

A COMPARATIVE STUDY FOR THE PROPERTIES OF MONTMORILLONITE (MMT) AND CARBON NANOTUBE (CNT) IN RAMIE/POLY(LACTIC ACID)(PLA) TERNARY COMPOSITES

A. Tao Yu, B. Yan Li*, C. Yi Chen

School of Aerospace Engineering and Applied Mechanics, Tongji University
1239 Siping Road, Shanghai, 200092, P. R. China

* Corresponding author (liyana@tongji.edu.cn)

1 Introduction

Recently, with the increasing pressure on the world's resources as well as concerns about the disposal of materials, biodegradable composites have received a lot of research attention. The feasibility of the production processes and the possibility of using renewable raw materials have made poly(lactic acid) (PLA) an attractive biodegradable polymer. Because PLA has high strength, thermal plasticity, and biocompatibility, it has been used as packaging materials and other products. Natural fibers such as ramie, sisal, jute and kenaf were extracted from different plant sources. It is known that natural fibers are cellulose fibers and their main chemical compositions are cellulose, hemi-cellulose and lignin, which account for more than 90% of the total weight. Natural fibers possess high specific strength and modulus. Combining natural fibers and PLA to make biodegradable composites sounds quite attractive. Many researches have been conducted on the processing and properties of this biodegradable composite and some applications have been fulfilled. However, some properties of natural fiber/PLA composites such as poor thermal stability and the mechanical properties limit their applications in automotive parts, building components, and aircraft interior parts. Therefore, it is worth finding a way to improve certain properties of the biodegradable composites.

During the past decade, nanotechnologies have been an extensive study area and offered variety of applications in improving the properties of polymers. Numerous investigations concerned with PLA/layered silicates composites indicated improved strength due to the dispersion of nano-scaled clay in the polymer matrix. CNTs have been applied for a variety of applications based on their unique electrical, optical, and mechanical properties. The exceptional mechanical properties of CNTs

have led them effective reinforcing fillers for polymer composites. CNT modified polymer composites have the potential for tailoring of the properties of materials with enhanced mechanical, thermal, and electrical properties.

In this study, ramie/PLA composites were prepared. The effect of MMT and CNT on the mechanical properties and the thermal properties of the composites was investigated.

2 Experimental

2.1 Materials

Poly(lactic acid) (PLA) ($M_w=140,000$) was supplied by Shanghai Tong-Jie-Liang Biomaterial Co. Ltd., China. Ramie yarn was purchased by Shanghai Qian-Cong Ramie Products Co. Ltd. (China). Sodium montmorillonite (Na^+ -MMT) was supplied by Zhejiang Fenghong Clay Co. Ltd. (China). Carbon nanotube with hydroxyl group (CNT-OH) and carbon nanotube with carboxyl group (CNT-COOH) (average diameter was less than 8nm, and the purity was more than 90 wt.%, the length CNTs: 50 μm) were supplied by Chengdu Organic limited corporation, China Academy of Sciences.

2.2 Preparation of the composites

In this paper, master batch method was adopted to prepare ramie/PLA/MMT and ramie/PLA/CNT ternary composites. MMT was modified through an ion-exchange reaction between organic cations and inorganic cations of MMT layers. Two kinds of CNT, i.e. CNT-OH and CNT-COOH, were used. Prior to the preparation of nanocomposites, PLA/MMT and PLA/CNT master batch were made by mixing PLA and org-MMT, PLA and CNT respectively using mixer after being dried at 80°C for 12h. Secondly, the master batches, ramie and

modified PLA were melt-mixing using a twin-screw extruder operated at 170 °C. The compositions are shown in **Table 1**. The composites obtained were then molded into sheets by hot pressing at 170°C and 20 MPa for 4 min, followed by cooling to room temperature at 5Mpa. The sheets were prepared for structure characterization and properties measurements.

Table 1 The compositions of the composites

	Ramie /wt%	PLA /wt%	MM T /wt%	CNT -OH /wt%	CNT- COOH /wt%
Ramie/PLA	10	90	-	-	-
Ramie/PLA/MMT	10	85	5	-	-
Ramie/PLA/CNT-OH	10	88	-	2	-
Rame/PLA/CNT-COOH	10	88	-	-	2

2.3 Characterization

Specimens of the composites were tested for tensile strength according to GB 13022-91 standard using a CMT5105 Materials Testing Machine (Shenzhen Sansi Material Instruments Ltd., China). Crosshead speed was set at 20 mm/min. The composites were tested for flexural strength under three point bending in a DXLL-5000 machine (Shanghai Jiedeng Instruments Ltd., China) in accordance with GB 1449-83. The size of the flexural testing samples used was 65mm × 10mm × 3.5mm. The machine was operated at a crosshead speed of 1.2 mm/min and a span of 60mm.

Thermal properties of the composites were analyzed by using TA Q20 Differential Scanning Calorimetry (DSC). The test temperature ranged between 20 and 200°C with heating rate of 10°C/min in nitrogen atmosphere. Dynamic mechanical analysis (DMA) was performed in three-point bending mode using a TA DMA Q800 Dynamic Mechanical Analyzer. The samples were cut from the sheets with typical dimensions of 60×13×2.4 mm. The test specimen dimensions were kept as consistent as possible in order to obtain an accurate comparison. Thermogravimetric analysis (TGA) was performed on a thermogravimetric analyzer (NETZSCH TA 449 C Jupiter) at a heating rate of 20 °C /min. Samples were examined under the presence of nitrogen (80ml/min) over a temperature range from ambient to 600°C.

3 Results and Discussion

3.1 Mechanical properties

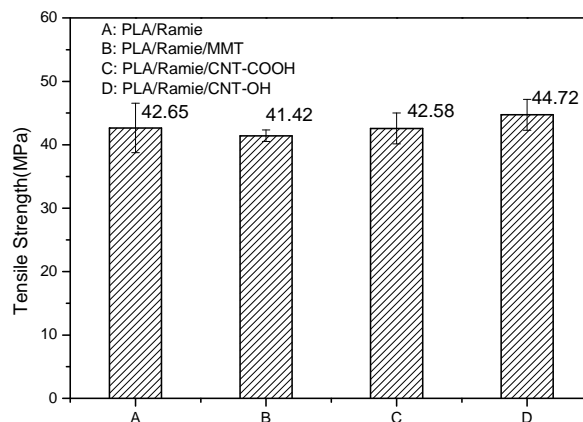


Fig. 1 Tensile strength of the composites

The mechanical properties of Ramie/PLA/nano material (MMT, CNT-OH or CNT-COOH) composites depend on the dispersion of ramie and nano materials and the interfacial strength between ramie and PLA.

Fig. 1 shows the tensile strength of the composites investigated. It can be seen that the tensile strength of ramie/PLA composite was 42.65 MPa. With the addition of MMT, CNT-OH and CNT-COOH, the tensile strength of the composite has nearly changed, which was around 42 MPa. The composite with CNT-OH shows the highest tensile strength reaching 44.72 MPa. It shows that the nano materials have almost no effect on the tensile strength of the composites.

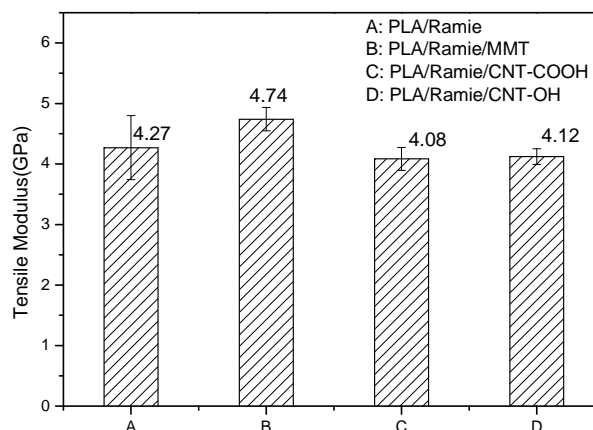


Fig.2 Tensile Modulus of the composites

The results of tensile modulus were shown in Fig. 3. Ramie/PLA composite has a lower tensile modulus than the composite with adding MMT, which was due to the MMT play a role as the reinforcement. The decrease in tensile modulus with addition of CNT-OH and CNT-COOH to ramie/PLA composite may result from the worse dispersion of the CNTs in the PLA matrix.

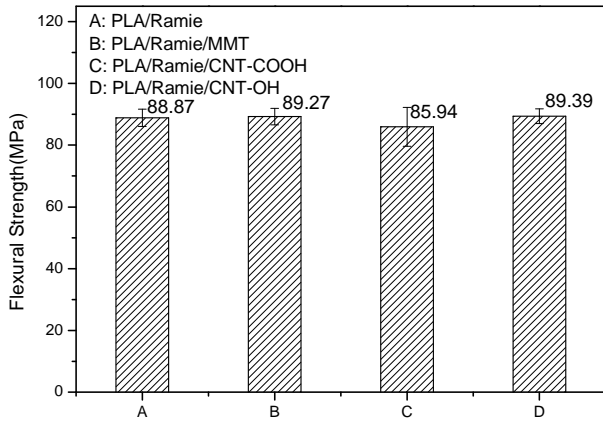


Fig.3 Flexural strength of the composites

The flexural strength of the composites was shown in Fig.3. The results of the flexural strength were similar with that of the tensile strength. The flexural strength of ramie/PLA composites with or without nano materials was around 88MPa.

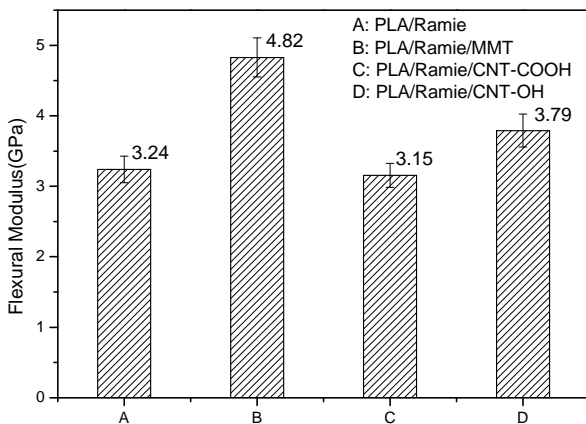


Fig.4 Flexural modulus of the composites

Fig.4 gives the flexural modulus of ramie/PLA composites. The flexural modulus of the composites increased significantly with addition of MMT and CNT-OH. MMT and CNT-OH adding into the

composites as filler can improve the stress transfer between ramie and PLA. However, the flexural modulus of the composites with CNT-COOH decreased slightly from 3.24 GPa to 3.15 GPa, which was due to worse dispersion of CNT resulting in the decrease of the interface strength between ramie and PLA.

3.2 Thermal properties

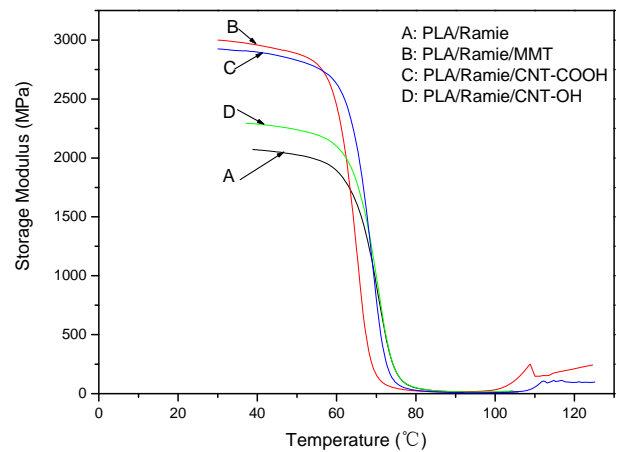


Fig.5 Storage modulus of the composites

The DMA data shows how exposure of the composites to elevated temperatures would affect the stiffness of the composite material. The dynamic properties reflect the amount of the energy in the composite stored as elastic energy and the amount of energy dissipated during the strain process. These properties are highly dependent on the existence of fillers: dispersion within the matrix, volume fraction, geometrical characteristics, and load transfer from the filler to the matrix. The storage modulus is closely related to the load bearing capacity of the material. From Fig. 5, the storage modulus of all samples decreases with temperature increasing, and there is a significant fall in the regions between 50°C to 80°C. And the storage modulus of the composites with nano materials is higher than that of ramie/PLA composite. This might be due to increase in the stiffness of the reinforcement imparted by nano material, which allows a greater degree of stress transfer from the matrix to the fiber. The composite with MMT has the highest storage modulus, which suggests the reinforced effect of MMT is higher than that of CNTs. The results of storage modulus at

room temperature were in accordance with the results of the f

Loss modulus reflects the amount of energy dissipated during the strain process. A good interface will bear a greater stress and a less energy dissipation. However, composite material with poor interfacial bonding will tend to dissipate more energy showing high magnitude of damping peak in comparison to a material with strongly bonded interface. Loss modulus of the ramie/PLA composites are shown in Fig. 6. The peak of ramie/PLA composites increased with the addition of nano materials which means the interface strength declined with adding nano materials.

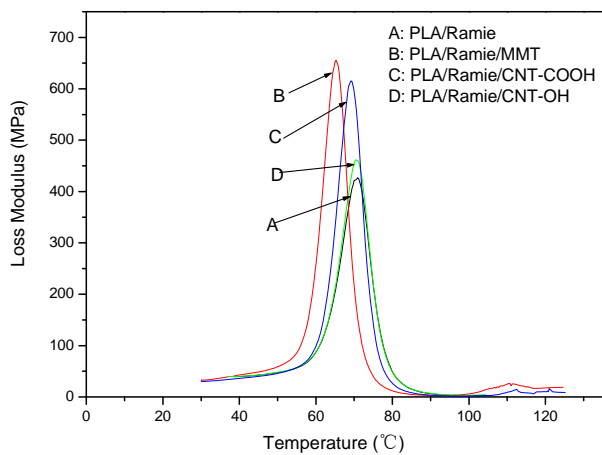


Fig.6 Loss modulus of the composites

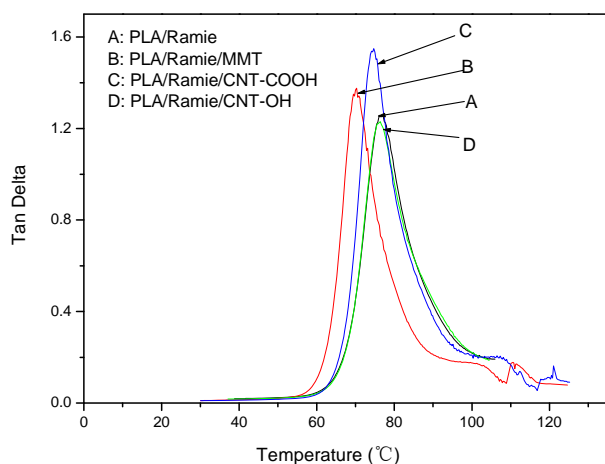


Fig.7 Tan Delta of the composites

The ratio of loss modulus to storage modulus is defined as mechanical loss factor or $\tan \delta$. The maximum heat dissipation occurs at the temperature where $\tan \delta$ is maximum indicating

the glass transition temperature (T_g) of the system. T_g of all the composites shifts to lower temperatures due to the nano materials present in the ramie/PLA composites, which can be associated with the increased mobility of the matrix chains due to nano materials decreased the interaction between ramie and PLA.

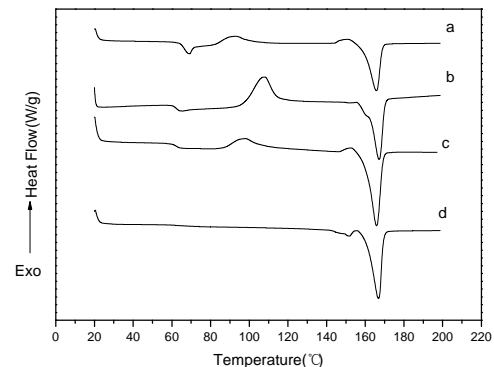


Fig.8 DSC curves of the composites: a, Ramie/PLA, b, Ramie/PLA/MMT, c, Ramie/PLA/CNT-OH, d, Ramie/PLA/CNT-COOH

The thermal properties of ramie/PLA composites are investigated by DSC. The curves are shown in Fig. 8 and the thermal properties data were listed in Table 2.

Table 2 Thermal properties of the composites

	$T_c/^\circ\text{C}$	$T_m/^\circ\text{C}$	$f_c/\%$
Ramie/PLA	111.4	167.3	22.5
Ramie/PLA/MMT	104.2	167.2	26.3
Ramie/PLA/CNT-COOH	-	166.8	28.8
Rame/PLA/CNT-OH	100.4	166.3	33.8

The crystallization temperature (T_c) appears at lower temperature with the addition of nano materials and the intensity of peak weakens accordingly. The nano size (MMT and CNTs) provide large surface due to their small size and thus it is reasonable to consider that the clay particles acted as a nucleating agent to enhance the ability of crystal during the process of crystallization.

The degree of crystallinity (f_c) was calculated as follows:

$$f_c = \frac{\Delta H_m}{\Delta H_{100\%}}$$

The melting enthalpy of the composite (ΔH_m) was determined by DSC. $\Delta H_{100\%}$ means the melting enthalpy of PLA when PLA overall melted, which was 93 J/g.

According to Table 2, f_c of the composites with nano materials exhibit an increase compared with that of ramie/PLA composite.

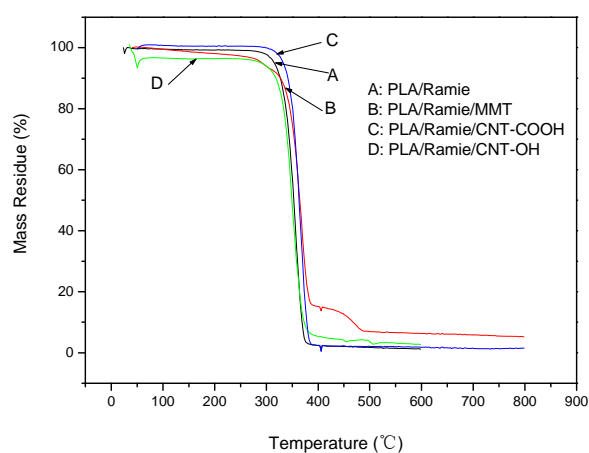


Fig.9 TGA curve of the composites

The thermal stability of ramie/PLA composites was investigated with thermal analysis, and the results are shown in Fig. 9. Thermal degradation of ramie/PLA shows completely in a single stage and occurs at 335.1°C. From Fig. 9, the composites with the addition of nano materials have similar TGA curves with ramie/PLA composites, which show higher degradation temperature than that of ramie/PLA composites. It might be due to nano materials hinder the diffusion of heat and volatile decomposition products. The hindered diffusion of volatile decomposition products caused by the barrier effect of the nano structure contributes to the increase of thermal stability of the nanocomposites.

4. Conclusions

Nano materials (MMT and CNTs) were added in the ramie/PLA composites. The mechanical properties results show that the addition of nano materials has nearly effect on the tensile strength and flexural strength, but the tensile modulus and flexural modulus is improved. The composites with MMT

have the highest mechanical properties. DMA results showed T_g decreased with the addition of nano materials. DSC results show that the T_m and f_c of the composites are improved the addition of nano materials, and the thermal degradation temperature of the composites also increases.

5. Acknowledgement

The authors would like to thank the support of the National Basic Research Program of China (973 program)(No. 2010CB631104) and the Post-doctoral Foundation of China (No.20090460655).

References

- [1] A. Rafael, H. Bruce and S. Susan. "An Overview of Polylactides as Packaging Materials". *Macromol Biosci*, Vol. 4, pp 835-864, 2004.
- [2] S. R. Suprakas and B. Mosto. "Biodegradable polymers and their layered silicate nanocomposites: In greening the 21st century materials world". *Prog Mater Sci*, Vol 50, pp 962-1079, 2005.
- [3] S. Gu, M. Yang, T. Yu, T. Ren and J. Ren. "Synthesis and characterization of biodegradable lactic acid-based polymers by chain extension". *Polymer International*, Vol. 57, No. 8, pp 982-986, 2008.
- [4] T. Yu, J. Ren, S. and M. Yang. "Preparation and characterization of biodegradable poly(lactic acid)-block-poly(ϵ -caprolactone) multiblock copolymer". *Polymers for Advanced Technologies*. Vol 21, pp 183-188, 2010.
- [5] G. Bhuvanesh, R. Nilesh and H. Jons. "Poly(lactic acid) fiber: An overview". *Prog Polym Sci*. Vol 32, pp 455-482, 2007.
- [6] L. Yu, Katherine D and Lin L. "Polymer blends and composites from renewable resources". *Prog Polym Sci*. Vol 31, pp 576-602, 2006.
- [7] T. Yu, Y. Li and J. Ren. "Preparation and properties of short natural fiber reinforced poly(lactic acid) composites". *Transactions of Nonferrous Metals Society of China*. Vol. Sp. Iss. 3, No. 19, pp.S651-S655, 2009.
- [8] T. Yu, J. Ren, S. Li, H. Yuan and Y. Li. "Effect of fiber surface-treatments on the properties of poly(lactic acid)/ramie composites". *Composites: Part A*. Vol. 41, pp 499 – 505, 2010.
- [9] J. Ren, T. Yu, H. Li, T. Ren and S. Yang. "Studies on morphologies and thermal properties of poly(lactic acid)/polycaprolactone/organic-modified montmorillonite nanocomposites". *Polymer Composites*, Vol. 29, pp1145-1151, 2008.

- [10] W. Chiu, Y. Chang, H. Kuo, M. Lin and H. Wen. "A study of carbon nanotubes/biodegradable plastic polylactic acid composites". *J Appl Polym Sci* Vol.108, pp 3024–3030, 2008.