

EFFECT OF PLASMA TREATMENT ON THE SPREADING OF MICRO DROPS THROUGH POLYLACTIC ACID (PLA) AND POLYESTER (PET) FABRICS

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Abstract:

The effect of oxygen plasma treatment on two polyester fibre types, polylactic acid and standard polyester, and the influence on their respective wetting characteristics is investigated. A novel analytical system, based on image analysis, was developed for measuring the rate of spreading and dynamic movement of liquid over the fabrics. The techniques of X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM) were utilized to examine the nature of the surface modifications after the plasma treatment. The analyses showed that the oxygen plasma treatment abraded the surface of the PLA fibres, but did not alter their chemical nature, whilst the surfaces of the PET fibres were less abraded, but had enhanced polarity due to an increase in carbonyl groups. The increased surface abrasion made little difference to the wetting or wicking rates of water on PLA fibres, but the increased polarity made a large difference to the rates on PET fibres.

Key words:

PLA, PET, plasma treatment, wetting, wicking.

Introduction

PLA is a biodegradable, aliphatic polyester derived from 100% renewable resources, such as corn and sugar beets. As a biodegradable polymer, it has tremendous potential applications where thermoplastic materials are employed [1]. The biodegradability of PLA makes it a promising material for many disposable products, such as baby nappies, plastic bags, and films. PLA is melt-spinnable and has good fibre- and film-forming properties, though its low melting point and high surface friction has limited its applications for garment manufacture. Nevertheless it has potential for use in blends with other fibres for sportswear where good wicking properties are required. PLA and standard polyester (PET) fibres are similar in that they each have ester groups though they differ because PET is an aromatic polymer and has linear chain while PLA is an aliphatic polymer (Figure 1) and has a helical chain [2].

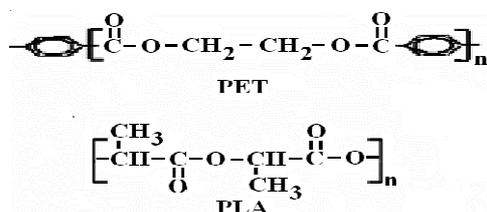


Figure 1. Chemical structure of PET and PLA.

Plasma is the coupling of electromagnetic power with a process gas which generates a medium comprising a dynamic mix of ions, electron, neutrons, photon, free radicals, meta-stable excited species and molecular and polymeric fragments. This allows the surface functionalisation of fibres and textiles without affecting their bulk properties [3]. The effect of plasma treatment depends on the combination of energy and flux of the excited species which are related to the power, pressure and time used for the treatment. Increasing the power will increase the intensity of the treatment, while increasing the pressure will reduce the energy per active species but will

increase the flux of these species on the surface of polymer. Decreasing the pressure will give more energy to each molecule/atomic gas species so may increase the etching effect, although it will reduce the density of species. Plasma treatment has potential for replacing many wet textile processes either completely or partially. The purpose of this investigation was to compare the effects of plasma treatment on PLA and PET fabrics and in particular to determine the potential for PLA to be modified by plasma for use to enhance its wetting properties. To date, relatively little has been published on the effects of plasma treatment on PLA fibres [4,5].

The idea of studying the spreading of drops on materials dates back to 1950s when Gillespie [6] developed a method to measure the radius of drops on filter paper at fixed time intervals. The studies showed that the spreading process could be divided into two phases (Figure 2), phase I when the liquid is still above the substrate, and phase II when the drop is completely contained by the substrate. In this second phase the liquid wicks through the fabric horizontally under the influence of capillary forces.

Gillespie developed the following equation to describe the spreading process:

$$R_t^2 [R_t^4 - R_0^4] = \frac{3\beta}{2} \left(\frac{3V}{2\pi h} \right) t \quad (1)$$

in which R_t denotes the radius of the stain at time t , R_0 the radius of the stain at time zero, V the volume of the liquid, and h the thickness of the substrate. The value of β is given by the term:

$$\beta = \frac{b q_s \gamma \cos \theta}{C_s^\circ \eta}$$

in which b is a constant characteristic of the substrate, q_s the permeability of the substrate, γ the surface tension of the liquid, η the viscosity of the liquid, θ the advancing contact angle, and C_s° the saturation concentration of the liquid in the substrate.

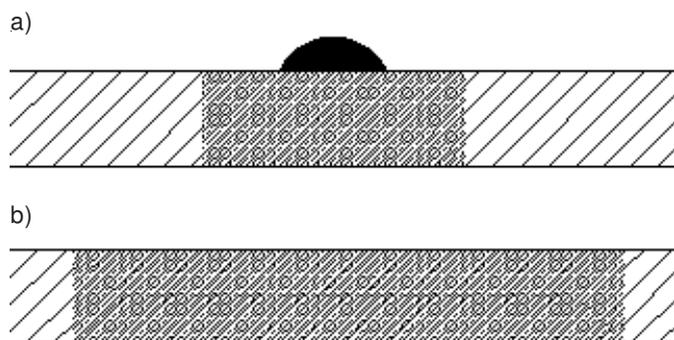


Figure 2. Schematic illustration of the two phases spreading; a) represents the first phase where part of the drop is still above the substrate, b) represents the second phase where all the drop is contained within the substrate.

Unlike filter paper, textile fabrics are not isotropic, so the area formed by a liquid spreading on a textile fabric is seldom a perfect circle. It is therefore more meaningful to measure the area covered by the spreading liquid. Another difficulty with measuring the spreading of the liquids on porous substrates is the speed with which the liquid front moves, in particular during the first phase. Kissa [7] measured the spreading area of a drop on textile fabric as a function of time. The area of a spreading liquid was photographed at uniform time intervals with an instant-picture camera. The area depicting the spreading liquid was cut out from the dried photograph and weighed. Kissa found that assuming that the fabric was impermeable to the liquid, the spreading rate could be represented by equation (2):

$$A = K(\gamma/\eta)^n V^m t^n \quad (2)$$

where:

- A - area of the liquid drop at time *t*,
- V - volume of the drop,
- γ - surface tension,
- η - viscosity, and
- K - capillary sorption coefficient.

In this study the equations developed by Kissa are applied to a more rigorous measurement of spreading behaviour using the image analysis of frames captured at fast rates, especially in the initial stages. Measurements of the dynamic change of shape of the spreading area of the liquid are also made.

Experimental

Fabrics

PLA fabric was supplied by Future Product Company Inc., Minnesota, Benson, MN 56215, USA, made of PLA polymer from Cargill Dow. The fabric was a 6.5 oz single Jersey knit with 16 course/cm, 12 wale/cm, using a fibre of denier 1.3. Differential Scanning Calorimetry showed the PLA fibres had a glass transition temperature of around 70°C and a melting temperature of around 170°C. The standard polyester used was a twill fabric, warp count 43 tex, weft count 47 tex, 67 ends/inch, 47 picks/inch, 229 g/m².

Plasma treatment

A low-temperature plasma machine CD-400 (Europlasma) was used. A number of preliminary experiments were conducted to find the optimum conditions of time, power and flux. The most effective gas was found to be oxygen under the conditions of

power of 200 watts, flux of 0.7 standard litre per minute (slm), and a treatment time of five minutes.

Before treatment the samples were washed with water at 60°C for 10 min, then left to dry in ambient conditions. Prior to treatment the samples were dried again in oven at 50°C in order to remove most of residual moisture.

A Hitachi S-4300 scanning electron microscope (SEM) was used to examine fibre surface topography. A Kratos Axis Ultra-DLD XPS system, available for access at Cardiff University, UK, was used to analyze the surface chemistry of the fibres.

Measurement of spreading

An Altra 20 camera, 1.5 megapixels, was used to measure the dynamic movement of the liquid over the fabric surface. The camera was mounted on a stereomicroscope, equipped with a C-mount and LED light, and connected to personal computer via its USB port as shown in Figure 3. The Altra 20 camera is compatible with Image Analysis 5 software, which was used to record the film and process the images.

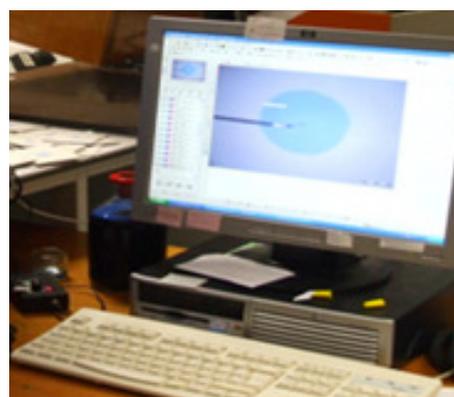


Figure 3. The image capturing and image analysis system.

For measurement of spreading rate, the fabrics were mounted in a cardboard holder of thickness 1.5 mm, cut as shown in Figure 4. The fabric was placed on a table without tension, and then the holder attached using double faced tape, ensuring that the tension on all edges was equal and the fabric was stretch-free.

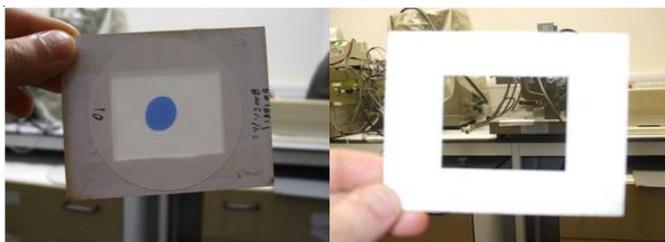


Figure 4. Cardboard frame used to attach the sample.

All the experiments were carried out in a conditioned room at a temperature of 22°C and relative humidity 65%. The testing liquid was a solution of 0.2 g/l of the dye C.I. Acid Blue 25. The dye was used to aid viewing of the liquid boundary during spreading, and chosen because it has no affinity for either of the fibre types. The drop was formed using a KDS 100 syringe pump and Hamilton syringe (100 µl) with a flat tip needle. The needle was tilted as shown in Figure 5. The drop took about 48 seconds to form and fall, having a drop volume of 13.5µl approximately.



Figure 5. The needle and the sample positioned on microscope stage.

The speed of the driver was adjusted at 1000 µl/h, to let the drop fall under gravity and to avoid any vibration or the effect of dynamic movement.

The software was adjusted to record, firstly for five seconds at four frames per second. After the first film had been recorded, the recording of second film started directly afterwards, with an interval of less than one second. For each sample the recording started approximately one second before drop falling. Due to a small variation in the initial size of the drop area, an average of ten measurements was taken. The tool "Free Hand" of the software measurement tools package was used to measure the spot area.

Results and Discussion

Topographical analysis

The SEM images of the plasma treated PLA fibres exhibited a scarred surface appearance (Figure 6) though it was apparent that some fibres were etched more than others. This uneven treatment could be an explanation for the variation in the spreading rates (Figure 11) and roundness of the spreading liquid areas (Figure 17).

In contrast, the SEM images showed that the plasma treatment caused a less pitted surface on the PET fibres than the PLA fibres (Figure 7). It is possible that the PLA fibres have a more porous surface structure which is more easily etched by plasma.

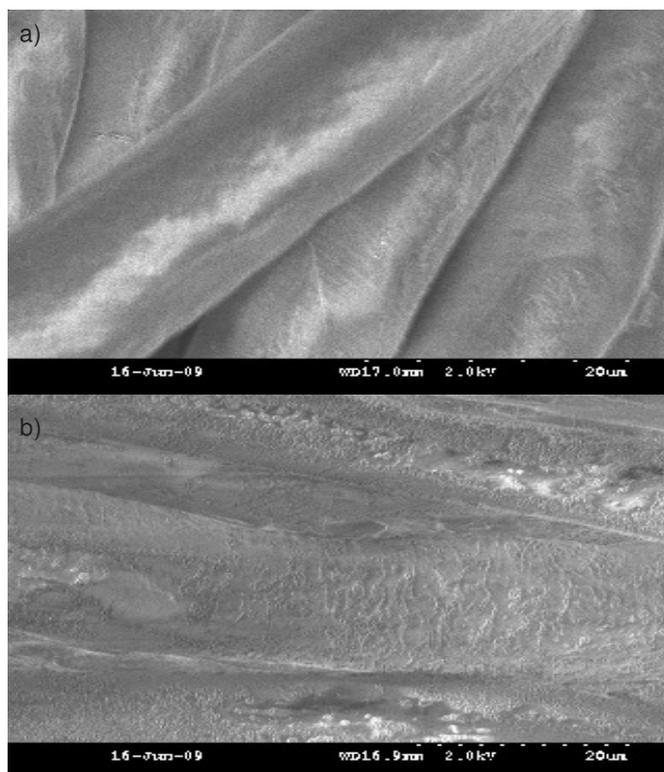


Figure 6. SEM images of PLA fibres; a) before treatment, b) after treatment.

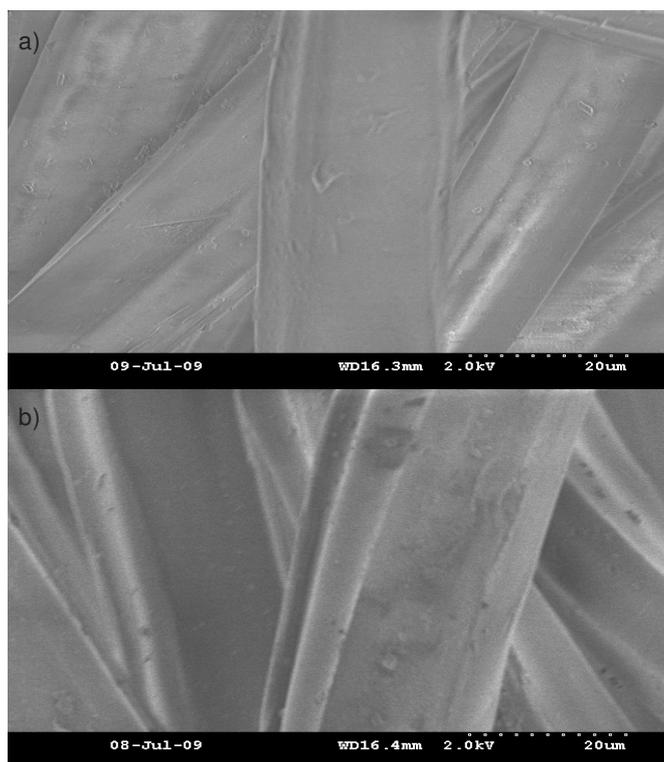


Figure 7. SEM images of PET fibres; a) before treatment, b) after treatment.

Surface Chemistry Analysis

The XPS C1s spectra of PLA fibres did not exhibit any differences of significance between the treated and untreated samples (Figure 8), indicating that no new chemical groups had been introduced into their surfaces by the plasma

Polylactic Acid

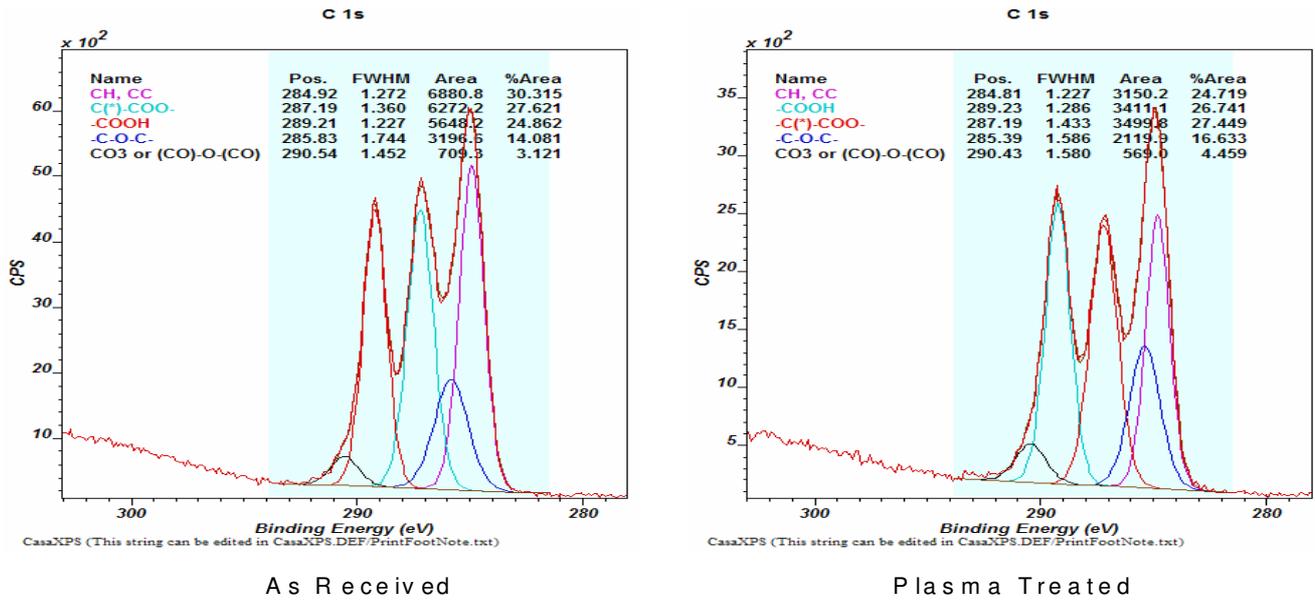


Figure 8. XPS C1s spectra of untreated and treated PLA fibres.

PET

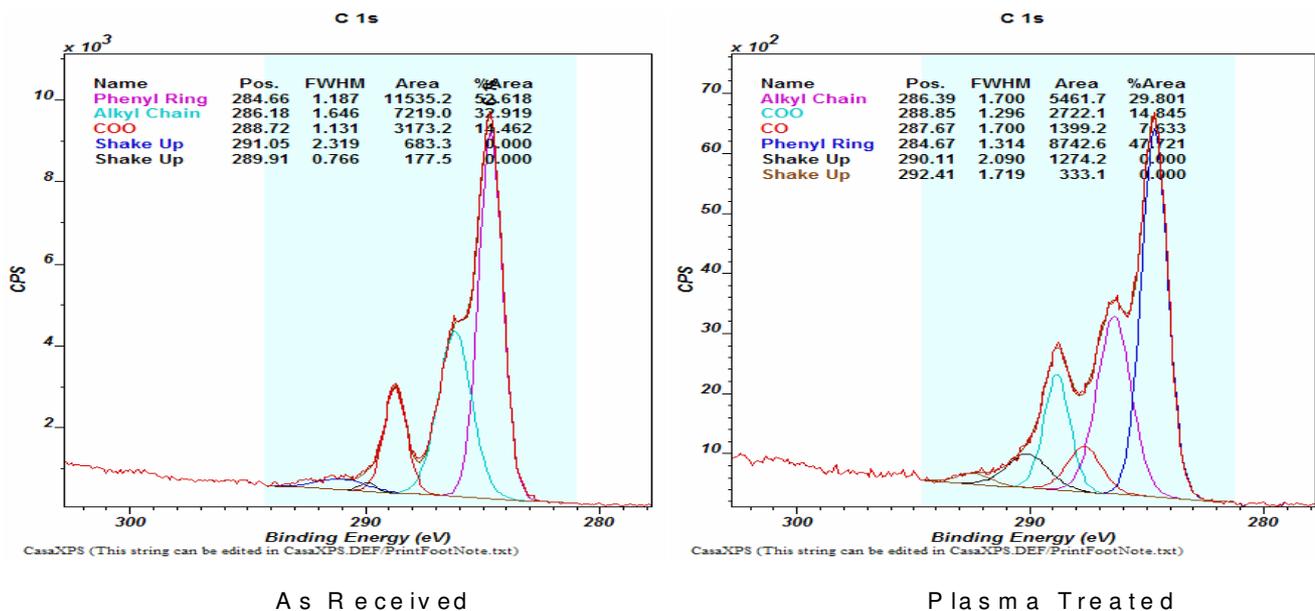


Figure 9. XPS C1s spectra of untreated and treated PET fibres.

treatment. In contrast the corresponding spectra for the PET fibres showed the presence of new carbonyl (CO) groups at 287.87 eV (Figure 9) in the treated samples.

Spreading Rate

The spreading rates of both the PLA and PET, both treated and untreated fabrics, are shown in the graphs in Figure 10. The curves show that the spreading of the water over the untreated fabrics exhibited two clear phases, as identified by Gillespie. Phase I lasted about one second; it is similar to feeding from a continuous reservoir. In phase II, when the whole amount of the drop was contained within the substrate, and the spreading continued under capillary action.

The PLA and PET samples showed different responses to

plasma treatment. On PLA the first phase (Figure 11) of the treated fabric lasted longer (about 2 seconds) than on the untreated fabric (about one second). The spot area of the second phase of the treated fabric increased gradually and slowly until it equalled, then exceeded that of the untreated area after about 1000 seconds.

The higher deviation from the average values in the treated samples of PLA (Figure 11) can be related to the unevenness of the plasma etching over the surface of substrate, with the result that the measured spreading rates depend on particular location where the drop falls.

The images in Figure 12 show the spreading of the drop on untreated (A) and treated (B) PLA fabric. The images of treated PLA fabric demonstrate a delay in the drop absorbing into the

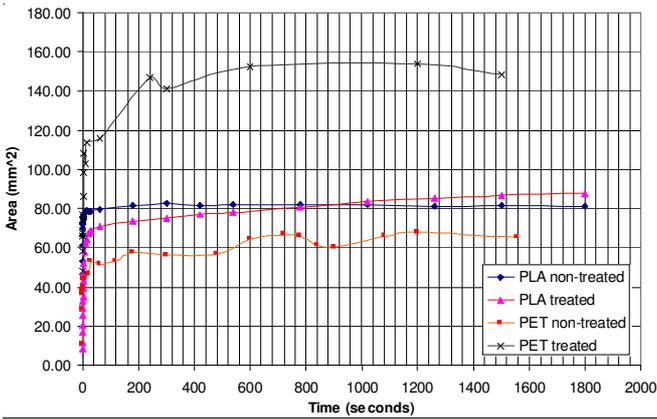


Figure 10. Spreading rate of droplets on PLA and PET fabrics.

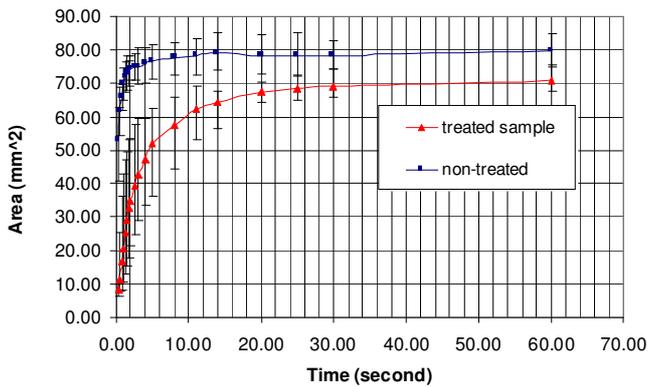


Figure 11. Initial spreading of droplet on PLA during first 60 seconds.

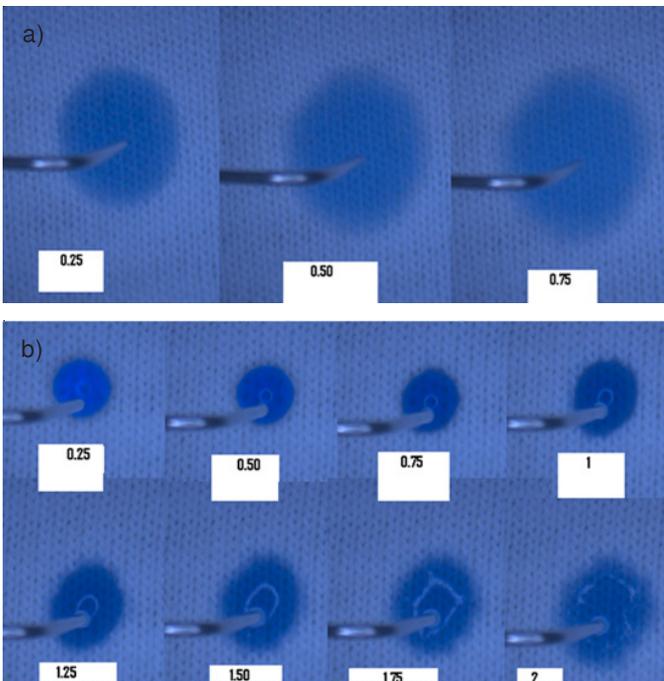


Figure 12. Frames of untreated; a) and treated, b) samples of PLA, showing the spreading at different interval times (seconds)

fabric, a consequence of the increase in roughness of the fibres.

The influence of the plasma treatment on the spreading process on the PET woven fabric was very different to that on

the PLA fabric (Figure 13). Again two phases exist and the first phase lasted about 1 second. However on the plasma treated fabric the overall rate of spreading was considerably higher than on the untreated fabric. The highly increased wicking rate of PET after plasma treatment can be related to the introduction of these new polar groups. The images in Figure 14 demonstrate the spreading process on untreated (a) and treated (b) PET fabric; the spot area takes a longitudinal shape in the direction of the warp, in contrast with the more circular shape on the knitted PLA. Also fingering patterns (spreading of liquid in irregular manner along individual yarns) were noticeable on the spot area of the woven PET fabric.

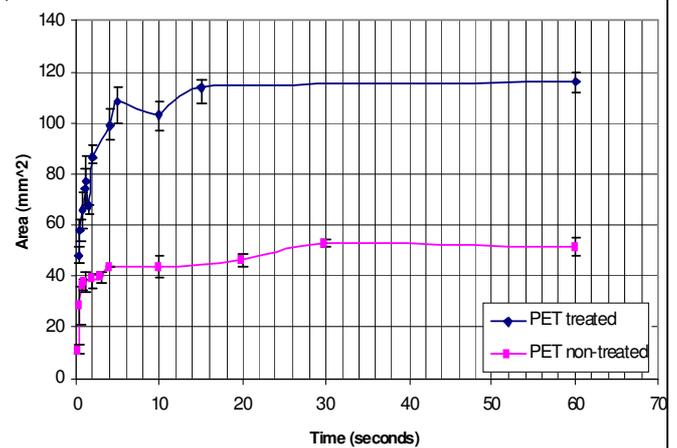


Figure 13. Spreading rates on PET woven fabric during first 60 seconds.

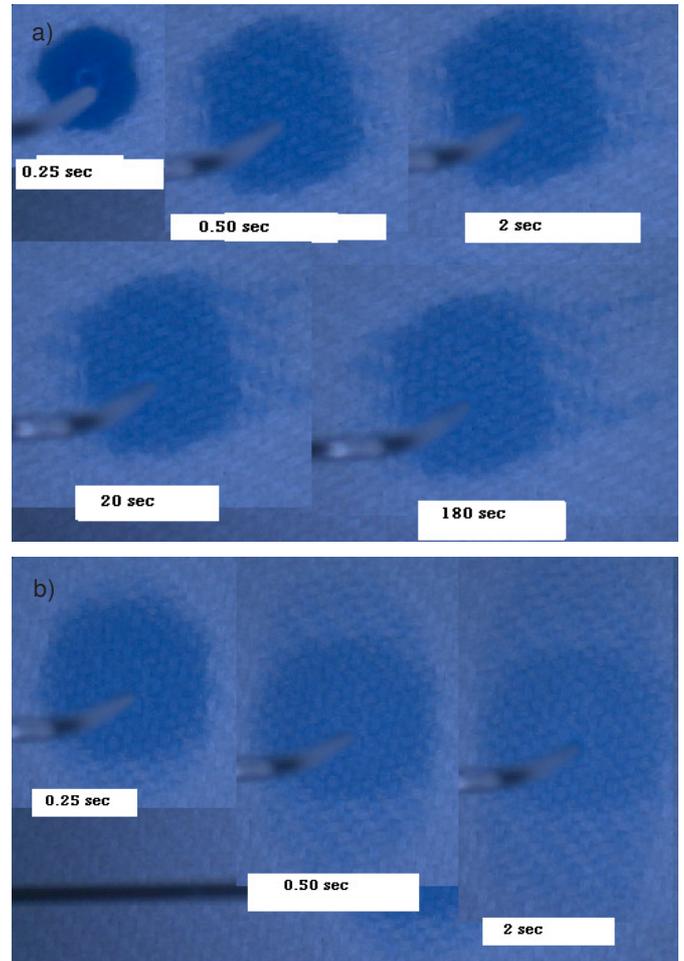


Figure 14. Frames of untreated (A) and treated (B) samples of PET, showing the spreading at different time intervals.

According to equation (2), for a given liquid with constant volume, a graph of log A vs log t should be linear with slope n. The greater the value of n, the greater the rate at which the area of the drop in the fabric increases. The logarithmic representation of spreading is shown in Figure 15. These logarithmic plots show two approximately linear phases for both PLA and PET fabrics, but indicating different responses to plasma treatment.

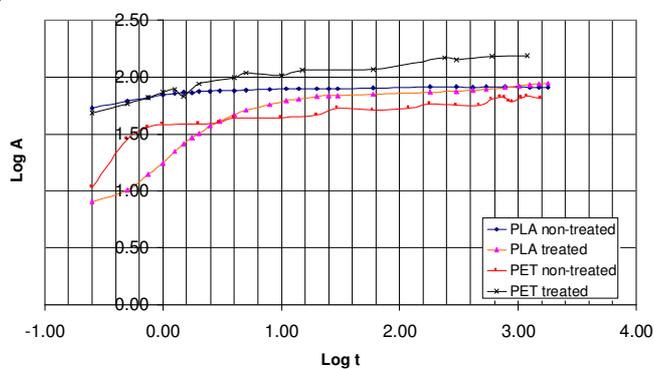


Figure 15. Logarithmic representation of spreading rates of PET and PLA.

The influence of the plasma treatment on the values of the slope, n, is demonstrated in Table 1. For the PLA fabric, plasma treatment gave higher values of n for both phases, indicating higher rates of wetting and spreading in each case. However the situation is more complex than this, because the overall drop area on the untreated PLA is higher than on the treated fabric. The images show (Figure 13) that on the untreated PLA, the water absorbs quickly into the fabric but spreads very little thereafter, as indicated by the very low value for n in phase II. On the treated PLA fabric, the increased hydrophobic character resulting from the rougher surface causes the drop to take longer to absorb into the fabric during phase I, but on doing so it spreads (through increased wicking) at a faster rate, as indicated by the higher value of n. The drop continues to spread in phase II, though not at such a high rate as it did in phase I. During the first 1000 seconds the spot of the treated samples covered a smaller area than on the untreated sample at any given time, showing the fabric wetted out less easily after treatment. After 1000 seconds the drop area on the treated sample was marginally higher, possibly due to the increased roughness in the amorphous regions which are more receptive to water.

In the case of the PET the value of n in the first phase is higher on the untreated fabric than on the treated fabric. The drop takes longer to be absorbed into the untreated fabric due to its hydrophobic nature, but with a greater rate of spreading, as the liquid still unabsorbed feeds the spreading. On the treated fabric absorption is instant and spreading is very rapid, due to the presence of new polar groups that increase hydrophilicity. In the second phase the values of n of both treated and untreated PET are reduced, with the value for the treated fabric

Table 1. Values of the slope n, before and after plasma treatment.

Slope	PLA		PET	
	untreated	treated	untreated	treated
Phase I	0.18	0.55	0.9	0.3
Phase II	0.02	0.12	0.06	0.11

being slightly higher than of the untreated fabric. This may be because the spreading of the liquid on the untreated fabric reaches equilibrium sooner than it does on the treated fabric. The final area on the treated fabric is greater, due to its increased hydrophilicity.

The Dynamic Change of Shape of Stain Area during Spreading The shape of the drop was studied by estimating roundness of the area R (3), where the M values are the central moments:

$$R = \frac{(M_{xx} - M_{yy}) - (4M_{xy}^2 + (M_{yy} - M_{xx})^2)^{0.5}}{(M_{xx} + M_{yy}) + (4M_{xy}^2 + (M_{yy} - M_{xx})^2)^{0.5}} \quad (3)$$

The roundness of the spreading area was expressed as a percentage of the ideal circular area as exemplified in Figure 16.

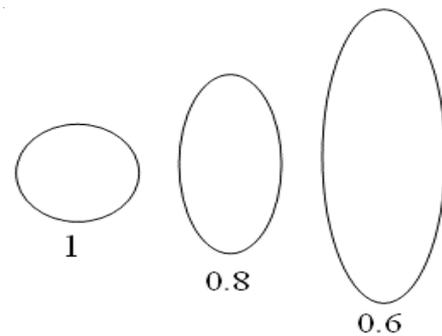


Figure 16. Schematic representation of expression of roundness.

The dynamic change of shape of the stain area during spreading was assessed for both PET and PLA before and after the plasma treatment. The change in roundness of the spreading liquid areas with time are shown in Figure 17. The images in Figure 12 and 14 show the shapes of the spot areas during spreading. The knitted untreated PLA exhibited a higher level of shape consistency during spreading than the untreated woven PET. However the shapes on the treated samples were less rounded in each case, which could be related to irregularity of plasma etching, as the plasma can etch the amorphous regions more than the crystalline regions. Woven PET exhibited decreasing circularity during spreading, the liquid moving in longitudinal shape, in the direction of the warp, and showed fingering patterns. The final spot shape of treated and untreated PET fabric exhibited the same level of roundness.

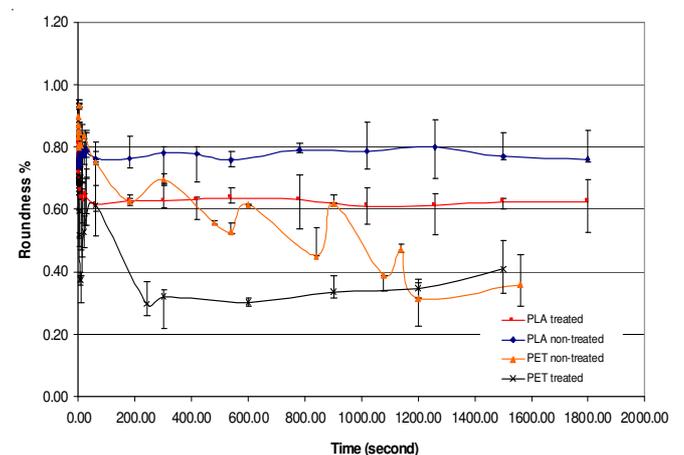


Figure 17. Roundness of the spreading areas of liquid.

Conclusions

The effect of oxygen plasma treatment on PLA fabric was one of topographical modification. The surface roughness of the fibres increased, which had the effect of increasing the time taken for the drop to penetrate the fabric. The PET fibres exhibited a different response to plasma treatment. New polar groups were introduced into the surface but there was less etching affect. However the increased polarity caused a very significant increase in the rate of spreading, much more than the etching effect seen on the PLA fibres. There seems to be little scope for modifying the wetting and wicking properties of the PLA fibres by plasma treatment using oxygen gas.

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Acknowledgments

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