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From PEF to rPEF: disclosing the potential of deep eutectic solvents in continuous de-/re-polymerization recycling

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PURPOSE OF THE ABSTRACT

With the rise of bio-based polymers' research and production, there is an emerging concern about their fate after usage, since some of them also tend to be persistent in the environment. Poly(ethylene 2,5-furandicarboxylate) (PEF), derived from C6 sugars like D-fructose or D-glucose [1], is widely known to be a viable replacement for conventionally used poly(ethylene terephthalate) (PET), mainly due to its relevant thermal and mechanical properties [2?5] as well as standout barrier features, with a 19 fold reduction in CO2 permeability compared to PET [6]. Despite its great potential and expected global production [7], its end-of-life (EoL) options are generally overlooked, as we have recently highlighted [8]. In this work, we report the design of urea:zinc acetate (U:ZnAc2) Deep Eutectic Solvent (DES) system for a continuous, mild and closed-loop recycling approach from PEF into rPEF (Figure 1). First, PEF was depolymerized by mild glycolysis using U:ZnAc2 (4:1 molar ratio) as a catalyst. Afterwards, the reaction mixture was repolymerized without any purification steps or additional catalysts in a novel one-pot approach, yielding again PEF (rPEF), as confirmed by 1H and 13C NMR, with a 69 % yield. When a co-catalyst was added, titanium(iv) tert-butoxide (TBT), a maximum yield of 91 % was achieved.
For the process' optimization, a series of Lewis Acid ESs were screened and tested for their efficiency in PEF depolymerization, and the reaction conditions were optimized to maximize the initial polymer's weight loss.
Additionally, if one wants to isolate intermediate products, that can be achieved by precipitation with water, allowing to confirm that bis(hydroxyethyl)-2,5-furandicarboxylate (BHEFDC) is the main intermediate product formed. The proposed recycling approach confirms, for the first time, the potential for DESs to catalyze PEF's de-/re-polymerization in a continuous way, as an efficient greener option to chemically recycle persistent PEF wastes (and beyond), promoting a more circular approach for its end-of-life.

FIGURES

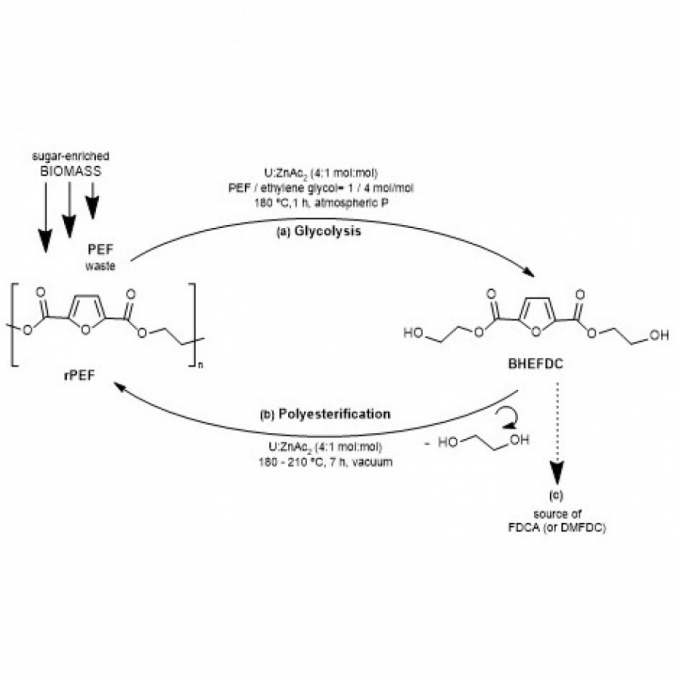

FIGURE 1

PEF continuous circular recycling method

PEF continuous circular recycling method through a DES-assisted mild glycolysis (a) and polyesterification (b) reactions, with potential recovery of FDCA (or its dimethyl ester) (c) also considered.

FIGURE 2

KEYWORDS

Poly(ethylene 2,5-furandicarboxylate) (PEF) | Deep Eutectic Solvent (DES) | Chemical Recycling | Polymer's End-of-Life

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