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MECHANICAL PROPERTIES OF LYOCELL FIBER REINFORCED POLYPROPYLENE COMPOSITES

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ABSTRACT

The major disadvantage of the hydrophilic natural fibers and hydrophobic polymer matrices is the poor compatibility between the fibers and matrices. In order to improve the affinity and adhesion between fibers (lyocell) and thermoplastic matrix (polypropylene) during manufacturing, maleic anhydride (MA) as a coupling agent has been employed. Physical properties such as void contents and water absorption rate were studied. Tensile and flexural tests were carried out to evaluate the composite mechanical properties. Tensile test results showed the higher strength and modulus of composite than pure polypropylene (PP). In addition, these properties were better for 2 wt% MA content than 1 wt% MA content. Thus, 2 wt% MA content ensured better interfacial adhesion between fibers and matrix. Like tensile properties, the flexural properties of the composites were not improved. However, between 1 and 2 wt% MA content, the composites containing 2 wt % MA showed better flexural properties than 1 wt % MA.

Keywords: Natural fibers, Polypropylene, Maleic anhydride, Interfacial bonding, Mechanical properties.

1. INTRODUCTION

In the recent years, considerable research and development have been done in natural fibers as reinforcements for thermoplastic resinous matrix. These reinforced plastics serve as an inexpensive, biodegradable, renewable, and nontoxic alternative to conventional fiber reinforced composites. The various advantages of natural fibers over man-made fibers like glass and carbon are low-cost, low density, competitive specific mechanical properties, reduced energy consumption, and biodegradability. The common thermoplastic materials that currently dominate as matrix materials for natural fibers are polypropylene and polyethylene while phenolics and polyesters are two widely used thermoset matrixes for the natural fibers. With a view to replacing the wooden fittings, fixtures, and furniture, organic matrix and resin reinforced with natural fibers, such as jute, kenaf, sisal, coir, straw, hemp, rice husk, bamboo, lyocell etc., have been explored in the past decades [1-21].

Recently, there is an increasing demand from automotive industries for materials with sound abatement capability as well as reduced weight for fuel efficiency. Natural fibers possess excellent sound absorbing efficiency and are more shatter resistant and have better energy management characteristics than conventional fiber reinforced composites. In automotive parts, such composites not only reduce the mass of the component but also lower the energy needed for production by 80%. Demands for natural fibers in plastic composites are forecast to grow at 15-20% annually in automotive applications and 50% or more in selected building applications [1].

However, the primary disadvantages of natural fiber reinforced plastic composites are (a) poor interfacial adhesion and dispersion in olefinic thermoplastic matrix materials due to hydrophilic character of cellulose [12], (b) high moisture absorption leading to dimensional instability, and (c) low permissible temperatures of processing and use due to their limited thermal stability. The hydrophilic groups present in unmodified cellulose are detrimental to the performance of the cellulose based composites if the fibers are exposed to the outside atmosphere. Water, in liquid or vapor form, can diffuse into the composite, and the properties (including dimensional stability) are hampered due to hydration. Similar to the study on cellulose based composites by Rowell [13], modification of cellulose by esterification may solve this problem by reduction in hygroscopicity. Sanadi *et al.* [14] pointed out that the processing temperature for cellulose based reinforced composites is limited to 200^{o}C although higher temperatures can be used for short periods of time.

The hydrophilic character of cellulose is usually incompatible with hydrophobic matrix material unless a compatibilizer or coupling agent is used [15]. This leads to poor interfacial adhesion between the fiber and matrix as well as poor fiber dispersion. Various coupling or compatibilizing agents are used for improving the interfacial adhesion, dispersion within the matrix, and compatibility of the system.

Surface modification of cellulose fibers with polypropylene-maleic anhydride copolymer resulted in improved mechanical properties of the cellulose--polypropylene composites as shown by Felix and Gatenholm [15]. Scanning electron microscopy (SEM) studies revealed improved dispersion and adhesion when the fibers were surface modified. Similar studies were reported by Karmaker and Youngquist [16] for jute fiber reinforced polypropylene composites, and by Chen *et al*. [17] for bamboo fiber reinforced polypropylene composites. Both of these studies used maleic anhydride-grafted polypropylene as coupling agent.

A study by Hendenberg and Gatenholm [18] showed improved stiffness in cellulose-thermoplastic composites containing polyethylene-polystyrene blend (70:30 proportion) as a matrix material when a functionalized copolymer (maleic acid anhydride grafted styrene-ethylene/butylene-styrene block copolymer) was used.

A study by Trejo-O'Reilly *et al.* [19] revealed the possible use of grafting agents bearing anhydride or isocyanate reactive groups for introducing non-polar characteristics to the surface of cellulose fiber in view of improving interfacial wetting with polymeric matrices. The interactions of various oligomeric (e.g. oligomeric isocyanate) and polymeric reagents, such as poly (styrene-co-maleic anhydride) and poly (styrene-co-3-isopopenyl-α,α'-dimethylbenzyl isocyanate) (PSTMI), with the OH groups on the surface of different cellulose materials were studied using Fourier transform Infrared Spectroscopy (FTIR), scanning electron microscopy (SEM), X-ray photoelectron microscopy, and elemental analysis. It was found that the accessibility of the OH groups varied as a function of the coupling agent in terms of molecular size and chemical nature. In addition, fiber surface property studies revealed considerable changes in contact angle of water when the appended moieties were long-chain hydrophobic structures like PSTMI.

Improvement in mechanical properties and interfacial wetting was noted for steam-exploded fiber from Yellow poplar (Liriodendron tulipifera) when the fibers were acetylated [20]. The thermal stability of the fibers was also improved when the fibers were extracted with water and alkali and later acetylated. Cellulose fiber surface treatment by pre-impregnation of henequen cellulosic fibers in LDPE-xylene solution improved the interfacial adhesion between the fiber and matrix as well as the shear properties of the composites [21]. Also the silane coupling agent (A- 172 Union Carbide) improved the properties of these henequen cellulosic fiber composites.

Lyocell is a new cellulosic fiber spun from wood or pulp in a closed amine oxide solvent system [12]. It is environmentally benign and has the shorter processing time than conventional viscose rayon in the production. Also, lyocell fibers are known to have good mechanical properties, good wettability, high tenacity, and good drapability as well as environmentally friendliness. Thus, these fibers have potential applications as reinforcements for polymer matrix materials to offer improved mechanical and physical properties. This urges to analyze various aspects of these composite systems to understand, improve and quantify their properties. The objective of the present study is to manufacture lyocell fiber reinforced polypropylene matrix composites followed by the evaluation of their mechanical as well as physical properties. Special attention is paid to the interfacial adhesion, uniform distribution of fibers, and proper alignment of fibers with a view to improving the mechanical properties of the composites.

2. EXPERIMENTAL

2.1 Materials

In this study, lyocell fibers were used as reinforcement which supplied by KOLON Inds. (USA). The diameter of single strand was 10 micron. The ultimate tensile strength of mono filament was 0.5-0.8 GPa. The elongation at break and initial elastic modulus were 6-8% and 10-16GPa, respectively.

Polypropylene (PP) supplied by Honam Petrochemical Corp. (Korea) was used as the matrix. The specific weight, the melting point, and the molecular weight of PP were 0.95 g/cm^3, 170^{o}C, and 10,000 g/mol, respectively. Maleic anhydride (MA) (Eastman, USA) was used as a coupling agent.

2.2 Composite Fabrication

Composites were prepared by compounding with extrusion and processing with compression molding. The fabrication process of the composites is outlined below.

PP and MA were melt mixed by twin-screw extruder (PRIM TSC 16TC, Thermo Electron Corp.) to form continuous rod of diameter 1.0mm. MA contents were varied from 1 to 2 wt%. After extrusion, the rods were vacuum dried for 24hrs. A grooved mold was used (250x250 mm^2) to distribute the fibers in matrix uniformly as shown in Fig. 1. Releasing agent was used for easy removal of composites. The lyocell fibers were laid along the grooves of the mold. The dried rods were then uniformly placed over the fibers. For compression molding, a hot press machine (Model: WES-A300, Wetech, Korea) was used. At first, mold was preheated at 150^{o}C temperature for 10min. Then the mold was compressed at 3ton pressure and 180^{o}C temperature for 20min to get a composite panel. This panel was formed with grooved in one side. Two grooved composite panels were then compressed to get the flat composite panel. The consolidation cycle was chosen as shown in Fig. 2. An adequate flow of matrix (reduction in viscosity) was allowed before any pressure was applied.

2.3 Voids Contents

The void contents of composite may significantly affect some of its mechanical properties (ASTM D-2734). Higher void contents usually mean lower fatigue

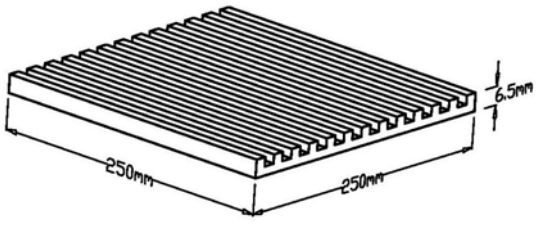


Fig 1. Grooved mold.

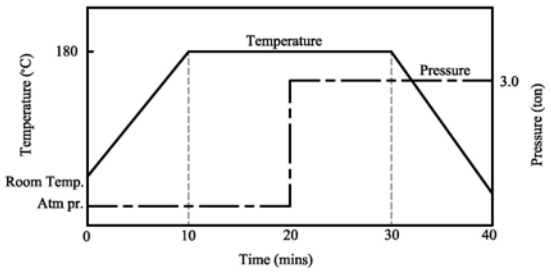


Fig 2. Time-temp-pressure cycle.

resistance, greater susceptibility to water penetration and weathering, and increased variation or scatter in strength properties. The void content is determined for the estimation of the quality of composites.

The densities of the composites were determined in accordance with ASTM-D792. The calculation was based the following equation:

$$M_d = a/(a+w-b) \quad (1)$$

where *a* represents apparent mass of specimen in air (g), *b* stands for apparent mass of specimen completely immersed and of the wire partially immersed in water (g/) and *w* stands for apparent mass of totally immersed sinker and partially immersed wire (g).

The theoretical densities and voids contents of the composites were determined in accordance with ASTM D 2734-94. The theoretica density was determined using the following equation:

$$T_d = 100/(R/D + r/d) \quad (2)$$

where T_d = theoretical density (g/cm^3), R = resin in composite (weight %), D = density of resin (g/cm^3), r = reinforcement in composite (weight %), and d = density of reinforcement (g/cm^3).

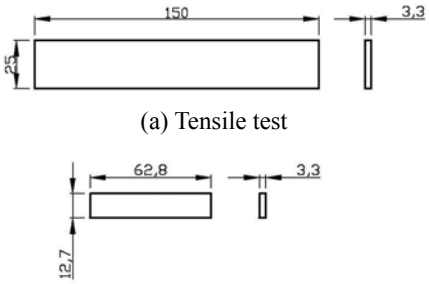
The void content was calculated from

$$V = 100(T_d - M_d)T_d \quad (3)$$

where V = voids contents (volume %).

2.4 Water Absorption of Composites

The mechanical properties of composites degrade if the composites absorb moisture. Thus, moisture absorbing capability of our lyocell fiber/PP composites is investigated in an attempt to know the degree of degradation of the mechanical properties of the composites. The tests were performed according to the ASTM D570-95 standard procedure for two and twenty four hour immersions (i.e. repeated immersion). Specimens of the composite panel were cut into dimensions of 76.2 mm in length by 25.4 mm in width by the thickness of the panel. The specimens were dried in an oven at 110^{o}C, cooled in a desiccator and weighed. The conditioned specimens were fully immersed in



(a) Tensile test

(b) 3-point flexural test

Fig 3. Dimensions of specimens (dimensions are in mm).

distilled water maintained at 23^{o}C. The two-hour immersion method is used for materials having a relatively high rate of absorption and thin specimens, which can gain an equilibrium water content in 2 hours. For the composite panels under consideration, both the two hours and twenty-four hours methods were used to compare the rate of absorption of water. Therefore, the specimens were removed from water after 2 hours, all surfaces were wiped off, and weighed. They were again placed in water, and weighed again after another 22 hours. Since there are no water soluble materials present in the composites, there was no need for any reconditioning. The percentage of water absorbed was calculated from

$$M(\%) = (M_t - M_o)/M_o \times 100 \quad (4)$$

where M_o is the mass of the dried specimen (g) and M_t is the mass of wet specimen (g).

2.5 Mechanical Properties

The tensile tests were carried out according to the ASTM D3039 standard (rectangular specimens) using a Universal Testing Machine (RB 301 Unitech M). The gage length was 25mm and the crosshead speed was 2.00mm/min. At the same time, strain was measured by an extensometer over a gage length of 25.0mm. The tensile modulus and strength were computed from the stress-strain curves.

According to the ASTM D790 standard, 3-point flexural test was performed by using the same Universal Testing Machine (RB 301 Unitech M) along with the flexural test fixture. The span length was 50mm and the test speed was 1.5mm/min. Figures 3(a) and 3(b) illustrate the specimens geometry for tensile and flexural test.

3. RESULTS AND DISCUSSION

3.1 Void contents

The experimental and theoretical densities are determined using Eq.s (1) and (2), respectively. Then, the void contents of composites are determined by using Eq. (3). Table 1 shows the densities and void contents of the lyocell/PP composites manufactured in the laboratory.

Table 1: Void contents of Lyocell/PP composites

Composite	Void (vol%)	M_d (g/cm^3)	T_d (g/cm^3)
1% MA	2.3	0.91	0.93
2 % MA	6.4	0.87	0.93

Table 2: Water absorption of Lyocell/PP composites

Immersion time	Water absorption (wt %)	
	1 % MA	2 % MA
2 hr	0.508	0.625
24 hr	6.29	7.62

The average void contents of the composites were found to be 2.3 and 6.4 %, respectively, for 1 wt % and 2 wt % of MA contents. A good composite should have less than 1 % voids. The amount of voids in our case is large due to the lack of uniformity of surface coverage and insufficient (gap-filling) melt-flow of oversized matrix particles. In addition, the use of water as a suspension medium for extruded PP rods during prepregging can absorbs water and cause these voids.

3.2 Water Absorptions

Water absorption of composites relates to composite properties such as dimensional stability. The results of the water absorption tests are summarized below in Table 2. It can be observed that the fiber-based composites showed significantly higher water absorption than pure PP due to the hydrophilic character of lyocell fibers. However, compared to water absorption of lyocell fibers, average of 52.6 ± 3.7%, composites exibit much lower water absorption values. Thses much lower values obtained for composites than for fibers themselves are because cellulose fibers are covered by PP layers that slow down the diffusion of water. Moreover, the hydrophilic –OH groups present in the lyocell fibers react with the acid anhydride group present in MA to form ester linkages. This reduces the water absorbing capacity in the lyocell/PP composites.

3.3 Mechanical Properties

The typical stress-strain curves for tensile test specimens of the composites are shown in Figure 4. It shows the effect of MA as a coupling agent on the tensile properties of the composites. It is observed that 2 wt % MA content shows better properties than 1 wt % MA content.

The improvement of tensile strengths of the composites can be observed from Fig. 5. The addition of 1 wt % MA increased the tensile strengths of the composites than the pure PP. The average tensile strength of the composites containing 1 wt % MA was 53.02 MPa. It was observed that with the increased of MA content from 1 to 2%, there was a relative rise in the tensile strengths. The average tensile strength of the composites

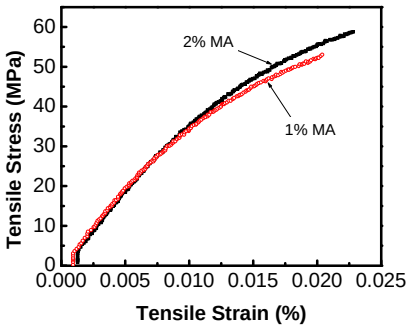


Fig 4. Stress-strain curves for tensile test specimens.

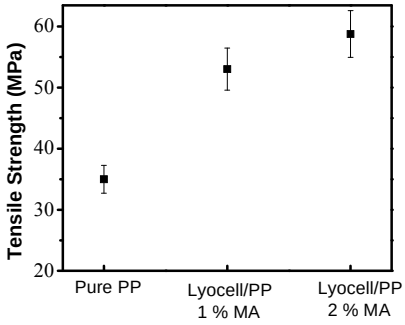


Fig 5. Tensile strength of Lyocell/PP composites.

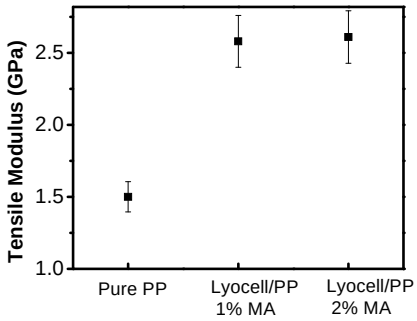


Fig 6. Tensile modulus of Lyocell/PP composites.

containing 2 wt % MA was 58.76 MPa. It ensures good interfacial adhesion between lyocell fibers and PP matrix.

Figure 6 shows the tensile modulus of lyocell/PP composites. Similar improvements were achieved in tensile modulus of the composites. The average tensile modulus of the composites containing 1 wt % MA content was 2.58 GPa while it was 2.61 GPa for the composites containing 2 wt % MA. The average elongations at break of 1 wt % MA and 2 wt % MA content composites were 5.2% and 6.8%, respectively.

The flexural properties of lyocell/PP composites were also studied (Figures 7, 8, and 9). The Typical stress-strain curves for flexural test specimens are shown in Fig. 7.

Figure 8 shows the flexural strength of the composites. The average flexural strength of the composites containing 1 wt % MA and 2 wt % MA were 32.58 MPa

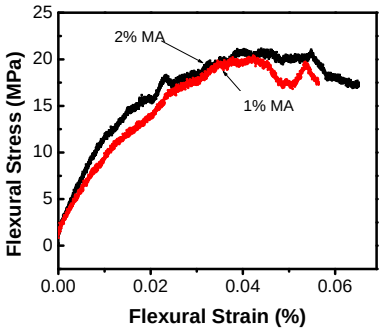


Fig 7. Stress-strain curves for flexural test specimens.

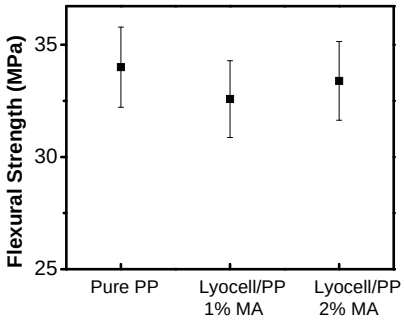


Fig 8. Flexural strength of Lyocell/PP composites.

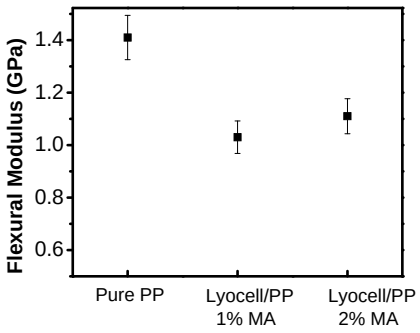


Fig 9. Flexural strength of Lyocell/PP composites.

and 33.39 MPa, respectivley. It ensures that increasing MA contents can improve the flexural properties of the composites.

Figure 9 shows the flexural modulus of the composites. Similar trends can be observed as flexural strengths. The average flexural modulus of the composites containing 1 wt % MA and 2 wt % MA were 1.03 GPa and 1.11 GPa, respectively. It is observed that the flexural properties of the composites were not improved as tensile properties. Although, the properties are lower than the pure PP, it is observed that composites containing 2wt % MA shows better properties than 1 wt % MA. Overall observation of flexural properties shows that increasing the amount of the coupling agent can result in improved flexural properties.

4. CONCLUSION

Lyocell fiber reinforced polypropylene matrix composites were successfully developed by compression molding technique and by using maleic anhydride as a coupling agent.

Results shows that average void contents of lyocell/PP composites are high. This is due to the lack of uniformity of surface coverage and insufficient (gap-filling) melt-flow of oversized matrix particles.

The improvement of tensile strengths and modulus of the composites can be observed. The tensile strengths of the composites were higher than the pure PP. It is observed that there is a relative rise in the tensile strengths and modulus upon increasing the content of the MA from 1 to 2%. It ensures that coupling agent can improve the interfacial adhesion between lyocell fibers and PP matrix.

The flexural properties for lyocell/PP composites do not show improvement. The results showed that increasing the amount of the coupling agent could improve the flexural properties.

It can be observed that the natural fiber-based composites show significantly higher water absorption than pure PP due to the hydrophilic character of lyocell fibers. However, compared to fibers, composites exhibit much lower abroption values.

5. ACKNOWLEDGEMENT

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