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Superficial Surface Treatment using Atmospheric Plasma on Recycled Nylon 6,6

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ABSTRACT

Polymers currently represent materials that are cost-effective, while its recycled nature is significant in terms of environmental protection. However, the surface properties of polymers often do not meet the demands of wettability, adhesion, and friction, among others. Atmospheric plasma treatment on the surface of polymers improves its physical-chemistry properties. In this work, a recycled nylon coating was prepared by the spin coating technique and characterized by Fourier transform infrared spectroscopy and X-ray diffraction. This coating was treated by atmospheric plasma, and Raman spectroscopy was performed to analyze the signals related to different functional groups present in the coating surface after plasma treatment. The action of plasma on the surface morphology was observed by scanning electron microscopy. The contact angle results showed an improvement in surface wettability.

1. Introduction

Nylon 6,6 was one of the first materials to be recognized as an engineered thermoplastic due to its mechanical properties, particularly when exposed to high temperatures or when brought into contact with solvents [1-3]. This polymer is a polyamide used for the manufacturing of machine components such as bearing cages, pneumatic connectors, and for making a variety of fixing products such as cable ties, fasteners, staples, and drills [4-5]. However, due to its low surface energy, weak chemical reactivity, and in the presence of a weak cohesion layer, it has little adhesion with other substances [6]. Consequently, surface properties such as chemical composition, hydrophilicity, and roughness are often aspects to improve for successful applications.

The polymer industry currently tends to focus on research aimed at surface treatment techniques for creating finished products [7-8]. One such (environmentally favorable) method is the use of plasma technology for modifying surface properties [9]. Plasma treatment has in recent years been used to improve adhesion, hydrophilicity, and surface roughness [10-12]. One of its main advantages is a chemical effect that is limited in terms of depth (10 nm or less) and does not affect the mechanical properties of a material [13-16]. Additionally, atmospheric discharge plasma has proven to be an effective alternative to conventional techniques for surface modification [17]. It can modify surfaces uniformly by forming oxygenated chemical groups on the surface, allowing for higher surface chemical reactivity [18-20].

Atmospheric plasma treatment on nylon 6,6 films was reported to modify material roughness and improve surface properties through the transformation of hydrocarbon and carbonyl groups into carboxylic groups while improving the adhesion of films [21]. However, there is currently no reported plasma treatment that works on polymeric films obtained from recycled materials.

In the case of nylon 6,6, which is used to produce parts for the automotive industry, the final disposal of polymeric waste is not well-regulated or established, giving rise to significant ecological impacts [22-25]. Accordingly, research focused on recycled polymers is of significant interest to the design of new materials that preserve their bulk properties and improve their surface properties.

This research proposes obtaining a coating from a waste polymer derived from automotive parts and improving its surface properties through atmospheric plasma treatment. The results gained from using recycled nylon

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6,6 can potentially provide valuable information about the interaction behavior of different components with plasma treatment [26].

2. Materials

2.1. Coating Preparation

Stainless steel specimens with a 2 cm diameter were prepared in triplicate using silicon carbide abrasive sandpaper (#600). The samples were then ultrasonicated in ethanol for 15 min and dried in an oven at 70°C for three hours.

Nylon 6,6 waste was purchased from a producer of automotive parts. A small scrap part was cut into small pellets. Then, 10 g of this polymer was added to 10 ml formic acid. After 10 min, 5 ml ethanol was added under constant stirring for 1 h at room temperature. All reagents and solvents used were reagent grade and manufactured by Sigma Aldrich-Merck.

The metal specimens were placed on a spin coater (Laurell, model WS-650MZ-23NPP) at 300 rpm. Then, a small amount of recycled nylon solution (0.5 mL) was dropped onto the substrate using a syringe, forming a film by letting it spin for 5 min. The wet coating was dried at room temperature.

2.2. Coating Characterization

The molecular composition of the formed coating was characterized by Fourier transform infrared (FTIR) **spectroscopy** [27-28] and compared with the nylon 6,6 commercial grade reactive as a means for identification. Fourier transform infrared spectroscopy with attenuated total reflection was performed in a Bruker ALPHA II system. The thickness of the transverse coating was measured using an Olympus optical microscope coupled with Raman spectroscopy. Then, the recycled nylon film and the coating on the substrate were analyzed using powder X-ray diffraction (XRD) (Bruker AVANCE diffractometer; Bruker AXS, Karlsruhe, Germany) with Cu Kα radiation (λ = 1.54 Å) in an angle range of 20°–70°.

2.3. Atmospheric Pressure Plasma Conditions

The recycled nylon 6,6 coatings were treated with atmospheric pressure plasma (APP) using atmospheric plasma equipment (©Diener Electronic GmbH+Co., KG model APC500 Spray Corona), with a line of air and a power generator of approximately 500 W at a voltage of 10 kV and gas pressure of 1500 torr. The distance between the electrode and the films was 4 cm. The APP treatment was performed for 60 s on the coatings. Optical emission spectroscopy (OES) of these atmospheric plasma conditions was previously reported for a relative humidity of 60% [29]. The ions characterized were OH and O due to the presence of H_2O and O_2 in the atmosphere.

2.4. Coating Characterization of Plasma Treatment

The recycled nylon 6,6 coatings were characterized before and after treatment with atmospheric plasma to analyze how the treatment influenced the surface properties. First, Raman spectroscopy [30-31] was performed using a Raman SENTERRA II (Bruker) with an Olympus microscope (20x objective), using a laser with a wavelength of 785 nm and 10 mW power and an integration time of 60,000 ms. Scanning electron microscopy (SEM) was performed using a JEOL JSM-IT500 instrument. For this analysis, the coatings were plated with silver to make the sample conductive.

Finally, to evaluate the wettability of nylon coatings treated and untreated with plasma, the contact angle was measured [32-33] via the sessile drop (10 μl) method using water as a liquid. The images were recorded with a Micro View 1000x digital microscope and the contact angle values were obtained from the geometric analysis of the images of drops using the software Image J (version 1.52p). Four measurements were taken for each surface to derive an average value.

3. Results and Discussion

3.1. Coating Characterization

The recycled nylon 6,6 coating was successfully formed on stainless steel.

Figure 1 shows the optical image of this coating in a transversal form with scale (μm), where it can be seen that the observed thickness is approximately 1.2 mm.

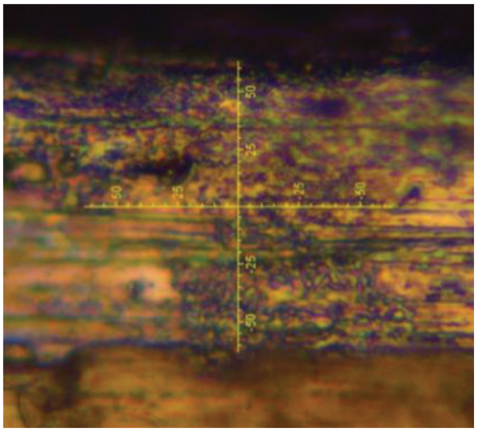

Figure 1: Optical image of the thickness of the recycled nylon 6,6 coating formed on stainless steel.

The recycled nylon 6,6 coating characterization by FTIR spectroscopy showed the same peaks that are characteristic of functional groups in reactive grade nylon 6,6 (Figure 2), indicating that the coating had been successfully achieved without decomposition in an acid medium. Factors such as the viscosity of the solution, the formation speed, and the evaporation of the solvent also influenced coating formation. In Figure 2, the FTIR spectra show the bands corresponding to the stretching vibration of the N-H group at 3302 cm^{-1}; the absorption bands relative to the C-H stretch are also observable in the region of 2950 to 2700 cm^{-1}. The absorption band corresponding to the stretching of the C = O group appeared at 1632 cm^{-1} for pure nylon. This signal was also observed for the recycled nylon coating and another displaced to 1698 cm^{-1} by intermolecular interaction. The deformation signal of N-H at 1533 cm^{-1} disappeared for the coating due to the intermolecular formation of a hydrogen bond between the hydrogen and carbonyl group (C = O–H). Finally, the stretching signal of the C-N bond appeared at about 1200 cm^{-1}, and the methylene group deformation was observed upto 685 cm^{-1}. The FTIR analysis confirmed the chemical structure of nylon reported in the literature [34].

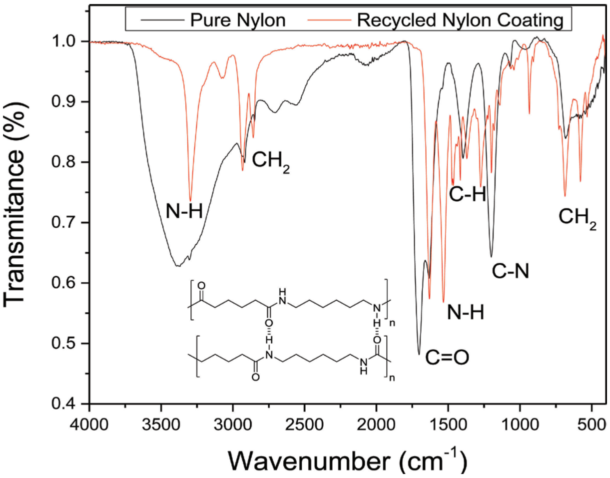

Figure 2: The FTIR spectrum of pure nylon 6,6 and recycled nylon 6,6 coating.

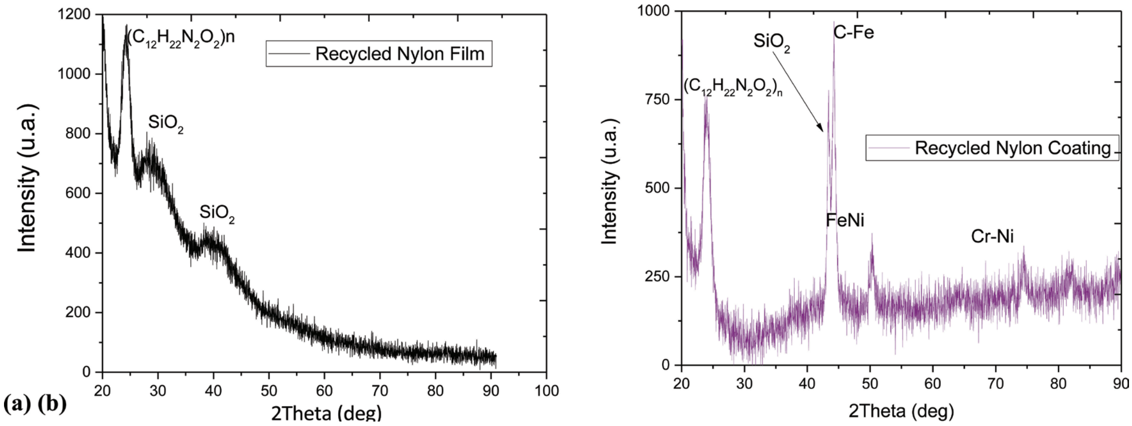

Figure 3: The XRD of (a) the recycled nylon film and (b) the coating deposited on the steel substrate.

The crystal structure of nylon 6,6 is monoclinic and the hydrogen-bonded sheets are sheared alternatively to form the α-phase; however, these also exist in the γ-phase [35]. Figure 3(a) shows the XRD spectrum of the recycled nylon film, where the characteristic peaks of the α-phase of nylon 6,6 at 2θ 21° and 24° can be observed, and are indexed as 200 and 002/202 reflections, respectively. The subsequent peaks corresponded to a silicon oxide (Si-O) polymer (fiberglass) present in the recycled nylon, which was used as reinforcement. These peaks were observed for the coating spectrum (Figure 3(b)), along with characteristic peaks for steel.

3.2. Coating Characterization of Plasma Treatment

The characterization of the coating surface before and after the plasma treatment was carried out by Raman spectroscopy, which presented a spatial resolution of 1 μm, unlike the 10 μm of FTIR. Figure 4 shows the normalized Raman spectra, where a strong peak can be observed corresponding to a Si-O bond vibration as a result of fiberglass being present in the recycled nylon. For the untreated coating, a band upto 1382 cm^{-1} could be observed corresponding to the molecular vibration of a methylene group (CH_2). The C = O vibration signal for the amide group appeared at 1761 cm^{-1} and another band was displaced to 1900 cm^{-1} due to the polarization from intermolecular interaction. For the plasma-treated coating, it was observed that the methylene group signal at 1382 cm^{-1} decreased due to its functionalization with OH groups. At 3184 cm^{-1}, a small band appeared for this group that was less detectable by Raman spectroscopy compared with FTIR. Additionally, the band at approximately 1200 cm^{-1} increased due to the C-O bond formation. Functionalization with carbonyl and hydroxy groups in nylon methylene groups was previously reported in [36]. Nevertheless, the functionalization of a surface with plasma will depend on the medium or gas used [37]. In the current plasma treatment, the H_2O molecules in the medium in contact with the ionization energy from plasma discharge generated high concentrations of OH radicals.

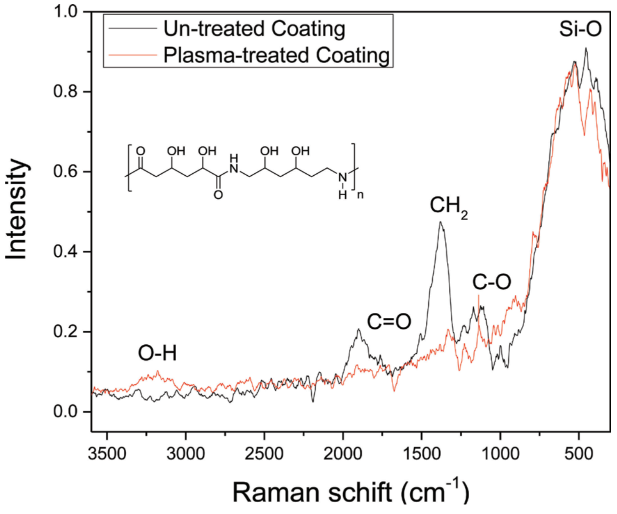

Figure 4: Raman spectrum of a recycled nylon 6,6 coating, both untreated and treated with APP.

The SEM image of the untreated plasma nylon coating showed an irregular layer with significant porosity on the surface morphology (Figure 5(a)).

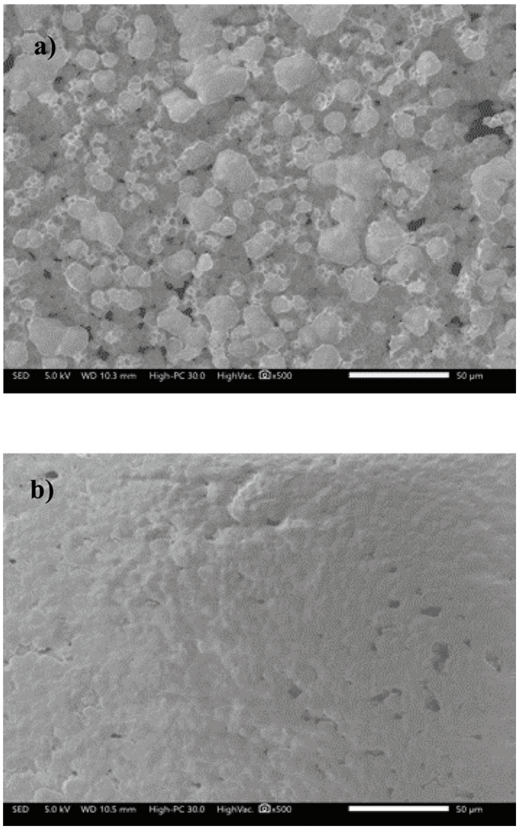

Figure 5: The SEM images of the morphology of the recycled nylon coating: (a) untreated and (b) plasma-treated.

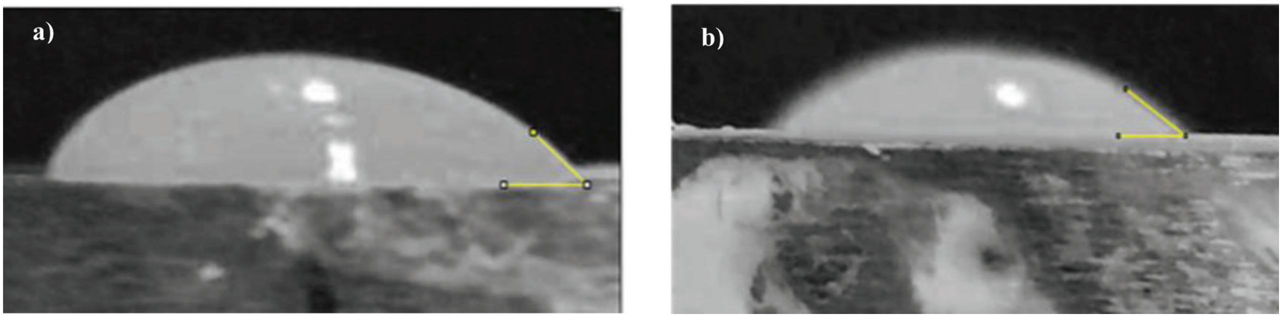

Figure 6: Images of the drop technique for measuring the contact angle: (a) no treatment; (b) plasma-treated.

The pores may potentially have formed due to the low solvent evaporation in the spin coating process.

However, following atmospheric plasma treatment on the coating, the surface appeared compact and less porous as shown in Figure 5(b).

This morphology was caused by plasma activation on the surface, which generated molecular interactions and etching.

The ability of atmospheric plasma to modify surfaces resulted from several factors, one of which was the high average energy of the free electrons present in the plasma, which was sufficient for breaking chemical bonds.

Wettability is an indicator of the adhesion properties of materials and has a relationship with surface energy. By increasing wettability or hydrophilicity, surface energy is also increased.

When the water contact angle value $\theta < 90°$, a hydrophilic surface is indicated. In this work, the recycled nylon coating presented a contact angle of 38.96° ± 3.42° as shown in Figure 6(a). When this coating was treated with atmospheric plasma, its wettability improved by 22% (Figure 5(b)). This happened due to the polar contribution of hydroxyl groups functionalized on the stainless steel surface.

Conclusions

A recycled nylon 6,6 coating was successfully obtained through chemical characterization, without suffering degradation when coming into contact with acid. Additionally, XRD analysis of the coating demonstrated the formation of fibers and the high crystallinity of the polymer.

The Raman analyses of the coating surface before and after the atmospheric plasma treatment showed the functionalized surface with hydroxyl groups. Accordingly, the wettability improved following the plasma treatment. The surface morphology observed by SEM presented a more homogenous surface after plasma treatment. These results are essential for improving surface properties to obtain better adhesion and high energy on coatings using recycled polymers.

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