

## STUDIES ON MECHANICAL, THERMAL, OPTICAL, PHYSICAL PROPERTIES AND CHARACTERIZATION OF PLA - EVA BLEND FILMS WITH EGMA COMPATIBILIZER

**R. GEETHA, B. KALAI SELVI, S. KOWSIKA, S. SALINI,  
\*S. SOUNDARARAJAN & S.K. NAYAK**

*Dept of Plastics Technology  
Central Institute of Plastics Engineering and Technology (CIPET),  
Guindy, Chennai -600032, Tamil Nadu, INDIA  
\* corresponding author email: bssrajan13@gmail.com*

### ABSTRACT

In this research a possible route to improve the toughness of poly(lactic acid) (PLA) by blending it with poly(ethylene-co-vinyl acetate) (EVA) having vinyl acetate content of 18%. PLA/EVA blends of 80/20, 70/30, 60/40 and 50/50 wt% were prepared by melt blending technique using a twin screw extruder, and blown film extrusion was done using a tubular blown film extruder. Ethylene Glycidyl Methacrylate (EGMA) copolymers was used as a compatibilizer to improve compatibility of the blends. All the blend compositions are characterized by DSC. In the PLA-EVA blend, as EVA concentration increases the tensile strength, and tear strength decrease. However, these tensile and tear strength are sufficient for food packaging applications. Among the three compositions, 80:20 % (wt.) yields best results. The MFI decreases with increasing EVA as EVA has higher melt viscosity and low in MFI. The luminous transmittance was decreased. Water Vapour Transmission Rate (WVTR) also decreases with increasing EVA content, since EVA has higher barrier properties. 50:50 % composition shows lower WVTR as compared to other compositions, although it has lower mechanical properties. The biodegradability rate is high in 80:20 % PLA-EVA composition due to high percentage of PLA compared to other PLA-EVA compositions.

**Keywords:** EVA, PLA, EGMA, TSC Extruder, Blown film extrusion, Testing, Characterization.

### INTRODUCTION

The alarming environmental problems had asserted the indispensable need for plastics with better biodegradability. Though biodegradable polymers, like poly(lactic acid) has better biodegradability, it may not be used on their own because of their techno-economic limitations. On the contrary, the conventional petrochemical polymers have superior properties with reduced environmental friendliness. An effective way to address this issue is to blend petrochemical polymers with biodegradable polymers [1].

Ethylene Vinyl Acetate (EVA) copolymer is a copolymer that exhibits good low-temperature toughness, and stress-crack resistance. EVA shows a good resistance to UV radiation. Further, it has a good clarity and useful in solar power panel lining. EVA polymers have been important for film manufacturing and because of their some what rubbery nature, gloss, permeability and good impact strength [2], they are of interest as stretch film for meat packaging and cling wrap purposes. Ethylene Ethyl Acrylate (EEA) copolymer is useful as a middle adhesive layer for coextruded laminated films [3]. Ethylene Vinyl Alcohol (EVOH) copolymer is obtained after hydrolyzing EVA copolymer, has excellent barrier properties to gases and moisture vapour. HDPE-EVOH-EVA may be used as barrier film for packaging cereals and the PS-EVOH-PS (Polystyrene-EVOH-Polystyrene) laminated/multilayer films

for coffee and cream food packaging [4]. Poly(vinyl acetate) (PVAC) emulsion is useful as paints and adhesives and are transparent [5].

Poly(lactic acid) is biodegradable and bioactive thermoplastic aliphatic polyester derived from renewable resources such as corn starch, cassava roots, chips or starch or sugarcane. Polylactide is well known for its good biocompatibility; biodegradability (mainly by simple hydrolysis). A wide range of degradation rates, physical and mechanical properties, can be achieved by varying its molecular weights and compositions in its copolymers. Poly L-lactide (PLLA) obtained from 100% L-lactide monomer, has a melting point of 170–183 °C and a glass-transition temperature of 55–65 °C while poly-D,L-lactide (PDLLA) obtained from mixture of D and L-lactide monomers) has  $T_g$  59 °C. Density of PLLA is 1.25–1.29 g/cm<sup>3</sup> and for PDLLA is 1.27 g/cm<sup>3</sup>.

PLA is water insoluble when its molecular weight is sufficiently high. However, when PLA is subjected to degradation, water penetrates the bulk of the polymer matrix and hydrolysis on the ester group takes place preferentially by attacking the chemical bonds in the amorphous phase, converting long polymer chains into shorter one, ultimately to low molecular weight water soluble oligomers and monomers.

Water soluble oligomers thus formed escape from the matrix into the surrounding aqueous medium. Degradation causes an increase in the number of carboxylic chain ends, which are known to autocatalysis the ester hydrolysis. As the aging time increases, soluble oligomers which are close to the surface can leach out before total degradation, whereas those which are located well inside the matrix remain entrapped and contribute totally to the autocatalytic effect. The hydrolysis mechanisms and behaviors of PLA are affected by numerous factors, including the materials and the hydrolysis media.

Many blends and alloys of PLA with EVA was reported in the literature some are given below. Do et al. [6] studied a novel enzymatic biodegradable route for PLA/EVA blends under agricultural soil of Vietnam. The morphological, thermal and mechanical properties were studied in order to elucidate the enzyme-based biodegradation mechanism of PLA and PLA/EVA under agricultural soil of Vietnam. It is clear that the PLA/EVA blends, and especially those containing 40 wt.% of EVA, were easier to be decomposed under Vietnamese agricultural conditions than pristine PLA. Moura et al. [7] studied characterization of EVA/PLA blends when exposed to different environments. In this work, the combination of several characterization techniques allowed to evaluate the durability of EVA, PLA and EVA/PLA blends with different compositions under UV radiation and microorganism's action. Singla et al. [8] studied physical blends of PLA with high vinyl acetate containing EVA and their rheological, thermo-mechanical and morphological responses. This study focused on comprehensive evaluation of thermo-mechanical, dynamic rheological and morphological response of PLA and PLA/EVA blends.

Siti Najihah Abdul Manan and Zurina Mohamad [9] studied tensile properties and morphology of PLA)/EVA. This study concluded that the best tensile strength is at 10 wt% of EVA loading in PLA/EVA blend. EVA is a good candidate to overcome the brittleness of PLA matrix. The morphology of PLA/EVA blend shows some changes at different EVA content thus giving different effect to the tensile properties. EVA domain act as reinforcing agent in PLA matrix at lower EVA content (5-10wt %). Sunder Kelkar and Pravin Kadam [10] studied the effect of EVA content on toughening of poly(lactic acid) by EVA copolymer having vinyl acetate content of 18%. PLA/EVA blends of various compositions were successfully prepared and characterized; using EVA having vinyl acetate content of 18%, with the motive to reduce the brittleness of PLA and make it easy processable.

Tsou et al. [11] studied preparation and characterization of PLA/EGMA copolymer blends. After modifying PLA with EGMA, both tensile and tear strength values of PLA/EGMA blown-film specimens in machine and transverse directions improve

significantly and reach the maximum values as their EGMA contents approach an optimum value of 6 wt%. Fortunati et al. [12] studied effect of ethylene-co-vinyl acetate-glycidylmethacrylate and cellulose microfibers on the thermal, rheological and biodegradation properties of poly(lactic acid) based systems. Poly(lactic acid)/ethylene-vinyl acetate-glycidylmethacrylate copolymer blends and their composites with cellulose microfibers were successfully produced by melt mixing. Yuan et al. [13] studied the research of EVA to PLA/E-AA-GMA blend materials toughening.

PLA is brittle, extremely poor fracture toughness and inferior processability. However, it is biocompatible and biodegradable [14]. Thus many projects are going on to improve its impact strength. The material is also less in usage, due to its high cost. Another material which is combined to blend with PLA is EVA. EVA has high impact strength which overcomes the disadvantage of low impact strength of PLA.

EVA is a petroleum-based product, and it has high impact strength property and good processability. EVA is used to overcome low impact strength and processing difficulties of PLA. PLA is a bio-based polymer which is biodegradable whereas EVA is biodegradable polymer. If photo-degradable additives such as benzophenone, metal dithiocarbamates (of Zn, Co, Ni, Fe) are added EVA can be photo-degradable and then when molecular weight is lowered, the low molecular weight fragments will be biodegradable. Also, in the presence of water due to hydrolysis, EVA will form EVOH which can be biodegradable like PVOH obtained after hydrolysis of poly(vinyl acetate) (PVAc) in the presence of bacteria and fungus which may be accelerated by enzymes. When combining these two polymers ie EVA and PLA by blending we can make a photo/biodegradable blend. However, EVA is incompatible. Hence, EGMA copolymer 2.5wt% optimum concentration is used as a reactive compatibilizer in this PLA – EVA blend to improve the interfacial adhesion and to reduce the interfacial tension between the EVA and PLA polymer chains. EVA has low  $T_g$  ( $T_g = -28^\circ\text{C}$ ) and hence improves the flexibility of PLA ( $T_g = +60^\circ\text{C}$ ) and reduces brittleness. Otherwise, PLA film will not form in the blown film extruder. Hence up to 20 - 50 wt% EVA copolymer was used. PLA is more fastly biodegradable than EVA and hence 50-80% was taken so that PLA-EVA blend will have higher rate of biodegradability.

In this present study, we want to make biodegradable film of PLA-EVA with various ratio (80:20, 70:30, 60:40, 50:50%) by melt blending using a twin screw extruder and then by blown film extrusion. Also the mechanical, thermal, optical properties of biodegradable films were determined. The films were characterized by DSC techniques. Soil burial biodegradability test for was also done and reported.

## EXPERIMENTAL

### Materials

Commercially available film grade PLA was procured from natur- Tec India pvt ltd, Chennai properties of which are given in Table 1.1. Commercially available film grade EVA was procured from Srinivasa polymers, Chennai properties of which are given in Table 1.2 and finally EGMA was procured from Ramachandra trading corporation. Its MFI ~ 5g/10min ( $190^\circ\text{C}/2.16\text{kg}$ ) and its density is  $0.94\text{ g/cm}^3$  at  $25^\circ\text{C}$ . Silicon oil was procured from Labkart scientific solutions. For list of tests and characterization experiments mention in our work. At least 2kgs of PLA-EVA blends is required in each proportion as listed in Table 1.3 and total raw material requirement in Table 1.4. For all the proportions mentioned 2.5% EGMA compatibilizer and silicon oil 1% will also be added.

**Table 1.1** Properties of PLA

Polymer	MFI (g/10min) 190 °C@2.16kg	Density (g/cm <sup>3</sup> )	T <sub>m</sub> (°C)	Processing temperature (°C)
PLA	14.5	1.24	160	185-195

**Table 1.2** Properties of EVA

Polymer	MFI (g/10min) 190 °C@2.16kg	Density (g/cm <sup>3</sup> )	VA content (%)	M <sub>p</sub> (°C)
EVA	2.5	0.935	18.2	87

**Table 1.3** Amount of material required for each proportion of blends

Material	Composition (%)	Quantity (kg)
PLA/EVA	100:0	2:0
PLA/EVA	80:20	1.6:0.4
PLA/EVA	70:30	1.4:0.6
PLA/EVA	60:40	1.2:0.8
PLA/EVA	50:50	1:1

**Table 1.4** Total amount of materials required

Material	PLA	EVA
Quantity(kg)	8	3

### Compounding by Twin Screw Extruder

EVA was mixed thoroughly with PLA 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 170-200°C as given below in Table 1.5.

**Table 1.5** Temperature for twin screw extrusion

ZONE-1	ZONE-2	ZONE-3	ZONE-4	DIE
170 °C	180 °C	190 °C	195 °C	200 °C

The extrudate, which looks 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 was 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 blows air on to the film. The film can be cooled.

After solidification at the frost line, the film moved into a set of nip rollers which collapsed the bubble and flatten 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. Film formation was very difficult with 100% PLA. Tubular film extrusion was done with the following temperature range as given below in Table 1.6.

**Table 1.6** Temperature for Blown Film Extrusion

ZONE -1	ZONE-2	ZONE-3	ZONE-4	DIE
160 °C	170 °C	180 °C	190 °C	200 °C

### Testing of Film Properties

The properties were determined as per ASTM standard [15] 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. 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.

### 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. Due to Covid-19 holidays the soil buried samples were not removed after 6 months.

## RESULTS AND DISCUSSION

### Melt Flow Index

The MFI of PLA-EVA blends are shown in following Table 2. The MFI of the PLA-EVA blends increased with increasing PLA content. The MFI of the PLA was high because of low melt viscosity, whereas the EVA was low because of high melt viscosity. Thus, by increasing the EVA content the MFI of the blend decreased gradually. PLA has low melt viscosity and hence during injection molding PLA drooling out from nozzle. Hence use of EVA improved the melt viscosity and mouldability.

**Table 2** Melt Flow index of PLA-EVA Blend granules

Material	Composition (%)	MFI(g/10min) 190°C@2.16kg
PLA/EVA	80/20	8.388
PLA/EVA	70/30	7.920
PLA/EVA	60/40	7.351
PLA/EVA	50/50	6.783

### Tensile Strength

Tensile strength of the samples was better in machine direction than their corresponding transverse direction (Table 3). Tensile strength decreased considerably with increasing percentage of EVA. Due to flexibility of EVA, mechanical strength decreased with increasing EVA content and due semi-compatibility of blends in the presence of EGMA compatibilizer. Among all compositions, 80:20% composition has higher tensile strength in both machine and transverse directions when compared to other compositions since PLA has higher tensile strength than EVA.

**Table 3** Tensile strength of PLA-EVA blend films

Sample	M/D (MPa)	T/D (MPa)
PLA:EVA / 80:20 %	36.879	15.533
PLA:EVA / 70:30 %	24.806	15.490
PLA:EVA / 60:40 %	24.382	2.870
PLA:EVA / 50:50 %	14.600	2.304

### Tear Strength

Tear strength results are shown in Table 4. which shows that tear strength in PLA/EVA blends decreased in both machine and transverse direction as the EVA concentration increased. In transverse direction, the polymer molecular orientation is perpendicular to applied force, hence tear strength in transverse direction higher than that of in machine direction.

**Table 4** Tear strength of PLA/EVA blend Films

Sample	M/D (N/mm)	T/D (N/mm)
PLA:EVA / 80:20 %	62.477	82.136
PLA:EVA / 70:30 %	29.624	57.665
PLA:EVA / 60:40 %	15.730	47.708
PLA:EVA / 50:50 %	13.718	45.088

### Luminous Transmittance

The transmittance values decreased with increasing EVA concentration (Table 5). Because PLA is amorphous, more transparent and EVA is semi crystalline, less transparent.

**Table 5** Optical properties of PLA-EVA blend films

Sample	Luminous Transmittance
PLA:EVA / 80:20	87.8
PLA:EVA / 70:30	85.7
PLA:EVA / 60:40	84.4
PLA:EVA / 50:50	82.1

### Water Vapour Permeability Test

Water vapour permeability decreased when EVA proportion was increased in PLA-EVA blend (Table 6). This is due to addition of PLA which has low barrier properties than EVA and hence high water vapour transmittance is obtained.

**Table 6** Water vapour permeability of PLA-EVA blend films

Sample	WVTR (g/m <sup>2</sup> /day)
PLA:EVA / 80:20	85.891
PLA:EVA / 70:30	63.184
PLA:EVA / 60:40	59.236
PLA:EVA / 50:50	55.287

### Biodegradability Test

Biodegradation of PLA/EVA blend increased with increasing PLA content (Table 7) in the blend because of higher biodegradability of PLA which has polyester groups in the main chain. This was done upto 7 months in soil burial method.

**Table 7** Biodegradability of PLA-EVA blend films

Formulations	Biodegradability (%)
PLA:EVA / 80:20	46.08
PLA:EVA / 70:30	40.50
PLA:EVA / 60:40	39.80
PLA:EVA / 50:50	30.7

### Differential Scanning Calorimeter (DSC)

The DSC was used to find whether the given blend is miscible or immiscible. It was also used to find the glass transition temperature, melting point and degradation temperature of the blend. If the glass transition temperature of the blend is nearer to glass transition temperature of polymer A or polymer B then the blend is said to be partially miscible. 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 a blends should be compatibilized using compatibilizer for the for successful use of the blend. Otherwise a immiscible blend will have poor properties without compatibilization.

**Table 8.1** DSC result of PLA-EVA blend (80:20%)

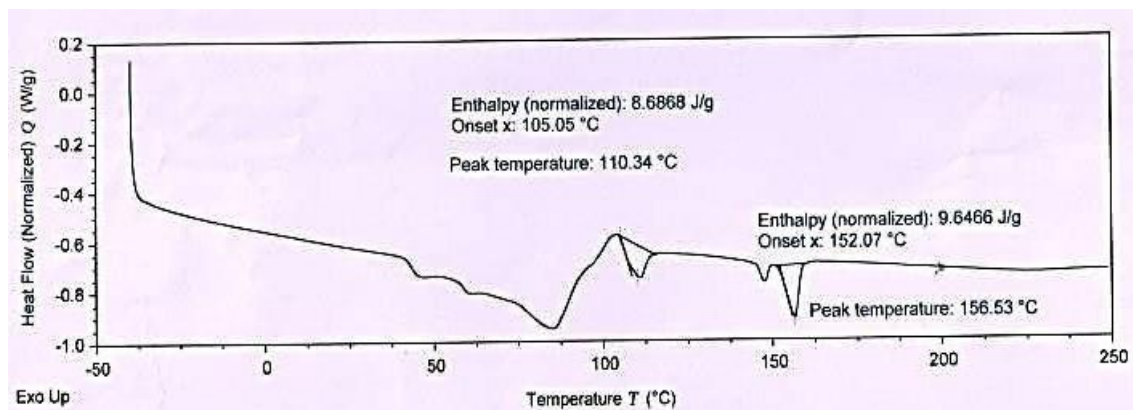
Material PLA-EVA	Melting point (°C)
80:20	156 (PLA) and 148 90 (EVA) 110 (Ethylenic units of EVA)

**Table 8.2** DSC result of PLA-EVA blend(70:30%)

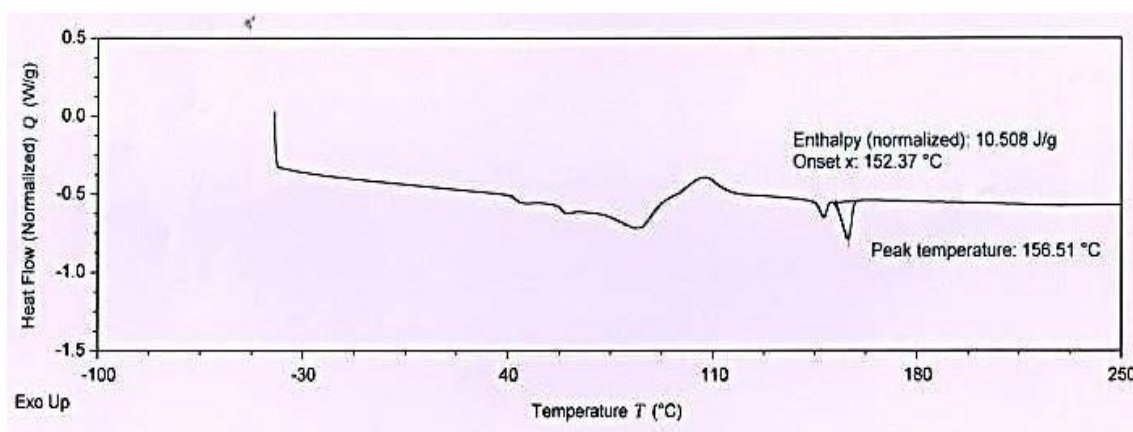
Material (PLA-EVA)	Melting point (°C)
70:30	156 (PLA) and 148 90 (EVA)

The  $T_m$  of amorphous PLA polymer matrix is splitted due to the semi-crystalline phase of PLA in the presence of semi-crystalline EVA resin matrix. PLA has  $T_g$  at 60 °C (Fig. 1 and 2). The  $T_g$  of EVA amorphous phase may at -28 °C. Since the  $T_g$  of PLA was not shifted/lowered towards  $T_g$  of EVA, the PLA/EVA blends were semi-compatible only that

too due to the reactive EGMA compatibilizer (2.5wt%) in all the EVA-PLA blends. EVA polymer may be dispersed as balls in PLA matrix in all the cases. The peak at 45 °C may be the melting temperature of amorphous VA phase. The peak at 110 °C is the melting temperature of crystalline ethylenic phase of EVA copolymer. The melting points of PLA and EVA are shown in Table 8.1 and 8.2.



**Fig. 1** DSC Curve of PLA:EVA- 80:20% Blend Film



**Fig. 2** DSC Curve of PLA:EVA-70:30% Blend Film

## CONCLUSION

In the PLA-EVA blend as the EVA concentration increases the tensile strength, and tear strength decreases. However these tensile and tear strength are sufficient for food packaging applications. Among the three compositions, 80:20 % (wt.) yields best results. The MFI decreases with decreasing EVA concentration since EVA has higher melt viscosity and low MFI. The luminous transmittance was decreased. WVTR also decreases when EVA content increases, since EVA has higher barrier properties. 50:50 % composition, shows higher WVTR as compared to other compositions, although it has lower mechanical properties. DSC thermograms show that the PLA- EVA blends are semi-compatible only that too due to the Reactive EGMA compatibilizer (2.5wt%) in all the EVA-PLA blends. The biodegradability rate is high in 80:20 % PLA-EVA composition due to high percentage of PLA compared to other PLA-EVA compositions. Generally the use of EGMA compatibilizer 0.5-2% is sufficient. Without EGMA the films may not be forming. Otherwise, uniform flow, uniform phases and uniform properties will not be obtained.



## REFERENCES

- [1] Arul Kumar K P and Soundararajan S. Studies on Mechanical, Barrier, Optical and Physical Properties of LDPE/PLA Blend for Packaging Films. *J. Polym. Mater.* 2016; 33: 491-502
- [2] Jaya Prakash N, Hari Prasad S, Nehru S, Et al. Synthesis, Characterization and Testing of Emulsion Polymerized Vinyl Acetate–Acrylamide Copolymers for Bio-Degradable Applications. *IOSR. Journal of Polymer and Textile Engineering (IOSR-JPTE)*. 2013; 1: 04-12
- [3] Brydson J A. *Plastics Materials*, 7<sup>th</sup> Ed. USA Butter worth Hein mann Publishers, 1999, 276-279.
- [4] Brydson J A. *Plastics Materials*, 7<sup>th</sup> Ed. USA Butter worth Hein mann Publisher. 1999, 394
- [5] Brydson J A. *Plastics Materials*, 7<sup>th</sup> Ed. USA Butter worth Hein mann Publishers, 1999, 389
- [6] Do Van Cong, Thai Hoang, Nguyen Vu Giang, et al. A novel enzymatic biodegradable route for PLA/EVA blends under agricultural soil of Vietnam. *Materials Science and Engineering C*. 2012; 32: 558–563.
- [7] Moura I, Botelho G and Machado A V. Characterization of EVA/PLA blends when exposed to different environments . *J Polym. Environment*, 2013; 22: 148-157
- [8] Singla R K, Zafar M T, Maiti S N. et al. Physical blends of PLA with high vinyl acetate containing EVA and their rheological, thermo- mechanical and morphological responses. *Polymer Testing*, 2017; 63: 398-406
- [9] Siti Najihah, Abdul Manan and Zurina Mohamad. Tensile Properties and Morphology of Polylactic Acid (PLA)/ Ethylene Vinyl Acetate (EVA). *Applied Mechanics and Materials*. 2015;735: 57-60.
- [10] Sunder Kelkar, Pravin Kadam, Shashank Mhaske et al. Toughening of poly(lactic acid) by Ethylene-co-vinyl acetate Copolymer having vinyl acetate Content of 18%: effect of ethylene co- Vinyl acetate content, *Advances in Materials Science and Engineering: An International Journal. (MSEJ)*. 2014; 1: 27-37
- [11] Chi-hui Tsoul, Ya-Ming Li, Wei-Hua Yao et al. Preparation and Characterization of Poly(lactic Acid)/ Ethylene Glycidyl Methacrylate Copolymer Blends. *Advanced Materials Research*. 2011;150-151: 139-143.
- [12] Fortunati E, Puglia D, Kenny J.M, et al. Effect of ethylene-co-vinyl acetate-glycidyl methacrylate and cellulose microfibers on the thermal, rheological and biodegradation properties of poly(lactic acid) based systems. *Polymer Degradation and Stability*. 2013; 98: 2742- 2751.
- [13] Wei Yuan, Jianping Liu, Xia Song et al. The research of EVA to PLA/E-AA-GMA blend materials toughening. *Advanced Materials Research*, 2012; 535-537: 1210-1213.
- [14] Kotiba Hamad, Mosab Kaseem and Fawaz Deri. Melt Rheology of Poly(Lactic Acid)/Low Density Polyethylene Polymer Blends. *Advances in Chemical Engineering and Science*, 2011; 1: P208-214.
- [15] ASTM Standards Annual Publication series – Volume 08-01.03