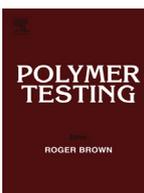




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A new device for in-line colorimetric quantification of polypropylene degradation under multiple extrusions

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ABSTRACT

An in-line colorimeter that is able to quantify color changes in real time during extrusion was developed and validated. It is composed of LEDs emitting at three different wavelengths and a photocell that measures the intensity of the light transmitted through the polymer melt flow. The colorimeter was validated at the bench by employing colored aqueous solutions and in-line during the extrusion of a colored polypropylene. Furthermore, it was used to in-line quantify the color changes in a polypropylene as generated over multiple extrusions due to thermo-mechanical degradation. The technique was proved to be fast and suitable to measure color changes in real time during extrusion.

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1. Introduction

Over recent years, several techniques have been used to monitor in real time the evolution of material properties during processing. These techniques, which can be qualitative and/or quantitative, include rheology [1], spectroscopic absorption [2], ultrasound attenuation [3], microscopy imaging [4] and light scattering [5], among others [6]. As the most important processing technique in the polymer transformation industry [7], the extrusion process shows potential for the application of inline and/or online measurements in order to characterize in real time the material and, ultimately, control the process. In fact, the real-time analysis of the material allows saving several steps of sample preparation that are required to perform off-line measurements, greatly reducing the amount of off-grade products.

During extrusion, high shear and temperature can cause a combination of thermal, mechanical, and chemical degradation in polymers [8]. This can lead to significant changes, not only in the rheological properties of the melt, but also in its optical properties. In particular, the chromophore groups, which often result from polymer degradation, absorb electromagnetic radiation in specific wavelengths of the visible spectrum, leading to the formation of color. Hence, to measure the color of the melt during extrusion may be, in principal, a good way to monitor the process.

While the human interpretation of color is subjective, the techniques and equipment developed in colorimetry can describe and quantify colors and any changes caused by formation/addition/alteration of the substances that may cause color in a material [9]. In fact, up to a critical concentration, the Beer-Lambert Law [10] allows establishment of a precise relationship between the concentration of chromophore groups and the intensity of the final color. Instrumental colorimetry started with the first

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standards and recommendations established by CIE (International Commission of Illumination) and the creation of models to describe color, such as the additive tristimulus model RGB (red, green and blue) based on a standard observer.

Several studies have proved that colorimetry is a valuable tool to evaluate the processing conditions and/or the changes in the material structure. In order to determine the residence time distribution of different polyethylene in a twin-screw extruder, Polance et al. [11] used a red dye as a tracer. By measuring the changes in the color of the material with a commercial colorimeter, they found that the residence time distribution of LDPE is narrower than that of LLDPE. Fornes et al. [12] studied the degradation and color formation in nanocomposites of polyamide and nanoclays. They were able to relate the color, as measured with a colorimeter, with both the double bonds in the organic surfactant and the ions present in the structure of the nanoclay. Reis et al. [13] observed an increase in the yellow color intensity of polypropylene/montmorillonite nanocomposites after multiple extrusions. That phenomenon was attributed, at least in part, to the oxidation of iron ions present as impurities in the nanoclay structure. Although these studies have been performed on the extruded material off-line, they anticipate the potential of an in-line device capable of measuring color in real time.

The degradation of polypropylene during extrusion occurs preferentially by chain scission due to the presence of an hydrogen linked to a tertiary carbon in the backbone chain [14]. It was observed by González-González et al. that, after multiple extrusions [15], a progressive reduction in the molecular weight distribution with increasing number of processing cycles. Canevarolo and Babetto [16] observed reductions on the average molecular weight and an increase in carbonyl and unsaturation indexes as the number of extrusions and the aggressiveness of the screw profile containing kneading discs increases. In addition, they found that the kneading element of 90° (KB90) caused a higher level of degradation.

Our research group has made several studies involving real time analysis during extrusion. Specifically, a turbidimeter that can be attached to the extruder die-exit was developed to measure the residence time distribution [5,17], and later used to study the degradation of single polymer [18] and the morphology of polymer blends [19,20] and nanocomposites [21]. Further changes in that device led to the development of a rheopolarimeter to quantify the flow birefringence during the polymer extrusion [22]. In this paper, we present a new in-line detector to quantify the light intensity attenuation at three particular wavelengths (colors) upon traversing the melt flow. In order to evaluate in real time the color changes during extrusion, the colorimeter is attached to the extruder exit. Here we present its validation at the bench and in the extruder as well as the results of its practical application to in-line monitoring the thermo-mechanical degradation of a homopolypropylene during multiple extrusions in a modular intermeshing co-rotating Werner&Pfleiderer ZSK30 twin-screw extruder.

2. Experimental

2.1. Materials

A commercial polypropylene homopolymer, H301 (MFI = 10g/10min) from Braskem, was used. For the validation of the colorimeter at the bench Yellow Acid 49 dye from Quimanyl was employed.

2.2. In-line colorimeter

The in-line colorimeter system is based on the turbidimeter developed earlier [5], which is mounted in a slit-die fitted at the extruder exit. It has two transparent windows of borosilicate glass allowing the measurement via transmitted light through the molten polymer flow. Four LEDs of high emission are located in one side of the die. Three of them match the RGB color system (red, green, blue), whereas a fourth one emits white light. A RGB LED, which is able to emit the three colors, was tested and discarded since it was not possible to properly align its light beams. The light emitted by the LEDs crosses the transparent window, the molten polymer flow and the second window, reaching a photocell fitted at the opposite side of the slit-die, as shown in Fig. 1. Each LED is lit for 1 second, one at a time consecutively. A single photocell synchronously senses the changes in the light intensity of each color. The whole control is done via software written in the LabVIEW platform, the data being recorded and presented on screen.

2.3. In-line colorimeter validation and calibration

The validation of the in-line colorimeter was performed in two different ways: firstly at the bench by using aqueous solutions of acid dyes with different colors. One litre of distilled water was added to a 2 litre capacity beaker containing a sunken pump. The pump forced the fluid to pass through the slit-die fitted on the in-line colorimeter. Constant volumes of a concentrated dye solution with known concentration were added stepwise while the change of the transmitted light intensity, due to the absorption, was monitored by the photocell. To get the baseline data, a flow of pure water was used.

To carry the second validation, the slit-die with the in-line colorimeter was attached to the extruder exit. A colored polymer masterbatch was prepared by tumbling polypropylene pellets with an ethanol solution of the dye. This procedure allows the dye to be adsorbed on the pellets' surface. In order to remove the solvent, those pellets were then vacuum dried. The resultant masterbatch was mixed with an appropriate amount of pure polypropylene to reach the desired color concentration. The mixture thus obtained was gravimetrically fed in the main hopper of the Werner&Pfleiderer ZSK30 extruder. The absorption on each color, during the steady-state extrusion, was recorded by the in-line colorimeter for a period not less than 15 minutes.

2.4. Polypropylene reprocessing

Neat polypropylene was processed in the same ZSK-30 twin screw extruder with K-Tron gravimetric feeders and a

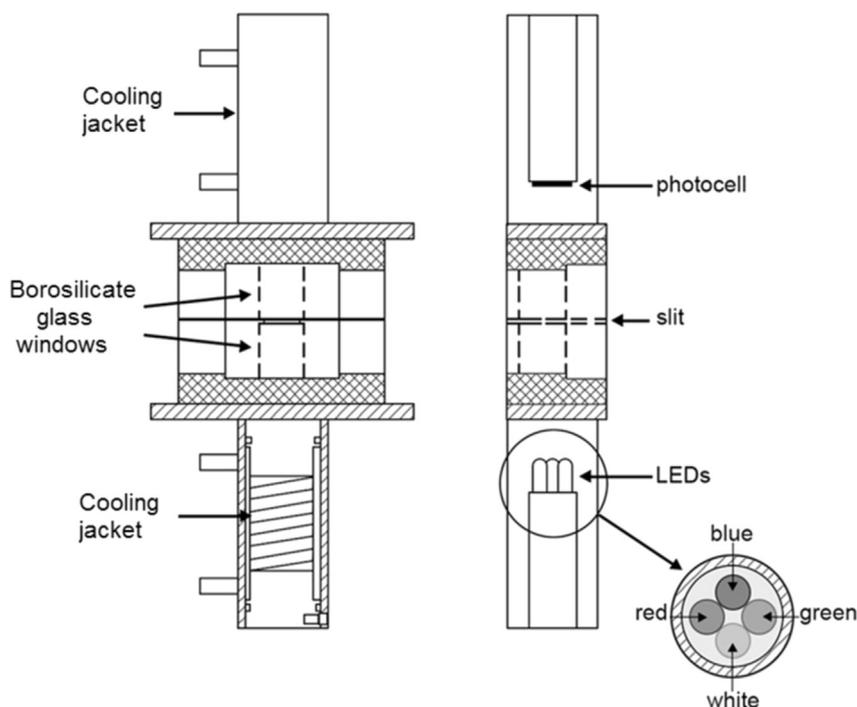


Fig. 1. Diagram of the extruder slit-die with the in-line colorimeter attached. In one side, it has a single photocell, whereas four LEDs set in the opposite side.

screw profile containing only conducting elements. No extra stabilization was added. It was processed at 100 rpm, 3 kg/h and with a constant temperature profile of 200 °C. After each extrusion, samples were collected to be used in additional off-line analysis, while the remaining material was extruded again under the same conditions, up to five times.

2.5. Rheological behavior

The rheological behavior of polypropylene after each extrusion cycle was evaluated in an Ares rheometer, model AGR2, equipped with plate-plate geometry. The tests were carried out at 180°C, in steady-state regime, with the shear rate $\dot{\gamma}$, ranging from 0.01 s⁻¹ to 10 s⁻¹.

2.6. Infrared and UV-Vis spectroscopy

Hot pressed films of the multi-extruded polypropylene were analyzed off-line, by FTIR and UV-Vis spectroscopy to validate the in-line measurements made during extrusion. A Nicolet 6700 FTIR, from ThermoScientific, at range of 400 to 4000 cm⁻¹, 64 scans and 4 cm⁻¹ of resolution, was used. The UV-Vis measurements for aqueous solutions were performed in a HP UV-Vis spectrometer in the range of 200 – 800 nm. The solid samples were analyzed in a Shimadzu UV-1800 since the previous spectrometer does not have support for solid samples.

3. Results

Fig. 2 shows the absorbance spectrum of YA49 yellow dye aqueous solutions, as measured in a commercial UV-Vis

spectrometer at increasing concentrations of the dye. A single and broad peak centered at 400 nm is observed. This wavelength is typical of a violet color, which is the complementary color of the yellow. In fact, the human eye recognizes colors as a combination of the non-absorbed wavelengths, resulting in a single sensation of the complementary color. In this case, the preferential absorption occurs on the violet/blue region of the white illuminating spectrum, so that the solution is perceived as yellow.

3.1. In-line colorimeter validation and calibration

In order to validate the in-line colorimeter, the data obtained at the bench, for the dyed solution flowing

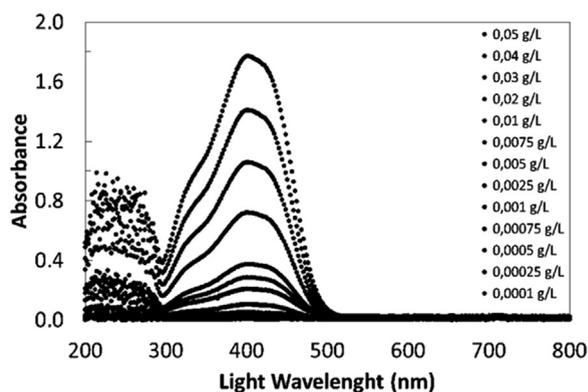


Fig. 2. Absorbance spectrum of YA49 yellow dye aqueous solution measured at increasing concentrations, in a commercial UV-Vis spectrometer.

through the slit-die, were compared with those obtained from a commercial UV-Vis bench spectrometer. The results for the absorbance at different concentrations are shown in Fig. 3. As expected, the main response of the in-line detector occurred under blue illumination (blue LED emits in the band ranging from about 430 to 510 nm), which corresponds to the region where yellow dye absorbs light, as shown in Fig. 2. In fact, Fig. 3 shows that the absorption of red (610 to 650 nm) and green (490 to 575 nm) LEDs emissions is negligible. Also, it can be seen that the response of both detectors, the in-house built and the UV-Vis commercial spectrometer, is linear, in agreement with Lambert-Beer law. However, the slopes are dissimilar, indicating a difference in the measured molar extinction coefficient (ϵ) of the yellow dye. This is not quite surprising since all LEDs used in our device show broader wavelength distributions in comparison to the commercial UV-Vis spectrometer, which works in a discrete way, measuring a single wavelength at a time. Hence, if the molar extinction coefficient is not constant in the emission band of the LED, different results may be obtained by the two detectors. Nevertheless, this fact does not have a significant impact on the in-line colorimeter quantitative performance as it does follow the Lambert-Beer law. Another important aspect concerns to the sensitivity of the detector. Based on the stability of the signal, the lower limit of detection of the in-line colorimeter for the YA49 dye was estimated in 0.01 g/L, which corresponds to an absorbance of 0.01. This means that, for some colored substances, measures at concentrations as low as 1 ppm can be performed.

A second procedure for the validation of the in-line colorimeter was performed in the extruder. Initially, in order to set the baseline, the pure polypropylene was extruded, with the absorption of the three colors being recorded for at least 400s after the steady state has been reached. Thus, the controls of the software were set to deliver zero absorption in the four measured wavelengths (red, green, blue and white). Immediately afterwards, the first gravimetric feeder, responsible for delivering the pure polymer, was switch off and a second gravimetric feeder delivering a mixture of pure PP and master pellets with the dye was put to run. The absorptions of all four colors at the

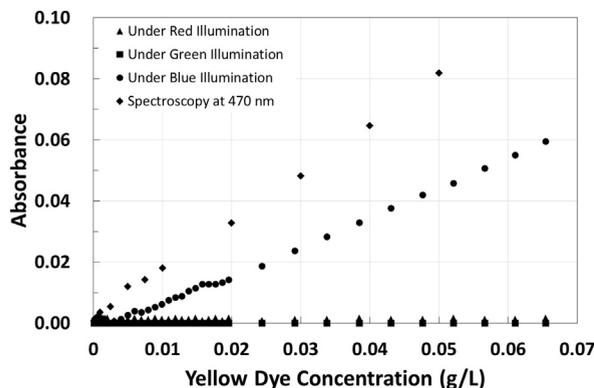


Fig. 3. —Data of light absorbance as a function of the concentration of the yellow dye YA49 aqueous solution obtained at the bench with the in-line colorimeter. The results from Fig. 2 for 470nm are also presented.

slit-die were measured with the in-line colorimeter. As discussed above, the absorbance of the green and red colors is negligible, occurring only with blue illumination and, therefore, in Fig. 4 only the absorbance on this color is shown. It can be seen that the steady state is reached about 450s after switching from pure to colored polymer, with represents the total residence time of the polymer inside the extruder. Moreover, as expected, the raising on the concentration of the dye intensifies the color and so the absorbance measured by the sensor. In addition, the signal obtained during the preparation of the master is also exhibited in the figure.

The absorbance average values, as calculated for the steady state, are presented in Fig. 5 as a function of the yellow dye concentration. Again, the linear behavior predicted by the Lambert-Beer law is observed. The data obtained in-line during the extrusion of molten polypropylene can be compared with the results obtained at the bench with aqueous solution. The absorbance of the yellow acid at a concentration of 0.02 g/kg in water is 0.02, while in molten polypropylene it is 0.033, both with very small standard deviations. The difference in the results is due to the great difference in polarity between the matrixes (water is polar and polypropylene is nonpolar) and temperature (room temperature for the aqueous solution and 240°C for the polypropylene extrusion). The polarity of the system affects the electron mobility in the structure changing the energy necessary for the electronic transitions, thus changing the molar extinction coefficient (ϵ) of the dye. The temperature changes the entropy of the system, also affecting the electronic transitions, and hence, ϵ . Another important fact is that none of the colored systems showed significant absorption under white illumination during extrusion, indicating insignificant turbidity and so lack of particles that would scatter light. Thus, the reduction of the measured transmitted light intensity under blue light illumination can be assigned only to absorption, the scattering being negligible. Therefore, this absorption quantitatively indicates the presence of chromophore

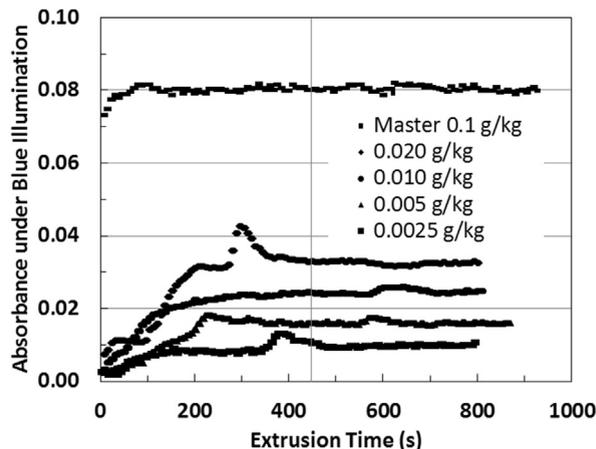


Fig. 4. —Absorbance under blue illumination measured in-line, in real time, as a function of extrusion time. An initial extrusion steady-state flow of pure polypropylene is switched, at about 100s, by a YA49 yellow colored flow of polypropylene at various dye concentrations, as indicated.

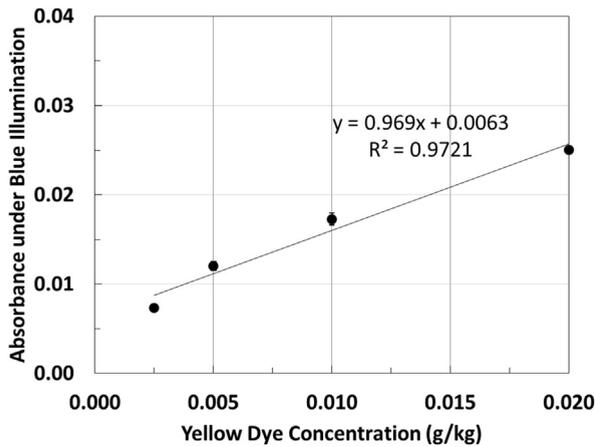


Fig. 5. Average normalized absorption measured in-line, under blue illumination, during steady-state extrusion of YA49 colored polypropylene as a linear function of dye concentration.

groups. In our view, the performance of the in-line colorimeter reported here, under these two well-controlled experiments, validates it to quantify in real time color changes at room and higher temperatures, particularly in the molten polymer flow. The absorption under white illumination acts as a limiting reference, signaling when the light scattering level is out of the in-line colorimeter measuring range.

3.2. Polypropylene reprocessing

After having been validated, the device was tested to quantify in real-time color changes due to the degradation of polypropylene subjected to multiple extrusions (reprocessing). The high shear rate and temperature applied in the extrusion process degrades the polymer. In the case of polypropylene, the main route for thermo-mechanical degradation is chain scission. In the presence of oxygen, this reaction leads to the formation of chromophore groups, such as carbonyl and double bonds. The polypropylene was extruded up to five times, while its color was measured in-line. Normalization was performed using the data from the first extrusion as blank. Fig. 6 shows the average absorption under all three colors illumination (Red, Green and Blue) as a function of the number of extrusions. For all, the absorption increases continuously with the increasing number of extrusions, indicating progressive degradation of the melt polymer. Hence, the degradation of PP appears to be associated with the formation of chromophore groups, which absorb in a wide range of the visible spectrum. Absorbance value on the fifth extrusion reaches averages closer to the highest absorbance obtained during the validation in-operation (0.03). The absorbance value during the first extrusion is below the minimum limit for the device detection, i.e., 0.005.

Fig. 7 shows the Whiteness Index (WI) obtained accordingly to ASTM-E311-10. This index quantifies the deviation of the color of the material relative to the pure white. Each new re-processing reduces the initial white (uncolored) material increasing the absorption in the

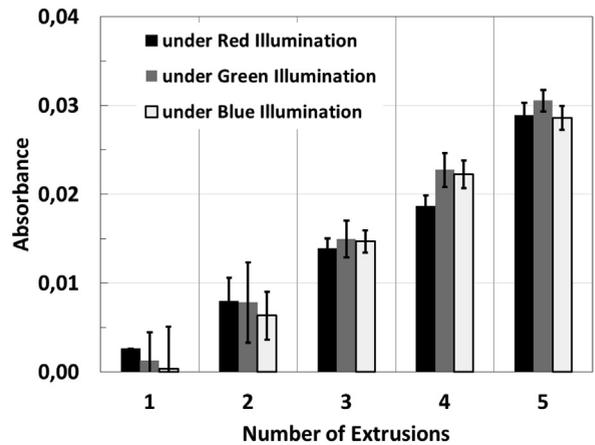


Fig. 6. The average absorption under each color illumination during the multiple extrusions of polypropylene.

visible range of the spectrum, coloring the polypropylene. For most of the polymers, the thermo-mechanical degradation tends to cause yellowness and then, commonly, another index is used: the Yellowness Index YI. According to the same standard, the YI can be determined only when the material does show a prevailing transmission (i.e. negligible absorbance) in the yellow band of the visible spectrum, 570 to 580 nm. Since the re-processed melt polypropylene shows high absorbance under green illumination (490 to 575nm), the yellowness index should not be estimated. Although it is possible to get the yellowness index of solid samples using a commercial colorimeter, the results could not be compared with the in-line measurements of the molten polymer; it would be affected by the crystallinity and surface irregularities of the solid sample.

The degradation of polypropylene was also confirmed by change in its rheological properties, as shown in Fig. 8. The rheological behavior shows a reduction of the viscosity (η_0), measured off-line in the plate-plate Ares rheometer, after the multiples extrusions, while the absorption under blue illumination measured in real time is increased. The reduction in viscosity indicates thermo-mechanical degradation of the material, which occurs preferentially

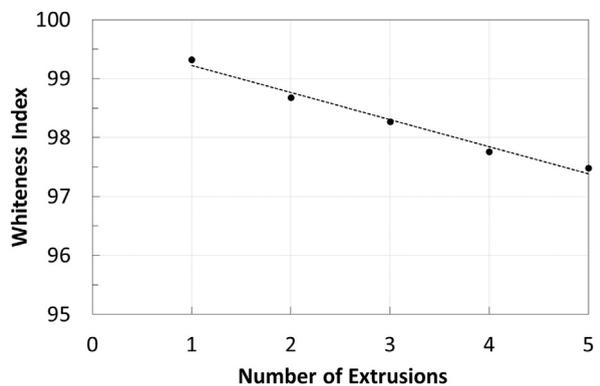


Fig. 7. Whiteness Index of pure polypropylene as a function of the number of reprocessing cycles.

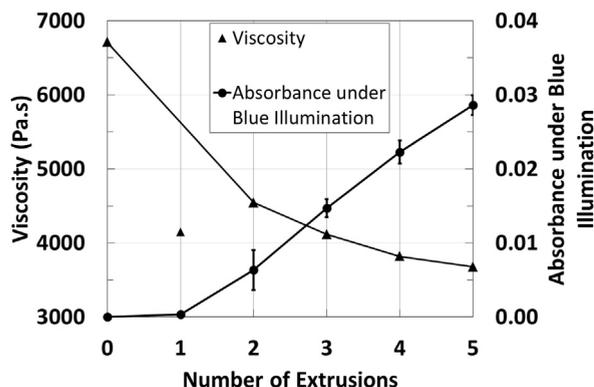


Fig. 8. Zero-shear viscosity, η_0 , of PP after each successive extrusion and the corresponding absorption under blue illumination as measured in-line by the colorimeter.

by chain scission, whereas the increment in light absorption indicates the formation of chromophore groups that absorb in the blue color region. Notwithstanding that the colorimetry shows no significant color variation in the first extrusion, there is a large reduction in viscosity, caused by the intense chain scission of the longer chains. The low absorbance observed in the first extrusion can be due to the thermal stabilizer present in the polypropylene, which significantly reduces oxidation while still active. As the number of extrusions increases, the reduction in the viscosity is still present, but at a lower rate, while the in-line blue light absorption increases steadily. These facts highlight the different levels of response given by different experimental techniques, and hence the need to be careful when comparing data from different experiments in order to properly quantify polymer degradation.

The multi-processed samples were also analyzed off-line using FTIR in order to quantify the formation of functional groups during the re-processing. However, this analysis could not reveal the presence of double bonds or carbonyl groups, probably due to their low concentrations. UV-Vis spectroscopy was also used to analyze the presence of chromophore groups. Samples as plates of about 1 mm thickness of the first, third and fifth extrusions were analyzed showing some differences in the UV region of the spectra, as presented in Fig. 9. After

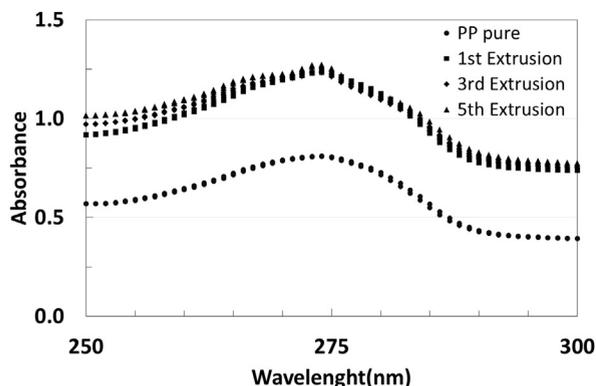


Fig. 9. UV-Vis spectra for neat PP and after one, three and five extrusions.

extrusion, the samples exhibited a new band near the 265 to 275 nm region, which can be associated with changes in the neighborhood of the group, i.e., the presence of other functional groups including some other similar chromophore groups. This effect is present in the FTIR spectrum of polypropylene grafted with maleic anhydride, where the insertion of two groups in side-by-side carbons creates an interaction, reflected as a new band near to 1980 cm^{-1} that is detected even at low concentrations, i.e., lower than 1.5 w% of carbonyl groups [23]. Thus, the change of the band in the region of 200–300 nm is a good indication of the insertion of new chromophore groups. However, if on one hand the changes in the absorption between extruded samples and neat PP show clearly the increase in double bonds, since the band at 275 nm is associated with the conjugated double bonds, on the other hand, the differences among the extruded samples are very small and, thus, difficult to quantify. In fact, a better quantification seems to be achieved by measuring the absorption under blue illumination with the in-line colorimeter.

4. Conclusions

An in-line colorimeter was successfully developed, validated and applied for real-time quantification of the color during the extrusion of polypropylene. It was shown that the device is able to sense colors, even at low concentrations, while keeping a linear response. It was able to measure changes in color for multiple extruded polypropylene, caused by the presence of chromophore groups formed during the thermo-mechanical degradation.

The relation between the degradation and the in-line measured color was investigated by employing off-line experimental techniques, namely rheology, FTIR and UV. A continuous reduction on the zero-shear viscosity (η_0) with the increasing number of processing cycles indicates the chain-scission degradation process. Probably due to its low concentration, the presence of carbonyl or double bonds could not be detected by FTIR. UV analyses have shown a new band in the region between 265 and 275 nm that can be associated with the formation of chromophore groups. However, the variations of the absorbance between the extruded samples are small and, thus, difficult to quantify.

The developed in-line colorimeter can indirectly monitor the oxidation and chemical modifications during processing and, therefore, it can be used as a tool to better control the extrusion process. Others studies using this in-line colorimeter to monitor reactive extrusion are currently under development by our research group.

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