

Modification of Stearic Acid in Ar and Ar-O₂ Pulsed DC Discharge

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Stearic acid (CH₃(CH₂)₁₆COOH) was treated with Ar and Ar-O₂ (10%) pulsed DC discharges created by a cathode-anode confined system to elucidate the role of oxygen in plasma cleaning. The treatment time (5 to 120 minutes) and plasma gas mixture (Ar and Ar-O₂) were varied, and the results showed that the mass variation of stearic acid after Ar-O₂ plasma exposure was greater than that of pure Ar plasma treatment. Thus, compared to Ar*, active oxygen species (O and O₂, in all states) enhance the etching process, regardless of their concentration. During the treatments, a liquid phase developed at the melting temperature of stearic acid, and differential thermal analyses showed that the formation of a liquid phase was associated with the breakage of bonds due to treatment with an Ar or Ar-O₂ plasma. After treatment with Ar and Ar-O₂ plasmas, the sample surface was significantly modified, especially when Ar-O₂ was utilized. The role of oxygen in the treatment process is to break carbonaceous chains by forming oxidized products and/or to act as a barrier against ramification, which accelerates the etching of stearic acid.

Keywords: *stearic acid, grafting, etching, cleaning by plasma*

1. Introduction

The surface properties of materials or mechanical parts play an essential role in the performance and life time of a product due to the effects of wear, corrosion or fatigue. Surface treatments such as painting, thin film deposition or thermochemical treatments are often employed to improve the properties of a material. However, because these techniques are sensitive to surface contamination, a cleaning step must be conducted to remove contaminants present on surfaces handled in the air.

The most commonly observed contaminants on the surface of materials are organic compounds such as oils and greases. Effective treatment methods for the removal of contaminants play an important role in the end performance of a product¹⁻³. The effectiveness of plasma cleaning processes depends on the type of gas (Ar, O₂, H₂, etc.), surface properties, discharge type (i.e., continuous current, microwave, radio frequency) and properties of the organic material⁴.

Under certain conditions, plasma treatments can affect the chemical bonds of a contaminant and strengthen them to the point where further removal is longer or impossible⁵. Significant improvements in the performance of plasma cleaning processes could be achieved by determining the interaction mechanisms between active species and the contaminant, which is currently unknown.

Several studies have been conducted to better understand the mechanism of the degradation of organic molecules via plasma treatment⁶⁻⁸. In these investigations, hexatriacontane (HTC), which possesses only simple C-C and C-H bonds, was evaluated, and the O/O₂ (in all states) ratio and temperature were key factors affecting the plasma etching or grafting of HTC. However, to understand how the plasma cleaning process occurs, many organic molecules with different types of bonds and functional groups must be studied to obtain a better representation of real organic contaminants.

Several studies have been performed on stearic acid (SA) to determine how carboxylic groups (COOH) react when exposed to chemically active species in the post-discharge area of an Ar-O₂ plasma^{9,10}. Through these treatments, several interaction mechanisms of SA with chemically active species were identified. By understanding the effect of the active species, different discharge treatments may be developed, and the influence of charged species (ions and electrons) and photons may be determined.

The aim of the present study was to understand the effect of the carboxylic group (COOH) of SA in Ar or Ar-O₂ plasmas in a DC discharge. Namely, the effect of the treatment time and plasma atmosphere (Ar and Ar-O₂) on the grafting and/or etching of SA was evaluated.

2. Experimental Set-up

Stearic acid (CH₃(CH₂)₁₆COOH), which has a linear structure containing C-C and C-H bonds and a carboxylic acid group on the chain end, was evaluated in the present study. The properties of SA are as follows: molar mass = 284.47 g.mol⁻¹; density = 0.847 g.cm⁻³; melting point = 342.6 K; ebullition point = 656 K. commercial SA used in the present study was 98% pure, and the remaining 2% of the material was composed primarily of hydrocarbons, oxalic acid and water. To prepare the samples, 1.2 g of SA was melted and poured into a crucible, as shown in Figure 1. Next, the crucible was capped to avoid temperature gradients until the material cooled to room temperature.

The experimental setup is depicted in Figure 1. The plasma reactor consisted of a cylindrical quartz tube with an inner diameter of 30 mm, and the plasma was created by a cathode-anode confined system

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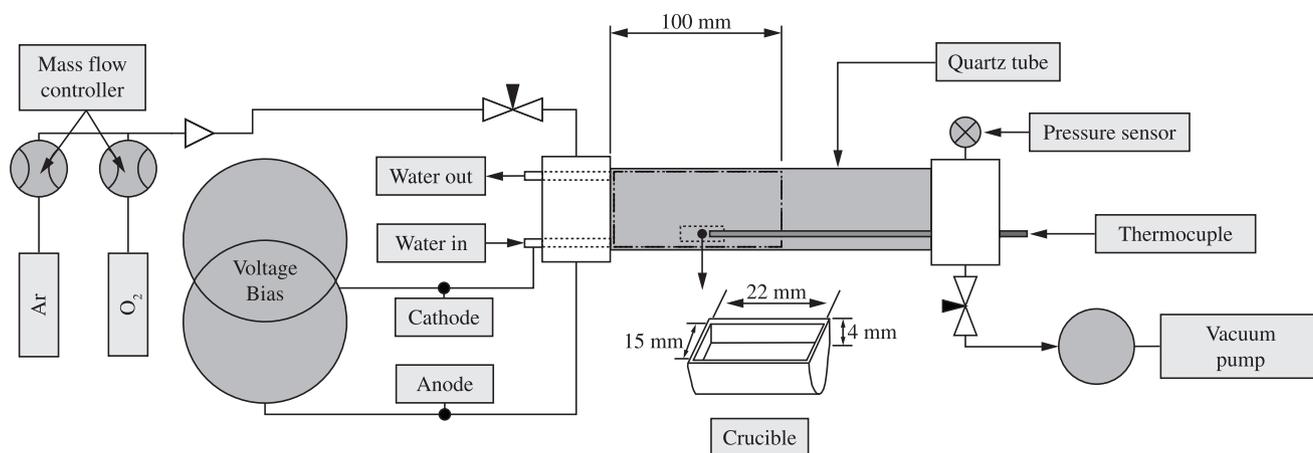


Figure 1. Experimental setup.

made of stainless steel. A complete description of the cathode-anode confined system has been presented by Pavanati et al. (2007)¹¹. The Teflon (PTFE) crucible was placed into the hollow cathode and was maintained at the floating potential. The temperature of the sample was controlled by a water-cooling system at the cathode. Because the samples were in direct contact with the cathode, the temperature of the samples could be controlled by changing the flow of water.

Prior to the plasma treatments, several tests were performed in the absence of the plasma. These experiments were conducted under conditions that were similar to those used in the plasma treatments to identify possible transformations induced by specific pressures, temperature and gas flows. The first series of tests was performed under vacuum (10^2 Torr) at 313 and 333 K for 5 to 120 minutes. The second series of treatments were performed under O_2 and/or Ar gas flow at a pressure of 3 Torr and temperatures of 313 and 333 K for 5 to 120 minutes.

The exposure time to the plasma (5 to 120 minutes) and the composition of the atmosphere (pure Ar or Ar- O_2 (10%) plasma) were evaluated in the present study. The other parameters were held constant, and the conditions presented in the work of Bernardelli et al. were employed (2009)¹²: plasma power: 8.5 W; voltage: 500 V; current: 0.17 A; flow rate: $100 \text{ cm}^3/\text{min}$; pressure: 3 Torr; pulsed DC bias frequency: 1.75 kHz; on period of the power supply (t_{on}): 70 to 90 μs ; off period of the power supply (t_{off}): 470 μs . Because the same current and voltages were observed in all of the treatments, the effect of the active species could be determined, regardless of their concentration.

Before and after each experiment, the samples were weighted with an analytical balance (precision $\pm 0.1 \text{ mg}$). The treatment process was characterized by the mass variation (MV) and mass variation rate, which was obtained according to the following equation:

$$MVR = \frac{\Delta m}{A \Delta t} \quad (1)$$

where A is the sample area (3.30 cm^2), Δm is the mass variation and Δt is the time of exposure to the plasma.

Before each treatment, the samples were analyzed by differential thermal analysis (DTA) using a STA NETZCHSTA model 409C device. X-ray diffraction (XRD) analyses were also performed before and after plasma treatment. In these experiments, a Philips X'Pert MPD diffractometer equipped with a $K\alpha$ copper radiation source was employed. The sample peaks were identified with Philips – PC Identify 2.1 software and the ISDD PDF-2 2001 database.

Elementary chemical analyses of samples treated in an Ar- O_2 plasma were performed via dynamic flash combustion using an elementary CHNS-O analyzer obtained from CE instruments (EA 1110 model). Due to the lower etching rate observed in a pure Ar plasma, the chemical composition of these samples was not analyzed. The oxygen concentration was estimated by determining the difference between the carbon and hydrogen concentration.

3. Results and Discussion

In the absence of a plasma, the mass variation and mass variation rate were equal to zero, and the formation of a liquid phase was not observed. Thus, modifications to the structure of SA were attributed to plasma treatment.

The DTA results of SA samples before plasma treatment are presented in Figure 2. The samples displayed only a solid to liquid phase transformation beginning at 342 K (which was equal to the melting temperature established by the manufacturer) and ending at 378 K. The observed temperature range was attributed to the presence of impurities in the study material, which possessed a purity of 98%. In the present analysis, two atmospheres (Ar and O_2) were employed, and similar changes in the volume/mass ratio were observed with both atmospheres. In the absence of the plasma, a phase transformation was not detected under an Ar or O_2 atmosphere.

The X-ray diffraction results of SA before and after 120 minutes of treatment in an Ar or Ar- O_2 plasma are presented in Figure 3. Prior to the treatment, SA possessed a crystalline structure and presented well-defined peaks in the diffraction patterns. After treatment, the samples displayed new peaks that could not be readily identified. In samples treated with Ar or Ar- O_2 plasmas, the elevation in the baseline in the 2θ gap from 15 to 25° was attributed to the formation of an amorphous phase. Figure 3 displays the diffractions observed at angles ranging from 23 to 25° . As shown in the figure, the peaks corresponding to samples treated in an Ar- O_2 plasma were less defined and wider than that of untreated samples and samples treated in an Ar plasma. After treatment with Ar- O_2 , the peaks shifted to the left, indicating that the lattice parameters increased. Thus, the nature of the SA degradation product in the presence of an oxygen-based plasma was different from that of a pure argon plasma.

The temporal evolution in the temperature of SA samples treated in Ar and Ar- O_2 plasmas is presented in Figure 4. Identical temperature profiles were observed in both atmospheres because the temperature was controlled by the cooling system of the cathode; thus, only a representative curve is shown in the figure. In the beginning

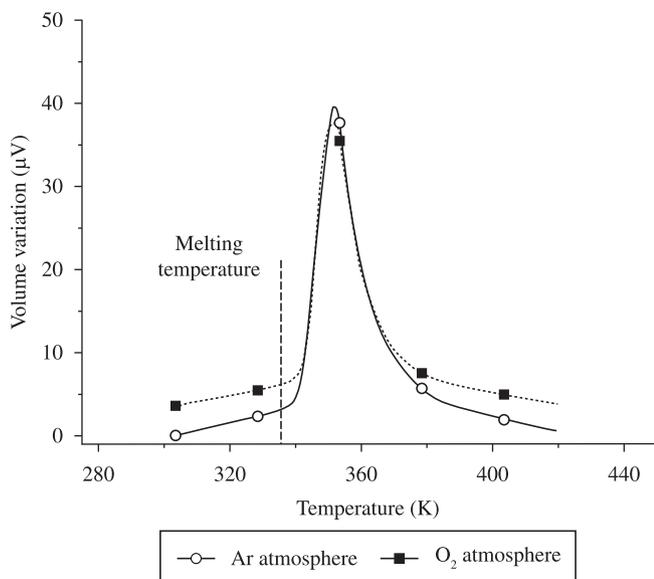


Figure 2. Differential thermal analysis of stearic acid prior to plasma treatment.

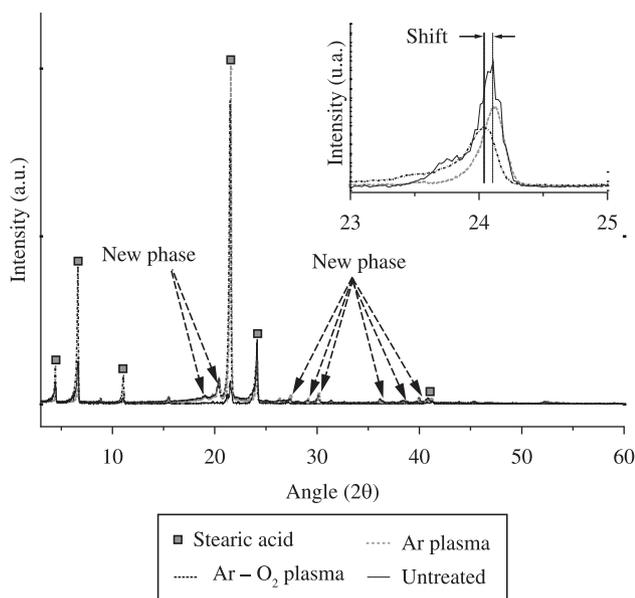


Figure 3. X-ray diffraction of stearic acid before and after (120 minutes) treatment with an Ar or Ar-O₂ plasma.

of the treatment process (approximately 10 minutes of exposure to the plasma), the temperature of the samples increased rapidly to 330 K and remained constant for the remainder of the procedure (120 minutes).

Because exothermal reactions occurred at the surface of HTC¹³, which increased the temperature of the sample, the cooling system used in the present study was helpful for understanding the temporal evolution of the temperature. In the current investigation, it is assumed that all of the transformations along the sample surface occurred at approximately the same temperature (330 K); therefore, the results obtained in different atmospheres were comparable.

At the beginning (about 5 minutes) of the treatment process, a liquid phase formed at the surface of the sample. In the DTA results, a liquid phase was observed at 342 K; thus, the formation of a liquid

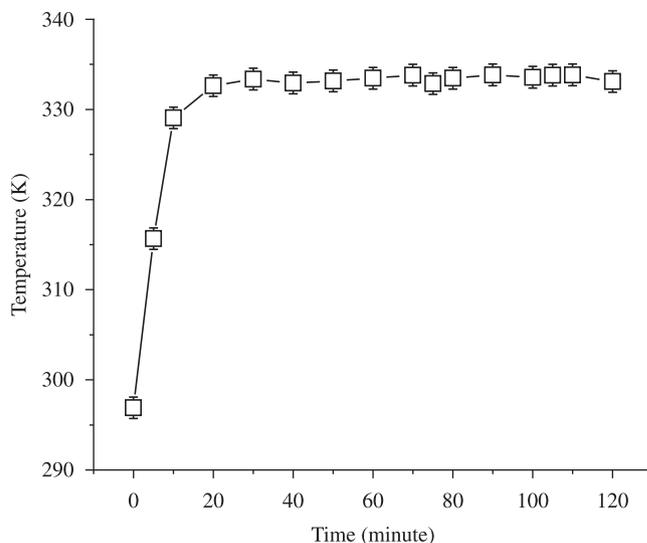


Figure 4. Temporal evolution of the temperature of the sample during treatment with an Ar or Ar-O₂ plasma.

phase in the plasma could not be attributed to heating. Rather, the production of a liquid phase was attributed to the breakage of bonds during the plasma treatment, as presented by Mafra et al. (2008)¹³. Moreover, in treatments conducted in the absence of plasma, a liquid phase was not produced, indicating that phase formation could be attributed to the reaction of SA with active species, rather than temperature measurement errors.

Using an Ar-O₂ plasma, the formation of a yellow layer was observed after 120 minutes of treatment. In contrast, when an Ar plasma was utilized, a color change was not apparent, indicating that an important structural modification occurred when an Ar-O₂ plasma was utilized. As discussed by Noel et al. (2009)¹⁴, when an O₂ plasma is employed, SA reacts with oxygen, which leads to the formation of a yellowish color.

Figure 5 shows the change in the mass variation over time in the Ar and Ar-O₂ plasma and the corresponding mass variation rate. When an Ar plasma was employed, the mass variation was significantly lower than that of an Ar-O₂ plasma. Thus, although the lattice parameter was reduced, physical etching could not promote the modification of SA. In contrast, when an Ar-O₂ plasma was utilized, a higher etching rate was observed throughout the entire treatment process. Specifically, the etching rate increased almost linearly in the first 75 minutes of treatment. Subsequently, the etching rate decreased, and only slight differences in the mass variation were observed at 90, 105 and 120 minutes of treatment. A reduction in the etching rate likely occurred due to the formation of a product that was resistant to plasma etching¹².

By evaluating the MRV results (Figure 5), transformations occurring at the sample surface at the beginning of the treatment process were identified. For instance, the MRV decreased within the first 20 minutes of treatment and then remained nearly constant until the end of the process. The observed reduction in the MRV indicated that reactions at the sample surface led to the self-protection of SA.

The results obtained in plasmas containing pure Ar and Ar-O₂ were compared to determine the role of active and charged species. In an Ar (respectively Ar-O₂) plasma, chemically active species such as Ar* (O and O₂, in all states) and charged species such as electrons and ions are present. If we assume that physical etching by Ar⁺ and O₂⁺ is similar under the proposed conditions, then active oxygen

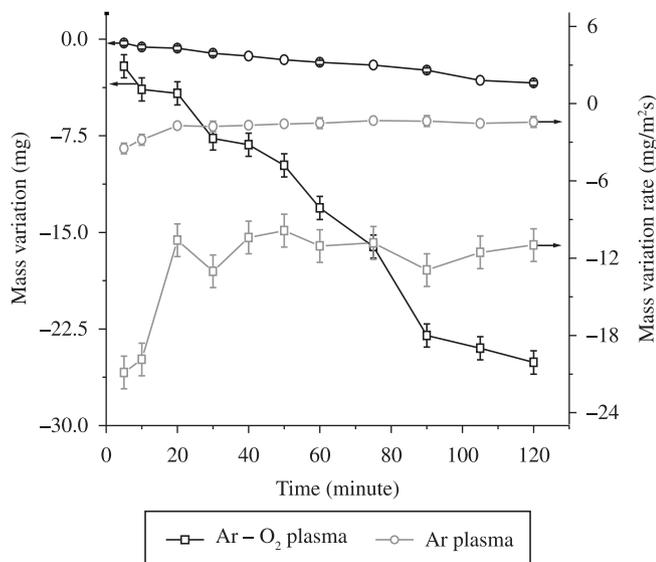


Figure 5. Temporal evolution of the mass variation due to treatment with an Ar or Ar-O₂ plasma. The mass variation rate (MRV) is also included.

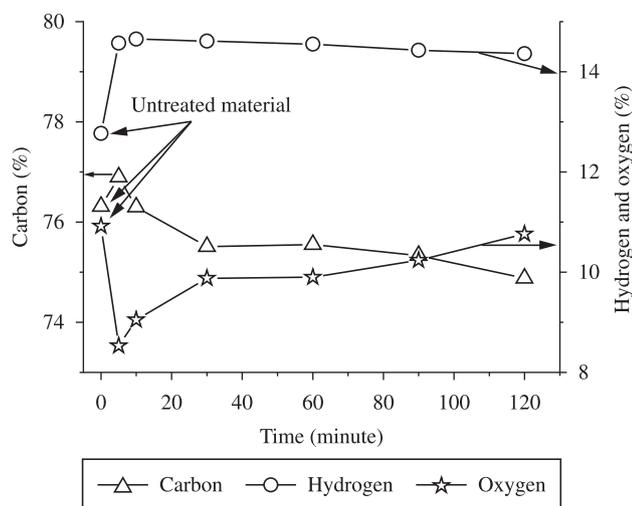


Figure 6. Relative amount of carbon, hydrogen and oxygen after treatment with an Ar-O₂ plasma.

species strongly enhance the etching process with regards to Ar* species, regardless of their concentration⁸.

Bernardelli et al. (2011)¹⁰ have shown that a significant increase in the mass of stearic acid occurs in the presence of chemical active species. In the present work, when working with charged species and photons (Ar plasma), the mass variation was low. Alternatively, when chemically active species, charged species and photons were present (Ar-O₂ plasma), high mass losses were observed. Thus, different species produced under the reaction conditions had a synergistic effect on the degradation of SA.

The results of the chemical analyses of samples treated with an Ar-O₂ plasma are presented in Figure 6. In the first 5 minutes of treatment, a sharp gravure of oxygen to the carboxylic acid of SA was observed. The abstraction of oxygen leads to an increase in the relative amount of carbon and hydrogen. Therefore, at this time, the carboxylic acid functional group was removed the surface of the sample. After

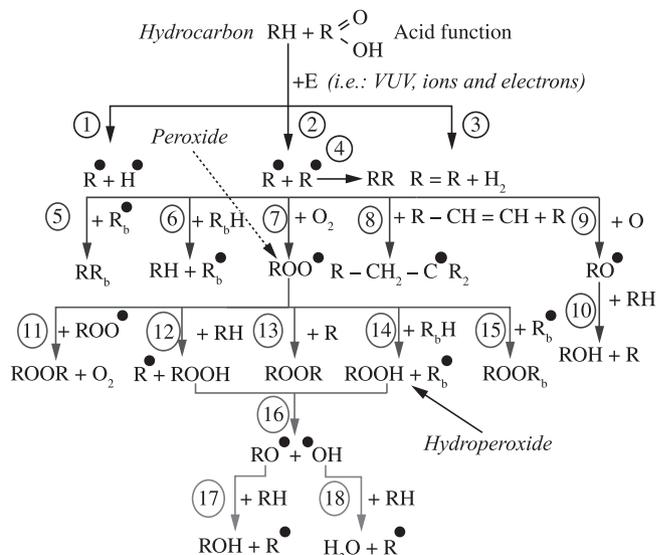


Figure 7. Reactions involving carbon chains that occur in an oxygen discharge^{7,12}.

5 minutes, the relative amount of oxygen increased, and the content of carbon and hydrogen decreased due to surface functionalization, which continued until 120 minutes of plasma exposure.

The chemical analysis results (Figure 6) were compared to the diffraction data (Figure 3), and a shift in the diffraction peaks of samples treated with an Ar-O₂ plasma was observed due to functionalization by oxygen. In particular, the introduction of oxygen increased the lattice parameters of the material. When samples were treated with an Ar plasma, the absence of oxygen improved the crystallinity of the sample. The observed enhancement in the degree of crystallinity could not be attributed to the functionalization of SA. Rather, the crystallinity of the sample improved due to the etching of the acid group by the plasma.

The main reactions that can occur between carbon chains and the oxygen plasma are presented in Figure 7^{7,15}. In the figure, E is any energy source (i.e., photons produced by VUV and UV, energetic ions or electrons) that is capable of breaking bonds¹⁵⁻¹⁷. The formation of alkyl radicals (R•) via reaction 2 can occur via the removal of hydrogen by oxygen⁷. After the formation of alkyl radicals, the oxidation of carbon-based molecules begins by the formation of a peroxide intermediate (reaction 7) or a radical alkoxy (reaction 9). The formation of a radical alkoxy can lead to reaction 10, and peroxides can participate in reactions 11-15. Hydroperoxides formed via reaction 12 and 14 can react with C-OH (alcohol), C=O (carbonyl, ketone or aldehyde), C-O-C (ether); COOH (acids), COOC (ester), etc. When an acid functional group reacts with the plasma, the formation of an alcohol, ketone and/or ether may be observed.

In the first 5 minutes of treatment, the formation of peroxides (ROO•) and alkoxy radicals (RO•) was limited, and the relative amount of oxygen decreased (Figure 6) due to the removal of the acid functional group (COOH) from SA. The carboxylic acid moiety is preferentially removed over C-C and C-H bonds due to the low treatment temperature (42 °C until 5 minutes) utilized in the present study. Under these conditions, the functionalization processes are difficult⁶.

From 5 to 120 minutes, the rate of the functionalization process increases (Figure 6), and the formation of byproducts via reaction 7 and 9 occurs more frequently. Oxidized volatile products (i.e.: alcohols, ketones, acids and esters) (reaction 16) are generated

preferentially, and a negative weight variation was observed for all of the treatments (Figure 5). Because the samples were immersed in a DC glow discharge, volatile products may be formed due to ionic, electronic or photonic bombardment (reaction 2).

The formation of products that are resistant to Ar-O₂ plasmas is likely due to the production of ramified chains (reactions 5 and 8) with double bonds (reaction 3) and functionalized chains (reaction 7). The formation of resistant products explains the observed reduction in the etching rate after 20 minutes of Ar-O₂ plasma treatment.

The results of the present study suggested that oxygen plays two different roles in the treatment process. In the beginning of treatment, oxygen breaks carbonaceous chains, forming oxidized products. In addition, oxygen acts as a barrier against ramification processes via reactions 5 and 8. Alternatively, the broken bond of carbon chains can be reformed through the reaction of oxygen with radicals, which results in chain closure^{17,18}.

During treatment with a pure Ar plasma, the main reactions that lead to the ramification process are reactions 5, 6 and 9. Reaction 3 may also occur, resulting in the formation of double bonds. These processes lead to the lowest amount of volatile products and the lowest MV (Figure 5). Reactions 7 and 9 occur in the presence of Ar*; however, this species has a weaker effect on the etching process of carbon chains⁸.

4. Conclusions

In the present study, experiments were conducted to understand the degradation of SA in Ar and Ar-O₂ plasmas, and the conclusions are presented hereafter.

According to the MV results, Ar-O₂ plasmas are more efficient at creating volatile compounds than Ar plasmas. Assuming that the concentration of active species is the same in both systems, O and O₂ are more reactive (Ar-O₂ plasma) than Ar* (Ar plasma) and increase the etching rate. The role of oxygen is to break carbonaceous chains by forming oxidized products. Because oxygen becomes attached to the ends of carbon chains, oxygen can also act as a barrier against ramification processes. This result was evidenced in the formation of larger amounts of the liquid phase when Ar-O₂ plasmas were employed.

According to the X-ray diffraction results, the structural changes observed in samples treated in plasmas containing oxygen were quite different from those observed with an argon plasma. Namely, the oxygen-based plasma led to the functionalization of organic compounds with oxygen atoms, while degradation in the argon-based plasma was due to the etching and ramification of carbon chains.

Although a mechanism for the degradation of SA by Ar and Ar-O₂ plasmas was proposed in the present study, new experiments and analyses (DRX, Chemical Analysis and DTA) are necessary to clarify the reaction mechanism. Thus, the degradation mechanism of plasmas will be the subject of a future study.

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