Optimization of adhesive performance of waterborne poly(urethane-urea)s for adhesion on high and low surface energy surfaces

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Abstract

Achieving adhesion to materials with a low surface energy is a challenge when designing new soft adhesives. With this question in mind, waterborne poly(urethane-urea) (WPUU) dispersions based on poly(ethylene oxide) (PEO) homopolymer and poly(ethylene oxide-b-propylene oxide-b-ethylene oxide) (PEO-b-PPO-b-PEO) and poly(propylene oxide-b-ethylene oxide-b-propylene oxide) (PPO-b-PEO-b-PPO) triblock copolymers were prepared. Adhesives cast from the dispersions exhibited better adhesion on a low surface energy polypropylene (PP) probe than on a high surface energy steel probe. Moreover, with the aim of improving the adhesive performance of the WPUUs for pressure sensitive adhesive (PSA) applications, bilayer systems were designed. They were prepared using two WPUUs with differing viscoelastic behavior (one more solid-like and the other one, more liquid-like) to create a gradient in the viscoelastic properties. This strategy led to adhesive materials that exhibited fibrillation during probe tack measurements using a steel probe, which is typical of PSAs. Finally, prototype adhesive tapes were prepared from one of the bilayer systems. These

adhesive tapes performed in a peel test in a similar way as a domestic commercial adhesive tape, making them interesting for that potential application.

Keywords: waterborne polyurethanes, pressure sensitive adhesive, soft adhesive, adhesive tape, bilayer adhesive, viscoelastic gradient

1. Introduction

Pressure-sensitive adhesives (PSAs) are a class of adhesives that can be applied to a broad range of substrates, requiring just light pressure and short contact time to join surfaces together [1–4]. The viscoelastic properties of polymers used in PSAs can be tuned to suit a particular application, from high-performance tapes to removable adhesives [2]. Materials to be used as a PSA need to fulfil the following requirements: a) be liquid-like enough to appropriately flow and wet the substrate, b) be solid-like enough to endure shear stress, and c) have the suitable viscoelastic properties to dissipate energy when being drawn into fibrils during debonding [4–6]. The glass transition temperature (T_g) of these materials, relative to the application temperature, plays a crucial role in defining their viscoelastic properties. Thus, control of the T_g value is essential [3,7] when designing PSAs [7].

Among all the different types of polymers, polyurethanes (PUs) are one of the most attractive categories considering their wide range of final properties, which allow them to find applications as coatings and adhesives [8]. PUs are made of two thermodynamically incompatible segments [9,10]: the macrodiol forms the soft segment whereas the hard segment consists of the diisocyanate and the chain extender [9,10]. As the relation between these two segments influences the mechanical properties, one can design PUs with different ranges of elastic modulus, deformation and strength [4]. Furthermore, molecular architecture [1,11] and molecular weight [4,12,13] strongly affect the viscoelastic properties of these materials and consequently their adhesion. Regardless of the different properties and segments of the huge variety of PUs, all of them present a urethane linkage, which is polar in nature, responsible for hydrogen bonding and which leads to high cohesive energy [4]. These characteristics make PUs attractive materials for adhesive applications. PSAs based on lightly cross-linked PUs have been developed [12,14], because cross-linking is necessary for the cohesion to achieve a high shear strength [3,6,14]. Concerning the cross-linking requirement, blends of triblock

1 copolymers have been used as base for PSAs. Triblock copolymers present the ability to self-
2 organize and as a consequence they can form physical entanglements that relax and allow flow
3 at high stress, leading to fibril formation [15]. A particular challenge for PSAs is adhesion to
4 surfaces with a low surface energy, when the thermodynamic work of adhesion is low.

5 Recently, due to the increased restrictions on the use of volatile organic compounds
6 (VOCs) [4,12–14], the interest of researchers and different sectors of industries has focused on
7 the development of more environmentally friendly adhesives. From this point of view,
8 waterborne polyurethanes (WPU)s are great candidates as adhesive materials since they
9 combine the properties of PUs with a reduction in the emissions of VOCs into the
10 atmosphere[16].

11 In this work, the adhesive properties of previously synthesized organic solvent-free
12 waterborne poly(urethane-urea)s (WPUUs) [10,17] were investigated. These WPUUs
13 presented different molecular architectures since they were synthesized using PEO
14 homopolymer as well as poly(ethylene oxide-b-propylene oxide-b-ethylene oxide) (PEO-b-
15 PPO-b-PEO) and poly(propylene oxide-b-ethylene oxide-b-propylene oxide) (PPO-b-PEO-b-
16 PPO) triblock copolymers as macrodiols. However, as these WPUUs are not cross-linked, we
17 propose here two different strategies to bring their adhesive properties closer to the required
18 standard for PSAs. One of the strategies is to blend different WPUU dispersions, since as
19 mentioned, it has been used with triblock copolymers. The other one is to prepare bilayer
20 materials with a gradient in the viscoelastic properties [15,18]. Carelli *et al.* [6] showed that
21 the adhesive properties of PSAs could be successfully improved by the introduction of a
22 gradient in the viscoelastic properties of a designed bilayer system, where one of the layers was
23 more dissipative, while the other one was more elastic. There are just a few published reports
24 using this approach for PSAs [6,18,19], and there are no reported investigations of using non-
25 cross-linked polymers in PSA bilayers. Accordingly, the research presented here introduces a

novel approach to the study and improvement of the adhesive performance of adhesives based on non-cross-linked PUs. To our knowledge, adhesive systems with a PSA-like performance have never before been derived from non-cross-linked WPUUs. These adhesives are more environmentally friendly than the classical solvent-borne material.

2. Experimental

2.1. Materials

The experiments were designed using previously synthesized and characterized waterborne poly(urethane-urea) (WPUU) dispersions [described in references 10 and 16]. The synthesized WPUUs were based on poly(ethylene oxide) (PEO) and amphiphilic triblock copolymers containing poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) blocks as macrodiols (Fig. 1). The hard segment of these WPUUs consisted of MDI as diisocyanate and neutralized 2'4-diamino-benzenesulfonic acid (DBSA) as a chain extender/internal emulsifier. Four different dispersions were considered in this work: PU0, PUEPE19, PUEPE29 and PUPEP27. In these sample names, PU refers to polyurethane. PU0 refers to PEO homopolymer macrodiol based WPUU, as it was denoted previously [10,17]. The WPUUs based on triblock copolymers, called PUEPE19 and PUEPE29, were synthesized with poly(ethylene oxide-b-propylene oxide-b-ethylene oxide) (PEO-b-PPO-b-PEO) triblock copolymer macrodiols of 1900 and 2900 g mol⁻¹ molecular weights, respectively. PUPEP27 was synthesized with a poly(propylene oxide-b-ethylene oxide-b-propylene oxide) (PPO-b-PEO-b-PPO) triblock copolymer macrodiol with a molecular weight of 2700 g mol⁻¹. In their names, E refers to the PEO block, P refers to the PPO block and the number refers to the molecular weight (in g mol⁻¹) of the soft copolymer segment. Table 1 shows details and some characteristics of these dispersions. Information on the techniques used to characterize the dispersions has been provided previously [10,17].

1 **Table 1.** Experimental solids content, glass transition temperature, weight-average molecular
 2 weight, dispersity index and theoretical hard segment content of the synthesized WPUUs.

Sample Name	Solids content	T_g	$\bar{M}_w$	$\bar{D}$	Theoretical
	(wt. %)	(°C)	(g mol ⁻¹)	($\bar{M}_w/\bar{M}_n$)	hard segment content (%)
PU0	24.1 ± 0.6	6	31,750	1.89	42.3
PUEPE19	24.7 ± 0.1	-52	26,740	1.79	28.4
PUEPE29	27.3 ± 0.1	-63	25,900	2.10	20.7
PUPEP27	25.9 ± 0.1	-66	14,650	1.27	21.9

Fig. 1. Reagents (diisocyanate, chain extender and macrodiols) used for the synthesis of the waterborne poly(urethane-urea)s and schematic diagram of the waterborne poly(urethane-urea)s based on the different macrodiols.

2.2. Probe-tack adhesion analysis

In order to perform the probe-tack analysis, WPUU dispersions were applied on glass substrates using a 200 μm cube applicator. Because of the low solids content, two successive depositions were required to achieve an adequate film thickness. The wet films were left to dry in air at room temperature and relative humidity (approximately 40%, but not controlled) for 24 h, to form a homogenous film. A digital caliper was used to measure the thickness of the films. 10 different representative areas of each film were measured. In these areas, given the sensitiveness to pressure of the polymer films, peel-off measurements were not carried out. Three successive depositions were required for PUPEP27 because it was the least viscous, and

hence it flowed out more during the deposition. The thickness of the dry films was in the range from 80 to 150 μm with the exception of PUPEP27, with a thickness of 200 μm .

The probe-tack analysis was carried out using a TA-XT Plus Texture Analyser (Stable Micro Systems, Godalming, UK) with a cell load of 1 kg. In order to investigate the effects of surface energy on adhesion, spherical probes (2.54 cm diameter) with two different surface energies were used: stainless steel (higher surface energy, $\gamma \approx 44.5 \text{ mJ m}^{-2}$ [20,21]) and polypropylene (PP) (lower surface energy, $\gamma \approx 32 \text{ mJ m}^{-2}$ [20,22]). The probes were brought into contact with the film for 1 s under a load of 4.9 N, whereas the test withdrawal speed was set at 0.1 mm s^{-1} . Five measurements were made for each test sample; the most representative curve for each is presented. The probe was cleaned with deionized water and acetone after each test. All probe-tack measurements were carried out at room temperature and humidity (typically 21 $^{\circ}\text{C}$ and 40% RH, but not strictly controlled).

The probe displacement, d , and the nominal force, F , were measured over time in each test. The initial contact area, A , of the probe on the film surface was measured by optical microscopy and using a caliper. For every test, the nominal engineering stress (σ) was calculated as

$$\sigma = \frac{F}{A} \quad (1)$$

and the engineering strain (ε) was determined by dividing d by the initial film thickness, h_{film} :

$$\varepsilon = \frac{d}{h_{film}} \quad (2)$$

The debonding energy (W_{deb}) was calculated from the area under the stress-strain curve as

$$W_{deb} = h_{film} \int_0^{\varepsilon_{max}} \sigma(\varepsilon) d\varepsilon \quad (3)$$

2.3. Adhesive performance optimization strategies

2.3.1 Bilayer systems

The first layer of the bilayer systems was prepared as detailed in section 2.2, going over the glass surface just one time. Once the first layer was dried, the second WPUU dispersion was cast directly on the flat film formed by the first layer using a cube applicator and then the second layer was left to dry for 24 h. For this second layer, cube applicators with three different thicknesses (50, 100 and 200 μm) were used in order to study the influence of the thickness of the second layer on the adhesion. The bilayer systems are listed in Table 2, whereas Fig. 2 shows a schematic illustration. The samples were denoted as bilayerXY-Z, where the X stands for the WPUU used for the first layer, the Y stands for the WPUU of the second layer (that will be in contact with the adherend), and the Z stands for the thickness of the cube applicator (in μm) employed for the application of the second layer. Here, it should be noted that, since the dispersions presented solids content of approximately 25 wt%, the final thickness of the films was approximately 25% of the applicator thickness. The morphology of the neat WPUUs was previously studied and was reported elsewhere[10,17].

Table 2. Bilayer systems using PU0 and PUEPE29 as the layers.

Sample	1 st layer		2 nd layer	
	WPUU	Applicator	WPUU	Applicator
		thickness		thickness
		(μm)		(μm)
Bilayer029-50	PU0	200	PUEPE29	50
Bilayer029-100	PU0	200	PUEPE29	100
Bilayer029-200	PU0	200	PUEPE29	200
Bilayer290-50	PUEPE29	200	PU0	50
Bilayer290-100	PUEPE29	200	PU0	100
Bilayer290-200	PUEPE29	200	PU0	200

Fig. 2. Schematic illustration of the arrangement of the bilayer systems for probe-tack adhesion measurement. Thicknesses refers to the thickness of the applicator.

2.3.2 Blending

Blends of PUEPE29 and PU0 in two different PUEPE29:PU0 mass ratios (based on the initial dispersion mass) of 1:1 and 2.3:1 were prepared by physical mixing of the dispersions using a mechanical stirrer at room temperature for 24 h. The mixtures are called Blend1 and Blend2.3, respectively. Blends were cast as detailed in section 2.2.

2.4. 180° peel-off test

In the pursuit of possible applications for prepared materials, a 180° peel test was carried out for the Bilayer029 system (denoted as Bilayer029-P). First, using a 120 μm spiral bar applicator a PU0 layer was cast on two different polymer surface sheets: a) polyethylene terephthalate (PET) and b) PP. The sheets had been subjected to a corona treatment, which increases their surface energy [23]. Films were left to dry at room temperature for 24 h. Then a second PUEPE29 layer was cast onto the first PU0 layer with a 60 μm cylindrical applicator and allowed to dry at room temperature for 24 h. Long strips of 25 mm wide were cut from the prepared sheets of PET or PP with Bilayer029-P. The adhesive side of the strips was pressed

onto an aluminum or glass surface. A TA-XT Plus Texture Analyser (Stable Micro Systems) in tensile mode with a load cell of 5 kg was used to determine the average force required to remove the strip from each surface at a constant test speed of 2 mm s⁻¹. A transparent, polypropylene-based PSA tape, sold commercially as Sellotape (Henkel, Winsford, UK), was also tested to compare with the performance of the WPUU adhesive tapes. In this case, a PET or PP backing layer was not used.

3. Results and discussion

3.1. Probe-tack adhesion

3.1.1. Analysis of waterborne poly(urethane-urea)s

A probe-tack curve, presented as stress versus strain, is rich in information [14,24,25]. The gradient of the linear region at low strain is related to the elastic modulus of the polymer in confinement. The stress reaches a maximum value, $\sigma_{\max}$, which indicates the point where debonding or cavitation begins, and then the stress falls. If a polymer has an elastic modulus that is too high, a type of interfacial failure (also known as brittle failure) follows, where the stress falls abruptly to zero without any further polymer deformation. However, if the polymer has a good balance of viscoelasticity, fibrillation will follow, which is observed as a stress plateau, consisting of a constant stress value as the strain increases, followed by failure by detachment at a strain of $\epsilon_{\max}$. Greater debonding energy follows from greater fibrillation, as energy is expended in the polymer deformation. A cross-linked polymer usually exhibit stress hardening during fibrillation, prior to clean detachment from the probe, without any cohesive failure.

As a general trend, $\sigma_{\max}$ is influenced by the thermodynamic work of adhesion, W_{adh} , which is the surface free energy associated with the creation of new surfaces after debonding a

joint. For the case of an adhesive poly(urethane-urea) based on a copolymer (CP) debonding from a probe (P), thermodynamic work of adhesion (per unit area) can be calculated from the Dupré equation [26]:

$$W_{adh} = \gamma_{CP} + \gamma_P - \gamma_{CPP} \quad (4)$$

where γ_i represents the interfacial free energy between the PSA poly(urethane-urea) (CP) and air, the probe (P) and air, or between the poly(urethane-urea) and probe (CPP). This equation shows us that to achieve a high thermodynamic work of adhesion, the interfacial energy, γ_{CPP} , should be minimized. The equation also explains why the work of adhesion on low surface energy probes (or other adherends) tends to be lower. For good adhesion on a substrate (or probe) with a low surface energy, the adhesive poly(urethane-urea) should have a high surface energy. Although this might lead to a higher interfacial energy between the adhesive and adherend probe [2,23], the thermodynamic work of adhesion would still be high. The energy of debonding, W_{deb} , is related to W_{adh} through the dissipation of the polymer, Φ , as $W_{deb} = W_{adh}(1 + \Phi)$. The viscoelastic properties of the polymer determine the value of Φ for a particular PSA.

Finding a suitable adhesive for low surface energy materials is still such a challenge, because most polymers in adhesives have a similar low surface energy and hence the thermodynamic work of adhesion is low. Note that the surface energy of PPO is in the range of 28 to 34 mJ m⁻² at room temperature [27,28], which is close to the value for the PP probe [29]. In contrast, the surface energy of PEO is higher (41 to 44 mJ m⁻²) [28,30]. The inclusion of PEO in a polymer could be advantageous to adhesion. Other polymers typically used in PSAs, such as poly(butyl acrylate) [31] and poly(ethyl hexyl acrylate) [32], likewise have a low surface energy (30–31 mJ m⁻²) and consequently typically show poorer adhesion on PP, polyethylene and other low energy surfaces [33]. Kowalski et al. [20] measured a surface energy of 30 mJ m⁻² for a model acrylic PSA.

A value of γ_{CPP} was estimated by using the surface energy values for PEO, PPO and the probes (PP or steel) that are available in literature [29,30,34], via the equation [26]:

$$\gamma_{CPP} = \left(\sqrt{\gamma_{CP}} - \sqrt{\gamma_P} \right)^2 \quad (5)$$

In this simple calculation, we are ignoring the separate polar and dispersive components and using the total surface energy. Moreover, these calculations do not consider the effect of the hard segment nor the different morphologies of WPUU on the surface and interfacial energies. (Specifically, there was no phase separation for PU0 while there was phase separation for the triblock copolymer-based WPUUs [10]). The hard segment content influences the final properties of the films, and this content is not the same for the various WPUUs. It depends on the molecular weight of the macrodiol. The hard segment content is higher when the molecular weight of the macrodiol is lower.

Table 3 presents calculated values of γ_{CPP} for the two probes for each of the four WPUUs. Values for a model acrylic PSA [20] are shown for comparison. γ_{CP} values for synthesized WPUUs were calculated considering the amount of PEO and PPO blocks in the macrodiol (Fig. 1). The value for the surface energy of PEO (42.8 mJ m⁻²) was taken from Roe *et al.* [30], while for PPO (31.7 mJ m⁻²) the value was taken from Kasemura *et al.* [34]. As PEO has a higher surface energy than PPO, the addition of the PEO block in the copolymer segment has the benefit of increasing the thermodynamic work of adhesion with the PP probe. Hence, PU0 has the highest W_{adh} of all the poly(urethane-urea)s with a calculated value of 74 mJ m⁻² for polypropylene and 87 mJ m⁻² for steel. In contrast, the standard acrylic PSA has the lowest values (62 mJ m⁻² and 73 mJ m⁻², respectively) for the same two materials. The triblock copolymer based poly(urethane-urea)s have values that are intermediate between PU0 and the standard acrylic PSA. Although the W_{adh} for the triblock copolymer based poly(urethane-urea)s is calculated to be higher for the stainless steel probe in comparison to the PP probe, the

calculated values for PP are more favorable for adhesion in comparison to the standard acrylic PSA.

Table 3. Surface energy (dispersive and polar components), calculated interfacial energy and thermodynamic work of adhesion of waterborne poly(urethane-urea)s.

Sample	γ_{CP}	γ_{CPP}	γ_{CPP}	W_{adh}	W_{adh}
		for PP	for steel	on PP	on steel
	(mJ m ⁻²)	(mJ m ⁻²)	(mJ m ⁻²)	(mJ m ⁻²)	(mJ m ⁻²)
PU0	42.8	0.8	0.02	74	87
PUEPE19	37.2	0.2	0.3	69	81
PUEPE29	36.1	0.1	0.4	68	80
PUPEP27	36.1	0.1	0.4	68	80
Reference PSA	30	0.03	1.4	62	73

The probe-tack curves obtained for the four WPUUs are presented in Fig. 3. PU0 and PUPEP27 have the lowest adhesive performance (smallest ϵ_{max} and no fibrillation). However, in the case of PUPEP27 the stress did not fall abruptly to zero after reaching σ_{max} , but fell gradually, because of cohesive debonding, and left residue on the probe afterward [35]. In the case of PU0, for both probes, and of PUEPE19 for the steel probe, a sudden decline of the stress to zero at ϵ_{max} occurred, which can be related to a clean interfacial detachment of the probe from the film, and is indicative of brittle failure [35]. For the steel probe, both PUEPE29 and PUPEP27 exhibited a gradual decrease of the stress, which corresponds to a liquid-like cohesive debonding [4,35]. This can be explained by their lower hard segment content in comparison to PU0 and PUEPE19 due to their higher molecular weight of the triblock

1 copolymers (Fig.1). In addition, PUPEP27 presented the lowest molecular weight of all
2 synthesized WPUUs (Fig.1). For the low surface energy PP probe, as can be seen in Fig. 3b,
3 two of the WPUUs (PUEPE19 and PUEPE29) presented short plateau-like segments in their
4 probe-tack curves. This observation indicates some partial fibrillation or at least some
5 extension of the poly(urethane-urea), which resulted in the greatest $\epsilon_{\max}$. However, these
6 polymers still exhibit a cohesive failure and leave residue on the probe, probably as a
7 consequence of the absence of cross-linking and associated strain hardening [6].

8 All three WPUUs based on triblock copolymers showed better probe-tack adhesion
9 than did the PU0, which is based on PEO only. This result can be explained by the relatively
10 high elastic modulus of PU0, reported elsewhere [36] to be 6.2 ± 1.7 MPa, which is far above
11 the acceptable range for PSAs, according to the Dahlquist criterion (which is on the order of
12 0.1 MPa) [7,35,37]. Triblock copolymer-based WPUUs presented lower elastic moduli and
13 fulfilled the Dahlquist criterion because of the addition of the PPO block, which presents $-\text{CH}_3$
14 side groups. The two WPUUs using PEO-*b*-PPO-*b*-PEO copolymers (PUEPE19 and
15 PUEPE29) exhibited a lower slope at low strain, indicating a lower elastic modulus in
16 confinement between the probe and substrate, in comparison to PUPEP27. The differences in
17 adhesive performance are attributed to the differences in their soft segments and viscoelasticity,
18 arising from the mentioned differences in hard segment content and molecular weight, which
19 determines Φ , rather than the influence of the thermodynamic work of adhesion, W_{adh} . Surface
20 energy effects are more likely to influence $\sigma_{\max}$. The surface energies of all WPUU films are
21 similar for a given probe, and the resulting $\sigma_{\max}$ is likewise similar.

22 In summary, none of the WPUUs performed as high performing PSAs that show
23 extensive fibrillation during debonding [38], however they presented some measurable
24 tackiness. Furthermore, it is notable that the poly(urethane-urea)s exhibit relatively good
25 adhesive performance on a low surface energy material (PP probe). This observation indicates

that – following optimization – they could be used as soft adhesives for substrates with a low surface energy, such as packaging material. Next, we consider how the performance of the WPUUs can be improved via a bilayer design.

Fig. 3. Representative probe-tack curves of the synthesized waterborne poly(urethane-urea)s for measurements carried out with (a) steel and (b) PP probes.

3.1.2. Probe-tack of bilayer systems based on PU0 and PUEPE29

As was demonstrated by Carelli *et al.* [6], adhesive properties can be modified by the preparation of bilayer systems with layers that exhibit different elastic and viscous properties in order to create a gradient in the viscoelastic properties. Taking into account the probe-tack results (Fig. 3), we selected two of the WPUUs with differing properties to use in a bilayer system design. The two candidates are PU0, which is more solid-like and has a high elastic modulus, and PUEPE29, which is more liquid-like, exhibited the highest $\epsilon_{\max}$ of all the WPUUs, and had a short plateau in the PP probe-tack tests (Fig. 3b). Table 2 lists the sample geometries that were investigated. Fig. 4a and 4b show the probe-tack curves obtained for the bilayer system in which PUEPE29 was cast on the glass substrate, and then PU0 was cast on top of it, so that it is in contact with the probe. These results indicate that the interfacial failure of PU0 (Fig. 3) prevailed for the three thicknesses of Bilayer290. There is no polymer extension

or fibrillation during the debonding process. In the case of the steel probe, $\varepsilon_{\max}$ values were superior to those found previously for PU0 but inferior to those of PUEPE29. The curves for the PP probe show inferior adhesion for all three Bilayer290 systems in comparison to the single polymers. The solid-like PU0 film dominates the debonding and interfacial failure result at relatively low strains. There is no benefit obtained from the creation of a bilayer.

Fig. 4. Representative probe-tack curves of the prepared different thickness bilayer systems measured with (a) (c) steel and (b) (d) PP probes. The sample names are defined in Table 2.

In contrast, in the case of Bilayer029 systems, in which the PUEPE29 film was on top and in contact with the probe, there is some benefit in using bilayers. When the PUEPE29 layer is thicker, the adhesive performance evidently is improved when using the steel probe. This

improvement can be appreciated in Fig. 4c, where a plateau appears for Bilayer029-100 and Bilayer029-200, which is similar to standard PSAs [4–6] with fibrillation and an adhesive debonding (not cohesive failure) [35]. The plateau was longer for Bilayer029-100, probably due to a decrease of the synergetic effect between the two materials in Bilayer029-200. Whereas the PUEPE29 films lacked sufficient cohesion to exhibit fibrillation, when this film is supported by a harder PU0 polymer, fibrillation is achieved. It is apparent that the PUEPE29 layer needs to be thick enough to achieve this improvement in the adhesive performance. Carelli *et al.* [6] similarly concluded that there is a minimum thickness required for the second layer in order to observe an impact in the adhesive performance.

For the PP probe, this bilayer was less effective. However, for Bilayer029-200, the detachment exhibited a cohesive liquid-like debonding [35] where the adhesive material left the residual on the PP probe. This phenomenon can be better understood by taking into account the liquid-like character of the PUEPE29 top layer as well as its thickness.

These results suggested that by preparing bilayers systems with a gradient in the viscoelastic properties, adhesive performance can be tailored and adjusted for different applications. PSA-like performance was observed when the softer polymer, supported by a harder polymer, was in contact with a steel surface.

3.1.3. Probe-tack of PU0/PUEPE29 blends

Polymer blending is one of the strategies to design materials with improved adhesion [13,38]. In particle mixtures, glassy (or hard) particles raise the elastic modulus but can lead to brittleness, and soft particles introduce energy dissipation and increase extensibility. In the bilayers, PU0, which is more solid-like (hard), was used in combination with PUEPE29, which is more liquid-like (soft). This raises the question as to whether the mixing of the hard and soft

particles will offer the same benefits as their use in a bilayer. Experiments were performed to answer this question.

The probe tack analysis from blends of PU0 and PUEPEP29 is presented in Fig. 5. Each of the two blends presented a higher strain at failure for the steel probe than for the PP probe. Blend1 behaved solid-like displaying brittle fracture on both probes. Blend1 exhibited a higher stress and strain for the steel probe; its performance was in between that observed for neat PU0 and PUEPE29 (Fig. 3a). In the case of Blend2.3, the performance on both probes during debonding was very similar: there was a gradual drop in stress, indicative of cohesive failure.

It is notable that Blend1 behaved more similarly to PU0 (Fig. 3a), whereas the curves for Blend2.3 were more similar to that of PUEPE29 (Fig. 3b). However, there was no improvement in the adhesive properties. As can be observed when comparing Fig. 5 to Fig. 3, the probe-tack performances of WPUU blends were inferior to the neat WPUUs, and even the small plateau observed in the case of PUEPE29 for the PP probe disappeared for the blends.

Fig. 5. Representative probe-tack curves of the different PU0/PUEPE29 blends using steel and PP probes.

Neither of the blends improved the performance of the neat WPUUs. This suggests that the strategy of preparing bilayers systems is better for optimization of the WPUUs for adhesive applications.

3.2. Comparison of probe-tack performances

As a means to draw conclusions, we next compare quantitatively the adhesive properties of the original WPUUs with the bilayer and the blends. We analyze the trends in the maximum stress and in the debonding energy.

3.2.1. Maximum stress, $\sigma_{\max}$

The maximum tack stress (Fig. 6) is influenced by the thermodynamic work of adhesion. As the composition of the WPUUs is changed, there are no significant differences in $\sigma_{\max}$. This result can be explained by the surface energies of the poly(urethane-urea)s being very similar.

Fig. 6. Maximum tack stress for the neat WPUUs, the blends, and the bilayers for (a) steel and (b) PP probes.

3.2.2. Debonding energy, W_{deb}

The debonding energy, calculated from the area under the stress-strain curve, is a good gauge of the overall adhesive performance, because it is a function of not only the maximum

tack force, but also the stress in the plateau region and the extent of fibrillation (which affects $\epsilon_{\max}$). As is shown in Fig. 7, the trends in W_{deb} are quite similar regardless of the probe. PUPEP27 displayed the highest value for W_{deb} for both probes despite its lower $\epsilon_{\max}$ since it was the thickest film of all, at the same time that Bilayer029-50 exhibits the lowest value for both probes. In the case of the Bilayer029 systems, it is evident that when increasing the thickness of the top PUEPE29 layer, the W_{deb} increases as a result, because there is a greater volume of extensible material. The positive effect of adding PUEPE29 is also observed in Blend2.3, as its W_{deb} is higher than that of Blend1, regardless of the probe.

Fig. 7. Debonding energy calculated from the area under the probe-tack curves for the various systems using (a) steel and (b) PP probes.

3.3. Application as adhesive tape

A 180° peel test was carried out in tensile mode, considering the plateau-like zone of the obtained curves as the peel force. The results are presented in Fig. 8. The first conclusion extracted from these results is that PET is not a satisfactory backing layer for the preparation of adhesive tapes based on Bilayer029-P because they detached fast from the PET backing layer under a low applied force. However, Bilayer029-P, deposited on a PP backing layer, was suitable for adhesive tapes. This was an unexpected effect taking into account that PET has a

higher surface energy than PP, even after corona treatment [39]. Nevertheless, it has been shown elsewhere that due to the inferior amount or lack of polar groups in polyolefin's structure, the corona treatment results in a more pronounced increase of their surface energy [39]. Moreover, how corona treatment is applied together with the storage of the film has a strong influence on the surface energy [39].

The peel force for glass surface was lower than that obtained by the commercial adhesive tape. On the contrary, the adhesive tape fabricated by applying Bilayer029-P on a PP backing achieved a higher peel force than the domestic adhesive tape on an aluminum surface. Note, however, that the adhesive layer in the domestic tape is significantly thinner than the bilayer. The adhesion energy is greater in thicker films that can dissipate more energy during debonding.

The results suggest that PU0 and PUEPE29 waterborne poly(urethane-urea) dispersions, applied on a PP surface to create a gradient in viscoelasticity, Bilayer029 configuration in this case, could potentially be used as an adhesive tape.

Fig. 8. Peel force determined by 180° peel-off test from glass (solid bars) and aluminum (striped bars) surfaces for the Bilayer029-P system with either PP (blue) or PET (green) backing layer. Results of a domestic tape (purple) are displayed for comparison.

4. Conclusions

Summarizing, VOC-free waterborne poly(urethane-urea)s, developed recently, showed adhesion to a high surface energy material (steel). Surprisingly, the same materials showed somewhat better adhesion to a low surface energy material (PP). This finding is partially attributed to the higher surface energy of the PEO block, which leads to a higher thermodynamic work of adhesion, and to the PPO block in triblock copolymer-based WPUUs that reduces the elastic modulus to fulfill the Dahlquist criterion. Consequently, these WPUU dispersions could be used as soft adhesives for attachment to low energy surfaces. Blending two of the WPUUs (in two different proportions) did not improve the adhesive performance, in comparison with the adhesive performance of the neat WPUUs. On the contrary, bilayer systems made from the same two WPUUs used in the blends, with a more liquid-like layer deposited on a more solid-like layer, led to a plateau in their probe-tack curves for steel, as a result of fibrillation. Thus, the preparation of a bilayer system is a successful approach for the improvement of the adhesive performance of WPUUs to achieve a PSA-like performance, meaning that they can be used as base of PSAs, leading to formulated PSAs by modification with surface agents in order to tailor the different properties. The top liquid-like layer provides tack, whereas the more solid-like underlayer contributes to the cohesion and enables fibrillation.

Building on the adhesive performance of the designed bilayer systems, adhesive tapes were prepared from the best-performing bilayer. The bilayer adhesive tape applied on a PP backing displayed a peel force in the range found for a domestic tape. The peel force exhibited

on an aluminum surface was superior to that of the domestic tape. However, the bilayer thickness was greater than the adhesive's thickness in the domestic tape, and further optimization is required to achieve acceptable performance in a thinner layer.

Acknowledgments

Financial support from Spanish Ministry of Science, Innovation and Universities and European Union (MICINN/FEDER and UE) in the frame of PGC2018-097699-B-I00, MAT2016-76294-R projects, from the Basque Government for PIBA 2019-44 project and from the University of the Basque Country (GIU18-216 research group) are gratefully acknowledged. I. D.-G. thanks the Basque Government for a PhD Fellowship (PRE_2018_2_0217) and for the grant to stay as a visiting PhD student at the University of Surrey (EP_2018_1_0065). We thank Joe Hall and Violeta Doukova (University of Surrey) for technical assistance.

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