Network design to control polyimine vitrimers properties: physical versus chemical approach

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Abstract

A family of biobased polyimine elastomeric vitrimers was synthesized by reaction between di- and trifunctional polyetheramines and a furan-based dialdehyde. By varying the triamine to diamine ratio and the molar mass of the diamine, a set of crosslinked networks with similar chemical structures but different crosslink densities was obtained. All these materials exhibit a vitrimeric behavior due to the dynamic nature of the imine bonds. This fundamental study clearly reveals that the crosslink density has a drastic effect on the relaxation properties of the vitrimers. For instance, the relaxation times and the activation energies are reduced when the crosslink density of the vitrimer networks decreased. This shows that the relaxation properties of vitrimers can be controlled by the sole modification of the network physical properties, without the introduction of a catalyst, a change in chemical structure or the introduction of additional chemical groups. In addition, a fast dual relaxation process has been clearly evidenced during stress relaxation experiments, which could potentially lead to double relaxation modes based on supramolecular interactions. The selective solubility of these polyimine networks was also demonstrated, opening interesting possibilities for chemical recycling whilst still offering robustness against aggressive conditions such as highly basic solutions. Finally, the dynamic properties and the high thermal stability of the designed polyimine networks provide an interesting reprocessability and tunable mechanical properties, showing the versatility of this sustainable family of vitrimer materials.

Keywords: vitrimer, covalent adaptable network, polyimine, biobased polymer

Introduction

Nowadays, two main categories of polymers can be found in the market: thermoplastics and thermosets. Thermoplastics are known to be easily remolded, reprocessed or recycled. However, they show limited mechanical properties, thermal and chemical resistances. Thermosets are usually formed of a three-dimensional network containing permanent and irreversible covalent bonds. They show higher dimensional stability, better mechanical and thermal properties and higher chemical resistances than thermoplastics. Nevertheless, once they are fully hardened, thermosets cannot be melted, which precludes their reprocessing and makes them difficult to recycle.

An elegant strategy to turn crosslinked polymer networks into reprocessable materials is to use crosslinking bonds that can be redistributed through the network. This can be performed either *via* strong supramolecular interactions¹⁻³ or dynamic covalent bonds.⁴⁻⁸ The latter are usually referred to as Covalent Adaptable Networks (CANs). They have later been divided into dissociative and associative CANs, according to the crosslink exchange mechanism. In dissociative CANs, chemical bonds are first broken before being formed again at another position, which implies that the network depolymerizes and loses its integrity during the process. The reversible Diels-Alder reaction between furans and maleimides is one of most commonly used crosslinking reaction in dissociative CANs.⁹⁻¹³ In associative CANs, also called vitrimers, the crosslinks can be redistributed through the network while maintaining a fixed crosslink density,^{8,14,15} allowing a certain fixed topology at low temperatures, but enabling reprocessing and recycling at higher temperatures. Various types of exchangeable reactions have been used for vitrimer synthesis, such as transesterification of esters,^{14,16-21} transesterification of boronic esters and/or dioxaborolane metathesis,²²⁻²⁵ transcarbonation,²⁶ transcarbamylation²⁷ or transamination of vinylogous urethanes.²⁸⁻³⁰

Imine exchange reactions have also been used as dynamic linkages in crosslinked polymer networks. They have been extensively studied by the group of Zhang, who combined various diamines with terephthalaldehyde and a trifunctional amine crosslinker to produce self-healable and recyclable polyimine networks,³¹⁻³⁵ which have later been employed to produce carbon fiber-reinforced recyclable composites.³⁶ Zheng et al.^{37,38} prepared similar polyimine vitrimers which combine flexibility, good mechanical properties and viscoelastic behavior. The lignin-derived monomer vanillin

was also used as aldehyde in polyimine vitrimers synthesis, yielding materials showing self-healing ability, good mechanical properties and recyclability.^{39–42} Our group recently developed a promising fully biobased polyimine vitrimer,⁴³ in which the network was formed by combining 2,5-furandicarboxaldehyde (FDC), directly obtained from fructose, with dimeric and trimeric biobased amines prepared from fatty acids. Compared to other vitrimers reported in the literature, this system showed reduced environmental impacts thanks to the use of fully biobased precursors and low temperatures for the synthesis and (re)processing steps.

A key point in the development of vitrimers is to control the relaxation properties of the materials, *i.e.* to tune the relaxation time and the activation energy. Reducing the relaxation time is particularly important to facilitate their recycling or to allow their processing *via* common industrial techniques, such as extrusion.⁴⁴ The control of the relaxation properties is usually achieved by a chemical control of the exchange reactions. Besides the choice of the nature of the dynamic linkage, the different strategies involve the introduction of various amounts and types of catalysts,^{18,26,45,46} the synthesis of networks carrying free chemical functions able to facilitate the exchanges,^{26,30,44,47,48} or the chemical design of structures able to accelerate the exchange reactions by side group effects.^{22,49} The influence of physical properties of the vitrimer networks, such as the crosslink density, has not been the topic of an in-depth investigation. A few studies hinted at an influence of the crosslink density on the relaxation properties (**Table S1**), however this was associated to a variation in the concentration of free chemical functions, such as OH groups in polyester or polycarbonate vitrimers,^{26,50–52} or to significant changes in the chemical structure,⁵³ making it difficult to decouple the different influences. The exchange of imine linkages through an associative pathway^{54,55} is efficient even in the presence of trace amounts of amine groups,⁵⁶ allowing the preparation of vitrimers without introducing an excess of chemical functions, unlike for instance transesterification vitrimers, making it a system of choice to study independently the influence of the network crosslink density.

The present work thus focuses on investigating thoroughly the influence of the network structure on the relaxation properties of vitrimers. The biobased dialdehyde (FDC) was combined with various non-toxic and largely available di- and trifunctional polyetheramines (**Table 1**), in a stoichiometric amine to aldehyde ratio, to produce a set of crosslinked networks having similar chemical structures

but varying crosslink densities. In addition, materials were synthesized with an excess of either amine or aldehyde, to draw a parallel with the chemical control. The materials were fully characterized to evidence how the network structure can influence the vitrimer properties, with a particular focus on the relaxation properties.

Table 1. Main characteristics of the polyetheramines

Polyetheramines	Abbreviation	Amine functionality	Molar Mass (g mol ⁻¹)
Jeffamine® D-230	D-230	2	230
Jeffamine® D-400	D-400	2	430
Jeffamine® D-2000	D-2000	2	2000
Jeffamine® T-403	T-403	3	440

Results and discussion

Synthesis of vitrimers

A mixture of diamine and triamine was reacted with the furan-based dialdehyde (FDC) to form the polymer tridimensional network (**Figure 1**). Tetrahydrofuran (THF) was chosen as solvent since imine condensation has been shown to be faster in THF than in other solvents,⁵⁷ leading to homogeneous materials with enhanced crosslinking.³¹ In addition, THF can potentially be biobased.⁵⁸ The triamine to diamine ratio and the diamine molar mass were varied to prepare a set of polyimine networks with a stoichiometric amine to aldehyde ratio, to study the influence of the crosslink density (**1 – 6**, Table 2). In addition, two materials were prepared with an excess of either amines or aldehydes to study the influence of free chemical groups on the material properties (**7, 8**, Table 2).

Figure 1. Synthesis of polyimine vitrimers from polyetheramines and FDC.

Table 2. Composition of the studied systems

System designation	Diamine (D)	Triamine (T)	T : D molar ratio	NH ₂ : CHO molar ratio
1	D-230	T-403	1	1 : 1
2	D-400	T-403	0.33	1 : 1
3	D-400	T-403	0.66	1 : 1
4	D-400	T-403	1	1 : 1
5	D-400	T-403	2	1 : 1
6	D-2000	T-403	1	1 : 1
7	D-400	T-403	1	0.95 : 1
8	D-400	T-403	1	1.05 : 1

To confirm the formation of imine linkages, a soluble linear polymer was also synthesized from the diamine D-400 and FDC. ¹H NMR spectrum confirms the appearance of imine linkages as well as the absence of remaining aldehydes and amines (**Figure S1**). For the tridimensional networks, polymerization was confirmed by FTIR measurements showing the disappearance of the vibration bands characteristic of primary amines at 1590 cm⁻¹ and of aldehydes at 1665 cm⁻¹, and by the appearance of the imine vibration band at 1637 cm⁻¹ (Supporting information, **Figure S2**).

Physical properties of polyimine networks

The thermal stability of the materials was first assessed by thermogravimetric analysis (TGA). All thermograms are available in the Supporting Information (**Figures S3 – S5**). They show similar degradation behaviors, suggesting that the mechanisms of thermal degradation are independent from the composition. The onset temperature (*i.e.* the temperature of 5 %wt loss of the material) was observed above 250 °C for all compositions, far above the processing temperature, and is only influenced by the diamine molar mass (**Table 3**). In addition, isothermal analyses were performed at 120 °C during 2 hours and revealed a weight loss below 1 %wt for all systems, confirming their stability during the processing and reprocessing steps (**Figure S6**).

Table 3. Summary of the main thermal properties

System designation	Varying parameter	T _{onset} (°C)	T _g (°C)	T _α (°C)	G' _{rub} (MPa)	ν (mol L ⁻¹)
T : D ratio						
2	0.33	257	– 15	-13	2.84	1.09
3	0.66	266	– 8	-7	4.49	1.72
4	1	260	– 4	-1	5.24	2.01
5	2	261	5	5	6.45	2.48
Diamine molar mass						
1	230	251	16	14	5.53	2.13
4	400	260	– 4	-1	5.24	2.01
6	2000	290	– 50	-45	1.79	0.73
NH ₂ : CHO ratio						
7	0.95 : 1	258	– 4	-3	3.52	1.35
4	1 : 1	260	– 4	-1	5.24	2.01
8	1.05 : 1	257	– 5	-4	4.61	1.77

Dynamic Mechanical Analysis (DMA) was then used to confirm the crosslinked nature of all materials, characterized by the appearance of a constant rubbery plateau (**Figure 2**). The crosslink density was calculated from the rubbery modulus using **Equation 1**:⁵⁹

$$\nu = G' / RT \quad (1)$$

where G' is the storage modulus on the rubbery plateau (at 40 °C), T is the temperature (in K), and R is the gas constant (8.314 J mol⁻¹ K⁻¹).

As expected, increasing the triamine to diamine ratio or reducing the diamine molar mass leads to an increase in the crosslink density (**Table 3 and Figure S7**). The amine to aldehyde ratio also influences

the network structure. The network synthesized with a stoichiometric amine to aldehyde ratio has a higher crosslink density compared to the systems with an excess of either amine or aldehyde (**Figure 2c, Table 3**). The excess of aldehyde reduces the molar ratio of triamine in the network and results in the lowest crosslink density. In presence of an excess of amines, the dialdehyde is the limiting reagent, meaning that some triamine reacts with less than three aldehydes, resulting in a lower crosslink density than in the stoichiometric network. All materials show a single relaxation within the studied temperature range, and the T_α globally increases with the crosslink density of the networks. Differential Scanning Calorimetry (DSC) was further used to measure the glass transition temperature (T_g) of the networks, and confirms the results obtained by DMA, with an excellent correlation between T_g and T_α (**Table 3, Figures S8 to S10**).

Figure 2. DMA thermograms according to the different varying parameters: (a) triamine to diamine ratio (b) diamine molar mass and (c) amine to aldehyde molar ratio.

Viscoelastic properties

The networks with the different crosslink densities were used to study the influence of the network structure on the viscoelastic properties. All the materials show the characteristic of vitrimers. They exhibit stress relaxation because imine bonds can be redistributed throughout the network. The

relaxation curves of vitrimer **4** are depicted on Figure 3a, similar data for the other vitrimers are given in the supporting information (**Figures S11 to S18 and Table S2**). The relaxation time (τ^*), obtained at $G(t)/G_0 = 1/e$, decreases when the temperature increases according to an Arrhenius law (Figure 3b). Relaxation times at temperatures higher than 65 °C became substantially fast. They reached the limit of significance for such an experiment and are thus not reported here. A single material, vitrimer **5**, shows a deviation from the Arrhenius law. Below 35 °C, it seems to follow a Williams-Landel-Ferry (WLF) equation (**Figure S19**).^{15,19,60} Nishimura et al.⁶⁰ showed that as the material temperature increases over T_g , it first behaves according to the WLF model before following the Arrhenius law (values lower than 25°C were not measured, as **5** did not reach τ^* at 20°C even after 60000 s).

Figure 3. (a) Stress relaxation of vitrimer **4** between 25 and 65 °C. (b) Arrhenius plot obtained from the relaxation times τ^* at different temperatures, used to calculate the activation energy.

Interestingly, our results show an important dependence of the relaxation time on the crosslink density. The relaxation times of the vitrimers at 45 °C have been plotted against the crosslink density in **Figure 4a**. Similar trends are observed at all temperatures between 25 and 65 °C, and are reported in the supporting information (**Figure S20**). For the vitrimers prepared with a stoichiometric amine to aldehyde ratio (dashed line on **Figure 4a**), decreasing the crosslink density leads to a strong reduction of the relaxation time. At 45 °C, τ^* can be reduced from about 500 to 25 s only by tuning the crosslink density of the network. A decrease of the relaxation time upon reducing the network crosslink density

had already been observed in CANs based on urethane reversion⁵⁰ or transcarbonation reactions,²⁶ but in both cases it was associated to varying amounts of free OH groups in the networks, which strongly influence the exchange reaction. Here, the control of the vitrimer relaxation time is achieved only by tuning the network crosslink density, without introducing any catalyst or change in chemical structure. Similar observations were recently reported in vitrimers based on dioxaborolane metathesis.²⁵ The reduction in relaxation time observed here (up to 20-fold decrease) is however unprecedented. The explanation of this result probably lies in the increased mobility of the polymer chains as the network crosslink density is reduced.^{25,26} This effect had already been evidenced in polyimine vitrimer composites with graphene, where an increase in graphene content led to an increase in the relaxation time caused by the reduced chain mobility.⁶¹ Surprisingly, when the crosslink density gets too low, the relaxation times increases again, showing that there might exist an optimum crosslink density to facilitate the exchange reactions. Recent results on transesterification vitrimers might corroborate this observation.⁶²

The vitrimers prepared with non-stoichiometric ratios between amines or aldehydes do not follow the same correlations to the crosslink density (blue triangles on **Figure 4a**). The vitrimer prepared with an excess of amine has reduced relaxation times with respect to the corresponding stoichiometric vitrimer of similar crosslink density. Indeed, the excess of amine eases the covalent bond exchanges by a transimination mechanism between free amines and imines in the network.⁵⁶ However, this study evidences that the introduction of an excess of amine reduces the relaxation time by two distinct factors. First, the excess of amine leads to a decrease in the crosslink density of the network, thus reducing the relaxation time. Second, the free amines in the network can catalyze the exchange reactions, leading to a further reduced relaxation time as compared to a system of similar crosslink density. The reduction of the relaxation times observed in vinylogous urethane vitrimers in the presence of excess amines^{44,47} or in polycarbonate vitrimers in the presence of free OH²⁶ might similarly be the resultant of these concomitant effects. In presence of a 5 mol% excess of aldehyde, the relaxation times are much higher than with a stoichiometric ratio. As a matter of fact, when amines are the limited components, no free amines should be present in the network, consequently leaving the

imine metathesis as predominant exchange mechanism. The latter is known to be much slower than transamination with free amines.⁵⁶

The dependency of the vitrimer activation energy on the nature of the chemical exchange reaction is generally accepted. Tuning of the activation energy can therefore be achieved by the addition of a catalyst^{18,44,45} or by a change in the chemical structure.⁴⁰ In the catalyst-free polyimine vitrimers prepared here, we observed almost constant activation energies for highly crosslinked networks, and on the other hand a marked decrease when the crosslink density was lowered (**Figure 4b**). The vitrimer with the lowest crosslinking density has an activation energy of 64 kJ mol⁻¹, very close to what our group previously obtained on a fully biobased polyimine vitrimer prepared with long chain di- and triamines based on dimer fatty acids.⁴³ The highly crosslinked systems have activation energies between 95 and 103 kJ mol⁻¹, in good agreement with relevant literature on vanillin-based polyimine vitrimers.^{41,42}

The activation energy is also influenced by the stoichiometry between amine and aldehyde groups (**Figure 4c**). As stated above, this observation is likely related to a change in the exchange mechanisms: the excess of amine favors a transamination mechanism between free amines and imine bonds, whereas the excess of aldehyde favors the imine metathesis exchange reaction.

Overall, these results show that the crosslink density of the vitrimer network has a very strong influence on the relaxation properties, which can be decoupled from the influence of the free chemical functions in the networks. It is thus an important parameter to consider while designing or comparing vitrimer materials, which until recently had been underestimated in vitrimer research.²⁵

Figure 4. (a) Relaxation times at 45 °C of the different vitrimers. (b) Activation energies depending on the crosslink density. (c) Activation energies depending on the amine to aldehyde ratio.

Detailed examination of the stress relaxation curves of the vitrimers measured at 25 °C show the appearance of a double relaxation mode. A relaxation of 6 to 21 % of the initial stress is observed within the first two seconds, followed by a slower relaxation process (**Figures 5a**). However, relaxation times τ^* were not affected by the double relaxation mode and follow the Arrhenius law.

This phenomenon disappeared at higher temperatures (**Figures S11 to S18**), suggesting that it arises from weak interactions that are easily broken as the temperature is raised. Stukenbroeker et al.³⁰ observed similar behavior in vinylogous urethane vitrimers and suggested that the fast relaxation was due to polar interactions in the material. In our case, we noticed that the intensity of the stress relaxation during the first 2 s seemed to depend on the weight fraction of FDC in the materials (**Figure 5b**), suggesting that some weak interactions between furan rings, such as π -stacking, could be responsible for the fast relaxation. This hypothesis would require further investigations, albeit the correlation on this particular point with Stukenbroeker et al.³⁰ seems to evidence a secondary relaxation phenomenon within these types of systems.

Figure 5. (a) Stress relaxation of vitrimers at 25 °C. (b) Stress relaxation after 2 s depending on the weight fraction of furan dialdehyde (FDC) in the vitrimers.

Creep recovery experiments were then used to evaluate the elastomeric material properties of vitrimers at different temperatures (**Figures S21 – S28**). The vitrimers were designed to carefully study the influence of the crosslink density, not to minimize creep, and they thus show relatively poor creep resistance, even at temperatures close to ambient. At higher temperatures, the exchange reactions allow the network to quickly rearrange its topology, leading to large deformations. After the release of the stress, a permanent deformation was observed (**Figure 6**). Logically, the crosslink density also impacts the creep behavior. As shown above, a decrease in crosslink density eases the exchange reactions, and has thus the tendency to increase the creep deformation. An excess of amine, which facilitates the exchange reaction, also lead to a strong increase in creep deformation (**Figure 6c**).

Figure 6. Creep recovery plots at 45 °C of vitrimers depending on (a) the triamine to diamine ratio, (b) the diamine molar mass and (c) the amine to aldehyde ratio.

These results evidence a contradiction in vitrimer material design: it is generally positive to reduce the relaxation time to improve processability and recyclability, but it also leads to a higher creep deformation, which can be a severe drawback for industrial applications.⁶³ Interestingly, the plots of the permanent creep deformation as a function of the relaxation time measured by stress relaxation show that the relaxation time can be reduced by a 5-fold factor without causing a significant increase in creep (**Figure 7**). This means that careful choice of network crosslink density can be a powerful tool to control the relaxation properties without compromising the material stability.

Figure 7. Permanent creep deformation of vitrimers depending on their relaxation time at 45 °C.

Similar plots at other temperatures are given in the supporting information (Figure S29).

Mechanical properties

Uniaxial tensile tests were then performed to study the influence of the network structure on the mechanical properties of the materials. Representative stress-strain curves are given in the supporting information (**Figures S30 to S32**). Results show that the mechanical properties are mostly influenced by the network crosslink density, as expected for polymer networks. An increase in the crosslink density globally causes an increase in Young modulus and stress at break, while it reduces the elongation at break (Figure 8). This confirms that at ambient temperature and with a short time scale of observation, vitrimer networks behave just as permanent crosslinked networks, following the same structure to mechanical properties relationships.

Figure 8. Influence of the networks crosslink density on the mechanical properties: (a) Young modulus, (b) stress at break and (c) elongation at break.

Swelling and solubility

Swelling and solubility of the different vitrimers have been tested in three organic solvents (THF, DMF and ethanol), neutral water and acid or basic solutions (1M HCl and 1M NaOH). Results are given in Table 4. All vitrimers showed good stability in neutral and basic solutions due to their crosslinked structures, however they were completely dissolved in acidic solution due to the acid-catalyzed hydrolysis of imine bonds.

In THF and DMF, there is a global trend towards a lower swelling when the crosslink density is increased (**Figure S33**), as expected in crosslinked materials.⁶⁴ As the crosslink density increases, the diffusion of the solvent in the vitrimer network becomes more difficult. The swelling ratios are relatively high, in agreement with previous reports showing that dynamic networks swell more than

permanent ones, because of exchange reactions that can occur during swelling tests.^{25,65} The differences in terms of swelling ratios between THF and DMF can then be related to the differences in exchange rate of imine bonds in these solvents. Vitrimer **2**, designed with a low crosslink density, was fully dissolved in DMF and THF.

Surprisingly, all the vitrimers except **5** were completely dissolved in ethanol, despite their crosslinked structures. In a recent study, Nicolaÿ and co-workers discussed the difference in swelling behavior and solubility between static and dynamic networks.²⁵ They mentioned the hypothesis that the solubility test might not be a sufficient proof, in certain cases, to show a vitrimeric behavior. Several parameters could control the solubility of vitrimers, without a necessary decrease of the overall network connectivity.^{25,65,66} These parameters can be (i) the crosslink density, (ii) the concentration of exchangeable bonds, (iii) the exchange rate of these dynamic bonds, (iv) the observation time and (v) the solvent quality. ¹H NMR spectra of the soluble fractions in ethanol still show the presence of imine linkages (**Figure S34**), and the absence of aldehyde or amine chain ends, indicating that the solubilization of the sample is not caused by a complete depolymerization. This rather suggests a reorganization of the system into soluble structures, such as linear, cyclic, or branched polymers, as suggested in the literature.^{25,66} The selective solubility of the polyimine networks requires further investigation on their solution behavior, but also opens interesting possibilities for chemical recycling, whilst still offering robustness against aggressive conditions such as highly basic solutions.

Table 4. Results of swelling experiments

Varying parameter		THF		DMF		EtOH		H ₂ O		HCl 1M	NaOH 1M		
		ν (mol L ⁻¹)	Swel. (%)	Sol. (%)	Swel. (%)	Sol. (%)	Swel. (%)	Sol. (%)	Swel. (%)	Sol. (%)	Swel. (%)	Sol. (%)	
T:D ratio													
2	0.33	1.09	-	100	-	100	-	100	26	0	100	9	1.7
3	0.67	1.72	659	21	342	15	-	100	17	3.2	100	9	2.1
4	1.00	2.01	336	8.9	213	6.2	-	100	12	3.9	100	9	0.0
5	2.00	2.48	317	5.4	149	9.2	433	50.4	42	1.1	100	8	1.1
Diamine molar mass													
1	230	2.13	783	20.1	255	9.2	-	100	21	2.7	100	8	1.5
4	400	2.01	336	8.9	213	6.2	-	100	12	3.9	100	9	0.0
6	2000	0.73	1003	25.0	448	23.8	-	100	4	2.2	100	3	0.0
NH ₂ : CHO ratio													
7	0.95	1.35	656	28.0	268	12.5	-	100	13	2.1	100	10	3.3
4	1	2.01	336	8.9	213	6.2	-	100	12	3.9	100	9	0.0
8	1.05	1.77	151	28.0	71	12.5	-	100	16	4.4	100	11	2.9

Reprocessability

The three materials presenting the highest crosslink density, and thus the highest mechanical properties, have been selected to test the reprocessability of the developed polyimine vitrimers (**1**, **4** and **5**). After each recycling step, consisting in cutting the samples into small pieces (< 2 mm) and pressing at 120 °C for 1 hour (**Figure S35**), the samples mechanical properties were evaluated (**Figure S36 to S38**).

Figure 9. Tensile properties of vitrimers **1**, **4**, and **5** after up to 5 recycling cycles: (a) Young modulus, (b) stress at break and (c) elongation at break.

Young moduli of these three vitrimers increase after each recycling step, except the last recycling step for **5** (**Figure 9a**). In particular, the Young modulus of **1** and **4** increased by 91 and 38 % after 5 recycling steps, respectively. Stress at break of **4** and **5** remained almost constant on average, whereas a gradual increase is observed for **1** from 0.72 to 2.07 MPa (**Figure 9b**). Elongation at break, which

had a similar initial value of around 30% for all three vitrimers, increased to reach 51% after 5 reprocess for **1** but decreased slightly for **4** and **5** to 17 and 25 %, respectively, after 4 recycling steps (**Figure 9c**). Overall, the two main trends that can be seen are the increase in mechanical properties of **1** (and to a smaller extend **4**) with increasing recycling steps, and the significant decrease observed during the last recycling step for **5**.

The increase in mechanical properties observed for **1** and **4** could be the result of an increase in the vitrimer crosslink density, caused by the multiple processing cycles, which raises the stiffness. This was confirmed by DMA measurement on **4**, which shows a slight increase in crosslink density after 5 recycling steps (**Figure S39**). Following these results, we tried to perform an additional curing step on the vitrimers after the first processing. This additional step, however, did not lead to a significant increase in crosslink density. Our hypothesis is that a global reprocessing step could help to achieve a network structure with enhanced crosslinking. The drop in mechanical properties of **5** after the 5th reprocessing could be due to an insufficient healing step, caused by a limited chain mobility (**5** displays the highest crosslink density), leading to an insufficient fusion of all pieces together, as already observed with other systems.⁴⁷ A more extensive study on these points related to reprocess of our polyimine vitrimer system would thus be required to gain a more accurate understanding.

Conclusion

In this work, a family of biobased polyimine vitrimers was synthesized using di- and trifunctional polyetheramines in combination with a furan-based dialdehyde. Upon variation of the triamine to diamine ratio and the diamine molar mass, networks with similar chemical structures but different crosslink densities were obtained. Thanks to the use of imine linkages, vitrimers could be prepared without introducing an excess of chemical functions, unlike for instance transesterification vitrimers. The study of their viscoelastic properties allowed us to gain important insights into the influence of the network structure on the relaxation properties of this family of vitrimers, which is suspected to have general implications for the field of vitrimer research. The crosslink density was found to have a drastic influence on the relaxation time, which can decrease by a 20-fold factor when the crosslink density is reduced. This point is highly relevant, since the control of the relaxation time of vitrimers is key to facilitate their recycling or processing by common industrial techniques such as extrusion. The activation energy was also found to be correlated in a similar manner to the crosslink density, albeit to a lesser extent. This study also revealed that weak interactions, such as π -stacking, can also influence the relaxation modes of vitrimer materials, requiring however deeper investigations. Overall, this polyimine vitrimer family was found to have high thermal stability, tunable mechanical properties and interesting reprocessability. To the best of our knowledge, this is the first extensive study undertaken on the influence of crosslink density in vitrimer materials, pointing out that the relaxation properties can be controlled by only tuning the physical properties of the networks. This physical control has also been put into perspective with chemical control, such as the introduction of an excess of reactive functions, which can only be used to tune the relaxation properties to a certain extent. The influence of the crosslink density has been so far underestimated and should therefore be considered as another valuable tool to control the relaxation properties of vitrimer materials, in concomitance with chemical control.

Experimental section

Materials

Different polyetheramines (Jeffamine® D series and T series) were provided by Huntsman (US). Their main characteristics are given in **Table 1**. 2,5-furandicarbaldehyde (*FDC*) was prepared by the oxidation of 5-hydroxymethylfurfural (HMF), as previously reported.⁴³ Briefly, HMF was oxidized by Dess-Martin Periodinane (1.2 equiv) in dichloromethane (CH₂Cl₂) at room temperature overnight. After purification and drying of the organic phase, the solvent was evaporated on a rotary evaporator and FDC was obtained as a yellowish powder (82% yield). ¹H NMR (CDCl₃, 400 MHz, δ): 9.85 (s, 2H, CHO), 7.33 (s, 2H, CH). IR (ATR): ν = 3127, 3102, 1665 cm⁻¹.

Tetrahydrofuran (THF, analytical reagent grade, 99.8%) and dimethylformamide (DMF, synthesis grade) were purchased from Fisher Scientific. Absolute ethanol (> 99.5%) was purchased from VWR. All chemicals were used as received without further purification.

Synthesis of vitrimer materials

The diamine, triamine and FDC were dissolved in THF, and the mixture was heated for 4 h at 40 °C. The mixture was then poured into a Teflon mold and the solvent was evaporated under a fume hood for 3 h followed by vacuum drying at 40 °C overnight. The casted films were then cured for one hour at 120 °C in a hot press, yielding the materials as dark red opaque elastomeric-like films.

Characterizations

Fourier Transformed Infrared (FTIR) spectra were collected on a ThermoScientific Nicolet iS10 spectrometer with a diamond ATR probe at room temperature. 32 scans were accumulated at a resolution of 4 cm⁻¹.

NMR spectra were recorded on a Bruker 400 MHz spectrometer at 25 °C. The samples were dissolved in CDCl₃ and 16 scans were collected.

Thermogravimetric Analyses (TGA) were performed under air flow (flow rate 25 mL min⁻¹) using a Q5000 IR apparatus from TA instruments. Samples (1 – 3 mg) were heated from 30 °C to 600 °C at a heating rate of 10 °C min⁻¹. In addition, isothermal analysis was performed at 120 °C during 2 h.

Differential Scanning Calorimetry (DSC) was conducted under nitrogen flow (flow rate 50 mL min⁻¹) using a Q200 apparatus from TA instruments. First, the sample was heated up to 150 °C at a heating

rate of $10\text{ }^{\circ}\text{C min}^{-1}$ and was kept 2 min at this temperature. Then, it was cooled down to $-70\text{ }^{\circ}\text{C}$ at a cooling rate of $5\text{ }^{\circ}\text{C min}^{-1}$ and was kept 2 min at this temperature. Finally, the sample was heated up to $150\text{ }^{\circ}\text{C}$ with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$. Glass transition temperature T_g was measured as the change in slope during the second heating run.

Rheological tests were performed on a Discovery HR-3 apparatus from TA instruments. The experiments were performed in parallel plate geometry using 25 mm sample disks. For stress relaxation experiments, a normal force of 1 N in compression mode and a strain of 2 % were applied to the material. The relaxation modulus $G(t)$ was followed over time at a constant temperature. The series of stress relaxation experiments were performed successively on the same sample. For creep experiments, a stress of 2000 Pa was applied using an axial force of 5 N for 1000 s before a 1000 s recovery period. The resulting strain was followed over time at a constant temperature.

Dynamic mechanical analyses (DMA) were carried out in torsion mode on a Discovery HR-3 apparatus from TA instruments using rectangular samples (16 mm x 5 mm x 1 mm). Measurements were taken from -60 to $40\text{ }^{\circ}\text{C}$ with a heating rate of $3\text{ }^{\circ}\text{C min}^{-1}$. The axial force was adjusted constantly to $1 \pm 0.5\text{ N}$. Strain was controlled at 0.05 % and oscillating frequency at 1 Hz. Storage and loss modulus, G' and G'' , were collected as a function of temperature. Relaxation temperature T_{α} was taken at the maximum of $\tan \delta = G''/G'$. The rubbery plateau was used to calculate the crosslink density at $40\text{ }^{\circ}\text{C}$ using **Equation 1**.⁵⁹

Uniaxial tensile tests were also performed on a Discovery HR-3 apparatus from TA instruments. The dog bone-shaped samples had an effective length of 14 mm, a width of 4.5 mm and a thickness of about 1 mm. The tensile measurements were performed using a preload of 0.05 N and pulling speed of $50\text{ }\mu\text{m s}^{-1}$ until sample failure. Reported values (elongation (%), stress at break (MPa), and Young Modulus (MPa)) are averages of at least four experiments with their corresponding standard deviations. The plotted tensile curves were selected to be representative of the average values.

Reprocessability was performed by cutting the samples into small pieces ($< 2\text{ mm}$) which were placed into the dog bone-shaped mold used for tensile test and pressed at $120\text{ }^{\circ}\text{C}$ for 1 h. Samples were reprocessed five times between which tensile tests were performed.

Solubility and hydrolytic stability experiments were carried out with about 200 mg of samples immersed for 24 h at room temperature in 5 mL of DMF, THF, ethanol, distilled water, 1 M HCl solution or 1 M NaOH solution. The solvent was then removed and the samples were dried under vacuum for 24 h at 50 °C. The soluble fraction and swelling ratio were calculated according to **Equation 2** and **3**, respectively.

$$\text{Soluble fraction (\%)} = 100 (w_i - w_d) / w_i \quad (2)$$

$$\text{Swelling ratio (\%)} = 100 (w_s - w_i) / w_i \quad (3)$$

where w_i , w_d , and w_s are the initial, dry, and swollen mass respectively.

Authors information notes

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Associated content

Supporting information presenting all additional figures and tables mentioned in the manuscript is available.

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