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Enhanced printability of thermoplastic polyurethane substrates by silica particles surface interactions

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ABSTRACT

- A new method development for surface treatment of thermoplastic polyurethane (TPU) substrates.
- The proposed method increases TPU surface energy (by 45%) and consequently the TPU wettability.
- Great increase of the TPU surface roughness (by 621%).
- Inkjet printed conductive ink was applied to the surface treated TPU substrate and significant improvements on the printability were obtained.

1. Introduction

Most polymers are hydrophobic and show a low surface energy. Therefore, they are difficult to adhere to other materials. In the case on ink-printing on polymers surface, the transfer and distribution of the ink on a substrate depends on the wettability and adhesion capabilities, among other factors of paramount importance that play a relevant role at their interface. The adhesion between the two materials, ink and polymer, is the sum of a number of mechanical, physical, and chemical forces between them. Such attractive forces at the interface depend on the mechanism of adhesion involved that mainly include:

- Substrate properties (chemical composition, surface porosity, wettability, etc.).
- Ink properties (chemical composition, rheological behavior, the rate of solvent evaporation, etc.).
- The superficial tension (ST) of the ink, and the surface energy of the substrate that will receive the ink; or better the difference between them.
- Functional groups and their intermolecular forces present in the ink/polymer system.
- Surfaces topologies (e.g., roughness) and mechanical locking mechanism between them.

Practically, this means, for example, that ink printing of polymeric substrates is rendered difficult. Intermolecular interactions between the fluid and substrate can be promoted in order to improve adhesion [1–3]. For this reason, a surface treatment of the polymer substrate is normally needed to promote compatibility and to improve adhesion forces by increasing the surface tension of the polymer, thus changing their hydrophilicity, increasing the surface contact area. Many adhesion-enhancing techniques have been explored in the literature, such as chemical roughening of the surface [1], resorting to the use of a primer (by dipping, brush or spray the substrate that can chemically alter the surface, e.g. silane coupling agents [4], but within the framework of printing polymer surface, corona discharge [2,5], plasma treatment [3,6–9] and flame treatment [2].

Plasma treatments are used to change the surface energy, to create functional groups at the surface, to induce mechanical roughness on the surface and to eliminate surface contaminants, such as silicone mold release agent, dirt, dust, grease, oils, and fingerprints. These contaminants also inhibit the shape of the drops, hence the printed image quality [10] and the adhesion.

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Nevertheless, plasma surface treatment is temporary, i.e., the surface treatment enhances the compatibility of the surface with the ink, but the exposure to air induces hydrophobic recovery [11]. Therefore, it is recommended to bond, coat, ink, or decorate the product as soon as possible just after the surface treatment. This adhesion improvement has been the subject of some studies. McDonald and Whitesides [11] published a study of polydimethylsiloxane atmospheric plasma treatment. It was showed that after the polymer surface treatment, adhesion and wettability increased, but a continuous exposure to air (5–30 min depending on the substrate) resulted in recovery of their hydrophobic nature. It is well known that the surface roughness can be controlled in order to modify the surface energy of the substrate [12]. An increment in the roughness of the polymer surface can be caused by a chemical treatment. These methods are preferred industrially over the plasma processes due to the much lower cost. The chemical treatment changes the surface characteristics (physical and chemical) in order to improve adhesion. In chemical treatment solutions, the adhesion is achieved by increasing the total area of interface between both layers leading to structural changes (by increasing the interface roughness) and interactions between the fluid molecules and the substrate. This type of treatment usually involves the use of expensive raw materials and it generates large chemical pollutants with high-environmental impact. Both on industrial and scientific studies polymer surface treatment has been used to promote the polymer receptivity to the ink. The adoption of such a solution, in addition to the inclusion of an extra step in the manufacturing process, increases the time and cost of production. Given the hydrophobicity of the polymers, a surface treatment to improve its adhesion ST and the ink is vital, but more effective, economic and low environmental impact solutions are required.

The increase of the polymer substrate surface energies through the modification of the surface roughness resorting to nanoparticles incorporation has so far not been reported in the literature. Therefore, the work presented here aims to develop a novel surface treatment for polymeric substrates with increased surface roughness and wettability. Thus, resorting to nanoparticles incorporation onto the polymer surface it is possible to achieve good results (compared to the existing solutions in the industry), with the particularity of offering an economically viable alternative.

2. Experimental

2.1. Materials

The substrate used in this study was a thermoplastic polyurethane, TPU, Avalon® 65AB from Huntsman (E = 7.5 MPa, 67 Shore A, and service temperatures range from −50 °C to 130 °C). In the proposed surface treatment method, nano silica particles (SP) were used. The SP consist on spherical particles and free of pores. Chemically speaking, they are made of silicon and oxygen atoms. AEROSIL 200 is a highly dispersed, hydrophilic fumed silica. One gram of AEROSIL 200 contains approximately 1 mol of silanol groups [13]. Table 1 lists the main properties of the AEROSIL 200 and summarizes the nanoparticle technical specification.

An organic semiconductor polymer based ink from Plextronics, *Plexcore*® OC RG-1100 was also used. This is a poly(thiophene-3-[2-(2-methoxyethoxy)ethoxy]-2,5-diyl) sulfonated conductive polymer ink, *Plexcore*®, with viscosity of 7–13 mPa s, a surface tension of 36.5 mN/m and a electrical resistivity of 0.25–2.5 Ω m [14]).

2.2. Sample preparation

TPU film was processed on a metallic mold spacer 210 mm × 125 mm with 1.5 mm thickness for 5 min at 190 °C (above the melting temperature of the TPU). Afterwards, the plates were quenched in water at room temperature (RT) (23 °C). All specimens were kept in a controlled RT for at least 3 weeks before performing any experimental tests according to ASTM 618-00.

Table 1
Nanoparticle technical specification.

Name	Particle D_{av} (nm) [13]	Surface area[a] (m^2/g)
AEROSIL 200	≈12	200 ± 25

D_{av}, main average diameter.
[a] Specific surface according to Brunauer–Emmett–Teller.

The surface roughness was modified in order to change the surface energies. Therefore, the spread of clay or silica particles on polymer surface was used as a way to increase the surface roughness resulting in the increase of the surface contact area. One gram of SP (particles loading of $1.96 \pm 3.3 \times 10^{-3}$ mg/cm^2) was added and manually spread on the TPU substrate surface. Then the TPU was heated up to 120 °C, below the polymer melting temperature (145 °C) and above the hard segments glass transition (66 °C), for 15 min. This allows the particles to sink in on the polymer surface, achieving a better particle–polymer interaction at their interfacial region.

The cleaning of the substrate is a required step, as this affects the surface wettability. The objective of cleaning and deionization is to eliminate surface contaminants such as silicone mold release, dirt, dust, grease, oils, and fingerprints and inhibit new particles to stick on the surface of the substrate. The substrates were cleaned, using the following procedure (in the presented order): baths in acetone, isopropyl alcohol, then washed with deionized water and finally dried under dried nitrogen flow.

The Inkjet printer used in this experimental work was the Xennia Carnelian Printer, a piezoelectric Drop-on-Demand (DoD) printer provided by Xennia Technology Ltd, equipped with Sapphire QS-256/10 AAA printed from Dimatix. All the available 256 nozzles were used in this printing study in order to get the highest as possible throughput and overlapping from 1 to 10 ink-jetted layers at drop spacing of 28.22 μm (900 DPI). After the applied ink, printed pattern was dried at 80 °C (this temperature was selected due to the limitation of the substrate working temperature).

2.3. Methods

2.3.1. Characterization of the substrate

The characterization of the substrates surface before and after the surface treatment was performed for assessment of the treatment effect on the substrate final properties. Critical substrate superficial tension (ST) was measured by contact angle using a contact angle measurement equipment (Dataphysics OCA15 plus with a min. resolution of ±0.05 mN/m). The standard procedure for determination of the critical surface tension of a solid substrate consists on the measurement of the contact angles between the substrate and a number of test liquids with various surface tensions, at room temperature. Before measuring, the substrate surfaces were clean using isopropyl alcohol at room temperature, and subsequently washing with distilled water and drying with dried nitrogen. The contact angle measurements were repeated with the three different liquids: water, ethylene glycol and diiodomethane. The ST was calculated according OWRK [15,16]. This procedure was repeated six times for each sample.

2.3.2. Adhesion tests

The evaluation of the adhesion between substrate-nanoparticles and substrate-ink was performed by the cross-cut tape test. Classified as a destructive tests, as the name suggests, the test allows analyzing compliance systems through damage [17]. For these