Synthesis of waterborne polyurethane-urea dispersions with chain extension step in homogeneous and heterogeneous media

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Graphical Abstract
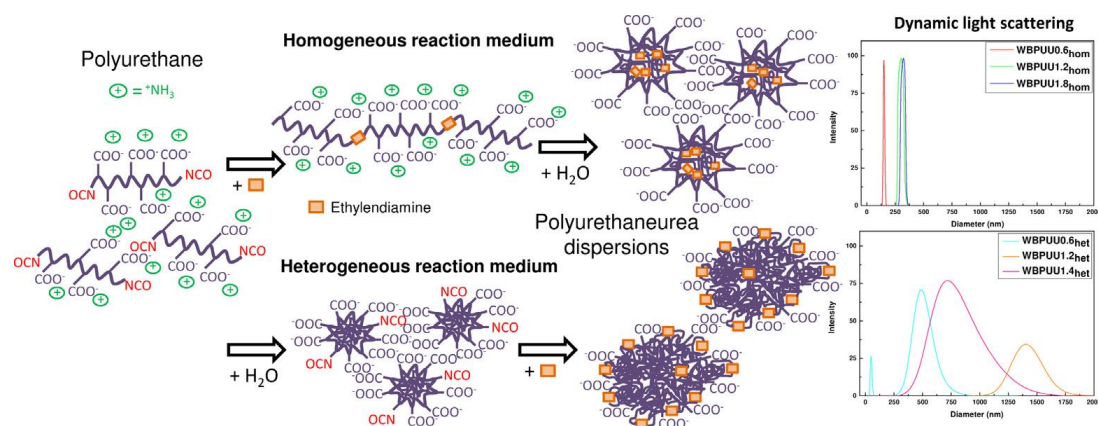
Abstract

Hypothesis: The possibility of tailoring the final properties of environmentally friendly waterborne polyurethane and polyurethane-urea dispersions and the films they produce makes them attractive for a wide range of applications. Both the reagents content and the synthesis route contribute to the observed final properties.

Experiments: A series of polyurethane-urea and polyurethane aqueous dispersions were synthesized using 1,2-ethanediamine and/or 1,4-butanediol as chain extenders. The diamine content was varied from 0 to 4.5 wt%. Its addition was carried out either by the classical heterogeneous reaction medium (after phase inversion step), or else by the alternative homogeneous medium (prior to dispersion formation). Dispersions as well as films prepared from dispersions have been later extensively characterized.

Findings: 1,2-Ethanediamine addition in heterogeneous medium leads to dispersions with high particle sizes and broad distributions whereas in homogeneous medium, lower particle sizes and narrow distributions were observed, thus leading to higher uniformity and cohesiveness among particles during film formation. Thereby, stress transfer is favored adding the diamine in a homogeneous medium; and thus the obtained films presented quite higher stress and modulus values. Furthermore, the higher uniformity of films tends to hinder water molecules transport through the film, resulting, in general, in a lower water absorption capacity.

Keywords: Waterborne polyurethane-ureas; 1,2-Ethanediamine; Homogeneous medium reaction; Heterogeneous medium reaction; Particle size distribution; Mechanical behavior

1. Introduction

Polyurethanes and polyurethane-ureas are part of a versatile polymer family composed by a macrodiol as soft segment (SS) and by an isocyanate and a low molecular weight diol or diamine chain extender as hard segment (HS) [1]. In the field of polyurethane and polyurethane-urea chemistry, and considering the concern on environmentally-friendly systems, the research on waterborne systems has been addressed by the addition of an internal emulsifier [2] forming part of the polymeric chain, providing stability to the particles formed during dispersion formation or phase inversion step. In this way, waterborne polyurethanes are taking over from the conventional solventborne counterparts reducing volatile organic compound emissions and resulting in stable dispersions with high solid contents, low viscosities, non-flammability, good adhesion and film-forming ability at room temperature [3]. In addition, the versatility and possibility of tailoring the properties of polyurethanes or polyurethane-ureas by designing SS-HS composition as well as reagents nature or synthesis procedure contribute to their extended use in a wide range of applications such as paintings,inks, coatings, adhesives and medicine [4–7].

Considering the nature of the chain extender and hence the reaction rate, generally diol chain extensions are carried out before phase inversion step, thus avoiding side reactions due to their lower reactivity with isocyanates comparing with water. Instead, due to their higher reactivity, diamine chain extenders can be added either prior to water addition (before phase inversion), leading to the reaction in homogeneous medium or once the dispersion is formed (after phase inversion), completing the polyurethaneurea reaction in heterogeneous medium. This last method is the most used for chain extension with diamines. The use of diamines as chain extenders generally favors the cohesion forces between urea groups comparing with urethane linkages [1,8], leading to systems with higher mechanical strength.

Therefore, in this work a systematic and comprehensive analysis of the synthesis process of a waterborne polyurethane-urea system has been carried out. Considering the few works studying the diamine chain extension step, this study has been focused on the synthesis of different polyurethane-ureas, where diamine extension was carried out both in homogeneous and heterogeneous media, besides varying diamine chain extender content. The corresponding polyurethane, i.e. a dispersion without diamine chain extender has also been synthesized in order to compare the influence of urethane or urethane and urea moieties in the polymer chain. The particle size and distribution of the dispersions has been analyzed and the prepared films has been characterized from the viewpoint of physicochemical, thermal, mechanical, thermomechanical and water absorption properties. Moreover, the hydrophilicity and morphology of the films has also been studied.

2. ExperimentalMaterials and methods

2.1. Materials

Polyurethane and polyurethane-ureas were synthesized using poly(e-caprolactone) diol (PCL) ($\overline{M}_w = 2000$ g/mol), provided by Solvay, as soft segment and isophorone diisocyanate (IPDI), provided by Bayer as the isocyanate. 1,4-Butanediol (BD) and ethylenediamine (EDA) supplied by Fluka and Panreac respectively, were used as chain extenders. 2,2-Bis(hydroxymethyl)pro pionic acid (DMPA), purchased from Fluka, was employed as internal emulsifier and triethylamine (TEA), provided by Fluka, was used to neutralize the ionic groups in the dispersion. PCL, BD and DMPA were dried under vacuum at 60 °C. Dry acetone, purchased from Panreac, and the catalyst dibutyltin dilaurate (DBTDL), supplied by Fluka were used without further purification.

2.2. Synthesis of waterborne polyurethane and polyurethane-ureas

Different waterborne polyurethane-urea (WBPUU) dispersions were synthesized by a two-step polymerization process, varying EDA content from 0 to about 4.5 (wt%).

The reaction was carried out in a 500 mL four neck jacketed reactor with an intracooler as a temperature controller. The reactor was equipped with a mechanical stirrer and a thermocouple connected to a computer for monitoring and controlling the reaction conditions. The synthesis was performed under nitrogen atmosphere and the reaction progress was followed by the dibutylamine back titration method according to ASTM D 2572-97. PCL, 0.037 wt % of DBTDL and IPDI were charged in the reactor at 80 °C and allowed to react until the amount of residual NCO groups reached the theoretical value. Once the mixture was cooled to 50 °C, and in order to effectively incorporate the internal emulsifier, previously mixed DMPA and TEA (dissolved in a small amount of acetone), were added. This procedure ensures the addition of DMPA as its triethylammonium salt. Then, the NCO terminated pre-polymer was heated to 80 °C and BD was added for the first chain extension with a diol. The system was cooled to 45 °C while the viscosity was adjusted with dry acetone. Afterwards, two alternative methods were chosen to carry out the second extension reaction with the diamine (EDA):

1. In the first method, EDA addition in homogeneous medium, EDA was dissolved in 30 mL of dry acetone and added at a flow rate of 0.5 mL min^{-1}. Thereafter, by the phase inversion process, a polyurethane-urea dispersion was obtained adding distilled water dropwise under vigorous stirring at 25 °C.

2. In the second method, EDA addition in heterogeneous medium, EDA was added after phase inversion.

In both cases the added amount of EDA was calculated assuming a chain extension of 80%. In either situation, acetone was removed using a rotary evaporator at 40 °C and 350 mbar, obtaining final dispersions with solid contents around 35 wt%. In addition, a dispersion without EDA has also been synthesized.

Polyurethane and polyurethane-urea films were prepared by casting dispersions in Teflon molds, which were allowed to dry at 25 °C and 50% of relative humidity during 7 days. Then, films were stored during 3 days at 25 °C at 800, 600 and 400 mbar respectively. Samples have been coded as WBPUUXy where X describes EDA molar ratio (0.6, 1.2 or 1.8) and sub-index y specifies a homogeneous (hom) or heterogeneous (het) medium for the EDA chain extension step. The dispersion without EDA addition is named WBPU. Table 1 shows the molar ratios of the reagents and the hard segment, EDA and DMPA content (expressed as percentage weight) of the synthesized polyurethane and polyurethane-ureas, both in homogeneous and heterogeneous media. Moreover, in Fig. 1 the scheme of the synthesis routes and the reagents molecular structure used in the polymerization process are represented.

Table 1. Molar composition and HS, EDA and DMPA content expressed as weight of percentage.

Designation	Molar composition					HS (wt%)	DMPA (wt%)	EDA (wt%)
	PCL	IPDI	DMPA	BD	EDA			
WBPU	0.5	3.15	0.5	2	0	48.61	3.44	0
WBPUU0.6$_y$	0.5	3.6	0.5	2	0.6	51.98	3.22	1.73
WBPUU1.2$_y$	0.5	4.2	0.5	2	1.2	55.59	2.98	3.20
WBPUU1.8$_y$	0.5	4.8	0.5	2	1.8	58.69	2.77	4.47

The y subindex denotes the EDA reaction medium, which refers to homogeneous or heterogeneous media.
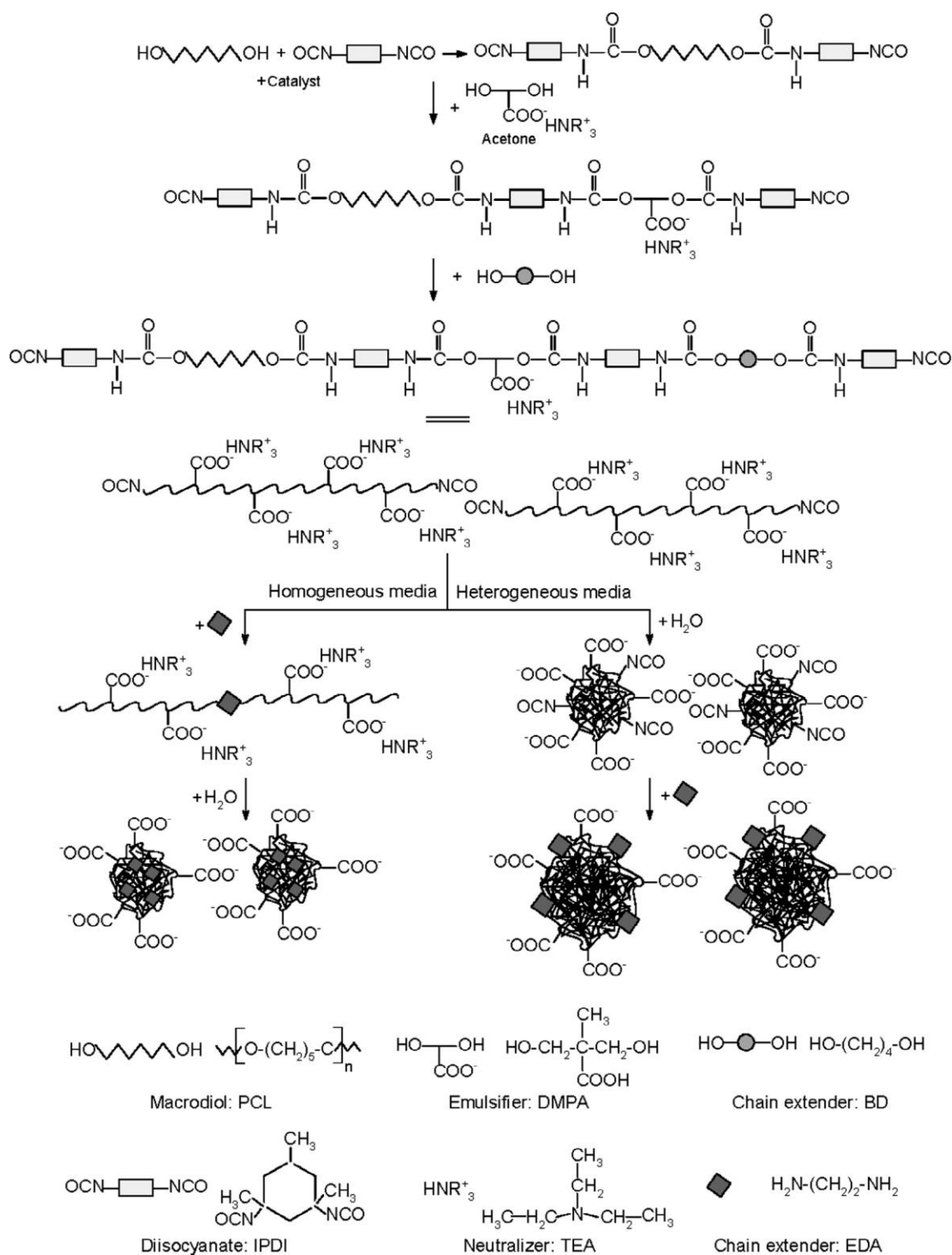
Fig. 1. Scheme of the synthesis routes and reagents used in the polymerization process.

2.3. Characterization

Dynamic light scattering (DLS) using a BI-200SM goniometer (Brookhaven) yielded particle size distributions of WBPU and WBPUU dispersions. A luminous source of He-Ne laser (Mini L-30, wavelength k = 637 nm, 400 mW) and a detector (BI-APD) placed on a rotary arm have measured the intensity of dispersed light at 90°. Samples, prepared diluting a small amount of polyurethane and polyurethane-urea dispersions in ultrapure water, were measured three times at 25 °C.

WBPUU morphology was analyzed by atomic force microscopy (AFM), in tapping mode, using a Nanoscope IIIa scanning probe microscope (MultimodeTM Digital instruments) with an integrated force generated by cantilever/silicon probes, applying a resonance frequency of about 180 kHz. The cantilevers were 125 μm long and had a tip radius of 5–10 nm. Samples were prepared by drying a drop of polyurethane-urea dispersions on glass supports via spin-coating (Spincoater P6700) at 200 rpm for 130 s.

The morphology was also studied by means of polarized optical microscopy (POM) using a Nikon Eclipse E600 in transmission mode obtaining images with a resolution of 500.

WBPU and WBPUU characteristic functional groups were determined by Fourier transform infrared spectroscopy (FTIR) using a Nicolet Nexus spectrometer provided with a MKII Golden Gate accessory (Specac) with a diamond crystal at a nominal incidence angle of 45° and ZnSe lens. Spectra were acquired in transmittance mode in the range from 4000 to 600 cm^{-1} averaging 64 scans with a resolution of 8 cm^{-1}.

Differential scanning calorimetry (DSC) measurements were carried out in a Mettler Toledo 822^e equipment, provided with a robotic arm and with an electric intracooler as refrigerator unit. Between 5 and 10 mg of WBPU and WBPUU films were sealed in aluminum pans and were subjected to a heating run from -75 to 180 °C at a scanning rate of 40 °C min^{-1}. From the obtained thermograms, glass transition temperature (T_g) was set as the inflection point in the heat capacity change. The maximum of endothermic peak was assigned to the melting temperature (T_m) and the area under that peak yielded the enthalpy of fusion (ΔH_m).

Mechanical behavior of WBPU and WBPUU films were analyzed in a MTS insight 10 testing machine provided with a 250 N load cell and using pneumatic grips to hold strip shape samples with dimensions about 8 mm in length, 2.5 mm in width and 0.4 mm in thickness. Tensile modulus, yield stress, stress at break and elongation at break of five specimens were averaged at a crosshead rate of 50 mm min^{-1}.

Thermomechanical behavior of the films was analyzed by dynamic mechanical analysis (DMA) in an Eplexor 100 N Gabo equipment. The measurements were conducted from -100 to 150 °C at a scanning rate of 2 °C min^{-1} in tensile mode, with an initial strain of 0.05% and operating frequency of 1 Hz.

Water contact angle (WCA) was measured in a Dataphysics OCA20 equipment for the analysis of WBPUU films hydrophilicity at room temperature. Six measurements were averaged by dropping 2 μL deionized water over polyurethane and polyurethaneurea films surface.

Water absorption measurements were also carried out for the analysis of WBPU and WBPUU films hydrophilicity in water at 25 °C. Around 15–20 mg of film were immersed in deionized water and weighed until no change was observed. Thereby, water absorption (WA) percentage was determined according to the following equation:

$$WA\ (\%) = \frac{W_t - W_0}{W_0} \cdot 100$$

where W_t and W_0 are the weights at t time and at initial time, respectively. Water absorption measurements for each sample were determined by triplicate.

3. Results and discussion

3.1. Polyurethane-urea dispersions

The dispersions particle size has no direct influence on the physical properties of polyurethane and polyurethane-urea cast films. However, particle size is a significant variable to consider depending on the final application of the polyurethane and polyurethane-urea dispersion [9,10]. Usually, small particle size dispersions are preferable for the preparation of deep penetrating coatings, whereas larger particle sizes promote the formation of fast drying coatings [9,11]. The distribution and average particle size of the polyurethane and polyurethane-ureas in this work, determined by light scattering are shown in Fig. 2 and Table 2 respectively. It has been observed that larger particles and broader particle size distribution profiles are obtained as EDA content increases. The addition of EDA results in higher HS content WBPUU, which causes a decrease in the flexibility of polymer chains hindering their ability to be dispersed into small particles [12]. In addition, the decrease in DMPA content as EDA content is increased, contributes to the formation of larger particles due to the lower repulsion forces generated among them [13]. In the case of WBPU, a bimodal distribution is observed, resulting in particles around 35 and 342 nm. The smaller particles present a narrow distribution whereas the distribution of larger sized particles is broader.
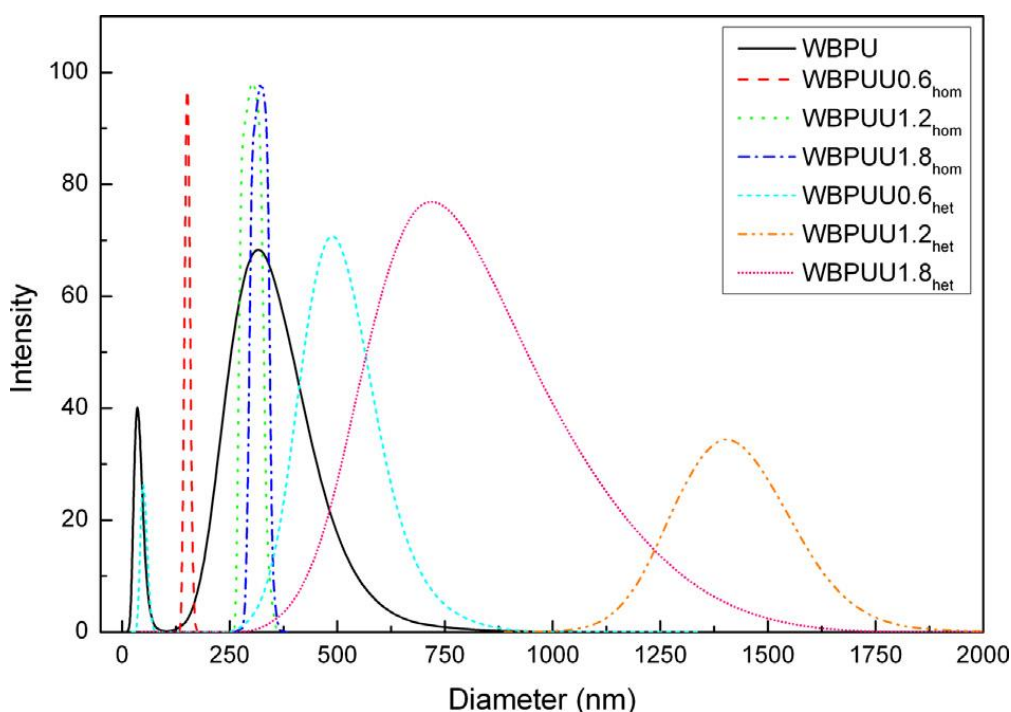

Fig. 2. Particle size distribution of polyurethane and polyurethane-urea dispersions.

The influence of the EDA chain extension step in the average particle size and distribution has also been examined. The results reveal that EDA reaction in homogeneous medium, leads to a narrow unimodal distribution with rather small particles. However, when EDA chain extension takes place in a heterogeneous medium, bimodal or very broad particle size distributions are observed. The broad peak consisting of larger particles could result from the growth of smaller particles during EDA chain extension step and possible agglomerations. It has to be noted that once phase inversion has occurred, NCO free groups can react with EDA or water, being the reactivity with EDA higher, and resulting in urea linkages in both cases. The reaction of NH_2 groups of EDA is supposed to take place mainly close to the particles surface. The NCO free groups positioned at or near the particle surface show greater accessibility than those located inside particles [14,15]. However, EDA and water molecules have also the ability to penetrate into the particles and react with remaining NCO groups. Therefore, despite the possibility of reactions inside the particles, it is expected that chain extension would mainly occur at the

particles surface [15], thus contributing to achieve larger particle sizes, as compared with their homologues synthesized in a homogeneous medium.

Table 2. Particle size of polyurethane and polyurethane-urea dispersions.

Sample	Particle size (nm)
WBPU	34.3 ± 1.1; 342.3 ± 41.0
WBPUU0.6$_{hom}$	153.4 ± 1.3
WBPUU1.2$_{hom}$	298.1 ± 1.4
WBPUU1.8$_{hom}$	308.6 ± 1.6
WBPUU0.6$_{het}$	56.8 ± 7.6; 483.5 ± 26.4
WBPUU1.2$_{het}$	1411.6 ± 412.2
WBPUU1.8$_{het}$	838.7 ± 179.7

AFM analysis was carried out in order to analyze the morphology of films formed from the dispersions. Fig. 3 shows height and phase images of polyurethane-ureas synthesized by EDA chain extension step in homogeneous medium. Analyzing those AFM images it can be observed that WBPUU0.6$_{hom}$ sample seems to present considerable cohesiveness between particles leading to a homogeneous film where spherical particles can barely be differentiated. Alternatively, as EDA content is increased, the cohesiveness between larger particles becomes weaker resulting in observable slightly isolated particles in the case of WBPUU1.8$_{hom}$. Since it was not possible to obtain AFM images of the other samples, an optical microscopy image of WBPUU0.6$_{het}$ sample is displayed where no homogeneously dispersed particles, heterogeneous in size, can be observed resulting in lower driving force for film formation. These results corroborate the above discussed DLS results.
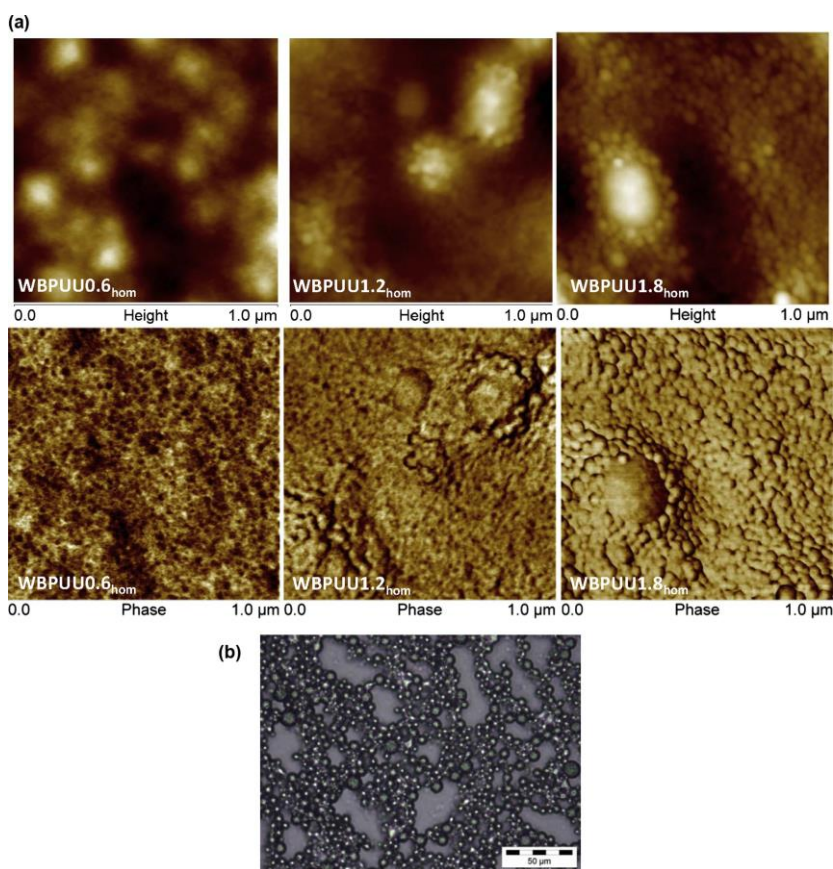

Fig. 3. (a) AFM height and phase images of polyurethane-ureas synthesized in homogeneous dispersion and (b) optical microscopic image of WBPUU0.6$_{het}$.

3.2. Polyurethane-urea films characterization

In Fig. 4, FTIR absorption spectra profiles of films are shown in order to identify the characteristic groups of polyurethane and polyurethane-ureas. The band at 2247 cm^{-1} associated with NCO groups is not detected in any spectra, so isocyanate conversion seems to be full in all synthesis.

The region between 3100 and 3500 cm^{-1} is attributed to urea and urethane N-H groups. Two peaks, located about 3320 and 3450 cm^{-1} are often observed, and they can be assigned to hydrogen-bonded and non hydrogen-bonded N-H of urethane and urea groups [1]. In this case, only a single peak around 3336 cm^{-1} is seen, suggesting that most N-H groups are involved in hydrogen bonds.
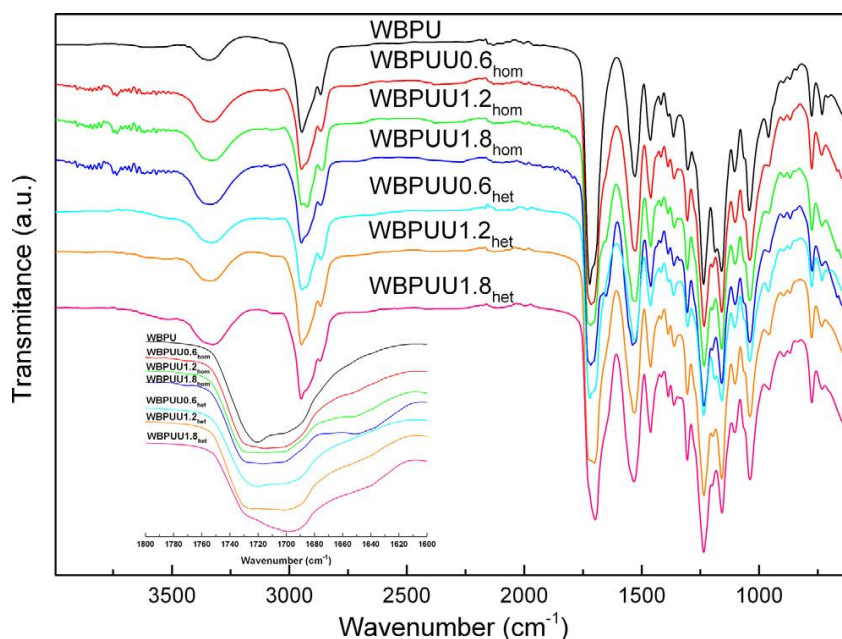

Fig. 4. FTIR spectra of polyurethane and polyurethane-urea films.

In the inset of Fig. 4, amide I region [16] located between 1745 and 1630 cm^{-1} concerning to carbonyl groups (C=O) can be observed. In that region, depending on the C=O groups nature and hydrogen bonding ability, stretching vibration peaks appear at different wavenumbers [1,6,17,18]. In WBPU a sharp peak can be distinguished around 1720 cm^{-1} and a shoulder about 1700 cm^{-1} attributable to the C=O of the free urethane and PCL ester groups, and C=O hydrogen bonded of urethane groups, respectively. In the case of EDA reaction in homogeneous medium, C=O carbonyl stretching region present different bands at about 1730 and 1701 cm^{-1}. In addition, a band close to 1650 cm^{-1} related with the hydrogen bonded urea C=O groups can be observed, becoming more noticeable as EDA content increases, therefore suggesting that EDA addition favors urea C=O hydrogen bonding interactions. In samples where the chain extension with EDA was performed in heterogeneous medium, similar bands to WBPU are observed. The peak about 1720 cm^{-1} shifts to higher wavenumber values (1720 cm^{-1} in WBPUU0.6$_{het}$, 1726 cm^{-1} in WBPUU1.2$_{het}$ and 1728 cm^{-1} in WBPUU1.8$_{het}$) as EDA content increases, probably due to the presence of a great amount of free C=O urethane groups. In addition, the relative intensity of the band about 1700 cm^{-1} increases due to the presence of more C=O of urea groups with EDA addition.

The bands related with the hydrogen bonded C=O urea groups, around 1640 cm^{-1} are perceptible at high EDA contents (WBPUU1.2$_{het}$ and WBPUU1.8$_{het}$) suggesting that urea C=O groups tend to associate in hydrogen bonding interactions when EDA content increases.

Fig. 5 shows DSC heating scans of polyurethane and polyurethane-urea samples. Soft segment glass transition temperature (T_{gSS}), melting temperature (T_{mSS}), and enthalpy (ΔH_{mSS}) as well as hard segment melting temperature (T_{mHS}), and enthalpy (ΔH_{mHS}) are summarized in Table 3. For WBPU, an endothermic peak about 50 °C related with the ordered soft domains has been observed. In WBPUUX$_{hom}$ systems, it was observed that EDA addition hinders the possibility of soft segments to arrange in soft crystalline domains, since no soft endothermic peak was detected, providing mobility and decreasing T_{gSS} as EDA content increases. However, in heterogeneous medium, WBPUU0.6$_{het}$ shows soft segment melting enthalpy. In this case, EDA is added after the polyurethane chains have adopted the conformation expected with core-shell particles, where PCL moves inside the particle, forming part of the core [13]. The amine tends to stay and later react close to the particle surface, as previously explained, and consequently, EDA will interfere in a lesser extent with PCL facilitating the ability to form soft crystalline domains. Nevertheless, ΔH_{mSS} decreases comparing with WBPU. At higher EDA contents SS crystallization is hindered. Around 80 °C, in both homogeneous and heterogeneous systems, an endothermic transition has been observed attributable to the short range ordering of hard segments [19]. It has been observed that the increase of EDA content decreases ΔH_{mHS} values and shifts the transition to higher temperature, due to stronger hydrogen bonding interactions. Moreover, in case of heterogeneous reaction medium higher and broader ΔH_{mHS} are obtained. When EDA reaction occurs after chains have adopted a conformation typical of particles, EDA tends to react in the outer shell of the particles remaining more accessible to interactions and thus favoring ordered structures.
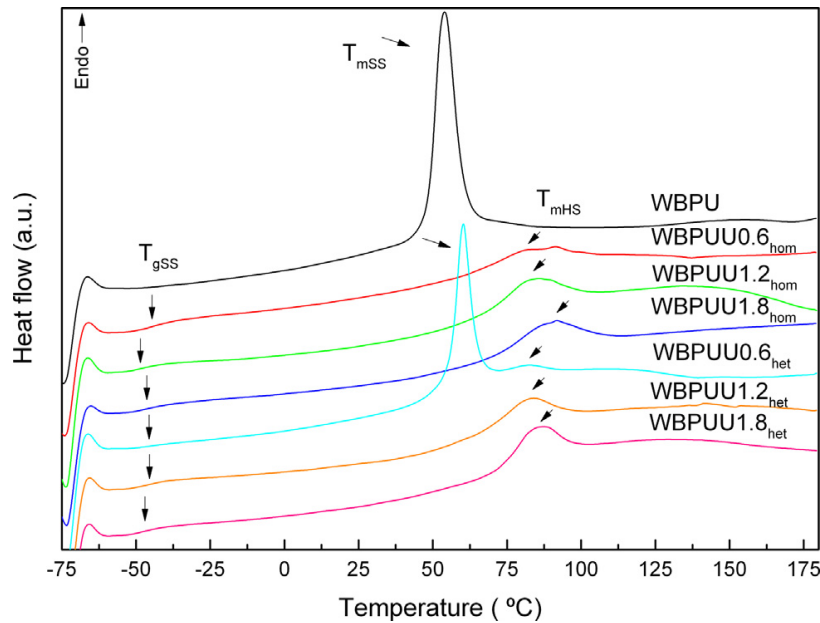

Fig. 5. DSC thermograms of polyurethane and polyurethane-urea films.

Table 3. Thermal properties of polyurethane and polyurethane-urea films.

Sample	T_{gSS} (°C)	ΔH_{mSS} (J g^{-1})	T_{mSS} (°C)	ΔH_{mHS} (J g^{-1})	T_{mHS} (°C)
WBPU	–	27.6	53.6	–	–
WBPUU0.6$_{hom}$	−44.4	–	–	13.5	81.5
WBPUU1.2$_{hom}$	−48.4	–	–	11.7	83.4
WBPUU1.8$_{hom}$	−46.4	–	–	10.8	91.9
WBPUU0.6$_{het}$	−45.7	13.5	60.5	3.3	82.1
WBPUU1.2$_{het}$	−45.7	–	–	15.1	82.7
WBPUU1.8$_{het}$	−47.1	–	–	14.6	85.3

Fig. 6 shows the mechanical behavior of WBPU and WBPUU films and yield stress (σ_y), stress at break (σ_y), modulus (E) and elongation at break (ε_b) values are summarized in Table 4. It has been observed a considerable improvement of polyurethane-ureas mechanical performance comparing with WBPU, behavior attributable to the stronger hydrogen bonding provided by urea groups as compared with urethane groups of hard segments [1]. The yield stress, stress at break and modulus values have improved considerably in WBPUU comparing with WBPU, even up 540, 1570 and 400%, respectively in WBPUU1.8$_{hom}$. The increase of EDA content results in a greater amount of urea groups thus leading to an increase of the hydrogen bonds as observed by FTIR resulting in tougher films [8]. In addition, in most of the samples high elongation at break values are observed. In the case of heterogeneous medium, and comparing samples with the same EDA content of the homogeneous series, except for WBPUU0.6$_{het}$, lower values of stress modulus and elongation at break are obtained. This could be related to a distinct pattern of the particles formation during the synthesis process. In homogeneous systems, a narrower size distribution together with lower average particle sizes has been obtained leading to an improved homogeneous cohesion between particles during the drying process of film formation. Therefore, interactions would be favored as observed in FTIR results, and the presumably lower amount of failure points, owing to the film homogeneity, would facilitate the stress transfer in the films. The larger values of yield stress, stress at break and modulus with sample WBPUU0.6$_{het}$ could be due to the additional stiffness conferred by the soft segment crystallization.
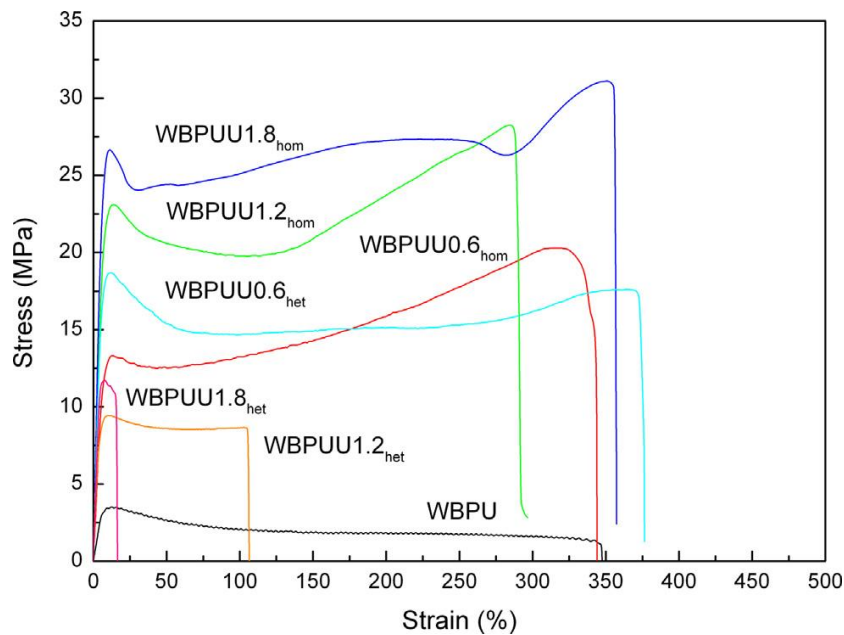

Fig. 6. Stress vs. strain curves of polyurethane and polyurethane-urea films.

Table 4. Mechanical properties of polyurethane and polyurethane-urea films.

Sample	Yield stress (MPa)	Stress at break (MPa)	Modulus (MPa)	Elongation at break (%)
WBPU	4.1 ± 0.7	1.8 ± 0.6	76.9 ± 14.4	337 ± 63
WBPUU0.6$_{hom}$	12.7 ± 0.5	20.6 ± 2.6	209.7 ± 14.9	329 ± 42
WBPUU1.2$_{hom}$	21.5 ± 1.3	26.6 ± 1.2	331.6 ± 13.9	296 ± 37
WBPUU1.8$_{hom}$	26.2 ± 2.2	29.7 ± 1.4	387.1 ± 51.5	343 ± 59
WBPUU0.6$_{het}$	14.5 ± 0.2	18.0 ± 0.8	337.7 ± 9.6	373 ± 22
WBPUU1.2$_{het}$	9.3 ± 0.5	8.5 ± 0.9	222.9 ± 28.6	113 ± 44
WBPUU1.8$_{het}$	11.5 ± 1.0	11.0 ± 1.0	279.0 ± 11.5	13 ± 3

The thermomechanical behavior of films has been studied by DMA by analyzing the evolution of storage modulus (E') and tan δ with increasing temperature, as observed in Fig. 7. It has been observed that at low temperatures all samples show similar E' values in the glassy state, followed by a drop between -50 and -25 °C attributable to the T_{gSS}, which is also reflected in a small peak in tan δ curve. Analyzing this peak, it can be observed that the transition is less pronounced in the case of the plain polyurethane, corroborating the results obtained by DSC, as T_{gSS} was hard to observe. Moreover, E' values for that polyurethane is slightly higher in this rubbery plateau, suggesting higher crystallinity of soft segments as compared to polyurethane-ureas [1]. With larger urea content, the T_{gSS} transition in the tan δ curve becomes more pronounced with almost unchanged temperature values. At higher temperatures, it can be appreciated that polyurethane WBPU presents lower thermomechanical stability comparing with polyurethane-ureas. Despite presenting around 90% higher E' values than in the case of WBPUU0.6$_{hom}$ and WBPUU0.6$_{het}$ at room temperature, when soft domains crystals melt about 50 °C, as observed in DSC results, the sample starts to flow. In polyurethane-ureas, the increase of EDA content provides greater thermomechanical stability due to the contribution of urea groups' interactions as observed by FTIR and DSC. In the case of homogeneous chain extension reaction, an improvement of about 55 and 100% has been observed in the thermomechanical stability temperature for WBPUU1.2$_{hom}$ and WBPUU1.8$_{hom}$ respect to WBPUU0.6$_{hom}$, whereas with heterogeneous system the improvement has resulted into about 75 and 120% for WBPUU1.2$_{het}$ and WBPUU1.8$_{het}$ respectively as compared to WBPUU0.6$_{het}$.
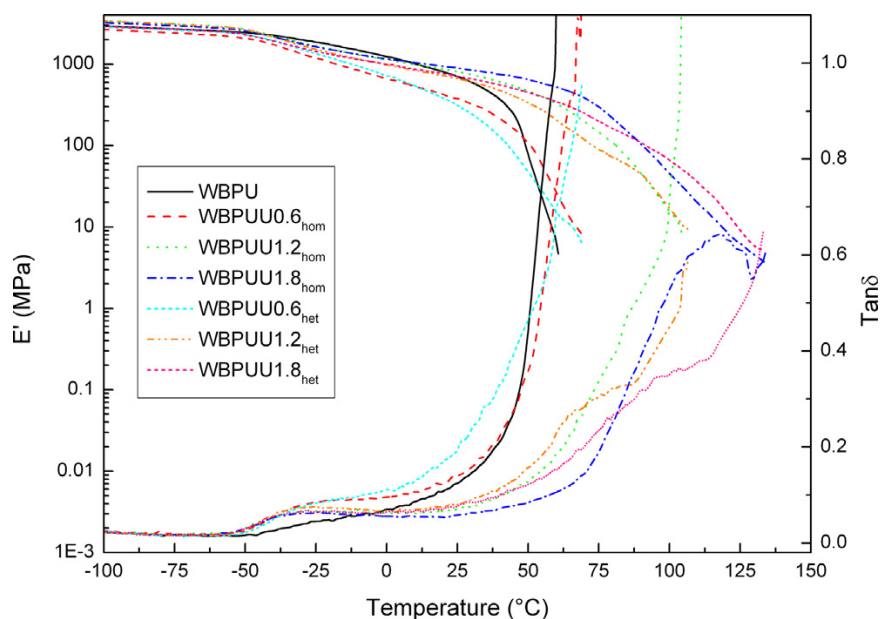

Fig. 7. Storage modulus and tan δ curves of polyurethane and polyurethane-urea films.

The hydrophilicity of polyurethane-urea films has been put into evidence through static water contact angle determinations, summarized in Table 5, as well as water absorption measurements at 25 °C displayed in Fig. 8. From the water contact angle values it can be observed that WBPU shows in general higher values as compared with polyurethane-ureas containing urea groups, which present higher polarity. In general, in both, EDA reaction in homogeneous and heterogeneous media, it has been observed a decrease in contact angle values as hard segment content increases, due to the greater density of urea groups. This drop is slightly lower in the case of EDA reaction in heterogeneous medium. Indeed, it could be influenced by the EDA addition after dispersion formation in the synthesis. As explained in DLS results, EDA would react preferably in the particle external boundary and probably would interfere with the location of the

ionic groups at the surface. In the case of WBPUU1.8$_{het}$, the higher surface roughness can also contribute to the increase of the water contact angle value [20].

Table 5. Water contact angle values of polyuretyhane and polyurethane-urea films.

Sample	Angle (°)
WBPU	87.4 ± 0.6
WBPUU0.6$_{hom}$	80.9 ± 1.0
WBPUU1.2$_{hom}$	75.5 ± 0.7
WBPUU1.8$_{hom}$	73.1 ± 1.3
WBPUU0.6$_{het}$	81.6 ± 1.1
WBPUU1.2$_{het}$	79.7 ± 0.8
WBPUU1.8$_{het}$	90.0 ± 0.7

As far hydrophilicity is concerned, and in order to study the behavior of films immersed in water, films have also been subject to weight change measurements. It can be observed that water absorption of WBPU reaches a maximum and then decreases due to the weight loss caused by hydrolytic degradation mainly closer to the surface [21].

With respect to EDA reaction in homogeneous medium, as the EDA content increases, a higher water absorption was observed, which can be due to a greater amount of urea polar groups, except for WBPUU1.8$_{hom}$, which could be related to the inhomogeneity of the film.
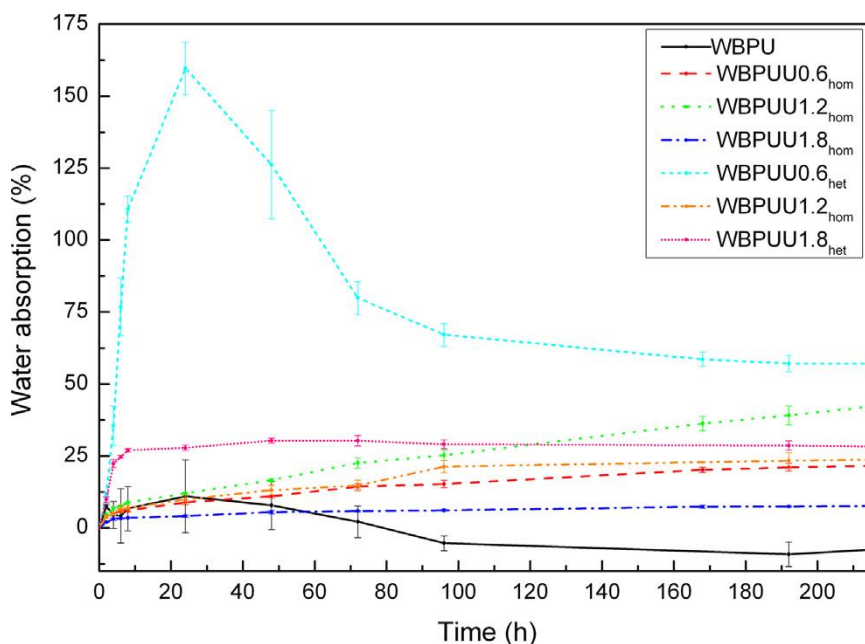

Fig. 8. Water absorption of polyurethane and polyurethane-urea films.

In the case of EDA reaction in heterogeneous medium, the same tendency is observed, being the observed values generally higher as compared to the corresponding homologues of the homogeneous series. This could be related with the film formation ability. The broader bimodal particle size distribution of the heterogeneous systems would lead to films with lower uniformity and cohesiveness among particles which may result in possible gaps among them and thereby, facilitate the transport of water molecules through the film. In the case of WBPUU0.6$_{het}$, a similar hydrophilic behavior to WBPU has been observed, corroborated by the similar soft and hard segment structures as observed in DSC results. Furthermore, the higher water absorption percentage achieved in WBPUU0.6$_{het}$ would be probably at the origin of the more severe

hydrolytic degradation of this sample due to the greater accessibility of water molecules to the hydrolysable groups [21].

4. Conclusion

In this work a series of polyurethane and polyurethane-urea dispersions, with varied EDA content and following two different chain extender addition procedures (in homogeneous or heterogeneous media), were produced. From these dispersions films were prepared and characterized.

As the EDA content increases, and thereby HS content, dispersions with larger particles were obtained as a result of the polymer chain flexibility reduction. Moreover, the used addition step also influences the particle size distribution. In homogeneous medium unimodal distributions with lower particle sizes were observed, whereas in heterogeneous medium broader distributions with larger particle sizes resulted, behavior attributed to the preferential EDA reaction at the particles' surface, once in this last case diamine addition follows particle formation.

Dispersions produced in homogenous medium with low EDA contents give rise to films imparting significant cohesiveness among particles, whereas slightly isolated particles start to be perceived as the EDA content increases. Moreover, DSC results revealed that soft segment crystallization ability was hindered by EDA addition, although endothermic transition related to short range ordering of hard segment domains was promoted.

Comparatively with polyurethane counterparts, polyurethaneurea presented better performance showing values of stress at yield, stress at break and modulus values up to 540, 1570, and 400%, respectively, while keeping proximate values of elongation at break. Also, a higher EDA content leads to improved stress and modulus, particularly if EDA is added in homogeneous medium. A narrow particle size distribution facilitated cohesiveness and interactions during film formation, thus favoring stress transfer. DMA results corroborated the thermomechanical stability conferred by EDA addition. An improvement of about 100% and 120% was observed in E0 values for samples $WBPUU1.8_{hom}$ and $WBPUU1.8_{het}$ respect to $WBPUU0.6_{hom}$ and $WBPUU0.6_{het}$ respectively.

Water absorption exhibited a growing tendency as the EDA content increased. If heterogeneous medium is used for chain extension, higher levels of water absorption are achieved in comparison with the corresponding homogeneous counterparts, attributable to the influence of particle size in the film formation process. Furthermore, a hydrolytic degradation behavior was observed in samples WBPU and $WBPUU0.6_{het}$.

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