

STUDIES ON MECHANICAL, OPTICAL AND BARRIER PROPERTIES OF BIODEGRADABLE PLA-PBAT BLEND FILM WITH EGMA COMPATIBILIZER AND MICRO ZnO

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Abstract

PLA-PBAT was melt blended using Twin screw compounding extruder in three ratios (60:40, 50:50, 40:60%) with EGMA as compatibilizer (2.5 wt%). Tubular blown films were made using a tubular blown film extruder. In one formulation (50:50%) micro ZnO 1% was also included. The PLA-PBAT blends were tested for their mechanical, thermal, optical and physical properties. Due to ductility/flexibility of PBAT, tensile strength in machine direction (M/D) decreases with increasing PBAT concentration. However, in the transverse direction (T/D) the tensile strength increases with increase in PBAT concentration. Tear strength results show maximum strength in proportion of 50:50 in both machine and transverse direction. The PLA-PBAT 50:50 % blend filled with ZnO 1% has higher tear strength in both machine and transverse direction. Improvement in the dart impact strength was observed. Luminous transmittance was increased, MFI increased with increase in PBAT composition. Water vapour transmission rate was not decreased by increasing PBAT content since PBAT has slightly higher gas permeability than that of PLA. A complete biodegradation (100%) of PLA/PBAT blend was achieved in all PLA-PBAT blends and with micro ZnO, because of high biodegradability nature of PLA and PBAT polyesters. The test was done up to 210 days in soil burial method.

Keywords: PLA; PBAT; EGMA; ZnO; TSC; blown film; mechanical property; optical property; thermal property; biodegradation.

INTRODUCTION

The alarming environmental problems had asserted the indispensable need for plastics with better biodegradability. Poly lactic acid (PLA) has 100% biodegradability, but PLA is amorphous and brittle, extremely low fracture toughness, narrow process ability (low melt viscosity) and the material is also less in usage, due to its high cost. For flexible packaging it is important to blend PLA with other flexible polymer materials like LDPE (low density polyethylene), EVA ethylene vinyl acetate copolymer), EVOH (ethylene vinyl alcohol copolymer).

Polymer blends and alloys of PLA with starch are reported in literature. Blends of PLA-Starch (20-50%) are fully biodegradable and green composites. But the materials are very brittle [1,2]. Chi-hui Tsou et al. in 2011 [3] studied preparation and characterization of poly(lactic acid)/ethylene glycidyl

methacrylate copolymer (EGMC) blends. After modifying PLA with EGMC, both tensile and tear strength values of PLA_xEGMC_y blown-film specimens in machine and transverse directions were improved significantly and reached maximum values as the EGMC content approached an optimum value of 6 wt%. Do Van Cong et al. in 2012 [4] studied a novel enzymatic biodegradable route for PLA/EVA blends under agricultural soil of Vietnam. Fortunati et al. in 2013 [5] studied effect of ethylene-co-vinyl acetate-glycidylmethacrylate and cellulose microfibers on the thermal, rheological and biodegradation properties of poly(lactic acid) based systems. Disintegration tests showed that the addition of EVA-GMA to PLA induces a slight delay of PLA disintegration, but after 21 days in composting conditions, the blends and composites resulted better degradability than PLA itself. Moura et al. [6] studied characterization of EVA/PLA blends when exposed to different environments with different compositions under UV radiation and microorganism's action.

PBAT has high impact strength which overcomes the disadvantage of low impact strength of PLA. PBAT (polybutylene adipate co-terephthalate) is a biodegradable random copolymer, specifically a copolyester of adipic acid, 1,4- butanediol and terephthalic acid (or from dimethyl terephthalate). PBAT has wide melting point, low elastic modulus and stiffness, but high flexibility and toughness. PBAT is fully biodegradable when composted due to the presence of butylene adipate groups. The high stability and mechanical properties come from the terephthalate portions. It is generally marketed as a fully biodegradable alternative to low-density polyethylene, having many similar properties including flexibility and resilience, allowing it to be used for many similar uses such as plastic bags and wraps.

PBAT is a petroleum based product and it has high impact strength and good processability. PBAT is used to overcome low impact strength and processing difficulties of PLA. PLA is a bio based polymer which is biodegradable whereas PBAT is also biodegradable polymer. When combining these two polymers by blending one can make a fully degradable blend but PLA and PBAT are immiscible. EGMA is used as a compatibilizer in this blend to improve the interfacial adhesion and to reduce the interfacial tension between the PLA and PBAT in this project.

Hongdilokkul et al. [7] studied the properties of films based on PLA/PBAT blend prepared by reactive compounding at the weight ratio of 80:20 together with peroxide as a reactive agent in a twin screw extruder. Carbonell-Verdu et al. [8] studied the compatibilization of poly(lactic acid)/poly(butylene adipate-co-terephthalate), PLA/PBAT (80:20%) binary blends by using cottonseed oil derivatives, *i.e.* epoxidized (ECISO) and maleinized (MCISO) cottonseed oil compatibilizers (1-7.5%). In 2012 Pukpanda and Sirisinha studied properties of poly(lactic acid) (PLA)/poly(butylene adipate-co-terephthalate) (PBAT) blends in the presence of antioxidant Irganox was studied [9].

In 2017 Wenhui Li et al. studied effects of PLA film incorporated with ZnO nanoparticle on the quality attributes of fresh-cut apple [10]. A novel nanopackaging film was synthesized by incorporating ZnO nanoparticles into a PLA matrix, and its effect on the quality of fresh-cut apple during the period of preservation was investigated at 4 ± 1 °C for 14 days. Six wt % cinnamaldehyde was added into the nano-blend film. Compared to the pure PLA film, the nano-blend film had a higher water vapor permeability (WVP) and lower oxygen permeability. It also had a remarkable inhibition on the growth of microorganisms. Therefore, Nano-ZnO active packaging could be used to improve the shelf-life of fresh-cut produce.

In 2016 Raja Venkatesan and Natesan Rajeswari studied, ZnO/PBAT nanocomposite films, ie investigation on the mechanical and biological activity for food packaging. Packaging of foods in high barrier materials is essential to attain food safety [11]. The role of ZnO loadings on poly(butylene adipate-co-terephthalate) (PBAT) structure were investigated, in addition to that packaging properties

such as barrier, thermal, and mechanical properties were studied. Antimicrobial films are developed based on PBAT and ZnO nanoparticles. The nanocomposites exhibit a significant increase in the mechanical and thermal stability. The resulting PBAT/ZnO nanofilms show superior antimicrobial activity against *Escherichia coli* and *Staphylococcus aureus*.

PLA blends of LDPE, EVA are not 100% biodegradable within six months as per ISO 17088 standard. Hence many research projects are going on to improve its flexibility, toughness, dart impact strength and biodegradability etc. of PLA flexible packagings. Other biodegradable polyesters such as PBAT, PBS, PHBV, PCL are available in the market to make 100% bio-degradable polymers and plastics. But these thermoplastic polyesters are of non-renewable origin and are costlier but the cost of PBAT is comparable with that of PLA. Hence in this research work we blended PLA with PBAT in three compositions (60:40, 50:50 and 40:60%), with micro ZnO in 50:50% and studied the mechanical, optical, barrier properties of PLA-PBAT blends with and without microclay ZnO filler. Zinc Oxide is white or light gray powder, non-toxic and odorless. Its specific gravity is 5.47, melting point of 1975 °C. It is soluble in acid and alkali, insoluble in water and alcohol, ZnO filled PLA-PBAT (50:50%) film had a lower oxygen permeability which is desired for packaging of food. Micro ZnO is of lower cost than nano ZnO.

Blending PLA and PBAT with ZnO becomes a natural choice to improve PLA-PBAT properties without compromising its biodegradability. In this study, our interest is to produce biodegradable film by blending of PLA-PBAT of 60:40, 50:50, 60:40% ratios using a Twin screw extruder and then blown film extrusion. The mechanical, optical and barrier properties of bio degradable film are studied. In one formulation (50:50%) micro ZnO 1% was also included to produce anti- microbial packaging film.

EXPERIMENTAL

Materials

Poly(butylene adipate terephthalate) (MFI 6g/10min) film grade was obtained from Natur Tec India Pvt ltd. Poly(lactic acid) (MFI 14.5 g/10min) film grade was obtained from Natur Tec India Pvt ltd. Ethylene glycidyl methacrylate (MFI 5g/10min) compatibilizer was obtained from Sigma Aldrich. Micro ZnO was procured from Ramachandra chemicals, Chennai.

Compounding by twin screw extruder

PLA-PBAT was mixed thoroughly with poly(lactic acid) in a high speed mixer and then EGMA was added and further mixing was carried out for uniformity. Silicone oil was added to this to improve lubricant behaviour. Then the mixed materials were blended in a twin screw compounding extruder using a temperature range 170-200⁰ C as given below:

Z - 6	Z - 5	Z - 4	Z - 3	Z - 2	DIE
170 °C	170 °C	175 °C	180 °C	190 °C	200 °C

The extrudate, which looked like long plastic strands, were then cooled in a water bath and then cut into granules.

Blown film extrusion

The blended material in a pellet form was pre-dried to remove moisture. The pre-dried pellet were successively compacted and melted to form a continuous, viscous liquid. This molten plastic was then forced, or extruded, through an annular die. Air was injected through a hole in the centre of the die, and the pressure caused the extruded melt to expand into a bubble. The air entering the bubble replaced air leaving it, so that even and constant pressure was maintained to ensure uniform thickness of the film. The bubble was pulled continually upwards from the die and a cooling ring blew air on to the film. The film was then cooled. After solidification at the frost line, the film was moved into a set of nip rollers which collapsed the bubble and flattened it into two flat film layers. The puller rolls pulled the film onto the wind up rolls. The film passed through idler rolls during this process to ensure that there was uniform tension in the film. Tubular film extrusion was done with the following temperature range as given below:

Z - 5	Z - 4	Z - 3	Z - 2	Z - 1	D - 1	D - 2
165 °C	175 °C	180 °C	180 °C	180 °C	180 °C	180 °C

Testing of film properties

The properties were determined as per ASTM standard [12] except WVTR which was determined as per BS standard. The tensile strength and elongation at break were determined using a UTM (Universal Testing Machine) as per ASTM D882 standard. The tear strength was determined as per ASTM D 1922 standard. Dart impact was determined as ASTM D 1709 standard. Luminous Transmittance (Clarity) was determined as per ASTM D 1003 standard. MFI was determined as per ASTM D 1238. Density was determined as per ASTM D 792 using extrudate obtained from MFI test. WVTR test was determined evaluated as per BS 2782 standard. The films were characterized by DSC as per ASTM D 3417 Standard.

Biodegradability test

Biodegradability of plastics can be determined in various test atmospheres. The film whose biodegradability has to be determined was cut as per specimen dimension and weighed before allowing it to compost in the soil. After, 210 days, the loss in weight of the film was measured. This determines the ability of the material to biodegrade. After 210 days, the loss in weight of the film was measured. Due to Covid-19 holidays the soil buried samples could not be removed by the project students just after 6 months as per ISO 17088 Standard and was removed only after 7 months.

RESULTS AND DISCUSSION

Melt flow index and density

The MFI of PLA-PBAT blends was shown in Table 1. The MFI of the PLA-PBAT blends increased with the increase in the PBAT content. The MFI of the PBAT was low (6 g/10min) and the MFI of PLA was 14.5 g/10 min. The melting point of PBAT is 110 °C and the melting point of PLA is 160 °C. The MFI was tested at 190 °C and at 2.16 kg load. At 190 °C PLA was having low melt viscosity and PBAT may be having still very low viscosity. Thus increasing the PBAT content has increased the MFI of the blend gradually. With ZnO 1% the MFI was not much changed. It was similar to PLA-PBAT 50:50%. But with ZnO 3% and 5 % very high MFI(>150 g/10 min) was obtained.

Table 1. Melt Flow index and density of PLA-PBAT blends with and without ZnO

Material	Composition (wt%)	MFI (g/10min) at 190 °C/2.16kg
PLA-PBAT	60:40%	13.951
PLA-PBAT	50:50%	17.583
PLA-PBAT	40:60%	18.505
PLA- PBAT+ZnO	50:50:1%	17.580

Tensile strength

Tensile strength of the samples was better in machine direction than their corresponding transverse direction. Tensile strength decreased considerably with increase in percentage of PBAT concentration. Due to ductility/flexibility of PBAT, tensile strength in machine direction (M/D) decreased with increasing PBAT concentration. But in the transverse direction (T/D) the tensile strength increased with increase in PBAT concentration. However the values were uniformly changing due to the EGMA reactive compatibilizer in between PLA and PBAT polymer material phases. With ZnO 1%, the tensile strength was little lowered in PLA-PBAT 50:50% blend in M/D and higher in T/D.

Table 2. Tensile Strength of PLA-PBAT blends with and without ZnO

Blend Composition wt%	Tensile Strength M/D (N/mm ²)	Tensile Strength T/D (N/mm ²)
PLA-PBAT (60:40%)	4.311	0.316
PLA-PBAT (50:50%)	3.011	1.142
PLA-PBAT (40:60%)	2.697	1.259
PLA-PBAT-ZnO (50:50:1%)	2.130	1.480

Tear strength

Tear strength results showed maximum tear strength in PLA-PBAT blends in proportion of 50:50% in both machine and transverse direction. In transverse direction orientation is perpendicular to the applied tear force, hence tear strength in transverse direction was higher than that of in machine direction. Up to 50% PBAT concentration, the tear strength increased but for 60% PBAT it decreased in both M/D and T/D.

The PLA-PBAT 50:50 % blend filled With ZnO1% had higher tear strength in both machine and transverse direction due to improvement in toughness as a results of slight cross-linking and intermolecular forces like in ionomers. In the presence of moisture, ZnO may form Zn(OH)₂ which may interact with PLA and PBAT end –hydroxyl and carboxyl groups. Hence tear strength was much improved particularly in machine direction from 30 N/mm to 74 N/mm.

Table 3. Tear strength of PLA/PBAT blend with and without ZnO

Blend Composition wt%	M/D (N/mm)	T/D (N/mm)
PLA-PBAT (60:40%)	10.594	60.027
PLA-PBAT (50:50%)	30.395	110.70 5
PLA-PBAT (40:60%)	17.705	65.809
PLA-PBAT-ZnO (50:50 :1%)	74.010	113.450

Dart impact strength

The dart impact strength increased due to higher flexibility of PBAT. Because PBAT is more ductile material than that of PLA which is amorphous, hard and brittle. Hence dart impact strength was increased with increase in concentration of PBAT content in PLA-PBAT blend. Higher dart impact strength was obtained with 60 % PBAT in PLA-PBAT blends. With ZnO 1% further the dart impact strength was improved like ionomer material. Because in the presence of moisture ZnO may form Zn(OH)_2 which may interact with end –hydroxyl and carboxyl groups of PLA and PBAT and thus making the blend ionomer like rubbery material. When ZnO concentration i\was 3 and 5% tubular blown film making was not at all formed.

Table 4. Dart Impact strength of PLA-PBAT blends with and without ZnO

Blend composition wt%	Weight (50 % failure) (g)
PLA-PBAT (60:40%)	63
PLA-PBAT (50:50%)	68
PLA-PBAT (40:60%)	73
PLA-PBAT-ZnO (50:50 :1%)	95

Luminous transmittance

The transmittance values were slightly decreased with increase in PBAT concentration. PLA is amorphous has higher clarity. PBAT is semi-crystalline and lower in light transmittance. Hence the luminous transmittance decreased with increase of PBAT content in PLA-PBAT blends. With ZnO the clarity was not lowered much than that of PLA-PBAT (50:50%) film.

Table 5. Optical properties of PLA-PBAT blends with and without ZnO

Blend composition wt%	Luminous transmittance
PLA-PBAT (60:40%)	84.0
PLA-PBAT (50:50%)	82.1
PLA-PBAT / (40:60%)	77.6
PLA-PBAT -ZnO (50:50 :1%)	81.6

Water vapour permeability test

Water vapour permeability showed a slight increase in trend with increase in of PBAT content in PLA-PBAT blend. Film with 40% PBAT has lower WVTR than the other two formulations. This is due to addition of PBAT which has little has gas permeability than that of PLA and hence higher water vapour transmittance rate. Due to addition of micro ZnO 1% in PLA-PBAT blend (50:50%) which has little lower voids and has better barrier properties than that of unfilled PLA-PBAT(50:50%) blend and hence lower water vapour transmittance rate was obtained.

Table 6. Water vapour permeability of PLA/PBAT blends with and without ZnO

Blend composition wt%	WVTR(g/m ² /day)
PLA-PBAT (60:40%)	0.2215
PLA-PBAT (50:50%)	0.2781
PLA-PBAT (40:60%)	0.3316
PLA-PBAT-ZnO (50:50:1%)	0.2037

Biodegradability test

A complete biodegradation (100%) of PLA-PBAT was obtained since both PLA and PBAT are truly biodegradable polyester. Within 180 days the PLA-PBAT blend films might have degraded more than 90% of the film as per ISO 17088 standard. The test was done up to 210 days in soil burial method since just after six months the buried samples could not be removed due to Covid-19 pandemic lockdown. Hence 100% biodegradation was achieved. Similarly the PLA-PBAT- ZnO 1% micro clay blend film achieved 100% biodegradation in 210 days.

Table 7 Biodegradability of PLA/PBAT blends with and without ZnO

Blend Composition wt%	Biodegradability (%) in 210 days
PLA-PBAT (60:40%)	100%
PLA-PBAT (50:50%)	100%
PLA-PBAT (40:60%)	100%
PLA:PBAT :ZnO/ 50:50:1%	100%

Differential scanning calorimeter (DSC)

DSC was used to find whether the given blend was miscible or immiscible. It was also used to find the glass transition temperature, melting point and degradation temperature of the blend. The following figure shows the conventional DSC thermogram of all three blends. It is known fact that if there is only one glass transition temperature for a blend then the blend is said to be a miscible blend. If there is individual glass transition temperature for polymer A and polymer B in the blends then the blend is said to be immiscible blend, such blends should be compatibilized using compatibilizer for the successful use of the blend. Otherwise, an immiscible blend will have poor properties without compatibilization.

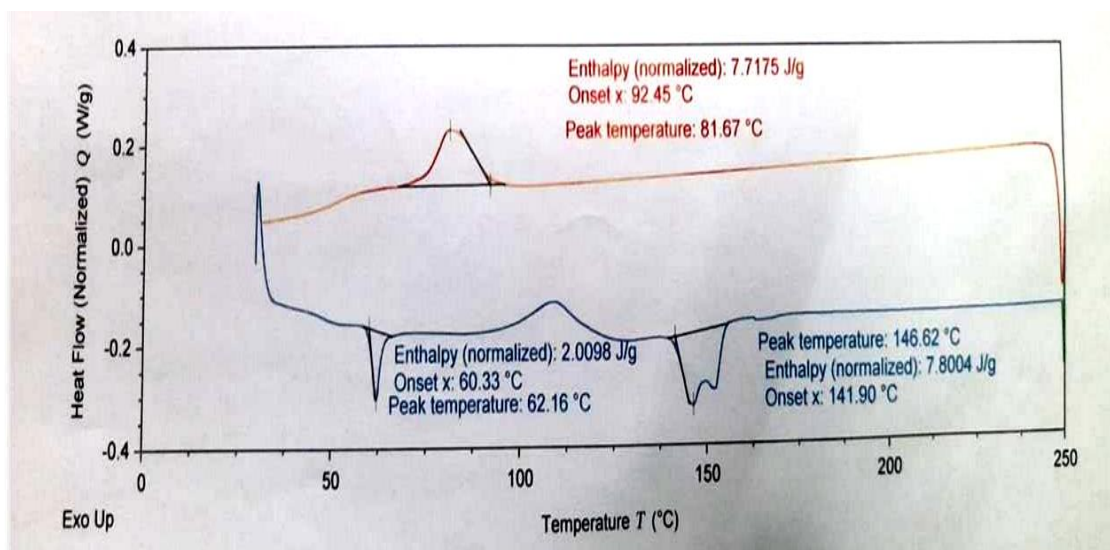


Fig. 1 DSC thermogram of PLA-PBAT 60:40%

The T_m (146.62-153 ° C) of amorphous PLA polymer matrix was splitted due to the presence of the semi-crystalline PBAT resin matrix. PLA has T_g at 60 °C (Fig. 1.). The broad peak at 110-115 °C was the melting temperature of PBAT. Since T_g of PLA was not shifted or lowered towards the T_g of PBAT ($T_g = -29$ °C, $T_m = 110-115$ °C of molecular weightt 145000), the PLA-PBAT blends may be semi-compatible only that to due to the reactive EGMA compatibilizer presence in the blends.

CONCLUSION

The PLA-PBAT blend has no improvements in tensile strength with increasing the percentage of PBAT, increases the tensile strength in T/D and decreases in M/D. However these improvements in tensile strength is sufficient for food packaging applications. Among the three composition 50:50 % (wt.) yields best results. There was an improvement in the impact strength of blends with higher PBAT content which shows that the blend is partially compatible in presence of EGMA reactive compatibilizer. MFI increased with increasing PBAT composition. Water vapour transmission rate was very slightly increased by increasing PBAT content, because PBAT has little lower barrier properties than that of PLA. All the films were found to be 100% biodegradable in soil in 210 days. The tensile strength decreased on adding ZnO, tear strength of the film increased, barrier properties were increased due to micro ZnO. With ZnO 3 and 5% concentration blown film forming was not obtained. Because in the presence of moisture, ZnO may form Zn(OH)_2 which may interact with PLA and PBAT end – hydroxyl and carboxyl groups and thus making the blend rubbery, which was unable to process the material into blown film.

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