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Published in:
ACS Macro Letters

DOI:
[10.1021/acsmacrolett.7b00011](https://doi.org/10.1021/acsmacrolett.7b00011)

Published: 15/02/2017

Document Version
Peer reviewed version

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Please cite the original version:
Myllymäki, T. T. T., Lemetti, L., Nonappa, N., & Ikkala, O. (2017). Hierarchical Supramolecular Cross-Linking of Polymers for Biomimetic Fracture Energy Dissipating Sacrificial Bonds and Defect Tolerance under Mechanical Loading. *ACS Macro Letters*, 6(3), 210-214. <https://doi.org/10.1021/acsmacrolett.7b00011>

Hierarchical Supramolecular Cross-Linking of Polymers for Biomimetic Fracture Energy Dissipating Sacrificial Bonds and Defect Tolerance under Mechanical Loading

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ABSTRACT: Biological structural materials offer fascinating models how to increase synergistically the solid state strength, toughness, and defect tolerance using nanocomposite structures by incorporating different levels of supramolecular sacrificial bonds to dissipate fracture energy. Inspired thereof, we show how to turn a commodity acrylate polymer, characteristically showing a brittle solid state fracture, to become defect tolerant manifesting noncatastrophic crack propagation by incorporation of different levels of fracture energy dissipating supramolecular interactions. Therein poly(2-hydroxyethyl methacrylate) (pHEMA) is a feasible model acrylate polymer showing brittle solid state fracture, where the weak hydroxyl-hydroxyl hydrogen bonds do not suffice to dissipate fracture energy. We provide the next level stronger supramolecular interactions towards solid-state networks by random copolymerization of a small fraction of methacrylates containing 2-ureido-4[1*H*]-pyrimidinone (UPy), capable of forming strong 4 parallel hydrogen bonds. Interestingly, such a p(HEMA-*r*-UPyMA) shows toughening by suppressed catastrophic crack propagation even if the strength and stiffness are increased. At the still higher hierarchical level, colloidal level crosslinking using oxidized carbon nanotubes with surface decorations, including UPy, COOH and OH surface groups leads to further increased stiffness and ultimate strength, still leading to suppressed catastrophic crack propagation. The findings suggest to incorporate a hierarchy of supramolecular groups of different interactions strengths upon pursuing towards biomimetic toughening.

Biological structural materials, such as spider silk, nacre, wood, bones and tendons, suggest that even if using mechanically inferior building blocks, remarkable combination of mechanical properties can be achieved, taken a proper self-assembly design is incorporated.¹⁻¹⁰ Therein, the synergistic mechanical properties typically arise from the self-assembled nanoscale structures, where stiff reinforcements are connected to soft, energy-dissipative matrices, involving hidden lengths and non-covalent sacrificial bonds at different scales.⁹ This has encouraged material scientists to pursue bioinspired nanostructured synthetic materials to combine fracture toughness with stiffness and strength.¹¹⁻²⁵ Therein, several types of biomimetic composites have been realized, including different kinds of combinations of hard and soft domains as connected via covalent and non-covalent interactions. They have allowed interesting mechanical properties, but combining high strength with fracture toughness and defect tolerance has remained challenging, especially if facile preparation is aimed. Therefore, novel molecularly engineered designs to create nanocomposites are needed. In synthetic materials, promoted toughening has extensively been studied in water-based nanocomposite hydrogels and double gels.^{26,27} By contrast, in the solid state, the interplay of supramolecular dynamics and binding strength becomes more subtle, especially if colloidal length scale is involved.^{24,25}

Here we suggest a biomimetic route where a hierarchy of different strengths of supramolecular interactions are used to pursue synergistic toughening and reinforcement using a commodity acrylate polymer to form network-like materials in

the solid state. Therein poly(2-hydroxyethyl methacrylate) (pHEMA) is a feasible model polymer, as it is glassy and brittle. It incorporates hydroxyl groups capable of mutual hydrogen bonds, obviously not sufficiently strong to act as sacrificial bonds to dissipate mechanical energy to allow toughening. It can be modified by incorporating a small fraction of stronger hydrogen bonding motifs by random copolymerization using 2-ureido-4[1*H*]-pyrimidinone (UPy) containing methacrylate repeat units, where the modified polymer is denoted here as poly(HEMA-*r*-UPyMA). UPy's form four complementary hydrogen bonds, with a high hydrogen bonding dimerization constant of $6 \times 10^7 \text{ M}^{-1}$ and $6 \times 10^8 \text{ M}^{-1}$ in CHCl_3 and in toluene, respectively.²⁸ UPy hydrogen bonded dimers can be dissociated by dissolution in highly polar solvents such as dimethyl sulfoxide (DMSO) or *N,N'*-dimethyl formamide (DMF) to facilitate processing, and re-associated by solvent exchange or by evaporation of the solvent.²⁹ The high strength of the UPy dimers arise from its parallel array of hydrogen bond donors and acceptors (DDAA), that have four attractive primary hydrogen bonds, four attractive secondary interactions and only two repulsive secondary interactions.³⁰ UPy has been used to construct a wide range of supramolecular assemblies and networks, and to promote self-healing and toughness.³¹⁻⁴¹

Still another higher level of physical cross-linking for the poly(HEMA-*r*-UPyMA) supramolecular network is suggested using colloidal units with numerous hydrogen bonding motifs. Beyond dynamic cross-linking, such units could also reinforce. Therein, carbon nanotubes (CNTs) offer great potential due to their exceptional mechanical, thermal and electronic

properties.^{42,43} Substantial efforts have been made to harness the properties of individual carbon nanotubes into bulk objects. Tensile strength of an individual multi walled carbon nanotube (MWCNT) can be 11-150 GPa.^{44,45} The lateral **dimensions** are usually few nanometers with lengths up to centimetre range.⁴⁶ CNTs have been applied in several nanocomposites where they promote strength and provide conductivity.⁴⁷⁻⁵⁰ However, CNTs connected to soft polymer matrix supramolecularly have offered poor mechanical properties.^{39,51}

UPy groups have been covalently attached to MWCNTs previously to form polymer composites and brittle self-standing films.^{38,39} To achieve any competitive materials involving CNTs, they need to be properly dispersed and debundled. Oxidation of CNTs is a common way to disperse CNTs in solvents and water.⁵² CNTs can be functionalized to achieve better stabilization in the solvent or to have added functionalities.^{52,53}

Figure 1. Scheme of the proposed biomimetic hierarchical supramolecular polymer cross-linking for sacrificial fracture energy dissipating bonds. a) Hydrogen bonds between the hydroxyl groups between pHEMA-chains constitute the weakest supramolecular interactions. b) Decorating the polymers by random copolymerizing of a small fraction of UPy-containing **repeat units** allows strong four-hydrogen bonds as the supramolecular cross-links. c) Oxidized CNT's decorated with UPy's, -COOH's and -OH's allow a palette of further hydrogen bonds to further crosslink p(HEMA-*r*-UPyMA) as the highest level cross-linker.

In this work, we explore whether polymeric solid state toughening, manifested as suppressed catastrophic crack propagation, can be obtained using supramolecular cross-linking at different scales. The suggested logic of this work is shown in Figure 1. The chains of pHEMA undergo only weak hydroxyl-hydroxyl hydrogen bonds (Figure 1a), and incorporating a small fraction of UPy-containing methacrylates provides additional stronger supramolecular interactions, effectively forming physical cross-links within the solid state, i.e., p(HEMA-*r*-UPyMA) (Figure 1b). Oxidized CNTs are decorated with UPy-surface groups in addition to the COOH, and OH-surface groups originating from the oxidation, and thus provide colloidal level cross-linking units for p(HEMA-*r*-UPyMA) with several supramolecular interaction sites (Figure 1c).

Two different molecular weights of pHEMA were explored: 2×10^4 g/mol and 1×10^6 g/mol (Sigma Aldrich). They were reacted with 2-(6-isocyanatohexylurea)-6-methyl-4[1H]pyrimidinone to derivatize different small fractions of OH groups with UPy (see SI for details). Subsequently, solely the higher molecular weight pHEMA is here addressed, as the smaller pHEMA molecular weight lead to poor mechanical properties. Too high (> ca. 4 mol %) UPy derivatization of hydroxyls of pHEMA resulted in difficulties in dissolution in DMF, whereas too low derivatization (2 mol %) lead to brittleness. Therefore, a composition where 4 mol % of the OH-groups have been modified using UPy is selected, denoted subsequently as p(HEMA-*r*-UPyMA). It is soluble in DMF at 60 °C, whereas at room temperature the mixture becomes turbid, but dissolves again upon heating. On the

other hand, pristine MWCNTs were first oxidized with a 1:3 mixture of conc. HNO_3 and conc. H_2SO_4 at 80 °C for 3 h, followed by centrifugation and washing with water until no sulphates were present, according to literature procedure.⁵³ OxCNTs were then dialyzed against DMF for complete solvent exchange and reacted with excess of 2-(6-isocyanatohexylurea)-6-methyl-4[1H]pyrimidinone using dibutyltin dilaurate (DBTDL) as a catalyst at 80 °C for 24 h to functionalize with UPy-groups. Unreacted reactant was removed by dialysis in DMF (see SI for details). The resulting composition is denoted as OxCNT-g-UPy. It can be dispersed in DMF, where the dispersion is stable for months. The two components, i.e., CNT-g-UPy and p(HEMA-*r*-UPyMA), were fully compatible without any clear phase separation as illustrated by the photograph of the composite dispersion (Figure 2b) and TEM micrographs of a cast film (Figures 2c and Figure S4). In contrast, pristine OxCNTs (i.e., without UPy units) precipitated from DMF immediately. Therefore, the UPy-groups ensure compatibility and adhesion between OxCNT phase and the p(HEMA-*r*-UPyMA) matrix. Films were prepared by solvent evaporation from a mixture consisting of p(HEMA-*r*-UPyMA)/CNT-g-UPy 99/1 wt/wt in DMF (30.4 mg/mL) at 80 °C on polytetrafluoroethylene beakers. For the mechanical testing, 2.25 mm wide and 5 mm long samples were cut from dry films of thickness 90-200 μm . The samples were incubated at room temperature at 50 % relative humidity (RH) for 24 h prior mechanical testing (see SI for details and Videos S1-S6).

Figure 2. Visual appearance and TEM of the OxCNT-g-UPy/p(HEMA-*r*-UPyMA) hybrids. a) A photograph of the dispersion of OxCNT-g-UPy in p(HEMA-*r*-UPyMA) 99/1 wt/wt in

DMF (30.4 mg/mL) illustrating the compatibility upon dissolving by heating. b) Photograph of a film cast from DMF at 80 °C. c) TEM micrograph of diluted sample of the nanocomposite film obtained upon casting over TEM grid with holey carbon support film, showing the nanoscale compatibility of CNT-g-UPy and p(HEMA-*r*-UPyMA).

Figure 3 shows the tensile stress-strain curves of the films for different compositions at 50% RH. The pristine pHEMA shows a modulus of 32 kPa, a clear yielding at ca. 2 MPa and beyond that the ultimate strength of 3.7 MPa is observed at the elongation of 216 % (Figure 3a, Table 1). Importantly, the fracture is brittle. By including stronger UPy hydrogen bonding motifs as supramolecular cross-linkers, p(HEMA-*r*-UPyMA) showed increased modulus to 54 kPa, increased yield strength of ca. 4 MPa, beyond which considerable yielding was observed. The maximum elongation was reduced in comparison to pristine pHEMA, but most importantly, the material demonstrated non-catastrophic crack propagation and suggests onset of necking (Figure 3b, Videos S1-S3). Upon typical tensile strength test, several cracks formed and the cracks propagated slowly. The local true stress-strain behavior near the crack tips was evaluated from the videos, and two examples are shown in Figure 3b. Considerable strain hardening is suggested therein. The evident scatter between the individual crack propagation is not surprising as the exact local nonuniformities in the samples can play a major role in the propagation of the exact crack tips. The increased modulus indicates that the reduced brittleness in p(HEMA-*r*-UPyMA) does not result from plasticization by incorporation of UPy and that synergistic increase of both toughness and stiffness is involved. Finally, the two-component nanocomposite p(HEMA-*r*-UPyMA)/OxCNT-g-UPy at the composition 99/1 wt/wt also showed high yield strength of ca. 4 MPa, i.e. close to that of p(HEMA-*r*-UPyMA), but larger ultimate strength 5.6 MPa. The modulus was considerably increased to 132 kPa. The increase in strength upon addition of CNT-g-UPy and the decoration of pHEMA with UPy was not surprising, as CNTs have been previously used to increase strength of polymeric materials.^{38,39} Interestingly, the nanocomposite does not undergo catastrophic failure (Figure 3c), but instead fail in a controlled manner, dissipating energy throughout the failure process. The initial crack that formed during elongation propagated slowly and showed onset of necking. In some samples, the crack propagation terminated, and a new crack was formed and continued propagation (Videos S3-S6). The controlled failure is an indirect evidence of successful incorporation of sacrificial bonds within the material. The onset of necking allows to evaluate the high true stresses at the site of the slowly progressing cracks (Figure 3c). As the crack propagates, the true stress in the material significantly increases before failure to reach the values between 20-60 MPa (Figure 3c) in comparison to the nominal value 5.6 MPa. The increased true stress points towards local alignment of CNT-g-UPy near the tip of the progressing crack.

That supramolecular interactions have a central role in the toughening and compatibility is shown by a control experiment where pHEMA without UPy and OxCNTs without UPy were mixed together in the same ratio as with the nanocomposite between CNT-g-UPy and p(HEMA-*r*-UPyMA). The maximum tensile strength, yield strength and the maximum elongation of the prepared films showed poor mechanical properties compared to those of untreated pHEMA (Figure 3a, Table 1). The ultimate strength was 1.85 MPa, ca. 50 % less than the untreated pHEMA. Also, the composite between OxCNTs and pHEMA did not show any fracture toughness, necking or controlled crack growth, but instead broke catastrophically. The results obtained from the mechanical tensile measurements and

error bars are summarized in Table 1. For completeness, Table 1 also shows the “work to fracture”, i.e. the integrated area below the stress-strain curves. We point out, however, that this param-

eter may not properly describe localized fracture properties, i.e. behavior of the localized propagation of crack tips.

Figure 3. Stress strain curves. a) Stress-strain curves of pHEMA, p(HEMA-*r*-UPyMA), and p(HEMA-*r*-UPyMA)/OxCNT-g-UPy. Pristine pHEMA shows a brittle fracture. Also pHEMA/OxCNT shows a brittle fracture. b) p(HEMA-*r*-UPyMA) shows suppressed catastrophic fracture and slow crack growth in tensile deformation. The true stress is evaluated at the site of onset of necking (see Videos S1-S3). Captures from two video-clips are shown to illustrate the slow crack propagation. As the sample is transparent, additional photos with artificially enhanced contrast at sample edges are shown below the actual photos (see insets) to illustrate qualitatively the onset of necking. c) p(HEMA-*r*-UPyMA)/OxCNT-g-UPy 99/1 wt/wt shows suppressed catastrophic fracture and slow crack growth in combination of increased strength. The true stress is shown at the site of onset of necking for three different samples (see Videos S4-S6). Captures from three video-clips are shown to illustrate the slow crack propagation.

Table 1. Mechanical tensile properties for the composite and for control samples

Sample	σ (MPa) ^a	ϵ_b (%) ^b	E (MPa) ^c	(MJ/m ³) ^d
pHEMA	3.70 ± 0.09	216.86 ± 6.82	0.032 ± 0.003	5.58 ± 0.15
pHEMA/OxCNT-g-UPy	1.85 ± 0.06	119.96 ± 0.03	0.022 ± 0.003	1.59 ± 0.08
p(HEMA- <i>r</i> -UPyMA)	3.46 ± 0.29	123.47 ± 12.4	0.054 ± 0.006	4.02 ± 0.40
P(HEMA- <i>r</i> -UPyMA)/OxCNT-g-UPy	5.62 ± 0.52	117.65 ± 3.07	0.135 ± 0.006	5.63 ± 0.40

^aNominal strength (ultimate tensile strength) ^bStrain at failure ^cYoung’s modulus ^dWork to failure

In conclusion, we have shown that decorating pHEMA with a small fraction of UPy-containing repeat units, i.e. p(HEMA-*r*-UPyMA) converts the polymer tough in the solid state, demonstrating slow and **noncatastrophic** crack propagation. At the same **time**, the modulus and yield strength increase ca. 245 % and ca. 200 %, correspondingly. The synergistic suppression of brittle crack propagation and increase of stiffness and strength suggest that the supramolecular cross-links act as sacrificial bonds in mechanical deformations, thus dissipating fracture energy. Further add-

ASSOCIATED CONTENT

Supporting Information.

The supporting information containing synthetic details, materials and methods, characterization data is available free of charge on the ACS Publications website.

ing a small weight fraction of **UPy-decorated** oxidized multiwall carbon nanotubes as colloidal cross-linkers, i.e. OxCNT-g-UPy, effectively additionally cross-links and reinforces p(HEMA-*r*-UPyMA), thus leading increased ultimate strength, still suppressing **catastrophic** crack propagation. The biomimetic design, where soft polymers are toughened via noncovalent supramolecular interactions at different scales, is suggested to be an effective way towards next-generation materials that are not only strong, but also dissipate energy during mechanical stress.

Supporting Information (PDF)

Video S1 Tensile measurement of p(HEMA-*r*-UPyMA) (mp4)

Video S2 Tensile measurement of p(HEMA-*r*-UPyMA) (mp4)

Video S3 Tensile measurement of p(HEMA-*r*-UPyMA) (mp4)

Video S4 Tensile measurement of p(HEMA-*r*-UPyMA)/OxCNT-g-UPy (mp4)

Video S5 Tensile measurement of p(HEMA-*r*-UPyMA)/OxCNT-g-UPy (mp4)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

Funding from Academy of Finland, Centre of Excellence in Molecular Engineering of Biosynthetic Hybrid Materials (2014-2019) and ERC Advanced Grant MIMEFUN are acknowledged.

Notes

Authors declare no competing financial interest.

ACKNOWLEDGMENT

This work made use of the facilities of Nanomicroscopy Centre, Aalto University.

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Table of Content Graphic

UPy-mediated
sacrificial bonds
Slow crack
propagation