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ORIGINAL PAPER

Immobilization of Chitosan Onto Polypropylene Foil via Air/Solution Atmospheric Pressure Plasma Afterglow Treatment

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Abstract
The combination of an atmospheric pressure plasma afterglow operated in air with wet grafting was utilized for the immobilization of chitosan on the surface of polypropylene foil. The plasma treatment results in a local modification of polymer surface along the sample axis with a modified zone of width 2 cm. Moreover, plasma treatment initiates etching and melting of the polymer on micro-level. Processing in combination with chitosan solution in-line prevents thermal effects and results in the formation of island-like chitosan structures. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR) reveal the presence of chemical groups typical for chitosan structure.

Keywords Atmospheric pressure plasma · Solution plasma processing · Polypropylene · Chitosan · Immobilization

Introduction

Nowadays, synthetic polymers are ubiquitous in everyday life. One such polymer, polypropylene, is used due to its superior mechanical properties, thermal stability, chemical inertness, non-toxicity and low cost. For example, a variety of housewares such as different bottles, containers, vessels, dishes, medical devices, membranes, filters and surgical bandages are fabricated of polypropylene. At the same time, some potential applications of

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this polymer are impossible because of poor wettability and the lack of chemically active groups on the surface that promote low adhesion, dyeability and printability of polypropylene-based materials. In addition, some applications, for instance biomedical, require protection from microbial biofilm formation, which cannot be provided by neat polypropylene. Nevertheless, all these limitations may be relatively easily overcome by modification of the polymeric surface.

Plasma-based techniques are widely utilized for the processing of polymer surfaces. The main advantage of plasma technologies lies in the modification of polymeric surface without influencing bulk properties. Moreover, plasma devices are environmentally friendly and relatively inexpensive to maintain. Different types of plasma reactors operated at low and atmospheric pressures were developed for the improvement of hydrophilicity of hydrophobic polymers, such as polypropylene, polyethylene, polyethylene terephthalate and polytetrafluoroethylene. In Choi et al. [1] and Rybkin et al. [2] authors particularly described the influence of oxygen plasma ignited in a low pressure reactor and of plasma in a liquid cathode system on polypropylene foils. A variety of publications demonstrate the effectiveness of atmospheric pressure discharges, such as glow discharge, dielectric barrier discharge, and different types of plasma jet, ignited in inert and reactive gases, for plasma treatment of polymer foils, fibers, membranes and non-woven materials [3–7]. Different characterization techniques successfully confirmed that plasma modification of polymer materials is a combination of etching and functionalization of the surface by polar oxygen-containing groups such as hydroxyl, carbonyl and carboxyl groups. Such groups crucially enhance surface energy and are chemically active, playing the role of brushes for subsequent chemical modification through the immobilization of other agents. One of such polymer, chitosan, exhibits attractive biocompatibility, biodegradability, extremely low toxicity and high antibacterial performance.

Chitosan is an aminosaccharide, commercially produced by deacetylation of chitin extracted from shells of shrimps or crabs. A variety of applications of chitosan and its derivatives were proposed in recent decades, such as for water purification from dyes, heavy metals and some organic pollutants [8–10], biomedicine [11] and food packaging [12]. It was shown recently that low molecular weight derivatives may be produced by degradation of high molecular weight chitosan during solution plasma treatment [13–15]. However, foils cast from such prepared solutions are characterized by low mechanical strength and high fragility. Therefore, the grafting of chitosan onto flexible polymeric supports appears to be a promising technique for further applications.

Several methods of atmospheric pressure plasma-initiated immobilization of chitosan on different polymeric materials were developed in recent years. Different variations of dielectric barrier discharge (DBD) in oxygen and air have been successfully applied for the activation of surfaces for direct immobilization of chitosan on polyethylene, polypropylene and polyethylene terephthalate foils [16, 17]. DBD was utilized for chitosan immobilization on non-woven materials based on polypropylene, polyester and polyethylene terephthalate, which find application in different areas [18–20]. Atmospheric air plasma jets are also widely used for polymer pretreatment before immersion into chitosan solution for immobilization, though not so often because of the small size of the modified zone on surface and the necessity to scan the sample for a uniform effect [21]. Chitosan was successfully immobilized not only on model substrates, such as foils or fabrics, but also on real objects. For instance, natural rubber latex medical surgical gloves were treated by air DBD plasma with subsequent chitosan grafting for bactericidal activity [22]. Another example is plasma-initiated chitosan immobilization onto polystyrene containers for grape packaging to prolong fruit shelf life [23].

The drawback of all plasma-based approaches presented above is their multi-stage character. All of them include as a minimum 3 steps: plasma treatment of polymer → transfer from the plasma device to a vessel with chitosan solution → chitosan immobilization. The challenge is how to overcome this inconvenience and make the process more straightforward. One solution is using a liquid cathode system, which was successfully applied for the in situ coupling of chitosan onto the surface of PP foil [24]. In current work, the same problem was solved using an atmospheric pressure plasma jet ignited in air. The combination of plasma processing with wet treatment in-line results in a fast and convenient technique for immobilization of chitosan onto polymer materials.

Experimental

Materials

Chitosan, natural co-polymer of (1 → 4)-linked 2-amino-2-deoxy-β-D-glucopyranose and 2-acetamido-2-deoxy-β-D-glucopyranose, with a molecular weight of 195 kDa was produced by deacetylation of chitin extracted from crab exoskeletons (Bioprogress Ltd.). The deacetylation degree determined by potentiometry was 82%. An aqueous solution was prepared by dissolving 1 g of chitosan in 100 ml of 2% acetic acid in water (Chimmed Ltd, GOST 61-75) at 50 °C under constant stirring for 2 h. After stirring, the mixture was left for 20 h at room temperature and a 1% (w/v) chitosan solution was obtained after the subsequent filtration.

Polypropylene (PP) foils with 20 µm thickness (TU RB 00204079.164-97, Mogilevkhimvolokno Ltd) were used as substrates. Prior to treatment, substrates 10 cm × 1.5 cm were cleaned with ethanol and deionized water.

Plasma Processing

The experimental set-up is presented in Fig. 1. DC atmospheric pressure glow discharge was ignited in the ambient air between an anode (a stainless steel nozzle with an inner diameter of 470 µm) and a cathode (a stainless steel triangular plate with the thickness of 1 mm). The interelecrode gap was 0.5 mm. A homemade DC supply was used to ignite the discharge at a current of 15 mA. The discharge voltage and power were 418 V and 6.3 W, respectively. The air was passed through the anode with a flow rate of 870 sccm. The high flow rate produced an afterglow directed downward from the cathode, which was applicable for polymer treatment.

PP substrates were mounted onto an 8 cm cylindrical sample holder rotating with a constant rate of 30 rpm. The distance between the sample holder and the cathode was set at 5 mm to ensure that substrates were treated in the afterglow of the discharge. The downside of the sample holder was immersed by 2 mm into a Petri dish containing 25 ml of the chitosan solution. Every point of the sample was treated for 0.1 s per cycle. Thus, when going through the rotating apex the substrates sequentially went into contact with the jet followed by the immersion in the chitosan solution. PP foils with immobilized chitosan were compared with neat PP foils and foils treated without the wet stage.

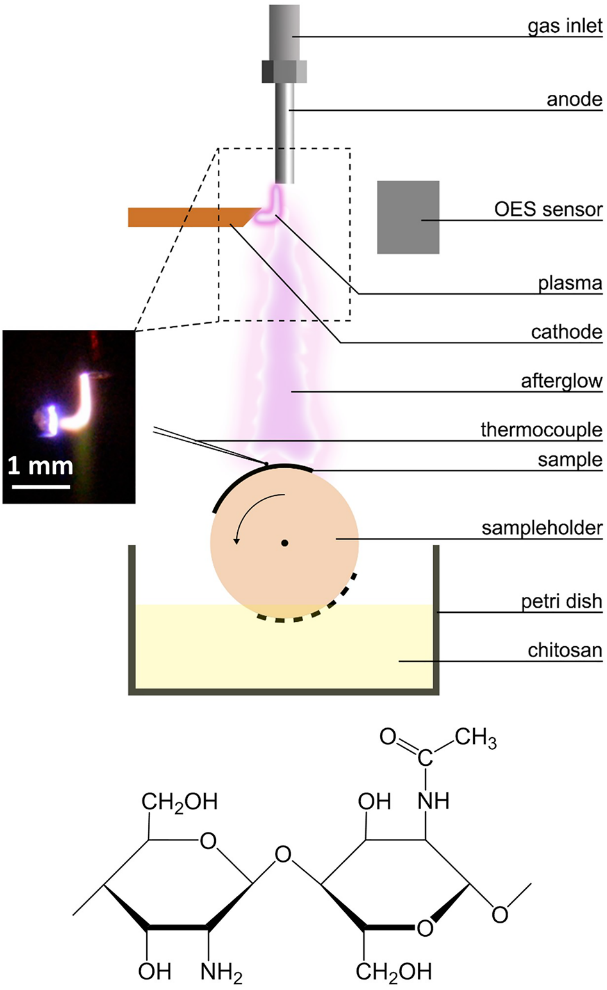


Fig. 1 Scheme of the experimental set-up and photo of the discharge

Characterization of the Foils

After plasma treatment, the PP samples were removed from the holder, rinsed with 2 w/v % acetic acid water solution for 15 min and then with deionized water for 15 min to remove loosely bound chitosan from the surface. Finally, the samples were dried in ambient atmosphere for at least 12 h.

The wettability of the foils was evaluated by a goniometer of custom construction. Static water contact angle (WCA) measurements were performed under ambient conditions using 2 µl deionized water droplets.

The chemical composition of the samples was studied by X-ray Photoelectron Spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). An Al Kα X-ray source (1486.6 eV, Specs) with a multi-channel hemispherical electrostatic analyzer (Phoibos 100 Specs) was used for XPS. Survey and high-resolution spectra were acquired with a pass energy of 40 and 10 eV, respectively. The spectra were charge-corrected using the position of aliphatic carbon at 285.0 eV.

Fourier transform infrared spectroscopy was carried out using a NICOLET 6700 FTIR spectrometer in a single attenuated total reflection (ATR) mode with a ZnSe crystal. 16 scans with spectral resolution 4 cm^{-1} were co-added to achieve a good signal-to-noise ratio. All measurements were performed at room temperature.

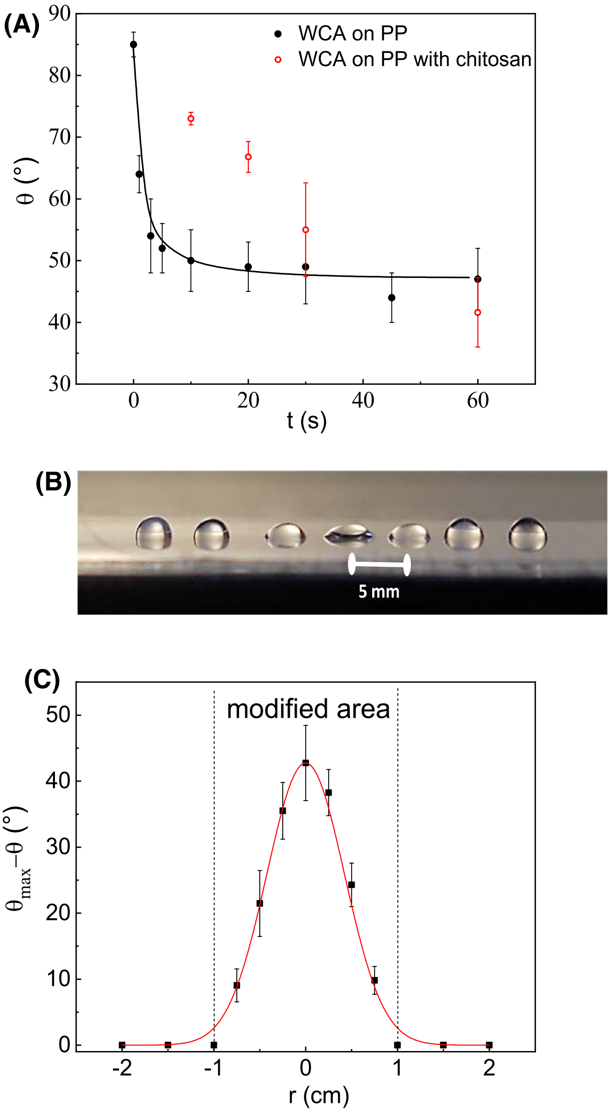
Atomic Force Microscopy measurements (AFM Ntegra Prima, NT-MDT) were performed in ambient environment in an amplitude modulation intermittent contact mode with standard silicon cantilevers (Multi75Al-G, spring constant is 3 N/m, tip radius is 10 nm). The height images were acquired with 256 × 256 data points and tilt was removed by subtracting second order polynomial from the raw data. The Scanning Electron Microscopy (SEM) measurements (Tescan Mira 3) were performed with an accelerating voltage of 10 kV in a secondary electron mode. The samples for SEM analysis were preliminarily metalized with a 3-nm gold film deposited by vapor phase deposition.

Results and Discussion

First, the changes in the wettability of the PP foils were studied without contact with chitosan solution for the preliminary estimation of the width of the area modified by the plasma treatment. It is well-known that air plasma modification of the originally hydrophobic polymers improves the surface wettability. In the case of PP foils used in the current study, the initial WCA was equal to 85°. Figure 2a shows a two-fold decrease of static WCA during the first 20 s of the treatment. However, further processing does not lead to any change of WCA. The value is stationary at about 47°, pointing at the hydrophilic character of the treated PP foil. This effect is explained by an enhancement of the polar component of surface energy, which results from formation of polar chemical groups on the polymer surface during and after the plasma processing. Moreover, the discharge configuration enables the local treatment of the polymer surface, as is demonstrated in Fig. 2b showing photos of water droplets placed transversally across the surface of the PP foil treated for 60 s. The corresponding values of WCA are plotted in Fig. 2c. The difference between the value of WCA outside and inside the modified area was used as a Y axis for more descriptive demonstration. The wettability is affected at a width of approximately 2 cm and is characterized by an inhomogeneous treatment profile. The dependence is fitted by a Gaussian distribution with a maximum located in the center of the sample, which underwent the most intensive treatment.

The cycling process of the treatment of PP foils by the afterglow of atmospheric pressure glow discharge with their subsequent immersion into 1% chitosan solution initiates the immobilization of chitosan on the polymer surface. The effect of chitosan grafting may be qualitatively confirmed by wettability test as well as by gravimetric measurement. The red point in Fig. 2a shows that WCA decreases after 60 s of plasma processing with chitosan solution in comparison with non-solution air plasma treatment. This result is consistent with the earlier reported hydrophilic character of PP/PET films assembled with chitosan using plasma [17]. PP substrate was weighed before chitosan immobilization, immediately after processing, and after washing by deionized water. The initial PP substrate had a weight of 27.9 mg. Immediately after chitosan immobilization the weight increased by 0.31 mg. However, after the sample was additionally washed by deionized water the weight increase was 0.25 mg. We conclude that washing by deionized water removed chitosan adsorbed physically on the surface. The weight increase indicates that chitosan was bound to the PP surface upon the cooperative plasma and wet treatment. Additionally, a

Fig. 2 **a** The time-evolution of WCA measured at the center of the sample, **b** the transversal distribution of water drops across the substrate and **c** the transversal distribution of WCA on plasma-treated PP surface (the sample of 10 × 5 cm size was taken for this measurement)



qualitative experiment with dyeing of the samples was performed to study the homogeneity of chitosan coverage. The first film was treated once for 60 s along the sample axis. The second film was treated in the same way 3 times step by step with a 3 mm shift of the treatment axis. Modified films were dyed with I.C. Active Blue 21, which interacts chemically with chitosan [25], to visualize the coverage of the PP surface. The samples were dipped into the dye solution for 10 min and then rinsed with deionized water. Figure 3 demonstrates photos of the foils after the single treatment and after the radial scanning treatment. It is seen that the films have a homogeneous blue color on the area near the treatment axis that indicates the chitosan immobilization. Moreover, radial scanning makes it possible to cover almost the full sample surface with chitosan.

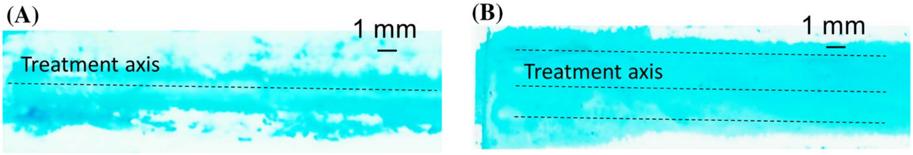


Fig. 3 PP film covered by chitosan using **a** single treatment and **b** radial scanning

The modification of the surface morphology of PP after plasma processing with the immobilization of chitosan is illustrated by Fig. 4. It shows the SEM images of neat PP foil (Fig. 4a), PP foil after non-solution plasma treatment for 60 s (Fig. 4b) and PP foil with grafted chitosan after solution plasma treatment for 60 s (Fig. 4c). It is worth noting that the polymer surface suffers significant transformations after the non-solution plasma treatment. PP foil becomes rougher because of the formation of structures with a lateral size of several μm. This may be explained by surface etching under the action of active species from plasma. Such effect is frequently observed after the plasma treatment of polymers. The surface of the foil processed with chitosan solution is covered by bigger objects. The accumulation of chitosan in the form of islands on polymeric foils is typical for step by step activation of the surface by atmospheric pressure plasma and immersion into chitosan solution [16, 17, 26]. However, our earlier in situ immobilization of chitosan onto PP performed in a system with a liquid cathode resulted in the formation of homogeneous chitosan film with thickness reaching 2 μm [24].

AFM measurements allow for more detailed analysis of the morphological features. Figure 5 shows AFM images of the surface of PP foil before and after the non-solution plasma treatment. As expected, the root-mean-square roughness (RMS) of the PP surface significantly increases from 7.1 ± 0.4 to 68 ± 6 nm. Upon closer examination, the surface pattern formed under the plasma action does not look as if given solely by etching. The formation of droplet-like structural defects was revealed. Such effect was reported and discussed previously for plasma treatment of PE and PP and several explanations were assumed [1, 7]. The first is polymer melting that occurs evidently because of local heating of the polymer surface. The measurements of temperature of the afterglow and of the surface of PP foil under the afterglow were performed by means of glazed copper-constantan thermopile. It was found that near the plasma zone, the temperature is around 373 K; however, this value can be understated due to the glass case of the thermopile. Up to the distance of 2 mm, the temperature gradually

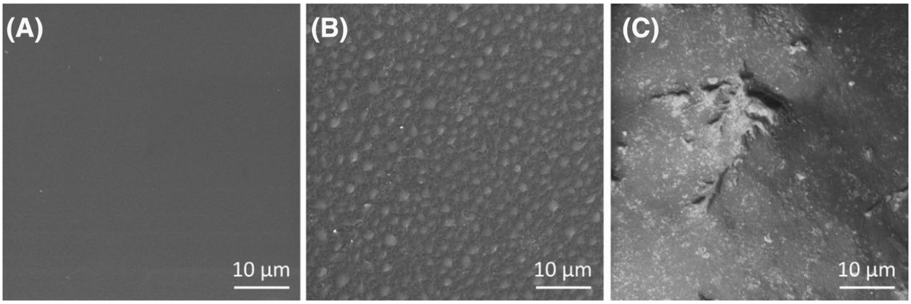


Fig. 4 SEM images of PP foil taken at their center: **a** without treatment; **b** after non-solution plasma processing; **c** with immobilized chitosan

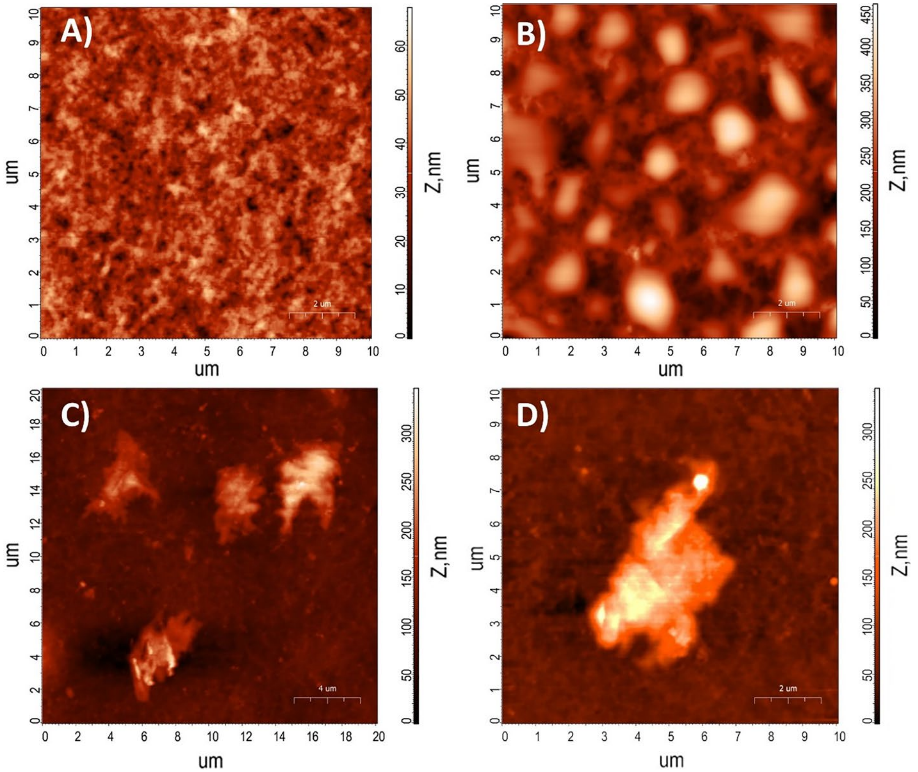


Fig. 5 The AFM micrographs of: **a** the original PP foil; **b** air plasma treated PP foil; **c** PP foil after plasma-assisted chitosan immobilization from solution and **d** the micrograph of the isolated chitosan island

decreases and then stays constant at about 310 K. At the same time, the surface of PP was heated up to 323 K during the 60 s of the plasma processing. However, the melting point of PP is significantly higher, about 130 °C. Nevertheless, the action of active species from plasma can initiate exothermic chemical processes on the polymer surface, leading to local heating and melting of the material. The second possible reason may be due to the inhomogeneity in the PP crystalline structure and different etching rates of different surface regions. As a result, the developed surface pattern was formed on PP. The third and most probable explanation of the droplet-like structures is based on surface oxidation reactions initiated by plasma action which result in the formation of so-called low molecular-weight oxidized materials (LMWOM) [27–29]. LMWOM tend to de-wet the hydrophobic polymer surfaces and form bumps on them. It is worth mentioning that the bumps could be easily removed from the surface by rinsing in polar solvents. Figure 5c shows AFM pictures of the surface of PP foil with chitosan structures and Fig. 5d demonstrates an isolated island. The microscopy results support SEM images that revealed the non-homogeneous character of the chitosan coating. The chitosan islands accumulated on the PP have an irregular shape and rough topography. At the same time, the surface is relatively smooth in between the islands without drop-like features. Nevertheless, the RMS roughness of the foil with immobilized chitosan is 43.9 ± 8.3 nm, which is significantly higher in comparison with the initial PP surface. The appearance of bumps on the surface of samples prepared by plasma-assisted immobilization of chitosan from solution may be explained by the specificity of the plasma solution processing. When PP foil passes through the chitosan solution, a thin aqueous layer forms on the polymer surface. After moving the sample into the afterglow region, the active species interact mostly with the liquid layer that serves as a barrier and prevents the underlying polymer surface from undesirable plasma action.

Figure 6 presents C 1s XPS spectra of the neat PP foil and PP foils after air plasma afterglow treatment and plasma assisted chitosan immobilization from solution. PP is a typical hydrocarbon polymer, so its spectrum demonstrates an intensive peak of aliphatic carbon with a small amount of oxygen-containing groups formed as a result of partial oxidation (96.3 at% of C and 3.7 at% of O). After the air plasma treatment, the concentration of oxygen significantly increases and a signal from nitrogen appears (79.7 at% of C, 19.5 at% of O and 0.8 at% of N), which points to intensive surface oxidation and the formation of new functional groups. The surface functionalization is also identified by the transformation of the shape of C 1 s peak in a higher binding energy region. Peaks corresponding to C–O bonds (hydroxyls, ethers) at 286.5 eV, C=O (carbonyls) at 288.0 eV and carboxyl groups at 289.0 eV were successfully identified. Chitosan immobilization on the PP surface results in a further increase of oxygen and nitrogen content (70.5 at% of C, 24.9 at% of O and 4.6 at% of N), which is accompanied by a noticeable change of the C 1 s peak. A significant increase of the peak at 286.5 eV is attributed to the increased concentration of hydroxyl, ether and primary amine groups available in the chitosan structure.

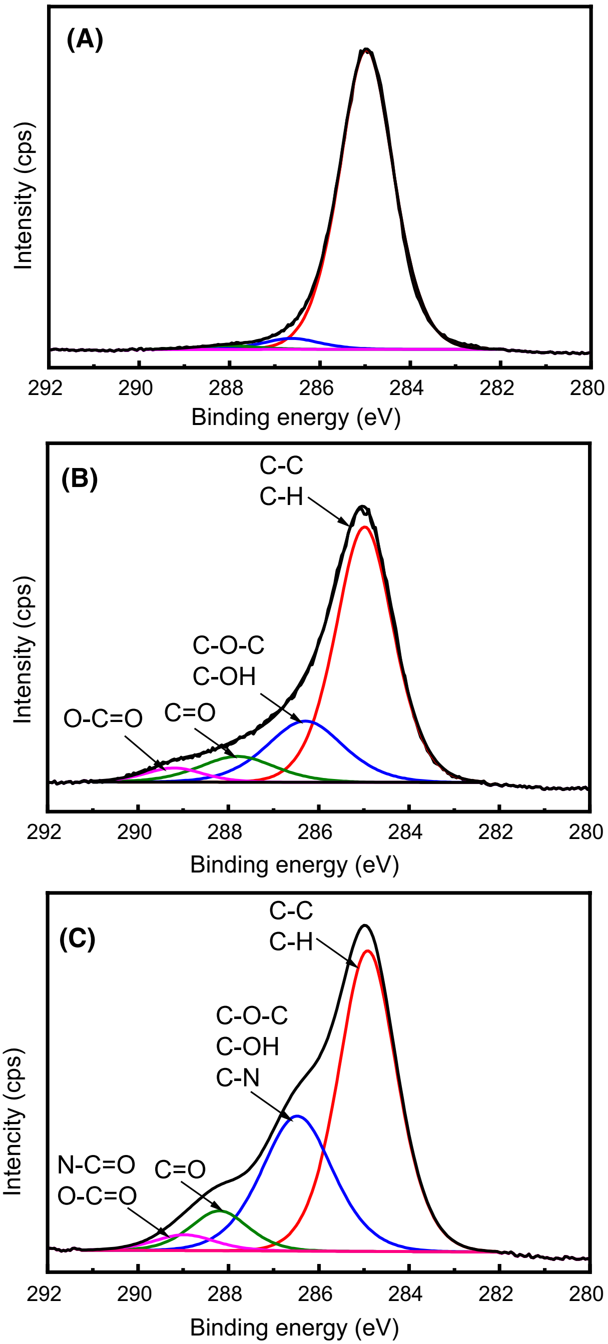
FTIR analysis provides complementary information. The FTIR-ATR spectrum of untreated PP (Fig. 7a) shows peaks at 2950 cm^{-1}, 2920 cm^{-1} and 2840 cm^{-1}, which correspond to CH_3 and CH_2 stretching, as well as characteristic peaks in the region of 800–1500 cm^{-1}. After air plasma processing, the appearance of extra signals at 1720 cm^{-1} and 1640 cm^{-1} corresponding to C=O stretching vibration indicates the effect of surface oxidation (Fig. 7b). The mechanism of surface oxidation after the atmospheric pressure air plasma treatment is supposed to be similar, as was repeatedly published [16, 23, 26]. Finally, the spectrum of PP foil with immobilized chitosan (Fig. 7c) is characterized by the presence of characteristic peaks in the range of 800–1200 cm^{-1}, corresponding to vibrations in pyranose rings. The bands at 1655 cm^{-1} and 1550 cm^{-1} correspond to amide I and amide II, respectively, and a wide band in the region of 3100–3600 cm^{-1} belongs to the overlapping stretching vibrations of amines and hydroxyls. Thus, FTIR-ATR spectra directly confirm the formation of the chitosan layer on the surface of PP.

The scheme of surface treatment of PP by atmospheric pressure air plasma has been previously described in work [30]. Atomic oxygen $O(^3P)$, electron excited molecules $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$, and ozone molecules are supposed to be responsible for the oxidation of PP surface. Nevertheless, the impact of $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ molecules in the oxidation of PP surface is negligible due to high quenching rates. In accordance with estimations published for atmospheric pressure plasma jets and in literature, the concentrations of these species in the plasma are high enough for $O(^3P)$ ($\sim 10^{14}$–10^{16} cm^{-3}) and for O_3 (10^{14}–10^{15} cm^{-3}), respectively [31–35]. The full set of reactions typical for the atmospheric pressure air plasma can be found in [30, 35]. In current work, the most important reactions of $O(^3P)$ formation and recombination are presented. The generation of atomic oxygen mostly occurs in the dissociation of O_2 molecules by electron impact and metastable $N_2(B^3\Pi_g)$ и $N_2(A^3\Sigma_u^+)$ impact. Moreover, $O(^3P)$ can be formed in the quenching reactions of excited state $O(^1D)$ by oxygen and nitrogen molecules.

$$O_2 + e \longrightarrow O\left(^3P\right) + O\left(^3P\right) + e$$

$$N\left(^4S\right) + NO \longrightarrow N_2(X, V = 11) + O\left(^3P\right)$$

Fig. 6 XPS spectra of: **a** untreated PP foil; **b** PP foil treated by air plasma jet for 60 s and **c** PP foil with chitosan immobilized using solution plasma processing



$$N_2(A^3S_u^+) + O_2 \longrightarrow N_2 + 2O\left(^3P\right)$$

$$N_2(B^3P_g) + O_2 \longrightarrow N_2 + 2O\left(^3P\right)$$

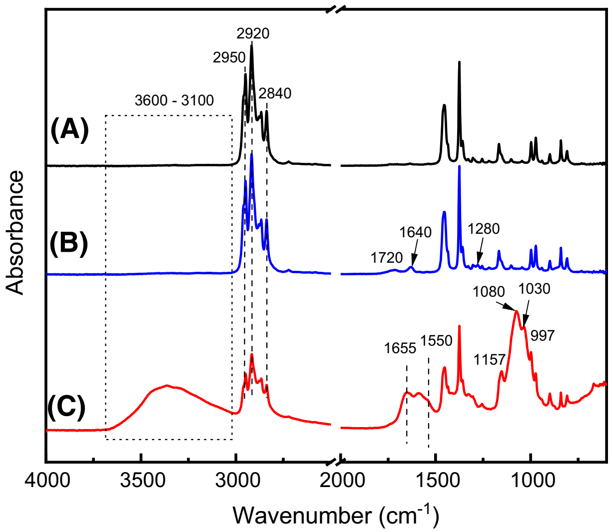


Fig. 7 FTIR-ATR spectra of: **a** PP original foil; **b** PP foil after 60 s treatment by air plasma jet and **c** PP foil with chitosan, immobilized on the surface

$$O(^1D) + O_2 \longrightarrow O(^3P) + O_2(b^1S_g^+)$$

$$O(^1D) + O_2 \longrightarrow O(^3P) + O_2$$

$$O(^1D) + N_2 \longrightarrow O(^3P) + N_2$$

The most probable pathways of $O(^3P)$ recombination are reactions with electron excited $O_2(b^1\Sigma_g^+)$ molecules, water molecules, and vibrationally excited N_2 molecules.

$$O(^3P) + e \longrightarrow O(^1D) + e$$

$$O_2(A^3S_u^+) + O(^3P) \longrightarrow O_2 + O(^1S)$$

$$O_2(b^1S_g^+) + O(^3P) \longrightarrow O_2 + O(^1D)$$

$$O(^3P) + H_2O \longrightarrow OH^{\cdot} + OH^{\cdot}$$

$$O(^3P) + N_2(X, V) \longrightarrow NO + N$$

It should be noted that for the most part processes characteristic of the plasma zone could not occur in the afterglow, especially electron impact reactions and all reactions with ions. Therefore, the concentration of atomic oxygen $O(^3P)$ should decrease with distance from plasma. The results of modelling published in [32, 36] show the decrease of $O(^3P)$ concentration down to 10^{12}–10^{14} cm^{-3} at distances up to 50 mm from plasma, which is also relatively high. Moreover, it can be found in both publications that ozone molecules are generated in the afterglow. The concentration of O_3 increases by several orders of magnitude. Additionally, in work [37] the lifetime of $O(^3P)$ was estimated as $\sim 10^{-5}$ s. Under current experimental conditions, the time of transport for active species from the plasma to the sample surface was estimated as $\sim 5 \times 10^{-6}$ s. Therefore, we can conclude that $O(^3P)$ atoms as well as ozone molecules could be responsible for the oxidation of PP and formation of carbonyl and carboxyl functional groups, which subsequently attach molecules of chitosan.

Conclusions

A combination of treatment by the afterglow of an atmospheric pressure glow discharge with subsequent immersion in chitosan solution in a cycling process results in the effective immobilization of chitosan onto the polymer surface. It was successfully demonstrated for polypropylene foil. The chitosan solution forms a thin liquid layer on the PP surface, which protects it from the excessive damage by the plasma. The biopolymer accumulates on PP in the form of island-like structures, which are distributed on the area subjected to the plasma action. The width of the surface area covered by chitosan is relatively small, which makes local modification possible. XPS and FTIR analysis reveals the presence of characteristic chemical groups confirming the success of chitosan immobilization on PP surface.

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