Review of the thesis

Organic-inorganic polymers – synthesis and characterization of hybrid polymers and nanocomposites

by Katarzyna Depa

The thesis deals with synthesis, characterization and study of specific organic-inorganic hybrid and nanocomposite systems. The theoretical part is worked out clearly and in detail. The experimental section is composed of two parts including smart nanocomposite poly(N-isopropylacrylamide) (PNIPAm) hydrogels and polysiloxane networks.

The thermosensitive PNIPAm hydrogels show thermally induced volume transition which is manifested by a force response at a particular experimental arrangement. The rate of the gel response on external stimulus is increased by incorporation of porosity by using a cryopolymerization technique. The reinforcement of gels or introduction of new applicable functions were achieved by using nanofillers – nanosilica, starch or polyaniline (PANI). In such a way the author prepared the smart systems responding to temperature, light or electrical current.

Polysiloxane composite networks exhibit a high electrical conductivity (with PANI filler) and moreover highly porous SiOC foams were prepared by using epoxy filler serving as a pore template at pyrolysis of the systems.

The main merit of the thesis consists in the following aspects.
Determination of a force response. The original application of PANI to prepare the conductive gel including the complex synthesis resulting in the deposition of PANI in the pore walls leaving the pores passageway intact. Synthesis of multistimuli responding gels.

I have the following comments and questions.

Modulus of gels increases with concentration of the monomer. This is explained by the author (p.51) by more robust porous structure (see morphology) and a more efficient PNIPAm crosslinking with the N,N’-methylene bis(acrylamide) (BAA) co-monomer, which yields a stronger pore wall material.

How can the gel modulus quantitatively evaluated with respect to the monomer concentration? Why the crosslinking is more efficient? BAA content is constant.

With respect to the moduli, some discrepancies between moduli of gels in Fig. 20 and Fig.11 should be explained.
Fig.11 shows the moduli of the non-porous gels – pure PNIPAm and nanocomposite PNIPAm/SiO2. Surprisingly, no reinforcement by SiO2 was found (G(PNIPAm)=6200 Pa, G(PNIPAm/SiO2)=6100 Pa). Fig.20 illustrates moduli of the corresponding porous gels. In this case the filled gel displayed the higher modulus by an order of the magnitude compared
to the neat gel; (G(PNIPAm) = 200 Pa, G(PNIPAm/SiO2) = 2000 Pa) and moreover, the moduli of the porous gels are much lower compared to bulk gels (3-30 times).

Generally, depending on the conditions of a synthesis, the porous cryogels often show even higher moduli than bulk gels due to the polymerization in a very high concentrated medium after water crystallization.

p.56 Porous gels filled with TiO2. Is there any interpretable reason for a significant increase in modulus of TiO2 filled gels prepared using 20 % monomer in Fig.7 ? The G value is more than 5 times higher than that for the comparable SiO2 filled gel (Fig.3). It is difficult to understand mainly in the connection with the swelling kinetics. The TiO2 filled gels show distinctly slower reswelling due to „less efficient pores‘ stabilization by TiO2 (in contrast to SiO2) against ‘gluing together‘ during deswelling.“ The pores‘ stabilization depends mainly on mechanical properties – modulus – of pore walls, but the modulus in some TiO2 gels is higher?

p.53 Interesting and possibly applicable approach of following the volume transition by measurement of the force response to a temperature change was shown.

„Force responses in the range between 0.3 and 1 N (=30-100 g) have been achieved (equilibrium state).“

The force in Fig. 5 does not seem to level off at this value. Why the force increase at cooling was followed only 20 s in spite of the fact that the reswelling significantly continues even after 90 s. What was the equilibrium force?

p.82 Polysiloxane-PANI composite. Interaction through H-bonding between phases was proved by FTIR. The strong peak at 1408 cm⁻¹ in the composite assigned to SiOH was supposed to form H-bond with PANI. However, in the neat matrix this peak is invisible? There could be a shift of the peak due to H-bonding, but how the new peak can appear?

p.83 „Although particulate fillers typically decrease the impact toughness of composites“. In fact, rubber nanoparticles are commonly used fillers for toughening of polymers.

Polysiloxane microcomposites with sacrificial epoxy filler as precursor of the very strong pyrolytic SiOC foams

p.88 Why larger pores are formed in the SiOC foams in case of a lower content of epoxy (sacrificial) filler?

The formal note. In p.40, there is a misprint \( \tan(\delta) = G'/G'' \). It should be \( \tan(\delta) = G''/G' \).

The research met the goal. The candidate prepared a series of interesting organic-inorganic nanocomposites, some of them displaying original smart properties. The thesis is of a high scientific quality. The author showed an ability to carry out an independent research and I recommend the thesis to the defense.

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