

HYBRID ORGANIC-INORGANIC NANOCOMPOSITE COATINGS PREPARATION AND CHARACTERIZATION

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Introduction

Sol-gel process (enabling the synthesis of ceramics and ceramics-like materials) belongs to the most important and the most utilized ways of up-to-date organic-inorganic (O-I) nanocomposite preparation [1]. This is due to the possibility of achieving of products involving advantages of both organic and inorganic material properties. The second benefit O-I nanocomposites is the possibility of preparation products with desired, often tailor-made properties on the very broad scale. Coatings a films with specialty properties are one of very often used O-I applications [2-7].

Experimental

Epoxy-based coatings were synthesized by two independent processes: sol-gel process consisting of hydrolysis and polycondensation (inorganic structure prepared *in-situ* from two functionalized organosilicon precursors containing glycidyl group, marked GTMS¹ and GMDES²) followed by polyaddition reactions (organic polymer network formation by reaction of commercial oligomeric diamine³ or triamine⁴ with glycidyl groups of GTMS- or GMDES-based condensates). Natural or synthetic additives (colloidal silica, montmorillonite, bentonite, laponite) either in the commercial or modified form were used as nanofillers. The technique of preparation was optimized with respect to the environmental aspects. This optimized procedure will be outlined together with possibilities of tuning of end-use coating properties. Solid-state NMR spectroscopy was used, i.a., for assessment of polycondensation and polyaddition degree. Dynamic mechanical analysis was used for the characterization of systems on the macroscopic level (dynamic moduli, temperature of glass transition, T_g). Atomic force (and other) microscopy methods were utilized for surface characterization of coatings or films

prepared in the presence or absence of nanoadditives.

Results and discussion

The mechanism and reaction kinetics of O-I coatings (in the presence/absence of nanofillers) was studied by solid-state NMR spectroscopy. It was found that while GTMS-based systems lead to very high polycondensation degree ($\geq 0,9$) both in the presence or absence of nanofillers, the degree of polycondensation for GMDES- based products is in all cases substantially lower ($\leq 0,7$). The presence of nanofillers can expressively influence (decrease) the polyaddition degree, i.e. the last step of O-I coating preparation.

Dynamic mechanical thermal analysis revealed that GTMS and D400 products (prepared at the equimolar [NH]/[glycidyl] ratio in the presence or absence of nanofillers) have T_g close to 10 °C, while GMDES and T403 products have higher T_g (ca. 20 °C). The shear modulus G' in the rubbery state is high ($\geq 10^8$ MPa). Figure 1 shows G' and $\tan \delta$ dependences for both studied O-I matrices. The nanofillers can influence dynamic mechanical properties depending on size, geometry and modification of nanofillers.

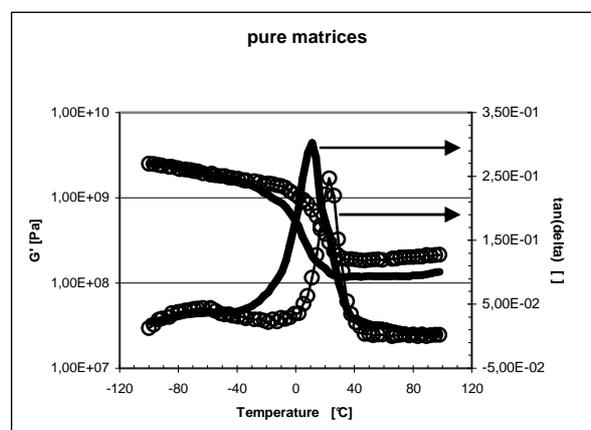


Fig. 1: Temperature dependences of storage shear modulus and $\tan \delta$ for coating made from GTMS-D400 (bold line) and from GMDES+T403 (circle)

¹ GTMS = [3-(glycidyoxy)propyl]trimethoxysilane

² GMDES = diethoxy-[3-(glycidyoxy)propyl]methylsilane

³ Jeffamine D400 (D400)

⁴ Jeffamine T403 (T403)

Surface properties were studied by several microscopy methods. In this contribution, atomic force microscopy results are shown.

Figure 2a shows AFM results of sample made from GMDES, T403 and bentonite for water systems, BW, (0.5 wt. %). Fig. 2b shows surface relief of sample of the *identical composition*, but small part of GMDES was used for the intercalation of bentonite before using in the coatings. On the Figure 2b is very well visible organ-like aggregate of μm -height order. The difference in composition of sample with intercalated GMDES is also visible on phase image (Fig. 2c). (Phase image of sample surface imaged in Fig. 2a is almost identical to top part of Fi. 2c, so that it is not shown here).

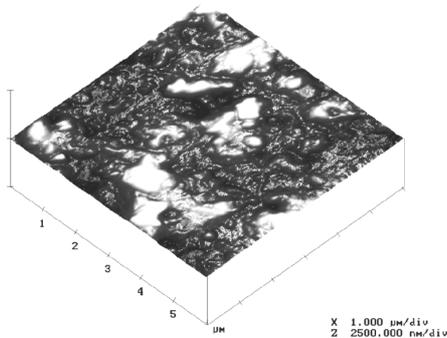


Fig. 2a: AFM height image of sample surface made from GMDES, T403 and bentonite for water systems, BW

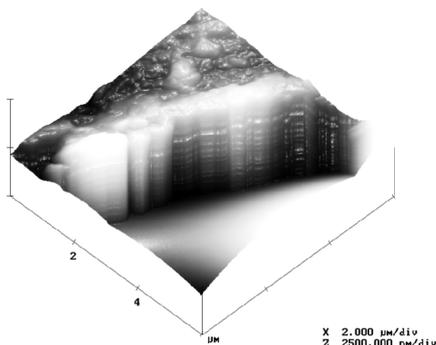


Fig. 2b: AFM height image of sample surface made from GMDES, T403 and bentonite for water systems with GMDES intercalated into BW

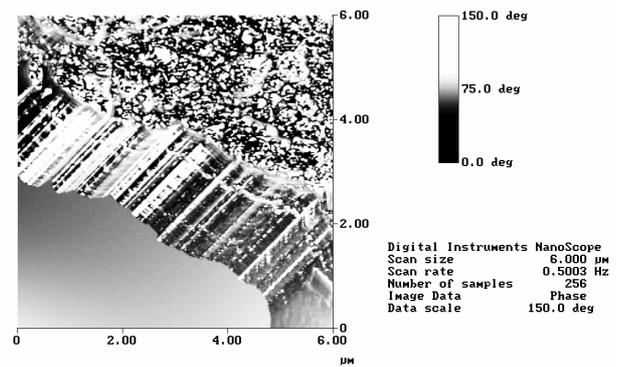


Fig. 2c : AFM phase image of sample surface made from GMDES, T403 and bentonite for water systems with intercalated GMDES

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