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Dynamic Covalent Chemistry for Architecture Changing Interpenetrated and Single Networks

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Abstract:

Interpenetrating networks (IPN) comprise two or more networks which are woven but not covalently bonded to each other. This is in contrast to simple, or single Networks (SN), which contain only one network that is covalently crosslinked. This study develops SNs and IPNs using 2-hydroxyethyl acrylate as the monomer and (2-((1-(2-(acryloyloxy)ethyl)-2,5-dioxopyrrolidin-3-yl) thio)ethyl acrylate) (TMMDA) as a thermoresponsive dynamic thiol-Michael crosslinker. In the case of the IPN and SN materials the TMMDA is used as a thermoresponsive linker in each network, since TMMDA undergoes dynamic covalent exchange above 90 °C. In this way the SN and IPNs are kinetically trapped in their as synthesized structures until exposed to thermal stimulus. The focus of this study is to investigate how dynamic bond exchange can modulate material properties, after the material has been synthesized using the SN and IPN materials as model systems. The dynamic nature of the thiol-Michael crosslinker allows the transition of IPNs into SN like structures above 90 °C resulting in similar polymer architecture in both SN and IPN. Surprisingly, upon heating the SN materials also changed their mechanical properties, upon activation of the dynamic thiol-Michael bonds. This enhancement is proposed to occur by thermally activating the thiol-Michael bonds and reducing the number of floppy loops at higher temperature.

Introduction:

The majority of polymers synthesized are static under ambient conditions and not adaptable. This gives polymer materials, especially thermosets, strength and stability but limits their recyclability and ability to be modified for various applications. Recently, materials with bonds that are exchangeable under relevant conditions called "dynamic" materials have drawn significant attention due to their unique functional properties such as self-healing, shape memory, adaptability and degradability.[1–8] These dynamic bonds are most frequently incorporated into the network through a crosslinker, enabling crosslinked thermoset materials to have adaptable properties.[9,10]

Dynamic linkages can be categorized into two types: non-covalent / supramolecular linkages [9,10] and dynamic covalent linkages.[8,11–16] Different dynamic bonds have different time scales that can span from seconds to days.[17–21] Boronic esters, imines, disulfides, Diels Alder adducts, anthracene dimers, Michael adducts and dynamic urea bonds [2,22–24] are common dynamic covalent bonds which exchange under external stimuli. Among them, thiol-Michael adducts has been studied widely in past few decades as a bioconjugation technique, ligation technique and a method to insert functional groups into polymers.[20–22,25–30] The facile "click" synthesis of the adducts, and relatively accessible reversible nature of thiol-Michael bonds are some attractive features of these thiol-Michael linkages as dynamic covalent bonds in polymer materials.[31,32]

Recently, several research groups introduced dynamic covalent bonds into single networks as well as interpenetrated networks. Interpenetrated networks, including the "Double Networks",

have become more popular due to its ability to enhance and introduce new properties to the material. [33–35]

Interpenetrated Networks comprise two or more networks which not covalently bonded each other, but rather they are interpenetrated or woven through each other.[36] The golden era of these Interpenetrated Networks (IPNs) started in 1914.[37–40] These networks can be thought of as "alloys" of crosslinked polymers.[41] Although the two networks are not covalently bonded to each other, networks cannot be isolated unless bonds are broken to extract the individual polymer chains. [41] The larger number of entanglements in IPNs create 'entanglement forces' or 'cohesive force' which can act as intermolecular locking forces within the networks.[42,43] Based on their synthesis IPNs can be categorized into groups such as simultaneous, latex, gradient, thermoplastic, semi and sequential IPNs. In simultaneous IPN, all monomers, activators and crosslinkers are mixed together, with both networks polymerized simultaneously. If the IPN is made from latex it is called a "latex IPN", where two latexes are combined with a crosslinker to form a film. A gradient IPN has a drift of composition or crosslinking density throughout the network. Thermoplastic IPNs are moldable and considered as blends of two polymers. Usually, they are crosslinked with physical crosslinkers instead of chemical crosslinkers. Semi IPNs contain one or more components which are soluble linear or branched polymers in a crosslinked network.[36] This article focuses on sequential IPNs where the monomer and crosslinker are initially polymerized into a network, followed by subsequent swelling and polymerization with additional monomer and crosslinker to make a second network. This results in an IPN material, although the same dynamic linker is used in both networks within the IPN, and the use of a crosslinker in all networks differentiates an IPN from a semi-IPN. [36,37,44]

In this study we introduce a thermoresponsive dynamic thiol-Michael bond into both SN and IPN materials through a crosslinker that dynamically exchange above 90 °C [30]. Although thiol-maleimide adducts can undergo hydrolysis under in the presence of water, leading to a non-dynamic linker, the absence of water, base or substantial quantities of free thiols in this system suggest that such hydrolysis and loss of dynamic maleimide functionality is likely to be limited in this system.[45]

Here SN refers to a network where there should be a pathway of covalent bonds between all parts of the material, as opposed to IPNs, where the two networks are connected by steric and entanglements, but not covalent bonds. The materials synthesized here contain the same dynamic linker in both networks in the IPN, allowing the material to undergo macromolecular changes or "metamorphosis".[46] The SN and IPN materials consist with same thiol-Michael crosslinker, based on the thiol-maleimide linkage, allowing transition between these two distinct architectures and adaptation of SN like materials. The main objective of this study is to compare mechanical and thermal properties of SN and IPNs, and to study how the activation of bond exchange can change the underlying material properties. Such macromolecular changes are possible due to the dynamic bonds in the material. The dynamic nature of the thiol-Michael crosslinker allows the transition of IPNs into SN upon thermal stimulus resulting similar polymer architecture in both SN and IPN. Surprisingly, the SN materials also had enhanced mechanical properties upon thermal stimulus, and this is interpreted as the network correcting defects such as loops through dynamic exchange, a process which could not occur in the absence of dynamic bonding. In this way the focus of this study is to use the SN and IPN materials as model systems to evaluate how activation of dynamic chemistry can lead to changes in the material's structure which impact the bulk material's properties.

Results and Discussion:

For the synthesis of crosslinked 2-hydroxyethyl acrylate (HEA) materials, (2-((1-(2-(acryloyloxy)ethyl)-2,5-dioxopyrrolidin-3-yl) thio)ethyl acrylate) (TMMDA) wt 2% was incorporated into both Single and Interpenetrated Network polymer matrix. The single network (SN) and interpenetrated networks (IPN) were synthesized using conventional radical polymerization of HEA in the presence of 2 wt% TMMDA using N, N-dimethylformamaide (DMF) as a solvent. A single polymerization was performed for the SN synthesis where the monomer conversion was over 99%. The SN material was dried, and then swollen in a second quantity of HEA, 2 wt% TMMDA and initiator to generate the IPN with 94% monomer conversion. (Scheme 1). It is important to note that with the very high conversion in the first polymerization of over 99% of the monomer, there will be essentially no pendant double bonds available for polymerization or incorporation into the first network. In this way the first network, or the SN, is fixed under these conditions, and unable to react further and have more chains covalently connected to it. Therefore, upon the swelling of the SN with new monomer and crosslinker, the polymerization can only occur in the voids between the existing polymer, thereby forming an IPN. It is important to note that the IPN polymerization conditions are different in the second network, which could lead to some difference in the primary chain architecture in the first and second networks of the IPN. These materials are denoted as PHEA-TMMDA-SN and PHEA-TMMDA-IPN respectively. The as synthesized materials are referred to as "cold", while materials that have been heated for 24h at 90 °C are referred to as "heated".

Tensile, self-healing, creep recovery, temperature and frequency sweep experiments were carried out to study the properties of the PHEA-TMMDA material, as synthesized and as a function of bond exchange. Figure S1 gives the differential scanning calorimetry (DSC) data for the

materials. DSC shows that all materials have glass transition temperatures between 0 and 10 °C, indicating that each material should behave as a soft elastomer at ambient temperature. Infrared spectra were collected before and after heating both the SN an IPN materials (Figures S2-S5), indicating that all materials had essentially the same composition, and that heating did not cause appreciable changes in the functional groups present.
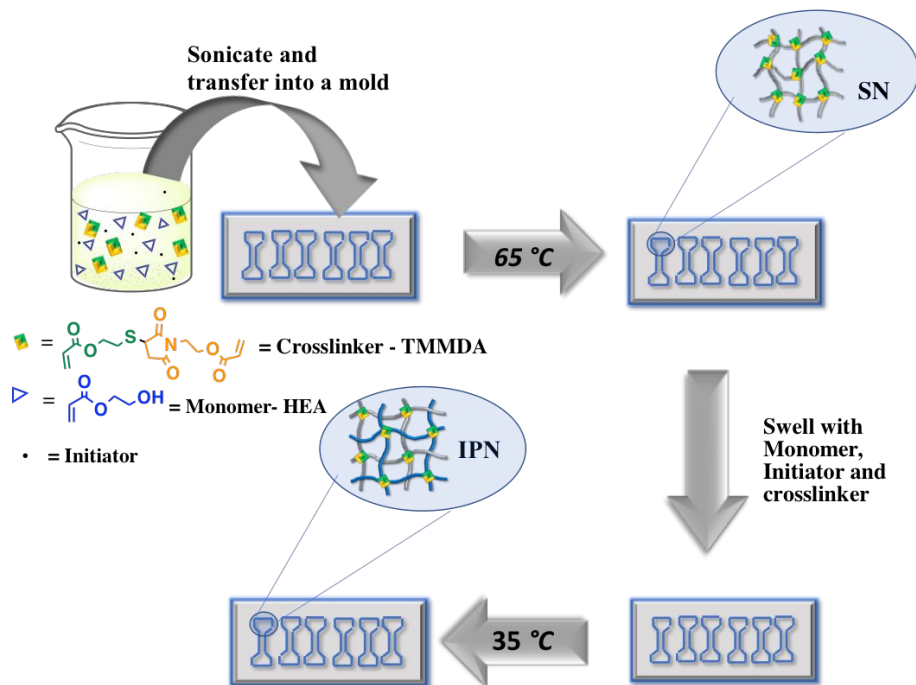
*Scheme 1: Schematic diagram of the synthesis of SN and IPN materials*

Temperature sweep experiments were carried out to study the behavior of the material during heating. As shown in the Figure 1a and 1b, temperature sweep results indicate that IPNs and SN have storage and loss moduli in the same order of magnitude, although the as synthesized IPN material had higher moduli. However, after heating the materials at 90 °C for 24 h before testing, the SN had a significant increase in the storage modulus (E') as seen in Figure 1a. The IPN materials also had an increase in storage modulus although this was relatively small increase in

the value of E' figure 1b. Indeed, the material properties after heating were similar for the IPN vs SNs, although the IPNs had a slightly higher value of E' at high temperature and a somewhat lower value of the loss modulus (E") across the whole temperature profile. Nevertheless, after heating the materials for 24 h at 90 °C, the mechanical properties of the SN closely matched the IPN structure, suggesting a shift towards similar morphologies. Similar effects are seen in the frequency sweep data given in Figure 2 where there is a substantial increase in E' for the SN material, with a modest increase in E' for the IPN material after heating the materials for 24 h at 90 °C. As with the temperature sweep data, the SN materials had lower moduli as synthesized compared to the IPN materials. After heating the samples at 90 °C for 24h the IPN and SN materials had similar mechanical properties. The enhanced mechanical properties of the IPN compared to the SN before heating are likely due to the two meshes of the IPN entangling and reinforcing each other.

The enhancement of mechanical properties of SN, and to a smaller extent the IPN, after heating could be due to the reduction of loops, or elastically ineffective linkers, created within the network during network synthesis. Johnson et al report that there could be loops created within the networks due to the self-crosslinking and internal crosslinking.[47–49] The networks were synthesized as relatively dilute polymerization solution, there is a higher possibility of having loops within the network. Intramolecular polymerization within chains is the one of the most common reason for those loops. Those loops can have a negative impact on the mechanical properties of the elastomers, since they do not percolate through the material and transduce forces, thus weakening the network and reducing the modulus.[48] The mechanical properties in the as-synthesized or cold SN are poorer than the IPN, since IPN has the second network which has enhanced entanglements and possibly lower total loops, since the second network is synthesized as a relatively more concentrated process. However, heating activates the bonds to exchange, and could reduce the

number of floppy loops created in the networks by allowing crosslinks to exchange into an network

with higher effective crosslink density. Figure 1C displays how heating can significantly reduce

the number of loops in the SN and increase the material's modulus. This is possible because the

TM dynamic bond exchange occurs after solvent is removed, enabling the unfolding of the loops

due to the higher concentration of polymer and crosslinker. It is important to note that the IR data

in Figures S2-S5 show no peak centered at 1640 cm^{-1},[50] which would correspond to unreacted

acrylic groups, and there is no appreciable change in the IR spectra before or after heating in these
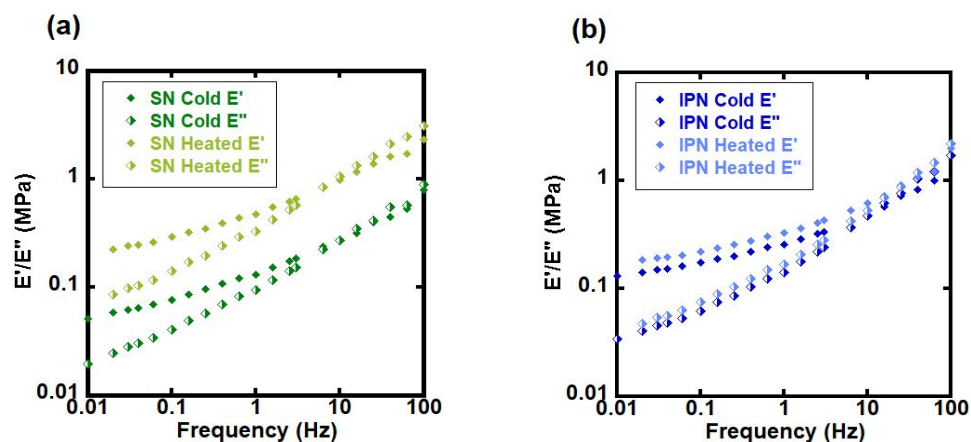
regions.

(a)

(b)
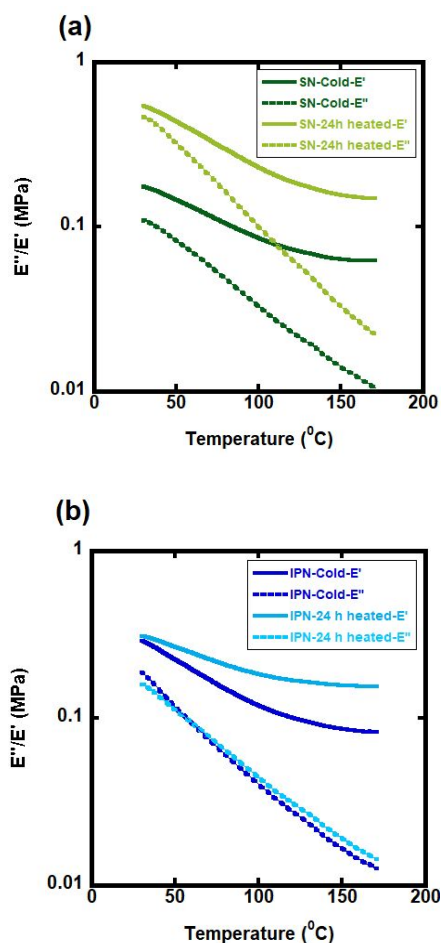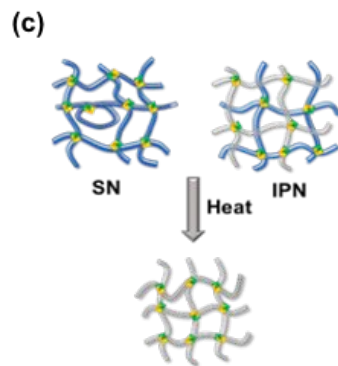
***Figure 1. (a) Temperature sweep results for cold SN and 24h heated SN. Storage(E') and loss modulus(E'')
of materials were shown. Samples heated at 90⁰C for 24 h denoted as '24h heated' and unheated samples
were denoted as 'cold'(b) Comparison of temperature sweep results for cold IPN and 24 h heated IPN. (c)
Schematic diagram of the transition of SN and IPN into a similar network.***

Stress-Strain curves for both the SN and IPN materials are given in figure 3. As shown in

figure 3, both cold SN and cold IPN followed a similar stress-strain profile. However, the IPNs

reached significantly higher peak stress and higher strain at break compare to SNs. IPNs had a

peak stress (σ_{peak}) around 148 kPa and strain at break (ε_{break}) around 4.7 where the SN had a σ_{peak}

around 95 kPa and ε_{break} of 4.6 respectively. (Table 1) The higher σ_{peak} and ε_{break} of the IPN could

be due to the higher effective cross-linking points per unit of IPN networks, as well as better

entanglements due to the IPN structure. A greater number of entanglements in the IPN induce

more 'entanglement forces' or 'cohesive forces.[42,43] These cohesive/entanglement forces can

behave as intermolecular locking forces of networks. This result higher strain at break point in

IPN. This data indicates that the IPN has higher stress-strain compared to SN due to its different

molecular architecture. Additionally, the 24-hour heated samples of both SN and IPN were tested

to investigate the effect of heating on the tensile properties. Interestingly, SN and IPN show

improvement of tensile strength once the materials are heated. Both heated materials show closely

similar stress values. The reason for the enhancement of tensile strength in the SN material is likely

due to the reduction of floppy, or elastically ineffective, loops created within the network. This

reduction in the elastically ineffective loops in the SN is likely to enhance both the σ_{peak}, as well

as the ε_{break}.

Figure 2. (a) Frequency sweep results for cold SN and 24h heated SN. Storage(E') and loss modulus(E'') of materials were shown. Samples heated at 90^0C for 24 h denoted as '24h heated' and unheated samples were denoted as 'cold'(b) Comparison of frequency sweep results for cold IPN and 24 h heated IPN

In addition, heating can enhance the strength of the IPN by inducing the transition of IPN

into a structure with fewer floppy loops as the material transitions to a SN like structure.

Interestingly, after heating and allowing bond exchange, the IPN materials had a slightly lower

ε_{break}. The lower ε_{break} of the IPN material after heating could be due to the second network in the

IPN having lower molecular weights than the first one, or clusters of higher crosslink density along

the backbone. As bond exchange promotes the transition from the distinct yet interwoven IPN to

a single network where all polymers are covalently bonded to each other, these defects now

become a part of the main polymer network. In particular, clusters of very high crosslink density

along the backbone, would likely form a relatively brittle material. Nevertheless, after heating the

σ_{peak} of the IPN material is similar to the SN material.

The mean Young's modulus for each material is given in Table 1, as determined from the Ogden model. Data shows that IPN has higher Young's modulus compare to the SN. Myung et al reports that higher physical entanglements of IPN lead to higher stiffness of the material which is proportional to the Young's modulus. [51] However, due to reduction of loops and concentrated polymer, both heated samples show an increase in the Young's modulus compared to the unheated samples.

Additionally, equations S1 and S2 allow the evaluation of the molecular weight between crosslinks (M_c) from the shear modulus (G), where G is determined from the low frequency limit of the frequency sweep DMA data in Figures 2. To evaluate M_c, the materials were assumed to be incompressible with a density of 1.29 g/mL [52,53] These data shows that the synthesized IPN has lower M_c value than SN. Larger M_c value suggests that the network has large distance between two crosslink points. Floppy loops in the network can lead to larger M_c. This suggests that SN has more loops compare to IPN.

In evaluating the contribution of floppy loops to the overall material, the mole ratio of monomer to crosslinker is 143:1, which would give on average 143 HEA monomers between crosslinkers, Therefore, the molecular weight between two crosslinking points should be around 16,600 g/mol, assuming perfect network percolation and no floppy loops. However, the experimental M_c values that we obtained are range from 39,000-153,000 g/mol which are much larger than the theoretical value determined from the stoichiometry, assuming no loops in the material. The significant discrepancy between the M_c determined from the modulus, and the M_c value anticipated from the monomer to crosslinker stoichiometry supports the hypothesis of the formation of floppy loops in the networks. A greater number of loops will decrease the number of crosslink points in the single

network leading higher M_c value. The heated SN and IPN materials had lower M_c values, which

is attributed due to the reduction of loops created in the network enabled by the dynamic chemistry.

Table 1: Properties of Materials, Stress at Break (σ_{peak}), Strain at Break (ε_{break}), Glass transition Temperature (T_g), Young's Modulus and average molecular weight between cross-links (M_c).

		σ_{peak} (kPa)	ε_{break} (mm/mm)	T_g (°C)	Young's Modulus (kPa)	M_c (kg/mol)
IPN	cold	150 ± 30	4.7 ± 0.7	3	31 ± 5	65
	24 h Heated	271 ± 7	3.9 ± 0.4	3	90 ± 10	49
SN	Cold	95 ± 7	5 ± 1	6	17 ± 3	153
	24 h Heated	230 ± 20	6.5 ± 0.5	9	40 ± 3	39
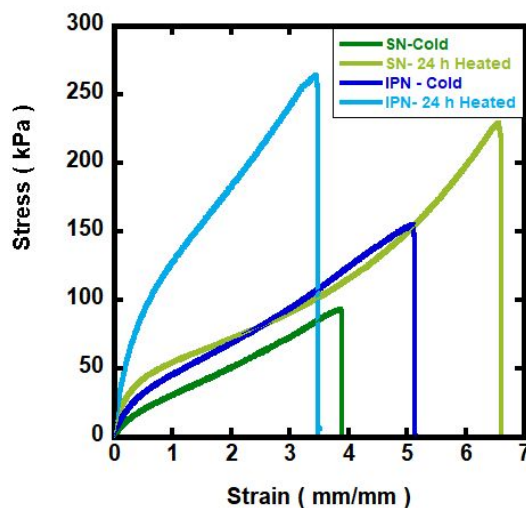
Figure 3: Stress-strain curves for SN and IPN. Samples heated at 90^0C for 24 h are denoted as '24 h heated' and unheated samples named as 'cold' samples.

Creep and creep recovery experiments were conducted to confirm the stability of the

material by applying a 10 kPa stress for 1 h, followed by a 2 h period of no applied stress to allow

recovery. Figure S6 shows the behavior of the materials under a stress of 10 kPa. Higher effective

cross-linking density and more entanglements of IPN make it more resistant to creep than the SN

in the cold, or as synthesized material. However, after both materials were heated for 24h at 90 °C

both materials behave as similar networks, although the IPN is still somewhat more creep resistant. This agrees with the general findings of the temperature sweep and frequency sweep data. Reducing elastically ineffective loops and increasing the effective crosslink densities in both materials upon heating leads to better creep resistance. Importantly, all materials show almost 100% creep recovery within 2 h due to the essentially static nature of the thiol-maleimide adducts at ambient temperatures.

The dynamic nature of the materials were investigated by conducting self-healing experiments. In this experiment, recovery properties of cut samples in both SN and IPN were measured as a function of temperature by activating thiol-Michael linkages at 90 °C, after the two ends were pressed together.[54] As shown in the Figure 4a IPN shows higher stress at each self-healing time point compared to SN in Figure 4b. However, both materials act as similar materials by showing similar stress-strain curves after 16 h of heating at 90 °C. At this temperature, dynamic Thiol-Michael crosslinker allows the transition of IPNs into SN resulting similar polymer architecture in both SN and IPN. The reason for this is the thiol-Michael linkages can activate and switch with other reacting groups within the network creating a similar network as SN. This results similar self-healing stress-strain curves for both SN and IPN. Differences remain between the stress strain and other mechanical characteristics of the materials, most likely due to a different backbone in the second network of the IPN compared to the primary chains of the SN and the IPN's first network. This difference in backbone of the first and second network of the IPN is could be due to the viscosity imparted by the first network, and the lower temperature of the second network synthesis.

DSC studies shows closer T_g values for both SN and IPN (Figure S1). This is consistent with the heating cycle transforming both networks into materials with similar thermal properties

and similar backbone mobility. (Table 1). Overall, these results indicate that dynamic bonds in polymer networks can both enhance a material's effective crosslink density, correct defects and allow macromolecular metamorphosis of one type of network into another.

(a)

(b)
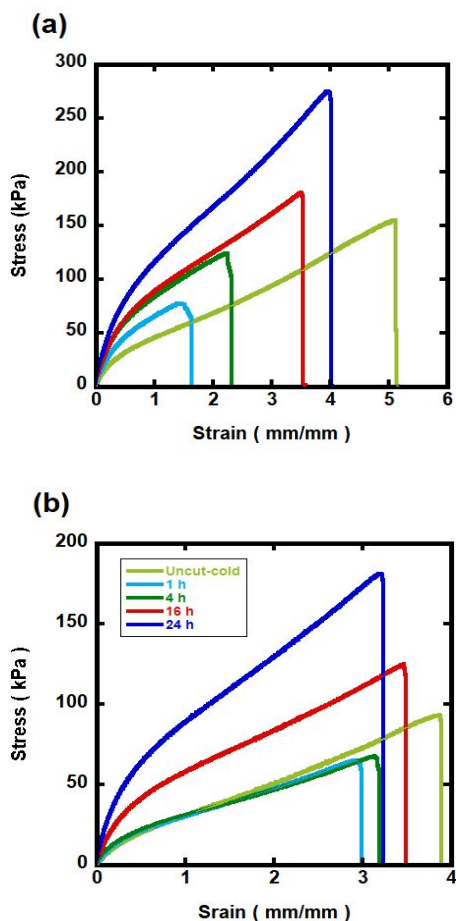
Figure 4. Stress-strain curves for the self-healing experiment. Unheated samples were denoted as 'cold'(a) Self-healing results of heated and unheated IPN materials. (b) Self-healing results of heated and unheated SN materials.

Swelling ratios were calculated in order to find the network structure (Figure 5). As is consistent with the mechanical characterization, the as prepared IPN (cold) materials have a lower swelling ratio than the SN, indicative of a tighter network and consistent with a lower molecular weight between crosslinks. The swelling ratio experiments show that heated samples have lower swelling ratios compared to the unheated samples. This is possibly due to the more crosslinking density and

more compact structure in heated samples. In addition,, heating created a significant difference of swelling ratios between SN cold and heated networks with compare to the IPN. This supports our hypothesis of loop reduction of SN by heating, and increasing effective crosslink density, with the difference being most significant for the SN materials after heating.
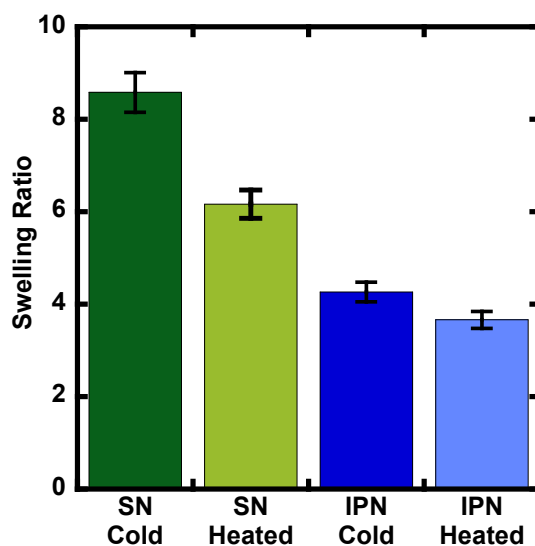
Figure 5: The swelling ratios of cold and heated networks were calculated after immersion in water

Conclusions:

In conclusion, IPN materials shows better thermal and mechanical properties such as tensile strength, creep and creep recovery, and modulus compare to SN. However, applying thermal stimulus to thiol-maleimide crosslinked materials, allowed materials to transform its network architecture resulting similar enhanced properties compare to the cold samples. In the case of the single network, activating the Thiol-Michael bonds can reduce the number of defects of the network such as floppy loops. In the case of interpenetrated materials, the dynamic exchange of thiol-maleimide bonds can shift a kinetically trapped interwoven structure towards a more uniformly linked network. In addition to allowing changes in the network structure, both materials displayed dynamic properties such as self-healing due to the incorporation of the thiol-maleimide

bonds. The ability to change the underlying architecture and potentially correct kinetically trapped defects in the synthesized materials are exciting possibilities enabled by dynamic bonding in polymer materials, enabling robust and tough materials to be created, even from materials with different and event defect containing polymers.

Conflicts of Interest

The authors declare no conflicts.

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