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Unusual Mechanical Performance of Amphiphilic Crosslinked Polymer Networks

Jinqi Xu,[†] David A. Bohnsack,[‡] Michael E. Mackay,[‡] and Karen L. Wooley*,[†]

Center for Materials Innovation and Department of Chemistry, Washington University, St Louis, Missouri 63130,
and Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing,
Michigan 48824

Received November 8, 2006; E-mail: klwooley@artsci.wustl.edu

Smart materials comprising natural and/or synthetic polymers and designed for application in aqueous environments that require minimal protein adsorption[1]—marine coatings, nanocarriers for drug delivery, scaffolds for tissue engineering, etc.—have seen a rapid rise in their investigation. These materials commonly have hydrophilic, hydrogel characteristics and properties (e.g., low mechanical strength) that introduce difficulties in handling and may impede their biological uses.[1,2] Our interest in the development of nontoxic, antibiofouling marine coatings requires mechanically robust or tough materials, both in the dry state and in the marine environment. These coatings rely upon limiting bioadhesion, which depends on the surface energy,[3] surface reconstruction,[4] and other properties of the materials,[5] including the elastic modulus.[6]

Recently, an amphiphilic crosslinked polymer network, composed of hyperbranched fluoropolymer and poly(ethylene glycol) (HBFP-PEG), has been developed with complex surface topographies, morphologies, and compositions distributed over nanoscopic dimensions.[7] Importantly, this complex material has exhibited superior abilities to inhibit protein adsorption and prevent marine organism settlement, which are related to its composition,[8] its heterogeneous surface properties, and the resulting surface reconstruction under water.[4a,7] In addition, the subsurface morphology provides nanoscale channels that have been shown to serve as a host environment for the uptake and promoted release of guest molecules.[7c] Because of the potential utility of the unique surface and subsurface properties of these materials, in applications that involve an aqueous environment, we have now investigated their mechanical properties, as prepared and after swelling in water. The stoichiometry of the HBFP and PEG were varied to alter the relative hydrophobic/hydrophilic balance and to control the domain sizes enriched in each of these two components. Interestingly, unlike hydrogels, water molecules were found to rigidify the amphiphilic networks, composed of a minority of PEG, whereas absorption of water molecules afforded the opposite effect when the materials were comprised of a PEG majority.

The amphiphilic networks were prepared and characterized as described previously.[7] The labile *p*-fluorine of the pentafluorophenyl groups present within HBFP ($M_n = 9000$ Da) underwent nucleophilic substitution by the terminal amino groups of bis(3-aminopropyl)-terminated PEG ($M_n = 1600$ Da) to interconnect the two immiscible components (Scheme S1 of Supporting Information (SI)), upon casting from tetrahydrofuran solution onto chlorotrimethylsilane-treated glass microscope slides. Such in-situ crosslinking trapped the thermodynamically driven phase segregation kinetically to provide nanoscopic features on the surface and throughout the bulk of the material.[7] The tensile properties of four systems, HBFP-PEG30, HBFP-PEG45, HBFP-PEG55 and HBFP-PEG63 (containing 30, 45, 55, and 63 wt % of PEG, respectively) were then investigated at 22 °C.

Dramatically different results were obtained by comparison of the dry samples (as prepared) versus those after swelling by water. As illustrated in Figure 1, the stress−strain curves for HBFP-PEG45 indicate a significant increase in elastic modulus (E) upon absorption of water (Figure 1a), whereas the data for HBFP-PEG55 exhibit a significant decrease in modulus under the same conditions (Figure 1b).

As the amount of PEG was increased from 30 to 45 wt %, E_{dry} increased ca. 4 times (Table 1 and Figure 2, variables are defined in the table). Upon further increase of the PEG amount to 55 or 63 wt %, E_{dry} reached ca. 12 MPa, 42 times higher than that of HBFP-PEG30. Coincidentally, ϵ_f decreased significantly from 880% to 80% upon the introduction of larger amounts of PEG, as expected, owing to the rigid, crystalline properties of the PEG-rich domains. X-ray diffraction studies[9] have shown that in-situ crosslinking of HBFP and PEG restricts the phase segregation process significantly, as compared with HBFP and PEG blends, but such crosslinked networks still contained the original two phases. Moreover, differential scanning calorimetry (DSC) studies of HBFP-PEG networks have demonstrated that the size of semicrystalline PEG-rich domains increases with the increment of PEG,[7b] even though individual components of hydrophobic HBFP and hydrophilic PEG were crosslinked covalently throughout the insoluble network. Therefore, nanoscopic and microscopic semicrystalline PEG domains may act as reinforcing fillers to improve the overall mechanical performance of HBFP-PEG (Figure 2).

As these films were swollen in water, they exhibited opposite mechanical performances (Table 1 and Figure 2). E_{wet} became much greater (ca. 10−50 times) than E_{dry} for HBFP-PEG30 and HBFP-PEG45, while E_{wet} decreased to be only ca. 10−20% of E_{dry} for HBFP-PEG55 and HBFP-PEG63. Hydrophilic PEG-rich domains within HBFP-PEG networks underwent swelling upon the addition of water, affording the complete disappearance of PEG crystallites and formation of DSC-observable PEG hydrate, but also causing an apparent inversion of the surface topography.[7b] The HBFP-PEG networks showed 38, 85, 112, and 140 wt % increase (and similar volume changes; Table S1 of SI) upon swelling with water as the PEG amounts increased from 30, 45, 55, to 63 wt %, respectively. Given the substantial water uptake for each system, we hypothesize that the semicrystalline PEG-rich domains acted as nano- and microchannels to absorb water molecules. This process eliminated crystallinity and led to entrapment of the water molecules in the HBFP-PEG30 and HBFP-PEG45, which contained PEG as the minor phase. It is further hypothesized that the uptake of water and swelling of the PEG-rich domains then deformed the amorphous HBFP-rich domains, both embrittling and rigidifying the entire networks; that is, $E_{wet} \gg E_{dry}$. In contrast, swollen HBFP-PEG networks performed as hydrogels as water-plasticized, soft, PEG-rich domains dominated the overall mechanical performance, giving $E_{wet} \ll E_{dry}$, when PEG amounts were large, 55 and 63 wt %.

[†] Washington University in Saint Louis.
[‡] Michigan State University.

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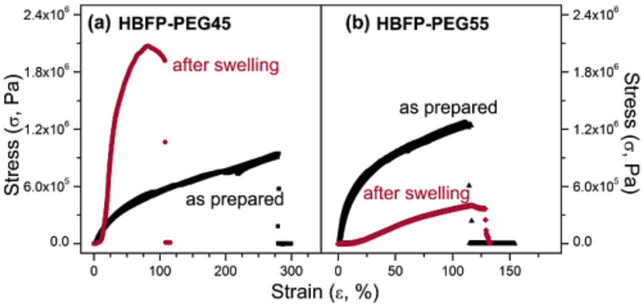

Figure 1. The stress−strain curves of HBFP-PEG45 (a) and HBFP-PEG55 (b) as prepared (black) and after (red) swelling in water.

Table 1. Summary of Mechanical Properties of Various HBFP-PEG Amphiphilic Networks before and after Water Swelling[a]

		before swelling in water			
films	PEG wt %	ultimate tensile strength (σ_{UTS}, MPa)	failure strain (ϵ_f, %)	E_{dry} (MPa)	E_{wet}[b] (MPa)
HBFP-PEG30	30	3.04 ± 0.42	880 ± 40	0.28 ± 0.05	14.5 ± 5.4
HBFP-PEG45	45	0.985 ± 0.057	30 ± 60	1.44 ± 0.24	13.0 ± 2.5
HBFP-PEG55	55	1.29 ± 0.22	13 ± 20	11.9 ± 1.8	0.95 ± 0.31
HBFP-PEG63	63	1.94 ± 0.89	80 ± 50	12.6 ± 2.2	1.92 ± 0.70

[a] Tensile measurements were performed on a RSA III instrument under ambient conditions. [b] After swelling in water for 5 min.

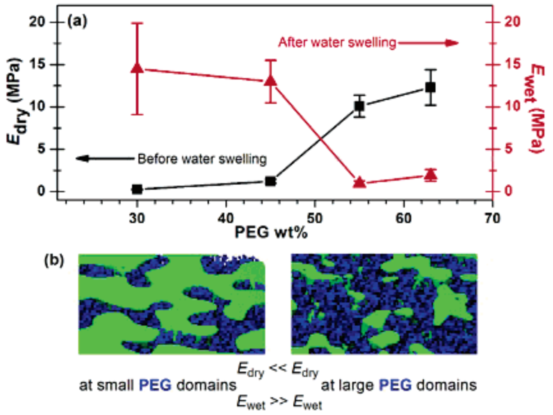

Figure 2. (a) Elastic moduli of HBFP-PEG with varying PEG wt % before (■) and after (▲) swelling in water; (b) schematic illustration of HBFP-PEG with PEG minority (left) and PEG majority (right).

Neither the testing speed for the tensile measurements nor swelling by D_2O (vs H_2O) gave a significant difference in the mechanical properties. It is interesting that the crossover point for crystalline PEG-based rigidification and water swelling-based rigidification appears to occur at ca. 50 wt % of the two polymer components (Figure 2).

It is well-known that phase-separating blends have co-percolative structures at concentrations between ca. 20% and 80% of a given component.[10] The significant increase of E_{dry} at PEG ≥ ca. 50 wt % suggests that a PEG-percolative structure is developed only above this concentration, perhaps due to the presence of a kinetic trapping of the phase segregation process (vide supra). In the swollen state, the majority PEG-rich phases were plasticized effectively, leading to the dramatic decrease of E. In contrast, as the minority PEG-rich domains swelled, the inverted percolated structure put the majority HBFP-rich phases under stress, resulting in $E_{wet} \gg E_{dry}$. Within the experimental time frame employed, it is possible that HBFP-PEG systems develop nonequilibrium percolating networks only when one phase is in majority, although this will be ascertained in future work. Moreover, the dynamics of the water molecules entrapped within each of the matrices is under investigation to better understand the unique properties of these materials.

In summary, we have demonstrated that the mechanical performance of HBFP-PEG amphiphilic networks depends on the amount of PEG present in the system. Water swelling in PEG-rich domains rigidifies or softens these materials, depending upon the size of the PEG-rich phases, relative to the hydrophobic HBFP network component. The unusual mechanical performance of HBFP-PEG45 with and without water may also contribute to their enhanced performance against bioadhesion in the marine environment, relative to common silicone elastomers and even other stoichiometries of HBFP-PEG.[4a] The tunability of their mechanical properties, the intrinsic characteristics of fluoro polymer and PEG, in combination with the nanoscopic surface and subsurface features, have suggested that these amphiphilic networks may be widely applicable in the design of novel biomedical devices. We are investigating these unique behaviors further to gain an understanding of their molecular and morphological origins.

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Supporting Information Available: Chemical structure of HBFP-PEG crosslinked networks, all stress−strain curves, and experimental details on film preparation, tensile measurement before and after water swelling, and swelling properties. This material is available free of charge via the Internet at http://pubs.acs.org.

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