Improvements in Surface Properties of Polypropylene, Polycarbonate and Polyurethane by Nonthermal Atmospheric Pressure Plasma Arc Jet in Air

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A R T I C L E I N F O

A B S T R A C T

Nonthermal plasma (NTP) is an interesting technique regarding improvements of surface properties of polymeric materials. Three polymers are considered in this study, namely polypropylene (PP), polycarbonate (PC) and polyurethane (PU) chosen for their diversity of use in technical applications. An atmospheric pressure plasma jet (APPJ) using air as working gas is constructed for the treatment of polymer specimens with moderate thermal load for different treatment time intervals and at different nozzle-specimen inter distances. PC specimen is found to suffer most from temperature increase, followed by PU then PP which withstand better the heat generated by plasma. After plasma treatment, surface properties of the considered polymers are investigated using water drop analysis, attenuated total reflectance Fourier transform infrared spectroscopy, surface tester profilometer, and reflectance spectrophotometer. Plasma improves surface properties as wettability, work of energy, surface energy, roughness, and dyeability of treated polymer surfaces. Those properties are found to increase with plasma exposure time; showing more pronounced effects on PU followed by PC and PP. This study can guide the decision of using a certain polymer type treated by plasma for achieving specific applications demanding higher performance of the polymeric material to face challenging practical conditions on wettability and dyeability.

1. Introduction

Polymers have wide range of applications in different manufacturing areas such as food packaging, surgical implants, and automotive industry. This is mainly due to some interesting properties they possess such as excellent thermal stability, light weight, and low cost [1,2]. However, the low surface energy of most of polymeric materials and their poor chemical reactivity negatively affect their use in many applications. They suffer from low wettability for liquids, poor adhesion to other materials and limited dyeability to many dyes and colorants. Remediations of such drawbacks have been attempted by using different techniques as chemical, thermal, or electrical surface treatments [3─5]. One of the most promising methods for polymer treatment was revealed to be the use of nonthermal plasma (NTP) [6]. NTP or as commonly called "cold" or "nonequilibrium" plasma has been recently used in various technical applications. In biomedical field, plasma applications can range from sterilization, wound healing to cancer fighting [7,8]. In agriculture, they expand from seeds treatment, crop growth, to food safety [9,10]. In environmental applications, they enlarge from wastewater remediation to air

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purification control [11,12]. Plasma constitutes mainly of electrons, ions, radicals, and UV radiations, which can initiate chemical and physical surface modifications on polymers' surfaces [13,14]. Plasma is mostly used as a dry process and affects mostly the surface rather than the bulk of polymers in environmentally friendly processes avoiding the use of harmful chemicals. As surfaces of polymers consist mainly of carbon and hydrogen, NTP will incorporate on them varieties of cross-linking and functional groups. This is due to the ability of plasma to insert active species on polymeric surfaces; causing the generation of free radicals in their polymeric chain. This includes oxygen-based functionalities (carbonyl, carboxyl, ether, peroxide, etc.) or nitrogen-based groups resulting in modifications to surface properties [15,16], such as improvement of surface energy of polymeric materials.

In this work, we will investigate the effect of NTP during surface treatments of three types of polymers: polypropylene (PP), polycarbonate (PC), and polyurethane (PU). Those three polymers are widely used in many technical applications in their pure or blend forms owing to their high mechanical strength, heat resistance, and chemical stability associated with low processing costs [17]. In spite their different natures and compositions, those three types of thermoplastic polymers have been used in this study due to their wide utilizations in common technical, industrial, and household applications. PP is a polyaliphatic polymer made from the combination of propylene monomers. It belongs to the group of polyolefins and is partially crystalline and non-polar. PP shows an extremely adaptable behavior, especially when used as protective film overcoats in many industrial applications, such as food packaging and surgical implants. However, it has low annealing temperature as drawback. PC is an amorphous transparent material containing aromatic rings with organic functional groups linked together by carbonate groups (–O–(C=O)–O–). PC is widely used in many engineering applications due to its behavior as strong and sturdy material while still being transparent in some grades. It can be easily molded, machined, colored, and possesses a high impact-resistance, but suffers from rather low scratch-resistance. PU is a polymer containing aromatic rings and composed of organic units joined by carbamate links, it contains two types of monomers, which polymerize one after the other. PU is a high-

performance material in all its forms as rigid or flexible foam, adhesives, coatings sand molds. It is a common material in many technical applications such as film in biomedical field or as insulation in walls and roofs in form of solid foams characterized by low stiffness, low thermal conductivity, and high compressibility. it can also be used in its solid rubber form.

Plasma treatments of many types of polymers, with the objective to ameliorate their surface properties, have been reported by many authors. Cheng et al. [18] have developed a new plasma generator, which can produce a stable cold plasma jet at atmospheric pressure using pure argon. They found that water contact angle of PP and polyethylene terephthalate (PET) fibers decrease after plasma treatment and it exhibits minor recovery in two months. Carrinoa et al. [19] have considered the enhancement of PP wettability and adhesion by the influence of AC electrical discharge cold plasma. Their analyses have demonstrated that voltage, voltage–time and the voltage–flow rate interactions significantly influence wettability. Mello et al. [20] have investigated surface modifications of PC by atmospheric pressure plasma jets (APPJ). They deduce that after the treatment, the PC surface became rougher, which also contributed to the reduction of water contact angles (WCA). They suggest that hydrophilic groups induced on the PC tended to agglomerate into granular structures that were loosely attached to the polymer surface and could be removed from the surface by water rinsing. Vijayalakshmi et al. [21] have analyzed polycarbonate film (PC) surface modifications induced by DC glow discharge low-pressure air plasma. The results show that, after plasma treatment, the root mean square (RMS) roughness of PC film was gradually increased with exposure time. Plasma treatment modified the chemical composition of the polymer surface and it made the surface to be highly hydrophilic. It was found that the air plasma treatment increases the polar component of PC film. Sanchis et al. [22] have examined surface modifications of PU film by low Pressure glow discharge with oxygen gas addition. Results show a much better surface wettability of the film even for short exposure times, with a considerable increase in the surface energy values. Besides functionalization, the surface wettability of the material improves because of a slight increase in surface roughness due to the etching effect of oxygen. Morozov et al. [23]

have studied the effect of plasma treatment of two elastic polyurethanes with different stiffness on bacterial adhesion. As a result, the relief and hydrophobicity of the surfaces changed such that the adhesion of bacteria decreased. Bacterial adhesion is affected mainly by the peculiarities of the relief structure: such that bacteria on the treated surfaces decreased by 50% or more.

Plasma can be produced using many types of NTP discharges [24]. Many authors have studied the applications of different discharge types to polymer surface treatment. For atmospheric pressure plasma jet (APPJ), Lommatzsch et al. [25] have considered the treatment of polyethylene (PE) samples surface for adhesion improvement. The improvement in adhesive bond strength is attributed to the incorporation of oxygen containing functional groups into the PE surface. Kostov et al. [26] have also used APPJ to study surface modifications of polymeric materials. The wettability of PE, PP and PET polymers has been enhanced using an atmospheric pressure argon jet in air. They established that if the process conditions, such as jet-to-sample distance, kind of treatment (static substrate or process with sample scanning) and the time of plasma exposure are properly chosen, the APPJ can uniformly modify a selected area of the sample. Liu et al. [27] have reported effects of operating parameters of dielectric barrier discharge (DBD) plasma on the polymer surface modification of polytetrafluoroethylene (PTFE), polyimide (PI) and polylactic acid (PLA) films in terms of changes in surface wettability and surface chemistry. It was observed that the plasma parameters have a selective effect on the changes observed for the polymers processed. Plasma processing time (treatment cycles) plays an important role in the treatment of PTFE and PI in this study, whereas the size of the electrode gap plays the dominant role in the treatment of PLA. For gliding arc (GA), Darvish et al. [28] have analyzed PP hydrophilicity improvement and aging effects. For corona discharge, results indicated that this treatment approach can be carried out in a single step and at atmospheric pressure without aging effects and without the unfavorable hydrophobic recovery phenomenon as delamination and incompatibility. Lindner et al. [29] have studied the surface energy of different treated polymers by corona discharge. It is shown that an "overtreatment" increases bond strength of laminated films, even though the surface energy does not increase further at higher corona dosages. Moreover, bond strength depends on the

amount of polar and dispersive bonds on the surface. Navaneetha Pandiyaraj et al. [30] have studied adhesive properties of some treated polymers surfaces. A glow discharge plasma has been used to modify the PP and PET film surfaces. Significant morphological and chemical changes were produced by the plasma treatment. The surface energy increase is basically due to the incorporated polar functional groups onto the surface of the PP and PET films causing decrease in contact angle and increase in surface energy. Czylkowski et al. [31] have focused on surface modifications of PC by an atmospheric pressure argon microwave plasma sheet studying the influence of the absorbed microwave power and the number of scans on the changes of the wettability, morphological and mechanical properties of the plasma-treated surface. Their results demonstrate the capability of the new atmospheric pressure plasma type in modifying the morphological and mechanical properties of PC surfaces for industrial applications.

The objective of this work is to make a comparative study of the improvement in surface properties of three polymers namely PP, PC and PU treated by APPJ operating in air. We will consider the effects of NTP on their wettability, adhesion, and roughness. Beside investigations of the surface properties of treated polymers, a study of the improvement of polymer dyability by APPJ, could introduce a rather affordable method to enhance polymer dyability without use of chemical materials, which is considered a challenging problem on the industrial scale. The results should guide the decision of using a certain polymer type treated by APPJ among the three polymers types considered to accomplish specific applications demanding higher surface performances.

2. Experimentation

2.1. Sample preparation

In this study, we use specimens of the three polymeric materials considered namely PP, PC and PU, as shown in Figure 1. Polymers samples have been provided from a local supplier; no special treatment was previously performed on the different polymeric specimens used. Their shapes and dimensions are as follows: PP of cubic shape with surface area 1.0 x 1.0 cm^2 and 1.5 cm thickness, PC of plate shape with surface area 1.0 x 1.0 cm^2 and 0.3 cm thickness, and PU of cylindrical shape of 2.5 cm diameter and 0.5 cm thickness. Before plasma

treatment, areas of PP and PU were polished using a Metkon Gripo 2V polisher machine (Bursa –Turkey) with 800-grade emery paper of grit sizes 1.2, this abrasive grade is chosen following the recommendation made by Bhowmik et al. [32], who had found that it gives the most effective polishing as related to enhancement of polymers surface energies. After polishing, the specimens were washed with distilled water and left dried in ambient air. PC specimen has not been polished using the above cited polishing machine but only hand polished with polishing cloths and was carefully washed and dried.
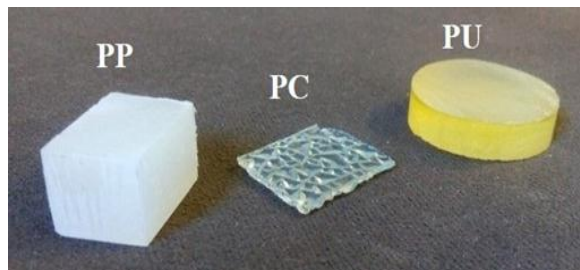

Fig. 1: Specimens of different polymeric materials: PP, PC and PU.

2.2. Experimental setup

An atmospheric pressure plasma jet (APPJ), shown in Figure 2, is constructed to generate plasma at moderate power (100 to 300 W), which can be applied to the surface of polymer specimens at certain distances from it and at certain treatment time intervals. The discharge occurs between a copper rod cathode of 14.3 mm diameter with a conic shape tip and a copper cylinder anode terminated by a convergent-divergent nozzle of 6.83 mm internal diameter. A ceramic tube of 17 mm outer diameter positioned in between assures electric and heat insulation. Air, generated by a compressor, is used as feeding gas to reach the discharge zone through a 30° inclined air inlet in the torch body with flow rate of 18 L/m. The treated polymer specimen is fixed in the XY plane and only the jet-specimen inter distance can be varied by moving the APPJ up and down. The power supply used is an AC step-up transformer of maximum output voltage 5.5 kV and 100 mA current. The 220 V─50 Hz input line voltage is fed to the transformer through a Variac autotransformer.
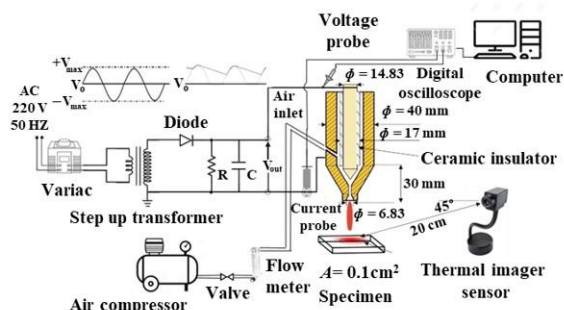

Fig.2: Setup of APPJ showing the power supply and torch details.

2.3. Infrared thermal camera

Infrared images of polymer specimen were obtained during plasma treatment using a thermal imager sensor FLIR A5sc (Oregon, USA) with spatial resolution of 2.78 mrad and spectral resolution of 7.5 -13 μm. The IR sensor is set 20 cm from specimen with an inclination angle of 45°. The sensor is focused on an area of 0.12 cm2 on the middle of the treated specimen of 1 cm2, as can be seen in Figure 2. The sensor is factory calibrated, and the values of the measuring conditions are fed to the original software program as follows: ambient temperature 25 °C, relative humidity 60 %. The IR emissivity e for the different polymer materials is taken as follows: for PP, e = 0.97; for PC, e = 0.8, and for PU, e = 0.9.

2.4. Wettability and contact angle

Wettability of a liquid on a solid surface, is characterized by the contact angle or wetting angle, which is the angle between the solid surface and the tangent to the surface of the liquid drop at that point. The water contact angle (WCA) θ can be determined by the sessile drop technique in which a droplet of distilled water is deposited by a syringe which is positioned above the sample surface, and a digital camera captures the image, which is analyzed by eye. The contact angle θ is given by Young's equation [33]:

$$cos\,\theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \qquad (1)$$

where γ_{sv} is the surface free energy of solid substrate against vapor or the surface tension of solid, γ_{lv} is the surface free energy of liquid against vapor

or the surface tension of liquid, and γ_{sl} is the solid-liquid interfacial free energy. Equation (1) shows that wetting is favored by a high solid surface tension, a low solid-liquid interfacial free energy, and a low liquid surface tension.

2.5. Work of adhesion

Work of adhesion W_a at the interface of solid-liquid-vapor systems is given by:

$$W_a = \gamma_{sv} + \gamma_{lv} - \gamma_{sl} \qquad (2)$$

The work of adhesion represents the energy per unit area of interaction between different phases. The solid-liquid contact angle θ determined by equation (1) can be rewritten as:

$$\gamma_{sl} = \gamma_{sv} - \gamma_{lv} \cos\theta \qquad (3)$$

Combining equations (2) and (3) gives:

$$W_a = \gamma_{lv} (1 + \cos\theta) \qquad (4)$$

Which is known as the Young-Dupré equation.

2.6. Surface energy of polymer

Surface free energy is a measure of the excess energy at the surface of a certain material rather than on its bulk. The surface energy of any substance can be determined by wetting it with one or more pure liquids of known surface tension and measuring the contact angle by the sessile drop methods described in section (2.4.1). By knowing the contact angle using two liquids, a polar and dispersive one, we can calculate accurately the two components of the solid surface energy using different models as described by Żenkiewicz [34]. A practical method using one liquid (water) can give a good, approximated value of the surface energy of a certain polymer as described by Good and Girifalco [35]. By knowing the contact angle θ, Eq. 3 can be written as:

$$\gamma_{sl} = \gamma_{sv} + \gamma_{lv} - 2\,\Phi(\gamma_{sv}\,\gamma_{lv})^{1/2} \qquad (5)$$

Where the parameter Φ is characterizing the interfacial interactions, and is given by:

$$\Phi = \frac{4\,(V_{sv}\,V_{lv})^{1/3}}{\left(V_{sv}^{1/3} + V_{lv}^{1/3}\right)^2} \qquad (6)$$

where V_{sv} and V_{lv} are the molar volume of solid and liquid respectively, which can be calculated knowing the density ρ and the molecular weight M of respective materials as one can calculate V as:

$V = M/\rho$. The expression of the solid surface energy can be approximated to:

$$\gamma_{sv} \approx \gamma_{lv}\left(\frac{(1+\cos\theta)^2}{4\Phi^2}\right) \qquad (7)$$

2.7. FTIR surface analysis of polymer surface

The technique of infrared analysis on polymer samples using attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy is a fast technique which allows the identification of chemical changes occurring on the polymer surface due to plasma treatment [36]. The measurements were performed using an FTIR spectrometer Vertex 70 (Bruker-Germany) equipped with vertical ATR device which is a surface sensitive method due to its inherent low depth of penetration. The spectrometer is continuously purged with nitrogen gas. The internal reflection element is a diamond crystal. A total of 32 scans per analysis was used with a resolution of 4 cm^{-1} are taken for spectrum integration in the wavenumber range from 4000 to 400 cm^{-1}. ATR-FTIR analysis is carried out on the untreated and plasma treated polymer specimens.

2.8. Surface roughness of polymer surface

Surface roughness accounts for fine irregularities on a solid surface, identifying smooth and rough ones. Consequently, it strongly influences the surface wettability marking the hydrophobic or hydrophilic characters of the surface imposed by substrate's chemistry and polar component of surface energy [37]. Roughness is acquired by the determination of surface morphology using a portable self-contained surface finish tester profilometer Surtronic 3+ (Taylor Hobson-UK) with a motorized drive and the following parameters: cut off length = 0.25 mm, measuring length = 4 mm, diamond Stylus Radius = 0.005 mm. The surface roughness of specimens is evaluated using R_a, which is defined as the arithmetic average value of all absolute distances of the roughness profile from the center line within the measuring length.

2.9. Dyeability of polymer surface by color measurement spectrophotometer

Color strength on polymer specimens is measured to assess dyeability improvement of polymeric surfaces due to plasma treatment. Color strength is defined as the ability of color pigment to impart color to a certain material. It depends on the colorant

absorption coefficient (K) and scattering coefficient (S). Measurements of the color strength for dyed polymer specimens are expressed as K/S [38]. Measurements of color strength are done at the maximum wavelength of the dye used using a reflectance spectrophotometer Hunter Lab Ultra-Scan Pro (Reston, Virginia, USA). The color strength (K/S value) is a value used to determine the depth of color of a dyed specimen using the Kubelka–Munk equation:

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \qquad (8)$$

where R is the reflectance of colored samples and K and S are the absorption and scattering coefficients, respectively.

3. Results and discussion

APPJ expands out of the nozzle with a jet of approximate diameter 4-6 mm reaching 2 cm long. The treatment time of few seconds is measured with a stopwatch and is taken to be the actual time period of plasma operation. The jet is directed on the middle part of the specimen and all further investigations are done on this treated region estimated to have a surface of 0.12 cm^2 in the middle of the specimen of area 1 cm^2. The three polymer types are placed at different nozzle-specimen inter distances of 3, 3.5, 4, 4.5 cm and plasma treatment time of 10, 20, and 30 s. Longer exposure time periods or shorter nozzle-specimen inter distances are not found to be suitable because of excessive heat load which may damage the specimen surface.

3.1. Specimen temperature analysis

Infrared thermal camera is used to obtain the temperature profile on polymeric surface at specific nozzle-specimen inter distances and treatment time periods. Figure 3 shows the thermal image of the PP specimen placed at 3 cm from the APPJ nozzle and exposed to plasma for 30 s. We can observe that the highest temperature occurs at a certain spot on the middle of the specimen (marked by red color) and radially decrease outward from the center of the specimen where the jet hit the treated area which be estimated as the jet diameter of about 4-6 mm on a specimen having dimension of 1cm x 1cm.
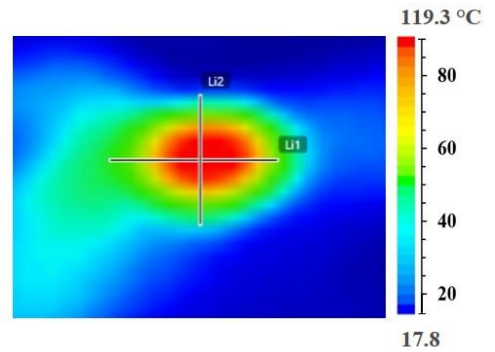

Fig. 3: Thermal image of the PP specimen placed at 3 cm nozzle-specimen inter distance for 30 s treatment time.

For the considered polymeric materials, PP, PC and PU their respective melting points MP are: 173 °C, 225 °C and 145.69 °C respectively. If we consider the values of temperatures recorded for the extreme conditions of 3 cm distance and 30 s treatment time given in Fig. 4, we found temperatures of 119.3 °C, 135.2 °C and 125.8 °C which indicates that the maximum treatment temperatures reached during treatment have not reached the MP avoiding thermal distortion of the treated polymeric surface. From this analysis, we can notice that shorter time and longer distance are more suitable considering heat load of the specimen during treatment.
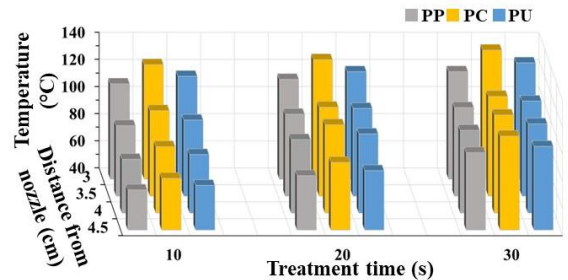

Fig. 4: IR camera temperature profile versus treatment time intervals at different nozzle-specimen inter distances for the three polymers considered.

3.2. Wettability of polymer surface by plasma

APPJ using compressed air as working gas is applied to the surface of specimens of PP, PC and PU. The change in wettability due to plasma at different treatment time periods and different inter distances nozzle-specimen is assessed by contact angle measurements. In Figure 5 we can see the change in water drop shape due to plasma treatment

time of 30 s for PP specimen located at 3.5 cm from torch nozzle. The flatness of the water drop indicates the enhancement of the wettability of the PP surface.
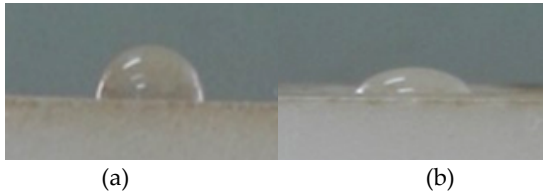

| (a) | (b) |

Fig. 5: Water drop on PP specimen. (a) untreated specimen (b) after 30 s plasma treatment and 3 cm nozzle-specimen inter distance.

After polishing the values of the contact angles are measured without plasma treatment this is denoted by ''untreated'' in Figure 6. By applying plasma for different time periods and at different nozzle-specimen distances, contact angles decrease with increasing treatment time and decreasing nozzle-specimen inter distances indicating better wettability. In Fig. 6 For larger time periods of 30 s, values for PC (135.2 °C) for distance 3 cm and PU for 3 cm (125.8 °C) and 3.5 cm (110.1 °C) could not be reported due to high temperatures imposed by plasma, which is near the transition temperatures Mp of corresponding materials.
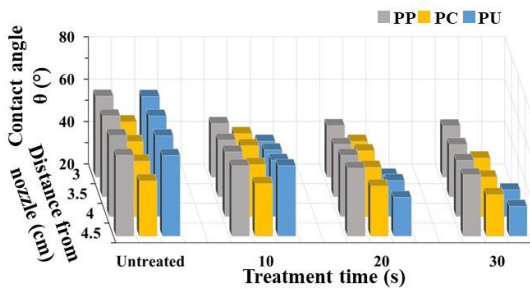

Fig. 6: Variation of the contact angle with plasma treatment time periods for different inter distance nozzle-specimen concerning the three polymers considered (note the direction of increase of the "distance from nozzle" on the z-axis).

Values of WCA of untreated polymers plotted in Fig. 6, seems to be lower than that reported in the literature for PP and PU, this may be due to polishing of the surface before treatment which may increase specimen surface roughness. However, for PC, angles of untreated specimen are comparable to that stated in [31]. Considering the values of temperatures in Figure 4 and that of contact angles in figure 6, one can notice that there is an inverse relationship between surface temperature recorded for each

polymer and the contact angles. Longer exposure time or closer distances produce high peak surface temperatures accompanied by lower reported contact angles. The change in wettability caused by plasma treatment is not expected to be permanent. Hydrophobic recovery observed by many authors, [39-41], can take place after plasma exposure depending on polymer type and discharge conditions. In our case we haven't recorded large noticeable change in contact angle after few hours from APPJ treatment which can give more opportunity during manufacture process related to wettability and dyeability improvement to be applied on the polymer treated surface.

3.3. Work of adhesion of different polymer

The work adhesion is calculated for the three polymers considered from water drop contact angle measurements data and by using Equation (4) applying surface tension of water: $\gamma_{H_2O} = 72.8 \text{ mJ/m}^2$. Figure 7 shows that work of adhesion values increase with increasing treatment time and decreasing nozzle-specimen inter distances, this indicates a better wettability. The surface energy values for the three polymers considered are calculated from water drop contact angle measurements data using Equation (7) and the physical parameters of considered polymers and water as follows:
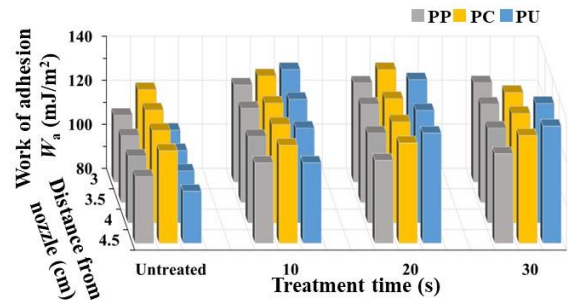

Fig. 7: Variation of the work of adhesion with plasma treatment time periods for different inter distance nozzle-specimen concerning the three polymers considered.

Table 1. Physical parameters of considered polymers and water.

Material	Density ρ g/cm³	Molecular weight M g/mol	Molar volume V cm³/mol
PP	0.905	42.08	46.59
PC	1.2	254.3	211.91
PU	1.19	600	504.2
Water	1	18	18
Surface tension of water		γ_{H_2O} = 72.8 mJ/m²	

Figure 8 shows effects of treatment time and nozzle-specimen distance on surface energy for the three polymers considered. We can notice that, for the three polymers considered, surface energy values increase with increasing plasma treatment time periods and decreasing specimen-nozzle inter distance.
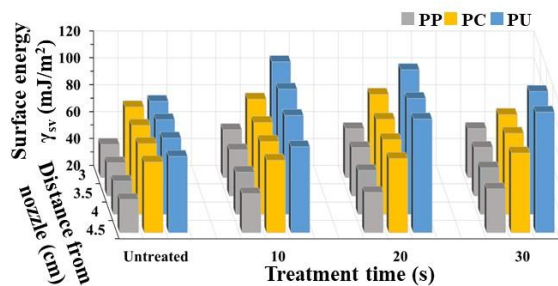

Fig. 8: Variation of the surface energy with plasma treatment time periods for different inter distance nozzle-specimen concerning the three polymers considered.

Generally, a surface with a low surface energy will cause poor wetting and therefore results in a high contact angle, which indicates that by increasing the surface energy we improve the wetting process. From figures 6, 7, and 8 for contact angles, work of adhesion and surface energy values; we can remark that PU is the most affected polymer by plasma especially at small distances from the nozzle followed by PP then PC which is the less affected by plasma treatment.

3.4. FTIR spectrum analysis

The ATR-FTIR spectra, for the untreated and plasma treated specimens, are illustrated in Figures 12 to14 for the three polymers in consideration, namely PP, PC, and PU.
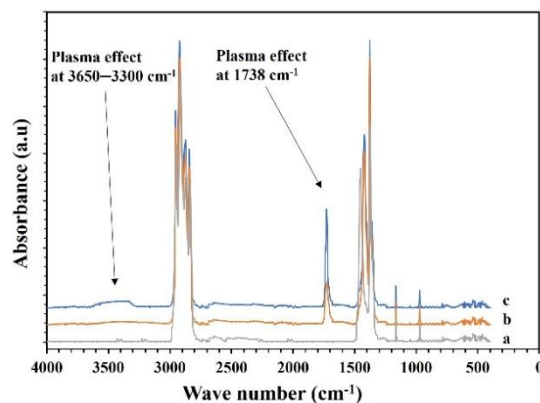

Fig. 9: ATR-FTIR spectrum for PP samples (a) untreated, (b) after 10 s treatment, (c) after 30 s treatment.

In Figure 9, the ATR-FTIR spectra for PP specimens are illustrated for untreated and plasma treated for exposure time periods of 10 s and 30 s. Plasma induces chemical changes on the surface of the polymer, this can be seen on the FTIR spectra where a very broad absorption peak between 3650 and 3300 cm^{-1} appears after treatment, which can be attributed to OH stretching vibrations. Moreover, a clear change can be seen in the region 1830–1580 cm^{-1} where a broad peak at 1738 cm^{-1} appears due to the presence of carbonyl (C=O) groups in ketones, aldehydes and carboxylic acids [42]. In Fig. 10, around 3000 cm^{-1}, due electronic distortion occurs due to measuring instrument limitations, which should be ignored in the signal analysis.
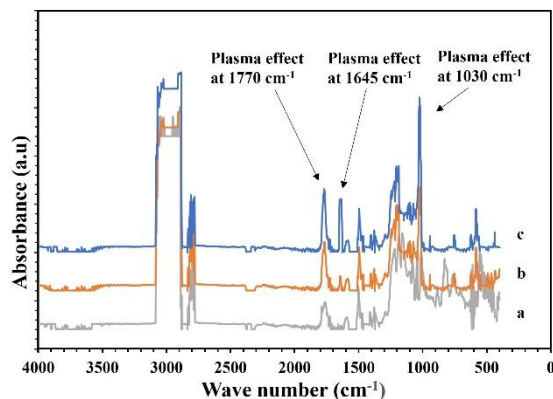

Fig. 10: ATR-FTIR spectrum for PC samples (a) untreated, (b) after 10 s treatment, (c) after 30 s treatment.

In Figure 10, the ATR-FTIR spectra for PC specimens are illustrated for untreated and plasma treated for plasma exposure time periods of 10 s and 30 s. We can identify in the spectrum the main bands, peaks and small peaks characteristic of PC. The increase in the absorption bands due to plasma treatment is visible at 1030 cm^{-1}, 1770 cm^{-1}, and 1645 cm^{-1}.
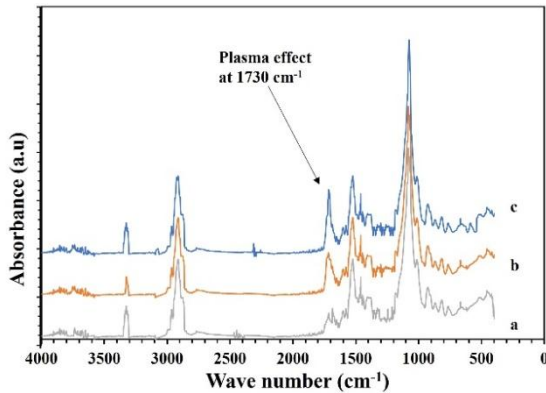

Fig. 11: ATR-FTIR spectrum for PU samples (a) untreated, (b) after 10 s treatment, (c) after 30 s treatment.

In Figure 11, the ATR-FTIR spectra for PU specimens are illustrated for untreated and plasma treated for plasma exposure time periods of 10 s and 30 s. We can note that peaks at 1730 cm^{-1} increase with increasing treatment time. The results of ATR-FTIR for the three polymers show that activated oxygen species could etch and oxidize the surface. The absorption bonds C=O, C─OH, and C─O can lead to formation of functional groups enhancing the hydrophilic character of the polymer surface after plasma exposure. For a more complete picture of the effect of NTP on polymer, Sanchis et al consider the loss of the degree of aromaticity on PU due to plasma [43] and Czylkowski et al has examined this effect on PC as already seen in [31].

3.5. Roughness analysis of polymeric surface treated by plasma

Effects of treatment time and specimen-nozzle distance on surface roughness are shown in Figure 12 for the three polymers considered.
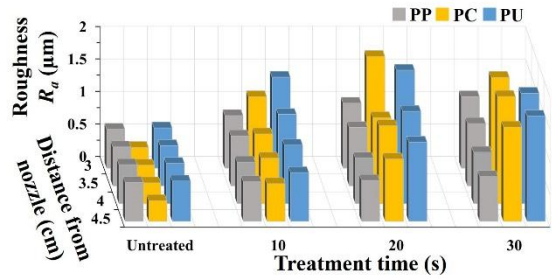

Fig. 12: Variation of the roughness with plasma treatment time periods for different inter distance nozzle-specimen concerning the three polymers considered.

We can notice that, for the three polymers considered, roughness values increase with increasing plasma treatment time periods and with decreasing nozzle-specimen inter distance. The phenomena of roughness increase on polymeric surfaces during NTP applications even at low power have been observed by many authors for different NTP discharge types. Mandolfino et al, [44] analyze the effect of plasma on surface characteristics of polypropylene samples. Felix et al [45], reports an experimental study on the temporal evolution of the roughness development of polymer surfaces exposed to argon non-thermal plasma under reduced pressure.
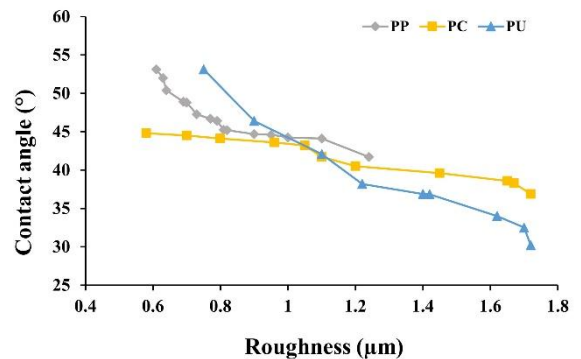

Fig. 13: Variation of contact angle θ with surface roughness for the three polymers considered.

Figure 13 demonstrates the lowering of the contact angle with increase of roughness. The decrease of contact angle values with roughness is associated with droplet spreading along the grooves, even small changes in surface roughness influence contact angle measurements leading to changes in wetting properties. The increased hydrophilicity of PP, PC and PU specimens with plasma treatment came from

the dual effect of oxidation of polymeric surface and introduction of oxygen-containing functional groups, which increases the surface energy, and enhances roughness [46]. For more accurate results one should consider that roughness can affect contact angle measurements, this may influence the values of the surface energy in figure 8. To take into account the effect of roughness on measured contact angle, one has to introduce a coefficient that accounts for high roughness. This have been proposed on an early paper by Wenzel [47] and on a more recent one by Cassie et al [48]. According to Wenzel, the relationship between roughness and contact angle is as follows:

$$cos\theta^* = r\,cos\theta \qquad (9)$$

θ^*= Measured (apparent) contact angle; θ= Contact angle with the smooth surface; r = Roughness coefficient: This specifies the ratio of the size of the overall surface to the surface projected geometrically onto a plane. Therefore, for perfectly flat surfaces, the value of r = 1, while for rough surfaces the value of r > 1. This correction using the roughness coefficient r given by Equation (9) has not been taken into account in this work but should be considered in upcoming investigations.

3.6. Dyeability

Measurements are carried for specimens of the three polymers considered namely PP, PC and PU. The surface of the untreated and plasma treated specimens are painted with red polyurethane pigment to investigate effects of plasma exposure for different treatment time intervals on the polymer dyeability, as shown in figure 14.
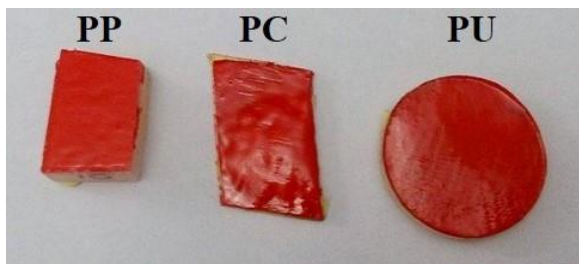

Fig. 14: Surfaces of specimens of PP, PC, and PU paint with red polyurethane pigment.

The specimens are set at 4 cm from the nozzle of the APPJ. After plasma exposure at different plasma exposure time, we paint the surface of untreated and treated samples by commercial liquid polyurethane red pigment past (supplied by a local manufacturer) and let them dry for 2 days. Measurements by color measurement spectrophotometer were done after 3 weeks at the maximum wavelength of the dye used of value 470 nm.
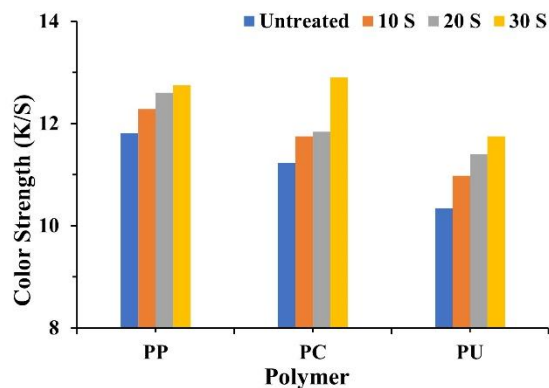

Fig. 15: The variation of color strength with treatment time for the three polymers considered.

Figure 15 shows the effect of APPJ treatment on the color strength (K/S) for untreated and plasma treated polymers' surfaces. Color strengths increase with increasing treatment time periods. This can be related to the increase in roughness and adhesion occurring due to plasma treatment. PC shows considerably better dyability with plasma treatment for large treatment time followed by PU and then PP, which is less influenced by dye and shows less color strength on the surface treated by plasma.

4. Conclusion

Cold atmospheric plasma discharge generated by an atmospheric pressure plasma jet has been used to treat the surfaces of different polymeric materials namely polypropylene, polycarbonate and polyurethane. The hydrophilic characters of the polymers have been found to be enhanced by plasma treatment through contact angle measurements of water drop on polymer surface. The contact angles decrease with increasing plasma treatment time periods and decreasing nozzle-specimen inter distance indicating better wettability of the three polymers treated by plasma. This decrease in contact angle is accompanied by change in work of adhesion and surface energy as well as surface roughness of

treated polymeric surfaces, which all consequently were found to increase with increasing treatment time and decreasing nozzle-specimen inter distances compared to untreated specimens. These phenomena occur for the three considered polymers; however, PU is the most affected polymer by plasma treatment followed by PC and PP which is the less affected by plasma treatment. ATR-FTIR measurements provide the chemical structure of the polymer surface layer and identify changes in the layer structure caused by plasma treatment. Air plasma treatment produces oxygen-containing functional groups, which are introduced in the polymer chain and are expected to improve surface wettability. Results show noticeable amount of hydrophilic C-O and C=O bonding species were created on the polymer surface after treatment turning the plasma treated material to be more hydrophilic and increase its roughness. Cold atmospheric plasma is a good candidate to replace chemical treatment for enhancing polymers surface properties concerning wettability, adhesive bonding and color dyeability which are very important properties in many technical and manufacturing applications.

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