COMPOSITES & POLYCON 2009
American Composites Manufacturers Association
January 15-17, 2009
Tampa, FL USA

New High Performance Natural Fiber Composites

by

M.-T. Ton-That[1,2*], J. Denault[1], F. Perrin[1], W. Leelapornpisit[2], W. Hu[1], and K. C. Cole[1]
[1]Industrial Materials Institute, National Research Council Canada, 75 blvd de Mortagne, Boucherville, Quebec, Canada J4B 6Y4; [2]Mechanical and Industrial Engineering, Concordia University, Montreal, Quebec, Canada

Abstract

Cellulose fiber composites have been used extensively for the construction industries in North America and they began to receive very much attraction in Europe, South America and Asia. In order to increase the competitiveness, it is important for the composites industry to reduce the consumption of energy and cost as well as to improve output and performance.

In this work, new formulations of cellulose fiber composites based on polypropylene (PP) and various cellulose sources, including wood fibers, flax and hemp fibers, and rice husk, etc., have been developed for melt processing. In order to reduce the processing cost and energy and the complications related to drying the cellulose sources, different types of cheap additives have been incorporated in the process in different ways. This new approach allows eliminating the cellulose drying step and the safety challenge related to the high flammability of the dried cellulose source thus reducing sufficiently the overall processing energy and cost. In addition it can also improve significantly the mechanical properties and the flame resistance of the composites.

Introduction

Although the pioneering work in natural fiber thermoplastic composites started in the 1970s, they are still undergoing substantial development even today. Wood fibre thermoplastic composites are gaining market share because of their advantages over wood and metal in terms of longevity, appearance, life-cycle cost, and value (1, 2). They are attractive, insect- and rot-resistant, and paintable, while they can be made to have the look of wood. In addition, they are stiffer and cheaper than plastic products while at the same time they can be worked, cut, glued and fastened with the same screws or nails as wood. On the other hand vegetable fibre thermoplastic composites are attractive to the automotive industry because of their low density and ecological advantages over conventional composites (3-5). As a result wood fibre composites have been used extensively for the construction industries in North America while vegetable fibre composites have been introduced into personal vehicles in Europe, South America, and Asia. In order to increase its competitiveness, it is important for the composites industry to reduce energy consumption and cost as well as to improve output and performance.

At this stage in the technology, the processing of natural fibre thermoplastic composites has been well explored (6, 7). However it is essential that the natural fibre reinforcement must be dried well before compounding with the polymer matrix in order to avoid degradation and formation of bubbles or voids. The drying process consumes a significant amount of energy and also exhibits a high safety risk owing to the highly flammable cellulose source. Several different approaches have been developed to overcome these problems, but each of them poses different challenges.

This paper presents a new method to overcome cellulose humidity and improve the mechanical properties and fire resistance of cellulose composites in which basic oxide filler is used. In principle, the humidity and wood acidity are absorbed or neutralized by adding basic oxides, such as calcium oxide, during processing. As a result, no drying of wood is required and degradation is limited. Wood fibres and two different types of flax fibres were used in this work.

Experimental

Two reground recycled polypropylenes PP1 and PP2 were obtained from Novoplas (Quebec, Canada). Virgin PP6100 SM (PP-a) was supplied by Montell. High melt flow index PP (PP-b) was provided by Unicolor (Quebec, Canada). Coupling agents (CA) based on maleic anhydride (MA) grafted polypro¬pylene, such as Epolene-43 (E43) (Mn = 9,100; ~ 4.81 wt% of MA), Epolene-3015 (E3015) (Mn = 47,000; ~ 1.31 wt% of MA), and Epolene-3003 (E3003) (Mn = 52,000; ~ 0.71 wt% of MA), all from Eastman Chemicals, were used in this study. Different spruce sawdusts were provided by JER Envirotech (Canada) while rice husk and flax fibers were kindly provided by Northern Wild Rice and Schweitzer-Mauduitz Canada. respectively. Calcium oxide (CaO) and aluminum oxide (Al2O3) were supplied by C. P. Hall Company and Malakof Industries Inc. respectively.

The composites were prepared by a twin-screw Extrusion Spec W&P 30 mm having L/D = 40, speed = 150-175 rpm, Tmax = 185°C. Samples were molded by

injection at T = 200°C. All samples contained 40 wt% cellulose fibers and 2 wt% coupling agent.

Transmission infrared spectra (FTIR) were measured on a thin film at room temperature (approx. 25°C) on a Nicolet Magna 860 Fourier transform instrument at a resolution of 4 cm-1. A JEOL JSM-6100 scanning electronic miscroscope (SEM) at a voltage of 10KV was utilized to analyze the dispersion of cellulose fiber into the PP matrix using polished surfaces, and the interface between cellulose and PP matrix on cryogenic fractured specimens. Tensile properties and un-notched Izod impact resistance were measured on the MTS Instron machine according to according to ASTM D638 and ASTM D256, respectively, at room temperature.

Results and Discussion

The effect of the basic fillers and coupling agent chemistry (molecular weight and grafting amount) on the formulation was examined and. The mechanical properties of the wood composites formulated with the same coupling agent E43 in the presence and absence of reactive fillers CaO and Al2O3 were reported in Figures 1. As indicated in Figure 1, the modulus and strength of the wood composites increases significantly with the presence of reactive fillers. This improvement can be due to the fact that the reactive filler interact with moisture and acid-like impurities in the wood during processing, thus reducing the degradation/oxidation of the composites. In addition reactive fillers can react with the maleic anhydride group of coupling agent (Figure 2) that can improve their interface with the PP matrix. As a result the reactive fillers can also be effective reinforcements for the PP matrix. CaO has a greater reinforcing effect on the composite properties than Al2O3 which can be due to its greater alkalinity thus its better reactivity with the coupling agent.

The interaction between CaO and coupling agent was studied by FTIR. Figure 2a shows the FTIR spectra of the thin film of PP, blend of PP and E43, blend of PP and CaO, and blend of PP, E43 and CaO while Figure 2b shows the spectra subtracted with the PP spectrum. The subtracted spectra of the CaO-E43-PP blend indicate that the peak (at 1710 cm^{-1}) assigned for carboxylic acid (dimer) of the maleic acid in the coupling agent E43 had disappeared and the new peak (at 1560 cm^{-1}) assigned for Calcium carboxylate was formed. Thus proves that the maleic acid group of the coupling agent can chemically react with the CaO particles. As a consequence, a good interface between the CaO surface and the PP matrix should be expected (Figure 3).

The quality of dispersion of the wood saw dust in the PP matrix is very good. Figure 4a illustrates a uniform distribution of saw dusts in the PP matrix, in which the saw dusts are well encapsulated by the matrix, without evidence of holes and voids. However, it was difficult to find out where the CaO particles are, hence, observation on the cryogenically fractured specimen was performed. Figure 4b reveals the presence of fine CaO particles in the matrix.

Figures 5 and 6 illustrate the effect of coupling agents on the composite performance. In the absence of CaO, with the same amount of wood content and coupling agent content, E3015 provides greater strength but lower modulus for the wood composites. This can be explained by the fact that E3015 has higher molecular weight, which provides better compatibility with the PP matrix. E43 has greater maleic anhydride content and lower molecular weight, it should interact better with the cellulose surface, however, it has poorer compatibility with the PP matrix due to its low molecular weight. The compatibility with the matrix seems to be more important for the strength. In the presence of CaO, E43 gives better strength and modulus than E3015. E43, which has a high amount of maleic anhydride grafting amount and lower molecular weight, should have better interaction with both the wood and the CaO particles. On the other hand the maleic content in E3015 is quite low (more than 3 times lower than in E43) which may not be sufficient for the interaction with both the CaO and the saw dust. Since CaO is more reactive than saw dust, E3015 likely reacts with CaO rather than with saw dusts. As the amount of CaO increases, the possibility for E3015 reacting with saw dust should reduces significantly. In other words, the E0315 becomes less effective in improving the interface between the saw dusts and the PP matrix. As a consequence, E3015 provides sufficiently lower strength with the increase of CaO amount.

Figure 6 shows that E3015 provides better ductility and toughness as a result of its higher molecular weight compared to E43. However, with the incorporation of CaO, ductility and toughness of samples formulated with E3015 were reduced dramtically, while those of samples formulated with E43 increased. Again, it can be explained by the poorer fiber-matrix compatibility in the E3015 due to the presence of CaO. At 10 wt% CaO, there is no significant difference in ductility and toughness between the two formulations formulated from the two coupling agents.

The effect of the PP type on the formulation was also studied. Figure 7 shows the tensile properties of the composites prepared from recycled PP1, recycled PP2, and pure PP Profax 1274. The positive effect of CaO in the mechanical performance of the wood composites was again confirmed in all three PP matrices.

The positive effect of CaO on the mechanical properties of the flax composites was also observed. Figure 8 demonstrates significant improvement in the modulus of

the composites fabricated from flax shives and flax straws (mixture of shives and fibers).

The presence of CaO was not only improved the mechanical properties but also the thermal stability and fire resistance of the cellulose composites. Figure 9 illustrates the limited oxygen idex of the flax PP composites in the presence and absence of coupling agent (MA). The presence of CaO in the formulation improves significantly the fire resistance of the composites. This can be due to the fact that CaO can disperse the energy during burning. It is also possible that CaO reacted with impurities in the fibers, which often have low molecular weights thus being more flammable.

Conclusion

The results show that the presence of basic oxides combined with coupling agent significantly improves the mechanical performance and fire resistance of the cellulose composites. These oxides absorb the humidity and neutralize the acidity of the wood reinforcement, thus limiting the degradation during compounding. The short-chain coupling agent E43 provides a better advantage since it has a higher mobility to impregnate the wood particle surface. While its high maleic anhydride content allows a better interaction with the basic fillers, thus enhance the reinforcing effect of the fillers. It was also found that CaO is one of the best fillers for cellulose composites due to its high reactivity and low cost.

Acknowledgements

The supply of cellulose sources by JER Envirotech and Schweitzer-Mauduit (Canada) for this project is highly appreciated. The authors would like to thank the Government of Canada for the funding via the ABIP program. W. Leelapornpisit and H. Wei would like to thank the National Science Research Council Canada for the financial support for the research fellowships (Grant# N00784).

References

1. T. Laufenberg, "The Future of Recycled Material Usage in Building Applications: Summary of Conference Viewpoints", Proceedings of the Conference on The Use of Recycled Wood and Paper in Building Applications, Madison, Wisconsin, USA, September 1996, 155-202.
2. A. K. Bledzki and J. Gassan, "Composites Reinforced with Cellulose Based Fibres". Prog. Polym. Sci., 1999; 24; 221-274.
3. M. Pracella, D. Chionna, I. Anguillesi, Z. Kulinski, E. Piorkowska, "Functional¬ization, Compatibilization and Properties of Polypropylene Composites with Hemp Fibres", Comp. Sci. Technol., 2006; 66: 2218-2230.
4. A. K. Rana, A. Mandal, B. C. Mitra, R. Jacobson, R. Rowell, A. N. Banerjee, "Short Jute Fiber-Reinforced Polypropylene Composites: Effect of Compatibilizer", J. Appl. Polym. Sci., 1998; 69: 329-338.
5. P. V. Joseph, K. Joseph, S. Thomas, C. K. S. Pillai, V. S. Prasad, G. Groeninckx, "The Thermal and Crystallization Studies of Short Sisal Fibre Reinforced Polypropylene Composites", Composites Part A, 2003; 34: 253-261.
6. A. K. Mohanty, M. Misra and L. T. Drzal, "Surface Modifications of Natural Fibers and Performance of the Resulting Biocomposites: An Overview", Compos. Interfaces, 2001; 8: 313-343.
7. X. Li, L. G. Tabil and S. Panigrah, "Chemical Treatments of Natural Fiber for Use in Natural Fiber-Reinforced Composites: A Review", J. Polym. Environ., 2007; 15: 25-33.

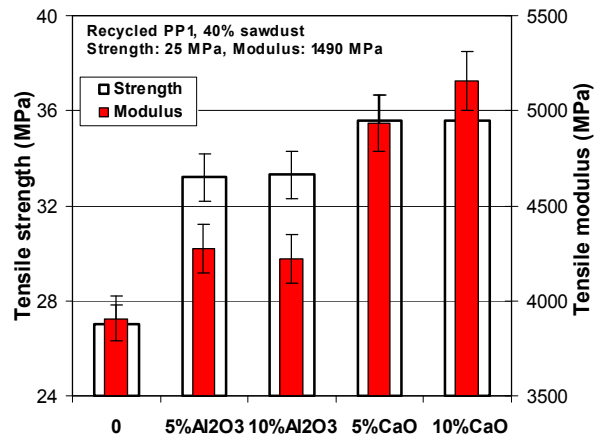
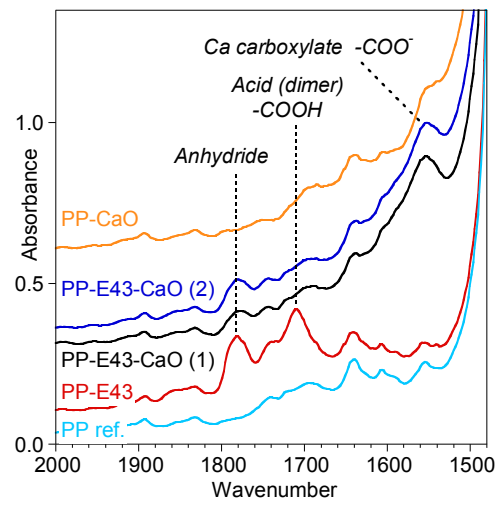
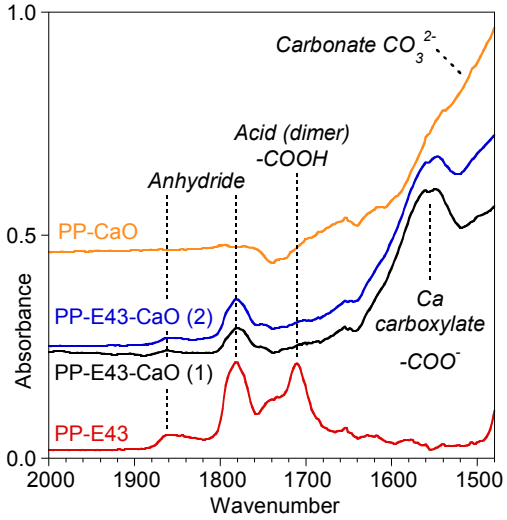


Figure 1: Tensile properties of the wood composites with different reactive fillers



a



b

Figure 2: FTIR spectra of PP, blend of PP and E43, blend of PP and CaO, and blend of PP, E43 and CaO a) original and b) after subtrated by PP spectrum

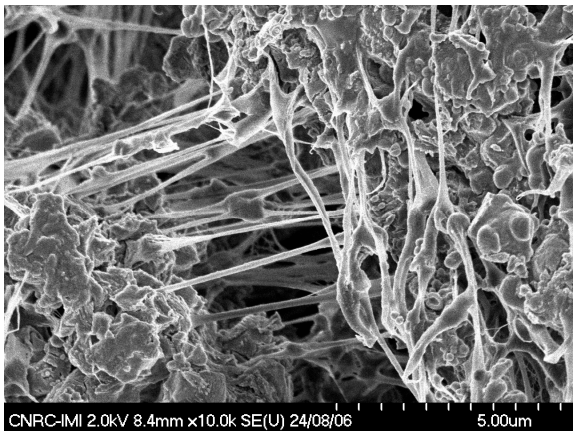
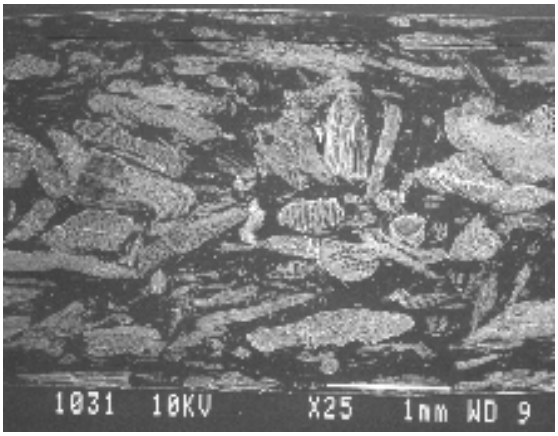
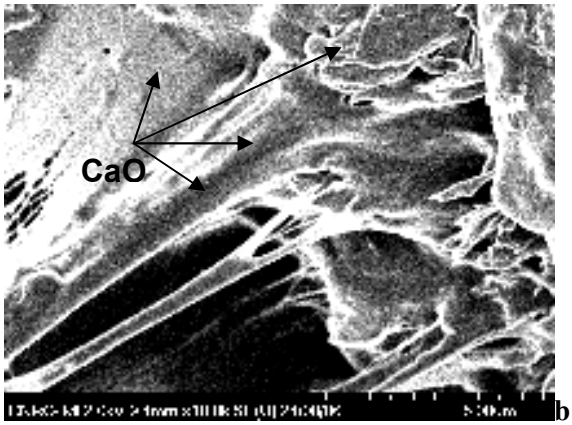


Figure 3. SEM image of the PP-E43-CaO blend specimen (cryogenic fracture)



a



b

Figure 4: SEM image of the wood composites a) dipersion of saw dust (polish specimen) and b) dispersion of CaO particles (fractured specimen)

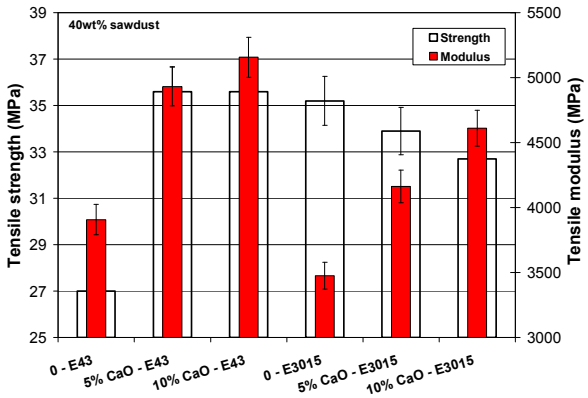


Figure 5: Tensile properties of the wood composites with different compatibilizers

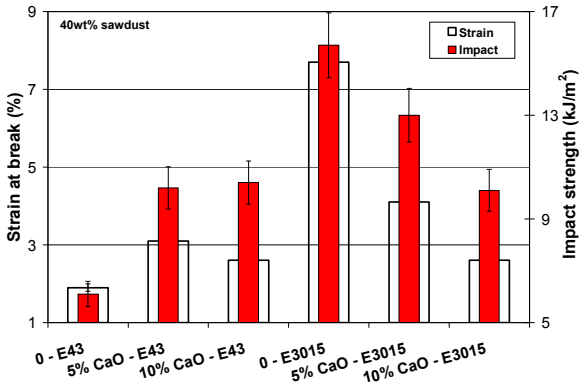


Figure 6: Ductility and impact resistance of the wood composites with different compatibilizers

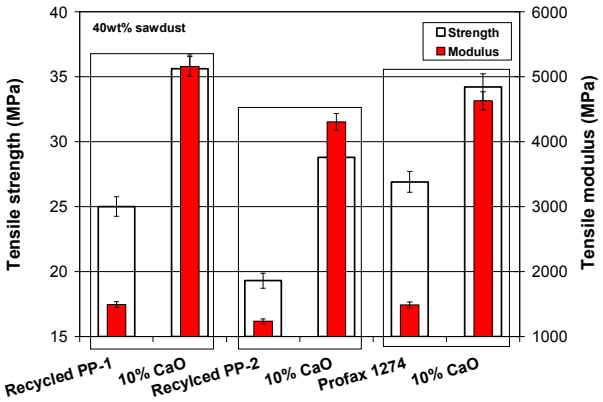


Figure 7: Tensile properties of the wood composites with different PP matrices.

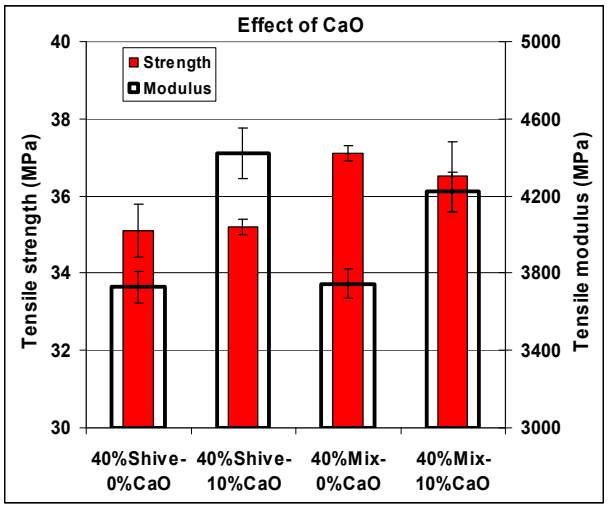


Figure 8: Tensile properties of the flax PP composites

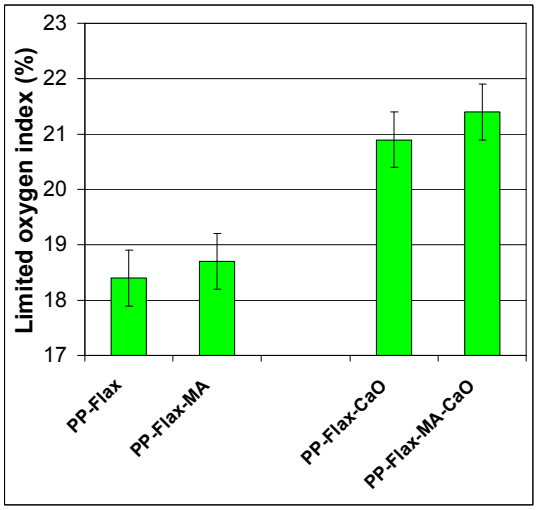


Figure 9: Limited oxygen index of flax PP composites