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# Interpenetrated Triple Network Polymers: Synergies of Three Different Dynamic Bonds

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## Abstract

An ongoing challenge in soft materials is to develop networks with high mechanical robustness while showing complete self-healing and stress relaxation. In this study we develop triple network (TN) materials with three different polymers with distinct dynamic linkers (Diels-alder, boronic acid-ester and hydrogen bonding). TN materials exhibit significant improvement of strength, stability and excellent self-healing properties simultaneously compared to their analogous double networks (DN). All the TNs (TN-FMA 5%, 7% and 9%) show higher tensile strength over all DNs. In addition, TN-FMA (9%) demonstrates excellent fracture energy over 20000 Jm<sup>-2</sup>, 750% elongation and fast stress relaxation. This highlights how dynamic bonding multiplicity and network structure can play a major role in improving the quality of dynamic materials.

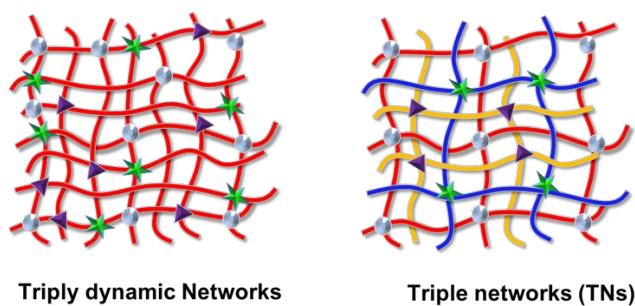
## Introduction

Tuning the network structure of interpenetrating networks (IPNs) has drawn a tremendous attention of scientific community due to resulting property enhancement.<sup>1</sup> These advanced structures lead to polymers with superior fracture energy, toughness, elasticity, and mechanical strength, making them promising candidates for various industries such as tires, seals, gloves, and other medicinal application.<sup>2-5</sup> IPNs consist of multiple networks that are not covalently crosslinked with each other but woven into a 'mesh' like structure by sterics and entanglements.<sup>2,6,7</sup> Interchain entanglement forces or cohesive forces lock the structure of the IPNs resulting improved

network percolation than that of Single Networks (SNs).<sup>8,9</sup> In contrast to IPNs, SNs comprise one type of network covalently bonded between all possible parts of the materials.<sup>10</sup> However, the reduced energy dissipation mechanisms of SNs resulted weak and poor toughness in materials and limited their functions in practical applications.<sup>11–13</sup> Double Networks (DNs), a subcategory of IPN were introduced in 2003 and significant research has been conducted to understand the origins of the superior properties of DN. <sup>1,11,14,15</sup> DN consist of two networks interpenetrated with each other, typically with highly disparate structures and crosslink densities, resulting in hydrogels or elastomers with excellent mechanical properties compared to their individual components.<sup>4,16</sup> However, most of these DN materials are static, with energy dissipation arising from irreversible cleavage of covalent bonds.<sup>17</sup>

Recently, the DN concept has been extended into Triple Networks (TNs) to optimize the material properties beyond those of the existing DN materials.<sup>5,12,18–22</sup> Most Triple Networks are formed by the addition of a third component into a DN, necessitating three network forming reactions.<sup>2,3</sup> Significant effort has been devoted to investigate the improvement of properties of TNs.<sup>3,5,11,21</sup> Yet, the majority of TNs developed to date non-dynamic linkers.<sup>3,5,23</sup> The incorporation of dynamic or reversible bonds into TNs is an interesting way of developing materials with better tunability and adaptiveness through a modular approach. Many studies have shown that SN materials have enhanced mechanical properties by the introduction of dynamic covalent and dynamic non-covalent bonds individually or as a combination into SNs and DN. <sup>24–29</sup> A combination of different crosslinks in one material offers complementary properties such as improved strength, fast shape recovery and toughness.<sup>27,30–32</sup> However, it is still a challenge to simultaneously obtain high mechanical properties and fast (within 1 day), complete self-healing recovery under ambient conditions.

Previous studies have reported triply dynamic networks and triple networks with enhanced mechanical properties.<sup>3,5,23,33</sup> Despite the excellent progress in materials synthesis and development there is still opportunities to enhance the triply dynamic materials' recovery healing times,<sup>33</sup> self-healing efficiency,<sup>5,23</sup> elasticity,<sup>3,5,23</sup> and fracture toughness.<sup>3</sup> As a critical example, Zhang et al. designed an outstanding triply dynamic material with high mechanical strength.<sup>33</sup> They combined the metal-coordination, hydrogen-bonded and dynamic covalent urethane linkers into a single polymer chain, which ultimately resulted triply dynamic SNs. These materials reached 100% self-healing efficiency at room temperature, although this required 130 h (over 5 days).<sup>33</sup> Since most materials in day-to-day life have high heat resistance, it is desirable to obtain fast self-healing materials under heat rather being slow at room temperature. In addition, Ducrot et al. synthesized TN polymer materials with excellent properties by introducing sacrificial bonds.<sup>3</sup> Although their materials showed excellent strength, their elongation and fracture toughness were relatively modest.<sup>3</sup> To the best of our knowledge, a modular approach to design complete dynamic TNs has not been explored yet. Existing reports either have TNs with dynamic bonds only in part of the networks, bypassing the benefits of a hierarchical sequence of dynamic linkers, or the triple dynamic linkers are on a common backbone, thereby without the benefit of modular network synthesis and interpenetration.

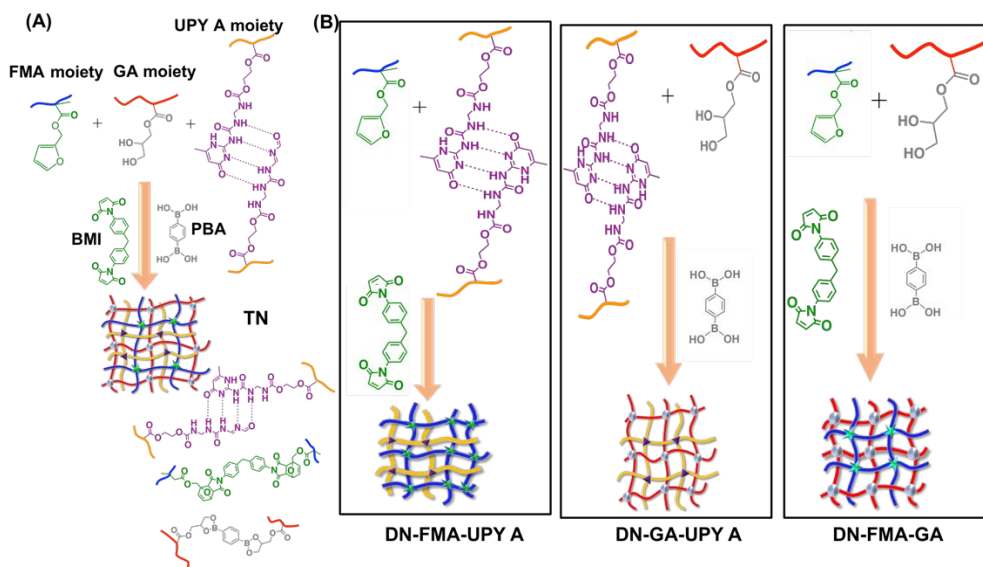


Scheme 1: Difference between triply dynamic networks and Triple network approaches

Diels-Alder chemistry, boronic ester chemistry and hydrogen-bonding (H-bonds) are three distinctive dynamic chemistries that can be used in building multidynamic networks. UPy units are one of the most popular H-bond crosslinking motifs due to their simple synthesis, high association constant and versatility.<sup>34</sup> UPy units form both end-to-end dimers via quadruple H-bond and stacks, thereby improving the mechanical strength, toughness as well as elongation due to the dissociation of UPy units upon stretching<sup>34</sup>. The pendant furan group in FMA can undergo a Diels-Alder reaction with an electron poor alkene. The Diels-Alder adducts are thermoresponsive motifs which are static under ambient conditions and dynamic upon heating via retro-Diels-Alder reaction. This static nature of Diels Alder adducts provide stable materials at room temperature exhibiting high creep resistance<sup>35,36</sup>. In contrast to these two linkers, the reversibility of the boronic ester and boronates can be activated even at the humidity in room temperature thus provide adaptable self-healing and reprocessable materials to many environments.<sup>37,38</sup> Combination of these three distinct linkers with different time scales will provide adaptable materials with high mechanical robustness. Further, incorporation of each linker onto its own polymer chain enables a modular approach to materials design, as well as facilitating effects such as entanglements and network dynamics typical of IPNs. Nevertheless, these chemistries have been employed individually or as pairs to design SNs and IPNs including DN and TNs to attain excellent mechanical properties.<sup>39-42</sup>

This study develops a novel triple network elastomer using a combination of dynamic covalent (Diels-Alder and boronate ester) and non-covalent (H-bonds) bonds to improve the mechanical robustness and dynamic characters of the materials. Polymers with pendant 2-ureido-4[1H]-pyrimidinone acrylate (UPyA), furfuryl methacrylate (FMA) and glyceryl acrylate (GA) were synthesized, combined, and finally crosslinked to acquire the TNs with an orthogonal

dynamic linker in each network (Scheme 2). Individual network components in the triple network elastomer were orthogonally crosslinked in one pot to yield the TN. Enhanced strength and fracture energies are expected, through the synergy between three unique linkers and the triple interpenetration, both of which are anticipated leading to an effective energy dissipation. Further, introducing UPy and boronic ester bonds can accelerate the dynamic exchanges under ambient conditions, yield efficient stress relaxation, in addition to the energy dissipation properties. Finally, the Diels-Alder units are introduced as static linkers at room temperature for strength and creep resistance, with full dynamic character upon heating leading to full self-healing in 24h.



Scheme 2: Schematic representation of the synthesis of networks (A) Preparation of TNs. BMI (1-[4-[[4-(2,5-dioxopyrrol-1-yl)phenyl]methyl]phenyl]pyrrole-2,5-dione) PBA (Phenyldiboronic acid) (B) Preparation of DNPs

## Results and discussion

Ethyl acrylate was used as the backbone monomer for all three polymers synthesized using free radical polymerization. Each polymer was synthesized by introducing the crosslinker separately. Each polymer synthesized was soluble in the polar mixed solvent of methanol: N,N-

dimethylformamide (DMF) in a 1:1 mixture. DNs and TNs were prepared by mixing particular polymers in 1:1 ratio/1:1:1 ratio (by weight) respectively. Polymers with each crosslinkers are denoted as poly-UPyA, poly-FMA and Poly-GA. Three types of DN materials with UPyA, GA and FMA were prepared to compare the material properties with TNs: DN-FMA-UPYA, DN-FMA-GA and DN-GA-UPYA. A series of TNs were prepared by using different amounts of FMA (5%, 7%, 9%) in the material and are named as TN-FMA (5%), TN-FMA (7%) and TN-FMA (9%). The FMA crosslink density alone was varied in the TN materials since the essentially permanent crosslinks at room temperature, arising from FMA based Diels-Alder linkages, can be used to modulate the materials strength and modulus. In contrast, efficient energy dissipation and transient hydrogen and boronic ester bond exchanges are anticipated while allowing a focus on the essentially permanent linkers under ambient conditions.

The materials were subsequently dried and analyzed by infrared spectroscopy. As seen in Figure S13, negligible amounts of solvents remained, with no peak at  $1500\text{ cm}^{-1}$  in any sample, which is attributed to the C-N stretch of DMF.<sup>43</sup> Tensile test, fracture energy test, frequency sweep, self-healing, creep recovery and stress relaxation were carried out to evaluate the properties of these materials.

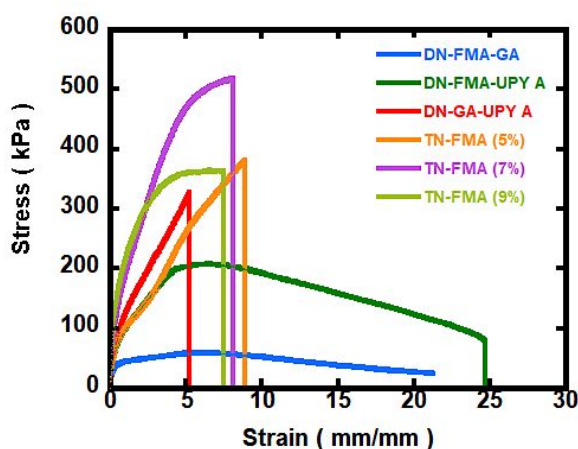
**Table 1:** Properties of materials, stress at break, strain at break, Fracture energy and glass transition temperature ( $T_g$ ). <sup>a</sup> Values are calculated as an average of the stress at break and maximum stress (n=3). <sup>b</sup> Values are calculated as an average of the strain at break and maximum strain

<i>Entry</i>	<i>Network Composition</i>	<i>Stress at break (kPa)</i>	<i>Strain at break (mm mm<sup>-1</sup>)</i>	<i>Fracture Energy (Jm<sup>-2</sup>)</i>	<i>T<sub>g</sub> (°C)</i>
1	DN-FMA-UPY A	110 <sup>a</sup> ± 30	20 <sup>b</sup> ± 5	34000 ± 3000	-12.2
2	DN-FMA-GA	25 <sup>a</sup> ± 4	20.5 <sup>b</sup> ± 0.7	7600 ± 500	-10.4
3	DN-GA-UPY A	290 ± 60	6.0 ± 0.7	3300 ± 600	-8.8
4	TN-FMA (5%)	370 ± 70	8 ± 1	6600 ± 100	-11.0
5	TN-FMA (7%)	510 ± 40	8.3 ± 0.9	10000 ± 1000	-9.3
6	TN-FMA (9%)	350 ± 50	6.7 ± 3.8	21000 ± 2000	-8.7

All materials show similar  $T_g$  values, determined by DSC. These DSC data (Fig.S1) reveals that both DNs and TNs have similar backbone mobility conferring similar thermal properties in all samples (Table 1). In the TN materials (Table 1, entry 4 to 6) there is a measurable increase in  $T_g$  moving from the 5% to the 7% FMA system, and a slight increase in  $T_g$  moving from the 7% to the 9% system. The increase in  $T_g$  with higher crosslink density is expected, although the small change between 7% and 9% FMA could be due to clustering of the Diels-Alder linkers, rather than well percolated crosslinkers through the matrix. Typical stress-strain curves for all materials are given in figure 1. DN-FMA-UPyA and DN-FMA-GA networks displayed large strain at break (~2000%) compared to all the other materials (Table 1). Although they have higher elongation, all DNs exhibit low stress values compared to TNs. Specially, DN-FMA-GA has a very low peak stress value of 50 kPa. This is possibly due to the limited number of chain intertwining and fewer



entanglement forces, combined with the rapid exchange of both the boronate and the UPy linkers in the particular DN systems. In contrast, TN materials exhibit greater number of entanglements, hence stronger intermolecular locking forces, which could lead to a stronger material. Increasing the FMA amount from 5% to 7%, raised the effective crosslinking points in the essentially permanent linkers, improving the tensile strength of the TN systems. However, further increasing the FMA percentage from 7% to 9% did not give substantial improvements in the tensile strength, with negative impacts on the strain at break. This could be due to the accumulation of Diels-Alder linkers as clusters within the network during the crosslinking process, which could be weaken the overall network structure.

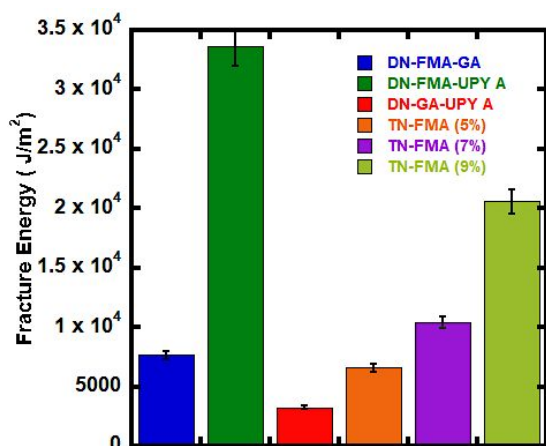


**Fig 1:** Stress-strain curves for all DNs and TNs

Fracture energy was measured by the paired “notched” and “pristine” approach described in the literature.<sup>44</sup> Notches were introduced into each “notched” specimen to half of the sample’s width. Each notched sample was extended to the break of the “notched” sample. The mean strain at which the notched samples fail, or fracture strain, is denoted as  $\epsilon_{\text{notch}}$ . The fracture energy ( $\Gamma$ ) is evaluated using the equation below:

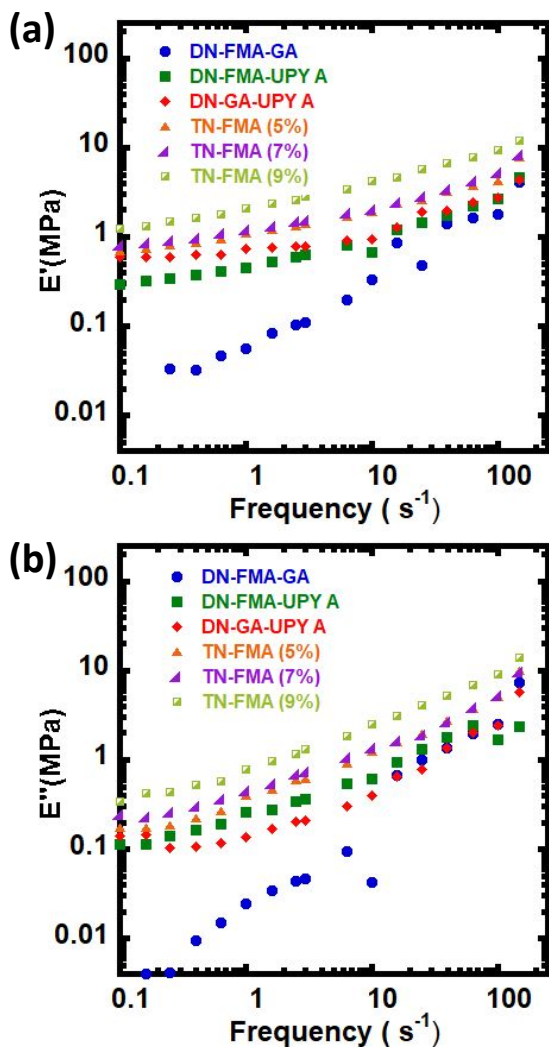
$$\Gamma = h \int_0^{\epsilon_{\text{notch}}} \sigma d\epsilon \quad (1)$$

Where  $h$  is the “pristine” sample’s initial height,  $\sigma$  is the “pristine” sample’s stress, and  $\varepsilon$  is the “pristine” sample’s strain. Calculated fracture energies for all the materials are shown in figure 2. In general, TN systems demonstrated relatively higher fracture energies compared to the DN systems except for the DN-UPYA-FMA. The DN-UPYA-FMA had the highest fracture energy ( $34000 \pm 3000 \text{ J/m}^2$ ) compared to all other materials. This excellent fracture energy is primarily due to the large fracture strain ( $\varepsilon_{\text{notch}}$ ) observed in DN-FMA-UPYA and was consistent with its excellent tensile properties shown in Fig 1. Otherwise, its fracture stress is closer to the TN-FMA (5%). The Fracture energies of TN materials improved with the increment of FMA percentages in the networks resulting the highest fracture energy for TN-FMA-(9%), which is  $21000 \pm 2000 \text{ J/m}^2$ . It is worth noting that, these novel TN materials can be modulated through crosslink densities to obtain superior fracture energies and tensile strengths without yielding. In contrast, the DN-UPYA-FMA material had excellent fracture energy but relatively poor tensile strength and significant yielding characteristics.



**Fig 2:** Fracture energy of DN and TN. Fracture energy was calculated by testing “cut” and “uncut” materials taking the average

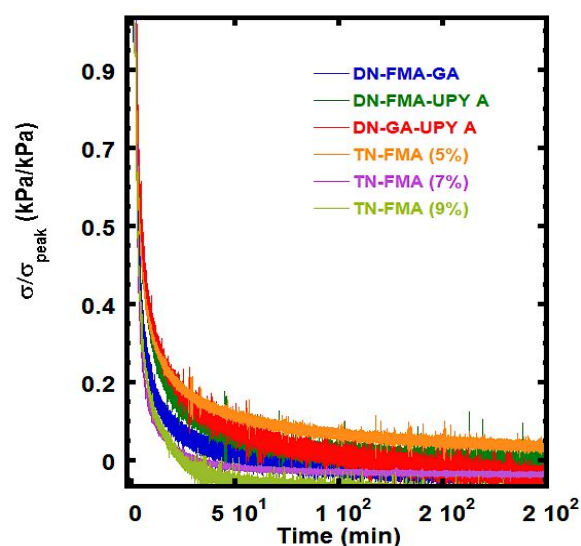
Further, the DNs, and TNs were characterized through the dynamic mechanical analysis experiments. Moduli of the materials were characterized by frequency sweep experiments as shown in figure 3. As predicted, TNs displayed a higher storage and loss moduli compared to DNs in frequency sweep experiments and was in accordance with our hypothesis. The superior internetwork entanglements and increment in effective crosslinking points contributed to improve the moduli in TN systems. This suggests that both the ability to store energy, through higher crosslink density, as well as dissipate energy through exchange of dynamic bonds is improved in the TN compared to the SN. In addition, these frequency sweep data revealed that the storage modulus and loss modulus increase with the FMA percentage in the system by showing the highest storage and loss modulus in TN-FMA (9%) and least in TN-FMA (5%). This agrees with the common trend where the crosslinking density is proportional to the storage modulus.<sup>10</sup>



**Fig 3:** Frequency sweep data for DN and TNs. (a) Storage modulus ( $E'$ ) and (b) Loss modulus ( $E''$ ) were shown.

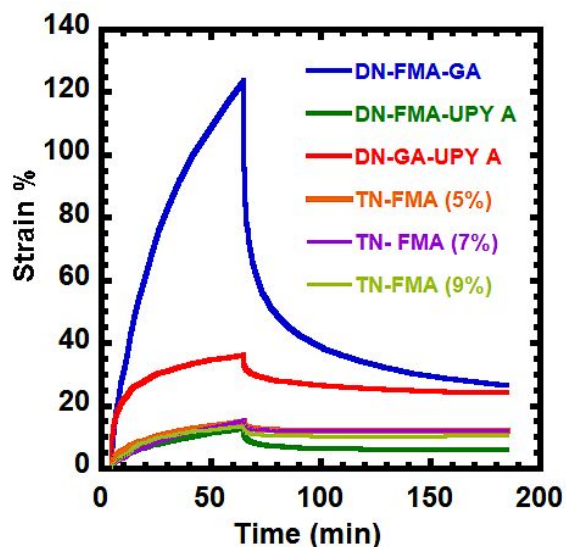
To investigate the bond exchange timescales, stress relaxation experiments were conducted by applying constant 20% strain. Figure 4 illustrates the stress relaxation curves for materials over 4 hours. Stress relaxation results revealed that all materials display essentially full relaxation within one hour under constant strain (Figure 4). The stress relaxation data were fitted with a stretch exponential function, yielding relaxation times on the order of 100 s for each system. The relaxation time and the exponent of the stretch exponential for each material are given in Table S1. Faster stress relaxations were observed for TNs compared to DN. However, TN-FMA (9%)

showed slower relaxation compared to TN-FMA (7%). This is possibly due to the cluster formations of the TN-FMA (9%) sample which led to poor homogeneity of crosslinkers. Relaxation of these each cluster can be varied resulting unexpected slower relaxation compared to TN-FMA (7%). This excellent stress relaxation could arise from the faster exchange dynamics of UPyA and Boronic ester dynamic systems at the room temperature,<sup>34,37,38</sup> while DA bonds contribute minimally due to its essential stimuli responsive nature at elevated temperature.<sup>35,36</sup>



**Fig 4:** Stress relaxation of materials. 15 points average of stress was calculated to plot the graph.

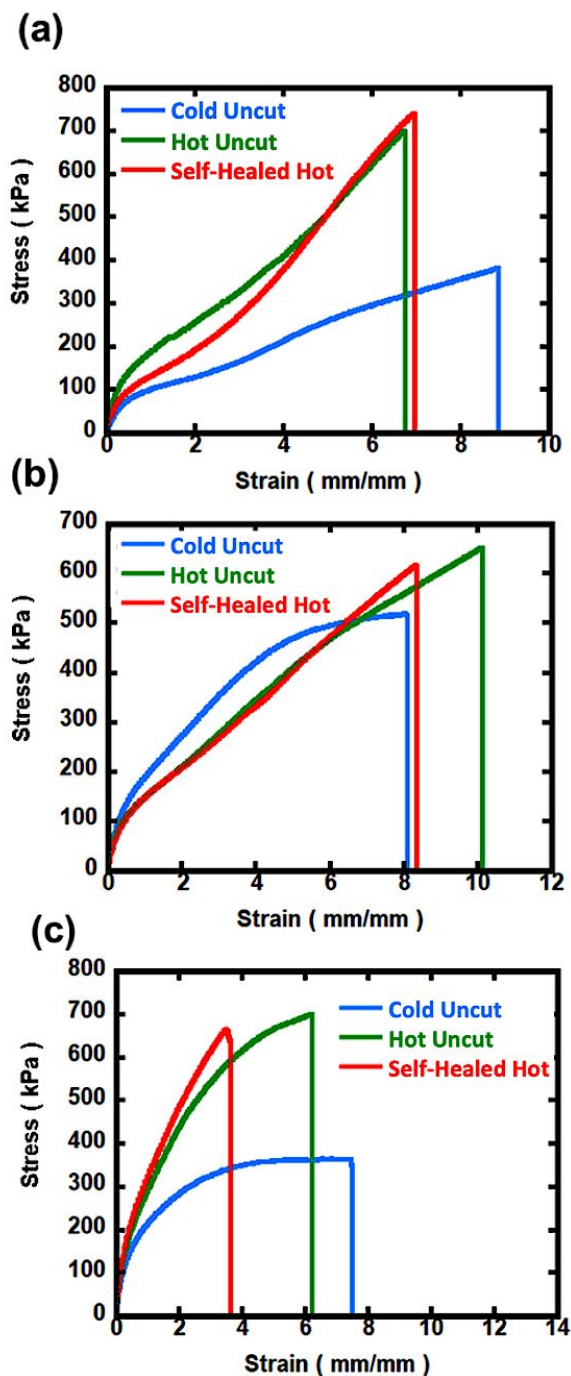
Stability of the materials at near ambient conditions were investigated by conducting creep and creep recovery experiments (Figure 5). Creep and creep recovery results indicated that all materials have high creep resistance except DN-FMA-GA and DN-GA-UPYA. In particular, the TNs had vastly superior creep properties to the DN-FMA-GA and DN-GA-UPyA Surprisingly, all TNs (5%, 7%, 9%) show similar creep and creep recovery.



**Fig 5:** Creep and creep recovery curves for all materials by applying 5 kPa stress for 1 h and 2 hrs. of applied stress for recovery.

The dynamic properties of the TNs were further evaluated using self-healing experiments as shown in figure 6. In this test, materials were heated at 90°C for 24 h. Heating improved the tensile stress of the materials, which could be due to the reduction of defects in the systems during heating.<sup>10</sup> All TNs showed essentially complete stress recovery within 24 h. This excellent self-healing and recovery of peak stress could be a consequence of the activation of exchange dynamics of all three reversible bonds in the systems with the addition of heat as an external stimulus. Both 5% and 7% materials displayed significantly greater self-healing profiles. However, TN-FMA (9%) samples showed ~60% recovery of the strain. The poorer healing in the TN-FMA (9%) materials could be due to the potential of crosslink-cluster formation in the network, which can inhibit effective exchange of all the DA linkers, limiting the full extensibility of the particular material. In this case, most of the crosslinks could recover, leading to good recovery in stress, yet cluster formation could prevent full percolation of the crosslinks, limiting elasticity. The DN-FMA-GA materials exhibited good self-healing efficiency than DN-FMA-UPY A and DN-GA-

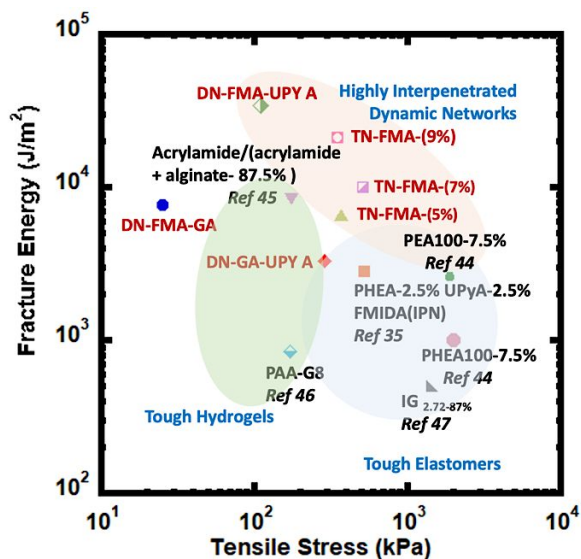
UPY A materials. However, the tensile stress of self-healed DN materials is still lower than TNs (Figure S2-S4).



**Fig 6:** Self-healing results for TN materials heated at 90°C for 24 hrs. Unheated materials is denoted as “cold uncut”. 24 h heated uncut materials are denoted as “hot uncut” (a) Self-healing curves of TN-FMA (5%) (b) Self-healing curves of TN-FMA (7%) (c) Self-healing curves of TN-FMA (9%)

A summary of the synthesized DN and TN materials in this work, as compared to other comparable materials in the literature<sup>35,44-47</sup> is given in Figure 7 in an Ashby plot. Foster and et al. reported doubly dynamic materials crosslinked with UPY A (2.5%) and FMA (2.5%) linkers.<sup>35</sup> In 2020, Cummings et al. designed dynamic hydroxyethyl acrylate and ethyl acrylate materials using UPY A crosslinker. In their study, they demonstrated the effect of the matrices on the properties of the materials.<sup>44</sup> Cao and et al synthesized strong poly(ethylacrylate)-based elastomers hydrogen bonded with ionic liquids at room temperature.<sup>47</sup> In their work, the tunability of materials properties using the effect of crosslinker concentration in the first network was studied. In 2020, Lei and the coworkers reported a polyacrylamide (PAA) hydrogel crosslinked with eight tandem repeats proteins (G8).<sup>46</sup> They studied the effect of the crosslinker composition for the mechanical behaviors of the PAA-G8 hydrogel.<sup>46</sup> Sun et al reported a stretchy tough hydrogel using acrylamide and alginate. They have changed the weight ratios of acrylamide to acrylamide plus alginate to study the reason of the higher stretchability of the materials.<sup>45</sup> In general, the TN materials show better strength and fracture energy combined properties, suggesting this is a viable strategy for new materials development.





**Fig 7:** Summary of Tensile stress, Fracture energy and the creep resistance of all DNs and TNs (labeled in red) compared to several materials in the literature.<sup>35,44–47</sup>

## Conclusion

In summary, we designed and synthesized a novel TN material with enhanced mechanical properties including tensile strength, good stability, fast relaxation, highest modulus while giving better self-healing efficiency. These TNs contained three orthogonal dynamic bonds, dynamic hydrogen bonds through the UPy linker, dynamic boronate esters, and thermally responsive furan-maleimide Diels-Alder adducts. The TNs were all stronger than their double network counterparts, confirming that network multiplicity has strengthened the polymer network. In addition, all TNs have higher creep resistance than the DN-FMA-GA and DN-GA-UPY A. The modular approach enables the synthesis of materials with distinct crosslink densities in each network to be synthesized. This leads to targeted properties such as, TN-FMA (9%) having a high fracture energy of  $20580 \pm 2212$  J/m<sup>2</sup> and the highest modulus. Additionally, due to the synergies of the crosslinks, all triple networks show ~100% self-healing stress recovery after heating at 90°C for 24 hrs.

## Conflicts of Interest

The authors declare no conflicts

## Acknowledgments

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