Upcycling of PET from recycled food packaging trays via vitrimers chemistry

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Abstract

Poly(ethylene terephthalate) (PET) recycling process is well established nowadays for PET bottles. On the other hand, recycling of PET from food trays (tPET) is still challenging because of its lower molecular weight and the possible presence of other polymers as a consequence of the use of multi-layered trays. In this work, end-of-life PET trays have been chemically modified through the melt reactive processing into a covalent associative network, in order to enhance its performance. In particular, upcycling of tPET was obtained by the reaction of diglycidyl ether of bisphenol A (DGEBA) in the presence of zinc acetylacetonate as a transesterification catalyst, to obtain a reversibly cross-linked material, i.e. a vitrimeric material, which retains recyclability while significantly enhancing mechanical properties of tPET. Indeed, rheological test demonstrated clear crosslinking of tPET vitrimers, with a high temperature relaxation explained by the exchange of covalent bonds. Dynamic mechanical analysis showed high thermomechanical resistance, while tensile test at room temperature demonstrated strong enhancement in tensile strength and elongation at break compared to tPET. The results reported in this paper opens to the upcycling of other low grades of PET, including textiles and other goods produced with previously recycled polymer, thus contributing to the establishment of a circular economy for PET, beyond bottles.

Keywords: Poly(ethylene terephthalate); upcycling; vitrimers; melt reactive blending

1. Introduction

Poly(ethylene terephthalate) (PET) is one of the most used polymer worldwide because of its set of properties, including good mechanical strength, thermal and chemical stability, processability and low permeability to gases. For this reason, its applications range from food and beverage packaging (mainly bottles and trays) to vehicle parts, electronic instruments and fibres [1-4]. Its large diffusion poses challenges for the end-of life management of PET household waste, as well as the dispersion of microparticles in water, mainly derived from PET fibres [5]. In fact, as PET is non-biodegradable, careful waste collection, separation and recycling are compulsory, both to reduce dispersion into the environment and to recover a high value material [6, 7]. Indeed, PET recycling methods, as well as for other thermoplastics such as LDPE, HDPE and PP, are already well established. In particular, PET recycling can be closed loop, that is increasingly used for bottles, or open loop, which is more common for coloured bottles and food packaging trays. The most common uses of recycled PET are in fibres, food packaging (usually blended with virgin PET) and other goods requiring mechanical strength. However, recycling of PET trays is still challenging, both because of the lower molecular weight compared to PET from bottles and because multilayers of different polymers are often used for food packaging, which are difficult to be sorted from mono-material PET trays. The consequence is that PET trays are often not sorted from mixed plastic, because of technical challenges or because the process is not economically sustainable, given the low value of the recycled material. When a recycled product is considered, the price of the recycled material and its lower mechanical properties compared to the virgin one may both represent severe limitations [1]. It is well-known the quality of mechanically recycled PET is lower than virgin material due the drop of the molecular weight and the presence of possible contaminations [1-3]. In particular, PVC contaminations may produce HCl during melt processing, that promotes chain scission, while residual moisture in PET causes hydrolytic degradation during the process [1, 8]. For this reason, the amount of PVC and water is required being less than 50 ppm for the former and less than 40 ppm for the latter before starting the extrusion [1, 2]. Besides, other variables (temperature, screw profile, screw speed, etc.) play an important role in the thermomechanical degradation of the polymer, which may rapidly lead to a decrease in molar mass, especially as low M_W degradation products can act as catalyst for a further deterioration [1, 2].

To compensate the chain scission during mechanical recycling, different strategies can be implemented, by the use of additives like stabilizers and chain extenders, or via a post processing

by solid-state polymerisation (SSP). The use of stabilizers such as metal-based structures (lead phthalate, butyl tin or antimony mercaptide, among a few to mention) helps preventing the negative effect of PVC, but SSP consists in heating the polymer between T_g and T_m to promote polycondensation while minimizing degradation reactions [1]. Karayanidis et al. [9, 10] demonstrated the effectiveness of the process for recycled PET samples heated at 230°C for 8 hours. However, the slowness and cost of whole process limits its practical application [10]. The use of chain extender additives is the most diffused process because it is relatively inexpensive and industrially viable [1]. Oxazolines [11], isocyanates [12], epoxides [13], pyromellitic dianhydride (PDMA) [14] and organic phosphites [15] are employed to join two or more PET chain-ends, leading to a significant enhancement in average molecular weight [1, 2]. Depending on the type of chain-extender, the final result can be constituted by longer or branched chains. In the latter case, controlling the amount of reactant and the reaction time, branching reaction can be varied, possibly leading to partial or even full cross-linking [1, 16]. While a cross-linked structure typically provides enhanced solvent resistance and improved mechanical and thermal properties, full and irreversible crosslinking impact on both processability and recyclability, thus colliding with sustainability needs [17].

Recently, a new type of reversibly cross-linked materials, referred to as vitrimers [18-25], were proposed and investigated. Vitrimers are cross-linked materials, thus having properties similar to thermosets, which can however undergo dynamic exchange or scission/reformation of their covalent bonds, allowing reprocessing the material at relatively high temperatures, thus reminding processability of thermoplastics. Dynamic exchange of bonds in vitrimers may be obtained with various chemical reactions, including transesterifications [26-32], boronic esters methathesis [25, 33], vinylogous urethanes exchange [34, 35] and others [36-41]. The first vitrimer concept were realized by Leibler et al. [19, 20, 32] via transesterification using diglycidyl ether of bisphenol A (DGEBA) in epoxy resin, using zinc acetate as trans-esterification catalyst, and the same approach was later applied to polyesters. Demongeot et al. [42] treated polybutylene terephthlate (PBT) in a reactive extrusion with DGEBA and zinc acetylacetonate ($Zn(acac)_2$) using trans-esterification chemistry. The process allowed obtaining an efficient cross-linking within a few minutes at 270°C, resulting in a material that combines crystalline properties of PBT, dimensional stability above the melting temperature, insolubility and a good processability for reshaping and recycling. Zhou et al. [43] incorporated PBT with glycerol and $Zn(acac)_2$ via solid state polymerization. Resulted materials showed the typical features of vitrimers, highlighting that thermal, rheological and mechanical

properties were tunable by controlling the glycerol content. It was also proven that several recycling steps did not significantly alter the thermomechanical properties of the material. Recently, Qiu et al. [44] report a method for reprocessable PET vitrimers using DGEBA and a polyol with a tertiary amine structure through reactive extrusion, due to the autocatalysis of the hydroxyl group and the tertiary amine structure on transesterification. Creep resistance improved than neat PET because of cross-linked networks.

This work addresses the valorization of end-of-life PET from food packaging trays, through the application of vitrimers chemistry, based on catalysed transesterification reactions carried out during one-step melt extrusion mechanical recycling.

2. Experimental

2.1 Materials

Poly(ethylene terephthalate) (PET) flakes coming from waste trays (tPET) were provided by the National Consortium for the collection and recycling of plastic packages (COREPLA, Italy), diglycidyl ether of bisphenol A (DGEBA) and zinc acetylacetonate ($Zn(acac)_2$) was supplied by Sigma-Aldrich. PET flakes were dried at 120°C for 12 h at least under static vacuum around -900 mbar. DGEBA and $Zn(acac)_2$ were also dried at 50°C for 5 h to remove residual moisture. Intrinsic viscosity (IV) for as received tPET was measured according to ASTM D4603 equal to 0.633 dL/g, corresponding to M_n=20,000 g/mol according to Moore Relationship $IV = 7.5 \cdot 10^{-4} M_n^{0.68}$.

2.2 Preparation of vitrimers

Reactive melt mixing was carried out into a co-rotating twin-screw mini-extruder DSM Xplore 15 cm^3 under nitrogen flow. As a typical example, 16 g of material, constituted by 96.5-100 wt % of tPET, 1.4-3.4 wt % of DGEBA and 0.1-1 wt % of $Zn(acac)_2$ was loaded in one step. To reduce loss of highly viscosity of DGEBA in the hopper, this was loaded into the extruder after spreading it over compression moulded tPET film, folded to contain the viscous liquid. The screw speed was set at 50 rpm during the material feeding and increased at 100 rpm during the mixing and the final extrusion. In different tests, the temperature was set at 250°C, 260°C or 270°C. The list of prepared formulations with the relative amount of DGEBA, $Zn(acac)_2$ and the process temperature during mixing is presented in Table 1. The choice of the percentage of reactants was inspired by previous literature reports for PBT vitrimers [42]. However, several tests were carried in a preliminary stage

(see Supplementary Information for details) to identify conditions providing sufficiently high cross-linking degree.

Table 1: List of prepared formulations.

Formulation code	tPET	DGEBA		$Zn(acac)_2$		Mixing T
	(g)	(g)	(wt %)	(mg)	(wt %)	(°C)
P0	16	0	0	0	0	250
P1D	15.78	0.22	1.36	0	0	250
P3D	15.46	0.54	3.40	0	0	250
P1D.3Za	15.73	0.22	1.36	48	0.3	250
P1D.3Zb	15.73	0.22	1.36	48	0.3	260
P1D.3Zc	15.73	0.22	1.36	48	0.3	270
P3D.1Za	15.44	0.54	3.40	16	0.1	250
P3D.1Zb	15.44	0.54	3.40	16	0.1	260
P3D.1Zc	15.44	0.54	3.40	16	0.1	270

The normal force on the screws, applied by the instrument, used as measure of viscosity, was recorded as function of the residence time. Even if the mixing time was set at 10 min, all samples were purged from the mixing chamber earlier, as soon as the normal force reaches 6500 N. On the one hand, reaching this limit supports for sufficient crosslinking of the material and on the other hand, purging of the material is necessary to avoid blocking of the compounder. Finally, the material was manually reduced in small pieces, dried (at 120°C for 12 h at least under static vacuum around -900 mbar) and used to prepare the samples for the following characterization through compression moulding. The hot compression moulding press (Collin P 200 T press) was set at 250°C for 4 min at 10 MPa. Pellets were placed inside different moulds: a 100 x 100 mm^2 mask made of aluminium foil (0.2 mm thick) for films, a 30 x 30 mm^2 and 1 mm thickness steel mold for DMTA and a 25 mm diameter and 1 mm thickness steel mold for rheology. All moulds were previously sprayed with a PTFE-based release agent sandwiched between two flat metal plates, internally covered with aluminium foils.

2.3 Characterization

2.3.1 Solubility test.

To evaluate crosslinking degree, 0.50 g of each formulation was immersed in 25 ml of a mixed solvent of phenol/tetrachloroethane (60/40 wt. %) and stirred at 120°C for 1 hour. Then, the solution was filtered, washed by acetone and dried in vacuum oven at 110°C for 2 hours. The residue on filter was weighted to calculate insoluble fraction.

2.3.2 Differential Scanning Calorimetry.

Crystallinity of PET formulations were measured by Differential Scanning Calorimetry (DSC). The analyses were carried out on a Q20 equipment (TA Instruments) under a nitrogen atmosphere. Each sample was about 7 mg and was heated from 25°C to 300°C at 10°C/min to remove thermal history, cooled (10°C/min) until 25°C to evaluate crystallization, finally it was heated again (10°C/min) to 300°C and this curve was considered for the glass transition temperature (T_g), cold crystallization temperatures (T_{cc}) and melting temperature (T_m). In order to evaluate the degree of crystallinity (X_c) of PET samples, enthalpy was compared to the value for 100% crystallinity of PET (ΔH_0=140 J/g) [45], according to the formula (1):

$$X_c = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_0 \cdot w} \quad (1)$$

where ΔH_m, ΔH_{cc} are the melting and cold crystallization enthalpy, respectively, and w is the weight fraction of tPET.

2.3.3 Thermogravimetric analysis

Thermal gravimetric analysis (TGA) analysis was performed with a Q550 equipment (TA Instruments), both in air and nitrogen atmosphere, range was 50-800°C, heating rate 10°C/min, using platinum sample holders.

2.3.4 Dynamic Thermomechanical Analysis (DMTA) measurement.

Bars with a cross-section of around 6 mm x 1 mm and a length of 30 mm were cut from compression molded squares and used to perform DMTA in tensile mode on a Q800 equipment (TA Instruments). Temperature scan was from 25°C to 270°C, at 3°C/min heating rate and 1 Hz frequency in strain-controlled mode, deformation amplitude at 0.05% and 0.005 N preload. All samples were conditioned at 23°C and 50% of relative humidity for at least 48 h before analyses. End of test criteria was set at 0.1 MPa threshold on E', to prevent flowing of the material.

2.3.5 Infrared spectroscopy.

To evaluate possible changes in the chemical structure of samples after the dynamic time sweep test, specimens were tested using a Frontier FT-IR spectrophotometer (Perkin Elmer) equipped with a universal ATR sampling accessory and a diamond crystal. The frequency range from 4000 cm^{-1} and 400 cm^{-1} for 16 scans and with 4 cm^{-1} resolution was used.

2.3.6 Rheology.

The rheological properties of materials were tested using an ARES rheometer (TA Instruments) operated with a 25 mm parallel plate geometry and 1 mm thickness samples. Dynamic frequency sweep tests were carried out to determine G', G'' and complex viscosity (η*) between 0.1 and 100 rad/s at 1% strain (linear viscoelasticity) and different temperatures (250°, 260°, 270°C). All rheological tests were performed under nitrogen atmosphere to avoid polymer degradation.

2.3.7 Mechanical tests.

The tensile properties of the samples, obtained by cutting compression molded films, with a dimension of around 20 x 10 x 0.2 mm^3 were tested on an Instron 5966 machine. Test were performed at room temperature using a 50 N loading cell, a strain rate of 1 mm/min and a gauge length of 20 mm. The samples were conditioned at 23°C and 50% of relative humidity for at least 48 h before analyses. A minimum of five specimens for each formulation were tested and results averaged to calculate mean values and deviations for elastic modulus, tensile strength and elongation at break.

3. Results and discussion

For the different prepared formulations (Table 1) the axial force measured during compounding was recorded, as a preliminary indication of the viscosity of the molten polymer *vs*. time (Figure 1). Indeed, viscosity strictly depends on the average molecular mass of PET chains and catalysed reactions occurring in the presence of DGEBA may lead to branching, chain extension and cross-linking, with obvious effects on the molecular mass. On the other hand, possible degradation processes due to the thermo-mechanical effect and/or to the presence of residual moisture may lead to decrease in molecular mass, by chain scission of PET [46-48].

The viscosity of P0 during extrusion is characterized by a slowly decreasing value, possibly due to limited thermomechanical degradation during the melt processing (Figure 1). When DGEBA is added

to tPET (Figure S1), viscosity was found to decrease with increasing the concentration of DGEBA, while maintaining similar trends *vs*. time. This may be explained by both the lower quantity of tPET into the extruder chamber and the presence of low molecular weight DGEBA, which is poorly reactive with PET chains. The situation is completely different when the catalyst is added to the PET and DGEBA mixture. Indeed, in the presence of the catalyst, the axial force increases abruptly after a few minutes, evidencing for rapid and extensive chain extension. The viscosity increase *vs*. time was expectedly found to depend on both the concentration of DGEBA and catalyst. At low DGEBA content (Figure 1a), increasing catalyst concentration results in faster viscosity increase, reaching the maximum force set (6500 N) after about 5 min mixing, when 0.3% wt. catalyst was added. On the latter formulation, increasing processing temperature to 260 or 270°C led to faster raise in viscosity, while the maximum force slightly decreased, probably due to concurrent degradation processes leading to chain scission. At higher DGEBA content (Figure 1b), the amount of catalyser needed to obtain rapid viscosity increase after a few minutes was found to be lower and the maximum concentration of $Zn(acac)_2$ was limited to 0.1% wt. to avoid blockage of the extruder. In these conditions, the force limit was reached after about 6 min when processing at 250°C, while faster reaction rates were observed increasing temperature to 260 or 270°C. However, compound produced at 270°C appears brownish, suggesting some extensive degradation occurred.

Different reactions have been reported to occur for polybutylene terephthalate during melt blending with DGEBA and Zn catalysers, the main processes corresponding to chain-extension by esterification or etherification as well as possible branching or transesterification [42]. The same reactions are expected to occur in PET (Scheme 1), with different extent, depending on the concentrations of DGEBA and catalyst. The effect of processing temperature was further explored to evaluate the rate of vitrimer formation during melt mixing, also taking into account the different reactions are expended to have different kinetics. A slightly higher rate of viscosity increase was found when processing at 260°C, compared to 250°C, whereas the raise in viscosity is clearly much faster when processing at 270°C (Figure 1), suggesting greater extent of crosslinking during processing. Because such a rapid viscosity increase is difficult to control in the used equipment and may easily lead to blockage of the extruder, processing at 270°C was not studied further.

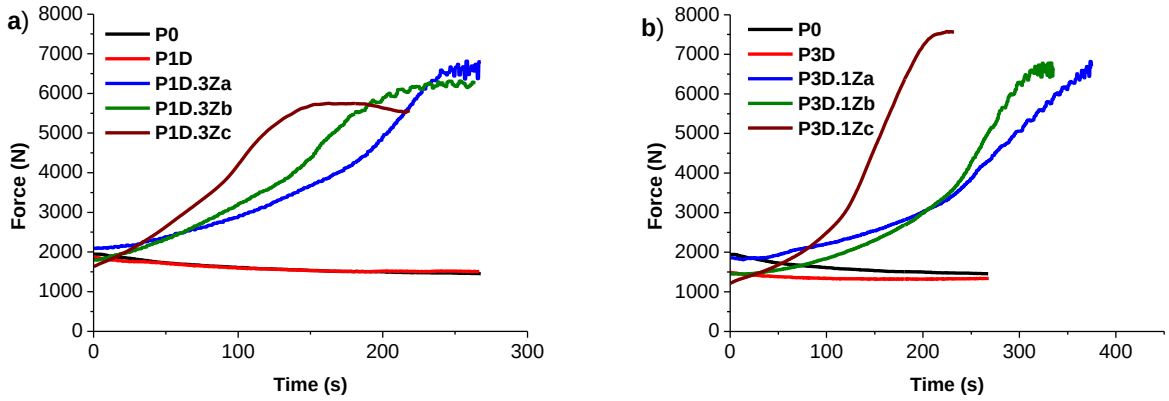
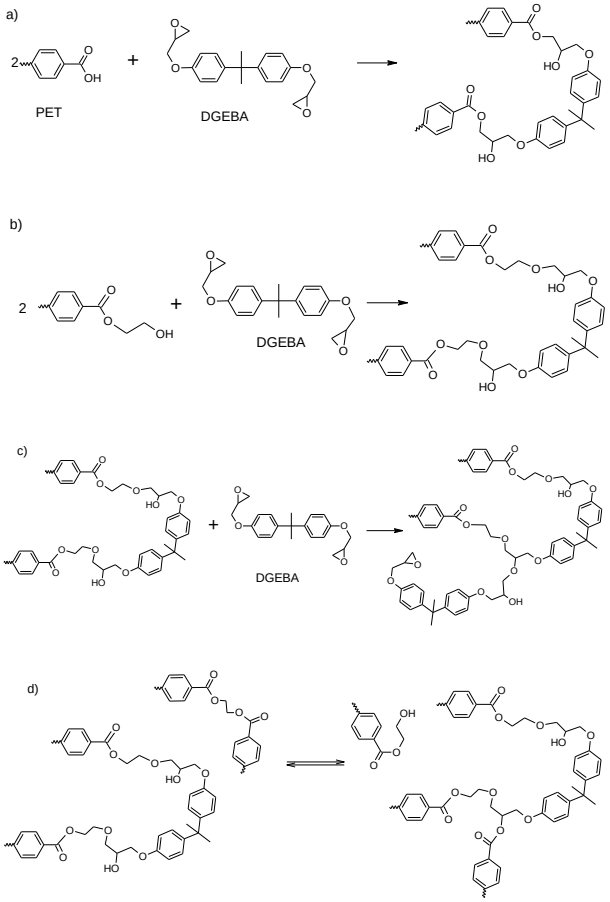


Figure 1: Variation of axial force as function as mixing time: a) tPET and DGEBA (1.36% wt.) with and without catalyst and at different temperatures, b) tPET and DGEBA (3.40% wt.) with and without catalyst and at different temperatures.



Scheme 1: Illustration of possible reaction during reactive extrusion: a) chain-extension by esterification, b) chain-extension by etherification, c) branching and d) the transesterification reaction, forming a cross-linked structure.

To investigate the extent of crosslinking in the different formulation and the different processing conditions, solubility tests were carried out. Linear PET chains can easily solubilize in a phenol/tetrachloroethane solution, whereas the cross-linked fraction remains insoluble and can be quantified as a solid residue after careful solvent removal. Neat tPET (P0) has cross-linked fraction close to zero (0.5%), the limited remaining likely corresponding to insoluble additives and impurities, taking into account of its recycled nature. On the other hand, the addition of DGEBA and $Zn(acac)_2$ leads to the formation of a considerable insoluble fraction. At low DGEBA content, P1D.3Za and P1D.3Zb, cross-linked fractions were found at ca. 33 % and 44 % (Figure 2), respectively, confirming processing at higher temperature leads to higher crosslinking extent. At higher DGEBA concentration, higher crosslinking fractions are expectedly found, namely ca. 67 and 75 % (Figure 2) for P3D.1Za and P3D.1Zb, respectively, confirming the effect of processing temperature. These results are consistent with result obtained by Demongeot et al. [42] for PBT, in which a 75 % cross-linking with 3.6 % wt. DGEBA and 0.1 % wt. $Zn(acac)_2$.

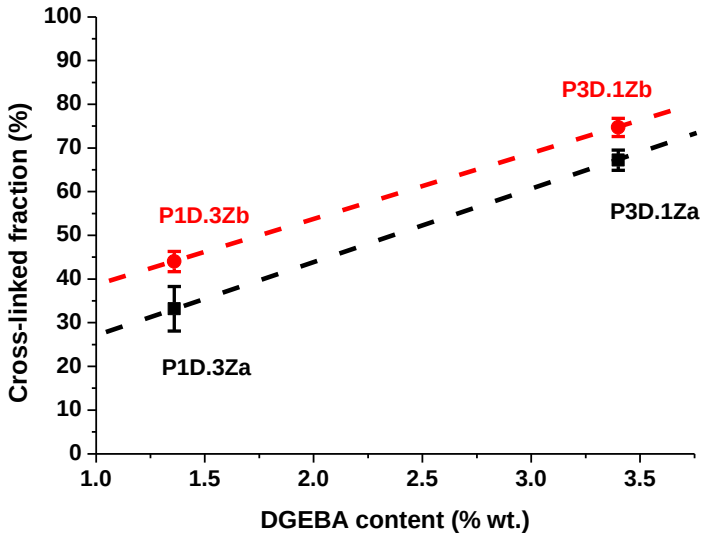


Figure 2: Cross-linked fraction as function as DGEBA content measured weighting the insoluble fraction after solubility test.

To investigate the effect of crosslinking on the crystallinity of tPET, non-isothermal DSC analysis was carried out. Significant differences were found for cross-linked PET compared to P0, as reported in Figure 3 and Table 2. In particular, the characteristic exothermic peak for crystallization during the cooling step (Figure *3*a) takes place at lower temperatures and with a lower intensity with the increasing of DGEBA (T_c=202.5°C for P0 and T_c =186.3°C for P3D), suggesting DGEBA to hinder crystallization. In the presence of DGEBA and catalyst, dramatic changes in the cooling plots were

observed, with further decrease T_c and broadening of the crystallization peak, that becomes barely visible for P3D.1Za. The hindrance to crystallization during cooling step is reflected in the second heating scan (Figure 3b), in which signals for cold crystallization process are visible. This is clearly visible for P3D.1Za (cold crystallization peak at 148°C), whereas a weaker signal is visible for P1D.3Za and barely observable for P1D and P3D. T_g values (around at 80°C) are not influenced by the modification on PET that is typical for a branching structure because it is not affect the free volume [49]. At the same time, T_m undergoes a significate decrease (Figure 3b and Table 2) with DGEBA content and even more in the presence of DGEBA and $Zn(acac)_2$, evidencing for the presence of lower stability crystals, in agreement with the constraints in crystallization. It is worth mentioning that PET is characterized by the presence of the typical double peak of fusion due to the coexistence of two crystalline populations with different thermal stability [50]. While P1D and P3D still preserve this feature, cross-linked materials appear to have a single and broad melting peak. In fact, the cross-linking prevents the formation of large and highly stable crystals by reducing the chain mobility. Processing temperature was found to have minor effects on the crystallinity of cross-linked PET, as presents in Supplementary Information (Figure S2 and Table S2).

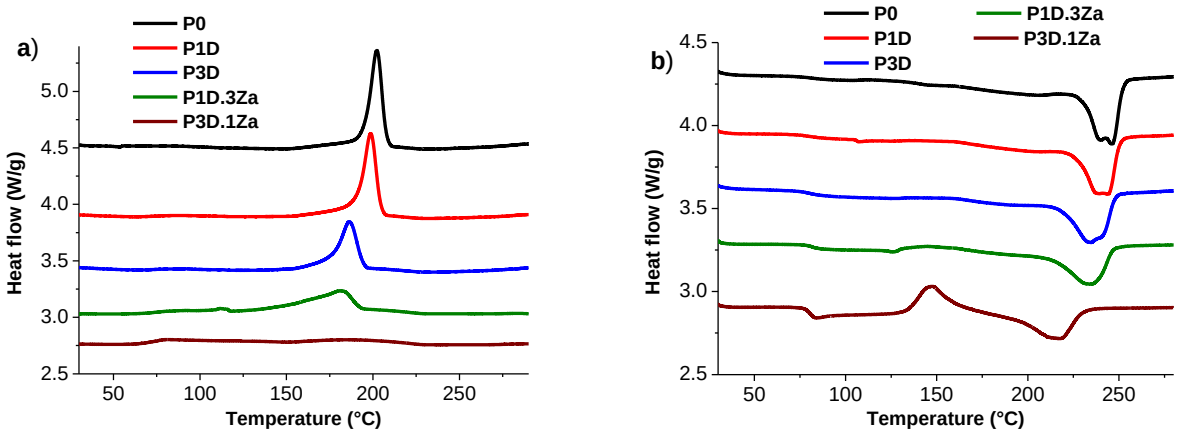


Figure 3: DSC thermograms: a) cooling step and b) second heating step for P0 and tPET with different amounts of DGEBA and, possibly, $Zn(acac)_2$.

Table 2: DSC results for P0 and tPET with different amounts of DGEBA and, possibly, $Zn(acac)_2$.

	Cooling		Second Heating						
	T_c (°C)	H_c (J/g)	T_g (°C)	T_{cc} (°C)	H_{cc} (J/g)	T_{m1} (°C)	T_{m2} (°C)	H_m (J/g)	X_c (%)
P0	202.5	51	82	-	-	240	246.5	34.7	25.2
P1D	198.9	53.2	80	159.3	9.7	238.5	244.3	33.7	10.6

P3D	186.3	42.6	80	158.4	5.3	234.7	240	32.6	20.2
P1D.3Za	180.7	40.5	81	145.3	8.2	235.1	-	26.2	13.1
P3D.1Za	-	-	80	147.8	22.7	217.8	-	23.4	0.5

Although the clear crosslinking observed at room temperature, the possibility to reprocessing PET/DGEBA was previously reported [44], thanks to the catalysed transesterification reaction. Indeed, all formulation reported in this work were found easily processable by compression moulding, which allows retaining recyclability. At the same time, the cross-linked structure is expected to deliver superior thermomechanical properties. As a first test to investigate dimensional stability at high temperature, specimens of the different formulations were hung upside above the melting temperature (260°C, 30 min) in a muffle furnace. Pictures of the specimens after the test (Figure 4), P0 is expectedly flown down under its own weight, leaving virtually no residue in the clamp. On the other hand, P1D.3Za and P1D.3Zb mostly retain their shape, while suffering deformation in the clamping region, which is clearly more severe for P1D.3Za. Specimens for high DGEBA content formulations (P3D.1Za and P3D.1Zb) appears much less deformed under their weight, directly reflecting the calculated crosslinking degrees. In all cases, browning of the specimens is also observed, likely due to the oxidation in air. Thermal volatilization was also evaluated by TGA, confirming no significant weight loss is obtained at 260°C and evidencing negligible differences between decomposition pathways of crosslinked PET vs. PET (Figure S3).

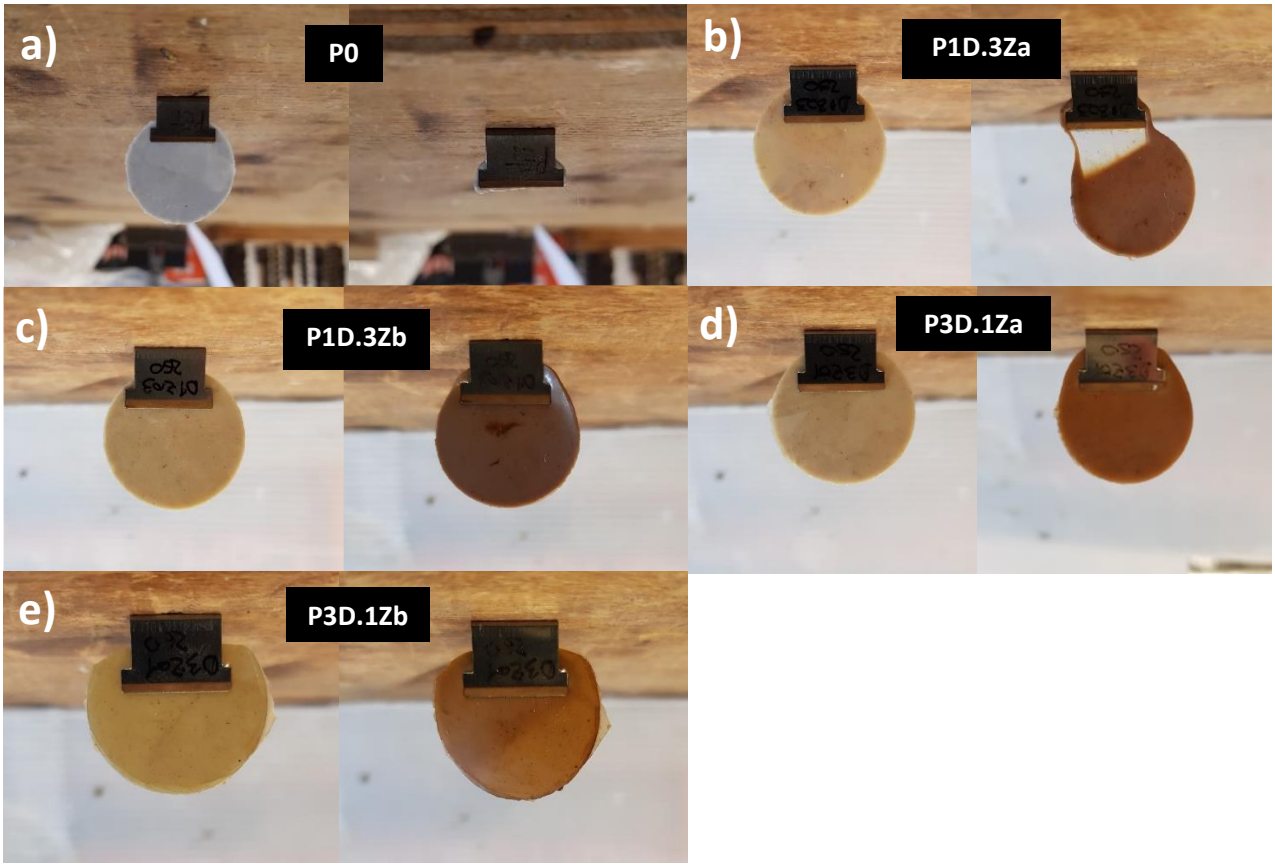


Figure 4: Compression moulded disks before (left) and after (right) 30 minutes at 260°C into a muffle furnace for a) P0, b) P1Z3a, c) P1Z3b, d) P3Z1a and e) P3Z1b.

To investigate thermomechanical properties of the different formulations, DMTA test were routinely carried out and the results of storage modulus (E′) and loss modulus (E′′) as function of temperature are presented in Figure 5. P0 shows a E' plateau in the glassy state around 2000 MPa, followed by a first drop in the modulus around 80-90°C, due to glass transition, to a rubbery plateau, until the final drop corresponding to the polymer melting. The specimens with DGEBA and catalyst exhibit slightly lower storage modulus compared to P0 in the glassy state (P1D.3Za ~ 1900 MPa, P1D.3Zb ~ 1500 MPa, P3D.1Za ~ 1800 MPa and P3D.1Zb ~ 1700 MPa), while the glass transitions temperature is similar to P0, in agreement with DSC results. The rubbery plateau for cross-linked tPET is considerably lower than P0, which is explained by the lower crystallinity. This is further confirmed by the increase in storage modulus upon cold crystallization, which is clearly visible around 126 °C for P3D.1Zb. Highly cross-linked formulations display a further plateau (approx. 0.3 MPa) above the melting region, which explains the capability of maintaining the specimens shape even above the melting temperature.

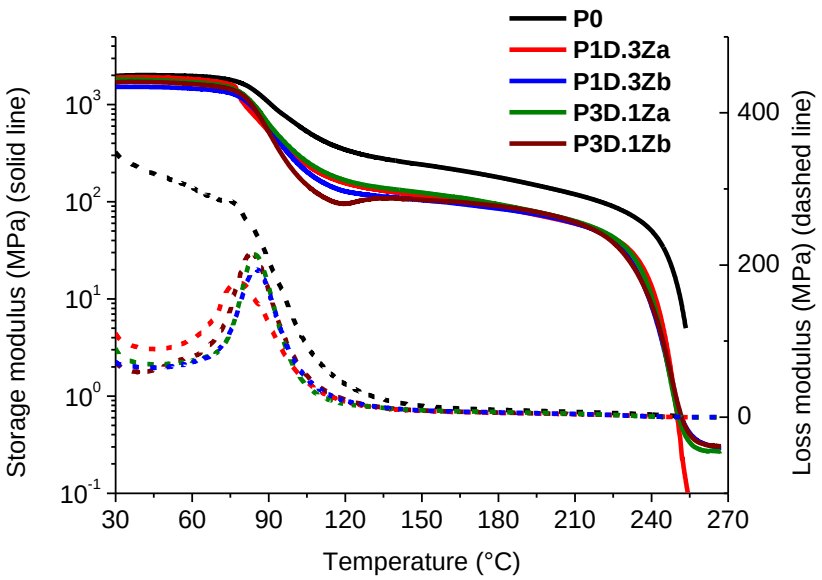


Figure 5: Storage modulus (solid line) and loss modulus (dashed line) vs temperature for P0, P1D.3Za, P1D.3Zb, P3D.1Za and P3D.1Zb.

Rheology analysis was also carried out to evaluate the crosslinking at high temperature and the dynamic of bonds exchange. Frequency sweep tests were conducted in linear viscoelastic regime in the range 0.1-100 rad/s and temperature between 250°C and 270°C. The obtained trends of G^{I} (storage modulus) and G^{II} (loss modulus) as a function of frequency are presented in Figure 6. P0 displays $G^{II} > G^{I}$ at each investigated temperature and over the whole tested frequency range, showing the typical behaviour of a non cross-linked polymer, whose rheological response is dominated by viscous flow above the melting temperature. P1D.3Za and P1D.3Zb show almost overlapped plots for G^{I} and G^{II}, with slight differences depending on the testing temperature. In particular, it should be noted that these samples show $G^{II} > G^{I}$ when tested at 250°C, while a transition from liquid-like to solid-like rheological behaviour is observed at higher temperatures. This finding suggests that crosslinking is not completed during processing and reactions may proceed at temperatures higher than 260°C in the rheometer. Irrespective of the testing temperature, the values of both moduli for these formulations are significantly higher as compared to P0; additionally, P1D.3Za and P1D.3Zb exhibit a power-law behaviour ($G^{I} \sim G^{II} \sim \omega^{n}$) [51, 52] which is very similar to that previously reported for poly(butylene terephthalate)-based vitrimers [43]. Furthermore, at 260 and 270°C a drop in the elastic modulus at low frequencies was observed, indicating the occurrence of relaxation phenomena at long time scale, which support the dynamic nature of crosslinking. A further increase of the DGEBA content induces the appearance of a clearly solid-like behaviour, with $G^{I} > G^{II}$, regardless of the testing temperature; besides, P3D.1Za and

P3D.1Zb show a frequency-independent elastic modulus in the whole tested frequency interval, indicating the formation of a cross-linked network with relaxation times relatively long compared to the tested time scales. It is worth mentioning that, as the material is not fully crosslinked, additional relaxation modes corresponding to networks strands, dangling chains, trapped loops as well as associative interaction between linear chains are possible, thus resulting in a rheologically complex behavior, as previously reported in other dynamically crosslinked systems [53, 54]. The loss angle tangent (tanδ) curves as a function of frequency (Figure S4) confirm that P0 is an obviously viscous material, whereas P3D.1Za and P3D.1Zb are elastic materials over the whole frequency and temperature ranges. The behaviour of P1D.3Za and P1D.3Zb is intermediate, with tanδ values dependent on the testing temperature. More specifically, for these samples tanδ is slightly higher than 1 when the testing temperature is 250°C, while it becomes less than 1 at higher temperatures. As already inferred from the analysis of the moduli curves, this behaviour can be associated with the increase of the crosslinking degree of these materials during the measurements performed at temperatures higher than 260°C, promoting a viscous-to-elastic transition of the rheological response.

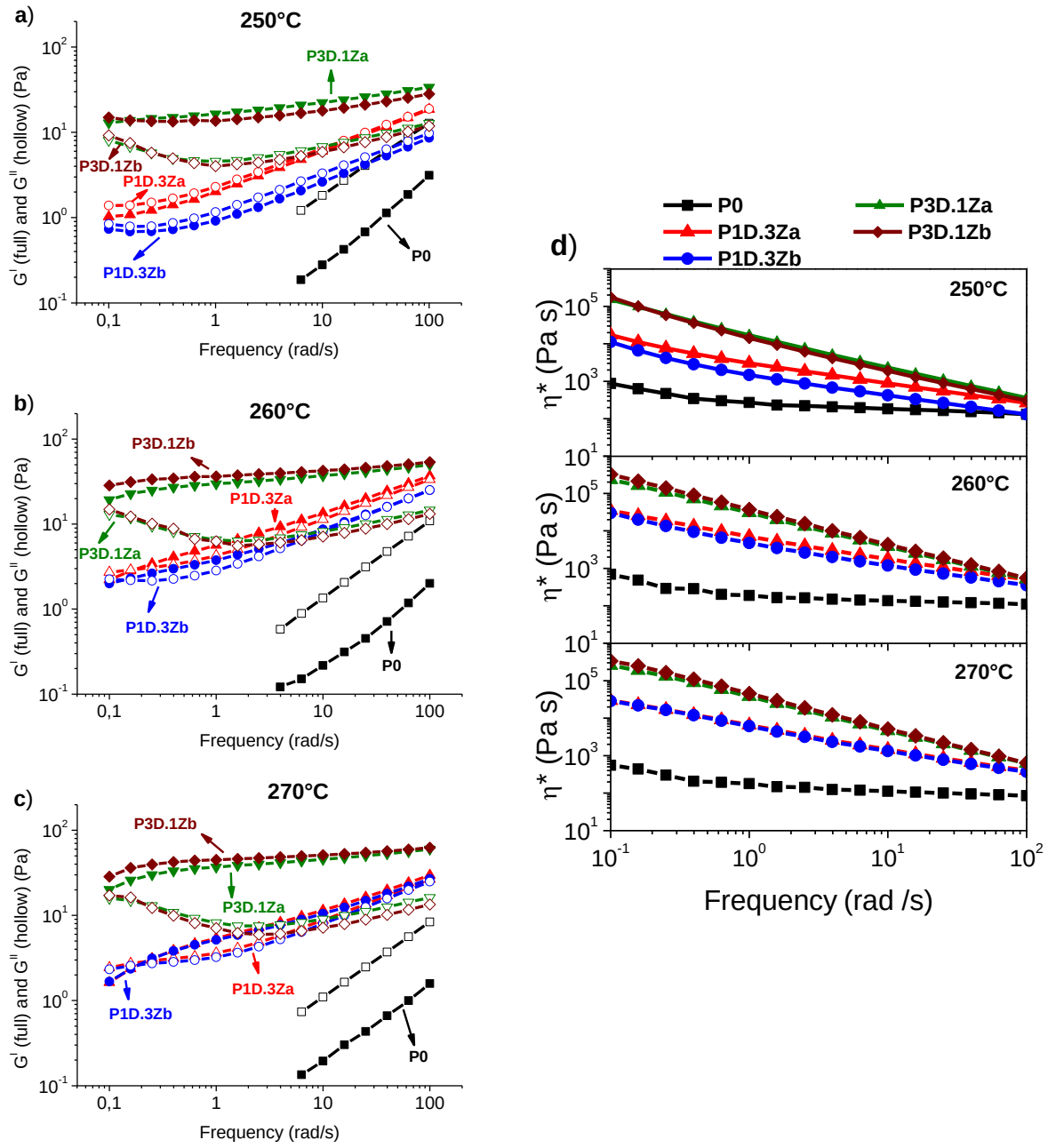


Figure 6: Elastic and viscous modulus for P0, P1D.3Za, P1D.3Zb, P3D.1Za and P3D.1Zb at a) 250°C, b) 260°C and c) 270°C in the range 0.1-100 rad/s. Complex viscosity measured by dynamic frequency sweep tests (d) for P0, P1D.3Za, P1D.3Zb, P3D.1Za and P3D.1Zb

Figure 6d reports the variation of the complex viscosity (η*) as function of frequency at different temperatures. All the investigated materials, regardless of the testing temperature, exhibit a similar behaviour, with a remarkable shear thinning involving a progressive decrease of the complex viscosity as the frequency increases. However, the samples containing DGEBA and catalyst exhibit significantly higher values of complex viscosity as compared to P0; in fact, at ω=0.1 rad/s P0 has

η*=549 Pa·s, whereas the values of P1D.3Za and P1D.3Zb are 2 orders of magnitude and P3D.1Za and P3D.1Zb 3 order of magnitude higher. The achievement of high values of complex viscosity implies improved melt strength, being this latter proportional to the zero-shear viscosity (η_0), which is the value of the complex viscosity in the Newtonian plateau appearing in the terminal region [55]. Typically, high values of melt strength are required to efficiently process polymers through many processing operations, such as blow moulding, film blowing and thermoforming, in which the elongational flow is dominant. Therefore, the obtained results highlight that the formulated materials exhibit enhanced melt strength with respect to neat tPET, thereby indicating the effectiveness of the proposed method in widening the processing window of end-of-life PET.

Mechanical properties at room temperature for the different formulations were measured by uniaxial tensile tests and the results are showed in Figure 7 and Table 3. Modulus, tensile strength and elongation at break are the main parameters to evaluate the performance of cross-linked materials, compared to P0. The elastic modulus, measure in the range of 2100 MPa for both P0, is slightly reduced in the cross-linked formulations, with minimum values for P1D.3Za and P3D.1Zb (Table 3). These values are consistent with DMTA results and the general decrease in stiffness is consistent with the reduction in crystallinity, measured by DSC on samples for mechanical testing (Table 3). It was previously reported that cross-linking has minor effect on the elastic modulus below T_g [56], whereas it value is directly influenced by the crystallinity. Beside stiffness, which is only relevant to small deformation, from an engineering point of view, strength and elongation at break are important parameters. P0 show limited tensile strength and elongation at break (Figure 7; σ=23.5 MPa, ε=1.2%) as a consequence of the low molar mass the recycled PET from trays, quantified in approx. Mn=20,000 g/mol. For this reason, the recycling of PET from trays is generally not found convenient and only PET from bottles is profitably recycled at present [57]. The formulation of recycled PET from trays to a vitrimeric PET, via the addition of DGEBA and $Zn(acac)_2$, allows dramatically improving tensile strength and elongation at break compared to P0. In fact, tensile strength increases to approx. 55 MPa for both P1D.3Za and P3D.1Za formulations, while best elongation at break was obtained for P1D.3Za in the range of 6%. These values are in line with results obtained by Qui et al. [44] for vitrimers obtained from virgin PET, thus further confirming potential for this method to upcycle low molecular weight PET grades.

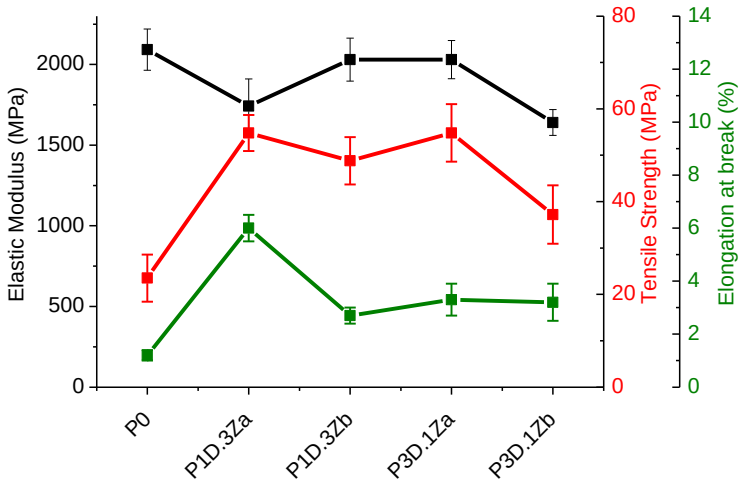


Figure 7: Mechanical properties of P0, P1D.3Za, P1D.3Zb, P3D.1Za and P3D.1Zb.

Table 3: List of mechanical properties of P0, P1D.3Za, P1D.3Zb, P3D.1Za and P3D.1Zb.

	Elastic Modulus (MPa)	Elongation at break (%)	Tensile Strength (MPa)
P0	2092 ± 128	1.2 ± 0.2	23.5 ± 5.1
P1D.3Za	1742 ± 168	6.0 ± 0.5	54.8 ± 3.9
P1D.3Zb	2030 ± 133	2.7 ± 0.3	48.8 ± 5.1
P3D.1Za	2030 ± 118	3.3 ± 0.6	54.8 ± 6.2
P3D.1Zb	1640 ± 80	3.2 ± 0.7	37.2 ± 6.3

Conclusions

Recycling of end-of-life PET trays is still limited by poor mechanical properties and consequently low profitability and application. Upcycling of tPET was addressed in this work and successfully obtained by melt compounding into a covalent associative network based on covalent bond exchange via transesterification. Reactive melt processing of tPET in the presence of a diepoxy (DGEBA) and transesterification catalyst ($Zn(acac)_2$) in different concentrations was carried out to optimize the extent of crosslinking while retaining sufficiently low viscosity for processability during compounding. The raise of molecular weight via chain extension and branching, was clearly observed after a few minutes of mixing, depending on the concentration of DGEBA and catalyst, as

well as the processing temperature. The presence of a partially cross-linked structure was confirmed by the solubility tests, yielding a crosslinked fraction up to 75%. Nonetheless, all formulations were demonstrated re-processable by compression moulding, evidencing for the reversibility of the covalent network and proving the possibility to further recycle the tPET vitrimers. DMTA and rheological tests proved high thermomechanical stability up to above the PET melting temperature, opening for possible application of tPET vitrimers in high temperature applications. Rheological test also highlighted a strongly enhanced melt strength, that is required in different polymer processing technology, such as blow moulding and thermoforming. Concerning mechanical properties at room temperature, tPET vitrimers exhibit a two-fold increase in mechanical strength. Overall, the use of vitrimers chemistry was demonstrated as a valid option to upcycle tPET to a high performance material. The same approach is envisaged for applications to other low-grade PET products, including the recycling of end-of life textile products.

CRediT author statement

Luciano Fabrizio: Investigation, Formal analysis, Writing - Original Draft; **Rossella Arrigo**: Methodology, Investigation, Formal analysis; **Maria Teresa Scrivani**: Methodology, Investigation; **Marco Monti**: Supervision, Funding acquisition; **Alberto Fina**: Conceptualization, Methodology, Formal analysis Writing - Review & Editing, Supervision, Funding acquisition

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Competing Interests

The authors have no relevant financial or non-financial interests to disclose.

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