Mechanical Properties Evaluation of a Recycled Flax Fiber-reinforced Vinyl Ester

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ABSTRACT: Flax fiber–vinyl ester composites are milled and mixed with virgin matrices to produce recycled composites. The effect of this powder incorporation on the mechanical properties of a thermosetting matrix (vinyl ester) and a thermoplastic matrix (polypropylene) is studied.

In the case of thermosetting matrix, flexural and tensile strength decrease with the addition of powder. For filler contents higher than 50 vol%, the strength reaches a constant value. Flexural and Young's moduli remain constant for different powder contents.

In the case of thermoplastic matrix, strength and modulus decrease when powder is replaced by fibers. Both, fibers and powder act as reinforcement as moduli increase. Impact properties are improved with the addition of powder and fibers in comparison with the pure matrix.

KEY WORDS: natural fibers, recycling, composites, vinyl ester, mechanical properties.

INTRODUCTION

THERE EXIST PROBLEMS in the disposal of end-of-life composites. The best disposal method is discussed in [1,2]. In the case of plastic materials, there are three available methods: landfills, biodegradation, and recycling. Each one has its own disadvantages. Plastics were put into landfills like many other materials. The increasing use of plastics, and the growing contamination stimulated the search for recycling and other disposal methods. Composite materials tend to be regarded as nonrecyclable and much of the waste currently produced is ultimately sent to landfill for disposal [3]. The reasons that

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natural products cannot replace the synthetic polymers are technical, economic, and humanitarian. Even though only a small fraction of plastics is present in the waste from the cities, it takes so many years for the complete biodegradation of these materials. Most of the polymers cannot degrade naturally by light, oxygen, water, or microorganisms, because of their carbon chains and lack of chromophores, and the energy content in plastics is wasted during the biodegradation process. Incineration can be another method of using the energy involved in plastics, but the emission of dioxin into the air is a disadvantage of such a procedure.

Recycling can be performed in different ways for thermoplastic polymers: (i) as materials by remelting or reshaping, (ii) as raw materials by degradation to monomers or petrochemicals [4].

Thermosetting composites is one of the materials that cannot be used for remelting or reshaping, but it is one of those especially interesting cases to study to use the scrap from processing or production.

Polymer matrices and composites can typically be recycled by three methods: chemical [5,6], powder production [7], or energy production. Chemical recycling includes processes like pyrolysis in which the material is heated to produce one or more recoverable substances. Powder production refers to processes in which thermosetting composites can be mechanically milled into particles that can be used later as filler in a new composite. Energy production is based on the possibility of incinerating the material to recover energy from its organic portion. Chemical recycling and powder production are the most suitable methods for recycling thermosetting matrix composites because these materials have a low organic content and produce low energy.

The product of milling in particle recycling can be used as filler in thermosetting or in thermoplastic matrices. For example, the automotive industry produces reinforced parts together with scrap. This scrap can be reused by milling it and making compound parts by compression molding (bulk molding compound). The other possibility is to sell this material to the thermoplastic composite industry.

The aim of this work is to determine the feasibility of recycling of a thermosetting composite material.

MATERIALS AND METHODS

Vinyl ester resin Derakane 411-350 from the Chemical Company Dow kindly supplied by Poliresinas San Luis, Argentina was used. The resin was reinforced with 30 vol% of flax fiber mat. Finflax (Finland) supplied the flax fiber. The plaques were fabricated by vacuum infusion. All plaques were postcured in an oven at 140°C for 120 min. A Perkin Elmer differential scanning calorimeter (DSC) was used in order to verify the complete curing of samples. A run was performed from 25 to 250°C at a heating rate of 10°C/min, under nitrogen. Specimens of 1 cm width were cut and then these small pieces were milled to get a powder. The milling machine used was a Janke and Kunkel – IKA. Tyler series sieves were used to separate the powder. The number of the sieves was 7 and they were put on a vibrator machine for 10 min.

Polypropylene Eltex-P HV200 from Solvay was used as the thermoplastic matrix. Polypropylene (PP) was mixed with 30 wt% of reinforcement. Samples were made by the combination of different amounts of flax fiber pulp and powder in the following relations (powder/fiber): 0/30, 10/20, 20/10, and 30/0. The polymer and the fibers were mixed in

an intensive mixer at 180°C for 15 min. The pellets were compression molded into thick plaques at 180°C and 500 MPa and then rapidly cooled down with running water. In order to release thermal stresses generated during molding, the plaques were annealed in an oven for 1 h at 100°C.

The same vinyl ester resin (Derakane 411-350) was used as thermoset matrix for the composites. Vinyl ester resin (using 2 wt% MEKP hardener, without any initiator) was mixed with different amounts of powder: 30, 50, 60, and 70 vol%. The mixtures of polymer and powder were prepared using an intensive mixer at room temperature. Due to the time required for mixing, it was not necessary to use any initiator. Hence the catalyst would be thermally activated during the high-temperature molding process. The mixed materials were compression molded into thick plaques at 80°C and 450 MPa for 60 min.

Flexural tests were performed on cut specimens from thermosetting composites of dimensions $11 \times 3 \times 80\,mm^3$ at a crosshead speed of 2 mm/min and a span value of 50 mm, according to ASTM 790-92. Tensile tests were carried out on specimens of dimensions $15 \times 3 \times 120\,mm^3$. The calibrated length was 50 mm and the crosshead speed was 2 mm/min, according to ASTM D D3039-00. A mechanical extensometer was used to record the actual elongation during the test.

Tensile dumbbells of thermoplastic composite specimens of 3 mm thickness and 10 mm width were machined from compression molded plaques. Tensile tests were performed according to ASTM D638-93 at a crosshead speed of 5 mm/min. A mechanical extensometer was used to record the actual elongation during the test. Flexural tests were done at a crosshead speed of 1.3 mm/min in accordance with ASTM D-790-92 on specimens of dimensions $15 \times 3 \times 80\,mm^3$, cut out from the plaques. The distance between supports (span) was 50 mm.

All these tests were carried out at room temperature on an Instron dynamometer 4467.

Puncture tests were conducted on disk samples of 90 mm diameter cut out from thermoplastic compression molded plates according to ASTM D256-84. These tests were performed in a falling weight Fractovis of Ceast at 3.5 m/s using the minimum striker mass (3.6 kg).

An optical microscope Olympus SZH10 was used to study the fiber dimensions and fiber aspect ratio (length/diameter) reduction during intensive mixing. The same microscope was used to study the fracture surface of thermoplastic composites. Fibers length distribution after intensive mixing was measured on isolated fibers after removal of the matrix by Soxhlet extraction at 180°C using xylene as the solvent.

RESULTS AND DISCUSSION

Milling Time for the Powder Preparation

In order to select the most efficient milling time, the size distribution of the powder was studied as a function of milling time using three different times. Figure 1 shows the results of this study. It can be seen, from this figure, that for milling times greater than 20 min, the powder size does not decrease any further. Due to this experimental observation, the milling time was set as 20 min. The resultant powder had cured resin particles and defibrillated fibers.

The energy consumption of this process is about 4.5 kW per kilogram of powder. The powder was sieved and the fraction larger than 840 μm was excluded (≈4 wt%).

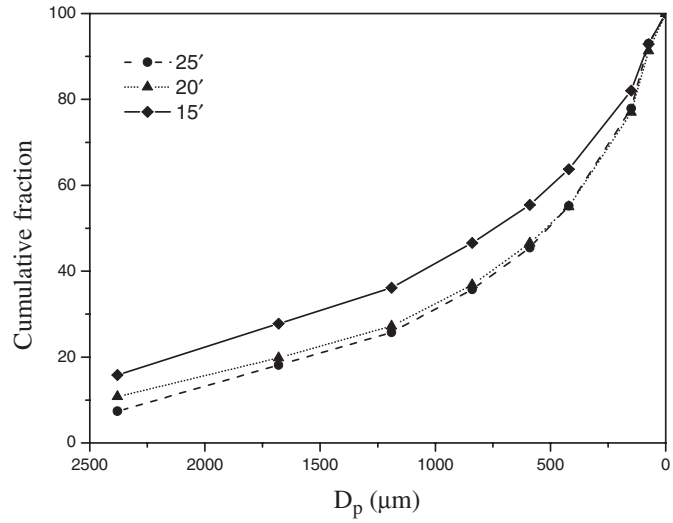

Figure 1. *Cumulative fraction vs particle diameter for different milling times: 15, 20, and 25 min.*

Table 1. Average fiber dimensions after milling obtained by optical microscopy.

Fiber	Average value
Length (μm)	201.86
Diameter (μm)	21.32
l/*d* (aspect ratio)	9.47

The average diameter (weight) was 220 μm. The average values of powder fibers dimensions after milling, obtained by optical microscopy, are shown in Table 1.

Thermosetting Composite Materials

Figure 2 shows the fiber length and diameter distribution in the powder fibers before and after mixing with the resin. The aspect ratio (length/diameter) increased from 9.47 (Table 1) to 12.5 due to a larger reduction in diameter than in length during the mixing. The true stress–strain curves obtained in flexural and tensile tests for thermosetting composite material are shown in Figure 3(a) and (b). The nonlinearity of these curves can be related with toughening mechanism that acts in composite materials. The initial linear portion of these curves is related to the elastic behavior of the studied materials, the deviation from linearity is an indication of initial matrix cracking. The rest of the drops in the curve are an indication of progressive failure of fibers in the longitudinal direction (axial splitting) producing fibrillation, and the fracture of the fibers in the perpendicular direction (transverse microcracking) with respect to the applied load. A low fiber–matrix adhesion generates a poor interphase, which produces the sliding of the fiber into the matrix and pullout. A macroscopic failure occurs when the fibers fracture [8].

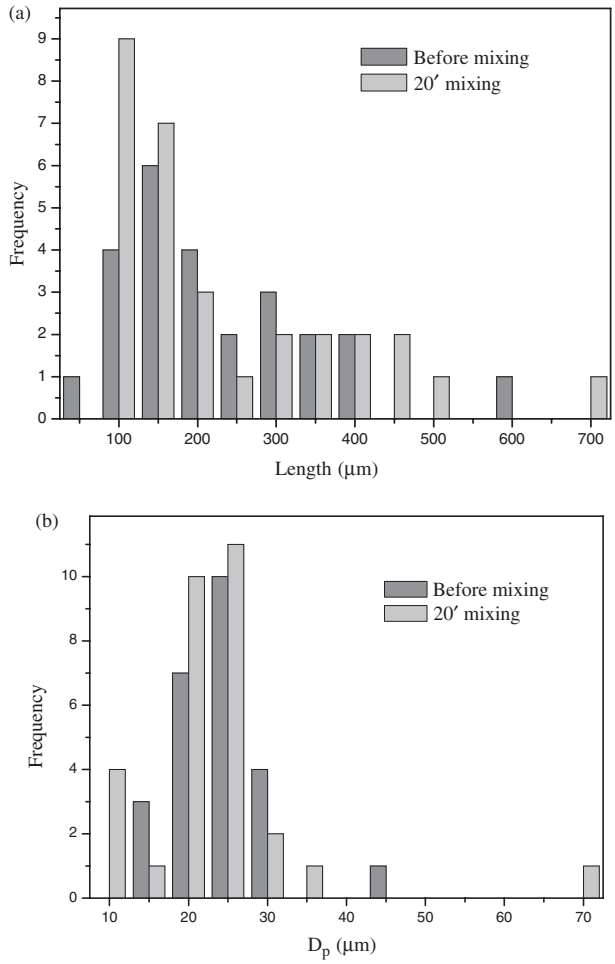

Figure 2. *(a) Fiber length distribution before and after mixing and (b) fiber diameter distribution before and after mixing.*

This nonlinearity tends to disappear when the powder content increases, because in this case the powder particles act as stress concentrators. These figures also show that elongation at break and displacement values decrease as the powder content rises.

In the case of tensile test, there is a significant difference between composites with 30 wt% of flax fiber mat and composites with 30 wt% of powder and it is related to the higher aspect ratio of mat fibers compared with powder particles and fibers in the powder [9].

Results of flexural tests are summarized in Table 2. It can be seen that the difference in strength between 30 vol% mat and 30 vol% powder composite is not important. This could be a consequence of the good compatibility between the vinyl ester resin and the vinyl ester cured particles that drives to a higher adhesion. This leads to the conclusion that the powder obtained by milling the original composites may have interesting commercial properties.

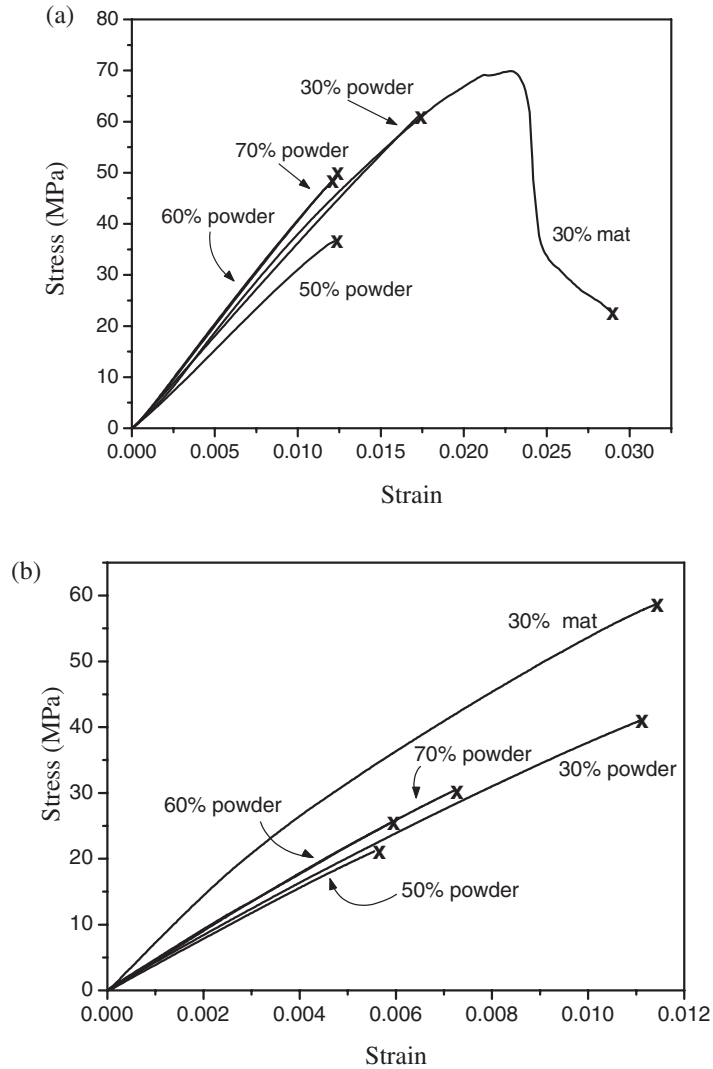

Figure 3. *(a) Flexural test results for thermoset composites based on vinyl ester with different powder content: 30, 50, 60, and 70 vol%, and a composite with 30 vol% of flax mat and (b) tensile test results for thermoset composites based on vinyl ester with different powder content: 30, 50, 60, and 70 vol% and also a composite made with 30 vol% of flax mat.*

On the other hand, as the powder content increases, the strength decreases due to dewetting and it may be due to the formation of a rigid interphase around the filler, which hinders the deformation. For filler contents higher than 50 vol%, flexural strength reaches a constant value of about 47 MPa. This result could be due to the reaching or overcoming of the percolation threshold for the crack propagation. When the percolation threshold is reached, particles are closer to each other and crack connectivity is higher, leading to easier crack propagation. The values obtained from the flexural modulus were similar for fiber and powder-filled composites for all filler contents studied in this work.

Table 2. Flexural and tensile results for thermosetting samples.

Filler (vol%)	Flexural tests (ASTM D790-93)			Tensile tests (ASTM D3039-00)		
	σ (MPa)	*E* (GPa)	*d* (mm)	σ (MPa)	*E* (GPa)	ε (%)
30% mat	71.1 ± 6.8	4.00 ± 0.60	3.20 ± 0.16	57.5 ± 1.6	6.88 ± 0.17	1.15 ± 0.08
30% powder	63.5 ± 4.4	3.65 ± 0.08	2.41 ± 0.12	38.7 ± 4.9	3.98 ± 0.11	1.00 ± 0.14
50% powder	46.7 ± 2.2	3.95 ± 0.32	1.53 ± 0.07	22.6 ± 1.8	3.97 ± 0.02	0.60 ± 0.02
60% powder	48.8 ± 3.1	4.12 ± 0.14	1.72 ± 0.11	27.9 ± 3.1	4.52 ± 0.08	0.65 ± 0.07
70% powder	49.0 ± 4.0	4.08 ± 0.21	1.53 ± 0.18	30.0 ± 1.4	4.64 ± 0.17	0.68 ± 0.07

Table 2 also shows the mechanical properties obtained from the tensile tests. The strength shows the same behavior as in flexural tests. Tensile modulus is higher than the flexural modulus. This is due to the shear deformation of the flexural modulus, so that, the flexural testing tends to underestimate the elastic modulus. Young's modulus is higher for the mat-reinforced vinyl ester than for powder-reinforced vinyl ester. Mat presents a higher aspect ratio than the powder material. This result can be explained in terms of the higher load transfer from the resin to the reinforcement in the first case. For different powder contents, the modulus values were similar.

Thermoplastic Composite Materials

Two different initial fiber lengths – short fibers (average length: 2.31 cm) and long fibers (5.94 cm) – were used, which correspond to the fiber lengths before intensive mixing process. Therefore, the real fiber size (diameter and length) distribution will be different after this process. Figure 4 shows the fiber length and diameter distribution after intensive mixing in composites with 30 wt% flax fibers. The average short fiber length was 1.34 ± 0.48 mm, and the average long fiber length was 3.19 ± 0.73 mm, with an aspect ratio of 15.8 and 35.1, respectively.

Figure 5 shows the stress–displacement curves obtained in flexural tests for PP matrix and different composites. It can be clearly seen from this figure that flexural strength is higher for long fiber composite than for short fiber composite and 30 wt% powder composites. This result can be explained in terms of the difference in the aspect ratio. As expected, long fibers have the highest aspect ratio and it leads to composites with higher mechanical properties [10].

Figure 6 shows the true stress–strain curves obtained in tensile tests for composites based on PP matrix and different powder to fiber ratios. Table 3 summarizes the results obtained from flexural and tensile tests in the case of thermoplastic composites. It can be seen that the tensile strength decreases as the fiber (regardless of its length) is replaced by powder. This result is also based on the difference in the aspect ratio of both fillers. Similar results are observed for Young's modulus.

The optical micrographs from the fractured surface of composites are shown in Figure 7(a) and (b). These figures reveal the existence of holes close to the powder particles and where one particle was included. In the case of 30 wt% of powder, the surface is plenty of holes. On the other hand, in the case of 30 wt% of fibers there are more fibers than voids. For composites with both, powder and fibers, there were holes and fibers in different ratios.

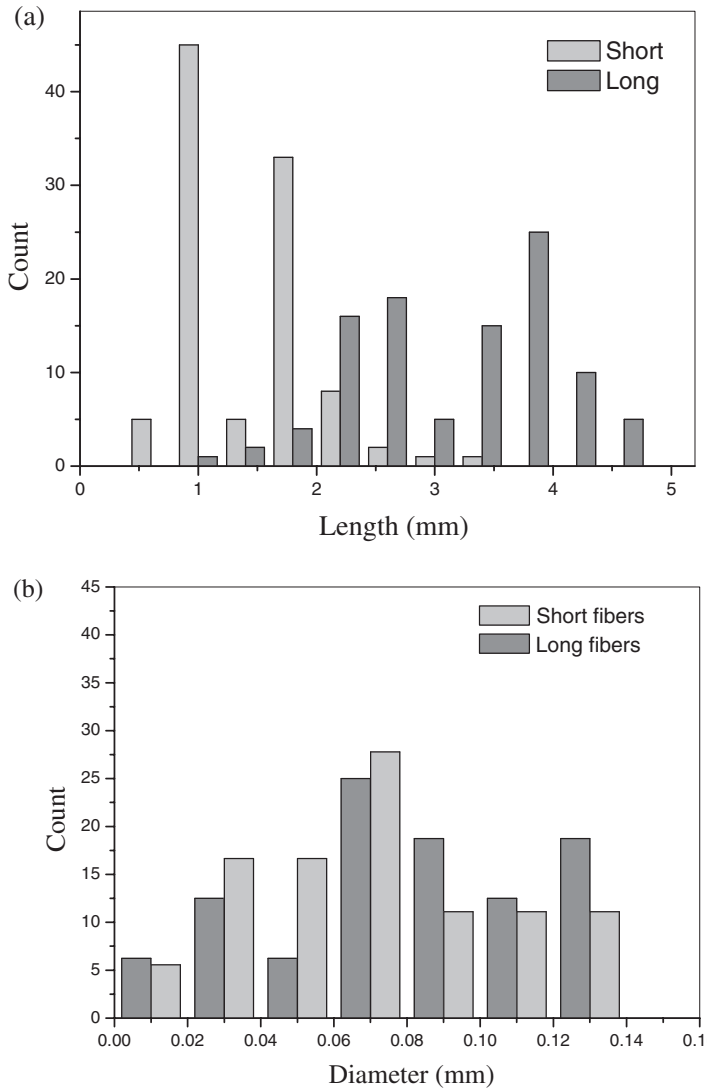

Figure 4. *(a) Fiber length distribution after intensive mixing in composites with 30 wt% flax fibers and (b) fiber diameter distribution after intensive mixing in composites with 30 wt% flax fibers.*

Figure 8 shows the load–displacement curves obtained in puncture test for some thermoplastic composites. Impact properties of the resultant material appear to be very poor. Many results were discarded. This figure shows the complete brittle failure. There is no crack propagation zone and the ductility index (defined as the ratio between propagation energy and total energy) equals zero. It can also be seen that the increase in powder content leads to poorer results, as expected. Another important result is the decrease of impact energy when the powder content increases (Table 3).

Table 3 also shows the comparison between different PP-reinforced materials and the obtained results in this work. The sample with 20 wt% of powder and 10 wt%

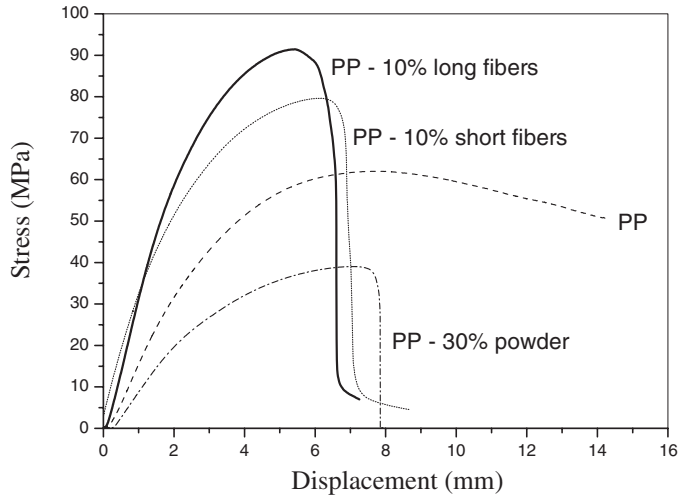

Figure 5. *Stress–displacement curves of composites based on PP and different powder to fiber ratios in weight: 30/0, 20/10 with long and short fibers obtained in flexural tests.*

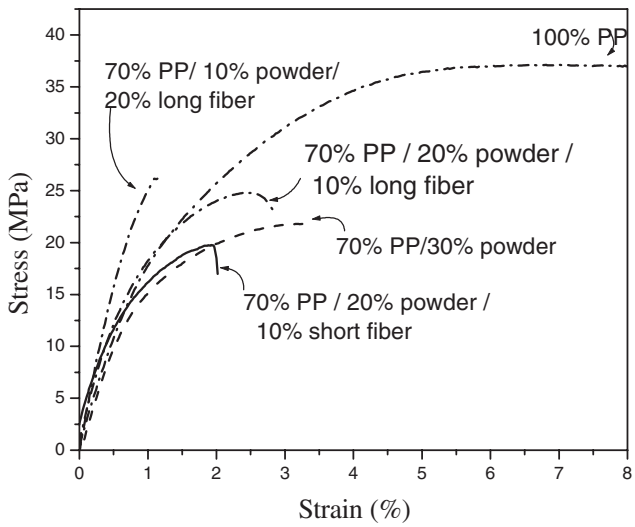

Figure 6. *True stress–strain curves obtained in tensile tests for composites based on PP matrix and different powder to fiber ratio (30/0, 10/20, 20/10).*

of fiber appears to have good mechanical properties, except for elongation at break values. The initial fiber length appears not to significantly influence the final properties, may be due to the reduction in length and diameter after processing. The powder obtained from milling of composite with 30 wt% of fiber mat could be used as filler material. In addition, impact property was found to increase, may be due to the dewetting process. The dewetting is a micromechanical deformation process that consumes energy [11]. However, a maximum value was found for 20 wt% powder and 10 wt% fibers; for higher content of

Table 3. Summarized results of this work and comparison with other composites.

Property	Tensile modulus (GPa)	Tensile strength (MPa)	Tensile elongation (%)	Flexural modulus (GPa)	Flexural elongation (%)	Impact energy (kJ/m)
100 wt% PP	2.1	36.9	8	1.60	61.30	0.35
70 wt% PP 30 wt% powder	2.2	21.2	3.26	1.98	41.45	0.66
70 wt% PP 20 wt% powder 10 wt% long fibers	2.5	23.8	2.2	1.93	44.95	1.17
70 wt% PP 20 wt% powder 10 wt% short fiber	2.5	21.5	1.85	2.03	40.16	1.19
70 wt% PP 10 wt% powder 20 wt% long fiber	3.0	26.1	1.15	2.35	26.59	0.74
PP 20 wt% talcum*	–	30	20	2.4	50	–
GMT*	5.5	80	1.6	5	120	–

*Reference: Ecofina web site.

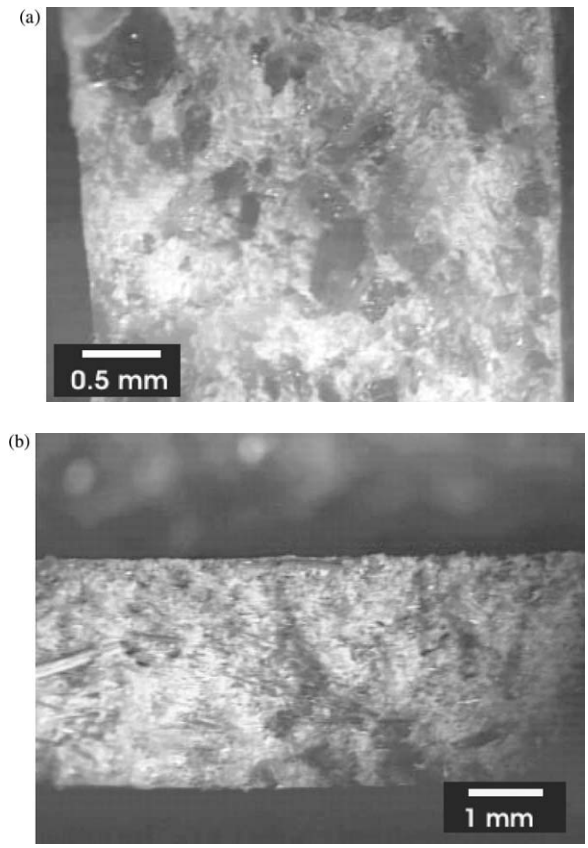

Figure 7. *(a) Optical micrograph of fracture surface of composites with 30 wt% powder and (b) optical micrograph of fracture surface of a composite with 30 wt% fibers.*

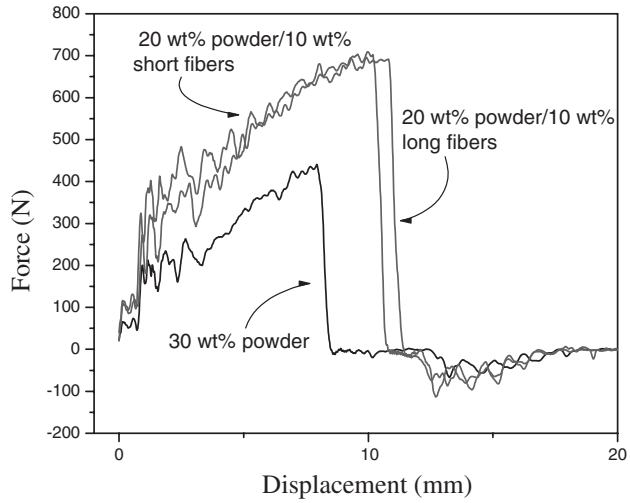

Figure 8. *Load–displacement curves obtained in falling weight test for thermoplastic composites based on PP and powder to fiber content with short and long fibers.*

fiber, the impact energy decreased and it could be due to the poor dispersion of the fibers in the composites.

CONCLUSIONS

Flax fiber–vinyl ester composites were milled and mixed with virgin matrices to produce recycled composites. The effect of this powder incorporation on the mechanical properties of a thermosetting matrix (vinyl ester) and a thermoplastic matrix (polypropylene) was studied.

For thermosetting matrix, it was shown that both flexural and tensile properties are lower than that of the original material (vinyl ester with 30 vol% fiber mat). These can be explained in terms of the stress concentration effect of the powder particles. For filler contents higher than 50 vol%, the strength reaches a constant value.

On the other hand, flexural and Young's moduli values did not change as the powder content increases.

For thermoplastic matrix, although the filler content was kept constant, it was shown that the strength decreases when the powder percentage increases in the filler. Both, fiber and powder act as reinforcement for the PP because their incorporation leads to a higher material modulus. Furthermore, the decrease in the reinforcement aspect ratio when fibers were replaced by powder drives to a lower modulus.

Finally, impact properties were improved with the addition of powder and fibers in comparison with the plane matrix.

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