Comparing Oxygen Plasma, Hydrogen Peroxide and Flame Treatments of Polyamide Tubes to Hydrophilic Coating Adhesion

Gean V. Salmoria[1,2], Izabelle M. Gindri[2], Waldemar F. M. Martins[1,3]

[1]Nimma, Department of Mechanical Engineering, Federal University of Santa Catarina, 88040-900, Florianópolis, Santa Catarina, Brazil.

[2]Laboratory of Biomechanical Engineering, University Hospital, Federal University of Santa Catarina, 88040-900, Florianópolis, Santa Catarina, Brazil.

[3]Nano Endoluminal S.A., SC 401, n° 4756, Office Park 1, 88032-005, Florianópolis, Santa Catarina, Brazil.

Abstract— *Hydrophilic-coated catheters reduce the endovascular friction between the device and blood and increase the biocompatibility of catheters. This study investigated three surface treatments to improve catheter surface. Oxygen plasma, hydrogen peroxide, and flame exposure coating equipment were manufactured. Polyamide 11 (PA11) catheter surfaces were treated and the influence of exposure time for each individual technique was studied. Treated samples were characterized by goniometry, scanning electron microscopy, infrared spectroscopy and scratch resistance of the hydrophilic coating deposited. Oxygen plasma, hydrogen peroxide, and flame surface treatments may considerably increase the wettability and adhesion properties of polyamide 11. The flame treatment during 60 s showed significant improvement in surface properties, in which both wettability and the adhesion of the hydrophilic coating were superior in comparison to the other samples. The devices developed in these work were able to coat and improve catheter surface properties.*

Keywords— Oxygen Plasma, Hydrogen Peroxide, Flame Treatments, Polyamide Tubes, Hydrophilic Coating.

I. INTRODUCTION

The incorporation of minimally invasive practices in surgical procedures has provided many facilities and benefits compared to equivalent traditional surgical techniques1. Through small localized incisions and using specific equipment, surgical management is restricted only to the diseased area and thus preserves the peripheral structures. This reduces the need for blood replacement, the length of hospital internment, the likelihood of infections, and the postoperative pain[1–6]. However, these new techniques also have some disadvantages. In the case of endovascular procedures one of the biggest problems is the trauma and injury caused to blood vessel walls due to friction during the introduction of the device[2,3,5,6]. Hydrophilic-coated catheters have contributed to further broadening the range of benefits offered by minimally invasive surgery through a significant reduction in the endovascular friction between the device and blood, as well as an increase in the biocompatibility of catheters. Hydrophilic coatings are polar materials and have high affinity for liquids of the same nature as blood, making the interface between them slide more easily[3]. Moreover, the hydrophilic coatings have given positive results in tests for cytotoxicity, systemic toxicity, and acute intracutaneous reactivity, among others, demonstrating that they also satisfy requirements related to biocompatibility[2,3]. Generally, methods to obtain a hydrophilic polymeric coating on another polymer component or device can be divided into three stages: (i) treatment of the device surface, (ii) deposition of the coating and (iii) curing of the coating. The surface treatment is necessary mainly due to a difference in polarity between the hydrophilic coating and the polymer device, factor which hinder the adhesion between them. The surface treatment of 7 polymeric devices can be accomplished by various methods ranging from wet to dry processes such as controlled oxidation using oxy-acids[6–8], plasma[9–12] and flame treatments[13]. Generally, techniques for surface modification are used to introduce polar functional groups that promote interaction at the interface between the device and polymer coating through intermolecular interactions, improving the wettability of the device[3,8,12,14]. This study investigated the use of oxygen plasma, hydrogen peroxide solution and flame exposure treatments to provide hydrophilicity to polyamide 11 (PA11) catheter surfaces. In particularly, the influence of exposure 64 times for each individual technique was evaluated with the aim of increasing the adhesion between the PA11 catheter and the hydrophilic coating. The wettability and adhesion of a hydrophilic coating were investigated. Treated samples were characterized by goniometry, scanning electron microscopy, infrared spectroscopy and scratch resistance of the hydrophilic coating deposited.

II. EXPERIMENTAL

2.1 Materials

Medical grade catheters of pure PA11 (AP Extrusion Incorporated, USA) with 1,130 mm of length, 3.8 mm of outside diameter and 0.6 mm of wall thickness were used as substrates in the present study. The catheters were cut to test samples with 40 mm of length and then washed with ethanol. The hydrophilic polyurethane oligomer based on aromatic polyisocyanate (Hypol JM, Dow Chemical Company, USA) was used as hydrophilic coating on PA11 samples surfaces.

2.2 Oxygen plasma treatment

An AC electrical discharge reactor, with a frequency of 50 Hz, was employed for the oxygen plasma treatment of the samples. Two aluminum electrodes were arranged in parallel inside the reactor. The electrical apparatus supplies a voltage of 2 kV at these electrodes, with 20 mA current maximum. Oxygen was confined in the reactor and submitted to pressures of around 8x10-1 Pa. The electric field created between the electrodes accelerates the gas particles, causing a chain reaction and increasing the concentration of ionized species. In this way the low temperature plasma (LTP) is generated. The exposure times were 1, 2, 3, 5 and 8 min.

2.3 Hydrogen peroxide treatment

A reflux system was employed for the hydrogen 95 peroxide treatment of the samples. An aqueous solution containing 20% of hydrogen peroxide was placed in a glass flask and closed. An electrical resistance was used to heat this solution to boiling point (102°C). The samples were fully submerged in this solution and treated one at a time. The exposure times were 0.5, 1, 2, and 4 h. Before characterization all samples were dried with paper towels.

2.4 Flame treatment

An apparatus built in the laboratory was used for surface treatment of the samples by intermittent exposure to the flame. The samples were held in the shaft and rotated perpendicularly to the flame of the torch to a constant frequency of 73 rpm. The exposure times were set at 5, 10, 20, 30 and 60 s to avoid causing changes, which could adversely affect the sample surface during treatment 13. The surface temperature of the samples was monitored by infrared thermometer. Because of the peculiarities of each technique, samples were previously evaluated by exposure to different times to define the optimal time interval for each technique investigation. The main criterion adopted was defining time range in which the surface of the samples showed no significant visual changes in sample color.

2.5 Contact Angle Determination

The technique of goniometry was used for the analysis of the variation in the contact angle as function of treatment time for the samples, at least 4h after the surface treatments. The equipment used was a Data Physics goniometer, model OCA-15, operated at ambient temperature and pressure. The contact angle was measured by the sessile drop method based on ASTM D724 - 99 (2003) and ASTM D5725 - 99 (2008). The radius of the base (b) and height (h) of the drop were measured and the contact angle was calculated using equation 12:

$$\text{Contact angle } (\theta) = \arcsin\left[\frac{2bh}{b^2+h^2}\right] \quad (1)$$

Two drops of deionized water were deposited for each time established in all the techniques, and two contact angles were measured per drop. The image of each drop was captured by the camera's high-resolution device connected to a computer.

2.6 Scanning Electron Microscopy (SEM) Analysis

For the image analysis by scanning electron microscopy of the PA11 samples, as well as the analysis of the scratch resistance of the samples coated with hydrophilic polymer, a XL-30 Philips scanning electron microscope was used. Before the tests, all samples were coated with a thin layer (20 nm) of gold.

2.7 Fourier Transform Infrared (FTIR) Analyses

The FTIR technique was used in reflectance mode (ATR) for the evaluation of possible chemical changes in the samples after treatment. The device used was a Perkin Elmer infrared spectrometer. The spectra generated were obtained from scans of the samples in the region from 3500 to 800 cm-1, at 4 cm-1 resolution.

2.8 Application of Hydrophilic Coating on PA11 Samples and Scratch Resistance Test

For a uniform application of the hydrophilic polymer on the surface of the PA11 tube samples the device shown in the diagram in Figure 1 was developed. The samples were fixed to a metal rod, which in turn was connected to the rotor shaft. While the sample was spinning at a constant speed, the hydrophilic polymer was applied on the surface until they were fully covered. The blade 0.1 mm from the surface uniformly regulated the thickness of the layer deposited. After the coating, the tubes were left rotating in the device for an hour for curing of the hydrophilic polymer. To analyze the direct influence of the increase in the free energy of PA11 on the adhesion of the hydrophilic polymer, tests were carried out to determine the scratch resistance of the coated samples. The apparatus developed for this test was based on ASTM D 7027-05 (Standard Test Method for Evaluation of Scratch Resistance of Polymeric Coatings and Plastics Using an Instrumented Scratch Machine). Figure 1 shows a simplified diagram of this device.

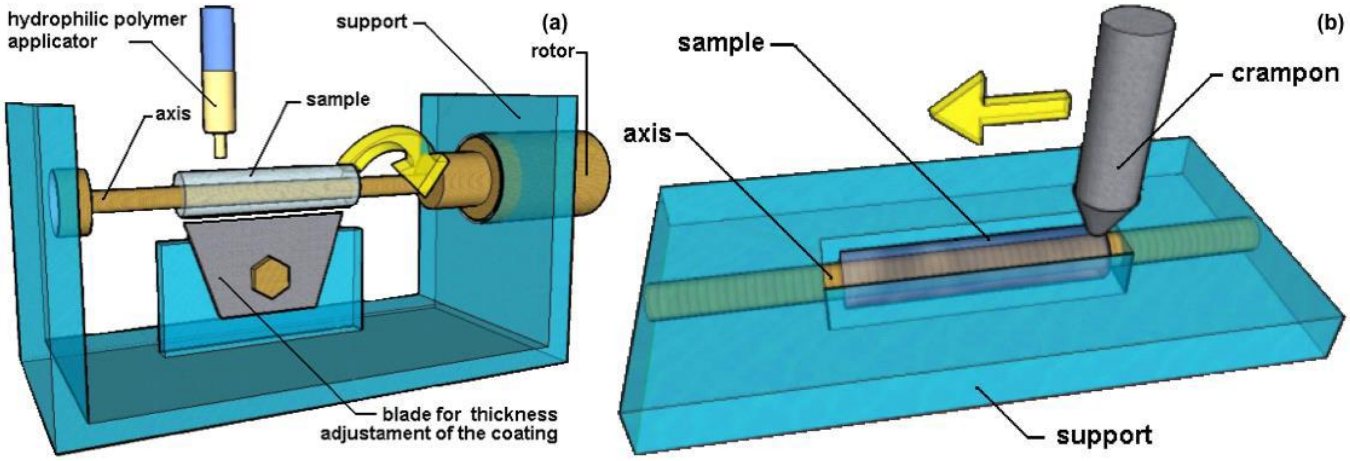

FIGURE 1: Set-ups of (a) coating and (b) scratching devices

Tests were performed on the samples by a conical metal tip that moved automatically at constant speed of 25 mm/min on the surface of the coated tubes. The tip was adjusted to form scratch marks around 0.1 mm. A qualitative analysis of the scratches on the surface of the samples was performed using the SEM images.

III. RESULTS AND DISCUSSION

Oxygen plasma, hydrogen peroxide and flame surface treatments were employed to increase wettability of polyamide 11 catheters surface. Surface hydrophilicity was evaluated through contact angle measurements and results are shown in Figures 2 a - c. The values correspond to the arithmetic means obtained in each exposure time period. The average contact angle of the untreated sample (time zero) was 84.2°.

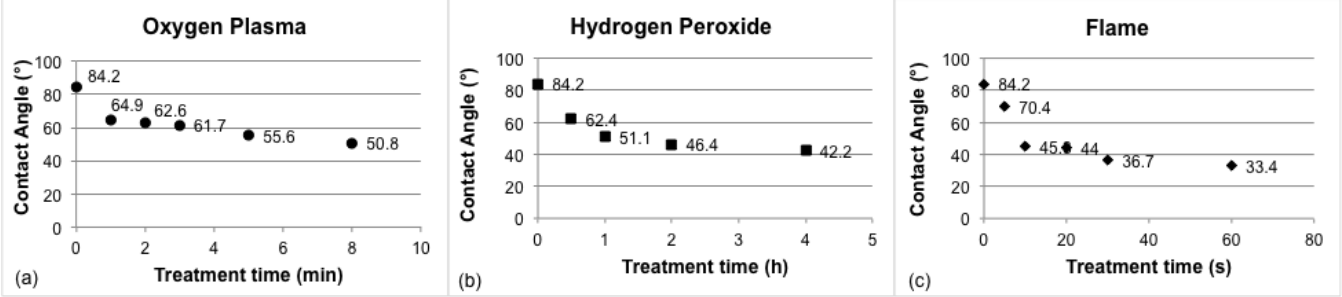

FIGURE 2: Contact angle v 177 ersus treatment exposure time for: a) plasma; b) hydrogen peroxide; and c) flame treatments

Samples treated with hydrogen peroxide and flame treatments presented the smallest contact angles, while the oxygen plasma resulted in a less expressive reduction. An important factor, which would lead to a reduction in the contact angles, is an increase in the surface energy of the tubes after treatment. The augmentation in the electrostatic interactions between droplets and the tubes surfaces by intermolecular interactions, such as hydrogen bonds can significantly increases the wettability 15. In an attempt to achieve a further increase in the wettability of the PA11 tubes, the samples were subjected to exposure times higher than those previously established for the hydrogen peroxide and flame treatment techniques, which were 7 h and 120 s, respectively. However, the contact angle for the hydrogen peroxide (7 h) and flame (120 s) treatments were 56.5 and 47.4, respectively, indicating an increase in the contact angle for both treatments after an optimum time. This change in the surface behavior may be related to a degradation of surface. This test confirms that the exposure times established in advance for the hydrogen peroxide (4h) and flame treatments (60s) can be considered as close to ideal under this study conditions. SEM was used to evaluate the surface of samples with lowest contact angle obtained for each technique. For comparison purposes, an untreated sample was also analyzed. As demonstrated in Figure 3 a, the surface of the untreated sample showed a flat region, with only some slight scratches. Higher roughness was noted on the surface of the sample treated by plasma for 8 min (Figure 6 b), characterized by irregular gaps. Samples treated with hydrogen peroxide, and flame treatments also presented irregularities on their surface, but with the detection of micro aggregates. The increase in surface roughness of samples submitted to the proposed treatments seems to be related to the increase in the contact angles, since this feature increase the contact area between the surface and water drop deposited.

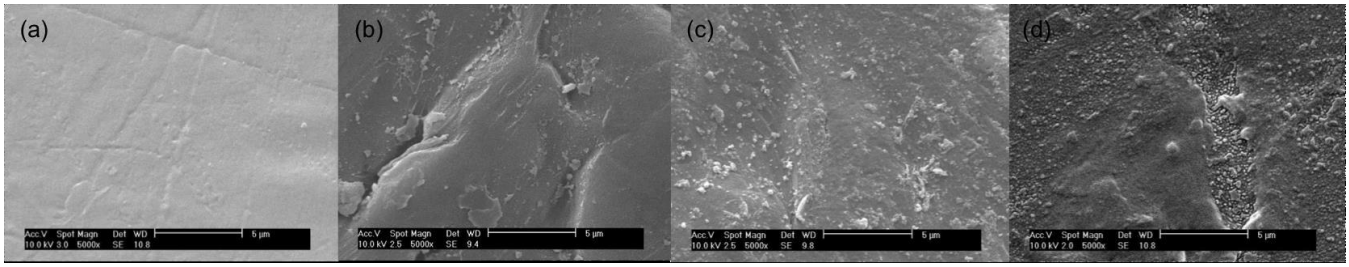

FIGURE 3: SEM images of the PA11 surfaces, magnification of 5000 times, samples: a) untreated PA11, b) treated by plasma during 8 min, c) by hydrogen peroxide during 4 h and d) by flame during 60 s.

Figures 4 a and b show the surfaces of samples treated with hydrogen peroxide for 7 h, and the flame for 120 s, respectively. Complete modification of material surface was observed in both conditions; however, hydrogen peroxide caused more pronounced changes. This characteristic corroborate with the hypothesis that after longer periods the samples surfaces started to degrade, resulting in the decrease of the contact angle. Furthermore the higher increase in surface roughness may be responsible for the increase in contact angle. A possible phenomenon that explains this behavior is the presence of micro features on the surface minimizing the contact area of the interface formed with the drop of water deposited, reducing the apparent wettability of the surface 13.

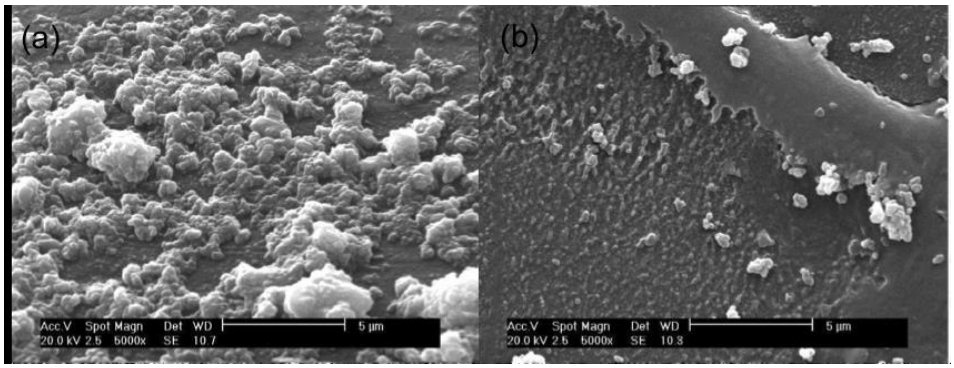

FIGURE 4: Micrographs of treated PA11 samples: a) 7 h with hydrogen peroxide, and b) 120 s with the flame.

Samples with the smaller contact angle values, as well as the untreated sample, were evaluated using FTIR. Figure 5 shows the spectra obtained at 3500 to 1200 cm-1 for the samples: untreated (Figure 5 a), treated with plasma for 8 min (Figure 5 b), hydrogen peroxide for 4 h (Figure 5 c) and the flame for 60 s (Figure 5 d).

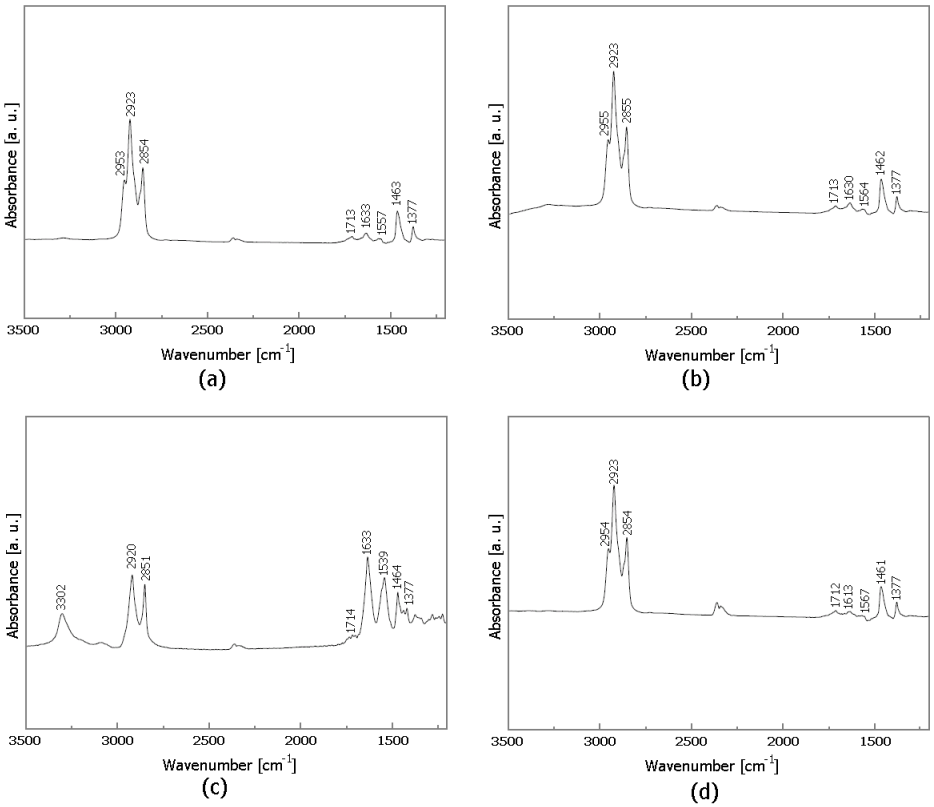

FIGURE 5: FTIR spectra of PA11 samples: a) untreated, and treated with b) plasma for 8 min, c) hydrogen peroxide for 4 h, and d) the flame for 60 s.

Characteristic bands of the hydrophilic coating were identified for the untreated sample and for samples treated with plasma and flame16, 17. The bands at 2953 and 2923 cm-1 correspond to the asymmetric axial deformation of the C-H bonds of the CH2 groups, respectively. The band at 2854 cm-1 corresponds to the symmetric axial deformation of C-H bonds of the CH2 group. The band at 1713 cm-1 corresponds to the vibration of axial deformation of C=O. The band at 1633 cm-1 corresponds to the axial deformation vibration of C = O (amide I band) and at 1557 cm-1 to the vibration of angular deformation of NH (amide II band). The bands at 1463 cm-1 and 1377 cm-243 1 refer to the symmetric angular deformations of CH2 [17-19]. On the other hand, the sample treated with hydrogen peroxide showed spectrum characteristics similar to the PA1118,19. FTIR provides information of a material volume within some μm of deep penetration; therefore it is suggested that most of the coating was removed due to the chemical treatment. Untreated sample and samples treated with hydrogen peroxide (4 h) and flame (60 s), which demonstrated the best results for contact angle, were selected for the scratch test.

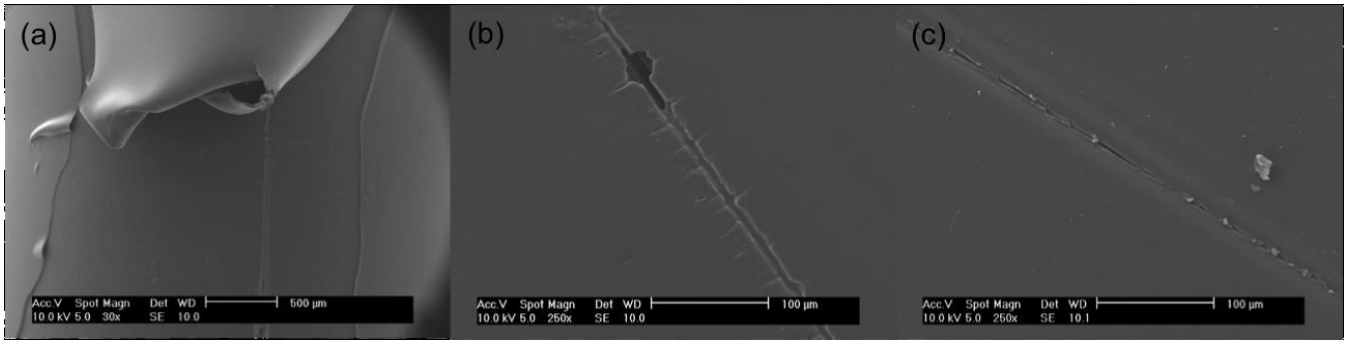

FIGURE 6. Micrographs of PA11 samples coated with hydrophilic film: (a) untreated PA11, and (b) treated with hydrogen peroxide during 4 h, and (c) treated by flame during 60 s.

In Figure 6 (a), the hydrophilic coating deposited on the untreated PA11 showed low adhesion to the surface, since there was a large detachment of the layer during the scratch test. Figure 6 (b) shows that sample treated with hydrogen peroxide during 4 h presents an improvement in the adhesion of the hydrophilic coating, compared with the untreated sample and small transverse cracks in the groove caused by the metal tip. This feature may be associated with the scratch of both coat and bulk materials. As observed in the FTIR results, the hydrogen peroxide treatment was observed to result in a thinner coating. On

the other hand, the sample treated with the flame for 60 s (Figure 6c) showed the best result regard to the adhesion of the hydrophilic coating. The scratch in this area is less clear, with no signs of coating detachment or tearing. This treatment was observed to result in the best emergent properties, where the coating had higher hydrophilicity and adhesion to the polymer. Future studies will evaluate the performance of this coating regard to its tribological and biocompatibility properties.

IV. CONCLUSION

The influence of exposure time for oxygen plasma, hydrogen peroxide solution and flame exposure treatments of polyamide 11 tubes was studied. It was observed that the treatment time directly affects the contact angle and there is an optimum time for each of the process investigated. SEM analysis of the surface of treated PA11 tubes allowed the observation of changes in the surface morphology and apparent roughness of the samples treated with different exposure times, and this could contribute for understand the behavior of contact angle as function of treatment time and wettability variation. FTIR results confirmed the presence of coating on samples treated with oxygen and flam as well as the thinning of the coated prepared via hydrogen peroxide. The scratch tests showed that the adhesion of the hydrophilic coating on the PA11 samples treated for 60 s with the flame presented a significant improvement over the adhesion comparing to untreated PA11 sample. The flame treatment was the most rapid and efficient process. A conclusion section must be included and should indicate clearly the advantages, limitations, and possible applications of the paper. Although a conclusion may review the main points of the paper, do not replicate the abstract as the conclusion. A conclusion might elaborate on the importance of the work or suggest applications and extensions.

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