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Blends of Low Molecular Weight of Poly Lactic Acid (PLA) with Gondorukem (Gum Rosin)

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Abstract. The utilization of plastic was increasing as well as the increasing its demand in wide range application. Consequently, the number of plastic litter will increase and make more serious environmental problems. This research concerns to minimize waste problems by designing biodegradable plastic. In this research, biodegradable plastic was made of poly lactic acid (PLA) and gondorukem (Gum rosin, *Resina colophonium*) as the plasticizer. The effect of gondorukem towards PLA properties such as rheology and degradability was investigated. The research divided into two steps: (i) the polycondensation of lactic acid (LA) and (ii) modification of obtained poly lactic acid. In the first step, polycondensation was done in N_2 atmosphere (138°C) for 30 hours and added 0.1 %w of $SnCl_2$ as catalyst. Bulk modification was conducted by blending of gondurukem in varied weight (0.5, 1, and 2 g in 10 g of PLA). Furthermore, the modified PLA was analyzed its molecular structure, biodegradability and rheological property. The presence of gondorukem enhanced the biodegradability of poly lactic acid. Gondorukem could act as the plasticizer. It is confirmed that the complex viscosity of PLA melt decreased upon the addition of gondorukem

INTRODUCTION

Plastics are used for food wrappers, drinking water bottles, food containers, baby toys, and many other plastic products. Plastic is a general term for polymers, materials that consist of long chains of carbon and other easily made elements of various shapes and sizes. Plastics are made by polymerization process which means composing, forming and connecting continuously the basic materials of plastic called monomer. Nowdays, vast majority of the plastics are originated from petroleum based hydrocarbons such as polypropylene (PP), polyethylene terephtalate (PET), polystyrene (PS), etc. It means these conventional plastics were made from nonrenewable resources.

Besides that, conventional plastics also contain non-plastic substances called additives. These additives are needed to improve the properties of plastics that function as dyes, antioxidants, ultraviolet light absorption, anti-stickiness, etc. The main negative impacts of plastics is the contamination of the environment because the conventional plastics made out of petroleum are non-biodegradable and non-compostable. As a result the amount of plastic waste continues to increase so that the environment is more polluted.

Last decade, researchers from academia and industry gave much attention to tackle the mentioned problem through the development of biodegradable plastic/polymer[1-3]. One of the most potent biodegradable plastic is poly lactic acid (PLA) [4]. Poly lactic acid was interesting to be projected and developed as replacement for conventional plastics in commodities application such as PP, PS, PET, etc. The mechanical properties of PLA are comparable to those plastics. However, PLA has major advantages, i.e., derived from renewable resources and easily degraded in landfill to nontoxic compounds [3].

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The main properties of PLA which considered in wide range applications are toughness, barrier properties, flexibility, degradability and thermal stability[5]. Thus, PLA need to be tailored to the required properties. In our previous works, degradability and elongation at break of PLA was increasing due to the presence of elastomer [2, 6]. The presence of elastomer was introduced through blending method. Other researchers have also reported their success to increasing flexibility of PLA through blending with flexible polymer such as epoxidized soybean [7], poly caprolactone [8, 9], etc. Onyari et.al [10] reported that gum arabic (GA) enhanced the biodegradability of PLA/GA blends.

Gondorukem, also called gum rosin, is a solid product derived from pine sap. It was produced by heating fresh liquid sap of pine tree to vaporize the volatile matters (terpene components). Its content is mostly diphenic acids, mainly abietic acid, isopimaric acid, laevoabietic acid, and pimaric acid [11]. By introducing gondorukem, the brittleness or stiffness of poly (lactic acid) was expected to decrease.

In this article, we report the effect of gondorukem towards PLA properties such as rheology and degradability. Rheological properties was analyzed using dynamic mechanical analysis (DMA) in melt phase. Degradation test of blend was carried out by burial it in the soil. The physical appearance of the tested specimens were monitored periodically.

EXPERIMENTAL PART

Monomer lactic acid in 88-92 % aqueous solution was kindly supplied by Bratachem with density of 1.20 ($20^o/4^o$). *M-xylene* (96%), chloroform and Stannous (II) chloride dihydrate (98%) were purchased from Sigma Aldrich. Methanol AR (99.5%) was purchased from Avonchem (UK). Gondorukem was purchased from local market in Surakarta, Indonesia. Further, all chemicals were used in this investigation without any purification. The addition of gondorukem was varied as tabulated in Table 1.

TABLE 1. List of the samples prepared for this study

Sample	Synthesized PLA, g	Gondorukem, g
A	9.5	0.5
B	9	1
C	8	2

Degradation test was performed by burying spicemens in the soil (approx. 5 cm) in ambient condition. The size of samples was about 1 x 1 x 0.3 cm. At certain time, samples were taken and washed intensively with distilled water at room temperature. The quantification of this reduction is determined by using Eq. 1.

Morphology of samples before and after buried in the soil was observed under scanning electron microscopy (SEM), JEOL JSM-6360A Japan, at 15kV. Rheological test was placed in the parallel plate geometry (Ø = 25 mm) in gap of 1 mm at 160°C. The Frequency range and percentage of strain were applied at 0.1-628 rad/s and 1%, respectively.

$$\% \text{ Degradation} = \frac{\text{Initial Weight} - \text{Final Weight}}{\text{Initial Weight}} \times 100\% \quad (1)$$

RESULTS AND DISCUSSION

Molecular Weight and Structure

Direct polycondensation of lactic acid was carried out in the 500 ml flat bottom three necked flask equipped with a dean stark trap. Stannous chloride ($SnCl_2$) was added about 0.1 %wt (calculated according to the amount of lactic acid) in nitrogen atmosphere for 18 hours.

The viscosity molecular weight (Mv) of PLA was determinated using Solomon-Cuita equation [12] and obtained about 1149.5 g/mol. It means that obtained PLA was still low molecular weight. Many reports described that PLA with high molecular weight needed to be applied in wide range application such as packaging, engineering application, etc. [13, 14].

TABLE 2. Comparison of absorption band between PLA from literature [15], gondorukem and its blends

Wave number of poly (lactic acid)					Chemical bonding	Notification
Garlotta [15]	**Gondorukem**	**Sample A**	**Sample B**	**Sample C**		
3571		3567	3578	3572	–OH	Weak intensity
2995, 2944	2980	2993	2990	3000	–CH–	asymmetric, symmetric
1759		1762	1755	1763.8	–C=O	
	1538.8	1540	1532	1529	–C=O	Weak intensity
1453	1449	1459	1444.1	1462	$–CH_3$	
1382, 1362	1400	1359	1370	1373	–CH–	asymmetric, symmetric
1268		1250	1260	1248	–C=O	
	1220.2	1218	1224	1222	–O-	
1194, 1130, 1093		1150,1132	1160,1124	1140,1130	–C–O–	
1047	1020	1032	1040	1025	–OH	
926,868	898.9	900	910	890	–C–C–	

Introduction of gondorukem as mentioned above is to enhance the PLA properties, especially its rheological property and biodegradability. The presence of gondorukem in PLA blends was detected qualitatively from FTIR spectra. The absorption band data of obtained PLA, gondorukem and its blends was summarized in Table 2. It can be highlighted that the presence of gondorukem can be compatible in the blends with PLA.

Rheological Test

The complex viscosity (|η*|) of polymer is a measurement of overall resistance to flow in melt phase. This parameter is related to chain mobility and free volume of polymer. The complex viscosity is very vurnerable to the macromolecular chain structure and some impurities added to the polymer [16].

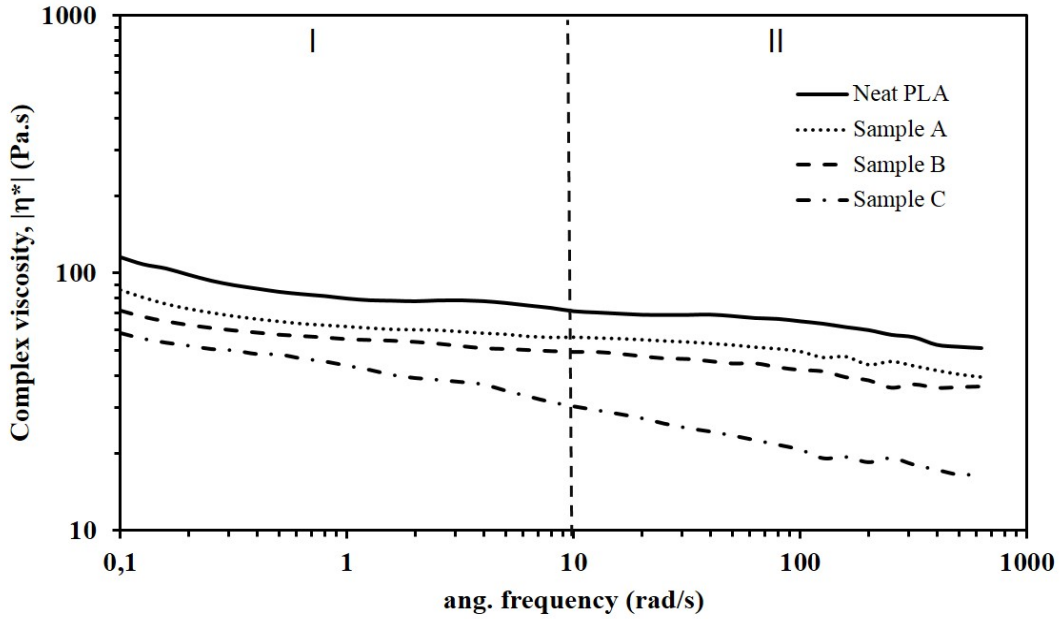

Figure 1. Frequency dependence of complex viscosity, |η*|, of PLA and its blends at 160°C

Fig. 1 presents the complex viscosity of PLA and its blends as a function of angular frequency at 160ºC. As depicted in Fig. 1, typical complex viscosity of all samples has a similar trend and can be divided into two virtual regions. First region is below 10 rad/s, the alteration of complex viscosity is not significantly appeared. It indicated that in this region the typical of complex viscosity is a Newtonian behavior. Compared to above 10 rad/s (as second region), it was showing a shear thinning response which attenuating complex viscosity as the frequency increased.

The measurement of complex viscosity was carried out on the all speciments. Obviously, the presence of gondorukem as an impurity affected the complex viscosity due to the chain mobility changes. The molecular chain mobility of PLA was becoming loose in the presence of gondorukem. The depletion phenomenon of the complex viscosity of melt PLA indicated that the inreasing free volume due to the plasticization of the gondorukem. Further evidence at 0.1 rad/s, the addition of gondorukem with ratio from 0 to 0.5/9.5, 1/9 and 2/8 (gram gondorukem/gram PLA) decreased the complex viscosity from 115 Pa.s to 85.7, 71.2 and 58.51 Pa.s, respectively.

Degradation Test

The specimens were buried in the soil as described in experimental part. The presence of gondorukem was proven to improve the degradability of PLA (see. Table 3). The significant effect was seen after the burial for 5 days. The increasing of gondorukem in PLA blends enhanced the percentage of degradation. In this study, Sample C (with ratio of PLA and gondorukem = 8/2) showed the highest value about 34.39%. It means that gondorukem might act as a degradation agent.

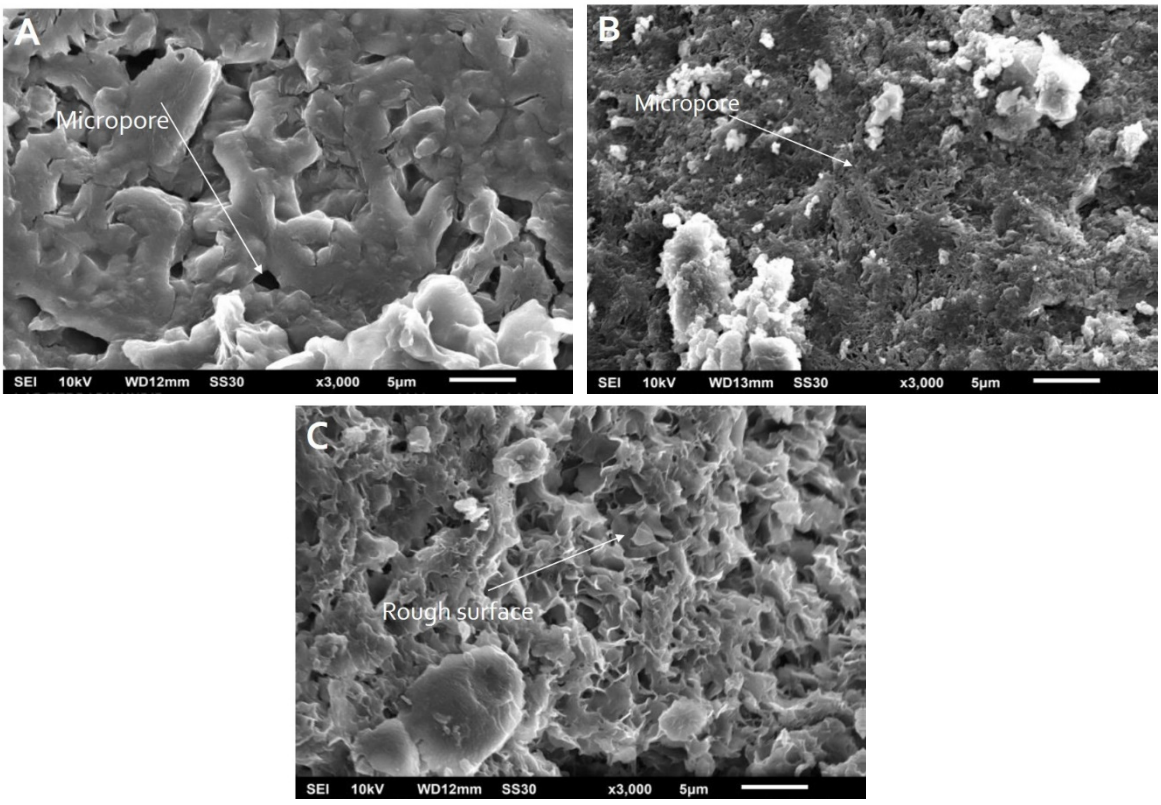

Figure 2. SEM micrographs of sample C in various burial times (1, 3 and 5 days)

Fig. 2 clearly depicts that the presence of gondorukem gave the significant effect on the degradability of PLA. The several micro holes appeared in PLA blends since 1 day after buried. Moreover, the micro-holes becomes more appearing in the increasung burial time. The formation of holes refers to the release of degradation products during the degradation test. Consequently, the weight of spicemens will decrease as tabulated in Table 3. Comparison between

Fig. 2A and Fig. 2C, the morphological surface of Fig. 2C is rougher than that of Fig. 2A, Indicating that the percentage of degradation is higher in Fig. 2C.

Table 3. Percentage of degradation for neat PLA and its blends with gondorukem

Sample	Initial Weight, g	Weight on the day, g					% degradation after 5 days
		1	2	3	4	5	
Neat PLA	1.2	1.09	1.12	1.02	0.99	0.97	19.17
A	0.89	0.82	0.78	0.73	0.67	0.64	27.79
B	1.89	1.79	1.62	1.51	1.43	1.35	28.09
C	2.25	2.02	1.85	1.72	1.61	1.48	34.39

CONCLUSIONS

The viscosity molecular weight PLA synthesized in direct polycondensation of lactic acid at 138°C for 18 hours is 1149,5 g/mol. To enhance the properties of this low molecular weight, obtained PLA was blended with gondorukem. The presence of gondorukem tended to decrease the complex viscosity of PLA. This phenomenon could be addressed to the increasing free volume and chain mobility of PLA due to the plasticization effect of gondorukem. Besides that, the degradability of PLA was also increasing which refers to existence of gondorukem.

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