

Manufacturing and Mechanical Properties of Sisal Fiber Reinforced Hybrid Composites

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ABSTRACT: PLA/PP polymer blends in various ratios (PLA:PP = 9:1, 4:1, 3:1, and 1:1), and their composites (PLA:PP = 1:1) with sisal fiber (10, 15 and 20 wt%) were fabricated using MAPP as compatibilizer. The aim of the work was to reduce the cost of biodegradable composites as well as to improve the impact strength of PLA using PP, a relatively cheaper thermoplastic. The developed composites were characterized for their morphological and mechanical properties. The tensile strength and modulus of the blends were decreased with increasing PP content whereas the strain at break and impact strength are increased. The tensile strength, modulus and water absorption were increased for hybrid composites with increasing fiber content.

Key Words: hybrid composites, sisal fiber, PP, PLA, mechanical properties

1. INTRODUCTION

Through the last few years there has been an increasing environmental consciousness, which has increased the interest to use natural fibers instead of man-made fibers in composites materials. Natural fibers have proven to be suitable reinforcement materials for composites thanks to a combination of good mechanical properties and environmental advantages such as renewability and biodegradability [1]. Sisal fiber is a hard fiber extracted from the leaves of the sisal plant. It is one of the most widely used natural fibers as a potential reinforcement of polymer composites because of its low cost, low-density, acceptable specific strength, good thermal insulation properties and renewability.

As a matrix, Poly (lactic acid) (PLA) is an example of a promising biopolymer prepared through a combination of biotechnology and chemistry. It is prepared from 100% renewable resources such as corn, sugar beets or rice [2,3]. It has a high strength and modulus and is inherently biodegradable in nature. However, its inherent brittleness and low toughness restricts its applications in markets. Blending PLA with other polymers presents a practical and economic measure to obtain

toughened products [4]. PLA blends with collagen, PBS, PMMA, PEG, PP and PEO have been reported to improve the properties, such as toughness, modulus and strength compared to the neat polymer [5,6]. However, most of these polymers that are blended with PLA are said to be partially immiscible and constitute multiphase blends with poor mechanical performance. In order to solve the problem of immiscibility, compatibilizers are used to reduce the interfacial tension and elevate the interface adhesion between the immiscible phases. To characterize the interfacial tension and interfacial adhesion, the rheological and morphological properties of the polymer blends have been analyzed both theoretically and experimentally over the last decades [7-9].

Polypropylene (PP) is one of the most extensively used plastics, it provides advantages in regard to economy (price), ecological (recycling behavior), and technical requirements (higher thermal stability and impact strength). In this study, PLA/PP blends at various ratios (PLA:PP = 9:1, 4:1, 3:1, and 1:1) were prepared by extrusion and injection molding process. Further, hybrid composites were prepared using PLA/PP blends (1:1) as matrix and sisal fiber as reinforcement at various fiber contents (10 wt%, 15 wt% and 20 wt%) and 5 wt% of

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poly (propylene)-graft-maleic anhydride (MAPP) was used as compatibilizer. The prepared composites were characterized for their morphological and mechanical properties.

2. EXPERIMENTAL

2.1 Materials

Poly(lactic acid (PLA), was provided by NATUREWORK CO. of American. PLA had weight-average molecular weight of 207 kDa (kilo daltons), density of 1.24 g/cm³ and temperature of 170°C. Polypropylene (PP) (injection grade), was obtained from Honam Petrochemical corporation, South Korea. Sisal fibers were bought from India, which are generally extracted from dried ripened leaves and used as reinforcement.

The coupling agent, Poly(propylene)-graft-maleic anhydride (MAPP) (Aldrich) and Sodium hydroxide (NaOH) (Dae-Jung Chemicals) were purchased and used as received.

2.2 Fiber surface modification

The sisal fibers were immersed in 5% NaOH solution for 5h at room temperature to eliminate hemicellulose as the ratio of 100g fiber to 2000 mL solution. After that, the fibers were washed with water until the fibers showed no residual NaOH (pH = 7) and dried in a vacuum oven at 70°C for 24 h. The dried alkali treated fibers were chopped in to 2-5 mm, stored in a sealed plastic bag for further characterization.

2.3 PP and PLA blends

PP and PLA were dried in a vacuum oven at 80°C for 12 h before use. Then the polymers were mixed using the twin-screw extruder. Melt extrusion performed by a double screw extruder. There are 5 different temperature zones on the extruder, which are 170, 180, 185, 185, and 180°C, respectively. The screw was rotated at 40rpm. The extrudate was cooled with water and cut into granulates of about 2mm length. Then the granulates were dried at 80°C overnight. Standard test specimens were prepared by injection-molding. The injection-molding temperature and pressure were 190°C and 60 MPa, respectively. Blends of PP and PLA were prepared in the ratios of:

- (1) 10% PP, 90% PLA; (2) 20% PP, 80% PLA;
- (3) 25% PP, 75%PLA; (4) 50% PP, 50% PLA.

2.4 Fabrication of Hybrid composites

Polymer blends (PLA:PP=1:1), sisal short fibers and MAPP were dried in vacuum oven for 24 h at 80°C. Then these materials were mixed first by melt-compounding using the twin-screw extruder and the standard test specimens were prepared by injection-molding using similar conditions as for blends preparation. Prior to the preparation of the composites, all the components were first dried in an oven at 80°C for at least 24 h. Similarly, composites (with 10 wt %) without were also

prepared for comparison.

2.5 Mechanical properties

2.5.1 Tensile strength

Tensile test was conducted according to ASTM D6389 (sample size of 165 mm × 13 mm (Narrow width) × 3 mm specimens) by a computerized Instron 3369 Universal testing machine. The tensile strength was measured at a cross-head speed of 5 mm/min.

2.5.2 Impact tests

Impact tests were performed employing an Izod impact testing machine, supplied by Comotech Testing Machines Co., Ltd, Taiwan, China. Rectangular strips of 64 mm × 12.7 mm × 3 mm were used as per ASTM 256-06 specifications. The impact test was carried out at room temperature and impact energy was reported in J/m. For each test, five replicate test specimens were taken and the average value was recorded.

2.5.3 Moisture tests

Moisture uptake was performed following ASTM D570-98. For each test, three test specimens (80 mm × 24.6 mm × 3.2 mm) were used. Prior to absorption experiments, the samples were dried in an oven at 50°C and then allowed them to cool to room temperature in a desiccator until the weight (dry weight) stabilized before weighing them to the nearest 0.001 g. The specimens were then immersed in distilled water at room temperature for 24 h. The specimens were taken out from the water and all surface water was removed with a clean dry cloth and immediately weighed (wet weight) to the nearest value 0.001 g. The percentage increase in weight during water immersion was calculated using the following equation (1).

$$MC = [(W_0 - W_{od})/W_0] \times 100 \quad (1)$$

where MC is moisture content, W_0 the initial and W_{od} is the final weight after drying.

2.6 Scanning electron microscopy

The morphological characterizations of the tensile and impact test fracture surface of composites were examined directly by scanning electron microscope JEOL JSM-6360. The scales were washed, cleaned thoroughly, air-dried and coated with 100 Å thick platinum in JEOL sputter ion coater and observed SEM at 20 kV. Similarly the composite samples were mounted on stubs with silver paste. To enhance the conductivity of the samples, a thin film of platinum was vacuum-evaporated onto them before the photomicrographs were taken.

3. RESULTS AND DISCUSSION

3.1 Tensile properties of PLA/PP blends

The results of the tensile properties such as tensile strength

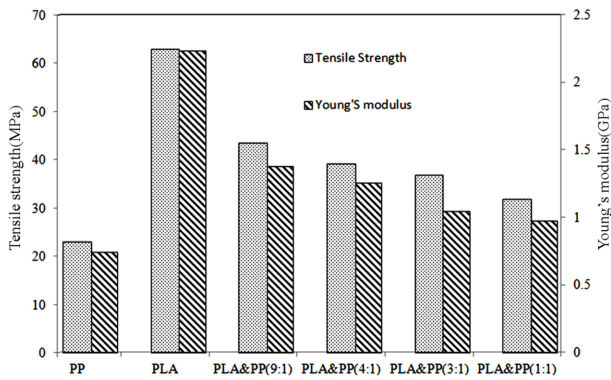


Fig. 1. Tensile properties of PP, PLA and their blends

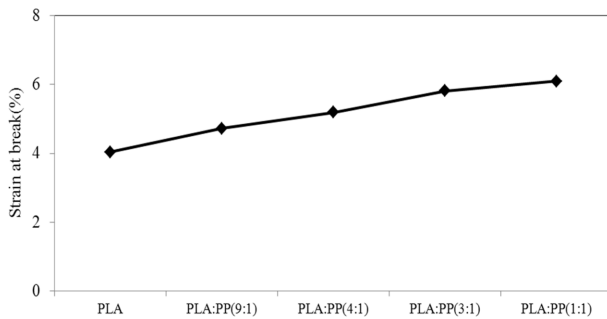


Fig. 2. Increasing tensile stain of PLA/PP blends with increasing PP content

and tensile modulus of virgin PP, virgin PLA and their blends are shown in Figs. 1 and 2. It is observed that the virgin PLA displayed a tensile strength of 62.96 MPa, with a tensile modulus of 2.23 GPa and a percentage strain at break of 3.92%. Due to its super elasticity, PP was not fractured under the testing condition. The incorporation of PP matrix to the tune of 10, 20, 25 and 50 wt % within the PLA matrix resulted in a decreased tensile strength and modulus in the resultant blends. However, the strain at break is increased with PP content increasing from 10% to 50%. PP incorporated within the PLA matrix probably acted as a toughening agent. This was probably due to incompatibility of hydrophobic PP with polar PLA or to the high polarity difference between the constituent polymers, which resulted in sharp boundaries between the two polymeric phases and led to the formation of voids and micro cracks when the samples were subjected to constant deformation [10]. However, the tensile strength and modulus of the all blends is higher than the pure PP.

3.2 Impact properties of blend matrix

The effect of PP content on the notched Izod impact strength of the PLA/PP blends of various compositions at room temperature is shown in Fig. 3. It was evident that virgin PLA displayed impact strength of 19.745 J/m, which increased to 21.01 J/m in the case of the blend with 50 wt % PP. Below 50 wt % PP, there was a significant decrease in the impact

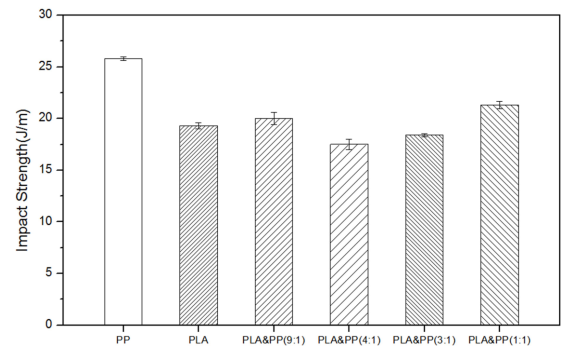


Fig. 3. Impact strength of PP, PLA and their blends

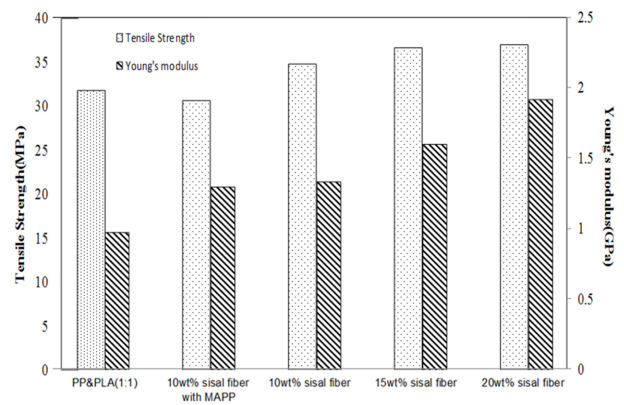


Fig. 4. Tensile properties of sisal fiber reinforce PLA/PP hybrid composites

strength of the blend. However, the blends prepared at PLA/PP ratios of 3:1, there was an increase in the impact strength compared to PLA/PP ratios of 4:1. This behavior was probably due to the high impact strength of the virgin PP matrix (25.76 J/m), which contributed to an enhancement in the absorbing impact energy in the blends. At a 1:9 ratio of PP/PLA there was an increase in the impact strength of virgin PLA from 19.745 to 20.2 J/m. However, in all cases where in the PP part was a major component, it formed a continuous phase with PLA domains as a dispersed phase, and the impact strength was lower compared with the PP matrix. This further confirmed that PLA and PP are incompatible in blends [11].

3.3 Tensile properties of sisal fiber reinforcing PLA/PP hybrid composites

Tensile properties of PLA/PP (1:1) composites which were reinforced by sisal fiber are showed in Fig. 4. Tensile strength and Young's modulus of PLA/PP matrix with MAPP were observed to increase with the addition of sisal fiber.

The results also indicate that the tensile properties are influenced by the presence of MAPP. For instance, tensile properties of 10 wt% fiber composites without compatibilizer were inferior to those with compatibilizer. In general, cellulose is not compatible with nonpolar PP matrix, it causes poor adhesion between fiber and matrix which results in lowering the

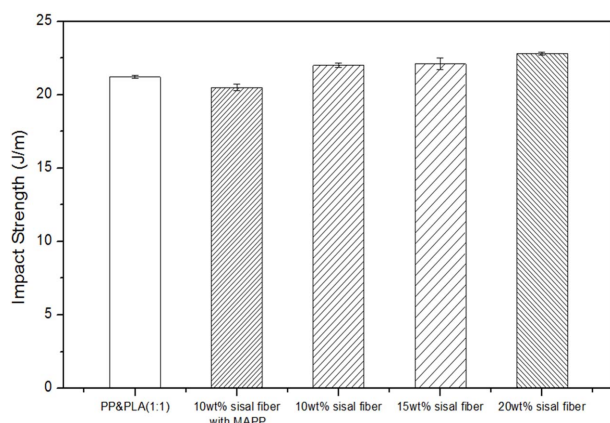


Fig. 5. Impact strength of sisal fiber reinforced PLA/PP composites

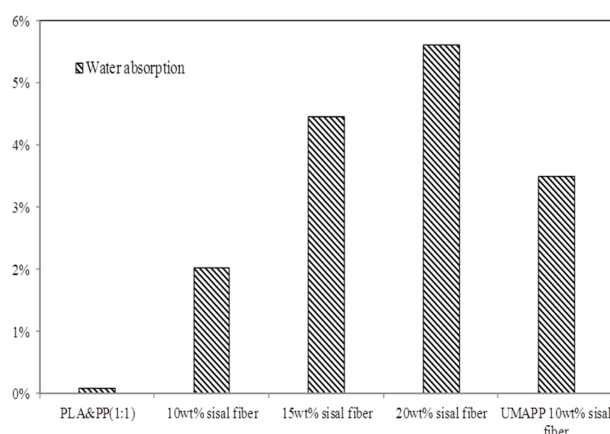


Fig. 6. Water absorption of sisal fiber reinforcing PLA/PP composites

mechanical properties. MAPP is not only used to modify fiber surface but also to achieve better interfacial bonding between PP and PLA and to improve the mechanical properties of the composites [12].

3.4 Impact properties of sisal fiber reinforced PLA/PP composites

Fig. 5 shows the impact strength of the sisal fiber reinforced PLA/PP hybrid composites. The blend matrix (PLA/PP) has an impact strength of 21.01 ± 0.1 J/m and after addition of sisal fiber and compatibilized (MAPP), the impact strength of the composite increased slightly. However, the sisal fiber composite without compatibilized (MAPP) showed low impact strengths compared to matrix. It might be due to the lack of bonding between the fiber and matrix (as we can see in Fig. 7a) and the incompatible nature of PLA and PP within the blend. In some cases the presence of too many fiber ends within the body of cellulose fiber-reinforced composites also may cause crack initiation and potential composite failure [10] and lead to crack in the matrix or at interface before the load transfer mechanism have occurred in all the extension as pos-

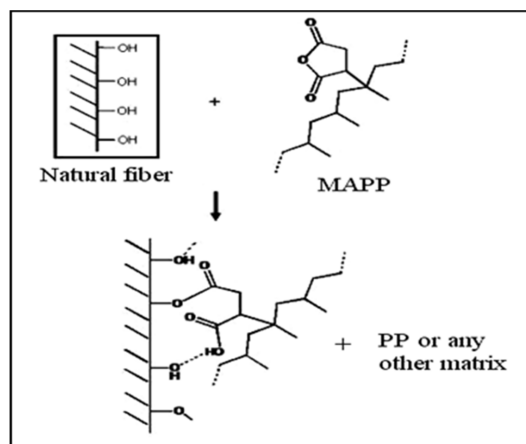


Fig. 7. Mechanism of interactions between coupling agent (MAPP) and the hydroxyl groups on the surface of natural fibers

sible, leading them to lower impact strength.

3.5 Water absorption properties

Moisture absorption of natural fiber/plastic composites is one major concern in their outdoor applications. They have an undesirable property, namely, hygroscopicity of their chemical constituents, thus affecting their long-term performance. For example, increased moisture decreases their mechanical properties. Provides the necessary condition for biodegradation, and changes their dimensions. Water absorption of PP/PLA and PP/PLA hybrid composites are shown in Fig. 6 and 7. It observed that PP-g-MAPP decreased the water absorption of sisal-PP/PLA composites. This is because of the fact that the incorporation of MAPP also provides hydrophobicity to the fibers because of the esterification of the anhydride groups of MAPP with the hydroxyl groups of the natural fibers and the establishment of hydrogen bond between the hydroxyl groups of the fiber and the remaining carboxylic group of the MAPP. The expected mechanism is shown in Fig. 7. As the sisal fiber content increased the water absorption decreased. This was attributed to the hydrophilic nature of the sisal fiber.

3.6 Morphology investigation of tensile fractured

The morphologies of tensile tested PLA/PP blend specimens were investigated by SEM and the pictures are shown in Fig. 8.

It can be observed that a smooth surface is obtained in pure PLA. However, it clearly reveals that many droplets remain at the fracture surface of PLA:PP = 1:1 blends and as the content of PLA increased, the quantity of droplets decreased. The droplet size was also found to decrease with increasing PLA content. This indicates the existence of a weak interfacial adhesion due to the incompatibility of PLA and PP.

Fig. 9 shows the SEM photographs of tensile fractured surfaces and interfaces of fiber reinforced PLA/PP (1:1) composites. Fig. 9(A) and 9(a) show the fractured surface

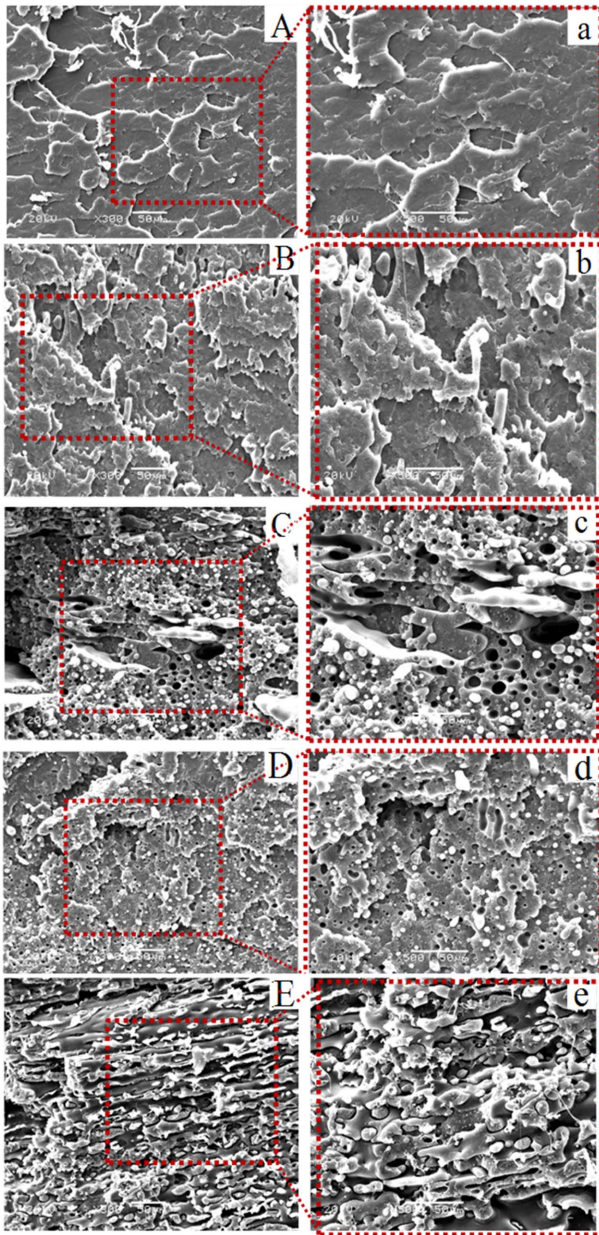


Fig. 8. Tensile fractured surface morphology of the PLA/PP blends: (a) PLA, (b) PLA:PP=1:1, (c) PLA:PP=3:1, (d) PLA:PP=4:1, (e) PLA:PP=9:1 (A/B/C/D/E $\times 300$, a/b/c/d/e $\times 500$)

morphology of 10 wt% Sisal fiber reinforced composites without MAPP. Some fibers pull out from matrix and many droplets can be found at the surface. Compared to that, we can't find droplets at the fracture surface in fig. B/C/D. It can be observed that the incorporation of MAPP in the blend led to improved miscibility between PLA and PP. This may be due to an increase in the mobility of chains at the interface caused by a chemical reaction between the end group of PLA and MAH group of MAH-g-PP. The compatibilized blends presented much finer spread phases than the non-compatibilized blend did. In addition, good adhesion between the sisal fibers and

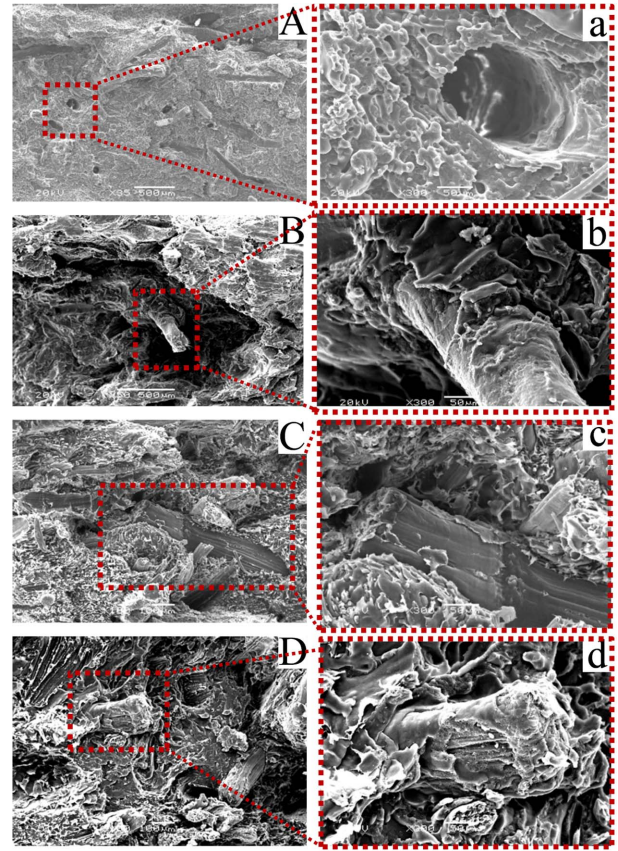


Fig. 9. Tensile fractured surface morphology of the PLA/PP/MAPP and sisal fiber blends: Sisal fiber content (a) 10 wt % UMAPP, (b) 10 wt%, (c) 15 wt %, (d) 20 wt %. (A/B/C/D $\times 300$, a/b/c/d $\times 500$)

matrix forms a strong interactions between fiber and matrix. So sisal fiber increased the tensile properties.

4. CONCLUSION

PLA/PP blends and their composites with sisal fiber (10, 15, 20 wt%) were prepared successfully by injection molding process. PLA/PP blends with 1:1 ratio show good impact strength as compared to others samples. Tensile strength, Young's modulus and impact strength of PLA/PP/sisal fiber hybrid composites with MAPP were observed to increase with increasing the fiber content. The incompatible nature of PLA and PP blends was clearly observed by SEM analysis, there were many droplets witnessed at the fracture surface and these droplets were disappeared by adding MAPP as compatibilizer. The MAPP used is not only to modify fiber surface but also to achieve better interfacial bonding between PP and PLA.

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REFERENCES

1. Oksman, K., "Mechanical Properties of Natural Fiber Mat Reinforced Thermoplastic," *Applied Composite Materials* Vol. 7, 2000, pp. 403-414.
2. Vink, E.T.H., Rábago, K.R., Glassner, D.A., and Gruber, P. R., "Applications of Life Cycle Assessment to Nature-Works. Polylactide (PLA) Production," *Polymer Degradation and Stability*, Vol. 80, 2003, pp. 403-419.
3. Kakiage, M., Ichikawa, T., Yamanobe, T., Uehara, H., and Sawai, D., "Structure and Property Gradation from Surface to Bulk of Poly(L-lactic acid)/poly(D-lactic acid) Blended Films as Estimated from Nanoscratch Tests Using Scanning Probe Microscopy," *ACS Applied Materials and Interfaces*, Vol. 2, 2010, pp. 633-638.
4. Gajria, A.M., Davé, V., Gross, R.A., and McCarthy, S.P., "Miscibility and Biodegradability of Blends of Poly(lactic acid) and Poly(vinyl acetate)," *Polymer*, Vol. 37, 1996, pp. 437-7444.
5. Anderson, K.S., and Hillmyer, M.A., "The Influence of Block Copolymer Microstructure on the Toughness of Compatibilized Polylactide/polyethylene Blends," *Polymer*, Vol. 45, 2004, pp. 8809-8823.
6. Girija, B.G., Sailaja, R.R.N., and Madras, G., "A Comparison of the Structure, Thermal Properties, and Biodegradability of Polycaprolactone/chitosan and Acrylic Acid Grafted Polycaprolactone/chitosan," *Polymer*, Vol. 46, 2005, pp. 147-155.
7. Ton That, M.T., Perrin Sarazin, F., Cole, K.C., Bureau, M.N., and Denault, J., "Polyolefin Nanocomposites: Formulation and Development," *Polymer Engineering and Science*, Vol. 44, 2004, pp. 1212-1219.
8. Manias, E., Touny, A., Wu, L., Strawhecker, K., Lu, B., and Chung, T.C., "Polypropylene/Montmorillonite Nanocomposites. Review of the Synthetic Routes and Materials Properties," *Chemistry of Materials*, Vol. 46, 2001, pp. 3516-3523.
9. Zhai, H., Xu, W., Guo, H., Zhou, Z., Shen, S., and Song, Q., Eur "Preparation and Characterization of PE and PE-g-MAH/Montmorillonite Nanocomposites," *European Polymer Journal*, Vol. 40, 2004, pp. 2539-2545.
10. Ho, C.H., Wang, C.H., Lin, C.I., and Lee, Y.D., "Synthesis and Characterization of TPO-PLA Copolymer and Its behavior as Compatibilizer for PLA/TPO Blends," *Polymer* Vol. 49, 2008, pp. 3902-3910.
11. Wojciechowska, E., Fabia, J., and Slusarczyk, C., "Manufacturing and Mechanical Properties of Sisal Fiber Reinforced Hybrid Composites," *Fibres & Textiles in Eastern Europe*, Vol. 5(53), 2005, pp. 126-128.
12. Folkes, M.J., and Belvis, M., (Ed.), "Short Fiber Reinforced Thermoplastics," Wiley, Herts, 1985, pp. 151-153.