Test equipment

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

Letícia Sausen Hamester [a], Pablo Andrés Riveros Muñoz [a], Sebastião Vicente Canevarolo [b, *]

[a] Programa de Pós-Graduação em Ciência e Engenharia de Materiais PPG-CEM/UFSCar, Brazil
[b] Departamento de Engenharia de Materiais DEMa, Universidade Federal de São Carlos (UFSCar), Via Washington Luiz, Km 235, CEP. 13-565-905, São Carlos, Brazil

A B S T R A C T

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

* Corresponding author.
   E-mail addresses: leticia.cosmos@gmail.com (L.S. Hamester), pabloarm@gmail.com (P.A.R. Muñoz), caneva@ufscar.br (S.V. Canevarolo).

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 Quimanil 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