# WOOD FIBER COMPOSITES FROM RECYCLED POLYOLEFIN

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## Abstract

Wood composites based on recycled polypropylene (PP) were fabricated by melt processing. Different formulations, involving two different types of coupling agents, two different types of reactive additives, and an impact modifier (IM), were used. The reinforcements were in the form of wood sawdust. The mechanical performance of the resulting composites was evaluated before and after conditioning in water for 1 and 7 days. The composites show superior mechanical properties when compared with the pristine matrix, and resist humidity very well. The results also demonstrate the effect of formulations on the performance of the recycled composites.

## Background

Although much of the pioneering work in wood-filled thermoplastic composites was done in the 1970s [1-3], only recently has there been substantial development. The market for thermoplastic wood composites in North America was 320,000 tonnes in 2000 and the volume is expected to more than double by 2005 [4].

Wood plastic composites are gaining market sharebecause of their advantages over wood and metal in terms of longevity, appearance, life-cycle cost, and value. They are attractive, insect and rot resistant, and paintable while they can be made to have a wood look. In addition, they are stiffer than plastic products while at the same time they can be worked, cut, glued and fastened with the same screws, nails, or staples as wood.

The great majority of reinforced thermoplastic composites available commercially use as their reinforcing fillers inorganic materials like glass, clays, minerals, etc. These materials are heavy and abrasive to processing equipment. In contrast with conventional reinforcements, wood and natural fibers possess the advantages of low cost, light weight and non-abrasiveness. Compared to natural fibers, wood fibers are very cheap, therefore it is not surprising that wood fibers are more attractive for composite production [5-16].

At this stage in the technology, the processing of wood thermoplastic composites has been well explored. Wood thermoplastic composites can be processed either by co-rotating or counter-rotating or parallel or conical twin-screw extruders, or single-screw extruders as well. Wood thermoplastic composites can be compounded by an inline or offline procedure, using continuous or batch processes. However it is essential that the wood reinforcement must be dried well before compounding with the polymer matrix in order to avoid degradation and formation of bubbles/voids. Furthermore, water in the extruded materials can also reduce extrusion speed, as well as destroy the surface finish and mechanical properties. Several different approaches have been developed to meet this requirement but each of them poses different challenges. For example, in a separate step, wood can be dried in a kiln or oven (suitably explosion-proofed due to the powdery nature of most wood). However, the cost can be high since the wood needs to be heated twice, first during drying and then in the processing step; the equipment occupies a large space; and it is also very difficult to store the dried wood. In a second approach, the drying is done together with processing in a twin-screw extruder (M. Hotchkiss, Farrel, Cincinnati), in which the wood is fed in first and the plastic part-way down the

barrel, or it can be done in a continuous mixer.  This gives the advantage of tremendous free volume and surface renewal capabilities but low output.  Recently, Davis Standard has introduced the Woodtruder into the market, which is a parallel, 28/1 L/D counter-rotating twin-screw extruder into which the wood is fed, and which has a single screw, side-injection extruder to feed melt plastics.  No material preparation is needed, with moisture removal via atmospheric and vacuum vents.  The advantages of this system include the low speed, low shear action, the separate melting process of polymer prior to addition of fibers, and the elimination of the cost of drying, size reduction, and blending operations but it complicates the process and requires high investment.

An alternative approach using chemical principles to resolve the drying problem and improve the wood composite performance is presented in reference 17.  In general, the humidity and wood acidity are absorbed/neutralized with/by basic oxides, such as CaO, during processing.  As a result no drying of wood is required and degradation is limited. However, according to the authors the amount of calcium oxide must be carefully calculated so that the water of the wood cellulose filler becomes finally 2-5% by weight, otherwise the composites will become very sensitive to humidity.  Since humidity in wood varies from one location to another, the method disclosed in this patent is difficult as the correct humidity of the wood is not always easy to determine.  In addition, the use of CaO requires surface treatment of the CaO.  This paper presents a method to overcome wood humidity and improve the mechanical properties of the wood composites in both dry and wet conditions in which the basic oxide-based filler is used without surface treatment.

## Experimental

Reground recycled PP and PP1 were obtained from Novoplas (Quebec, Canada) in the form of an injection grade with MI = 5 and 8 g/min, respectively.  Virgin PP6100 SM was supplied by Montell.  High melt flow index PP (PP HMI) was provided by Unicolor (Quebec, Canada). Compatibilizers based on maleic anhydride (MA) grafted polypropylene, such as Epolene-43 (acid number AN = 45; $M_n$ = 9,100; ~4.81 wt% of MA), Epolene-3015 (AN = 15; $M_n$ = 47,000; ~1.31 wt% of MA), and Epolene-3003 (AN = 8; $M_n$ = 52,000; ~0.71 wt% of MA), all from Eastman Chemicals, were used in this study.  An impact modifier, ethylene-propylene rubber DSM Sarlink 419 (EPR), was also used in some formulations.

Spruce sawdust (>2% moisture) was provided by JER Envirotech (Vancouver, Canada). The sawdust was screened to obtain an average particle size of 0.5 mm and homogenized prior to processing.

Calcium oxide CaO was supplied by The C.P. Hall Company with max 92 wt% CaO. Aluminum oxide $Al_2O_3$ was obtained from Malakof Industries Inc with min 95 wt% $Al_2O_3$.

The sawdust was dry-blended with the polymer pellets then fed into a twin-screw extruder Extrusion Spec W&P 30 mm having L/D = 40; speed = 150-175 rpm; $T_{max}$ = 185°C.  For testing, samples were molded by injection (BOY 30A injection machine at T = 200°C). Table I provides the formulations for the various composites studied.  Example numbers starting with the letter 'C' are comparative examples.

Density measurements were made with a pycnometer AccuPyc 1330.  Water absorption was determined by measuring the weight gain or loss after immersing the sample in water for 1 to 7 days.

Microstructural observations of the composites were made using a JEOL JSM-6100 scanning electron microscope (SEM).  Observations of the dispersion of the cellulosic filler in

the polyolefin matrix were made using a Leitz Dialux 20 optical polarised microscope (OM), and of their interface using SEM.

*Table I:  Composition of the composites*

| **Composition** | | | | | |
|---|---|---|---|---|---|
| Sample | Cellulosic filler | Polyolefin | Graft polyolefin | Basic reactive filler | Other additive |
| C1 | 40% CF1 | 58% PP | 2% E43 | | |
| 2 | 40% CF1 | 53% PP | 2% E43 | 5% CaO | |
| 3 | 40% CF1 | 48% PP | 2% E43 | 10% CaO | |
| C4 | 40% CF1 | 53% PP | 2% E43 | | 5% EPR |
| C5 | 40% CF1 | 48% PP | 2% E43 | | 10% EPR |
| C6 | 40% CF1 | 53% PP | 2% E43 | | 5% $CaCO_3$ |
| 7 | 40% CF3 | 53% PP | 2% E43 | 5% $Al_2O_3$ | |
| 8 | 40% CF3 | 48% PP | 2% E43 | 10% $Al_2O_3$ | |
| 9 | 40% CF3 | 48% PP | 2% E43 | 5% CaO | |
| 10 | 40% CF3 | 43% PP | 2% E43 | 10% CaO | |
| C11 | 40% CF3 | 58% PP | 2% E3015 | | |
| C12 | 40% CF3 | 53% PP | 2% E3015 | 5% CaO | |
| C13 | 40% CF3 | 48% PP | 2% E3015 | 10% CaO | |
| C14 | 40% CF1 | 58% PP | 2% E3003 | | |
| C15 | 40% CF1 | 43% PP | 2% E3003 | 10% CaO | 5% EPR |
| 16 | 40% CF9 | 58% PP1 | 2% E43 | | |
| 17 | 40% CF9 | 48% PP1 | 2% E43 | 10% CaO | |
| 18 | 40% CF9 | 48% PP1 | 2% E43 | 5% CaO | 10% GF/PP |
| C19 | 30% CF8 | 68% PP6100SM | 2% E43 | | |
| 20 | 40% CF9 | 48% PP6100 SM | 2% E43 | 10% CaO | |
| C21 | 40% CF9 | 48% PP HMI | 2% E43 | 10% CaO | |
| 22 | 40% CF9 | 48% HMI | 2% E43 | 10% CaO | |
| 23 | 40% CF10 | 48% HMI | 2% E43 | 10% CaO | |

Interaction between the basic reactive filler and the graft polyolefin was studied by means of transmission infrared spectroscopy at room temperature on a Nicolet Magna 860 Fourier transform instrument at a resolution of 4 cm$^{-1}$.

Flexural properties (ASTM D790) were measured using a bending test where the sample length was 12.5 mm, the test speed was 1.3 mm/min, and the span was 48 mm.  Impact resistance (ASTM D256) was evaluated using an un-notched IZOD impact test.  All tests were conducted at ambient temperature.  To evaluate the resistance to humidity, samples were immersed in water for different periods of time between 1 and 7 days and then tested.

## Results and Discussion

With reference to Table II, comparing sample C1 to samples 2 and 3 illustrates that cellulose-filled thermoplastic composites (ex. 2 and 3) have significantly improved mechanical properties over a similar comparative composite (ex. C1) which does not have a basic reactive filler (e.g. CaO).  Furthermore, the level of improvement provided by composites in this work is superior when compared with the results reported in reference 17.

Comparing examples 2 and 3 to comparative examples C4, C5 and C6, it is also evident that the use of a basic reactive filler (e.g. CaO) provides more significant improvement in tensile and flexural properties than the use of an impact modifier (e.g. EPR) or a simple filler (e.g. CaCO3) in a similar composite.

As evidenced by examples 7 and 8, the use of $Al_2O_3$ as the basic reactive filler also leads to significant improvement in flexural properties and impact resistance of the composite.  Although the level of improvement to flexural properties and impact resistance is not as high as with CaO, the use of $Al_2O_3$ provides more improvement in tensile strain at break than CaO.  Thus, the use of CaO or $Al_2O_3$ will depend on the specific application to which the composite will be put.

Similar results were obtained using different cellulosic fillers and recycled polypropylenes, for example, samples 3, 10, C13, C15, 17, 20, C21, 22, and 23.

Referring to examples 9 and 10, it is evident that increasing the amount of CaO from 5 wt% to 10 wt% results in no reduction in mechanical properties (except for tensile strain at break), but rather results in a great improvement in mechanical properties.  Additionally, even when the amount of CaO is 15 wt%, there is no reduction in such mechanical properties.  This is in contradiction with reference 17, which teaches that the amount of CaO needs to be controlled carefully and kept small or there will be a reduction in the mechanical properties of the composite.

Comparative examples C11, C12 and C13 illustrate that the presence of CaO in a composite containing E3015 (acid number < 35 mg KOH/g) as coupling agent provides significant improvement to mechanical properties when CaO is 5 wt%, but that the improvement becomes negligible as the amount of CaO is increased beyond 5 wt%.  This illustrates that the balance between the amount of basic reactive filler in the composite and the acid number of the graft polyolefin is an important consideration in respect of improvements to the mechanical properties of the cellulose-filled thermoplastic composite.

The importance of balance between the amount of basic reactive filler and acid number of the graft polyolefin is further illustrated by examples C14 and C15 in which E3003 was used.  E3003 has an even smaller acid number than E3015.  While there is a small improvement in modulus with the addition of CaO, there is a significant reduction in both strength and impact resistance at all levels of CaO in the composite.

Example 17 illustrates that similar improvements to mechanical properties resulting from the approach presented here can be obtained using hardwood sawdust and another type of recycled polypropylene.  In addition, example 18 illustrates that the addition of glass fiber can

further increase the mechanical properties, especially the strength and impact resistance.

*Table II:  Mechanical properties of the composites*

| Sample | Tensile Properties | | | Flexural Properties | | | Impact |
|---|---|---|---|---|---|---|---|
| | Young's Modulus (MPa) | Stress (MPa) | Strain at Break (%) | Elastic Modulus (MPa) | Stress (MPa) | Strain (%) | Impact Resistance (kJ/m$^2$) |
| C1 | 4180 | 34 | 2.2 | 2036 | 50 | 4.8 | 8.9 |
| 2 | 5100 | 34 | 1.9 | 2420 | 52.1 | 4.1 | 9.8 |
| 3 | 5511 | 37.8 | 1.7 | 4243 | 68.3 | 2.7 | 10.6 |
| C4 | 4297 | 30.5 | 2.6 | 1921 | 46.5 | 5 | 10.2 |
| C5 | 3662 | 28.5 | 3.3 | 1834 | 44.5 | 5.4 | 11.2 |
| C6 | 4654 | 35.2 | 2.1 | 2368 | 54.5 | 4.3 | 10.1 |
| 7 | 4275 | 33.2 | 3.4 | 3460 | 58.1 | 3.2 | 11.2 |
| 8 | 4220 | 33.3 | 3.6 | 3397 | 57.9 | 3.2 | 11.1 |
| 9 | 4933 | 35.6 | 3.1 | 3914 | 61.2 | 2.8 | 10.2 |
| 10 | 5157 | 35.6 | 2.6 | 4252 | 62.5 | 2.6 | 10.4 |
| C11 | 3476 | 35.2 | 7.7 | 2482 | 62 | 5.4 | 15.67 |
| C12 | 4164 | 33.9 | 4.1 | 3210 | 59.3 | 3.6 | 13.0 |
| C13 | 4611 | 32.7 | 2.6 | 3752 | 58.1 | 2.9 | 10.1 |
| C14 | 3591 | 30.4 | 4.2 | 2664 | 57.7 | 4.4 | 11.03 |
| C15 | 4027 | 27.8 | 2.8 | 2967 | 51.4 | 3.4 | 8.85 |
| 16 | 3288 | 24.1 | 3.5 | 2580 | 44.3 | 3.5 | 7.6 |
| 17 | 4305 | 28.8 | 2.2 | 3432 | 52.0 | 2.7 | 4.5 |
| 18 | 4361 | 30.6 | 2.8 | 3657 | 54.3 | 2.9 | 10.0 |
| C19 | 3372 | 23.9 | 3.7 | 2202 | 41.7 | 6.1 | |
| 20 | 4627 | 34.2 | 2.3 | 3806 | 61.6 | 2.7 | 5.9 |
| C21 | 2619 | 24.9 | 3.0 | 2021 | 45.9 | | |
| 22 | 2923 | 25.2 | 2.3 | 2635 | 45.4 | | |
| 23 | 2903 | 23.5 | 3.1 | 2161 | 43.1 | | |

The type of polypropylene used must also be considered. Virgin polypropylene leads to higher mechanical properties compared to recycled polypropylene as illustrated by comparing examples 17 and 20.

For a virgin PP with very high melt index and low performance, similar improvements in the mechanical properties by using CaO have also been obtained (C21 & 22).  However, it also needs to be stressed here that sample 23 has the same components and formulation as sample 22, except that 22 was made from dried wood (<2% moisture) whereas 23 was made from wet wood (17.5% moisture).  From the 10 wt% CaO and the water content of the wood in 23, the calculated water content of the wood must be less than 5 wt% as requested in reference 17.  As

indicated in Table II, the mechanical properties of the sample 23 are poorer than those of 22 and have no significant improvement compared with the C21.

Table III shows that the use of CaO can inhibit thermal degradation of the composites as reflected by the higher temperatures at a weight loss of 10 wt% ($T_{10\%}$) and 20 wt% ($T_{20\%}$) and the weight loss at 500°C as measured by TGA. As CaO absorbs humidity in the wood to transform to $Ca(OH)_2$, at high temperature it will release $H_2O$, therefore its presence should slow down the burning process.

*Table II!: Thermal properties of the composites*

| | | Thermal properties | |
|---|---|---|---|
| | $T_{10\%}$ (°C) | $T_{20\%}$ (°C) | Weight loss at 500°C (wt%) |
| C21 | 334 | 364 | 91 |
| 22 | 346 | 398 | 73 |

Table IV provides the results of water absorption tests on various cellulose-filled thermoplastic composites. Amounts in the composition are given in weight percent based on the weight of the composite. Example numbers starting with the letter 'C' are comparative examples.

*Table IV: Water absorption of the composites*

| | | Water absorption | | |
|---|---|---|---|---|
| | Composition | Water Absorption (%) | | |
| | | 24 h in water | 24 h in water, 24 h in air | 7 days in water |
| C100 | | 0.6 | 0.35 | 1.85 |
| C101 | 40% CF1 + 56% PP 2% + 2% E43 + 2% SA | 0.4 | 0.25 | 0.95 |
| C102 | 40% CF1 + 58% PP + 2% E43 | 0.35 | 0.2 | 0.9 |
| 103 | 40% CF1 + 53% PP + 2% E43 + 5% CaO | 0.55 | 0.25 | 1.25 |
| 104 | 40% CF1 + 48% PP + 2% E43 + 10% CaO | 0.55 | 0.3 | 1.45 |

It is evident from Table IV that even though a basic reactive filler such as CaO is present in the composite in amounts as high as 10 wt%, the extent of water absorption can be kept low, which is in contradiction to the teachings of reference 17. Furthermore, the mechanical properties of the composites of examples 103 and 104 remained unchanged even after conditioning in water up to 7 days.

FT-IR studies (not shown here) confirmed that a chemical reaction had taken place between the maleic anhydride group of E43 and the basic reactive filler (CaO or $Al_2O_3$) during extrusion of the cellulose-filled thermoplastic composites. This can explain the synergistic impact of these two ingredients on the mechanical performance.

## Summary and Next Steps

The results show that the presence of basic oxides like CaO and $Al_2O_3$ has significantly improved the mechanical performance of the wood 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 MAgPP E43 provides a better advantage since it has a higher mobility to impregnate the wood particle surface. The loss in mechanical properties resulting from the short-chain molecules of E43 is limited by the presence of basic oxide fillers. Besides the reinforcing effect, these fillers can react with the MA group of E43 to increase the effective molecular weight of the E43, thus improving the composite performance.

The presence of basic oxide fillers should improve the flame resistance and decay resistance. Further experiments involving these aspects are under consideration.

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