All-inorganic and hybrid self-healing hydrogels

Euzébio Skovroinski (PQ)[1], Rodrigo J. de Oliveira (PQ)[2], André Galembeck (PQ)[3,4]*. andre@ufpe.br

[1] Programa de Pós-Graduação em Ciência de Materiais, UFPE, 50670-901, Recife, PE, [2] Departamento de Química, UEPB, 58109-970, Campina Grande, PB, [3] Departamento de Química Fundamental, UFPE, 50670-901, Recife, PE, [4] Centro de Tecnologias Estratégicas do Nordeste/MCTI, 50740-540, Recife, PE.

Palavras Chave: *self-healing, hydrogels, hybrid materials, inorganic polymers*

Abstract

Self-healing in Al/Fe-polyphosphate gels and their hybrids with polyaniline result from H-bonding and Al-PO_4 interactions.

Introdução

Many different strategies have been reported to make self-healing gels, which can regain their pristine properties after being scratched, cracked or even broken. Amongst the strategies being employed, supramolecular self-assembly is the only one in which the healed zone is, in principle, structurally identical to the bulk material. Polyphosphates form hydrogels when associated to metal ions such as Al^{3+}, Fe^{3+} and Ca^{2+} and react faster than the previously reported metallo-based hydrogels, where the self-healing capability arises from the dynamics of the metal-ligand association, where both a relatively high Coulomb potential and bond lability are mandatory to the resulting properties.

Resultados e Discussão

Al/Fe-polyphosphate (AFPP) hydrogels were prepared starting from Na polyphosphate, Al(NO3)3 and Fe(NO3)3 aqueous solutions. The hybrid hydrogels were prepared by aniline *in-situ* polymerization, using Fe^{3+} ions as initiator. The hybrid hydrogels (AFPP/PAni) present the green color, typically observed for the Pani in its conducting form and the Pani amount is 3.0%. The samples absorb and desorb water vapor reversibly, if exposed to high and low relative humidity (RH) environments, respectively.

The self-healing behavior is presented in Figure 1. A free standing AFPP hydrogel film (1.a) was sliced (1.b), then each piece was pressed by handling (1.c,d) and rejoined (1e). The resulting single piece was molded into a cube (1.f), which was then compressed (1.g) to finally restore its original shape (1.h). AFPP/PAni samples behave equally.

Self-healing was also investigated by Environmental Scanning Electron Microcopy (ESEM) with a previously vacuum-dried AFPP/Pani sample. The sample was, initially under 34.2% RH and, as the relative humidity within the microscope chamber was raised, the sample swelled and the surface was smoothened. The smaller particles, initially dispersed throughout a large particle surface, merged with the latter and can no longer be distinguished. The larger particle keeps its shape, with smoother surfaces and edges, when the RH inside the microscope chamber reached 92.7%.

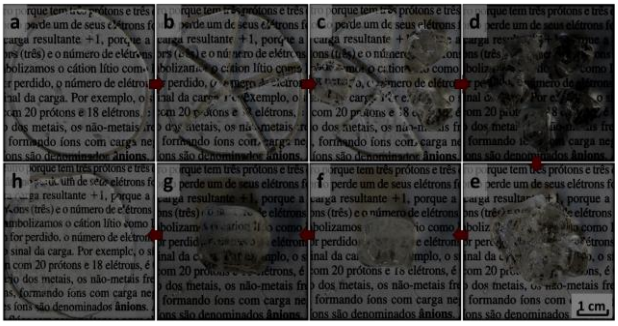

Figure 1. Self-healing behavior in Al/Fe-polyphosphate hydrogels.

The self-healing behavior can be explained by the time scale for water molecules to be exchanged by other ligands in the Al^{3+} coordination sphere, which is about a few seconds; this is proper to the network quickly accommodate to external tension and compression, breaking and reforming bonds in compliance with the external forces. Water molecules strongly attached to this structure account for the hygroscopicity that is essential to the hydrogels to show plasticity.

Conclusões

The plastic behavior and rapid self-healing result from the efficient water diffusion through the sample surfaces and the lability of the Al-phosphate bonds responsible for network formation and stability.

Agradecimentos

Às agências FACEPE, CNPq e CAPES. À F. Rangel (CETENE) pelas medidas de ESEM.

Skovroinski, E.; de Oliveira, R.J.; Galembeck, A. *Macromol. Mat. Eng.*, **2016,** submitted.