Macromol. Symp. **2004**, *212,* 343-348

Hybrid Organic-Inorganic Coatings and Films Containing Conducting Polyaniline Nanoparticles

Milena Špírková,[1] Jaroslav Stejskal,*[1] *Jan Prokeš*[2]

[1] Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic
[2] Faculty of Mathematics and Physics, Charles University Prague, 121 16 Prague 2, Czech Republic

Summary: Hybrid organic–inorganic coatings and free-standing films made from [3-(glycidyloxy)propyl]trimethoxysilane, amino-terminated poly(oxypropylene) (Jeffamine D-230), colloidal polyaniline nanoparticles and, in some cases, colloidal nanosilica were prepared and characterized. HCl or 4-methylbenzene-1-sulfonic acid were used as catalysts for the sol–gel process and pH tuning, water–propan-2-ol mixture as a solvent. Electrical and mechanical properties and surface morphology of films were studied. The coatings were blue and non-conducting, or green and conducting, depending on preparation conditions. They have a smoother surface than *in-situ* polymerized polyaniline films.

Keywords: atomic force microscopy; films; hybrid networks; mechanical properties; polyaniline dispersion particles

Introduction

Organic–inorganic (O–I) hybrid materials with an *in-situ* formed inorganic phase rank among nanocomposites with interesting properties. They can be prepared by the sol–gel process consisting in the hydrolysis and subsequent polycondensation of alkoxysilanes. The polycondensation reaction results in a multiplicity of structures ranging from monodisperse silica particles to polymer networks depending on the reaction conditions used.[1–3] Another way of their preparation consists in the use of alkoxysilanes bearing polymerizable functional groups[4,5] (glycidyl, amino, isocyanate, methacryloyl, etc.). Then the final product is obtained as a result of two independent polymerization reactions: inorganic structures are formed by sol–gel process of alkoxysilane groups and the organic polymer network by classic polymerization reactions (polyaddition, radical polymerization, etc.).

DOI: 10.1002/masy.200450840

We have prepared and characterized a series of hybrid O–I coatings and free-standing films made from [3-(glycidyloxy)propyl]trimethoxysilane (GTMS), amino-terminated poly(oxypropylene) (Jeffamine D-230) and submicrometer colloidal polyaniline (PANI) particles. In some cases, colloidal silica (SiO_2) was added as well. The O–I networks were formed by two independent reaction mechanisms: by the sol–gel process and epoxy–amine addition reaction. The influence of the PANI concentration and reaction conditions on properties of hybrid O–I polymeric products is reported in the present study.

Experimental

Materials. GTMS (Aldrich, 98 %) and Jeffamine D-230 (D230, Huntsman Corp; M~230, total amine content 8.45 mequiv g^{-1}) were used as received. PANI particles (37 wt.% PANI, 63 wt.% silica, average particle diameter 430 nm) were prepared by dispersion polymerization of aniline hydrochloride[6] in the presence of nanocolloidal silica[7] (Ludox AS-40, Aldrich; average particle size 35 nm). Propan-2-ol (Lachema, Czech Republic), hydrochloric acid (Lachema, Czech Republic) and 4-methylbenzene-1-sulfonic acid (TsOH, Fluka, Switzerland) were used as received.

Preparation of free-standing films and coatings. GTMS was mixed with water, propan-2-ol, a dispersion of PANI–SiO_2 particles and, in some cases, with colloidal silica (SiO_2) particles at laboratory temperature. Acid conditions (pH 4) for the hydrolysis of alkoxy groups were adjusted with dilute hydrochloric acid or TsOH; D230 was then added. Due to the alkaline character of Jeffamine, pH of the resulting reaction mixture increased up to 8–9. This means that the polycondensation and thermal curing took place under alkaline conditions. Several films were also prepared under acid conditions (after addition of D230, pH was adjusted to 3–4 by addition of HCl or TsOH). The reaction mixture was spread on a glass or polypropylene sheet with a ruler of adjustable 50–500 μm thickness and heated for 2 h at 80 °C and for 1 h at 105 °C.

Methods of characterization. *Static mechanical properties* were measured with an Instron model 6025 (Instron). Specimens of the size 25×6×0.1 mm were tested at laboratory temperature at a test speed of 3.33×10^{-2} mm s^{-1}. All reported values are averages from five independent measurements. *Dynamic mechanical properties* of the films were studied using an ARES apparatus (Rheometric Scientific). A specimen of the size 17×7.5×0.1 mm was measured by oscillatory shear deformation at a constant frequency of 1 Hz and the rate of heating 3 °C min^{-1} to obtain temperature dependences of storage and loss shear moduli, $G'$and G'', from −100 °C to +100 °C. *Conductivity* was measured by the two-probe method with a Keithley 6517 electrometer after deposition of gold electrodes on both sides of films. *Atomic force microscopy* under ambient conditions used a commercial atomic-force microscope (MultiMode Digital Instruments NanoScope Dimension III) in contact mode with Olympus oxide-sharpened silicon nitride probe (OMCL TR-400). The normal force of the tip on the sample was reduced not exceeding 10 nN.

Results and discussion

Tensile properties. The ultimate goal was the preparation of mechanically resistant durable coatings, either electrically conducting (acid polycondensation) or non-conducting (alkaline polycondensation). PANI-free hybrid polymers were tested as well[8] (Table 1, samples 1 and 2). Static mechanical characteristics, i.e., the strain at break ϵ_b, stress at break σ_b, Young modulus E and toughness w of free-standing films were determined from stress–strain dependences.

It was found that the introduction of PANI–SiO_2 and SiO_2 particles influence tensile properties after alkaline polycondensation. If we choose, e.g., toughness as the criterion of tensile properties, the order of decreasing toughness was: silica-containing films > PANI–SiO_2 composite > silica-free products (Table 1, samples 1–3). When the polycondensation is carried out in acid medium, the strain at break is the only parameter comparable with alkaline polycondensation. Other tensile characteristics were reduced (Table 1).

Dynamic Mechanical Analysis. Properties of networks depend strongly on temperature and change mainly in the region close to the glass transition temperature, T_g. The dynamic mechanical properties were measured for sample 7 in Table 1 in the temperature range from −100 to +100 °C. Figure 1 shows temperature dependences of the storage and loss shear moduli, $G'$and G'', and the loss factor, tan δ. The sample is characterized by two glass-transition temperatures T_g; the first at ca −75 °C corresponds to T_g of poly(oxypropylene), while a more distinct transition at *ca* +10 °C reflects the glass transition of the organic phase immobilized by inorganic structures.

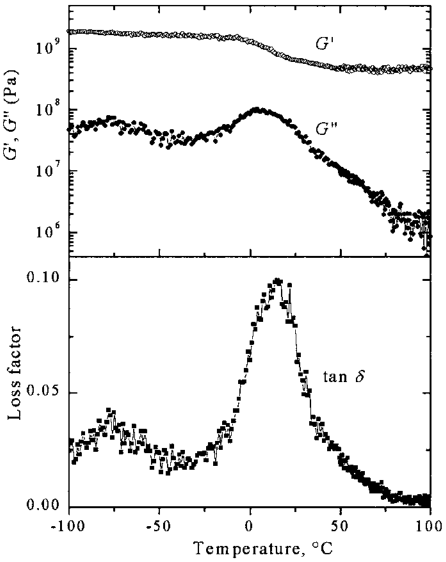


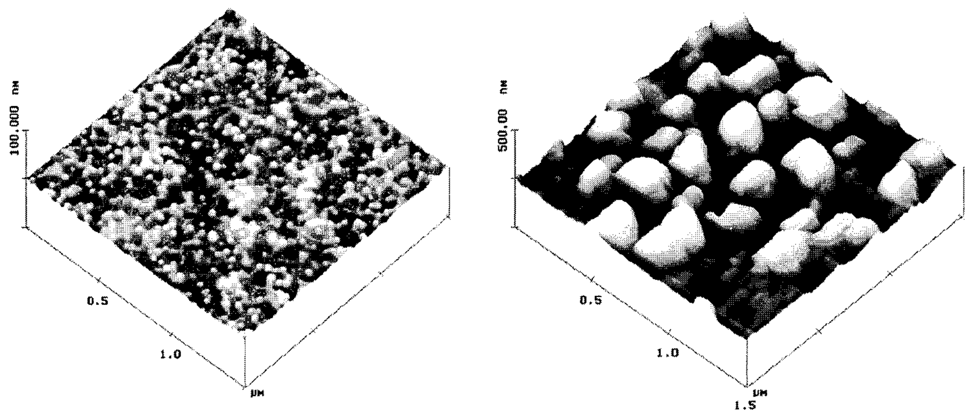
Figure 1. The storage and loss shear moduli, $G'$and G'', and the loss factor, tan δ, of a typical O–I composite comprising PANI–SiO_2 and SiO_2 nanoparticles (sample 7 in Table 1).

Table 1. Composition of reaction mixtures, electrical conductivity σ, the strain at break ε_b, the stress at break σ_b, Young modulus E and toughness w (the energy per unit cross-section necessary to break the sample).

No.	PANI–SiO_2/GTMS/ SiO_2/D230[a], wt.%	Catalyst/ medium[b]	σ S cm^{-1}	ε_b %	σ_b MPa	E MPa	w kJ m^{-2}
1	0/80.4/0/19.6	HCl/B	2.7×10^{-12}	2	8.4	892	1.3
2	0/68.4/15.0/16.6	HCl/B	2.3×10^{-12}	2.1	15.3	1060	3.2
3	7.4/74.5/0/18.1	HCl/B	2.5×10^{-12}	3	7.2	570	2.6
4	7.4/74.5/0/18.1	HCl/A	5.8×10^{-4}	1.3	1.1	75	0.7
5	6.5/64.4/15.0/14.1	HCl/A	3.8×10^{-4}	2.6	2.5	92	1.3
6	7.6/75.9/0/16.5	TsOH/A	2.4×10^{-6}	2.2	0.7	56	0.4
7	6.5/64.4/15.0/14.1	TsOH/A	6.4×10^{-4}	3.5	3.7	156	1.5

[a] The molar ratio of reactive NH end-groups /epoxy, $r = 0.9–1$.
[b] Polycondensation and thermal curing at A: pH 3–4; B: pH 8–9.

Atomic-Force Microscopy. The surface morphology was investigated by atomic-force microscopy using a contact mode. The products based on organic–inorganic hybrid matrix included (a) colloidal PANI–SiO_2 particles and (b) PANI–SiO_2 and SiO_2 particles. For comparison, a PANI film prepared in situ on glass by dispersion polymerization of aniline in the presence of nanocolloidal silica[9] was also characterized. The surfaces of individual products differ substantially (Fig. 2): while the coating containing only PANI–SiO_2 particles embedded in the matrix has a very flat and regular surface (not shown here), the coatings of type (b) containing both PANI–SiO_2 and small SiO_2 nanoparticles can be clearly observed on the surface (Fig. 2a). Profile height differences are units of nm in both cases. The films grown during the dispersion polymerization of aniline have rough surface (Fig. 2b) due to adhering individual PANI–SiO_2 particles on the substrate.



(a) (b)

Figure 2. 3D images of sample surfaces (contact mode): (a) hybrid O–I coating containing PANI–SiO_2 and SiO_2 nanoparticles (sample 7 in Table 1), (b) coating prepared by direct polymerization of aniline in the presence of SiO_2 nanoparticles. *z*-Scales are (a) 100 nm and (b) 500 nm.

Electrical properties. The preparation under alkaline conditions (Table 1, samples 1–3) yields blue and non-conducting products as expected from the presence of PANI base. Green and conducting coatings comprising protonated PANI are obtained under acid reaction conditions (samples 4–7). The conductivity of the order of 10^{-4} S cm^{-1} can be regarded as reasonably high as the film contains only ca 3 wt.% of PANI and the system is well below a typical percolation limit of 16 vol.%.

Conclusions

A series of electrically conducting and non-conducting hybrid O–I coatings containing colloidal polyaniline particles was prepared and characterized. Conducting films are produced when the polycondensation and thermal curing proceed under acid conditions. Their mechanical properties can be tuned by conditions of preparation.

Acknowledgements

The authors wish to thank the Grant Agency of the Czech Republic (203/01/0735) and the Grant Agency of Academy of Sciences of the Czech Republic (K4050111) for financial support. Dynamic mechanical measurements were kindly performed by Dr. A. Strachota from the Institute.

[1] C.J. Brinker, C.W.Scherer, "*Sol-Gel Science*", Academic Press, San Diego 1990.
[2] L. Matějka, K.Dušek, J. Pleštil, J. Kříž, F. Lednický, *Polymer* 1999, *40*, 171.
[3] D.A. Loy, B.M. Baugher, C.R. Baugher, D.A. Schneider, K. Rahimian, *Chem. Mater.* 2000, *12*, 3624.
[4] L. Matějka, O.Dukh, J. Brus, W.J. Simonsick, B. Meissner, *J. Non-Cryst. Solids* 2000, *270*, 34.
[5] M.W. Daniels, L.F. Francis, *J. Colloid Interface Sci.* 1998, *205*, 191.
[6] J. Stejskal, *J. Polym. Mater.* 2001, *18*, 225.
[7] J. Stejskal, P. Kratochvíl, S.P. Armes, S.F. Lascelles, A. Riede, M. Helmstedt, J. Prokeš, I. Křivka, *Macromolecules* 1996, *29*, 6814.
[8] M. Špírková, J. Brus, D. Hlavatá, H. Kamišová, L. Matějka, A. Strachota, *Surf. Coat. Int.*, in press.
[9] A. Riede, M. Helmstedt, V. Riede, J. Zemek, J. Stejskal, *Langmuir* 2000, *16*, 6240.