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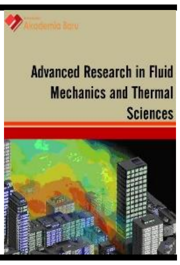

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Effects of Tributyl Citrate Plasticizer on Thermomechanical Attributes of Poly Lactic Acid

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ABSTRACT

Unique physicochemical and barrier attributes of a biodegradable and sustainable polymer called poly (lactic acid) (PLA) is promising for various applications. Conversely, the issues related to the rigidity and fragility of this polymer that limits its wide usage needs to be inhibited. To surmount these shortcomings, various plasticizers have been incorporated into PLA to soften and make it useful for food packaging. In this research, tributyl citrate (TBC) was inserted as plasticizer into PLA matrix to modify its properties. The impact of varying TBC contents on the morphology, thermal and dynamic mechanical behaviour of PLA/TBC composites were evaluated. FESEM images of PLA composites revealed homogeneous fractured surfaces. The crystallinity of PLA/TBC composites was increased with the addition of plasticizer without altering its transparency. The values of the storage modulus and glass transition temperatures, the cold crystallization temperatures as well as the melting temperatures were discerned to be lowered. Furthermore, the dynamic mechanical analysis disclosed a drop in the storage modulus of 2.11 GPa at 7 wt·% of TBC inclusion, indicating enhanced flexibility of TBC modified PLA. It was asserted that the inflexibility and brittleness associated with pristine PLA can considerably be improved by activating it with the additive plasticizer TBC.

Keywords:
PLA; TBC; plasticizer; thermomechanical traits; storage modulus

1. Introduction

Plastics (a spin-off from petroleum-based engineered materials) have been dominating the packaging industry because of their abundance, softness, lightness, transparency, flexibility, durability, and low cost. In addition, plastics are exceptionally stable and tolerant against external biotic and abiotic stresses [1-4]. However, the slow natural decomposition of used plastics remains an environmental concern. Therefore, a biodegradable, sustainable, low-cost, soft and environmental affable material alternative to plastic has been constantly demanded.

Biodegradable polymers are a green material that has been widely used in various industries such as food packaging, shopping bags, sacks, textiles, prosthetics and also in medicals applications. The

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industrial researches on the production of green materials from natural resources have been dedicated due to their minimal environmental footprint after the use [5, 6]. In this regard, Poly (lactic acid) (PLA) as linear aliphatic thermoplastic polyester are the most extensively researched and utilized biodegradable and sustainable green material because of its abundance in natural and renewable resources including corn, beet and sugarcane [7, 8]. Due to its notable sustainability, complete biodegradability, biocompatibility, and good physical properties, high strength and modulus, and good transparency, PLA became attractive for the packaging industry and become a potential substitute for several conventional polymers derived from petrochemical processing [9, 10].

However, it has some drawbacks that limit the use of PLA in certain applications. PLA suffered from various issues such as low thermal stability, weak barrier characteristics, brittleness, poor melt strength, and low crystallization rate mediated processing difficulty are detrimental unless inhibited [11, 12]. In fact, these shortcomings limit the practical applications of PLA in the field of automotive, electronics and films production for food packaging. Thus, constant efforts have been made to improve the thermomechanical and other attributes or to get emergent properties of PLA via the activation of different additives such as plasticizers [13–15], polymer blends [16] and nanofillers [17].

Brittleness and stiffness of PLA could be altered by blending with plasticizer. Inclusion of plasticizers enhanced flexibility and reduce the flaws by retaining the primary properties of PLA such as drawability and ductility [14]. Over the years, varied plasticizers including polyethylene glycol (PEG), oligomeric lactic acid (OLA), polypropylene glycol (PPG), tributyl citrate (TBC) and acetyl triethyl citrate (ATC) have successfully been combined with PLA to achieve its improved properties [18-20]. Generally, the efficiency of a plasticizer is evaluated depending on its ability to lower the glass transition temperature (T_g) and enhance the toughness which is decided by the plasticizer and polymer miscibility, type of plasticizer and its content [18].

The application of PLA in flexible films is restricted due to its low ductility. PLA low ductility is mainly due to its glass transition temperature (T_g), which is approximately 60°C. Since T_g is higher than room temperature, films produced with this polymer tend to be rigid. In line with this, the present research is directed towards composites PLA with TBC for the preparation of plasticized PLA using film casting and hot press methods. Subsequently, the effect of TBC loadings in PLA blend properties was investigated. Morphology, thermomechanical and transparency properties that imparted on the PLA-TBC composites at different contents of plasticizer were evaluated to assess the most adequate formulation. The melting and crystallization behaviour of PLA composites have been studied systematically.

2. Methodology

2.1 Materials

Poly (lactic acid) PLA 2002D was obtained in pellet form from Natureworks Co., Minnetonka, USA. Analytical grade tributyl citrate (TBC) (purity of 97.00%, Sigma Aldrich) was utilized as plasticizer to prepare the proposed PLA/TBC composites.

2.2 Preparation of PLA/TBC Composites

The PLA–TBC mixture was prepared via pre-treatment of PLA pellets wherein the humidity was eliminated. In this process, PLA pellets were the first oven-dried in the vacuum at 60°C for 24h. Then, the weighed PLA was dissolved in a beaker containing 50 mL of THF solvent followed by stirring using a magnetic hotplate at 60°C for 6h. Next, the desired TBC plasticizer was added to the PLA solution with constant stirring for about 2h. Later, the resultant mixture was cast onto a Petri dish and air-dried at room temperature for 24h to let adequate solvent evaporated, forming a thin film of modified PLA/TBC of different thicknesses. The sample was then heated in the oven at 60°C for 24h to ensure total solvent removal. Later, the sample was pressed in a hot compression machine to eliminate air bubbles and to get even film with 30 mm thickness. The plasticized PLA composites were designated as pPLA as shown in Table 1.

Table 1
Identification of abbreviations for neat PLA and plasticized PLA composites

Samples	PLA (%·w/w)	Plasticizer (%·w/w)
PLA	100	0
pPLA05	95	5
pPLA07	93	7
pPLA10	90	10

2.3 Characterizations of PLA and PLA/TBC Composites

The surface morphologies of the fractured specimens were examined using FESEM Hitachi SU8020. Prior to scanning, samples were coated with a thin layer of platinum to create a conducting surface on the composites to prevent specimen charging by the electron beam.

Dynamic mechanical analysis (DMA) was conducted on a TA instrument (DMA Q 800) in tensile mode. The sample of dimension (30 mm × 8 mm × 0.5 mm) was heated from 25 to 160°C at 2°C/min scanning rate with regulated sinusoidal strain.

Thermal behaviour of the composites was analyzed using a TA Instruments (DSC Q20 series). Melting and crystallization curves were obtained by heating about 5 mg of composites, sealed in an aluminum pan with an empty sample pan served as a reference.

Prior to cooling scan, a sample was first heated from 30°C to 180°C at a scanning rate of 10°C/min and held in the molten state for 2 min to remove the thermal history. Then, the sample was cooled from 180°C to 30°C at a scanning rate of 2°C/min. After cooling, the sample was further heated from 30°C to 180°C with the same scanning rate as the cooling rate. The second heating scan was obtained to determine the thermal behaviour of the composites. The degree of crystallinity (X_c) of the composites was calculated using Eq. (1).

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_m^*} \times 100 \quad (1)$$

where ΔH_{cc} (in J/g) is the enthalpy of crystallization and ΔH_m (in J/g) is the enthalpy of fusion of the PLA composites. ΔH_m^* (in J/g) is the heat of fusion of 100 % PLA was observed to be 93.1 J/g [21].

The thermal characteristics of the composites were determined by thermogravimetric analysis (TGA) using a TA instruments (Q-500). Samples of about 5.0 mg were heated in nitrogen atmosphere from 50°C to 600°C at a heating rate of 10°C/min and the purging gas flow rate of 20 ml/min. The room temperature ultraviolet–visible (UV-Vis) absorption spectra in the wavelength range of 200–800 nm was recorded to determine composites optical transmittance behaviour.

3. Results

3.1 FESEM Images and EDX Spectra of Neat PLA and PLA/TBC Composites

Figure 1 (a)-(d) shows the FESEM images of neat PLA compared with pPLA composites containing 5.0, 7.0 and 10.0 wt·% of TBC.

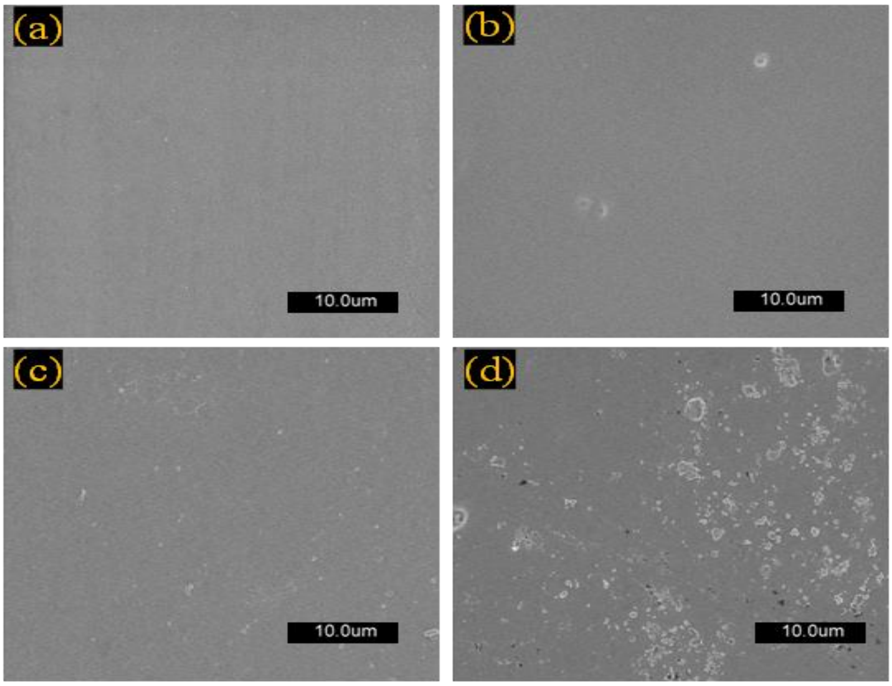

Fig. 1. FESEM images at 5000× magnifications for (a) neat PLA, (b) pPLA05, (c) pPLA07 and (d) pPLA10

The FESEM images of neat PLA all pPLA revealed regular structure with some smoothly breakable and almost flat surface morphology in the absence of large cracks or agglomerated structures or pores. This clearly indicated the fragile semi-crystalline polymeric character of as-prepared neat PLA. Furthermore, TBC (plasticizer) did not disclose any phase segregation, confirming its excellent conjunction with the polymer networks.

3.2 Dynamic Mechanical Properties of Neat PLA and PLA/TBC Composites

Figure 2 displays the temperature-dependent variation in the storage modulus (E') of neat PLA and pPLA composites. The E' of pPLA composites were lower than the neat PLA, implying an enhancement in the elastic modulus of TBC in the composites. Furthermore, with the rise in TBC contents from 5 to 10 wt·% the value of T_g was decreased. As depicted in Table 2, with the decrease of T_g value the value of E' started dropping. Overall, the values of E' for all composites were steadily decreased with the increase in temperature except a rapid decay in the region of T_g within 59.9 to 45°C, however above 80°C the value of E' was increased due to cold crystallization of PLA.

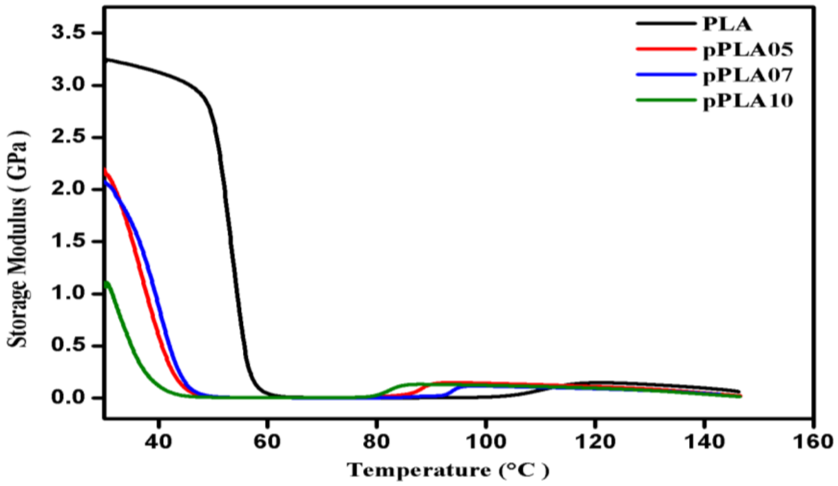

Fig. 2. Temperature dependent variation in the storage modulus of neat PLA and pPLA

Figure 3 shows the temperature dependent variation in the loss modulus (E") of neat PLA and pPLA composites. The finite value of E" clearly indicated the viscosity (often called the flow of the material) of the polymer after melting. Values of E" of the composite films were decreased with the increase in TBC contents, implying a reduction in the melt viscosity of the composites. Furthermore, polymeric chains have cooperative movements, leading to the mechanism of energy dissipation due to the decrease in the E". However, when the TBC content in PLA was higher (10.0 wt.%) the peak value of E" moved towards lower temperatures and then dropped. The result shows that at the higher contents of TBC in PLA matrix act simultaneously like a good solvent or plasticizer, thereby increasing the viscosity of the TBC in PLA composites [6].

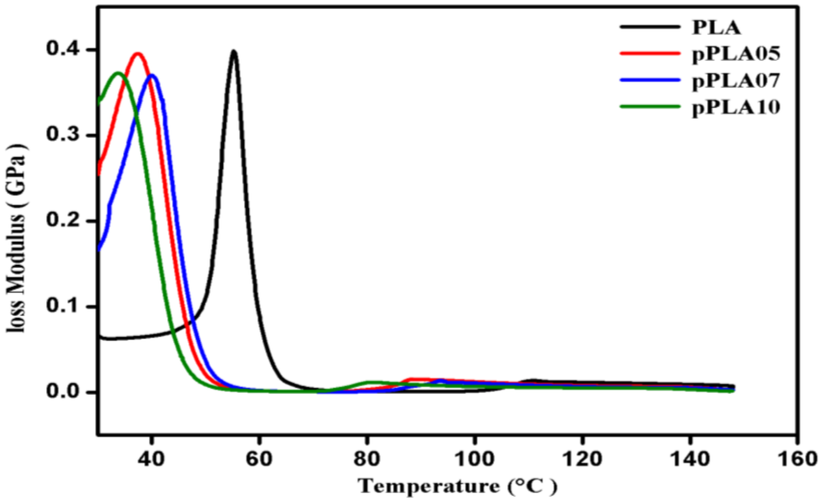

Fig. 3. Temperature dependent variation in the loss modulus of neat PLA and pPLA

Figure 4 represents the temperature dependent variation in the damping factor of PLA and pPLA composites. The value of T_g obtained from DMA which was marked as the temperature where the value of E" or damping vector (tan δ) was maximum. In fact, tan δ provided the resistive effect of the composites and the peak value of T_g tend to separate the glassy domain from the elastic one. Also, the damping factor is related to the motion of polymeric chains and small chemical groups inside the complex networks. The value of T_g of neat PLA and pPLA composites was estimated from the peak of temperature dependent variation in tan δ which showed a shift to the lower temperature with the increase in TBC. Table 2 depicts the values of dynamic mechanical properties of neat PLA and pPLA composites obtained from DMA results.

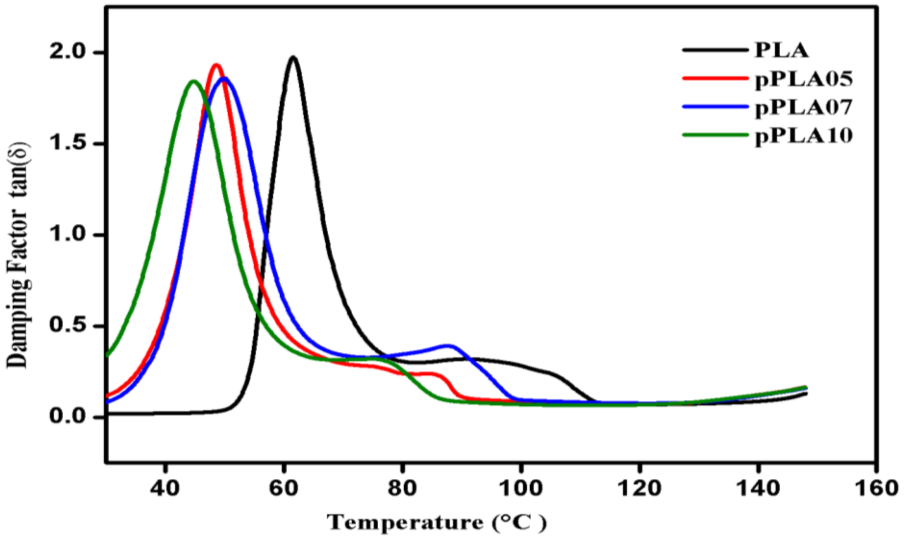

Fig. 4. Temperature dependent variation in the damping factor of neat PLA and PLA composites

Table 2
Dynamic mechanical properties of neat PLA and pPLA

Samples	E′ (GPa)	E″ (GPa)	T_g (°C)	tan δ
PLA	3.13	0.08	59.9	1.97
pPLA05	2.52	0.27	48.5	1.93
pPLA07	2.11	0.18	50.0	1.89
pPLA10	1.40	0.37	45.0	1.91

The peak value of tan δ of the composite film containing 7 wt·% of TBC (pPLA07) was lower (1.89) than pPLA with 5 and 10 wt·% TBC. It was concluded that the decrease in damping factor could affect the interfaces and thus increased the adhesion of the interface as observed in pPLA07. Thus, the weak bonding of the interface led to more energy dissipation compared to good bonding. In addition, the lower value of tan δ peak indicated the limitation in the molecular movement in the polymeric network, suggesting an improvement in the interfacial bonding of pPLA than neat PLA.

3.3 Thermal Characteristics of Neat PLA and PLA/TBC Composites

Figure 5 shows the thermal response in the heat capacity of neat PLA and pPLA composites under the first heating cycle. The heating curve of neat PLA consisted of two endothermic peaks and one broad exothermic. However, the heating curves of pPLA revealed an exothermic event related to the cold crystallization followed by an endothermic event corresponded to fusion in which the peak for T_g was not evidenced.

Irrespective of TBC contents, the T_c peaks of the pPLA were shifted towards lower temperatures. The presence of plasticizers in the PLA matrix promoted crystallization during heating while shifting the T_c toward lower temperatures. This enhanced favorable crystallization process that attributed to the increased movement of the polymer chains because of the existence of plasticizers in PLA matrix. Table 3 summarizes the thermal properties of neat PLA and pPLA composites.

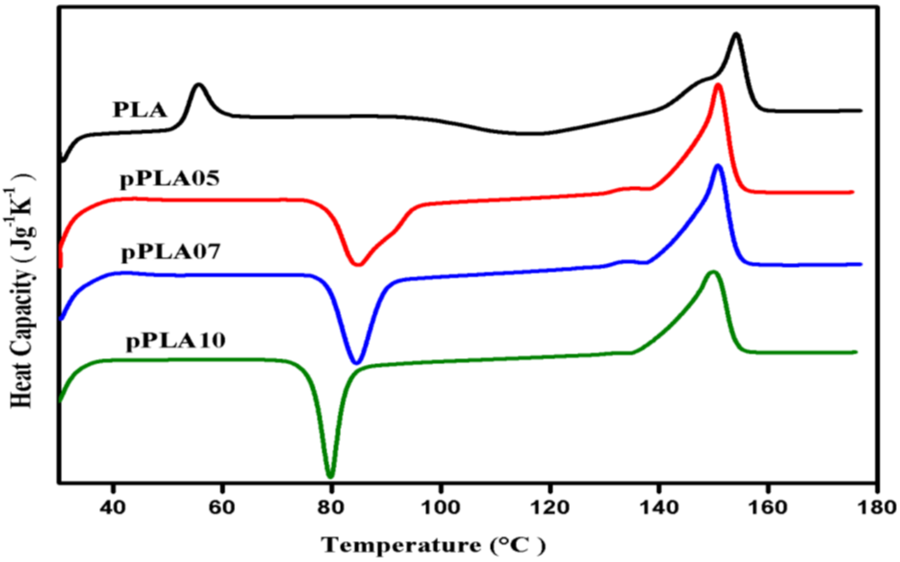

Fig. 5. Heat capacity (DSC curve) of neat PLA and pPLA composites under the first heating cycle

Figure 6 displays the temperature dependent heat capacity changes of neat PLA and pPLA for the second heating cycle. The DSC profiles of pPLA manifested only T_m while T_c and T_g are disappeared, indicating the emergence of good crystallinity in the composites after the cooling cycle which agreed with the previous report [22]. The main reason for the undetected or ill-defined (obscure) T_g peak in the second heating cycle was ascribed to the formation of crystalline domains on cooling that prevented or hindered the movement of the amorphous domains, in addition to because it was cooled at a slower rate (2°C/min) whilst in the first heating was at higher scanning rate (10°C/min).

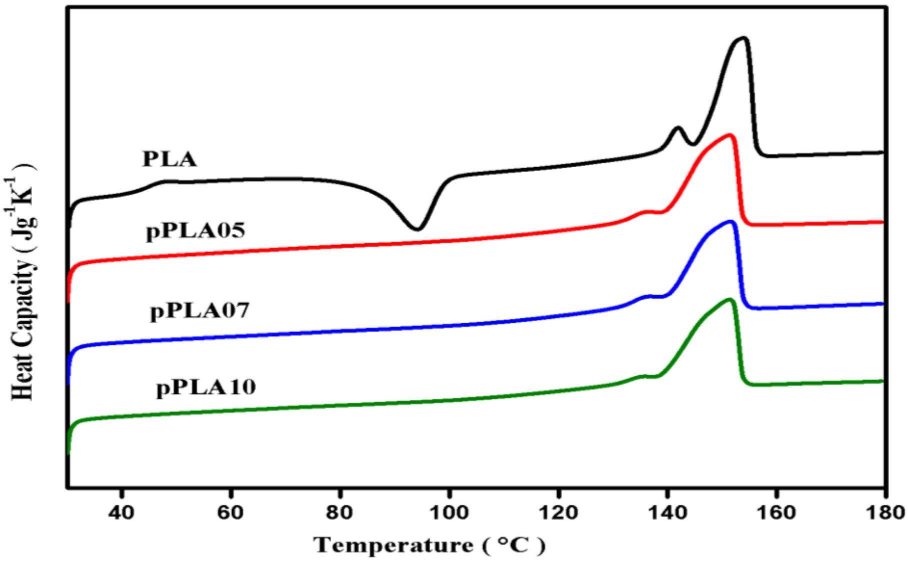

Fig. 6. Heat capacity (DSC second heating curve) of neat PLA and pPLA

The achieved crystallinity of pPLA composites was superior compared to neat PLA (17.52%), after the cooling cycle where the extent of crystallinity in pPLA composites was increased from 36.73 to 38.34% (Table 3) as TBC increased from 5 to 10 wt·%., respectively. This improvement in the crystallinity of pLA composite indicated its significant role in controlling the morphology and structures of the final products. This behavior was also reported for PLA plasticized with PEG [23]. The observed modification in the structural properties of the proposed plasticized composites clearly implied the TBC inclusion assisted improved molecular movements of different chain segments which favored the rearrangements of the polymer chains in the crystalline phases over a longer temperature range. Therefore, the crystallization dip was absent because PLA already existed in the complete crystalline phase during the cooling scan. Conversely, it is not preferred to add large amounts of plasticizers which could cause phase segregation and reduce the compatibility between polymer and plasticizer as reported earlier [24].

Table 3
Thermal parameters of neat PLA and plasticized PLA composites films

Composites	T_g (°C)	T_c (°C)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_{m1} (°C)	T_{m2} (°C)	ΔH_m (J/g)	χ_c %
PLA	53.0	92.10	94.2	18.8	141.9	153.00	37.7	17.52
pPLA05	-	88.60	-	-	135.6	151.80	34.2	36.73
pPLA07	-	89.00	-	-	134.98	151.55	35.9	38.56
pPLA10	-	88.30	-	-	134.75	151.47	35.5	38.13

Neat PLA shows two melting peaks, due to tiny and irregular crystallites have enough time for melting and recrystallization process which can majorly be explained by melt-recrystallization model [25]. The degree of crystallinity (Table 3) was determined from the melting where the crystalline content formed during the cold crystallization and would not be representing the actual sample. The crystallinity was calculated in terms of thermal properties from the difference of ΔH_m and ΔH_{cc}. Generally, the addition of plasticizers to PLA lowers the T_g and enhances the crystallinity. The crystallinity of the neat PLA showed the predominance of amorphous state however the presence of plasticizer enhanced crystallization, indicating TBC inclusion mediated greater mobility of the chains that assisted the formation of crystals.

3.4 Thermogravimetry Analysis of Neat PLA and PLA/TBC Composites

Thermogravimetric analysis (TGA) gives information on weight loss because of degradation as a function of temperature. Figure 7 and 8 show the degradation temperature of neat PLA and pPLA composites.

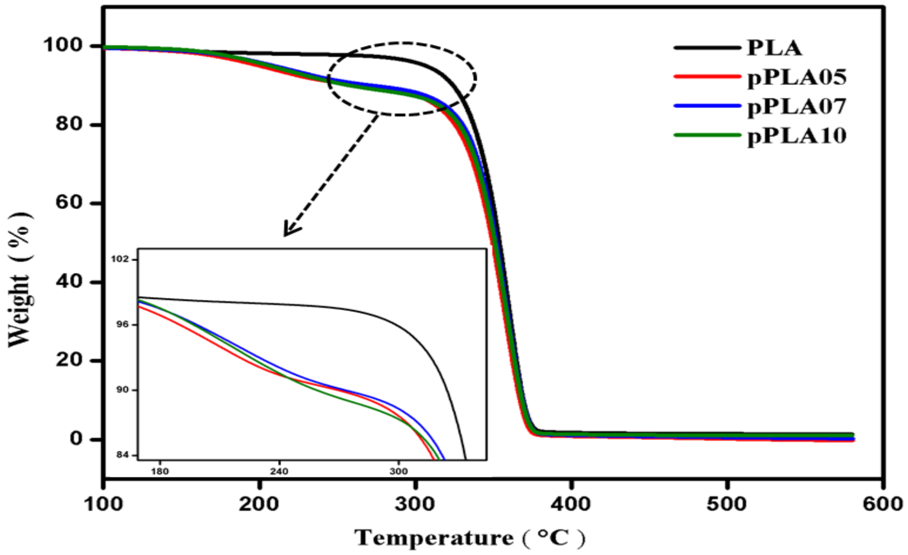

Fig. 7. TGA curve of neat PLA and pPLA composites

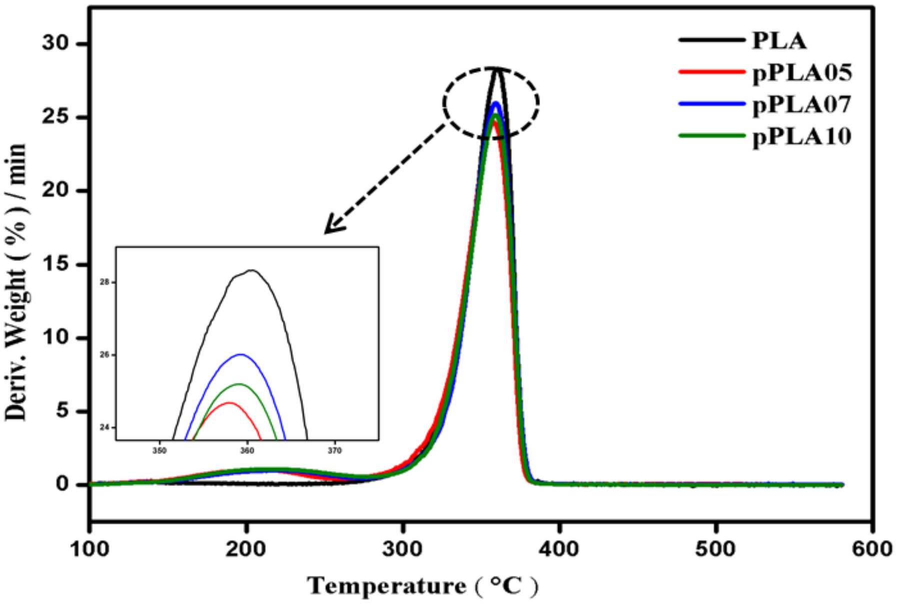

Fig. 8. DTG curve of neat PLA and pPLA composites

The neat PLA started decomposing at 284.6°C because of the change in the ester or losses of end groups from the primary polymeric chain through radical reactions and by non-radical concerted reactions [26]. The initial decay temperatures (T_{onset}) that occurred at 5% (T5%) and 50 % (T50%) of mass loss which was utilized as the measure of the onset and half degradation temperature, respectively. Table 4 provides the temperature for the highest rate of decomposition (dw_{max}) of neat PLA and pPLA composite obtained using derivative data analysis (DTG).

The decomposition temperatures for the (T_{onset}) and (T_{end}) of composites were calculated at 50% of weight loss which showed a systematic shift towards lower temperature with the increase in TBC contents. The shift in the temperature was ascribed to the greater free volume of the system imposed by the plasticizers. This, in turn, caused a reduction in intermolecular interactions of the PLA matrix chains with the addition of citrates.

Table 4
Comparison of TGA and DTG properties of Neat PLA and pPLA

Composites	T_{onset} (°C)	T50% (°C)	T_{end} (°C)	dw_{max} (%·min^{-1})	Char Residue at 525 °C
PLA	288.7	353.8	378.5	360.2	1.44
pPLA05	186.8	351.9	376.9	358.7	0.2
pPLA07	186.7	351.6	376.1	358.6	0.5
pPLA10	186.3	350.9	375.5	358.3	1.2

3.5 Transparency of Neat PLA and PLA/TBC Composites

Figure 9 shows the measured UV-Vis transmittance spectra of neat PLA and TBC incorporated PLA films (pPLA) in the wavelength range of 200 to 800 nm. The transmittance of neat PLA film was approximately 89%. However, the transmittance of the pPLA was slightly lowered with the increase in TBC contents in the PLA matrix. It is important to note that the optical absorption and transmission properties of polymer-based materials are vital for food packaging applications. It is universally accepted that transparent packaging of edible stuff provides a close view to the consumers before purchasing the products. In addition, displayed colour and look of the food products often attract the customers when presented by the stores in a better way. Thus, similar transmittance of the PLA/TBC blends yet with excellent thermal stability and biodegradable characteristic as that of neat PLA can be achieved. Briefly, the observed visible transmittance was very effective for the plasticized biodegradable materials for further development.

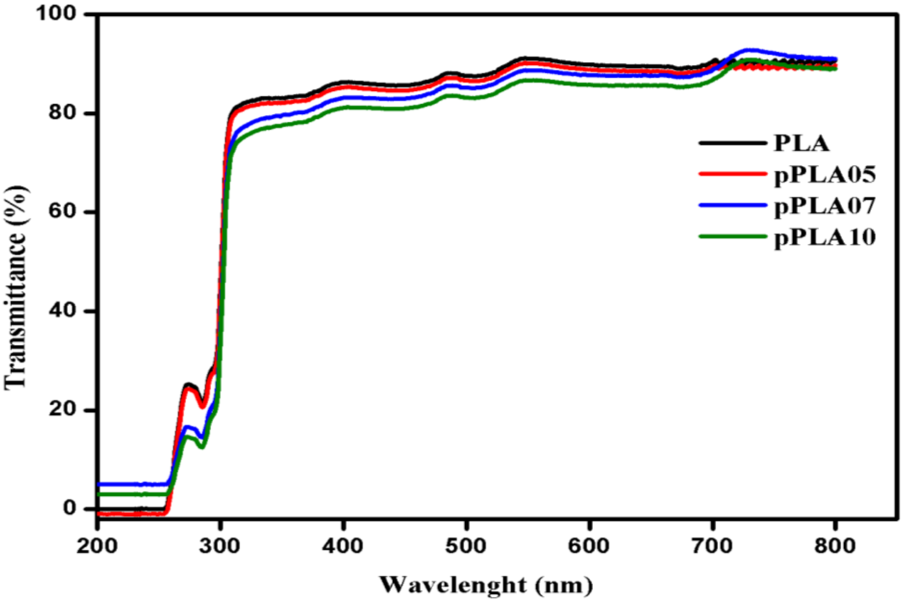

Fig. 9. Transmittance spectra of neat PLA and pPLA films

4. Conclusions

The PLA/TBC composites were prepared via solution casting and hot compression techniques. Inclusion of TBC into the PLA matrix lowered the T_g value compared to neat PLA which was ascribed to the enhancement of the polymer chains mobility in the presence of the plasticizer. Consequently, it imparted greater flexibility and higher crystallinity to the PLA chains in the PLA/TBC composites. The addition of TBC into the PLA matrix weakened the interaction strengths between the polymer chains within the matrix, resulting in more flexible materials. Meanwhile, the crystallinity of the PLA/TBC composites was enhanced with the increase in the plasticizer content. TGA results showed a drop in the onset and end temperature of degradation for PLA/TBC composites with the increase in TBC content. Inclusion of TBC decreases stiffness and brittleness of PLA as observed in DMA results. The value of E' and T_g of the PLA/TBC composites attained maximum for 7 wt·%. SEM images revealed the best miscibility and interfacial adhesion between PLA and pPLA that was observed at 7 wt·% of TBC. All the proposed PLA/TBC films showed excellent visible transparency, improved flexibility and biodegradability. It was asserted that the proposed PLA/TBC composite films may contribute toward the development of sustainable and biodegradable transparent material useful for food packaging and other applications.

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