Effects of aging on the adhesive properties of poly(lactic acid) by atmospheric air plasma treatment

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ABSTRACT: The aim of this study was to analyze the durability of a plasma treatment on the surface of poly(lactic acid) (PLA). We used atmospheric-plasma treatment with air to improve the wettability of PLA by evaluating the aging effect under controlled conditions of relative humidity (RH) and temperature (25% RH and 25°C). We studied the durability of the atmospheric-plasma treatment by measuring the contact angle, calculating the surface energy, and observing changes in the resistance of the PLA–PLA adhesive bonds. These techniques allowed us to evaluate the hydrophobic recovery phenomenon that the PLA surface suffered as a consequence of the aging process. The results provide the maximum storage time of PLA treated with atmospheric plasma at which the sample retained its good adhesion properties; this time was lower than 3 days under normal atmospheric conditions. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43040.

INTRODUCTION

One of the most interesting biopolymers in the research field is poly(lactic acid) (PLA). There is an increasing demand for this kind of polymer because of the renewable origin of the raw material for its production and also because of its biodegradable properties. PLA is the second most produced bioplastic on a large scale and is preceded only by starch.[1–12]

Packaging is the industrial field in which PLA is the most demanded polymer; it is mainly used for short-life products. PLA is satisfactorily replacing traditional commodity polymers for these applications. The main features of this biopolymer are its high mechanical strength, transparency, and processability. PLA is a linear polyester obtained from 100% renewable materials produced from lactic acid. On the other hand, lactic acid is produced by the anaerobic fermentation of substrates with carbon, which can be either pure (glucose, lactose, etc.) or impure (starch, molasses, etc.) with microorganisms such as bacteria *Lactobacillus, Pediococcus, Lactococcus,* and *Streptococcus,* or some fungus, such as *Rhizopus oryzae.* Industrially, saccharose from sugar cane and beet is used along with glucose.[12–21]

Nowadays, one of the most demanding sectors for PLA is packaging; it is mainly in demand for short-life products, such as disposable dishes, glasses, straws, feeding bags, films, and cosmetic containers. Design is a very important factor in the packaging sec-

tor and, in most applications, adhesion is needed. Because of the intrinsically low surface wetting properties in polymers, the surface hydrophilicity on the substrate needs to be improved. To achieve this, a technology of surface modification based on atmospheric plasma is used. This technology is a really versatile technology because a vacuum is not needed; furthermore, it is adaptable to automatic production and capable of working continuously in a production line. Also, because of its lack of waste, this is an environmentally friendly process. This surface modification treatment increases the resistance properties of adhesive joints on the polymeric surface because it enhances their wettability. The effect of the atmospheric-plasma surface treatment over polymeric surfaces is an important surface activation; it increases the polymer surface energy and, therefore, its hydrophilicity. These allow a better adhesive–polymer interaction and improves adhesion. However, these surface activation effects are not permanent, and the enhancement on the surface wettability decreases with time. This aging phenomenon is called *hydrophobic recovery.*[22–28]

With respect to atmospheric plasma on the PLA surface, plasma treatment promotes an increase in the surface energy of 59% from values of around 37.10 mJ/m^2 to values close to 58.92 mJ/m^2. This treatment of the PLA surface induces the appearance of new activated species, such as carboxyl (—COOH), carbonyl (—CO), hydroxyl (—OH), peroxide (—ROOR—), hydroperoxide (— ROOH), ether (—COC—), ester (—COOC—), and other functional groups, which change over

Table I. Contact Liquids and Their γ_s, γ_s^d, and γ_s^d Values

Test liquid	γ_s^d (mJ/m^2)	γ_s^p (mJ/m^2)	γ_s (mJ/m^2)
Water	22.0	50.2	72.2
Glycerol	34.0	30.0	64.0
Diiodomethane	48.5	2.3	50.8
Formamide	32.3	26.0	58.3

time to achieve a stable state.[29–36] The reduction of this active groups acts negatively on the wettability properties achieved with treatment. The main plasma-acting mechanism of the atmospheric-plasma surface treatment is the chemical functionalization of the treated surface, so it is important to determine the durability of the treatment and to quantify changes in the wettability along with time; these changes cause the aging process.[22–24,33,37–40]

In this study, the effects of the time after the atmospheric-plasma treatment on the PLA substrate were evaluated. The aging process conditions were as follows: 25% relative humidity (RH) and a temperature of 25°C for 21 days; these are usual conditions in industrial environments. Furthermore, the hydrophobic recovery phenomenon was determined by PLA–PLA joint resistance; this depends on the aging time. In these unions, a biodegradable adhesive was used to maintain ecofriendly characteristics in this study. It is important to take into account the aging factor to implant this technology in industrial processes because it affects the storage time of a product waiting for a postprocess. We determined the maximum storage time of PLA samples through analysis of the hydrophobic recovery process to optimize the industrial process in terms of adhesion.[41–47]

EXPERIMENTAL

Materials and Sample Preparation
Poly(lactic acid) (PLA; commercial grade, PLA 6201D) was supplied in pellet form by Nature Works LLC (Minnetonka, MN). The material was injected into a gloss mirror finished with dimensions of 160 × 60 × 2.2 mm^3 under manufacturer recommended conditions.

Four different liquids were used for contact angle (θ) measurements and subsequent surface energy calculations. The liquids were stabilized diiodomethane (99% purity, Acros Organics Geel, Belgium), double-distilled water, formamide, and glycerol (99%, extrapure for analysis, reagent grade, acros organics (ACS), from Scharlau Chemie S. A., Scharlab S. L., Barcelona, Spain).

These test liquids were selected to cover a wide range of polar (γ_s^p) and dispersive (γ_s^d) components of the liquid total surface energy (γ_s), as shown in Table I.

Commercial adhesive-grade EcoPoxy Fast Hardener supplied by Ecopoxy Systems Co. (Providence, EEUU (USA)) was used to form PLA-PLA adhesion unions. Ecopoxy is a partially biobased adhesive with epoxidized soybean oil, and it finds typical applications as a polymer adhesive.

Atmospheric-Plasma Surface Treatment
PLA samples were subjected to atmospheric-plasma treatment with a plasma generator (model Plasma JetRD1004, Plasmatreat

GmbH, Steinhagen, Germany). The plasma generator worked at 50/60 Hz, 230 V, and 16 A with a frequency of 17 kHz and a discharge voltage of 20 kV. The plasma treatment was applied with a rotating torch ending in a nozzle with a rotation speed of 1900 rpm.

Atmospheric plasma was applied with nozzle–sample distances of 6 and 10 mm. The treatment rates were set as 100, 300, and 700 mm/s. The samples used were 60 × 20 × 2.2 mm^3 in size.

Aging
The durability of the atmospheric-plasma surface treatment was studied through surface θ measurements for different storage times (from 3 h to 21 days). The storage conditions of the PLA samples were a temperature of 25° and an RH of 25%.

θ and Surface Energy
An Easydrop Standard Instrument (model FM140, Krüss, Hamburg, Germany) was used to measure θ. The maximum error in the θ measurement did not exceed ±4%. The software used was Drop Shape Analysis SW21. This process was realized with four different test liquids with different polarities to calculate the surface energy.

The Owens–Wendt method was used to calculate the surface energy. With this method, we were able to determine both disperse and polar additive contributions. Equation (1) represents the equation for the surface energy calculation.

$$\gamma_l(1+\cos\theta)/2(\gamma_l^d)^{1/2}=(\gamma_s^p)^{1/2}\left[(\gamma_l^p)^{1/2}/(\gamma_l^d)^{1/2}\right]+(\gamma_s^d)^{1/2}$$

(1)

where γ_l is the surface tension of the liquid, γ_s is the surface tension of the solid or free surface energy, and d and p refer to the dispersive and polar components of each phase, respectively. This expression is plotted linearly by the following equation: $y = ax + b$

If $(\gamma_l^p)^{1/2}/(\gamma_l^d)^{1/2}$ is represented versus $\gamma_l(1 + \cos\theta)/2(\gamma_l^d)^{1/2}$ as a linear interception of this line on the axis, the slope of the line gives $(\gamma_s^p)^{1/2}$, whereas $(\gamma_s^d)^{1/2}$ is the intersection of the beeline with the y axis. The sum of γ_s^d and γ_s^p is the surface free energy ($\gamma_s = \gamma_s^p + \gamma_s^d$).

Mechanical Characterization
The test used to evaluate the PLA–PLA adhesive joints strength was the determination of the shear strength by the block-shear method according to standard ISO 13445. Five samples, 25 × 25 × 2 mm^3 in size with adhesive joints from 10 to 12 mm, of each treated surface were subjected to a shear rate of 300 mm/m in an Ibertest ELIB 30 (Ibertest SAE, Madrid, Spain) at room temperature.

IR Thermography
To evaluate the effect of the plasma treatment on the PLA surface in terms of degradation caused by high temperature, a thermal vision camera (IR 980, Cantronic Systems, Inc., Coquillan, Canada) was used. The dispositive allowed us to obtain thermal images in the range of temperatures −20 to 600°C with a precision of ±5°C

RESULTS AND DISCUSSION

Effect of Aging on the PLA Treated by Atmospheric Plasma
An aging study of the PLA substrate was carried out to determine the treatment durability before the atmospheric-plasma

Table II. θs for Different Test Liquids with Different Aging Times of the PLA-Treated Sample with a 6-mm Reach and Treatment Rates of 100, 300, and 700 mm/s

		Distance 6 mm							
		Water		Formamide		Diiodomethane		Glycerol	
Advance rate (mm/s)	Aging	θ	deviation	θ	deviation	θ	deviation	θ	deviation
100	0 h	44.0	2.1	21.6	2.8	21.4	2.8	36.9	4.7
	12 h	45.7	0.3	24.6	1.4	31.6	1.9	45.2	1.1
	1 day	45.8	0.4	24.2	0.7	31.9	1.7	45.5	1.9
	5 day	48.9	0.6	27.6	0.4	36.6	0.8	48.3	1.6
	10 day	53.7	2.7	39.1	3.5	38.6	4.4	61.4	4.3
	14 day	62.3	4.0	43.7	0.5	40.6	0.7	68.4	0.8
	21 day	68.7	0.7	43.9	0.3	40.7	0.2	70.3	6.6
300	0 h	53.4	2.8	24.3	2.3	29.5	2.1	48.6	1.0
	12 h	53.8	1.9	33.0	1.5	30.6	5.6	56.7	2.8
	1 day	54.0	2.3	33.9	1.2	31.1	5.0	57.9	3.8
	5 day	56.1	0.7	37.9	0.2	34.1	1.6	61.4	1.0
	10 day	60.1	3.6	41.5	0.4	36.8	1.3	65.9	1.0
	14 day	64.6	1.9	44.9	1.8	39.7	0.5	72.2	3.3
	21 day	73.3	2.6	52.0	1.6	40.1	0.6	73.7	2.5
700	0 h	61.6	2.6	42.1	1.2	33.2	4.1	64.2	2.9
	12 h	63.4	0.9	43.0	1.0	34.6	2.2	64.8	4.2
	1 day	64.4	0.8	43.1	1.0	36.4	0.9	64.8	1.3
	5 day	65.3	0.3	44.1	1.2	39.6	0.7	65.7	3.6
	10 day	66.9	0.3	45.5	5	40.1	1.5	67.4	0.2
	14 day	72.3	0.3	50.9	4.7	40.6	1.0	71.0	1.2
	21 day	72.5	0.4	52.1	2.1	40.8	0.7	76.5	3.2

treatment. In this study, we took measurements of θ on the PLA substrate with four different contact liquids with different polarities for different samples with storage times from 0 h to 21 days at 25°C and 25% RH.[30,48–53]

In previous studies on the effects of atmospheric plasma on the PLA surface, it was concluded that low treatment rates and short distances between the nozzle and substrate were the most effective. In this study, distances of 6 and 10 mm and treatment rates of 100, 300, and 700 mm/s were chosen to quantify hydrophobic recovery on the PLA polymeric substrate.[29]

In Table II, a summary of the θ results for different aging times are shown. For each analyzed treatment rate, an increasing trend of θ was observed for a distance of 6 mm. No significant changes in θ were observed at low storage times. Then, an increase in θ was observed over 21 aging test days. This effect was produced because of the realignment and disappearance of unstable species generated by the atmospheric-plasma treatment over the substrate; this reduced the surface polarity and subsequent wettability of PLA, and these effects were quantified by the increasing θ.[33,37,54–56]

A loss in the surface wettability with increasing θ was observed for water for 5 days after the treatment at a treatment rate of 100 mm/s, and an 11% increase in the angle was observed. An increase of 5% in the angle was observed for the higher treat-

ment rates 300 and 700 mm/s. After 21 days of storage, the water θ increased up to 56, 37, and 17% for treatment rates of 100, 300, and 700 mm/s, respectively. A lower angle was observed on the treated PLA than on the nontreated PLA when the 21st day was reached. This corroborated the fact that although there was a loss of wettability because of the loss of surface functionalization of the PLA caused by the initial action of the atmospheric plasma, this treatment not only was a chemical modification but also produced an etching of the surface material. This caused an increase in the substrate wettability because the physical modification did not change along with the aging time.[7,37,56–61]

Shown in Table III is a summary of the obtained values of θ for samples treated at different rates and nozzle–substrate distances with different storage times. An increase in θ was observed along with the aging time under treatment conditions of 10 mm for all of the treatment rates used.

For treatment conditions of 10 mm and 100 mm/s, a significant hydrophobic recovery in the hours after the plasma treatment is shown in Table III. Only 3 h after treatment, the increase in the value of θ of water was 29%; this was indicative of a fast hydrophobic recovery. This marked increase in θ occurred because under these conditions of the application of the plasma treatment (optimum conditions, according to previous studies), the maximum surface activation or polarity was achieved. Precisely

Table III. θs for Different Test Liquids at Different Aging Times of a PLA Sample Treated to 10 mm and with Treatment Rates of 100, 300, and 700 mm/s

		Distance 10 mm							
		Water		Formamide		Diiodomethane		Glycerol	
Advance rate (mm/s)	Aging	θ	deviation	θ	deviation	θ	deviation	θ	deviation
100	0 h	26.8	1.4	18.6	2.8	23	2.8	46	2.1
	12 h	47.6	1.8	27.8	2.4	31.5	1.4	60.0	1.2
	1 day	48.2	2.1	27.5	0.6	31.4	0.7	62.3	0.2
	5 day	51.7	0.3	37.4	0.7	33.3	1.4	68.0	0.5
	10 day	63.3	0.4	42.3	0.3	36.7	3.4	70.4	0.3
	14 day	70.9	2.5	49.5	0.1	40.3	1.6	76.2	1.2
	21 day	73.0	1.0	51.8	2.6	40.5	3.7	76.4	1
300	0 h	40.4	2.9	25.2	2.0	30.6	2.7	54.1	2.6
	12 h	50.9	2.5	26.4	1.4	33.0	0.6	57.3	1.3
	1 day	51.2	0.7	27.5	0.6	33.6	0.8	59.5	0.5
	5 day	54.5	1.6	32.7	3.0	37.9	0.1	65.0	0.7
	10 day	63.4	1.2	37.5	0.1	39.4	4.0	68.3	0.3
	14 day	67.2	2.9	50.2	0.1	40.1	0.8	75.1	1.6
	21 day	70.6	3.4	51.2	1.5	40.2	0.9	75.7	2.1
700	0 h	51.9	2.5	29.7	2.4	39.5	1.2	62.5	0.5
	12 h	54	0.9	36.9	0.2	39.7	1.6	63.0	0.6
	1 day	54.1	1.6	37.0	0.2	39.7	1.8	63.1	0.3
	5 day	57.9	0.8	38.6	0.8	40.1	1.9	65.2	2.7
	10 day	65.0	1.5	42.7	0.7	40.5	3.1	69.7	1.8
	14 day	72.5	1.5	50.8	1.5	40.8	2.8	72.2	3.7
	21 day	73.6	2.6	51.3	0.9	40.9	2.7	73.1	2.9

because of the chemical instability of these active species reacting quickly to more stable states with the same atmosphere, they quickly lost their functionality at higher values of θ. After 21 days of atmospheric aging, with water as a reference, θ on the surface of PLA increased by 56% under low treatment rates. Increases in θ of 37 and 17% for rates of 300 and 700 mm/s, respectively, were produced at high treatment rates.[54,55]

A marked hydrophobic recovery was observed for the treated PLA; this hydrophobic recovery was more accentuated in the first aging hours. After analysis of the evolution of θ for 21 aging days in the PLA sample, the variation of the surface energies during the same aging period were studied.[62–65]

Figure 1 shows the variation of γ_s, γ_s^p, and γ_s^d against the air-aging time for treated PLA with a distance of 6 mm and different treatment rates.

A decrease in the variation of the surface energy, mainly, γ_s^p, for 21 aging days under storage conditions is shown to be due to the restructuring of the active species on the PLA surface sample treated with atmospheric plasma. This surface energy decreased up to 28% at 21 days for treated samples with a 6 mm distance and a 100 mm/s treatment rates. Under the same conditions, γ_s^p decreased to a value of 9.47 mJ/m^2; this was close to that obtained without treatment (6.79 mJ/m^2). However, γ_s^d had a slightest variation and remained in the 26–33 mJ/m^2 range.

For a 300 mm/s treatment rate, the decreases in the surface energy after the aging process were about 25 and 15% for 700 mm/s. γ_s^p decreased from 17.51 mJ/m^2 for the nonaged sample to 6.78 mJ/m^2 for the 300 mm/s treatment rate. At a high treatment rate (700 mJ/m^2), γ_s^p decreased from 12.37 to 7.23 mJ/m^2 after 21 days of atmospheric aging. A higher realignment of polar modules inserted and activated on the polymer surface during the atmospheric treatment was promoted with increasing aging time.[66,67]

Figure 2 shows the variation in γ_s values and their γ_s^p and γ_s^d values with respect to air-aging time for PLA atmospheric-plasma-pretreated samples with a distance of 10 mm and different treatment rates.

The decreases obtained in the surface energy after 21 days of aging were 36.7, 28.7, and 18% for treatment rates of 100, 300, and 700 mm/s, respectively. This lower surface energy was mainly due to the loss of polarity of the PLA treated with plasma. γ_s^p also presented a clear decrease. For 100 mm/s, γ_s^p decreased from 32.83 to 6.92 mJ/m^2 after 21 days of storage. For higher treatment rates (300 and 700 mm/s), this decreased from 26.24 to 8.14 mJ/m^2 and from 20.49 to 6.81 mJ/m^2, respectively.
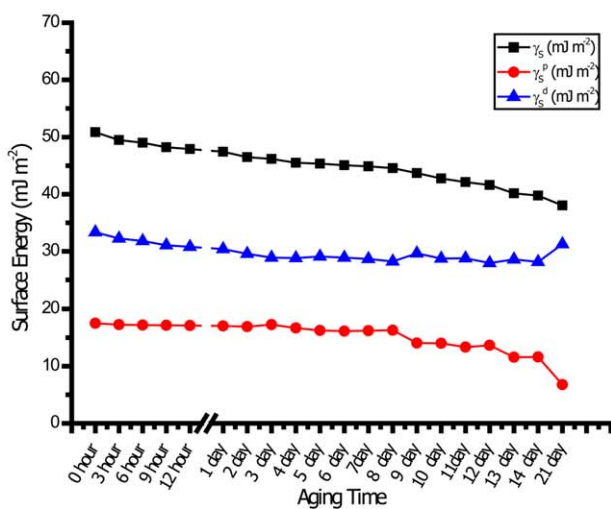
The high polarity or functionalization generated by atmospheric plasma caused a fast reaction in the active species on the PLA surface with air elements; in the aging process, in this way, the
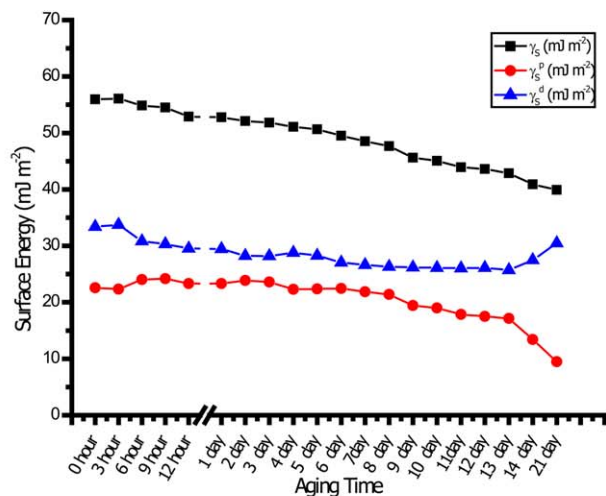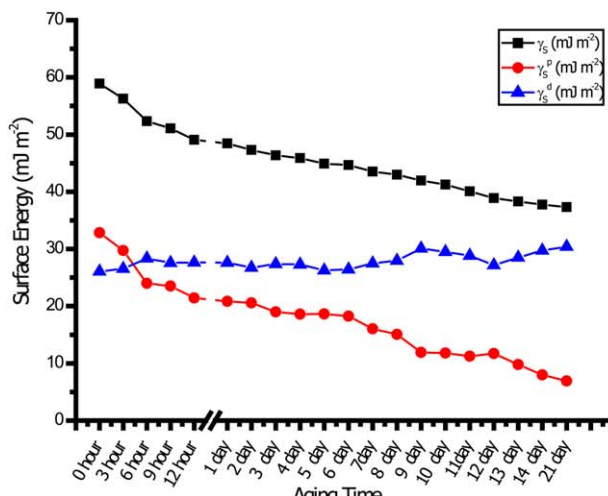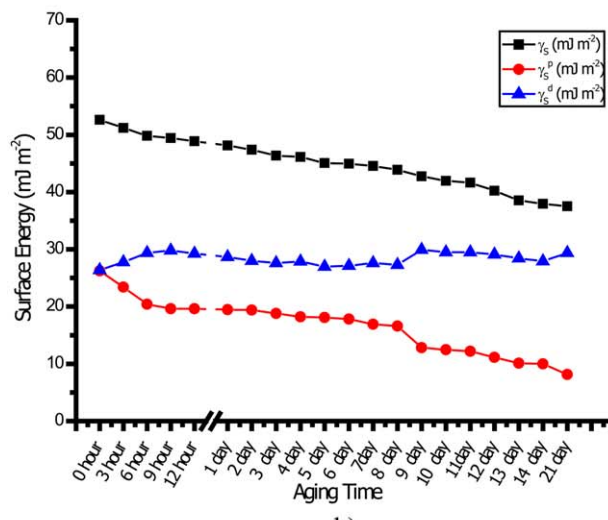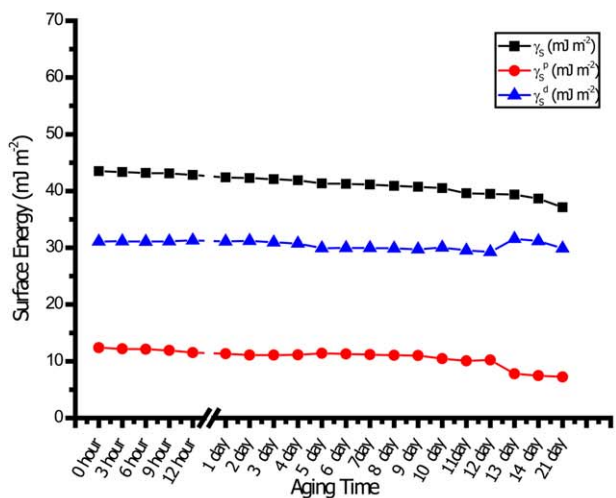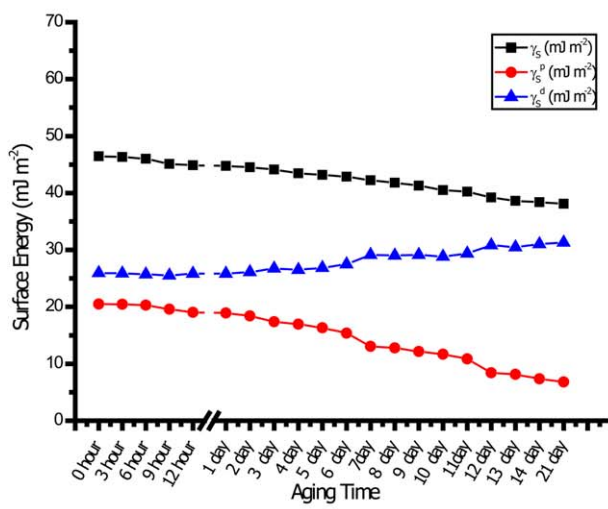
Figure 1. Variation of γ_s, γ_s^P, and γ_s^d of the PLA substrate with different aging times for the treated sample with a nozzle–sample distance of 6 mm and treatment rates of (a) 100, (b) 300, and (c) 700 mm/s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 2. Variation of γ_s, γ_s^P, and γ_s^d of the PLA substrate with different aging times for a treated sample with a nozzle–sample distance of 10 mm and treatment rates of (a) 100, (b) 300, and (c) 700 mm/s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Best Time for Curing the PLA–PLA Adhesive Joints

Curing time (min)	Strength (N/cm^2)	
	Untreated PLA	PLA with plasma treatment[a]
15	21.73	19.60
30	33.03	26.00
45	35.83	33.76
60	40.00	75.83
75	50.05	114.20
90	50.63	150.10
105	49.23	149.90
120	49.40	149.20
135	47.73	150.00
150	48.40	149.43
165	49.10	149.10
180	48.73	149.80

[a] Distance = 6 mm, advance rate = 100 mm/s.

γ_s^p values decreased mainly in the first hours after plasma treatment. After 21 aging days, both γ_s and its γ_s^p and γ_s^d reached values close to those of the untreated sample.

The aging process was closely related to the instability of the polar species generated on the surface treated with atmospheric plasma and was the result of the continuous chemical reactions suffered by free radicals generated on the surface by plasma treatment with oxygen and humidity existing in the environment. Also, the free rotation of hydrophilic polar groups into the PLA structure reduced the surface wettability.[49,50,58,65,68,69]

Effects of the Variation of the PLA Adhesive Properties on the Aging Process

The effect of the aging of PLA on their adhesive properties was quantified with plasma-treated PLA sheets joined with a commercial adhesive. This study was realized with optimized process conditions of the plasma at two distances, 6 and 10 mm, and three treatment rates, 100, 300, and 700 mm/s.[62,70,71]

Previously, the optimal curing time of the bioadhesive used was determined experimentally. The maximum strength of the PLA–PLA adhesion joints with the shear stress is represented in Table IV for surface conditions of PLA with and without atmospheric-plasma treatment at 6 mm between the PLA surface and plasma nozzle and with an advance treatment rate of 100 mm/s.

A progressive increase in the maximum adhesive shear strength was observed for the untreated surface to reach a maximum of 50.63 N/cm^2 for 90 min of curing. For higher times, the shear strength values remained almost constant. A similar effect was observed with the atmospheric-plasma treatment of the samples. The maximum shear strength value of the adhesion joint, 150.10 N/cm^2, was obtained for curing times of 90 min. There was no enhancement of the adhesion joint shear strength for higher curing times, insomuch as ranks were maintained at 150–149 N/cm^2 for times of 180 min. So, the optimal curing time was 90 min; this value was used in later tests.

Once the optimal curing time of the bioadhesive was determined, the effect of the aging time over the PLA–PLA adhesion joint was analyzed. Figure 3 shows the variation of the maximum shear strength of the PLA–PLA adhesion joints as a function of the aging time. For atmospheric-plasma-treated samples with a nozzle–substrate distance of 6 mm and different treatment rates (100, 300, and 700 mm/s), we observed that the shear strength decreased with aging time, and this fact corroborated the variation of the surface energy with the aging time, as described previously.

In this way, for a treatment rate of 100 mm/s, the shear strength obtained immediately after atmospheric-plasma treatment was 150.03 N. After 6 aging days, there was a loss of maximum shear strength in the adhesion joint of 15%; this reached 53% at 21 days. However, at the end of the analyzed period, the maximum shear strength was higher than that of the untreated PLA–PLA adhesion joint (50.10 N/cm^2). For a higher plasma treatment rate on the PLA surface (300 mm/s), the maximum strength value was 133.50 N/cm^2. After 21 aging days, the maximum shear strength decreased to 73.05 N/cm^2; this was a 45% decrease. For a rate of 700 mm/s, this decrease was about 60%.

Figure 4 plots the maximum adhesive PLA–PLA adhesion shear strength during the aging time for plasma-treated PLA with a distance of 10 mm and different rates (100, 300, and 700 mm/s). In the same way as in the previous case, there was a trend toward a decrease in the maximum shear strength with aging time.

In a comparison of the experimental results for different treatment rates, there were always losses in the maximum adhesion shear strength with aging time.

With a 10-mm PLA–nozzle distance, a maximum shear strength was obtained for a low treatment rate (100 mm/s), and a value of 168.7 N/cm^2 in the PLA–PLA adhesion joints was obtained immediately after plasma treatment. After 6 days of shear aging with a shear strength loss of 6%, a value of 158.80 N/cm^2 was
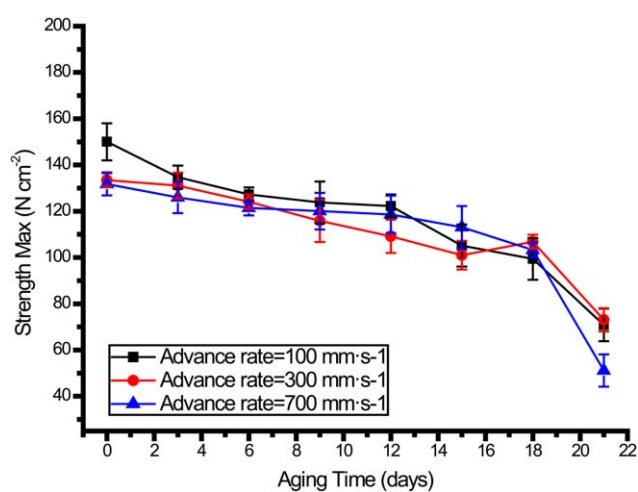

Figure 3. Variation of the maximum shear strength on the PLA–PLA adhesion joints as a function of the aging time for treated PLA samples with a nozzle–substrate distance of 6 mm and treatment rates of (a) 100, (b) 300, and (c) 700 mm/s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
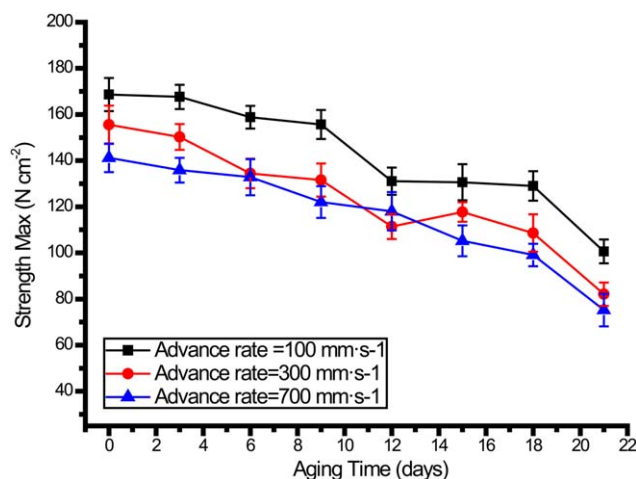
Figure 4. Variation on the maximum shear strength on the PLA–PLA adhesion joints as a function of the aging time for treated PLA samples with a nozzle–substrate distance of 10 mm and advance treatment rates of 100, 300, and 700 mm/s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

obtained. For higher treatment advance rates (300 and 700 mm/s), the maximum obtained values were 155.5 and 141.18 N/cm^2, respectively; this decreased with aging time. At the end of the analyzed aging period (21 days), samples treated at 10 mm suffered decreases of 40, 47, and 47% in the maximum shear strength for rates of 100, 300, and 700 mm/s, respectively. In general, the study of the variation of the adhesive properties of PLA during the atmospheric aging process showed a negative effect of the hydrophobic recovery phenomenon on their wettability properties of the plasma-treated PLA surfaces.

Nevertheless, after the aging test, although there was a loss of adhesion because of the loss of wettability of the PLA surface caused by the hydrophobic recovery effect, this was still higher than that of the adhesion joint of the untreated PLA for all of the plasma treatment conditions. After 21 aging days of the plasma-treated PLA surface at a 10-mm PLA–nozzle distance and for advance rates of 100, 300, and 700 mm/s, the PLA–PLA adhesion joints presented values of shear strength that were 50.2, 39, and 33.4%, respectively, higher than that of the untreated PLA.

Although there was an important hydrophobic recovery effect, most of the wettability achieved with atmospheric plasma was not lost entirely. As the microetching mechanism on the PLA surface was a physical effect, which increased the roughness of the PLA surface, this phenomenon was not recovered during the aging time; because of that, the maximum shear strength on the plasma pretreated PLA–PLA adhesive unions was still higher than that of the untreated PLA–PLA unions, even after 21 aging days. This corroborated the results obtained previously for the variations of both θ and the surface energy on the PLA surface as a function of the aging time. On the other hand, plasma treatment with a PLA–nozzle distance of 10 mm provided better results.

Comparatively, the maximum value of the shear strength (168.7 N/cm^2) was observed in the experimental results for a distance of 10 mm and a slow treatment rate of 100 mm/s. This value was higher than those of the treated samples with a distance of 6 mm and the same treatment rate (150.00 N/cm^2). This was due to the atmospheric-plasma aggressiveness in very low distances between the plasma nozzle and PLA; this produced a degradation on the PLA surface that reduced the adhesion effect. On the PLA surface and in general in polymers, it is possible to find very low-molecular-weight species oxidized because of the atmospheric air contact. These species can be deleted or actuated as initiators of the degradation process after atmospheric-plasma treatment.

A thermal camera was used to determine whether excessive heating and subsequent degradation were produced on the PLA surface by the atmospheric plasma. This heating could produce certain polymeric surface degradation with very short treatment times.[33,54,55,72–74]

Figures 5 and 6 show the thermal images of the PLA surfaces during the plasma treatment for 6- and 10-mm nozzle–substrate distances, respectively. As shown, a decrease in the surface temperature according to the increase in the nozzle–substrate distance was observed. Both figures are followed by a graphic where chromatic spectra are shown, where the variation in the colors is related to the temperature change. Blue is used for low temperatures, and red is used for high temperatures. Temperatures higher than 100°C are represented by white.

For a nozzle–substrate distance of 6 mm (Figure 5), the highest temperatures in both tests were reached at a value of 127.6°C.
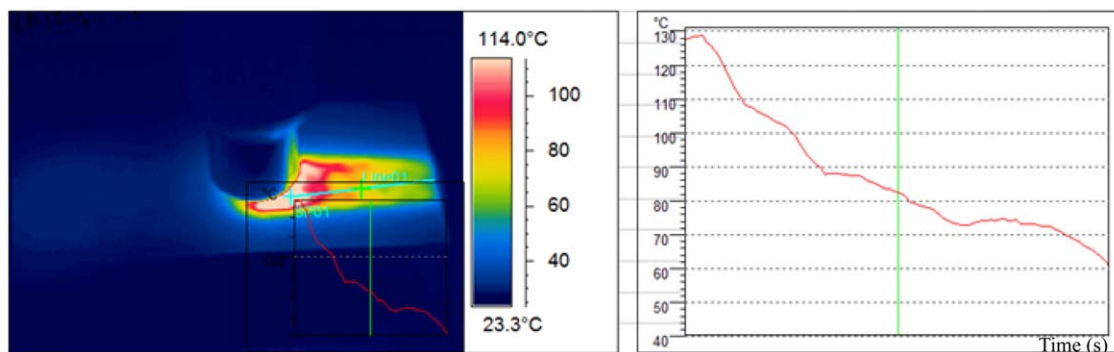

Figure 5. Image obtained from a thermal camera for a nozzle–substrate distance of 6 mm and a treatment rate of 100 mm/s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6. Image obtained from a thermal camera for a nozzle–substrate distance of 10 mm and a treatment rate of 100 mm/s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
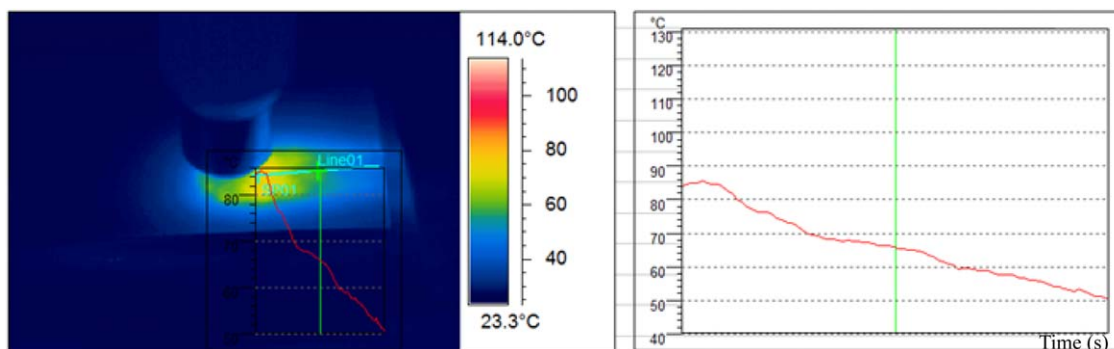
Just after, a decrease in the temperature was observed; here, the temperature reached 61°C. For the same analysis at a nozzle–substrate distance of 10 mm, the maximum temperature decreased significantly (33%) in comparison with that at 6 mm, which was 84.6°C, and immediately after that, it decreased to approximately 50°C.

The thermal degradation of the PLA surface was produced by treatment with high heating at a low distance (6 mm), although it was ephemeral and had a negative influence on the surface energy values obtained under these conditions. For this reason, the surface energies and shear strength of the PLA–PLA adhesion joints treated with atmospheric plasma at a distance of 6 mm were lower than those at 10 mm.

The optimal storage time of this substrate at the industrial level after the atmospheric-plasma treatment will depend on the needs of the product. In the range of 3–6 days of storage, the adhesion shear strength remained at values close to 160 N/cm^2; this allowed the use of treated samples with improved adhesive performance.

CONCLUSIONS

PLA samples treated with atmospheric plasma were strongly affected by the storage time. In this way, θ values on the sample surface increased with the storage time, and subsequently, the surface energy decreased. This fact had repercussions for the loss of hydrophobicity of the PLA substrate. The low durability of the plasma effects over PLA caused an important loss in the surface wettability, and this had negative repercussions for the adhesive properties of the material.

When PLA samples were stored under typical industrial conditions (25°C and 25% RH), there was an important loss in the surface wettability. γ_s^P was the most influential on the loss of wettability because of the decrease in the PLA functionalization and surface activation promoted by previous atmospheric-plasma treatment. The instability of polar volatile species generated on the plasma-treated surface, the continuous chemical reactions between free radicals generated by the plasma treatment and oxygen or humidity, and the free rotation of the hydrophilic polar groups into the PLA structure reduced the surface wettability.

The variation of the shear strength in the adhesion joints of the PLA–PLA samples during the aging process under atmospheric conditions showed the negative influence of the hydrophobic recovery phenomenon on the adhesive properties of PLA. However, although there was a loss of adhesion with aging time, the adhesion remained higher than that of PLA surface without plasma treatment for all of the conditions analyzed.

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