Investigation of the Ultraviolet Irradiation on Blend Films of PS/PCL

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Abstract — In this work, an investigation was carried out on the effect of ultraviolet light on different films. Polystyrene (PS), poly (caprolactone) (PCL), and blended films of PS/PCL were produced. Ethyl acetate (AE) was used as a solvent, and PS and PCL solutions were prepared by dissolving 250 mg in 2.5mL of AE under mechanical stirring at room temperature. The blended solutions of PS/PCL (PS/PCL) were prepared with different mass proportions, such as 90:10, 80:20, 70:30, and 60:40 into 2.5 mL of EA. The solutions were dripped with 500 µL on a glass substrate, and the films were produced with mechanical rotation of N=2000 RPM for 15 seconds using a Spin coater. The films were submitted to ultraviolet light for t=60 minutes and morphologically analyzed by optical microscopy, chemically by IR spectroscopy, and superficially by contact angle and wettability; this last analysis also investigated the effect of ultraviolet light at t=0, t=30, and t=60 minutes. The exposure of ultraviolet light on the films affected its morphologies. IR spectra showed that the photodegradation increased for larger PCL amounts into the blend. The contact angle measurements showed that after exposure to ultraviolet light, the hydrophobicity of the films increased. Therefore, the presence of PCL in the polymer mixture promoted the photodegradation of the PS/PCL films, making it attractive for developing new packaging.

Index Terms—Polymeric blend, poly (caprolactone), polystyrene, photodegradation.

I. INTRODUCTION

The use of conventional synthetic polymers has indispensable applications for the daily life of the modern world [1]. On the other hand, the appeal involving environmental problems caused by the inappropriate disposal of these materials implies the need for measures taken to reduce the environmental impact [2]. The development of new materials and methodologies has been investigated by researchers and scientists aiming the biodegradability these materials [2], [3].

Polystyrene (PS) is one of the most used polymers in the packaging industry [4]. It is a homopolymer resulting from styrene polymerization, and has several benzene rings in its polymeric chain, highly hydrophobic, transparent, easy pigmentation, low cost, and its attractive physical-mechanical characteristics and versatility for processing [4], [5]. PS-based polymers are applied in the manufacture of insulators, electrotechnical materials, resin varnishes, cell phone plastics, plastic cups, packaging, and others [6]-[8]. Naturally, polymeric materials exhibit photodegradation from solar irradiation along time, initiating oxidative reactions, causing the loss of color, altering the brightness, fragility, and formation of fractures [9], [10]. During the degradation process, chain break and cross-linking processes occur, causing surface and chemical changes [11]. The photodegradation mechanisms of the most common polymers are well established. However, the behavior of polymeric materials about UV irradiation is still poorly understood due to the great complexity of the interactions between the components [12].

The PS is degraded under environmental conditions, such as light, heat and humidity. However, it is considered a non-biodegradable polymer, i.e., it does not degrade by the action of microorganisms [13]. However, the mixtures of polymers involving the presence of biodegradable polymers can be an alternative to reduce ecological problems.

Traditional biodegradable polymers most used are PCL, polyhydroxyalkanoate (PHA), polyhydroxybutyrate (PHB), polybutylene succinate (PBS), poly(L-Lactide) (PLA), poly(L-lactic acid) (PLLA), and poly(D-lactic acid) (PDLA) [14]. These polymers have potential applications in the industrial packaging area; however, their disadvantage is mainly in the cost compared to plastics [14], [15], i.e.: PS, polypropylene (PP), low density polypropylene (LDPE), high density polypropylene (HDPE), polyvinyl chloride (PVC), and others [16].

PCL is a biodegradable polymer, aliphatic and synthesized by the caprolactone monomer ring opening. it has interesting properties, such as biodegradability, biocompatibility, and good mechanical property [17], [18], including impact resistance.

Studies have reported in the literature the production of blends of biodegradable and non-biodegradable polymers, specifically on PCL and PS, e.g., blends of PLA/PS, PBS/PS, PCL/PS, PCL/LDPE, PCL/PP, PCL/PVC, and others [16]. Although these blends have potential industrial applications, studies on their performance are needed. In this context, investigations on photodegradation of polymers have been carried out, including the PCL [3].

França et al. [3] observed that the PCL was severely affected by UV irradiation and presented photodegradation when exposed to UV irradiation for 9 weeks; PCL showed changes in mechanical and thermal properties, in the morphological characteristics, and modification in the FTIR spectra in the carbonyl groups at 1725 cm⁻¹. Martins-Franchetti et al. [19] produced PCL/PVP blend and found
changes in the blend when exposed to UV irradiation, specifically structural and morphological changes. On the other hand, the authors reported that the PCL/PVP blend was more resistant to photodegradation than the PCL and PVP individually.

This work aimed to investigate the chemical, morphological, and superficial influence of films formed by PS/PCL blends exposure to UV irradiation.

II. MATERIALS AND METHODS

A. Materials

PCL with MM=80,000 g/mol – Sigma aldrich, PS with MM=10,000 g/mol – Piramidal company, and ethyl acetate (EA, 99.85%, Anidrol). Potassium bromide (KBr, Produtos Quimicos Eireli). Deionized water (0.5 μS/cm, Deionized Water – Anidrol). Potassium bromide (KBr, Produtos Quimicos Eireli). Deionized water (0.5 μS/cm, Anidrol).  Potassium bromide (KBr, Produtos Quimicos Eireli). Deionized water (0.5 μS/cm, Anidrol). Potassium bromide (KBr, Produtos Quimicos Eireli). Deionized water (0.5 μS/cm, Anidrol). Potassium bromide (KBr, Produtos Quimicos Eireli). Deionized water (0.5 μS/cm, Anidrol). Potassium bromide (KBr, Produtos Quimicos Eireli). Deionized water (0.5 μS/cm, Anidrol). Potassium bromide (KBr, Produtos Quimicos Eireli). Deionized water (0.5 μS/cm, Anidrol).

B. Preparation of Solutions and Films of PS, PCL, and PS/PCL Blend

PS solution was prepared by dissolving PS (250 mg) in 2.5 mL of EA under mechanical stirring at room temperature for 4 hours. PCL solution was prepared similarly to the PS solution, except for the mechanical stirring time, which was 2 hours. The solutions blended with PS and PCL were prepared with different mass proportions (PS: PCL), such as 90:10, 80:20, 70:30, and 60:40 dissolved in 2.5 mL of EA. The mechanical stirring time was 7 hours at room temperature.

In order to prepare the films, each solution was deposited on a glass substrate (2.5×2.5 cm) with volume of V=500 μL, which were submitted to the Spin coater (SPIN COATER, VTC-50A) with rotation speed N=500 RPM for 1 second soon afterward of N=2,000 RPM for 15 seconds. All the films were prepared at room temperature.

C. Investigation of UV Irradiation on the PS/PCL Films

A Box equipped with 4 lamps, wavelength of 365 nm (UV-A/UV-B), and 9 Watts each was used to investigate the films under UV irradiation. The films were exposed to UV irradiation at 8 cm distance for 60 minutes. Fig. 1 shows the schematic illustration of the experiment performed.

D. Characterization by Infrared Spectroscopy – IR

The FTIR spectra were obtained by spectrometer (Thermo Electron – Model Nicolet iS10), 32 scans, and ranging from 400 to 4000 cm⁻¹ with 4 cm⁻¹ resolution. The films were mixture with potassium bromide (KBr) in a 1:100 ratio and pressed at 80 kN pressure for 1 minute.

E. Characterization by Optical Microscopy – OM

Trinocular metallographic optical microscope (Fortel – Model MCB100) equipped with 40X optical lens was used to observe the film morphology that were exposed to UV irradiation.

F. Characterization by Wettability and Contact Angle – CA

Contact angle measurements (θ) were obtained using deionized water (10 μL) on the films-surface at room temperature. The digital microscope (DINO-Lite plus, 1000x resolution) was used to observe the water drop photographed at 120 s. The CA measure were obtained from images using the LB-ADSA directory of the software ImageJ.

III. RESULTS AND DISCUSSIONS

In the Fig. 2 is shown the IR absorption spectra of PS film. The main vibrational bands of PS founded in this work are in concordance with the literature [20],[21]. The bands in 3058 cm⁻¹ and 3024 cm⁻¹ are attributed to the C—H aromatic stretching vibration. Methylenes of the polymeric chain of PS were observed in 2922 cm⁻¹ and 2850 cm⁻¹. The absorption peaks in the positions at 1602, 1494, and 1452 cm⁻¹ correspond to the aromatic C=C stretching of the benzene ring. In 758 cm⁻¹ and 696 cm⁻¹ are attributions that show the existence of a unique substituent in the benzene ring, the C—H out-of-plane bending vibration [20]. Fig. 2 also shows the absorption peaks in the position at 3450 cm⁻¹ that correspond to the O—H group. This functional group does not belong to the chemical composition of PS; however, it shows the presence of hydroxyl from water that may come from moisture.

In the Fig. 3 is shown the IR absorption spectra of PCL film. The absorption peaks in the positions at 2939 cm⁻¹ and 2866 cm⁻¹ corresponding to the asymmetric and symmetric CH₂ stretching, respectively. It was observed the carbonyl stretching at 1725 cm⁻¹. The position at 1472 cm⁻¹ is
attributed to the angular deformation C—H, whereas at 1295 cm\(^{-1}\) corresponding to the C—O and C—C stretching in the crystalline phase. The bands at 1238 cm\(^{-1}\) and 1171 cm\(^{-1}\) are the positions of asymmetric and symmetric COC stretching. The OC—O stretching was founded in the position at 1190 cm\(^{-1}\). All bands observed in this study are in concordance with the literature [22].

The mixture of polymers with different ratio was investigated to understand the miscibility and interaction between the polymers. The Fig. 4 shows the spectra of the blends before exposure to UV irradiation in the 1800–1000 cm\(^{-1}\) region. The peaks at 1600, 1492, and 1452 cm\(^{-1}\) are specific and unique peaks of the PS; note that these peaks do not appear in PCL spectra. It was observed the same with the peaks at 1294, 1239, and 1170 cm\(^{-1}\) that belong only to the PCL. Obviously, the blend is composed of PS and PCL characteristics. In addition, the peak intensity at 1733 cm\(^{-1}\) increases with the increase in the amount of PCL in the composition of the PS/PCL blend.

Fig. 4 also shows two vibrational positions highlighted, such as 1733 cm\(^{-1}\) and 1190 cm\(^{-1}\), attributed to the carbonyl stretch and the OC—O stretch of the PCL, respectively. The position of the carbonyl stretch shifted from 1725 cm\(^{-1}\) to 1733 cm\(^{-1}\), and the peak at 1190 cm\(^{-1}\) does not appear in the PS/PCL films at any mixing ratio (compare the Fig. 3 and Fig. 4). This result shows that the interaction between the polymers caused the displacement of peak due to the interaction between C—H and O=C. This effect corroborates with other blends using PCL in the mixture [23].

The inhibition of stretching vibration by 1190 cm\(^{-1}\) may have occurred due to the interaction between C—H and OC—O, what prevents it from vibrating. The results showed no chemical bond between the polymers because no new chemical bond was observed [24].

PS/PCL blends were exposed to UV irradiation for 60 minutes. The comparison between the IR absorption spectra is shown in Fig. 5. The peak at 1733 cm\(^{-1}\) attributed to the carbonyl group is important to analyze the effect of UV irradiation. Peak intensity increases with the increase in the amount of PCL in the blend, as shown in Fig. 4; on the other hand, after UV irradiation, the peak intensity is reduced in all PCL concentrations. The reason for this may be the photodegradation of the PCL present in the blend. Besides, the same effect is observed in the 1500 – 900 cm\(^{-1}\) regions, as shown in Fig. 5.

The PS/PCL film (90:10) showed changes in its morphology after UV irradiation. Fig. 6a shows that phase formation between the polymers presented by two distinct regions, a light region related to PS and a dark one to PCL [25]. Fig. 6b shows the PCL region in spheres format after UV irradiation. This effect in the morphology may have occurred due to its low melting temperature \(T_m = 55.8 \, ^{\circ}\)C [7], making it sensitive to UV irradiation.

Fig. 6c and 6d show the results of the measurements of the CA and wettability test of the PS/PCL film (90:10), respectively. The UV irradiation on the films was investigated at 0, 30, and 60 minutes times.

The CA measurements showed that there was an increase from \(\theta = 83.20 \pm 0.50^\circ\) to \(\theta = 84.60 \pm 0.40^\circ\) and \(\theta = 85.00 \pm 0.50^\circ\). The results show an increase in the hydrophobicity of the PS/PCL film (90:10) after UV irradiation. In Fig. 6d, it is possible to observe the water drop on the films at different times of UV irradiation. In all cases, the water drop behavior of wettability test was a half-moon with contact angle values below 90\(^{\circ}\), characterizing the films as hydrophilic [27].
Fig. 6. OM images of PS/PCL films (90:10) before (a) and after (b) UV irradiation, contact angle measurements (c), and wettability tests (d).

The morphologies of the PS/PCL film (80:20) after and before the UV irradiation are shown in Fig. 7a and 7b, respectively. In the Fig. 7b is shown a scattering of the PCL region after UV irradiation, reinforcing the hypothesis of its sensitivity to UV irradiation due to the low melting temperature. The PS/PCL film (80:20) presented a significative increase in the contact angle measurements. The increase was of $\theta = 72.40 \pm 0.4^\circ$ to $\theta = 82.02 \pm 0.5^\circ$ and $\theta = 82.40 \pm 0.5^\circ$ at 0, 30, and 60 minutes, respectively. The increase in the PCL amount into blended film resulted in the CA measurement decrease.

After UV irradiation, the CA measurement increases to $82.40 \pm 0.5^\circ$ at 60 minutes. This result reveals that PCL is the polymer most affected by UV irradiation. Fig. 7d show the half-moon behavior (<90°) of the water drop on films also characterized as hydrophilic.

Fig. 7. OM images of PS/PCL films (80:20) before (a) and after (b) UV irradiation, contact angle measurements (c), and wettability tests (d).

The Fig. 8a and 8b show the OM images of PS/PCL film (70:30), whereas the OM images of PS/PCL film (60:40) are presented in Fig. 9a and 9b. Obviously, regardless of the amount of PCL within blended film, there is the formation of phases between the polymers.

PS/PCL film (70:30) presented CA measurements of $\theta = 72.00 \pm 0.40^\circ$ at 0 minutes (see Fig. 8c), it this value is similar compared to value of PS/PCL film (80:20) that was $\theta = 72.40 \pm 0.4^\circ$, on the hand, for the PS/PCL film (60:40) the CA was of $\theta = 69.60 \pm 0.50^\circ$ (see Fig. 9c). The Fig. 8d and Fig. 9d shown the half-moon behavior (<90°) of the water drop on the PS/PCL films (70:30) and (60:40) characterized as hydrophilic.

Fig. 8. OM images of PS/PCL films (70:30) before (a) and after (b) UV irradiation, contact angle measurements (c), and wettability tests (d).

Fig. 9. OM images of PS/PCL films (60:40) before (a) and after (b) UV irradiation, contact angle measurements (c), and wettability tests (d).

IV. CONCLUSION

We conclude that the mixture between the polymers to produce the PS/PCL blend caused a shift in the peak positioned at 1725 cm$^{-1}$ to 1733 cm$^{-1}$ due to the interaction between the C—H and O=C groups. UV irradiation reduced the intensity of the IR spectra of the PS/PCL blend for all concentrations with PCL. Probably due to photodegradation of the PCL present in the mix. The PCL increased the hydrophilicity of the PS/PCL films with the increase in amount of PCL; the same effect was observed in PS/PCL films exposed to UV irradiation. In all cases, the wetting behavior of water drop was a half-moon with AC values below 90°. Our study suggests that the presence of PCL in PS/PCL films changed the surface of films and promoted its photodegradation, making it attractive for the development of new packaging.
ACKNOWLEDGMENT

The authors thank the Amazonas State Research Support Foundation – FAPEAM (062.00113/2016), Coordination for the Improvement of Higher Education Personnel – CAPES, and Federal University of Amazonas – UFAM.

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