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PREPARATION AND CHARACTERIZATION OF PLASTICIZED POLY(LACTIC ACID) AND POLY(ε-CAPROLACTONE) BLEND WITH POLY(ETHYLENE GLYCOL) (PEG) AND TRIETHYL CITRATE (TEC)

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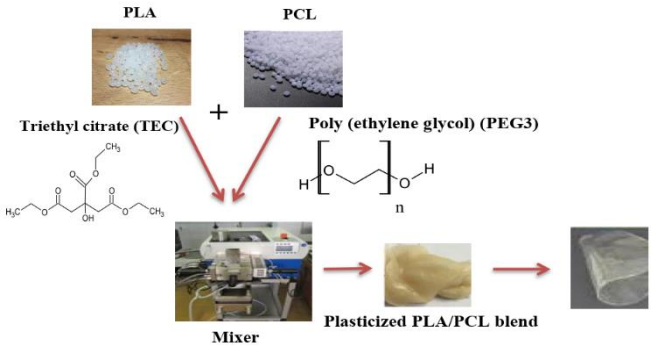
This study investigated the effect of the bioplastisizeres Poly(ethylene glycol) (PEG) and Triethyl citrate (TEC)) on the properties of Polylactic Acide/poly(ε-caprolactone) (PLA/PCL) blends. The addition of PEG_3 and TEC influenced the properties of 80PLA/20PCL blends. Were analyzed by Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), UV-Vis spectroscopy, opacity and Melt flow index (MFI), FTIR results showed that intermolecular hydrogen bonding between the hydroxyl groups in the PLA/PCL blend and the ester group of TEC and PEG_3. The X-ray diffraction showed that increasing crystallinity with increasing plasticizers content in the blends. Analysis by UV-Vis spectroscopy showed that the two plasticizers: TEC and PEG_3 have no effect on the color change of the films. The effect of the concentration of plasticizer on the opacity of the films was negligible. The value of the MFI was observed for all samples are higher than those of treated PLA.



INTRODUCTION

As a completely degradable polyester polymer material, polylactic acid (PLA) has received increasing attention from scholars due to its good biocompatibility, high modulus, and high strength mechanical properties. With the introduction of PLA, its development has been limited by its inherent disadvantages of low elongation at break, poor impact strength, and brittleness, thereby requiring the toughening modification of PLA.[1–5] To overcome these drawbacks, many approaches have been reported. This includes the incorporation of fillers, copolymerization, or blending with other polymers.[6–8] PLA offers various applications in different sectors, such as packaging, biomedical, and structural.[9,10–13]

Blending is a more conventional and economical method for modifying polymer properties, which has been investigated by various authors.[14–15] Ductile polymers with a low glass transition temperature (T_g) can significantly improve the toughness of brittle polymers such as PLA by blending.[15] Biopolymers such as poly (ε-caprolactone) (PCL) and poly (ethylene glycol) (PEG) have been studied to improve the properties of PLA. PCL is a semicrystalline biodegradable thermoplastic with a low Tg of

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−60 ◦C, making it very flexible at ambient temperature.[16,17] However, PEG is another polymer that can be blended to improve PLA properties, thus broadening its potential applications. PEG is used primarily as a plasticizer to enhance the elasticity of PLA.[18,19]

The plasticizers provide PLA with improved biodegradation properties, as reported by Arrieta et al.[20] Polyethylene glycol (PEG) with diferent molecular weights has been extensively used as a plasticizer for PLA, as it shows exceptional miscibility.[21,22] Citrate esters such as triethyl citrate (TEC) and acetyl tributyl citrate (ATBC) have been widely used as plasticizers in PLA formulations, exhibiting excellent ductile properties. Maiza *et al*.[23] reported plasticized PLA formulations with up to 30 wt% TEC or ATBC with a noticeable decrease in the glass transition temperature (T_g). Adipate esters have also been widely used in PLA plasticization.[24]

In this study, two types of bio-plasticizeres, namely, the triethyl citrate (TEC) and the poly (ethylene glycol) (PEG_3) are used as plasticizer to 80PLA/20PCL blend.[25] The aim of this study was to investigate the effects of plasticizer loadings on the rheological properties of the PLA/PCL blend, as well as to investigate the interaction between PLA/PCL and plasticizers. This material has great potential as alternatives to the conventionally used polymers, such as polypropylene, as a biodegradable or green biomaterial in the packaging industry.

MATERIALS AND METHODS

1. Materials

The selected commercial Polylactic acid (PLA) grade 2002D purchased from NatureWorks LLC (Minnetonka, MN, United State). Its average molecular weight (Mw), Tg and Tms are about 160,000–220,000 g mol^{-1}, 60 °C and 156 °C, respectively. Its specific gravity is 1.24, and its melt flow index is between 5–7 g 10 min^{-1} at 210 °C/2.16 Kg. The poly ε-caprolactone (PCL) (CAPA 6,800, Mw = 80.000 g mol^{-1}) used in this study was a commercial product from Perstorp Polyols Inc (Toledo, OH, USA). Its melting point and Tg reported by the supplier are 58–60 °C and –58 °C, respectively. Poly (ethylene glycol) (PEG3) (Mw = 6000 g mol^{-1}, CAS No. 25322-68-3 purchased from Sigma Aldrich (France)) and triethyl citrate (TEC) (CAS NO. 77-93-0 purchased from Sigma Aldrich, France) (Figs. 1a–d).

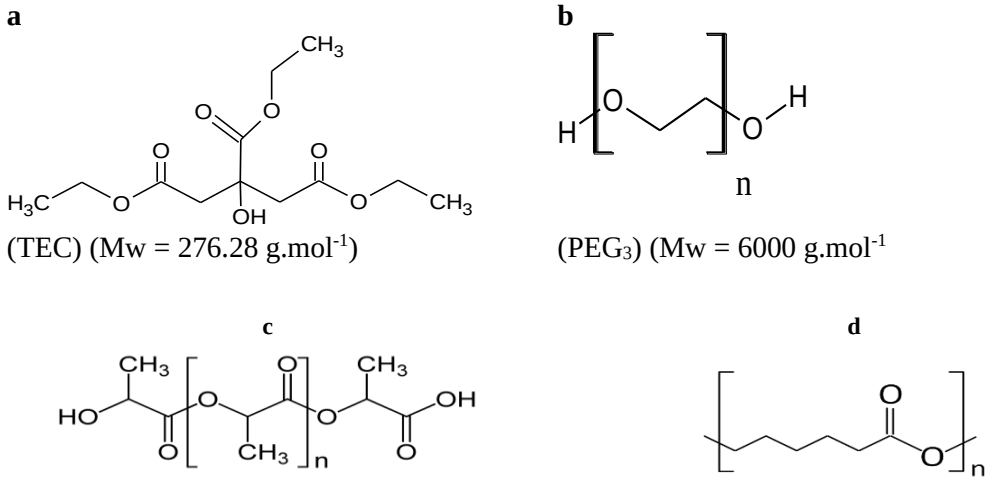

Fig. 1 – Chemical structure of: a) EC; b) PEG_3; c) PLA; d) PCL.

2. Sample preparation

PLA pellets and PCL powder were dried in a hot air oven at 60 °C and 30 °C, respectively, for 12 hours before melt blending. The ratio of PLA/PCL formulated for melt blending was 80/20 by weight percentage. The 80PLA/20PCL blends were prepared by the melt blending method using a Brabender plastograph LP2100 (Duisburg, Germany). The volume of the mixing chamber is 60 cm^3. The obtained samples were cut into small pieces and then compression moulded into 2mm thick sheets and thin films at the same temperature (190 °C) for 7 min and the blend rotation speed was 30 rpm using a hydraulic press (CARVER) at a pressure of 75Pa. Prior to blending, PLA and PCL

were desiccated in a vacuum oven at 50 °C for 24 h. The plasticizers TEC and PEG_3 were blended to 80PLA/20PCL at various concentrations. Table 1 summarizes the compositions of each formulation.

Table 1

Composition of treated PLA, 80PLA/20PCL, and plasticized 80PLA/20PCL with TEC and PEG_3 plasticizers

Formulation	PLA/PCL (%)	TEC or PEG_3 (%)
Treated PLA	–	–
PCL	–	–
80PLA/20PCL	100	–
80PLA/20PCL–TEC5	95	5
80PLA/20PCL–TEC10	90	10
80PLA/20PCL –TEC15	85	15
80PLA/20PCL –TEC20	80	20
80PLA/20PCL –TEC30	70	30
80PLA/20PCL – $PEG_3$10	95	10
80PLA/20PCL – $PEG_3$20	80	20
80PLA/20PCL –$PEG_3$30	90	30
80PLA/20PCL – (TEC+PEG_3)20	80	20

3. Characterization

3.1. Fourier transform infrared (FTIR) spectroscopy

Fourier transform infrared (FTIR) spectroscopy Chemical structure modification of plasticized PLA/PCL isevaluated by FTIR spectroscopy in transmission from 400 cm^{-1} to 4000 cm^{-1} with a Perkin Elmer FTIR Spectrum 1000 spectrophotometer (Waltham, MA, USA).

3.2. X-ray diffraction (XRD)

Diffraction (XRD) The XRD study was carried out using a Bruker D8 Advance diffractometer (Billerica, Massachusetts, USA) with Cu-Ni radiation (λ=1.54184 nm). The diffractogram was scanned in ranges of 6–70° at a scan rate of 0.05° min^{-1}.

3.3. Melt flow index (MFI)

Melt flow index (MFI) is the mass flow rate index, expressed in grams, extruded isothermally 10 min under constant load through a die of standard dimensions was measured by using Dynisco Polymer test machine (Franklin, USA) according to ASTMD1238 at 190 °C and 2.16 Kg.

3.4. Opacity

The film opacity was determined by measuring light transmittance at wavelengths ranging from 200 nm to 600 nm at room temperature using a UV-Vis spectrophotometer instrument (Shimadzu Co. UV-2550, Tokyo, Japan). The opacity of the film was calculated by the equation:

$$\text{Opacity} = \frac{AB_{600}}{d} \quad (1)$$

Or: AB_{600} absorbance at 600 nm and d thickness of film (mm)

RESULTS AND DISCUSSION

1. Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra of treated PLA, PCL and plasticized 80PLA/20PCL blend with TEC and PEG_3 are shown in Figs 2a–b. Three distinguished absorption bands at 2997 cm^{-1}, 2947 cm^{-1} and 3504 cm^{-1} corresponding to C-H aliphatic stretching (doublet), and O–H stretching vibrations were found in the spectra of the treated PLA and plasticized PLA/PCL at 3656 cm^{-1}, 3503 cm^{-1} and at 3650 cm^{-1}, 3503 cm^{-1} with TEC and PEG_3, respectively. The C=O stretching vibrations and vibrations of C-O bonds in ester groups (PLA and PCL) show peaks at 1752 cm^{-1} and at 1746 cm^{-1} for plasticized PLA/PCL with TEC and PEG_3, respectively, the intensity of these peaks is increased. The decrease of the peak density of two distinguished absorption bands centered at 955 cm^{-1} and 865 cm^{-1} corresponding to the motions of C–O[26] and C–C[27] stretching vibrations, respectively, with the addition of 30% of TEC or PEG_3 and the reduction of the peak intensity at 1454 cm^{-1}. It was also observed that the CH_2 stretching absorption bands of the PLA/PCL blend shift to higher frequencies with the presence of TEC and PEG_3 in the blend. This may be because of molecular interactions between the PLA/PCL blend and

plasticizers. It is believed hydrogen bonding could occur between the C=O group in TEC and PEG_3 and terminal hydroxyl groups of the PLA and PCL main chains in the PLA/PCL blend. The interaction between PLA/PCL and plasticizers (TEC and PEG_3) may also be attributed to possible hydrogen bonding between the hydroxyl groups in the PLA/PCL blend and the ester group of TEC and PEG_3.

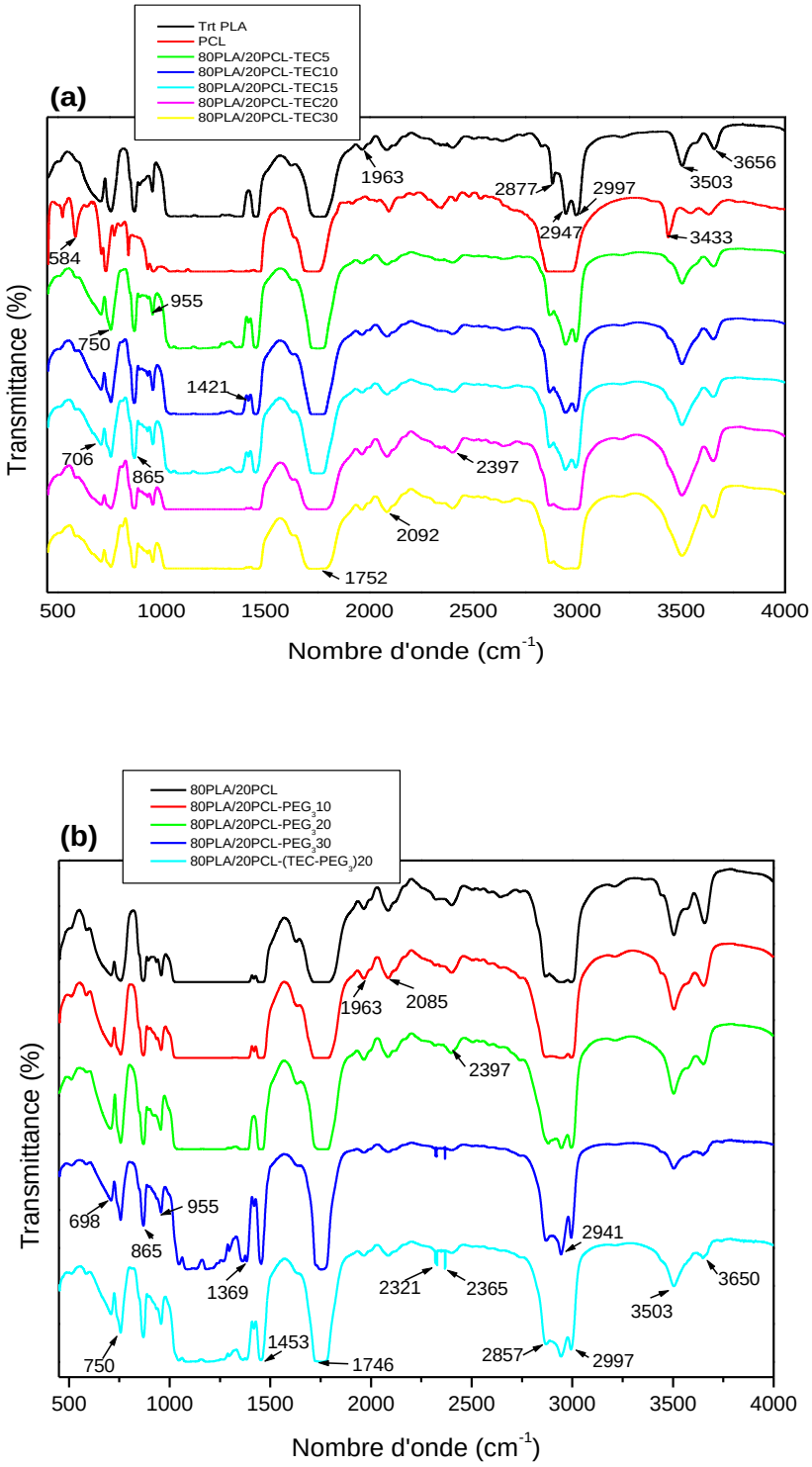

Fig. 2 – Fourier transform infrared (FTIR) spectra of treated poly (lactic acid) (PLA), PCL, 80PLA/20PCL and plasticized 80PLA/20PCL with: a) TEC and b) PEG_3 at various concentrations.

2. XRD

XRD patterns of treated PLA, PCL, 80PLA/20PCL and plasticized 80PLA/20PCL are shown in Fig. 3, indicating that PCL is highly crystalline, while PLA is amorphous or slightly crystalline. A weak characteristic PLA crystalline peak located at 2θ=16.8°, superimposed on a broad amorphous peak background, was visible as PCL was added to PLA, implying that the PLA was composed of most amorphous and small amounts of crystalline. The crystalline peaks of PCL were located at 2θ = 21.8°, 23.7° and 29.5°.

The PCL spectrum has shown several peaks between 15° and 40°, with two high-intensity and other low-intensity peaks between 20° and 25° and between 35° and 40°, respectively. Moreover, the peaks were sharp and distinct, which indicated that the sample was a crystalline material. Similar findings are in accordance with those reported works. 48–50 In addition, the spectrum of the other blends has shown the same crystalline peaks overlapping the amorphous curve of PLA. The peak intensities vary with the variation of TEC and PEG_3 content. The XRD observation of increasing crystallinity with increasing plasticizers content in the blends could. 80PLA/20PCL-TEC30 and 80PLA/20PCL-(TEC+PEG_3)20 have shifted towards lower angles between 15° and 20°, which probably indicates the variation in the distance between parallel planes of atoms. According to Bragg's law, if the spacing of the crystallographic planes changes, the Bragg angle should decrease towards lower 2θ values.[28]

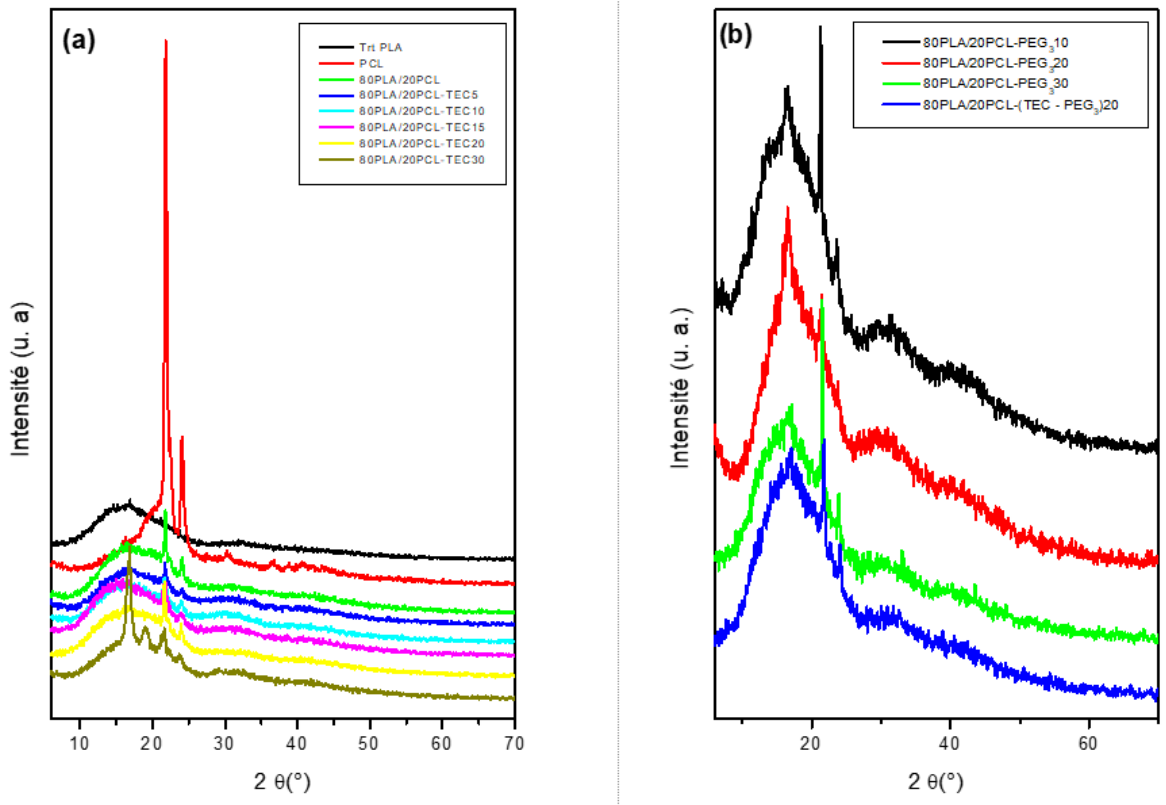

Fig. 3 – X-ray diffractograms of treated poly (lactic acid) (PLA), PCL, 80PLA/20PCL and plasticized 80PLA/20PCL with: a) TEC and b) PEG_3 at various concentrations.

3. UV-Vis spectroscopy

Because the aspect of packaging could influence the decision of consumers, high transparency in food packaging is required. The UV-Vis light transmittance of treated poly (lactic acid) (PLA), poly (ε-caprolactone) (PCL), 80PLA/20PCL and plasticized 80PLA/20PCL with TEC and PEG_3 were measured are shows in Fig. 4a and Fig. 4b. The spectra clearly show that whatever the level of plasticizer, the general appearances of all spectra are identical. All the maximum absorbance range is between about 208–214 nm. Both plasticizers (TEC and PEG_3) have no effect on the color change of the films. In the same field, there appear weak staining is due to the effect of film thickness.

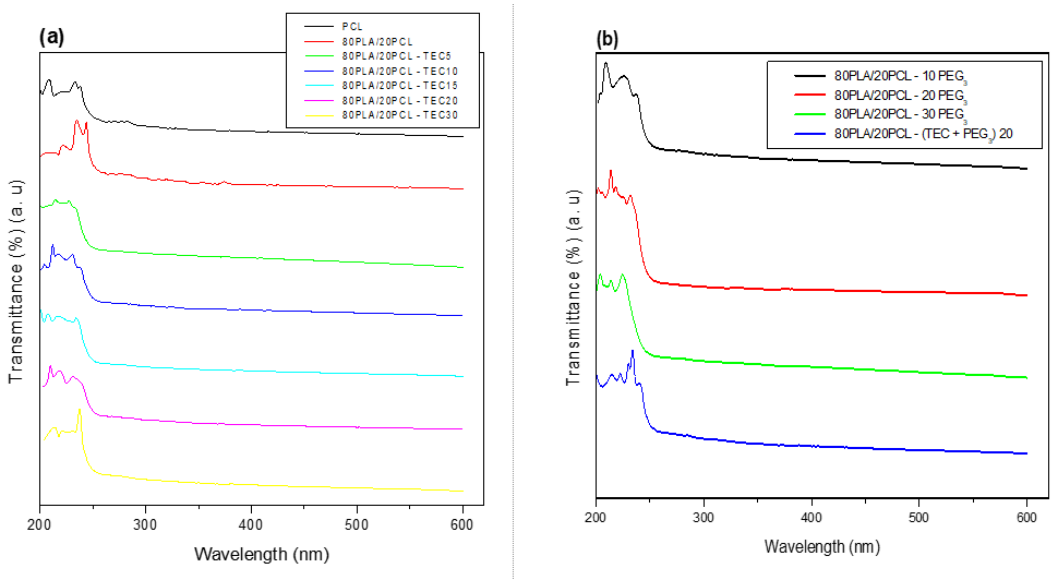

Fig. 4 – UV-Visible spectra of treated poly (lactic acid) (PLA), PCL, 80PLA/20PCL and plasticized 80PLA/20PCL with: a) TEC and b) PEG_3 at various concentrations.

4. Opacity measurement

Transparency is a very important technical parameter to evaluate and validate certain food packaging materials. In the recent scientific literature, several methods (*i.e.* transmittance, opacity, haze, and absorbance) have been used.[29] The opacity of the treated PLA, PCL, 80PLA/20PCL and plasticized 80PLA/20PCL films with TEC and PEG_3 at various concentrations is shown in Figs. 5(a, b), respectively. High opacity values indicate that the films were less transparent. As shown in Fig. 5, the opacity value of the 80PLA/20PCL films plasticized with citrate esters (TEC or PEG_3) was slightly lower than that of the treated PLA films. This was possibly due to the increased free volume resulting from the greater mobility of PLA/PCL chains and to the decrease in crystallinity. For the placticizers, varying the concentration and type of plasticizer did not significantly alter opacity. The incorporation of TEC and PEG_3 into PLA/PCL films decreased the transparency of the PLA films to a certain extent.

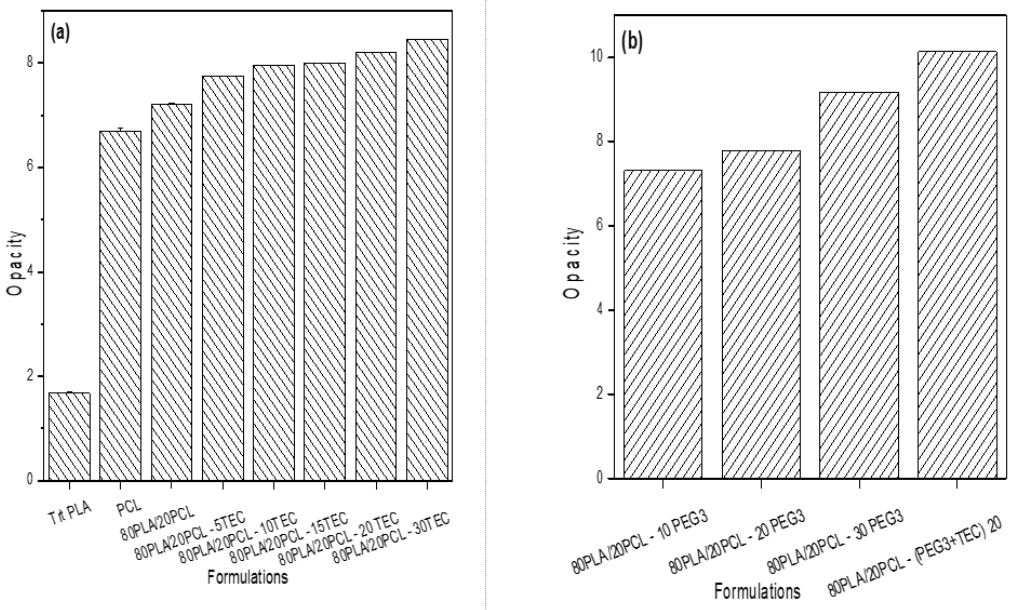

Fig. 5 – Opacity analysis of treated poly (lactic acid) (PLA), PCL, 80PLA/20PCL and plasticized 80PLA/20PCL with: a) TEC and b) PEG_3 at various concentrations.

5. Melt Flow Index (MFI)

MFI achieves an empirical parameter that is infuenced by diferent factors, among them: conditions of measurement, physical properties, molecular weight, molecular weight distributions, levels of branching and molecular structure.[30] The importance of the obtained MFI value is that it can be used as an initial screening for the selection of processing techniques. For example, a MFI value between 3 and 13 is related to extrusion blow molding or injection molding.[31]

Figure 6 displays the MFI values and their corresponding formulation. The treated PLA sample showed the lowest MFI (4.6 g/10 min). The addition of a plasticizer increases the polymer chain mobility which implies a reduction in viscosity and increase of MFI of plasticized 80PLA/20PCL. The reason why MFI values of plasticized 80PLA/20PCL blends with TEC were higher than those with PEG_3, could be associated with the plasticizer, since the plasticizer provides higher chain mobility to the blend. Maiza *et al*.[29] investigated the higher molecular weight of citrate in the studied exhibited a greater plasticizing effect to the PLA.

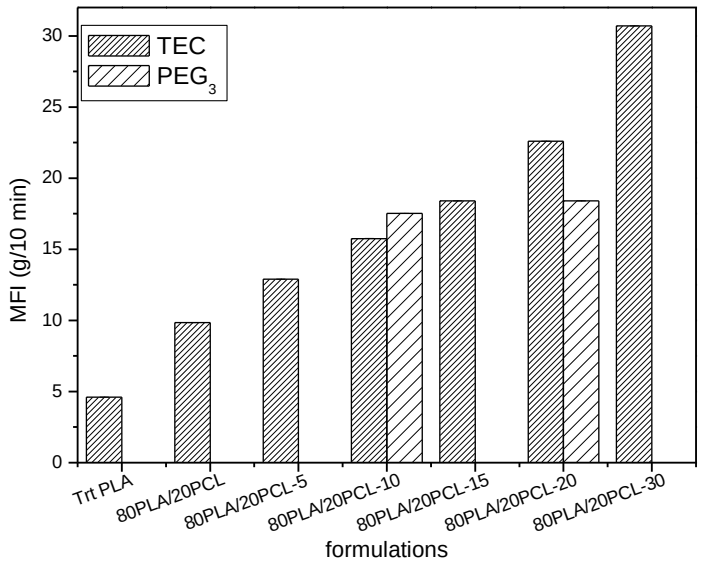

Fig. 6 – Variation of MFI of treated poly (lactic acid) (PLA), PCL, 80PLA/20PCL and plasticized 80PLA/20PCL with: a) TEC and b) PEG_3 at various concentrations.

CONCLUSIONS

In this study, the characterization of treated PLA, PCL, 80PLA/20PCL and plasticized 80PLA/20PCL with TEC and PEG_3 by using the simple melt blending method was reported. FTIR results showed that intermolecular hydrogen bonding between the hydroxyl groups in the PLA/PCL blend and the ester group of TEC and PEG_3. XRD confirmed that PLA is partially amorphous. Moreover, PCL sample was also confirmed to be a highly crystalline material. UV-Vis spectroscopy shows that the two plasticizers: TEC and PEG_3 have no effect on the color change of the films. The value of the melt flow index (MFI) was observed for all samples are higher than those of treated PLA. The opacity values of the 80PLA/20PCL films plasticized with TEC and PEG_3 were slightly lower than the value observed for the treated PLA film. Finally, it can be said that the higher molecular weight of plasticizers exhibited a greater plasticizing effect to the 80PLA/20PCL.

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