

Vitrimeric Epoxy-Amine Polyimine Networks Based on a Renewable Vanillin Derivative

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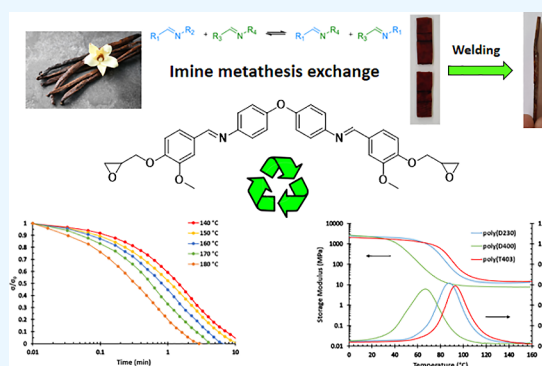
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ABSTRACT: A series of bio-based polyimine vitrimers was obtained and characterized. A diimine-diglycidyl monomer (DIDG) was synthesized by condensing vanillin with 4,4'-oxydianiline (ODA) and further glycidylation with epichlorohydrin. This compound was cross-linked with three different Jeffamines (Jeff230, JeffD400, and JeffT403) with a different number of poly(propylene glycol) units in their structure and different functionalities. Trimethylolpropane triglycidyl ether (TMPTE) was added to the formulation to improve the thermal, mechanical, and thermomechanical properties. All of the materials prepared showed T_g 's above 66 °C, good vitrimeric behavior being the maximum relaxation rate reached by the material prepared from JeffD400, which also allows the most extensive degradation when treated with an acidic aqueous solution. These polyimine vitrimers can entirely relax the stress in less than 10.5 min at 150 °C without any added catalyst. All of the materials prepared could be satisfactorily recycled up to 200 °C also presenting an excellent self-welding ability.

KEYWORDS: vanillin, vitrimers, imine metathesis, covalent adaptable networks, recyclability, self-welding



1. INTRODUCTION

Covalent adaptable networks (CANs) have attracted considerable interest in the last few years due to their ability to be reshaped or self-repaired and present a promising solution in the recyclability of thermosetting materials.^{1,2} These materials possess dynamic and exchangeable covalent bonds in their cross-linked structure which can be activated with external stimuli, such as temperature or light, enabling the alteration of their behavior from a viscoelastic solid to a material with a fluid-like plastic flow.

One of the most important types of CANs are vitrimers, reported for the first time by Leibler and co-workers.³ In them, the bond exchange is produced in a concerted way, without any intermediate state, without losing the network integrity and always keeping the cross-linking density constant.⁴ Many organic reactions have been studied as a potential dynamic process in vitrimers such as transesterification,^{5–8} disulfide metathesis,^{9–11} transamination of vinylogous urethanes,^{12,13} trans-thiocarbonylation,^{14,15} and imine exchange,^{16–19} among others.

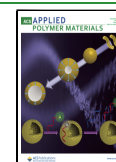
Imine exchange can occur in networks with imine bonds, easily formed by a condensation reaction between aldehydes or ketones and primary amines. In general, imines can participate in three types of equilibrium-controlled reactions: hydrolysis, amine–imine exchange, and metathesis (see Scheme 1), but only the lattermost takes place concertedly, in an associative-type mechanism, therefore leading to vitrimeric materials.

Imine metathesis-based materials have attracted the interest of many academic researchers for a long time. Zhang et al.²⁰ designed a catalyst-free malleable polyimine network from commercially available aldehydes and amines that could be reprocessed by applying water or heat to obtain efficiently recycled samples without the loss of mechanical performance. After that, the same group went further in their investigation and tested polyimine vitrimers as binder materials in carbon fiber reinforced composites (CFRC) by adding a single layer of twill weave carbon fiber resulting in CFRCs that could be easily molded into shapes with three-dimensional (3D) curvatures, demonstrating a green approach to recyclable composites.²¹ Geng and co-workers²² synthesized polyimine materials based on lignin-derived vanillin that demonstrated self-healing properties, which could be mechanically recycled and were able to form again after degradation under acidic conditions, showing a promising approach to the sustainability of these materials. Later on, Abu-Omar et al.²³ described the preparation of an epoxy monomer containing imine bonds in its structure which was able to react with amines, affording a

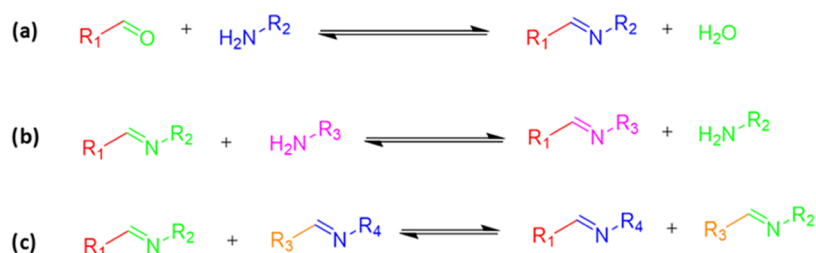
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Scheme 1. Three Types of Reversible Imine Reactions (a) Imine Condensation, (b) Amine–Imine Exchange, and (c) Imine Metathesis



thermoset material with high mechanical performance and good vitrimeric behavior with low relaxation times even at low temperatures. They also demonstrate the high malleability of their materials and the self-welding properties of the imine-containing polymer, showing similar values when tested in a tensile test and compared to the pristine sample.

Nowadays, biomass-derived products are gaining interest worldwide since they avoid the use of fossil raw materials and help to find greener synthetic procedures for eluding the depletion of petrochemical-derived compounds. One of the most used bio-based compounds to produce vitrimers is lignin.^{24,25} Its derivative, vanillin, obtained by the alkaline oxidation of lignin, is also widely used for the synthesis of polymers, especially imine vitrimers, due to its aldehyde and phenol groups that can be easily modified to get a suitable functionality as well as for its aromatic structure that provides high thermal and mechanical properties to the obtained materials.^{22,26–29}

Taking all this into account, in the present article, we report the synthesis and characterization of a series of polyimine vitrimers. A diimine-diglycidyl monomer (DIDG) that has not been previously described was synthesized in high yields via a two-step procedure with an excellent yield. Then it was cured with three Jeffamines (Jeff230, JeffD400, and JeffT403) with a different number of poly(propylene glycol) units in their structure and different functionality, in stoichiometric epoxy/NH ratios. Trimethylolpropane triglycidyl ether (TMPTE) was also added to the mixtures to obtain better homogeneities and improve the final mechanical properties. As far as we know, no diimine-diglycidyl have been reported. The presence of epoxy groups in the diamine structure opens the possibility of further cross-linking with many curing agents, which enhances the versatility in the characteristics of the final vitrimeric materials. Previous studies in imine derivatives from vanillin report the synthesis of diphenolic or amino-phenol compounds that react with some epoxy resins.^{30–32}

Fourier transform infrared (FTIR) spectroscopy was used to check the completion of the curing reaction. The thermal stability of the polyimine vitrimers was evaluated by thermogravimetry and the thermomechanical properties and vitrimeric behavior by dynamic mechanical thermal analysis (DMTA). All cross-linked materials could be mechanically recycled under certain conditions, and very similar properties were obtained compared to the pristine samples. Moreover, chemical degradation could be performed, and the percentage of weight degraded could be related to the polymer's structure. Materials also revealed good self-welding properties, which open a huge window of industrial applications.

2. MATERIALS AND METHODS

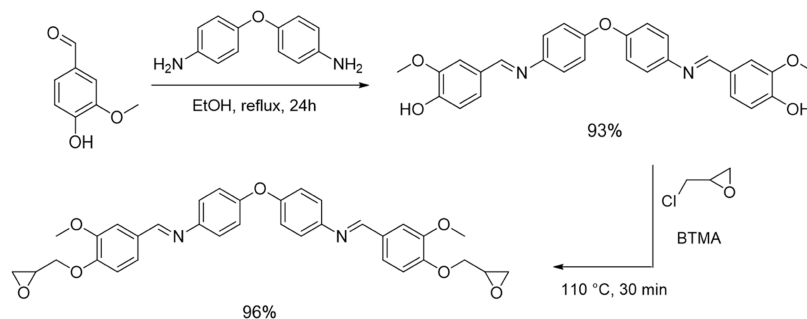
2.1. Materials. The following chemicals were purchased from Sigma Aldrich: 4,4'-oxydianiline (ODA, 97%), (±)-epichlorohydrin (ECH, ≥99%), benzyl trimethylammonium chloride (BTMA, 97%), trimethylolpropane triglycidyl ether (TMPTE), and trimethylolpropane tris[poly(propylene glycol), amine terminated] ether (JeffT403, average M_n 440). 4-Hydroxy-3-methoxybenzaldehyde (Vanillin, 99%) was obtained from ACROS Organics. Poly(oxypropylene) diamines (JeffD400 and JeffD230) from Huntsman. Sodium hydroxide (granulated, NaOH) and absolute ethanol (EtOH) were purchased from Scharlau. Dichloromethane (DCM) and hexane were obtained from VWR Chemicals. All of the reagents were used as received.

2.2. Synthesis of the Diimine-Diphenol Derivative (DIDP). The synthesis of DIDP was achieved according to the literature procedure.³³ In a 250 mL three-neck round bottom flask equipped with a magnetic stirrer, thermometer, and reflux condenser, vanillin (12.0 g, 78.8 mmol) was dissolved in absolute EtOH (80 mL), followed by the addition of 4,4'-oxydianiline (ODA, 7.9 g, 39.4 mmol). The reaction mixture was magnetically stirred and heated at reflux for 24 h. After this time, a precipitate appears, and it was cooled down to room temperature, filtered through a Büchner funnel, washed with cold EtOH, and dried in a vacuum at 60 °C for 12 h to give DIDP as a greyish-yellow solid with a yield of 93%. Mp = 163.4 °C. ¹H NMR (DMSO-*d*₆, δ in ppm): 9.72 (s, 2H), 8.48 (s, 2H), 7.52 (d, 2H), 7.33 (dd, 2H), 7.28 (dd, 4H), 7.05 (dd, 4H), 6.89 (d, 2H), 3.85 (s, 6H). ¹³C NMR (DMSO-*d*₆, δ in ppm): 159.55, 154.71, 150.14, 147.99, 147.32, 127.95, 124.03, 122.47, 119.19, 115.34, 110.31, 55.55.

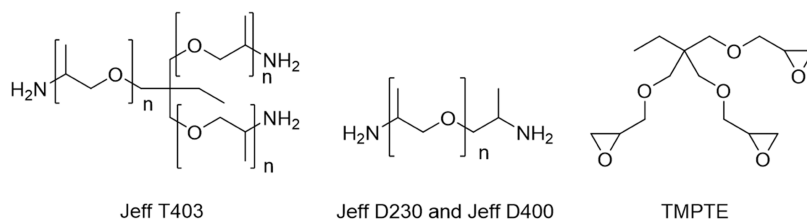
2.3. Synthesis of Diimine-Diglycidyl Derivative (DIDG). A 250 mL three-neck round bottom flask, equipped with a magnetic stirrer, thermometer, and reflux condenser, was charged with DIDP (8.5 g, 18.1 mmol) and epichlorohydrin (ECH, 100.7 g, 1.1 mol). Then, the temperature was set to 110 °C and benzyl trimethylammonium chloride (BTMA, 0.34 g 1.8 mmol) was added to the mixture. The reflux was maintained for 30 min and then cooled down. Then, 50 mL of dichloromethane was added, and extractions with distilled water (neutral pH) were performed. The organic layer was dried over anhydrous MgSO₄, filtered, and concentrated under reduced pressure. The residual amount of epichlorohydrin was eliminated by mixing with hexane and evaporating in the rotary evaporator several times. DIDG was obtained as a light-yellow solid with a yield of 96%. Mp = 144.9 °C. ¹H NMR (DMSO-*d*₆, δ in ppm): 8.54 (s, 2H), 7.57 (d, 2H), 7.43 (dd, 2H), 7.31 (dd, 4H), 7.10 (d, 2H), 7.07 (dd, 4H), 4.39 (dd, 2H), 3.90 (dd, 2H), 3.86 (s, 6H), 3.37 (m, 2H), 2.87 (dd, 2H), 2.73 (dd, 2H). ¹³C NMR (DMSO-*d*₆, δ in ppm): 159.38, 154.87, 150.60, 149.11, 147.09, 129.56, 123.71, 122.58, 119.22, 112.57, 109.63, 69.81, 55.47, 49.60, 43.83.

2.4. General Procedure for the Preparation of Polyimine Vitrimers. Polyimine vitrimers were prepared by mixing DIDG and TMPTE in a 3:1 molar ratio with the corresponding Jeffamine in stoichiometric epoxy/NH proportions in a vial until a good dispersion of the solid diimine-diglycidyl compound in the mixture was obtained. Then, prepared formulations were poured into rectangular Teflon molds of 30 × 5 × 1.5 mm³ dimensions and cured in an oven at 150 °C for 3 h to obtain transparent solid rectangular films. The materials were coded as poly(X), where X indicates the Jeffamine used in each material.

Scheme 2. Schematic Route for the Synthesis of the Diimine-Diglycidyl Derivative (DIDG)



Scheme 3. Structures of the Hardeners Used in the Preparation of the Polyimine Materials



2.5. Methods. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian VNMR-S400 NMR spectrometer. $\text{DMSO-}d_6$ was used as a solvent. All chemical shifts are quoted on the δ scale in part per million (ppm) using the residual protonated solvent as the internal standard (^1H NMR: $\text{DMSO-}d_6 = 2.50$ ppm; ^{13}C NMR: $\text{DMSO-}d_6 = 39.52$ ppm). Differential scanning calorimetry (DSC) analyses were carried out on a Mettler DSC3+ instrument calibrated using indium (heat flow calibration) and zinc (temperature calibration) standards. Samples of approximately 8–10 mg were placed in aluminum pans with pierced lids and analyzed under an N_2 atmosphere with a gas flow of $50 \text{ cm}^3 \text{ min}^{-1}$. Dynamic studies between 30 and $250 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ were performed to determine the melting points. A Jasco FT/IR-680 Plus spectrometer equipped with an attenuated total reflection accessory (ATR) (Golden Gate, Specac Ltd, Teknokroma) was used to record the FTIR spectra of the mixture before and after the curing procedure. Real-time spectra were recorded in the wavenumber range between 4000 and 600 cm^{-1} with a resolution of 4 cm^{-1} and averaged over 20 scans. The disappearance of the characteristic absorbance peak of the epoxy group at 915 cm^{-1} and the appearance of the peak corresponding to O–H at 3300 cm^{-1} were used to confirm the completion of the reaction. The thermal stability of the materials was evaluated using a Mettler Toledo TGA 2 thermobalance. Cured samples weighing around 10 mg were degraded between 30 and $600 \text{ }^\circ\text{C}$ at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ under an N_2 atmosphere with a flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$. The thermomechanical properties were studied using a DMA Q800 (TA Instruments) equipped with a film tension clamp. Prismatic rectangular samples with dimensions of around $30 \times 5 \times 1.5 \text{ mm}^3$ were analyzed from 0 to $200 \text{ }^\circ\text{C}$ at 1 Hz, with 0.1% strain at a heating rate of $2 \text{ }^\circ\text{C min}^{-1}$. Tensile stress-relaxation tests were conducted in the same instrument using the film tension clamp on samples with the same dimensions as previously defined. The samples were first equilibrated at the relaxation temperature for 5 min and a constant strain of 1% was applied, measuring the consequent stress level as a function of time. The materials were tested only once at one temperature. The relaxation-stress $\sigma(t)$ was normalized by the initial stress σ_0 , and the relaxation times (τ) were determined as the time necessary to relax $0.37\sigma_0$, i.e., ($\sigma = 1/e\sigma_0$). With the relaxation times obtained at each temperature, the activation energy values (E_a), were calculated using an Arrhenius-type equation

$$\ln(\tau) = \frac{E_a}{RT} - \ln A$$

where τ is the time needed to attain a given stress-relaxation value ($0.37\sigma_0$), A is the pre-exponential factor, and R is the gas constant. From the Arrhenius relation, the topology freezing temperature (T_v) was obtained as the temperature at which the material reaches a viscosity of $10^{12} \text{ Pa}\cdot\text{s}$. Using Maxwell's relation and E' determined from DMTA (assuming E' is relatively invariant in the rubbery state), τ^* was determined to be around 10^5 s in our systems. The Arrhenius relationship was then extrapolated to the corresponding value of τ^* to determine T_v in each sample. The recycled samples were obtained by cutting the cross-linked polymers and hot-pressing in a Specac Atlas manual 15 T hydraulic press at 3 MPa into an aluminum mold at $180 \text{ }^\circ\text{C}$ for 2 h. Recycled samples were die-cut to the same dimensions from the new film obtained and tested again in the DMA analyzer for their mechanical characterization under the same conditions as previously described. The chemical degradation of the materials was investigated by first weighing the sample of the cured material and then keeping it in a 1 M HCl aqueous solution for 24 h at room temperature under stirring. Then, the samples were dried under vacuum at $90 \text{ }^\circ\text{C}$ for 12 h, weighed and the gel fraction was calculated. Final materials were tested until break in tensile mode at room temperature using an electromechanical universal testing machine (Shimadzu AGS-X) with a 1 kN load cell at 10 mm/min and using Type V samples with a thickness of 1 mm according to the ASTM D638-14 standard. Three samples of each material were analyzed, and the results were averaged. Self-welding studies were performed by cutting a poly(D230) sample of a cured material in two parts and then overlapping in an oven at $180 \text{ }^\circ\text{C}$ for 2 h under a pressure of 3 MPa. After that, the samples were tested in the tensile test under the same conditions as previously described.

3. RESULTS AND DISCUSSION

3.1. Synthesis of the Diimine-Diglycidyl Monomer (DIDG). DIDG was prepared via a two-step procedure, including the synthesis of an intermediate diimine-diphenol compound (DIDP) and the further glycidylation reaction of the phenol groups with ECH (Scheme 2). Both products were characterized by nuclear magnetic resonance (NMR) spectroscopy (Figures S1–S4).

The first step is the condensation reaction between bio-based vanillin and ODA, in which the diimine-diphenol compound is obtained in a high yield without needing any catalyst. The appearance of the proton signal at 8.48 ppm

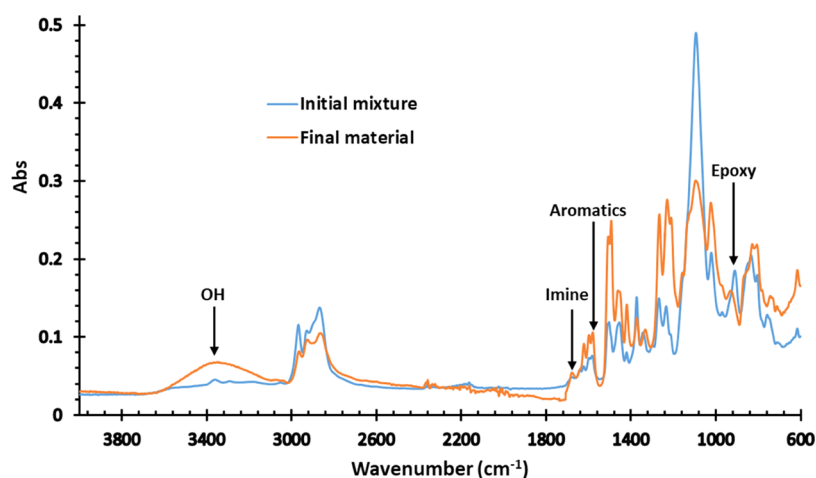


Figure 1. FTIR spectra of the initial mixture (blue) and final material poly(D400) (orange).

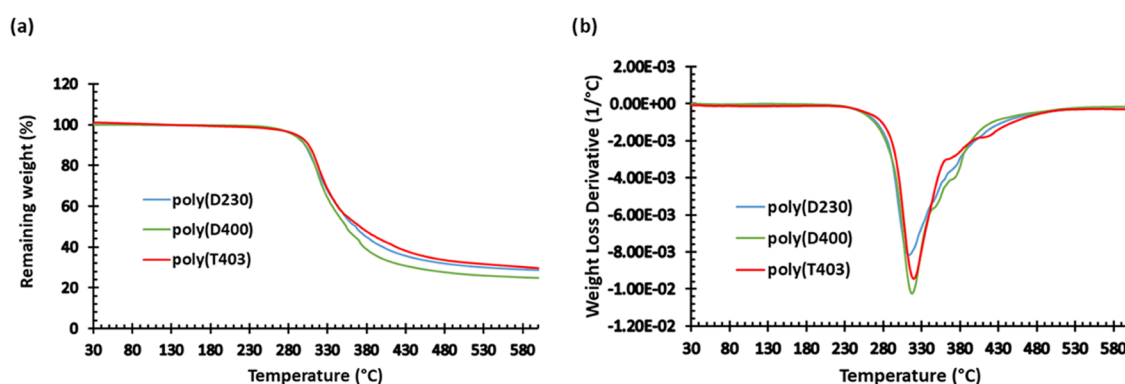


Figure 2. (a) Thermogravimetric curves and (b) DTG curves of all polyimine materials recorded under an N_2 atmosphere.

corresponding to the methine of the imine group and the disappearance of the aldehyde signal of the starting vanillin confirmed the structure of the intermediate DIDP compound. ^{13}C NMR corroborated the purity of the compound by the complete disappearance of the aldehyde signal and the appearance of the carbon signal of the new imine bond formed. The glycidylation reaction was performed with a large excess of ECH using BTMA as a phase transfer catalyst and heating the mixture to $110\text{ }^\circ\text{C}$ for 30 min. The proton signals corresponding to the glycidyl groups appeared between 4.75 and 2.75 ppm, and the phenol signal was no longer visible in the spectrum, demonstrating that glycidylation had taken place. ^{13}C NMR also showed the presence of carbon signals corresponding to the epoxy groups of DIDG, confirming the successful synthesis of the expected diimine-diglycidyl compound, which was not previously reported.

3.2. Study of the Curing Procedure. The synthesized DIDG and the different Jeffamines (Jeff400, Jeff230, and JeffT403, see Scheme 3) were used in the preparation of the vanillin-based vitrimers containing dynamic imine bonds. DIDG has a high melting point and molecular weight due to its high content of aromatic rings, which will give high rigidity to the materials and make it very difficult to achieve homogeneity in the samples. For this reason, as well as to endow the final networks with greater flexibility and to reach a better dispersion of the solid compound in the mixture without reducing the cross-linking density, an aliphatic trimethylolpropane triglycidyl ether (TMPTE) was added to the formulations in a 3:1 molar ratio between DIDG and TMPTE. The curing

temperature was set to $150\text{ }^\circ\text{C}$ to guarantee that DIDG melts during the procedure and to ensure the complete homogeneity of the mixture during the curing process. The need to melt the solid compound in the mixture hampers the proper kinetic study. All cross-linked materials were prepared under stoichiometric epoxy/NH conditions and cured according to the procedure previously described in the Experimental Section to obtain reddish transparent samples.

FTIR spectra of the initial mixtures and the final materials were recorded to determine if the curing process had been completed. Figure 1 shows the FTIR spectra of the initial mixture and the final material for the poly(D400) derivative. As it can be seen, after thermal treatment, the band at 910 cm^{-1} attributed to stretching of the epoxy groups disappears, while a broad band at around 3300 cm^{-1} corresponding to the O–H groups generated during the epoxy-amine reaction appears, which indicates that this curing process was effective. It is also noteworthy that the band at approximately 1657 cm^{-1} corresponding to the imine group remained unchanged during the curing process, confirming that the final materials still contain these dynamic groups.

3.3. Thermal Characterization of the Materials. The thermal stability of the polyimine vitrimers was studied by thermogravimetry (TGA). Figure 2 shows the TGA curves and their derivatives for the materials prepared, and Table 1 presents the most significant data extracted.

As it can be observed, all of the materials reveal similar degradation patterns with one main peak with a maximum between 300 and $320\text{ }^\circ\text{C}$, which can be assigned to the

Table 1. Thermogravimetric Data of all of the Polyimine Materials Prepared

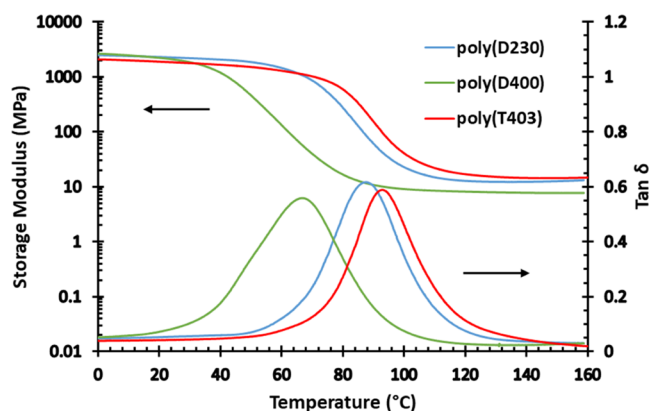
sample	$T_{1\%}^a$ (°C)	$T_{2\%}^b$ (°C)	T_{\max}^c (°C)	char yield ^d (%)
poly(D230)	230.5	263.3	313.2	28.7
poly(D400)	226.4	258.0	315.1	24.8
poly(T403)	231.2	265.2	317.5	29.6

^aTemperature of 1% of weight loss. ^bTemperature of 2% of weight loss. ^cTemperature at the maximum rate of degradation. ^dChar residue at 600 °C.

degradation of the poly(hydroxyl-amine) network because of the high content of labile C–N bonds.³⁴

As can be seen in Table 1, all of the samples lose 1% weight at temperatures above 226 °C, slightly increasing this value with the cross-linking density, which depends on Jeffamine characteristics. Their thermal stability is conferred by the cross-linking density provided by the high functionality of the monomers as well as for the significant content of aromatic rings in the network. In terms of mechanical recycling, thermal stability is essential to ensure that the material does not begin to degrade at the recycling temperature. These values of the initial degradation temperature allow for the treatment of the material up to 200 °C without fear of degradation. In addition, the char yield of all of the materials is relatively high due to the presence of nitrogen and aromatic rings in the network, but it decreases when the functionality of the starting Jeffamine is lower and when the cross-linking density decreases.

The thermomechanical properties of the polyimine vitrimers were determined by DMTA analysis. Figure 3 shows the evolution of the $\tan \delta$ curves and the storage moduli (E') with temperature for all of the materials. The data extracted from these studies are summarized in Table 2.

**Figure 3.** Evolution of $\tan \delta$ and storage modulus with temperature of all polyimine vitrimers.

As observed, fully cured polyimine vitrimers exhibit T_g values (taken from the maximum of $\tan \delta$ curves) between 66 and 93 °C depending on the Jeffamine used as the curing agent. As expected, poly(D400) exhibits the lowest T_g value, in accordance with a more open network structure provided by the higher mobility and flexibility of the structure, while poly(T403) has the highest T_g . Nevertheless, the T_g of poly(D400) is slightly higher in comparison to DGEBA-JeffD400, which is reported to be 62 °C.³⁵ Although it would seem that a greater molecular weight provided by the poly(propylene ether) units in JeffT403 would lead to a lower T_g , the higher functionality reduces the mobility of the network. Furthermore, the storage moduli in the glassy state are very similar in all cases, with values of around 2000 MPa indicating a relatively high rigidity. Contrarily, in the rubbery state, it can be seen that the higher the cross-linking density, the higher the value of the storage modulus in this state.

3.4. Study of the Vitrimeric Behavior. Stress-relaxation tests were performed by DMTA to investigate the time and temperature-dependent relaxation behavior and, consequently, the vitrimeric nature of these materials. The results are shown in Figure 4, and the characteristic data are tabulated in Table 3. The stress-relaxation curves reveal that these polyimine vitrimers can relax the stress extremely fast, reaching the reference relaxation value of 63% ($\sigma = 0.37\sigma_0$) at 150 °C in less than 1.75 min for poly(D230), 0.85 min for poly(D400), and 1.90 min for poly(T403) without needing any external catalyst, which highlights the high speed of the exchange reaction. As it is also possible to be seen, all of the materials can relax the stress entirely in less than 10.5 min at the same temperature.

As seen in Table 3, poly(D400) is the material that can relax stress the fastest due to the higher flexibility of the network, allowing the imine groups to undergo the exchange reaction easily. On the other hand, poly(D230) has a shorter chain and poly(T403) has a more closed network, and consequently, mobility is more restricted in both cases, thus the interchange is more challenging to occur.

When viscosity is controlled by the exchange reaction, in vitrimeric materials, a relationship between temperature and viscosity similar to the inorganic silica materials is achieved, which follows an Arrhenius-type temperature dependence.³⁶ Based on this, to perform an extensive study of the vitrimeric behavior of these polyimine materials, the stress-relaxation time at different temperatures for a relaxation value of 63% ($\sigma/\sigma_0 = 0.37$) was obtained from Figure 4a–c. Using an Arrhenius-type equation, the activation energy (E_a) of the rearrangement process can be determined (see Table 3). These values also indicate that the sensitivity of the imine metathesis to a change in temperature could be significant depending on the cross-linking density and the chain length of the starting Jeffamine.

Table 2. Thermomechanical Data of all of the Virgin and Recycled Imine Vitrimers

sample	virgin			recycled		
	E'_{glassy}^a (MPa)	E'_{rubbery}^b (MPa)	$T_{\tan \delta}^c$ (°C)	E'_{glassy}^a (MPa)	E'_{rubbery}^b (MPa)	$T_{\tan \delta}^c$ (°C)
poly(D230)	2230	13.1	87.4	1700	11.2	85.4
poly(D400)	2000	7.7	66.8	1950	4.3	66.1
poly(T403)	1835	14.9	92.8	2000	12.6	93.2

^aGlassy storage modulus at $T_g - 50$ °C determined by DMTA. ^bRubbery storage modulus at $T_g + 50$ °C determined by DMTA. ^cTemperature at the maximum of $\tan \delta$ peak at 1 Hz.

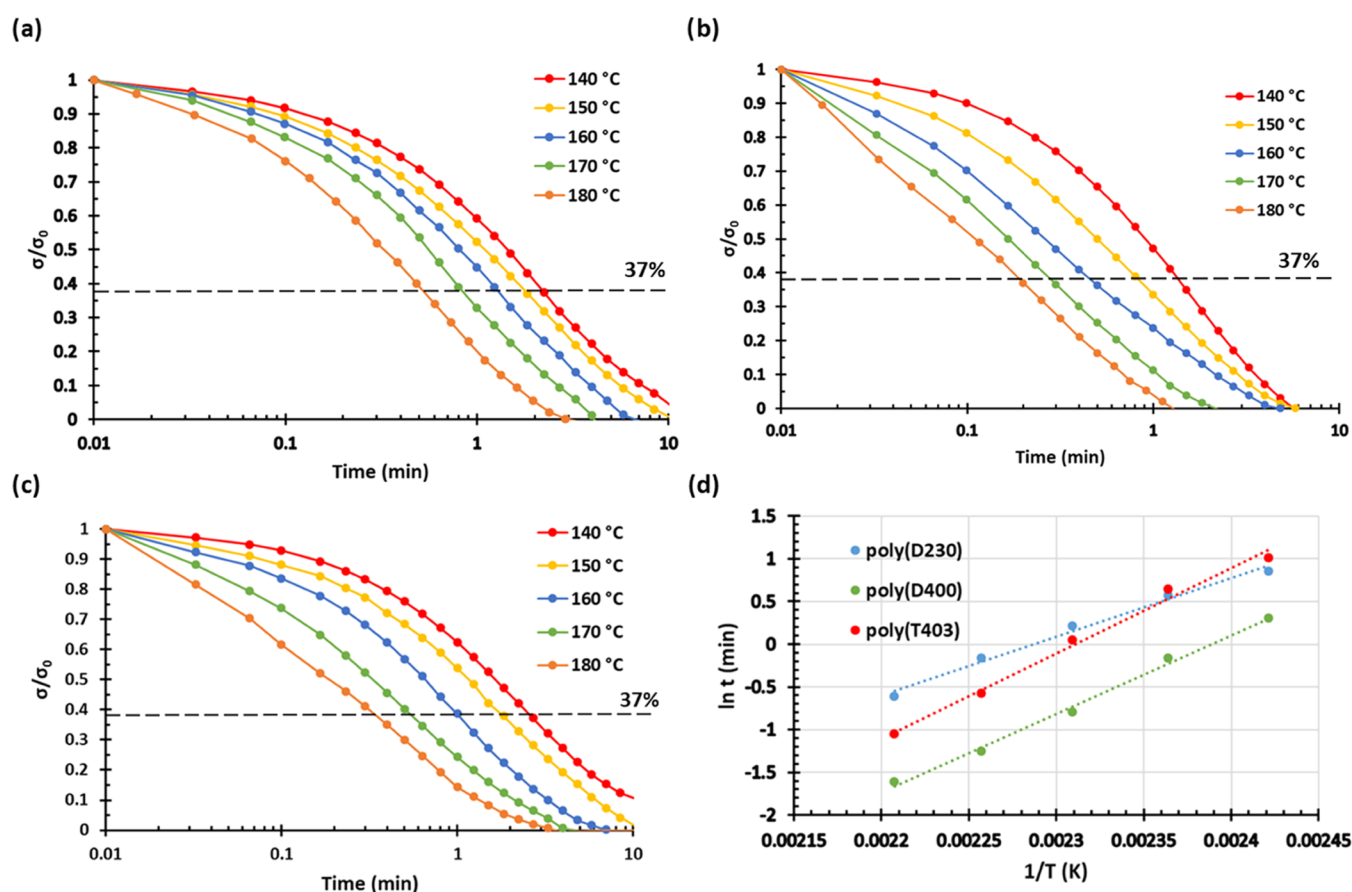


Figure 4. Normalized stress-relaxation plots as a function of time at various temperatures during 10 min for poly(D230) (a), poly(D400) (b), and poly(T403) (c) samples, and (d) Arrhenius plot of relaxation times against the inverse of the temperature for the different polyimine vitrimers.

Table 3. Relaxation Times, Topology Freezing Temperature, Activation Energy, and Adjusting Parameters for the Arrhenius Equation of all Samples Prepared

material	$\tau_{0.37}^a$ (min)	$\tau_{100\%}^b$ (min)	T_v (°C)	E_a (kJ mol ⁻¹)	$\ln A$ (min)	r^2
poly(D230)	1.75	10	27.3	57.0	15.67	0.99
poly(D400)	0.85	6	39.0	76.5	21.98	0.99
poly(T403)	1.90	10.5	58.7	83.0	23.07	0.99

^aTime to reach a value of $\sigma/\sigma_0 = 0.37$ at 150 °C. ^bTime to reach total relaxation at 150 °C.

The topology freezing temperature (T_v), which by definition is the temperature when the material reaches a viscosity of 1012 Pa·s, can be determined from the Arrhenius plot.³ This temperature accounts for the temperature below which chemical exchanges are negligible and can be used to compare bond exchange capabilities in vitrimers. In these imine vitrimers, it is possible to see that the T_v values are low and much lower than T_g . In this case, the critical factor in determining the relaxation behavior is T_g because, in the glassy state, the lack of segmental motions hampers the exchange reaction between imine units. Therefore T_v is not real, just hypothetical since it is necessary to exceed the T_g so that the network achieves certain mobility and the exchange reactions can start.^{36,37} Despite that the correlations are very strong, it is noteworthy that limited errors in activation energy give significant errors in the relaxation time and, consequently, in the T_v .

Since no free primary amine groups exist in the network, the exchange mechanism produced must be imine metathesis.

3.5. Recycling Process. To investigate the recyclability of the three different polyimine vitrimers prepared, the materials were cut into small pieces and hot-pressed at 3 MPa in an aluminum mold for 2 h. The recycling temperature selected was 180 °C, which ensured the topological rearrangement and guaranteed that no degradation will occur, as it was determined by thermogravimetry that at this temperature for 2 h no weight was lost. As it can be seen in Figure S5 the recycled material shows good transparency, indicating that the recycling process has been successful.

DMTA analysis was performed to study the thermomechanical properties of the recycled samples and compare them with the virgin ones. The $\tan \delta$ curves and the storage modulus as a function of temperature for all of the recycled and virgin materials can be seen in Figure 5, and the data obtained from them are presented in Table 2.

As can be seen, very similar $\tan \delta$ curves and $T_{\tan \delta}$ values were obtained for the virgin and recycled samples, demonstrating that the recycling process hardly affects the thermomechanical properties of the final materials.

Moreover, to check if the chemical structure has been changed after the recycling process, FTIR analyses of the virgin and recycled poly(D400) were performed. As can be seen in Figure S6, no significant changes between both samples can be observed, indicating that the chemical structure has not been altered.

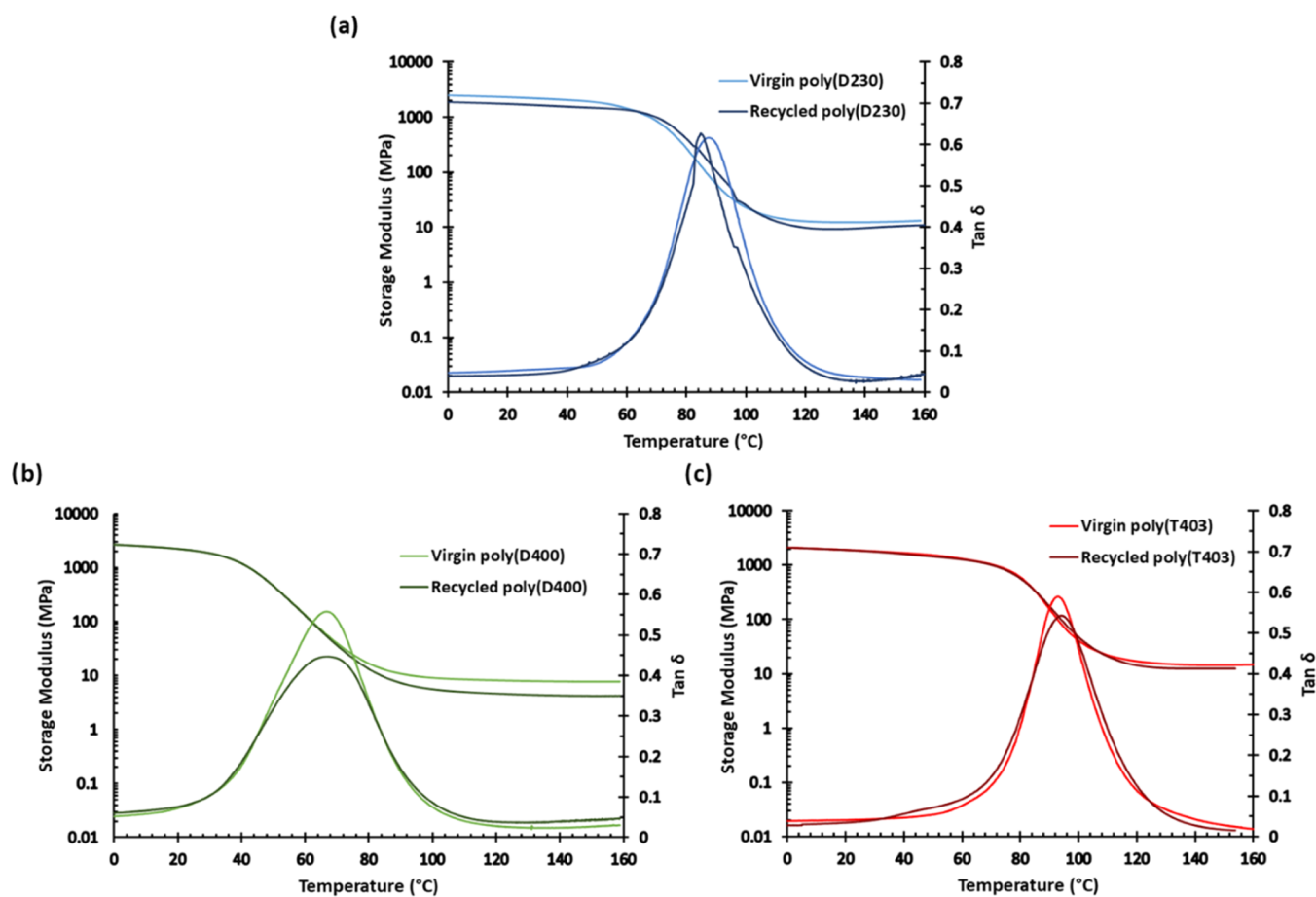


Figure 5. Dependence of tan δ and storage modulus vs temperature before and after recycling of poly(D230) (a), poly(D400) (b), and poly(T403) (c).

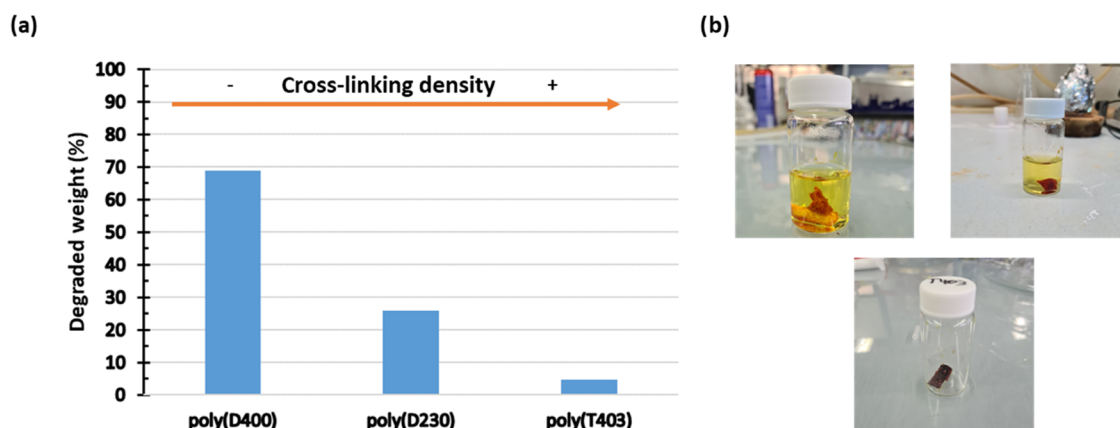


Figure 6. (a) Degraded weight percentage of each polyimine material and (b) photographs of the samples after the chemical degradation.

The goodness of the recyclability of poly(D230) was confirmed by the tensile strength comparing the virgin and the recycled material. Figure S7 shows the stress–strain curves of both samples, which are quite similar, with a slightly more rigid behavior in the case of the recycled one. This can be explained by the presence of some defects in the recycled material due to the harsh conditions of the recycling process.

3.6. Chemical Degradability. All materials were introduced in a 1 M HCl aqueous solution for 24 h at room temperature under stirring to investigate the chemical degradability of the imine vitrimers since it is known that

imine bonds can be easily hydrolyzed under acidic conditions. After that, it can be noticed in Figure 6 that the solution became yellowish, indicating the hydrolysis of the imine bonds. Nevertheless, a trend is observed for the materials since poly(D400) was degraded until 68.8% of its initial weight, but poly(T403) only 4.8%. This fact is in accordance with the increase in the cross-linking density, which is given by the functionality and chain length of the starting Jeffamines. Higher functionality means more non-exchangeable covalent bonds in the material and a fewer proportion of degraded sample under the same conditions. The presence of TMPTE in

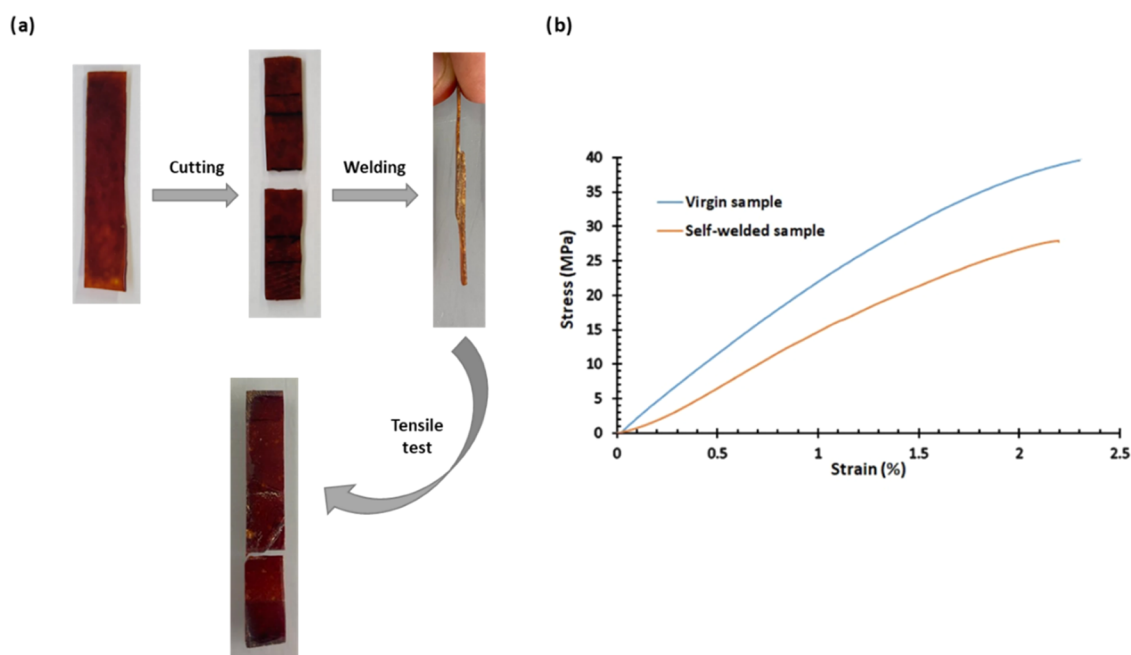


Figure 7. (a) Self-welding process and (b) tensile properties of virgin and welded poly(D230).

the formulation, with a trifunctional structure without imine groups, hinders the complete solubilization of the material when hydrolyzed in an acidic medium.

3.7. Self-Welding Studies. Polyimine materials proved to have self-welding abilities thanks to imine metathesis that can occur at the interface of two overlapped pieces of the materials. To study this phenomenon, a rectangular film of poly(D230) was cut into two pieces and then overlapped under the same conditions of the recycling procedure to ensure that the exchange reaction occurred in the overlapping area. As can be observed in Figure 7a, the two parts of the polyimine material were attached. The virgin and the welded samples possessed similar dimensions, so they were subjected to the tensile test. Figure 7a also shows that the sample was broken at a random site rather than the overlapping area, demonstrating that this part is not the weakest. Nevertheless, the tensile strength and elongation at break (Figure 7b) were slightly lower compared to the virgin polyimine due to the stress concentration factor at the end of the part where both pieces overlapped as well as the lack of uniformity in the transverse section of the sample.

4. CONCLUSIONS

A bio-based diimine-diglycidyl derivative of vanillin has been successfully synthesized and cross-linked with three Jeffamines (JeffD230, JeffD400, and JeffT403) with different molecular weights and functionalities. Trimethylolpropane triglycidyl ether (TMPTE) was added to facilitate processing and increase flexibility and cross-linking density.

All of the materials obtained have a T_g higher than 65 °C and high thermal stability ($T_{1\%} > 225$ °C), allowing safe recycling up to 200 °C.

The exchange reaction occurs via imine metathesis and only needs about 10 min to completely relax stress at 150 °C in all cases without adding any external catalyst. The topology freezing temperatures (T_v) were calculated using the Arrhenius dependence of relaxation with temperature and resulted in lower T_v than the T_g values, meaning that once this

temperature is overpassed, the exchange reaction takes place immediately.

The materials could be recycled under pressure at 180 °C for 2 h without changing their thermomechanical characteristics.

Imine groups in the network allow the chemical degradation of the material in aqueous HCl, but the addition of TMPTE to the formulation hinders the complete degradation. The structure of the Jeffamine, used as the curing agent, affects the hydrolysis extent because of the different cross-linking densities of the network.

Self-welding studies were performed in all of the polyimine vitrimers under pressure at 160 °C in a conventional oven demonstrating their great capability for this application.

The partially bio-based character, the high relaxation rate, recyclability, chemical degradability, and self-welding characteristics make these materials very interesting for future industrial applications.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsapm.2c01604>.

Structural characterization of the synthesized products and some supporting images of the recycled materials (PDF)

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Author Contributions

A.R. conducted the synthesis of the monomers and materials, mechanical tests, and wrote the original draft. P.H. performed the recycling tests and part of welding experiments. X.R., S.D.I.F., and A.S. validated the studies, made conceptualization, supervised the work, and reviewed and edited the final manuscript.

Notes

The authors declare no competing financial interest.

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