Experimental report

01/02/2019

Proposal: 9-12-472 **Council:** 4/2016

Title: Structural Characterization of Hybrid PVA/ZnO NPs Hydrogels

Research area: Soft condensed matter

This proposal is a new proposal

Main proposer: Alessandra LUCHINI

Experimental team: Yuri GERELLI
Alessandra LUCHINI
Giuseppe VITIELLO
Luigi PADUANO

Local contacts: Lionel PORCAR

Samples: (C2H4O)n
(C2H4O)n, ZnO NPs

Instrument	Requested days	Allocated days	From	To
D22	2	2	28/01/2017	30/01/2017

Abstract:

Poly Vinyl Alcohol (PVA) and inorganic nanoparticles have been used for the obtainment of nanocomposites with several technological applications, from food and detergent packaging to artificial tissue and contact lenses. In particular, a promising system is represented by PVA matrix containing ZnO nanoparticles (ZnO NPs) showing improved mechanical properties, higher resistance to UV-radiation exposure and optical fluorescence properties. Even if a large variety of hybrid hydrogel based on PVA and inorganic nanoparticles has recently been proposed, a detailed structural characterization is missing. Here we propose to perform SANS measurements on PVA-ZnONPs hydrogels with increasing ZnONPs concentration, investigating their structure simultaneously on the mesoscopic and microscopic scale. Being water one of the components of a hydrogel (about 80%w/w), SANS represents the best approach to obtain structural information without compromising the sample hydration. We believe that the collected information will be extremely relevant for the rational design of hybrid hydrogel with potential application in several technological fields, such as food and detergent packing.

Structural Characterization of Hybrid PVA/ZnO NPs Hydrogels

Introduction

Poly Vinyl Alcohol (PVA) is a water-soluble biodegradable and biocompatible semicrystalline polymer (diffraction peaks were observed for q>2 $Å^{-1}$[1]), which have been largely used for the obtainment of nanocomposites with several technological applications, from food and detergent packaging to artificial tissue and contact lenses. In particular, a promising system is represented by PVA matrix containing ZnO nanoparticles (ZnO NPs) showing improved mechanical properties, higher resistance to UV-radiation exposure and optical fluorescence properties. Hence, the combination of PVA and ZnO NPs results in a hybrid material with high potential for different applications such as industrial packaging [2-4].

PVA hydrogel present a hierarchical structure. As reported in the references [5,6], in the range $\sim 10^{-2}$ $Å^{-1}$ < q < $\sim 10^{-1}$ $Å^{-1}$, the scattered intensity is mainly governed by a spherical form factor due to the polymer crystallites. On the other hand, in the range $\sim 10^{-5}$ $Å^{-1}$ < q < $10^{-2} Å^{-1}$ the scattered intensity scales with a power law due to the mass fractal structure of the hydrogel on the mesoscopic length-scale. Here we performed SANS measurements on PVA-ZnONPs hydrogels with increasing ZnONPs concentration, investigating their structure simultaneously on the mesoscopic and microscopic scale. Being water one of the components of a hydrogel (about 80%w/w), SANS represents the best approach to obtain structural information without compromising the sample hydration.

Experimental method

PVA/ZnO hydrogels were prepared through the freeze & thaw protocol [1]. More specifically, a 11% w/w PVA solution was prepared by mixing the polymer with D_2O and subsequently heating up the solution to 85° under vigorous stirring until it became clear. ZnO NPs were prepared according to the wet-chemical method reported elsewhere [4]. The synthesized nanoparticles were re-dispersed in a 1% w/w PVA solution, which was subsequently used to dilute to 11%w/w PVA solution to 10%w/w (PVA content). Different amount of ZnONPs were used to prepare the hybrid PVA films at different ZnO NPs concentration: 1) PVA:ZnONPs 0.3 w/w; 2) PVA:ZnONPs 0.2 w/w; 3)PVA:ZnONPs 0.15 w/w. 2ml of the PVA and ZnONPs solutions were used to prepare ~ 1mm thick films, which were subsequently treated with 3 cycles of freezing and thawing.

Samples were prepared using two different PVA, PVA 99% hydrolyzed and Mw=100000$gmol^{-1}$(PVA_b) and PVA 99% hydrolyzed and Mw=170000$gmol^{-1}$(PVA_c). Hence, the data collected on the samples prepared with PVA_b and PVA_c aimed at probing the impact of the polymer molecular weight on the overall hybrid hydrogel structure.

SANS measurements were performed on D22. Neutrons with a wavelength spread $\Delta\lambda/\lambda \leq 0.2$ were used. A two-dimensional array detector at three different wavelength (W)/collimation (C) /sample-to-detector(D) distance combinations $W_{6Å}C_{2.8m}D_{1.4m}$, $W_{6Å}C_{5.6m}D_{5.6m}$ and $W_{6Å}C_{17.6m}D_{17.6m}$) measured neutrons scattered from the samples. These configurations allowed collecting data in a range of the scattering vector modulus $q = 4\pi/\lambda \sin(\theta/2)$ between 0.002 $Å^{-1}$ and 0.59 $Å^{-1}$, with θ being the scattering angle. The raw data were converted from 2D

detector image to 1D curve then corrected for background and empty cell scattering by using the GRASP software.

Results and discussions

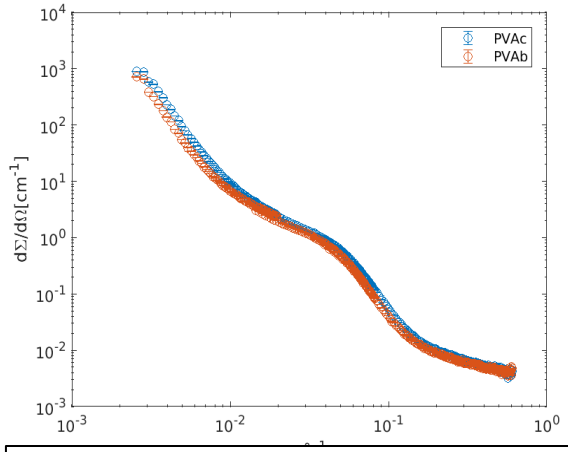

Figure 2: Experimental data collected for the films prepared with PVA_c and PVA_b as reported in the legend.

Figure 1 shows the experimental data collected for the PVA films without ZnONPs. The data were initially collected as reference and confirms the expected structural differences in the PVA_b and PVA_c film. Indeed, while the overall shape of the curve is very similar for the two films, the small shift of the PVA_c curve (reported in red) towards smaller q-values in the mid-q region (0.08-0.8) might suggest a larger size of the polymer crystallites.

Figure 2 shows the data collected in the case of PVA_b for the hybrid films with different PVA:ZnONPs ratios. Interestingly, the presence of the nanoparticles did not dramatically affect the overall curve shape. The data were analyzed (fit not shown) by summing a spherical form (to describe the polymer crystallite and eventually monodispersed nanoparticles) and a power law to take into account the larger polymer structure and potential nanoparticle aggregates). As a result, it is hard to distinguish from the curves collected in D_2O the contribution of the polymer and the nanoparticles to the overall film structure. In future experiments, films should be prepared with a D_2O : H_2O mixture to match out the PVA contribution to scattered intensity, which would allow to better understand the presence of the nanoparticles in the film as monodispersed NPs or NP aggregates. Furthermore, a higher NP loading should be as well explored to better enhance the effect of the ZnONPs on the film structure.

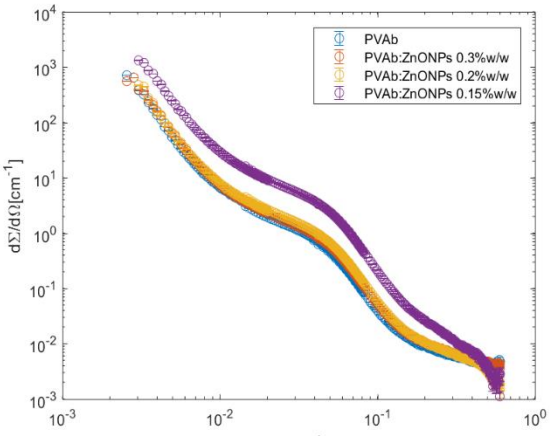

Figure 1: Experimental data collected for the film prepared with PVA_b and different ZnONPs content as reported in the legend.

References:

1] R. Ricciardi, Chemistry of Materials, 2005, 17, 1183-1189

[2]V.A. Bershtein, RSC Advances, 2012, 2, 1424-1431

[3]H. N. Chandrakala, Journal of Material Science, 2012, 47, 8076-8084

[4]S.Chouhan, Fibers and Polymers, 2015, 16, 1243-1254

[5]R. Rhodes, Journal of Colloid and Interface Science, 2010, 334, 261-271

[6] G. Mangiapia, Journal of Phyical. Chemistry B 2007, 111, 2166-2173