Tuning Dual Dynamic Network Materials through Polymer Architectural Features

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Abstract:

Dynamic materials are known for their applications in self-healing, adhesive, and shape memory applications. Interpenetrating Networks (IPNs) are types of materials that can hold dual dynamic crosslinkers to show complementary chemical and mechanical properties. There has been a number of research on exploring the dynamic chemistries involved in IPN materials. Not only the bond type, but polymer network architecture also play an important role in governing IPN material properties. In this study, we show that network architectural features are as much as important as studying the dynamic chemistries using an IPN system with quadrupole hydrogen (H) bonding and thiol-Michael (TM) bonding. We have varied network types, chain lengths, dynamic bond compositions, crosslink density and crosslink distribution within the system to explore the effect on the thermomechanical properties. The synergetic effect of H and TM bonds revealed excellent stress relaxation and self-healing at room temperature and elevated temperatures. Increment of chain length and crosslink density enhanced the strength of the materials as high as 3.5 MPa while crosslink distribution boosted the creep resistance under an applied force. Further, complementary H and TM bonding assisted in improving the adhesive properties in these materials to hold up to 2kg weight with the adhered wood strips.

Keywords: Polymer Architecture; Dynamic Bonds; Mechanical Properties; Responsive Materials; Structure-Property Relationships

Introduction:

Dynamic chemistries involve bond breakage or reformation autonomously or as a response to external stimuli.[1] In recent years, polymer materials with dynamic bonds have become a hot topic within the field of polymer chemistry. The exchanging nature of dynamic bonds often assists the synthesis of materials with innovative properties including shape memory, adhesive, self-healing and malleability.[2–7] Depending on the nature of the bond exchange, dynamic bonds can be further categorized as dynamic non-covalent and covalent bonds.[8,9] Dynamic non-covalent bonds often display a rapid and autonomous exchange while dynamic covalent bonds typically have relatively slower exchange rates and often only in response to external stimuli. Both dynamic covalent and non-covalent chemistries have been used in polymer material chemistry. Due to the fast exchange of dynamic non-covalent bonds, materials tend to show better self-healing properties at ambient temperature yet they are susceptible to creep (permanent shape deformation) when subjected to external forces. Instead, materials linked with dynamic covalent bonds are often stable against creep, but they only show self-healing behavior when exposed to external stimuli. However, there are some exceptions such as boronic esters which can exchange at room temperature and show creep deformation.[6] It was found that the incorporation of two or more dynamic chemistries together should result in materials with complementary properties.[10–15]

Interpenetrating networks (IPN) are considered to be combinations of two or more chemically distinct polymers in network form, where they coexist in a matrix.[16] In an IPN, at least one of the networks is polymerized and/or crosslinked in the presence of the second network.[17–20] Broadly speaking, there are two types of IPNs: Full IPNs, and Semi IPNs. In full IPNs both the polymer components are crosslinked networks, where semi IPN consist of only one polymer as a network, with the other being uncrosslinked polymers.[16,21,22] Thus far, a number of studies have been carried out to synthesize the IPN materials with a variety of dynamic covalent and non-covalent chemistries such as metal-ligand interactions, hydrogen (H) bonding, Diels-alder, boronic esters, disulfide, and urethane chemistries.[23–27] This study will focus on incorporating thiol-Michael (TM) chemistry along with quadruple H bonding through the 2-ureido-4-pyrimidone (UPy) to obtain intertwined networks with synergistic properties. TM chemistry has been used in many materials and bio-related applications such as conjugation, surface modification, biomolecular synthesis and modifications.[28] Recent work has established that TM bonds are essentially static in ambient temperature but dynamic at elevated temperatures.[29] Owing to these

properties, TM materials can provide creep resistance at ambient conditions and display self-healing ability at elevated temperatures. Further, despite their dissociative mechanism, TM linkers maintain network integrity far above their exchange temperature, presumably due to the high equilibrium constant favoring the associated state.[30] In contrast, H bonding, for instance through the UPy linker, can offer faster bond exchanging at ambient temperature which can enable reversible rearrangements and remolding to IPN networks.[2,31,32]

Aside from the chemistry involved, network characteristics and primary chain architecture is another important factor that governs the macroscopic properties of the polymers such as elasticity, strength, swelling, and permeability.[33–37] Chemical composition and topological structure have been identified as the two main categories that are responsible for the macroscopic property changes in polymer networks.[33] The molecular formula and the connectivity between atoms determines the central design of a polymer strand. Instead, topology defines the connectivity between two or more polymer strands in a polymer matrix. Factors such as polymer chain length, composition, crosslink density and crosslink distributions and network types can not only impact the network topological features but the macroscopic material properties as well.[38,39] These architectural and topological features could affect the polymer materials despite what chemistry is involved within their polymer matrixes.[40–42] These observations lead to an important question that how far the architectural features can push the macroscopic properties of the materials that consist of one or more dynamic bonds. There have been several studies exploring the impact of architectural features of dynamic material properties with only one linker.[37,43,44] However, compared to the studies focused on architectural features in singly occupied dynamic materials, only fewer studies have been conducted to investigate the impact of polymer microstructure and architectural features on the dual dynamic systems.

This study presents a detailed analysis of how the architectural features such as network types, chain lengths, compositions of the polymers, crosslink densities, crosslink distributions and network types affect the dynamic, mechanical and thermal properties of single and interpenetrating networks. The thiol-Michael and quadrupole hydrogen bonded UPy units are used as a model system to investigate the impact of polymer and network micro structure on the properties of the dual dynamic IPN or single network (SN) systems. Of particular interest is the question of crosslink distribution in the networks. In addition to studies of crosslink density and chain length, this work proposes two distinct types of polymer architecture. One has the linkers uniformly distributed

across the polymer backbone, while the other has segmented or blocky type structure, where the TM or UPy linkers are limited to just the ends of the polymers. The impact of such architectural features is important, showing that the underlying polymer can significantly impact the material's strength, toughness, and dynamic properties. As a potential application of the materials hot melt adhesive properties is examined, highlighting the powerful potential of these materials.

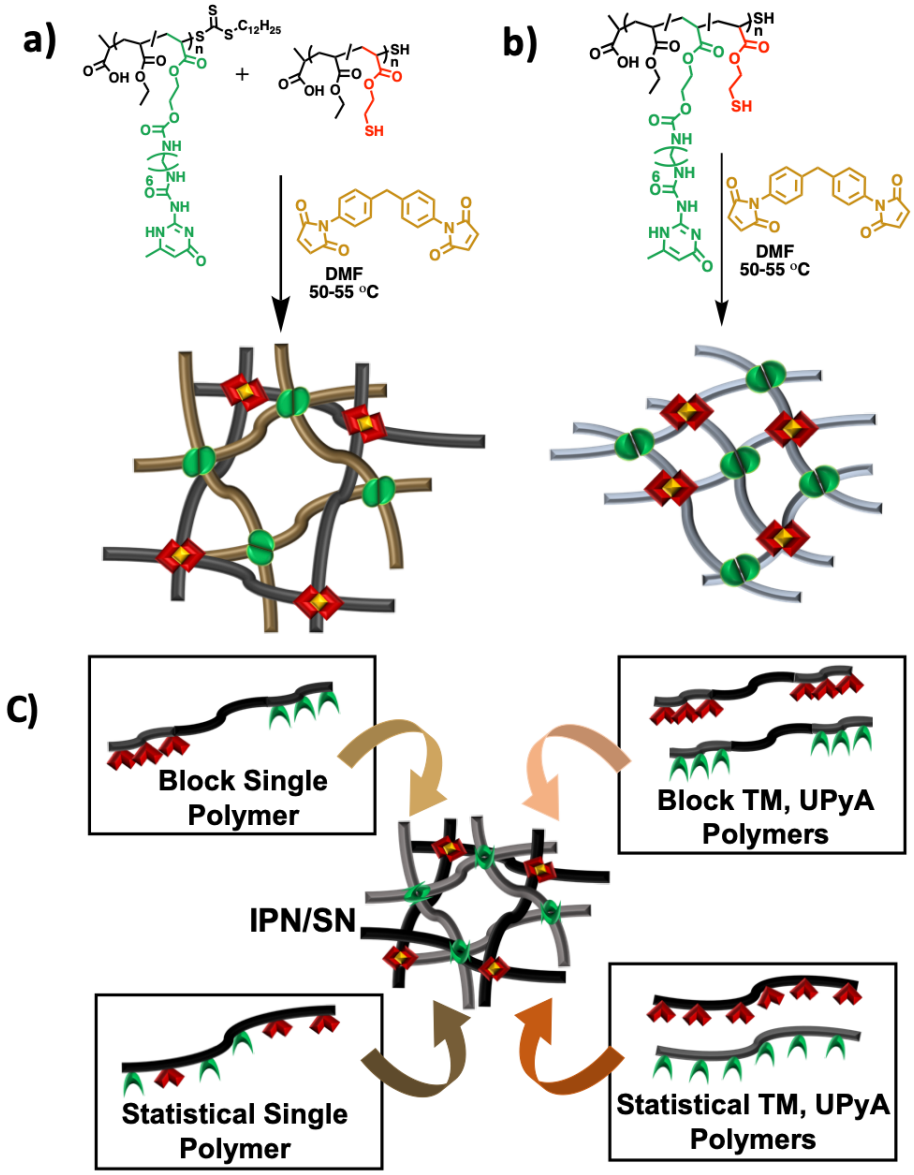
Results and Discussion

Synthesis of Polymer Networks

In preparation of dual dynamic networks, H bonding and thiol crosslinkers were introduced to the polymer chains through 2-(((6-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido)hexyl)carbamoyl)oxy)ethyl acrylate (UP yA) and 2-((ethoxycarbonothioyl)thio) ethyl acrylate (XEA) respectively. Polymers containing ethyl acrylate (EA) as a backbone forming monomer, UPyA and XEA were synthesized through RAFT polymerization using (2-propionicacid)yldodecyl trithiocarbonate (PADTC) as the chain transfer agent (CTA). 2-ureido-4-pyrimidones (UPy) units in UPyA units can dimerize through quadrapole H bonding to the IPNs.[45,46] Deprotection of the xanthate group in XEA with a primary amine liberates free thiols that react with 1,1′-(Methylenedi-4,1-phenylene)bismaleimide (BMI) to form thermoresponsive thiol-michael (TM) covalent bonds.[47] UPyA and deprotected XEA polymers were mixed together in targeted ratios to form entangled IPN networks in the presence of BMI crosslinker. To compare the network arrangements SNs and IPNs were made with both the dynamic non-covalent and covalent linkages included as shown in Scheme 1 a and b. The distinct primary chain structures considered in this study are shown in Scheme 1c.

Comparisons of the network composition were carried out varying the mixing ratios of UPyA and TM polymers (2:1, 1:1 and 1:2). To compare the effect of chain lengths, IPNs were synthesized using UPyA and TM polymers with 50, 100 and 150 degree of polymerization (DP). Similarly, single networks were synthesized using polymer chains bearing dual dynamic linkers with different chain lengths (100DP and 150 DP). Crosslink densities of UPyA and TM polymers were varied from 6% to 10% within the polymer chains to compare the effect of the crosslink densities of polymer IPN properties. Further, to compare the effect of crosslink distribution on material properties and inspired by thermoplastic elastomers, ABA type polymers were synthesized where

"A" blocks contained the dynamic linkers and "B" blocks contained only the backbone forming monomer. All the polymers were synthesized with narrow molecular weight distributions (Table S1-S6, Figure S1-S3). The number averaged molecular weights (M_n) calculated through NMR analysis agreed with the theoretical values and the dispersity values (M_w/M_n) were below 1.35, indicating good control polymerization of the UPyA and TM polymers (Table S7).



Scheme 1: Synthesis of a) IPN and b) SN and c) the different architectures of polymers used for both IPN and SN synthesis. Block single polymer is made including both the crosslinkers in one chain as ABA type block polymers. Block TM, UPyA polymers represent the ABA type block polymers with the crosslinkers as end blocks. Random single polymer chains include both TM and

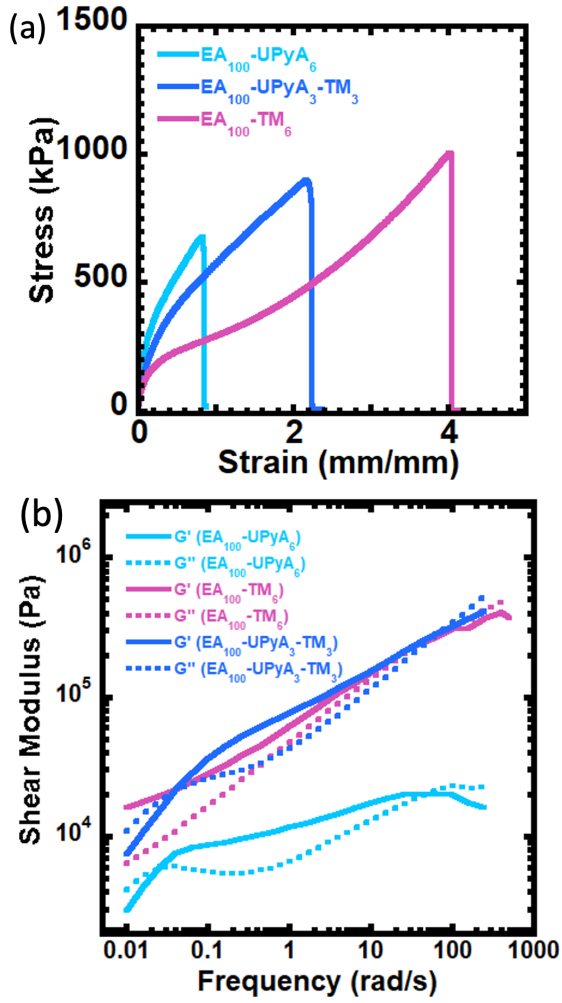
UPyA linkers in random manner. Statistical TM and UPyA polymers consist of either TM or UPyA linkers in random manner.

A summary of the mechanical and thermal properties of the synthesized IPN and SN network materials are shown in table S8 and table S9 respectively. All these materials were analyzed through DSC, IR (Figure S4-S7 and S17), Rheology (Figure S8-S14), Tensile testing, Creep and recovery, stress relaxation. Adhesion properties of these materials were analyzed through lap shear strength calculations (Equation S1).

The properties of the IPN networks will be discussed with respect to their architectural features such as network type, composition, chain lengths, crosslink density and crosslink distribution along the backbone. Further their effect on strength, creep deformation, stress relaxation and glass transition temperatures will be correlated with the underlying architectural features. Initially, to evaluate the impact of each component of the material, tensile and rheological studies were performed on materials containing a primary chain length of 100 units of EA, and 6% total crosslinker. However, in one system a single network of only 6% UPyA was synthesized, in another system a only 6% TM was used, while the other was an IPN with 6% total crosslinker with half of the crosslinkers being H-bonded UPyA linkers, and 50% being from the TM linkers. As shown in Figure 1a, the IPN comprised of the combination of the H-bonded UPy polymer and the TM dynamic covalent linkers has the strength similar to the covalently crosslinked polymer, with the elasticity which bridges the two materials. Additionally, the rheological data provide important insights into each material properties. The frequency sweep data indicate that at sufficiently low frequencies, in the order of 10^{-2} rad/s corresponding to a timescale of ca. 100 s, the EA_{100}-$UPyA_6$ material shows a crossover and becomes dominated by its loss term below this frequency, while above this crossover, the material behaves as a low modulus rubber. This timescale of 100s is consistent with the bond exchange timescale of the UPy linker.[48] A similar transition is seen in the temperature sweep data transitioning from a rubber to a rheological liquid with increasing temperature in Figure 1c. In contrast the covalently crosslinked material (EA_{100}-TM_6) shows rubber-like behavior, transitioning to an approximately flat rubbery plateau. The Hybrid IPN (EA_{100}-TM_3-$UPyA_3$) shows both characteristics in its rheological properties. The material has a modulus consistent with the covalently crosslinked system at intermediate frequencies, but shows a crossover to become dominated by energy dissipation at both sufficiently low frequencies of ca

10^{-2} rad/s, or at sufficiently high temperatures of 55 °C. This energy dissipation is consistent with the hydrogen bonded UPy units, while the enhanced modulus is consistent with the covalent TM crosslinker.

In general, IPN materials overcame the limitations present in the SN dynamic materials giving materials with comparatively improved performance based on the characteristics of both UPyA and TM linkers. The IPNs had superior tensile strength, rheology properties, and creep resistance, while maintaining acceptable stress relaxation behavior.



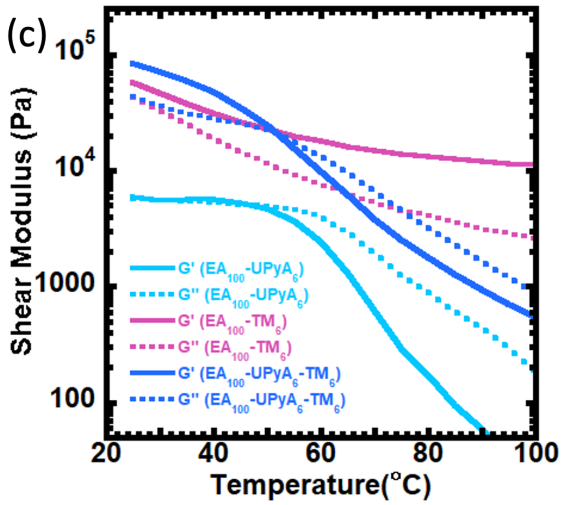


Figure 1: Stress-strain curves and rheology data of 100 DP 6% UPyA (EA_{100}-$UPyA_6$), 6% IPN (EA100-TM_3-$UPyA_3$), and 6% TM (EA_{100}-TM_6) materials. a) stress-strain curves, b) frequency sweep data at 25 °C and 1% strain c) temperature sweep data at 0.1 Hz and 1% strain.

Impact of Architectural Features on Materials Properties.

1. Network type

Dual-dynamic interpenetrating networks consist of two types of dynamic bonds within their matrixes. These materials can be synthesized using two main strategies: mixing two polymers containing two different dynamic linkers (IPN) or synthesizing materials with single polymer with both the dynamic crosslinkers (SN). In both strategies, the crosslink density and the network composition remain same. Recent work has shown that network type greatly affects the properties of the materials.[49] Even though both network types contained the same composition, they can alter the chain entanglements and the likelihood of the two crosslinkers associating to form dynamic bonds.[50] Since the IPN materials contain the crosslinkers in different chains, they have a higher chance forming intermolecular crosslinking and chain entanglements within the matrix, as shown by recent simulations.[50] On the other hand, due to the large space between analogous linkers, SN has fewer possibility to form interchain crosslinking but higher chance for intrachain crosslinking resulting in floppy loops.[51] Such floppy loops can adversely impact mechanical, dynamic and thermal properties.

The data in Figure 2a and Figure 2c show that the IPN materials had superior creep resistance and tensile strength than SN materials. However, SN materials showed faster bond relaxation at room temperature than the IPN materials (Figure 2b). The higher number of chain entanglements and elastically effective crosslink points is the likely reason why the IPN materials have greater tensile strength and creep resistance compared to SN materials. However, the same factors can reduce the rate of stress relaxation (SR) in IPN materials. Since the IPN is likely to have a higher effective crosslink density, which can hinder the movement of dynamic H bonds within the matrix and cause fewer exchanges and adaptation to the strain applied. In contrast, in the SN the lower density of elastically effective linkers facilitates exchange of H bonds at ambient environment to relax the stress and allow deformation under applied forces. In earlier studies, we observed that when these materials strain to 100% at their length, IPN displayed better stress relaxation than the analogous SN materials.[49] However, when the applied strain decreases to 25% from the original strain at break, SN materials displayed greater stress relaxation compared to the IPN materials.[52,53] Still, these materials exhibited more than 70% stress relaxation within 20 mins (Table S10). From previous experience with stress relaxation behavior at elevated temperatures,[29] these materials could display even faster relaxation times (within seconds) at elevated temperatures.

Both the IPN and SN materials showed efficient self-healing upon heating to 90 °C, although these IPN materials had superior self-healing after 24 hrs at ambient temperature (Figure 2C). This is most likely due to the greater effective H-bond density in the IPN materials compared to SN materials, which arises from the inter chain crosslinking within the IPN. In the IPN, more H-bonds can form due to the H-bonded chains being free to adapt and move through the matrix and create more linkages, rather than being restrained by the TM linkers on the same chain, as occurs in the SN. With the higher the number of H bonds, more exchange reactions take place to offer superior self-healing under ambient conditions.

Further, the T_gs observed for the analogous IPN and SN materials (PEA_{100}-$UPyA_3$-TM_3) were -0.25 °C and 3.75 °C respectively. IPN materials have a greater tendency to form intermolecular dynamic interactions in between polymer chains than SNs.[50] Instead, SN materials contain fewer effective linkers within the matrix with a higher possibility of intramolecular dynamic bonds (loop formation) rather than intermolecular linkages. As reported previously, larger loops along the polymer chains can restrict the movements of longer polymer chains with respect to the

temperature increment.[54] Further, the presence of loops reduce the free volume exhibit within the polymer matrix resulting higher glass transition temperatures in SN through confining chain mobility. Another factor is that the increased mobility of the H-bonded part of the IPN material reduces the T_g compared to the IPN, as these chains experience fewer barriers to mobility through the matrix.[50] In addition, both the SN and IPN materials displayed similar T_{cross} values in temperature sweep experiments (Table S9). Finally, as shown in Figure 2d, the frequency sweep rheological data were similar for the IPN and SN materials, with both having a cross-over consistent with the timescale of UPy unit's exchange.

Overall, IPN materials displayed better creep resistance and tensile strength than the SN materials while SN materials had faster stress relaxation and higher T_gs compared with their IPN analogues. The major difference between these materials is in the availability of elastically effective crosslinking points within the network matrix, consistent with earlier simulation results.

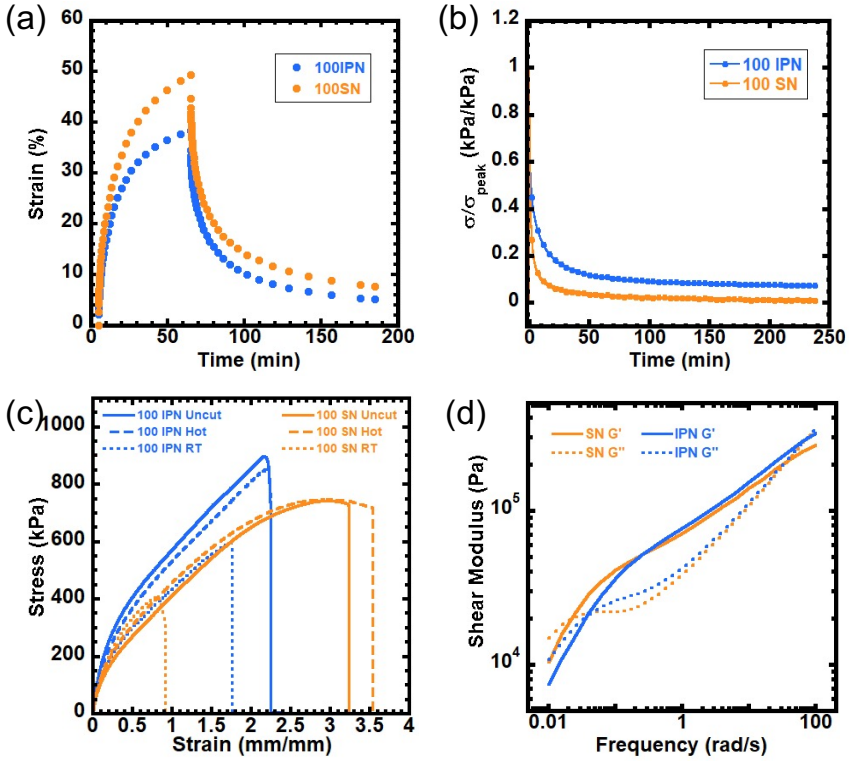


Figure 2: 100 DP 6% IPN (PEA_{100}-$UPyA_6$ + PEA_{100}-TM_6; (1:1 wt%)), 6% SN (EA100-TM_3-$UPyA_3$) material properties. a) Creep and recovery b) Stress relaxation at room temperature after strain to 25% of their ε_{break}. c) Stress-strain curves with uncut (solid lines), 24 hrs hot healing (dashed lines), and 24 hrs room temperature (rt) healing (dotted lines). d) Frequency sweep rheology at 25 °C (0.1 Hz and 1% strain).

2. Impact of composition in material properties

To evaluate the impact of polymer composition in material properties, the ratios of UPyA and thiol polymers were varied within the IPN matrixes. The mixing ratios of the UPyA polymer and thiol polymer were varied from 2:1 to 1:2. This has the potential to impact the relative dynamics of the overall exchange efficiency at ambient temperatures, which is dominated by H-bonded UPy linkers. The creep deformation and recovery experiments of Figure 3a showed significant changes with the polymer mixing ratios. As the content of UPyA increased, materials tend to deform further under applied force and displayed sluggish recovery, presumably due to the faster dynamic exchanges caused by the UPyA at room temperature which lead to a permanent shape deformation. As the TM dynamic bond content increases within the systems, the materials displayed some resistance to shape deformation and recovered back to original position relatively faster once the load was released. All the materials showed almost full relaxation within four hours of time period and importantly, relaxed more than 70% of the stress within first 30 mins. However, the materials with higher UPy loading relaxed the stress more efficiently (Figure 3b), as a result of having faster dynamic exchanges within their system. Rapid H bond exchanges allows to relax the in-built stress within the materials which caused by the strain.

The composition of the IPN materials directly impact the tensile and shear modulus of the materials (Figure 3c and d). The introduction of additional dynamic covalent bonds reinforces the material, whereas the introduction of more dynamic non-covalent interactions causes higher elasticity and lower strength to the materials, as seen in Figure 3c. The self-healing at 90 °C was not impacted by the fraction of UPy and TM linkers, although surprisingly at room temperature the system with the highest UPy content had the poorest self-healing. This could be due to the possible clustering of the UPy units, which still leads to efficient dynamic exchange under load, such as in creep or stress relaxation experiments, but such clusters may inhibit interpolymer exchange as required for self-healing.

Further as shown in Table S9, decreasing the relative fraction of UPy linkers increases the temperature crossover points in temperature sweep experiments, and makes materials more static in the temperature range. Materials with more noncovalent interactions (2:1 UPyA/TM) showed the lowest glass transition temperature of –4.9 °C due to the faster chain movements with the increment of the temperature. Both 1:1 And 1:2 UPyA/TM systems had higher T_g values than the 2:1 UPyA/TM system at –0.3 °C and –2.4 °C respectively. Figure 3d shows the frequency sweep rheological data, with all three compositions having similar moduli. However, the system with an

excess of UPyA based linker showed a crossover to being dominated by energy dissipation at a slightly higher frequency, which is most likely due to the increased loading of H-bonded UPy units.

In conclusion, the composition of the dual dynamic systems plays a vital role in governing the properties of the materials. Superior creep resistance and tensile strength were observed with higher dynamic covalent crosslink density within the matrix due to their essentially static nature in the ambient conditions. However, the materials with higher H-bonding linker densities displayed faster relaxation and lower T_gs due to the faster exchanges of H-bonds and faster movements of polymer chains in the matrix.

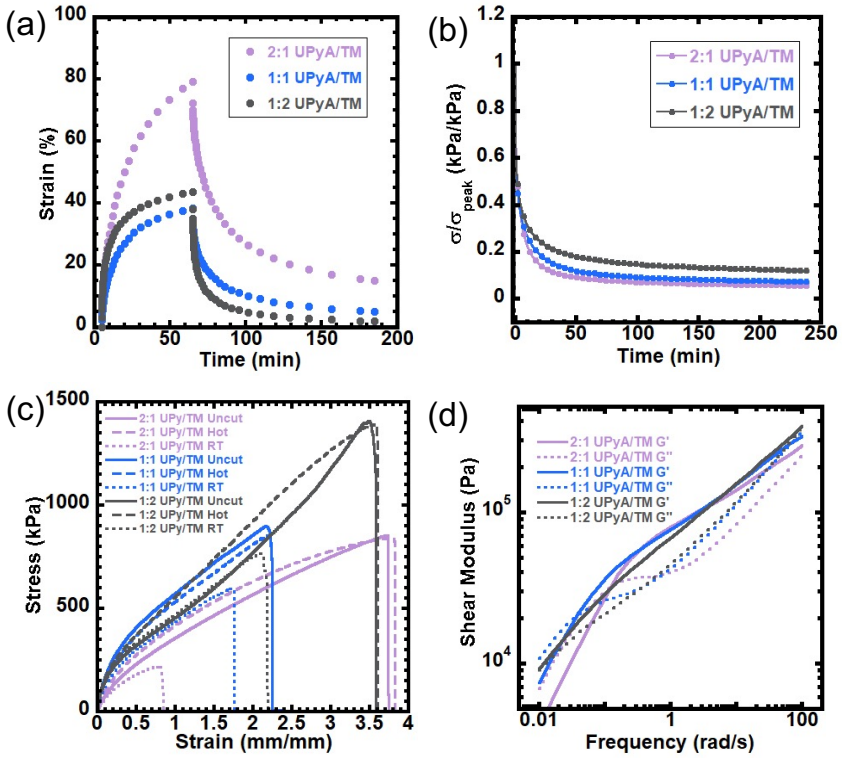


Figure 3: 100DP 6% 2:1 UPyA/TM IPN (PEA_{100}-$UPyA_6$ + PEA_{100}-TM_6; (2:1 wt%)), 100DP 6% 1:1 UPyA/TM IPN (PEA_{100}-$UPyA_6$ + PEA_{100}-TM_6; (1:1 wt%)), 100DP 6% 1:2 UPyA/TM IPN (PEA_{100}-$UPyA_6$ + PEA_{100}-TM_6; (1:2 wt%)), material properties. a) Creep and recovery b) Stress relaxation at room temperature after strain to 25% of their ε_{break}. c) Stress-strain curves with uncut (solid lines), 24 hrs hot healing (dashed lines), and 24 hrs room temperature (rt) healing (dotted lines). d) Frequency sweep rheology at 25 °C (0.1 Hz and 1% strain).

3. Impact of Chain length.

Chain length is a critical architectural feature that can impact the thermomechanical properties of the dynamic materials. In order to study the effect of the polymer chain length in IPN properties, statistical polymers were synthesized with 50, 100 and 150 DPs, while retaining the same density of crosslinkers along the backbone. Both IPN and SN structures were synthesized with distinct chain lengths. Increasing the chain length promotes chain entanglements and total network percolation within the matrix. As seen in Figures 4a and b, the chain length impacts the SN and IPN materials differently in creep and stress relaxation. The highly intertwined IPN matrix and presence of stable covalent bonds can establish stability against the permanent shape deformation and improve the strength of the materials in room temperature. As predicted, the IPN materials based on polymers with higher DP displayed better creep resistance and relatively slower stress relaxation. Interestingly, the SN material at chain length 150 displayed poorer creep resistance and recovery than the corresponding polymer at chain length 100. This could be due to the longer chain length in the less mobile and adaptable SN structure inhibiting creep recovery due to significant needs for segmental rearrangement.

Figure 4c evaluates the tensile properties of both IPN and SN materials at both chain length 100 and chain length 150. As expected, at higher chain lengths the strength of the material was enhanced, and the modulus increased. When considering the self-healing efficiency, Figure 4c indicates that higher chain lengths lead to small reductions in self-healing at 90 °C, and substantial reductions in self-healing at room temperature. This is most pronounced at in the SN system which displayed very poor room temperature self-healing. The longer chains in SN system seems to build a higher barrier to segmental rearrangement and restrict the chain movements to bridge across the interface generated by the cut. A IPN material based on chain length 50 polymers showed poor mechanical properties and yielding during tensile testing experiments (Figure S15). This suggests that at chain length 50, the chain entanglements and the number of crosslinks per chain are not sufficient enough to create a well-defined percolated network. Consistent with the trend that SN materials have lower effective crosslink density, the 50 DP SN system turned in to a viscous liquid and could not retain the material shape.

Materials with 150DP in SN and IPN systems displayed higher T_g compared to 100DP materials as a result of having more entwined chains within their matrix and reduced mobility. With the increment of DP, T_g values varied 3.72 °C to 8.25 °C for SN materials where IPN

displayed a variation from -0.3 °C to 2.13 °C. The presence of higher chain entanglements in 150 DP materials also broaden the viscoelastic solid temperature range of both IPN and SN materials by increasing the T_{cross} temperatures in temperature experiments. The rheological data in Figure 4d indicate that the effect of chain length is relatively minimal on the rheological properties, although both the 150 DP materials did not show crossovers in lower frequency region (0.01-10 rad/s). This is consistent with chain dynamics and relaxations being inhibited in the longer polymers.

As shown below, polymer chain length could affect the material properties such as creep resistance, stress relaxation, T_gs, tensile strength and rheological properties. Longer chain lengths offer more chain entanglements and higher probability of forming elastically effective crosslinks within the polymer matrix, thereby restricting the chain movements. Tensile strength, T_gs and creep resistance increase with the degree of entanglements and density of effective crosslinks within the system. Conversely, the IPN system restrict the chain movements in the materials and cause slower stress relaxation.

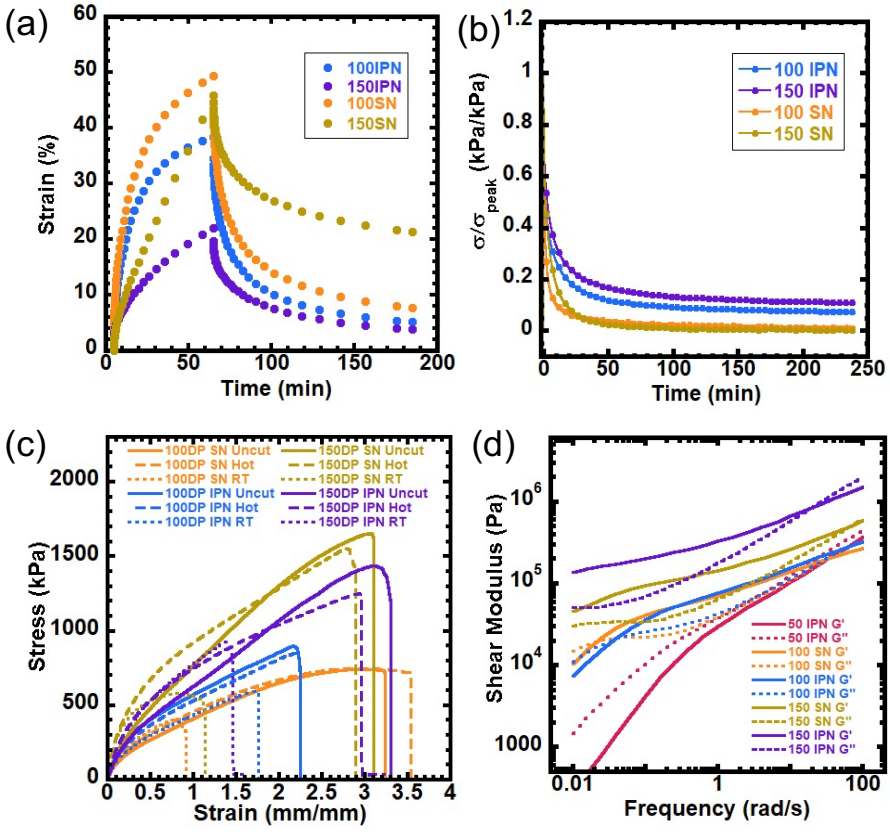


Figure 4: : 50DP 6% IPN (PEA_{50}-$UPyA_3$ + PEA_{50}-TM_3), 100DP 6% IPN (PEA_{100}-$UPyA_6$ + PEA_{100}-TM_6), 100DP 6% SN (EA100-TM_3-$UPyA_3$), 150DP 6% IPN (PEA_{150}-$UPyA_9$ + PEA_{150}-TM_9), and 150DP 6% SN (EA150-$TM_{4.5}$-$UPyA_{4.5}$) material properties. . a) Creep and recovery b) Stress relaxation at room temperature after strain to 25% of their ε_{break}. c) Stress-strain curves with uncut (solid lines), 24 hrs hot healing (dashed lines), and 24 hrs room temperature (rt) healing (dotted lines). d) Frequency sweep rheology at 25 °C (0.1 Hz and 1% strain).

4. Crosslink density

Crosslink density within the polymer matrix considered to be a crucial factor in determining the material's thermal and mechanical properties. With more crosslinkers in the system chain mobility could be reduced, and the density of linkers per unit volume could be enhanced, thereby increasing the material strength. To determine the effect of crosslink density IPN materials were prepared using polymers containing 6% and 10% UPyA and XEA crosslink moles. Upon mixing equal volumes of UPyA and crosslink polymers the IPN materials were obtained with 0.03 and 0.05 crosslink densities of both UPy and TM linkers in the matrix. The SN materials were synthesized with 3% and 5% crosslink moles in both UPyA and XEA linkers to obtained materials with 0.03 and 0.05 crosslink densities of both UPy and TM linkers in the matrix.

Figure 5 shows that as expected, increasing the crosslink density enhanced the strength in both IPN and SN materials. Further, due to the stability of the covalent crosslink points at room temperature, more crosslink points increase the material's stability against the creep deformation. Hence, both the single and IPN networks with higher crosslink densities showed better creep resistance against the applied force. In addition, due to the presence of faster exchanging H bonds in the system, all these materials essentially showed good stress relaxation properties as seen in Figure 5b, and Table S10. However, materials with higher crosslink densities required a longer time to reach mechanical equilibrium, due to the presence of a higher density of essentially static TM crosslink points under the studied conditions. In addition, the presence of more crosslink points can limit the chain mobility of IPN and SN materials and increase the thermal energy requirement for backbone to relax.[55] This causes an increase of glass transition temperatures with increasing crosslink density. As a result, we observed as increment of T_g in SN materials from 3.7 °C to 6.3 °C and IPN materials from -0.3 °C to 2.2 °C respectively. Additionally, with the higher crosslink density, the materials became significantly stronger, as seen in Figure 5c, with a slight decrease in elasticity. Despite the increase in strength, the self-healing at 90 °C was still excellent in these systems. This is important to note, since earlier work showed that with higher crosslink

densities, the self-healing can be adversely impacted.[53,56] The likely reason for the essentially quantitative self-healing at 90 °C was the synergies of the H bonded UPy and dynamic covalent TM linker. This is especially relevant when compared to the room temperature self-healing, where the systems with 10% crosslink density have room temperature self-healing efficiencies in the order of 0-15%, compared to 50-60% efficiency for the 6% crosslink density. The ineffective self-healing in 10% materials could arise from the restriction of UPyA linker movements through larger static crosslinking points (TM) at room temperature. This restraint prevents the assembly of two UPyA linkers to form H-bonding at ambient conditions.

Most importantly, changing the crosslink density in SN from 6% to 10% increases the crossover temperature from 50 to 65 ºC in temperature sweep rheology (Figure S12), while 10% crosslink density in the IPN materials allowed materials to stay in the rubbery state continued over the temperature range from 25 to 180 ºC (Figure S11). Additionally, Figure 5d shows the frequency sweep data, indicating that the materials with higher crosslink density also had higher moduli, as anticipated, and the materials lacked a clear crossover to a viscous regime. This is most likely due to the materials having a higher density of essentially static TM linkers, which limit the extent of energy dissipation and flow in these materials.

Crosslink density governs the strength, rheological, and creep performances of the dual dynamic systems. Increasing the density of crosslinking points enhances the material's tensile strength, creep resistance and the temperature needed for the transition between glassy to rubbery state. However, higher static crosslinking points at room temperature causes comparatively sluggish stress relaxation in the material.

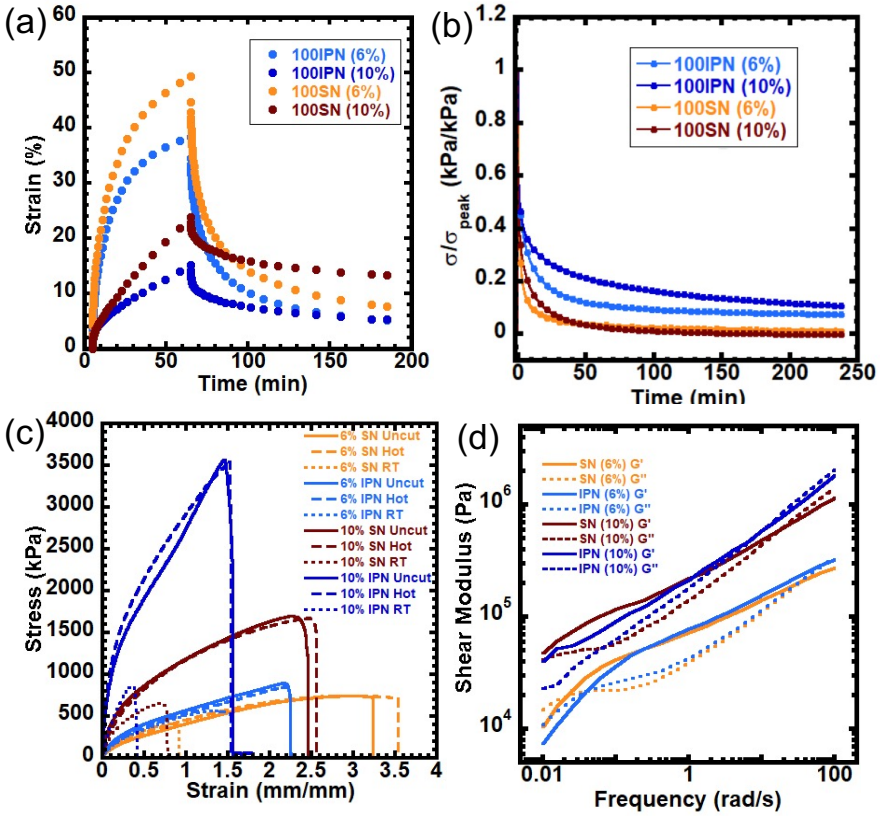


Figure 5: 100DP 6% IPN (PEA_{100}-$UPyA_6$ + PEA_{100}-TM_6), 100DP 6% SN (EA100-TM_3-$UPyA_3$), 100DP 10% IPN (PEA_{100}-$UPyA_{10}$ + PEA_{100}-TM_{10}), and 100DP 10% SN (EA100-TM_5-$UPyA_5$) material properties. a) Creep and recovery b) Stress relaxation at room temperature after strain to 25% of their ε_{break}. c) Stress-strain curves with uncut (solid lines), 24 hrs hot healing (dashed lines), and 24 hrs room temperature (rt) healing (dotted lines). d) Frequency sweep rheology at 25 °C (6%:0.1 Hz and 1% strain, 10%: 0.1 Hz and 0.1% strain).

5. Crosslink distribution

Recently, crosslink distribution has been identified as one of the major factors that determines the thermal, mechanical and dynamic properties of the materials.[43,48,57,58] The crosslink distribution within the polymers can be altered using different polymerization strategies such as gradient polymerization and block polymerization. Our previous studies on thermoplastic elastomers showed that the block lengths can clearly affect the mechanical properties of the materials and 40% of end A block segments could result the highest strength for materials with ABA type block polymers.[59] Hence, for the comparison with 6% crosslinked IPN materials, ABA type polymers were synthesized with (EA_{20}-XEA_3)-EA_{40}-(EA_{20}-XEA_3) and (EA_{20}-$UPyA_3$)-EA_{40}-(EA_{20}-$UPyA_3$)

composition and mixed them in 1:1 weight ratios to synthesize the crosslink materials with 0.06 collective crosslink density. In these block polymers UPyA and XEA crosslinkers were distributed within the end "A" blocks equally in random manner. Each A blocks consist of 20% chain length from the total backbone length, with the remaining 60% of the backbone from the central B block. To compare the SN materials with the statistical polymers, ABC type block polymers were synthesized with 3% UPyA crosslinker in the first "A" block, and 3% XEA crosslinker in the terminal "C" block in the end with the composition of (EA_{20}-$UPyA_3$)-EA_{40}-(EA_{20}-XEA_3).

These blocky-type polymers should cause local concentration of analogous crosslink points, where statistical polymers will have random crosslink points within the matrix. The crosslink clusters could impact the creep behavior, material strength, stress relaxation and transition temperatures in materials. It has been reported that the microphase separation within the matrix could enhance the creep resistance of the dynamic materials.[43] Similarly, Figure 6a shows enhanced creep resistance in blocky SN and IPN materials than their analogous materials consist with statistical polymers. Despite of their varied crosslink distributions, all the SN and IPN materials displayed good stress relaxation at room temperature as a result of having autonomously exchanging H bonds as seen in Figure 6b.

In addition, materials with blocky polymers showed lower young's modulus than the materials with statistical polymers. The ABA type IPN materials and ABC type SN materials displayed higher strain at break and peak stress than the analogous statistical materials as seen in Figure 6c. Interestingly, the ABC SN material had very similar tensile properties to the ABA IPN type, material, suggesting that the ability to concentrate and cluster dynamic UPy units together and to cluster dynamic TM linkers together leads to similar bulk properties. In both cases, this is superior to the statistical SN or IPN. Similarly, when considering self-healing efficiency at elevated temperature, all materials statistical or segmented, showed very similar properties with essentially complete recovery after 24 hrs. When comparing the self-healing at room temperature, the ABA-type segmented IPN showed similar efficiency to the statistical IPN, with both having self-healing efficiencies of ca. 50-60% at room temperature. However, notably the ABC SN material showed the fastest rate of self-healing of any material, as seen in Figure 6a and S23. Surprisingly, the segmented ABC-type SN material showed one of the poorest room temperature self-healing characteristics. This is especially surprising when contrasted against its exceptional self-healing at 90 °C. This difference in self-healing of the ABC-type SN material at elevated vs room

temperature could be due to several factors. The ABC-like structure is likely to restrict the mobility of the UPy rich segment in the SN, without having a corresponding density of UPy segments uniformly distributed throughout the matrix, in a way that is not the case in the IPN. This clustering and restriction of mobility is likely to inhibit room temperature self-healing in the ABC-type SN compared to its statistical counterpart. However, at elevated temperatures, the TM and UPy based linkers are both dynamic, and in these cases the local clustering and connection between the domains could enhance the self-healing of both TM and UPy linkers, since a bridging event of the across the cut would also place a TM linker close to the cut.

There were major differences in T_g between analogous materials with block and statistical polymers. The statistical IPN and SN materials displayed T_gs of -0.3 °C and 3.7 °C whereas the ABA-type IPN materials displayed a T_g of -4.2, which is very similar to the ABC-type SN which had a T_g of -4.3 °C. This reduced in the T_g in the segmented polymers is most likely due to the presence of long segments of poly(EA), which has a T_g of -26 °C as a uncrosslinked polymer.[60] Interestingly, despite reducing the T_g, segmenting the crosslinkers increased the crossover temperature by 10 °C for the ABA-type IPN compared to the statistical IPN, while reducing the crossover by 5 °C for the ABC-type SN compared to the statistical SN. Surprisingly, even though it is known that the association of segments can slower the dynamics of the materials,[48] in SN materials the segmentation tend to facilitate the exchange dynamic and reduce the working temperature of the 10% SN materials. This is also reflected in the frequency sweep data in Figure 6d. All four materials had relatively similar moduli, however, the ABA-type IPN had a crossover at lower frequency than the statistical IPN, the ABC-type SN had a crossover to a dominant viscous response at higher frequency than the to the statistical SN.

Generally, crosslink distribution controls the behavior of the dynamic linkage behavior. Block polymers tend to display phase separation behavior and localization of similar linkages, while statistical polymers display random crosslink distribution within the matrix. Materials with block architecture showed superior creep resistance compared to the statistical materials. Further localization of the dynamic linkages caused lower glass transition temperatures in blocky materials. However, both types of materials displayed similar tensile strengths and stress relaxation behaviors.

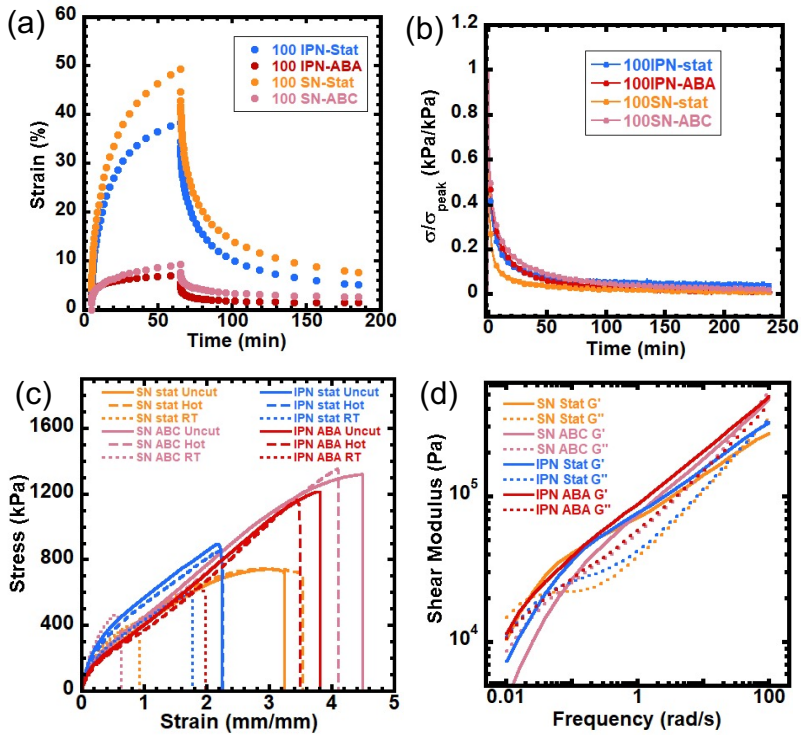
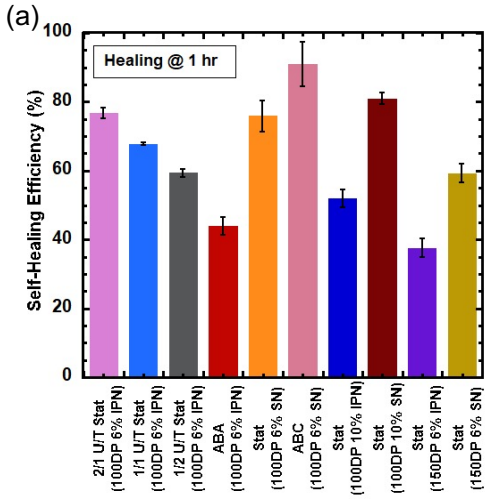


Figure 6: 100DP 6% statistical IPN (PEA_{100}-$UPyA_6$ + PEA_{100}-TM_6), 100 DP 6% ABA type IPN ((EA_{20}-TM_3)-EA_{40}-(EA_{20}-TM_3) + (EA_{20}-$UPyA_3$)-EA_{40}-(EA_{20}-$UPyA_3$), 6% statistical SN (EA100-TM_3-$UPyA_3$), and 100 DP 6% ABC type SN ((EA_{20}-$UPyA_3$)-EA_{40}-(EA_{20}-TM_3) material properties. a) Creep and recovery b) Stress relaxation at room temperature after strain to 25% of their ε_{break}. c) Stress-strain curves with uncut (solid lines), 24 hrs hot healing (dashed lines), and 24 hrs room temperature (rt) healing (dotted lines). d) Frequency sweep rheology at 25 °C (0.1 Hz and 1% strain).

Self-Healing:

Due to the presence of both H bonds and TM bonds, the IPN and SN materials can exhibit self-healing at room temperature and elevated temperature. At room temperature, H bonds exchange autonomously while elevated temperature provides external inducement to activate the TM bond exchanges.[29] Hence, UPyA linkers are mostly responsible for room temperature healing while both TM and UPyA linkers contribute to self-healing at elevated temperature through dynamic exchanges. IPN and SN materials were sliced to two pieces at the middle, pressed them against and let to heal at room temperature (24 hrs) and elevated temperatures for 1, 4, 7, 16, and 24 hrs . The IPN materials were healed at 90 ºC while the SN materials healed at slightly lower temperature (70 ºC) to avoid any melting.

Mostly, the free volume, length of the polymer chains, crosslink points and the nature of the dynamic bonds affect the self-healing ability of the IPN materials. It was clear that SN materials showed excellent self-healing ability under elevated temperature while IPN materials performed better at room temperature (Figure 7a and 7b). Most of the SN materials essentially displayed full recovery of its original stress after 7hrs of heating time. Among all the materials, segmented SN materials displayed the best healing ability under elevated temperature while the segmented IPN materials showed slower healing under the heat. Generally, all the materials displayed 40% or above self-healing ability under the heat with respect to the stress of the uncut materials. Further, all the dual dynamic systems displayed over 20% or above self-healing ability at room temperature after 24 hrs. Figure 7c shows the time needed to reach at least 90% self-healing at elevated temperatures, showing that SN structures, ABA IPN/ABC SN or shorter chain length and crosslink densities all lead to more rapid self-healing.



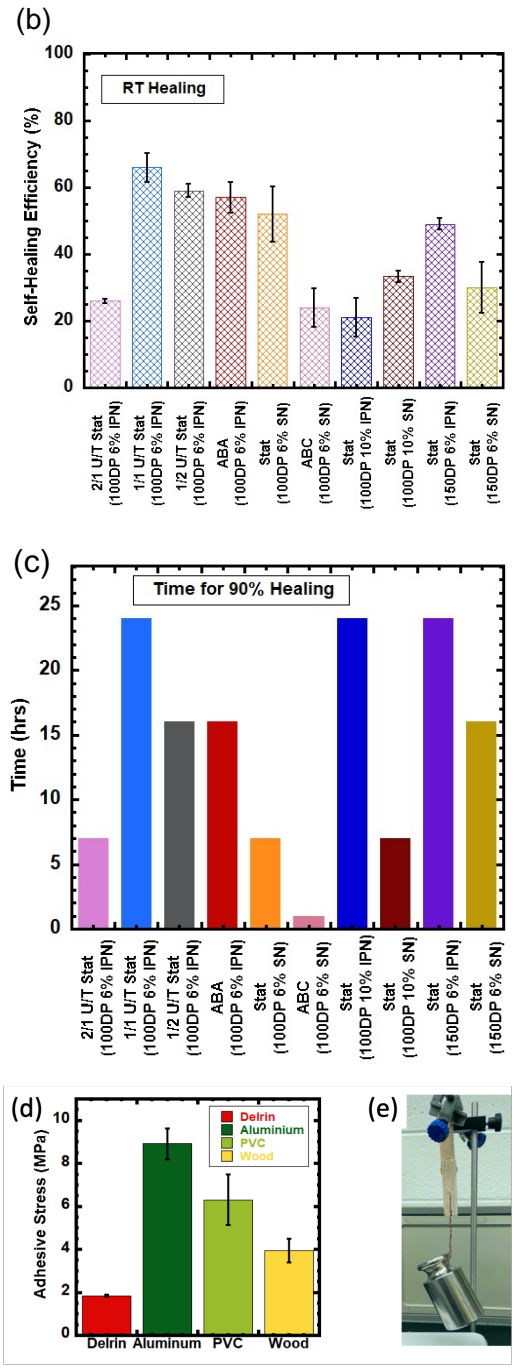


Figure 7: a-c) Comparison of the self-healing performances in dual dynamic IPN system. a) Summary of the self-healing performances of dual dynamic IPN systems at elevated temperature (90 ºC for IPN and 70 ºC for IPN) after 1hr. b) Summary of the self-healing performances of dual dynamic IPN systems at room temperature after 24 hrs. c) Summary of the time scales taken to reach 90% recovery from its original stress. d) Adhesive properties of 100DP 6% IPN (PEA_{100}-$UPyA_6$ + PEA_{100}-TM_6; (1:2 wt%))1:2 UPyA/TM IPN materials, e). Photograph of 2 kg weight hanging with the aid of adhered wood strips.

Adhesive Properties:

Generally, the presence of dynamic bonds provides enhanced adhesive properties to the materials because the dynamic properties allow the material to adapt the substrate and enhance adhesion. [61–65] Since the IPN materials contain thiol-Michael and H bonds within the matrix, these materials should be able to show strong adhesive properties through thiol and H bonds to the surfaces. Further, materials containing covalent adaptable networks can provide superior adhesive properties compared to traditional thermoset adhesives due to their shape changing ability upon stimuli application.[66] To evaluate the adhesive properties, the 1:2 UPyA/TM IPN (PEA_{100}-$UPyA_6$ + PEA_{100}-TM_6; (1:2 wt%)), material was sandwiched in between two identical surfaces and pulled with 1mm/min strain rate until the two surfaces detach from each other. To evaluate the adhesive properties with respective to the surface roughness, Delrin, Aluminum, polyvinyl chloride (PVC) and wood surfaces were selected as adhesive surfaces. The lap shear strength was calculated using the maximum force divided with the area of polymer between two adhesive surfaces (equation S1). As shown in the figure 7d, IPN materials displayed maximum adhesive properties with aluminum strips and lowest with Delrin surfaces. Further they showed good adhesive properties with comparatively rough wood surfaces as well as smooth Delrin surfaces. The adhesion to Delrin and PVC are notable since these are both polymers with somewhat low surface energy, which is typically challenging in adhesive applications.[67–70]The dynamic IPN adhesive between two wood surfaces with IPN materials is enough to hold even 2 kg weight (Figure 7e).

Conclusion:

In conclusion, we have synthesized IPN and SN materials using dual dynamic crosslinkers UPyA and thiol-maleimide adducts. In this system the quadruple hydrogen bonded UPyA can exchange with autonomously at ambient temperature. Instead, the thiol-maleimide crosslinkers give stimulus responsive linkers which are essentially static at room temperature and exchange in response upon heating. IPN and SN materials were synthesized with varied network type, composition, chain lengths, crosslink density, and crosslink distribution to study the impact of architectural features on dynamic, thermal and mechanical properties of the dual dynamic crosslinked systems. We observed these architectural features can directly impact the chain entanglements, crosslink points, free volume, distance between crosslinks and phase behavior of the dual dynamic systems. Most

interestingly, the segmentation of the polymers had unique impacts on the material properties, with blocky polymers that contain the dynamic linkers in only the terminal segments having superior mechanical properties to those which have statistical distributions of crosslinkers. In addition, due to the dynamic nature of the quadrupole H bonds and thiol-Michael bonds, these materials display superior adhesive properties on Delrin, Aluminum, PVC and wood surfaces and able to hold weights with adhered surfaces.

Supporting Information

Experimental details, polymer molecular and spectroscopic characterization data, additional materials thermal characterization data, and mechanical characterization data

Acknowledgements

This material is based upon work supported by the National Science Foundation under Grant No. (DMR-1749730) to D.K.. D.K. would also like to acknowledge support from the Robert H. and Nancy J. Blayney Professorship. N.D.A.W would like to acknowledge support from Miami University as a Dissertation Scholar.

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