

24th COBEM - 2017



24th ABCM International Congress of Mechanical Engineering  
December 3-8, 2017, Curitiba, PR, Brazil

COBEM-2017-0489

## EFFECT OF FLAME TREATMENT IN THE COATING ADHESION ON POLYPROPYLENE SUBSTRATE

Elisa Medeiros

Ricardo Brandes

Hazim Ali Al-Qureshi

Derce de Oliveira Souza Recouvreur

Federal University of Santa Catarina, Graduate Program in Engineering and Mechanical Sciences, Joinville, Brazil  
elisamede@gmail.com, ricardobrandes@gmail.com, hazim.ali@ufsc.br, derce.recouvreur@ufsc.br

**Abstract.** Some of the polymers largely used, such as Polypropylene (PP), have poor superficial properties making necessary a pre-treatment before coating the paint film. There is a number of pre-treatments related to the PP surface improvement, the most known at the industry is the flame process because it is possible to achieve the necessary level of surface energy in a short processing time. The flame process applied on polypropylene substrates increases the adhesion for painting films. Thus, the main objective in this work was to produce PP samples treated by flame treatment and perform morphological, chemical and surface tension characterizations. Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and Dyne Test Inks were employed to evaluate the material properties. The morphological analysis presented a superficial modification and the chemical analyses showed the formation of new functional groups after the flame treatment. This treatment increased the surface tension of the samples by approximately 20%. These results proved the efficacy of the flame treatment in the increase of the surface energy and in the adherence of the coatings applied to the PP substrates.

**Keywords:** polypropylene, flame treatment, adherence, coating, painting.

### 1. INTRODUCTION

The polypropylene (PP) is a polymer largely used industrially due to its good general properties and low cost (Maddah, 2016). However, PP suffers due to its surface properties, which make it a polymer with low surface adhesion, paint and biocompatibility, reducing its use in some applications (Ryntz and Yaneff, 2003). In fact, the coating adhesion at polymeric substrates is still a big issue. The adhesion depends of the surface wettability proprieties and free surface energy (Mazzola, 2011). For the PP, the lack of adhesion is due to the absence of polar groups and this can result in coating failings (Chashmejahanbin, 2014; Wanke, 2012). Thus, in order to improve the PP coating capacity, chemical pre-treatments can be employed on the surface of the polymer aiming to increase the adhesion of the coating (Ryntz and Yaneff, 2003; Lima and Santos, 2015). Flame treatment is a low cost option with good efficiency (Garbassi, *et al.*, 1987; Sutherland, *et al.*, 1991; Strobel, *et al.*, 1996). The flame treatment consists in material surface exposure to an oxidant flame generated through a hydrocarbon combustion. The resultant thermal oxidation allows the polar groups introduction at the surface by a partial break in the molecular chains (Etienne, 2011). The surface activation in polyolefins by flame treatment is based on the free radical degradation mechanism. The polypropylene oxidation process involves the C-H bonding break through the polymer surface by the high temperature generated for the combustion process and the inclusion of oxygen based groups making available new hydrophilic points for interaction between coating and substrate (Farris, *et al.*, 2010), as can be seen in Fig. 1.

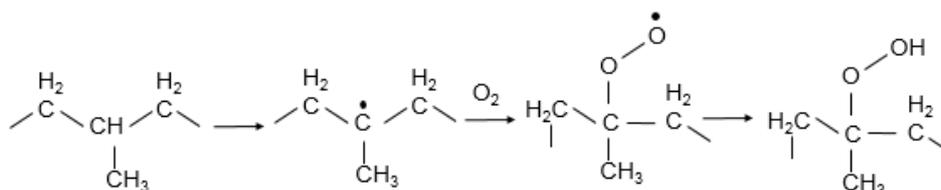


Figure 1 – PP thermal oxidation reaction by flame treatment.

It is of extreme importance to study the influence of flame treatment on the performance of painted polyolefins with respect to adhesion of the applied coating. Therefore, the main objective of this work was to produce and evaluate the influence of surface treatment by flame on polypropylene substrates in improving adhesion properties of coatings for industrial applications. The characterization techniques that were used to evaluate this treatment were the Dyne Test Inks in order to analysis the wettability of the substrate surface, the Fourier Transform Infrared Spectroscopy in order to analysis the chemical modifications of the surface of the material and the Scanning Electron Microscopy in order to verify the morphological changes.

## **2. EXPERIMENTAL PROCEDURE**

### **2.1. Materials**

Polypropylene high impact copolymer containing 15% of mineral filler (Hifax TYC 900P) supplied by the Lyondell Basell Industries was the selected polymer used for the production of the samples. The materials used for the coating of the samples were polymers based on polyester and acrylic polyurethane being that the set of coatings were composed by primer, base-coat and clear-coat all supplied by the PPG Industries Inc. All products used hold solvent technology. In the primer and clear-coat products was added a catalyst to promote the cure of these polymers.

### **2.2. Preparation of Polypropylene Samples**

The samples were produced by the injection molding process. After injection, the samples were cut according to the dimensions required for each test and characterization techniques. Then, the samples were painted according to a series of well-defined operations ranging from substrate preparation to application of a coating assembly. The surface preparation of the samples was performed by surface cleaning with isopropyl alcohol to remove oils and grime, followed by an ionized air curtain to neutralize the static loads and finally the flame treatment to increase the energy of surface of the substrate. The flame treatment and paint coating were applied in a robotized industrial paint line. The process steps were the manual cleaning, ionized air curtain passage, pre-treatment of flame, application of primer, application of base, application of varnish and stove of cure. A burner from Ipros with 200mm of flame width supported by a robot was used to carry out the flame process, allowing to control the process parameters that can influence the flame treatment efficiency. The treatment was performed in the samples under a scanning speed of 650 mm/s.

### **2.3. Scanning Electron Microscopy Analysis**

The morphologies of the samples were characterized by SEM. The SEM analysis were performed with a Shimadzu SS-550 microscope. The PP samples with and without the flame treatment were placed on an aluminum support and the surface was covered with a layer of gold around 30 nm with the Shimadzu IC-50 Ion Coater device. A conductive tape was added at the top of the samples to do contact with the metal support and the electrons were accelerated with a voltage of 10 kV.

### **2.4. Fourier Transform Infrared Analysis**

As a result of the flame process, a variety of chemical groups containing oxygen are formed on the surface of the polymer, phenomena such as cross-linking can be present. The FTIR test is used to identify chemical composition and functional groups. So, the samples were analyzed by FTIR to verify the chemical modifications. The FTIR analyzes were carried out using a Thermo Nicolet (Avatar 370/DTGS) equipment. The analyzes were performed with 64 readings for each measurement.

### **2.5. Wettability Analysis**

To characterize the wettability of the samples the Dyne Test Inks was applied, which is composed of a set of standard paints that allow to control the effectiveness of the surface activation media. Pens with tensoactive liquid were used in different surface tension scales. The pens used were of the Polymix brand with tensions ranging from 30 to 54 dynes/cm<sup>2</sup>. In this test were used a group of pens with known surface tension values. The liquid was applied to the surface with the tip of the pen by drawing a continuous strip with a minimum length of 7cm on the surface of the material to be analyzed. After application, the behavior of the liquid film on the surface was observed for 3 seconds. The wettability was related to which the ink film remained intact. The surface tension evaluation by the Dyne Inks method was performed in samples of PP without and with flame treatment.

### 3. RESULTS AND DISCUSSION

#### 3.1. SEM Evaluation

Scanning electron microscopy analyzes were performed to verify the change in the roughness of the samples. For this, samples of PP with and without flame treatment were analyzed. Mazzola, *et al.*, 2011 found variations in the morphology of the samples after buckling when observed in the SEM at an increase of 20000 $\times$ . Ferris, *et al.*, 2010 analyzed samples with different initial roughness and they observed a reduction in roughness, although less significant for samples with smaller initial roughness. Analyzing the micrographs obtained by SEM, it is possible to observe morphological differences in the surface of the samples with and without the flame treatment, as can be seen in Fig. 2.

It is possible to observe higher porosity in the samples without treatment Fig. 2 (a), whereas in Fig. 2 (b), samples that received the flame treatment, a more homogeneous surface can be observed. Considering the analyzes presented by Ferris, *et al.*, 2010 that for totally smooth samples the reduction of roughness was not very accentuated, a correlation can be performed with the samples analyzed in this study, where samples were injected in a mold without texture, that is, extremely smooth. This fact justifies a not significant change in the morphology of samples after flame treatment. Another factor to be considered is that the equipment used for the microscopic analysis did not allow to obtain images with quality and magnification necessary to analyze in more detail the morphological alterations of the samples.

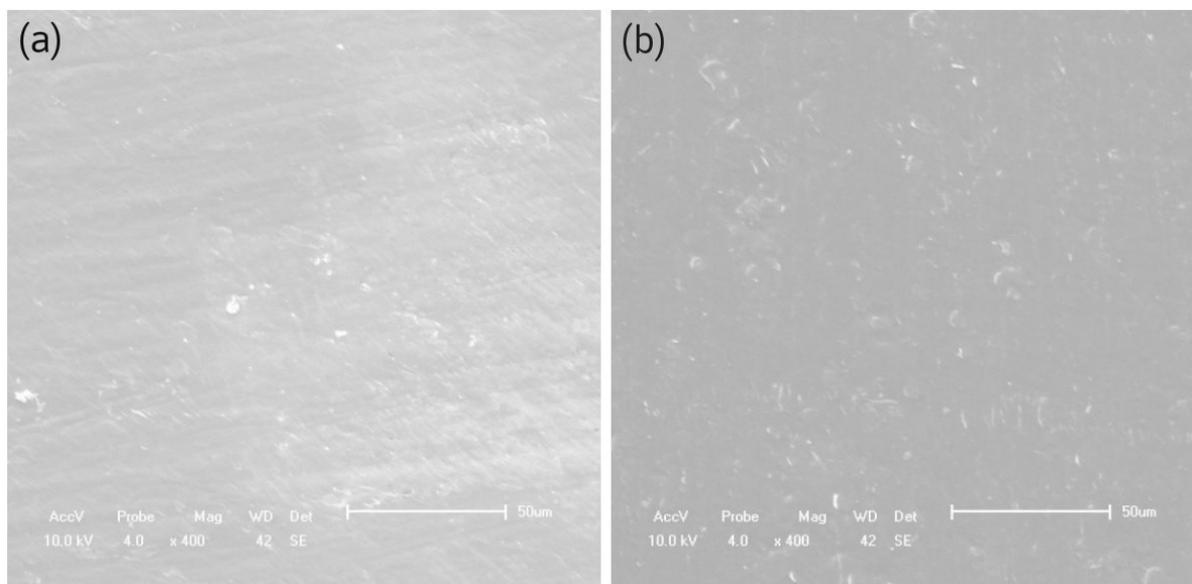


Figure 2. Micrographs obtained from SEM. In (a) - PP without flame treatment and in (b) PP with flame treatment.

#### 3.2. FTIR Evaluation

Fourier Transform Infrared Spectroscopy analyzes were performed on samples without flame treatment and with flame treatment. Untreated and treated samples were measured under three different regions. This chemical analysis can verify by infrared spectroscopy the specific functional groups formed in the materials, therefore it would be possible to know the new functional groups formed on the treated sample after the flame treatment. Ferris, *et al.*, 2010 showed that PP parts treated by flame contain oxygen in the form of hydroxyl groups, with approximately 20 to 30% and other groups such as carboxyl and carbonyl. So, it is expected to find these groups in the samples after the flame treatment. The PP samples without flame treatment were taken as the basis for the analyzes on the effect of flame treatment. In the spectrum that refers to the sample of untreated PP, according to Fig. 3, the bands are identified at approximately 1000, 1500 and 3000  $\text{cm}^{-1}$ , which indicate the groups,  $-\text{CH}_3$ , C-C and C-H, respectively (Wanke, *et al.*, 2012).

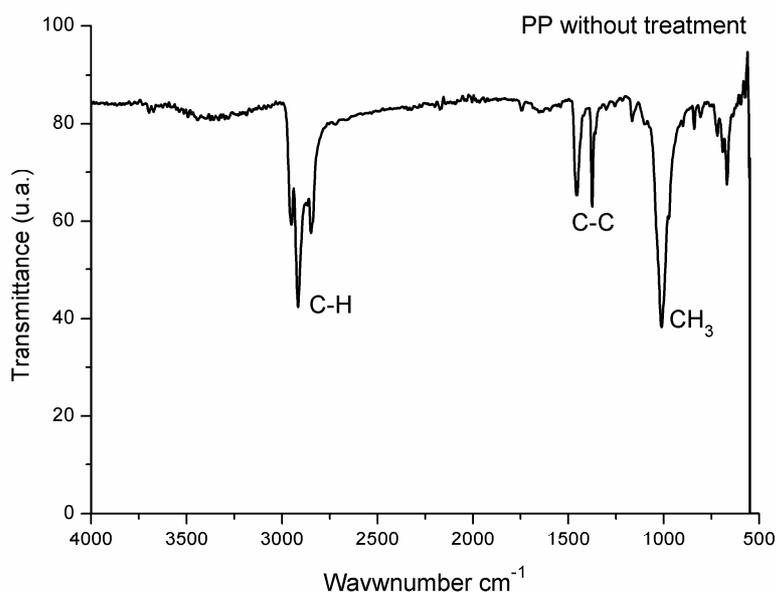


Figure 3. FTIR spectrum of the PP sample without flame treatment.

The samples with flame treatment were measured in three different samples and no variations were observed in the spectra present, as shown in Fig. 4. After the flame treatment the spectra indicate the formation of new functional groups due to the appearance of new bands in the PP, as can be observed in Fig. 4 in the absorption peaks of 1600 [C=O] and 3200 [O-H]. Thus, FTIR analyzes showed the formation of new groups functional groups for the PP sample after the flame treatment and the groups created were carbonyl [C=O] and hydroxyl [O-H]. The formation of these groups confirms the theory that the flame treatment is based on the oxidation of the substrate surface, that means, inclusion of oxygen for the formation of new polar groups increasing the surface tension of the substrate. The results obtained are consistent with other studies on the flame treatment.

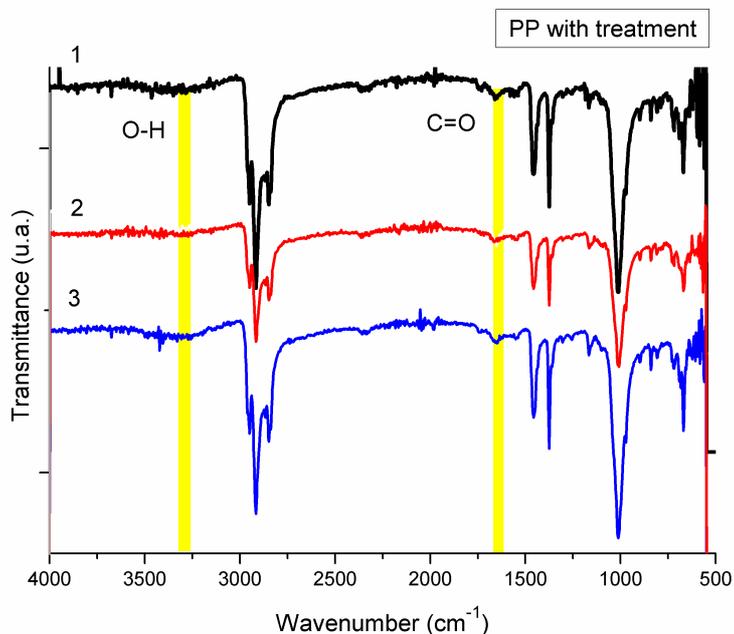


Figure 4. FTIR spectrum of the PP sample with flame treatment.

### 3.3. Wettability Evaluation

The wettability (surface tension) of the samples was verified through the Dyne Test Inks, which pens with active surfactant at different levels of surface tension were used. The surface tension was evaluated in two stages, PP samples

without the flame treatment and PP samples with the flame treatment. The Dyne Test Inks performed on the sample without flame treatment, Fig. 5, shows that the trace identified as B, 38 dynes, it presented the most homogeneous behavior. According to the Dyne Inks methodology, it is possible to verify that the traces A and C are dotted, this means that the substrate has a different surface tension compared to the liquid used of 36 and 40 dynes, respectively. Thus, it is possible to infer that the surface tension of the PP, before the flame treatment was of 38 dynes/cm<sup>2</sup>.

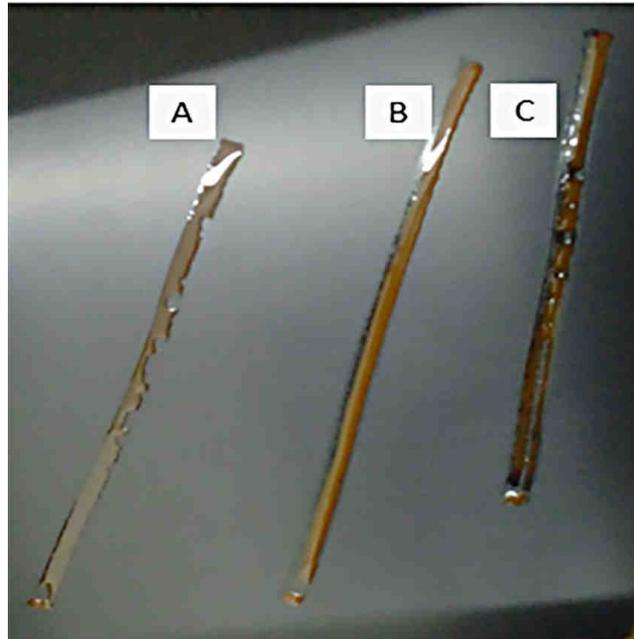


Figure 5. Results of the Dyne Test Inks in the PP samples without flame treatment. The pens with tensoactive liquids were used in (A) 36 dynes, (B) 38 dynes and (C) 40 dynes.

The surface tension was evaluated after the flame treatment. Fig. 6 presents the results of surface tension after the treatment with a speed of 650 mm/s and it is verified that the film of 46 dynes (trace A) remains continuous while that of 48 dynes (trace B) shows discontinuities. So, the surface tension reached by PP with the flame treatment was of 46 dynes/cm<sup>2</sup>. If we compare this value with the surface tension of the PP without this treatment, 38 dynes/cm<sup>2</sup>, we can prove the efficacy of the flame treatment due to the increased surface tension, which it reached an increase of 8 dynes/cm<sup>2</sup>. Farris, *et al.*, 2010 measured surface tension values for samples of polyolefin materials using different processing conditions of the flame treatment and found values ranging from 40 to 52 dynes/cm<sup>2</sup>, with gains between 15 and 30% in surface tension depending on the treatment applied. These results are in agreement with those found in this research.



Figure 6. Results of the Dyne Test Inks after flame treatment, (A) 46 dynes and (B) 48 dynes.

Through a simple and rapid evaluation of the surface tension, by means of the Dyne Test Inks, it was possible to prove the efficacy of the flame treatment in order to increase the PP surface tension. Therefore, Dyne Test Inks is a practical tool to control this property of the substrate, since it allows to determine the minimum surface tension that the

substrate must reach to ensure a good adhesion to the coating to be applied. Gains of the order of 20% were achieved with flame treatment.

#### 4. CONCLUSION

Regarding the morphological aspect of PP, SEM analysis showed slight differences in the morphology between PP samples with and without flame treatment, especially in relation to the porosity of the samples. It has been found that the flame treatment alters the morphology of the material. FTIR analyzes have shown that the flame treatment is able to introduce new functional groups on the surface of the substrate through oxidation. In the analyzes carried out in this work were identified the formation of hydroxyl and carbonyl groups after the flame of PP. However, this behavior was not very accentuated as found by other authors. The flame treatment proved to be effective in improving the wettability of PP, which was verified by the increase in the surface tension of the samples that suffered the treatment, achieving a gain in the order of 8 dynes/cm<sup>2</sup> which corresponds to an increase of 20%. These results demonstrated that the surface treatment of PP can improve its surface properties, enabling the use of this material in applications that require coating anchoring, such as the painting of automotive parts.

#### 5. ACKNOWLEDGMENTS

Authors acknowledge the Federal University of Santa Catarina for supported this study.

#### 6. REFERENCES

- Chashmejahanbin, M.R., Salimi, A., Langroudi, A.E., 2014. "The study of the coating adhesion on PP surface modified indifferent plasma/acrylic acid solution". *International Journal of Adhesion & Adhesives*, Vol. 49, p. 44-50.
- Etienne, B., 2011. "Guide Théorique sur la Technique de Flammage pour pieces plastiques avant peinture". Document Base Métier Ingénierie Renault.
- Farris, S., Pozzoli, S., Biagioni, P., Duó, L., Mancinelli, S., Piergiovanni, L., 2010. "The fundamentals of flame treatment for the surface activation of polyolefin polymers - A review". *Polymer*, Vol.51, p. 3591-3605.
- Garbassi, F., Occhiello, E., Polato, F., Brown, A., 1987. "Surface effect of flame treatments on polypropylene". *Journal of Materials Science*, Vol. 22, p. 1450-1456.
- Lima, P.M., Santos, J.C.C., 2015. "Efeito da flambagem do polipropileno na aderência de tintas e tensão superficial do polímero". In: *Anais do 13º Congresso Brasileiro de Polímeros*, Natal, Brazil.
- Maddah, A.H., 2016. "Polypropylene as a promising plastic: a review". *American Journal of Polymer Science*, Vol. 6, p. 1-11.
- Mazzola, L., Bemporad, E., Carassiti, F., 2011. "Flame treatment on plastic: A new surface free energy statistical prediction model and characterization of treated surfaces". *Applied Surface Science*, Vol. 257, p. 2148-2158.
- Ryntz, R.A. and Yaneff, P.V., 2003. "Coatings of polymers and plastics". Marcel Dekker, Inc., New York, 1<sup>nd</sup> edition.
- Strobel, M., Branch, M.C., Ulsh, M., Kapaun, R.S., Kirk, S., Lyons, C.S., 1996. Flame surface modification of polypropylene film. *Journal of Adhesion Science and Technology*, Vol. 10, p. 515-539.
- Sutherland, I., Brewis, D.M., Health, R.J., Sheng, E., 1991. "Modification of polypropylene surfaces by flame treatment". *Surface and Interface Analysis*, Vol. 17, p. 507-510.
- Wanke, H.C., Barbosa, L.G., Hübner, J.V.M., Horowitz, F., Mauler, R.S., Oliveira, R.V.B., 2012. "Recuperação hidrofóbica de polipropileno tratado por VUV ou Plasma". *Polímeros*, Vol. 22, p. 158-163.

#### 7. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.