POLITECNICO DI TORINO
Repository ISTITUZIONALE

Critical analysis of the thermal stability of transesterification vitrimers for 3Dprinting applications based on digital light processing

Original
Critical analysis of the thermal stability of transesterification vitrimers for 3Dprinting applications based on digital light processing / Romano, A., Konuray, O., Román, F., Calventus, Y., Fernándezfrancos, X., Roppolo, I., Sangermano, M.. - In: POLYMER INTERNATIONAL. - ISSN 0959-8103. - ELETTRONICO. - 73:4(2024), pp. 280-286. [10.1002/pi.6592]

Availability:
This version is available at: 11583/2986547 since: 2024-03-04T16:57:34Z

Publisher:
Wiley

Published
DOI:10.1002/pi.6592

Terms of use:

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright

(Article begins on next page)

14 September 2026

Check for updates

Research Article

Received: 18 July 2023 Revised: 16 October 2023 Accepted article published: 17 November 2023 Published online in Wiley Online Library: 1 December 2023

(wileyonlinelibrary.com) DOI 10.1002/pi.6592

Critical analysis of the thermal stability of transesterification vitrimers for 3D-printing applications based on digital light processing

Angelo Romano,[a] Osman Konuray,[b] Frida Román,[c] Yolanda Calventus,[c] Xavier Fernández-Francos,[b*] Ignazio Roppolo[a] and Marco Sangermano[a]

Abstract

3D-printable vitrimers processed by digital light processing (DLP) have been recently developed, based on the transesterification reaction of β-hydroxyester structures from mono- and diacrylate monomers employed in the formulation. These materials show promising repairability and recyclability, in addition to other interesting features such as shape memory and shape reconfigurability. It has been reported that structural changes taking place due to transesterification promote network rearrangement and an enhancement of the thermomechanical properties. However, the elevated temperatures required for the network reconfiguration cast some doubts on their applicability in real-life scenarios. In this paper, we analyze the effect of the thermal treatment on the thermomechanical properties and relaxation behavior of these materials and discuss the underlying mechanism explaining the observed changes. We identify some critical issues related to use of a monoacrylate containing β-hydroxyester moieties, and propose solutions to overcome the most relevant drawbacks.
© 2023 The Authors. *Polymer International* published by John Wiley & Sons Ltd on behalf of Society of Industrial Chemistry.

Supporting information may be found in the online version of this article.

Keywords: 3D-printing; vitrimer; digital light processing (DLP); thermal stability; relaxation dynamics

INTRODUCTION

Several strategies have been reported in recent years for the incorporation of vitrimer functionality, based on transesterification reactions, into 3D-printed thermosetting materials. In one such report, Zhang *et al.*[1] described a set of acrylate-based vitrimers, processed by digital light processing (DLP). Printable formulations consisted of a combination of bisphenol A glycerolate diacrylate and 2-hydroxy-2-phenoxypropyl acrylate, a suitable photoinitiator for the 3D-printing process and $Zn(acac)_2$ catalyst for the activation of dynamic bond exchange by transesterification reactions of β-hydroxyester structures present in the network structure.[1] It was reported that thermal treatment at an elevated temperature, 180 °C, increased the thermomechanical properties of the materials due to the network rearrangement taking place as a consequence of the transesterification reactions; repair and reprocessing of the printed materials was demonstrated, showing great application potential.[1,2] Similar materials were studied by Rossegger *et al.*[3] but using glycerol-1,3-diglycerolate diacrylate and trimethylolpropane triacrylate as crosslinking monomers, and employing an organic phosphate covalently bound to the polymer network as transesterification catalyst. The effect of the incorporation of multifunctional thiols into the network structure was also recently studied.[4] These materials also showed a significant enhancement in thermomechanical properties after thermal treatment at 180 °C, substantial repair capabilities and triple shape-memory effect.[4]

Previously, Shi *et al.* devised a procedure for the 3D-printing and recycling of epoxy-based vitrimers, which were processed by direct ink writing and thermally postcured in order to achieve the ultimate material properies.[5] Recycling and reprinting of the ink were accomplished by redissolution of the solid waste in ethylene glycol, the excess being removed under vacuum in order to produce a printing ink with comparable properties to the initial one. Chen *et al.* formulated an ink for DLP 3D-printing based on a dual-curing process,[6] consisting of (1) a photocuring stage in the 3D-printer leading to the polymerization and crosslinking of polyacrylates and monoacrylates with hydroxyl end groups and (2) a thermal curing stage based on epoxy–anhydride reaction. Recycling of the printed components was achieved by

* *Correspondence to: X Fernández-Francos, Thermodynamics Laboratory ETSEIB, Universitat Politècnica de Catalunya, Barcelona, Spain. E-mail: xavier.fernandez@upc.edu*

a *Department of Applied Science and Technology, Politecnico di Torino, Torino, Italy*

b *Thermodynamics Laboratory ETSEIB, Universitat Politècnica de Catalunya, Barcelona, Spain*

c *Heat Engines Department ESEIAAT, Universitat Politècnica de Catalunya, Terrassa, Spain*

© 2023 The Authors. *Polymer International* published by John Wiley & Sons Ltd on behalf of Society of Industrial Chemistry.

This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

redissolution in ethylene glycol using a suitable catalyst. Due to the absence of photocurable reactive groups, this recycled component needed to be incorporated into an acrylate component in order to enable re-printing.

By way of contrast, Casado *et al*. designed a dual-curing 3D-printable vitrimer formulation for DLP 3D-printing[7,8] based on (1) the radical photopolymerization of 1,3-diglycerolate diacrylate, glycidyl methacrylate and poly(ethylene glycol) methacrylate for the 3D-printing stage followed by (2) an epoxy–acid reaction between glutaric acid and epoxy groups from DGEBA and polymerized glycidyl methacrylate. The effects of different combinations of catalysts and the network structure on the dual-curing process and the bond exchange dynamics were studied. Recycling and repairing of the 3D-printed objects were demonstrated.

The possibility of repairing and recycling these materials offers a great opportunity for the reduction in waste material once the end life of the printed components is achieved, or else when a piece is damaged and it is therefore discarded. However, this recycling and repair procedure is always accompanied by a certain loss in thermomechanical properties. For instance, the "wet" chemical recycling processes employing ethylene glycol as reactive solvent introduce flexible aliphatic moieties into the recycled component, leading to changes in the structure and properties after each recycling cycle.[5,6] In the case of the "dry" recycling processes, elevated temperatures are required in order to activate the internal bond exchange reactions taking place within the material.[1] It is commonly reported that thermal treatments after the printing process produce an increase in thermomechanical properties that is generally ascribed to the network rearrangement taking place during transesterification.[1–4] Zhang *et al*. did not observe changes in the composition of ester bonds, therefore deeming the materials thermally stable.[1] In a further work, they reported that no changes were observed in the hydroxyl group region.[2] However, Rossegger *et al*. observed a decrease in the content of hydroxyl groups that was ascribed to the side reactions leading to further crosslinking.[4] A detrimental effect on the relaxation dynamics was reported as a consequence, but the materials were claimed to be thermally stable.[4]

In order to shed light on the thermal stability and thermomechanical properties of such 3D-printable vitrimers, the material developed by Zhang *et al*.,[1] coded as Base-Zn, was taken as reference. For comparison purposes, a similar material containing triazabicyclodecene (TBD) as transesterification catalyst, namely Base-TBD, and another one without catalyst, Base-nocat, were also studied. In spite of its reported drawbacks when employed in 3D-printable formulations,[3] TBD was chosen for its established performance as transesterification catalyst, comparable to that of $Zn(acac)_2$ in epoxy–carboxylic acid vitrimers.[9,10] The effect of the thermal treatment on the materials was studied using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), Fourier transform infrared (FTIR) spectroscopy and gas chromatography–mass spectrometry (GC–MS).

EXPERIMENTAL

Materials

The acrylate components of the formulations bisphenol A glycerolate diacrylate (bisGDA) (484 g mol^{-1}), 2-hydroxy-3-phenoxypropyl acrylate (PPA; 222.2 g mol^{-1}), zinc(II) acetylacetonte hydrate (Zn; *ca* 278 g mol^{-1}) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) were purchased from Sigma-Aldrich (Madrid, Spain) and used without further purification. The radical photoinitiator diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO; 348.4 g mol^{-1}) was donated by Ciba (Basel, Switzerland).

The formulations Base-Zn and Base-TBD were prepared by mixing the acrylate components (10 wt% bisGDA and 90 wt% PPA) and the transesterification catalyst (6 phr of Zn or 5 phr of TBD for Base-Zn or Base-TBD formulations, respectively) and homogenizing by magnetic stirring on a hot plate at a temperature of *ca* 60 °C until complete dissolution. An amount of 2 phr of radical photoinitiator TPO was added to the previous mixture at room temperature and homogenized by magnetic stirring. A material without transesterification catalyst, Base-nocat, was also prepared and analyzed for comparison purposes.

Preparation of samples

UV-cured samples were prepared in a prismatic rectangular mold (*ca* 50 × 12 × 1 mm^3) made of polypropylene covers and polytetrafluoroethylene spacers. The liquid formulations were injected into the mold using a syringe and cured in an Asiga flash chamber, 3 min on each side, followed by prolonged exposure for 30 min in a Photopol Vacuum UV oven, in order to ensure uniform and maximum conversion of acrylate groups.

Analytical techniques

Differential scanning calorimetry

A Mettler DSC821e DSC instrument equipped with a sample robot and Haake EK90/MT intracooler was used to measure T_g of the UV-cured materials and to analyze the effect of the thermal treatment. T_g was taken as the half-way point of the heat capacity step observed in a scan at 10 °C min^{-1}, following the DIN 51007 standard method. Samples were held for controlled periods of time at temperatures of 160, 170, 180, 190 and 200 °C and T_g was subsequently analyzed. Consecutive cycles at the same isothermal temperature with increasing time were applied to the samples. A nitrogen dry gas flow of 50 cm^3 min^{-1} was used in all experiments.

FTIR spectroscopy

The evolution of functional groups was monitored using a temperature-controlled Bruker Vertex 70 FTIR spectrometer equipped with an attenuated total reflection accessory (GoldenGate™, Specac Ltd). Spectra were collected in the mid-infrared region between 600 and 4000 cm^{-1} with a resolution of 4 cm^{-1}, averaging 20 scans per spectrum. The UV-cured samples were pressed against the diamond window in the hot plate at 180 °C and scanned at regular intervals.

Dynamic mechanical analysis

Stress relaxation experiments were performed using a TA Instruments DMA Q800 on 20 × 12 × 1 mm^3 (length × width × thickness) samples using a three-point bending configuration with a preload force of 0.01 N and 1%. Each sample was heated at 10 °C min^{-1} to the desired temperature of 180 °C, stabilized and held at that temperature for 5 min before the start of the relaxation process.

Thermogravimetric analysis

TGA was performed at 10 °C min^{-1} using a Mettler TGA/DSC1 equipped with a sample robot and Hubercryostat (precision of ±0.1 °C). Fully cured samples were analyzed under isothermal conditions and under 200 cm^3 min^{-1} of nitrogen purge.

© 2023 The Authors.
Polymer International published by John Wiley & Sons Ltd on behalf of Society of Industrial Chemistry.

10970126, 2024, 4, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/pi.6592 by Politecnico Di Torino Sist. Bibl Del Polit Di Torino, Wiley Online Library on [04/03/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

The materials were also analyzed isothermally at 160, 170, 180, 190 and 200 °C.

GC–MS analyses

The Base-Zn material was degraded by heating 2 g of the material at 180 °C, for 2 h, in a sealed vial. The detection of the derived volatile products was performed with an HP6890 gas chromatograph and 5973 mass selective detector (Agilent Technologies, Waldbronn, Germany), using an HP-5MS capillary column (30 m × 0.25 mm × 0.25 m) provided by Agilent.

Kinetics analysis

Data from the thermogravimetric experiments under isothermal conditions were analyzed using an isoconversional isothermal integral method.[11] The apparent activation energy E_w at a given weight loss w was determined at regular intervals of 1% weight loss, by means of the following expression:

$$\ln t_{w,i} = C + \frac{E_w}{R \times T_i}$$

where $t_{w,i}$ is the time needed to reach a weight loss w at a given temperature T_i, R is the gas constant and C is a constant. Linear representation of $\ln t_{w,i}$ with respect to the reciprocal temperature $1/T_i$ at a given degree of weight loss w for all the temperatures should yield a straight line with slope E_w/R.

RESULTS AND DISCUSSION

Specimens of the different materials were prepared following the procedures detailed in the previous section. Given that the materials were not processed by 3D-printing, no ink was included in the formulations. Samples containing TBD were exposed to sufficiently long UV irradiation in order to overcome any detrimental effect of TBD on the photopolymerization kinetics.[3]

Figure 1 compares the thermal stability of UV-cured samples of Base-Zn and Base-TBD materials. Figure 1(a) shows that, when heated at 10 °C min^{-1}, the thermal degradation process is complex: a first process takes place at a slower rate and lower temperatures, up to a weight loss of *ca* 30%; this is followed by a sharper degradation process at higher temperatures, leading to the decomposition of the network structure. Both materials start to lose weight appreciably at about 200 °C but, as the temperature increases, the weight loss rate of Base-TBD increases, eventually leading to a thermal degradation of the network structure taking place at lower temperatures than that for the Base-Zn material. If no transesterification catalyst is used, the thermal stability is considerably higher (see Fig. S1 in supporting information). All the materials had a comparable value of T_g, around 25–28 °C, after the photocuring process, indicating that the network structure was similar. Therefore, the clear difference in thermal stability between the materials must be caused by factors other than incomplete degree of cure or looser network structure.

The analysis under isothermal conditions Fig. 1(b), and (see Fig. S1 in supporting information) shows a significant weight loss within a few hours of thermal treatment, *ca* 20–25 wt% in 12 h at 180 °C or in 4 h at 200 °C for Base-Zn and Base-TBD materials. The weight loss is also notable after 12 h at 160 °C. In the absence of transesterification catalyst, the stability is much higher and a weight loss of only *ca* 7 wt% after 12 h at 180 °C is reached (see Fig. S1 in supporting information). The initial weigh loss rate for the Base-Zn material is higher than for the Base-TBD material, but

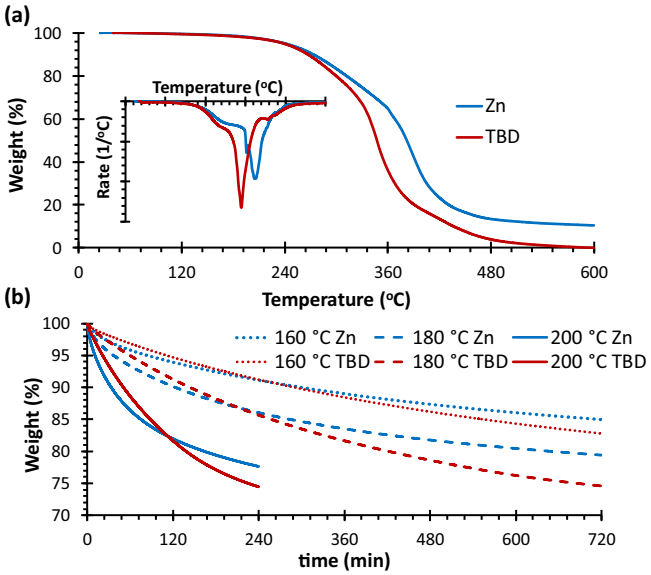


Figure 1. Results of TGA of Base-Zn and Base-TBD formulations (a) at a heating rate of 10 °C min^{-1} (the inset shows the rate of weight loss) and (b) isothermally at 160, 180 and 200 °C.

eventually Base-TBD degrades at a higher rate, in agreement with the dynamic data. Zhang *et al.* reported that stress relaxation of Base-Zn was nearly complete within 100 min at 200 °C.[1] This corresponds to a weight loss of *ca* 17% according to the thermogravimetric data in Fig. 1. This significant lack of thermal stability contrasts with previous statements reported in the literature.[1,2,4]

Such a significant weight loss, as determined by thermogravimetry, would have a significant impact in terms of dimensions of the processed samples. Indeed, the appearance of the materials changed significantly after the thermal treatment. Figure 2 shows that the Base-Zn material was colorless and transparent at the beginning, but after 8 h at 180 °C it showed a significant yellowing. An intense smell was detected in the oven during and after the thermal treatment, which was indicative of the evaporation of volatile products, in agreement with the thermal stability data. Moreover, it was also noticed that the dimensions of the sample had changed. From the caliper measurements shown in Fig. 2, a reduction in length of about −8.3% could be determined. A reduction in width and thickness was also observed. Assuming that the change is similar in all three dimensions, it is possible to roughly estimate a volume change of −23%. Noticeably, the weight loss after 8 h at 180 °C for Base-Zn is nearly 20 wt%, which is comparable to the volumetric change estimated before (Fig. 2).

This significant loss of volatiles during the thermal treatment evidenced by TGA raises some concerns to be considered from a practical point of view. From a standpoint of quality, this change in dimensions would probably render the material unusable if such thermal treatment is employed for on-site repair, given that dimensional precision is a strict requirement of the application. This would be less of a concern in a recycling scenario, since the material is usually reprocessed fully (e.g. by grinding and hot pressing). The release of volatile organic compounds during thermal treatment calls for suitable control in order to minimize emissions and prevent associated risks.

The increase in the thermomechanical properties of the materials upon thermal treatment deserves some consideration as well. The analysis of T_g of the material at different isothermal

© 2023 The Authors.

Polymer International published by John Wiley & Sons Ltd on behalf of Society of Industrial Chemistry.

10970126, 2024, 4, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/pi.6592 by Politecnico Di Torino Sist. Bibl Del Polit Di Torino, Wiley Online Library on [04/03/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

Figure 2. Dimensional and color changes taking place in Base-Zn material after thermal treatment. The left-hand image shows a UV-cured (untreated) sample and the right-hand image shows the same sample after 8 h at 180 °C.

conditions shown in Fig. 3 by DSC revealed an increase from *ca* 25 up to 60–65 °C for the Base-Zn material and up to 70–80 °C for the Base-TBD material. The changes in T_g were faster when thermal treatment was carried out at higher temperatures. A certain increase in T_g was expected taking into consideration previous results of Zhang *et al.*[1] Rossegger *et al.* had also described an increase in T_g after 4 h of thermal treatment at 180 °C, which was attributed to additional crosslinking taking place.[4] However, unlike the results reported by Zhang *et al.*,[1] no clear stabilization in T_g is observed within 4–6 h at 180 °C (nor at any other temperature; Fig. 3). The change in T_g was slower and more limited when no catalyst was used (Fig. S2 in supporting information).

Moreover, T_g was compared with the weight loss at the different temperatures (see Figs S4 and S5 in supporting information for complete results of isothermal TGA), revealing some interesting features. The results in Fig. 4 show that there is a fairly good correlation between the evolution of T_g and weight loss at any of the temperatures of thermal treatment tested. A higher weight loss and change in T_g is observed for the Base-TBD material. Also observed was a similar correlation in weight loss and T_g for Base-Zn and Base-TBD materials, while the uncatalyzed material followed a different trend (Fig. S2 in supporting information) In light of these results, it is hypothesized that the change in thermomechanical properties would be a side effect of the thermal degradation taking place, rather than an intended and desirable effect resulting only from the network rearrangement caused by the transesterification.[1,2]

When the stress relaxation profiles of the samples were analyzed (Fig. 5), it was noticed that the relaxation of the UV-cured Base-Zn material at 180 °C was fast, in excellent agreement with the data reported by Zhang *et al.*[1] Noteworthy, the relaxation of the Base-TBD material was initially slower than that of Base-Zn, but then it increased and overtook. This kinetic effect has striking similarities with the isothermal thermogravimetric curves shown in Fig. 1 (see also Fig. S3 in supporting information), indicating that there is an apparent connection between the occurrence of transesterification reactions during relaxation and the observed weight loss. It must be stressed that transesterification is possible without catalyst, as reported in the literature,[12] but it takes place at considerably lower rate, producing a very slow stress relaxation process (Fig. S3 in supporting information). It can also be seen that the relaxation of the Base-Zn sample after 3 and 6 h of thermal treatment at 180 °C becomes progressively slower, an effect that was also detected by Rossegger *et al.*[4] These results also suggest

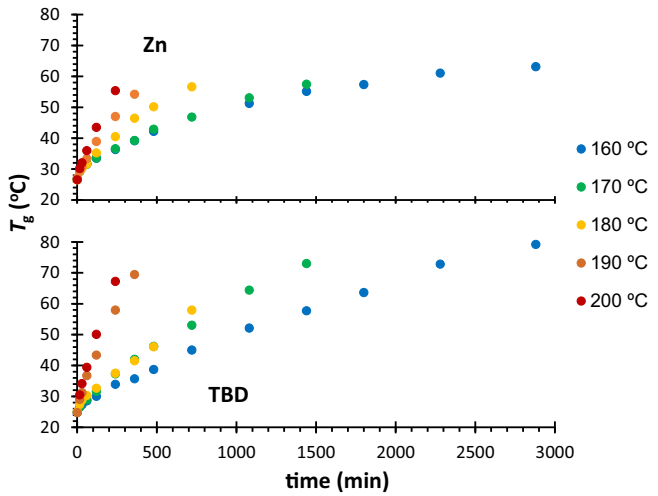


Figure 3. Evolution of T_g of Base-Zn (upper graph) and Base-TBD (lower graph) materials during thermal treatment at temperatures ranging from 160 to 200 °C.

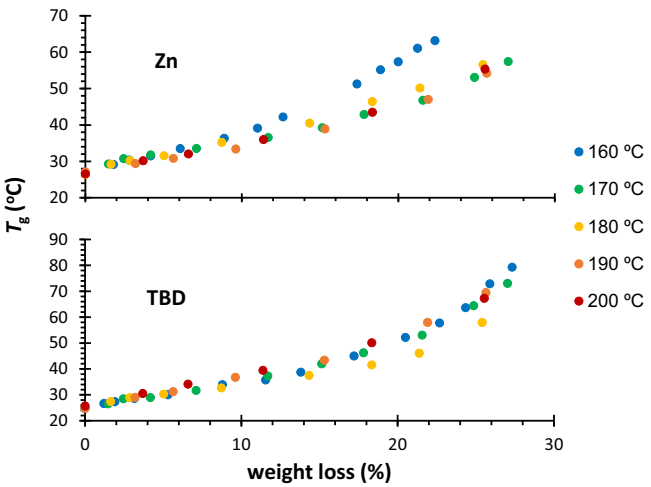


Figure 4. Comparison of T_g of Base-Zn (upper graph) and Base-TBD (lower graph) against weight loss during thermal treatment at temperatures ranging from 160 to 200 °C.

© 2023 The Authors.
Polymer International published by John Wiley & Sons Ltd on behalf of Society of Industrial Chemistry.

10970126, 2024, 4, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/pi.6592 by Politecnico Di Torino Sist. Bibl Del Polit Di Torino, Wiley Online Library on [04/03/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

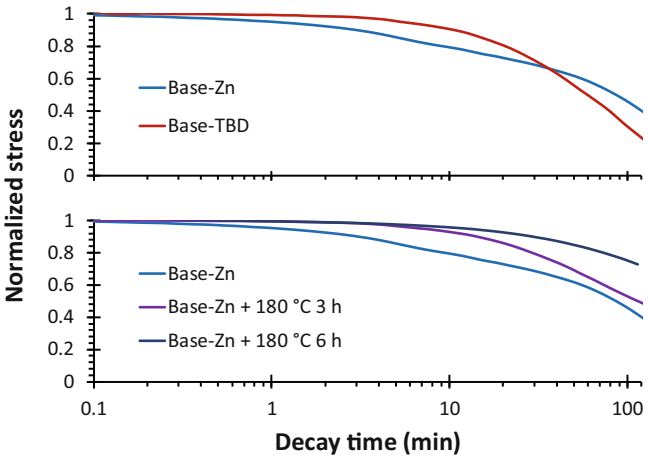


Figure 5. Stress relaxation at 180 °C of UV-cured Base-Zn and Base-TBD materials (upper graph) and Base-Zn materials after thermal treatment for several hours at 180 °C (lower graph).

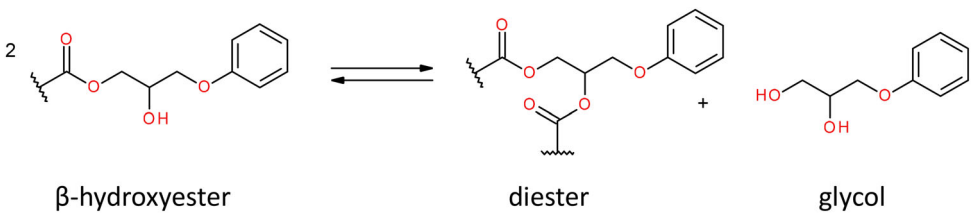
that there is an effect of the weight loss and the change in thermomechanical properties on the kinetics of the relaxation process.

In order to shed more light on the observed phenomena, the kinetics of the degradation process taking place between 160 and 200 °C (complete degradation data are shown in Figs S4 and S5 in supporting information) were studied making use of the method described in Kinetics analysis section. The results (Fig. S6 in supporting information) reveal that that the apparent activation energy of the process is around 70–90 kJ mol^{-1} for both materials, slightly higher for Base-Zn. This value is in the same range of activation energies commonly reported for transesterification-based vitrimers using different catalysts.[7,13,14] Such a coincidence suggests that there is a connection between the observed weight loss, the change in thermomechanical properties and the kinetics of the bond exchange process.

In order to interpret all these observations, one must consider the structural changes occurring when transesterification reactions are activated at elevated temperature. Transesterification reactions in β-hydroxyester structures are assumed to reach a temperature-dependent equilibrium, leading to a significant fraction of glycol and diester structures.[14,15] Scheme 1 shows the transesterification reactions taking place on the short side chains present in the material as a consequence of the use of PPA.[1] This reaction leads to the transformation of a β-hydroxyester structure into a diester attached to the polyacrylate backbone and a small glycol molecule, 2,3-dihydroxypropylphenyl ether. This small molecule may be sufficiently volatile to leave the material as it is being produced at elevated temperatures such as 160–180 °C. Gamardella *et al.* also reported that thermal treatment of polythiourethane vitrimers at elevated temperatures for an exceedingly long period could produce structural changes affecting the thermomechanical properties of the reprocessed materials.[16] Taplan *et al.* used TGA as additional evidence of the occurrence of retro aza-Michael reactions in β-aminoester materials produced from small monoamines (with a size comparable to that of the 2,3-dihydroxypropylphenyl ether molecule) as model compounds, observing evaporation of the monoamines under isothermal treatment at elevated temperature.[17]

In order to validate the hypothesis, it was decided to monitor the thermal treatment process in more detail by FTIR analysis. Zhang *et al.* argued that the samples were stable because the ester band remained unchanged,[1] as expected in vitrimers based on transesterification reaction.[13] However, other regions of the IR spectra were not analyzed. Figure 6 shows the results of the FTIR analysis of Base-Zn material. In order to facilitate the analysis, the spectra were normalized with respect to the ester band at 1730 cm^{-1}. Notable changes can be observed upon comparing the spectra before and after 5 h of thermal treatment at 180 °C. There is a significant decrease in the hydroxyl O—H stretch band at around 3500 cm^{-1}, a feature that was attributed to further crosslinking by Rossegger *et al.*[4] However, it can be noticed that several other signals decrease: peaks at 754 and 690 cm^{-1} (hydrogen wag of monosubstituted phenyl rings), the bands around 1400 and 1600 cm^{-1} (C—C ring stretch), the peaks at 1038 cm^{-1} (alkyl—O stretch in aryl–alkyl ethers) and 1235 cm^{-1} (aryl—O stretch in aryl–alkyl ethers), 2800–3000 cm^{-1} (aliphatic C—H stretch), among others. Similar changes were observed in the analysis of the Base-TBD material. The analysis of the volatile products evolved at 180 °C by GC–MS (see Figs S7–S13 in supporting information) indicated that they are composed mainly of phenolic derivatives and some aliphatic moieties, in good agreement with the experimental FTIR data and the proposed mechanism.

The volatilization of the 2,3-dihydroxypropylphenyl ether molecule would shift the equilibrium towards the formation of the diester (Scheme 1), eventually leading to the complete transformation of the original β-hydroxyester structure into diester and volatilized glycol. The evaporation of this aromatic glycol and formation of diester structures are consistent with the evolution of the FTIR spectra, since carbonyl ester groups remain attached to the polyacrylate polymer backbone, while aromatic and hydroxyl signals would decrease. The progressive formation of diester structures would lead to an effective increase in the crosslinking density, which could explain the observed increase in T_g.[1,2] However, it is likely that the evaporation of the small glycol molecule, which would act as plasticizer, also plays a significant role in the observed increase in T_g. Moreover, the decreasing content of hydroxyl groups in the material will produce a decelerating effect on the network relaxation kinetics, based on the transesterification reaction, as already reported[4] and observed in Fig. 5. Reprocessing ability of the materials would become worse with each



Scheme 1. Transesterification taking place in the side chains coming from the PPA monomer.

© 2023 The Authors.
Polymer International published by John Wiley & Sons Ltd on behalf of Society of Industrial Chemistry.

10970126, 2024, 4, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/pi.6592 by Politecnico Di Torino Sist. Bibl Del Polit Di Torino, Wiley Online Library on [04/03/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

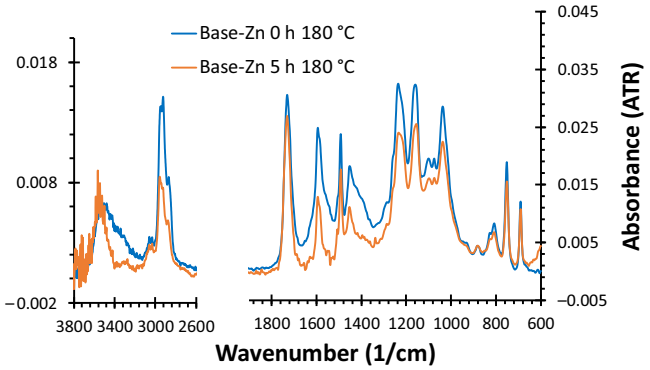


Figure 6. FTIR spectra collected during isothermal treatment of Base-Zn material at 180 °C. The spectra are normalized with respect to the carbonyl ester C═O stretch band at 1730 cm^{-1}.

thermal treatment cycle until stabilization eventually takes place, once this irreversible transformation has taken place to a sufficient extent.

Taking into consideration that half of the aromatic moieties from PPA would transform to the volatile glycol molecule, it is expected that transesterification reactions would produce a maximum weight loss of 34 wt% with respect to the bisGDA + PPA mixture, and about 31–32 wt% of the total formulation mass for Base-Zn and Base-TBD formulations. A closer look at the isothermal degradation curves shown in Fig. 1 evidences that the weight loss of Base-Zn and Base-TBD is significant, as discussed above. Indeed, a weight loss of *ca* 25% is reached for Base-TBD materials. The dynamic thermograms in Fig. 1(a) show a change in the thermal degradation behavior around 30% weight loss (70% remaining weight). Such a coincidence between this threshold value and the calculated weight loss confirms that the first degradation step corresponds to the quantitative volatilization of the glycol molecules formed by the transesterification equilibrium (Scheme 1), followed by the thermal degradation of the remaining acrylate network. The observed differences in degradation kinetics between Base-Zn and Base-TBD materials (Fig. 1) must therefore be related to the different kinetics of the bond exchange process (Fig. 5) depending on the type and concentration of the transesterification catalyst.

The results presented in this work evidence that transesterification-based vitrimer materials that are being studied for 3D-printing applications based on DLP[1–4] suffer from significant drawbacks that limit their practical application. It is also evidenced that, in addition to network relaxation dynamics and thermomechanical and mechanical properties, thermal stability of these materials needs to be analyzed in a more detailed way, under realistic processing conditions.

Most of the observed effects are a consequence of the use of PPA as co-monomer in the formulations for 3D-printable vitrimers. Its use is appealing because of its low viscosity and the elevated concentration of β-hydroxyester groups in the resulting network structure, allowing fast bond exchange. However, transesterification process leads to the formation of volatile glycol moieties that leave the material at the elevated temperatures required for the activation of the dynamic bond exchange, and to the formation of a denser crosslinked network structure with a reduced amount of available hydroxyl groups for further transesterification bond exchange. Carrying out thermal treatment at elevated pressures would probably ameliorate this problem, but small glycol molecules would remain in the material, which could eventually evaporate.

In order to overcome this drawback, different solutions can be found at the material design level. It is hypothesized that the use of longer-side-chain acrylates with β-hydroxyester structures would help to mitigate the problems detected in this work. Such acrylates might be easily prepared from acrylic or methacrylic acid and suitable longer-chain monoepoxides. The use of diacrylates such as bisGDA or glycerol-1,3-diglycerolate diacrylate in higher proportion would make their application difficult because of their high viscosity, but they might be considered for hot printing stages.[18] One might also consider other epoxy acrylates commercially available or the preparation of diacrylates by reaction between suitable diepoxides and acrylic acid. Another interesting approach could be the *in situ* generation of β-hydroxyester bonds during processing by means of a dual-curing processing scheme starting from low-molecular-weight precursors.[6] Indeed, Casado *et al*. already reported promising results in that respect.[7,8] Starting from commercially available monomers, they prepared materials with elevated thermal stability, reprocessing and repair capabilities, and whose relaxation kinetics were minimally impacted by thermal treatment.[7,8] It is expected that these research directions could lead to the development of materials with enhanced thermal and mechanical properties and recyclability with realistic application prospects in the context of printed parts processed by DLP.

CONCLUSIONS

Current vitrimers designed for application in DLP printing processes, based on the transesterification of β-hydroxyester structures, suffer from several drawbacks due to the occurrence of irreversible transformations during their inevitable thermal treatment. Because of the use of short-side-chain monoacrylates, transesterification at elevated temperatures leads to the formation small structural fragments which are easily volatilized. Such transformation produces an apparently beneficial effect on the thermomechanical properties. However, a number of negative side effects are observed, such as a loss of dimensional stability and a decrease in relaxation kinetics, compromising the reprocessability. This imposes severe limits to the practical application of such materials. In order to overcome these drawbacks, it is proposed to incorporate acrylate monomers with structures less likely to produce small and volatile molecules upon thermal treatment. Alternatively, appropriate dual-curing procedures can be employed to incorporate β-hydroxyester structures into the network structure.

ACKNOWLEDGEMENTS

This work was funded by the Spanish Ministry of Science and Innovation (MCIN/AEI) through R&D project PID2020-115102RB-C22, and also by Generalitat de Catalunya (2021-SGR-154 and BASE3D). XF-F and OK acknowledge the Serra-Húnter program (Generalitat de Catalunya).

SUPPORTING INFORMATION

Supporting information may be found in the online version of this article.

© 2023 The Authors.
Polymer International published by John Wiley & Sons Ltd on behalf of Society of Industrial Chemistry.

10970126, 2024, 4, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/pi.6592 by Politecnico Di Torino Sist. Bibl Del Polit Di Torino, Wiley Online Library on [04/03/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License

REFERENCES

1 Zhang B, Kowsari K, Serjouei A, Dunn ML and Ge Q, *Nat Commun* **9**: 1831 (2018).
2 Luo C, Zhang B, Zhang W, Yuan C, Dunn M, Ge Q *et al.*, *J Mech Phys Solids* **126**:168–186 (2019).
3 Rossegger E, Höller R, Reisinger D, Fleisch M, Strasser J, Wieser V *et al.*, *Polymer (Guildf)* **221**:123631 (2021).
4 Rossegger E, Höller R, Reisinger D, Strasser J, Fleisch M, Griesser T *et al.*, *Polym Chem* **12**:639–644 (2021).
5 Shi Q, Yu K, Kuang X, Mu X, Dunn CK, Dunn ML *et al.*, *Mater Horizons* **4**: 598–607 (2017).
6 Chen Z, Yang M, Ji M, Kuang X, Qi HJ and Wang T, *Mater Des* **197**: 109189 (2021).
7 Casado J, Konuray O, Roig A and Fernández-Francos XR, *Eur Polym J* **173**:111256 (2022).
8 Casado J, Konuray O, Benet G, Fernández-Francos X, Morancho JM and Ramis X, *Polymers (Basel)* **14**:5102 (2022).
9 Capelot M, Unterlass MM, Tournilhac F and Leibler L, *ACS Macro Lett* **1**: 789–792 (2012).
10 Poutrel Q-AA, Blaker JJ, Soutis C, Tournilhac F and Gresil M, *Polym Chem* **11**:5327–5338 (2020).
11 Vyazovkin S, Burnham AK, Criado JM, Pérez-Maqueda LA, Popescu C and Sbirrazzuoli N, *Thermochim Acta* **520**:1–19 (2011).
12 Capelot M, Montarnal D, Tournilhac F and Leibler L, *J Am Chem Soc* **134**: 7664–7667 (2012).
13 Montarnal D, Capelot M, Tournilhac F and Leibler L, *Science* **334**: 965–968 (2011).
14 Altuna FI, Hoppe CE and Williams RJJ, *Eur Polym J* **113**:297–304 (2019).
15 Altuna FI, Hoppe CE and Williams RJ, *Polymers (Basel)* **10**:43 (2018).
16 Gamardella F, Muñoz S, De la Flor S, Ramis X and Serra A, *Polymers (Basel)* **12**:2913 (2020).
17 Taplan C, Guerre M and Du Prez FE, *J Am Chem Soc* **143**:9140–9150 (2021).
18 Steyrer B, Busetti B, Harakály G, Liska R and Stampfl J, *Addit Manuf* **21**: 209–214 (2018).

© 2023 The Authors.

Polymer International published by John Wiley & Sons Ltd on behalf of Society of Industrial Chemistry.

10970126, 2024, 4, Downloaded from https://onlinelibrary.wiley.com/doi/10.1002/pi.6592 by Politecnico Di Torino Sist. Bibl Del Polit Di Torino, Wiley Online Library on [04/03/2024]. See the Terms and Conditions (https://onlinelibrary.wiley.com/terms-and-conditions) on Wiley Online Library for rules of use; OA articles are governed by the applicable Creative Commons License