

MECHANICAL PROPERTIES OF POLYLACTIC ACID AND NATURAL RUBBER BLEND USING CALCIUM CARBONATE AND VETIVER GRASS FIBER AS FILLER

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1 General Introduction

Poly (lactic acid) (PLA) is an important biodegradable polymer because it has less harmful effect on environment compared to fossil fuel based plastics. However, its inherent brittleness, low-melt viscosity, and low-heat distortion temperature of PLA have restricted its applications [1]. In order to improve mechanical properties of PLA, several polymers were blended with PLA such as polycaprolactone (PCL) [2-4], polybutylenesuccinate (PBS) [5], poly (butylene succinate-co-L-lactate) (PBSL) [6] and poly (butylene adipate-co-terephthalate) (PBAT) [7,8]. Generally, these blends showed considerably higher toughness than pure PLA. However, a significant decrease in tensile strength and modulus of the blends can be observed. Moreover, these polymers come from petroleum resource, whose price tends to increase in the future. Therefore, the material from renewable resource has received a lot of attention from researchers. In our previous study, natural rubber (NR) was used to improve toughness of PLA [9]. Impact strength and elongation at break of PLA was increased when adding NR. Moreover, by using NR-g-GMA as compatibilizer for PLA and NR blend, impact strength and elongation at break was improved. However, tensile strength and modulus of PLA/NR blend with and without NR-g-GMA were decreased, which can greatly limit its engineering applications. Therefore, these properties needed to be improved for many potential applications of PLA. Adding fillers into plastics is usually implemented to improve their mechanical properties. In this study, calcium carbonate (CaCO₃) and vetiver grass fiber were used as filler and it was expected to improve mechanical properties of PLA/NR blend.

2 Experimental

2.1 Materials

Thai natural rubber (grade STR 5L) were purchased from Thaihua Latex Co., Ltd. A commercial grade of PLA (PLA 4042D) was purchased from NatureWorks LLC. NR-g-GMA was prepared in our laboratory. The details on synthesis and characterization of NR-g-GMA were given in our previous study [9]. Vetiver grass fiber, with 2 mm in length and its aspect ratio of 6.15 was modified by heat treatment method using the temperature of 180°C for 4 hours before mixing. CaCO₃ (Hicoat 801) was provided by Sand and Soil Co., Ltd. and it was dried in an oven at 70 °C for 6 hours to eliminate moisture before used.

2.2 Blends and composites preparation

The compositions of PLA blends and PLA composites are shown in Table 1. Before mixing, PLA was dried in an oven at 70 °C for 4 hours to eliminate moisture. All compositions of each PLA blends and PLA composite were mixed using an internal mixer (Hakke Rheomix, 3000p) at temperature of 170 °C with a rotor speed of 60 rpm for 10 min. Compression molding (LabTech, LP20-B) were used to prepare the specimens. The melting temperature of 165 °C and mold temperature of 25 °C were used. The impact test was performed according to ASTM D256 using an Atlas testing machine (model BPI). Tensile properties were obtained according to ASTM D638 using an Instron universal testing machine (UTM, model 5565) with a load cell of 5 kN.

Table 1. Blends and composites composition

Symbols	PLA (wt.%)	NR (wt.%)	NR-g-GMA (wt.%)	Vetiver fiber (phr)	CaCO ₃ (phr)
PLA	100	-	-	-	-
PLA/NR	90	10	-	-	-
A	90	9.5	0.5	-	-
B	90	9.5	0.5	10	-
C	90	9.5	0.5	-	5
D	90	9.5	0.5	-	10
E	90	9.5	0.5	-	20

3 Results and discussion

3.1 Impact properties

Fig.1. shows impact strength of PLA, PLA blends and PLA composites. It was shown that impact strength of neat PLA was 19.06 kJ/m². When adding NR impact strength was increased to 39.52 kJ/m², which is about 2 times higher than that of neat PLA. The impact strength of PLA/NR blend with NR-g-GMA (69.83 kJ/m²) was greatly improved by the addition of NR-g-GMA. This indicated that the compatibility between PLA and NR was improved when NR-g-GMA was used as a compatibilizer. With the addition of CaCO₃ into PLA/NR blend with NR-g-GMA, impact strength of the composite was increased. In contrast, the addition of vetiver grass fiber into PLA/NR blend with NR-g-GMA led to the decrease of impact strength. This may be due to the fact that the addition of vetiver grass fiber was possibly increased the number of void in PLA composites. Therefore, these voids were served as a local area for crack initiation and caused the failure at lower stress. Somnuk et.al also observed this behavior in vetiver grass fiber - PP composite [10]. Fig.2. shows impact strength of PLA and PLA composites at various CaCO₃ content. To study the effect of CaCO₃ content on mechanical properties of PLA composites, CaCO₃ content was varied from 5 to 20 phr in PLA composite with NR and using NR-g-GMA as compatibilizer. The experimental results show that impact strength of PLA composites decreased with increasing CaCO₃ content. This behavior can be related to the probable tendency to form CaCO₃ agglomerates, resulting in a poor dispersion of CaCO₃ on the PLA matrix.

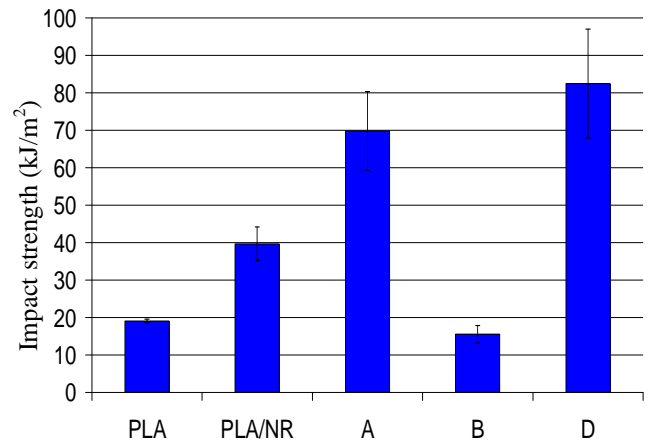


Fig.1. Impact strength of PLA blends and PLA composites.

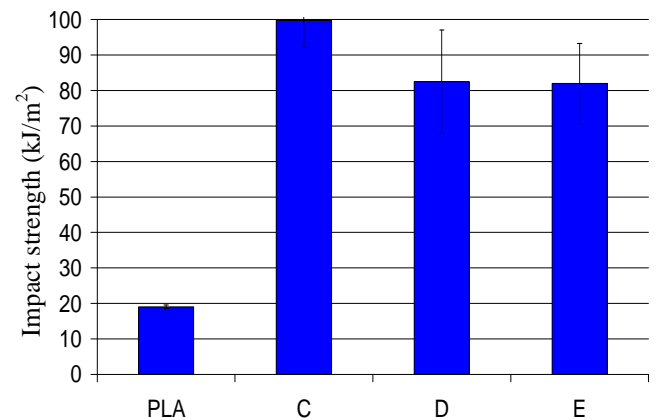


Fig.2. Impact strength of PLA and PLA composites at various CaCO₃ content.

3.2 Tensile properties

Table 2 shows tensile strength, modulus and elongation at break of PLA blends and PLA composites. PLA/NR blends with and without NR-g-GMA show higher elongation at break than that of neat PLA. However, tensile strength and modulus of PLA/NR blend with and without NR-g-GMA was lower than those of neat PLA. The reduction in these mechanical properties was due to the result of the rubbery nature of NR. With the addition of CaCO₃ into PLA/NR blend with NR-g-GMA, modulus of the composite was increased but tensile strength and elongation at break were decreased. However,

elongation at break of this composite was still higher than that of neat PLA and PLA/NR blend without NR-g-GMA. With the addition of vetiver grass fiber into PLA/NR blend with NR-g-GMA, elongation at break of the composite was lower. However, modulus and tensile strength of this composite was higher than those of PLA/NR blend with and without NR-g-GMA. The increase of modulus when using CaCO_3 and vetiver grass fiber as filler is because the high modulus of CaCO_3 and vetiver grass fiber. The effect of CaCO_3 content on tensile strength, modulus and elongation at break of PLA composite were also studied. The results show that modulus and tensile strength increase with increasing CaCO_3 content. However, elongation at break decreases with increasing CaCO_3 content. These changes are usually associated with the increasing brittleness of the composites.

Table 2. Tensile strength, modulus and elongation at break of PLA blends and composites.

Samples	Tensile strength (MPa)	Elongation at break (%)	Modulus (GPa)
PLA	52.99±0.65	10.84±1.64	0.63±0.04
PLA/NR	29.66±1.56	74.51±9.06	0.51±0.04
A	28.3±0.99	403.45±23.50	0.52±0.02
B	30.19±1.50	25.14±3.62	0.61±0.04
C	24.38±0.54	278.64±17.32	0.62±0.03
D	25.94±0.43	244.75±19.41	0.64±0.02
E	26.14±0.61	232.23±19.46	0.68±0.04

3.3 Thermal properties

TGA curves of NR, PLA, PLA blends and PLA composites are shown in Fig.3. It is evident that the thermal degradation of PLA and NR showed only single step of weight loss. The onset degradation temperatures of PLA and NR were 290.76 °C and 305.33°C, respectively. The final degradation temperature of PLA and NR were noticed at 409.67 °C and 490.62 °C, respectively. This indicated the higher thermal stability of NR compared to that of PLA. The onset degradation temperature of PLA/NR was 294.20 °C, which is about 4°C higher than PLA. The slightly increase in thermal stability of PLA/NR has been attributed to the higher thermal stability of NR. Moreover, PLA/NR blend with NR-g-GMA showed higher onset degradation temperatures (301.59°C) than that of PLA/NR. The increase in

thermal stability of PLA/NR when using NR-g-GMA as compatibilizer might be attributed to the higher interaction and better dispersion of NR in PLA matrix. An increase in thermal stability of PLA due to the good interaction between the blend components was also reported in other PLA blends and composites [11]. The onset degradation temperature of PLA composite was lower than this of PLA and PLA blend. Moreover, it was found that the onset degradation temperature was decreased with increasing CaCO_3 content (Fig.4.). This may be due to the fact that the basic nature of CaCO_3 may have catalyzed the depolymerization of the ester bonds of PLA, and thus, it was thought to be responsible for the reduced thermal stability [12].

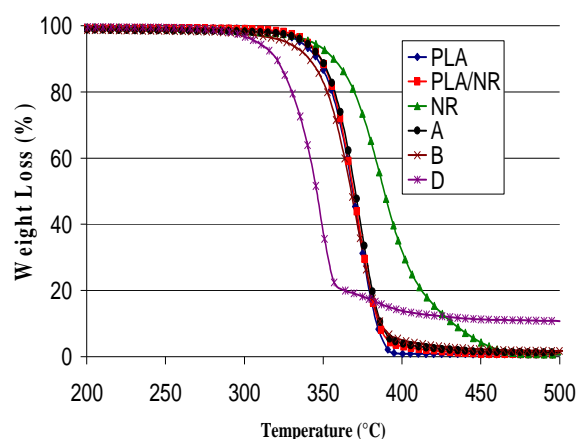


Fig.3. Impact strength of PLA blends and PLA composites.

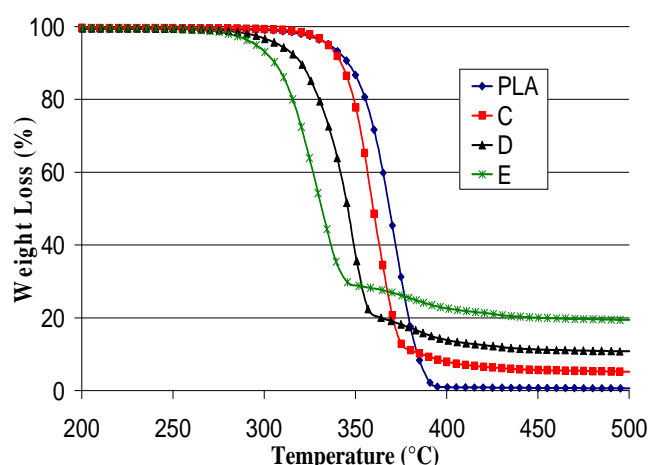


Fig.4. Impact strength of PLA blends and PLA composites at various CaCO_3 content.

4. Conclusion

The addition of NR-g-GMA in PLA/NR blend greatly improved the impact strength of the blend. With the addition of CaCO₃ into PLA/NR blend with NR-g-GMA, impact strength and modulus of the composite were further increased with a loss in tensile strength. In contrast, the addition of vetiver grass fiber into PLA/NR blend with NR-g-GMA led to an increase in tensile strength and modulus and a decrease in impact strength and elongation at break.

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