

## Manuscript Details

<b>Manuscript number</b>	REACT_2020_168_R1
<b>Title</b>	Recyclable poly(thiourethane) vitrimers with high Tg. Influence of the isocyanate structure
<b>Article type</b>	Research Paper

### Abstract

Networked poly(thiourethane) materials with Tgs around 130 °C, derived from two aliphatic isocyanates (isophorone diisocyanate, IPDI and 4,4'-methylene bis(cyclohexyl isocyanate), HMDI) and one aromatic diisocyanate (toluene-2,4-diisocyanate, TDI) have been prepared with the same trithiol as comonomer (trimethylol propane tris(3-mercaptopropionate), S3) in stoichiometric proportions in the presence of dibutyltin dilaurate (DBTDL) as the catalyst. The higher reactivity of TDI allowed the preparation of this material in absence of catalyst. The evolution of the curing process has been followed by FTIR. Thermomechanical studies have been performed to determine their viscoelastic properties and their vitrimeric behaviour. The materials were able to reach a complete relaxation stress state thanks to the exchange process of the thiourethane moiety. Among them, TDI derived material experimented the fastest relaxation. The materials were also characterized by thermogravimetry and tensile tests. The recycled materials obtained by grinding the original thermosets and hot-pressing the powder have been fully characterized by mechanical, thermomechanical and FTIR studies, which allowed to confirm their recyclability without appreciable changes in the network structure. The presence of DBTDL in the materials has been proved to be necessary to reach a good recyclability.

<b>Keywords</b>	Vitrimers; poly(thiourethane); thermosets; recyclability; covalent adaptable networks.
<b>Taxonomy</b>	High Performance Polymer, Crosslinked
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<b>Opposed reviewers</b>	Christopher Bowman, John Torkelson

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## **Research Data Related to this Submission**

There are no linked research data sets for this submission. The following reason is given:  
Data will be made available on request



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Prof. Dinu

Tarragona, March 12<sup>th</sup> 2020

Dear Prof. M. Valentina Dinu:

I submit our revised manuscript entitled "Recyclable poly(thiourethane) vitrimers with high  $T_g$ . Influence of the isocyanate structure" to be taken in consideration for acceptance in Reactive and Functional Polymers together with the answer to the reviewer comments.

Thank you very much for the quick response and the great level of the reviewers that commented on our paper. I hope we have solved all the issues they found in our manuscript

Looking forward to your reply, I send my regards.

Prof. Angels Serra

## **Reviewer 1**

The manuscript analyzes properties of poly(thiourethane) vitrimers prepared with both aliphatic and aromatic diisocyanates cured with a stoichiometric amount of a commercial trithiol, using DBTDL as catalyst. In a previous paper of the same team (Ref. 30), a single poly(thiourethane) vitrimer was studied in detail. The influence of the diisocyanate structure and catalyst amount on mechanical properties, stress relaxation and recyclability of the vitrimers is clearly described in the present study. The selected poly(thiourethane) vitrimers exhibit glass transition temperatures in the range of 120 – 130 °C. This makes these results of interest because there are few previous reports describing vitrimers with these relatively high values of glass transitions temperatures. I recommend publication of this manuscript with a minor revision to consider the following comments:

### **1. Introduction: p.2. It is stated that thermoplastics can be molten.**

*Thank you very much for your comment. We agree with the reviewer and we have added the following paragraph:*

“Thermoplastics depending on their structure are subdivided into semicrystalline and amorphous polymers. The firsts have a relatively sharp melting point after which they can flow. The others become soft after their glass transition and more fluid as additional heat is applied. These characteristics allow them to be easily processed and recycled, but they are relatively weak, and they can suffer degradation by heat, solvents and environmental attack.”

### **2. Introduction: p.2. Leibler and coworkers reported the malleability of both epoxy-carboxylic acid and epoxy-anhydride networks.**

*According to the reviewer’s comment, we have changed this sentence in the text.*

“With this approach, a “third” class of polymers, called vitrimers, has been discovered in 2011 by Leibler and co-workers, who reported the malleability of both epoxy-carboxylic acid and epoxy-anhydride networks.”

### **3. Experimental section 2.8: p.8. Indicate how viscosity was calculated at temperatures where the strain rate was not constant in the period following the elastic response of the material.**

*According to the reviewer’s suggestion, we have added the following paragraph in the experimental section:*

“The viscosity ?? (Pa·s) was obtained from the creep plots, considering the linear part of variation of the strain and fitting it with a linear regression. The strain rate  $\dot{\epsilon}$  was determined from the slope of the linear fit. The viscosity ?? was calculated using the following expression:

$$\eta = \frac{\sigma}{\dot{\epsilon}} \quad (3) \text{ and represented in front of } T_g/T$$

thus obtaining the Angell fragility plot”.

### **4. Experimental section 2.10: p.8-9. As described in few reports in the literature, the effectiveness of the recycling process depends on the size of the powder generated in the**

grinding process. Provide the mesh size (or a related value) of the powder obtained by grinding.

According to the reviewer's suggestion, we have calculated the mesh size of the powder. From the image below the distribution of the particle size could be calculated. The average size of the powder is 1.2 mm with a standard deviation of 0.6 mm and the maximum size is around 2.4 mm. The sizes are detailed in the text.

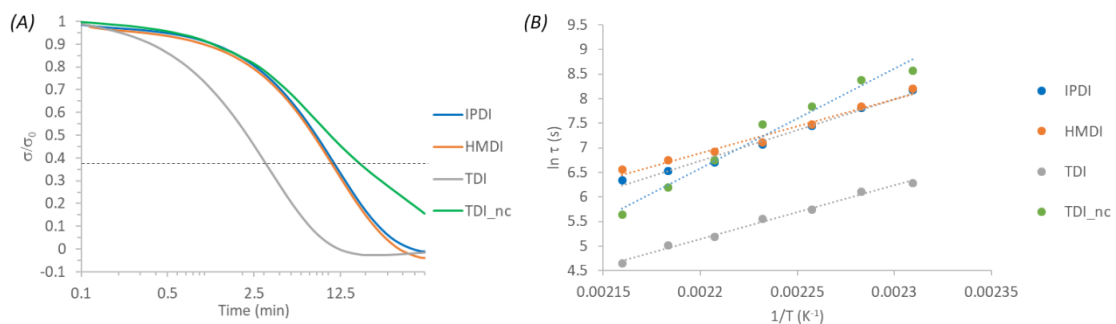


5. p.11: sentence before Table 2: Use upper case for all references.

Thank you very much for your observation, we have changed it in the manuscript.

6. Is there any explanation for the negative values of stress relaxation for the vitrimer prepared with TDI (and DBTDL), before reaching the zero value (as shown in Fig. 5A)?

We have changed Figure 5A, performing a new test with a sample completely free of defects, and this behaviour is now minimized.



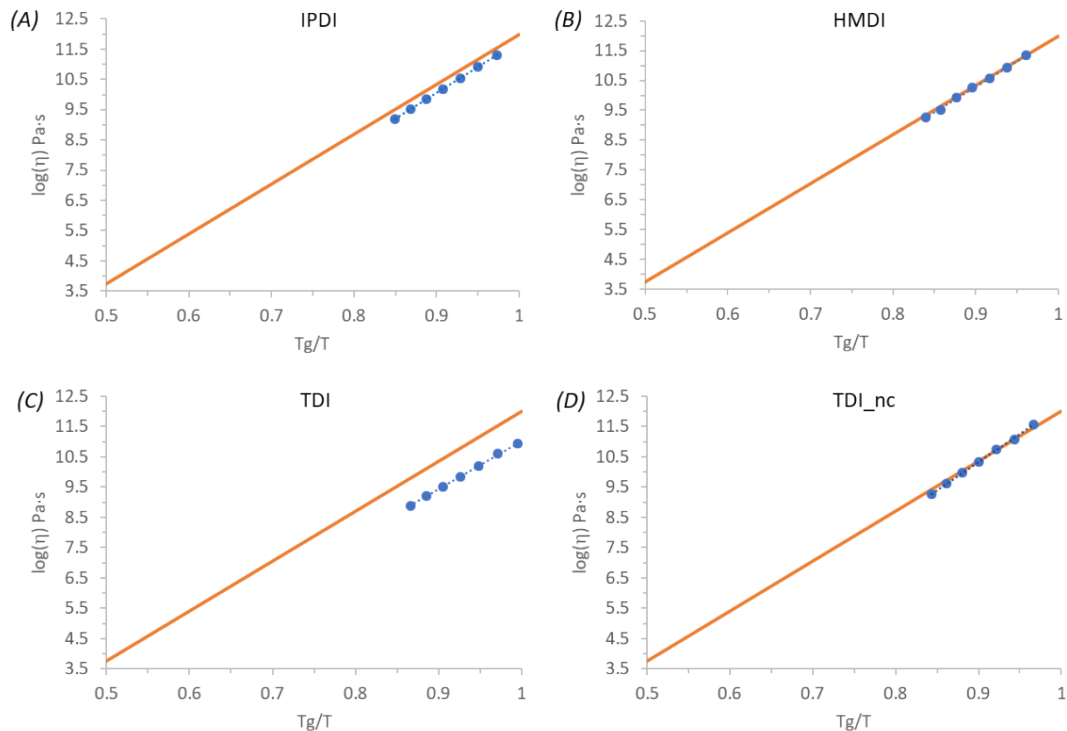
7. p.16: Activation energies for the viscosity arising from Angell plots should be calculated and compared with those obtained in relaxation tests.

According to the reviewer's comment, we have calculated the activation energies of the different materials prepared and added in Table 3.

Sample	Relaxation experiment				Creep experiment	
	$\tau_{1/e,180^\circ\text{C}}$ (min)	$T_v$ (°C)	$E_a$ (kJ/mol)	$r^2$	$E_a$ (kJ/mol)	$r^2$
IPDI	11.1	117±5	107±5	0.99	130± 7	1.00
HMDI	10.7	110±8	92±6	0.98	130± 4	0.99
TDI	2.9	88±4	91±3	0.99	115± 5	0.99
TDI_nc	18.4	137±7	186±14	0.98	144±9	0.99

The activation energies calculated from creep experiments (from Angell Fragility Plots) are slightly different from the ones calculated by relaxation experiments but follow the same trend. Therefore, the lowest  $E_a$  is obtained for TDI materials in the presence of catalyst and the higher one is in absence of DBTDL. The aliphatic PTUs show the same  $E_a$ , as expected.

New Angell Plots are represented in Figure 7 (with the corresponding correction needed for the calculation of activation energies).



**8. p.19:** The glassy modulus of thermosets does not depend on crosslink density (the explanation provided to explain the low value of the HMDI material). It depends on the cohesive energy density and the intensity of a beta-relaxation, if present.

According to the reviewer's observation, we have changed the paragraph:

*“The rigid structure of the isocyanates selected is reflected in the notable high moduli reached in all the samples, being the lowest value for the HDMI vitrimers thanks to its more flexible structure.”*

**9. p.21: Discussion related to Fig. S5: It is not evident that the shape of the FTIR spectrum for the uncatalyzed TDI sample has changed after recycling. The whole spectrum has lower intensity but there is no apparent change in the location and relative intensities of peaks (at least in a first visual inspection).**

*Thank you very much for your comment, we have changed the sentence:*

*“On the other hand, in absence of catalyst, only the intensity of the peaks of the FTIR spectrum of the recycled TDI-nc is changed”.*

-Reviewer 2

-Serra and coworkers report an interesting follow-up on their earlier work on thiourethanes as dynamic covalent bonds for the design of vitrimer networks that can be regarded as the sulfur-analogs of classical PU networks, that become malleable through rapid thiocarbamylation reactions (<https://doi.org/10.1016/j.eurpolymj.2019.109361>)

In this new report, a comparison of different materials is made that have been obtained by using different isocyanates. All materials have been properly analysed, and the results are presented in a logical fashion, which is very easy to read, and also quite informative and interesting. It seems this paper is thus a very good fit for the reactive&functional polymers journal

*We are grateful to your positive comments*

When preparing and revising their manuscript for final submission for publication, I only have two comments that the authors should take into consideration. The length of these comments does not reflect their severity, but is necessary to convey the level of detail needed to put them into context.

1. The conversion of NCO is monitored by IR and it seems to be leveling off somewhat below 100% conversion (figure 1). The manuscript states that a full conversion of isocyanates is achieved by a post-curing step at higher temperature. However, a full isocyanate conversion can still be interpreted in two ways: either they do indeed go on to react with the remaining thiols that were not affected during gelation at a lower temperature, or the NCO's are forced to make 'secondary' crosslinks to other reactive moieties, such as the thiourethane N-H, or with other isocyanates. This may not seem to be an overly important point, but these secondary cross-links would add some non-dynamic permanent cross-links, and would also result in a lot more free thiol-SH in the networks, compared to what is expected based on stoichiometry. Especially this 'excess' of free thiols may be of high importance for the exchange mechanism (see point 2). Some kind of experimental quantification or qualification of what happens during the post-curing step would thus be helpful and informative.

*Thank you very much for your excellent comments and suggestions. It is true that in the FTIR/ATR spectra taken to evaluate the formation of the different formulations at 130 °C we don't get a full conversion of the isocyanate band, but after post-curing the isocyanate band has disappeared completely. The spectra of the final materials are shown in the supporting information, where we can clearly see the absorptions of thiourethane and ester carbonyl groups coming from the thiol. To see if some other bands corresponding to unexpected groups such as*

*ureas, isocyanurates or thioallophanates are formed, we have recently performed structural studies during the curing process with the same isocyanates and a thiol without any carbonyl ester absorption with the aim to see clearly if these undesired groups are formed. The results we obtained is that when using DBTDL as the catalyst, only thiouretane absorptions appear, which accounts for a click character of this reaction in these conditions. However, with other Lewis acid catalysts some other carbonyl absorptions are formed, and in this case, the click characteristics are lost. We are studying the vitrimeric characteristics of these samples to see the effect of these unexpected groups in the relaxation behaviour. This work is still not finished. It is true that the thiol absorption is weak in the FTIR, and for this reason it is not conclusive, but we have not seen any remaining signal in its absorption region after curing.*

2. The discussion of the dynamic bond exchange mechanism deserves some closer attention. In their earlier report on these dynamic polythiourethane (PTU) networks, aliphatic PTUs were prepared from a 1:1 ratio of SH and NCO, using DBTDL as a catalyst for the gel formation. There, a 'safe' metathesis exchange reaction scheme is shown, without explicifying if the exchange happens through reversal to isocyanates and thiols, or through nucleophilic association of a free thiol, but the latter is implied (which would be required to have true 'associative' vitrimer-like bond exchanges). Here, at least in the graphical abstract, the same non-explicit scheme is shown, but the manuscript text is in several places more explicit on mechanistic aspects, which may be misguided and misleading, and requires some careful consideration, and in my opinion, some revision. Although not much experimental work on the reaction kinetics is reported that would allow to make a distinction between different types of exchange mechanisms, authors do spend quite a bit of discussion on mechanistic issues both in their previous as well as in their current report. I am not convinced by the argument that I will paraphrase as 'no free isocyanates can be detected in heated samples, so the mechanism through debonding to NCO is not happening'. Absence of proof is not proof of absence, and the dissociation is expected to be endothermic by a substantial amount. Shifting the equilibrium to the debonded state with a build-up of a significant concentration of free NCO is highly unlikely to happen below 200°C, but can be kinetically highly meaningful, and a dissociative process is perfectly reasonable at this temperature: the free isocyanate will react as quickly to a new bond as it is formed. A crucial point in this discussion, which is often overlooked, is that either mechanism (dissociative or associative) requires the presence of free thiols as 'acceptors' for the new TU-bonds. In an associative mechanism, thiols must first make a new bond to a TU moiety (tetrahedral carbon intermediate), and in a dissociative mechanism wherein the reactive intermediate has a very short life time (eg for an endothermic formation of NCO and SH), the debonding event will not result in an effective exchange, unless it is statistically likely that the debonded state encounters another reactive polymer chain segment. In the small molecule exchange 'model reactions', even if no free thiols are present at the start due to slight off-stoichiometry, some degree of free thiols will arise through dissociation to NCO and minor side reaction of this reactive moiety (eg allophanate-type quenching on the TU NHs), resulting in a small amount of reactive free thiols which may be hard to detect by standard analysis.

So, even though NCO cannot be detected in heated materials, its reversible formation may still be involved in the exchange process. Torkelson and coworkers looked more into the mechanistic issue in his recent paper (Macromolecules 2019, 52, 21, 8207-8216), using aromatic PTUs and DBU/PPh<sub>3</sub> as a catalyst. He nicely shows that if the ratio of SH to NCO is 1:1, a dissociative mechanism dominates. But even if you have a small excess of SH, this dissociative exchange is surpassed by a much faster associative mechanism. This is why my first point on possible free



thiols may be of interest. Furthermore, authors seem to hold the point in this paper that there are no free thiols and the exchange is happening through associative trans-thiocarbonylation, which are contradictory positions.

In all, to my opinion, the difference in exchange mechanisms are over-emphasized and over-simplified in the discussion presented by the authors in this paper, and conclusions are quite premature in the absence of a good mechanistic study to validate these points. Limiting the discussion on p14 to a simple difference in intrinsic reactivity between aromatic and aliphatics is misleading, and should not be done. On page 21, the strongly phrased sentence:

"our evidences lead us to conclude that a predominant associative exchange mechanism occurs in the presence of DBTDL at the range of temperatures tested." should be removed or rephrased to a more conditional tense: on page 14 the authors use 'could', but on page 21 a strong conclusion is forwarded without data to support it. This conclusion does not affect the overall conclusions and validity of the interesting reported results, but it should be revised nonetheless, taking into account the wider mechanistic perspectives I have tried to offer herein. Mechanistic discussion need to take into account at least also differences in thiol availability, as done in Torkelson's work.

In conclusion, I strongly recommend publication of this fine paper, if authors can 'soften' their mechanistic discussion a bit

*Thank you very much for your positive recommendation and we also thank you for your suggestions, discussions and the time you employed in your extremely accurate revision. The mechanism adopted in the structural rearrangement that occurs in the relaxation is of course a controversial point. Up to now only two mechanisms are proposed. One is the thermal breakage of thiourethane moieties to form isocyanates and thiol and the other is a typical nucleophilic substitution in the thiourethane groups by attack of thiols. In our first article on this topic, we tried to confirm if trans-thiocarbonylation occurred by using model compounds (without any excess of thiol groups) and since we confirmed this process, we get to the conclusion that the mechanism was different from the nucleophilic substitution promoted by thiols. We couldn't see any traces of free isocyanate and free thiol and therefore we arrive to the conclusion that the mechanism was not dissociative but associative, and the vitrimeric behaviour observed seemed to support this conclusion. In addition, by DSC we couldn't see any endotherm corresponding to the dissociative process, although the heat absorbed could be inappreciable and/or overlapped with the exotherm produced by the subsequent formation of thiouretanes. However, we agree that the absence of proofs is not a conclusive evidence and it is true that a dissociative mechanism with a quick recovering of the thiourethane moieties can occur. Thus, in our opinion, there is a third possibility, which is the occurrence of a concerted metathesis mechanism, catalysed by DBTDL. DBTDL increases the electrophilicity of thiourethane carbon that can be attacked by the sulphur of the thiourethane group. Although not reported before, this could be an alternative to the dissociative mechanism in a concerted manner. To reach the conclusion if this mechanism is concerted or the bonds break and after that they are quickly reformed is not easy. Therefore, the possibility of a concerted mechanism will be explored by DFT studies with help of some colleagues. In the article: Trans-Carbonylation Enabled Intrinsic Plasticity for Thermoset Shape Memory Polyurethane by Ning Zheng, Zizheng Fang, Weike Zou, Qian Zhao\*, Tao Xie they reach the conclusion that trans-carbonylation by OH attack was negligible, but they did not mention the possibility of urethane dissociation and thiouretanes (by TGA) seems to be more stable than urethanes are. It is true that at high temperatures both urethanes and thiouretanes dissociate, but it is not easy to confirm that at the relaxation temperatures this*

*process occurs. In fact, by FTIR we couldn't see any isocyanate absorption when reaching these temperatures, but it is true that just once dissociated the groups formed could react instantaneously and the absorption could be too weak to be appreciated. We have tested what happens in the presence of an excess of thiol and the relaxation is slower. In case of a nucleophilic substitution the relaxation rate should increase by adding more thiol or adding a more nucleophilic thiol (as an aromatic one), but this was not observed. The use of a strong base as catalyst, that in principle should increase the nucleophilicity of the thiol by forming thiolate does not produce any type of acceleration. Since we don't have any defined evidence of the mechanism, we preferred to add a non-explicit scheme in the graphical abstracts.*

*We have eliminated the paragraphs in pages 14 and 21, according to the reviewer's comments and we have also eliminated the rearrangement scheme from the graphical abstracts.*

## **Highlights**

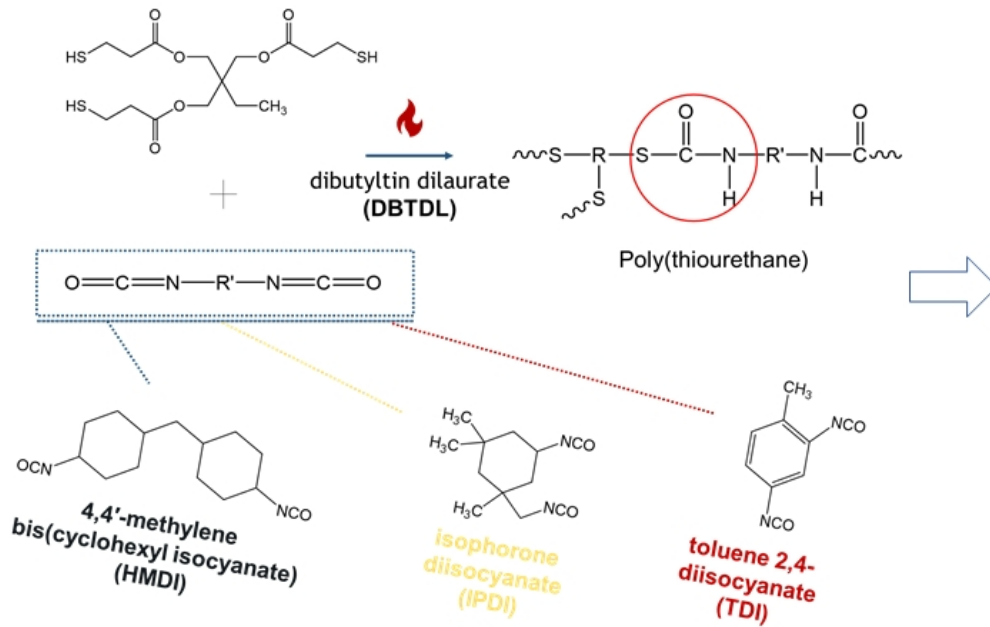
High Tg poly(thiourethane) vitrimeric materials have been studied

Vitrimeric characteristics have been demonstrated

Influence of isocyanate structure has been studied

Recycling potentiality has been demonstrated.

## Poly(thiourethane) formation

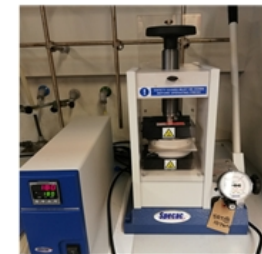


## Recycling of poly(thiourethane)

Original polymer



Grinded polymer



Heated under pressure



Recycled polymer



# RECYCLABLE POLY(THIOURETHANE) VITRIMERS WITH HIGH $T_g$ . INFLUENCE OF THE ISOCYANATE STRUCTURE

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## Abstracts

Networked poly(thiourethane) materials with  $T_g$ s around 130 °C, derived from two aliphatic isocyanates (isophorone diisocyanate, IPDI and 4,4'-methylene bis(cyclohexyl isocyanate), HMDI) and one aromatic diisocyanate (toluene-2,4-diisocyanate, TDI) have been prepared with the same trithiol as comonomer (trimethylol propane tris(3-mercaptopropionate), S3) in stoichiometric proportions in the presence of dibutyltin dilaurate (DBTDL) as the catalyst. The higher reactivity of TDI allowed the preparation of this material in absence of catalyst.

The evolution of the curing process has been followed by FTIR. Thermomechanical studies have been performed to determine their viscoelastic properties and their vitrimeric behaviour. The materials were able to reach a complete relaxation stress state thanks to the exchange process of the thiourethane moiety. Among them, TDI derived material experimented the fastest relaxation. The materials were also characterized by thermogravimetry and tensile tests.

The recycled materials obtained by grinding the original thermosets and hot-pressing the powder have been fully characterized by mechanical, thermomechanical and FTIR studies, which allowed to confirm their recyclability without appreciable changes in the network structure. The presence of DBTDL in the materials has been proved to be necessary to reach a good recyclability.

## Keywords

Vitrimers; poly(thiourethane); thermosets; recyclability; covalent adaptable networks.

## 1. Introduction

Traditionally, polymers are classified in two main types: thermoplastic and thermosets depending on their thermal behaviour. Thermoplastics depending on their structure are subdivided into semicrystalline and amorphous polymers. The firsts have a relatively sharp melting point after which they can flow. The others become soft after their glass transition and more fluid as additional heat is applied. These characteristics allow them to be easily processed and recycled, but they are relatively weak, and they can suffer degradation by heat, solvents and environmental attack. On the other hand, thermosetting polymers, thanks to their permanent covalent bonds in the network structure, show outstanding mechanical and thermal properties, allowing them to be widely used in industrial applications where high mechanical performances and dimensional stability are required. However, their permanent three-dimensional structure hinders reshaping, reprocessing, or recycling once they are cured, resulting in a serious environmental issue. For these reasons, they are considered among the most difficult materials to be recycled.<sup>1,2</sup>

With the aim to combine the advantages of both type of polymers, thermoplastics and thermosets, in the last decades many researchers have focused their attention on the field of dynamic polymers. They were designed by incorporating reversible covalent bonds into the polymeric network to obtain the so called CANs (covalent adaptable networks).<sup>3,4,5</sup> With this approach, a “third” class of polymers, called vitrimers, has been discovered in 2011 by Leibler and co-workers, who reported the malleability of both epoxy-carboxylic acid and epoxy-anhydride networks.<sup>6</sup> These materials can lead to topological rearrangement via transesterification, keeping constant their crosslinking density.<sup>7</sup>

To develop new CANs, different reversible exchange reactions have been explored, such as: transesterification,<sup>6,8</sup> transamination,<sup>9,10</sup> disulfide exchange,<sup>11,12</sup> transalkylation,<sup>13</sup> siloxane equilibrium,<sup>14</sup> dioxaborolane metathesis,<sup>15</sup> amine-urea exchange,<sup>16</sup> and transcarbamoylation.<sup>17,18</sup>

If we focus our attention on the family of vitrimers based on poly(urethane) structures, it should be mentioned that Tobolsky and co-workers in 1956<sup>19</sup> observed that poly(urethane)s could experiment chemical stress relaxation at high temperature. However, this article had not attracted much attention and the explanation of this behaviour was not completely clarified. Recently, carbamate exchange has been recognized as the responsible of the vitrimeric behaviour of poly(urethane) thermosets, and it constitutes one of the most used mechanism in the preparation of dynamic networks.<sup>20-24</sup> Poly(urethane)s, thanks to their structural versatility, have a broad range of applications in different industrial fields as elastomers, coatings, rigid foams and adhesives.<sup>25</sup>

Poly(thiourethane)s (PTUs) are related to their oxygen counterparts, showing comparative properties due to the presence of similar hydrogen bonding, but they possess several advantages. The formation of PTUs from isocyanates and thiols is described as a *click-type* reaction; therefore, it is not accompanied by side-reactions contrary to what occurs in the poly(urethane) synthesis.<sup>26,27</sup> Moreover, poly(thiourethane) thermosets show a high refractive index thanks to the presence of sulphur into the backbone of the polymeric structure, making them good candidates for optical applications.<sup>28,29</sup>

Recently, our research group<sup>30</sup> has demonstrated that PTUs derived from 1,6-hexamethylene diisocyanate (HDI) and trimethylolpropane tris(3-mercaptopropionate) (S3) can behave as vitrimers when stoichiometric ratios of thiol-isocyanate were reacted in the presence of a Lewis acid catalyst, such as dibutyltin dilaurate (DBTDL). The reversible thiocarbamate exchange has been demonstrated by means of equilibrating model compounds. Moreover, the influence of the proportion of catalyst in the vitrimeric characteristics of poly(thiourethane) thermosets has been demonstrated. Similarly, Torkelson and co-workers<sup>31</sup> reported that thiourethane linkages, formed from an aromatic diisocyanate monomer, follow associative and dissociative reversible pathways, depending if an excess or a stoichiometric amount of thiol has been added to the formulation. In both cases, they use the simultaneous presence of two different catalysts, triphenylphosphine and 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU) and the crosslinked materials have an elastomeric nature. By using model compounds and by means of TGA coupled with gas-chromatography and mass spectrometry they proved the dissociative character of exchange mechanism, but these aromatic poly(thiourethane) materials do not lead to significant changes when the material was reprocessed.

Although both articles focused on the reprocessable character of poly(thiourethane) networks, the relaxation rates were very different, about 8 min to reach a value of  $\sigma/\sigma_0 = 1/e$  at 180 °C in the case of our previous studies, and less than 10 s at 150 °C in the Torkelson's work. These differences could be related to the aromatic character of the isocyanate selected as the monomer, the lower crosslinking density they reached, due to the presence of the long poly(propylene oxide) structures in the isocyanate monomer, which leads to  $T_g$ s around -25 °C, and the differences in the catalysts and their proportions.

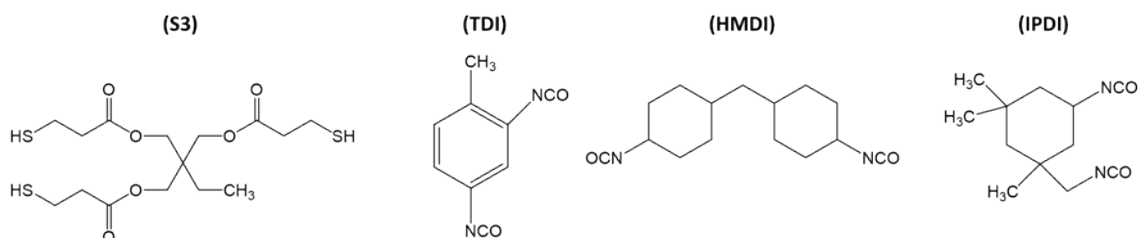
Despite the previous work reported on this topic, the nature of the stress relaxation and reprocessing of this class of materials remains quite unexplored. Herein, we investigate the potentiality of this class of dynamic polymers based on poly(thiourethane) networks, to obtain vitrimers with high glass transition temperatures ( $T_g$ ) and a fast exchange mechanism. This remains one of the most challenging goals in this field, since almost all the vitrimers reported in the literature show  $T_g$ s lower than 100 °C, which limits their applicability in some industrial fields, where high thermal and mechanical performance at elevated temperature is required. In the literature, we found only few reports on reprocessable thermosets with high  $T_g$ : a self-healable epoxy-anhydride thermoset based on renewable vanillin and guaiacol starting compounds with a  $T_g$  of 187 °C,<sup>32</sup> but with broad relaxation processes, a lignin-based vitrimer for recoverable adhesive with  $T_g$  in the range from 95 to 133 °C,<sup>33</sup> and a vitrimer based on silyl ether exchange reported by Guan et al. with a  $T_g$  of 125 °C.<sup>34</sup>

It should be taken into account, that the viscoelastic properties of vitrimers at high temperatures are firstly controlled by the velocity of the dynamic exchange mechanism responsible of the vitrimeric behaviour, which can be accelerated by increasing the amount of catalyst,<sup>8,30</sup> or by the presence of unreacted groups in non-stoichiometric systems. Secondly, the macroscopic flow can be influenced by the network architecture. The introduction of flexible structures seems to increase the rate of the exchange mechanism, leading in some cases to elastomeric characteristics.<sup>35</sup>

Encouraged by the results of our previous work, we selected three different diisocyanates with a rigid structure to prepare PTUs with high  $T_g$  and to explore the influence of the macromolecular architecture on their viscoelastic properties at high temperatures. Two of the diisocyanates selected are aliphatic: isophorone diisocyanate (IPDI) and 4,4'-methylene bis(cyclohexyl isocyanate) (HMDI) while toluene 2,4-diisocyanate (TDI) was selected as an aromatic one. We chose trimethylolpropane tris(3-



mercaptopropionate) (S3) as trifunctional thiol. The structure of these compounds is represented in Scheme 1. Thiol and isocyanate groups were reacted in stoichiometric proportions and a Lewis acid (dibutyltin dilaurate, DBTDL) was used as the catalyst. Taking advantage of the high reactivity of aromatic isocyanates, we prepared a PTU, derived from TDI, in absence of catalyst to study its possible vitrimeric behaviour.



**Scheme 1.** Structure of the starting compounds

## 2. Experimental part

### 2.1 Materials

Trimethylolpropane tris(3-mercaptopropionate) (S3), toluene 2,4-diisocyanate (TDI) and dibutyltin dilaurate (DBTDL) from Sigma-Aldrich were used as received. Isophorone diisocyanate (IPDI) and 4,4'-methylene bis(cyclohexyl isocyanate) (HMDI) from Acroos Organics were used without previous purification.

### 2.2. Preparation of the formulations

The different diisocyanates and S3 were mixed in stoichiometric proportions: 2 mol of S3 per 3 mol of the selected diisocyanate. The catalyst, DBTDL, was first dissolved in the isocyanate and the corresponding amount of thiol was then added. The formulations with aliphatic diisocyanates were prepared with 4 phr of DBTDL (parts of catalysts per hundred parts of thiol), while the formulations with TDI were prepared with 2 phr of DBTDL or without, due to the higher reactivity of the aromatic diisocyanate towards thiol. The mixtures were manually stirred until homogeneity at room temperature, and freshly used.

**Table 1.** Formulations used to prepare poly(thiourethane) thermosets

Sample	Formulation	Diisocyanate (g)	Thiol (g)	DBTDL (g)
IPDI	S3_IPDI_4%DBTDL	1.67	2.00	0.08
HMDI	S3_HMDI_4%DBTDL	1.97	2.00	0.08
TDI	S3_TDI_2%DBTDL	1.31	2.00	0.04
TDI_nc	S3_TDI_0%DBTDL	1.31	2.00	-

For a better understanding, the formulations detailed in Table 1 have been designed with an acronym that represents the isocyanate chosen in the preparation of the material. TDI\_nc accounts for the material prepared from TDI without any catalyst.

### 2.3. Sample preparation

For DMTA analysis, films were prepared by pouring the formulations on pre-silanized glasses and using Teflon spacers to ensure a homogeneous thickness of 0.5 mm. The formulations were cured at 80 °C, 100 °C, 125 °C for 1h at each temperature and 160 °C for 2 h. In the case of free catalyst formulation, a post curing at 175 °C for 2h was required. The films were die-cut to obtain a rectangular specimen of 20 x 5 x 0.5 mm<sup>3</sup> dimensions.

### 2.4. FTIR analysis

To monitor the evolution of isocyanate/thiol groups during the isothermal curing at 130 °C and to quantitatively determine the rate of curing, a FTIR spectrometer Bruker Vertex 70 with an attenuated total reflection accessory with thermal control and a diamond crystal (Golden Gate Heated Single Reflection Diamond ATR Specac-Teknokroma) and equipped with a mid-band liquid nitrogen-cooled mercury-cadmium-telluride (MCT) detector was used. Real-time spectra were collected in absorbance mode with a resolution of 4 cm<sup>-1</sup> in the wavelength range 4000 to 600 cm<sup>-1</sup> averaging 10 scans for each spectrum. The spectra were corrected for the wavelength dependence of the absorbance in ATR devices. The characteristic absorbance peak of the isocyanate at 2280 cm<sup>-1</sup> (vibration of -N=C=O groups) was used to monitor the conversion of the isocyanate group during thiol-isocyanate reaction. Absorbance of each scanned sample were

normalized with that of the S3-ester group at 1720  $\text{cm}^{-1}$ . Isocyanate group conversion ( $X_{NCO}$ ) were calculated by Eq. 1.

$$x_{NCO} = 1 - \frac{A_{2280}}{A_{2280,0}} \quad (1)$$

where  $A_{2280}$  and  $A_{2280,0}$  are the normalized absorbances of the isocyanate peak at 2280  $\text{cm}^{-1}$  at a given reaction time and at the beginning of the curing process.<sup>36</sup>

### 2.5. Dissolution experiments

Dissolution experiments of cross-linked polymers were performed by the following procedure. Pieces of poly(thiourethane) samples of 0.2-0.3 g, which were weighed before the experiment, were placed into a vial. The vial was filled with 1,2-dichlorobenzene, closed and heated at 150 °C for 24 h and then the vial was cooled down to room temperature. The polymer sample was washed by dichloromethane and the sample was then dried under reduced pressure at 80 °C overnight. After cooling down to room temperature, the sample was weighed, and the gel fraction was calculated.

### 2.6. Thermal degradation studies

The thermal stability of the cured samples was studied by thermogravimetric analysis (TGA), using a Mettler TGA/SDTA 851e thermobalance. All experiments were performed under inert atmosphere ( $\text{N}_2$  at 100 mL/min). Pieces of cured samples of 10-15 mg were degraded between 30 and 600 °C at a heating rate of 10 °C/min.

### 2.7. Stress relaxation tests

Tensile stress relaxation tests were conducted in a DMA Q800 analyser using a film tension clamp on samples with the same dimensions as previously defined. The sample was firstly equilibrated at 160 °C and left isothermally at this temperature for 3 min, then a constant strain of 1.5 % (to ensure the material is within the linear range) was applied on the sample and the consequent stress level was measured as function of time. Then the strain was removed, and the process was repeated every 5 °C until the final test temperature, 190 °C, is reached. The relaxation stress  $\sigma(t)$  was normalized by the initial stress  $\sigma_0$  and the relaxation times ( $\tau$ ) were determined as the time necessary to relax  $0.37 \cdot \sigma_0$  i.e. ( $\sigma = 1/e \cdot \sigma_0$ ). With the relaxation times obtained at each temperature, the

activation energy values  $E_a$  were calculated for each vitrimer, using an Arrhenius-type equation:

$$\ln(\tau) = \frac{E_a}{RT} - \ln A \quad (2)$$

where,  $\tau$  is the time needed to attain a given stress relaxation value ( $0.37\sigma_0$ ),  $A$  is a pre-exponential factor and  $R$  is the gas constant. From the Arrhenius relation, the temperature of topology freezing ( $T_v$ ) was obtained as the temperature at which the material reaches a viscosity of  $10^{12}$  Pa·s. Using Maxwell's relation and  $E'$  determined from DMTA (assuming  $E'$  being relatively invariant in the rubbery state),  $\tau^*$  was determined to be around  $10^5$  s in our systems. The Arrhenius relationship was then extrapolated to the corresponding value of  $\tau^*$  to determine  $T_v$  in each sample.

To compare the time to reach the complete relaxation of the stress (i.e. a normalized stress less than  $10^{-2}$ ) of the poly(thiourethane) vitrimers obtained with different diisocyanates, a single stress relaxation test was performed at the temperature of  $180$  °C with the same constant strain of  $1.5$  %.

## 2.8. Creep experiments

Creep and recovery properties were studied in tension by the same DMA Q800 apparatus equipped with the film tension clamp. All the samples were stretched under a stress of  $0.1$  MPa at  $180$  °C for  $30$  min, then the stress was immediately released, and the sample was left to recover for  $30$  min.

For the determination of the viscosity at each temperature needed for the representation of the Angell fragility plot, a series of creep experiments were carried out on films at temperatures between  $130$  and  $180$  °C, increasing  $10$  °C in each scan. To perform the tests, the selected temperature was equilibrated for  $3$  min and then a stress level of  $0.1$  MPa was applied for  $30$  min. The viscosity  $\eta$  (Pa·s) was obtained from the creep plots, considering the linear part of variation of the strain and fitting it with a linear regression. The strain rate  $\dot{\epsilon}$  was determined from the slope of the linear fit. The viscosity ?? was calculated using the following expression:

$$\eta = \frac{\sigma}{\dot{\epsilon}} \quad (3) \text{ and represented in front of } T_g/T$$

thus obtaining the Angell fragility plot.

## 2.9. *Dilatometry tests*

Dilatometry experiments in tension were performed with the film tension clamp in the DMA Q800 analyzer on the different PTU samples with the same dimensions as described before. The length of the sample was continuously measured while increasing the temperature at a heating rate of 1 °C/min from 25 to 250 °C. A slight stress of 0.01 MPa was applied during the experiment to avoid buckling.

## 2.10. *Recycling*

Original and recycled samples were tested until break in tensile mode at room temperature using an electromechanical universal testing machine (Shimadzu AGS-X) with a 1000 N load cell at 5 mm/min and using Type V samples according to ASTM D638–14 standard. Three samples of each material were analyzed and the results were averaged.

The recycled samples were obtained by grinding the crosslinked polymers, and hot pressing into an aluminium mould at 165°C for 2.5 h with 8 MPa. **In order to analyse the average size of the powder obtained, a micrograph was taken with an optical microscope. The image taken was processed and analysed obtaining the average value and the maximum size of the particles.** The new film obtained were die-cut in Type V samples and were tested under the same conditions.

# 3. **Results and discussion**

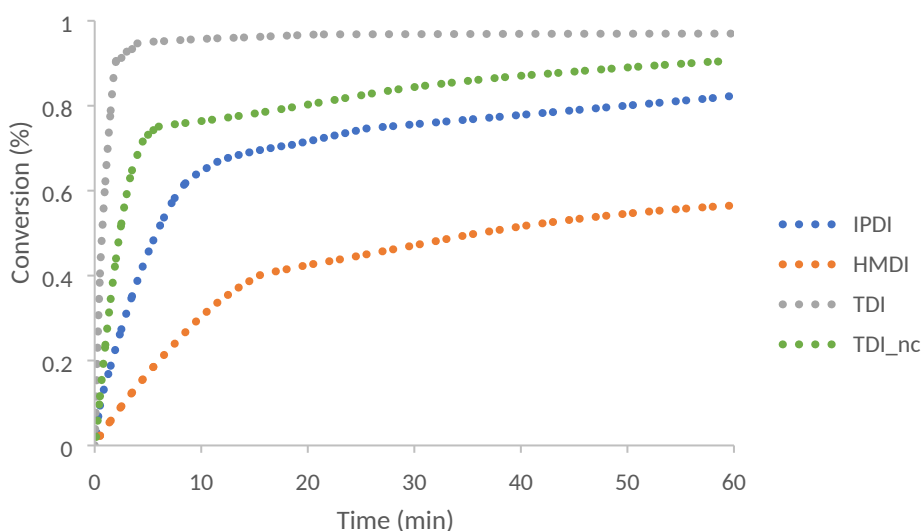
## 3.1 *Study of the curing process*

Although the preparation of poly(thiourethane) thermosets can be accomplished with the help of basic and acid catalyst, their vitrimeric characteristics are enhanced by the presence of a Lewis acid. In our previous papers,<sup>26,30</sup> we determined that small amounts of DBTDL as the catalyst (0.5-1 phr) were enough to reach fully crosslinked poly(thiourethane) networks. However, the amount of catalyst had a great influence in the rate of the relaxation process when studying their vitrimeric behaviour. Thus, 4 phr of DBTDL were added in the preparation of the vitrimer obtained from HDI and S3 to shorten the relaxation time. According to that, we selected this proportion of DBTDL for preparing the samples with the aliphatic isocyanates selected, but the high reactivity of the aromatic diisocyanate forced us to reduce the amount of catalyst to 2 phr. Since this

compound was highly reactive, we also prepared samples with S3, without any catalyst, reaching a fully cured material.

The evolution of the thiol-isocyanate reaction during the curing process was followed by FT-IR spectroscopy to investigate the kinetics of the reaction and how the different isocyanate monomers could influence the rate and curing schedule. In the spectrum, the reduction of the isocyanate peak, at  $2280\text{ cm}^{-1}$ , was accompanied by the appearance of N-H st. ( $3350\text{ cm}^{-1}$ ) and carbonyl st. ( $1670\text{ cm}^{-1}$ ) of the thiourethane groups, which are indicative of the poly(thiourethane) formation. The carbonyl absorption of the thiourethane groups is partially overlapped with the carbonyl ester absorption of the thiol, taken as the reference band, and the deconvolution has been done in order to extract quantitative information.

The isothermal curing temperature in the FTIR/ATR experiments for kinetics evaluation was set at  $130\text{ }^{\circ}\text{C}$  and the evolution of the curing process was followed by the diminution of the isocyanate band. Figure 1 shows the conversion curves against time for all the formulation studied. As we can see in the figure, all the reactions proceed quickly during the first minutes and then they slow down. However, it is evident that the aromatic isocyanate, TDI, leads to the fastest reaction, even without catalyst. Among the aliphatic diisocyanates, the reactivity of IPDI is higher than HMDI. Since a plateau is reached at long reaction times, higher temperatures must be used in order to reach full cure. Therefore, to cure the samples for mechanical and thermal characterization we performed a post-curing at  $160\text{ }^{\circ}\text{C}$  for 2 h and proved the full conversion by FTIR (see Fig S1, in supporting information).



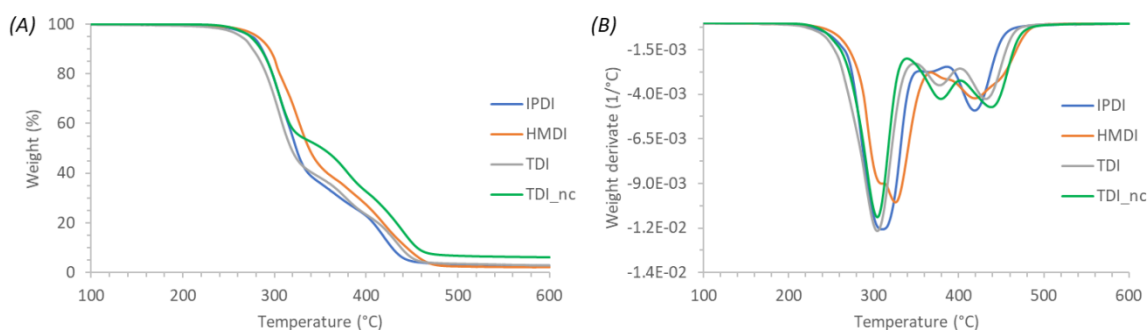
**Figure 1.** Kinetic profile at 130 °C of the conversion of NCO group in the different poly(thiourethane) formulations obtained from FTIR analysis.

### 3.2. Characterization of the thermosets

To prove the thermosetting character of the poly(thiourethane)s prepared we determined the gel content of all the samples in 1,2-dichlorobenzene, for 24 h at 150 °C which are collected in Table 2. Once, the solvent was completely removed the gel content was higher than 95% in all the materials tested, verifying their thermosetting nature.

The thermal stability of the PTUs was analysed by TGA and the weight loss and the derivative curves are shown in Figure 2. The data extracted from these experiments are collected in Table 2.

As we can see in Figure 2A, there are not many differences among all the materials evaluated, neither in the stability nor in the degradation processes. The degradation mechanism is quite complex, with three different stages although partially overlapped. The reversion of the urethane to isocyanate in poly(urethane)s (PUs) between 120-250 °C is described in the literature.<sup>37,38</sup> Thus, we can deduce that in PTUs this reversion could also occur. However, in Figure 2B the first degradation process leading to weight loss begins at 220 °C, with a maximum degradation rate above 300 °C. This indicates a higher thermal stability of PTUs in front of PUs. The peaks at higher temperatures can be attributed to the  $\beta$ -elimination processes of the esters present in the network structure.



**Figure 2.** (A) TGA curves and (B) DTG curves of the different poly(thiourethane)s prepared.

In Table 2, we can see that the temperature for the 2% of weight loss is around 260 °C for the PTUs based on aliphatic monomers. When the isocyanate is TDI, this temperature

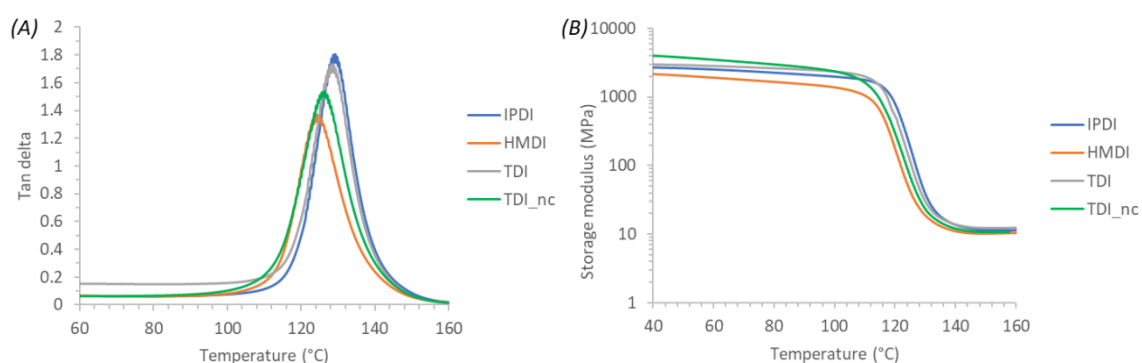
is slightly lower ( $T_{2\%}=243$  °C), indicating that the aromatic PTUs are less stable at high temperatures than the aliphatic ones. However, the material prepared from TDI without any catalyst begins to degrade at higher temperature, indicating that the first degradation process is catalysed by DBTDL. The thermoset that shows the highest stability is the one obtained from HMDI isocyanate. The lower temperature of initial degradation in aromatic poly(thiourethane)s in comparison with the aliphatic ones could be related to a partial dissociative character of the aromatic, as it has been previously reported.<sup>2130-31</sup>

**Table 2.** Gel content, thermal stability and thermomechanical data of the thermosets prepared

Sample	Gel content (%)	$T_{(2\%)}^a$ (°C)	$T_{max}^b$ (°C)	$T_{tan\delta}^c$ (°C)	FWHM <sup>d</sup> (°C)	$E^e$ (MPa)
IPDI	97	255	310/379/419	129	12.6	11.5
HMDI	95	262	325/367/419	124	13.6	10.7
TDI	99	243	304/378/431	128	13.0	13.9
TDI_nc	98	258	304/379/438	126	14.4	11.0

- Temperature of the 2% of weight loss
- Temperature of the maximum rate of the three-step degradation
- Temperature of the maximum of the  $\tan \delta$  peak.
- Full width at half maximum of the  $\tan \delta$  peak.
- Relaxed modulus determined at the temperature of the maximum of  $\tan \delta$  peak + 30 °C

In order to investigate the thermomechanical behaviour of all the materials prepared from the three diisocyanates selected, a DMTA analysis has been conducted. Fig. 3A and 3B show the evolution of  $\tan \delta$  and storage modulus with temperature. The main data extracted from these curves are collected in Table 2.



**Figure 3.** (A)  $\tan \delta$  and (B) storage modulus evolution with temperature for the different materials prepared.

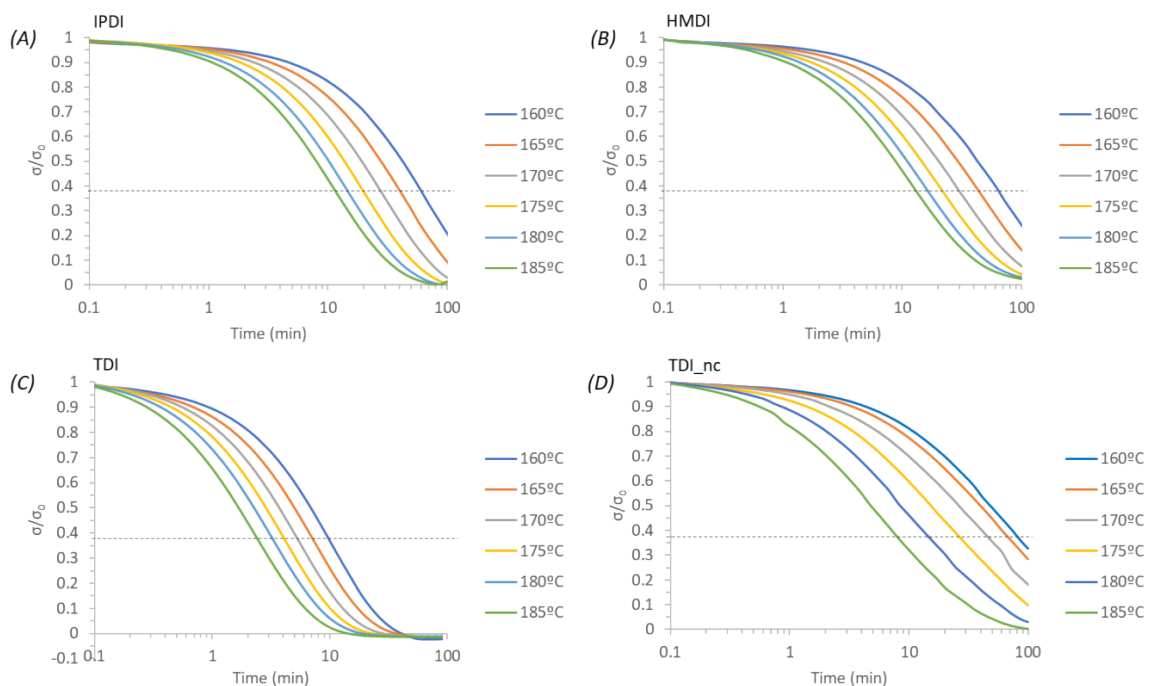


All the curves of the materials prepared show a  $\tan \delta$  peak higher than 120 °C, without many differences among them. The  $\tan \delta$  curves are quite narrow indicating the formation of uniform network structures (see Table 2) with a FWHM around 13 °C, thanks to the click reaction mechanism. The relaxation of the materials takes place sharply with a significant change in the moduli from the glass to the rubbery state. There are no significant differences in the relaxed moduli, but the thermoset prepared from TDI in the presence of catalyst leads to the highest value meaning that the use of DBTDL as the catalyst in TDI formulations seems to increase slightly the degree of crosslinking achieved.

### 3.3. Vitrimeric characterization

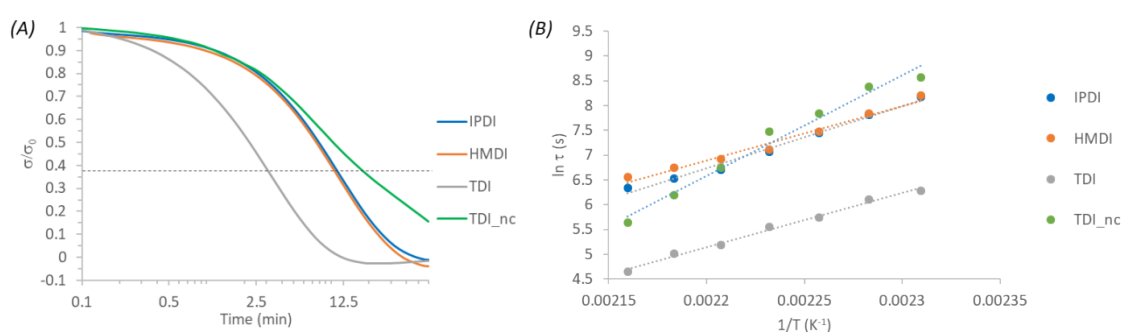
The viscoelastic properties at elevated temperatures were determined by stress relaxation experiments in DMTA to investigate the influence of the structure of the isocyanate in the different PTUs prepared.<sup>30</sup> At the selected temperatures, a constant strain of 1.5 % was applied on the samples and the stress was followed as function of time and the characteristic relaxation times ( $\tau_{1/e}$ ) were determined as the point when a relaxation value of 1/e ( $\sigma/\sigma_0=0.37$ ) was reached.

The stress relaxation curves of the different PTUs are presented in Figure 4, where we can see that all the materials can completely relax the stress at high temperature, showing the expected vitrimeric characteristics.



**Figure 4.** Normalized stress relaxation plots as a function of time at various temperatures from (160 to 185 °C) during 100 min for the different poly(thiourethane) samples. The value of  $\sigma/\sigma_0 = 0.37$  is highlighted.

For comparative purposes, the stress relaxation curves at 180 °C of the different PTUs are presented in Figure 5A and the characteristic relaxation times ( $\tau_{1/e,180^\circ\text{C}}$ ) are collected in Table 3.



**Figure 5.** Normalized stress relaxation behaviour at 180 °C (A). Arrhenius plot of relaxation times against the inverse of temperature measured by stress-relaxation experiments for the PTUs prepared (B)

As we can see in Figure 5A, the relaxation process of the aromatic poly(thiourethane) prepared with DBTDL as the catalyst is the fastest one, reaching the 63 % of stress relaxation in only 2.9 min. On the other hand, the TDI sample without DBTDL needs 18.4 min to reach the same relaxation level under the same conditions. This means that although DBTDL is not required to reach a complete curing it affects considerably the rate of rearrangement of the groups responsible of the network relaxation. In a previous paper<sup>30</sup> we demonstrated that trans-thiocarbamoylation can occur in this type of materials, allowing the network to relax and opening the possibility of reshaping. In that work, it was put in evidence that the amount of catalyst affects considerably the relaxation rate. Taking all these results into account, we can state that the trans-thiocarbamoylation reaction is the limiting step of the relaxation process. It can also be observed in Figure 5A that there is no difference in the relaxation rate between aliphatic PTUs.

As shown in Figure 4, there is a clear dependence of the relaxation time on the temperature for all the PTUs prepared, fitting perfectly with an Arrhenius-like relaxation behaviour (see Figure 5B). By the Arrhenius equation, the activation energy ( $E_a$ ) of the exchange mechanism and the topology freezing transition temperature,  $T_v$  (the

temperature at which the material reaches a viscosity of  $10^{12}$  Pa·s, i.e.  $\tau \approx 10^5$  s) could be determined and the values are collected in Table 3. It should be noted, in Figure 5B, the different behaviour of the TDI material without catalyst in reference to the others. This material relax faster than the aliphatic PTUs at high temperature, but slower at low temperature. Again, this could be related to the differences in the exchange mechanism in the sample without catalyst that can experiment variations in the associative/dissociative competitive mechanisms at different temperatures. Nevertheless, the fastest material in the relaxation process is the aromatic PTU in all the temperature range, even with 2 phr of DBTDL, less proportion than in aliphatic PTUs.

**Table 3.** Time to reach a value of  $\sigma/\sigma_0=0.37$  at 180 °C, topology freezing temperature, kinetic and adjusting parameters for the Arrhenius equation.

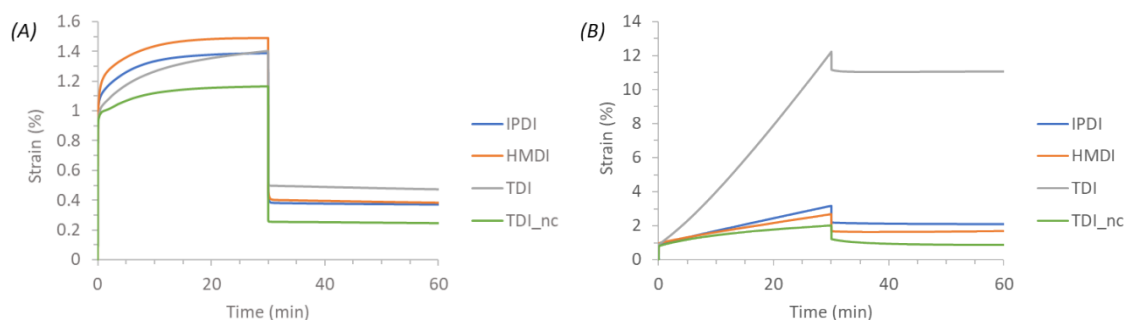
Sample	Relaxation experiment				Creep experiment	
	$\tau_{1/e,180^\circ C}$ (min)	$T_v$ (°C)	$E_a$ (kJ/mol)	$r^2$	$E_a$ (kJ/mol)	$r^2$
IPDI	11.1	117±5	107±5	0.99	130± 7	1.00
HMDI	10.7	110±8	92±6	0.98	130± 4	0.99
TDI	2.9	88±4	91±3	0.99	115± 5	0.99
TDI <sub>nc</sub>	18.4	137±7	186±14	0.98	144±9	0.99

The aliphatic structures rend values of  $E_a$  in the range of 92 to 107 kJ/mol, slightly higher than those determined for hexamethylene diisocyanate derived materials (which was 72 kJ/mol).<sup>30</sup> The role of the catalyst in the rearrangement process is evidenced by the value of the activation energy, reducing it from 186 to 91 kJ/mol in TDI derived materials. The former activation energy is in agreement with the value of 183.7 kJ/mol reported by Xie et al.<sup>39</sup> who prepared a catalyst-free polyurethane thermoset based on an aromatic diisocyanate (4,4'-methylene bis(phenyl isocyanate)).

It should be mentioned that the materials obtained in this work (except that prepared without catalyst) present a hypothetical  $T_v$  lower than  $T_g$  (from DMTA characterization) although at temperatures below  $T_g$  no segmental movement occurs to allow the exchange reaction. By heating above the  $T_g$  of the materials, the segmental movement starts gradually while the exchange reactions are already fast, and the exchange reaction becomes the dominating factor for the stress relaxation.<sup>9,34,40</sup> For this reason, the materials

prepared, especially the aromatic poly(thiourethane) with catalyst, have a very fast relaxation process.

To further analyze the viscoelastic properties of the PTUs and to confirm that the PTUs behave like a viscoelastic liquid at elevated temperatures, the effect of the temperature on the creep behaviour was studied. Figure 6 shows the creep behaviour for all the samples at 130 °C (temperature around  $T_{\tan\delta}$ ) and at 180 °C (temperature around  $T_{\tan\delta} + 50$  °C to assure a high mobility).

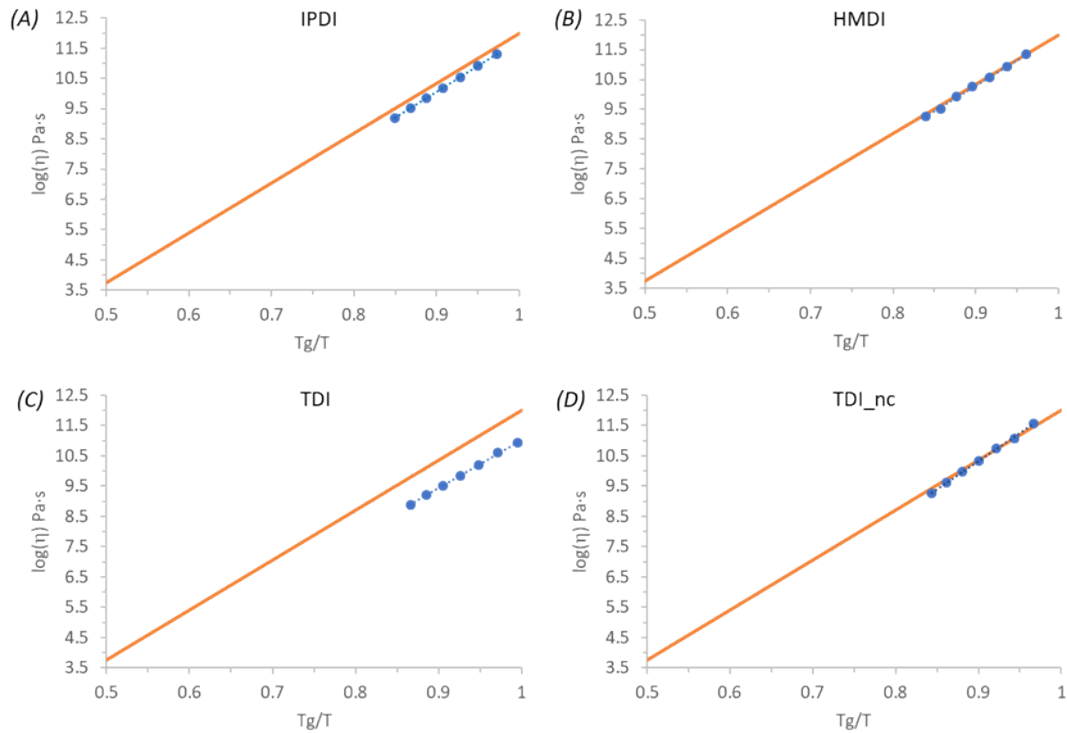


**Figure 6.** Creep recovery curves at 130 °C (A) and 180 °C (B) for all the PTUs prepared

Thermosets generally exhibit good resistance to creep thanks to their permanent network structure, presenting a constant deformation in time when a constant external stress is applied, and no plastic deformation appears when the stress is released. Contrarily, our materials, when tested at 130 °C with a constant stress, increase the deformation progressively, presenting a slight plastic deformation when the stress returns to zero. This increase in deformation with time (deformation rate) is higher at higher temperature (180 °C) confirming that the PTU vitrimers behave like a viscoelastic liquid. At this temperature, the materials recover only their initial elastic response and a permanent deformation remains due to the topological rearrangement of the network structure. The material prepared from TDI in the presence of DBTDL shows a very high deformation rate at 180 °C and, consequently, a very high plastic deformation, confirming the outstanding vitrimeric characteristics of this material.

From the creep experiments, the viscosities at different temperatures can be deduced for each sample and represented in the Angell fragility plot. In this plot (Figure 7) the variation of the viscosity with the inverse of temperature, scaled to  $T_g$ , is presented for all the materials. At temperatures higher than their  $T_g$ , all of them behave as “strong glass formers” like inorganic silica materials. The exchange reactions follow an Arrhenius law,

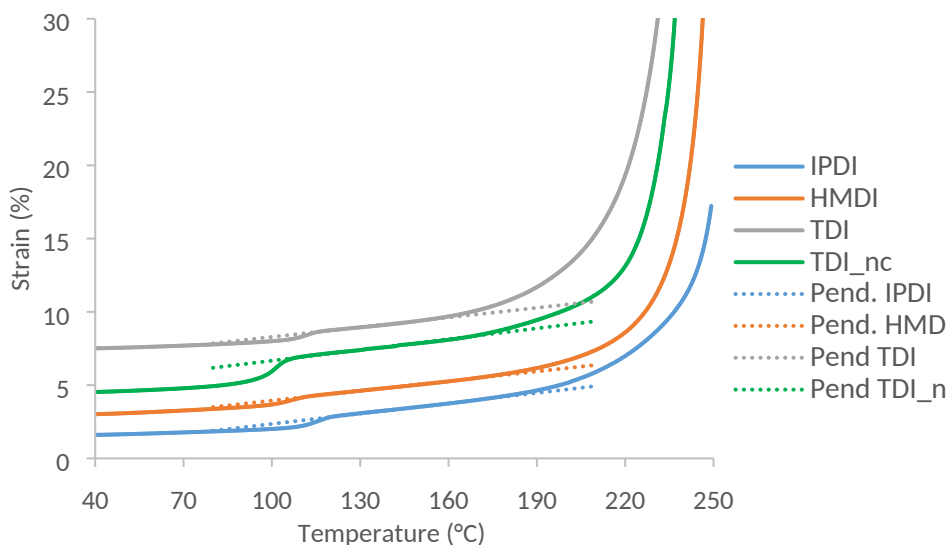
in contrast to the behaviour of thermoplastic materials, which are “fragile liquids”. From these plots it is possible to obtain the activation energy for all the materials tested (results are presented in Table 3). As it can be seen, the activation energies are slightly different from those obtained from relaxation tests but follow the same trend: the lowest  $E_a$  is



obtained for TDI materials in the presence of catalyst and the highest is in absence of DBTDL. The aliphatic PTUs show the same  $E_a$ , as expected.

**Figure 7.** Angell fragility plot representing the logarithm of the viscosity as a function of the inverse temperature, scaled to  $T_g$  (assuming  $T_g$  as  $T_{lam\delta}$ ), for the different materials. The relation for silica is included as a reference of an ideal strong liquid.

Network relaxation was also analysed by dilatometry experiments and the behaviour for all the samples is collected in Figure 8. Classical thermosets exhibit a lower thermal expansion coefficient (CTE) in reference to the non-crosslinked polymers and above their  $T_g$  the CTE remains constant for a permanently crosslinked network, In Figure 8 two changes in the slope of CTE can be appreciated, a first one at  $T=T_g$ , after which the slope remains constant, as observed in thermosetting polymers. The second change occurs when the exchange reactions start, leading to a significant increase in CTE, typical of the vitrimeric behaviour.



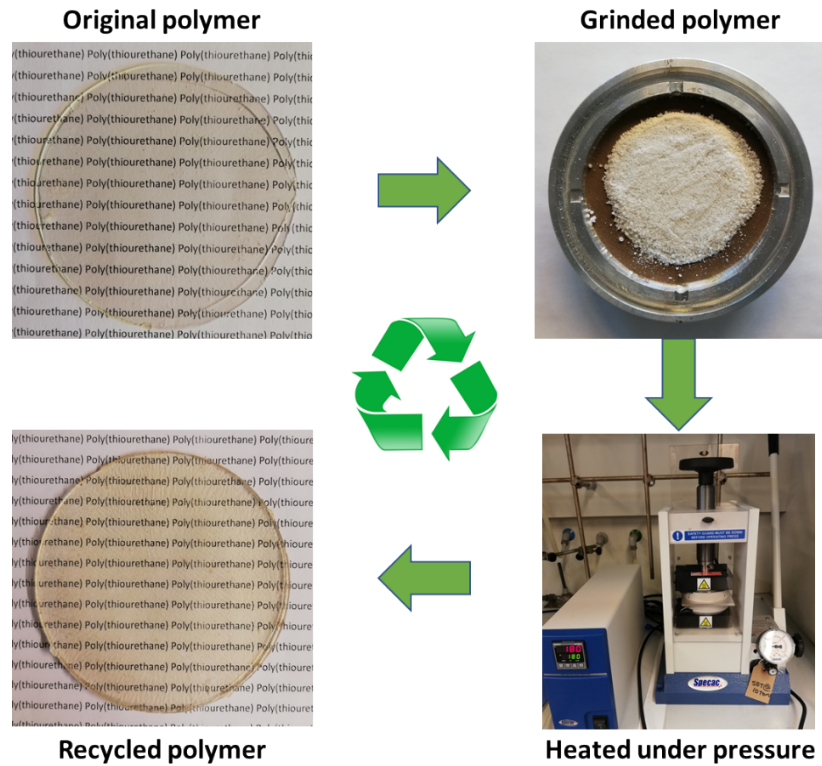
**Figure 8.** Dilatometry experiments performed with a heating rate of 1 °C/min for the different materials (the curves are shifted only for a better understanding).

### 3.4. Recyclability

To investigate the recyclability of the crosslinked PTUs prepared, the materials were grinded into small particles and the powder obtained was hot pressed at 165 °C for 2.5 h to obtain the recycled films. **In order to determine the average size of the powder obtained, a micrograph was taken with an optical microscope and the particle size measured. The average size measured was 1.2 mm with a standard deviation of 0.6 mm and the maximum size was 2.4 mm.**

As we can see in Figure 9, the original materials show good transparency and an excellent uniformity, properties that are quite well preserved with only a slight colour change after recycling.

To fully characterize the original and the recycled samples, they were subjected to uniaxial tensile test until break, DMTA and FTIR analysis. Dog-bone-shaped samples (Figure S2) of all the original and recycled poly(thiourethane)s were tested with a universal tensile machine. The stress-strain behaviour of the virgin materials were registered and compared with the recycled ones.



**Figure 9.** Photographs of the original, grinded and recycled sample, together with the hot press device used in the reprocessing.

**Table 4.** Tensile data of the original and recycled PTUs and DMTA data of the reprocessed materials. For comparison purposes, the DMTA data of original materials in Table 2 have also been included. The mean value of three different samples tested is shown. Coefficients of variations are less than 7 % for stress and strain results and less than 5 % for the tensile moduli.

Original						
Sample	$E^a$ (GPa)	$\sigma_{max}^b$ (MPa)	$\epsilon_{max}^c$ (%)	$T_{tan\delta}^d$ (°C)	FWHM <sup>e</sup> (°C)	$E'^f$ (MPa)
IPDI	5.1	154.8	4.4	129	12.6	11.5
HMDI	3.1	140.7	5.9	124	13.6	10.7
TDI	5.2	155.4	3.3	128	13.0	13.9
TDI_nc	4.8	126.5	3.2	126	14.4	11.0
Recycled						
Sample	$E^a$ (GPa)	$\sigma_{max}^b$ (MPa)	$\epsilon_{max}^c$ (%)	$T_{tan\delta}^d$ (°C)	FWHM <sup>e</sup> (°C)	$E'^f$ (MPa)
IPDI	3.4	92.1	4.5	127	13.6	10.7
HMDI	2.9	83.0	4.0	124	14.0	10.5
TDI	5.5	106.0	2.1	127	13.0	13.6
TDI_nc	3.8	82.8	2.5	120	23.4	10.8

a. Tensile modulus at room temperature.

b. Stress at break

c. Strain at break.

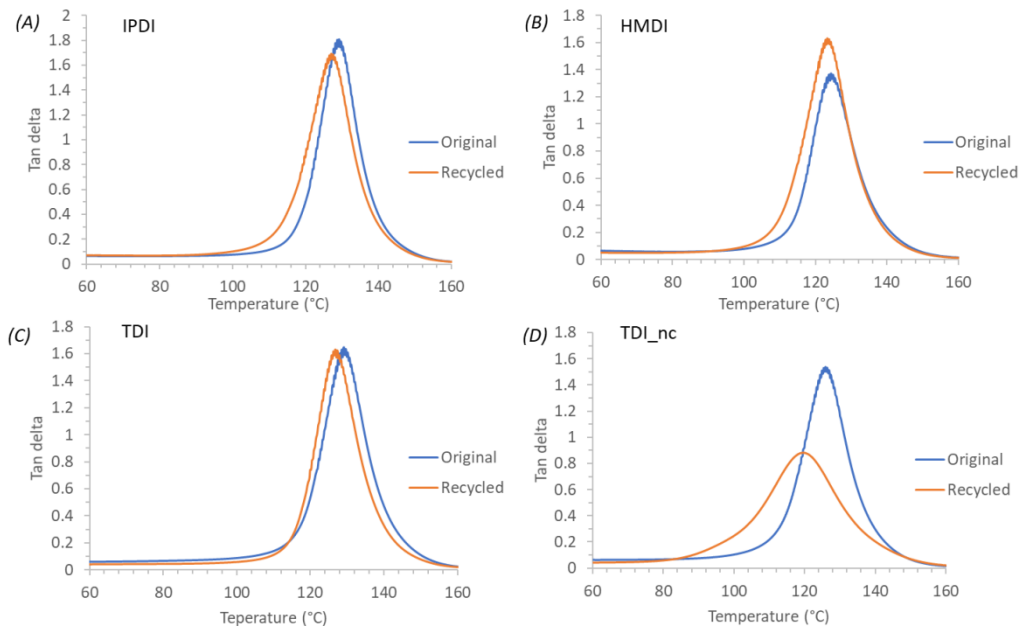
d. Temperature of the maximum of the  $\tan \delta$  peak.

e. Full width at half maximum of the  $\tan \delta$  peak.

f. Relaxed modulus determined at the temperature of the maximum of  $\tan \delta$  peak + 30 °C

Results from the tensile tests show that all the original materials are relatively rigid at room temperature and do not experiment high deformations before breaking due to their crosslinked character. **The rigid structure of the isocyanates selected is reflected in the notable high moduli reached in all the samples, being the lowest value for the HDMI vitrimers thanks to its more flexible structure.** With respect to the stress and strain at break values, the materials behave similarly, being again the HDMI the one that presents higher ductility. The TDI-nc is the one with lower strength, probably due to its network heterogeneity and slightly lower crosslinking density.

It can be appreciated in Table 4 that all materials behave mechanically quite well after the recycling process. The rigidities of the recycled samples remain similar while their strength is around 70% of the original value for the aromatic PTU with catalyst and 60% for the aliphatic ones. It is important to remark the extremely harsh conditions of the recycling process. The mechanical grinding can affect the integrity of all the bonds forming the network structure and not only those in thiourethane groups. The fact that the materials are not elastomers but thermosets with a high  $T_g$  and rigidity, also complicates the achievement of high quality samples.



**Figure 10.** Dependence of  $\tan \delta$  versus temperature of the different materials prepared before and after recycling.



To compare the thermomechanical behaviour of the original and recycled samples,  $\tan \delta$  curves extracted from DMTA analysis are presented in Figure 10 and the most typical data are collected in Table 4. In Figure 10, it can be appreciated that the thermomechanical behaviour of the aliphatic materials is almost similar in the original and the recycled samples, remaining the shape of  $\tan \delta$  curves unaltered with only a slight shift to lower temperatures within experimental error. The recycled materials derived from the aromatic TDI show a different behaviour depending on the presence or absence of catalyst. In TDI sample prepared with DBTDL the maximum of the  $\tan \delta$  peak remains practically unaltered, but the material TDI-nc shows a much broader peak and is shifted at lower temperatures, which indicates a loss of the homogeneity during recycling and changes in the network structure. From this result, it is again evident the important role of DBTDL as the catalyst in the vitrimeric behaviour. To ensure that the slight changes in the  $\tan \delta$  behaviour found in the materials are only due to the harsh conditions of the recycling process and not to a change in the crosslinking density, the storage moduli were determined and they are compared in Figure S3. In this figure, it can be observed that the glassy and rubbery moduli remain unaltered after recycling in all the samples, although some slight changes in the transition process can be observed. These differences can be due to the harsh recycling conditions previously mentioned, that has obviously slightly altered the network structure, but not the crosslinking density. To prove that the variations are only due to the recycling process, we have subjected an original TDI sample with catalyst to a series of two relaxation cycles and verifying that the peak of  $\tan \delta$  and the storage modulus remained constant, as can be seen in Figure S4. The DMTA analyses confirm that the material is fully reshapable.

To reveal the underlying mechanisms of network rearrangement and to know if changes in the chemical structure of the materials after recycling have occurred, the FTIR spectra of the original and recycled materials were recorded and compared (see Figure S5). The FTIR spectra of the PTUs prepared in the presence of DBTDL remain almost identical after the recycling process, showing any significant chemical degradation, which proves the recyclability of this class of materials in the presence of catalyst. On the other hand, in absence of catalyst, **only the intensity of the peaks of the FTIR spectrum of the recycled TDI-nc is changed.**

## **Conclusions**

In this work we have developed different reprocessable and recyclable poly(thiourethane) thermosets starting from commercially available aromatic and aliphatic diisocyanate monomers and a trithiol in the presence of DBTDL as the catalyst. The resulting materials show high homogeneity and transparency with glass transition temperatures around 130 °C. Although the reactivity of aromatic diisocyanates allows the preparation of aromatic PTUs without catalyst, the materials obtained are not fully recyclable.

The materials prepared can undergo topological rearrangement by exchange reactions allowing a complete stress relaxation and reorganization of the network, faster in the materials prepared from the aromatic isocyanate.

The catalyst plays an important role in the rearrangement process, evidenced by the shift in the value of activation energy of the exchange reaction, reducing it from 186 to 91 kJ/mol in TDI derived materials.

By performing mechanical, thermomechanical and FTIR analyses before and after the recycling process, it has been proved that the materials in the presence of catalyst kept their crosslinked network structure and their mechanical performance.

These characteristics confer these materials promising possibilities for practical and smart technological applications in different fields thanks to their high glass transition temperature and transparency, and good mechanical performance combined with the ability of being recyclable under harsh conditions.

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There are no conflicts to declare.

Francesco Gamardella, Experimental Part, edition and writing

Xavier Ramis, supervision and review

Silvia De la Flor, supervisión; validation

Angels Serra, supervision, writing; validation; conceptualization



## SUPPORTING INFORMATION

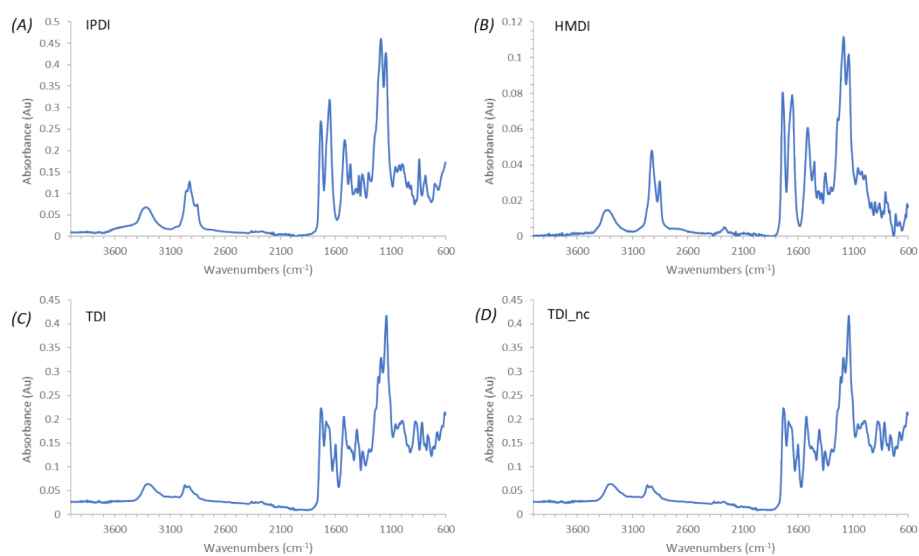
### RECYCLABLE POLY(THIOURETHANE) VITRIMERS WITH HIGH $T_g$ . INFLUENCE OF THE ISOCYANATE STRUCTURE

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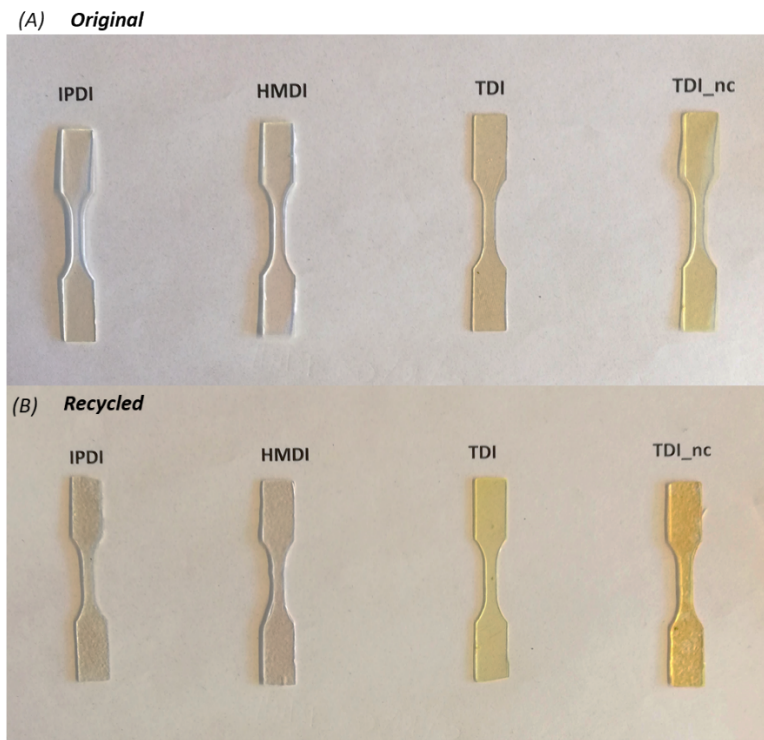
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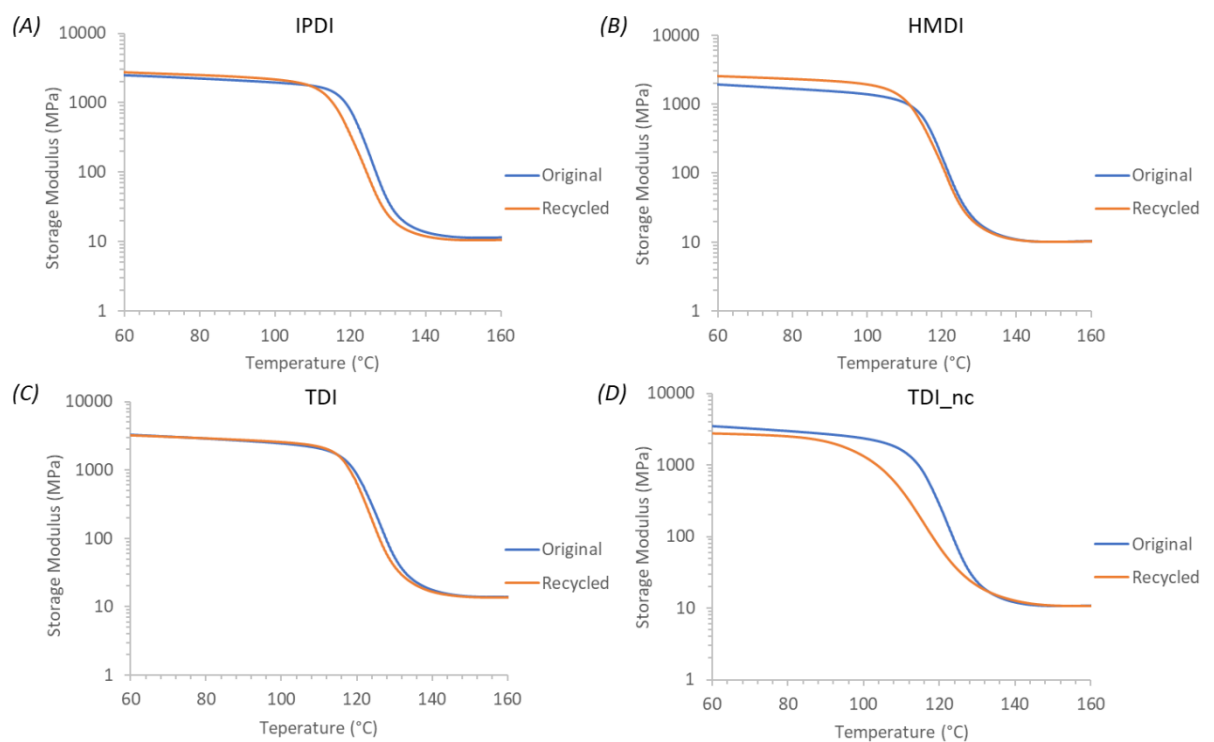
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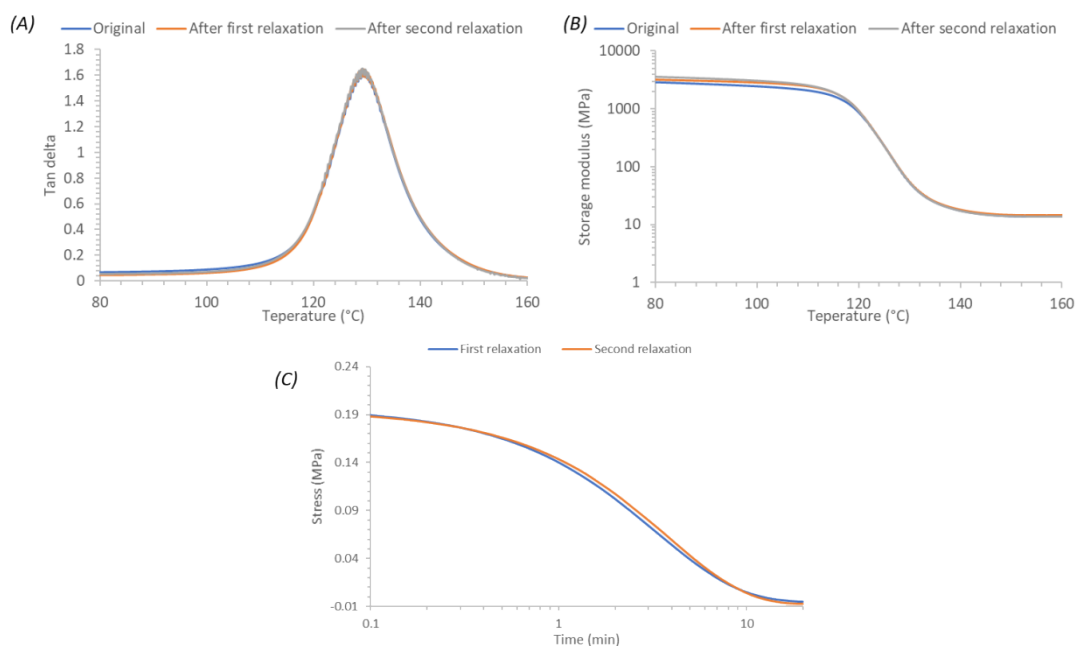
**Figure S1.** FTIR of cured poly(thiourethane)s registered at room temperature



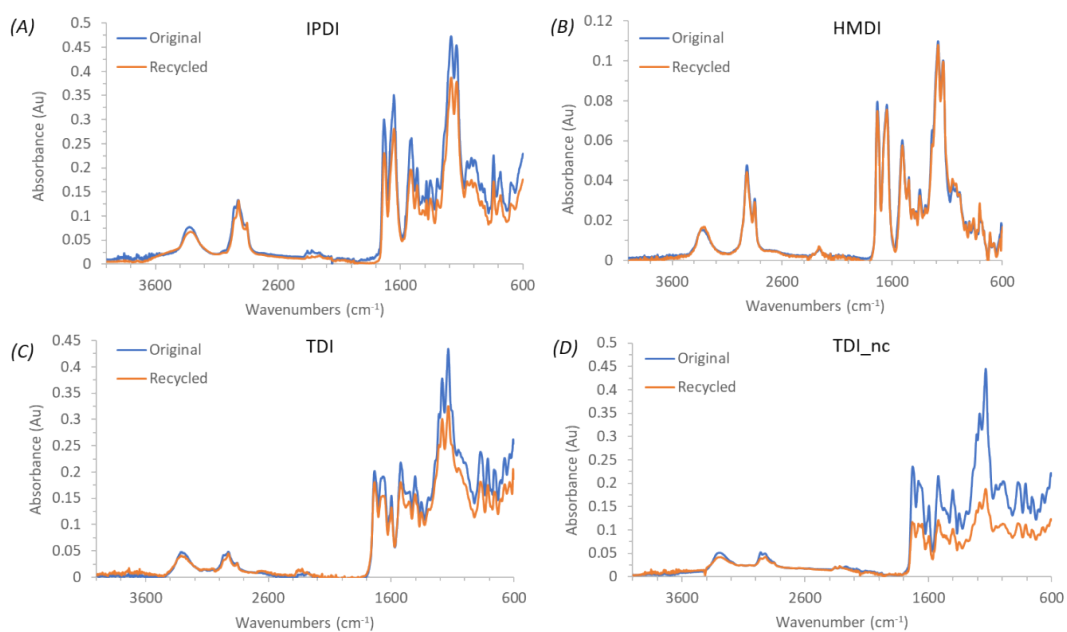
**Figure S2.** (A) Original and (B) recycled dog-bone PTU samples.



**Figure S3.** Storage modulus evolution with temperature of poly(thiourethane)s before and after recycling.



**Figure S4.** (A) Evolution of  $\tan \delta$  and (B) storage modulus against temperature of the TDI based PTU with a 2% of DBTDL sample before and after two relaxation processes at 180 °C. (C) Evolution of the two-stress relaxation process in front of time.



**Figure S5.** FTIR of poly(thiourethane)s before and after recycling registered at room temperature