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Vitrimerization of poly(butylene succinate) by reactive melt

3 mixing using Zn(II) epoxy-vitrimer chemistryFirstname Lastname ¹, Firstname

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6 Abstract: Vitrimers constitute a new class of covalent adaptable networks (CANs), in which thermally stimulated associative exchange reactions allow the topological rearrangement of the dy-7 namic network while keeping the number of the bonds and crosslink density constant. The current 8 9 study proposed a solvent-free method to synthesize vitrimers by reactive melt mixing using a commercial biobased/biodegradable polyester, poly(butylene succinate), PBS. More specifically, a two-10 step process was followed; the first step involved reactive mixing of PBS with the crosslinker (di-11 glycidyl ether of bisphenol A, DGEBA) and the transesterification catalyst (Zinc(II) acetylacetonate 12 hydrate, Zn(acac)2) in a twin-screw mini-compounder, in order to incorporate the epoxy groups in 13 14 the polymer backbone. The second step (vitrimerization) comprised a crosslinking process of the homogenous mixtures in a vacuum oven at 170 °C, resulting in the formation of a dynamic cross-15 linked network with epoxy moieties serving as the crosslinkers. By tuning the crosslinker content (0 16 17 - 10% mol with respect to PBS repeating unit) and the Zinc(II) catalyst to crosslinker ratio (0 to 1), tailor-made vitrimers were prepared with high insolubility and improved melt strength. Moreover, 18 19 PBS vitrimers could still be reprocessed by compression molding after the crosslinking, which enables recycling process. 20 21 This work was made possible by the "Basic Research Programme, NTUA, PEVE 2020 NTUA" [PEVE0050] of the National Technical University of Athens and is gratefully acknowledged. 22

> **Keywords:** poly(butylene succinate); epoxy-based vitrimers; polyesters; crosslinking; reprocessability; recycling;

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