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Water Sorption and Electrical/Dielectric Properties of Organic-Inorganic Polymer Blends

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Summary: Organic-inorganic polymer blends (OIPB) were obtained by reaction of organic and inorganic oligomers. The organic oligomer was synthesized with 2,4-toluene diisocyanate (TDI) and oligooxypropylene glycols (OPG) with various molecular weights (MW). The inorganic component was a water solution of sodium silicate. The OIPB obtained are hydrophilic and have great water sorption ability (the relative weight of sorbed water reaches 2000 %). The kinetics of water sorption and the changes of electrical conductivity during sorption were studied. Sorption ability, and mechanical, electrical and dielectric properties of OIPB depend on molecular weight of OPG: conductivity increases with increasing MW, whereas the sorption ability correlates with the mechanical properties. The influence of the inorganic phase content on the electrical and dielectric properties was studied as well.

Keywords: blends, conductivity, hydrophilic polymers, mechanical properties, water sorption

Introduction

Organic-inorganic polymer blends (OIPB) are a new class of composites which began to be studied the last ten years.[1-4] These composites are formed from mixtures of organic and inorganic components during the process of their joint polymerization. This process can be carried out both at room and higher temperatures. The structure of polymer blends is characterized by the existence of three phases, including the phase of organic polymer, the phase of inorganic polymer and the phase of interaction product between organic and inorganic components.

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In previous research we have studied OIPB based on polyisocyanates and sodium silicates. These composites were hard materials with extremely high resistance to aggressive media (acids, alkalis) and to γ–radiation.[5] Using of an organic oligomer with free isocyanate groups instead of the low molecular polyisocyanate results in elastic properties of the synthesized polymer blends. These composites exhibit also other interesting properties, for example high water sorption ability and relatively high conductivity.

The aim of this work is the study of water sorption ability, mechanical characteristics, electrical conductivity and dielectric properties of OIPB based on the organic oligomer with various molecular weights.

Experimental

The materials were obtained on the basis of 2,4-toluene diisocyanate (TDI), oligooxypropylene glycols (OPGs) with various molecular weights (MW) and functionality equal to 2 and 3 (two or three OH-groups at the ends of a molecular chain, in the first case the chain is linear, in the second one the chain has star (branched) configuration). OPGs marked 1052, 2102, 3603 and 5003, according to MW and functionality (for example OPG-1052 means MW=1050 and functionality 2), were used. Water solution of a sodium silicate (SC) was used as inorganic component and OIPB was obtained in two stages. First, the organic oligomers were synthesized from TDI and OPGs. Depending on MW and functionality of OPG, organic oligomers were obtained with various molecular weights and branching of the molecular chains. In the second stage, OIPBs were obtained as a result of reactions between oligomers and SC and were marked OIPB-1, OIPB-2, OIPB-3, OIPB-5, following the designation of OPGs. For comparison with OIPB, samples of pure polyurethane without inorganic phase were obtained by hardening of the organic oligomers with atmosphere moisture and marked PU-1, PU-2, PU-3 and PU-5.

After mixing of the organic and inorganic components, the mixture was put in a teflon die, where samples of OIPBs with 30 mm diameter and 1 mm thickness were formed at room temperature. The samples of PUs were obtained in the same way.

The kinetics of water sorption was studied by a gravimetric method with samples, which were immersed in water. For evaluation of volume changes of OIPG during sorption, the samples of OIPB were taken out of water for short time at predetermined times and their thickness and diameter were measured. At the same time electrical dc conductivity of the samples was also measured by using the teraohmmeter E6-13 under constant voltage 10 V and flat brass electrodes.

For the investigation of the dielectric properties dielectric relaxation spectrometry (DRS) in wide ranges of frequency and temperature and thermally stimulated depolarization current (TSDC) techniques were used. For DRS measurements the complex dielectric permittivity, $\varepsilon^*=\varepsilon'-i\varepsilon''$, was determined as a function of frequency (10^{-2}-10^{6} Hz) in the temperature range –60 to 80 °C. The sample was sandwiched between gold-coated brass electrodes. A Schlumberger Frequency Response Analyzer (FRA SI 1260) supplemented with a buffer amplifier of variable gain (Chelsea Dielectric Interface) in combination with the Novocontrol Quatro Cryosystem was used. TSDC corresponds to measuring dielectric losses as a function of temperature at a fixed frequency in the range 10^{-2}-10^{-4} Hz. A home-made TSDC equipment was used for measurements in the range –185 to 30 °C.

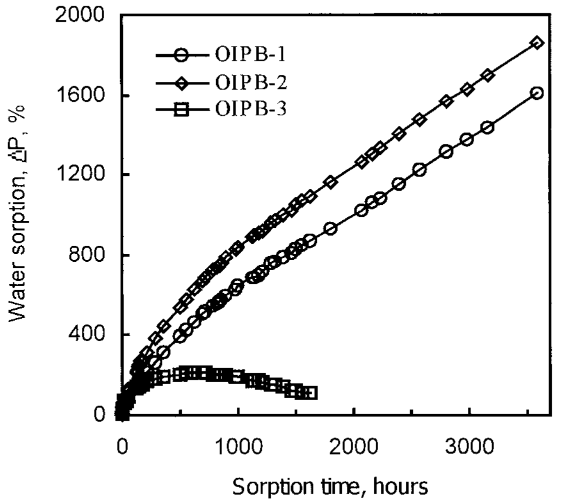
Mechanical characteristics of OIPB were obtained with standard stress-strain measurements.

Results and Discussion

The kinetics of water sorption was studied for OIPBs based on various OPGs. Increase of OPG molecular weight (1050 to 2100) at the same functionality 2 results in the increase of the amount of water sorbed and of the rate of sorption (Fig. 1), whereas the kinetics is strongly different for OIPB based on OPG 3603 with functionality 3. The kinetics curve of OIPB-3, with the presence of a maximum which corresponds to equilibrium sorption, allows to calculate various sorption parameters, such as diffusion D, sorption S, permeability N coefficients and relative weight of sorbed water ΔP_{max}. They were calculated as:[6]

$$D = 0{,}0494\,(d^2/\tau_{1/2}); \qquad S = P_w / V_{max}; \qquad N = D \cdot S; \qquad \Delta P_{max} = 100 \cdot P_w / P_0;$$

where d is the sample thickness, $\tau_{1/2}$ is the time at which $1/2(\Delta P_{max})$ is achieved, P_w is the maximal weight of sorbed water, P_0 is the weight of the dry sample, V_{max} is the sample volume when ΔP_{max} is achieved. The values of the sorption parameters are given in a Table 1.



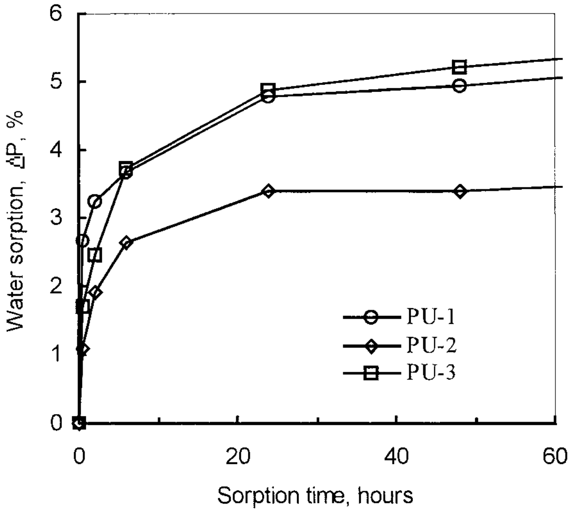


Fig. 1. Kinetics of water sorption of OIPBs and PUs based on OPG with warious molecular weights and functionalities. The weight ratio of organic/inorganic phases is 80/20 for all composites. ΔP was calculated as $100 \cdot (P-P_0)/P_0$, where P is the weight of the sample after exposition to water.

Table 1. Sorption parameters of OIPB-3 and PU-3.

Composite	Diffusion coefficient, D	Sorption coefficient, S	Permeability coefficient, N	Relative weight of sorbed water, ΔP_{max}
	cm^2/s	g/cm^3	g/(cm·s)	%
OIPB-3 with 20 wt. % of the inorganic phase	$3.06 \cdot 10^{-9}$	0.609	$1.86 \cdot 10^{-9}$	210
PU-3	$1.80 \cdot 10^{-7}$	0.041	$7.38 \cdot 10^{-9}$	4.6

It is seen from Table 1 that the diffusion coefficient D of PU-3 is two orders of magnitude higher than D of OIPB-3 because of the large differences in time $\tau_{1/2}$, the value of equilibrium sorption is achieved much faster in PU-3 than in OIPB-3 (see Fig. 1). Sorption coefficient S and weight of sorbed water ΔP_{max} are much higher for OIPB-3 than for PU-3, indicating great sorption capacity of OIPB-3 due to the hydrophilic properties of the inorganic phase. Fig. 1 shows that the sorption capacity of OIPB-1 and OIPB-2 (based on OPG with functionality 2) is much higher than for OIPB-3 and reaches nearly 2000 % for the exposition time used. Consequently, the volume of water sorbed by the inorganic phase is controlled by the mechanical characteristics of the organic matrix.

These data are in agreement with the results obtained for the mechanical properties of OIPB. Fig. 2 shows that OIPB-2 has the highest elongation, whereas OIPB-3 has the lowest elastic characteristics.

These results show that the inorganic component of the blend is responsible for water sorption. Swelling of the particles of the hydrophilic inorganic phase during water sorption is controlled by the expansion of the organic matrix, in which the microparticles of mineral component are distributed. The most rigid organic matrix of OIPB-3 allows to swell the inorganic particles to a definite limit during the sorption process, then the mineral gel structure is destroyed under the compressing stress of the matrix and decreasing of the sorption is observed. As a result, IOPB-3 exhibits a sorption curve with maximum (see Fig. 1). In the elastic organic matrix of OIPB-1 and OIPB-2 such an effect is not observed and the increase of composite weight (and of the volume, consequently) reaches nearly 2000 % for the sorption time used.

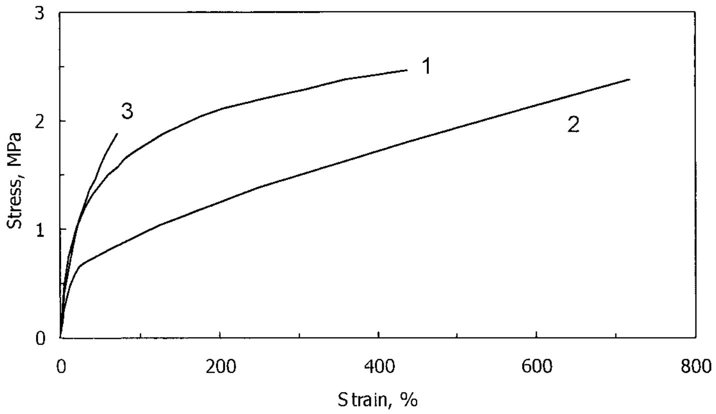


Fig. 2. Mechanical properties of OIPB-1 (1), OIPB-2 (2) and OIPB-3 (3) with inorganic phase content 20 wt.%.

Investigation of the cycling swelling of OIPB in water showed that the process of water sorption is reversible and the elastomer maintains its sorption and mechanical properties after water desorption (Fig. 3, cycles 1). A substitution of water by the electrolyte (aqueous solution of $CuCl_2$) greatly reduces the value of sorption (cycles 2). Probably this effect is a result of ionic reactions in the inorganic phase and of substitution of Na^+ by Cu^{++} on the particles surface of inorganic phase. The next cycle of water sorption (cycle 3) recovers the hydrophilic properties of OIPB.

Electrical dc conductivity of OIPB-3 during the process of cycling sorption is shown in Fig. 4. A sharp increase of conductivity can be seen (of two orders of magnitude) in the first moments of sorption, when the level of sorption is still less than 10 %, whereas afterwards the increase of conductivity is very slow (Fig. 4, curves 1). The conductivity of the composites during sorption of the electrolyte is enhanced, as compared with the cycles of water sorption (curves 2). The dependence of conductivity during the third cycle of water sorption is similar to curves 1, but the absolute values higher (curves 3). Consequently, immersion of the composite in the electrolyte makes the hydrophilic structure more sensitive to water sorption and increases the ionic conductivity.

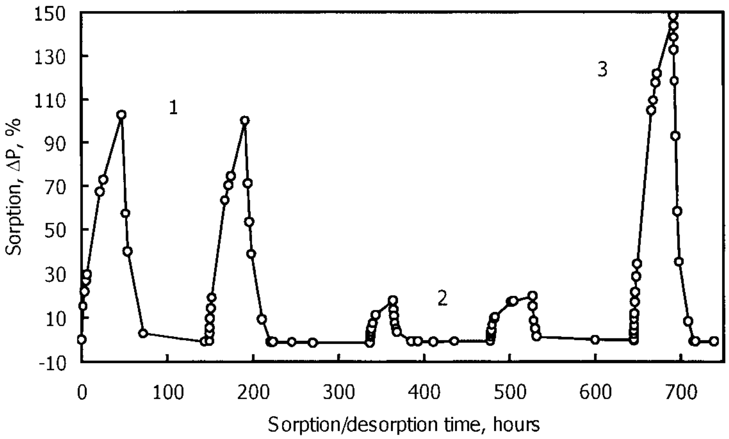


Fig. 3. Cycling regime of the sorption of OIPB-3 (with inorganic phase content 20 wt.%) in water (1, 3) and in aqueous solution of $CuCl_2$ (2).

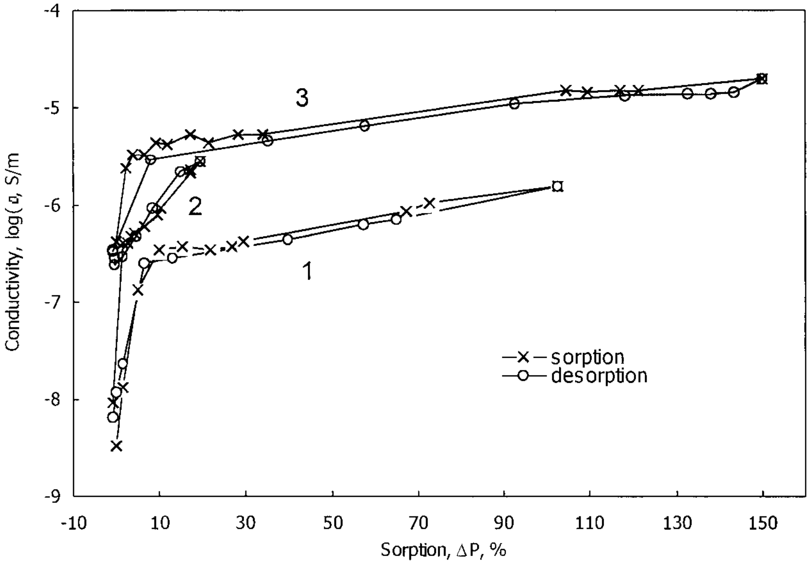


Fig. 4. Dependence of dc conductivity on water sorption during the process of cycling sorption-desorption. The numbers near the curves correspond to the numbers of the sorption/desorption cycles in Fig. 3.

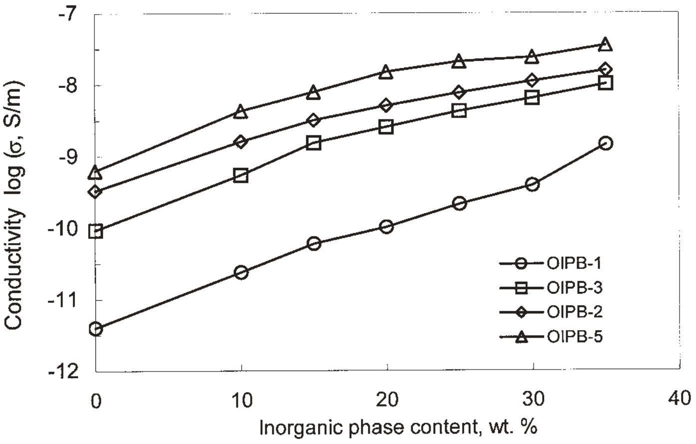
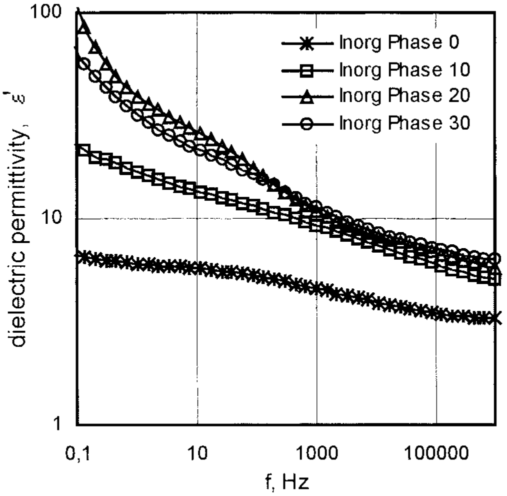


Fig. 5. Influence of the inorganic phase content on conductivity of OIPBs.

Fig. 5 demonstrates the influence of inorganic phase content and kind of OIPB on dc conductivity of these systems. Conductivity increases with the molecular weight of OIPBs, by two orders of magnitude with increase of the molecular weight of OPG from 1050 to 5000. Probably increase of the molecular chain length facilitates the transport of a charge along a chain. Functionality of OIPBs and mechanical characteristics of the polymer matrix do not affect conductivity. The dependence of conductivity on the inorganic phase content is similar for the OIPBs based on various OPGs. Increase of the inorganic phase content to 30 % leads to the rise of conductivity by almost two orders of magnitude.

DRS results show that the relaxation spectra of OIPBs are changed under variation of composition and temperature. Fig. 6 shows comparative plots of dielectric permittivity ε' and dielectric losses ε'' as a function of frequency, at room temperature, for OIPB-1. Similar results were obtained also with the other OIPBs. The most striking result in Fig. 6 is the overall increase of mobility in the composites as compared to the pure matrix. The high values of ε' at low frequencies in the composites are due to conductivity effects, as indicated also by the increase of ε'' in the same frequency range. In $\varepsilon''(f)$ a loss peak is observed at about 1 kHz in the pure PU-1 matrix. Measurements at several temperatures show, in agreement with TSDC



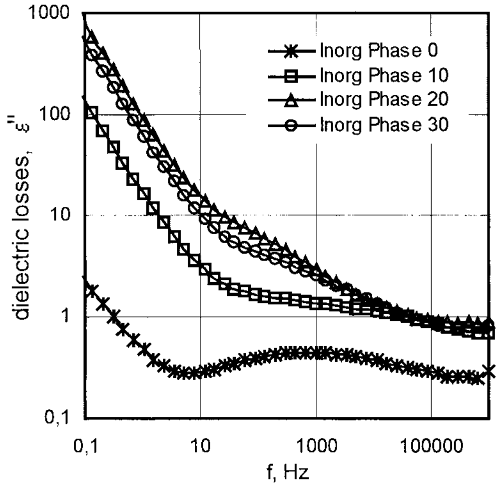


Fig. 6. Dependence of dielectric permittivity and dielectric losses on frequency at room temperature for PU-1 and OIPB-1 with various content (in wt.%) of the inorganic phase.

measurements and preliminary DCS measurements, that this peak is due to the α relaxation associated to the glass transition of the matrix. The peak is present also in the OIPBs, but it is masked by a larger peak at lower frequencies, tentatively attributed to interfacial Maxwell-Wagner-Sillars polarization. It is interesting to note that the overall dielectric response of the OIPBs with 20 and 30 wt. % inorganic phase is very similar, suggesting a kind of saturation. This is reflected also in the TSDC plots not shown here.

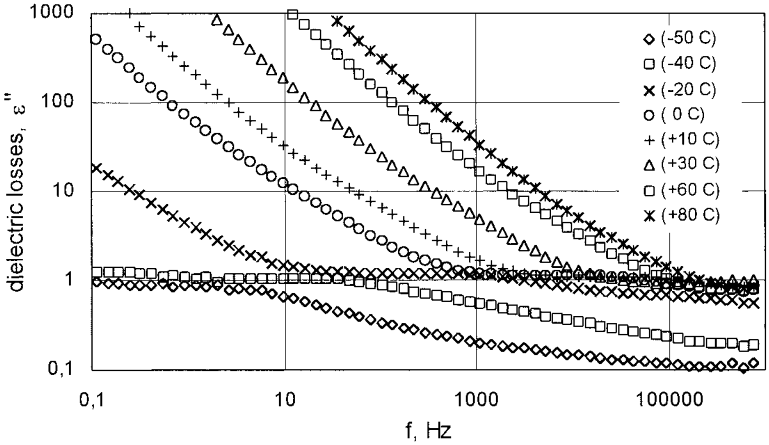


Fig. 7. Dependence of dielectric losses on frequency at various temperatures for OIPB-3 with inorganic phase content 20 wt.%.

Fig. 7 shows ε''(f) for the OIPB-3 with 20 wt. % inorganic phase. A change of the response is observed at temperatures higher than about –40 °C, associated to the glass transition. The α loss peak shifts to higher frequencies with increasing temperature. At high temperatures/low frequencies high values of ε'' are measured related to conductivity effects. Analysis of these and similar dielectric data is now in progress to extract quantitative information on the various mechanisms of molecular mobility.

Conclusion

Organic-inorganic polymer blends (OIPBs), obtained by polymerization of urethane oligomers with various molecular weights and aqueous solution of sodium silicate, demonstrate elastic mechanical properties which are typical for elastomers. Due to the presence of the inorganic mineral phase in the organic matrix, OIPBs possess hydrophilic properties with very high sorption capacity (about two 2000%). Cycling process sorption/desorption is reversible and shows that the electrical conductivity of OIPBs is changed during the sorption/desorption process by several orders of magnitude due to ionic conductivity in the inorganic phase in the presence of water. The electrical conductivity of OIPBs depends on the molecular weight of oligomers and content of the inorganic phase and is determined by formation of the conductive inorganic structure in the polymer matrix. Dielectric characteristics depend on the inorganic phase content and temperature and show increase of the polymer chains mobility in OIPB, as compared with pure PU.

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