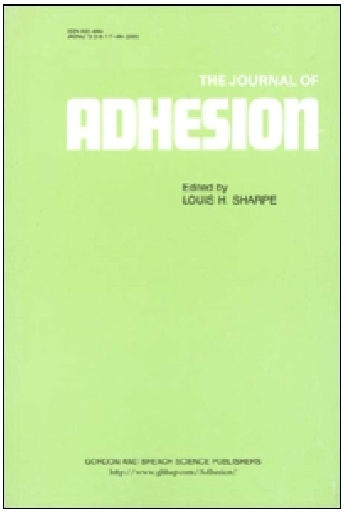

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Influence of the Chemical Structure of Urethane-Based Thickeners on the Properties of Waterborne Polyurethane Adhesives

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To analyse the parameters that influence the thickening mechanism of waterborne polyurethane adhesives, different hydrophobically modified ethoxylated polyurethane based thickeners (HEUR) were used. The thickeners were characterized by proton nuclear magnetic resonance (^{1}H-NMR) and gel permeation chromatography (GPC). The thickened adhesive solutions were characterized by flow rheology, pH, particle size measurements, solids content, and confocal microscopy. The thickened solid adhesive films were characterized by ATR-IR spectroscopy, parallel plate rheology, dynamic mechanical thermal analysis (DMTA), and differential scanning calorimetry (DSC). The adhesion was measured by a T-peel test of leather/polyurethane adhesive/SBR rubber joints. The addition of the different HEUR thickeners increased the viscosity of the polyurethane dispersion to different degrees. Furthermore, whereas the un-thickened polyurethane dispersion showed a Newtonian rheological behaviour, a shear-thinning rheological behaviour was observed in the thickened dispersions due to thickener-thickener and polyurethane-thickener interactions. The viscosity of the thickened polyurethane adhesive solutions increased with the degree of hydrophobicity and the molecular weight of the thickener. The addition of different thickeners increased the pH values due to the ionic adsorption, which is one of the interactions that contribute to the thickening mechanism of the polyurethane thickeners, besides hydrogen bonding and van der Waals hydrophobic interactions (micelles). The entanglement of the thickened polyurethane adhesives was studied by confocal microscopy. Although the addition of the thickeners did not affect the thermal properties of the polyurethanes, the T-peel strength of leather/adhesive/SBR rubber joints was influenced by the rheological properties of the thickened adhesives.

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1. INTRODUCTION

Waterborne polyurethane adhesives are one of the most interesting alternatives to the current solvent-based polyurethane adhesives used in the footwear industry as they meet the restricted European environmental legislation (Directive 1999/13/CE) with regard to the emission of organic solvents to the atmosphere.

In comparison with the solvent-borne adhesives, for their application in the footwear industry, the polyurethane dispersions offer a low viscosity, requiring the addition of thickeners to improve their rheological properties [1], which greatly influence the handling, storage, and application of a waterborne adhesive [2]. Previous studies analysed the influence of the amount of a hydrophobically modified ethoxylated urethane thickener (HEUR) in the rheological, thermal, and adhesive properties of a waterborne polyurethane adhesive [3].

Previous studies [4–7] have shown that the interactions that take part in the thickening mechanism of HEUR in polyurethane adhesives have been described in terms of ionic adsorption, hydrogen bonding, and van der Waals hydrophobic interactions (*i.e.*, micelle formation). Therefore, the degree of hydrophobicity of a HEUR thickener is a key parameter in determining its extent of interaction with the polyurethane dispersion. Thus, in this study several urethane-based thickeners differing in viscosity and pH values, solids content, nature of surfactant, degree of hydrophobicity, and molecular weight were added to a waterborne dispersion. The structure of a hydrophobically modified ethoxylated urethane consists of a hydrophilic backbone modified with terminal hydrophobic groups, which impart an associative character. According to Barmar *et al.* [8], a HEUR thickener consists of a polyoxyethylene unit (POE), urethane or urea groups, and terminal hydrophobic groups (aliphatic amines or alcohols). The molecular weight influences the thickening mechanism, as well as pH value and degree of hydrophobicity of the thickener. Previous results by Kaczmarski and Glass [9] have shown that the degree of hydrophobicity can be calculated from ^{1}H-NMR spectra of the polyurethane thickeners.

Although some technical literature has dealt with the effects of adding thickeners to water-based coatings, few papers related to the effects of incorporation of thickeners on waterborne adhesives have been published and, to our knowledge, no paper has been devoted to the effect of the degree of hydrophobicity of the thickener on the properties of thickened waterborne polyurethane adhesives in the footwear industry. In this study, the effects of adding several urethane-based thickeners with different chemical structures, their influence on the rheological, thermal, and adhesive properties of waterborne polyurethane adhesives, and a proposal of a thickening mechanism were addressed. To our knowledge, this is the first study in the existing literature dealing with the effect of different thickeners on the properties of waterborne polyurethane adhesives.

2. EXPERIMENTAL

2.1. Materials

A commercial waterborne polyurethane dispersion (Dispercoll® U54, Bayer AG, Leverkusen, Germany) was used. Some properties of the dispersion are given in Table 1. Five commercial urethane-based (HEUR) thickeners having different surfactants, POE chain lengths and structure from Borchers (Langenfeld, Germany), Cognis Iberia (Barcelona, Spain), and Coatex-Omya (Barcelona, Spain) were used, and some of their properties are given in Table 2.

2.2. Preparation of the Thickened Waterborne Polyurethane Adhesives

Five waterborne polyurethane adhesives were prepared by adding 1.5 wt% of the different urethane-based (HEUR) thickeners to the polyurethane dispersion. The polyurethane dispersion (DPU) was mixed with 1.5 wt% urethane-based thickener by stirring at 300 rpm

TABLE 1 Some Properties of the Commercial Waterborne Polyurethane Dispersion Dispercoll® U54

Property	Value
Brookfield viscosity	345 ± 5 mPa s⁽¹⁾
Solids content	50 ± 1 wt%⁽²⁾
pH	7.5 ± 0.1⁽³⁾
Density	1.07 g/cm^{3}⁽⁴⁾
Particle size	184 ± 1 nm

(1)UNE-EN ISO 2555:2000. Spindle no. 2, 30 rpm, 21°C.

(2)UNE-EN 827:1996.

(3)UNE-EN 1245:1999.

(4)DIN 51 757.

TABLE 2 Some Properties of the Commercial Urethane-Based Thickeners (HEUR) Used in this Study

Polyurethane thickener (HEUR)	Nomenclature	Brookfield viscosity(1) (mPa · s)	pH(4)	Solids content(5) (wt%)
COAPUR®2025	C20	3500(2)	8.1 ± 0.2	25.3 ± 0.1
BORCHI®GEL	B75	3630(2)	8.1 ± 0.1	50.0 ± 0.1
L75 N	C83	8200(3)	8.1 ± 0.2	51.1 ± 0.1
COAPUR®830 W	C60	7900(3)	6.0 ± 0.1	51.0 ± 0.1
COAPUR®6050	D16	8525(3)	7.7 ± 0.3	43.0 ± 0.1
DSX®1516				

(1)UNE-EN ISO 2555:2000. 40 rpm, 21°C.
(2)Spindle no. 4. 40 rpm, 21°C.
(3)Spindle no. 5. 40 rpm, 21°C.
(4)UNE-EN 1245:1999.
(5)UNE-EN 827:1996.

for 30 min at room temperature in a glass reactor. The nomenclature of the thickened polyurethane adhesives is given in Table 3.

For some experiments, solid thickened polyurethane adhesive films were used. The films were prepared by placing about 80 g of the thickened waterborne adhesives in a PTFE mould and allowing them to dry at room temperature for 10 days to ensure the complete removal of the water in the film. Adhesive solid films of about 1 mm thick were obtained.

2.3. Experimental Techniques

Characterization of the Polyurethane Adhesive Solutions

Flow rheometer. The viscosity of the adhesive solutions was measured in a Rheolab MC100 Physica rheometer (Reologica Instruments, Inc., Bordentown, NJ, USA). The measurements were carried out at

TABLE 3 Nomenclature of the Thickened Polyurethane Adhesive Solutions

Polyurethane dispersion	Polyurethane thickener	Thickener content (wt%)	Adhesive nomenclature
Dispercoll® U54	BORCHI®GEL		DPU/1.5B75
	L75 N		DPU/1.5C20
	COAPUR®2025		DPU/1.5C83
	COAPUR®830 W	1.5	DPU/1.5C60
	COAPUR®6050		DPU/1.5D16
	DSX®1516		

23°C by using 100 mL of solution in the rotational mode using concentric cylinders and the spindle Z2 (according to DIN 53019). Controlled shear rate experiments were carried out as follows. The shear rate was increased from 0 to 2 s^{-1} in 30 s and maintained for 300 s to provide a homogeneous solution. Then, the shear rate was gradually increased from 2 to 50 s^{-1} in 120 s, and maintained for 10 s; afterwards, a decrease in shear rate from 50 to 2 s^{-1} in 120 s was carried out. Finally, the shear rate was gradually decreased from 2 to 0 s^{-1} in 30 s. The pseudoplasticity of the adhesive solutions was quantified by means of the shear thinning index (STI), which was calculated as the ratio between the viscosities measured at shear rates of 2.5 and 25 s^{-1}, respectively. The thixotropy was calculated as the thixotropic area (TA) between the up and down runs of the flow curves.

pH measurement. The pH values of the adhesive solutions were measured at 23°C in a pH-meter (HI 8418, of Hanna Instruments, Inc., Woonsocket, RI, USA) provided with a silver reference electrode.

Particle size distribution. The average particle size distribution of the adhesive solutions was measured in a Coulter LS230 apparatus (Beckman Coulter, Inc., Miami, FL, USA), provided with laser diffraction and polarised light detectors. Approximately 1 g of the adhesive solution was added to 50 mL of distilled deionised water for measurement. It was assumed that the particles are polystyrene dispersed in water, and all measurements were referred to the refraction index of polystyrene (1.6) and water (1.333).

Confocal microscopy. The mechanism of thickening of the waterborne dispersion was studied by using a TCS SP2 Leica confocal microscope (Leica Microsystems GmbH, Heidelberg, Germany). A schematic diagram of a confocal microscope is given in Fig. 1. A laser excitation source with a wavelength of 488 nm (corresponding to sodium fluorescein) strikes the sample which emits light of a higher wavelength. The emitted light comes not only from the focal plane, but also from higher and lower planes. The light emitted from the focal plane passes through the confocal microscope's pinhole, but not the light from higher and lower planes, which is focused above or below the pinhole and not passing through it. In this way, the image is formed only with the light emitted from the focal plane. To acquire three-dimensional images, several images of different focal planes are obtained and reconstructed by means of the microscope software.

A small amount of sodium fluorescein (0.001 wt%) was added to the different urethane-based thickeners before adding to the dispersion, in such a way that the only component able to emit fluorescence was the

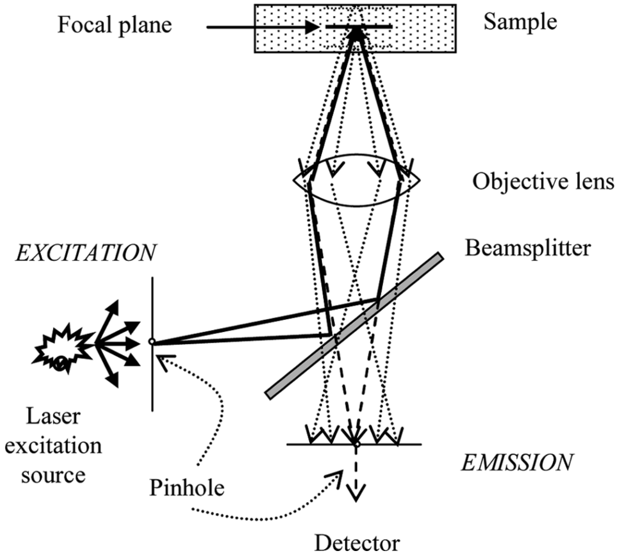

FIGURE 1 Schematic diagram of confocal microscope.

thickener. For analysis, three drops of each adhesive were placed into microscope slides.

Surface tension measurements. Surface tension values of the thickened polyurethane adhesive solutions were obtained in a Cahn DCA-322 dynamic contact angle analyzer (Thermo Fisher Scientific, Inc., Waltham, MA, USA) by using the Wilhelmy plate method. A microscope slide was held in a fixed vertical position, attaching it to a microbalance which measures the force to separate the sunken slide in to from the adhesive.

Characterization of the Polyurethane Thickeners

Proton nuclear magnetic resonance (^{1}H-NMR). ^{1}H-NMR spectra of the urethane-based thickeners were recorded in a Fourier Transform Bruker 300 MHz spectrometer model AC-300 (Bruker Española S.A., Madrid, Spain). 10 mg of the urethane-based thickeners were dissolved in 4 ml of deuterated chloroform. TMS was used as the internal reference.

Molecular weight distribution. The average molecular weights of the urethane-based thickeners were obtained by gel permeation chromatography (GPC), using a Waters peristaltic pump model 510 HPLC (flow rate of THF was 1 mL/min) and a Waters 410 refraction index detector (Waters Corporation, Milford, MA, USA). Three heated (37°C) Shodex columns from Showa Denko K. K. (Ridgeville, SC, USA) were used. 30 mg of the urethane-based thickeners were dissolved in 10 mL of tetrahydrofurane (THF).

Characterization of the Polyurethane Adhesive Films

Infrared spectroscopy (IR-ATR). The chemistry of the thickened polyurethane adhesive films was analysed in a Nicolet 510 infrared spectrophotometer (Nicolet Instrument Technologies Inc., Madison, WI, USA), provided with Fourier transform analysis (FTIR). The measurements were carried out by using the attenuated total reflectance (ATR) technique, and the Golden Gate single reflection diamond was used as prism. An incidence angle of the laser beam of 45° was used and 120 scans were recorded and averaged.

Parallel plate rheometer. The rheological properties of the thickened solid polyurethane films were determined in a shear stress-controlled Bohlin CS50 rheometer (Bohlin Instruments, Ltd., Gloucestershire, UK) using a plate-plate geometry (upper plate diameter = 20 mm), a frequency of 1 Hz, a target strain of 0.005, and a gap between the plates of 0.4 mm. The temperature was varied from 200 to 20°C by using a cooling rate of 5°C/min.

Dynamic mechanical thermal analysis (DMTA). The viscoelastic properties of the thickened polyurethane adhesive films were measured in DMTA Mk III equipment (Rheometric Scientific Inc., Loughborough, UK) and the two-point bending system (single cantilever) was used. The experiments were carried out by heating the sample from −80 to 80°C with a heating rate of 5°C/min, a frequency of 1 Hz, and a strain of 64 μm.

Differential scanning calorimetry (DSC). The thermal properties of the thickened polyurethane adhesive films were measured in a differential scanning calorimeter Mettler Toledo DSC 30, equipped with a temperature programme control Mettler Toledo TC10A (Mettler-Toledo GmbH, Schwerzenbach, Switzerland). Approximately 10 mg of polyurethane films were placed in aluminium pans and the experiments were carried out under nitrogen atmosphere (flow = 30 mL/min) by using a heating rate of 10°C/min. Four consecutives run were carried out: *i)* heating from −100 to 110°C followed by an isothermal heating at 110°C for 3 min in order to remove the thermal history of the sample; *ii)* sudden cooling down to −100°C; *iii)* second heating run from −100 to 110°C; and *iv)* cooling down to

25°C followed by an isothermal heating at 25°C for 45 min (to study the crystallisation kinetics of the polyurethane).

T-peel strength measurements. The adhesion properties of the waterborne polyurethane adhesives containing different urethane-based thickeners were studied by T-peel strength tests of leather/polyurethane adhesive/vulcanized styrene-butadiene (SBR) rubber joints. The formulation of the sulphur vulcanized SBR rubber is given in Table 4. Both the leather and the SBR rubber were standard materials of INESCOP (Elda, Spain). Bovine chromium tanned leather without a finish was used in this study. This leather has a tensile strength of 22 MPa, an elongation at break of 52%, and a chromium content less than 5 wt%. Before the joint formation the leather surface was roughened in a roughening machine (Superlema S.A., Zaragoza, Spain) operating at 2800 rpm. A P100 aluminium oxide abrasive cloth (Due Emme Abrasivi, Pavia, Italy) was used, and about 0.5 mm leather was removed. The SBR rubber was roughened, eliminating about 0.5 mm rubber, followed by halogenation with 2 wt% trichloroisocyanuric acid solution in ethyl acetate. The halogenation reaction lasted for 1 h at room temperature.

Once the surface treatments of the different materials were carried out, the polyurethane adhesive was applied to each strip using a metering rod (5.2 mils = 132 μm) and was left to dry in open air for 1 h. After solvent evaporation, a thick solid adhesive film was formed, which was immediately heated at 80°C by infrared radiation (re-activation process) in a temperature controlled heater ACN 02/01 (Automática y Control Numérico, Elda, Spain). The heated strips were joined under a pressure of 0.7 MPa for 10 s.

TABLE 4 Formulation of the Sulphur Vulcanized Styrene-Butadiene Rubber Used in T-Peel Tests

Component	Percentage (phr)[a]
SBR 1205	60.00
NR (WF)	40.00
Precipitated silica	33.33
Zinc oxide	1.67
Stearic acid	1.00
Polyethyleneglycol	1.67
Paraffin antioxidant	0.67
Plasticizer	3.30
Sulphur	2.30
2-mercaptobenzothiazol	1.50
Tetramethyl thiuram	0.33

[a] phr: Parts per hundred parts of rubber.

The T-peel strength measurements were performed in an Instron 1011 universal test machine (Instrom Ltd., Buckinghamshire, UK) using a crosshead speed of 100 mm/min. The adhesive strength was obtained at different times (2 min, 1, and 72 h) after the joint formation.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Polyurethane Thickeners

Figure 2 shows the ^{1}H-NMR spectra of the polyurethane thickeners. The signal at 1.3 ppm can be ascribed to hydrophobic groups (aliphatic amines or alcohols), whereas the signal at 3.6 ppm corresponds to the hydrophilic groups (polyoxyethylene unit-POE). The signal at 7.3 ppm

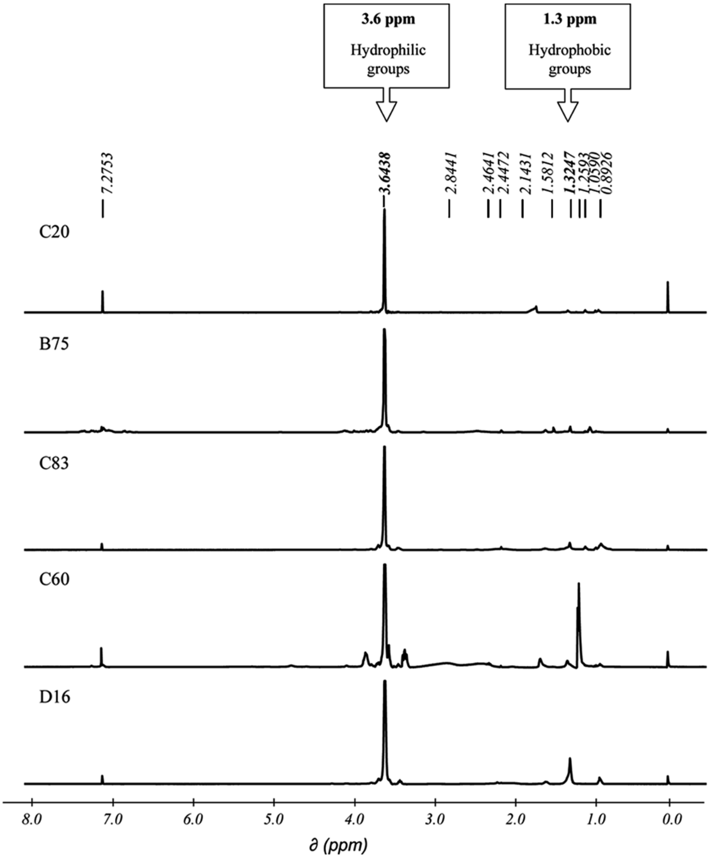

FIGURE 2 ^{1}H-NMR spectra of the urethane-based thickeners.

TABLE 5 Intensities in the ^{1}H-NMR Spectra of the Urethane-Based Thickeners Corresponding to Characteristic Signal of Hydrophobic and Hydrophilic Groups and Hydrophobicity Degree

HEUR	Intensity at 1.3 ppm (Hydrophobic groups)	Intensity at 3.6 ppm (Hydrophilic groups)	Hydrophobicity degree
C20	216	66852	0.32
B75	266	64802	0.41
C83	320	71132	0.44
C60	7144	61500	11.62
D16	567	80411	0.71

is due only to the solvent, deuterated chloroform ($CDCl_3$). The degree of hydrophobicity of each thickener (Table 5) was calculated as the ratio of the intensities at 1.3 ppm with respect to 3.6 ppm [7,10]. The lowest degree of hydrophobicity values correspond to C20, B75, and C83 thickeners, whereas the C60 shows the highest value.

Table 6 includes the average molecular weights of the urethane-based thickeners obtained by gel permeation chromatography (GPC). The lowest Mw values correspond to C60 and C20 thickeners, followed by B75 and C83, whereas the D16 shows the highest value.

3.2. Characterization of the Thickened Polyurethane Adhesive Solutions

The critical micelle concentration (CMC) of the thickened polyurethane adhesive was studied with the aim of selecting the optimum amount of thickener to be added to the polyurethane dispersion. The CMC is the concentration above which micelles are formed [11]. As a typical example, the variation of the surface tension as a function of the C60 thickener content is given in Fig. 3. Two straight lines with different slopes were obtained, which indicate a sudden change related

TABLE 6 Average Molecular Weights and Polydispersity of the Urethane-Based Thickeners

HEUR	M_n	M_w	M_z	(M_w/M_n)
C20	19100	20830	31950	1.31
B75	20100	25650	32300	1.28
C83	20360	25570	35450	1.26
C60	18250	20830	24460	1.14
D16	23800	32830	44410	1.38

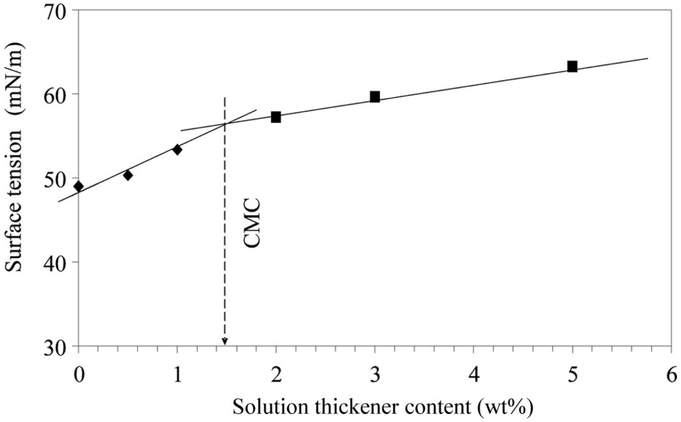

FIGURE 3 Variation of the surface tension as a function of the C60 thickener content.

to the formation of a micellar network. According to the Fig. 3, the two straight lines cross at a thickener concentration of 1.5 wt%, so this amount was selected for all thickeners to add to the polyurethane dispersion.

The addition of the different thickeners does not produce significant changes in the solids content not in the mean particle size of the polyurethane adhesives (Table 7). The mean particle size of the polyurethane adhesives was quite similar in all solutions (181–185 nm) and it was not influenced by the addition of the thickeners. However, an increase in pH values of the waterborne polyurethane dispersion was observed, regardless of the thickener used. The urethane-based thickeners used in this study are non-ionic and do not produce ions in water. However, the non-ionic thickeners are soluble in water because of the

TABLE 7 pH, Solids Content and Mean Particle Size Values of the Thickened Polyurethane Adhesive Solutions

Polyurethane adhesive	pH	Solids content (wt%)	Mean particle size (nm)
DPU	7.5 ± 0.1	50.0 ± 0.1	184 ± 1
DPU/1.5B75	8.2 ± 0.1	50.3 ± 0.1	182 ± 2
DPU/1.5C20	8.2 ± 0.1	50.1 ± 0.1	183 ± 2
DPU/1.5C83	8.1 ± 0.2	50.6 ± 0.1	181 ± 3
DPU/1.5C60	8.2 ± 0.1	51.1 ± 0.1	183 ± 2
DPU/1.5D16	8.4 ± 0.2	50.3 ± 0.1	185 ± 2

high affinity of POE chains for water caused by strong dipole-dipole interactions (*i.e.*, hydrogen bonds). Then, after adding the thickener to the polyurethane dispersion, the POE chains in the thickener are protonated and they are able to interact electrostatically with the ionic groups of the polyurethane dispersion (*i.e.*, ionic adsorption). Therefore, the increase in the pH value of the polyurethane dispersions can be ascribed to interactions between the protonated POE chains in the thickener and the ionic groups of the polyurethane dispersion (negatively charged). In this way, the ionic adsorption could explain the increase in the pH and this is one of the interactions which take part in the thickening mechanism of the polyurethane thickeners [3,8,12].

The variation of the viscosity as a function of the shear rate for the waterborne polyurethane adhesive solutions without and with the different thickeners is given in Fig. 4. The waterborne polyurethane adhesive without thickener (DPU) shows a Newtonian behaviour (*i.e.*, the viscosity does not vary by changing the shear rate), and the addition of the urethane-based thickeners increases the viscosity of the polyurethane adhesive solution to a different degree for each thickener. Furthermore, a shear-thinning behaviour is observed (*i.e.*, the viscosity decreases with increasing shear rate [3,13,14]) and thixotropy (*i.e.*, the increase in viscosity with increasing time) is imparted to the waterborne polyurethane adhesive solution by all thickeners except for D16. Previous studies [3,13] have shown that

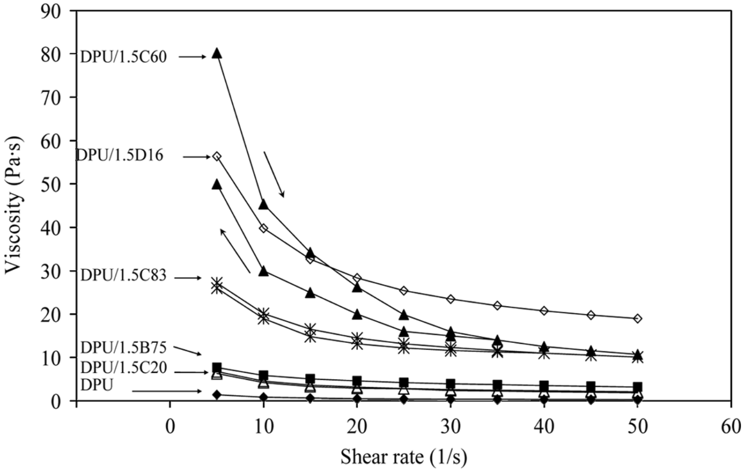

FIGURE 4 Variation of the thickened waterborne polyurethane adhesive viscosity as a function of the shear rate. Arrows show the runs corresponding to the increase and decrease in shear rate.

the existence of pseudoplasticity and thixotropy in the thickened adhesive solutions can be ascribed to the creation of the intermolecular networks among hydrophobic groups of the thickener and also to the interactions between the thickener and the polyurethane dispersion.

The pseudoplasticity of the polyurethane adhesive solutions was quantified by the shear thinning index (STI), the values of which are given in Table 8. Whereas the rheological behaviour of the polyurethane dispersion without thickener is Newtonian (STI ≈ 1), all the thickened adhesives exhibit pseudoplasticity (STI > 1), depending on the thickener used, and thixotropy (quantified by the thixotropic area) is also obtained (except in DPU/1.5D16), indicating the creation of thickener-thickener and polyurethane-thickener interactions. The application of the Casson model [15] to the rheological curves exhibiting pseudoplasticity allows one to calculate the yield stress (σ_o)—minimum necessary stress to allow the adhesive to flow—and the viscosity at infinite shear rate (η_∞)—the viscosity of the solutions without any kind of interactions (Table 8). The addition of the different thickeners produces a noticeable increase in the values of yield stress, which is in agreement with the increase in the viscosity, and the viscosity at infinite shear rate increased, regardless of the thickener (except in DPU/1.5D16 which shows the highest value of viscosity and σ_o).

According to the degree of increasing viscosity imparted to the waterborne dispersion by adding different thickeners, three groups can be distinguished (according to the viscosity values at 40 s^{-1}): *i*) adhesives containing C20 and B75 thickeners show a slight increase

TABLE 8 Some Rheological Properties of the Thickened Polyurethane Adhesive Solutions

Adhesive	$\eta^{(1)}$ (Pa · s)	STI$^{(2)}$	TA$^{(3)}$ (Pa/s · cm^3)	$\sigma_o{}^{(4)}$ (Pa)	$\eta_\infty{}^{(5)}$ (Pa · s)
DPU	0.35	1.1	–	–	–
DPU/1.5B75	2.31	2.3	0.5	1.5	0.9
DPU/1.5C20	3.53	2.3	2.0	3.2	0.8
DPU/1.5C83	11.03	2.2	4.0	5.9	0.9
DPU/1.5C60	12.55	9.1	15.1	9.0	0.8
DPU/1.5D16	20.78	4.6	–	15.0	–

(1) Viscosity at 40 s^{-1}. Temperature = 23°C.

(2) STI: Shear thinning index, calculated as the ratio between the viscosities measured at shear rates of 2.5 and 25 s^{-1}.

(3) TA: Thixotropic area in the curves of Fig. 4.

(4) σ_o: Critical yield stress.

(5) η_∞: Viscosity at infinite shear rate.

in viscosity; *ii*) adhesives containing C83 and C60 thickeners show a moderate increase in viscosity; and the *iii*) adhesive containing D16 thickener shows a marked increase in viscosity.

The variation of the polyurethane adhesive's viscosity as a function of the adhesive's weight average molecular weight (Mw) of the different thickeners is given in Fig. 5. The viscosity of the thickened waterborne polyurethane adhesive solution increases with the molecular weight of the thickener (except for the solution containing C60 thickener). When the molecular weight of the thickener increases, the length of its chains increases and it can be expected that the number of interactions with the polyurethane chains also increases; therefore, an increase in the viscosity of the adhesive solutions should be produced [7,9]. However, the increase in the molecular weight alone is not sufficient to explain the great variations in viscosity of the thickened waterborne adhesive solutions, since both hydrophilic and hydrophobic groups could contribute to the length of the thickener chain. Thus, additional factors must affect the increase in viscosity of the thickened waterborne adhesive solutions, such as the degree of hydrophobicity of the thickener [6,7]. Figure 6 shows the variation of the viscosity of the thickened waterborne adhesive solutions as a function of the hydrophobicity degree of the thickeners. The viscosity of the thickened waterborne adhesive solutions increases with the degree of hydrophobicity of the thickener because of the increase in the number of hydrophobic groups, which contribute to the thickening

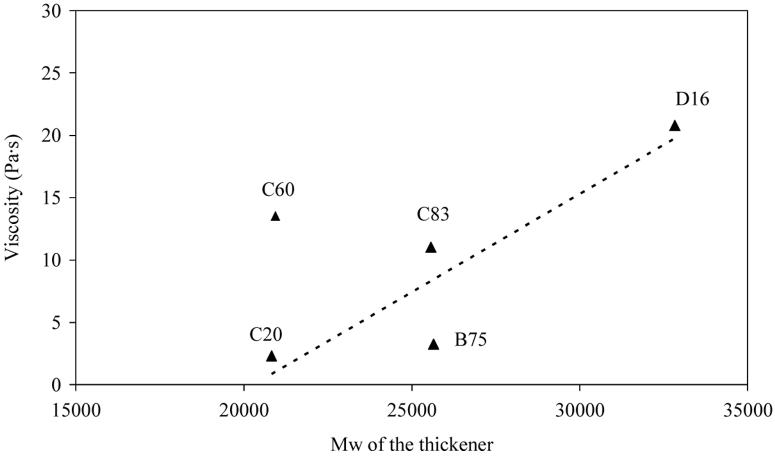

FIGURE 5 Variation of the thickened waterborne polyurethane adhesive viscosity as a function of the weight average molecular weight (Mw) of the thickeners.

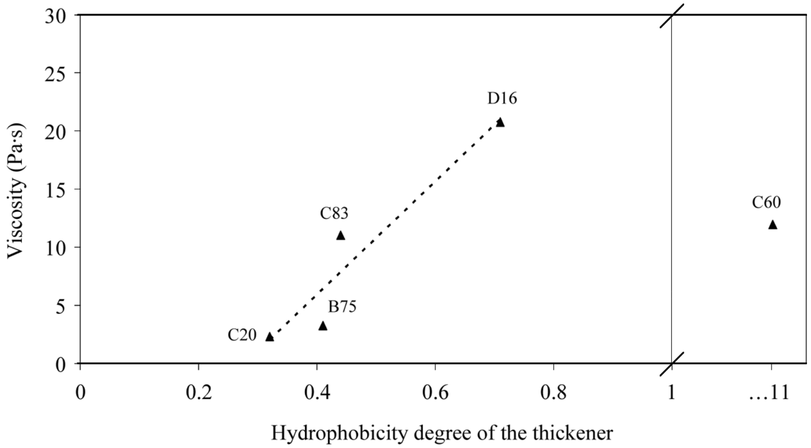

FIGURE 6 Variation of the thickened waterborne polyurethane adhesive viscosity as a function of the degree of hydrophobicity of the thickeners.

mechanism by van der Waals hydrophobic (*i.e.*, micelle) interactions; hydrogen bonds contribute also to the thickening mechanism. The rheological behaviour of the thickened waterborne adhesive solution containing C60 (Fig. 4) could be ascribed to its great hydrophobic groups contribution (Table 5) which should enhance the net interactions with the polyurethane chains giving important increases in both STI and AT values; however, these interactions are destroyed by increasing the shear rate, giving a noticeable decrease in viscosity at $40\,s^{-1}$.

For the very first time in the existing literature, in this study the mechanism of thickening of the polyurethane adhesive solutions was evidenced by confocal laser microscopy. The confocal laser micrographs (Fig. 7) show the entanglement of the polyurethane (noticed as more dense whiter images) produced by adding the thickeners which can be ascribed to the existence of interactions between the thickener and the polyurethane, in agreement with previous studies [3,13,14]. Figure 7 shows the influence of the entanglement produced by two different thickeners, taken as representative examples, which is more noticeable for the DPU/1.5D16 adhesive solution.

3.3. Characterization of the Solid Thickened Polyurethane Adhesive Films

The chemical properties of the solid thickened polyurethane adhesive films containing different thickeners were analysed by ATR-IR

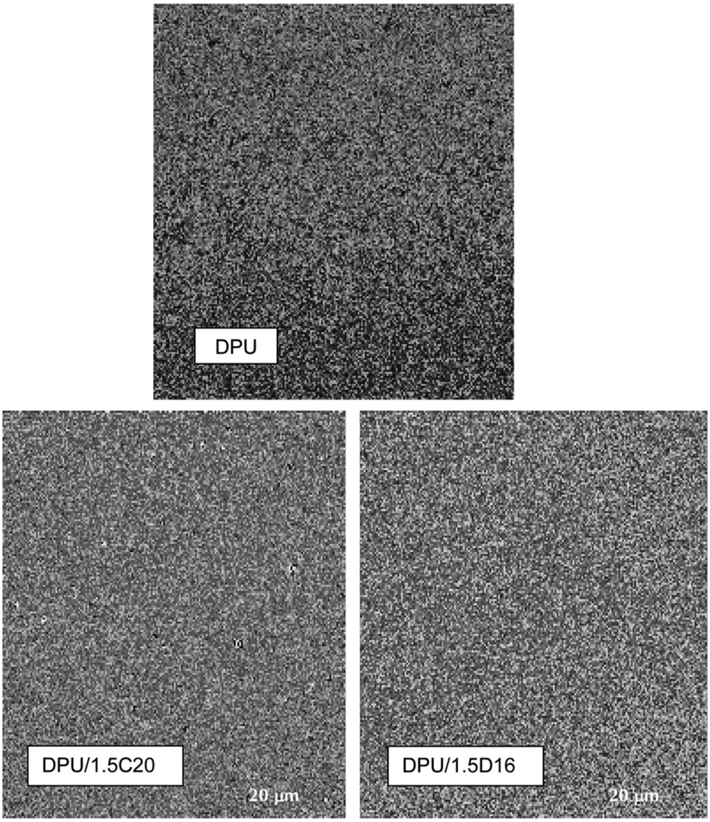

FIGURE 7 Confocal laser micrographs of DPU and some thickened waterborne polyurethane adhesive solutions.

spectroscopy. All the polyurethanes showed relatively similar ATR-IR spectra with the main IR bands of polyurethane [3]. Figure 8a shows the ATR-IR spectra of the polyurethanes without and with 1.5 wt% thickeners. The addition of the different thickeners did not produce changes in the chemical properties of the thickened polyurethanes as no new absorption bands appeared in the ATR-IR spectra.

The addition of the different thickeners produces an increase in the intensity of the broad N-H stretching band centered at about 3300 cm^{-1} (Fig. 8b) indicating the existence of hydrogen bonding. Furthermore, the ATR-IR spectra of the polyurethanes containing the different thickeners show a higher intensity of the C=O stretching band at 1719 cm^{-1} (Fig. 8c), confirming the creation of hydrogen bonds between the urethane groups of the polyurethane and the thickener [4,16].

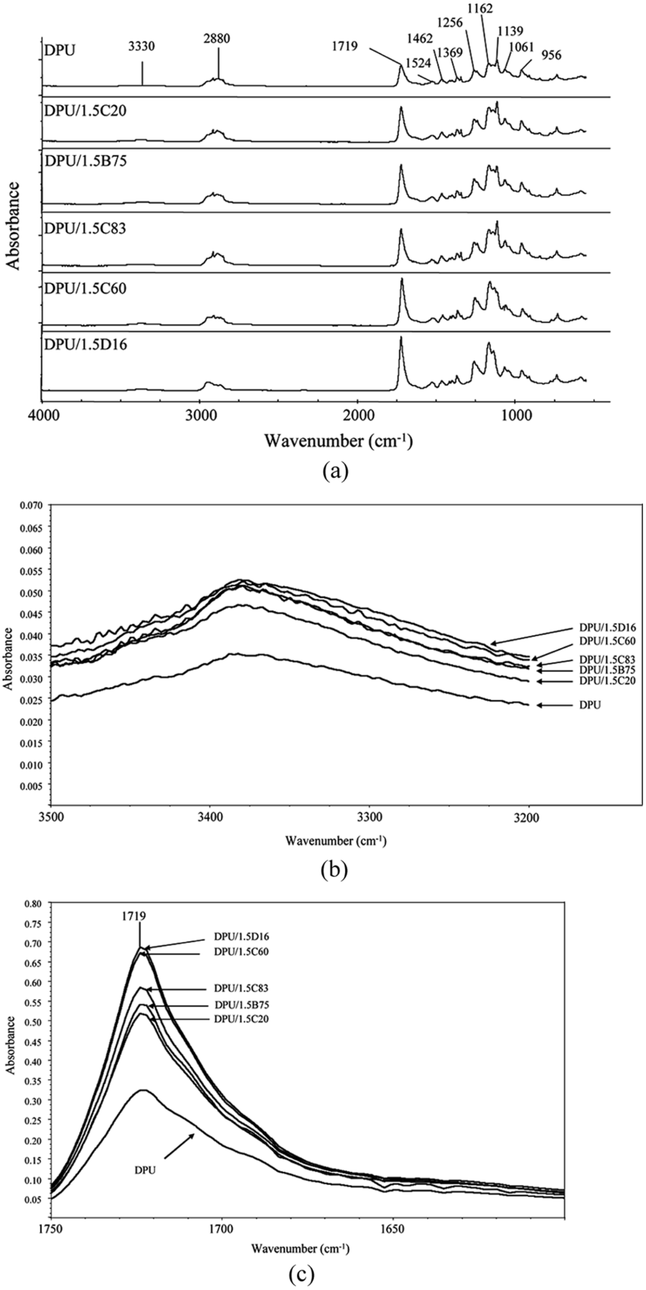

FIGURE 8 (a) ATR-IR spectra of the polyurethanes without and with 1.5 wt% thickeners. (b) 3200–3500 cm^{-1} region. (c) 1600–1750 cm^{-1} region.

The physical interactions (ionic adsorption, hydrogen bonding) between the polyurethane and the thickener can also be evidenced by parallel plate rheology experiments.

Figure 9 shows the variation of the elastic modulus (*G′*) as a function of the temperature for the thickened polyurethane films (parallel plate rheology experiments). The elastic modulus of the polyurethanes decreases as the temperature increases and the addition of the thickeners affects the modulus of the polyurethane differently, depending on their nature: *i*) addition of C20 and B75 thickeners decrease the elastic modulus (with regard to DPU); *ii*) addition of C83 and C60 thickeners slightly increase the elastic modulus (with regard to DPU); and *iii*) addition of D16 thickener greatly increases the elastic modulus (with regard to DPU). Furthermore, the addition of the thickeners produces a shift of the temperature value at the cross-over between the elastic and viscous moduli and the same three groups can be distinguished (Table 9). Thus, the values of temperature and, to a lesser extent, the moduli at the cross-over between the elastic and viscous moduli were *i*) smaller than DPU values in the adhesives containing B75 and C20 thickeners; *ii*) slightly greater than DPU values in the adhesives containing C83 and C60 thickeners; and *iii*) greater than DPU values in the adhesive containing D16 thickener.

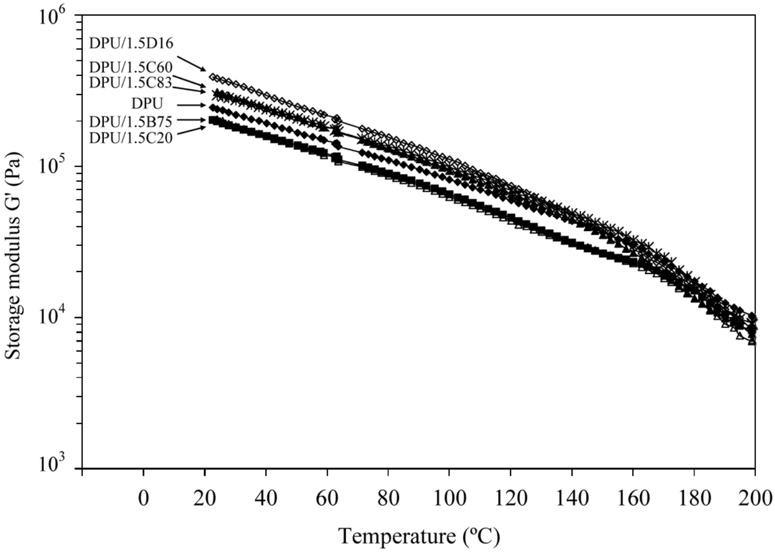

FIGURE 9 Variation of the elastic (*G′*) modulus as a function of the temperature for the thickened polyurethane films. Parallel plate rheometer experiments.

TABLE 9 Temperature ($T_{cross\text{-}over}$) and Modulus ($G_{cross\text{-}over}$) Values at the Cross-Over Between the Elastic and Viscous Modulus Curves of the Thickened Polyurethanes

Polyurethane	$T_{cross\text{-}over}$ (°C)	$G_{cross\text{-}over}$ (Pa)
DPU	145	$3.8 \cdot 10^4$
DPU/1.5C20	138	$3.2 \cdot 10^4$
DPU/1.5B75	140	$3.1 \cdot 10^4$
DPU/1.5C83	148	$4.1 \cdot 10^4$
DPU/1.5C60	145	$3.8 \cdot 10^4$
DPU/1.5D16	152	$4.4 \cdot 10^4$

The increase in the elastic modulus as well as in temperature and moduli values at the cross-over can be mainly ascribed to the existence of polyurethane-thickener interactions [13,14]. On the other hand, the decrease in the adhesives DPU/1.5C20 and DPU/1.5B75 can be attributed to their smaller hydrophobic group content (Table 5).

The viscoelastic properties of the thickened polyurethane films were studied by DMTA. Figure 10 shows the variation of the storage modulus (*E'*) as a function of the temperature for the polyurethanes containing different thickeners. After the glass transition (recognized as an inflection in the curves), a rubbery plateau appears in which an increase in the storage modulus and a decrease in the rubbery plateau slope are produced by adding the thickeners. The decrease in the slope of the rubbery

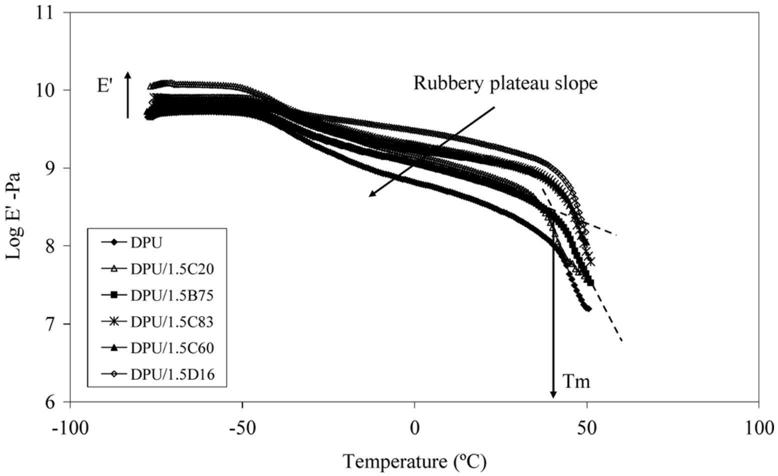

FIGURE 10 Variation of the storage modulus (*E'*) as a function of the temperature of the thickened polyurethane films. DMTA experiments.

plateau means that the elastic modulus is maintained higher by increasing the temperature, *i.e.*, greater polyurethane-thickener interactions are produced. Thus, the lowest rubbery plateau slope corresponds to the polyurethane containing D16 thickener, followed by those containing C60 and C83 thickeners. At about 40°C, a sudden decrease in the storage modulus is produced because of the softening of the polyurethanes. The value of this melting point temperature (Tm) increases with the addition of the thickeners (Table 10), particularly for the polyurethanes containing D16, C60, and C83 thickeners. All these trends can be ascribed mainly to the existence of polyurethane-thickener interactions.

The thermal properties of the thickened polyurethanes were studied by differential scanning calorimetry (DSC). The DSC thermograms corresponding to the second heating run (Fig. 11) shows the T_g of the soft segments located at low temperature, followed by the crystallisation of the soft segments (exothermal peak), as well as the melting of the soft segments, located at higher temperature (46°C). All polyurethanes showed a similar value of T_g (around -54°C) and crystallization temperature (T_c) (around -19°C), as well as similar melting (38–40 J/g) and crystallization (44–47 J/g) of soft segment enthalpy values, which indicated that the addition of the different thickeners did not disturb the degree of phase separation between the hard and soft segments in the polyurethane (Table 11).

The adhesion properties of the thickened waterborne polyurethane adhesives were obtained from T-peel tests of roughened leather/thickened waterborne polyurethane adhesive/roughened + halogenated ed SBR rubber joints. The immediate (2 min and 1 h after joint formation) and the final adhesive strength (72 h after joint formation) are given in Fig. 12. The smallest values of adhesive strength correspond to the joint produced with the adhesive containing the D16 thickener, whereas the highest values of final adhesion, obtained 72 h after the joint formation, correspond to the joints produced with the dispersion

TABLE 10 T_m and Rubbery Plateau Slope Values of the Thickened Polyurethanes Calculated from DMTA Curves

Polyurethane	Rubbery plateau slope	T_m(°C)
DPU	0.014	37.2
DPU/1.5C20	0.013	37.7
DPU/1.5B75	0.013	38.4
DPU/1.5C83	0.010	42.2
DPU/1.5C60	0.009	40.8
DPU/1.5D16	0.008	41.4

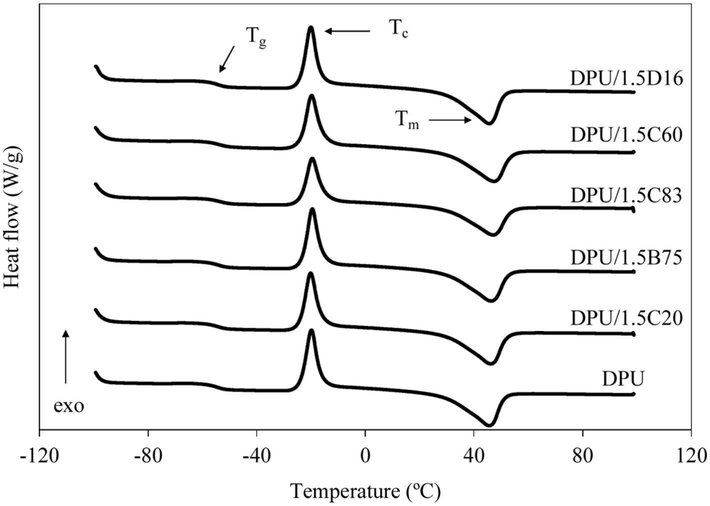

FIGURE 11 DSC curves corresponding to the second heating run of the thickened polyurethane films.

without thickener and DPU/1.5B75 adhesive. 2 min after the joint formation, a cohesive failure (C) was obtained and up to 1 h, an adhesion failure to the leather (A1) was observed.

Because of the high viscosity of the DPU/1.5D16 adhesive, the penetration in the pores of the leather should be inhibited, and thus a poor contact and a lower adhesive strength are produced. Moreover, the smallest values of adhesive strength can be due to an inadequate coalescence of the adhesive film, because the reactivation temperature used (80°C) was lower than the softening temperature of the thickened adhesives obtained from parallel plate rheology experiments.

The experimental results obtained in this work and in previous studies [3] allow one to conclude that several interactions take part

TABLE 11 Some Values Obtained from DSC Thermograms (Second Heating Run) of the Thickened Polyurethanes

Polyurethane	Tg (°C)	Tm (°C)	ΔHm (J/g)	Tc (°C)	ΔHc (J/g)
DPU	−54	46	46	−20	39
DPU/1.5C20	−54	46	46	−20	38
DPU/1.5B75	−54	46	44	−19	40
DPU/1.5C83	−53	47	39	−19	40
DPU/1.5C60	−54	47	47	−20	38
DPU/1.5D16	−55	45	45	−20	40

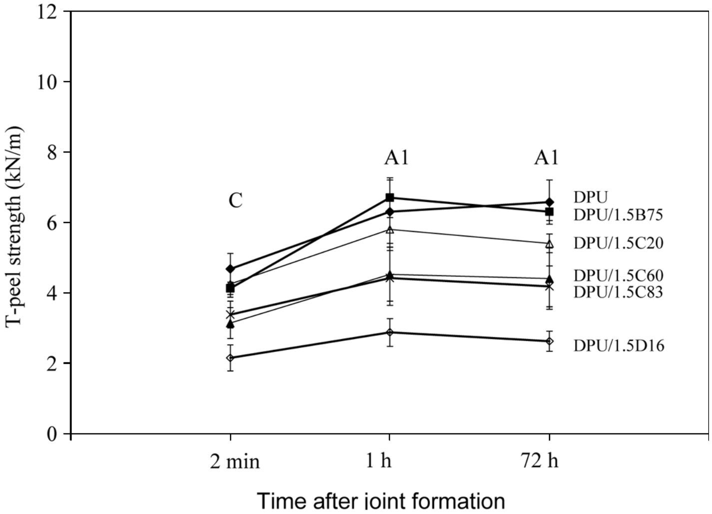

FIGURE 12 Variation of T-peel strength as a function of the time in roughened leather/thickened waterborne polyurethane adhesive/roughened + halogenated SBR joints. Locus of failure: C = Cohesive failure in the adhesive, A1 = Adhesive failure to the leather.

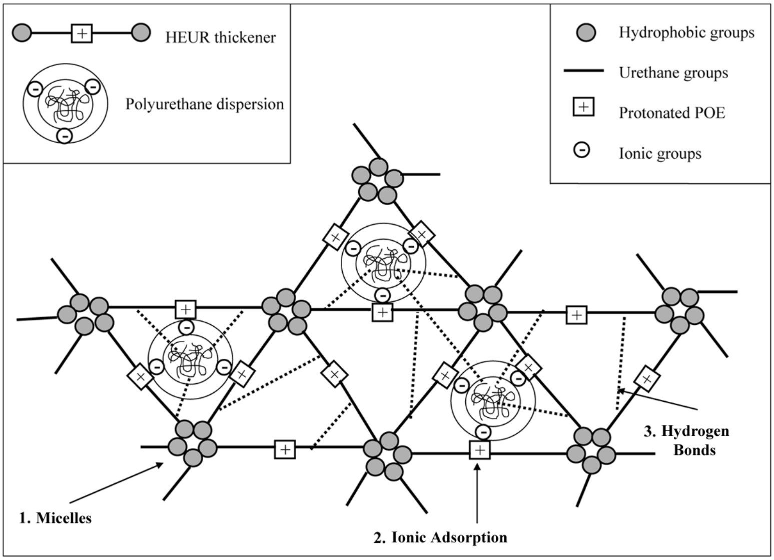

FIGURE 13 Schematic diagram of the thickening mechanism of waterborne polyurethane adhesive containing urethane-based thickener through the formation of 3D micelle network.

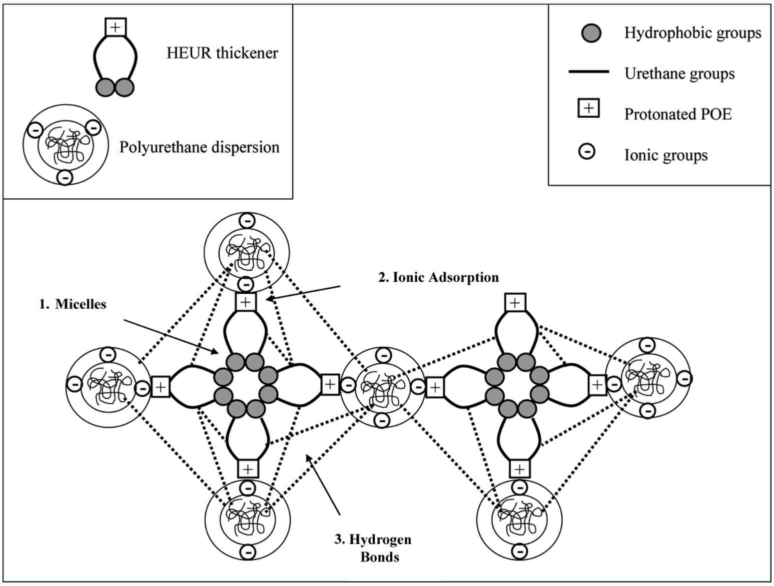

FIGURE 14 Schematic diagram of the formation of flower-like micelles by interaction between the hydrophobic groups of the thickener in each micelle.

in the thickening mechanism of polyurethane adhesive dispersions by adding urethane-based thickener: *i)* interactions between the terminal hydrophobic groups of the thickener itself throughout the creation of van der Waals hydrophobic forces (*i.e.*, micelle formation); *ii)* interactions by ionic adsorption of the POE chains of the thickener with the ionic groups on the surface of polyurethane particles; *iii)* interactions by hydrogen bonds between urethane groups of the polyurethane dispersion and the urethane-based thickener. Figure 13 shows a schematic diagram of the thickening mechanism of waterborne polyurethane adhesive containing urethane-based thickener through the formation of a 3D micelle network. Furthermore, Fig. 14 shows a schematic diagram of the formation of flower-like micelles by interaction between the hydrophobic groups of the thickener in each micelle.

4. CONCLUSIONS

1.5 wt% of different urethane-based thickeners was selected as critical micelle concentration (CMC) to add to a waterborne polyurethane dispersion with the aim to analyse the effect of the degree of hydrophobicity of the thickener on the thickening mechanism in waterborne polyurethane dispersions.

The addition of the HEUR thickeners increased the viscosity of the waterborne polyurethane dispersion to different degrees and shear-thinning behaviour was observed due to thickener-thickener and polyurethane-thickener interactions. The viscosity of the thickened waterborne polyurethane adhesive solutions was increased by increasing both the degree of hydrophobicity and the molecular weight of the thickener. Moreover, the addition of the thickener increased the pH values of the waterborne polyurethane dispersion due to ionic adsorption, which is one of the interactions that contribute to the thickening mechanism of the urethane-based thickeners. Furthermore, the ATR-IR spectra showed the existence of hydrogen bonding between urethane groups in the solid polyurethane films. Therefore, the ionic adsorption, the van der Waals hydrophobic interactions, and the hydrogen bonding favoured the thickening mechanism of the waterborne polyurethane adhesives by the addition of urethane-based thickeners.

An improvement in the rheological properties of the polyurethane was produced due to the formation of an entangled structure favoured by the thickener. According to the variation in viscosity, and the rheological and viscoelastic properties, three groups of thickened adhesives were distinguished, the adhesive containing D16 thickener providing the best values. On the other hand, the thickener addition did not disturb the miscibility between the hard and soft segments in the polyurethanes and phase separation was not affected.

The adhesive strength of leather/thickened waterborne polyurethane adhesive/SBR rubber joints was influenced by the rheological properties of the thickened adhesives. The penetration in to the leather pores was inhibited by the adhesives with a high viscosity, giving a decrease in adhesive strength and an adhesion failure to the leather.

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