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RECYCLING AND REUSE OF PULTRUDED POLYMER GLASS-FIBER COMPOSITES AND RESIN WASTE

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ABSTRACT

In this study we present the viability of recycling a pultruded glass fiber composite and reusing the methacrylate resin waste accumulated during the pultrusion process to prepare a new pultrusion resin and fabricate pultruded composites again, to enhance sustainability. First, the pultruded composite was recycled by solvent extraction of the polymer matrix and filtering of the fibers. In parallel, waste resin that dripped from the die entrance was subjected to solution polymerization to obtain reusable polymer pellets. The polymer that was recovered from both recycling techniques was used to produce a suitable pultrusion resin by mixing it with methyl methacrylate. Finally, new glass fiber composites were successfully fabricated with the resin prepared with recycled polymers.

1 INTRODUCTION

Nowadays, fiber-reinforced polymer composites (FRPC) are widely utilized in several important sectors such as aeronautics, tanks & pipes, wind turbines, marine, transportation, electrics & electronics, and construction. From the production point of view, FRPC are considered as eco-friendly materials in terms of carbon footprint compared to traditional materials (concrete, steel, etc.). However, the rapid increase in demand for FRPC (from 50 kilotons in 2010 to more than 160 kilotons in 2020) led to an increase in their production, which contributes to the waste problem all over the world. As the waste amounts of FRPC are expected to spike in the future, given that incineration causes global warming issues and landfill disposal regulations are becoming stricter, FRPC wastes must be recycled as much as possible [1–7].

FRPC mainly consist of two primary components: fibers as the main reinforcement material and a polymer matrix that binds and surrounds the fibers. A FRPC's polymer matrix can be either a thermoset or a thermoplastic polymer, but a vast majority of global FRPC production and consumption consists of thermoset matrices [5]. Due to the market dominance of thermoset FRPC, recycling methods have primarily focused on these composites. The methods fall into three main categories, which are mechanical, thermal, and chemical processes [8]. In mechanical recycling, waste FRPC is pulverized by a milling or grinding machine to obtain matrix-rich powder and fiber-rich aggregates. Matrix-rich powder is reused as filler and fiber-rich aggregates are used as reinforcement material to produce new composites. This is a simple, inexpensive recycling method compared to others and environmental impact is also very low as there is no harsh chemical use or gas emission. However, new materials produced using recycled powder and aggregates exhibit very low mechanical strength and have significantly low market value [9,10], due to the significantly reduced fiber size. The most common thermal recycling methods are pyrolysis and fluidized beds. Pyrolysis involves recovering fibers by decomposing the polymer matrix and obtaining oil and gas products within a temperature range of 450 – 700 °C under an inert atmosphere. The gas products and other hydrocarbons are later used for low calorific energy sources. The liquid phase (tar and other heavy liquids) could be used as oil and other products. In a fluidized bed, the polymer matrix is decomposed in hot and oxygen-rich air flow (450 – 550 °C) to reclaim fibers. Recovered fibers in this method are clean and char-free. Although the recovered fibers in thermal recycling are considered more valuable, they require more energy and are less environmentally friendly compared to those from mechanical recycling [11,12]. Chemical recycling is based on recovering the matrix as useful solvents, monomers and reclaiming unharmed, full-length fibers by solvolysis. This method uses solvents, acids, and catalysts to break down the thermoset polymer matrix into smaller organic compounds and the temperature requirements are generally less than 350 °C. The fiber quality obtained from this method is better than thermal recycling but efficiency is relatively low and energy requirements are high due to the need for high temperature and pressure for prolonged times [12–15]. In summary, each recycling method has its own advantages and disadvantages, considering factors such as retaining mechanical strength, the value of recycled materials, recycling ratio, cost, and environmental impact. The recent introduction of recyclable thermoplastic FRPC is gaining significant interest, offering easier recycling compared to thermosets, as the polymer matrix can be reclaimed as a reusable material without a change in its chemical structure [16–21]. Therefore, waste from thermoplastic FRPC can be recycled using innovative methods that are cost-efficient, environmentally friendly, and capable of recovering both the polymer matrix and fiber phase without damage. The status of the thermoplastic-oriented recycling methods can be found in a recent review by Bernates et al. [22]. Among these methods, the dissolution method involves dissolving the thermoplastic matrix using its solvent, filtering to recover the fibers, and then precipitating in its non-solvent to reclaim the matrix. Alternative to precipitating, evaporating can also be used to increase the yield and avoid a second separation step. Recent studies have shown that this recycling method is promising due to its simplicity, scalability, low cost, and high efficiency with a high reclaiming ratio for both fibers and matrix. Moreover, reclaimed polymer and fibers are then used to fabricate new composites in so-called closed-loop recycling where recycled material is used for the same production [23–25].

To the best of our knowledge, a recycling method for pultruded thermoplastic FRPC waste and resin waste, involving reclaiming matrix and fibers separately by a dissolution method and the preparation of a recycled resin to reuse in the same pultrusion process has not been previously proposed. The work presented here had the following objectives:

- Recycling the manufacturing waste generated from thermoplastic pultrusion,
- Reclaiming unharmed and reusable fibers suitable for other fiber-reinforced composite processes,
- Reclaiming the polymer matrix to prepare resin for pultrusion,
- Repurposing resin waste to produce reusable polymer and prepare a resin for the same pultrusion process.

2 MATERIALS AND METHOD:

2.1 Materials:

The FRPC waste rods (Ø = 9mm, fiber ratio ≈ 70 %) used in this study are manufacturing parts from our previous experiments on thermoplastic acrylic resin pultrusion. A halogenated solvent (HS) was employed for the dissolution recycling method. Methacrylate-based monomers and free radical polymerization initiators were used in subsequent resin preparation, polymerization, and pultrusion.

2.2 Methods:

This study on recycling thermoplastic pultrusion waste involves two recycling routes, as depicted in Figure 1. One of them is focused on thermoplastic FRPC waste that involves reclaiming fibers and polymer matrix by dissolution method and reusing the polymer matrix to prepare a new resin, and subsequently produce new pultruded FRPC (Figure 1A, bigger cycle). The other one is to utilize the resin waste collected during pultrusion to prepare a new resin, and produce new pultruded FRPC (Figure 1B, the smaller cycle). Both methods are described in detail below.

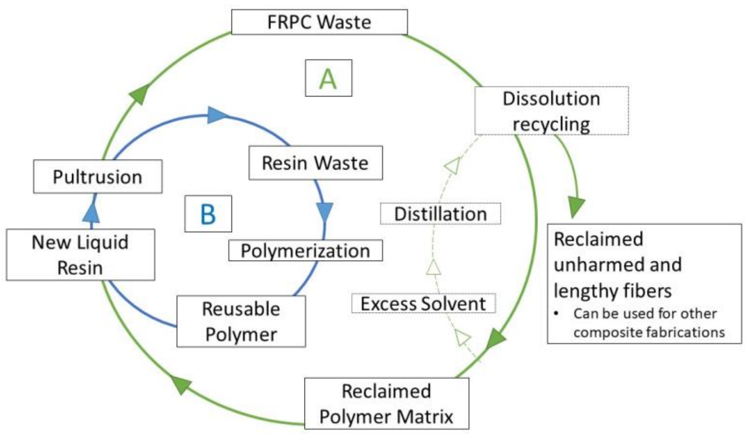

Figure 1. The recycling processes : (A) the bigger green circle represents the recycling route for FRPC waste; (B) the smaller blue circle represents the recycling of resin waste.

2.2.1 Recycling the FRPC waste

Thermoplastic FRPC rod wastes were cut into small pieces (length ≈ 5cm), weighed, placed in a jar, and solvent was added. The container was closed with a cap and kept overnight at room temperature to dissolve the matrix. The mixture was filtered and the glass fibers were reclaimed. The excess solvent of the filtrate was recycled using a rotary evaporator at 40 ^{o}C. After this step, the diluted solution was poured into aluminum molds, and a polymer matrix was obtained after evaporation of the remaining solvent at room temperature. Then, the casted polymer was dried in the oven at 60 ^{o}C to remove the residual solvent. The dried polymer product was crushed into smaller pieces with a blender and then pulverized using a benchtop grinder. The reclaimed polymer was then used to prepare a new liquid resin for pultrusion, and the fabrication of a new pultruded composite was carried out on a pultrusion machine (Ashirvad AIHP-HGR-06, Gujarat, India) equipped with a creel stand for fiber roving, roving guide stands, a resin impregnation bath, a hydraulic pulling system, an automatic section cutter, a 100 cm long stainless steel die having a 9 mm diameter cavity.

2.2.2 Recycling the resin waste

The resin waste that had dripped from the entrance of the die, and the remaining resin in the resin bath was collected during the pultrusion processes. It was poured in a round bottom reaction flask and an equal volume of solvent was added. The polymerization reaction was carried out in a constant temperature oil bath at 60 ^{o}C for 2 hours. After the polymerization, the solution was poured into an aluminum mold for solvent casting. The casted polymer was then dried in the oven at 60 ^{o}C to remove the residual solvent. The dried polymer was crushed into smaller pieces with a blender and then converted into powder via a benchtop grinder. The obtained polymer was used to prepare a liquid resin for pultrusion, which was carried out using the pultrusion machine mentioned in the previous section.

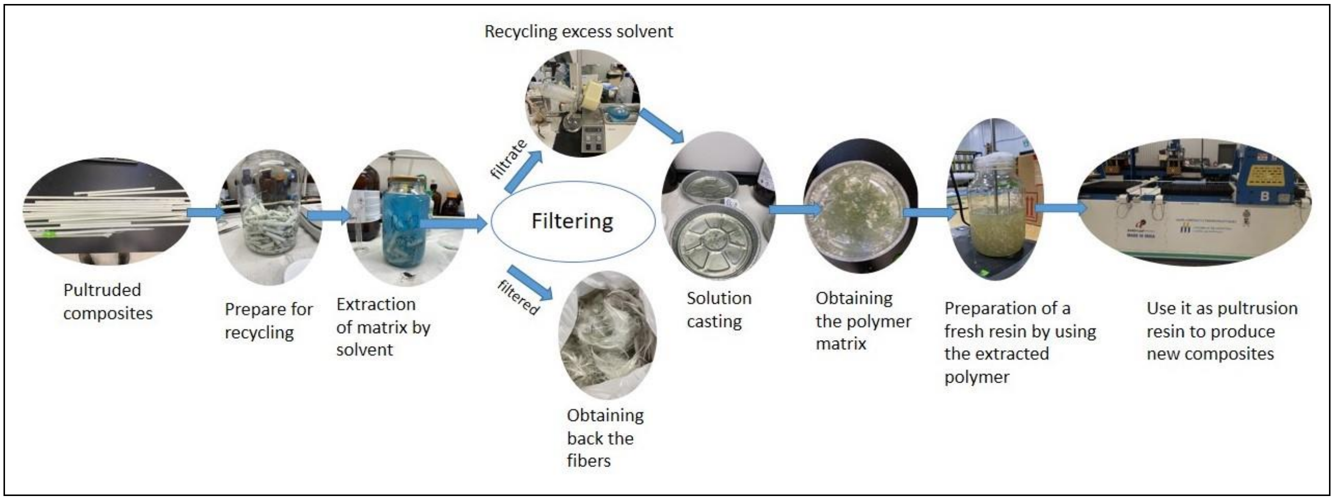

Figure 2. Schematic of the recycling and reusing steps involved in the pultruded composites production process.

3 RESULTS AND DISCUSSION

3.1 *Recycling the FRPC waste*

Both polymer matrix and fibers were reclaimed successfully by employing the dissolution recycling method. Fibers were not affected by solvent treatment at room temperature and were recovered in an unharmed condition. The reclaimed polymer matrix was found to have a molecular weight between 91 – 95 kDa. The polymer recovery yield was calculated assuming that all the composite pieces had a 30 % polymer matrix content, as

$$P_c = m_c \times 0.3 \tag{1}$$

$$Yield = (P_r/P_c) \times 100 \tag{2}$$

where m_c, P_c and P_r are the composite weight, the theoretical polymer weight in the composite, and weight of the obtained (recycled) polymer, respectively.

It was observed that the volume of the solvent affected the recovery yield of the polymer matrix. Table 1 summarizes the relation between the polymer recovery yield, the V_s/m_c ratio where V_s is the solvent volume, and the GPC of the polymers. Increasing the solvent/FRPC composite waste ratio (V_s/m_c) to 5 provided a 71.1% recovery.

Reclaimed polymer was used to prepare a new pultrusion resin and a FRPC was successfully fabricated using this new resin. The new pultruded FRPC showed an acceptable flexural strength of 390 MPa.

Table 1. Recovery yields vs. solvent/composite ratio and GPC results of the reclaimed polymer matrix

V_s/m_c	Yield (P_r/P_c x 100)	Mw (kDa)	PDI
1.94	56.2 %	92.0	2.81
2.29	65.3 %	94.8	2.54
4.94	71.1 %	91.1	2.82

3.2 Recycling resin waste

Resin waste was polymerized and a polymer with 130 kDa average molecular weight (PDI: 1.9) was obtained. This polymer was then used for preparing pultrusion resin, and a pultruded glass fiber composite was fabricated. The FRPC prepared with this resin also showed a good flexural strength 399 MPa. Figure 3 shows the flexural test results of FRPC obtained from both recycling routes.

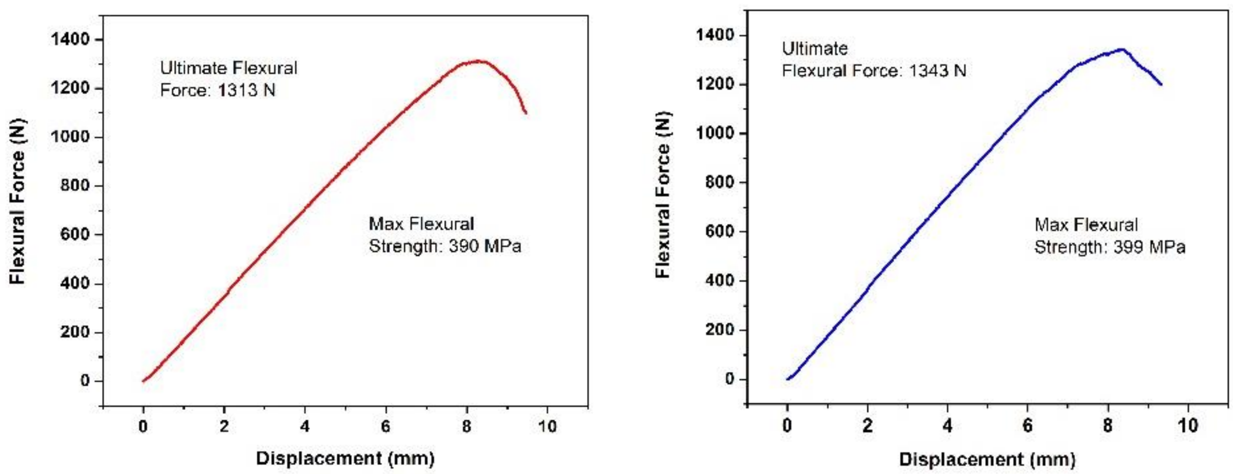

Figure 3. Flexural test results of the pultruded FRPC from both recycling routes.

4 CONCLUSION

This study proposed a recycling method for pultrusion wastes, including resin and FRPC, that could be applied to faulty parts and unused waste resin in a real manufacturing setting. Results showed that both the fibers and the matrix can be reclaimed efficiently. All the steps in this method can be considered environmental-friendly and cost-efficient. Thanks to the suitability of the FRPC and the method, a semi-industrial scale reproduction of the new FRPC was achieved. Additionally, the newly fabricated FRPC showed good mechanical strength. Therefore, we believe that most of the waste materials during the pultrusion can be recycled into new useful FRPC without losing too much market value. Moreover, the method is proven to be scalable and may also offer in-house recycling.

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