Biodegradation of POM/PLA Multifilament in Sea Water

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Abstract.

Multifilaments of POM/PLA (70/30 by weight) were produced using a melt spinning process. The effect of addition of additives, PEG and EBS (0.5, 1 and 1.5 phr) to improve the flexibility and reduce the static electricity on the fiber. The tenacity and percent extension at break of multifilaments were measured. POM/PLA/PEG exhibits good results of polymer high tenacity and extension at break. Increasing the additive contents improved the mechanical property of multifilaments. High mechanical property POM/PLA with addition of 1 phr PEG exhibit satisfy mechanical property. The degradation test of multifilaments was carried out in sea water compared with in tap water for 120 days. The degradation of multifilaments in was observed to be higher than in tap water. The rate of degradation increased after 90 days. High and more than 10 % of weight loss was observed after 120 days. The fiber size of POM/PLA/PEG (1 phr) by SEM measurement.

Keywords. -

1. INTRODUCTION

The environmental concerns on wastes from non-degradable petroleum-based plastic have been recognized as they are harmful to sea animals. As a result it is needed to develop the industrial manufacturing of biodegradable polymers to replace the conventional polymers. The investigation on development of biobased and biodegradable polymers has been continuously reported [1-4]. Poly (lactic acid) (PLA) is the best known biodegradable polymer made from renewable resources such as corn, tapioca and sugar cane [5,6]. PLA has high mechanical property but its glass transition temperature (Tg) is high (ca 55 oC). Then, PLA is rigid and brittle at room temperature [6]. This drawback limits the PLA applications including extrusion and fiber products. To improve the mechanical property of PLA, copolymerized lactide with other monomers have been reported. However, the

scale-up of copolymerization processes has not reported due to unprofitable reasons [7-10]. Blending of PLA with other polymers or copolymers that have the recompensed properties of PLA was reported. This method could moderately improve the mechanical properties of the polymer [11-20].

In a fishing net or seine manufacturing process, conventional polymers used to produce the nets are polypropylene (PP) and nylon 6. They exhibit high mechanical property and good processability for fiber fabrication. But PP and nylon 6 are non-degradable polymers and their wastes are not degraded and floating on the sea surface. These wastes are harmful to sea animals. Decompose of nets under severe environment is a source of microplastic pollutions. Therefore, investigation of new materials that their wastes can be degraded to replace PP and Nylon 6 is the eminent problem solving method.

Polyoxymethylene (POM) is an engineering plastics used in automotive industry due to their high mechanical property, high fracture toughness and crystallinity, excellent abrasion and fatigue resistance [21-23]. Goossens et al. reported the study on improvement of physicochemical properties of epoxy/POM blends [24]. For the textile industry POM must be modified by copolymerize the oxymethylene monomer with oxyethylene to increase the polymer toughness and flexibility

Furthermore, due to the high capacity of fishing net utilization the application of POM for seine manufacturing with modification the mechanical and physical property by blending POM with biodegradable polymer, PLA will produce the partly biodegradable polymer for seine production. We have reported the production of POM/PLA multifilament that exhibited excellent elongation.

In the melt spinning process of POM/PLA blend, the electrostatic from the fiber flowing through the air produced repulsion force is the difficulty problem of multifilament winding. In the polyethylene (PE) and polypropylene (PP) melt spinning process, oil spraying to fiber extruded prior to the winder as antistatic materials has been used to solve the electrostatic. However, oil spray could not apply to PLA for anti-electrostatic additive due to oil affects the crystallinity and stability of polymer chain.

In this research we studied the fabrication process of multifilament from POM/PLA blends. The ratio of POM/PLA was 70/30 [25]. The effect of 2 types of additives: poly (ethylene glycol), PEG and N,N’-Ethylene bis-stearamide, EBS, as anti-electrostatic additive to solve the processing problems was investigated. There are 2 types of mechanical properties tests: normal and knot. Then select good formula for degradation measurement. We studied degradation of POM/PLA fiber in sea water and tap water. Compare morphology of fiber before and after degradation test. For the actual application of multifilament for seine fishing in the sea, the biodegradation of fishing net was evaluated. The results will be significant to the application of POM/PLA blends as an environmental friendly material for seine production. The fiber fabrication process and effect of POM on product property was measured.

2. EXPERIMENTAL PROCEDURE

2.1. Experimental Materials

Poly(lactic acid), (PLA), grade TP4000 was purchased from Unitika Ltd., Japan, (Density = 1.25 g/cm3). Polyoxymethylene (POM), Iupital V20-HE, (Density = 1.39 g/cm3) were produced by Mitsubishi Gas Chemical Corporation, Japan. Poly(ethylene glycol), (PEG, MW 20,000) was purchased from Sanyo Chemical Industries Company Ltd., Japan. N,N'-Ethylene bis-stearamide (EBS) was purchased from Tarak Chemicals Company Ltd., China.

2.2. Multifilament preparation

The POM and PLA pellets were first dried in an oven at 80°C for 8 h prior to processing. Multifilament yarns of polyoxymethylene (POM) and poly(lactic acid) (PLA) blends were prepared by a melt-spinning method using single screw extruder (ThermoHaake Polydrive) equipped (Figure 1). The ratios of the POM/PLA fibers studied were 70/30 by weight with additives (PEG and EBS) 0.5, 1.0 and 1.5 wt%. The polymers and additive were mixed together and processed with dry blend method. The spinning conditions are as follows table 1. After that, the final multifilament was subjected to secondary winding to make extension of the fiber for 6.5 and 7.5 times (6.5x and 7.5x).

Table 1 The melt spinning conditions of POM/PLA multifilament

Die	24 holes (diameter has 0.32 mm/hole)
Temperature (^{o}C)	180, 190, 200 (Zone Extruder) 210 (Connecter) and 210 (Die)
Screw speed	8 rpm
Winding speed (m/min)	500

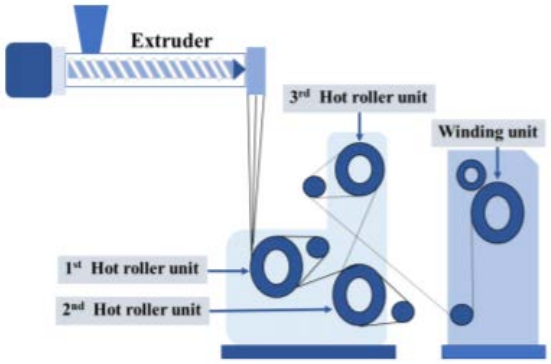

Figure 1 Fiber melt spinning process

2.3. Thermal property analysis

Thermal analysis of multifilament was recorded on a differential scanning calorimeter, Perkin Elmer, DSC 8000 under nitrogen atmosphere with a heating rate of 10°C/min from 30 to 250°C.

2.4. Tensile property measurement

The tensile strength and elongation at break (%) of the fiber were measured using an Instron universal testing machine (INSTRON5569) according to the ASTM standard method D3822-01. The mechanical property of the fiber was testing with a load cell of 50kN with gauge length of 25 mm and test speed of 50 mm/min. Figure 2 show 2 types of fiber test: normal type and knot type.

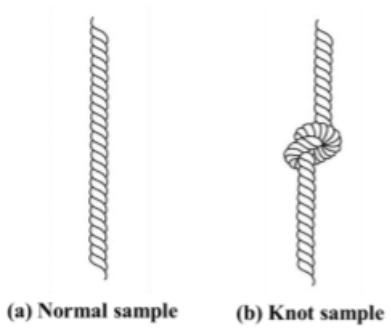

Figure 2 Tensile test samples

2.5. Degradability of POM/PLA multifilaments

Multifilaments of POM/PLA blend produced by a melt spinning process was cut for 30 cm length. The fibers were packed in a nylon tea bags. For the biodegradability test of multifilaments in sea water, natural sea water was collected at 1 m depth from the sea surface from Laem Chabang Port, Chon Buri, Thailand. The salinity was 30 ppt. The degradation test of multifilament was carried out compared with the tap water. The sample bag was soaked in the test sink. The sampling of test samples was done after 15, 30, 60, 90 and 120 days. The temperature, salinity and pH of the solution was recorded daily. The samples taken from each period were dried and weighed to calculate the percent weight loss.

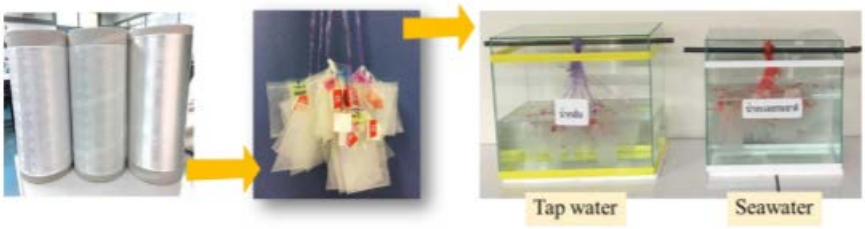

Figure 3 Degradability of POM/PLA fibers in sea water and tap water

3. RESULTS AND DISCUSSION

3.1 Thermal property analysis

The thermal property analysis of POM/PLA (70/30 w/w) blend with and without additive was carried out using a DSC analysis. The results are shown in Figure 4, 5 and Table 1.

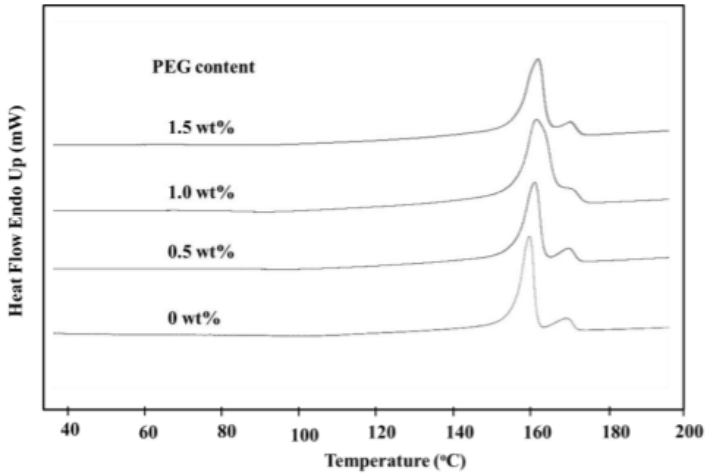

Figure 4 DSC Thermogram of POM/PLA fiber with PEG (winding speed 500 m/min)

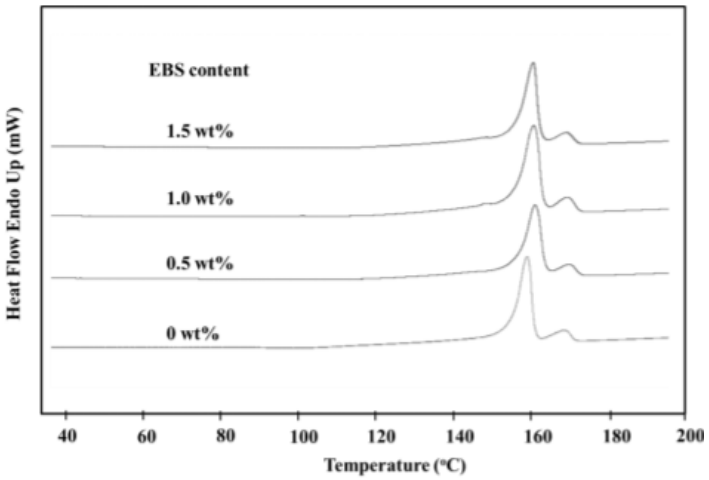

Figure 5 DSC Thermogram of POM/PLA fiber with EBS (winding speed 500 m/min)

Table 2 DSC Thermogram data of POM/PLA fiber at winding speed 500 m/min

Sample	Plasticizers (phr)		Tm POM (°C)	ΔHm POM (J/g)	Tm PLA (°C)	ΔHm PLA (J/g)	Xc POM (%)	Xc PLA (%)
POM	-		160.27	68.82	-	-	21.11	-
PLA	-		-	-	175.47	32.75	-	35.22
POM/PLA (70/30)	-		159.28	59.22	169.95	7.23	18.17	7.77
	PEG	0.5	160.52	48.95	169.52	6.23	15.02	6.70
		1	161.11	45.92	170.69	5.83	14.09	6.27
		1.5	161.57	42.98	170.05	3.67	13.18	3.95
	EBS	0.5	161.41	49.37	170.25	6.30	15.14	6.77
		1	161.02	48.44	169.84	5.39	14.86	5.80
		1.5	160.96	45.63	169.70	5.17	14.00	5.56

Figure 4 and 5 show DSC thermogram of POM/ PLA fiber with PEG and EBS, respectively. The increasing of additive contents shows no significant effect on melting temperature of POM/PLA fiber. The enthalpy of melting and percent crystallinity were calculated and showed in Table 2. The degree of crystallinity (Xc) of POM and PLA was determined by using Eq (1)

$$Xc = \frac{\Delta H_m}{\Delta H_m^0} \times 100\% \quad (3.1)$$

where ΔH_m is the heat of fusion of POM or PLA sample measured, ΔH_m^0 is the heat of fusion of 100% crystalline POM (326.3 J/g) or PLA (93 J/g) [25]. Table 2 shows DSC

thermogram data of POM/PLA fiber with PEG and EBS additive. The melting temperature (Tm) of neat POM, neat PLA was observed at 160 and 175 °C. For the POM/PLA fiber without additive, Tm of POM not change but Tm of PLA reduced may be POM molecules enhanced the mobility of PLA molecules. The Tm of POM and PLA blend show two melting peaks confirmed the phase separation of the two polymers. Due to the polymer blends of POM and PLA at low temperature are miscible in the melt state. [26, 27] The immiscibility of POM and PLA is accounted for by the weak interactions between the carboxyl groups of PLA and the methylene groups of POM [25]

3.2. Mechanical Properties

The tenacity and extension at break of POM/PLA multifilament with PEG and EBS addition at drawing extension of 6.5 and 7.5 times compare normal and knot test are shown in Figure 6 and 7. For normal test the tenacity (Figure 6) of 7.5 times extension is higher than 6.5 times and PEG shows higher tenacity than EBS. For knot test, the drawing 7.5 times is slightly higher than 6.5 times extension but the PEG and EBS additives are not significantly different. The percent extension at break measurement in Figure 7 shows contrast results of normal test. Drawing at 6.5 times exhibits higher percent extension at break than 7.5 times. The knot test also shows similar trend but lower value. The effect of PEG and EBS was not clearly observed. For effect of the additive contents for both PEG and EBS shows similar tendency of increasing the tenacity and extension at break while increasing the additive contents from 0.5 to 1.5 phr. It was found that PEG has higher effect than EBS.

3.3 Degradation of Multifilament in Sea Water

The degradation of POM/PLA/PEG (1 phr) multifilament in sea water and tap water was carried out for 120 days. The fibers were soaked in the solution medium and sampling at 15, 30, 60, 90 and 120 days. Weight loss of fibers was calculated to compare the percent of degradability. Slow degradation of fibers in tap water was observed while the degradation rate increased after 90 days. The degradation of fibers in sea water was much higher than tap water which indicated the effect of salinity to the ester scission. Rate of degradation in sea water was clearly observed after 90 days. The results verified that the POM/PLA/PEG multifilaments were degraded under the sea water condition.

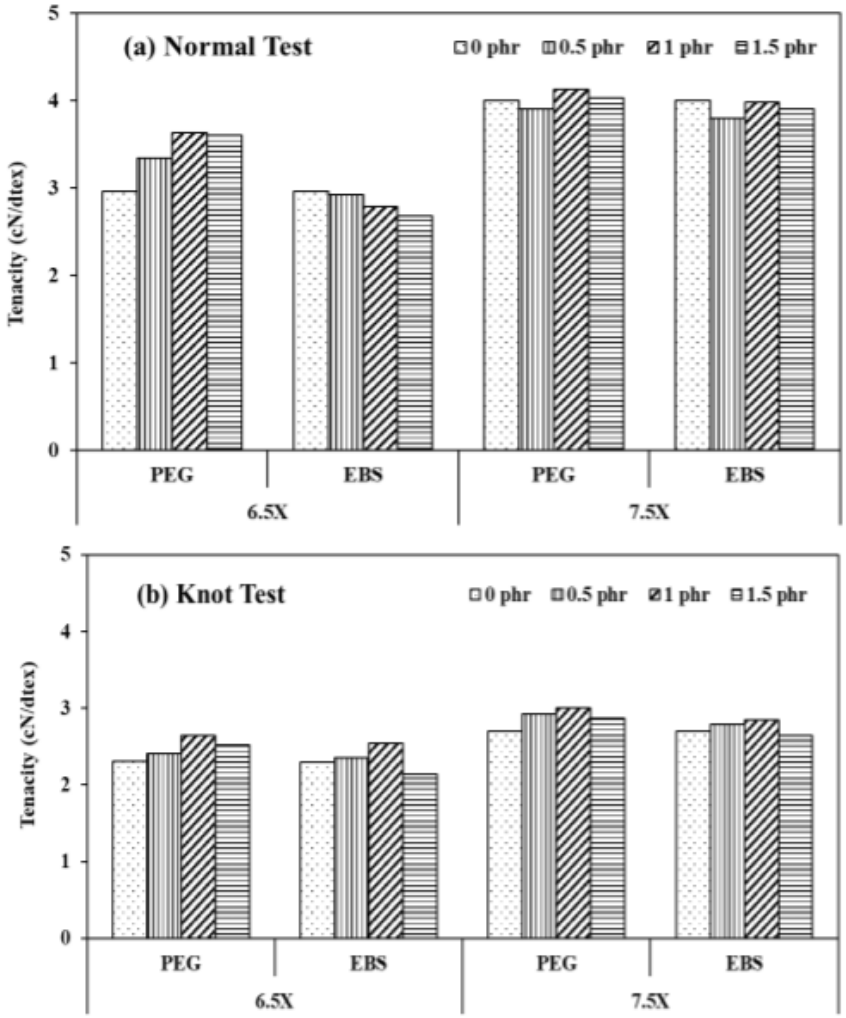

Figure 6 Tenacity of POM/PLA fibers with PEG and EBS additives at 6.5 and 7.5 times extension.

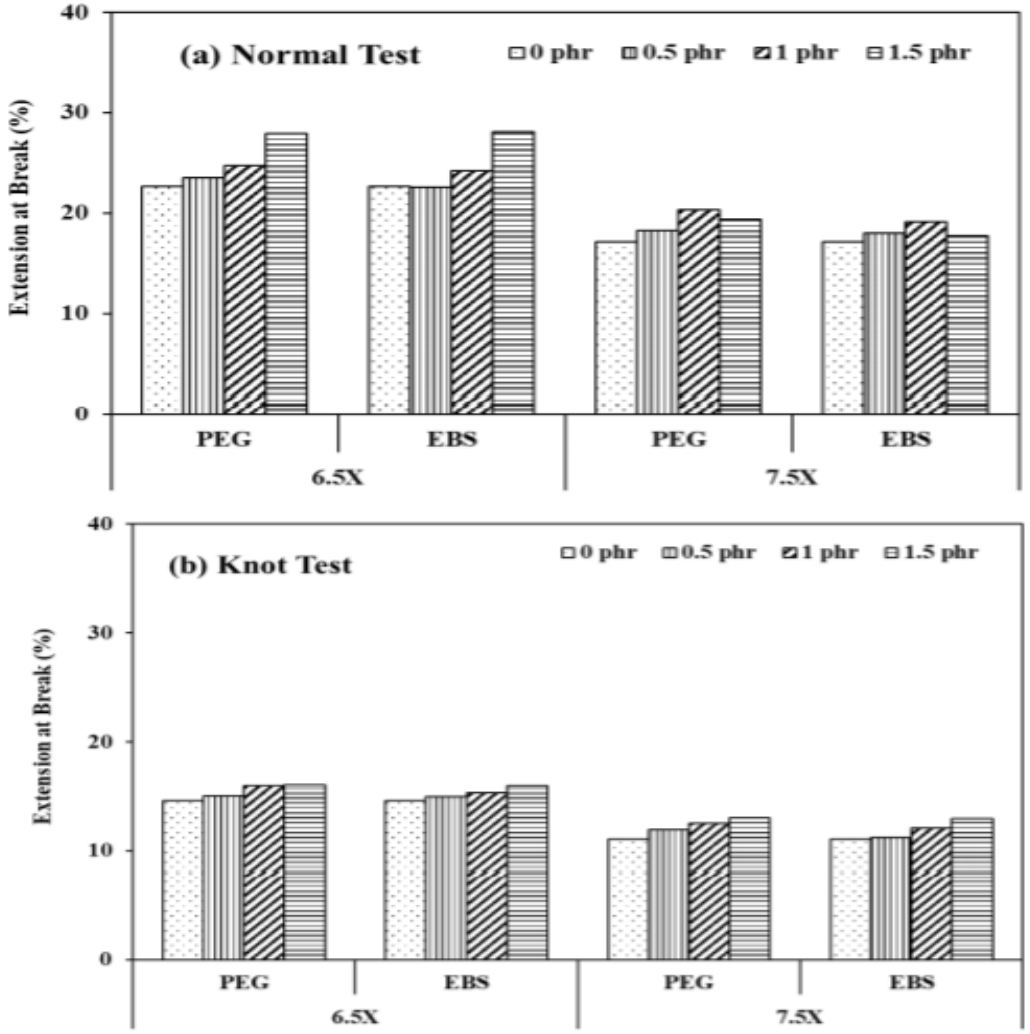

Figure 7 Extension at break of POM/PLA fiber with PEG and EBS additives at 6.5 and 7.5 times extension

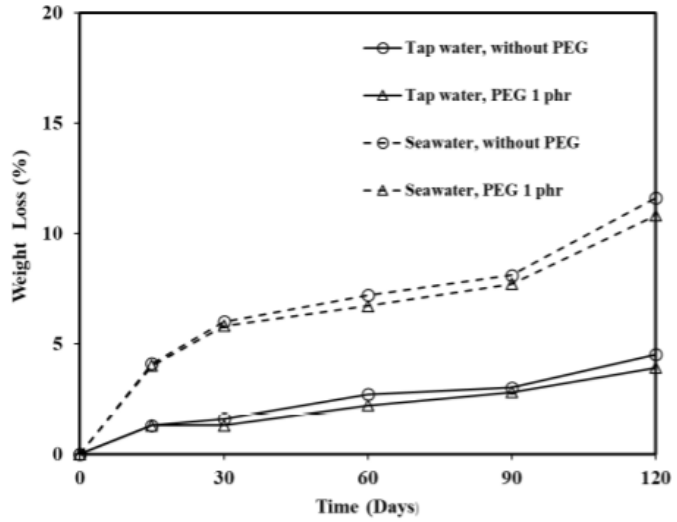

Figure 8 Degradation of POM/PLA/PEG (1 phr) multifilament in sea water and tap water

3.4 Degradation of Multifilament in Sea Water

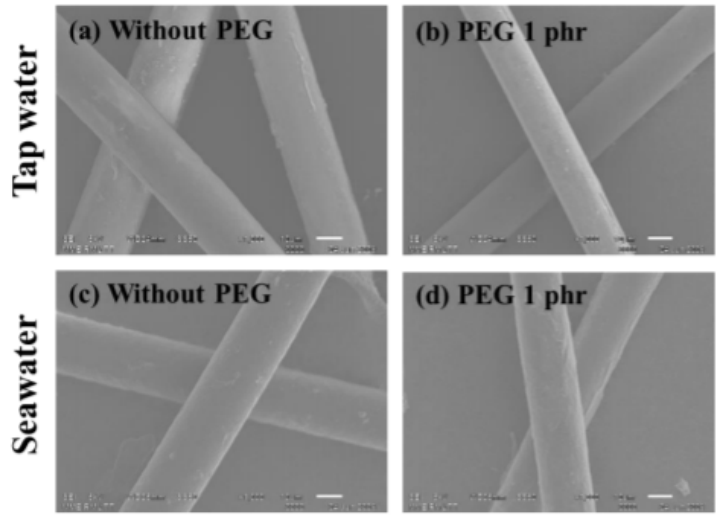

Figure 9 SEM image of fiber after 4 months in water

The SEM image of morphology of POM/PLA/PEG (1 phr) multifilament are shown in Figure 9. The diameter and surface of fibers with addition of PEG (1 phr) show decrease in

diameter and the surface is rough due to surface degradation. The results are in agreement with the weight loss measurement in Figure 8.

4. CONCLUSION

Multifilaments of POM/PLA with addition of additives, PEG and EBS, were produced using a melt spinning process. PEG exhibits high tenacity and extension at break. The additive contents improve the mechanical property of multifilaments. The addition of 1 phr PEG to POM/ PLA exhibit satisfy mechanical property. The degradation of multifilaments in sea water was observed to be higher than in tap water. The rate of degradation increased after 90 days and more than 10 % of weight loss was observed after 120 days. The fiber surface shows decrease in fiber size for POM/PLA/PEG (1 phr) which verified by SEM measurement.

5. ACKNOWLEDGEMENT

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