A comparison of plasma and electron beam-sterilization of PU catheters

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Abstract
Polyurethane (PU) catheters made of Pellethane 2363-80AE® were treated in two different ways: a new treatment with low temperature plasma that could be used to decontaminate reusable polymer devices in hospitals, and an e-beam (EB) irradiation. Polymer structure and bulk properties were studied by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), infrared spectroscopy (FTIR) and size exclusion chromatography (SEC). Although PU was strongly modified by the e-beam irradiation leading to branching of polymer chains, it had no or little impact on the thermo-mechanical properties of the catheters and on the hard/soft segment organization of PU. For plasma-treated samples, no modification in the polymer bulk was observed, confirming that plasma treatment might be considered as an alternative to e-beam irradiation. The analysis of surface modifications showed an evolution of superficial topology and chemical composition (grafting of oxygen and nitrogen species) of the catheters after treatment, with a more polar and hydrophilic surface.

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1. Introduction
PU is often used in medical devices because of its interesting mechanical and chemical properties as well as its biocompatibility (Pinchuk, 1994; Ulrich and Bonk, 1984). Some of these properties are due to the segmented structure of PU with hard (diisocyanate and polyl) and soft segments (polyether/polyester). These segments are only partly miscible and organize themselves into microdomains with different levels of organization (Seymour and Cooper, 1973). Polyurethane cannot be sterilized by steam autoclaving, because this process may induce degradation and loss of shape. Electron beam radiation is a possible means of sterilization, but hospitals usually do not have e-beam at their disposal. Moreover, irradiation is known to produce changes in the bulk polymer, such as scission, cross-linking and oxidation of polymer chains (Chapiro, 1995). For PU, different kinds of degradation processes may occur. For example, the formation of quinoid structures in the polymer (Ravat et al., 2001a, 2001b, 2000) and photo Fries rearrangement with C–N cleavage (Wilhelm et al., 1998) were reported. Low temperature plasma appears to be a good alternative to existing sterilization processes. Plasma treatment is known to change the surface structure through etching or grafting, but generally, it does not significantly damage the material in bulk (Gorna and Gogolewski, 2003b). It is cheap and easy to use, and allows reusing of expensive medical devices such as endoscope tubular sheaths.

In this paper, we describe polymer modifications observed after treatments by a cold nitrogen atmospheric plasma (Ganciu et al., 2003) and an electron beam irradiation. We focused on the following:
- Chain degradation, by evaluating branching, scission and cross-linking of the polymer chains, as these degradation processes might generate potential leachables like oligomers and change the mechanical properties of the catheter.
- Hard/soft segment reorganization.
- Degradation of the additives that could reduce polymer stability and create potential toxic and leachable compounds.
- A preliminary study on surface modifications induced by plasma treatment.

2. Experimental
2.1. Polymer

The polyurethane studied is a Pellethane 2363–80AE® (Dow Chemical). It is a poly(etherurethane) with aromatic groups. Soft segments are polyethers based on the poly(tetramethylene glycol). Hard segments are constituted of urethane groups.
(derived from methylene diphenylisocyanate) and of a chain extender (1, 4-butanediol) (Fig. 1). The polymer was supplied in the form of catheters by the company Vygon, Ecouen, France. The catheters studied had an external diameter of 4 mm, and their wall thickness was 0.75 mm.

2.2. Plasma

We used a new atomic nitrogen source created by the “Physique des Gaz et des Plasma” Laboratory at Univ Paris-Sud 11, France (Ganciu et al., 2003). The pulsed corona discharge was produced between needles. The experiment was conducted in nitrogen at atmospheric pressure and at a voltage of about 10 kV; a frequency of around 10 kHz and a mean power of 15 W. The nitrogen source was an alphagaz (Air Liquide) nitrogen bottle (water < 3 ppm, O₂ < 2 ppm and C₆H₆ < 0.5 ppm) with a nitrogen flow of 40 L/min. A significant amount of atomic nitrogen was produced and propagated over a long distance (Larbre et al., 2004). It was thus able to decontaminate surfaces in the afterglow area (Pointu et al., 2005). Three 30 cm-long catheters were treated together, in such a way that only the external surface was exposed to plasma and treated. The catheters were threaded on a quartz support and closed by quartz caps at the open extremity (Fig. 2). The duration of the treatment varied from 10 to 150 min.

2.3. Irradiation

Samples were irradiated by a 10 MeV electron accelerator at the company Ionisos, (Orsay, France) using 10-kW power. The samples were exposed to 3 different irradiation doses: 25, 75 and 150 kGy; all irradiations were done in steps of 25 kGy.

2.4. Additive extraction

In order to quantify and identify the phenolic antioxidants present in the polymer, we used a dissolution/precipitation process. 3 g of polymer were dissolved at reflux at around 50 °C in 50 mL of THF (HPLC grade Carlo Erba). After complete dissolution, polyurethane was precipitated by slowly adding 100 mL of cold methanol (Carlo Erba HPLC grade) while stirring. Polyurethane was removed from the solution containing additives by filtration on paper and the precipitate was carefully rinsed with methanol. The solution was then evaporated with a rotavapor at 60 °C (under vacuum) in order to obtain a dry residue potentially containing additives, oligomers and degradation products. Five extractions were made on each type of sample.

To estimate the amount of lubricant (ethylene bis stearamide) in the polymer, an extraction at reflux with ethanol was carried out while stirring (10 g of PU in 250 mL of ethanol). After 2 days of extraction, the polymer was separated from the extraction solution, which was then evaporated. The dry residue was a mixture of PU oligomers and lubricant. It was purified by adding THF to dissolve the oligomers. Ethylene bis stearamide (EBS) powder was obtained after centrifugation of the THF solution. The EBS residue was controlled by FTIR analysis and weighed. Oligomer fractions in THF and EBS powder were almost pure (FTIR analysis). Two extractions were carried out on non-treated samples.

2.5. Antioxidant analysis

The solution was filtered on a 0.45 μm Teflon filter. The chromatographic apparatus was made up of a gradient pump (Spectrum Systems P4000 (TSP), with a flow rate of 1 mL/min), an automatic injector AS 3000 Spectra System (TSP), and an UV detector Spectra System 6000 (TSP); the detector was a photodiode array ranging from 210 to 350 nm. The column was a LiChrocart 250–4 RP select B (5 μm) LiChrosphere (Interchim) and the injection volume was 20 μL. Data acquisition was made using the Chromquest software (TSP, version 3.0). Identification of the additive was performed by comparing retention times of pharmaceutical additive standards (different kinds of Irganox® from Ciba and BHT from Sigma, all belonging to the positive list of European Pharmacopoeia (EDQM, 2007)) with the retention times of the peaks found on the chromatogram of the extracted solutions. Quantification was carried out by constructing a calibration plot with several standard concentrations. We used an HPLC method which had been previously developed in our laboratory in order to analyze additives in pharmaceutical polymers. This method uses three mobile phases composed of a mixture of one up to five solvents (methanol, acetonitrile, THF, water and ethyl acetate, all HPLC grade), and a gradient elution that consists of linear gradients from one mobile phase to another.

2.6. FTIR

The spectrometer apparatus was a Perkin Elmer Spectrum 2000. It was used in the ATR mode with a diamond crystal (golden gate-Specac) and in transmission mode. The ATR was used for analyzing the external surface of the catheter (the catheter was pressed on the crystal). Analysis in transmission was made on films obtained by casting: a catheter was dissolved in THF and solution was cast onto glass before THF evaporation. We used the height of the band to express its intensity. The wavelength range was from 4000 to 600 cm⁻¹ with a resolution of 4 cm⁻¹ and 16 scans. Spectra were performed on five different samples.
2.7. Differential scanning calorimetry (DSC)

DSC scans were performed on a TA Instrument Q1000 and on a Perkin Elmer DSC7. The temperature range investigated was between 40 and 220 °C. Aluminium pans were used. The heating rate was 20 °C/min. Polymer mass was between 5 and 15 mg. Five different samples of each type were analyzed.

2.8. Thermogravimetric analysis (TGA)

TGA was used to study polymer degradation. Two apparatuses were used, a Perkin Elmer TGA7 and a TA Instrument Q500. The temperature range was between 35 and 800 °C under a nitrogen blanketing. The scanning heating rate was 20 °C/min. Three different samples of each type were analyzed.

2.9. Size exclusion chromatography (SEC)

Three SEC columns from Polymer Laboratories were used: two mixed-B 10 μm columns (300 mm × 7.5 mm) and one PLgel 10 10 μm (pore size: 100Å) column (300 mm × 7.5 mm). The columns were thermostated at 30 °C in a Shimadzu CTO 10A oven. The solvent was THF with a flow rate of 1 mL/min. The pump was an HP 1050. The detector was a Jasco UV-1575 with the wavelength set at 254 nm (PU maximal absorption).

Toluene was added to the polymer solution (5 μL/mL of polymer solution) and used as a flow rate marker. Polymeric concentration was 1 mg/mL and the injected volume of the solution was 20 μL. Five injections were performed for each sample. Data were acquired through Azur software (Datalys) and treated by Cyrus software (Polymer Laboratories).

2.10. Wettability

Samples were analyzed during the few hours following treatment. Contact angle measurements were carried out after a liquid drop deposition, using a G40 (Krüss™, Germany) goniometer coupled to the Drop Shape Analysis DSAv1.80 software. Three liquids were used: diiodomethane (CH2I2, Merck Schuchardt OHG), ethylene glycol (HOCH2CH2OH, E. Merck Darmstadt), and milliQ water. Ten drops deposited on each tube sample of at least two liquids.

The solid (S)–liquid (Li) adhesion work

\[ W_{S,L} = \sigma_s + \sigma_{li} - \sigma_{sl} \]  

may also be written as

\[ W_{S,L} = \sigma_{li}(1 + \cos \theta_i) = 2(\sigma_s^p \sigma_{li}^d)^{1/2} + 2(\sigma_s^d \sigma_{li}^p)^{1/2} \]

where \( \theta_i \) is the contact angle between a droplet of the liquid in thermal equilibrium on a horizontal surface, \( \sigma_s \) the surface tension of the deposited liquid, and \( \sigma_{sl} \) the solid–liquid surface energy.

From Eq. (3) the polar and dispersive contributions to the solid surface energy may easily be calculated knowing \( \sigma_{li}^p \) and \( \sigma_{li}^d \) for at least two liquids.

2.11. X-ray photoelectron spectroscopy (XPS)

The apparatus is a Thermo Electron VG Escalab220XL located at the CEFS2 centre of the Institut Lavoisier de Versailles. X-ray excitation was provided by the AlKα line of a twin anode. Spectrometer calibration was performed using the Thermo Electron procedure and was completed by a self-consistent check on sputtered copper and gold samples based on the ASTM E902-94 recommendation. The binding energy position of the Au4f7/2 line was 84 eV.

Pass energies of 50 eV (survey spectra) and 20 eV (C1s, O1s and N1s) were chosen for the electron detection which is performed in a Constant Analyser Energy mode. Electrons are detected perpendicularly to the sample surface. Samples were analyzed only few hours after treatment and protected from air contamination before analysis by storage under vacuum after treatment. C/O and C/N atomic ratios were calculated with survey spectra using the respective peak areas corrected by the different sensitivity factors. Atomic ratios are obtained using the Thermo Electron “Avantage XPS software”. Curve fitting was performed by XPS peak4.1 (freeware written by Raymund Kwok). Energies were corrected by using the C1s for C–C bond at 285 eV.

2.12. Atomic force microscopy (AFM)

AFM was performed to image the surface modification of the catheter with plasma treatments. The AFM used is an apparatus of DIGITAL Instruments 3100, located at LMN (Laboratoire des milieux nanométriques, Evry Val d’Essonne University). The tapping mode was chosen to avoid mechanical modifications of the soft polymer surface. Several images were acquired and the root mean square roughness, \( R_q \), was calculated to 1 μm².

3. Results and discussion

3.1. Influence of the treatment on the degradation of the polymer

3.1.1. FTIR

Degradations in PU are generally studied by FTIR analysis. The C–O–C stretching vibration (1100 cm⁻¹) and methylene bands corresponding to ether functions decrease with ether scission (Wilhelm et al., 1998). Characteristic bands of degradation products such as formates appear at 1140 and 1725 cm⁻¹ (Wilhelm et al., 1998). If a quinoid structure is obtained, a decrease in both NH and CH₂ stretching band intensities are observed. If a photo Fries rearrangement occurs, bands of the urethane components (at 3327, 1700, 1730, 1529, 1220, and 670 cm⁻¹) and para substituted aromatic ring band at 816 cm⁻¹ decrease, while a new band at 840 cm⁻¹ characteristic of 1,2,4 tri-substituted aromatic ring appears (Wilhelm et al., 1998).

We studied the surface of the PU catheter (on a depth of 1–2 μm) by FTIR-ATR analysis, and its bulk by analysis in transmission mode of cast PU films. In both cases, no significant differences were observed in the spectra between non-treated and treated samples (either plasma or irradiation), see Fig. 3. Variations in the absorbance (A) of characteristic bands of ether and urethane linkages (C–O–C at 1103 cm⁻¹ and C≡O stretching vibrations at 1700 and 1730 cm⁻¹) were studied by choosing the band at 1413 cm⁻¹ (aromatic band) as a reference band (McCarthy et al., 1997). No variation in the \( A_{670}/A_{1413} \), \( A_{1700}/A_{1413} \), and \( A_{1013}/A_{1413} \) ratios of band absorbance was observed after plasma or irradiation treatment (Fig. 4). No bands of functional groups such as hydroxide, peroxide (characteristic of polymer oxidation)
were observed, even by subtracting the spectra of non-irradiated sample to those of the irradiated ones. These results are in agreement with those of Guignot et al. (2001) on Tecoflex, an aliphatic polyetherurethane, which showed that for the smallest irradiation doses (<100 kGy), no significant FTIR spectra modification was detected.

![Fig. 3. ATR–FTIR spectra of Pellethane® after and before treatment (plasma and irradiation). Spectrum of the untreated PU is in black. Spectra of irradiated and plasma-treated PU are in grey. All spectra are superimposed.](image)

![Fig. 4. Evolution of the relative absorption ratio of the 1730 cm⁻¹/1413 cm⁻¹, 1700 cm⁻¹/1413 cm⁻¹ and 1103 cm⁻¹/1413 cm⁻¹ bands with plasma treatment time or irradiation dose. The two x-axes are of illustrative purposes only and do not imply a similarity between plasma and irradiation exposure levels.](image)
3.1.2. SEC

Although no chain degradation was shown by FTIR analysis, scissions of the chains were evidenced by SEC performed on the beta irradiated samples, for which the weight distribution showed an enlargement (Fig. 5). It was attributed to both scissions and branching of the polymer chain, although branching was the predominant phenomenon. Indeed for the highest doses, a new peak clearly appeared at an elution time of about 16 min (Fig. 5). It was characteristic of a new distribution of higher molecular weight.

The modification of the chromatogram was in agreement with the evolution of $M_n$ and $M_w$ (Fig. 6). Between 0 and 25 kGy, only a slight decrease in $M_n$ (3%) was observed because of chain scission. The scission process was increased at the 150 kGy dose, with a 15 000 g/mol drop in $M_w$, compared with the non-irradiated sample (25% decrease). However, scission remained quite low even at the highest irradiation doses: only one C–O ether group or urethane group/per 2 chains was affected by the scission at 150 kGy. This explains why we did not observe significant modification in the FTIR spectra.

The evolution of $M_w$ was more significant. If the increase of $M_w$ for the 25 kGy sample was quite small (8%), an increase of 55% and 200% was observed for 75 and 150 kGy irradiation, respectively. As a consequence the polydispersity index ($I_p$) reached 5.5 for the 150 kGy irradiated sample.

The predominance of either scission or branching/cross-linking depends on the radiation (beta or gamma) (Woo and Sandford, 2002), the irradiation dose (Guignot et al., 2001), the nature of polyurethane (Abraham et al., 1997) and the irradiation atmosphere (Chapiro, 1995). Sterilization in air or under oxygen generally leads to chain scissions (Chapiro, 1995). For PU submitted to gamma irradiation, mostly scissions were reported in the literature (Gorna and Gogolewski, 2003a), even for Pellethane® 2363 analogues (Shintani et al., 1990). However, for Pellethane 2363 submitted to electron beam radiation, we showed on the contrary that the predominant phenomenon was chain branching, in spite of the fact that our samples were irradiated in air. For plasma treatment, no modification of the mass distribution was observed. This apparently contradicts previous results obtained by Gorna and Gogolewski (2003b), who showed that significant mass decrease was observed after cold plasma treatment. However, these authors used a gas with a higher oxidant power than N₂, our discharge gas; moreover we worked at atmospheric pressure in the post-discharge area, in a configuration there were neither aggressive ionic species nor UV radiation.

![Fig. 5. SEC chromatogram of a Pellethane® solution for the different irradiation doses.](image)

![Fig. 6. Variations of the number average molecular weight ($M_n$) (a), of the weight average molecular weight ($M_w$) (b) and of the polydispersity index ($I_p$) with the irradiation dose.](image)
3.1.3. DSC
Scission and branching of polymer chains occurring during irradiation could explain some of our DSC results. A small decrease (2°C) of the glass transition temperature ($T_g$) was observed by DSC analysis of the 150 kGy sample (Fig. 7). It might be due to the chain scissions and branching that occurred at this dose and increased the free volume. Indeed, chain ends introduce a supplementary free volume that allows $T_g$ to decrease, by decreasing the chain length (Fox and Gibbs, 1950). The influence of branching may be more complex (Jayakannan and Ramakrishnan, 2000; Kricheldorf et al., 1995; Puskas et al., 2006) but generally it lowers $T_g$ too, by limiting chain packing and creating free volume (Bamford et al., 2006; Kritskaya et al., 2007).

$T_g$ variations caused by chain scissions have already been described by Abraham et al. (1997) for Biomer® PU, in which the soft segment $T_g$ decreased by 3°C after a 50 kGy gamma irradiation.

3.1.4. TGA
Scission might also explain the small variations in TGA thermograms. For PU degraded during TGA in nitrogen, one would expect to find two successive stages, the first one mainly related to the hard segments of the polymer and the second one, mostly to the polyether segments (Guignot et al., 2001; Herrera et al., 2002). Two degradation stages were indeed observed for the PU catheters (Fig. 8). The first degradation stage (hard segments) was always quite complex. For the derivative weight signal, two close peaks were observed and other shoulders were detected. The shape of the derivative weight signal for the first degradation stage fluctuated even if the degraded percentage was relatively reproducible (around ±1% for the non-irradiated samples).

Contrary to other observations (Abd El All, 2007), no variation in the temperature of thermal decomposition peaks was observed after both plasma and e-beam treatments: stability of hard and soft segments in PU was not affected by the modification of the polymer chains. Because the scissions of soft segments may generate small highly volatile oxidized polyether fragments which might disappear during the first mass loss step, Guignot et al. (2001) observed for a polyetherurethane (Tecoflex) a mass loss increase of 8% during the first degradation stage for the sample irradiated at 1000 kGy with respect to the non-irradiated sample. For our samples the trend was not obvious, because the differences were small (±2%), with a scattering of the results that increased with the irradiation dose (Fig. 9).

3.2. Influence of the treatment on the organization of the polymer
Phase separation is known to play an important role in PU properties. Hydrogen bonds (H bonds) in PU have a strong influence...
on phase separation between hard and soft segments. H bond may either exist between two hard segments, binding carbonyl function of one urethane to the N–H function of another urethane, or between hard (N–H) and soft domains (C–O–C) (Brunette et al., 1982; Lee et al., 1987, 1988; Sung and Schneider, 1975). If there are mostly N–H–C–O bonds, there is an extensive phase separation. If N–H function interacts with soft segments (ether), there is a dispersed phase of hard segment mixed with soft ones.

3.2.1. FTIR

Phase separation between hard and soft segments may be evaluated by the proportion of N–H–C–O bonds and studied by FTIR analysis of the N–H stretching vibration (Brunette et al., 1982; Lee et al., 1987, 1988; Sung and Schneider, 1975). If there are mostly N–H–C–O bonds, vN–H is located at around 3330 cm\(^{-1}\). If N–H function interacts with soft segments, vN–H is at around 3295 cm\(^{-1}\). In this case, the absorbance of the stretching band of the C–O groups (1703 cm\(^{-1}\)) that corresponds to the one bound to the N–H (Seymour et al., 1970), is smaller.

Modifications in H bonding after irradiation were observed by Ravat et al. (2000). By studying C–O vibration of our samples, we concluded there was no modification of hydrogen bonding after plasma or irradiation treatment for our samples (Fig. 4).

3.2.2. DSC

Endotherms obtained with PU were attributed to different levels of packing order in the hard domains (Seymour and Cooper, 1973); the endotherm occurring at the lower temperature (\(T_I\)) corresponds to the disruption of short order ranges (< 100 °C) (Seymour and Cooper, 1973). Endotherms between 100 and 200 °C (\(T_{II}\)) are due to the disruption of long order range and are associated with the onset of partial intersegmental mixing (Koberstein and Rusell, 1986; Leung and Koberstein, 1986; Saiani et al., 2001, 2004). The ones (\(T_{III}\)) at higher temperatures (> 200 °C) can be attributed to the melting of a crystalline state in the hard domains (Seymour and Cooper, 1973). The endotherm at \(T_I\) has been explained by some authors as an enthalpic relaxation due to ageing. It was associated with the hard segments glass transition that occurs in the same temperature range (Chen et al., 1997, 1998; Koberstein et al., 1992).

On the first heating of our samples, there was a small endotherm around 80 °C, and a broad endotherm between 100 and 180 °C, with two main endothermic maxima at around 135 and 160 °C. On the second heating, the second endotherm was not modified but the first one disappeared and a calorific capacity (\(C_p\)) jump around 83 °C was observed (Fig. 7). The second endotherm characteristic of hard segment organization was not modified upon irradiation (Fig. 7) or plasma treatment (Fig. 10). DSC scans of Pellethane\(^{®}\) were in agreement with our

![Fig. 10](image-url). DSC thermograms obtained for Pellethane\(^{®}\) (20 °C/min heating rate; 40–220 °C). First (a) and second heating (b) for plasma-treated and non-treated samples.
previous FTIR results that showed that there was no modification in phase separation and organization between soft and hard segments.

3.3. Effect of the treatment on the additives of the polymer

3.3.1. Study of polymer extracts

After extraction by a precipitation/dissolution process, and analysis of the extract by HPLC, two phenolic antioxidants were found in Pellethane®: the first one was the BHT (butylhydroxytoluene) (60 ppm ± 5), which could result from the degradation of the second one: Irganox 1076® (Octadecyl 3,5-di-(tert)-butyl-4-hydroxyhydrocinnamate) (2100 ppm ± 100). The lubricant ethylene bis stearamide (EBS) was estimated to 25 000 ppm ± 7000.

As the irradiation dose increased, a significant decrease in the extractable level of Irganox 1076® was observed (Fig. 11). The decrease might be due to the degradation of the antioxidant or to the formation of covalent bonds between antioxidant and the polymer chains. Such kind of bonding was already reported by Allen et al. (1991). No degradation of antioxidants was observed in our samples after plasma treatment (Fig. 11).

3.3.2. Study of the material surface (FTIR)

Ratner and Briggs showed by XPS and SIMS measurements (Briggs, 1987; Ratner, 1983; Ratner et al., 1988) that there was a pre-existent superficial EBS layer on Pellethane® polyurethanes.

![Fig. 11. Evolution of the extractable Irganox 1076® amount in Pellethane® with irradiation dose or plasma treatment time. The two x-axes are of illustrative purposes only and do not imply a similarity between plasma and irradiation exposure levels.](image)

![Fig. 12. FTIR–ATR spectra modifications resulting of EBS exudation/migration after irradiation. Characteristic EBS bands are denoted by (*). (a) Initial spectra. (b) Subtracted spectra (treated–untreated) are given for irradiated PU. Subtracted spectra were given for 150, 75 and 25 kGy irradiation doses.](image)
The modification observed in our FTIR spectra indicated that there was a very slight diffusion of the lubricant toward the polymer surface after irradiation (Fig. 12): a new band at 2916 cm$^{-1}$/C=O and a very slight shoulder at 3307 cm$^{-1}$/C=O appeared. These bands are characteristic of the presence of the lubricant EBS. This observation was more obvious after subtraction of the spectra of the non-irradiated sample. The result clearly showed three characteristic bands of EBS at 3307, 2916 and 2848 cm$^{-1}$. The dose of irradiation seemed to have no effect on the intensity of EBS diffusion toward the interface. For plasma-treated samples the same phenomenon was revealed by spectra subtraction, but this effect was much less obvious than after irradiation.

3.4. Effect of the plasma treatment on the surface: a preliminary study

Non-treated catheters were compared with 40 min-treated catheters.

3.4.1. Surface topography (AFM)

In order to avoid additive clusters onto the surface, catheters were washed with ethanol before analysis. The breaking of chemical bonds during plasma treatment resulted in the ablation of low molecular weight compounds. The AFM image (Fig. 13a) shows that the etching was not homogeneous. After treatment, the surface was smoothed (Fig. 13b) and the roughness $R_q$ initially around 3.5 nm decreased to 1.5 nm. This might be due to a selective attack of soft polyether segments. This has been already observed with other plasmas (Wilson et al., 2003).

3.4.2. Chemistry modification (XPS)

C/O and C/N atomic ratios were modified for treated sample (Table 1) and showed enrichment in the oxygen (1.8 factor) and in nitrogen (1.4 factor). Incorporation of oxygen containing species with N$_2$ plasma treatment has already been observed (Sanchis et al., 2008; Weibel et al., 2006). O$_2$ is very reactive and can react during or just after treatment on the plasma activated surface (free radicals are generated by chain scissions). Indeed the experiments were not performed under vacuum.

Table 1  

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<td>Before treatment</td>
<td>8</td>
<td>52</td>
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<td>After treatment</td>
<td>5.5</td>
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For C1s, C–C bond amount on the surface decreases compared with more polar bonds whose energies are between 286 and 288 eV (Fig. 14a). Plasma can produce complex mixtures of functionalities and attribution of new C1s peaks is difficult. C=N, C=N–C, C–O, N–C–O species might be implicated. N1s peak (Fig. 14b) was broadened after treatment suggesting the existence of nitrogen in a greater variety of environments. O1s shape was modified too with a decrease in C–O–C bond, and a C–O bond increases (Figs. 14c and d).

Those chemical modifications are coherent with both polyether erosion seen by AFM (less C–O–C bond) and new functionality grafting (C1s, O1s and N1s evolution).

3.4.3. Wettability

After treatment, the wettability of the catheters appeared modified. For all studied liquids, the contact angle was reduced. Calculations according to the Owens–Wendt model showed a significant increase in the surface energy of the treated samples, and especially in its polar component (Table 2). This may be correlated to the increase of C–O and N functionalities onto the surface.

4. Conclusions

Beta irradiation on PU catheters leads to significant degradation of the catheter. Antioxidants were consumed, and there was considerable chain branching. However, these degradations did not extensively modify the thermo-mechanical properties of the catheters or the soft/hard segments organization of PU. Unfortunately, the degradation products of antioxidants and the oligomers formed by chain scissions (even if these scissions were quite limited) are mobile species that could migrate from the polymer to the biological fluids. Moreover, they were evidenced even at the lowest irradiation dose that is commonly applied for sterilization of medical devices. Therefore, their toxicity should be studied.

Contrary to e-beam irradiation, plasma treatment did not damage the bulk of the polyurethane catheter nor affect the additives. These results were expected since plasma is generally known to mostly affect the polymer surfaces. Moreover, the conditions of plasma discharge used (gas, atmospheric pressure and post-discharge treatment) did not favour the existence of aggressive species (ions, UV radiations or atomic oxygen) that could be involved in the damaging of the polymer chains. They were however checked, because these treated PU are designed for medical applications. The study of surface modification on a few nanometers depth (no modification were observed by ATR on a micrometer scale) was essential, because the surface state has a

Fig. 13. AFM tapping mode images of washed catheters on a 1 $\times$ 1 $\mu$m$^2$ box: (a) non-treated and (b) 40 min treated.
significant impact on the biostability and the biocompatibility of polymers. The results showed that the chemical composition changed after plasma treatment, with an enrichment in polar species (O and N). Topology was also modified due to a smoothing effect of the treatment. A thorough study of surface modifications and their evolution with time following plasma treatment is currently in progress.

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Table 2
Contact angle measurements, surface energy and polarity of the catheter surface before and after 40 min of plasma treatment.

<table>
<thead>
<tr>
<th></th>
<th>Before treatment</th>
<th>After treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water angle (deg)</td>
<td>96 ± 4</td>
<td>54 ± 4</td>
</tr>
<tr>
<td>EG angle (deg)</td>
<td>81 ± 4</td>
<td>47 ± 4</td>
</tr>
<tr>
<td>Diodomethane angle (deg)</td>
<td>61 ± 4</td>
<td>41 ± 4</td>
</tr>
<tr>
<td>Surface energy (mJ/m²)</td>
<td>25.5</td>
<td>47.5</td>
</tr>
<tr>
<td>Polar component (%)</td>
<td>4.5</td>
<td>35</td>
</tr>
</tbody>
</table>

Percentage of polar component is defined as the ratio \(s_p/s_d\) × 100.

References


