Quantity or Quality: Are Self-Healing Polymers and Elastomers Always Tougher with more Hydrogen Bonds?

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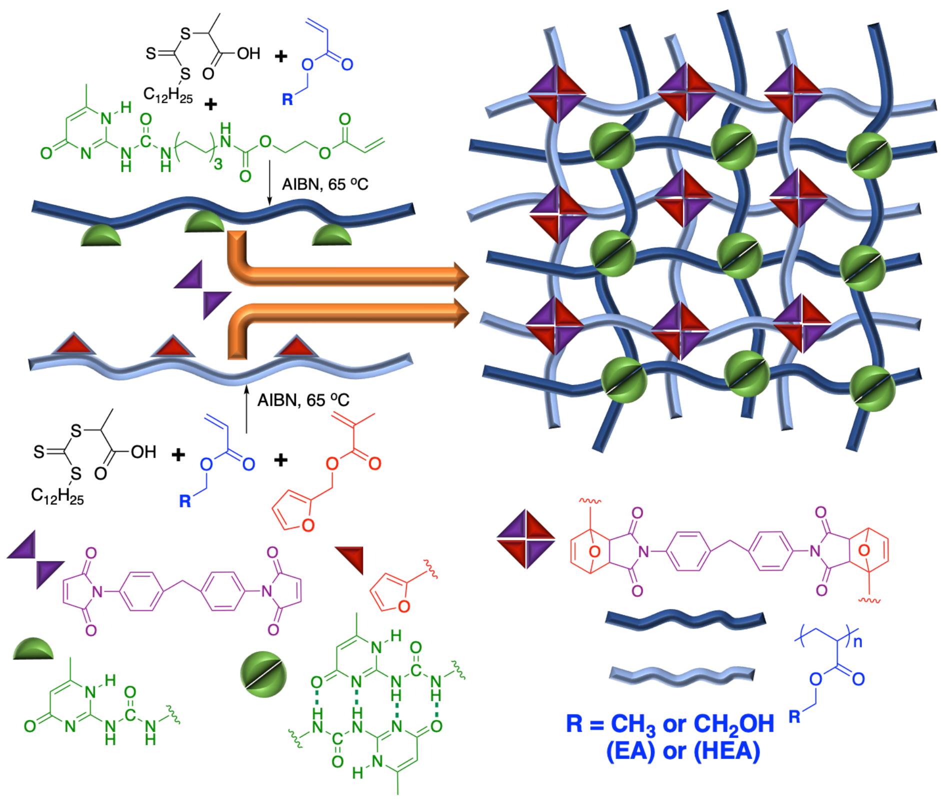
ABSTRACT: Polymer materials containing dynamic bonds have many potential applications including adhesives, elastomers, and coatings with long lifetimes. Interpenetrated networks (IPNs) were studied, where one network had covalent linkers, and the other network had dynamic quadruple hydrogen-bonded 2-ureido-4[1H]-pyrimidinone (UPy) linkers. IPNs typically have superior mechanical properties to each component network. IPNs had either non-polar poly(ethyl acrylate) (PEA) or hydrogen-bond rich poly(2-hydroxyethyl acrylate) (PHEA) matrices. Although the PHEA materials have more hydrogen-bonds, the self-healing, toughness and fracture energies were poorer than the PEA systems. This suggests that strong and dynamic hydrogen-bonds, even at the potential expense of total hydrogen-bonds, should be chosen for applications that require toughness such as high-performance coatings, sealants or elastomers.

KEYWORDS: Hydrogen-bonds; toughness; fracture energy; polymer network; interpenetrated network; dynamic bonds; self-healing polymers; RAFT polymerization.

Dynamic bonds have made substantial impacts on polymer materials, enabling materials to have extended useful lifetimes, improving toughness, or enhanced performance in challenging environments.[1] Realized and potential applications of dynamic polymers are numerous including coatings, sealants, advanced elastomers, rubbers, self and rehealable materials and even biomedical applications.[1-4] These applications arise from the dynamic bonding increasing toughness and enabling the material to be reprocessed or recover from damage. Dynamic bonds fall into two categories, dynamic covalent or dynamic non-covalent bonds.[5,6] Dynamic covalent bonds use strong covalent bonds which typically require external stimuli to activate them towards exchange.[5] In contrast, dynamic non-covalent or supramolecular bonds tend to be active under ambient conditions with relatively fast exchange under ambient conditions.[7] There are many examples of non-covalent bonds including host-guest interactions, metal-coordination, and hydrogen-bonds.[6] Hydrogen bonds have often been used to make dynamic and self-healing materials which exchange and heal under ambient conditions.[2,6] Due to the large number of functionalities that can introduce hydrogen bonds to a material, "sacrificial" or engineered hydrogen bonds have been commonly added to polymer materials to increase performance in self-healing or toughness tests.[8,9] High performance polymer materials can be engineered by combinations of dynamic covalent and non-covalent bonds such as hydrogen bonds.[7,8,10-12] In these cases the dynamic covalent bonds can provide material integrity, with the non-covalent bonds introducing dynamics under ambient conditions.[10,13] Recent work has also shown that network and macromolecular architecture can further impact material mechanics. Interpenetrated networks (IPN), with one network entangled but not linked to the other, have enhanced toughness, fracture energy and strength.[13-16]

One of the most commonly used and accessible strong hydrogen-bonded linkers is the quadruple hydrogen bonded 2-ureido-4[1H]-pyrimidinone (UPy) linker, with dimerization constants that can exceed 10^6 M^{-1}.[17,18] This linker has been incorporated into polymer materials to induce thermoreversibility,[19] self-healing,[20], shape memory,[21,22] responsive adhesive properties,[23] and enhanced toughness[24,25] through exchange of these H bonds. As with all other hydrogen-bonded interactions, solvent effects can impact association constants for UPy units, with less polar solvents favoring stronger association of UPy units.[25,26] Earlier work has incorporated the UPy units into both polar polymer matrices rich in hydrogen bond donors and acceptors,[10,13] as well as non-polar matrices which should favor strong association of the UPy units.[14,27] In polar matrices, such as poly(2-hydroxyethyl acrylate) (PHEA), the association of UPy units is likely to be substantially weakened,[19,28,29] but there is a larger *quantity* of hydrogen-bonds from the UPy units and the OH and carbonyl groups in the monomer.[30,31] In contrast, in non-polar matrices such as poly(ethyl acrylate) (PEA) the association of UPy unit is likely to be enhanced, or a higher *quality* UPy bond, although the backbone monomers do not form a hydrogen-bonded network. Typically, a material's toughness and ability to tolerate fractures before failing improves with "sacrificial" hydrogen-bonds,[8] although it is currently unclear if quality of UPy association or quantity of hydrogen bonds, even at the potential expense of UPy association, leads to superior toughness and self-healing properties. By modifying only one terminal hydrogen of PEA to an OH group in PHEA, difference in pendant group mobility should be small, and sidechain flexibility is likely to play a minimal part in overall material properties.[32] Earlier work showed IPN materials give superior mechanical properties by allowing more non-covalent bonds to form.[33] Therefore, IPN materials containing UPy linkers in one network and essentially static Diels-Alder adducts in the other network are used as model system. This model system is designed to provide evidence on whether materials are toughened through the strength of hydrogen bond association (*quality*) or total number of hydrogen-bonds (*quantity*). In particular, for UPy containing polymers we investigate whether polymer materials are toughened through the increased association constant of UPy hydrogen bonds in non-polar PEA matrices,[26] leading to improved *quality* of hydrogen-bonds. Alternatively, we test if UPy containing polymer materials are toughened with the greater *quantity* of hydrogen-bonds in a PHEA matrix, which contains hydrogen-bonds at each repeat unit, despite the potential decrease in the UPy association constant in hydrogen bond rich matrices.

A series of IPNs were synthesized with different matrices (hydrogen bond rich PHEA and non-polar PEA), chain lengths (primary chain lengths of 50 vs 100) and crosslink densities (5 mol% total crosslink density or 7.5 mol% total crosslink density). Note crosslink density is evenly split between non-covalent UPy units and covalent Diels-Alder units. Polymer molecular weight data is given in Table S1 for PEA materials and Table S2 for PHEA materials. Primary chain lengths were controlled by reversible addition-fragmentation chain transfer (RAFT) polymerization.[34] Table S1-S2 gives the molecular weight data for the RAFT polymers synthesized as determined by size exclusion chromatography (SEC) and nuclear magnetic resonance (NMR). Representative SEC traces are given in Figure S1 and representative NMR spectra used to calculate molecular weight averages are given in Figures S2-S3. Note the SEC derived molecular weights were determined using conventional calibration against poly(methyl methacrylate) standards, making them apparent molecular weights. Nevertheless, generally narrow molecular weight distributions were obtained indicating good control over polymer architecture, and the NMR analysis in Table S1-S2 indicates that the obtained polymer composition is close to the targeted composition, with PHEA based materials having substantially more hydrogen-bond donors than PEA based materials. The synthesis of the materials is given in Scheme 1.



Scheme 1. Synthesis and structure of IPN materials based on HEA (R=CH_2OH) or EA (R=CH_3) with UPy (green) hydrogen-bonded crosslinker and furan-maleimide (red-purple) covalent crosslinker.

Copolymers of ethyl acrylate (EA) or 2-hydroxyethyl acrylate (HEA) with either furfuryl methacrylate (FMA) or 2-(((6-(3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)ureido)hexyl)carbamoyl)oxy)ethyl acrylate (UPyA) were synthesized by RAFT polymerization using an approach developed in the literature.[14] To generate the IPNs, the UPyA copolymer was mixed with the FMA copolymer and 1,1′-(Methylenedi-4,1-phenylene)bismaleimide as a crosslinker for the FMA units, taking advantage of the Diels-Alder "click" chemistry properties.[35] Equal mass proportions of the non-covalent (UPyA) network forming polymer and the covalent (FMA) network forming polymer were used in each IPN, although IPNs of different backbone chain lengths and crosslink densities were used. It is important to note that the same backbone forming monomer (EA or HEA) was used for both the UPyA and the FMA polymers to limit the potential for phase separation. N,N-dimethylformamide (DMF) was used in the IPN synthesis, and removed after the material was formed.

A code was developed to describe the materials, for instance PEA_{100}-5% is a material with average chain length of 100 units with 5% crosslink density, and overall Diels-Alder crosslink density of 2.5 mol% and a UPyA crosslink density of 2.5 mol%. Typical infrared spectra of the materials are given in Figure S4 with the OH stretch clearly visible in the PHEA materials and absent in PEA materials. These infrared spectra are consistent with those reported for PEA,[14] and PHEA,[4] based materials.

Table 1. Thermal and mechanical properties of the IPN materials. Errors represent standard error of mean.

Material	T_g (°C)	σ_{peak} (kPa)	ε_{break}(mm/mm)	E (kPa)
PEA_{100}-5%	-5	480±40	1.9±0.2	490±60
PEA_{100}-7.5%	1	1900±100	1.00±0.04	2900±200
PEA_{50}-7.5%	0	1260±40	1.74±0.07	1100±200
$PHEA_{100}$-5%	17	290 ± 60	2.54±0.06	190±50
$PHEA_{100}$-7.5%	19	2000±200	0.7±0.1	4500±400
$PHEA_{50}$-7.5%	13	900±200	1.12±0.04	1000±200

To evaluate the performance of the 6 materials, tensile, self-healing and fracture energy experiments were performed. Table 1 gives the tensile and thermal properties of each material. All materials had glass transition temperatures (T_g) near or below room temperature as determined by differential scanning calorimetry (DSC). The DSC measured T_g of homopolymers of PHEA were found to be -14 °C and -17 °C for $PHEA_{50}$ and $PHEA_{100}$, respectively. Similarly, the DSC measured T_g of homopolymers of PEA were found to be -32 °C and -30 °C for PEA_{50} and PEA_{100} homopolymers, respectively. In all cases, crosslinking to the IPN materials increases the rigidity of the backbone and raises the T_g, with small variations in T_g due to composition and chain-length, with the material with the highest crosslink density and chain length having the highest T_g.

It is important to note that under the testing conditions of ambient temperature (22 °C), all materials are above the glass transition temperature, leading to soft elastomeric material. This is reflected in the Young's Modulus values calculated using the Ogden model,[36] showing similar Young's modulus (E) values in the same order for paired PHEA and PEA materials. Young's modulus values are in the range of 0.2-5 MPa as shown in Table 1, typical for elastomeric materials.[37]

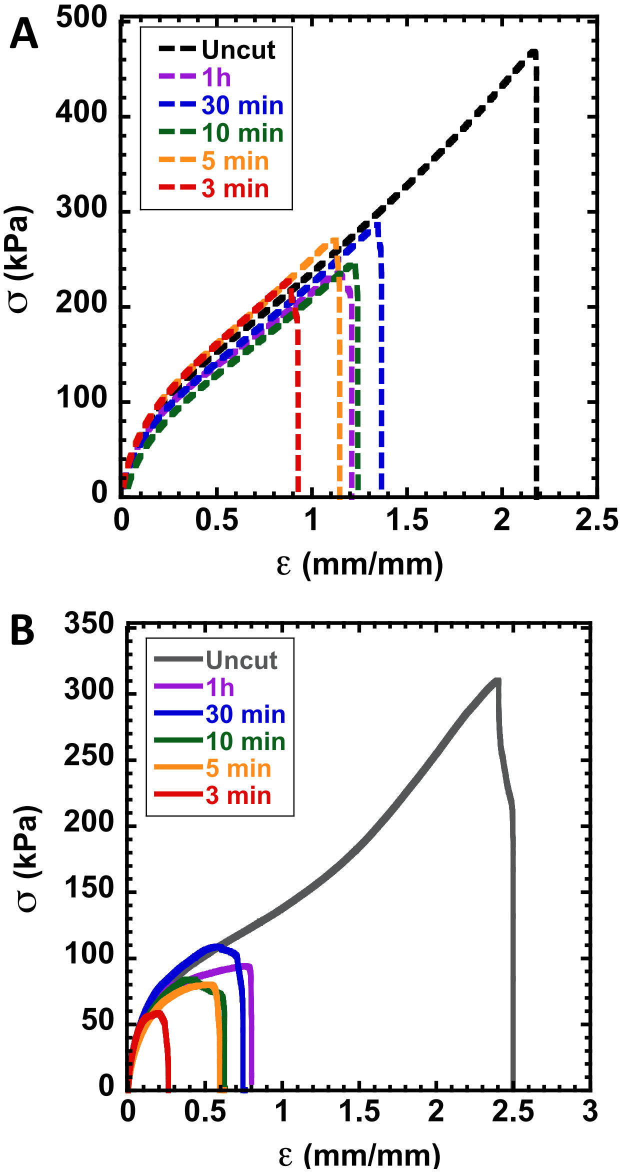


Figure 1. A) Self-healing at ambient temperature of PEA_{100}-5%. B) Self-healing at ambient temperature of $PHEA_{100}$-5%.

Each material's peak stress (σ_{peak}) and strain at break (ε_{break}) was evaluated by tensile testing. As anticipated higher crosslink density led to larger σ_{peak}, but made the materials less elastic reducing ε_{break}. Higher chain lengths led to an increase the number of elastically effective linkers that percolate the network, increasing σ_{peak}.[14,38] In general the HEA based materials had similar or slightly lower σ_{peak} values compared to the comparable EA material, however, due to the presence of covalent crosslinkers there is only a relatively small difference between the tensile properties of PHEA and PEA based materials.

To explore the dynamics and efficacy of hydrogen-bonds in the polymer networks, self-healing experiments were performed at room temperature. Earlier work showed that the covalent linkers are essentially static at room temperature, with self-healing attributed to exchange of hydrogen-bonds.[10,13,14] As seen in Figure 1, the PEA_{100}-5% material recovered approximately half of the σ_{peak} and ε_{break} compared to the uncut material. In contrast, the $PHEA_{100}$-5% recovered only about one quarter to one half of the σ_{peak} and ε_{break} of a typical uncut material. After 10 min there is minimal increase in recovered mechanical properties after self-healing consistent with the seconds to minutes timescale of UPy exchange.[27]

The superior performance of PEA_{100}-5% compared to $PHEA_{100}$-5% suggests that the self-healing is promoted by the stronger hydrogen-bonded associations in the non-polar PEA matrix. Although PHEA has a greater number of potential hydrogen-bonds, this did not lead to improved self-healing. Figure S5 and Figure S6 compare the self-healing of the PEA_{100}-7.5% with self-healing of the $PHEA_{100}$-7.5% material and the self-healing of the PEA_{50}-7.5% material with the self-healing of the $PHEA_{50}$-7.5% material, respectively. All PEA based materials displayed superior self-healing to the PHEA based materials of the same composition. The self-healing data suggests that the UPy crosslinkers are more efficiently bonding in the PEA matrix compared to the PHEA matrix.

To further evaluate the impact of matrix hydrogen-bond characteristics on the materials energy dissipation and defect tolerance, toughness and fracture energy calculations were performed. Material toughness (Φ) was calculated as the area under the stress-strain curve in a tensile test as follows:[39]

$$\Phi = \int_0^{\varepsilon_{\text{break}}} \sigma \, d\varepsilon \qquad (1)$$

Where σ is the engineering stress, ε is the applied strain up to $\varepsilon_{\text{break}}$. Fracture energy was determined using the paired notched pristine approach outlined by Zhao et al.[40] One set of rectangular samples were notched ½ the width and subjected to tension until break. This gives the mean notched specimens strain at break ($\varepsilon_{\text{notch}}$). The energy needed to break this material was determined by applying tension to a pristine sample to the same strain and calculating the energy under the unnotched sample's stress-strain curve. The fracture energy (Γ) is determined by the following equation:[40]

$$\Gamma = h \int_0^{\varepsilon_{\text{notch}}} \sigma \, d\varepsilon \qquad (2)$$

Where h is the unnotched sample's initial height and σ, and ε are the unnotched specimen's stress and strain.

As seen in Figure 2A, the EA and HEA materials had similar toughness values for the DP_{100}-5% and DP_{100}-7.5%, although the DP_{50}-7.5% EA materials had a slightly higher toughness than the HEA material. These data suggest that the stronger binding of UPy units in the non-polar EA matrix at least offsets the greater number of hydrogen-bonds in the HEA matrix. However, the toughness includes contributions from both the covalent network and the non-covalent UPy network. Therefore, fracture energy were calculated to determine the impact of total energy dissipative interactions, including UPy hydrogen-bonds, matrix hydrogen bonds and other non-covalent interactions, including entanglements and dispersion forces.

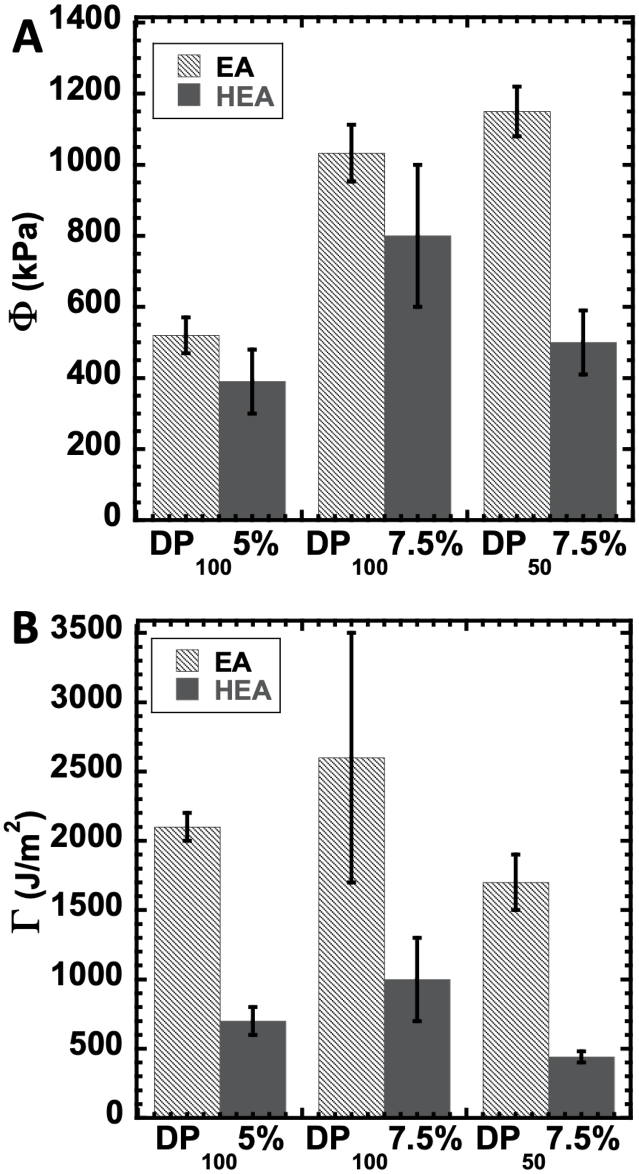


Figure 2. A) Toughness (Φ) and B) fracture energy (Γ) for PEA100-5%, PEA100-7.5%, PEA50-7.5%, PHEA100-5%, PHEA100-7.5%, and PHEA50-7.5%. Note that the DP label was used to denote the degree of polymerization to facilitate direct comparison of the materials. Error bars represent standard error of mean.

Figure 2B showed that the EA materials have superior fracture energies compared to the HEA networks of the same composition. It is noteworthy that the fracture energies (Γ) show larger discrepancies between the PEA and the PHEA series than the toughness values (Φ). This could be because the toughness includes contributions from both non-covalent and covalent linkers, while fracture energy is primarily dictated by energy dissipation driven by non-covalent hydrogen-bonds. The poor fracture energy and self-healing results of the PHEA materials suggest that despite HEA matrices increasing the *quantity* of hydrogen-bonds in the material, the PHEA derived hydrogen bonds are relatively weak and may disrupt or compete with the strong UPy linkers. This disruption of strong UPy hydrogen bonds can lead to a decrease in fracture energy and toughness, as well as reducing the self-healing efficiency. In contrast, the non-polar EA matrix promotes the formation of strong UPy hydrogen-bonds, since the matrix does not compete with hydrogen-bonding between UPy units, leading to enhanced self-healing and higher fracture energies. Despite the lower quantity of potential hydrogen-bonds in EA matrixes, the increased association constant of the UPy units, or increased *quality* of UPy hydrogen bonds, more than offsets this decrease in total number of hydrogen-bonds. Presumably, at very low densities of UPy crosslinker, the large number of hydrogen-bonds in HEA would surpass the small number of hydrogen-bonds possible from the UPy units. However, within typical crosslink densities studied, such as the 2.5-3.75 mol% UPy the ability to form high quality hydrogen-bonds is critical, even if comparing against a system with an overall reduced number of hydrogen-bonds. These results hold under the tested conditions at the compositions studied, and suggest that *quality* of hydrogen bonds may be more important than *quantity* in these model systems.

In conclusion, IPNs containing covalently crosslinked Diels-Alder networks and quadruple hydrogen bonded 2-ureido-4[1H]-pyrimidinone (UPy) crosslinked networks were synthesized in two matrices of different hydrogen-bonding capabilities. One system used a non-polar poly(ethyl acrylate) matrix (PEA), and the other used a polar and hydrogen-bond rich poly(2-hydroxyethyl acrylate) (PHEA) matrix. The room temperature self-healing data for the PEA system was superior to the PHEA system, suggesting that the increased association constant of UPy units in the PEA matrices, or increased *quality* of UPy hydrogen bonds, is more important than the total hydrogen-bonds in the studied PHEA systems, or *quantity* of hydrogen bonds. Toughness and fracture energy measurements corroborate the self-healing experiments, indicating that in the studied systems, the increased association strength of hydrogen-bonded UPy units in the tested non-polar PEA matrices improves the mechanical properties, despite the PHEA matrices having more hydrogen-bonds. This work suggests that a materials performance can be enhanced by focusing on introducing stronger dynamic non-covalent bonds to a polymer material. This will enable the design and realization of tough adhesives, elastomers, sealants, and hydrogels for future applications in the materials and biomedical spaces.

ASSOCIATED CONTENT

Supporting Information. Experimental details, polymer characterization data and additional materials characterization data are available.

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