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Poly (lactic acid)/Epoxidized Natural Rubber Blends Foams with Nanofillers Cellular Compressed Foaming: Effect of Nanofillers Blends Foam on Physiology, Compressive Strength, Thermal Stability and Morphology

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Abstract: *The effect of the nanoparticles included nanosilica and nanotitania that altered the biodegradable foams from Polylactic acid (PLA) and Epoxidized natural rubber (ENR) with sodium hydrogen carbonate ($NaHCO_3$) and citric acid (CA)to act as blowing agents. All compositions were integrated with a co-rotating twin screw extruder. The biodegradable foams were prepared by a compression molding process with various ratios of the nanoparticles. The properties of the biodegradable foams with nanoparticles were investigated for mechanical properties in terms of compressive properties by a universal testing machine in which the thermal behavior of the foams were investigated with the thermal stabilization of the foams by using thermogravimetric analysis (TGA). Lastly, physical properties including morphology were studied by a scanning electron microscope (SEM) to investigate the structure inside the final foams and study the density of the biodegradable foams.*

***Keywords*:** *Poly(lactic acid, Blends, Epoxidized natural rubber, Nanosilica, Nanotitania, Biodegradable foams.*

1. Introduction

In recent years, the polymeric petroleum base obtained has used plastic abundantly; however, this has become popular and retained good mechanical and thermal properties. The effect of petroleum plastics has become nondegradable [1]. Foams as one of the forms of packaging have been discovered in developing countries. The foams' structure comprises plastic parts with a foaming agent to result in a cellular foam structure [2]. The reaction between the polymeric base as a matrix phase and foaming agent as an additive has produced a porous polymer. In addition, the heat enhances the foaming agent to decompose as gas molecules, especially carbon dioxide. These gas molecules tend to intermingle completely in the matrix phase. On the other hand, the high content of the foaming agent showed deficiencies. Hemmasi et al. (2011) investigated the various foaming agents as azodicarbonamide at 2, 4 and 6 percent by weight. The composites consisted of HDPE, EVA and rice hull, which discovered that the high foaming agent content increased the cell's size whereas they reduced the cell's density [3]. However, Farsheh et al. (2011) studied a PVC wood plastic composite incorporated with foaming agent as 0, 3 and 6 percent by weight. The result indicated the increment of the foaming agent was added in terms of the cell's density and cell's size [4].

Polylactic acid (PLA) is a thermoplastic polymer that can be a biodegradable polyester. PLA is used in a wide range of applications because of the biodegradability, low toxicity, biocompatibility and good mechanical and thermal properties [5]. PLA is used in packaging, disposable products, the textile industry and surgical

implants [6]. The process is to improve PLA plastic; such as, injection molding, cast film solution, extrusion of blow molding and compression molding.

The compression molding technique with the foaming agent is applied in a bio-based polymer, which would receive more attention and more allurement because of global warming that has considerable increased and must be monitored closely. Gao et al. (2014) studied polylactic acid foam that was produced by a compression molding process. The PLA foam received a low density in comparison with unadulterated PLA. Besides the polymer foams decreased the tensile strength from 26.6 to 4.6 MPa at 2 percent of the foaming agent [7].

Natural rubber is an economic crop in Thailand [8]. Moreover, the global quantity of rubber is increasing and is used in various fields; such as, the automobile industry and medical devices [9]. Natural rubber has a good abrasion resistance, elasticity and flexibility. The structure of natural rubber, is represented by polymer as a high crystalline and amorphous structure, consists of cis-1,4-polyisoprene [9,10]. Najib et al. (2009) prepared rubber foams with sodium bicarbonate. The foams could absorb the energy by more than 99.85 percent and appeared tough at 4.43 J $mm^{-2}\times10^{-5}$ at 4 percent of the foaming agent. However, the toughness decreased the enlargement of the foaming agent [11].

The blends of PLA and natural rubber has been researched in many works. Mat Desa et al. studied the polymer blends of PLA and rubber. The results showed that the rubber could improve the impact strength and elongation at the breaks successfully, but it decreased the crystallinity [12]. Nanoparticles or nanofillers were filled into the polymer to improve the mechanical and thermal properties. In addition, they are non-toxic [13] and are used with a foam preparation in order to control the porous size. Ji et al. (2013) investigated the PLA/silica nanocomposite to the morphology and cell density. After that, the silica nanoparticles could disperse in the average cell size whereas the incorporation of excess nanosilica indicated the aggregates of the nanosilica [14].

In this research the compression molding foams were prepared from PLA/ rubber with 2 percent of the foaming agent to investigate the nanoparticle foams. The characterization of the compressive properties

2. Materials and Methods

2.1. Materials

PLA pellets (grade 2003D) from NatureWorks,USA with a density of 1.24 g/cm^3. Epoxidized Natural Rubber with epoxidized group 50% or ENR50 with density of 0.95 g/cm^3 were purchased from Muang Mai Guthrie, Thailand. ENR50 was added to decreased the brittleness and to increase the elasticity of the polymer blends by cutting ENR into small pieces with size around 0.5-1 cm by using a hydraulic cutting machine provided by the Rubber Research Institute of Thailand. Sodium hydrogen carbonate in molecular weight of 84.01 g/mol from QRëC, New Zealand and citric acid from Gammaco, Thailand were acted as the blowing agent together to generated the porosity of biodegradable foams.

2.2. Foam Preparation

The proportions of raw materials to produce the biodegradable foams were shown in Table1. The PLA/ENR blends foams were mixing in co-rotation twin screw extruder with temperature profile ranging from 170ºC to 200ºC and screw speed 60 rpm. Then foams samples were prepared by compression molding with molded dimensions 15×15×1 cm at 200ºC with a pressing step of 100 bars for 7 minutes followed by cooling for 5 minutes. Cut blends foams specimens in the size of the width 1 × length 10 for testing and characterization.

TABLE 1: Weight Proportions of Samples Composition.

Sample name	PLA (%)	ENR (%)	Blowing agent (phr)		Nanoparticles (phr)	
			$NaHCO_3$	Citric acid	Nanosilica	Nanotitania

P20E80	20	80	1.0	1.0	-	-
P20E80C5	20	80	1.0	1.0	0.5	-
P20E80C10	20	80	1.0	1.0	1	-
P20E80C15	20	80	1.0	1.0	1.5	-
P20E80T5	20	80	1.0	1.0	-	0.5
P20E80T10	20	80	1.0	1.0	-	1
P20E80T15	20	80	1.0	1.0	-	1.5

2.3.Testing and Characterization.

Mechanical property investigated by compressive force of the test samples was determined by using universal testing machine with testing speed of 20 mm/min. and having 500 KN capacity load cells of testing machine. Thermal properties of the test samples were investigated with thermal stabilization of the test samples were characterized by thermogravimetric analysis (TGA). The TGA analyses were conducted by heating from 25ºC to 800ºC, at a scanning rate of 20ºC/min under a nitrogen atmosphere to examine the thermal stabilization of samples. About Physical properties investigated about the morphological properties of all samples were evaluated by scanning electron microscope (SEM) and density of biodegradable foams was characterized according to ASTM D792.

3. Results and Discussions

The mechanical properties of the PLA/ENR foams in the part of the compressive strength were shown in Table 2. The compressive strength was presented at 26.6±1.62 N/10cm^2 and the deformation distance of 25.04±0.55 mm. Then the nanosilica and nanotitania were considered in the compressive properties. When the increment of low SiO_2 and TiO_2 content could improve the mechanical properties to 48.16 N/10 cm^2 and 30.08±4.34 N/10cm^2 respectively, the deformation was decreased to 15.53±0.40 mm and 9.55±1.01 mm., respectively because the lower content of the nanofillers would control the range of the porous size. In addition, the acceleration of the nanoparticles content might be agglomerated and affect the decrease in the compressive properties and elongation. Furthermore, more than 0.5 percent of the fillers could not significantly maintain the value of the mechanical properties as shown in the PLA/ENR/1.5 percent of SiO_2 and 1.5 percent of TiO_2 that exhibited 34.70±0.86 N/10cm^2 and 22.07±7.44 N/10cm^2 [14]. The step of the nanoparticles could indicate the limit of packing a filler's content.

TABLE 2: The Mechanical and physical Properties of the PLA/ENR Blends Foams.

Sample name	Compressive force (N)	Deformation(mm)	Density(g/cm^3)
P20E80	26.6± 1.62	25.04±0.55	1.065
P20E80C5	48.16±0.85	15.53±0.40	1.032
P20E80C10	34.70±0.86	12.44±0.72	1.039
P20E80C15	40.58±4.75	10.67±0.98	1.061
P20E80T5	30.08±4.34	9.55±1.01	1.056
P20E80T10	34.06±3.32	11.18±2.46	1.050
P20E80T15	22.07±7.44	8.64±0.16	1.058

The density of the PLA/ENR blended foams with and without nanoparticles was shown in Table 2. The density of the neat PLA exhibited at 1.26 g/cm^3 in which the incorporation of epoxidized natural rubber in the matrix could decrease in density. The natural rubber had a low density at about 0.95 g/cm^3, so the density of the blends with a foaming agent reduced dramatically at 1.065 g/cm^3. Nevertheless, the nanoparticles were incorporated in order to increase the compressive properties, as they could invariably control the porous size. The climbing nanoparticles caused to append the density. Moreover, the higher fillers might be agglomerated particles [15]. Actually, the comparison between nanosilica and nanotitania were different in the size of the particles whereby the silica was larger than titania. The small particles could aggregate with difficulty whenever they fluctuated.

TABLE 3: TGA Thermograms Result at 10% Weight Loss (T10) and 90% Weight Loss (T90) of PLA/ENR Blends Foams.

Sample name	T_{10} (°C)	T_{90} (°C)
P20E80	283.0394	437.3226
P20E80C5	285.6036	437.4683
P20E80C10	286.6161	439.6194
P20E80C15	288.7394	442.0634
P20E80T5	279.5495	438.4616
P20E80T10	285.5192	439.1341
P20E80T15	286.2670	442.3845

The thermal stability of the PLA/ENR blended foams was observed from the initial degradation temperature (T_d), which had a 10 percent (T_{10}) weight loss and a final degradation temperature that showed a 90 percent weight loss (T_{90}) from the result of the TGA thermograms that was listed in Table 3. The increment on the thermal stability of the samples showed when the samples were more than the nanoparticle content because the thermal stability of the nanosilica could generate a high residual weight in the samples and the high crystallinity of the nanosilica displayed degradation of more than 400°C. The same result from the study was the effect of the nanosilica on the thermal behavior of the copolymer by Yazdimamaghani et al. (2013) [16] and the glass manufacturer that used silica as a main component at very high temperature. A study by Ramimoghadam et al. (2014) studied the effect of titania on the thermal stability of the film in which TiO2 or titania was the decomposition of the organic group's residuals of titania and the condensation effect of theTiO_2 anatase phases (forming a crystallinity phase) [17]. Bagheri et al. (2013) studied about anathase phase of titania in which the Anatase phases of TiO2 showed the TGA curve to be around 350-450° C [18]. In addition, adding more nanoparticle content led to an increase in the thermal stability of the samples.

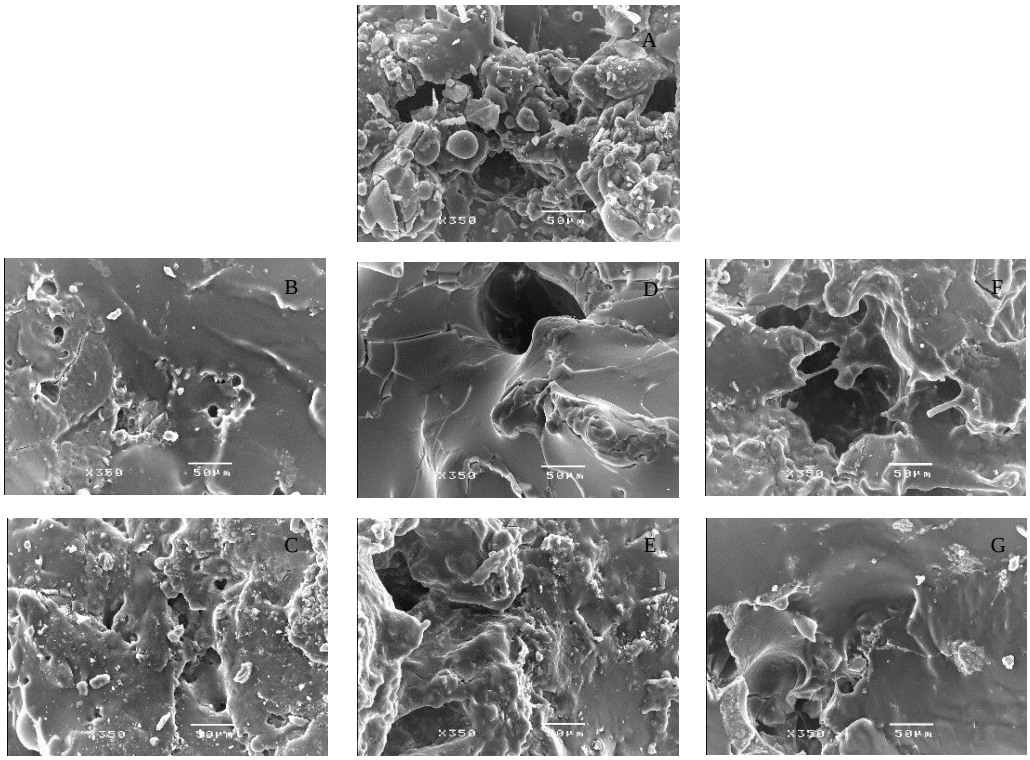

Fig.1: SEM images (×350 magnifications) of (A) P20E80, (B) P20E80C5, (C) P20E80T5, (D) P20E80C10, (E) P20E80T10 and (F) P20E80C15 (G) P20E80T15

The SEM images of the PLA/ENR foams at 350 magnifications were shown in Fig 1. Non-nanoparticles were shown in Fig. 1A. The least amount of the nanoparticles content in the PLA/ENR blended foams at 0.5 phr showed the nanosilica and nanotitania dispersed to be more porous and the control of the similar porous size in

all of the samples were shown in Fig. 1B and 1C. The excess of the nanoparticles content was shown in Fig.1D and 1E. Furthermore, the effect of greater nanoparticle content shows more agglomeration of nanoparticles-nanoparticles interaction in which this effects of the nanofiller were shown in Fig. 1F and 1G that affected the pores in the blended foam with regards to the size and dispersion. The increment of porous size in foam and less dispersion of the porous in the blends foams was shown. In addition, the high nanoparticle content showed a greater effect on the foam. Consequently, these results can successfully confirm the result of the compressive property, density and thermal stability of blended foams.

4. Conclusion

Biodegradable foams were prepared consisting of PLA, ENR, $NaHCO_3$, CA with and without nanoparticles. Biodegradable foams without nanoparticles exhibited low thermal stability, low compressive force and high deformation distance. On the other hand, adding 0.5 percent of nanoparticles could improve the thermal stability of the samples, but in terms of mechanical and physical properties adding a higher nanoparticle content than 0.5 percent showed a decrease of those two properties because the agglomeration of the nanoparticles in the samples was shown in the SEM images of the blended foams while this could confirm the compressive properties, deformation and density of the blended foams.

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6. References

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