

Nanoscale Structure of High Strength Poly(ethylene glycol)/Poly(acrylic acid) Interpenetrating Network Hydrogels from Small Angle Scattering

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Abstract – High strength hydrogels with water contents above 80 wt.% have been synthesized by interpenetrating a poly(ethylene glycol) (PEG) network with poly(acrylic acid) (PAA). Small angle x-ray and neutron scattering (SAXS/SANS) are used to determine the structure of PEG/PAA interpenetrating polymer network (IPN) hydrogels. SAXS/SANS show that PEG networks have an ordered structure with dense crosslink junction points spaced 10-15 nm apart; while PAA networks have a poorly defined structure. PEG/PAA IPNs have scattering profiles that suggest the occurrence of nanoscale phase separation. This structure could lead to the observed enhancement of mechanical properties in PEG/PAA IPNs.

Hydrogels are hydrophilic polymer networks that can imbibe large amounts of water, but are insoluble due to the presence of network crosslinks. Hydrogels are attractive materials for soft tissue replacement as they have water contents near that of natural tissue (80-95 wt.%) and have a high rate of cell nutrient diffusion. Despite these attractive properties, applications of hydrogels are often limited by their extremely fragile nature. Interpenetrating polymer network (IPN) hydrogels have been shown to exhibit an order of magnitude increase in tensile elastic modulus and fracture strength compared to single networks of each component [1, 2]. The enhanced mechanical properties of IPN hydrogels broaden their use to a number of applications requiring high mechanical strength.

To determine the molecular level structural basis for the enhanced mechanical properties observed in poly(ethylene glycol)/poly(acrylic acid) (PEG/PAA) IPN hydrogels, small angle x-ray and small angle neutron scattering (SAXS/SANS) techniques are employed. The first PEG network is formed by UV photopolymerization of diacrylate or diacrylamide terminated PEG macromonomers. This forms an ordered structure with dense crosslink junction points spaced 10-15 nm apart (molecular weight dependent) as evidenced by a correlation peak in the scattering pattern. When this PEG network is interpenetrated with PAA, SANS reveals that the PEG network maintains its ordered structure at low pH. At physiological pH PEG/PAA IPNs show two reasonably well defined features at $q \approx 0.3 \text{ nm}^{-1}$ and $q \approx 4.0 \text{ nm}^{-1}$ as shown in Figure 1. In these features, the intensity drops off as q^{-4} suggesting that the scattering is not from polymer fractals, but rather from phase separated domains on the nanoscale. This nanoscale phase separated structure may be responsible for the enhanced elastic modulus and fracture strength of PEG/PAA IPN hydrogels.

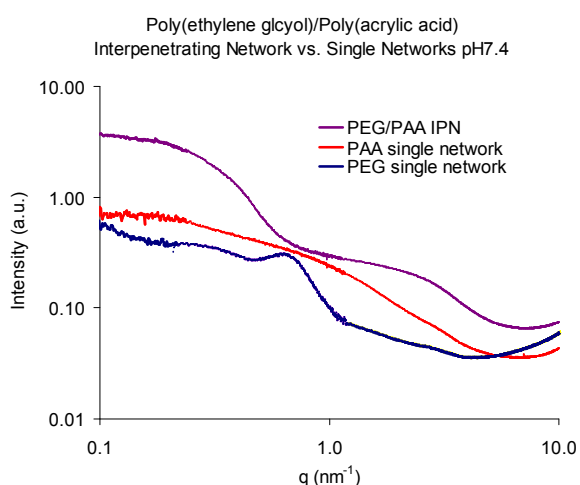


Figure 1: SAXS profiles for PEG/PAA IPN (top), PAA single network (middle), and PEG single network (bottom).

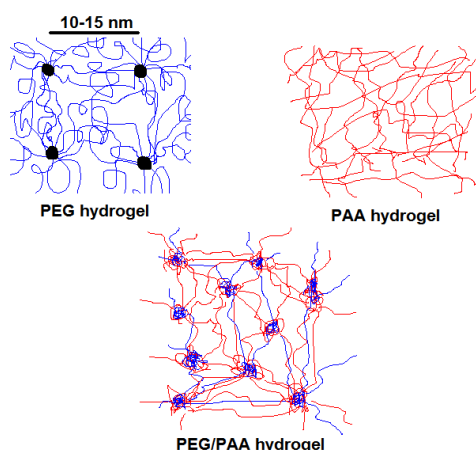


Figure 2: Sketches of molecular level structures that are consistent with the SAXS/SANS data for PEG hydrogels (top left), PAA hydrogels (top right), and PEG/PAA IPN hydrogels (bottom).

References

- [1] J.P. Gong, Y. Katsuyama, T. Kurokawa, and Y. Osada, *Advanced Materials* 15 (2003), 1155-1158.
[2] D. Myung, W. Koh, J. Ko, Y. Hin, M. Carrasco, J. Noolandi, C. N. Ta, and C.W. Frank, *Polymer* 48 (2007), 5376-87.