METHODOLOGY TOWARDS RELIABLE DESIGN WITH RECYCLED HIGH-PERFORMANCE FIBER REINFORCED COMPOSITES FOR AUTOMOTIVE STRUCTURES

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ABSTRACT

A controlled, extreme case of recycling short fiber reinforced polyphthalamide (PPA) was investigated with an aim to develop a guide that ties together mechanical, thermal, and statistical influences that mechanical recycling has on the material. This methodology intends to establish a foundation upon which more accurate design guidelines can be developed, enabling a higher utilization rate of recycled material in advanced applications. Short fiber reinforced PPA is frequently utilized as metal replacement in high-performance applications. Current cost barriers and sustainability goals for certain industries, such as automotive, present a need for its recyclability to be further investigated. Mechanical recycling of carbon and glass fiber reinforced PPA was conducted, to produce controlled recycled (R1) material. This process was then repeated to produce the twice recycled (R2) material. Tensile testing showed a decrease in tensile strength of approximately 12-13% with each round of recycling. The distribution in tensile properties within material batches was then studied using the two-parameter Weibull distribution function, and it was observed that the consistency of material properties was negatively impacted with each round of recycling. Differential scanning calorimetry (DSC) was conducted to gain insight into the impact of recycling on the material’s thermal characteristics. Finally, a fiber length distribution analysis was conducted for both glass and carbon fibers from each material batch; as expected, a decrease in fiber length as well as broadening of each distribution was measured for both fiber types over the course of consecutive recycling. Connecting microstructural impact of recycling to the mechanical degradation was hence achieved. A generalizable approach by way of this work can be further utilized as a template for other high-performance thermoplastic polymers that have similar barriers to implementation at high scales because of their lack of controlled and predictable recycling data.

1 INTRODUCTION

Within the automotive industry, strict goals of increasing the use of recycled or renewable plastics in new vehicles have been established in order to meet sustainability goals driven by material waste and energy consumption. For example, Ford Motor Company has pledged to use 20% recycled or renewable plastics by 2025 [1]. With the continued development of thermoplastic polymer composites within automotive structures today, the need to establish closed loop recycling has become an increasingly pressing area of focus within the automotive industry; however, there are several barriers that impede further integration of recycled content at larger scales [2]. The main obstacles hindering the growth in the recycled fiber market include initial cost, processing consistency, reliability of incoming waste sources, environmental sustainability, and reliability of long-term performance of recycled fiber composite parts [3,4].

Driven by the automotive industry’s paradigm shift towards hybrid molding (conventional molding in combination with continuous fiber composites) and short fiber- reinforced injection molded thermoplastics, more research is needed to develop re-integration of waste from manufacturing and end-of-life structures. However, these efforts must address the variability in processing, microstructural defects, as well as the consistency in performance of such structures over their service life. This is to address the distinct need by manufacturers that are called to implement closed loop recycling within their companies but have limited data for reliable prediction of their recycled material. Because of this, over-design of recycled composite structures can occur, in turn adding unnecessary cost and weight to a structure [5]. This domino effect highlighting the importance of efficient design guidelines is shown in Figure 1.

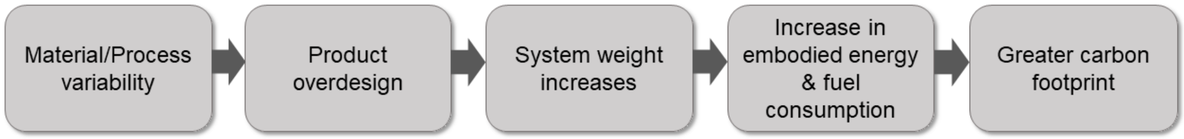

Figure 1: Diagram displaying the downstream effects that can occur from material and process induced variability, thus highlighting the importance of reliable design guidelines and thorough recycling data. Graphic adapted from [5]

This downstream effect is especially important for high performance polymers that are continuing to be developed for automotive applications where weight savings are critical, in which recyclability has not yet been thoroughly evaluated for re-use in higher performance applications. One example of this class of material that was the focus of this work is polyphthalamide (PPA).

Fiber-reinforced PPA offers distinct advantages over traditional polyamides commonly used in automotive today, including: higher strength and stiffness, improved dimensional stability, improved chemical resistance over a wider temperature range, as well as impact performance [6]. While cost is an initial barrier for this material, recycling could offer a more cost-feasible pathway of integration into automotive that also offers mechanical performance advantages [7]. Specifically developed for structural applications, this material's high performance under extreme conditions can be utilized by automotive to further increase weight savings in vehicles without compromising performance or safety.

The following work presents research centered around assessing the impact that mechanical recycling has on glass and carbon reinforced polyphthalamide (PPA/CF/GF), in the form of injected molded tensile samples. Tensile testing was conducted and analyzed via Digital Image Correlation (DIC). In addition, the two-parameter Weibull distribution function was utilized to assess the reliability and failure distribution between material batches. Calorimetric studies using Differential Scanning Calorimetry (DSC) was also conducted to observe a trend that mechanical recycling induces for crystallization and melting behaviors. Lastly, the fiber length distribution of both glass and carbon fibers from each batch of material was measured and analyzed. These physical, chemical, and statistical results are then presented as a foundation of comparison on which to build on in future work, where applications for recycled PPA can be further characterized.

2 MATERIALS AND METHODS

2.1 Materials

The material used in this study was Solvay Specialty Polymers' Amodel® AXS-1655 HS BK 324, which is a hybrid glass and recycled carbon fiber reinforced polyphthalamide (PPA). For clarity it is useful to note that although the carbon fibers in the original material are recycled, the nomenclature for this research designates the as-received material as "virgin", whereas the once-recycled and twice-recycled batches are referred to as "R1" and "R2", respectively as it refers to the entire material system.

2.2 Manufacturing and Mechanical Recycling

The material was first dried at 120 °C for 8 hours according to the manufacturer's specifications. The material was then injection molded into ASTM d638 bars. During the initial molding cycle of the virgin tensile bars, an excess of approximately 50 tensile bars were molded and collected to be reground along with their sprues.

The material was then re-fed straight into the injection molding machine and used to mold the R1 batch of tensile bars. A portion of that batch was then reground again, and then directly fed into the injection molding machine to mold the final batch of R2 tensile bars. A diagram of this process can be seen in Figure 2.

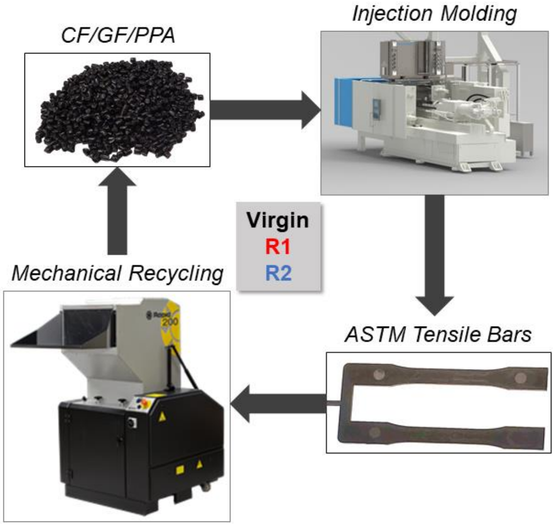

Figure 2: Manufacturing loop in which the virgin material is injection molded into tensile bars. A portion of those bars were then ground and then fed directly into the injection molding machine to produce the once recycled, or R1 tensile bars. This process was then repeated to produce the twice recycled, or R2 tensile bars

2.3 Tensile Testing

The tensile bars were then tested in tension on an MTS 100 kN load frame, while simultaneously conducting Digital Image Correlation (DIC). The DIC was conducted using two 5MP cameras (Correlated Solutions, Inc). Collection and post-processing analysis were done using VIC-SNAP and VIC-3D, respectively.

2.4 Weibull Distribution Function

Due to the brittle nature of the material, as well as the increase in variability that the incorporation of recycled content introduces, a two-parameter Weibull analysis can be utilized [8]. Beyond studying the reliability of a data set, this method also allows for ties between performance consistency and physical defects to be quantified. This simple method is important to quantify more realistic design margins for recycled composite parts. The two-parameter Weibull probability distribution function (PDF) is given by:

$$f(x) = \frac{\beta}{\alpha}\left(\frac{x}{\alpha}\right)^{\beta-1} \exp[(\frac{x}{\alpha})^{\beta}]. \tag{1}$$

Where β is the shape parameter or Weibull modulus, α is the scale parameter, and x denotes the tensile strength in this case. The cumulative distribution function (CDF) is obtained by integrating Equation 1 [9,10]:

$$F = 1 - \exp[-(\frac{x}{\alpha})^{\beta}]. \tag{2}$$

A probability plot is then obtained by linearizing Equation 2:

$$\ln\left(ln\left(\frac{1}{1-F}\right)\right) = \beta\ln(x) - \beta\ln(\alpha) \tag{3}$$

From this function, the failure rate distribution over time can be visualized. This can be used, for example, to measure the shape parameter which indicates how consistent the tensile strength is between samples [9].

A high shape parameter indicates high consistency, whereas a low shape parameter can indicate the presence of defects that ultimately increase the spread of the dataset [11]. From this probability plot, the impact of recycling on the mechanical properties of the material can be studied by calculating the likelihood of failure, repeatability of stress at fracture, as well as the overall reliability of a part.

2.5 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is a widely used technique that can be applied to study the same crucial characteristics of polymers. In the case of recycled PPA, this technique was used to investigate if mechanical recycling had any impact on crystallization and melting characteristics.

For the DSC, a Q100 DSC (TA Instruments) was used. Approximately 5 mg of material from each batch was placed in a hermetic aluminium pan. A heating, cooling, and heating program was conducted, where an initial temperature was equilibrated at 30 °C and held for two minutes. The sample was then heated to 400 °C at a rate of 10 °C/min. It was held at 400 °C for two minutes, then cooled to 30 °C at the same rate of 10 °C/min. It was then held at 30 °C for two minutes, before a second cycle of heating was then conducted to 400 °C at a rate of 10 °C/min, and the final temperature was held for two minutes. The data was then analyzed using OriginLab.

2.6 Fiber Length Distribution Analysis

Fiber length distribution is important to relate the recycling and manufacturing impact to the degradation in mechanical performance. Because this work is focused on injection molded material, the fiber length attrition that occurs during manufacturing should also be considered in addition to the fiber breakage during the grinding process. During injection molding, fiber breakage occurs as the material passes through the plastification unit and goes through complex and severe thermo-mechanical flow patterns [12]. Both carbon and glass fibers within the PPA material were measured for the virgin, once recycled, and twice recycled batches to study the attrition of fiber length and impact on fiber length distributions.

To measure the distribution of fiber lengths of both carbon and glass fiber types, the fibers were first separated from the matrix. For the glass fibers this was done via an ashing process, and for the carbon fibers this was accomplished through chemical digestion. The fibers were then put into a slurry, and drop casted onto glass.

The fibers were then imaged using an optical microscope, with a minimum of 200 fibers imaged for each sample. The images were then analysed using ImageJ, where each fiber was measured. The data was then plotted with the Analysis ToolPak in Excel, where the average fiber length and standard deviations were also calculated.

3 RESULTS AND DISCUSSION

3.1 Mechanical Degradation: Tensile Strength

Results from the tensile tests showed a decrease in tensile strength and elongation to break after each round of recycling, as seen in Figure 3. This is indicative of degradation or defects introduced by recycling, as can be expected. The modulus was relatively unaffected.

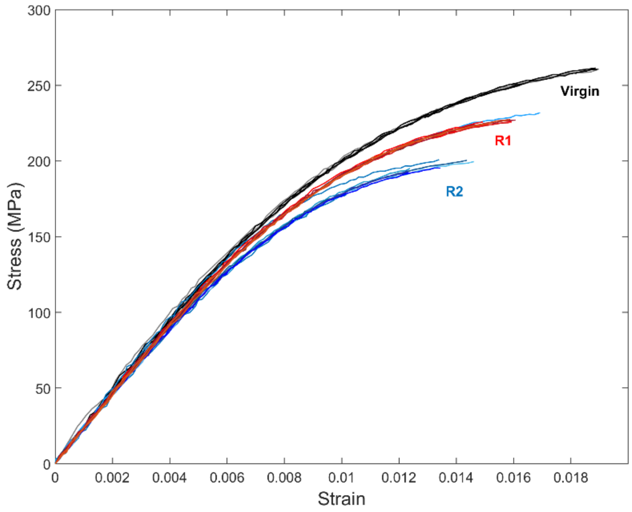

Figure 3: Impact of mechanical recycling on tensile strength of PPA/CF/GF

It can also be seen that the consistency in tensile strength was impacted by mechanical recycling. As the material was recycled more rounds, it could be seen that tensile strength from sample to sample within that batch had higher variability. The average tensile strength of the virgin samples was 259 MPa. The R1 samples had an average tensile strength of 224 MPa, and the R2 samples had an average tensile strength of 197 MPa. This variability in performance that is a prevalent issue in recycled fiber reinforced thermoplastics was further quantified in Section 3.2 by utilizing Weibull statistics.

3.2 Statistical Impact: Weibull Analysis

The tensile data can be visualized in a Weibull probability plot, as seen in Figure 4. It can be seen that the change in slope, or shape parameter was relatively insignificant between the virgin and R1 batches, but showed a significant decrease when comparing virgin and R2 batches. The solid lines connect the first and third quartiles of data for each sample set, which determines the fit of the line. It can be seen from the data point's horizontal proximity to the extended fit line how consistent the data points are, and the distance of the data points from the solid line reflect how variable the outlying samples are from the second and third quartiles [13].

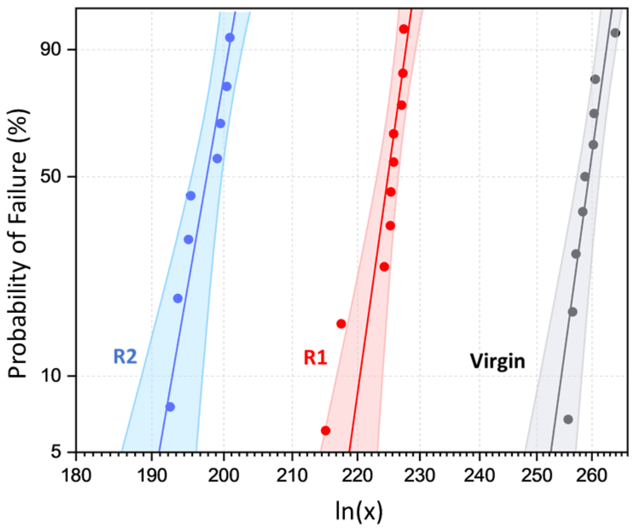

Figure 3: Weibull probability plot displaying the broadening of tensile strength distributions corresponding to number of rounds of recycling

This plot offers a more thorough look at the consistency of performance of each sample set and can be used to compare the probability of failure over time. Since the virgin material has a steeper shape parameter indicative of a smaller distribution of performance properties, it can be seen from the plot that the virgin material is more likely to fail over a much smaller range of tensile strengths as compared to the R2 material. It is also clearly seen from the plot that R1 and R2 data sets have more data points that lie out-of-line with the projected fit line determined by the second and third quartiles of their respective distributions, indicating less consistent properties.

Values for the shape and scale parameters for the virgin, R1, and R2 material batches are annotated in Table 1, quantifying the impact of recycling on the characteristic life and the variability within each distribution, respectively.

	Virgin	R1	R2
Scale parameter (α)	260.39	225.68	198.54
Shape parameter (β)	96.22	94.62	76.61

Table 1: Impact of recycling on the scale (α) and shape (β) parameters respectively, indicating both a decrease in characteristic life limit as well as a decrease in consistency of tensile strengths for each batch

3.3 Chemical and Thermal Degradation

It is important to characterize the chemical degradation of the matrix caused by thermal cycling in order to assess the viability of recycled material undergoing repeatable thermal exposures. A first qualitative look into the impact on thermal stability was considered here by conducting calorimetric analysis (DSC). Results from the DSC can be seen in Figure 5.

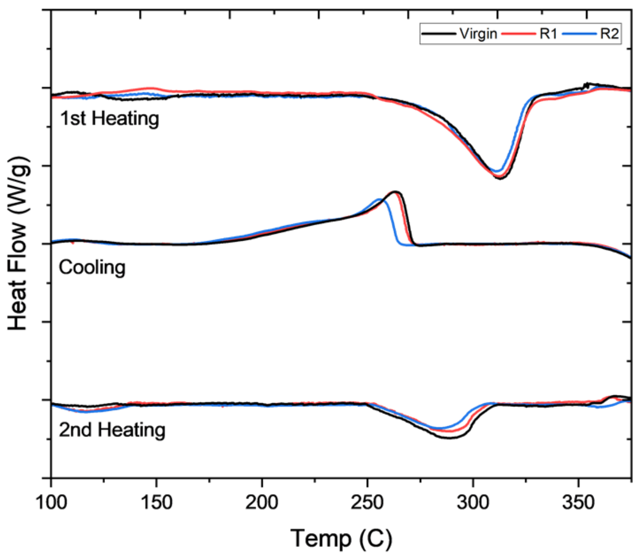

Figure 5: Differential scanning calorimetry (DSC) scans of virgin, once recycled (R1), and twice recycled (R2) carbon and glass fiber reinforced PPA. Exo up

The first heating cycle reflects a combination of intrinsic material properties and thermal conditions during the manufacturing of the part. The second heating cycle represents a clearer view of the material properties which is the focus of this work. It can be noted that this work primarily focused on establishing a trend between recycling of PPA and its melting behaviour, and that other features captured by DSC are not discussed in detail in this work. It can be observed by the cooling and secondary heating curves that recycling resulted in a slight suppression of both melting and crystallization temperatures. Select crystallization and melting parameters were calculated in Table 2. This trend has not been well documented in literature for polyphthalamide but shows agreement with previously reported trends in adjacent studies for different recycled thermoplastic materials [14,15].

	Virgin	R1	R2
T_m Peak (°C)	287.33	286.34	283.61
% Decrease in ΔH_f	N/A	33.17	23.38
T_c Peak (°C)	263.29	261.71	255.74
% Decrease in ΔH_c	N/A	1.24	8.8

Table 2: Peak melting and crystallization temperatures, and comparison of changes in enthalpy of fusion (ΔHf) and enthalpy of crystallization (ΔHc) due to recycling

It was observed that the peak crystallization and melting temperatures decrease slightly with each round of recycling. Integration of the crystallization and melting curves showed that the enthalpy of crystallization as well as the enthalpy of fusion also decreased with each round of recycling, which could be attributed to degradation of the material. It is known that mechanical and thermal exposure of a polymer often results in molecular reconfigurations, such as chain scission and/or crosslinking of the molecule [16]. This typically impacts the chain mobility. A decrease in molecular weight is known to lower the glass transition temperature as well as the melting characteristics [17]. As the degree of degradation increases, a lowering of the melting temperature will occur. Recycled material is expected to have lower thermal stability because of thermal ageing, meaning the recycled PPA material could start to decompose at a slightly lower temperature than the virgin material. It should be noted that the study did not take any effect from stabilizer packages into account. While the glass transition temperature is not clearly visible by DSC for this material, the slight suppression in both peak crystallization and melting temperatures supported this notion and indicated that some degradation had occurred. While this data showed agreement with this trend, the overall impact seen was not significant due to the material's high thermal stability. Future work would benefit from additional characterization of recycling's impact on molecular weight, as well as further quantification of defects and chemical degradation within each batch.

3.4 Impact on Fiber Length Distribution

The distributions of fiber lengths for both carbon and glass types from each batch of material can be seen in Figure 6. All distributions were formed after imaging a sample size of 200 fibers from each batch.

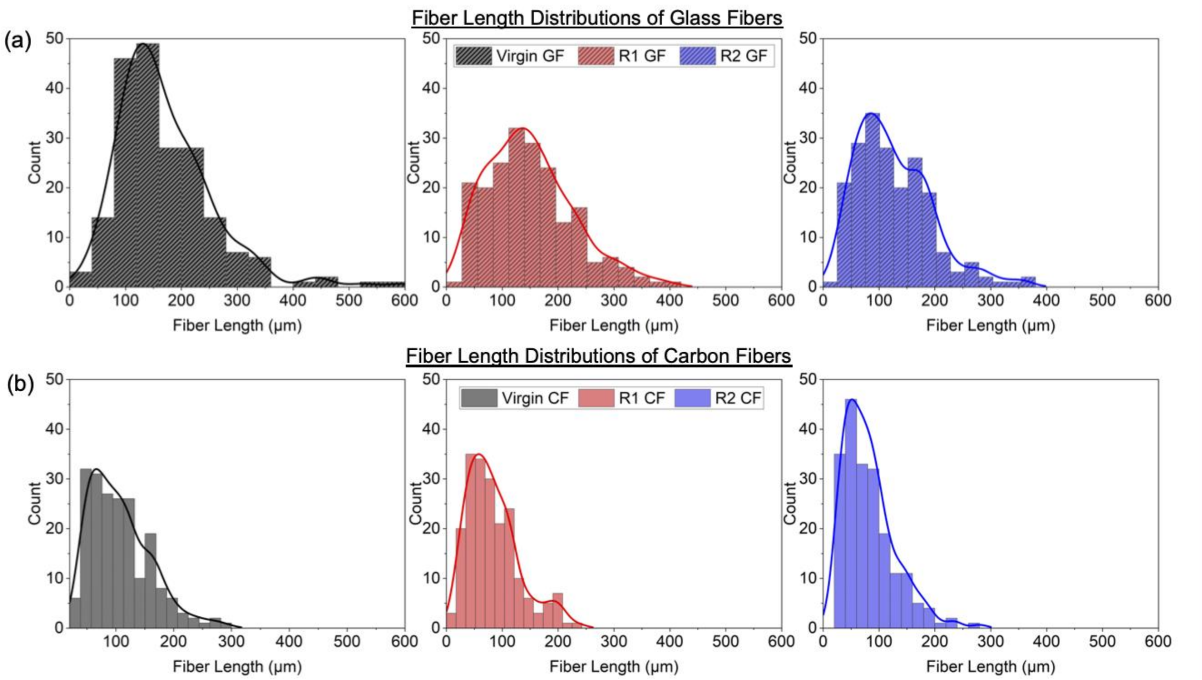

Figure 6: Fiber length distributions for (a) the glass fibers and (b) the carbon fibers present in the PPA/CF/GF. The gray plots represent their as-received distributions, the red plots represent their respective distributions after one round of recycling (R1), and finally the blue plots represent the distributions for the material that has been recycled twice (R2)

A summary of key features from these distributions are summarized in Table 3.

		Glass Fibers	Carbon Fibers
Virgin	Avg. Fiber Length (μm)	170.9	106.8
	% Fibers < Avg. Length	48.5	51.5
R1	Avg. Fiber Length (μm)	149.7	83.6
	% Fibers < Avg. Length	54.5	50
R2	Avg. Fiber Length (μm)	126.1	81.8
	% Fibers < Avg. Length	56	52.5

Table 3: Impact of recycling on fiber length distributions for both glass and carbon fibers

As anticipated, consecutive rounds of injection molding and recycling induced fiber breakage. The breakage of longer fibers into shorter fibers affected the shape of the distributions, and increased the left-hand side of the distributions with each round of recycling. The glass fibers experienced this to a greater degree, as they were originally longer and the shorter carbon fibers were more likely to retain their length to a higher degree and therefore had a smaller range of fiber lengths observed.

The decrease in fiber length for both carbon and glass fibers greatly impacted the mechanical properties of the material. To further quantify reliable design guidelines with a recycled fiber reinforced thermoplastic material, it is important not only to quantify the mechanical and chemical degradation that occurs within the fiber and matrix materials, but to also assess which has a greater impact on the performance of the part under the load cases and service environments the part is to be designed to withstand.

4 CONCLUSIONS

The work presented indicated progressive degradation in mechanical, thermal, and statistical properties of recycled PPA/CF/GF as a result of repetitive mechanical recycling. Tensile strength decreased an average of ~12-13% with each round of recycling, and a Weibull analysis displayed a decrease in Weibull modulus which corresponds to a decrease in consistency of tensile strength properties within sample batches. Calorimetric analysis showed a slight suppression of melting and crystallization behaviors consistent with molecular chain scission caused by recycling. Finally, the average fiber length decreased with recycling for both fiber types, and a broadening of fiber length distributions were observed.

It was shown that controlled recycling can ensure that PPA/CF/GF remains a strong candidate for metal replacement in automotive structures under controlled recycling conditions. Further research into the recycling methods and resultant effects aims to assist in quantifying design guidelines to expand potential applications, as well as to build a foundation of characterization from which more sustainable pathways can be built from using this high-performance material. This methodology of quantifying the impact that controlled recycling has on the mechanical, chemical/thermal, and statistical properties of this material system can be further expanded on as an approach for the efficient design of recycled composite structures. Additionally, this approach will also benefit the design of new virgin polymer composite applications that will need to consider the recyclability from the very beginning of the design stage. By way of this methodology, confidence in a wider range of recycled material systems can hopefully be increased through the maturing of thorough recycling databases and the quantification of trends that will aid in the refinement of design margins.

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