Effect of plasticizers on melt processability and properties of PHB

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Some results regarding plasticization of poly(3-hydroxybutyrate) (PHB) using triethyl citrate (TEC), acetyl *o*-tributyl citrate (ATBC) and tributyl citrate (TBC) are presented. The blends were obtained by melt mixing procedure on a Brabender Plastograph at a temperature of 180^{o}C, rotor speed of 60 rpm and mixing time of 6 minutes. The amounts of plasticizers varied from 10 wt.% to 30 wt.% relative to PHB. The effect of plasticizer content on the melt viscosity, thermal properties (DSC), spectral characteristics (ATR-FTIR), tensile properties and water permeability was investigated in order to improve the processability and properties of PHB.

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1. Introduction

Nowadays, food packages market is in ongoing growth in order to accomplish world population's requirements. Thus, many efforts are focused on developing specific packages having tailored properties such as mechanical, thermal, optical and barrier in order to assure integral product quality [1].

The most well-known packaging materials that meet these criteria are those based on petrochemical sources. However, these conventional plastics, manufactured from fossil fuels are non-renewable and, furthermore, they have a strong impact on environment.

Biopolymers produced from various natural resources are considered attractive alternatives for non-biodegradable petroleum-based plastics since they are renewable, environmentally friendly and biodegradable [2]. It is estimated that consumption of biopolymers will grow to approximately 100 million metric tons/year by 2020 in Europe [3]. Poly(3-hydroxybutyrate) (PHB) is a polyester and one of the most widely investigated members of the family of the polyhydroxy alkanoates (PHAs). It is fully biodegradable, partially crystalline with a high melting temperature (175 ^{o}C) and high degree of crystallinity [2, 4]. PHB offers many advantages over traditional petrochemically derived plastics for food packaging applications, being completely biodegradable and nontoxic [3].

However, PHB is still expensive, stiff and brittle [5]. Its slow crystallization rates lead to tacky products (e.g. fibres, films, etc.) [6]. PHB is very sensitive to processing conditions and exhibits a very narrow processing window [7, 8]. The narrow processing window arises from its high crystallinity and high melting temperature of the crystalline domains. A high processing temperature (close to or above T_m) is required where unfortunately the thermal degradation becomes significant. Such thermal degradation leads to random scission of polymer chains, resulting in a decrease in molecular weight and further reduction of the melt strength [9]. In principle, this problem can be overcome either by the reduction of crystalline melting point to lower the processing temperature or by some means of reforming links in the polymer being adopted (e.g., crosslinking) [9].

The toughness and processability of PHB can be improved by incorporation of the hydroxyvalerate (HV) monomers in the bacterial fermentation process [6, 10] or by introduction of additives, like plasticizers [3] and nucleating agents [11] and formulations of composites and blends based on PLA [12], PCL [13], cellulose/wood fiber [4, 14, 15], poly(glycidyl methacrylate [9], etc.

Generally, plasticizers are added to both synthetic and bio-based polymeric materials to impart flexibility, improve toughness, and lower the glass transition temperature. Plasticizers constitute about one third of the global additive market, with a worldwide consumption of over 4.6 million metric tonnes in 2003 [6].

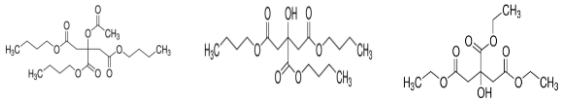
So far, as plasticizers for PHB have been reported Lapol 108 (polyester plasticizer) [12], acetyl tributyl citrate (ATBC) [16], poly(ethylene glycol) (PEG) [17], glycerol [18], limonene [19], etc. Generally, all investigated PHB-based blends were prepared by solvent technique and contained 10 wt.% of plasticizer. Few papers described preparation of plasticized PHB by melt technique. Thus, Kurusu et al. [20] investigated the incorporation of three industrial plasticizers, tri(ethylene glycol) bis(2-ethylhexanoate), triethyl citrate and tributyl citrate in PHB via melt-mixing and studied the effect of these additives through ageing and after annealing.

In this paper, the plasticization of poly(3-hydroxybutyrate) using triethyl citrate (TEC), tributyl *o*-acetylcitrate (ATBC) and tributyl citrate (TBC) has been studied by melt mixing procedure on a Brabender Plastograph at a temperature of 180°C, rotor speed of 60 rpm and mixing time of 6 minutes. The amounts of plasticizers varied from 10 wt.% to 30 wt.% relative to PHB. The effect of plasticizer content on the melt viscosity, thermal properties (DSC), spectral characteristics (ATR-FTIR), tensile properties and water permeability was investigated in order to improve the processability and properties of PHB.

2. Experimental

2.1 Materials and Methods

In the current study, PHB in the powder form was used; it was kindly supplied by BIOMER CO KRAILING (Germany), batch no. 19T302/12/2106. Three types of food grade plasticizers were selected: tributyl citrate (TBC), ≥ 97.0 %, batch no. BCBM 9410V were purchased from ALDRICH; tributyl *o*-acetylcitrate (ATBC), batch no. 201406120011 was bought from PROVIRON (Belgium); and triethyl citrate (TEC) L12639, batch no. 10182084 was purchased from ALFA AESAS (Germany). Their chemical structure and properties are shown in Figure 1 and Table 1.



ATBC **TBC** **TEC**

Fig.1. Chemical structure of ecological plasticizers

Table 1. Properties of the used plasticizers

Plasticizer	Molecular weight (g mol^{-1})	Density (g L^{-1})	Solubility parameters
Tributyl citrate (TBC)	360.44	1.043	18.8 (J cm^{-3})$^{1/2}$ [21]
Tributyl *o*-acetylcitrate (ATBC)	405.5	1.045 – 1.055	18.7 (J cm^{-3})$^{1/2}$ [21]
Triethyl citrate (TEC)	276.28	1.137	22.7- 23.8 MPa$^{1/2}$ [20,22]

2.2 Preparation of the blends

Melt blending of PHB/plasticizer blends was carried out in a Brabender Plastograph at temperature of 180°C, rotor speed 60 rpm and mixing time 6 minutes. Before melting, PHB was dried at 50°C for 24 h. Three types of blends (polymer/plasticizer) were prepared with the composition of polymer to plasticizer as follows: PHB/ATBC - 90/10, 80/20 and 70/30 (wt/wt), PHB/TBC - 90/10 and 80/20 (wt/wt) and respectively PHB/TEC - 90/10, 80/20 and 70/30 (wt/wt). The plasticizer was mixed with PHB before being loaded into the Brabender Plastograph. Once the melted products were obtained, were prepared sheets with dimensions (200 x 200 x 1) mm and films with thickness of max. 100 µm by compression-molding using a hydraulic press, at 175°C and 150 atm pressure for 3 min. Specimens for characterization were cut from plates.

2.3 Characterization

2.3.1 Melt blending processing approach

Processing behavior was evaluated by analysis of processing characteristics following the torque − time curves registered during blending in the Brabender mixer. Thus, torque and melt viscosity of the prepared blends were evaluated to constant values of 6 min at 60 rpm based on rheological data reported earlier conforming equations (1) and (2) [23]:

$$M = C_0 S^a \quad (1)$$

where: M is torque; S is the rotor speed (rpm); C_0 is a constant depends on temperature; a is a constant.

$$\zeta = K\dot{\gamma}^n \quad (2)$$

where: ζ is shear stress; $\dot{\gamma}$ is shear rate; K and n are the power law parameters.

Based on the equations (1) and (2) it can be deduced that the torque recorded on Brabender is an indirect indication of shear stress, while the rotor speed (rpm) is an indirect indication of shear rate. Thus, the melt viscosity η is given as the ratio of shear stress to shear rate, and herein can be obtained from the ratio of torque to rotor speed (equation (3)) [24]:

$$\eta = K(M/S) \quad (3)$$

where K is a constant depends on temperature.

2.3.2 Fourier transformation infrared (FT-IR) spectroscopy studies

In order to evaluate the influence of plasticizers on PHB blends, the films were analyzed by Fourier Transform Infrared Spectroscopy in Attenuated Total Reflectance mode (FTIR - ATR) using a ZnSe crystal with an incidence angle of 45°. All spectra represent the average of 20 scans recorded at 4 cm^{-1} resolution in a 2000 to 750 cm^{-1} range, using air as background.

2.3.3 Differential scanning calorimetry (DSC) measurements

Thermal analysis of materials was carried out on a DSC analyzer (823^e Mettler Toledo). Small amounts (about 5 mg) of dry samples were placed into aluminum pans, sealed and first heated between 30 and 200^{o}C at a scanning speed of 10^{o}C /min. The samples were then cooled to 30^{o}C at a cooling rate of 10^{o}C /min and heated again to 200^{o}C at 10^{o}C /min. An empty aluminum pan was used as reference. Melting temperature (T_m) and enthalpy of fusion (ΔH_f) were obtained from the second melting endotherms. Calibration was performed using an indium indium (m.p. = 156.6 ^{o}C; ΔH_f = 28.45 J/g).

The blend crystallinity degree was calculated using the following equation [25]:

$$X_c\ \% = 100 \times \Delta H_f / \Delta H_f^0 \quad (4)$$

where: ΔH_f is the melting enthalpy of the specimens (J/g); ΔH_f^0 is the enthalpy value for a theoretically 100% crystalline PHB (146 J/g) [26].

2.3.4 Mechanical properties

Mechanical properties were measured using an Instrom 3345 (USA) Testing. Tensile strength, elongation at break and Young's modulus were determined on a dumbbell-shaped sheet with the following dimensions: 13 mm, 73 mm and 1 mm in width, gage length and thickness, respectively, with the crosshead speed of 10 mm min^{-1}. At least five samples were tested for each composition, and the average value with a standard deviation (SD) was reported.

2.3.5 Water vapor permeability

Water vapor transmittance rate (WVTR) of the samples was determined with PBI-Dansensor L 80-5000. A dry room with a specified relative humidity is separated by a wet room where the atmosphere is saturated with water vapor at a known temperature through a sheet of material to be tested. Changing humidity in the dry chamber is achieved by water vapor passing through the tested material and is detected by a humidity sensor that is able to provide an electrical signal that is measuring relative humidity in the dry room. The time required to increase humidity to a certain amount is measured and converted into a transmission rate of water vapor. The permeability of the samples was performed at 23°C.

3. Results and discussion

3.1 Processing characteristics of PHB/plasticizer blends

In Fig. 2 are shown the plastograms of plastified PHB melted at a temperature of 180^{o}C, rotor speed of 60 rpm and mixing time of 6 minutes.

The addition of plasticizer led to the lower level of torque and lower melt viscosity, as it can be seen from Figures 2 and 3.

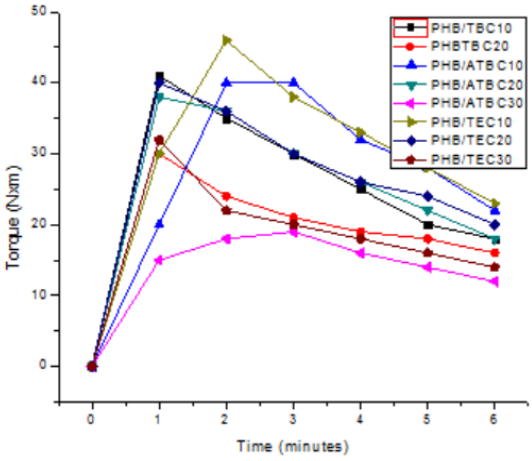


Fig.2. Brabender torque-time profiles of plastified PHB

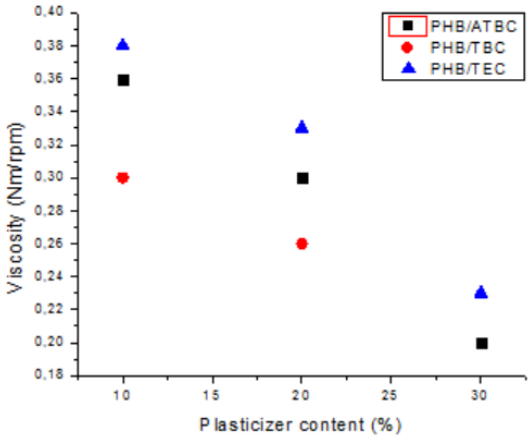


Fig.3. Melt viscosity index of plastified PHB at different loadings of plasticizer

From Fig. 2 is observed that at 6 minutes the torque decreased as the plasticizer content increased. With increasing of plasticizer content, the viscosity decreased for all types of plasticizers (Figure 3). This decrease indicates that the chains of PHB are easily deformed and their frictional resistance is not optimum.

All plasticizers used were found very suitable to plasticize the PHB, among which TBC is the most effective plasticizer for significantly improvement of PHB processability. Melt viscosity index of PHB blends decreased as follows: TEC-10 > ATBC-10 > TBC-10; TEC-20 > ATBC-20 > TBC-20; TEC-30 > ATBC-30.

3.2 FTIR-ATR Analysis

The effect of three plasticizers on FTIR spectrum on PHB is presented in Figure 4. Neat PHB (as powder) was used as reference.

From literature, the main bands of PHB are assigned to C–O–C stretching at 1188 cm^{-1} [27], C-O-C stretching at 1227 cm^{-1}, wag CH_3 at 1380 cm^{-1} [28], assym. CH_3 at

1456 cm^{-1} and crystalline C=O at 1724 cm^{-1} [28, 29]. Characteristic bands associated to plastified PHB are shifted to lower wavenumber, as the plasticizer content increases. Therefore, neat PHB shows a band at 1182 cm^{-1} that is shifted to 1180 cm^{-1} and to 1178 cm^{-1} for PHB/ATBC-10 and respectively PHB/ATBC-20.

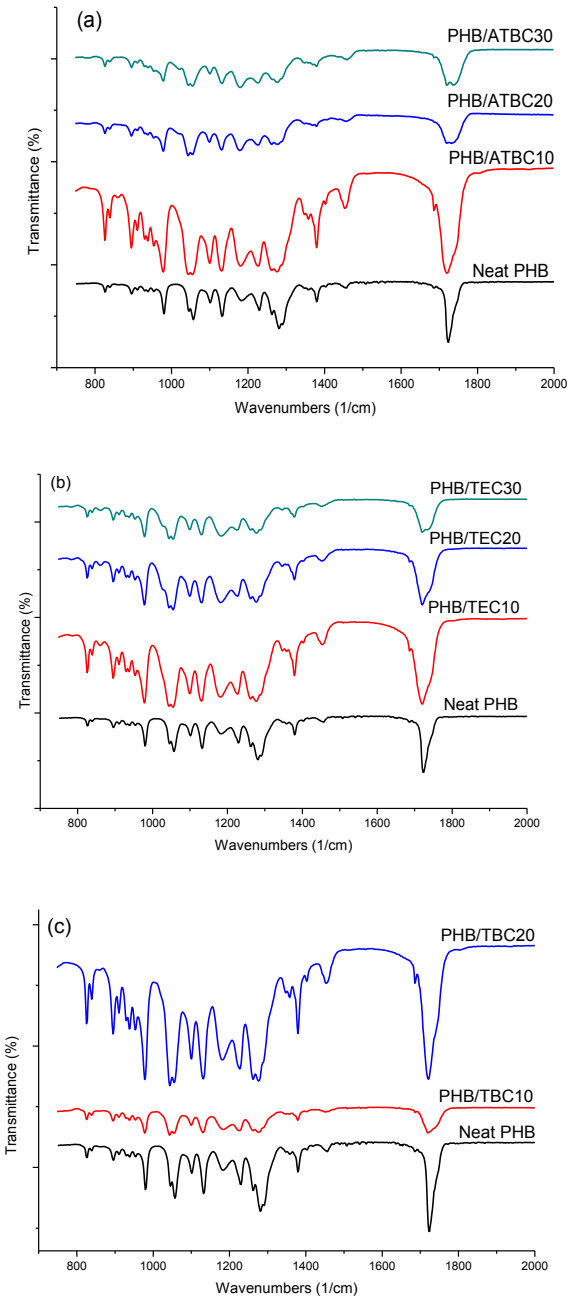


Fig. 4. Effect of plasticizer type and concentration on FTIR spectrum of PHB/plasticizer films(a) Plasticized with ATBC; (b) Plasticized with TEC; (c) Plasticized with TBC

The crystalline band at 1724 cm^{-1} is shifted to 1720 cm^{-1} for PHB/ATBC-10, PHB/ATBC-30, PHB/TEC and PHB/TBC-20 samples and to 1718 cm^{-1} for PHB/ATBC-20 and PHB/TBC-10 samples. This indicated that plasticizer could decrease the wavenumber of the characteristic peaks. The same decrease of wavenumber to lower frequency was observed by Wang et al. for characteristic bands of PLA/carbon black composites with increasing plasticizers content [30].

3.3 DSC Spectra

The thermal properties as T_c, T_m, ΔH_f and X_c of PHB/plasticizer blends, obtained from the second heating, are summarized in Table 2.

Table 2. DSC results of PHB/plasticizer blends

Sample code	T_c (°C)	T_m (°C)	ΔH_f (J/g)	X_c (%)
PHB pure	87.1	173.5	89.0	60.9
PHB/ATBC10	81.1	166.9	82.8	56.7
PHB/ATBC20	80.7	167.3	78.8	53.9
PHB/ATBC30	80.8	158.2	67.2	46.0
PHB/TEC10	79.7	168.1	80.0	54.8
PHB/TEC20	70.2	168.4	61.6	42.2
PHB/TEC30	65.2	162.8	59.7	40.9
PHB/TBC10	75.4	171.9	85.7	58.6
PHB/TBC20	69.8	168.1	75.4	51.6

The data from Table 2 revealed that the enthalpy of PHB fusion, ΔH_f, decreased from 89.0 J/g to 67.2 J/g for PHB with 30% ATBC, to 59.7 J/g for PHB with 30% TEC and respectively to 75.4 J/g for PHB with 20% TBC. In addition, the T_c value of blends showed lower values than pure PHB.

The effect of plasticizer content on T_m and X_c of PHB/ plasticizer blends is also shown in Figure 5. The pure PHB powder showed one endotherm peak at 173.5°C. A depression of T_m was observed in all PHB/plasticizer blends in comparison with pure PHB (Fig. 5 (a)). Erceg et al. [16] investigated the effect of acetyl tributyl citrate (ATBC) on the thermal stability of PHB by DSC and showed that ATBC leads to significant decrease in T_m. From Fig. 5 (a) is observed that once the plasticizer content increased, the T_m decreased. As a result, the processing temperature window is increased. This is in good agreement with lower viscosity recorded for PHB loaded with plasticizers, making them the easier for processing.

From the melting temperature of PHB blends, it can be concluded that the efficiency of plasticizers was higher in the order: TBC-10 > TEC-10 > ATBC-10; TEC-20 > TBC-20 > ATBC-20; TEC-30 > ATBC-30.

From Fig. 5 (b) is observed that X_c decreased with loading of plasticizers. With increasing of plasticizer contents, the PHB microcrystals or ordered chains could be more easily moved to unpack into a little dense or perfect crystalline structure [31]. The X_c of pure PHB was 60.9%. The lowest value of X_c is recorded by PHB/TEC30 blend (40.9%).

It is noted that the trend of decrease of PHB/plasticizer blends crystallinity (X_c) degree is obvious in the order: TBC-10 > ATBC-10 > TEC-10; ATBC-20 > TBC-20 > TEC-20; ATBC-30 > TEC-30.

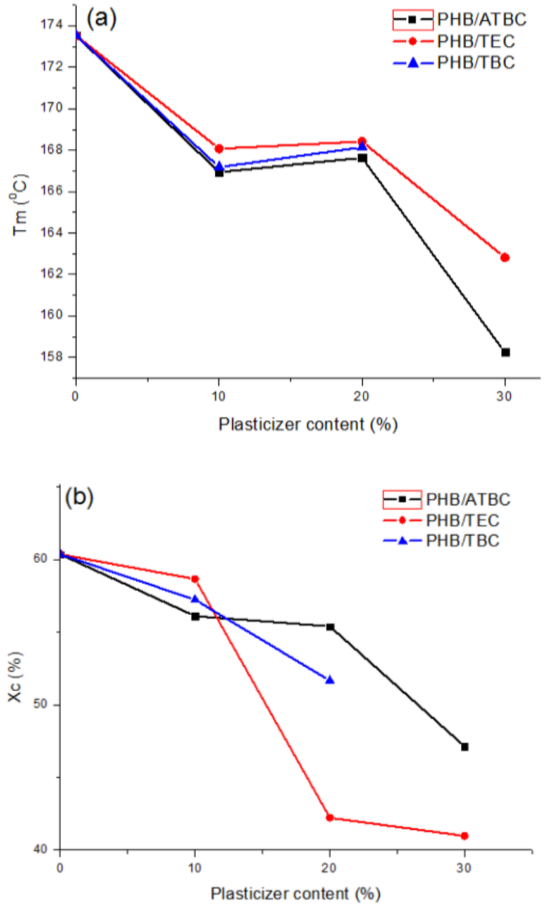


Fig. 5. Thermal properties of PHB/plasticizer blends (a) Melting temperature; (b) Degree of crystallinity

3.4 Tensile properties

The effect of type and concentration of plasticizer on the mechanical properties of PHB/plasticizer blends (tensile strength, elongation at break, and Young's modulus) are shown in Figure 6.

From Figure 6 is evidenced that loading of plasticizer leads to improve of elongation at break with the detriment of tensile strength. The addition of ATBC decreased the tensile strength of PHB blends at about 25% for blend containing ATBC in content of 20% and respectively at 59% for 30% ATBC compared with PHB/ATBC-10 sample. Also, TEC led to a decrease of tensile strength with 27% for blends containing 20% TEC and with 51% for 30% TEC since a lower decrease at 16 % was recorded for PHB/TBC-20 (Figure 6 (a)). It is showed a significantly increase of elongation at break for PHB/ATBC-30, PHB/TBC-20 blends (95% higher than PHB/TBC-10) and for PHB/ATBC-20 (62% higher than PHB/ATBC-10) (Figure 6 (b)). PHB/TEC blends display a maximum elongation at break of 31% for loading of 30% TEC. These results were in agreement with the outcome of other researchers that found that increase in the PEG content reduced the tensile strength and increased the elongation at break of pure PHB [17].

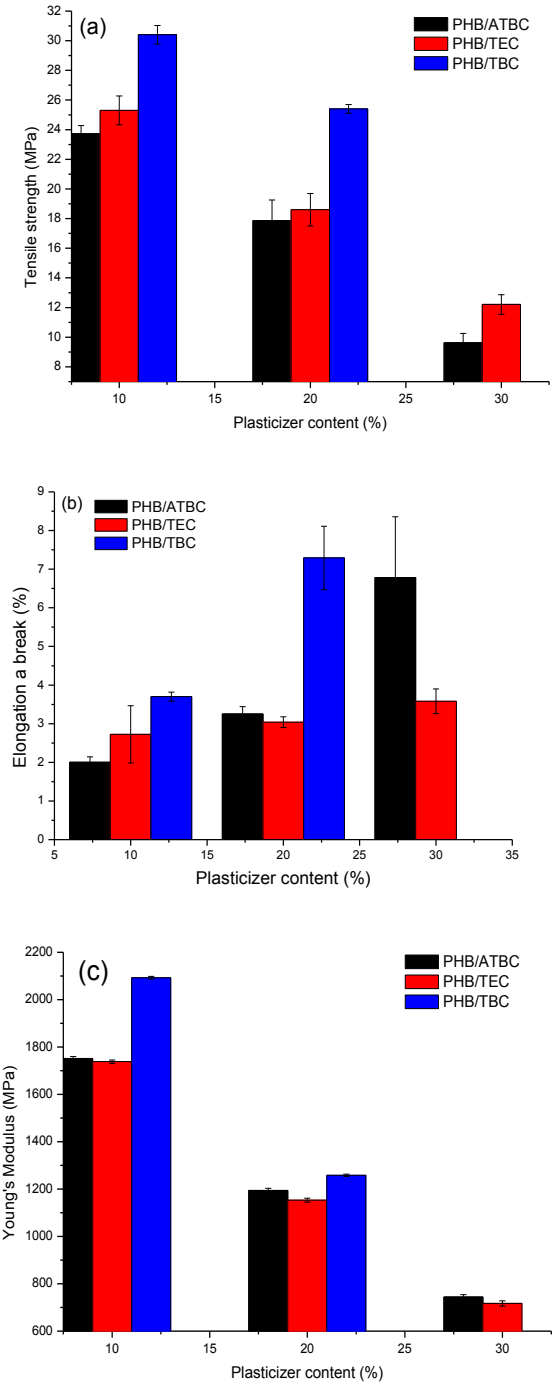


Fig. 6. Effect of plasticizer type and concentration on tensile properties of PHB/plasticizer blends (a) Tensile strength; (b) Elongation at Break;(c) Young's Modulus. Error bars represent standard error, n = 5

It is recognized that plasticization reduces the relative number of polymer–polymer contacts thereby decreasing the rigidity of the three-dimensional structure thereby allowing deformation without rupture [6]. Young's modulus follows the same decreased trend than evidences of tensile strength variation (Fig. 6 (c)).

It should be noted that the solubility parameters of PHB that has been reported to range between 18.5 and 20.1 $MPa^{1/2}$ [32] [37.85 - 41.12 $(J/cm^3)^{1/2}$] are closed to

those of TEC [48.69 $(J/cm^3)^{1/2}$]. This indicated that PHB should interact well with TEC. The highest solubility parameter of TEC may result in the higher strain at break compared to the blends containing ATBC and TBC. However, the rank of these solubility parameters cannot explain the lowest elongation at break of the PHB containing TEC. This can be due to the lowest molecular weight of TEC (276.28 g/mol) causing the lowest intermolecular attraction of PHB leading to the lowest elongation. Tensile properties reveal that the most efficient plasticizer is TBC followed by ATBC. Depending on desired properties of the final products it could be selected the optimal concentration of plasticizer.

3.5 Water vapor permeability

Water vapor transmittance rate (WVTR) of the films prepared by the plasticization of PHB with ATBC, TEC and respectively TBC is presented in Figure 7.

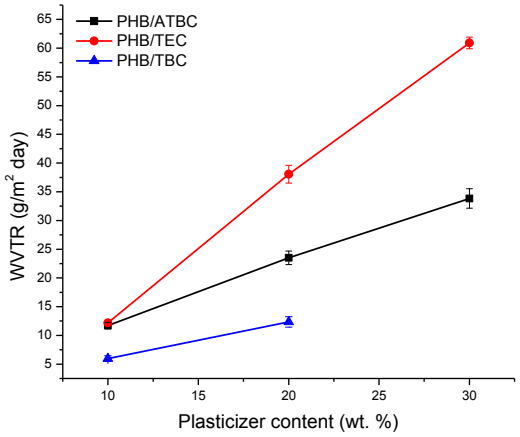


Fig.7. WVTR of PHB/plasticizer films

Data showed in Fig. 7 emphasize that WVTR is dependent on the type and level of plasticizer. It was found to be in the range of 5.97 to 6.90 g/m^2 day. A higher WVTR is recorded by PHB/TEC blend.

It is known that the degree of crystallinity influences inversly proportional the permeability of samples. A higher degree of crystallinity is usually related with low permeability of the films (as crystals restricting chain mobility) [27]. From Figure 6, is shown that PHB/TBC10 reached the higher value for X_c, and PHB/TEC blends recorded the lowest X_c this being in accordance with the permeability variation.

4. Conclusions

The results of this study evidenced the effect of three types of plasticizers, named acetyl *o*-tributylcitrate, triethyl citrate and tributhyl citrate on melt processability and properties of PHB.

The addition of plasticizer led to the lower level of torque. The melt viscosity index of PHB blends decreased as follows: TEC-10>ATBC-10>TBC-10; TEC-20> ATBC-20>TBC-20; TEC-30 >ATBC-30. PHB/plasticizer blends exhibited a wider melt-processing window. FT-IR spectroscopy revealed that the increase of plasticizer leads to reduction of the wavenumber for the characteristic bands of PHB (1182 cm^{-1}, 1724 cm^{-1}). Incorporation of plasticizers into PHB decreased tensile strength and Young's modulus, but increased the elongation at break. WVTR was found to be dependent on the type and content of plasticizer. TBC and ATBC were the most compatible and efficient plasticizers on improving the thermal, mechanical and barrier properties of PHB. The optimum concentration could be up to 20% depending on the desired properties of final products.

The findings of this study will also provide foundation for further developments of bioactive food packaging from PHB, ecological plasticizers and bioactive compounds.

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