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3D printing with biobased PEF for carbon neutral manufacturing

Fedor A. Kucherov, Evgeny G. Gordeev, Alexey S. Kashin, and Valentine P. Ananikov*

Abstract: *We demonstrate the utility of biomass-derived poly(ethylene-2,5-furandicarboxylate) (PEF) as an efficient material for Fused Deposition Modeling (FDM) 3D printing. A complete cycle from cellulose to printed object has been performed. PEF-printed objects created in the present study demonstrated higher chemical resistance than objects printed with commonly available materials (ABS, PLA, PETG). The studied PEF polymer has shown key advantages for 3D printing: optimal adhesion, thermoplasticity, lack of delamination and low heat shrinkage. The high thermal stability of PEF and relatively low temperature that are necessary for extrusion are optimal for recycling printed objects and minimizing waste. Several successive cycles of 3D-printing and recycling were successfully demonstrated. The suggested approach for extending additive manufacturing to carbon neutral materials opens a new direction in the field of sustainable development.*

Dependence on non-renewable natural resources, non-recyclability and environmental CO_2 pollution are undoubtedly matters of paramount importance.[1] Biobased materials and sustainable feedstock will inevitably replace fossil hydrocarbons in the near future.[2] Materials that are derived from renewable sources and low-waste manufacturing methods should be combined to develop advanced technologies.[3] These topics define a new paradigm of carbon neutral cycle processes, and the introduction of purely biobased compounds is now an urgent task.[4]

3D printing, also known as additive manufacturing, refers to a collection of processes used to build freestanding objects from computer aided design (CAD) instructions.[5] Additive manufacturing is inherently waste-free method for accessing products of varying complexity, in contrast to subtractive manufacturing methods such as machining and milling. For practical use, Fused Deposition Modeling (FDM) is the most commonly used 3D printing method that allows rapid design, prototyping and production.[6] The general principle is simple and attractive: a thermoplastic filament is extruded through a hot nozzle onto a moving table, depositing a small amount of polymer layer by layer.[5-6]

The most common filament materials are polylactic acid (PLA), acrylonitrile butadiene styrene (ABS) and polyethylene terephthalate glycol-modified (PETG), among many others. However, most of the commercially available materials suffer from several drawbacks that limit their use in the direct application of the prototype in a real environment in contact with chemicals. Plastic products made from PLA, ABS and PETG lose their structural integrity with exposure to organic solvents. Polymers with high solvent resistance such as polypropylene (PP) demonstrate low adhesion to the build plate and relatively high heat shrinkage, which leads to the delamination of layers, accumulation of defects during printing and a loose surface of the model. In this work, we describe poly(ethylene-2,5-furandicarboxylate) (PEF), a completely biobased «green» polymer that is suitable for 3D-printing and has many practical advantages.

A full sustainable development cycle starting from cellulose was implemented (Figure 1A). Cellulose or carbohydrates were directly converted to 5-(hydroxymethyl)furfural (HMF) using a procedure developed earlier.[7]

Transformation of biomass to HMF is actively studied worldwide, and the production of HMF at the plant-scale is now available. [8] Oxidation of HMF leads to 2,5-furandicarboxylic acid (FDCA), which can be esterified with methanol to yield the corresponding methyl ester derivative (FDE). FDCA and FDE are important building units for the synthesis of a variety of polyesters.[8,9] Multistep melt polycondensation of FDE with ethylene glycol proceeds *in vacuo* using titanium (IV) isopropoxide as the catalyst (1.25 mol%). The target polyester was obtained after re-precipitation from methanol as a white powder in excellent yield (97%).

The filament was fabricated by melting powdered polymer in the oven, followed by formation of the raw piece by hot drawing to a standard diameter (2.85 mm). The 3D-printing was performed using an easily available Ultimaker^2 machine. No additional hardware modifications for printing with PEF are required, and common printing parameters were used (Figures 1B-C). All of the stages in the printing process were performed using standard procedures, thus confirming the excellent compatibility of the prepared PEF material.

Several sample objects were produced to study 3D-printing performance (Figure 1D). PEF was extruded through the nozzle well, producing smooth layers with considerable printing speeds. No signs of delamination were observed in the produced objects To evaluate print quality and dimensional changes from digital model to printed part, we measured the linear dimensions and diameters of vertical holes (Figures S5, S6 in Supporting Information). Remarkably, the difference between predetermined shape and printed model was minimal due to low thermal shrinkage (~1.8% for PLA, ~3.4% for ABS, ~2.5% for PEF).

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Supporting information for this article is given via a link at the end of the document.

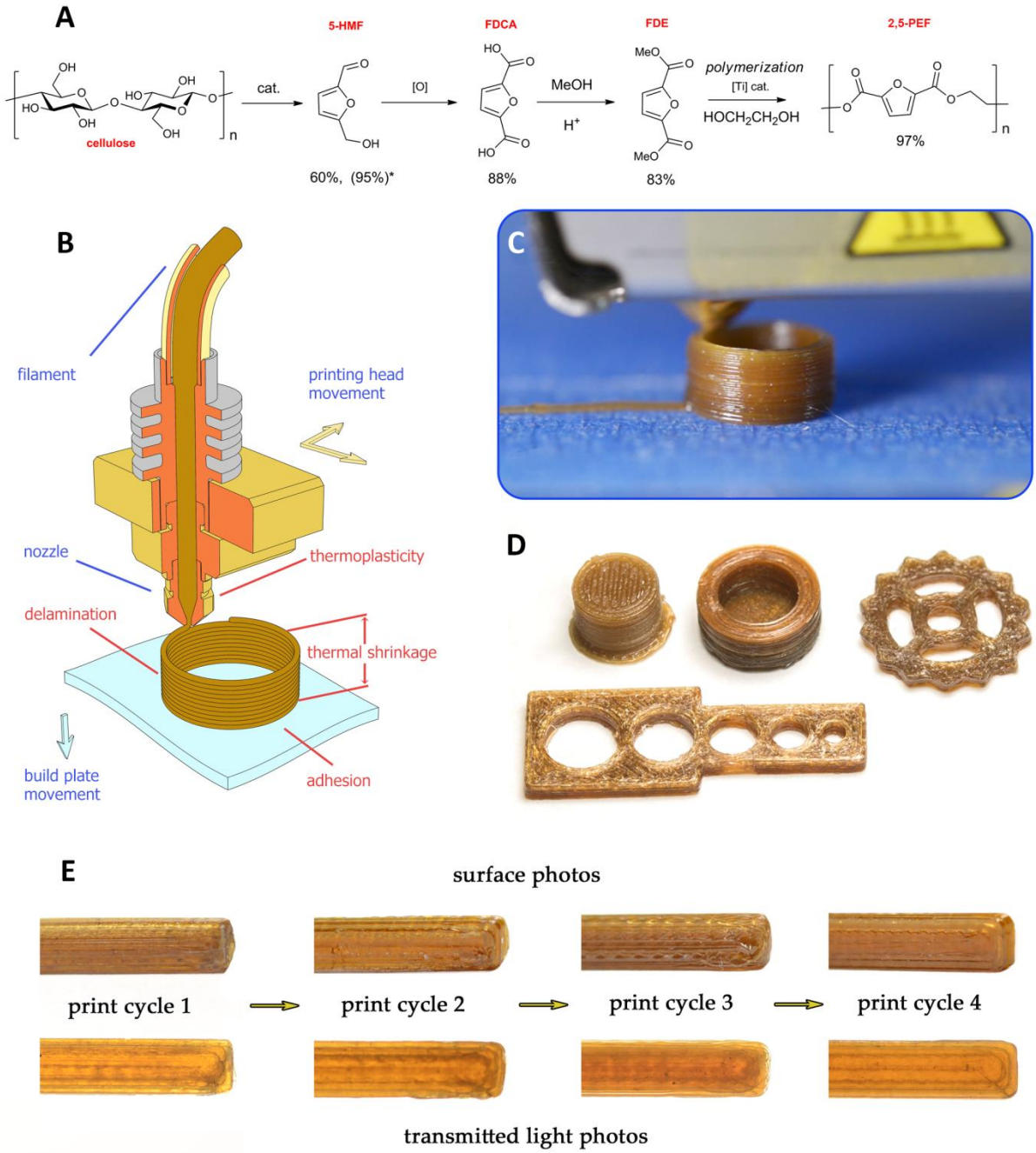

Figure 1. 3D-printing with poly(ethylene-2,5-furandicarboxylate): A - Reaction scheme of synthesis of PEF from biomass and from fructose (*). B ï General scheme of Fused Deposition Modeling and key characteristics of 3D-printing (shown in red). C - 3D-Printing process with PEF on the Ultimaker^2 FDM platform (extrusion temperature 215°C, build plate temperature 60°C, material flow 105% w/o retraction, layer height 0.15 mm, printing speed 40 mm/s, travel speed 100 mm/s, cooling fan enable). D - Examples of 3D-printed objects produced from PEF. E - Recycling in several 3D printing cycles with each stage represented by the surface photo (top) and transmitted light photo (bottom).

For practical applications, the key point is resistance to liquid phase environment. Since one of the main drawbacks of conventional materials is sensitivity to organic solvents, a dedicated assessment of PEF and comparison with PLA, ABS, PETG were performed.

Methylene chloride (DCM) was selected as the most challenging aggressive test. A relative stability test was conducted wherein the printed object was placed in a vial filled with DCM and an appropriate indicator (metallic ball) was applied on top (Figure 2). The indicator clearly shows the point of loss of structural integrity (metallic ball drops upon destruction of the cylinder).

Cylinders printed with PLA, ABS and PETG soften and lose their structural integrity within 250 seconds and, after 500 seconds, break down completely. Amazingly, the PEF-printed model fully preserves its stability and shape.

Even a prolonged 24-hour experiment showed that the PEF model retained the initial shape and was not crushed in this challenging test (video is provided in Supporting Information). Another experiment was performed to determine the durability of a thin layer of the materials (Figures S1, S2 in Supporting Information). As expected, PEF was superior in this stress test compared to models produced from PLA, ABS and PETG, which lost structural integrity in the DCM medium after ~ 5 minutes.

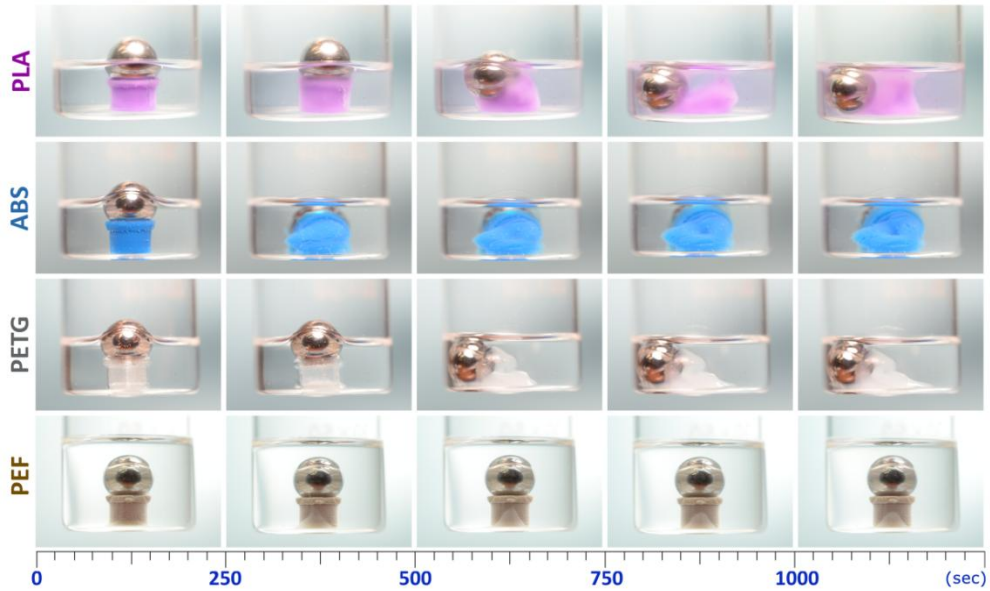

Figure 2. Comparative stability test of PEF and common materials by treatment of printed objects (dimensions: 7x5.6 mm, 0.6 mm wall/bottom) in dichloromethane. Time in seconds is shown on the horizontal axis.

Resistance to an aggressive liquid phase environment is a key parameter and, inspired by PEF's unusual stability, we performed a detailed structural study. To evaluate the character and extent of damage due to contact with the solvent, a series of electron microscopic studies of the object surface were performed (Figure S4 in Supporting Information). SEM images of untreated material demonstrated a solid structure of the surface layer due to full fusion during printing.

Sample preparation for microscopy includes treatment of the surface of the PEF-printed tablet with a drop of DCM (20 µl) (Figure S4). After 5 minutes, the solvent had completely evaporated. Microscopy analysis of a cut of the treated material clearly reveals that the solvent was not able to penetrate deeply into the solid; only ~50 µm of the material was affected (Figure S4). SEM images reveal the specific morphology of PEF during interaction with DCM. The polymer noticeably did not dissolve and swelling was not observed. Porous spherical nanostructures were formed on the surface (Figure S4).

An important point is to compare intrinsic electronic properties of PEF with polyethylene terephthalate (PET). Currently, PET is one of the most used non-sustainable oil-derived polymers, with an annual production of approximately 56 million tons.[10] In a number of applications, such as the production of multi-ton scale materials, PEF is considered a «green» replacement for PET.[8-11] The present study demonstrated good processability of PEF in FDM-based printing with uniform extrusion and negligible thermal shrinkage.

It is known that unmodified PET is poorly suited for 3D-printing. Thus, despite the structural similarity between PEF and PET, their properties differ significantly in terms of their applicability to 3D-printing. The properties of the polymer material are defined by the fundamental features of its structure, e.g., the mobility of elementary units and the characteristics of the secondary structure of macromolecules. To reveal plausible differences in molecular structure, we performed preliminary DFT calculations to model intermolecular arrangement in PET and PEF (Figure 3).

The all-trans conformation of PET units forms a linear structure, a noticeable difference from PEF (*cf.* Figures 3A, B and 3F, G). The studied PEF units form a spiral motif in which five-membered rings at the opposite ends are perpendicular to each other. The fundamental difference between benzene ring (Ŭ = 0Á) and furan ring (Ŭ = 49°) suggests that spiral motifs and diverse non-linear architectures may be expressed in the latter case (Figures 3C, H).

The presence of the spiral motif and twisting of polymer chains (cf. Figure 3D and 3I) may be a key factor to introduce higher stability against delamination and attractive practical properties.

The difference between PET and PEF can be considered at the molecular structure and electron density levels. A PET chain in the ñall transò form contains segments with a symmetrical arrangement of polar groups, whereas in PEF segments, furan rings result in less uniform charge distribution. The calculated dipole moment for a PET segment is almost zero (0.06 D), whereas for PEF segment a much greater value of µ = 3.3 D was found. In PET segments, the oxygen atoms of COO groups are the only sources of negative electrostatic potential. The additional oxygen atom in the furan ring of PEF results in expansion of the negative electrostatic potential region (Figures 3E, J).

The presence of cyclic geometry arrangements and spiral motifs may be an important factor to preserve structural integrity during treatment. Thus, the lower symmetry of the furan ring and additional oxygen atom in PEF chains result in the greater polarity of the PEF polymer compared to PET. Of course, the present DFT calculations for polymer units should be considered as preliminary assessment only, since computational study does not take into account larger model and far-order interactions, which govern important polymer properties.

Recycling and re-using the material are important practical requirements. We have found that objects printed with PEF can be completely recycled - printed objects were melted, converted to filament and used in 3D printing again (Figure 1E). This useful

feature allows the recycling of printed objects, including any filament residues and technical leftovers, without a notable degradation of the polyester. The high thermal stability of the polymer allows the melting of scraps at 250 °C until a uniform material is obtained. The refining process was carried out without any drop in printing quality (Figure 1E). Comparative DSC study and elemental analysis after each 3D printing step with re-cycled material showed very good performance and no evidence for changing composition/oxidation. Reliable stability towards oxidation on air was evaluated by continuous heating of the material (see Supporting Information).

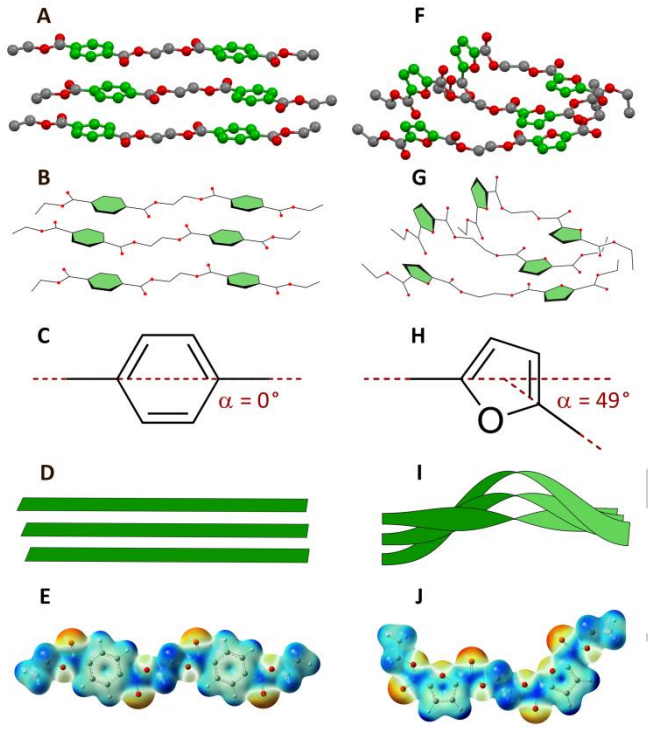

Figure 3. Molecular structure of fully optimized PET and PEF segments in interchain complexes (BP86/def2-SVP D3BJ). **A, F,** ball and stick model; **B, G,** simplified stick model; **C**, **H,** angular deviation from linearity in benzene and furan rings; **D, I,** simplified schematic view of secondary structures; **E, J,** electrostatic potential surfaces for shown segments.

Finally, 3D printing with different nozzle sizes, layer heights and printing time was carried out to confirm reliable performance of the developed PEF material (Figure S30 in Supporting Information). The material was completely suitable for rapid 3D printing with low resolution and slow 3D printing with high resolution. The quality of the 3D printed object with PEF was superior in terms of fusion of layers and high quality smooth surface as compared to a standard PLA material (Figure S31 in Supporting Information).

In conclusion, we have demonstrated a process whereby polymeric material was synthesized from biomass, processed into filament and used in 3D printing. This opens up stimulating opportunities for such a material in sustainable development, especially considering the significant potential for possible modifications and the introduction of co-polymer and additives.

Biobased PEF can be recycled several times without noticeable loss of 3D printing characteristics. Overall, PEF production depends only on biomass-derived carbon sources: HMF and ethylene glycol (Figure S3 in Supporting Information). The life cycle of this 3D printing material is fully compatible with carbon neutral concepts and represents a sustainable technology. More detailed studies are anticipated in the near future to evaluate several important properties of biomass-derived polymers and to carry out dedicated optimization for better 3D-printing performance.

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Keywords: 3D printing Å5-hydroxymethylfurfural Åsustainable development Åcarbon neutral cycle

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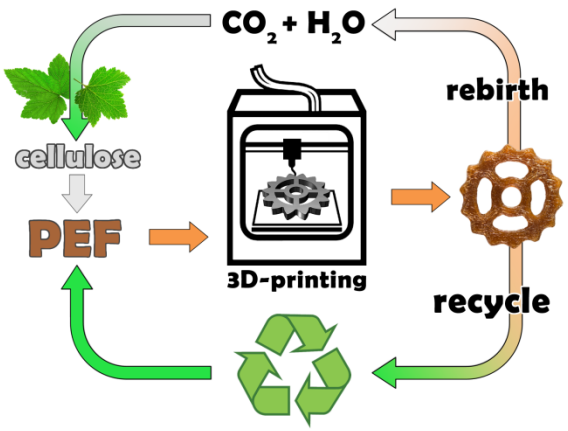

Sustainable 3D printing: biomass-derived poly(ethylene-2,5-furandicarboxylate) (PEF) was utilized as an efficient material for Fused Deposition Modeling (FDM) 3D printing. A complete cycle from cellulose to printed object has been performed. PEF-printed objects created in the present study demonstrated higher chemical resistance than objects printed with commonly available materials.