Water absorption behavior of mechanically recycled PP and PA6 composites reinforced with natural fibers and glass fibers

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Abstract

The recyclability of natural fiber and glass fiber reinforced polypropylene composites and glass fiber reinforced nylon composites have been studied through injection molding and mechanical grinding. Mechanical properties of virgin and recycled composites were assessed through flexural, tensile, and impact tests. No significant degradation in the mechanical properties of natural fiber composites was observed after subjecting the composites through several rounds of recycling and water absorption at ambient temperature in tap water. However, severe degradation in the mechanical properties was observed for glass fiber composites. For instance, after five cycles of recycling, only 59% of flexural strength and 64% of flexural modulus was retained for glass fiber reinforced nylon composite. This is mainly due to severe attrition in glass fibers caused by recycling as evidenced by studies on fiber length distribution. Water absorption tests conducted at room temperature and subsequent environmental conditionings such as freeze-thaw cycling and extended freeze cycling only affected nylon composites. At saturation point, water absorption for nylon composites was 7.7% by wt. after 45 days of immersion, which significantly affected the mechanical properties. The tensile strength of the nylon composites reduced from 88.4 MPa to 36.2 MPa, and modulus reduced from 5.6 GPa to 1.8 GPa after saturation.

1. Introduction

The extensive use of thermoplastics and their composites in our society is causing growing concerns due to its adverse effects on our environment [1]. There are several ways to reutilize polymers for sustainable models such as reuse, chemical recycling, and mechanical recycling. Of these, the latter two are the most widely practiced methods of recycling [2]. This study focuses on the mechanical recycling of polymer composites with various mineral and natural fillers. In general, mechanical recycling includes regrinding and reprocessing the polymer composite to produce a new component. The main problem with this type of recycling includes degradation in mechanical properties due to the shortening of fibers, damage on the surface of the fiber, delamination on the wall of natural fiber, fiber-matrix debonding, thermomechanical degradation on coupling agent, and reduction in molecular weight [3]. Poor retention of mechanical properties leads to recycled material generally being downgraded for the next cycle of an application. Although there have been attempts to use additives to upgrade the mechanically recycled polymer composites [4].

In the automotive industry, the use of polymer composites continues to grow due to its contribution to lightweighting, which directly impacts fuel economy. Metal components in automotive vehicles are replaced by plastics or composites resulting in lightweight vehicles. A reduction in 10% weight leads to a 3% to 7% improvement in fuel efficiency [5]. High-density fillers such as glass fibers or minerals (talc, calcium carbonate) are generally used to reinforce the polymer matrix to improve the mechanical properties of the composite without sacrificing the overall cost of the component. However, mechanical recycling reduces the reusability of these composites. The length of the fiber, which directly relates to the improvement in the mechanical properties, is greatly reduced due to the brittle nature of glass fibers. Fiber attrition has also been observed in injection molded components where the fibers must navigate through thin and convoluted sections. Additionally, the reduction in the molecular weight of the polymer matrix due to thermomechanical degradation could further exacerbate the issue with recycling. In contrast to glass fiber reinforcement, composites reinforced with natural fiber exhibit very little to no changes in mechanical properties after recycling [6]. This is because natural fibers can withstand external mechanical forces and are less likely to break due to their complex internal compositions [6] [7]. Injection molding is a widely utilized manufacturing method for polymer composites in the automotive industry. The presence of a resin-rich layer at the surface of injection molded components protects the hydrophilic natural fillers from moisture intrusion.

In this study, various natural fiber and glass fiber composites are investigated for degradation in mechanical properties due to grinding and reprocessing, and the effect of recycling on water absorption behavior. Tensile tests, flexural tests, and impact tests were conducted to assess the mechanical properties of dry (control) and saturated specimens subjected to various hygrothermal conditions. To further investigate the cause of degradation in tensile and flexural properties, measurements of fiber length distribution are carried out.

2. Materials

Table 1 shows the list of composite materials considered in this study. There are three natural fiber reinforced composites, one hybrid composite, and four composites with mineral fillers (talc and glass fibers).

Table 1 Thermoplastic composites considered in the study

Notation	Matrix	Filler	Filler type
WF	PP Copolymer	20% Wood pine fiber	Natural fillers
RH	Recycled polyolefin (PP and PE)	10% Rice hull	
C20	PP	20% Cellulose	
CGF	PP	10% Cellulose 15 Long glass fiber	Hybrid
T40	PP Homopolymer	40% Talc	Mineral fillers
GB	PP	29% Talc 7% Glass bubbles 5% Short glass fiber	
GFC	Chemically coupled PP	30% Short glass fiber	
LGF	PP	30% Long glass fiber	
NGF	Nylon 6	15% Short glass fiber	

3. Experimental work

3.1. Sample preparation and recycling

Figure 1 shows the mechanical recycling process adopted in this study. During the first cycle, virgin pellets are fed into the injection molding machine to fabricate test specimens. A set number of specimens are collected for mechanical and physical characterization. The rest of the specimens are ground and then oven-dried at 105ºC for four hours. In the second cycle, the oven-dried pellets are injection molded and the process is repeated up to five cycles. All specimens were prepared via injection molding using the parameters presented in Table 2.

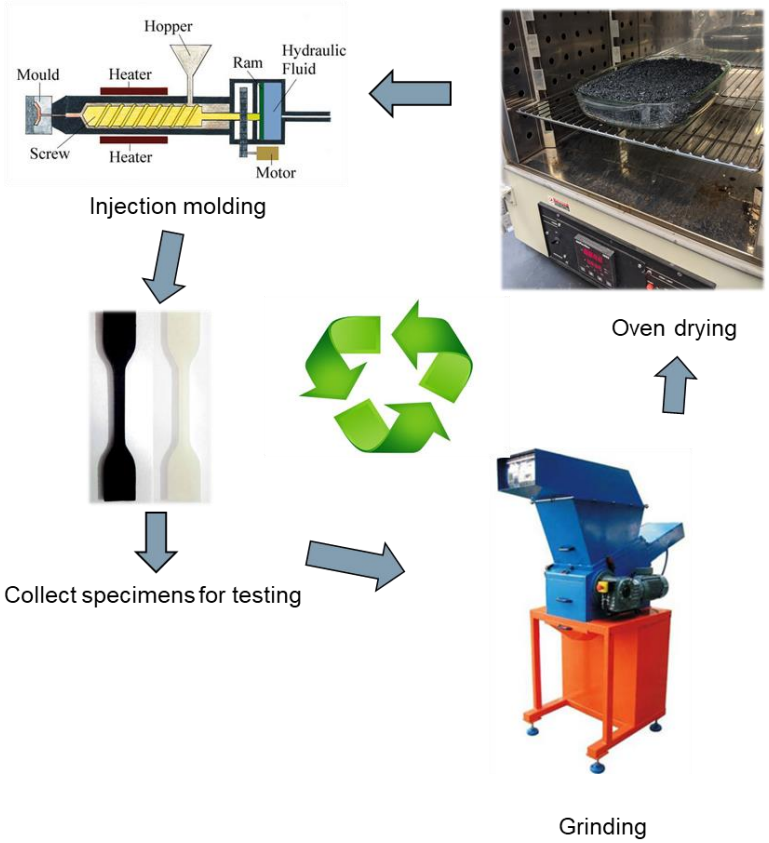


Figure 1 Recycling steps used in this study for thermoplastic composites

Table 2 Processing parameters for injection molding

Barrel temperature (from hopper to nozzle):	
PP composite	182, 188, 191, 193, 193°C
Nylon composite	238, 243, 246, 249, 249°C
Back pressure	689.5 kPa
Hold pressure	1999.5 kPa
Screw speed	70 rpm
Injection time	
Hold time	1 sec
Cooling time	25 sec
Total cycle time	
Mold temperature:	
PP Composites	29.4°C
Nylon composite	60°C

3.2. Water absorption tests

Before starting the water absorption tests, specimens were conditioned at 23°C and 50% relative humidity for at least seven days before taking the initial dry weight measurement. Water absorption

tests were carried out by immersing the specimens in tap water per ASTM D570. While immersing the specimens in water, spacers were kept between the flat surface of the specimens to allow water absorption. Absorption tests were performed on three sets of specimens for each type of composite at 23°C. Each set of specimen consists of seven specimens.

Weight measurements were taken after 1, 2, 3, 7, 14, and every two weeks thereafter until the specimens saturated. The procedure for taking readings for specimens immersed at 23°C is as follows: the specimens were taken out from the water one at a time, placed vertically to allow water to drain for 30 s, then surface moisture was wiped off, weight measurement was taken and the specimen is placed back in the water. Water absorption percentage was calculated by using the following equation:

$$\%M = \frac{M_{wet} - M_{dry}}{M_{dry}} \times 100$$

Where, %M is the percentage of water absorbed, M_{wet} is the mass of the specimen (g) subjected to water absorption for a certain time, M_{dry} is the initial dry mass (g).

3.3. Freeze-thaw exposure

Since these materials are to be used for exterior application, composite materials were subjected to freeze-thaw exposure. Following ASTM D7032, one set of specimens saturated at 23°C were subjected to -29°C for 24 h, followed by thawing at 23°C for 24 h. This completes one freeze-thaw cycle. Specimens were subjected to five such cycles. These specimens were subsequently conditioned at 23°C for at least seven days while immersed in water for the assessment of mechanical properties through tensile and flexural tests.

3.4. Re-drying

To determine mass loss due to water absorption, specimens saturated at 23°C were re-dried in an oven at 50°C. Specimens were periodically weighed until the average change in weight was less than 5 mg.

3.5. Mechanical tests

Instron Dual Column Universal Testing System (Model 3366) was used for both tensile and flexural tests. Tensile tests were conducted on Type V specimens (ASTM D638) at a loading rate of 5 mm/min until failure or up to a maximum engineering strain of 10%, whichever occurred first.

A 5 kN load cell was employed to monitor the force in the specimen and an extensometer was used to directly monitor the strain in the gage length. A 500 N load cell was used for quasi-static three-point flexural tests. Specimens were loaded at a strain rate of 5% per min until failure or up to a maximum strain of 5%, whichever occurred first. Calculation of strain was based on the deflection in the middle of the specimen monitored from the crosshead displacement of the machine per ASTM D790.

All the test specimens were conditioned at 23ºC for at least seven days. For instance, the specimens subjected to freeze-thaw cycling were conditioned by immersing them in water at 23°C for at least seven days before testing. While performing tests on wet specimens, the specimens were taken out of the water one at a time and weight measurements were taken following the procedure outlined earlier and placed in the Instron and tested.

Notched Izod impact testing was also conducted on the control specimen using a pendulum arm impact tester (Model 43-02-03) per ASTM D256. Specimen preparation included creating a standard type V notch using a notch cutter (Model TMI 22-05) on rectangular bars. At least ten specimens for each composition were tested where each specimen was clamped with a constant force.

3.6. Fiber length distribution measurements

Fiber length distribution of glass fiber composites is carried out by burning the specimen in an oven at 600ºC for 2 hours. The retracted fibers are then gently mixed in an acetone solution by pouring between two beakers for at least 5 minutes. Then the resulting solution is poured onto a glass plate and observed under a microscope once the acetone has evaporated.

For natural fiber composites, the fibers are extracted by dissolving the composites in Decalin. Small pieces of composites with Decalin are placed in a round-bottom flask, which is immersed in an oil bath heated at 150ºC. Mixing was carried out using a magnetic stirrer and a complete dissolution of the composites took place in 45 mins. The viscous mixture was then allowed to cool before diluting with acetone solution to be observed under a microscope.

4. Experimental results

4.1. Mechanical properties

4.1.1. Tensile properties

Tensile strength, tensile modulus, and strain to failure for control samples are presented in Figure 2. As expected, natural fiber-reinforced composites have the lowest tensile properties. Both wood fiber and rice hull reinforced composites did not fail within 5% strain, while all other composites failed below a tensile strain of 5%. The GB composite with talc, glass bubbles, and glass fiber was

found to be the most brittle one with a strain to failure of only 1.67%. Long glass fiber PP composite has the best overall tensile properties.

After recycling, there is a significant decrement in the tensile strength of glass fiber reinforced composites (Figure 3). Whereas, a marginal effect was found on natural fiber-reinforced composites or talc composite due to recycling. The effect of recycling on modulus is not as pronounced as strength. In general, strain to failure increases slightly with recycling. For nylon glass fiber composite, strain to failure after the fifth cycle is very high (~8%) compared to 2 – 2.5% for earlier cycles (Figure 3). This could be attributed to the moisture present in the nylon matrix in the later cycles, which act as a plasticizer. Yield stress decreases with water absorption due to an increase in chain mobility in the presence of water [8]. It is worth noting that no appreciable changes in appearance were observed after recycling. The least retention of properties for glass fiber reinforced composites was observed after five batches of recycling. Natural fiber-reinforced composites and talc reinforced composites were least affected by recycling with retention of more than 90% tensile strength property. Whereas, glass fiber reinforced composites have about 60-70% modulus property retention after five batches of recycling.

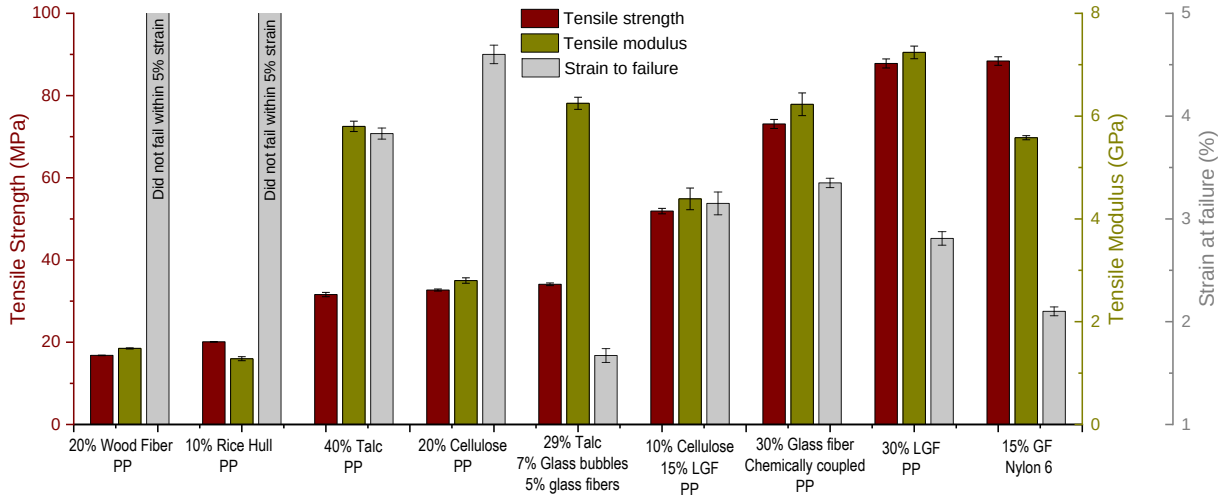


Figure 2 Tensile properties of control samples for thermoplastic composites

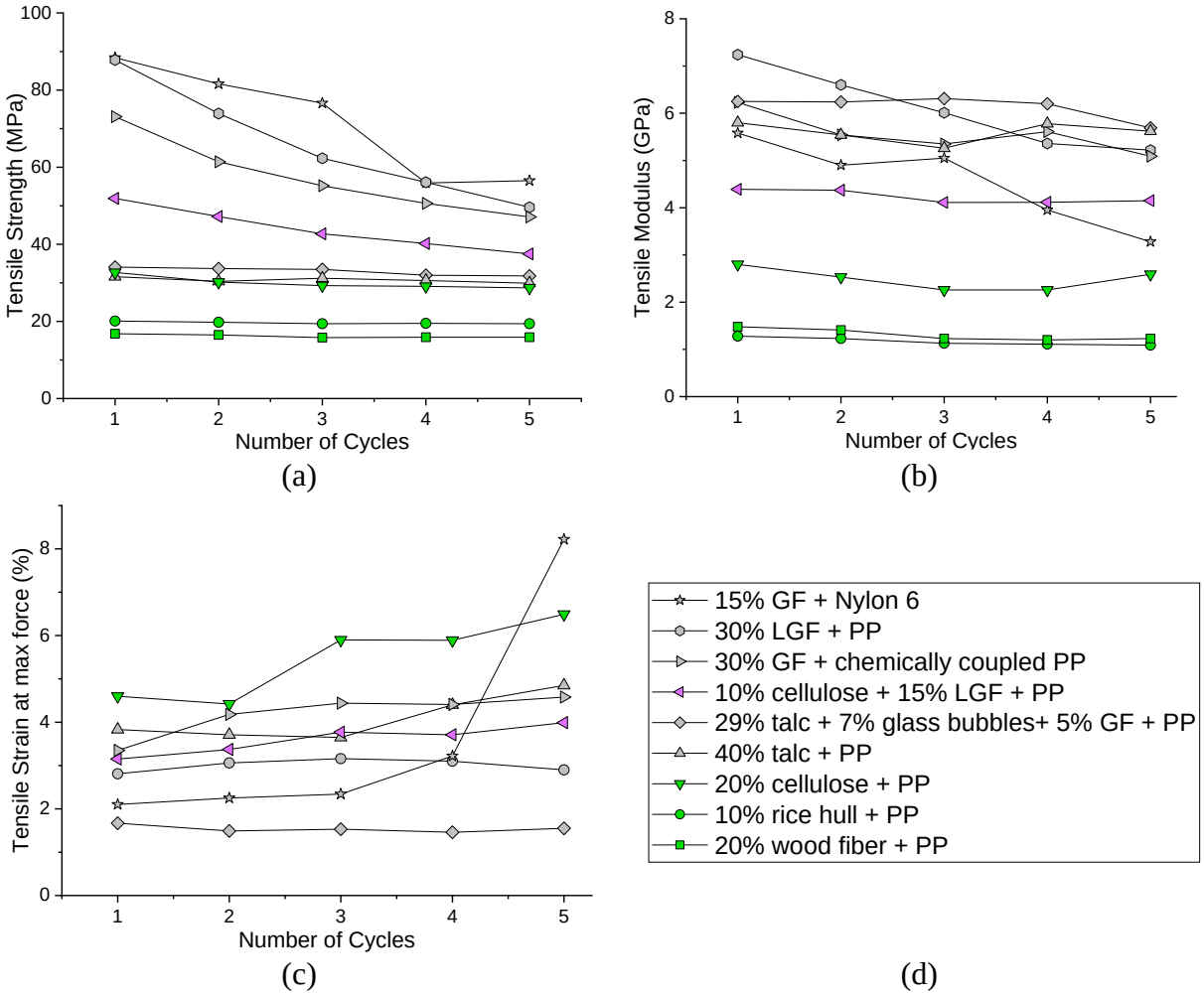


Figure 3 Thermomechanical degradation of tensile properties after mechanical recycling (a) tensile strength, (b) tensile modulus, (c) tensile strain at maximum force, (d) legend

4.1.2. Flexural properties

Results on the flexural properties of control samples are similar to the tensile properties. Long glass fiber composites have the overall best flexural properties (Figure 4). Whereas, natural fiber reinforced PP composites have the lowest flexural properties. Trends of decrement in flexural properties after recycling are also similar to tensile properties. A significant decrement was observed in the flexural strength of glass fiber reinforced composites, especially the ones with long glass fibers. A decrement in modulus is not as significant as flexural strength. Recycling has a marginal effect on natural fiber-reinforced composites or talc composite.

Similar to tensile properties, the least retention of properties was observed for glass fiber reinforced composites after five batches of recycling with retention of only 60-70% strength properties after

recycling (Figure 5). More than 90% of tensile strength property retention was observed for natural fiber-reinforced composites. Talc reinforced composites seem to be unaffected by recycling.

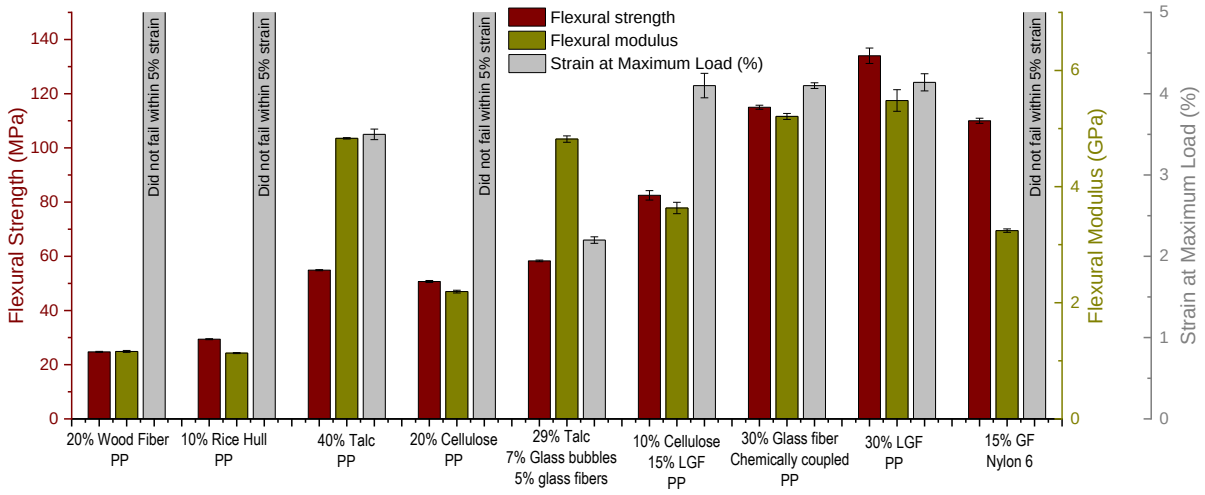
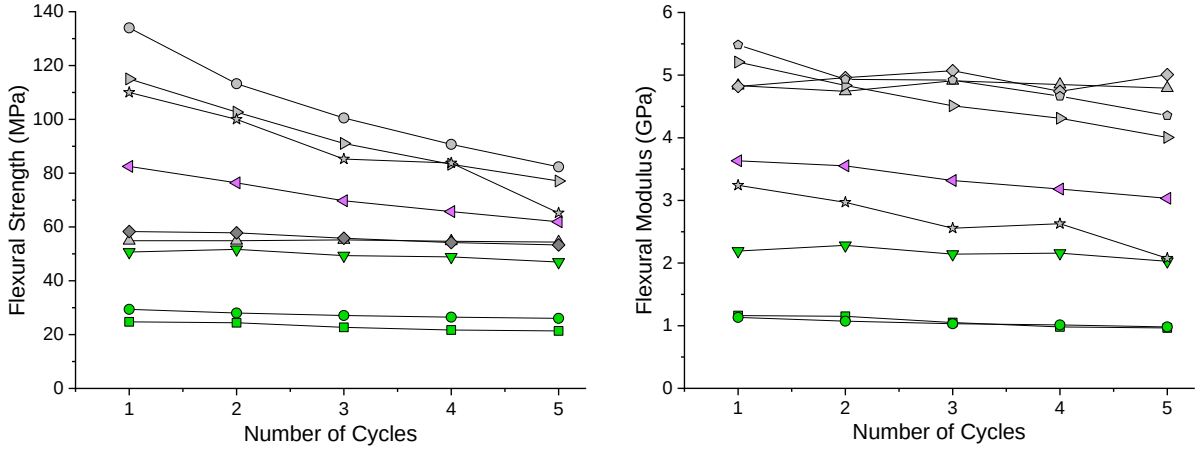
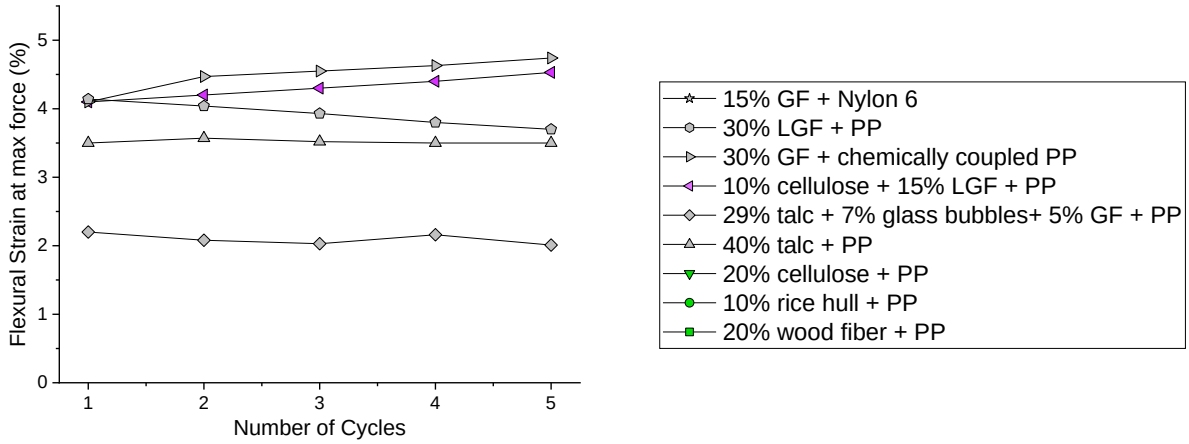


Figure 4 Flexural properties of control samples for thermoplastic composites





(c) (d)

Figure 5 Thermomechanical degradation of flexural properties after mechanical recycling (a) flexural strength, (b) flexural modulus, (c) flexural strain at maximum force, (d) legend

4.1.3. Impact properties

As expected, wood fiber and rice hull reinforced composites have the highest impact resistance and are least affected by recycling (Figure 6). Impact resistance of glass fiber reinforced composites is severely affected by recycling. For long glass fiber reinforced polypropylene composite, after five recycles, impact resistance is only 39% of the first cycle.

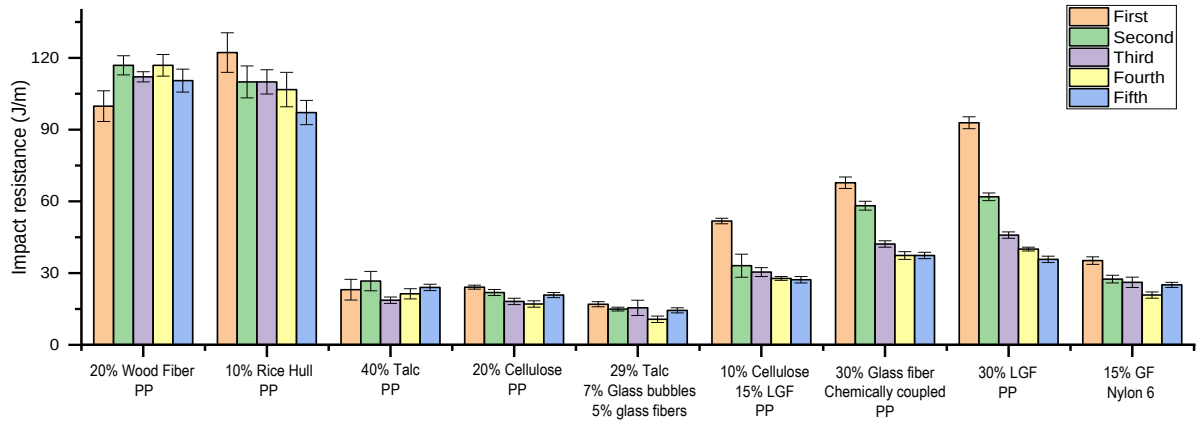


Figure 6 Degradation in impact properties after mechanical recycling of the composites

4.2. Water absorption tests

Only glass fiber reinforced nylon composites showed water absorption at 23ºC with the maximum intake being 6.5% to 7.7% (by wt.) at saturation. The percentage of water absorption at saturation decreased slightly with recycling. No dimensional instability (warping) or changes in physical appearance was observed for nylon composites after immersion in water. However, thickness swelling of about 6.5% was observed. All other composites did not absorb water even after 45 days of immersion.

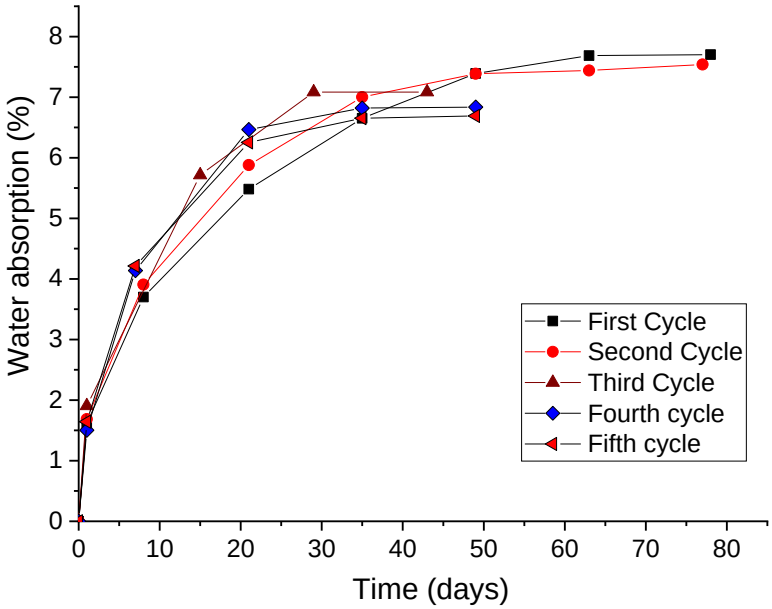


Figure 7 Water uptake (by wt.) for glass fiber reinforced nylon composites

4.3. Hygrothermal effects on mechanical properties

Strength and modulus properties decreased significantly after subjecting the saturated nylon composites to hygrothermal conditions. Subjecting saturated specimens to five cycles of freeze-thaw did not have any significant effect on the mechanical properties of the nylon composites. Water absorption had irreversible effects on the mechanical properties since they could not be completely regained after redrying the saturated specimens. Loss in mechanical properties is attributed to an increase in chain mobility in the presence of water. Under wet conditions, cellulose PP composites are better than glass fiber reinforced nylon composites (Figure 8).

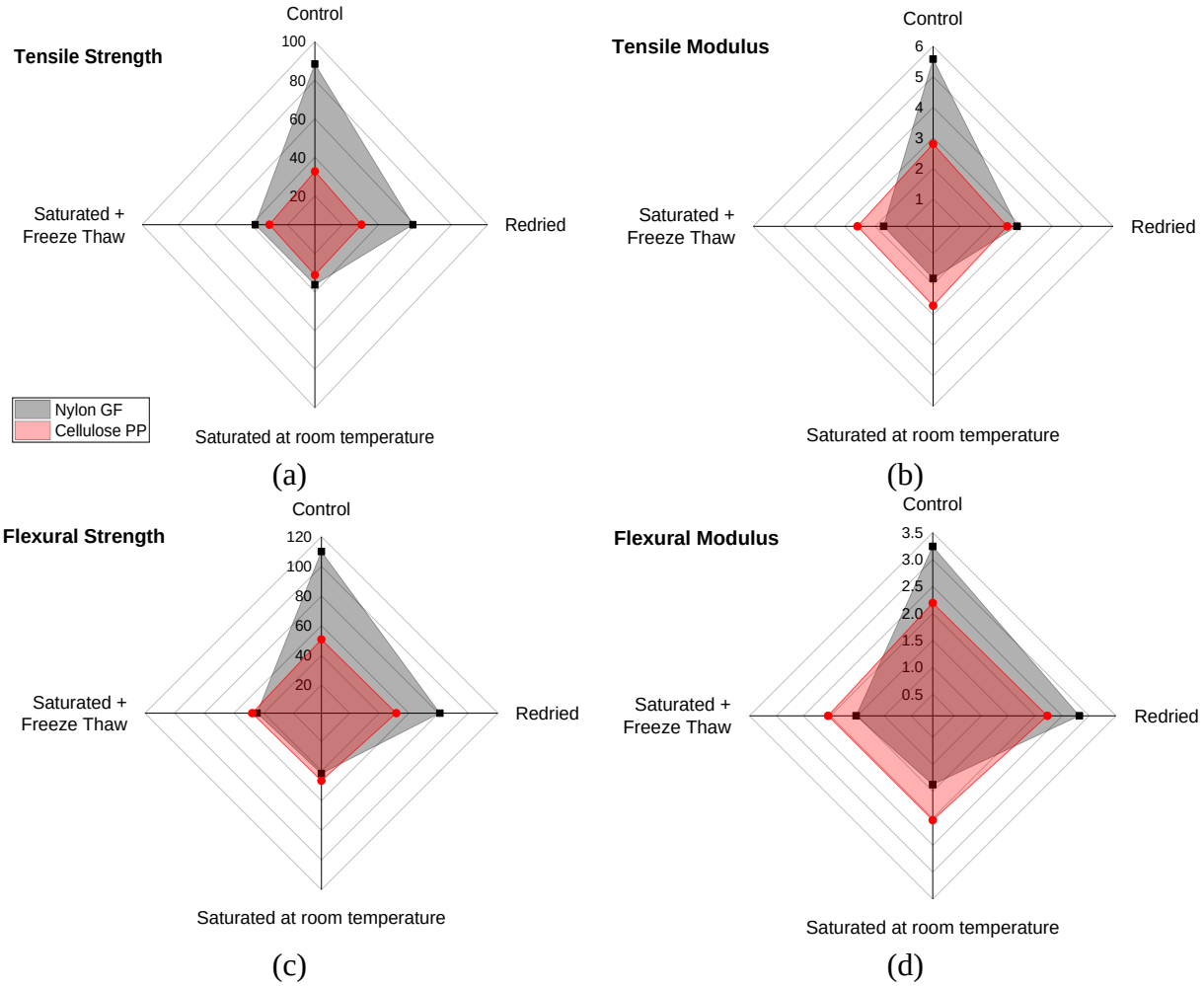


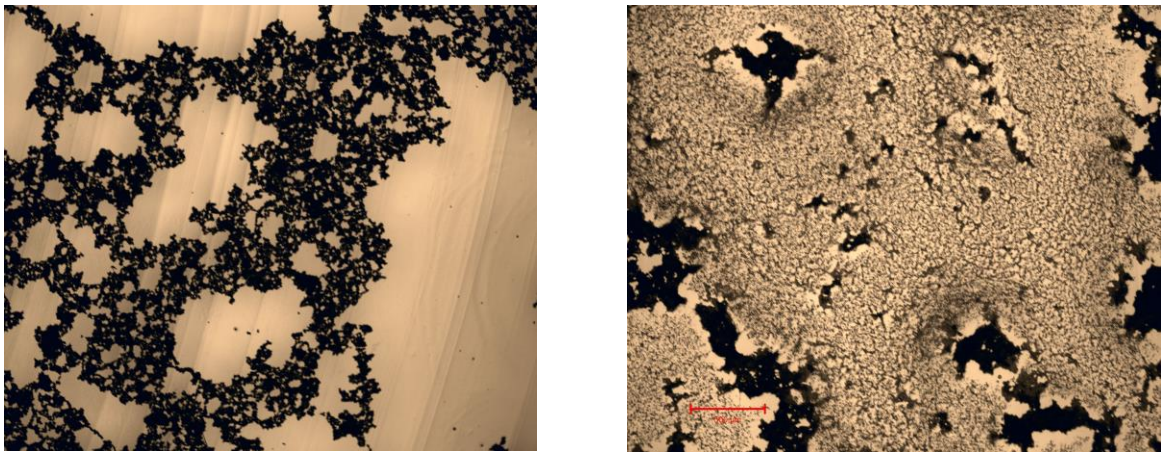
Figure 8 Comparison between hygrothermal effects on mechanical properties of glass fiber reinforced nylon composites and cellulose reinforced polypropylene composites

4.4. Fiber length distribution

The extraction of rice hull and wood fiber from the pellets show that the filler contents have been completely pulverized (Figure 9). The original size of both the fillers is 1-2 mm range before compounding. A separate study on the effect of Decalin on the filler at high temperature (150ºC) and shear-induced by magnetic stirrer show no alteration on the particle size. The cause of pulverization observed in the pellets can be attributed to the high shearing caused during compounding. This suggests that the natural fillers may not be contributing much to the increment in the mechanical properties of the composites. Improvements in the mechanical properties of natural fiber composites can be achieved by optimizing the processing parameters during compounding.

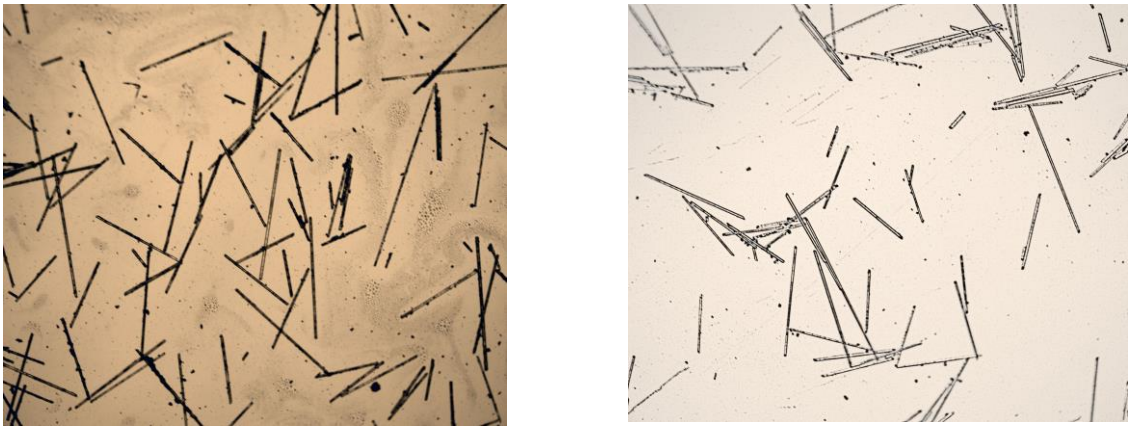
Figure 10 shows short glass fibers (GFC) and long glass fibers (LGF) extracted by burning the polymers. The short glass fibers were extracted from pellets as received. The average length of

GFC in the pellet form is 523 μm, whereas the original length of the fibers before compounding is 6 mm. Similarly, the average length of long glass fibers after the first cycle of injection molding is 706 μm, while the original length of LGF is 12 mm. Figure 11 and Figure 12 show that significant fiber attrition occurs after recycling and processing, which is the leading cause for the degradation in mechanical properties.



(a) (b)

Figure 9 Optical microscope images of (a) rice hull and (b) wood fiber extracted from as received pellets after Decalin treatment



(a) (b)

Figure 10 Optical microscope images of (a) short glass fibers and (b) long glass fibers extracted by burning as received pellets in an oven

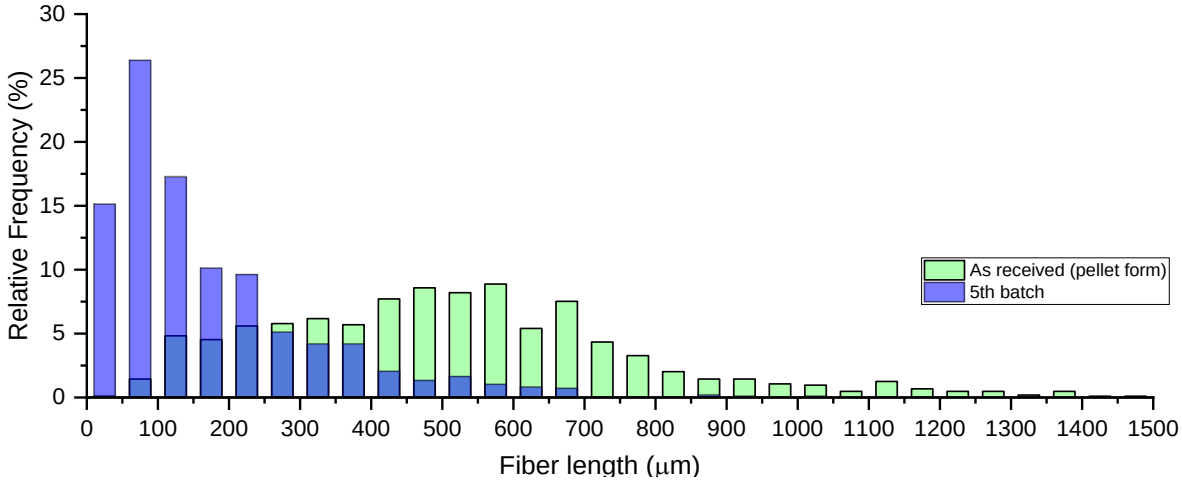


Figure 11 Fiber length distribution of short glass fibers from as received pellets and after 5th batch of recycling

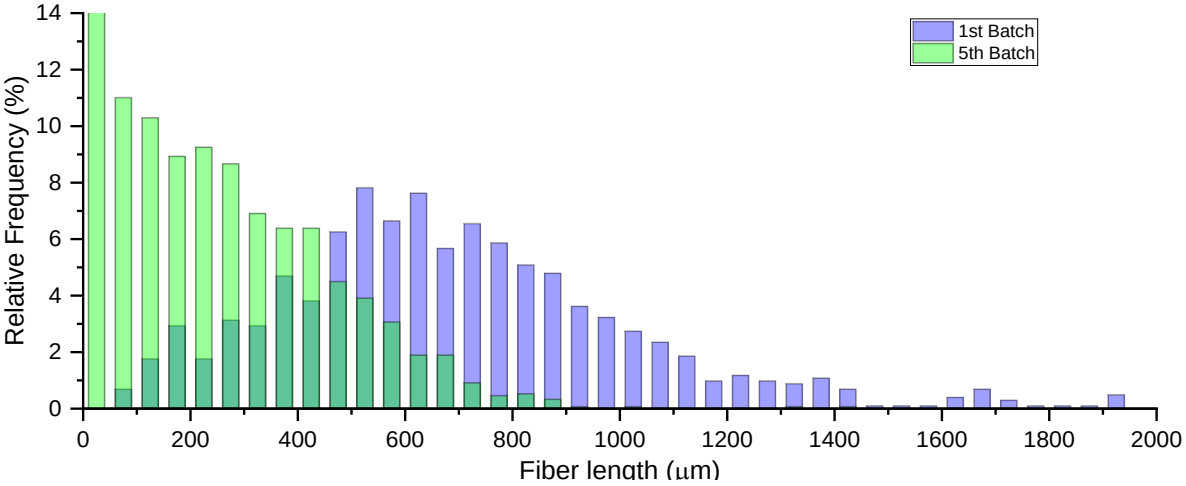


Figure 12 Fiber length distribution of long glass fibers from as received pellets and after 5th batch of recycling

5. Conclusions

Following are the conclusions drawn from this study:

- Effect of mechanical recycling (regrinding) on tensile, flexural, impact properties were studied on nine types of composites.

- Mechanical properties of natural fiber composites were not significantly affected by recycling retaining more than 90% of the original properties.
- Tensile and flexural strength properties of glass fiber reinforced composites were significantly affected by recycling retaining only 60-70% of the original values.
- Talc filled composites were unaffected by mechanical recycling.
- Impact properties of long glass fiber composite were also significantly affected, retaining only 39% of the original value after five batches of recycling.
- Only nylon composite was found to absorb water with 6.5% to 7.7% absorption at saturation.
- Cellulose composites were at par or better than nylon composites under wet conditions.
- Optical images of rice hull and wood fibers extracted from as received pellets show that the filler has been pulverized during the compounding process.
- Fiber length distribution of glass fibers shows significant attrition after mechanical recycling.

6. References

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