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Communication

Composite Recycling with Biocatalytic Thermoset Reforming

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ABSTRACT: Carbon fiber reinforced polymers (CFRPs, or composites) are increasingly replacing traditional manufacturing materials used in the automobile, aerospace, and energy sectors. With this shift, it is vital to develop end-of-life processes for CFRPs that retain the value of both the carbon fibers and the polymer matrix. Here we demonstrate a strategy to upcycle pre- and postconsumer polystyrene-containing CFRPs, cross-linked with unsaturated polyesters or vinyl esters, to benzoic acid. The thermoset matrix is upgraded via biocatalysis utilizing an engineered strain of the filamentous fungus *Aspergillus nidulans*, which gives access to valuable secondary metabolites in high yields, exemplified here by (2*Z*,4*Z*,6*E*)-octa-2,4,6-trienoic acid. Reactions are engineered to preserve the carbon fibers with much of their sizing so that the isolated carbon fiber plies are manufactured into new composite coupons that exhibit mechanical properties comparable to those of virgin manufacturing substrates. In sum, this represents the first system to reclaim a high value from both the fiber fabric and polymer matrix of a CFRP.

Carbon fiber reinforced polymers (CFRPs) are composite materials comprising carbon fibers embedded in a polymer matrix, commonly a thermosetting polymer such as an epoxy,[1−3] unsaturated polyester,[4,5] or vinyl ester[6] system cross-linked with vinyl monomers, the latter acting as a reactive diluent, processing aid, and catalyst.[7,8] CFRPs are attractive manufacturing materials in the energy, aerospace, and automotive sectors[1−3,9] because of their high strength- and stiffness-to-weight ratios and resistance to corrosion, moisture, and chemical pollutants.[10] CFRPs are generally landfilled at end-of-life, because the strong three-dimensional cross-linking network of the polymer matrix makes recycling difficult and repairs impractical.[1−3,9] By 2030, 6,000−8,000 CFRP commercial aircraft will reach their end of service,[11] and by 2050, the retirement of wind turbines will have generated 483,000 tons of CFRP waste, while the demand for carbon fibers and CFRPs is projected to reach 190 kilotons.[10,11] It is therefore imperative to establish viable recycling methods for these composites.

Current options for CFRP recycling include mechanical, thermal, and chemical processes.[1] Mechanical recycling involves shredding CFRPs into smaller pieces, destroying the value of the continuous fiber. Thermal recycling involves energy-intensive pyrolysis (≥450 °C) in which the polymer matrix is discarded as valueless oils and gases, and the high temperatures degrade the mechanical properties of the fibers. Emerging chemical recycling methods, mainly comprising solvolysis of epoxy systems, are attractive when effective chemistries can be found, as some harvest the matrix as valuable chemicals while recovering fibers and retaining the fabrics' architecture and their mechanical properties.[1,12] Here, we show an upcycling chemistry new to the composite space in which tandem chemical and biocatalysis are used, respectively, to cleave and upgrade a polyolefin-containing composite matrix to high-value products, the first approach to use a waste composite matrix as a manufacturing substrate for fine chemicals.

We exhibit our method on polyester and vinyl ester thermosets. These materials feature durability, low cost, effective fiber-matrix adhesion, and negligible composite shrinkage.[10] Such materials are commonly cross-linked by vinyl monomer polymerization; our case features styrene, as it is both economical and has attractive properties, such as a low molecular weight, high reactivity, and easy processing.[8] Polystyrene (PS)-containing composites are not limited to CFRPs;[13] there is an increasing effort to incorporate postconsumer PS, other organics,[14,15] and natural fibers into composites.[16,17]

Partenheimer established conditions for homogeneous liquid phase aerobic oxidation of PS to benzoic acid utilizing a system comprising acetic acid and metal/bromide catalysts in high yields (≤88%).[18] Oxidative methods utilizing acetic acid and hydrogen peroxide enabled the recovery of both the carbon fibers and resin system via formation of peracetic acid in situ as demonstrated by Varughese,[19] while recovery of value from both the fiber and matrix utilizing transition metal catalysts in postconsumer composites was demonstrated by Skrydstrup.[20] Beckham illustrated a tandem biocatalytic method to convert polymer waste into small molecules via bacterial metabolism.[21] Taking inspiration from these works, our composite matrix cleavage proceeds in two steps: (1) presoaking the composite in benzyl alcohol and tripotassium phosphate trihydrate, $K_3PO_4{\cdot}3H_2O$, and (2) digesting with manganese(II) and

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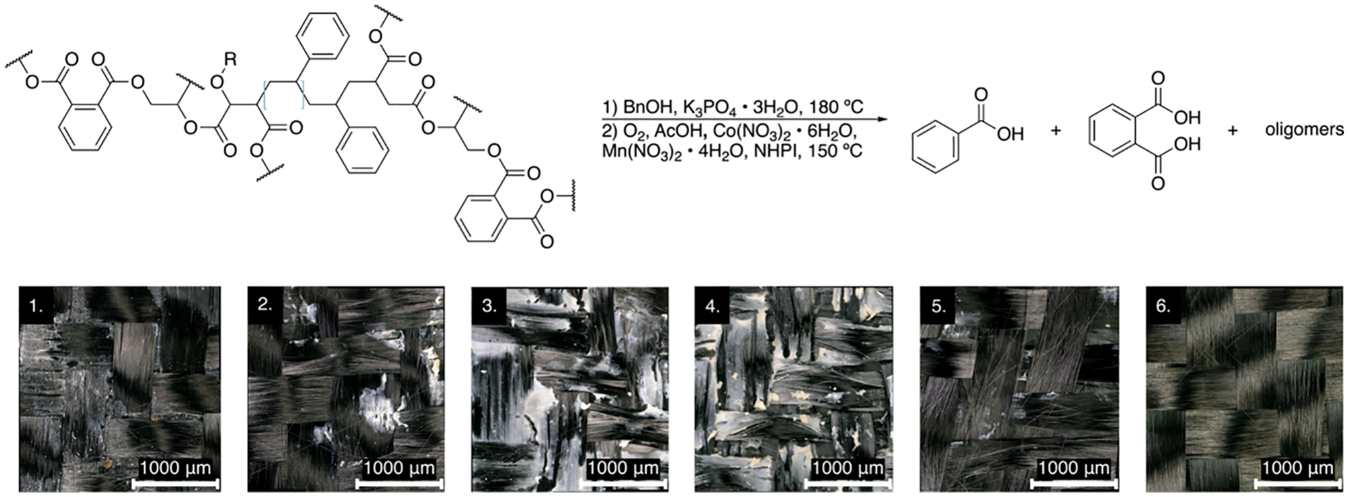

Figure 1. Top: proposed reaction for CFRP digestion. Bottom: resulting carbon fibers from the digestion of preconsumer CFRPs. Reaction conditions were optimized to obtain clean carbon fiber plies that retained their plain weave pattern and are summarized in Table S4.

cobalt(II) nitrate salts. We first used CFRP panels featuring a FiberGlast Part #77 polyester molding resin. To measure the composition of both materials, the matrix was first digested with sulfuric acid and hydrogen peroxide at 100 °C, separating the polymer matrix from the fibers. This provides an accurate quantification of fiber versus polymer content (Tables S1–S3).

In the first step, composite panels (50.8 × 38.1 mm) are incubated in benzyl alcohol and $K_3PO_4 \cdot 3H_2O$ for 24 hours at 180 °C. This appears to swell the composite and enables more extensive intercalation of the reagents of the subsequent step. While we used a similar approach with neutral benzyl alcohol when cleaving epoxy composites by catalytic oxidation,[2,12] here we add a base to cleave the polyester cross-links. The swelling and disconnection are visible, as the pretreatment causes matrix cracking near the surface, yielding a white crystalline substance on the surface of the carbon fiber plies. Infrared spectra of the crystalline material and clear-yellow benzyl alcohol solution resulting from the pretreatment reveal that only the resulting solid contains esters (Figure S13).

Initial attempts at oxidative matrix cleavage (vide infra) without pretreatment involving smaller panels (25.4 mm × 25.4 mm) and a catalyst loading of 4–7 wt % (relative to the composite) for metal catalysts and NHPI yield clean carbon fibers; however, with larger composites suitable for remanufacture, only partial digestion of the matrix is achieved (Table S4, entry 1), thus justifying the added step.

The solvolysis product, pretreated polymer still affixed to the fibers, is further processed with conditions we introduced for converting PS to benzoic acid.[22] We adapt these conditions to yield clean carbon fiber plies that retain their plain weave pattern, which are visually observed and easily imaged via light microscopy (Figure 1, bottom). Optimization of reaction conditions is summarized in Table S4. Notably, $K_3PO_4 \cdot 3H_2O$ is required for complete digestion, an observation evident when comparing entries 2 and 6 in Table S4. Increasing the reaction time and amount of acetic acid in the reaction mixture leads to more complete digestion with a lower catalyst loading. However, this formulation can leave residual polymer matrix on the fibers (Table S4, entry 5). Characterization via ^{1}H NMR reveals that all entries in Table S4 produce benzoic acid, phthalic acid, and oligomers of different chain lengths (Figures S15–S22).

The reaction conditions in Table S4, entry 6, yield a clean fiber fabric and are used to isolate benzoic acid for fungal upgrading. Using these conditions, benzoic acid is isolated in yields of 93–102% relative to the polystyrene content in the composite. Although most of the benzoic acid yield is attributed to polystyrene conversion, some of the yield can be credited to the conversion of residual benzyl alcohol[23] remaining in the composite after pretreatment, even with thorough washing with acetone. Similar reaction conditions are applied to postconsumer CFRPs (50.8 × 38.1 mm) consisting of polystyrene cross-linked with vinyl esters and chopped, unaligned carbon fibers. This results in a yield of 16–25% for benzoic acid. The complete isolated and recovered composition for pre- and postconsumer composites is summarized in Table S5.

Prior to upgrading, the crude oxidation product is purified via a series of filtrations, extractions, and crystallizations to remove the oligomers and phthalic acid as, although phthalic acid does not inhibit growth, it cannot be metabolized by the fungi.[22] Although the final purification step of recrystallizing benzoic acid removes most of the remaining oligomers in the sample, a yellow impurity cocrystallizes with the product and is detected by elemental analysis (Table S6). The impurity does not inhibit fungal growth.

We previously upgraded PS-derived benzoic acid to secondary metabolites via the model fungal organism *Aspergillus nidulans*,[22] wherein polymer digest was the sole carbon source. This, in conjunction with its diverse secondary metabolite profile, makes *A. nidulans* the ideal candidate for the biochemical upcycling of CFRP-derived benzoic acid into a valuable fungal metabolite. Here, we upgrade the composite matrix to (2*Z*,4*Z*,6*E*)-octa-2,4,6-trienoic acid, OTA. OTA is an intermediate in the biosynthetic pathway for (+)-asperlin, a molecule with antitumor, antibiotic, and anti-inflammatory properties.[24,25] OTA is of particular interest because its conjugated backbone readily lends itself as a potential feedstock compound with synthetic chemistry applications,[26] such as ketonization, Kolbe coupling, and olefin coupling. Thus, we demonstrate here the formation of a versatile platform chemical from a waste stream of industrial scale.

In *A. nidulans*, the production of OTA requires the expression of two genes, *alnA* (AN11191 using the

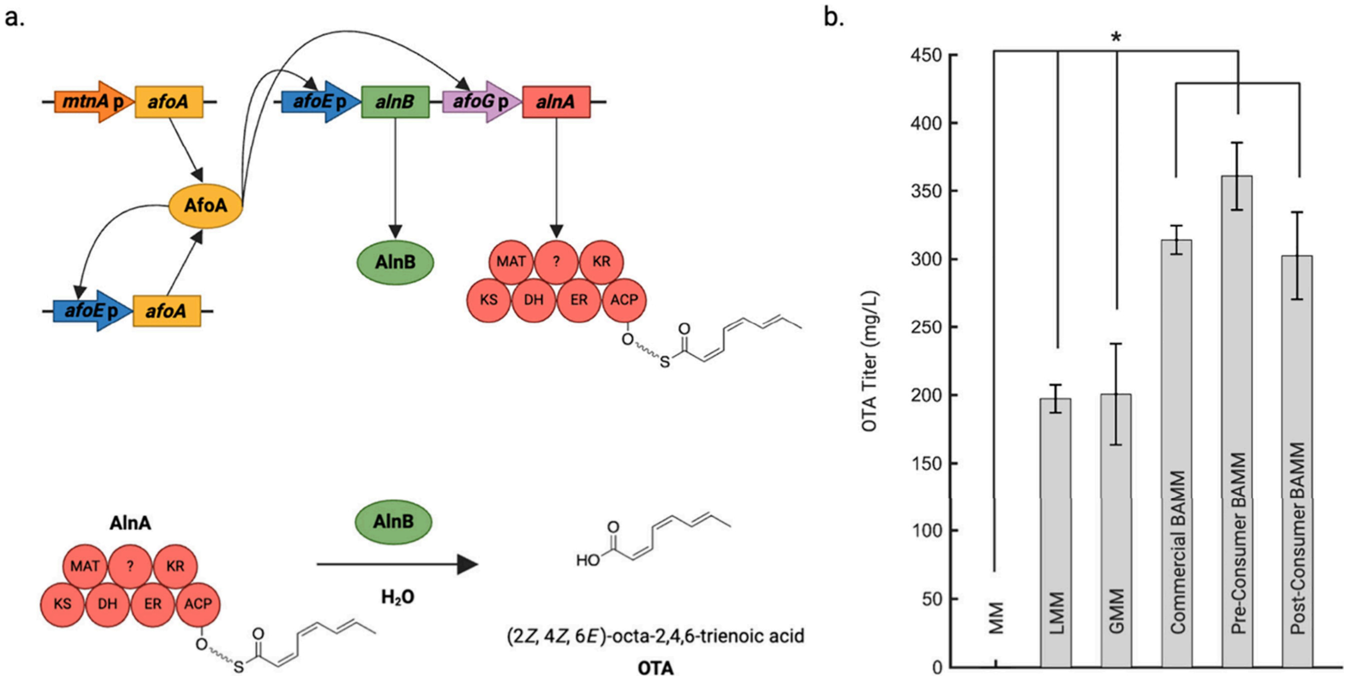

Figure 2. (a) Schematic of the genetic design of LO11055 and biosynthesis of OTA. The promoter of AN11489, which we identify as a metallothionein gene and hereby designate *mtnA*, was inserted to constitutively express AN1029 (*afoA*), whose gene product, AfoA, is a strong transcription factor. AN11191 (*alnA*) and AN11199 (*alnB*) produce AlnA and AlnB, the two proteins responsible for OTA synthesis, and were placed under the control of the AN1036 promoter [*afoG*(p)] and the AN1034 promoter [*afoE*(p)], respectively. AfoA binds to these promoters to drive the transcription of *alnA* and *alnB*. Additionally, a copy of *afoA* under control of *afoE*(p) was inserted, creating positive feedback. (b) Comparative OTA production by medium type: MM, minimal medium; LMM, lactose minimal medium; GMM, glucose minimal medium; BAMM, benzoic acid minimal medium. Commercial BAMM was prepared using commercially sourced benzoic acid, whereas preconsumer and postconsumer BAMM were prepared using benzoic acid derived from preconsumer and postconsumer composite materials. OTA titers were quantified using HPLC-DAD. Bars represent means, and error bars represent standard deviations. $^*p < 0.05$.

FungiDB.org gene designation), which is a polyketide synthase (PKS), and *alnB* (AN11199), which is thought to be required for the release of OTA from the PKS. We previously developed an OTA-producing strain, LO4912, by replacing the native promoters of *alnA* and *alnB* with a regulatable *alcA* promoter.[25] To achieve higher yields and eliminate the need for induction, we engineered a strain with a strong constitutive promoter system that employs a positive feedback loop, after our recent success with a similar system in the production of the fungal secondary metabolite asperbenzaldehyde.[22] In the resultant strain LO11055, the feedback loop promotes the expression of *alnA* and *alnB*, which drives OTA biosynthesis (Figure 2a).

Thus, we use LO11055 for the biosynthetic conversion of CFRP-derived benzoic acid into OTA. In a representative experiment, LO11055 is inoculated into liquid minimal media (MM) containing 10 g/L of glucose (GMM), 15 g/L of lactose (LMM), or 10 g/L of benzoic acid obtained commercially, isolated from a preconsumer composite source, or isolated from a postconsumer composite source. A minimal medium without a carbon source is used as a negative control. We find that LO11055 successfully utilizes benzoic acid from all three sources to grow and produce OTA. The OTA titer is determined via HPLC-DAD with statistical significance quantified by the unpaired *t* test (Figure 2b). Notably, three benzoic acid sources (commercial, FiberGlast Part #77-derived, and postconsumer-derived) yield OTA at statistically significant higher titers than either GMM or LMM. This was surprising given that LMM and GMM, in particular, are excellent carbon sources that support rapid growth. Benzoate utilization in *A. nidulans* has been studied extensively,[27,28] and the results may give clues as to why benzoic acid is converted more efficiently into OTA than glucose or lactose. Benzoate is converted by benzoate *para*-hydroxylase into *para*-hydroxybenzoate, which is, in turn, converted to protocatechuic acid.[27−29] Protocatechuic acid is converted to 3-oxyadipate, which feeds into the TCA/glyoxylate cycle. Oxaloacetate from the TCA cycle is converted by AcuF to phosphoenylpyruvate, which is converted to pyruvate, which is converted to acetyl-CoA. Acetyl-CoA is converted to malonyl-CoA by acetyl-CoA carboxylase. Acetyl-CoA and malonyl-CoA are the building blocks of polyketides, and the structure of OTA indicates that it is synthesized from four malonyl-CoA molecules. We speculate, therefore, that the greater yields of OTA from benzoic acid media relative to glucose or lactose media are due to benzoic acid being converted to malonyl-CoA by a mechanism that bypasses the longer glycolytic pathway that converts carbohydrates, such as lactose or glucose, into pyruvate. All carbon-source-containing conditions also outperform previously reported bacterial-biosynthesized OTA yields by 172−185%.[26] The elevated yields of OTA associated with composite-derived benzoic acid as the sole carbon source are promising results that hold up the stepwise chemical/biocatalytic approach as a new and productive paradigm for upcycling composite polymers not yet touched by modern methods for epoxy recovery.

Many reports of composite recycling schemes recover fibers, but few show their utility as manufacturing substrates. We imaged our recovered carbon fibers, rCF, via scanning electron microscopy (Figures S3−S7) after cleaning them following the procedure described in the Supporting Information. These rCFs appeared clean and free of surface damage. X-ray photoelectron spectroscopy (XPS) reports the change in the surface chemistry of the fibers after recycling (Figures S8−S10 and Table S7). XPS data show that sizing functionalities, such as hydroxyl and carboxyl groups, diminish but do not disappear during recycling. We restore diminished sizing by employing a nitric acid treatment, as shown in Figure S10.

Single-fiber tensile strengths of virgin and recovered CFs were measured and summarized in Figure S11 and Tables S8−S10. We find that rCFs retained >97% of the tensile strength and >99% of the modulus of virgin fibers. Cleaned but not resized rCFs are readily remanufactured into a second-generation composite with aerospace-grade resin films, cured through a vacuum bag only (VBO, nonautoclave) process. Cross sections of the second-generation composite were polished and examined by light microscopy (Figure S12). The second-generation composite is well consolidated, demonstrating the viability of upcycling intact carbon fiber fabrics under the proposed conditions.

The production of both OTA and a second-generation composite coupon from the same starting CFRP sample illustrates the first case of remanufacturing both the CFRP polymer matrix and reinforcing fibers, the latter without disruption of the alignment or pattern. While minimal disruption of sizing is observed by XPS, the fabric is remanufactured directly or readily resized with nitric acid. Thus, we provide the first method that fully recovers value from both fiber and matrix components of pre- and postconsumer polystyrene containing CFRPs. The procedure is not only rapid, occurring within one week, but also results in high yields of OTA, 172−185% more than in previous reports utilizing bacteria instead of fungi. Recovered carbon fibers are readily used to produce a second-generation composite with negligible loss of material properties and minimal, reversible changes to the fibers' surface chemistry.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.4c10838.

> Procedures for optimization of reaction conditions, compound and recovered fiber purification, media recipes and fungal metabolism, *Aspergillus nidulans* strain engineering, NMR spectra and chemical shift data, IR spectra, UV−vis spectrum, XPS spectra, and SEM images (PDF)

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

CFRP, carbon fiber reinforced polymer; OTA, (2*Z*,4*Z*,6*E*)-octa-2,4,6-trienoic acid; *A. nidulans*, *Aspergillus nidulans*; PKS, polyketide synthase; HPLC-DAD, high performance liquid chromatography with diode-array detection; MM, minimal medium; GMM, glucose minimal medium; LMM, lactose minimal medium; BAMM, benzoic acid minimal medium; rCF, recovered carbon fiber

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