Surface Modification of Polycaprolactone Monofilament by Low Pressure Oxygen Plasma

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ABSTRACT: Surface modification of polycaprolactone filament has been carried out using a low pressure oxygen plasma to introduce active centers in the form of radicals, peroxides, and hydroperoxides on the surface. Evaluation by 2, 2-diphenyl-1-picrylhydrazyl method shows that there is an optimum value of exposure time, gas pressure, and discharge power for the generation of the maximum concentration of such groups. The plasma exposure time was thereafter varied to study the extent of the surface modification introduced by the plasma. It was found that only a short time of exposure to the oxygen plasma was necessary to make the surface highly wettable and polar with increased surface energy and work of adhesion. Surface chemical analysis by X-ray photoelectron spectroscopy revealed that this happens because of oxidation of the top layer of the filament, which occurs primarily by the breaking of bonds and incorporation of oxygen containing functionalities. Morphological and topographical observations by scanning electron microscopy and atomic force microscopy revealed that etching is pronounced at longer exposure times leading to a rougher surface with hill-valley features. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Polycaprolactone (PCL) has been the material of choice for drug delivery and tissue engineering applications on the ground of its ease of processability, good biocompatibility and slow resorbablity.[1,2] However, there are problems with the PCL surface in terms of hydrophobicity as well as poor cytocompatibility. Cheng et al. have shown that human dermal fibroblast and human myoblast cells show poor cell attachment and proliferation on PCL surface.[3] Zhu et al. have found very similar observations on endothelial cell culture on PCL membrane.[4] One way to overcome this impediment is to functionalize the surface keeping the bulk properties intact. Out of various strategies to modify the surface, the low pressure plasma based modification is particularly interesting in that modification process is limited to surface region only and even a complex shaped scaffold of very delicate polymer can be modified easily in a cleaner way.[5]

Plasma treatment using non-polymerizable gases such as Ar, N_2, O_2, and CO_2 is able to alter surface wettability, and may alter topography and morphology of polymeric systems. However, it does not result in the generation of proper, unique functionality on the surface which may be required for biomolecule immobi-

lization. Techniques which modify the surface by generating nonspecific functional groups are of less significance from the point of view of bioconjugation of polymer.[6,7] Plasma-induced grafting holds the key here. Plasma-induced grafting using vinyl monomers and surface bound initiators offers a way to tailor the surface with selective functional groups in a controlled fashion.[8] Monomers such as acrylic acid (AA), methacrylic acid (MMA), vinyl phosphonic acid (VPA), and vinyl sulfonic acid (VSA) have been grafted onto PCL via free radical polymerization following the plasma treatment.[3,4,9] Each active center (radical, peroxide or hydroperoxide), generated as a result of plasma treatment, is the potential site for initiating graft polymerization. Cheng et al. and Zhu et al. have shown that concentration of immobilized collagen/gelatin is largely dependent on the degree of grafting.[3,4] Saxena et al. have found that degree of grafting very closely follows the peroxide concentration.[8] Since, concentration of active centers plays a significant role on the degree of grafting, it becomes very important to optimize it. Several parameters, such as apparatus, discharge and procedural parameters can influence the plasma treatment at the same time.[10] Zhang et al. have found that longer exposure and higher power do not yield more peroxides on polyurethane films.[11]

Also, peroxide concentration has been found to be intrinsically associated with the gas pressure.[12] Concerning the importance of these parameters, the present work aims to optimize concentration of active centers onto PCL filament by varying process parameters, such as plasma exposure time, gas pressure and discharge power. Since, the plasma treatment includes a number of concurrent processes such as functionalization, etching, degradation, and cross-linking; it becomes interesting to study the surface properties as a function of time as the sample is exposed to oxygen plasma near the optimized point. The extent of modification is characterized by contact angle, spectroscopic, and microscopic techniques.

EXPERIMENTAL

Materials

Polycaprolactone (PCL), $M_v \sim$ 70,000–80,000 (determined by viscometry) used for this study was supplied by Sigma-Aldrich Chemicals. Monofilaments were prepared by melt spinning of polymer at 210°C and were collected at a circular speed of 38 m/min by passing through a cooled water bath at 4°C. This was followed by drawing at an overall draw ratio of 7 and heat setting in taut condition at 48°C in a water bath for 10 min. The diameter of the final filament was 127 $\pm$ 3 μm.

Methanol from Merck (India) was used for washing filaments prior to the plasma treatment. The filaments were later dried at room temperature under reduced pressure for 24 h. O$_2$ gas cylinders used for plasma generation were purchased from a local supplier. 2, 2-Diphenyl-1-picrylhydrazyl (DPPH) used for peroxide estimation was procured from Fluka.

Liquids used for contact angle measurements were deionized water (purified by Millipore Water Purification System) and formamide (procured from G. S. Chemical Testing Lab & Allied Industries, New Delhi). These were used as received.

Plasma Treatment

Plasma treatment of PCL monofilaments was carried out under oxygen plasma in a capacitively coupled RF reactor operating at 13.6 MHz.[13] The monofilament was mounted in a zig zag manner over a sample holder and rotated at 40 rpm by a motor to ensure homogeneous plasma treatment.[14] The cylindrical vessel was first evacuated to 10^{-5} Torr and then oxygen gas was introduced under the control of mass flow controller. Variables for plasma treatment were—exposure time (0–120 s), gas pressure (10–100 mTorr), and discharge power (10–90 W). Finally, the valve was opened and sample was exposed to ambient atmospheric air. Within 5 min of plasma treatment, it was subject to subsequent analysis.[12]

Determination of Active Centers' Concentration

The concentration of active centers formed on the PCL surface after oxygen plasma treatment was determined using DPPH method.[8,15] The samples were placed in glass ampoules of 10 cm^3 containing 1 $\times$ 10^{-4} M deaerated toluene solution of DPPH. The ampoule was kept at 70°C for 2 h to accomplish the reaction. The DPPH molecules consumed were calculated spectrophotometerically by Perkin–Elmer's UV–visible Lambda 35 from the difference in absorbance at 520 nm between the control and plasma-treated sample, and a calibration plot of concentration of DPPH vs. absorbance. Error bars were calculated by taking measurements on at least 10 samples.

Contact Angle Measurements

Dynamic contact angle measurements on individual filaments were performed under ambient conditions using DCAT 21 Tensiometer from Dataphysics. Two liquids selected for contact angle measurements were deionized water and formamide. The filament was placed onto the sample holder and was immersed into and withdrawn out from the liquid while simultaneously measuring the force acting on the filament. The contact angle was obtained from the force and diameter of the filament by in-built software based on Wilhelmy technique.[16] At least five to six samples were taken for measurement of contact angle.

Surface energy calculations were performed from the values of advancing contact angles with two different liquids water and formamide using Wu's harmonic mean equation.[17]

$$\sigma_L(1 + \cos \theta_L) = 4\left(\frac{\sigma_L^d \sigma_S^d}{\sigma_L^d + \sigma_S^d} + \frac{(\sigma_L^p \sigma_S^p)}{\sigma_L^p + \sigma_S^p}\right) \quad (1)$$

where θ_L is the contact angle and σ_L, σ_L^p and σ_L^d are the total surface energy of a liquid and its polar and dispersive components respectively.[18] Total surface energy is related to its polar and dispersive components by the following equation:

$$\sigma_S = \sigma_s^p + \sigma_s^d \quad (2)$$

The work of adhesion was calculated using the Young–Duprě equation: [19]

$$W_A = \sigma_L(1 + \cos \theta) \quad (3)$$

where W_A is work of adhesion (in mN/m), θ is the contact angle and σ_L is the total surface energy of the testing liquid.

X-Ray Photoelectron Spectroscopy

The surface chemical analysis of the filament was carried out using X-Ray Photoelectron Spectroscopy (XPS). A Phi Electronics Quantum 2000 Scanning ESCA Microprobe was used for this purpose which operated with a monochromatic AlK$_\alpha$ X-ray source in a constant angle energy mode. The detection angle was 45°. Pass energy of 108 eV was used to record wide-scan spectra.

Surface Morphology and Topography

The surface morphology of silver coated filaments was studied using Zeiss EVO 50 scanning electron microscope (SEM) operating at 20 kV. The surface topography of filaments was examined in air at room temperature by atomic force microscopy (AFM) imaging using Solver Pro SPM (NT-MDT, Russia). It operated in the semicontact mode using a NSG 10 series tip. Five to ten different locations, free of any manufacturing defect, on each sample were analyzed and roughness observations were quantified in terms of RMS values, S_q from Nova 1.0.26.1644 software. Ten point height, S_z was also obtained from the same software. Scanning size of each image for comparison was kept 2.5 μm $\times$ 2.5 μm and these were scanned at a rate of 1 Hz.

RESULTS AND DISCUSSION

Optimization of Active Centers' Concentration

Oxygen plasma has been reported to introduce active centers on the surface of various polymers and has been evaluated by DPPH method.[12,14] It becomes interesting to know what happens to their content on the surface of PCL when factors affecting plasma treatment are varied. Figure 1(a) shows the effect of plasma exposure time on the consumption of DPPH by unit area of surface. With the increase in the plasma exposure time, their concentration on the surface increased rapidly; passed through a maximum at 35 s, and then decreased slowly. Thus, longer exposure did not result in the generation of more active centers on the surface. Similar observations on treatment of polymers had been made by several workers and maximum in peroxide concentration have been found to be 30 s for polyurethane (PU) film, 40 s for polycarbonate (PC) membrane, and 3 min for high density polyethylene (HDPE) sheets.[11,15,20] This phenomenon has been explained by considering that produced peroxides are partly converted into inactive species which do not yield radicals, even after prolonged plasma exposure.[15] Considering the mechanistic studies of plasma modification in the presence of oxygen gas, the initial rapid increase may be due to creation of more macro radical sites by plasma created species or vacuum ultraviolet radiations (VUV).[14,21] These active sites react fast with oxygen molecules to form peroxy radicals which may create hydroperoxides by abstraction of hydrogen during plasma exposure or by reaction with humid air in the post plasma process.[21–23] During plasma exposure, abstraction of hydrogen is a relatively slow process. Thus, it is quite likely that these reactive radicals participate in other reactions which do not result in creation of active centers. This is further complicated by the fact that PCL containing ester is quite susceptible to etching and degradation in oxygen plasma which would increase further with the exposure time.[17,24] Thus, as a result of various competing processes; a maximum in the active centers' concentration with the plasma exposure time was expected. The optimum exposure time was found to be at 35 s. Interestingly, this observation is in contrast to our earlier studies on polypropylene (PP) filament where the peroxide concentration increased with the exposure time.[8]

The effect of gas pressure on active centers concentration is presented in Figure 1(b). Here, the optimum pressure was found at 70 mTorr. Explanation is associated with number of reactive plasma particles and their kinetic energy. The mean free path and kinetic energy of plasma particles are closely dependent on the gas pressure and, for a given power feed, increase with the decreasing pressure.[25] At very low pressure, there will be less number of active plasma particles which can cause surface modification. At very high pressure, the intensity of collisions among plasma particles increases. This decreases their mean free path and kinetic energy, and therefore, the particles loose kinetic energy before colliding with the surface, resulting in less generation of active sites.[26] Further, the plasma is unstable at very high pressure and sample may be damaged by heat.[11] Thus, it is expected that there will be maximum surface modification at an intermediate pressure. Such a maximum was actually observed when the gas pressure was varied from 10 mTorr to 100 mTorr at 40 W power and 35 s treatment time.
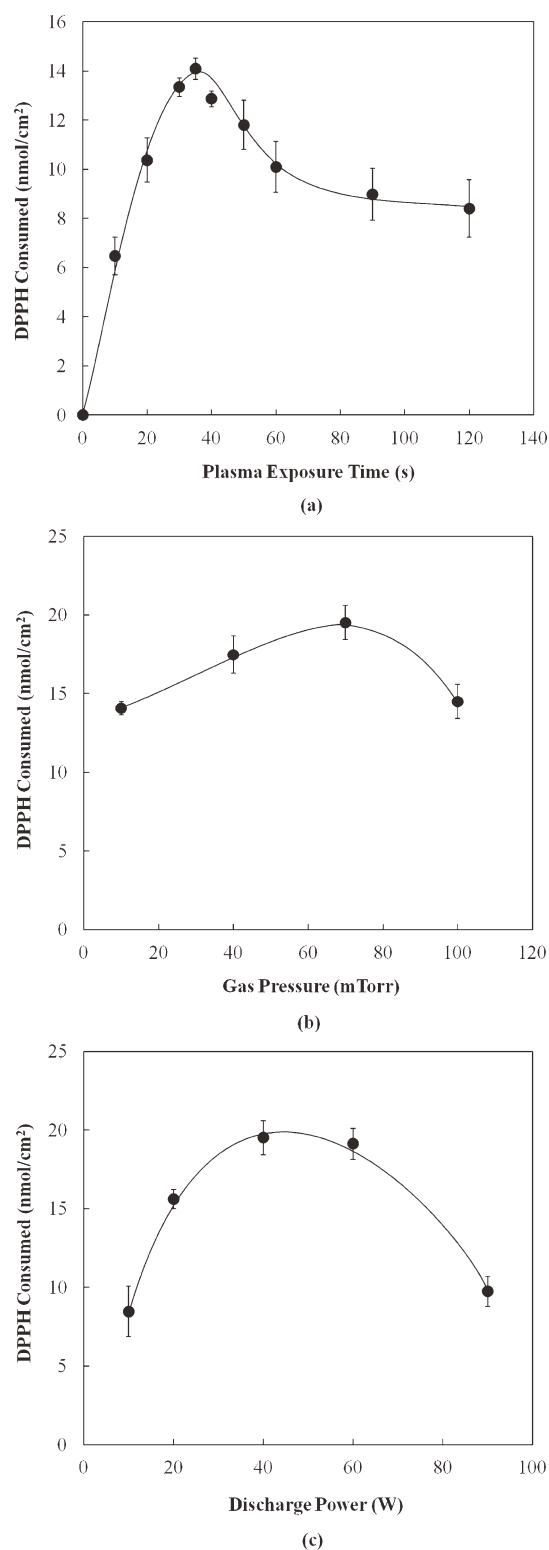

Figure 1. (a) Effect of the plasma exposure time on DPPH consumption. Plasma treatment conditions: Discharge Power: 40 W, Gas Pressure: 10 mTorr, Air exposure: 5 min; (b) Effect of the gas pressure on DPPH consumption. Plasma treatment conditions: Plasma Power: 40 W, Plasma exposure: 35 s, Air exposure: 5 min; (c) Effect of the discharge power on DPPH consumption. Plasma treatment conditions: Gas Pressure: 70 mTorr, Plasma exposure: 35 s, Air exposure: 5 min.
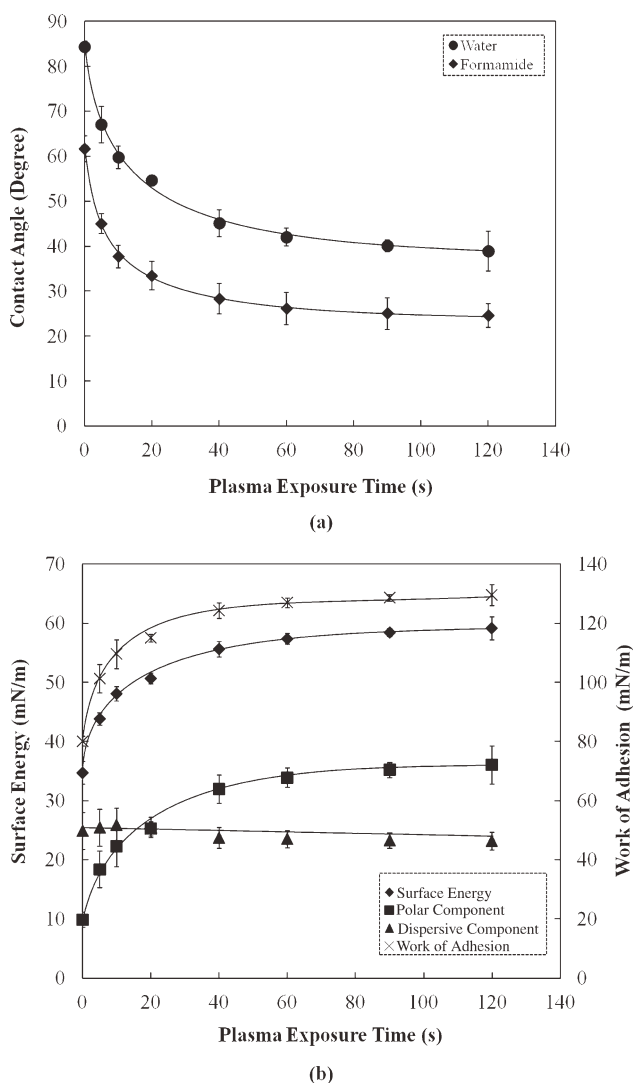
(a)

(b)

Figure 2. (a) Effect of the plasma exposure time on contact angle of PCL filament with deionized water and formamide under ambient conditions. Sample preparation conditions: Plasma discharge power, 40 W, Gas Pressure: 70 mTorr; (b) Effect of the plasma exposure time on surface energy, polar component, dispersive component and work of adhesion, W_A of PCL filament.

The effect of the plasma discharge power on concentration of active centers is shown in Figure 1(c). The maximum concentration was observed at 40 W of discharge power. With the increase in the discharge power, their concentration increased. This is due to transfer of more energy to the gaseous medium which causes an increased rate of excitation or the increased rate of initiation. After 40 W of discharge power, the active centers' concentration decreased, indicating the passivation of active species on the polymer surface.[11,27] Hence, the optimized plasma treatment conditions for the generation of maximum concentration of active centers were 35 s plasma treatment time, 70 mTorr gas pressure and 40 W discharge power. These optimal conditions were used to prepare samples for further experiments; however, plasma exposure time was varied.

Hydrophilic Analysis: Contact Angle, Surface Energy, and Work of Adhesion Measurements

Contact angle is a relatively simple, sensitive, and rapid technique to monitor the wettability of a solid surface following any treatment.[28] Measurements of advancing contact angle with two different liquids, deionized water and formamide, are presented in the Figure 2(a). Untreated PCL filament's advancing contact angles with deionized water and formamide were 84° and 61° respectively. Interestingly, a short exposure of oxygen plasma for 20 s could bring down the advancing contact angle with deionized water from 84° to 54°. Advancing contact angle followed a decreasing trend with the increase of plasma exposure time. However, decrease was rather slow after 40 s of plasma exposure. This means that the most of the wettability enhancement occurred during first few seconds of plasma treatment and thereafter the effect was less pronounced.

The decrease in contact angle is indicative of changes in surface energy taking place at the filament's surface. In order to interpret these changes, surface energy calculations were performed using Wu's harmonic equation and values of advancing contact angles.[17] The untreated filament had low surface energy of 34.7 ± 1.9 mN/m, major part of which came from the dispersive component (24.8 ± 3.1 mN/m, 72%) as shown in the Figure 2(b). Surface energy and polar component (9.8 ± 1.3 mN/m, 28%) increased initially with exposure time which then finally saturated at a final value of 59.1 ± 1.9 mN/m for surface energy of which polar component constituted 35.9 ± 3.2 mN/m (60%), while dispersive component remained almost unaffected in the whole process. This suggests that polar component is primarily responsible for increase in total surface energy with plasma treatment. Hence, the surface of polymer became more polar after plasma treatment. Very similar observations have been reported by Hirotsu et al. while studying the effect of the oxygen plasma treatment on the blended sheets of PCL/PC.[29]

Surface energy is an important factor which affects several surface and interfacial properties, such as adsorption, wetting, and adhesion.[30] Increase in total surface energy can be an indication of increasing adhesive force. Work of adhesion increased with the plasma treatment time and finally saturated near 40 s with a final value of 129.5 ± 3.5 mN/m at 120 s.

Chemical Composition Analysis: XPS Observations

In order to elucidate changes in chemical composition arising out of plasma treatment on top surface of PCL filament, XPS

Table I. XPS Data of the Oxygen Plasma-Treated PCL Filament

Sample no.	Time (s)	Atomic concentrations (%)	
		C	O
1	0	75.1	24.9
2	10	74.0	26.0
3	20	67.5	32.5
4	40	65.9	34.1
5	60	64.5	35.5
6	90	66.9	33.1
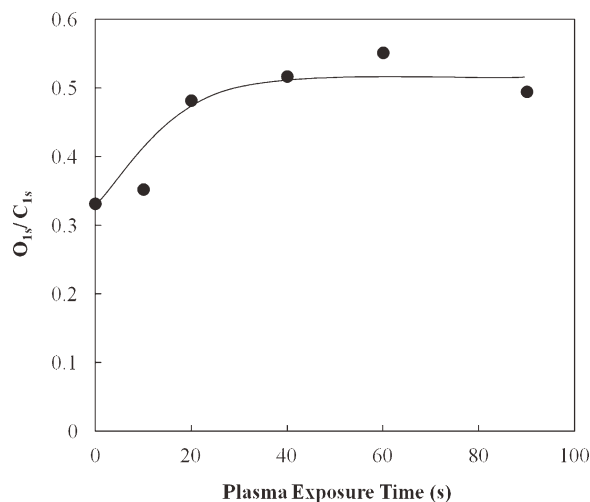
Figure 3. Variation of O_{1s}/C_{1s} ratio with the plasma exposure time.

high as 0.5. Interestingly, most significant increment occurred within 40 s of plasma treatment. This is consistent with decrease in contact angle and increase in surface energy with treatment time. Thus introduction of oxygen in the topmost surface is primarily responsible for wettability enhancement.[31,32] Incorporation of oxygen can be explained in two ways—one is the direct reaction of polymer with oxygen plasma in the chamber, and the other is the reaction of generated active sites with air and water vapor.[33]
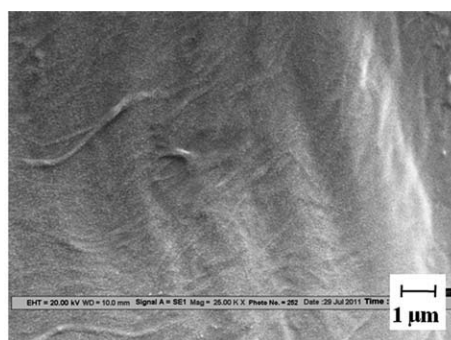
Morphological and Topographical Analysis: SEM and AFM Observations

SEM micrographs of pristine and plasma-treated samples show pronounced differences in surface morphological features (Figure 4). An exposure of oxygen plasma for 40 s showed very little changes from that of untreated one. However, at longer plasma exposure, surface roughness became dominant feature and increased more with plasma exposure time.
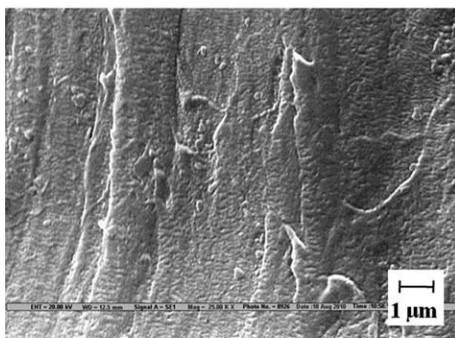
These observations were supported by AFM. AFM image of pristine filament shows relatively flat surface with presence of fibrils in the direction of filament long axis (Figure 5). As the plasma exposure time increased, the surface started filling with small conical protrusions. Further, these conical protrusions became nano hills whose ten point height (S_z), which expresses surface roughness by selecting five maximal heights and hollows, increased with exposure time and fibrillar features were superseded by newly developed nano hills and valleys (Figure 6).
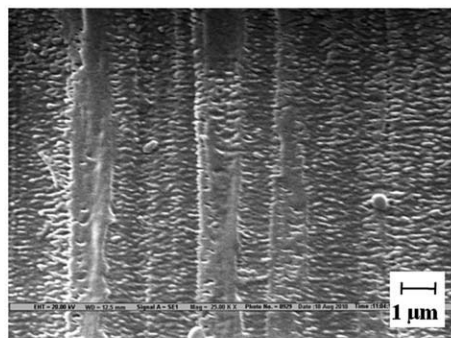
analysis was carried out. Wide scan survey of PCL filament revealed that C and O are the main elements present on untreated and plasma-treated filaments from the values of Table I; however, percentage atomic concentration of O and C changed with treatment time. Figure 3 shows the variation of O_{1s}/C_{1s} with treatment time. Pristine PCL filament has the same ratio as expected from stoichiometry of monomeric unit of PCL. After 90 s of plasma treatment O_{1s}/C_{1s} ratio became as

(a) Pristine PCL

(b) Plasma Treatment, 40 s

(c) Plasma Treatment, 90 s

(d) Plasma Treatment, 120 s

Figure 4. SEM of PCL filament exposed to oxygen plasma for different treatment times: (a) pristine PCL; (b) plasma treatment, 40 s; (c) plasma treatment, 90 s; (d) plasma treatment, 120 s. Sample preparation conditions same as in Figure 2.

Figure 5. AFM of PCL filament exposed to oxygen plasma for different treatment times: (a) pristine PCL; (b) plasma treatment, 40 s; (c) plasma treatment, 90 s; (d) plasma treatment, 120 s. Sample preparation conditions same as in Figure 2.
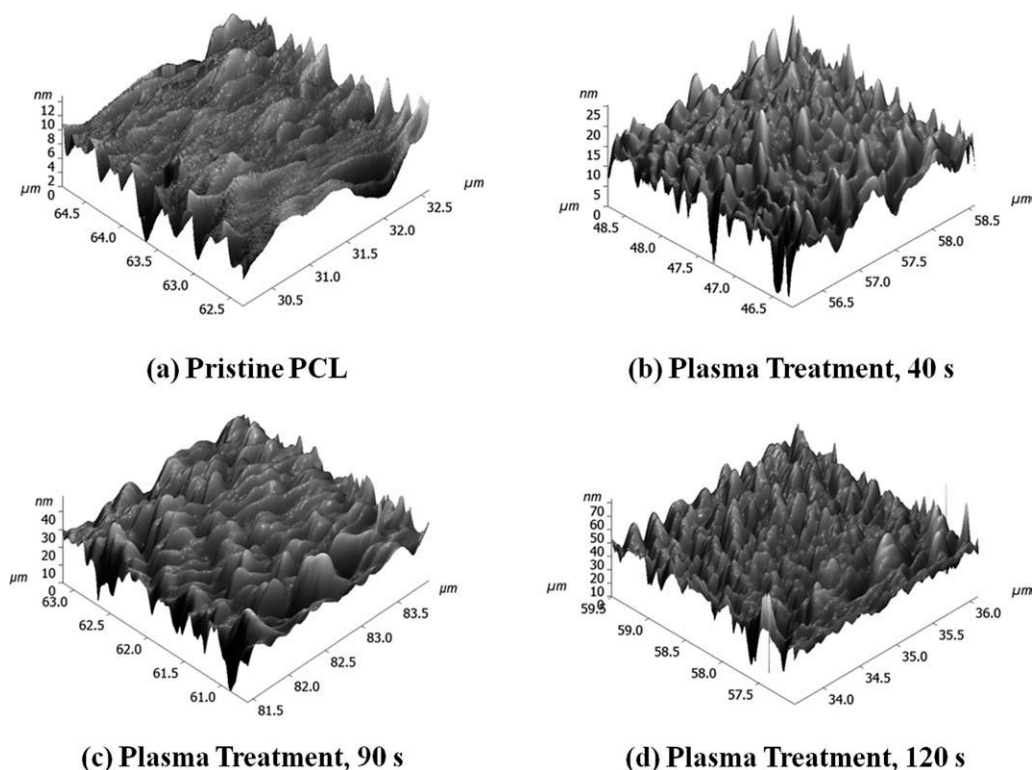
These developments were reflected in quantification of surface roughness in terms of RMS values (S_q) and ten point height (S_z) as shown in Figure 6. RMS surface roughness of untreated filament was 1.2 ± 0.1 nm, which increased rapidly with exposure time, especially after 40 s (2.4 ± 0.5 nm). At 90 s, it was 4.1 ± 0.4 nm, which finally reached to 5.5 ± 1.0 nm at 120 s. The values for ten point height (S_z) also increased from 7.1 ± 1.5 nm for untreated one and kept increasing with plasma exposure time within the studied range. It was 16.1 ± 3.2 nm at 40 s, 27.2 ± 6.8 nm at 90 s and reached to 30.6 ± 6.8 nm at 120 s. These may be due to several factors, such as melting because of an increase in the surface temperature, degradation of polymer surface and more importantly anisotropic etching effect of oxygen plasma.[34,35]

CONCLUSIONS

Surface of the PCL filament has been modified by the application of low pressure oxygen plasma treatment. Active centers generated on the surface have been optimized by varying exposure time, gas pressure, and discharge power. There is an optimum value of exposure time, gas pressure and discharge power to obtain maximum concentration of active centers which comes out at 35 s, 70 mTorr, and 40 W. As a result of plasma exposure, surface hydrophilicity improves, surface energy, and work of adhesion increase with treatment time. This is primarily due to incorporation of oxygen containing polar functionalities on the surface as observed by XPS and contact angle analysis. SEM and AFM observations further reveal that plasma treatment transforms morphology and topography of PCL filament significantly with exposure time from relatively smooth surface to rough surface with prominent hill-valley feature.

Figure 6. Effect of the plasma exposure time on root mean square roughness, S_q and ten point height, S_z.

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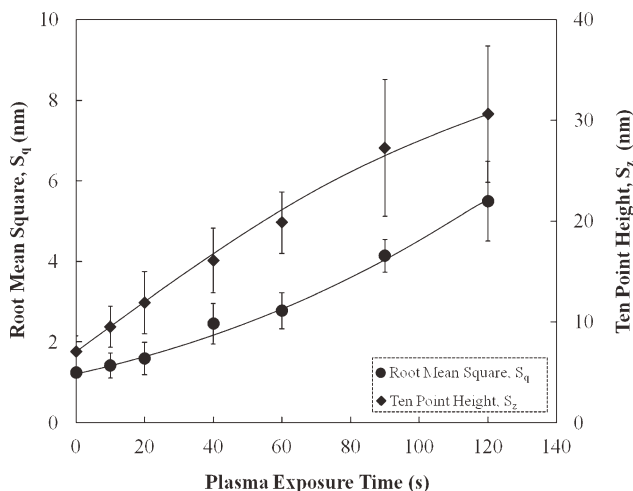2. Pitt, C. G. Biodegradable Polymers as Drug Delivery Systems; Marcel Dekker: New York, **1991.**

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