

# Thiol–Ene Networks with Tunable Dynamicity for Covalent Adaptation

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Cite This: *ACS Appl. Polym. Mater.* 2023, 5, 1651–1656

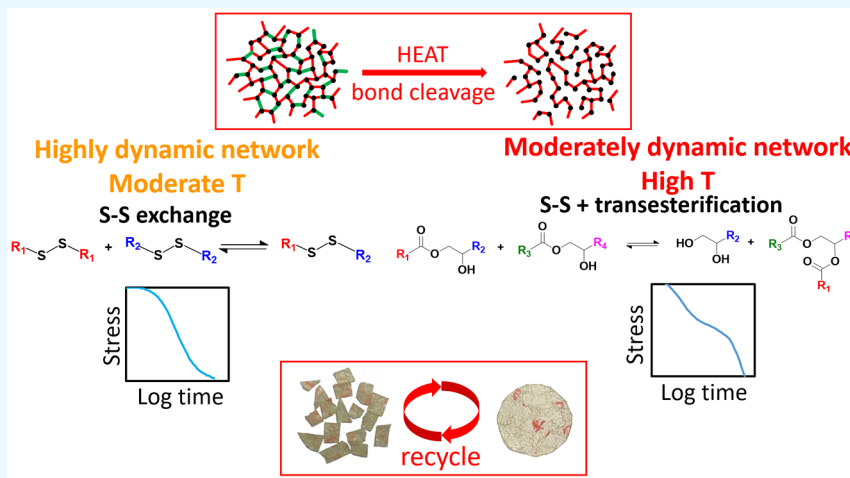
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**ABSTRACT:** To be fully recyclable, covalent adaptable networks must ultimately be able to overcome all topological restrictions and flow. By using a statistically based method, it was shown that the extent of stress relaxation in disulfide-containing thiol–ene polymers is closely correlated to the fraction of permanent cross-links. Given sufficient disulfide content, the cured materials can be recycled at moderate temperatures with no apparent loss in tensile properties. Since the materials also feature ester bonds, even when the disulfide content is low, one can increase the reprocessing temperature to trigger transesterification reactions which ensure full stress relaxation and recyclability.

**KEYWORDS:** covalent adaptable network, vitrimer, thiol–ene, disulfide exchange, transesterification, structural fragments

The recent paradigm of reprocessable yet densely cross-linked macromolecules has inspired many researchers in the fields of organic chemistry, polymer science, and material engineering. This emergent class of polymeric materials was coined as “vitrimers” some 12 years ago by the Leibler group,<sup>1</sup> who, in their pioneering research, reported that polyesters prepared from epoxides and fatty acids had interesting flow properties previously ascribed exclusively to vitreous silica. At high temperatures, these materials became malleable thanks to transesterification reactions that take place at bulk scale and through an associative bond exchange mechanism allowing the material to “flow” without any loss in overall network connectivity. In the years that followed, many such covalent adaptation mechanisms based on different chemistries were employed at the macromolecular level. There are excellent papers reviewing these versatile materials.<sup>2–4</sup>

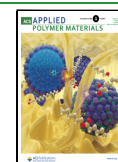
Among the numerous dynamic polymer systems, those that contain S–S bonds that can undergo disulfide metathesis appear to allow very fast network adaptation, oftentimes without requiring any catalysts.<sup>5,6</sup> Even more contemporary is

the design of networks containing both disulfide and ester functionalities that can concomitantly undergo disulfide exchange and transesterifications and hence achieve synergy in relaxing strain-induced stresses. This stress relaxation property is the most commonly studied manifestation of dynamic networks. Recently, Chen et al. reported such a material wherein the two exchange reactions can be simultaneously and synergistically triggered, leading to very fast stress relaxation.<sup>7</sup> Later, Mauro and Mija reported similar disulfide-ester dually relaxing polyepoxide materials with particular focus on material properties.<sup>8</sup> Similar epoxy-based vitrimers have also been prepared using amine curing agents.<sup>9</sup>

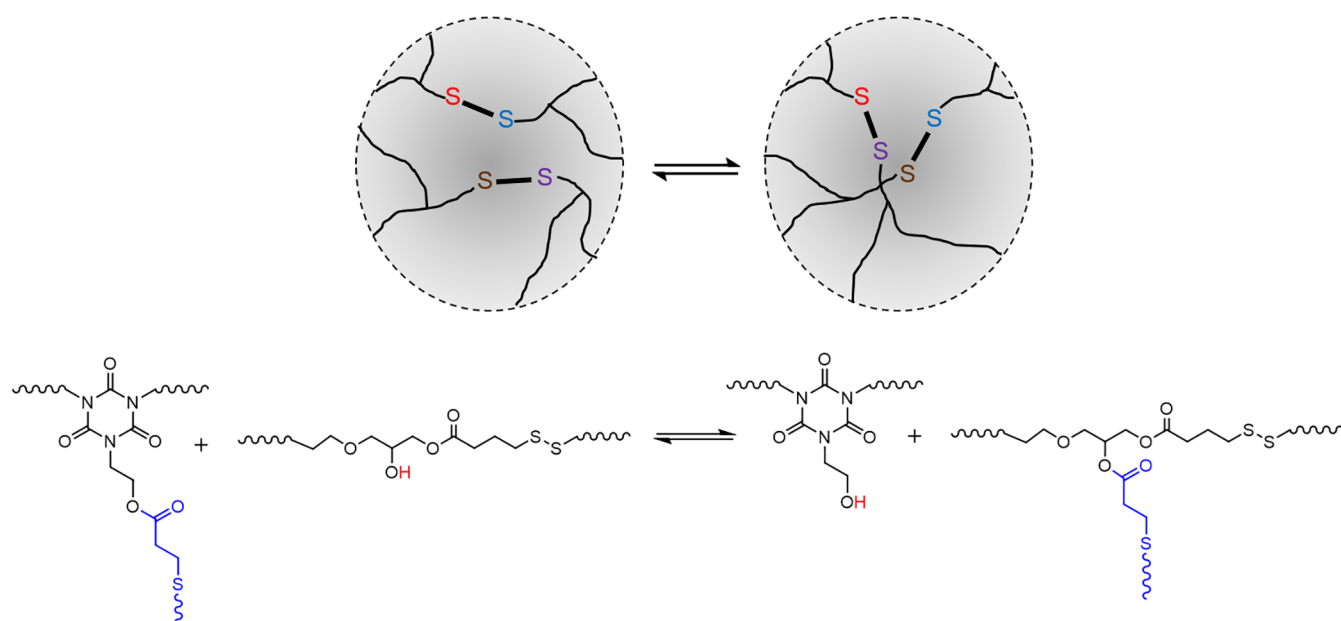
**Received:** December 12, 2022

**Accepted:** January 10, 2023

**Published:** February 10, 2023



**Scheme 1. Disulfide Exchange within the Dynamic Network at Low Temperature (top) and Transesterification between the Crosslinks and  $\beta$ -Hydroxyls of the Dynamic Network (bottom)**



In some applications, it might be desirable to control the extent of dynamic behavior. One method to achieve this would be the incorporation of permanent structures into the dynamic network. Wang et al.<sup>10</sup> demonstrated this approach on an epoxy polymer cured with mixtures of disulfide-containing and disulfide-free carboxylic acids at varying proportions. Most recently, Alfarhan et al. studied disulfide-containing thiol-ene networks and their depolymerization via base-catalyzed thiol-disulfide exchange that yields repolymerizable thiol oligomers.<sup>11</sup>

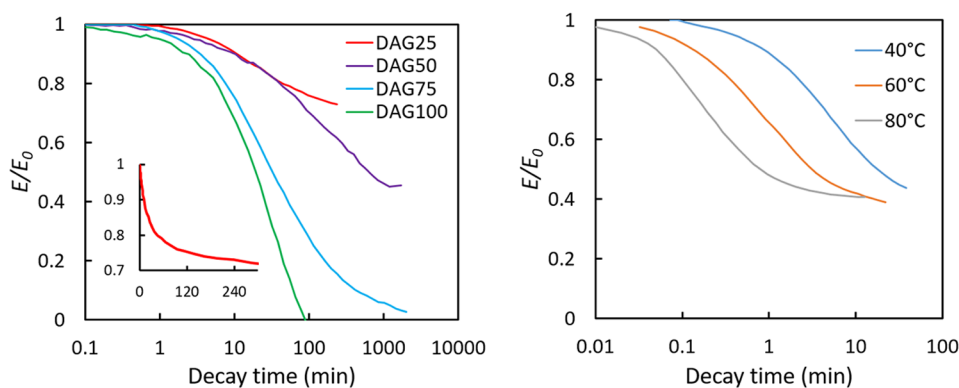
Inspired by all these dually dynamic networks, here we describe a family of thiol-ene polymers that are covalently adaptable primarily via disulfide exchange and secondarily via transesterification reactions, triggered at different temperatures. As a result, the dynamic behavior is manifested in a sequential manner, allowing two levels of reprocessability to the materials. In this work, we limit our focus on the primary adaptation mechanism, namely, disulfide exchange, and try to establish a relationship between the network structure governed by this exchange reaction and recyclability of the cured material. In particular, we use a statistical analysis method, originally intended to study the network build-up process by considering the structural fragments in the network.<sup>12</sup> In our analysis, a fully cured network will be assumed and the main variable will be the disulfide content of the network. We will investigate the extent to which disulfide content impacts network permanency (i.e., nonrecyclability).

To prepare our test materials, we first synthesized a disulfide containing allyl monomer via base-catalyzed epoxy-acid reaction of 4,4'-dithiobutyric acid (DTBA) and allyl glycidyl ether (AGE) catalyzed by trimethylamine, at 100 °C for 1h, followed by 12 h at room temperature, after which the allyl monomer, coded as DAG, was obtained with negligible impurities. The NMR spectrum is given in Figure S1 (Supporting Information). We later prepared photocurable monomer mixtures using this dynamic allyl in conjunction with 1,3,5-triallyl-1,3,5-triazine-2,4,6-trione (TATATO), a disulfide-free allyl. The latter monomer provides the ultimate network

with permanent cross-links, thereby allowing regulation of dynamic behavior. As cross-linker, we used tris(2-(3-mercaptopropionyloxy)ethyl isocyanurate (3TI). Tributylphosphine (TBP) was used, along with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), both at 0.5% (w/w) loading, to promote disulfide exchange. DBN also ensures the basicity required by transesterification. In all formulations, 2% (w/w) of diphenyl-(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) was used as photoinitiator, along with 0.25% of a radical scavenger, namely, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) in order to avoid early cure during sample preparation. The structures of all chemicals used are given in Figure S2 along with descriptions of the experimental methods employed (Supporting Information).

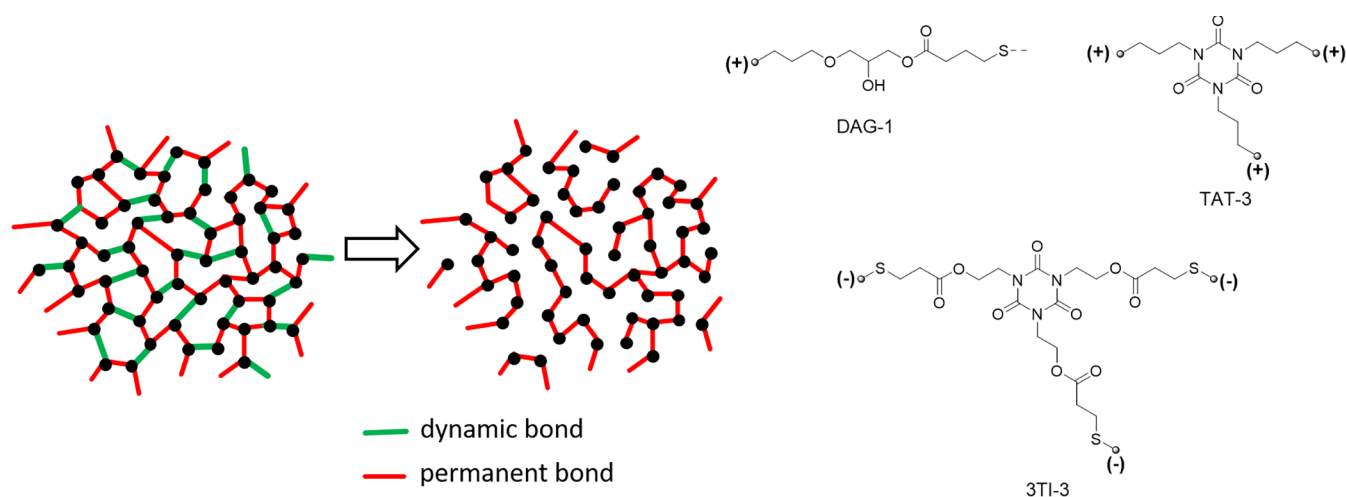
To ensure our cured materials are exclusively thiol-ene polymers, we use stoichiometric mixtures of our thiol and allyl components and thus avoid any subsequent disulfide-ene reaction, which would change the network structure drastically.<sup>13</sup> The materials are simply coded as DAG $x$ , where  $x$  denotes the weight percent of the disulfide-containing DAG monomer, so that the weight percent of the disulfide-free allyl monomer TATATO is (100 -  $x$ ). The photocured thiol-ene polymers have  $T_g$  ranging between 0 and 25 °C obtained by dynamic mechanical analysis (DMA), taken as temperatures at  $\tan \delta$  peaks. The curves are given in Figure S3. The higher the TATATO content, the higher the average allyl functionality and thus the  $T_g$ . Moreover, as can be seen in Figure S3, all formulations exhibit narrow  $\tan \delta$  peaks with high amplitude, suggesting homogeneous network structures. The networks feature both disulfide and  $\beta$ -hydroxy ester bonds that would undergo disulfide exchange and transesterification reactions, respectively (Scheme 1).

By using stoichiometric thiol:ene proportions and by employing a phosphine catalyst, we ensure the first exchange is predominantly between the disulfides themselves, rather than between disulfides and thiols.<sup>14,15</sup> By DMA using 3-point-bending configuration and a fixed strain of 1%, we obtained



**Figure 1.** Normalized DMA 3-point-bending stress relaxation curves of DAG25, DAG50, DAG75, and DAG100 at 60 °C (left) and of DAG50 (containing 1% DBN by weight) at various temperatures (right). Curve of DAG25 is repeated as inset with a nonlogarithmic scale.

**Scheme 2. Structural Change of the Network upon Total S–S Bond Cleavage (left) and Basic Structural Fragments for the Statistical Analysis (right)**

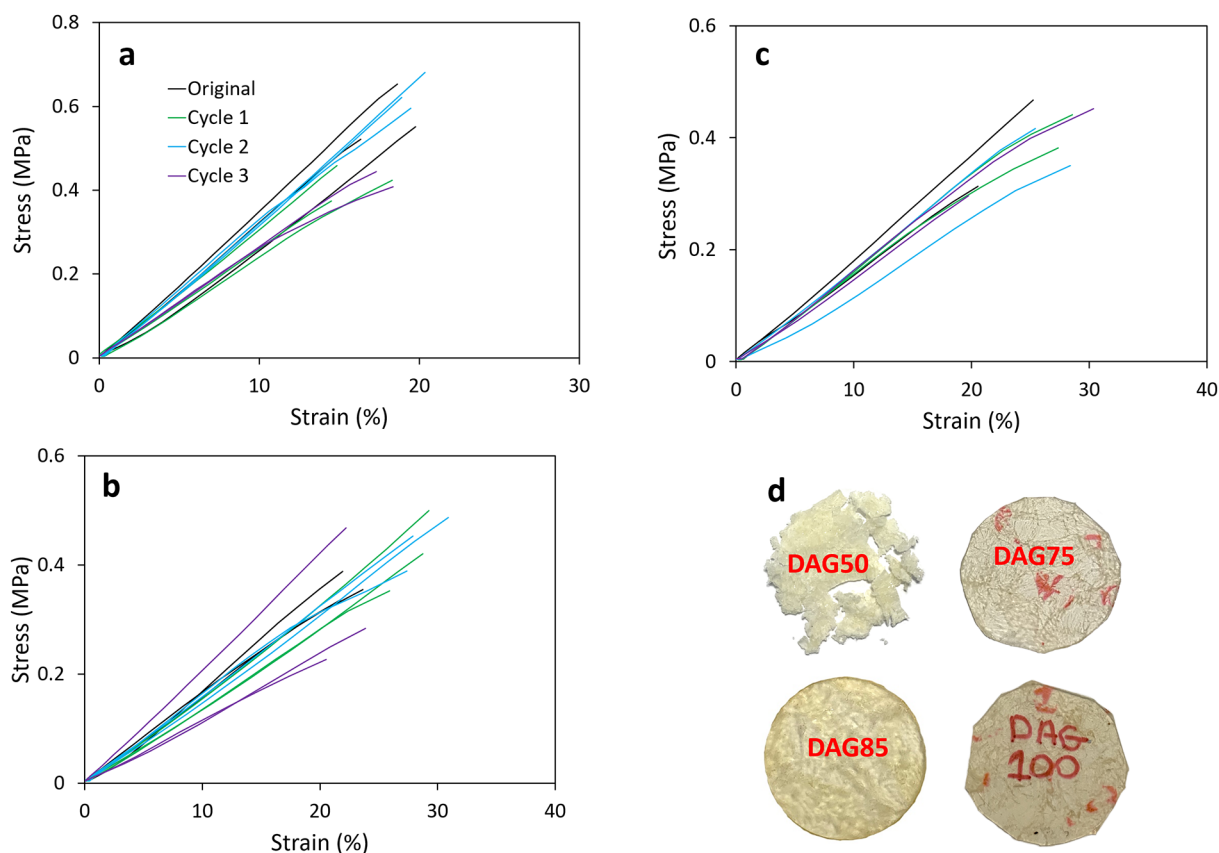


stress relaxation responses of cured materials with different DAG contents (Figure 1).

As can be seen from Figure 1 (left), the extent of stress relaxation seems to be correlated with the DAG (and thus the disulfide) content. This result resembles that shown by Li et al. in their study of dynamic bond exchange in thiol-epoxy networks with reduced creep.<sup>16</sup> It also hints that the predominant adaptation mechanism under these conditions (i.e., moderate temperatures and in a time scale of minutes to hours) is disulfide exchange. In the materials with incomplete stress relaxation, the relaxation continues at longer time scales, albeit at very low rate, due to a slow transesterification at low  $T$ . For instance, in DAG25, the relaxation is slowed markedly when a normalized relaxation modulus of ca. 0.75 is reached, a value which correlates to the disulfide-free fraction of the network. This inflection point is more clearly visible when the curve is viewed in a nonlogarithmic scale, which is given as an inset of Figure 1 (left). The temperature dependence of stress relaxation (Figure 1, right) is accurately captured by an Arrhenius-type model, with an activation energy of 70 kJ/mol, a value comparable to that of previously reported vitrimers based on disulfide exchange.<sup>8,9,17,18</sup> As can be seen from the same figure, the curves are truncated when the relaxations practically come to a halt (i.e.,  $E/E_0 \cong 0.5$ ). The linear regression is performed after normalizing these truncated

curves. The linear Arrhenius plot is given in Figure S4. The similarity of the activation energies reported and the correlation between the final relaxation modulus and permanent network content suggest that the relaxation mechanism is a concerted disulfide exchange, most likely a metathesis reaction, during which the network connectivity is maintained.

The correlation between the extent of stress relaxation and the disulfide content can be analyzed from a theoretical point of view. A statistical analysis method is employed here, based on the structural fragments approach.<sup>12</sup> At the root of the analysis lies the assumption that, at moderate temperatures, the adaptation mechanism of the fully cured material is exclusively disulfide exchange, with no transesterification reaction taking place. During the recycling process, the material would be subjected to constant strain (e.g., while being remolded under pressure), so eventually all the S–S bonds of the thiol-ene network would be exchanged from the original stressed state to a relaxed state. The dynamic bond exchange process relieves the stress of the network strands, through a reduction in the amount of effective cross-links in the network structure. In practice, this is equivalent to considering that S–S bonds are cleaved in the network relaxation process so that the remaining stress, if any, results from the remaining cross-links constituting the permanent (i.e., nondynamic) part of the network (Scheme



**Figure 2.** Tensile response of DAG75 (a), DAG85 (b), and DAG100 (c) after three reprocessing cycles and circular discs of each material obtained from the hot press after the first cycle (d).

2, left). The fraction of permanent cross-links in the network structure,  $f_{\text{xlinks}}$ , upon cleavage of all S–S bonds, could therefore be used as a predictor of the expected stress relaxation.

Under this asymptotic condition, the structural fragments based on DAG, TATATO, and 3TI would be as in Scheme 2 (right). The number after the dashes denotes the functionality of each fragment. The fragment based on TATATO is shortened as TAT-3 for convenience. The cleaved disulfide bond is depicted as two dashes (- -).

In this scheme, each (+) bond must be connected to a (-) bond. The analysis disregards the effects of substitution and intramolecular cyclizations. It could be argued that the analysis maintains a decent level of accuracy since the studied system lacks subordinate functional groups or long, cyclization-prone chains. The ultimate goal is to relate the adaptable content of the network (i.e., the thiol–ene dynamic network formed by the reaction of DAG with 3TI) to the fraction of permanent cross-links,  $f_{\text{xlinks}}$ . Following this methodology, for each structural fragment, one must define (i) the probability of being attached to a certain bond of opposite polarity (defined as  $P_{(+)}$  or  $P_{(-)}$ ) and (ii) the probability that any of its arms has a finite ending (defined as  $Z_{(+)}$  and  $Z_{(-)}$ ). For a given structural fragment to contribute to the soluble fraction, all its bonds must be attached to finite chains. Permanent cross-links are determined under the condition that all three arms of fragments with three bonds are infinite. The detailed mathematical treatment is given as Supporting Information. This calculation yields theoretical values of  $f_{\text{xlinks}}$  of 0.83, 0.57, and 0.16 for the formulations DAG25, DAG50, and DAG75.

Indeed, they have a remarkable correlation with the final normalized relaxation moduli ( $E/E_0$ ) of DAG25, DAG50, and DAG75 with values of 0.71, 0.42, and 0.003, respectively. This indicates that the fraction of permanent cross-links  $f_{\text{xlinks}}$  could serve as a predictor of the expected stress relaxation. Discrepancies may be caused by nonidealities such as intermolecular cyclization, which would have reduced the connectivity of the network structure. Moreover, as stated previously, the possibility of transesterifications at low temperatures is not completely discarded.

For a material to be fully recyclable, it must be able to flow completely. On one hand, this is equivalent to assuming that there is no permanent network structure upon cleavage of the S–S bonds, that is,  $f_{\text{xlinks}} = 0$ . This is accomplished when  $Z_{(+)}$  and  $Z_{(-)}$  are both equal to 1. A threshold value can be calculated using a recursive approach and making use of the concept of expected weight pending from the bonds (defined as  $W_{(+)}$  and  $W_{(-)}$ ). Details of this treatment are given as Supporting Information. A generalized expression follows for the critical ratio between dynamic ene groups (i.e., coming from the DAG monomer) and the total ene groups:  $r_{\text{DAG,crit}} = 1 - [(f_{\text{ene,nodyn}} - 1) \cdot (f_{\text{thiol}} - 1)]^{-1}$ . Above this ratio, there is no permanent network and the materials can relax completely. Here,  $f_{\text{thiol}}$  is the thiol functionality and  $f_{\text{ene,nodyn}}$  is the nondynamic allyl monomer functionality. It must be noted that this is equivalent to applying the renowned expression by Flory and Stockmayer. For our monomers, a value of 0.75 can be calculated for  $r_{\text{DAG,crit}}$  which corresponds to a DAG weight ratio of 0.89. This means that, theoretically, a fully recyclable formulation would have to contain a minimum of 89% DAG by

weight. It should be noted that this expression would yield the same result as the one derived by Li et al. for a different dynamic bond exchange system.<sup>16</sup> The  $r_{\text{DAG}}$  values of all formulations are given in Table S1.

To demonstrate, recycling experiments were conducted with various formulations. Fully cured materials were ground to bits which were then placed in a hot press at 60 °C and were subjected to a pressure of 8.9 MPa for 1 h. In DAG50, grain boundaries were still visible after the process, indicating incomplete network adaptation (Figure 2d). According to the theory, DAG75 should not be fully recyclable. However, it was shown earlier that DAG75 exhibited practically complete stress relaxation (Figure 1, left). Here it was confirmed that when ground DAG75 was kept in the hot press for 1 h, a disk with uniform appearance was obtained (Figure 2d). This was somewhat unexpected since complete stress relaxation took several hours in DMA. It is therefore evident that pressure in the hot press seems to have accelerated covalent adaptation by enhancing the physical contact and promoting dynamic bond exchange at the interphase between the ground pieces.

Rectangular samples cut from these recycled DAG $\alpha$  materials with dimensions 30 × 5 × 1 mm<sup>3</sup> were tensile tested in a TA Q800 DMA instrument, using tension film clamp and a preload force of 0.01 N, and results are presented in Figure 2a–c. For each formulation and each cycle, at least 2 samples were tested. Alterations in tensile response after reprocessing can be deemed to be within acceptable limits. Each formulation maintained its Young's modulus and fracture strain, the averages of which are given in Table 1.

**Table 1. Mean Tensile Properties of Cured Materials**

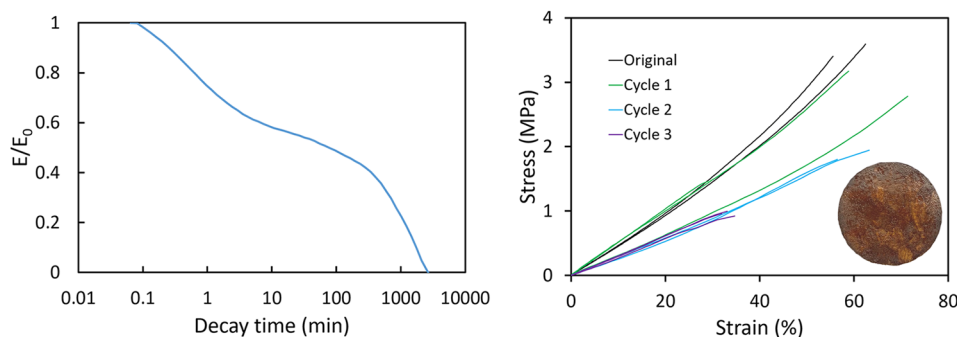
	$E$ (Mpa)	frac strain (%)
DAG75	3.23	18.9
DAG85	1.69	22.6
DAG100	1.73	26.4

Despite the failure to recycle DAG50 at moderate temperatures, it exhibited full stress relaxation, albeit at 160 °C and over significantly longer time scales (Figure 3, left). This is believed to be due to transesterifications that take place between the  $\beta$ -hydroxyesters of the DAG-3TI network and the esters on the cross-linking arms of TATATO-3TI (See Scheme 1, bottom). The material recycled at 160 °C showed repeatable tensile properties after the first reprocessing cycle (Figure 3, right). Nevertheless, some detrimental effect of reprocessing is observed after the second processing cycle. The Young's

modulus dropped from 4.87 to 3.11 MPa between cycles 1 and 2. A third cycle did not impact Young's modulus, but it reduced the mean fracture strain from 63.7 (cycle 2) to 37.8% (cycle 3).

Apparently, at moderate temperatures, disulfide exchange takes place exclusively, with little to no transesterification reaction, as is also suggested by the results of our statistical analysis. Subsequently, at higher temperatures and/or given sufficient time, transesterification reactions allow the cured material to fully relax strain-induced stresses. To the best of our knowledge, such a sequentially triggered dual-adaptation behavior has not been documented before. As can be seen in Figure 3 (left), at 160 °C, the normalized relaxation modulus starts to flatten at ca. 10 min. This is followed by several hours of practically stagnant behavior, after which a slow relaxation process commences, driven by transesterifications. Full relaxation is achieved after 35 h.

All in all, either by providing sufficient disulfide content or by increasing the processing temperature, full recyclability can be achieved in these thiol–ene dynamic networks. One caveat of high-temperature reprocessing is the possible thermal degradation that jeopardizes mechanical properties especially after consecutive processing cycles. Whereas the former strategy relies solely on disulfide exchange which are very fast, the latter strategy relies on transesterifications which are several orders of magnitude slower. The statistical analysis showed that to be able to recycle exclusively by disulfide exchange, DAG contents higher than 89% by weight are required. Experiments showed, however, that full recycling at low temperature is possible for DAG loadings as low as 75% by weight. The discrepancy between the theoretical prediction and the experimental findings is believed to be a result of some intramolecular cyclization during cure, and some slow transesterifications occurring at low temperatures. The underlying assumption of the analysis was that all S–S bonds would be cleaved if strain is maintained. One can also study a strain-free case by introducing the chemical equilibrium constant for disulfide exchange and derive expressions for the relevant network parameters based on the same fragments. However, an additional bifunctional allyl fragment containing an uncleaved S–S bond, whose fraction depends on the equilibrium constant, would have to be defined for such an analysis. To further increase the accuracy of the analysis, the effect of intramolecular cyclization can also be considered by defining cyclization probabilities in a number of ways. A comprehensive modeling study is underway in which all these aspects are included.



**Figure 3.** Normalized relaxation modulus of DAG50 at 160 °C (left). Tensile response of recycled DAG50 material in 3 reprocessing cycles (right). A photo of the circular disc obtained from the hot press is given as an inset.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsapm.2c02136>.

Experimental methods, NMR spectrum of the DAG monomer, chemicals used in the study, DMA  $\tan \delta$  curves of all formulations, analysis of stress relaxation kinetics, and calculation of network parameters using the statistical network build-up model based on structural fragments (PDF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

The authors acknowledge the funds provided by the Spanish Ministry of Science and Innovation (MCNI/AEI) through R&D projects PID2020-115102RB-C21 and PID2020-115102RB-C22, and also by Generalitat de Catalunya (2017-SGR-77 and BASE3D). O. Konuray and X. Fernández-Francos acknowledge the Serra Húnter programme (Generalitat de Catalunya).

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