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RECYCLING OF THERMOPLASTIC COMPOSITES: QUALITY AND DURABILITY

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ABSTRACT

This paper describes the effects of reprocessing on the physical and mechanical properties of composites based on radiata pine *(Pinus Radiata*) fiber in a polypropylene (PP) matrix. Composites, containing 40 wt% fiber with 4 wt% maleated polypropylene (MAPP) as a coupling agent, were reprocessed up to eight times. Tensile strength (TS) and Young's modulus (YM) were found to decrease with increased reprocessing by up to 25% for TS and 17% for YM (after reprocessed 8 times). Hygrothermal ageing was also carried out by immersing specimens in distilled water at 50°C over a 9 month period. The diffusion coefficient of moisture absorption was obtained for composites by measuring water uptake of specimens at regular time intervals. It was found that the diffusion coefficient and the equilibrium moisture contents of composites decreased with increased number of times the materials were reprocessed. After hygrothermal ageing, tensile strength (TS) and Young's modulus (YM) of both virgin and reprocessed composites were found to decrease.

Keywords: Composites, Recycling, Weathering, Coupling Agent.

1. INTRODUCTION

It is estimated that globally, more than 6 million tonnes of polymer matrix composite products are manufactured each year, largely dominated by glass fibre reinforced polymers [1]. Furthermore, the amounts used are increasing annually. Concern for the environment, both in terms of limiting the use of finite resources and the need to manage waste disposal, has led to increasing pressure to recycle materials at the end of their useful life. In the metals industries, for instance, materials recycling operations are already well established and are driven by economics [2]. Polymers are generally more difficult to recycle and the economic incentives to recycle have been less favourable, particularly when waste disposal in landfills is relatively cheap. However, waste management is now a high priority within the European Union. As a consequence, it is already illegal to landfill composites waste in many EU countries. The "End-of-Life Vehicle Directive" (Directive 2000/53/EC) regulates the disposal of vehicles and the requirements include that from 2015, 85% of the weight of all "End-of-Life" vehicles must be re-used or recycled, a further 10% may be subject to energy recovery with a maximum of only 5% of the vehicle allowed to be disposed of in landfill. As vehicles have a life expectancy of more than 10 years, vehicles currently being manufactured must meet the 2015 requirements [2]. As a consequence of increasing legislation, there is a need for recycling routes to be established [2]. Although there are governmental regulations recycled materials are avoided, not only due to their physical properties, but mainly because of their surface appearance. Indeed, many designers are reluctant to use them as they can be rejected by the market. However, this is an attitude that can change, as demonstrated in Brazil where around 15% of all rigid plastics and films consumed, are recycled and returned to industry [3]. Some states in the US are also concerned with recycling. For example, in Michigan, the recycling rate is close to 100 % and proves the potential for recycling plastic waste as well as changes in market attitude [4].

One major factor determining the route for recycling of composites is whether the matrix is thermoplastic or a thermoset plastic. Thermoplastics can be melted and therefore lend themselves more readily to recycling by reshaping. Indeed, there is much interest in the area of thermoplastic matrix composites, particularly in the automotive area, due the readiness with which they are expected to be recyclable. Thermoset matrix composites are less obviously recyclable due to the inability to remould them. However, increased adoption of these materials, along with increased cost of landfill and the use of more expensive fibres than are commonly used in thermoplastics, in particular carbon fibre, has driven interest in re-use of these materials. Potential techniques that could be in used for these materials include mechanical break-down, thermal recycling as well as chemical recycling. Although these techniques could also be used for thermoplastic matrix composites, energy considerations would suggest remoulding to be a much more desirable option. Due to the ability to melt thermoplastics, mechanical break-down into granules for use in the original processing stream is the most obvious technique for recycling fiber reinforced thermoplastics. However, for fiber reinforced thermoplastics, fiber breakage induced by grinding and subsequent processing (e.g. injection moulding) leads to reduction of material properties. For these reasons, recycling by dissolution of the polymer matrix, often at elevated temperatures has also been considered. The simplicity of mechanical recycling and its relatively low cost give it the greatest potential, particularly for short fiber reinforced thermoplastics, for which fiber breakage during reprocessing has a lower impact on reinforcing properties than for long fiber reinforced plastics [5].

No post-consumer based recycling studies have been carried out on agro-based fiber composites [6] but there have been a number of studies on reprocessing. Agro-based fibers are less brittle and softer than glass fibers and are therefore more likely to retain properties during recycling. Bourmaud and Baley [7] compared reprocessing of hemp and sisal with glass fiber reinforced polypropylene (PP) composites. They observed reduction of both tensile strength (TS) and Young's modulus (YM) for all composites, with greater reduction found for glass fiber reinforced PP (about 52% for TS and 40% for YM) than PP reinforced with sisal (17% for TS and 10% for YM) or hemp (13% for TS and 1% for YM) after being reprocessed seven times. Walz et al. [8] studied reprocessing of 50 wt% kenaf fibre reinforced PP composites. Both tensile and flexural properties were found to decrease (by about 20%) with increased number of times the materials were reprocessed (up to nine times). A similar trend was shown by Joseph et al [9] for 20 wt% sisal fibre/LDPE matrix composites.

Cellulose fibres contain many hydroxyl groups (-OH) and readily interact with water molecules by hydrogen bonding. In contrast to glass fibres, where water adsorption only occurs at the surface, cellulose fibres can interact with water throughout their bulk. Moisture penetration into composite materials occurs by three different mechanisms. The main process consists of diffusion of water molecules inside the microgaps between polymer chains. The other mechanisms are capillary transport into the gaps and flaws at the interfaces between fibres and polymer because of incomplete wettability and impregnation, and transport by microcracks in the matrix, formed during the compounding process [10]. The capillary mechanism involves the flow of water molecules into the interface between the fibres and the matrix. It is particularly significant when the interfacial adhesion is weak and when the debonding of the fibres and the matrix has started. In addition, transport by microcracks includes the flow and storage of water in the cracks, pores or small channels in the composite structure. These imperfections can be originated during the processing of the material or due to environmental and service effects. The diffusion coefficient is the most important parameter for water absorption as this shows the ability of solvent molecules to penetrate inside the composite structure. Over short times, such that $M_t/M_\infty \leq 0.5$, the following equation can be used to determine the diffusion co-efficient [11]:

$$\frac{M_t}{M_\infty} = \frac{4}{L}\left(\frac{D}{\pi}\right)^{0.5} t^{0.5} \tag{1}$$

where M_t is the moisture content at time t, M_∞ is the moisture content at the equilibrium, L is the thickness of the sample and D is the diffusion coefficient. D, can be obtained from the slope of the linear part of the plot of Mt versus the square root of time t.

It is difficult to entirely eliminate the absorption of moisture in composites without using expensive surface barriers [12]. Good wetting of the fibre by the matrix and adequate fibre–matrix bonding can decrease the rate and amount of water absorption in the interface region of the composite [13]. Optimization of interfacial adhesion between cellulose-based fibres and thermoplastics has been the focus of a large amount of research conducted during the last two decades [14]. Coupling agents in wood fibre reinforced plastic composites play an important role in improving compatibility and adhesion between polar wood fibre and non-polar polymer matrices by forming bridges of chemical bonds between the fibre and the matrix. So far, more than forty coupling agents have been used in production and research. Among them, maleated polypropylene (MAPP) is the most popular one [15]. Several authors have investigated hygrothermal ageing of natural fibre composites. Panthapulakkal et al. [16] studied water absorption of agro-residue reinforced high-density polyethylene composites and found the tensile strength and Young's modulus to decrease despite the presence of compatibilizers. Espert et al. [17] found that the water absorption of natural fibre/PP composites followed the kinetics of a Fickian diffusion process, where the kinetic parameters are influenced by the fibre content, the type of matrix and mainly, the temperature by means of the Arrhenius law. Mechanical properties were found to be dramatically affected by water absorption. Prior to this current study, fibre content had already been optimised (from 30, 40 and 50wt%) to give the highest composites tensile strength [18] and Maximum tensile strength of composites was found for 40 wt% fibre content with 4 wt% MAPP. In this study, effects of reprocessing on the mechanical and hygrothermal behavior was studied.

2. MATERIALS AND METHODS

2.1 Materials

Radiata pine (Pinus Radiata) bleached wood fiber (Kraft) was supplied by Tasman Pulp & Paper Co Ltd, New Zealand. The average fiber length was 2.36 mm and the fiber diameter was 25 µm. The lignin content of the fiber was zero. The matrix polymer was a standard polypropylene (PP) powder with a density of 0.9 g/cc supplied by the Aldrich Chemical Company, Inc and MAPP (AC 950P) with a saponification value of 35-40 mg KOH/g, a density of 0.93 g/cc and free maleic anhydride content of less than 0.5% was supplied by Honeywell international, Inc, USA.

2.2 Methods

Composite fabrication: Composites were fabricated with

40 wt% fiber with MAPP and PP using a TSE-16-TC twin-screw extruder with a 15.6 mm screw blade diameter at 180oC (maintaining 5 different temperature zones 100, 130, 160, 180 and 175oC from feed zone to exit die) and a screw speed setting of 100 rpm. Prior to extrusion, wood fiber, PP and coupling agent were dried in an oven at 80oC for a minimum of 48 hours. Following extrusion, the material was pelletised into lengths of less than 5 mm and injection moulded into specimens for tensile and 4-point bend testing using a BOY 15-S injection moulder. Specimens for tensile testing were randomly selected from approximately one hundred and fifty of each type to evaluate the mechanical properties. The remaining specimens were granulated and injection moulded. Again specimens were randomly selected from these recycled reprocessed materials for physical and mechanical property evaluation. The procedure of injection moulding and granulation was repeated for a total of eight times.

Water absorption: Water absorption studies were performed following the ASTM D 570-98: Standard Test Method for Water Absorption of Plastics. Six specimens of tensile and bending from every batch were submerged in distilled water at 50^{o}C. The specimens were removed from the water after certain periods of time, weighed in a high precision balance to find the amount of water taken up and then resubmerged in water.

Tensile testing: Tensile testing was carried out according to the ASTM 638-03: Standard Test Method for Tensile Properties of Plastics using an Instron-4204 tensile testing machine fitted with a 5 kN load cell operated at a cross-head speed of 5 mm/min. An Instron 2630-112 extensometer was used to measure the strain. Six specimens were tested for each batch with a gauge length of 50 mm.

Digital microscopy: Following mounting, grinding and polishing, the fiber distribution and alignment of the fiber in the composites was observed using an Olympus B X 60 microscope.

Scanning Electron Microscopy (SEM): The fractured surfaces of the tensile test specimens were examined using a Hitachi S-4000 field emission scanning electron microscope, operated at 5 kV. Samples were mounted with carbon tape on aluminium stubs and then sputter coated with platinum and paladium to make them conductive prior to SEM observation.

Extraction of fiber from composites: Fiber was extracted by dissolving the matrix in hot xylene at 110oC followed by soxhlet extraction in xylene for 72 hours.

Fiber length measurement: The length and fiber distribution of virgin and extracted fiber from the composites was measured using a Kajaani FS-200 electronic sequential fiber analyzer. Fiber count of about 15,000-20,000 was used to determine the fiber length distribution.

Thermogravimetric analysis (TGA): Thermogravimetric analysis was carried out using a TA Instruments n SDT 2960 Simultaneous DTA-TGA in air (flow rate 150 ml/min) with a heating rate of 10oC/min. The temperature range scanned was from 25oC to 600oC. The weights of all specimens were approximately 10 mg. Alumina open crucible was used for sample holding..

Differential scanning calorimetry *(DSC)*: DSC was carried out using a TA Instruments DSC 2920 Differential scanning calorimeter in air (flow rate 50 ml/min) with a heating rate of 10oC/min. The temperature range scanned was from 25oC to 200oC. The weights of all specimens were approximately 10 mg. Aluminium open crucible was used for sample holding.

3. RESULTS AND DISCUSSION

3.1 Effects on Reprocessing

Reprocessing was carried out for 40 wt% fibre (with 4 wt% MAPP) reinforced composites. Very little change on TS and YM was found for PP during reprocessing Figs 1 and 2).

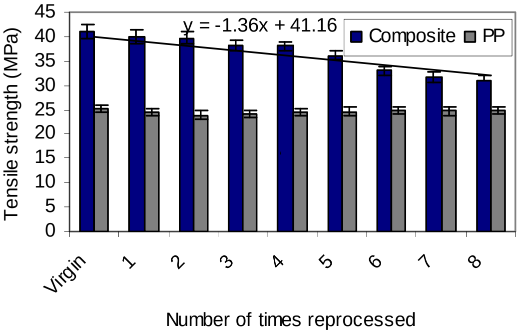


Fig 1. Tensile strength versus number of times reprocessed.

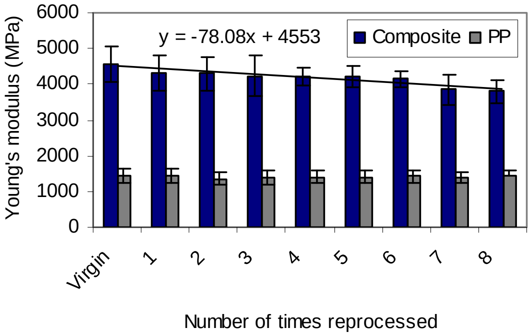


Fig 2. Young's modulus of composites versus number of times the materials were reprocessed.

The TS and YM of composites decreased with increased number of times the materials were reprocessed in a linear fashion. The virgin composites showed an average TS of 41 MPa and YM of 4553 MPa which reduced after being reprocessed 8 times to 31 MPa and 3800MPa respectively.

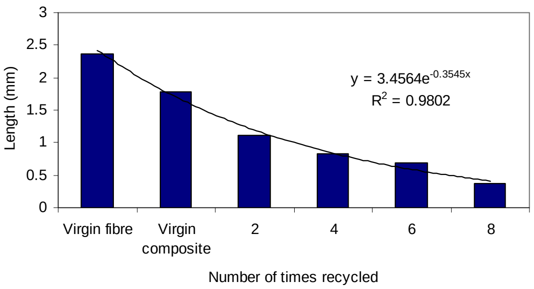
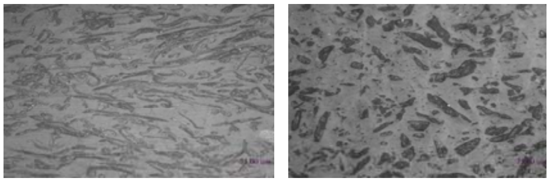


Fig 3. Weighted average fibre length of virgin fibre and the fibre extracted from composites.

One of the reasons for the changes in mechanical properties is likely to be due to the fact that reprocessing resulting some fibre damage. The average fibre length was found to decrease from 2.36 mm for virgin fibre to 0.37 mm for the fibre extracted from the 40 wt% fibre composites reprocessed 8 times (Fig. 3). The shorter fibre lengths and the increased fines percentage with reprocessing were also observable by light microscopy (Fig 4). The reductions of fibre length would be expected to reduce reinforcing efficiency, leading to the observed reduction in TS, YM.



Virgin 8 times reprocessed

Fig 4. Fiber distribution in virgin and reprocessed composites.

3.2 Durability of Reprocessed Composites

Moisture absorption increased with increased soaking time for virgin and reprocessed composites until saturation at about 5 months (Fig. 5).

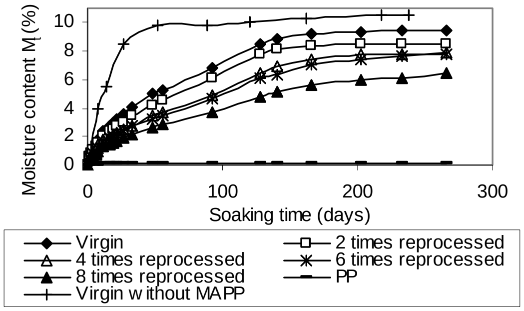


Fig 5. Moisture content of composites and PP versus hygrothermal ageing time.

As no significant weight gain was found for PP during this period, it seemed likely that moisture only penetrated into the composites through the fiber and fiber matrix interface. Both the equilibrium moisture content and diffusion coefficient decreased with increased number of times the materials were reprocessed respectively from 9.42% and 2.54x10-13 m2/s for virgin composites to 6.41% and 1.01x10-13 m2/s for composites reprocessed 8 times (Table 1).

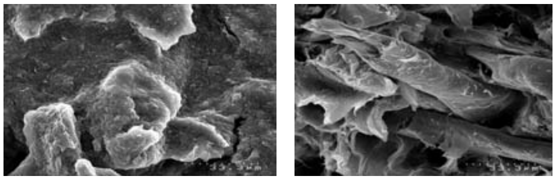
Table 1: Equilibrium moisture content and diffusion coefficient of virgin and reprocessed composites (with and without MAPP).

Composites	Equilibrium moisture content M∞(%)	Diffusion coefficient D (m2/s)
Virgin Without MAPP	10.51	5.70x10-13
Virgin (with 4 wt% MAPP)	9.42	2.54x10-13
2 times reprocessed	8.46	1.53x10-13
4 times reprocessed	7.93	1.19x10-13
6 times reprocessed	7.75	1.10x10-13
8 times reprocessed	6.41	1.01x10-13

The decrease in moisture content and diffusion coefficient with increased number of times the materials were reprocessed was explained by a number of effects. As the fiber length decreased with increased number of times the materials were reprocessed, it was considered that it would have been more difficult to form finite clusters which serve as passages for water molecules to travel through the lattice from one side to another. Also, reduction of micro-voids as evaluated by the increased density of composites with increased reprocessing would be expected to result in a decrease in moisture content and diffusion coefficient.

Table 2: Mechanical properties of 40 wt% fiber virgin (with and without MAPP) and reprocessed composites (made with 4 wt% coupling agent) before and after ageing.

Composites	TS (MPa)		YM (MPa)	
	Unaged	Aged	Unaged	Aged
Without MAPP	23	17.5	3619	1226
With 4 wt% MAPP	41	27.7	4553	2734
2 times reprocessed	40	26.3	4295	2776
4 times reprocessed	38	25.2	4215	2847
6 times reprocessed	33	23.5	4148	3002
8 times reprocessed	31	22.7	3800	2769



a) Unaged b) Aged

Fig 6. Effects of hygrothermal ageing showing SEMs of a) fracture surface of an unaged virgin composite, b) fracture surface of an aged virgin composite.

TS and YM after have been observed to decrease after hygrothermal ageing for virgin and reprocessed composites (Table 2) and it can be seen that the extent of reduction in properties decreased with increased number of times the materials were reprocessed. After ageing, reductions in TS of 33% and YM of 40% were found for virgin composites compared to reductions for both TS and YM of 27% for composites reprocessed eight times. This was considered to be due to the equilibrium moisture content decreasing with increased number of times the materials were reprocessed, and therefore having less effect on behaviour. Degradation of fibre and fibre matrix interface bonding was highlighted to explain the physical and mechanical properties of composites (Fig. 6).

3.3 Effects of Recycling on Thermal Stability

The melting temperature (Tm) of PP in composites was found to be reduced slightly from 171oC for virgin composites to 167oC for composites reprocessed eight times which was considered to be due to reduced molecular weight as a consequence of thermo-mechanical degradation and chain.

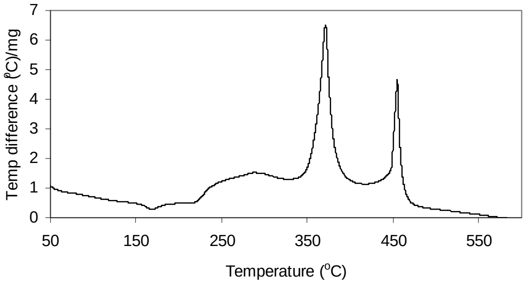


Fig 7. DTA trace of virgin composite.

Three stages of decomposition have been observed for virgin and reprocessed composites (Fig. 7), starting with dehydration and decomposition of volatile components at around 250°C, followed by rapid weight loss for oxidative decomposition and finally slow decomposition corresponding to formation of char as the temperature increased. Kinetic parameters for the various stages of thermal degradation were determined from the TGA graphs using the following equation, given by Broido [19].

$$\ln\left(\ln\frac{1}{y}\right) = -\frac{E_a}{RT} + \ln\left(\frac{RZ}{E_a\beta}T_m{}^2\right) \qquad (3)$$

where y is the fraction of nonvolatilized material not yet decomposed, Tmax is the temperature of maximum reaction rate, β is the heating rate, Z is the frequency factor and Ea is the activation energy. Initially, plots of lnln(1/y) versus 1/T for various stages of decomposition were drawn and found to be linear, suggesting good agreement with the Broido equation. The activation energies, Ea determined from the slopes of these plots are given in Table 3.

Table 3: Thermal properties of composites

Type	Stage	Wt. loss (%)	Temp. range (oC)	Tmax (oC)	Ea (kJ/mol)
Virgin	1st	61	226-351	285	85
	2nd	31	351-436	371	68
	3rd	7	436-508	455	60
8 times re-processed	1st	30	230-340	289	87
	2nd	52	340-447	412	71
	3rd	15	470-512	470	81

Tmax and Ea for PP in composites have been found to increase with increased number of times the materials were reprocessed. The positions of weight loss on the TGA traces of composites (Fig. 8) increased number of times the materials were reprocessed suggesting increased thermal stability. The increase in thermal stability has been considered to be due to an increase in crystallinity of PP resulting from molecular weight reduction.

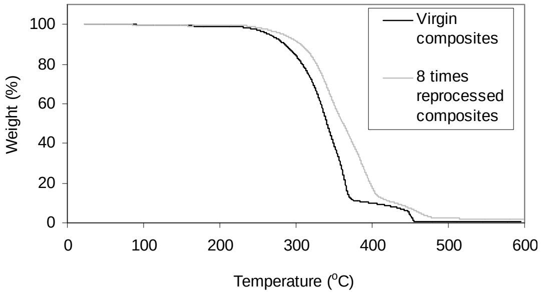


Fig 8. TGA trace of virgin and reprocessed composites.

4. CONCLUSION

Mechanical break-down is also the most progressed recycling method for thermoplastic matrix composites. Research based on reprocessing of thermoplastic matrix composites shows some reduction of tensile strength and Young's modulus,with poor surface appearance but increased failure strain and better moisture resistance. Reductions of fibre length and polymer degradation have been highlighted to explain the change in properties of reprocessed composites. Overall, issues of contamination and separation will also need to be addressed for increased mechanical recycling and therefore the development of infrastructure and systems For 40 wt% fibre reinforced composites reprocessed 8 times, a 25% reduction in TS and 16% reduction in YM was found. The reduction of TS, YM was considered to be due to fibre damage that occurred during reprocessing as evaluated by the associated reduction of the average fibre length from 2.36 mm for virgin fibre to 0.37 mm for the fibre extracted from the composites reprocessed 8 times. Moisture absorption increased with increased soaking time for all composites until saturation at about 5 months. Equilibrium moisture content and diffusion coefficient decreased with increased number of times the materials were reprocessed. For virgin and 8 times reprocessed composites, the equilibrium moisture contents were respectively 9.42% and 6.41% and the diffusion coefficients were 2.54x10-13 m2/s and 1.01x10-13 m2/s. TS and YM was found to decrease after hygrothermal ageing. A 33% reduction of TS and 40% reduction of YM was found for virgin composites and 27% reduction of both TS and YM was found for composites reprocessed 8 times. However, the extent of reduction was lower for reprocessed composites. Degradation of fibre and fibre matrix interface bonding was highlighted to explain the physical and mechanical properties of composites.

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