from the DSC thermograms of the second heating run.

4
5 **Plate-plate rheology.** The viscoelastic properties of the PU films were measured in
6 a DHR-2 rheometer (TA Instruments, New Castle, DE, USA) using parallel plates
7 (upper plate diameter = 20 mm). One piece of PU film was placed on the bottom
8 plate heated at 150 °C and, once softened, the upper plate was lowered onto the
9 bottom plate to set a gap of 1 mm. Then, the temperature was increased to 200 °C
10 and the excess PU film dough was carefully trimmed off by using a spatula.
11 Experiments were performed in the region of linear viscoelasticity by decreasing the
12 temperature from 200 to 30 °C in a Peltier system by using a cooling rate of 5 °C/min.
13 A frequency of 1 Hz and a strain amplitude of 0.05% was used.

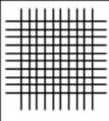
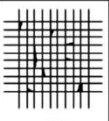
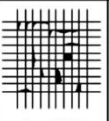
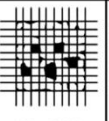

14
15 **Thermogravimetric Analysis (TGA).** The thermal stability of the PU films before
16 and after accelerated aging was studied in TGA Q500 equipment (TA Instruments,
17 New Castle, DE, USA) under nitrogen atmosphere (flow rate: 50 mL/min). 10-15 mg
18 of PU film was placed in a platinum crucible and heated from 25 to 800 °C at a
19 heating rate of 10 °C/min.

20
21 **Adhesion properties of the PU coatings (cross-cut tests):** The adhesion of the PU
22 coatings on stainless steel 304 before and after accelerated aging were obtained by
23 cross-cut tests according to ASTM D3359-02 standard [18]. The cross-cut test
24 determines the percentage of 1x1 mm squares of a polymeric coating on a substrate
25 removed by means of standard adhesive tape.

26 The coatings were prepared by pouring 4 mL of PUD over stainless steel 304 plates,
27 leaving a wet film of 20 µm thick by means of RDS8 Meyer rod (about 10 µm thick
28 solid film). Then, the water was removed in an oven at 50 °C overnight. A multi-blade
29 cutting device 0302001 (Neurtek Instruments S.A., Eibar, Spain) was used for making
30 6 parallel cuts on the coating surface in perpendicular direction; afterward, standard
31 Tesa[®] adhesive tape was applied on the coating squares and the tape was pulled out
32 accounting for the number of removed coating squares. Three replicates were carried
33 out and averaged.

34
35 The cross-cut adhesion values were ranked according to the scale given in ASTM
36 D3359 standard [18] that is summarized in Figure 2. A cross-cut adhesion value of
37 5B means excellent adhesion, i.e. all coating squares remain on the coated stainless-
38 steel plate -, and a cross-cut value of 0B means poor adhesion, i.e. the most coating
39 squares are detached from the stainless steel plate.

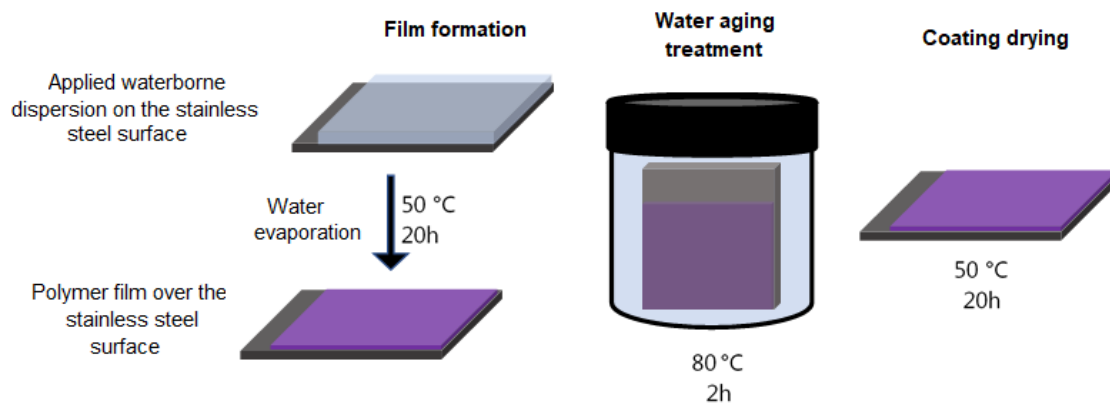
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Example for adhesion range by percent						65%~
Classification	5B	4B	3B	2B	1B	0B

2 **Figure 2.** Cross-cut adhesion scale for coatings according to ASTM D3359 standard
 3 [13].

4 **Accelerated aging.** The aging resistance of the PU films and PU coatings on stainless
 5 steel 304 was tested by immersion in water at 80 °C for 2 hours. The scheme of the
 6 procedure used to develop the accelerated aging treatment is shown in **Figure 3**.
 7 After water immersion, the films were dried at 50 °C for two hours.

8



9

10 **Figure 3.** Scheme of film formation and aging treatment for the coatings

11

RESULTS AND DISCUSSION

Characterization of the polyester polyols

The number average molecular weight of the polyester polyols (PBAs) was varied between 780 and 2610 g/mol, for changing the soft segment content of the polyurethanes. The polydispersity of PBAs was near 2 irrespective of the molecular weight, and the acid number of the PBAs decreases because of the increase of the chain length (Table 1). On the other hand, as it is expected, the increase of the molecular weight increases the glass transition temperature (T_g), and the melting (T_m) and crystallization (T_c) temperatures also increase because of the interactions between polyester groups are more numerous, this restricts the mobility of the chains.

Table 1. Some properties of the polyester polyols.

Polyol	\bar{M}_n (g/mol)	\bar{M}_w (g/mol)	PDI	Acid number (mg KOH/g polyester polyol)	T_g^* (°C)	T_m^* (°C)	T_c^* (°C)
PBA800	780	1750	2.2	82	-24	45	14
PBA2000	1980	3960	2.0	49	6	53	24
PBA2600	2610	5640	2.2	32	6	54	25

*Values obtained from the second run of DSC thermograms.

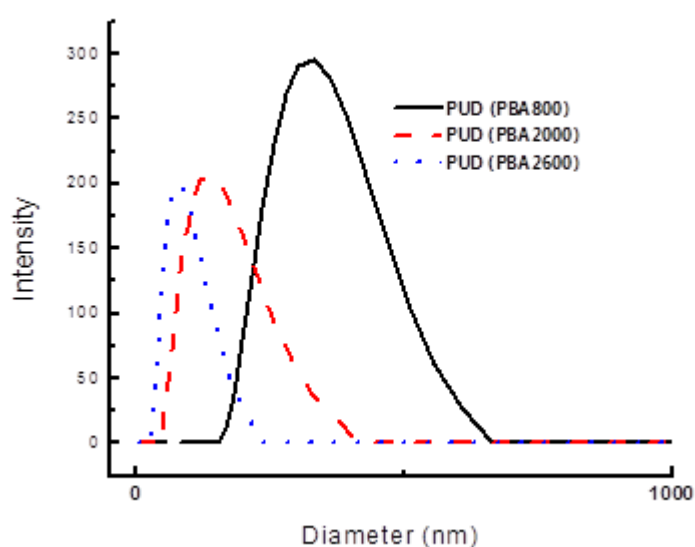
Characterization of waterborne polyurethane dispersions

The synthesis conditions and the colloidal properties of the samples are shown in Table 2. The hard segment content was calculated considering the mass fraction of short reactants (IPDI, DMPA, EDA) related to the total mass of the reactants (IPDI, DMPA, EDA, PBA). The dispersions were stable at least 4 months after preparation.

Table 2. Some properties of the PUDs synthesized with PBAs of different molecular weight.

PUD	Hard segments (%)	Mean particle size (nm)	Surface tension (mN/m)	pH	ζ Potential (mV)	Solids content (wt%)
PUD (PBA800)	41	308	47±1	8.5±0.1	-46,4	29.4± 1.0
PUD (PBA2000)	31	92	48±1	8.2±0.1	-48,3	37.3 ± 0.4
PUD (PBA2600)	28	78	53±1	7.8±0.1	-47,8	36.7 ± 0.8

1 In Figure 4 is shown the particle size distribution for the polyurethane dispersions
2 obtained with the different synthesized polyols, it can be seen that at a higher
3 molecular weight of the used polyol decrease the mean particle size, this behavior is
4 due the increased the flexibility of the chains, which allows the fragmentation of the
5 prepolymer to primary particles of the dispersed phase to smaller and more
6 homogeneous particles.
7 At higher proportions of hard segments, it is more difficult to fragment those primary
8 particles and could appear some hindrance of soft segments to have an effective
9 packaging, so that bigger particle size are obtained, similar results were previously
10 reported [19]



11 **Figure 4.** Particle size distributions of PUDs synthesized with different molecular
12 weights.

13 In Table 3 is possible to observe that increasing the length of the soft segments
14 decrease the pH, due the improving diffusion of the triethylamine between the
15 chains increases the proportion of neutralized DMPA, which favors the ionic
16 interactions that promote cohesion, giving place to increased surface tension.

17 **Characterization of the polyurethane films before aging**

18
19 The ATR-IR spectra of the PU samples are shown in **Figure 5**. There, it is possible to
20 identify the N-H stretching band of urethane and urea and the -CH₂ symmetric and
21 asymmetric stretching of soft segments at ≈ 3300 and ≈ 3000 - 2800 cm⁻¹ respectively,
22 in the zone between 1725 and 1600 cm⁻¹ it is possible to find the carbonyl stretching
23 signals of urethane, ester and urea carbonyls [20].

1 The shoulder at 1645 cm^{-1} corresponds to the stretching of the hydrogen-bonded
 2 carbonyl. It is generally accepted that the bonded carbonyls are mainly located in
 3 the hard domain and the free carbonyls come from the soft and hard segments
 4 dispersed, so the bigger proportion of bonded carbonyls for PUD(PBA800) indicates
 5 a lower degree of microphase separation between the hard and soft segments [9].
 6 The signal about 1543 cm^{-1} corresponds to N-C stretching. The several bands at
 7 $1237\text{-}1138\text{ cm}^{-1}$ correspond to the stretching of C-O-C bonds in the soft segment.

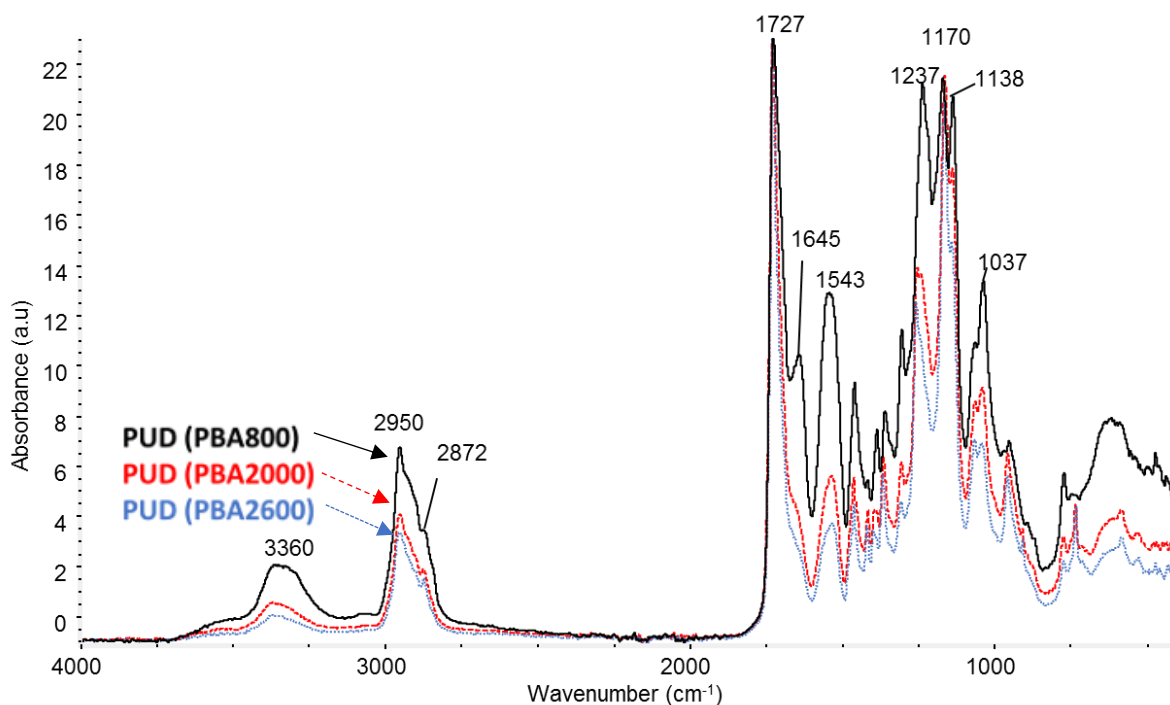


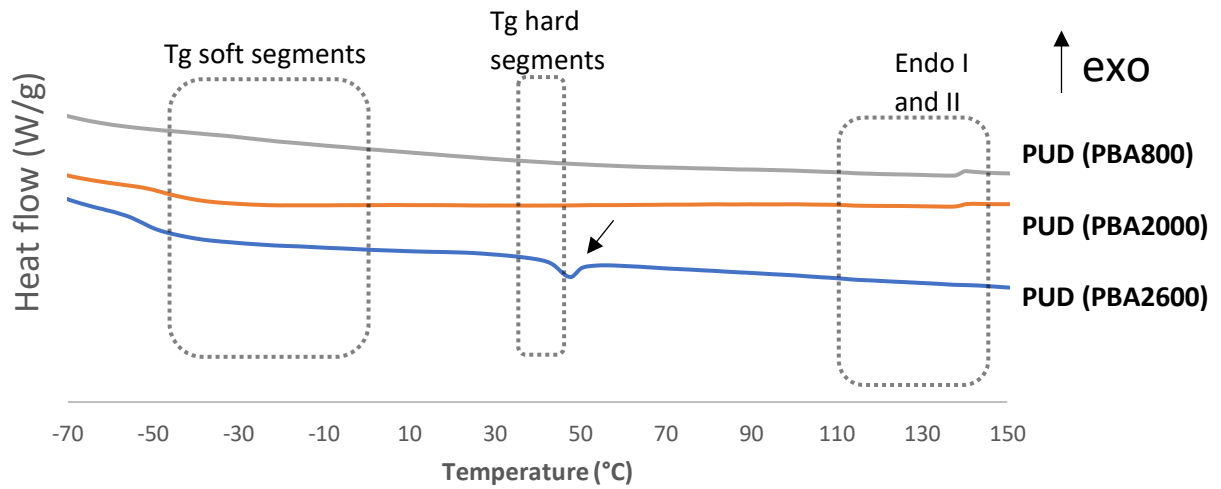
Figure 5. ATR-IR spectra of PU films synthesized with polyols of different molecular weight

8 In Figure 6 is shown the DSC thermograms of the PU film made with different
 9 molecular weight polyols, the thermal changes for all polyols are registered in Table
 10 3. The first glass transition temperature (T_{gS}) can be attributed to the beginning of
 11 the mobility of the soft segments, it is noticed from Table 1 and Table 3, that the
 12 incorporation of the soft segments on the PU elastomeric chain restricts the mobility
 13 of the polyols, decreasing the T_g values [21,22]. The second glass transition (T_{gH})
 14 corresponds to the mobility of hard segments in the PU matrix, due to the similar
 15 composition and proportion of hard segment fraction, the T_g doesn't show important
 16 differences [23].

17
 18 The absence of melting peaks in the samples is evidence of its amorphousness, the
 19 slightly melting peak observed on PUD(PBA2600) corresponds to the melting of
 20 crystalline domain that coincides with the melting temperature of the pristine polyol,

1 evidencing that the soft segments fractions are isolated, which is an indicative that
 2 using longer polyol chains, the materials show greater phase separation degree [24].

3
 4 Small endotherms changes **I** and **II** have been ascribed to the break-up of short-
 5 range and long-range ordered hard segment domain interactions respectively [10],
 6 it can be seen that for more segmented materials, the energy necessary to break the
 7 short-range ordered domains interactions increase due to the more isolated and
 8 organized domains.



21 **Figure 6.** DSC thermograms of PU films synthesized with polyols of different molecular
 22 weightl. Second heating run.

23
 24 **Table 3.** Some thermal properties of PU films made with polyols of different
 25 molecular weights. DSC experiments.

PU	T _{gs} (°C)	T _{gh} (°C)	Endo I (°C)	Endo II (°C)
PU (PBA800)	-27	26	113	138
PU (PBA2000)	-48	22	113	137
PU (PBA2600)	-53	27	120	-

27
 28 The thermograms are represented in Figure 7 and relevant data of decomposition
 29 are summarized in

1 **Table 4.** The first weigh loss could be attributed to free or bonded (ionic or hydrogen
2 bonds) water, because of incomplete drying and DMPA decomposition.

3

4 The thermal stability of hard segments is represented by the second and third loss
5 corresponding to the degradation of urethane and urea linkages. [25]

6 For all the samples, the remaining weight was 2%, they present a similar
7 decomposition rate, except the PUD based on PBA800, which decomposes earlier
8 than the others, at 160°C this sample has lost 5% of his weight, while for the others
9 more than 200°C are needed. This could be due to the higher content of hard
10 segments and the proximity of urethane and urea groups that have a lower thermal
11 resistance.

12

13 The thermal stability of the soft segments is represented by the maximum
14 decomposition peak at 350 °C. It is possible that when the hard and soft segments
15 are well distributed, more energy would be needed to reach and break the soft
16 segment chains, as can be seen in the higher value of temperature at maximum
17 decomposition for the most homogenous (less segregated) film -PUD(PBA800)-, it
18 could suggest that the miscibility of the phases protects the soft segments against
19 thermal degradation.

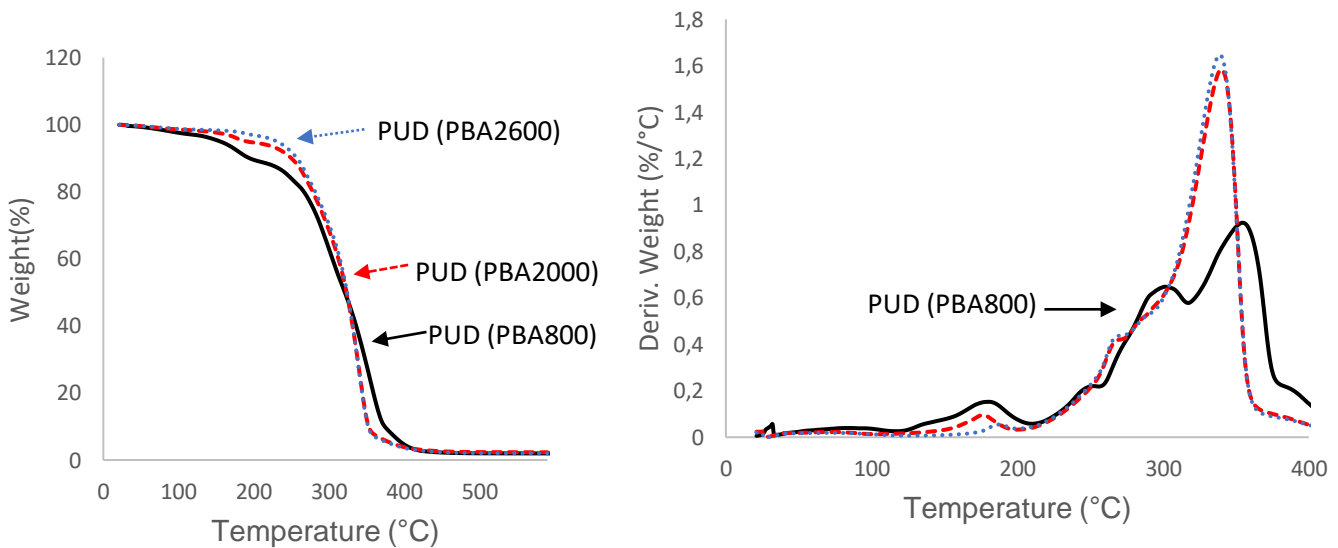


Figure 7. a) Thermogram and **(b)** Weight derivative of PU with different molecular weights

20

21

22

1 **Table 4.** Data extracted from TGA analysis

2

Sample	Loss at 5% T (°C)	Loss at 50% T (°C)	Max. Decomp. T (°C)
PUD(PBA800)	157	323	358
PUD(PBA2000)	202	333	350
PUD(PBA2600)	240	334	349

3
4 The storage and loss modulus and $\tan \delta$ of each sample with temperature were
5 recorded. The values in the crossover point for modulus and temperature are in
6 **Table 5.** Briefly, there is a crossover point ($G' = G''$) where the viscoelastic behavior
7 changes from a mainly solid, liquid-like ($G' > G''$) to an elastic liquid-like behavior
8 ($G'' > G'$). This crossover point represents the melting temperature of the crystalline
9 domains, or their crystallization temperature [26,27]. The temperature and moduli at
10 which this crossover occurs are similar in all the samples, hence the rheological
11 properties of the melt polyurethane films are not significantly affected by the
12 differences in the molecular weight of the used polyol, in the worked range. In
13 addition, these temperatures are similar to the melting temperatures of the polyols
14 obtained by DSC presented in **Table 1.**

15
16 It is worth to mention that the PU made with the shortest polyol presents their
17 crystallization temperature in a wider range (30-60°C), where their storage and loss
18 moduli have similar magnitude, as it can be seen in **Figure 8.** Since the soft segments
19 are related to the viscous moduli and the hard segments to the elastic moduli, it is
20 an indication that the sample with the shortest molecular weight presents lower
21 ordered crystalline segments, in smaller proportion and more dispersed, that is, it
22 has a greater miscibility of phases compared to the materials obtained with longer
23 soft segments.

24 This characteristic can lead to gel-like behaviors with tacky properties because it has
25 values of $\tan \delta$ close to the unit in a considerable range at room temperature, which
26 can be very useful when you want to design materials with potential use as pressure-
27 sensitive adhesives.[27]

28
29 **Table 5.** Temperature and modulus at the cross-over between the storage and loss
30 moduli of the polyurethane films.

31

Sample	Modulus at the cross-over (Pa)	Temperature at the cross-over (°C)
PUD (PBA800)	161000	30-60

PUD (PBA2000)	119000	56
PUD (PBA2600)	115000	56

1

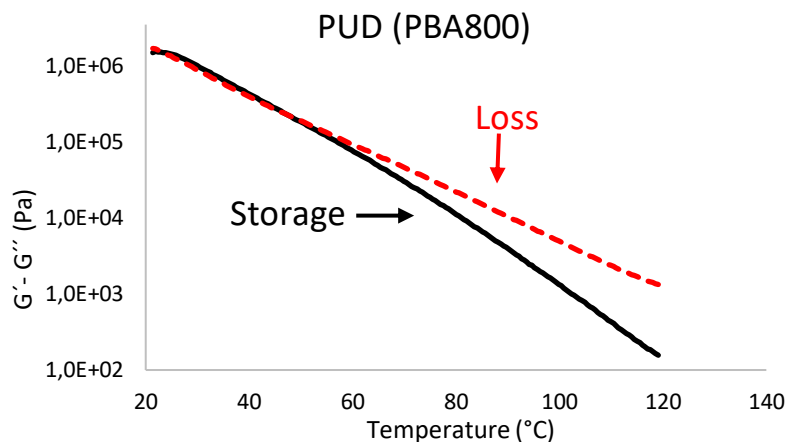


Figure 8. Rheological analysis of temperature sweep experiments of PU (PBA800) film.

2

3

Characterization of PU films after severe accelerated aging

4

5

In **Table 6** it can be seen that the sample synthesized by using the lower molecular weight polyol shows the best resistance to the accelerated aging in water, due to the high content of hard segments and the close proximity between them, the films swell but there is not visible degradation compared to the other films which dissolve in some proportion, as it can be seen in the pictures in the milky appearance of the aqueous phase

10

11

12

In ATR-FTIR experiments, the band near at 1453 cm^{-1} can be ascribed to the stretching of OC-O⁻ groups from carboxylic acid, which is a product of the hydrolysis of ester groups of polyesters polyol, previously described in the literature[11]. Focusing the attention on this signal, it is possible to compare the degradation rate of each sample, the comparative spectra of each pristine sample and after their aging experiments are shown in Figure 9.

17

18

19

After annealing treatment, as it can be seen in Figure 10(a), the most affected sample is the one synthesized with the shortest molecular weight polyol, it is due to the closeness of the thermally unstable urethane groups, which when broken can expose easily the soft segments to the degradation.

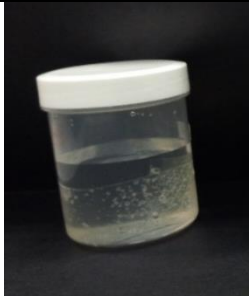
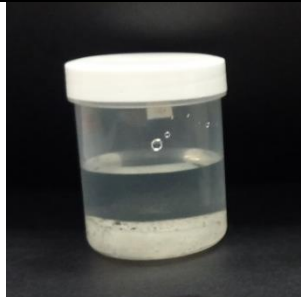
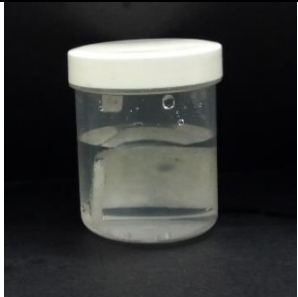
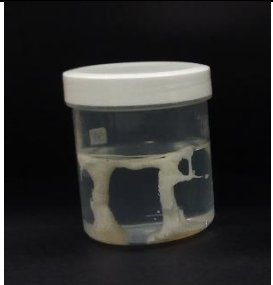
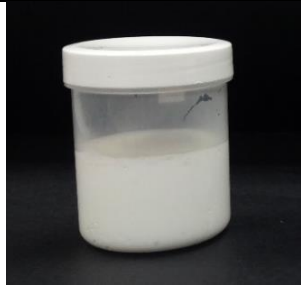
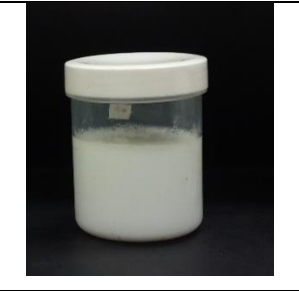
22

23

1 Figure 10 (b) presents the ATR-IR spectra of the samples thermally aged on water, it
 2 is possible to notice that the increase in the molecular weight promotes the
 3 degradation of the soft segments by hydrolysis, due the increasing proportion of
 4 hydrolyzable ester groups in the chain.

5

6 **Table 6.** PU films before and after immersion in water at 80 °C

	PUD (PBA800)	PUD (PBA2000)	PUD (PBA2600)
Immersed films before water heating			
After water immersion (80°C, 2h)			

7

8

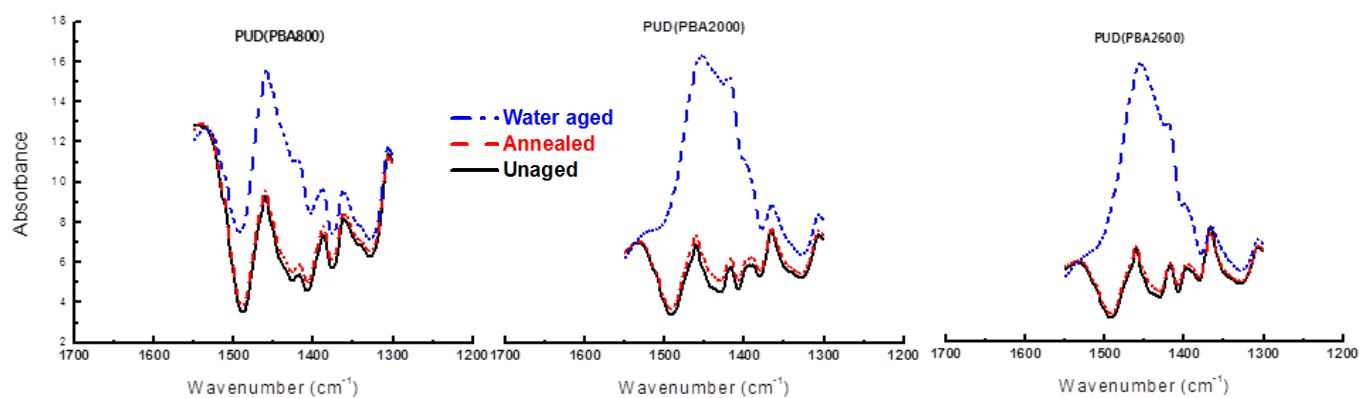


Figure 9. 1600-1300 cm^{-1} zone of ATR-FTIR spectra

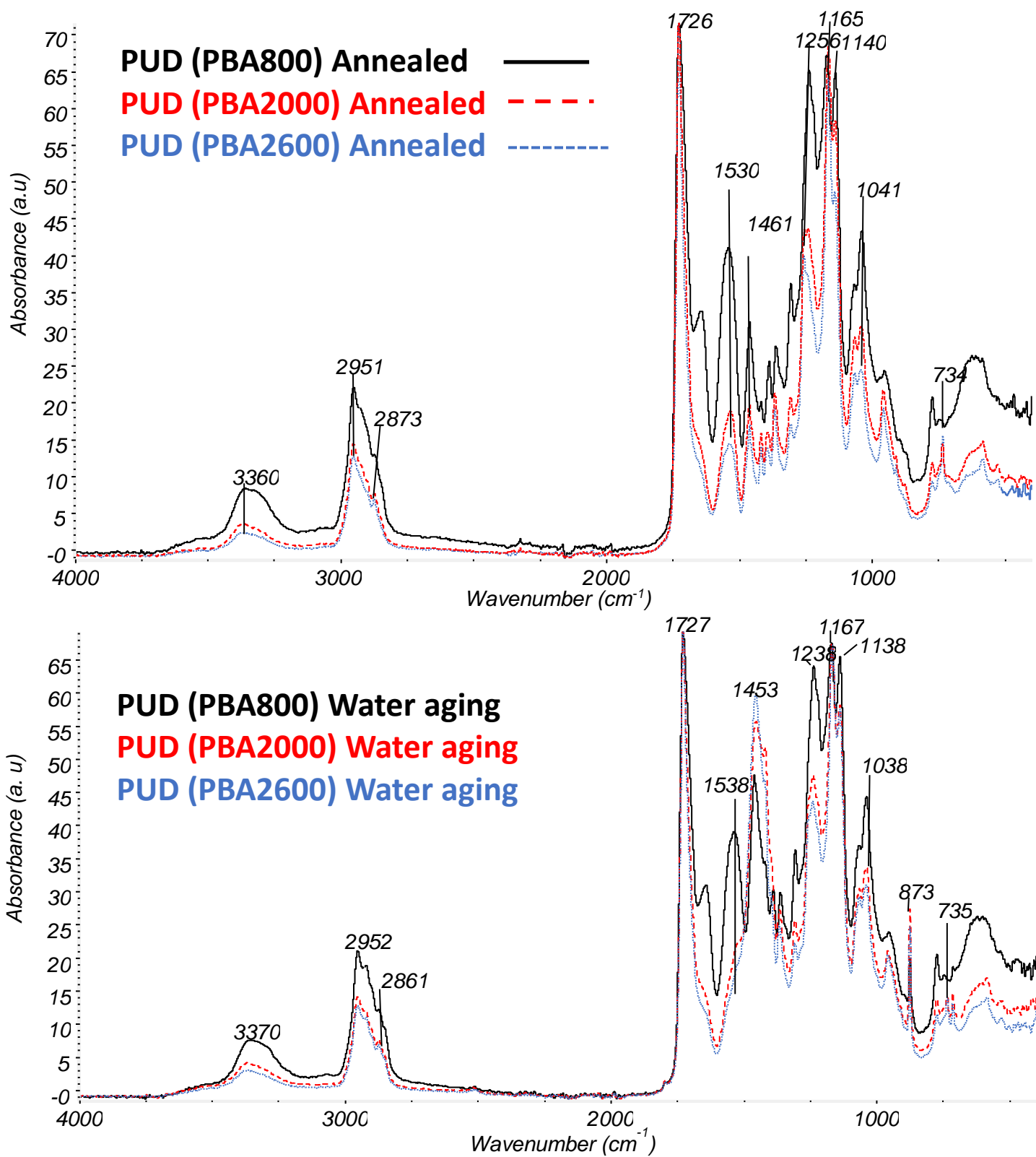


Figure 10. ATR-IR spectra of aged films. (a) After annealing treatment (b) After water immersion

1 The effect on DSC thermograms, of the films after the aging treatment, is shown in
 2 **Table 7**. The T_g of hard and soft segments didn't change in a significant way, so the
 3 miscibility of the hard and soft segments phases was not affected by aging
 4 treatments.

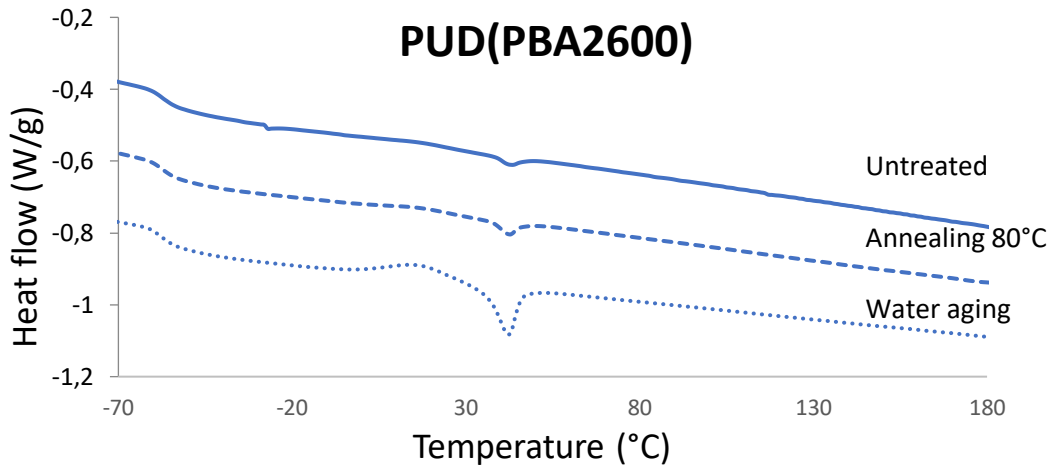
5
 6 The values of endotherm **I** indicate that for PU's synthesized with shorter polyols, the
 7 annealing treatment increases the thermal resistance of the short-range ordered
 8 hard segment domains.

9
 10 In **Figure 11**, where **UA** refers to unaged, **AN** to annealed or thermal aged and **WA**
 11 to water aged samples, it can be seen that aging under hot water increases the
 12 melting enthalpy in the most segmented material -PUD(PBA2600)-, due the polarity
 13 of the largest polyol chain and the ionic nature of the PU, more water can be
 14 absorbed in the material through Van der Waals interactions, which favors
 15 secondaries bonds between chains, increasing crystallinity and the need of more
 16 energy to melt the soft segments as it has been reported before[14].

17
 18 **Table 7.** Thermal transitions of PU films made with different molecular weights

Sample	$T_g(1)$ (°C)			$T_g(2)$ (°C)			Endo I (°C)		
	UA	AN	WA	UA	AN	WA	UA	AN	WA
PUD (PBA800)	-39	-37	-33	26	26	25	113	123	116
PUD (PBA2000)	-51	-51	-49	26	26	26	113	125	116
PUD (PBA2600)	-53	-53	-53	27	29	covered	120	111	117

19
 20



21
 22 **Figure 11.** Accelerated aging effect on DSC thermogram of PU made with PBA2600

1 In Table 8 the maximum decomposition temperature of the samples before and after
2 aging treatment according to TGA experiments it is shown, it can be seen that when
3 higher molecular weight polyols are used, the temperature at which the
4 decomposition rate is maximum decreases due to the decrease in the content of the
5 hard segments and the increase of soft segments content, which facilitates a greater
6 diffusion of radical species that promote the thermal decomposition in the polymer.

7
8

Table 8. Maximum decomposition temperature according to TGA experiments

Sample	Temperature of maximum decomposition velocity (°C)		
	UA	AN	WA
PUD (PBA800)	358	356	347
PUD (PBA2000)	350	340	342
PUD (PBA2600)	349	346	340

9

Aging effect of coatings on a stainless-steel plate

10
11

PU coatings on stainless-steel sheets

12

13
14 The water contact angle before aging treatment is summarized in Table 10, it can be
15 seen that there are not important differences, so that the reviewed changes in the
16 molecular weight of the polyols don't affect the contact angle.

17

18 The result of the cross-hatch analysis before aging treatment is in Figure 11, where
19 it can be seen how the only place where the coating is detached is in the grids. In
20 general, as it can be seen from these results by using polyols of lower molecular
21 weights, improves the adhesion. The higher content of hard segments and the
22 shorter soft segments can improve the cohesion of the films, avoiding the detaching
23 from the surface.

24

25 In Table 9, it can be seen how the hot water affects the coating applied over stainless
26 steel sheets which are not evidenced in the unaged samples. On the surface of the
27 polymeric coating appears some pinhole like empty bubbles, maybe due to hot
28 points caused by water evaporation. According to the count of degradation points,
29 is visible that PU's based on the longer polyols are more susceptible to water
30 degradation due to the higher content of soft segments which have the lower
31 melting temperature.

32

1 As can be seen in Table 10, the water contact angle of the samples increases after
 2 the annealing treatment which promotes the segmentation in of the films allowing
 3 the migration of the less polar fraction to the surface.



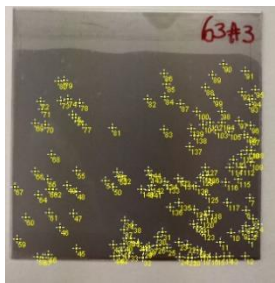
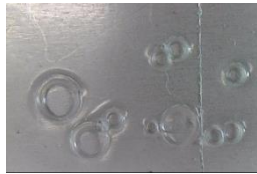
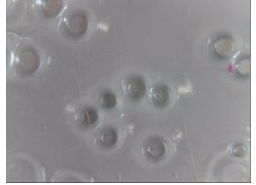
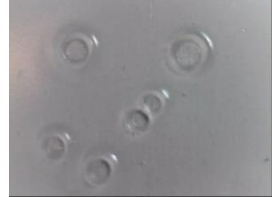
4

5 After water aging experiments the contact angle over the coating is reduced due to
 6 the incorporation of water onto the bulk, it is more evident as increase the molecular
 7 weight of the used polyol due to the more hydrophilic character of the long soft
 8 segments.

9

10 Despite the bubbles over the surface, the behavior of the coatings as the adhesive
 11 is not affected in a significative way, as is shown in Table 11. In general, the
 12 samples of aging experiments maintain the same adhesion properties.

13 **Table 9.** Degradation of coatings after water immersion




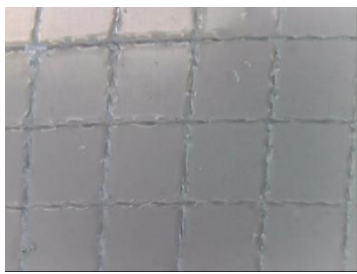
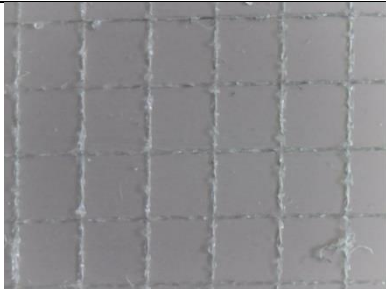
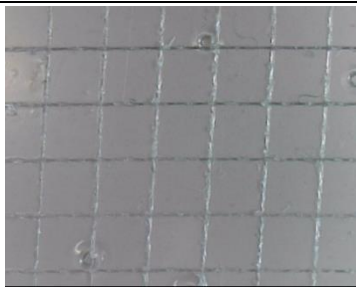

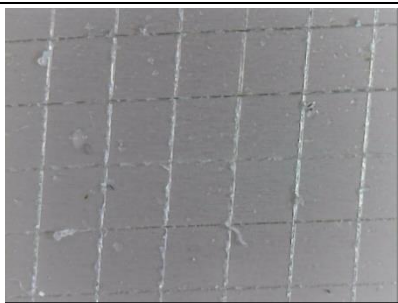
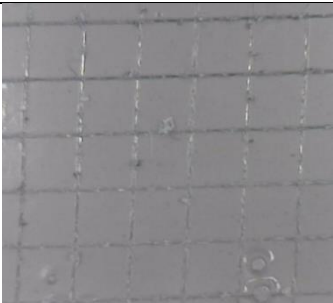
Degradation points after aging in water 80°C-2h			
Sample	PUD (PBA800)	PUD (PBA2000)	PUD (PBA 3000)
	111	160	144
Counting			
Detail			

14

15 **Table 10.** Effect of aging treatments on water contact angle

Sample	Unaged (°)	Annealing 80°C 2h (°)	Water aging¹⁶ 80°C, 2h (°)
PUD (PBA800)	73 ± 1	79 ± 3	75 ± 2
PUD (PBA2000)	75 ± 1	76 ± 2	70 ± 2
PUD (PBA2600)	71 ± 1	73 ± 1	60 ± 1

1 **Table 11.** Crosshatch analysis after aging treatment

Coating	Unaged	Annealed	Water aged
PUD (PBA800)			
Thickness	47		
Classification ASTM D 3359 – 02	4B	4B	4B
PUD (PBA2000)			
Thickness	118		
Classification ASTM D 3359 – 02	4B	4B	4B
PUD (PBA2600)			
Thickness	97		
Classification ASTM D 3359 – 02	4B	4B	4B

2

3

4

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 6 and to CODI for the economic and time support on the project 785 registered in the
 7 act 2018-19331.

8

9

Acknowledgments

Conclusions

In this work, it was demonstrated that increasing the molecular weight of the polyol included in the PU chains and decreasing the hard segment content allows the fragmentation of the dispersed phase in smaller and more homogeneous particles. The inclusion of the polyols on the polyurethane chains restricts the mobility of them, decreasing the T_g of the soft segments once they are incorporated in the elastomeric PU.

According to the rheology, the ATR-IR and the DSC experiments, it was found that the shortest polyols give place to enhanced miscibility between hard and soft segments and using longer polyols promotes the phase segmentation.

The sample with improved miscibility presents a higher maximum decomposition temperature of soft segments in TGA experiments due the closeness of the thermally unstable urethane groups, which can expose easily the soft segments to degradation, this hypothesis is supported by the ATR-IR experiments where the hydrolysis of soft segments by annealing is enhanced compared with more segmented materials.

In addition, the poorly segmented polyurethane exposes a wide temperature range in which the material presents its melting.

The more segmented materials, which were synthesized with the largest polyols, show strong hydrolysis of the soft segments when they are submitted to water aging treatments, but they withstand heat treatment in a better way than polyurethanes that show more segmentation.

The enhanced phase segmentation promotes the absorption of water, increasing the crystallinity of the materials trough Van der Waals interaction between water and the PU chains.

Despite the bubbles over the surface, the adhesive behavior of the coatings over the stainless steel is not affected in a significant way.

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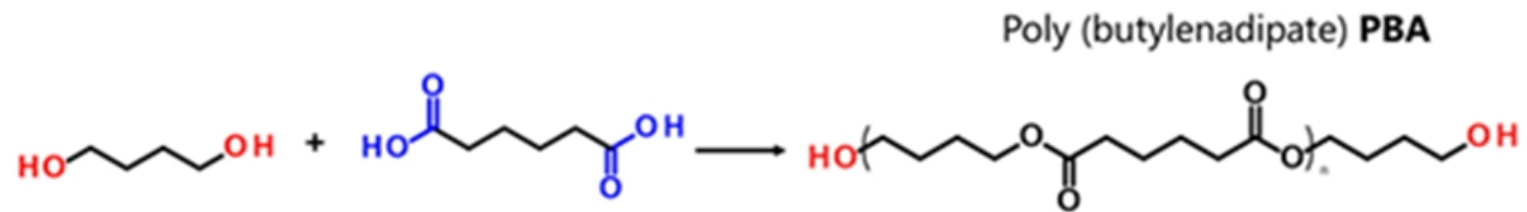


Figure 1. Scheme of reaction to obtain poly(butyleneadipate)

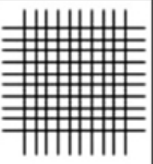
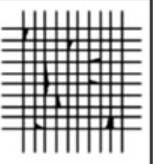
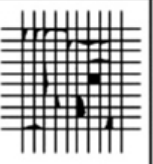
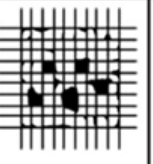
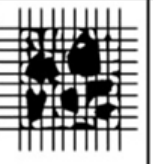
Example for adhesion range by percent	 0%	 ~ 5%	 5 ~ 15%	 15 ~ 35%	 35 ~ 65%	65%~
Classification	5B	4B	3B	2B	1B	0B

Figure 2. Cross-cut adhesion scale for coatings according to ASTM D3359 standard [13].

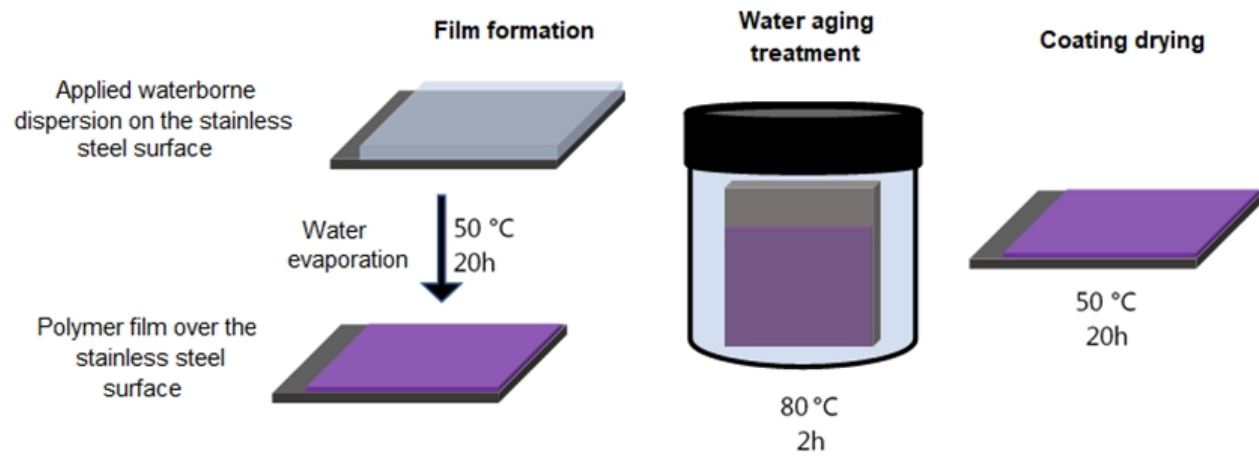


Figure 3. Scheme of film formation and aging treatment for the coatings

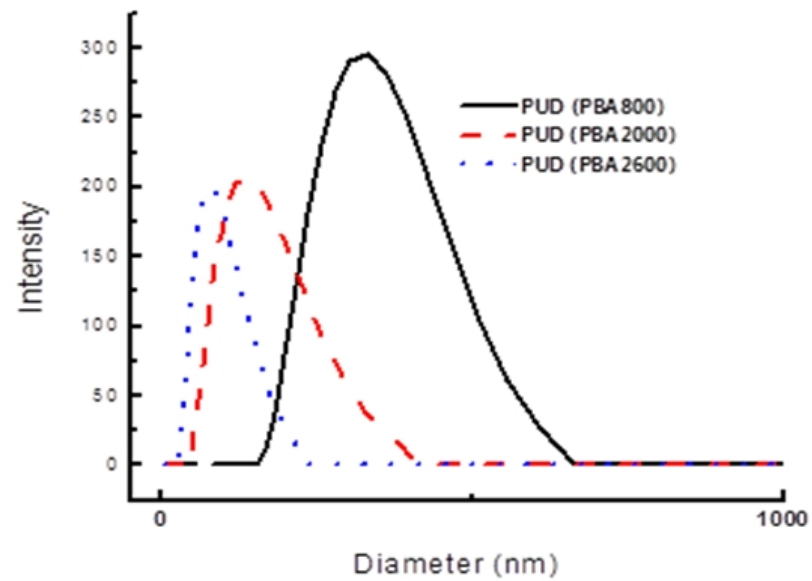


Figure 4. Particle size distributions of PUDs synthesized with different molecular weights.

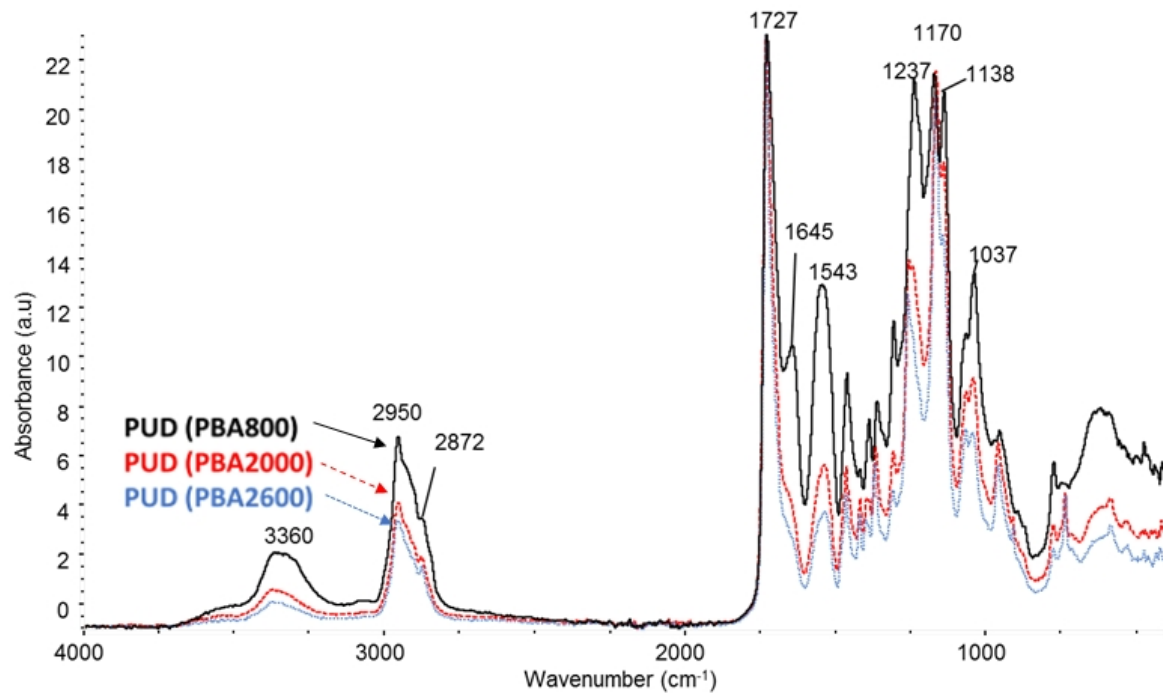


Figure 5. ATR-IR spectra of PU films synthesized with polyols of different molecular weight

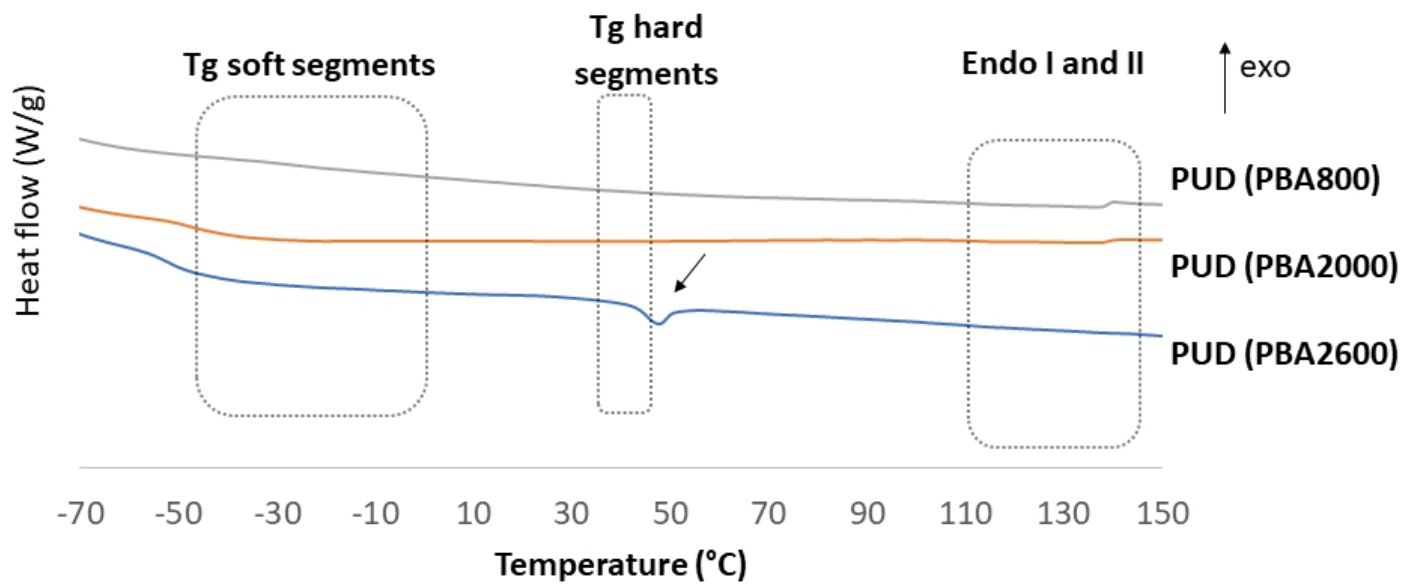


Figure 6. DSC thermograms of PU films synthesized with polyols of different molecular weight. Second heating run.

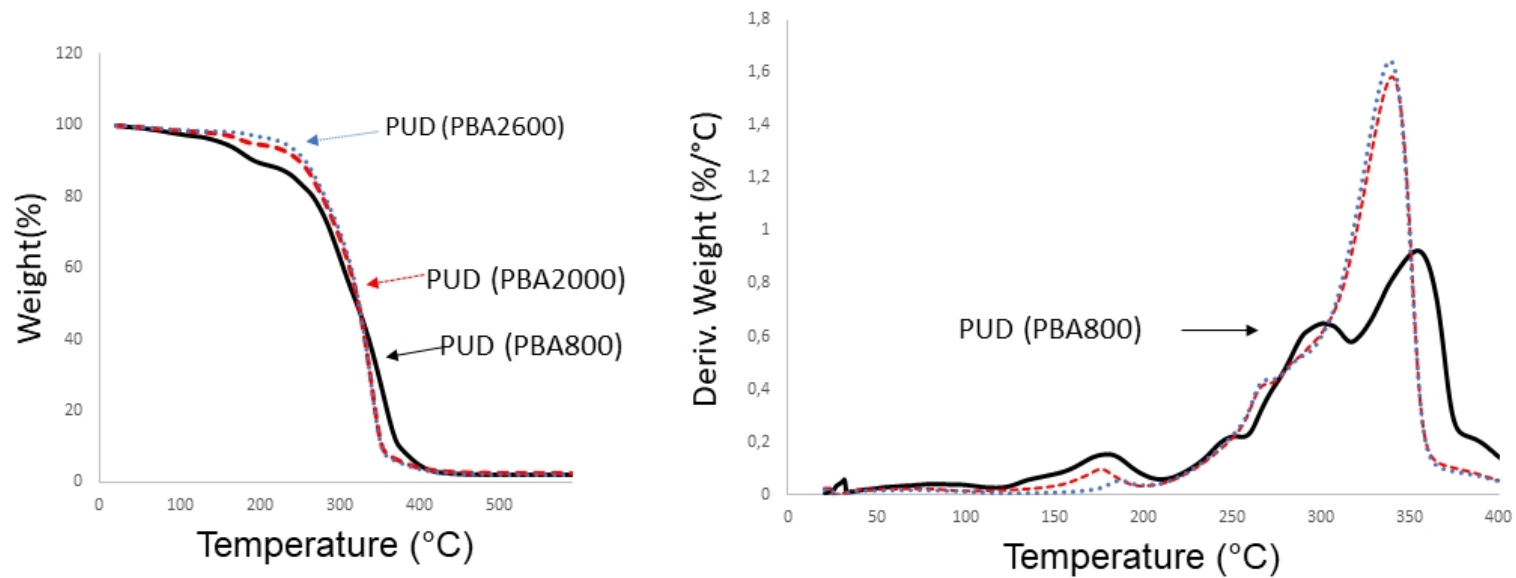


Figure 7. **a)** Thermogram and **(b)** Weight derivative of PU with different molecular weights

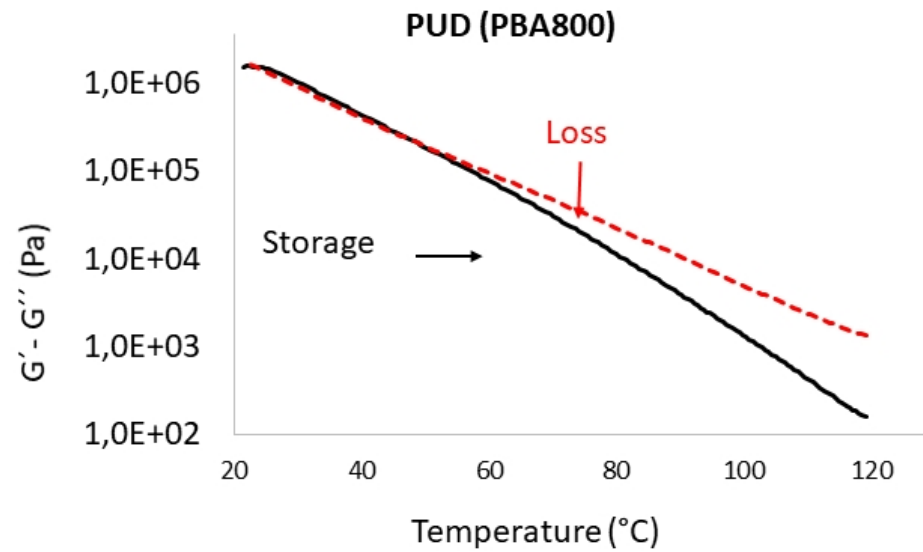


Figure 8. Rheological analysis of temperature sweep experiments of PU (PBA800) film.

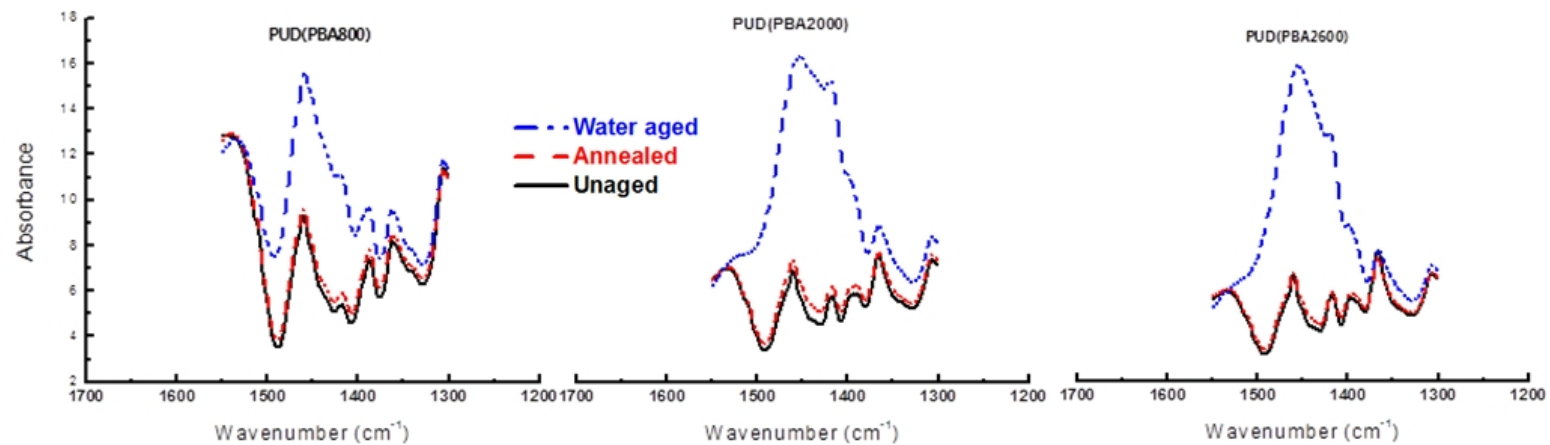


Figure 9. 1600-1300 cm⁻¹ zone of ATTR-FTIR spectra

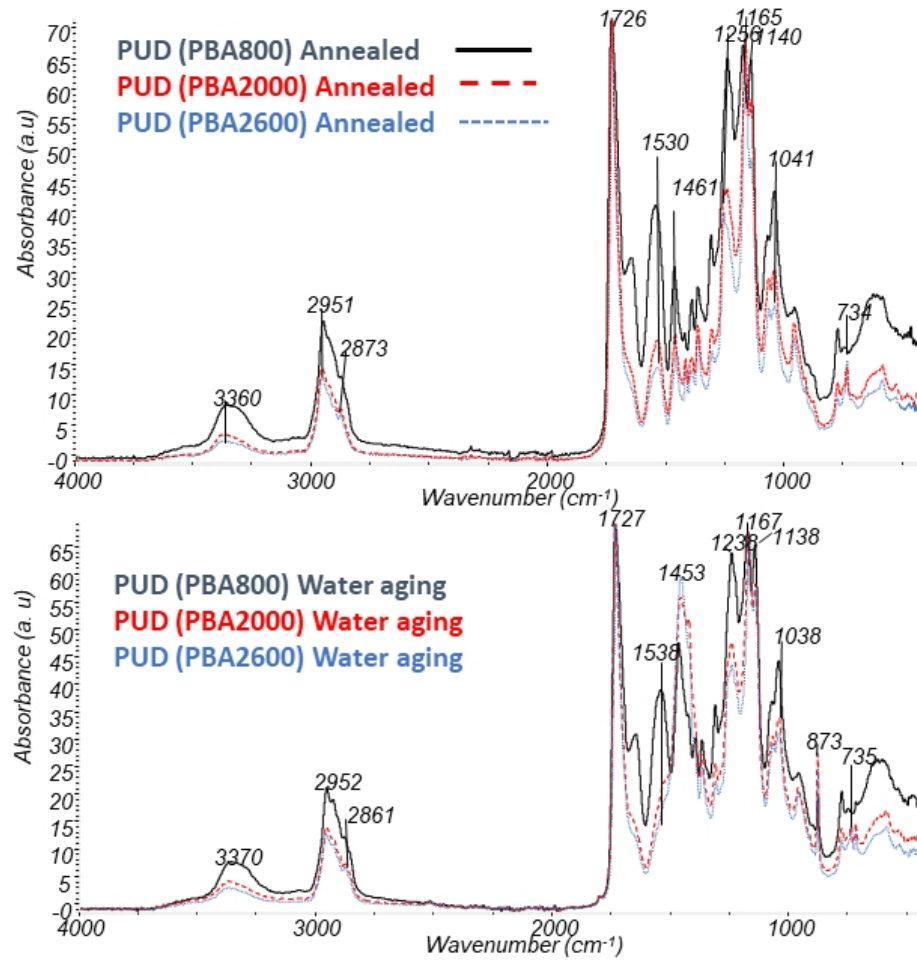


Figure 10. ATR-IR spectra of aged films. (a)After annealing treatment (b) After water immersion

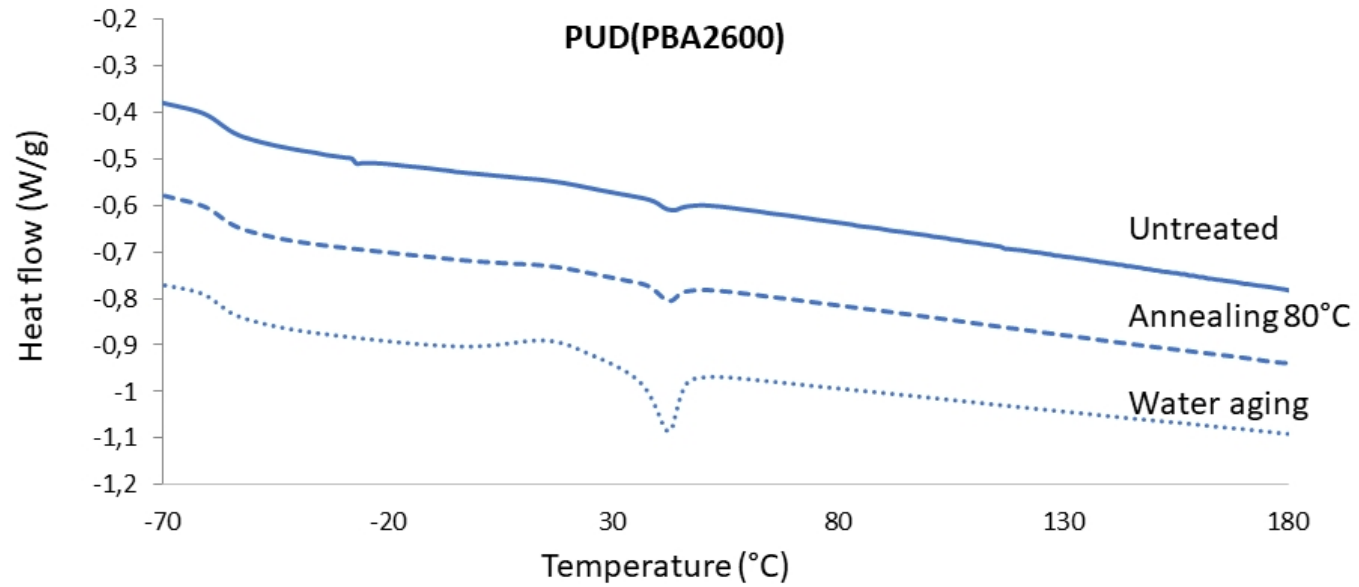


Figure 11. Accelerated aging effect on DSC thermogram of PU made with PBA2600

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Editorial Department of Progress in Organic Coatings

Dear Editor of Progress in Organic Coatings,

We confirm that this manuscript has not been published elsewhere and is not under consideration by another journal. All authors have approved the manuscript and agreed with the submission to Colloid and Polymer Science. This study was supported by a Colciencias in the frame of the project code 1115-452-21346, corresponding to the convocatory number 452 to 2008. The authors have no conflicts of interest to declare.

Thank you very much for your consideration.
Yours Sincerely,



Prof. Víctor Hugo Orozco
Universidad de Antioquia
Laboratorio de Investigación en Polímeros
Bloque 2, Laboratorio 2-303
Tel.: +57 3174370257
E-mail: hugo.orozco@udea.edu.co,

Authors:

Anny C. Ospina¹
Víctor H. Orozco^{1*}
Luis F. Giraldo¹
José Miguel Martín-Martínez²

¹ *Laboratorio de Investigación en Polímeros, Instituto de Química, Universidad de Antioquia, 050010 Medellín, Colombia*

² *Adhesion and Adhesives Laboratory, University of Alicante, 03080 Alicante, Spain*