The Influence of Surface Treatment on Tensile Properties of Three Type Natural Fibers Reinforce Polyprolene Composites

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ABSTRACT

The surface modification effects of triethoxysilane (AS), methacrylic propyl trimethoxy silane (MS), and maleic anhydride grafted polypropylene (MAPP) on the cellulose (CE), sawdust (SD) and wheat straw (WS) have been studied by tensile test at room temperature and fracture morphology observation on composites reinforced by these natural fibers. The results revealed that MAPP was the most effective coupling agent, and SD composites exhibit the best performance compared to CE and WS composites. Optimum conditions for coupling agents were found to be 1 wt % for silane coupling agents and 5 wt % for MAPP. SEM analysis confirmed tensile test results, proving better adhesion with the employment of MAPP. Void and crack formations around the fibers were observed to decrease with MAPP treatment. Silane treatment did not provide an observable enhancement in adhesion between fiber and matrix.

INTRODUCTION

Natural fibers are drawing considerable attention as substitute candidate for synthetic fibers in recent years. The mechanical properties of natural fiber reinforced composites highly depend on the interface adhesion property between the fibers and the polymer matrix as have been reported by many researchers [1-2]. Natural fibers contain hemicelluloses, lignin, cellulose and pectin and are rich in hydroxyl groups, natural fibers tend to be strong polar and hydrophilic materials whilst polymer materials are a polar and exhibit significant hydrophobic [3]. In other words, there are significant problems of compatibility between the fiber and the matrix due to weak interface. The bond strength has been successfully improved by modifying the fiber surface with either chemical or physical surface treatment such as heat treatment, plasma treatment, silanization and acetylation [4-6].

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In this work, three natural fibers, namely cellulose (CE), sawdust (SD) and wheat straw (WS) treated with three coupling agents, (3-aminopropyl)-triethoxysilane (AS), methacriloxy propyl trimethoxy silane (MS), and maleic anhydride grafted polypropylene (MAPP) were used as reinforcement for polypropylene (PP) matrix. Effects of fiber type and treatment method on mechanical properties of composites were studied.

EXPERIMENTAL

Materials and Treatment Method.
Isotactic PP in pellet form was used as polymeric matrix material. CE, SD and WS were used as reinforced fibers. Surface modification of CE, SD and WS with silane coupling agent was carried out in solution. Aqueous ethyl alcohol solution was prepared and silane coupling agent (0.5, 1, 2.5% w/w of fiber) was added to the solution. The solution was mixed with a mechanical mixer for 15 minutes for hydrolysis reaction of silane coupling agent to take place. Then the fibers were added to the solution of silane coupling agent and left for 45 minutes under agitation for condensation and chemical bonding of silanes and cellulose fibers. Treated fibers were washed with ethanol to remove excess coupling agents. Afterwards, the solution was introduced into a rotary evaporator at 333K under vacuum for 1 h until fibers were dried.

Preparation of Composites.
Chopped dried short untreated (referred as UF) or treated fibers and PP pellets were compounded with fiber content of 10, 20, 30wt% by using ThermoPrism twin screw extruder for good mixing of fiber and polymer. The extruded composite material was palletized and dried at 350K for 48 hours and then injection molded using an injection molding machine.

Characterization Methods.
Tensile behaviors of PP and PP composites were tested on a Zwick machine at room temperature, with a load cell of 250 kN, following normative ASTM D3039. Composite fracture surface morphology was observed and analyzed with HITACHI S-4700 field emission scanning electron microscopes. All samples were sputter-coated with platinum and palladium to provide enhanced conductivity.

RESULTS AND DISCUSSION

Tensile Strength and Breaking Strain.
Fig.1 is a typical example of stress-strain curve belongs to PP/SD composites at 30wt% fiber content and optimum treatment conditions. Generally speaking, incorporation of CE into PP had decreased tensile strength as well as toughness and break strain. Young’s Modulus of composites increased with employment of CE. AS
and MS treatment had increased tensile strength to some extent, but MAPP treatment had a distinct positive effect on tensile strength. Composites treated with MAPP had almost recovered the tensile strength loss due to incorporation of fibers. Increase in Young’s Modulus is also much more pronounced for MAPP treated composites. AS and MS did not have a distinct effect on Young’s Modulus and strain at break. Strain at break of MAPP treated composites had decreased compared to untreated, silane treated composites. Another interesting point is MAPP treatment prevented stress relaxation in the composites, that is there was no yielding in MAPP treated composites whereas untreated, AS and MS treated exhibited yielding phenomenon. Fig.2 shows tensile strength of CE, SD and WS loaded composites as a function of fiber loading. It can be seen that tensile strength decreased with increasing fiber loading. At 40wt% fiber loading, the decline was 41.9, 42.4 and 44.4% for CE, SD and WS/PP composites, respectively. Fig.3 illustrates the effect of coupling agents on tensile strength of CE, SD and WS/PP composites at 30wt% loading. This graph shows that MAPP has a great coupling efficiency compared to AS and MS. Another conclusion is MAPP is more effective coupling agent for SD/PP composites since increase in tensile strength is much more pronounced for SD/PP composites compare to two other composite systems. Although 30% fiber was employed, there was almost no tensile strength decrease for SD/PP composites compared to neat PP.

![Figure 1](image1.png)

**Figure 1.** A typical stress-strain curve of PP/SD composite at 30wt% fiber loading (a)pure PP (b) untreated (c)MS treated (d)AS treated (e) MAPP treated composites.

![Figure 2](image2.png)

**Figure 2.** Effect of fiber loading on tensile strength of PP/C, SD and WS composites.

Fig. 4 shows effect of fiber loading on elongation at break and energy to break of PP/CE composites. It was observed that loading had an adverse effect on both elongation at break and energy to break. It has to be mentioned that elongation at break and energy to break of pure PP is 418% and 12 N•m, respectively. Only 10wt% loading of CE had a great impact on elongation and toughness of composites. Elongation at break decreased from 418% to about 8% and energy to break decreased from 12 N•m to 0.35 N•m. These observations show that incorporation of particles causes a brittle behavior in composites compared to ductile thermoplastic matrix, even at low fiber loadings. This is because particles or fibers restrict deformation capacity in elastic zone as well as plastic zone. Restricted deformation capacity in the elastic zone causes increase in modulus whereas restricted deformation capacity in the plastic zone causes decreased elongation at break and toughness. Fig. 5 and Fig. 6 illustrate the deviation of strain at break and energy to break of CE, SD and WS composites with AS, MS and MAPP treatment, respectively. Considering error bars,
AS and MS treatment did not change strain at break and energy to break of composites significantly for three types of composites, but MAPP significantly reduced the two responses. The reduction in strain at break was 33.5, 33.9, and 44.8% for CE, SD, and WS/PP composites, respectively. Similarly, reduction in energy to break was 10.0, 21.4 and 33.3% for CE, SD, and WS/PP composites, respectively. MAPP have reduced strain at break and, consequently energy to break values of composites due to enhanced adhesion between fiber and matrix. Better adhesion yields to more restriction of deformation capacity of composites, thus catastrophic failure occurs after small strain deformations. It would be expected that silane coupling agents would decrease strain at break and toughness of composites due to enhancement of adhesion between polymer and fiber but it seems that limited enhancement of the interface was not reflected in toughness of the composites.

**Figure 3.** Effect of coupling agent on tensile strength of PP/CE, SD and WS composites.

**Figure 4.** Effect of CE loading on strain at break and energy to break of PP/CE composites.

**Figure 5.** Effect of fiber and treatment on strain of PP/CE, SD, WS composites at 30% fiber.

**Figure 6.** Effect of fiber and treatment on break energy of PP/CE, SD, WS composites at 30% fiber.

**Fracture Morphology.**

Fig.7-9 show fracture surfaces of CE, SD and WS without treatment or with 3 different surface treatments, respectively. At the first sight, it can be easily observed that all types of fibers were well dispersed in the matrix, regardless of surface treatment employed. This observation proves that efficient mixing of fibers in the
matrix was achieved via melt mixing of fibers and PP in Rheomixer and compression molding in the polymer press.

![Image](image1.png)

**Figure 7.** SEM micrographs of (a) untreated (b) AS treated (c) MS treated (d) MAPP treated CE/PP composites at 30 wt% loading and x100 magnification.

![Image](image2.png)

**Figure 8.** SEM micrographs of (a) untreated (b) AS treated (c) MS treated (d) MAPP treated SD/PP composites at 30 wt% loading and x100 magnification.

![Image](image3.png)

**Figure 9.** SEM micrographs of (a) untreated (b) AS treated (c) MS treated (d) MAPP treated SD/PP composites at 30 wt% loading and x100 magnification.

In Fig. 7, particulate structure of cellulose can be observed. Fig. 8 and 9 reveal that SD and WS were predominantly in fiber form and WS has higher fiber length and aspect ratio than SD. SD and WS composites consist of fibers. It can be seen that fibers were oriented randomly along the matrix. When effect of surface treatments on fracture surface of composites were compared, it was observed that AS and MS did not cause a change on the fracture surface of composites for both CE, SD and WS composites whereas MAPP treatment changed fracture mode significantly. Comparison of surface treatments shows that surface roughness of composites treated with MAPP is significantly lower than that of untreated or AS and MS treated composites. Decreased surface roughness with employment of MAPP is a cause of enhanced stress transfer between fiber and matrix via enhanced fiber matrix adhesion. Fiber or particle pull out from the matrix in the presence of a tensile load is an indicator of lack of adhesion between fiber and matrix and increases surface roughness of fracture surface. These observations were also confirmed by tensile test results. Tensile strength of composites significantly increased with employment of MAPP for all composite types. AS and MS did not yield a significant increase in tensile strength since adhesion could not be improved.
Fig. 10-12 depicts a more detailed view of the same composites in the same sequence at 1000 times magnification. Detailed view of fracture surface of composites enables a deeper understanding of interface and nature of fracture. As seen in Fig.9-(a-c), cellulose particles exhibited poor wetting by polymer matrix. Particles were not covered with a polymer layer and there were voids around the particles. This is a proof that PP was easily separated from C along the interface because of low interfacial adhesion. On the contrary, MAPP treated PP/CE composites were well embedded in the matrix with surface coverage by the matrix as seen in Fig.9-d. In Fig.10-a, fiber pull out accompanied by void formations could be observed for untreated PP/SD composites. AS and MS treatment improved interfacial adhesion to some extent. There is less fiber pull out and more interfacial adhesion as seen in Fig.10-(b, c). In addition to fiber pull out as the mode of fracture, fiber breakage can also occur for MAPP treated composites, as seen in Fig.11-d for PP/WS composites. This is an evidence of effective stress transfer between fiber and matrix.

![Figure 10](image10)

**Figure 10.** SEM micrographs of (a) untreated (b) AS treated (c) MS treated (d) MAPP treated CE/PP composites at 30wt% loading and x1000 magnification.

![Figure 11](image11)

**Figure 11.** SEM micrographs of (a) untreated (b) AS treated (c) MS treated (d) MAPP treated SD/PP composites at 30wt% loading and x1000 magnification.

![Figure 12](image12)

**Figure 12.** SEM micrographs of (a) untreated (b) AS treated (c) MS treated (d) MAPP treated WS/PP composites at 30wt% loading and x1000 magnification.

Mechanical properties had shown that there is a significant decrease in elongation at break and toughness of composites when MAPP treatment was employed. In the light of SEM observations, it is evident that MAPP decreased fiber pull-out by increasing fiber-matrix adhesion and decreased void formations around the fibers. Voids around the fibers and fiber pull out of the composites would have increased energy dissipation while fracture of composites, which has a positive impact on
toughness of composites. It is obvious that voids around fibers increased the path of crack penetration in the transverse direction. Decreased surface roughness of fracture surface of composites with employment of MAPP is a direct evidence of decreased path distance during crack propagation, decreasing elongation at break and toughness of composites accordingly. Ichazo suggested another explanation to decreased elongation at break with employment of MAPP [7]. They suggested that this behavior of elongation at break when composites contain MAPP can be due to acidic nature of functionalized compatibilizers since these compatibilizers can accelerate degradation of cellulose fibers at the processing temperature, and this, in turn leads to fragilization of cellulose fibers.

SUMMARY

Three natural fibers, cellulose, sawdust and wheat straw were modified by three coupling agents, (3-aminopropyl)-triethoxysilane (AS), methacryloxy propyl trimethoxy silane (MS), and maleic anhydride grafted polypropylene (MAPP) respectively and were used as reinforcement for PP matrix. Tensile strength of the PP/fiber composites tends to decrease with increasing fiber volume fraction. MAPP treatment exhibited the best performance especially for PP/SD composites. The increase in tensile strength with employment of MAPP was up to 50% for the PP/SD composites whereas AS and MS treatment provided at most 14.2% increase in tensile strength at 30wt% fiber loading. Break strain and toughness of composites declined drastically even at low fiber loadings. MAPP treatment give rise to decline in toughness due to enhanced interactions between fiber and matrix whereas silane treatment did not have an obvious effect on toughness of PP/fiber composites. Interfacial interactions were considerably improved via MAPP treatment. Silane treatments also had the same effect but to a lesser extent. SEM studies confirmed mechanical test results, proving better adhesion with the employment of MAPP.

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