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Preparation of poly(thiourethane) networks by using a novel acidic organocatalyst. Evaluation of their vitrimer-like behaviour

--Manuscript Draft--

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Abstract:	In this work, a novel acidic catalyst, isopropyl methane sulfonate, has been tested for the preparation of a series of poly(thiourethane) thermosets (PTU)s. The advantage of this compound is that in addition to being free of metals, by heating at temperatures above 100 °C, it releases methane sulfonic acid, which is the true catalyst allowing to maintain the formulation liquid at room temperature for a longer time than when using the more common dibutyltin dilaurate (DBTDL) catalyst. The materials obtained were characterized by thermogravimetry and thermomechanical analysis, which allow determining higher initial degradation temperatures than using tetraphenyl borate amidinium salts as basic organic catalysts. The PTUs prepared with this catalyst show good vitrimeric-like characteristics, with faster relaxation on increasing the amount of catalyst. The materials could be recycled without losing their chemical structure and mechanical performance.
Suggested Reviewers:	Alberto Jiménez Rey Juan Carlos University alberto.jimenez.suarez@urjc.es He is an expert in vitrimers and in thermosets
	Weiping Du Donghua University duweiping@dhu.edu.cn He is an expert in poly(thiourethanes)
Opposed Reviewers:	
Response to Reviewers:	

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Tarragona, December 22th 2022

Dear Prof. Dinu:

Hereby, I submit our revised manuscript entitled “Preparation of poly(thiourethane) networks by using a novel acidic organocatalyst. Evaluation of their vitrimer-like behavior” to be accepted for publication in Reactive and Functional Polymers

We have answer to all the reviewer’s comments and did the new characterizations they asked us to do.

Looking forward to your reply, I send my best regards and my best wishes for Christmas and New Year. Good luck in 2023

Prof. Angels Serra

ANSWER TO THE REVIEWERS

Reviewer #1: This work studied the use of isopropyl methane sulfonate (IMS) as a latent catalyst to substitute DBTDL (instantaneous catalytic effect) in the preparation of vitrimer-like poly(thiourethane) thermosets. Over the past decade, there have been countless papers published in the area of vitrimer-like polyurethane thermosets (check Google Scholar). The type of strategy presented in the paper is not new as addressed by the authors themselves. Nevertheless, the catalyst is new with better synthetic and processing conditions, and the study is reasonably good. I would like to recommend the publication of this manuscript in Reactive & Functional Polymers after addressing the following two minor issues.

First of all, we want to thank you for your very positive comments about our work and also for your dedication in reviewing the article.

1. *Throughout the manuscript, the term "vitrimer-like" popped up quite a lot (I am aware that "3.4. Vitrimeric characterization" is a solid study). The authors might want to shed some light on the potential of "poly(thiourethane) vitrimers" from the tensile tests based on the continuously re-processed samples for at least 3 times (only once in this work).*

   Thank you for your comment. We agree with the reviewer that only one recycling process is not enough to be completely sure to assert the high potential of these materials for recyclability. To this aim, a thorough study determining the optimal combination of time, pressure, and temperature for the recycling process is needed because, as it is mentioned in the paper, extremely harsh conditions could destroy definitely the network integrity avoiding new recycling cycles. As the aim of our paper was to present the ability of these materials to be recycled, as a proof of concept we only perform one recycling process without an in-depth study of the best recycling conditions.

   We have added the following paragraph in the text to empathize this:

   “Nevertheless, it is important to highlight that a thorough study determining the optimal combination of time, pressure, and temperature for the recycling process is needed to ensure these materials' high capability for recyclability”.

2. *The ester compound, IMS can experiment a β-elimination process that leads to the loss of propylene at temperatures higher than 100 °C, with the formation of the methane sulfonic acid, which catalyzes the reaction of isocyanate and thiol. No doubt about this. However, one just wonders where the eliminated propylene molecules would go.*
   This is a good question. Propylene goes into the atmosphere. At the beginning we were afraid that bubbles would form in the material, but luckily that doesn't happen. Because the formation of propylene takes place when the mixture is still in its initial liquid state, the propylene is not trapped.

Reviewer #2: In this article, the authors tested the catalytic activity of isopropyl methane sulfonate for thiol-isocyanate reaction and exchange reaction of thiourethane bonds. The advantage of this catalyst was the long-term stability of the starting monomers in the presence of the catalyst, which was due to the on-demand activation nature of this catalyst. Concretely, *the catalyst was decomposed to leave methane sulfonic acid at a certain high temperature via ß-elimination process, acting as a catalyst and enhancing the electrophilic character of the isocyanate carbonyl group. The catalyst also worked for activation of thiourethane exchange in the cross-linked materials, and they investigated the effects of the catalyst fraction as well as the kinds of isocyanate monomers and branch numbers at the cross-link point.*

I admitted the importance of such storable catalysts and the data were well supported by the data. Therefore, I could recommend this study for publication, after addressing the concerns below.

First of all, we want to thank you very much for your very positive comments about our work and also for your dedication in reviewing the article.

1. *The authors should add more relevant reference about vitrimer or vitimer-like materials with thiourethane exchange, for example, DOI: 10.1039/d0py01050b and doi.org/10.1021/acs.macromol.9b01359.*

Thank you very much. We have included the references you suggested in the text with a short comment.

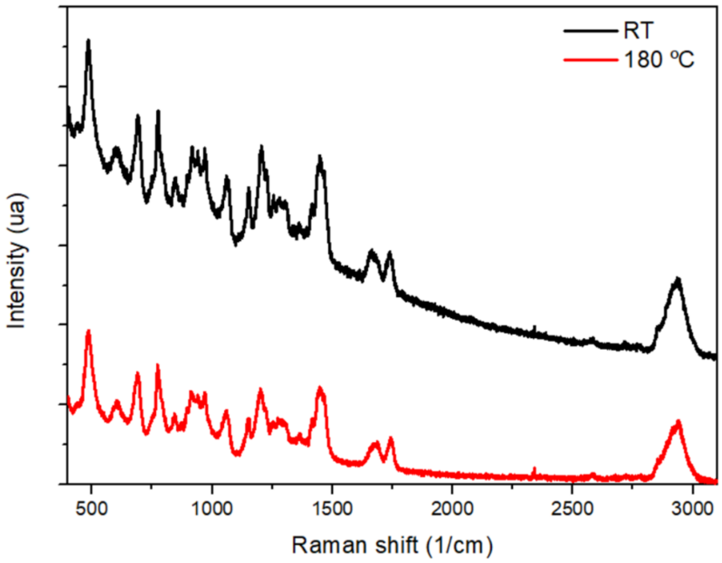
"Torkelson's group reported the vitrimeric-like behavior by studying the solvolysis of PTUs with alcohols, allowing to recover of monomeric thiols.[31] Similarly, Bowman et al. proposed the depolymerization of networked poly(thiourethane)s to lead to liquid oligomers which can be further re-crosslinked without any loss of performance.[32]"

2. *Mechanism of the exchange reaction in the present system:*

The authors mentioned that the exchange reaction involved in the present system was "the dissociation of the thiourethane group to isocyanate and thiol". How this can be concluded? As mentioned in the above reference, there is another exchange reaction, i.e., the exchange reaction between the free thiol and thiourethane bonds, and in this case, the reaction proceeds in an associative manner. The detection of thiol signal is quite difficult in FT-IR, but could be much easier using Raman spectroscopy (DOI: 10.1039/C8RA07157H). Thus, the authors should try Raman to specify the exchange mechanism based on the experimental fact.

In a previous study on polythiourethanes (ref. 23), we could observe that the crosslinked material followed an Arrhenius dependence of the relaxation time with the temperature. Moreover, it can be solved in DMSO, although not in 1,2-dichlorobenzene concluding that the material has a vitrimer-like behavior. According to the paper Brutman, J.P., Fortman, D.J., De Hoe, G.X., Dichtel, W.R. Hillmyer, M.A. J. Phys. Chem. B. 2019, 123, 1432-1441 on polyurethane materials. The fact that the material can be solved in DMSO demonstrates the dissociative nature of the exchange pathway. It should be considered the higher polarity of DMSO in comparison to dichlorobenzene. We never detected thiol or isocyanate by FTIR, which probably could have been detected if the exchange reaction was not as fast. It is true that the thiol band is very weak in FTIR, but the absorption of isocyanate is strong.

As you recommend, we have performed Raman studies, and by this technique, the formation of thiol at 2600 cm^{-1} cannot be observed at the interchange temperature (180 °C).



We have added a comment in the text:

“The fact that the material could be solubilized in DMSO but not in dichlorobenzene evidenced the dissociative character of the thiourethane exchange.[38] However, we couldn’t detect the formation of isocyanate groups by the appearance of the absorption at 2250 cm^{-1} in the FTIR spectrum recorded at 180 ºC or the appearance of the band at 2600 cm^{-1}, attributable to the thiol group thiols in the Raman spectrum at the same temperature. This indicates that although the exchange reaction is dissociative, the coupling reaction is extremely fast, and the dissociated fragments cannot be detected.”

3. Determination of Tv:

The authors estimated Tv by extrapolation of the Arrhenius plots of relaxation time and modulus. Although the obtained Tv was similar between samples, this estimation was not accurate since this is just an extrapolation. For more straight estimation, I recommend the authors to perform temperature-ramp creep for more accurate comparison of activation temperature of the bond exchange (see for example, DOI: 10.1021/acsapm.2c00230 and DOI: 10.1016/j.polymer.2020.122804).

Thank you very much for your comments. We totally agree with you that other complementary tests, as isothermal creep and temperature-ramp creep, would give us a more accurate approach to the activation temperatures. In fact, we have performed dilatometry and isothermal creep experiments in our previous article (ref. 30). Unfortunately, we don’t have access to the equipment due to technical problems and we cannot perform these experiments for the present article. We will keep it in mind for a next study.

4. Discussion about the plateau modulus:

Since the present network structure is quite simple, the authors should compare the experimental modulus and theoretical modulus based on the molecular characteristics. Similar vitrimer design using trifunctional and tetrafunctional thiols was reported (doi.org/10.1021/acs.macromol.2c00560), and see how the branch numbers at the cross-link point can affect the modulus.

Thank you very much for your suggestion. We have calculated the theoretical storage moduli in the rubbery state by using the ideal rubber elastic equation and the so-called phantom model following the references 35 and 36 included in the text. We have added the following comment:

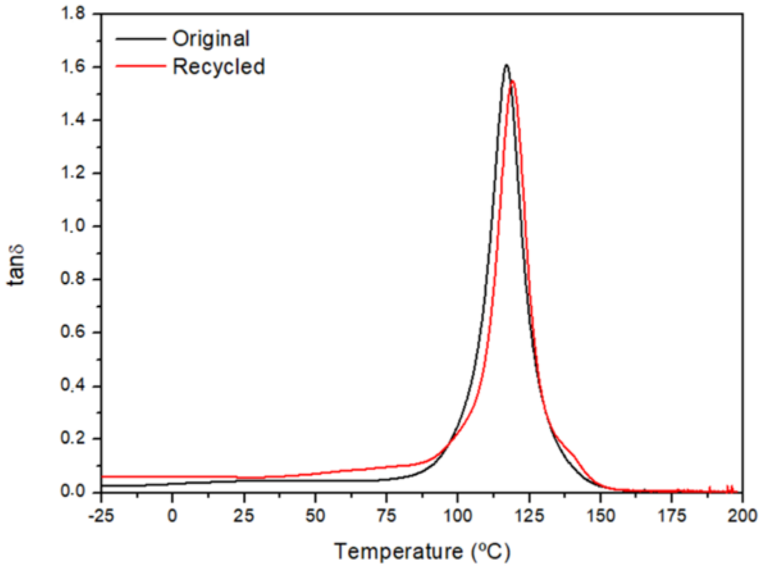
"The rubbery moduli of the HDI-formulations agree reasonably well with the theoretical ones, whereas theoretical modulus of IPDI-containing formulations is underestimated, possibly due to low mobility of IPDI. In any case, experimental and theoretical modules for each isocyanate are proportional to the branch numbers at the cross-link point, higher for S4 formulations."

5. The authors also discuss the difference of relaxation properties based on the literature, doi.org/10.1021/acs.macromol.2c00560

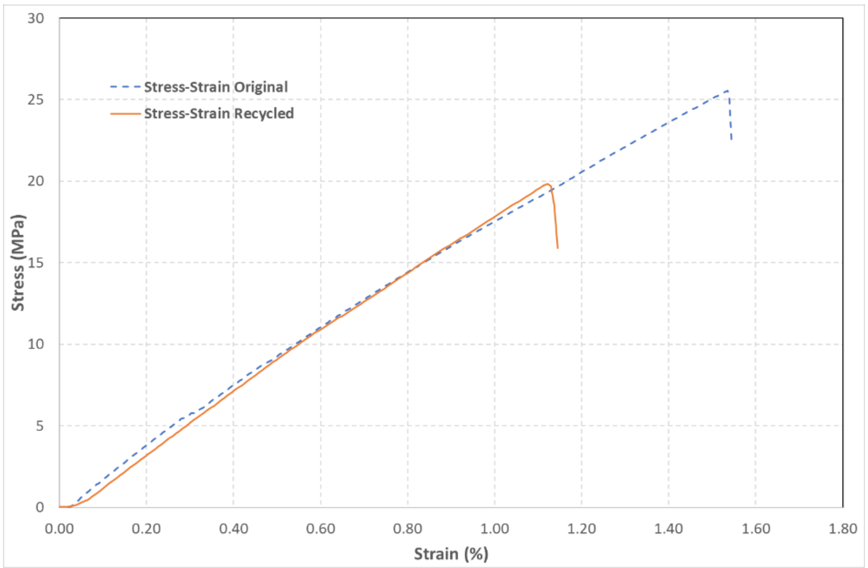
As discussed before the relaxation properties of the materials are directly related with the theoretical storage moduli in the rubbery state calculated by the Phanton model. However, it is difficult to stablish a correlation between f and the relaxation properties with only two values (S3 with f = 3 and S4 with f =4), since IPDI and HDI have a different structure.

6. The authors should show the graphs of DSC and tensile tests (before and after healing), only the summary of values were not insufficient.

Thank you very much for your suggestion. We have not registered DSC curves of these materials but we studied by DMTA if the thermomechanical characteristics are similar and we added to the text the tan δ curves for the original and recycled material. The curves of the original and recycled material have been included in Figure 11, with a short comment.



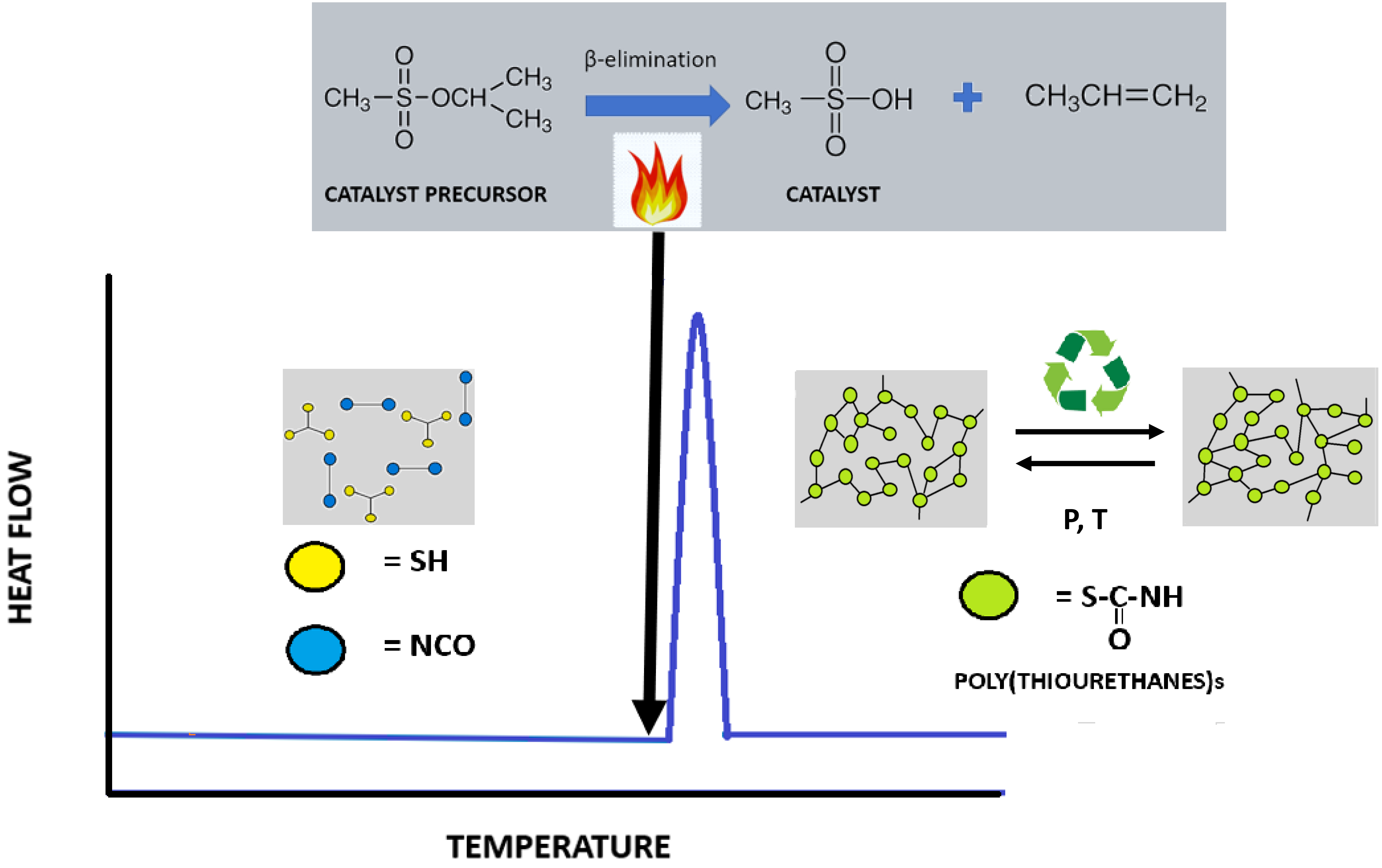
We have also added the graph for the stress-strain behaviour of one selected sample (from the three done) before and after the recycled process (Figure 12).


Stress-Strain Original
Stress-Strain Recycled
Stress (MPa)
Strain (%)
0
5
10
15
20
25
30
0.00
0.20
0.40
0.60
0.80
1.00
1.20
1.40
1.60
1.80

Highlights

- A new acidic organocatalyst has been studied in the synthesis of poly(thiourethane)s.
- This new catalyst allows the manipulation of the formulations for long time.
- Isopropyl methane sulfonate liberates, when heating at about 100 °C, the true acidic catalyst.
- The thermosets obtained show a good stress relaxation at 190 °C.
- The materials can be safely recycled at temperatures of 170 °C.

Graphical Abstract



Preparation of poly(thiourethane) networks by using a novel acidic organocatalyst. Evaluation of their vitrimer-like behaviour

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Abstract: In this work, a novel acidic catalyst, isopropyl methane sulfonate, has been tested for the preparation of a series of poly(thiourethane) thermosets (PTU)s. The advantage of this compound is that in addition to being free of metals, by heating at temperatures above 100 °C, it releases methane sulfonic acid, which is the true catalyst allowing to maintain the formulation liquid at room temperature for a longer time than when using the more common dibutyltin dilaurate (DBTDL) catalyst. The materials obtained were characterized by thermogravimetry and thermomechanical analysis, which allow determining higher initial degradation temperatures than using tetraphenyl borate amidinium salts as basic organic catalysts. The PTUs prepared with this catalyst show good vitrimeric-like characteristics, with faster relaxation on increasing the amount of catalyst. The materials could be recycled without losing their chemical structure and mechanical performance.

Keywords: poly(thiourethanes); latency; vitrimers; organocatalysis; recyclability.

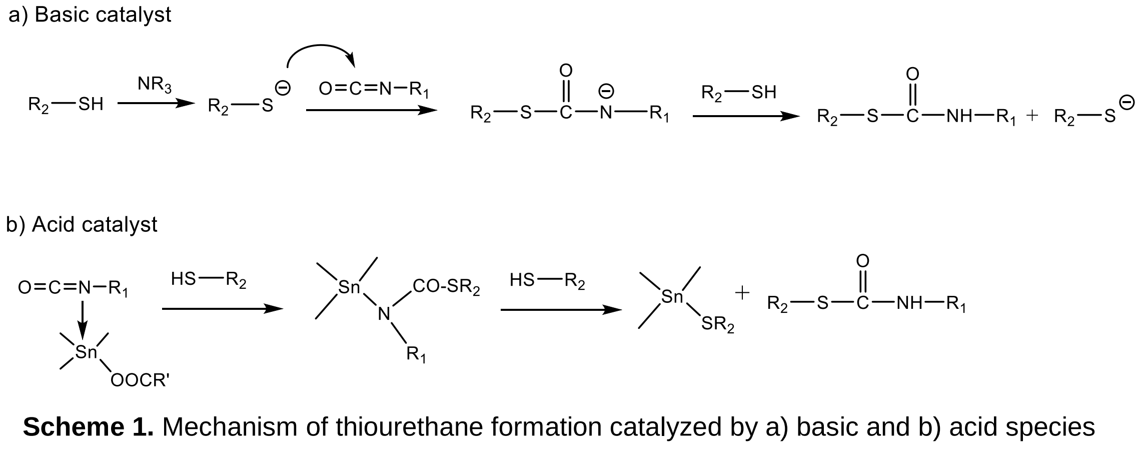
1. Introduction

In today's world, so scarce in resources and with serious environmental problems, the recycling of thermosetting materials is one of the challenges that must be addressed to find out a solution in a short time.[1,2] On the other hand, the use of highly toxic metal catalysts to obtain this type of materials is another of the environmental and health issues to be solved. Moreover, production wastes due to the poor stability of the formulations before their application have a negative impact not only on the economic costs but also contribute to the environmental problems that arise from the lack of recyclability of thermosetting materials. It should be commented that when their service life is over, most of the thermosets are landfilled or incinerated.[3,4] The present paper aims to contribute to solving all these three issues.

The recycling and reshaping of thermosets have been tackled by adding reversible functional groups in the network structure so that at high temperatures above T_g, the network acquires some mobility due to the exchange between reactive groups. Under these conditions, the material can be manipulated to be able to be repaired[5] or change its shape to be reused.[6,7]

The incorporation of dynamic covalent bonds in the network structure allows obtaining recyclable and reusable materials while maintaining their mechanical performance at the service temperature, which characterizes thermosetting materials.[8] These materials have been named globally as covalent adaptable networks (CANs) and a high number of covalent groups, which define the material characteristics, have been selected for such applications like esters,[9] imines,[10] urethanes,[11] vinylogous urethanes,[12] disulfides,[13] boronic esters[14] and triazolium salts,[15] among others.

In previous studies of our group, we investigated the preparation, reprocessability, and recyclability of poly(thiourethanes) (PTUs), which are the sulfur analogs of poly(urethanes) (PUs). The applications of PUs are very broad, representing nearly 5 % of total polymer production.[16] In contrast, poly(thiourethanes) have not been largely studied, although they have good physical and mechanical characteristics and better optical properties. In addition, they are more biocompatibleand it has been described that their formation does not lead to by-products as allophanate, according to the click nature of thiol-isocyanate reactions.[17,18,19] As it is reported, the preparation of PTUs can take place by two different mechanisms, according to the acid or basic characteristics of the catalyst, which are shown in Scheme 1:

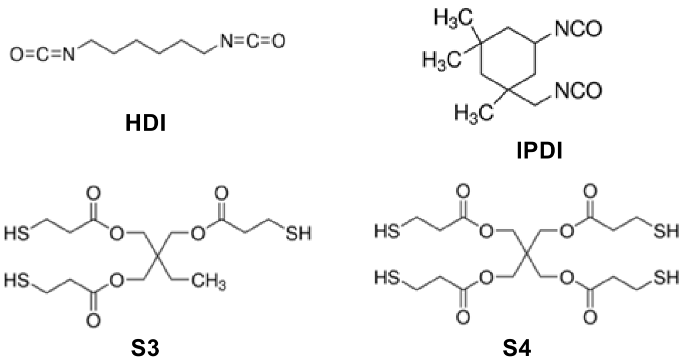


Scheme 1. Mechanism of thiourethane formation catalyzed by a) basic and b) acid species

As bases, trimethylamine[20] or amidine compounds as 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)[21] have been used. The reaction is usually too fast, making the manipulation of the formulation difficult because of the short pot life. To solve this limitation, we proposed the use of latent systems that liberate the corresponding base on heating.[22] These compounds are amidinium salts derived from tetraphenyl boric acid and different tertiary amines, which release the base only when heated above 100 °C, which allows safe storage and application and temporal control of the curing process. Moreover, the use of these salts is advantageous in comparison to the use of free amines since it allows a substantial increase in the proportion of amine in the material, which helps to accelerate the relaxation of the network structure, facilitating the recyclability of PTUs.[23]

As an acid catalyst, the most extensively used is dibutyltin dilaurate (DBTDL).[24,25] This Lewis acid starts the reaction even at room temperature, which is also a disadvantage for storing the formulations before their application. In addition, the EU has classified this compound as toxic for reproduction and suspected to be mutagenic.[26] Brönsted acids, as methane sulfonic, acetic, trifluoroacetic, and triflic acids have been tested.[27] The combination of methane sulfonic acid, as Brönsted acid, with nucleophilic phosphines was also reported by Bowman's group who observed induction times up to 20 min without affecting the final conversion reached.[27] Thus, to reach a fully temporal control in the production of PTU thermosets avoiding the use of metals, it is necessary to look for other acidic catalysts.

In the present study, we propose the use of isopropyl methane sulfonate (IMS) as a source of methane sulfonic acid.[28] This ester compound can experiment a β-elimination process that leads to the loss of propylene at temperatures higher than 100 °C, with the formation of the methane sulfonic acid, which catalyzes the reaction of isocyanate and thiol. As monomers, we selected 1,6 hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI) as isocyanate sources, and trimethylolpropane tris(3-mercapto propionate) (S3) and pentaerythritol tetrakis(3-mercapto propionate) (S4) as the thiols. Scheme 2 shows the structure of these compounds.



Scheme 2. Structure of the monomers used in the poly(thiourethane) synthesis

Since the poly(thiourethanes) behave as vitrimer-like polymers in the presence of DBTDL or tetraphenylborate amidinium salts, and their proportion influences the relaxation time, in the present study, we will characterize the materials prepared with the new acidic catalyst from the thermomechanical point of view. We will also compare them with their analogous prepared using DBTDL as the catalyst. The vitrimeric-like behavior was attributed to the trans-thiocarbamoylation process of thiourethane groups, which at high temperature revert to isocyanate and thiol groups that immediately react. This quick reaction allows maintaining practically the same number of crosslinking points and consequently reducing the viscosity progressively on increasing the temperature following an Arrhenius behavior.[23,29,30] Torkelson's group reported the vitrimeric-like behavior by studying the solvolysis of PTUs with alcohols, allowing to recover of monomeric thiols.[31] Similarly, Bowman et al. proposed the depolymerization of networked poly(thiourethane)s to lead to liquid oligomers which can be further re-crosslinked without any loss of performance.[32]

2. Experimental part

2.1 Materials

Trimethylolpropane tris(3-mercapto propionate) (S3), pentaerythritol tetrakis(3-mercapto propionate) (S4), and hexamethylene diisocyanate (HDI) from Sigma Aldrich were used without previous purification. Isophorone diisocyanate (IPDI) and isopropyl methane sulfonate (IMS)from Acros Organics were used as received.

2.2 Preparation of the formulations

Thiols (S3 or S4) and diisocyanates (HDI or IPDI) were mixed in stoichiometric proportions: 1 mol of thiol group per mol of isocyanate group. The amount of catalyst was calculated as grams of catalysts per hundred grams of thiol (phr). The mixtures were manually stirred until complete homogenization.

2.3 Sample preparation

The formulations prepared were placed on Petri dished covered with adhesive Teflon to avoid sticking to the glass, and they were heated at 140 °C for 15 min. Then, the materials were removed from the mold and the curing processes were completed in a hot-press at 180 °C for 45 min under a pressure of 15 MPa. The cured sample were cut while heating to obtain rectangular specimens of about 20 x 5 x 0.5 mm

2.4 Calorimetry study

A differential scanning calorimeter (DSC) Mettler DSC-3$^+$, calibrated using an indium standard (heat flow calibration), and an indium-lead-zinc standard (temperature calibration) was used to analyze the curing evolution. Samples of approximately 5–10 mg were tested in aluminum pans with a pierced lid in an inert atmosphere (N_2) with a gas flow of 50 cm^3/min. The dynamic studies were performed in a temperature range of 0–250 °C with a heating rate of 10 °C/min.

The enthalpy (Δh) released while curing the mixtures was calculated by integration of the calorimetric signal using a straight baseline with the help of the STARe software. The glass-transition temperature (T_g) of the cured materials was determined by heating a small piece between 0 to 250 °C at 20 °C/min. Temperatures were calculated with the help of the STARe software.

2.5 Thermal stability

The thermal stability of the cured samples was evaluated by thermogravimetric analysis (TGA), using a Mettler Toledo TGA2 STAR System thermobalance. All experiments were performed under an inert atmosphere (N_2 at a flow of 50 cm^3/min). Pieces of cured samples of 10–15 mg were degraded between 30 and 600 °C, with a heating rate of 10 °C/min.

2.6 Infrared spectroscopy

Fourier-transform infrared (FTIR) spectra were recorded with a spectrometer Jasco FT/IR 6700, in absorbance mode, with a resolution of 4 cm^{-1}, in the wavelength range from 650 to 4000 cm^{-1} and with 32 scans of each spectrum. The instrument is equipped with an attenuated total reflection accessory with thermal control (Golden Gate Heated Single Reflection Diamond-ATR Specac-Teknokroma).

2.7 Raman spectroscopy

Raman spectra were recorded with a spectrometer Raman Renishaw InVia, with a resolution of 1 cm-1 in the spectral range from 400 to 3100 cm-1. The device is equipped with a Linkam heating plate accessory that allows to record the spectra from room temperature to 200 °C.

2.8 Thermomechanical properties

The viscoelastic and thermomechanical properties were evaluated with a DMA Q800 analyzer from TA Instruments, using a film tension clamp. Cured samples were die-cut in rectangular specimens of dimensions about 20 x 5 x 0.5 mm^3.The evolution of tan δ and dynamic modulus with the temperature was analyzed. The samples were tested at a heating rate of 2 °C/min from -25 to 100 °C, with a frequency of 1 Hz and 0.1 % of strain.

2.9 Stress-relaxation tests

Tensile stress relaxation tests were conducted using samples with the dimensions previously defined. The samples were equilibrated at 155 °C and left at this temperature for 5 min. Then, a constant strain of 1.5 % (to ensure the materials were within the linear range) was applied, and the consequent stress level was measured as a function of time for 90 minutes. After releasing the stress, the temperature was progressively increased 5 °C, and the process was repeated until a final temperature of 190 °C was reached. Relaxation stress $\sigma(t)$ was normalized to the initial stress (σ_o), and the relaxation time (τ) was determined as the time necessary to relax $0.37\sigma_o$.

With the relaxation times obtained at each temperature, the activation energy values (E_a) and the pre-exponential constant (A) were calculated by using an Arrhenius-type equation:

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

where τ is the time needed to attain a given stress-relaxation value ($0.37\sigma_o$), A is the 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 DMA (assuming E' is relatively invariant in the rubbery state), τ^* was determined for each material. The Arrhenius relationship was then extrapolated to the corresponding value of τ^* to determine the T_v for each sample.

2.10 Recycling

The cured materials were cut into small pieces and hot-pressed at 15 MPa into an aluminum mold at 180 °C for 90 min. Original and recycled samples were die-cut in dog-bone shapes from the film obtained and tested in the tensile mode in a Shimadzu AGS-X universal testing machine with a 1000 N load cell at 10 mm/min at room temperature. Three samples of each material were tested, and the values obtained were averaged.

3. Results and discussion

3.1 Study of the curing process

In technological applications, curing catalysts showing a certain degree of latency are of great importance, as the prepared formulations can be maintained in their initial state for a while, enough to allow the manufacture of pieces or the complete coating of surfaces during the working time. Therefore, the use of such catalysts as curing agents has great economic and environmental effects, as they help reduce the waste of useless formulations. Thus, we propose the use of isopropyl methane sulfonate (IMS) as a catalyst to substitute dibutyltin dilaurate (DBTDL) in the preparation of poly(thiourethane) thermosets since DBTDL starts the reaction instantaneously when added to the reactive mixture reducing the pot-life.

The curing of the thiol/isocyanate formulations that contained 1phr of IMS was studied by calorimetry (DSC). Figure 1 shows the calorimetric curves for all the combinations of monomers. Table 1 collects the main data extracted by this technique.

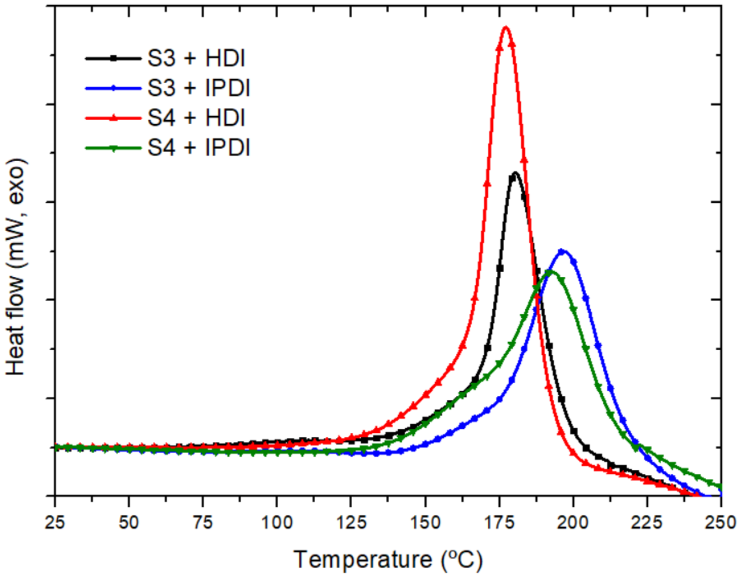


Figure 1. Calorimetric curves of the dynamic curing of the different formulations prepared with 1 phr of IMS at 10 °C/min

As we can see from the curves, the heat release begins at temperatures above 100 °C. When the reaction starts, it is quite fast, especially in the mixtures containing HDI as the diisocyanate monomer. This seems to confirm a certain latent character of this acid precursor, which upon reaching the required temperature for the β-elimination process, abruptly releases propylene and leaves methane sulfonic acid in the reactive mixture, acting as a catalyst and enhancing the electrophilic character of the isocyanate carbonyl group. The different reactivity of both isocyanate groups and the rigidity of the cycloaliphatic ring in the IPDI broadens the calorimetric curve, which extends to higher temperatures.

Table 1. Main calorimetric data extracted from DSC studies of the curing of the formulations studied

Monomers	**Proportion of catalyst** (phr)	T_{max}[a] (°C)	Δh[b] (kJ/eq)	T_g[c] (°C)
S3 + HDI	1	181	56	29
S3 + HDI	4	170	57	30
S3 + HDI	10	164	57	30
S3 + IPDI	1	197	66	106
S3 + IPDI	4	184	67	106
S3 + IPDI	10	178	67	106
S4 + HDI	1	179	65	56
S4 + HDI	4	168	66	56
S4 + HDI	10	163	66	57
S4 + IPDI	1	193	56	124
S4 + IPDI	4	181	57	124
S4 + IPDI	10	175	57	126

a. Temperature of the maximum of the exotherm
b. Enthalpy released in the thiol-isocyanate reaction by equivalent of isocyanate
c. Glass transition temperature of the cured material

From the data in Table 1, it can be seen that the enthalpy evolved is of 56 to 67 kJ per isocyanate equivalent, slightly lower than the enthalpy obtained by using 1-imidazolium tetraphenylborate salt, as the base latent catalyst,[22] or DBTDL.[30] This could be explained because the acid formation by the β-elimination process is an endothermic process overlapped with the curing exotherm.

To know the effect of the catalyst proportion on the curing process, mixtures of HDI and IPDI with S3 and S4 with different proportions of acid precursor were prepared. The main calorimetric data are also collected in Table 1, and Figure 2 represents the curves for the formulations obtained with HDI and S3 as an example.

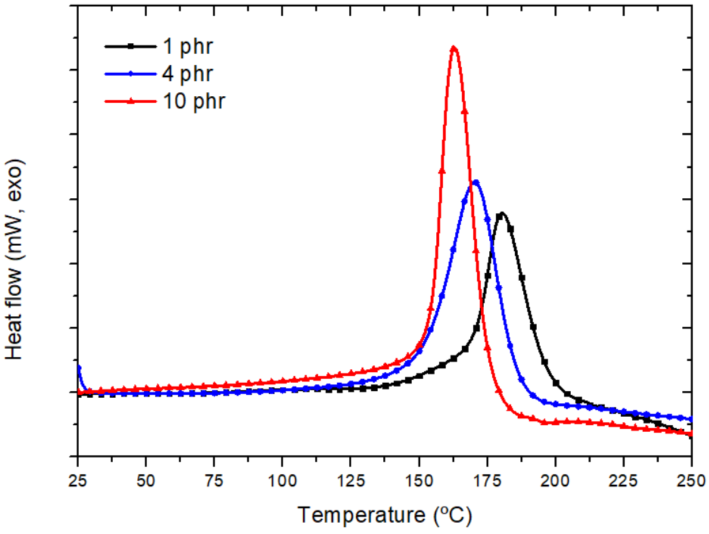


Figure 2. Calorimetric curves of the dynamic curing of formulations prepared with stoichiometric proportions of S3 and HDI with different proportions of isopropyl methane sulfonate at 10 °C/min

The increase of the proportion of catalyst in the curing evolution mainly affects the reaction rate, and the exothermal curve is higher and thinner on increasing the amount of catalyst. At the same time, the temperature of the maximum of the exotherm shifts to a lower temperature. However, the enthalpy evolved is similar, which indicates that the curing process reaches the same extent. Thus, the use of this acid allows for an increase in the amount of catalyst, without compromising the stability of the formulation before application. This could be advantageous in terms of stress relaxation rate without losing the ability to manipulate the formulation for quite a long time once it has been prepared compared to formulations catalyzed by DBTDL.

The glass-transition temperature (T_g) of the materials after isothermal curing does not show any variation in increasing the amount of acid precursor. Samples with cyclic isocyanate (IPDI) present higher glass-transition temperatures, related to the lower mobility of the network structure, than samples obtained from the linear isocyanate (HDI). Moreover, samples containing tetrathiol (S4) have a higher T_g value than the ones obtained from S3 due to the higher crosslinking degree achieved. Consequently, samples obtained from a stoichiometric formulation of S4 and IPDI presented the highest T_gs, ranging from 29 to 126 °C on changing the monomer's structure.

FTIR spectra were recorded to confirm that the curing process had been completed. In Figure 3, the spectra of the HDI + S3 with 1 phr of the acid precursor before and after curing are overlapped.

As we can see, the stretching band at 2250 cm^{-1} of the isocyanate has completely disappeared in the spectrum of the cured material, whereas new N-H and N-CO-S stretching absorptions appear at 3350 and 1655 cm^{-1}, respectively, and the N-H bending at 1515 cm^{-1}. This indicates the full conversion of isocyanate in thiourethane groups. The thiol band at 2580 cm^{-1}, due to its weakness, cannot be barely observed. The ester absorption at 1730 cm^{-1} of the thiol monomer remains constant and has been previously used as a reference band in kinetic studies by this technique.[22]

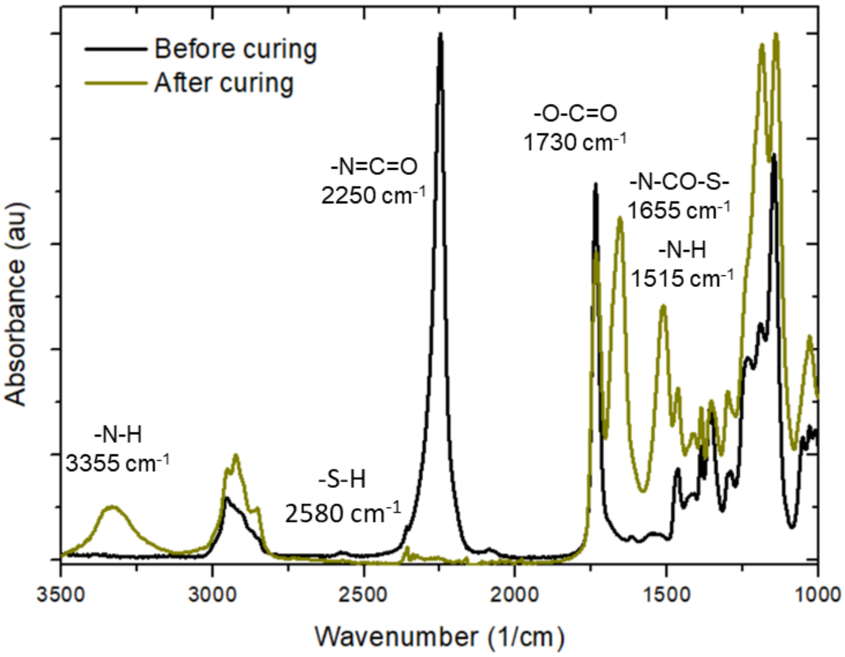


Figure 3. FTIR spectra of the stoichiometric HDI with S3 with 1 phr of isopropyl methane sulfonate before and after curing.

Several mixtures were stored for 30 days in a chamber at 20 °C to investigate if the use of IMS as a catalyst leads to a latent character of the curing system. We investigated by FTIR the evolution of the isocyanate bands and their apparent fluidity. The formulations remain liquid to be applied for more than 20 days, but the isocyanate band started to decrease slightly after 24 h. HDI formulations showed higher reactivity than those with IPDI, which were liquid for more than 30 days. The presence of S3 in the formulation increased the reactivity compared to S4.

3.2 Thermal stability

Thermal stability of the prepared poly(thiourethane) thermosets was evaluated by thermogravimetry. The primary data obtained are presented in Table 2, and in Figure 4, the derivative of the weight loss curves of all the samples prepared with 1 phr of the catalyst are shown.

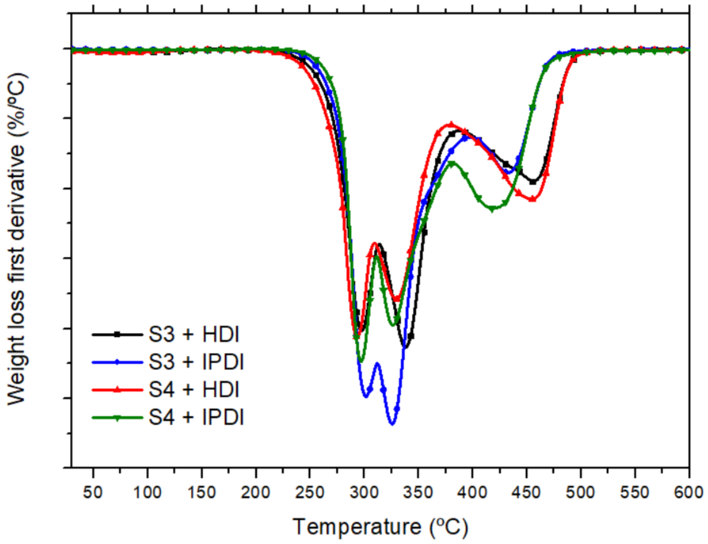


Figure 4. DTG curves of the materials prepared from the different monomers with 1 phr of isopropyl methane sulfonate registered in N_2 atmosphere at 10 °C/min

As shown in Figure 4, the degradation mechanism is quite complex, with three different steps for all the materials studied. However, the shape of the curves is similar to that obtained by using DBTDL as the catalyst.[23] This indicates that the degradation mechanism does not change. Looking at the values presented in Table 2, we can observe that the initial degradation temperature decreases on increasing the proportion of catalyst, but this effect is practically negligible. The initial degradation temperature, a parameter of utmost importance for mechanical recycling, is 10 °C higher in the case of the material S3 + IPDI than when using DBTDL as the catalyst[30] and much higher than similar materials prepared with tetraphenylborate salts as latent base catalysts.[23] This constitutes an advantage when using IMS in terms of the recycling capability of the final thermoset. As expected, the main difference in thermal stability depends on the network structure. IPDI materials start the degradation at higher temperatures than those with HDI, and the higher crosslinking reached by S4 enhances the thermal stability in front of S3.

Table 2. Thermogravimetric data of all the materials prepared in N_2 atmosphere

Monomers	**Proportion of catalyst** (phr)	$T_{2\%}$[a] (°C)	$T_{5\%}$[a] (°C)	T_{max}[b] (°C)	**Char Yield**[c] (%)
S3 + HDI	1	248	272	297/332/456	2.6
S3 + HDI	4	247	269	300/333/457	2.6
S3 + HDI	10	244	268	303/338/458	3.0
S3 + IPDI	1	268	283	302/326/433	2.3
S3 + IPDI	4	266	282	303/328/433	2.5
S3 + IPDI	10	265	282	305/331/434	2.6
S4 + HDI	1	247	269	293/330/455	3.4
S4 + HDI	4	245	269	295/333/456	3.6
S4 + HDI	10	245	267	297/334/455	3.7
S4 + IPDI	1	273	286	297/326/456	3.2
S4 + IPDI	4	272	284	298/328/456	3.4
S4 + IPDI	10	270	284	300/329/456	3.6

a. Temperatures of initial degradation (2 and 5% of weight loss)
b. Temperatures of the maximum degradation rates of the three steps
c. Remaining weight percentage at 600 °C

On increasing the proportion of catalyst, the temperatures of maximum degradation rates of the three steps do not change significantly. However, the first and second steps are slightly shifted to higher temperatures on increasing the amount of catalyst.

We investigated by FTIR the residue after degradation at 220 °C for 24 hours. The spectra before and after degradation are represented in Figure 5.

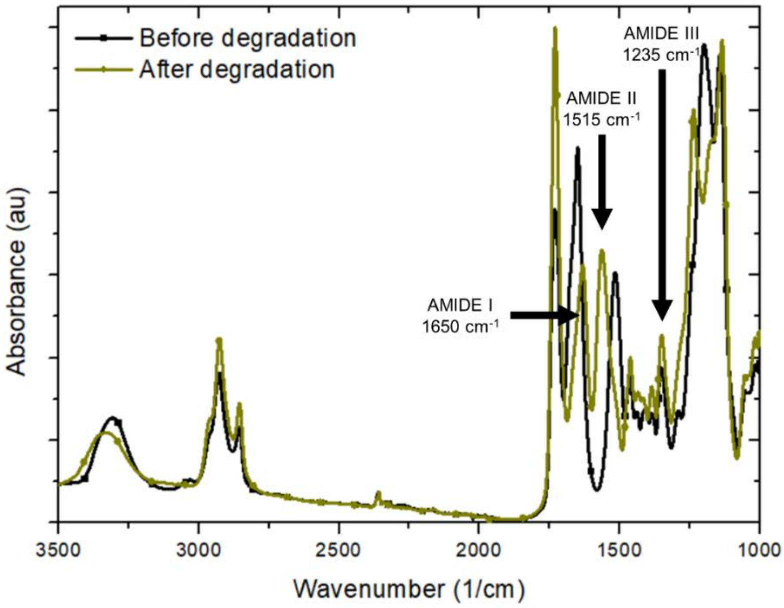


Figure 5. FTIR spectra of the material obtained from a stoichiometric HDI/S3 formulation with 1 phr of IMS before and after degradation at 220 °C for 24 hours.

In the spectrum of the degraded material, the absorption of the carbonyl group of the thiourethane moiety at 1730 cm^{-1} has disappeared, appearing new bands typical of secondary amides at 3300 cm^{-1} (N-H st.), 1650 cm^{-1} (C=O st., amide I), 1515 cm^{-1} (N-H bending, amide II) and 1235 cm^{-1} (C-N symmetric vibration, amide III).[33] In any case, isocyanate groups were detected. This is in contrast with the results reported by Rogulska et al.[34] They determined that the gases that evolved during degradation were formed by carbonyl sulfide, isocyanate, and carbon dioxide. According to that, their proposed mechanism led to the formation of amine residues and not amides, as we have clearly identified.

3.3 Thermomechanical characterization

The materials prepared with 1 phr of IMS were characterized by DMA to determine their thermomechanical behavior. To know if there is an effect of the catalyst proportion, a sample obtained from HDI and S3 with 10 phr of the acid precursor was also investigated. In Figure 6, the tan δ curves and storage moduli of the materials prepared with 1 phr of IMS are plotted. The main values extracted are presented in Table 3.

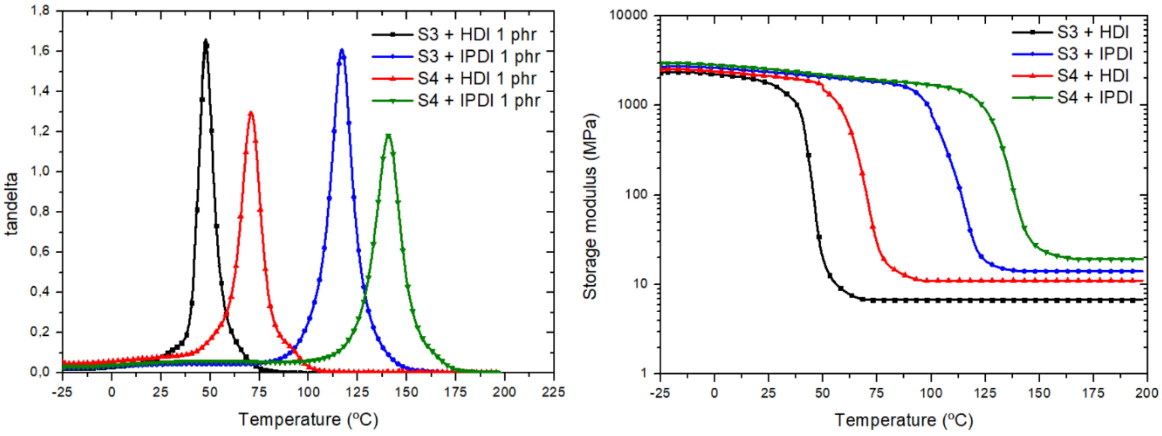


Figure 6. Evolution of tan δ (left) and storage moduli (right) with temperature of the different poly(thiourethane)s prepared with 1 phr of isopropyl methane sulfonate

Table 3. Main data obtained from DMA analysis of selected materials

Monomers	**Proportion of catalyst** (phr)	$T_{\tan\delta}{}^{a}$ (°C)	**FWHM**[b] (°C)	$E_{glassy}{}^{c}$ (MPa)	$E_{rubbery}{}^{c}$ (MPa)	$E_{rub,\,theor}{}^{d}$ (MPa)
S3 + HDI	1	49	9.6	2209	6	7
S3 + IPDI	1	118	13.3	2697	14	8
S4 + HDI	1	70	12.0	2512	11	12
S4 + IPDI	1	141	15.5	2948	19	13
S3 + HDI	10	48	10.5	2338	9	7

a. Temperature of the maximum of the tan δ peak.
b. Full width at half maximum of the tan δ peak.
c. Storage modulus determined $T_{\tan\delta}$ -30°C and at $T_{\tan\delta}$ +30 °C
d. Theoretical rubbery storage modulus determined using the ideal rubber elastic equation and the so-called phantom model.[35,36]

The shape of the *tan δ* curves shows the high homogeneity of the network structure in all the PTUs, thanks to the click nature of the thiol isocyanate reaction with this catalyst.

The values of FWHM of the curves are similar to those obtained using DBTDL or imidazolium tetraphenylborate as the catalysts.[22] This value increases slightly with the functionality of the thiol and the proportion of catalyst. However, the maximum of the *tan* δ curves appears at lower temperatures when using IMS as the catalyst instead of DBTDL. IPDI, because of its more rigid structure, leads to materials with higher $T_{tan\delta}$, reaching 141 °C when S4 was used as the comonomer. The use of high proportions of IMS does not affect this value.

Storage moduli in the rubbery and glassy states are slightly higher for IPDI-derived materials and increase with the functionality of thiol, as expected. Higher proportions of IMS barely increase both moduli. When comparing the values obtained with those previously reported using a basic organocatalyst,[22,37] we can state that when using IMS they are slightly lower in the rubbery state, which accounts for a more open network, but slightly higher, with a slightly higher crosslinking density, than when using DBTDL.[30]

The rubbery moduli of the HDI-formulations agree reasonably well with the theoretical ones, whereas theoretical modulus of IPDI-containing formulations is underestimated, possibly due to low mobility of IPDI. In any case, experimental and theoretical modules for each isocyanate are proportional to the branch numbers at the cross-link point, higher for S4 formulations.

3.4. Vitrimeric characterization

In previous papers of our group, we reported that trans-thiocarbamoylation reaction could proceed in networked poly(thiourethane)s at elevated temperatures in the presence of acidic[29,30] and basic catalysts,[23] and the higher the proportion of catalyst, the quicker the relaxation process at the proper temperature. We demonstrated that this type of materials has a vitrimeric-like behavior with the dissociation of the thiourethane group to isocyanate and thiol and a very fast reforming that leads to a diminution of the viscosity on heating that follows an Arrhenius type evolution. The fact that the material could be solubilized in DMSO but not in dichlorobenzene evidenced the dissociative character of the thiourethane exchange.[38] However, we couldn't detect the formation of isocyanate groups by the appearance of the absorption at 2250 cm^{-1} in the FTIR spectrum recorded at 180 ºC or the appearance of the band at 2600 cm^{-1}, attributable to the thiol group thiols in the Raman spectrum at the same temperature. This indicates that although the exchange reaction is dissociative, the coupling reaction is extremely fast, and the dissociated fragments cannot be detected.

We performed DMA experiments to investigate the effect of the monomer structures of the different PTUs prepared and the ability of the acidic catalyst present in the material on the stress relaxation behavior. The temperatures selected were well above the T_g to allow some movement of the network structure to perform the exchange process.

Figure 7 shows the dependence of the relaxation process on the network structure and the effect of a higher proportion of IMS.

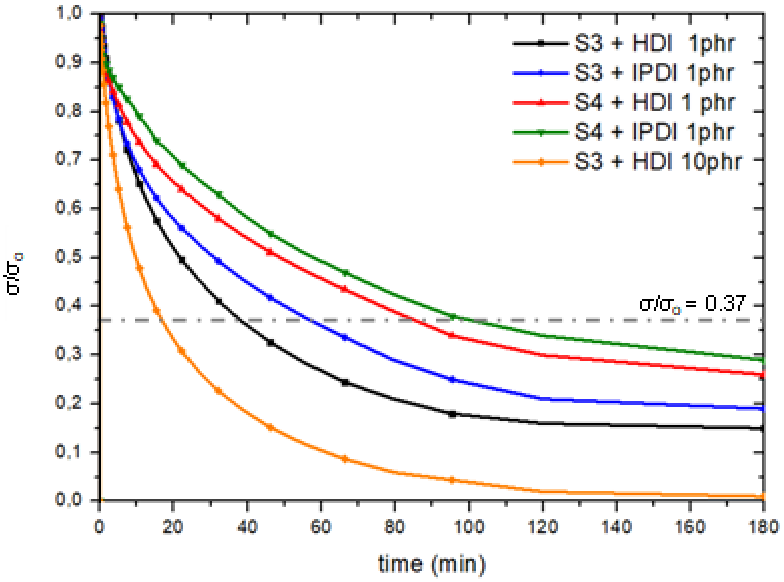


Figure 7. Normalized stress relaxation behavior at 185 °C for all the PTUs prepared with 1 phr of IMS and for HDI/S3 material with 10 phr of catalyst.

As we can see in Figure 7, there is an apparent reduction of the relaxation time when 10 phr of acid catalyst is in the material because of the increase in the exchange reaction rate, similar to that observed in PTUs catalyzed by DBTDL.[29] The addition of 10 phr of IMS to the formulation leads to a final methane sulfonic acid content in the material of 7 phr after the elimination of propylene on curing. The more flexible and open network in HDI/S3 materials (see black curve) leads to the lowest relaxation time of all the materials with the same amount of catalyst. The increase of the crosslinking density produced by substituting S3 with S4 in the formulation and/or HDI with IPDI (black and red curves for HDI systems and blue and green curves for IPDI systems) increases the relaxation times.

Table 4 presents the times needed to reach the point at which the stress decreases to 1/e (37%) of its initial value ($\tau_{0.37}$) at the tested temperatures, in this case, 180 and 185 °C. The increase from 1 to 10 in the catalyst proportion reduces this value to half. However, this value is higher than previously studied acids[29,30] or bases.[23] It was reported that at 180 °C the formulation with S3 + HDI has a $\tau_{0.37}$ of 126 min with 1 phr of DBTDL, but only 20 min with 4 phr.[29] Thus, we need a proportion of isopropyl methane sulfonate higher than 10 phr to reach a similar relaxation rate. On the other hand, the use of tetraphenyl borates of amidine salts, such as DBN, DBU, and TBD, allows reaching this relaxation time in less than 2 min at the same temperature. However, the initial degradation temperature is around 210 °C, which limits the recycling to be performed at temperatures not higher than 130 °C.

It must be noted that 180 °C was not enough to achieve the 63% of relaxation of the stresses for the S4 + IPDI sample with 1 phr of catalyst, so a minimum temperature of 185 °C must be used to reach this value, although it takes about 100 min. This longer time is due to the higher crosslinking density introduced by the use of S4, together with the rigidity of the IPDI structure.

Table 4. Main data extracted from stress relaxation experiments

Monomers	**Proportion of catalyst** (phr)	$\tau_{0.37}$ [a] (min)	$\tau_{0.37}$ [b] (min)	E_a [c] (kJ/mol)	***lnA***	r^2	T_v [d] (°C)
S3 + HDI	1	48.2	38.0	247	57.0	0.9959	157
S3 + IPDI	1	69.2	57.5	257	59.5	0.9995	164
S4 + HDI	1	141.2	85.2	272	63.0	0.9967	167
S4 + IPDI	1	-	99.8	280	65.0	0.9984	171
S3 + HDI	10	28.2	16.7	149	32.3	0.9919	135

a. Time to reach $\sigma/\sigma_o = 0.37$ at 180 °C.
b. Time to reach $\sigma/\sigma_o = 0.37$ at 185 °C.
c. Activation energy of the exchange process
d. Topology freezing temperature calculated as defined in Section 2.8

Stress-relaxation tests were performed at different temperatures to further characterize the vitrimeric-like behavior of the materials. Figure 8 shows the relaxation curves for the HDI + S3 formulation with 10 phr of catalyst as an example. As is expected, the higher the temperature, the shorter the time to relax the stress.

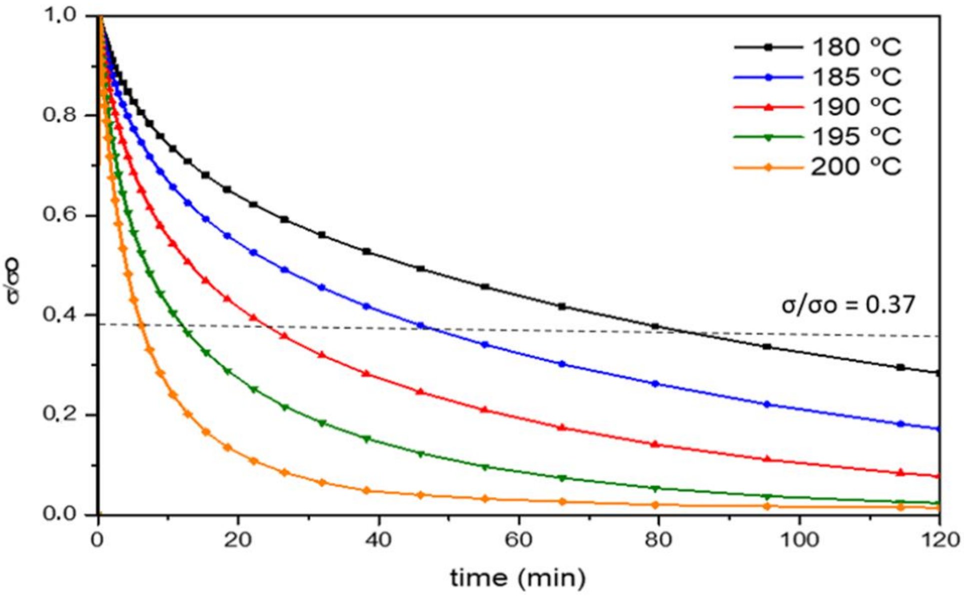


Figure 8. Normalized stress relaxation plot as a function of time at several temperatures from 180 to 200 °C during 120 min of sample S3 + HDI with 10 phr of IMS.

Vitrimer-like materials, although dissociative from the mechanistic point of view, present a decrease of viscosity with the temperature following Arrhenius' law, like inorganic silica. From the times to reach a relaxation stress σ/σ_0=37% at each tested temperature and using an Arrhenius-type equation, we determined the activation energy (E_a) of the rearrangement process for the materials prepared. The values obtained are presented in Table 4, while Figure 9 shows the Arrhenius plots. It should be noticed that the activation energy values calculated are quite high compared to those obtained for DBTDL materials (from 102 to 72 kJ/mol, for 1% to 4% phr of catalyst).[29] As occurred for DBTDL PTUs, on increasing the amount of catalyst, the activation energy is reduced. In the case of IMS, this decrease is notable and goes from 247 to 149 kJ/mol.

When comparing the materials prepared with the same proportion of catalyst, it can be observed that the activation energy (and *lnA*) increases more noticeably when changing S3 by S4 with the same monomer (around 10% of increase) than when changing HDI by IPDI with the same thiol (with only an increase of around 4%).

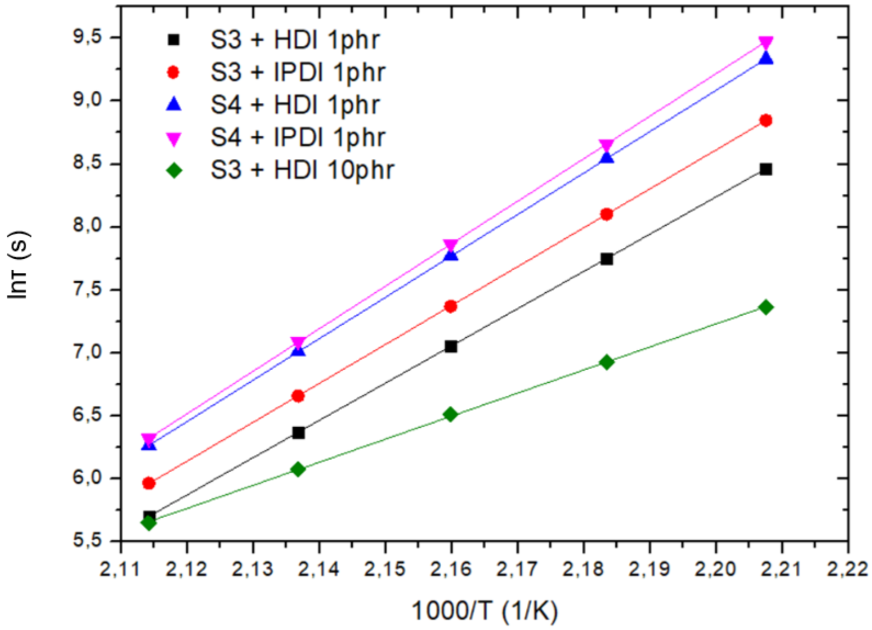


Figure 9. Arrhenius plot of relaxation times against temperature for all the materials prepared.

From the Arrhenius equation derived from these plots, we could determine the topology freezing transition temperature (T_v), defined as the temperature at which the material reaches a viscosity of 10^{12} Pa·s. As we can see in Table 4, these temperatures are similar for all the materials with the same amount of catalyst and around 20 °C lower when the catalyst proportion is 10 phr. The T_vs obtained for DBTDL catalyzed PTUs were lower, between 132 and 96 °C, for 1 and 4 phr of DBTDL.[29]

3.5. Recycling

To test the recyclability of the prepared PTUs we selected the S3 + IPDI sample due to its higher T_g that warranty a reliable mechanical behavior at room temperature. To prepare the recycled material we cut the sample S3 + IPDI (with 10 phr of catalyst) into small pieces and placed them on an aluminum mold and then it was hot-pressed at 15 MPa and 170 °C for 90 min. This temperature is suitable for recycling, as isothermal TGA results proved that at this temperature during 100 min, less than 1 % in weight was lost. The process was repeated several times, and the FTIR spectra of the samples were recorded after each process. Figure 10 shows the overlapped FTIR spectra.

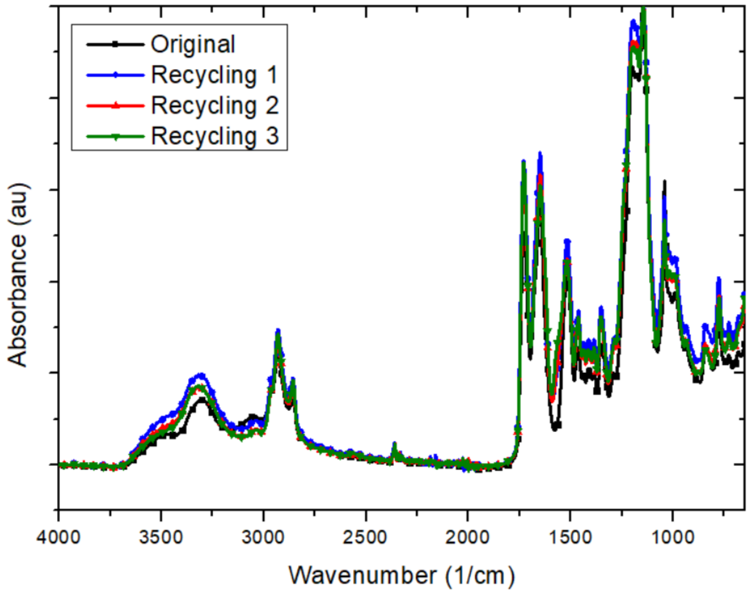


Figure 10. FTIR spectra of the original material obtained from S3 + IPDI formulation with 10 phr of catalyst and after three consecutive recycling processes

As shown in Figure 10, the spectra are practically superimposable without significant variations even after the third recycling process. The tan δ curves for the original and recycled material were registered, and as can be seen in Figure 11, they are very similar, which confirm the good recyclability of these materials.

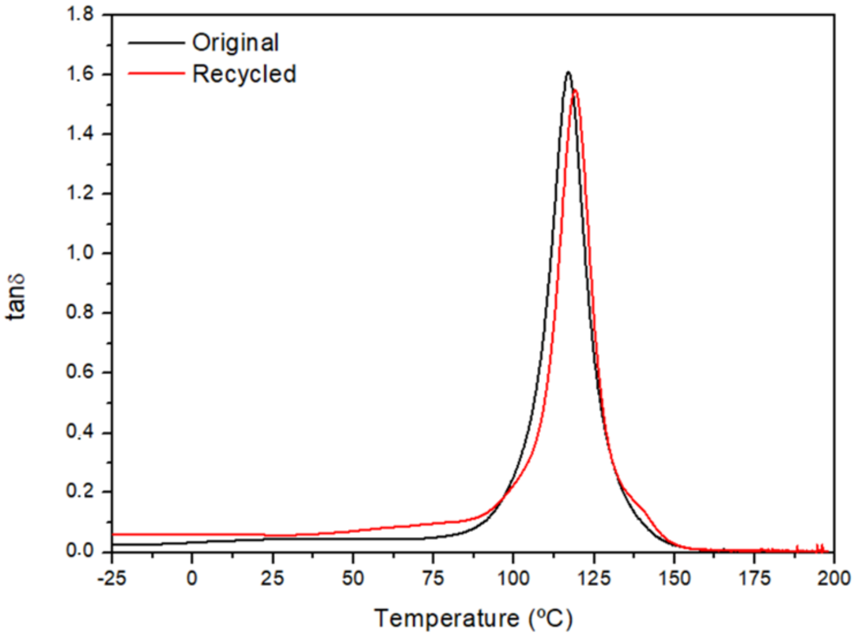


Figure 11. Evolution of tan δ with temperature of the original and recycled S3 + IPDI sample with 1 phr of isopropyl methane sulfonate

The films obtained after recycling were die-cut in dog-bone shapes and they were tested in tensile in a universal testing machine. The stress-strain behavior of the virgin materials was registered and compared with the recycled ones. The stress-strain behavior of one selected sample (from the three done) is presented in Figure 12 and the parameters extracted are presented in Table 5.

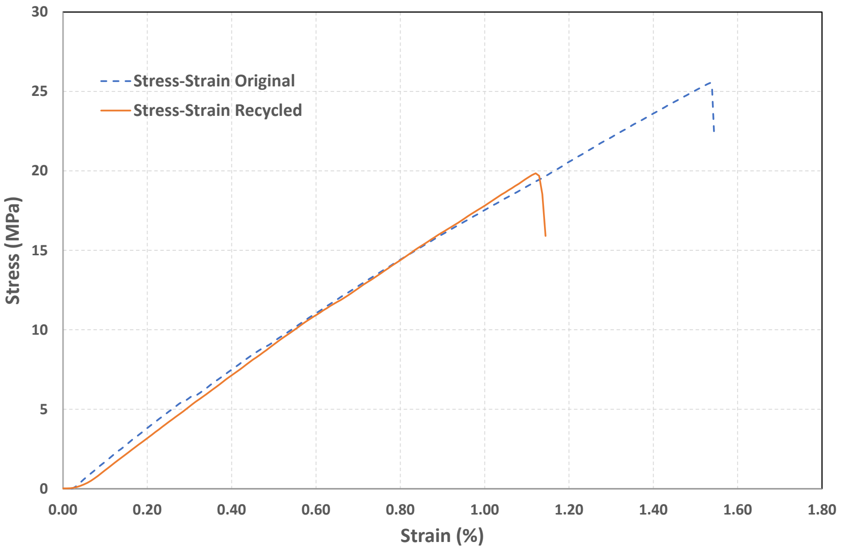


Figure 12. Stress-strain behavior of the original material obtained from S3 + IPDI formulation with 10 phr of catalyst and after a recycling processes.

Table 5. Main data extracted from tensile test at break for original and recycled samples

Material	**Stress at break** (MPa)	**Strain at break** (%)	**Tensile modulus** (MPa)
Original	24.0 ± 3	1.5 ± 0.6	1779 ± 95
Recycled	21.6 ± 5	1.2 ± 0.9	1850 ± 110

As we can see from the values of the table all the materials behave quite similar before and after being recycled. The stiffness is more or less the same and the strength is slightly lower in the recycled sample due to the extremely harsh conditions of the recycling process. Nevertheless, it is important to highlight that a thorough study determining the optimal combination of time, pressure, and temperature for the recycling process is needed to ensure these materials' high capability for recyclability.

4. Conclusions

A new acidic organocatalyst, isopropyl methane sulfonate, has been tested for the preparation of poly(thiourethane) networks. This compound, when heated to temperatures above 100 °C, releases the corresponding acid, which is the true catalyst. This allows the prepared formulations to be kept in the proper viscosity range for a much longer time than when using DBTDL as a catalyst. This behavior allows for increasing its proportion up to high content, which is convenient to accelerate the relaxation process of PTUs vitrimer-like materials.

The PTUs prepared with this catalyst show glass transition temperatures that mainly depend on the monomer's structure and not on the proportion of catalyst. However, these temperatures are slightly lower than the ones obtained from previously reported PTUs obtained by using DBTDL. From the width of the tan δ curve, it is inferred that the materials were highly homogeneous because of the click nature of the thiol-isocyanate reaction. No side reactions could be detected by FTIR spectroscopy.

The initial degradation temperatures of the materials prepared are slightly higher than similar reported materials prepared with DBTDL and much higher than the ones prepared with tetraphenyl borate amidinium salts, which constitutes an advantage when using this organocatalyst in terms of the recycling capability of the thermosets.

The materials present a vitrimeric-like behavior with an Arrhenius-type decrease of the viscosity with temperature, with activation energies higher than when using DBTDL. This value decreases by increasing the amount of catalyst. Consequently, the times needed to relax are shortened when the proportion of catalyst in the material increases. The time needed to achieve the stress relaxation mainly increases with the crosslinking density and slightly with the rigidity of the monomer structure.

FTIR spectra, thermomechanical analysis and mechanical results of the original and recycled samples demonstrated that the material can be recycled maintaining their chemical structure and mechanical performance.

Acknowledgments

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Declaration of interests

☒The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Author Statement

F.G. performed the experimental work. A.S. and S.F. wrote and corrected the paper. X. R., S. F. and A.S. validated the studies, made conceptualization, supervised the methodology and results and were the responsible of funding acquisition and project administration.