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Dielectric Properties and Molecular Mobility of Organic/Inorganic Polymer Composites

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Summary: Microstructure-dielectric properties relationship and molecular mobility of organic/inorganic polymer composites (OIPCs), consisting of polyurethane (PU) and sodium silicate (NaSi), were investigated in this work. Broadband dielectric relaxation spectroscopy (DRS) and thermally stimulated depolarization current (TSDC) techniques were employed. Our interest was focused on the study of the glass transition mechanism and conductivity relaxation. The influence of the molecular weight of PU and inorganic phase content on the dielectric properties of the composites was of particular interest. Glass transition temperature shifts to higher temperatures with the addition of NaSi. The overall molecular mobility was found to increase in the composites, compared to the pure PU matrix. The results are more intense for the composites based on the PU with low molecular weight.

Keywords: conductivity relaxation; dielectric properties; glass transition; molecular mobility; organic/inorganic polymer composites

Introduction

Organic/Inorganic Polymer Composites (OIPC) is a new fascinating class of materials, which began to be studied the last few years.[1-2] These materials are formed from mixtures of organic and inorganic components during their joint polymerization. The structure of these composites is characterized by the existence of three phases, namely the phase of the organic polymer, the phase of the inorganic component and the phase of interaction between the organic and inorganic components, ie. they are three-phase systems.[3] These materials may have wide range of practical applications, because they combine the properties of both the organic and inorganic components. At the same time, these materials hold interest from

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fundamental point of view. Changing of the chemical composition of the organic and inorganic phases can modify the properties of the final compound, and, as a result, materials with desirable properties can be obtained.

In this work broadband dielectric relaxation spectroscopy (DRS) and thermally stimulated depolarization current (TSDC) techniques were used to investigate the properties of OIPCs, based on polyurethane (PU). Two different PUs with molecular weights of 1050 and 3600 and functionality equal to 2 and 3 respectively were used. This results to structures with two different chain configurations. Water solution of sodium silicate (NaSi) was used as the inorganic component. The inorganic phase content was varied in the range 0-30 wt. %. Molecular mobility, glass transition mechanism and conductivity relaxation were studied. These composites have high water sorption ability, high elasticity and higher conductivity compared to materials consisting of polyisocyanate and NaSi.[4]

Experimental

Organic/inorganic polymer composites (OIPC), consisting of a polyurethane organic phase and a mineral inorganic phase were prepared by the joint polymerization of the urethane oligomer with the water solution sodium silicate.

Urethane oligomer was obtained on the basis of 2,4– toluene diisocyanate (TDI) and oligo oxypropylene glycol (OPG) with various molecular weights (MW) and different functionality equal to 2 or 3 (two or three OH- groups at the ends of molecular chain). In the first case the polymer chain is linear, in the second one the chain has branched configuration. The molar ratio TDI:OPG was 2:1 for the OPG with functionality 2 and equal to 3:1 for the trifunctional one. OPGs were labeled 1052 and 3603 according to their molecular weight and functionality (for example OPG-1052 means MW=1050 and functionality 2, while OPG-3603 means MW=3600 and functionality equal to 3). The inorganic component of the composites was sodium silicate (NaSi) that exists in water solution in the form of inorganic oligomer.

OIPCs were prepared in two steps. Firstly, the organic oligomers were synthesized from TDI and OPG. In the second step, OIPCs were obtained as a result of the reaction between oligomers and NaSi. The inorganic content was varied between 0 and 30 % wt. for all the composites studied.

For the investigation of the dielectric properties, dielectric relaxation spectroscopy (DRS) in a wide frequency and temperature range and thermally stimulated depolarization current (TSDC) techniques were employed. For DRS measurements, the complex dielectric permittivity, $\epsilon^*=\epsilon'-i\epsilon''$, was determined as a function of frequency (10^{-2}-10^{6} Hz) and temperature (-60 to 80 °C).[5] 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 method consists of measuring the thermally activated release of frozen-in polarization and corresponds to measuring dielectric losses as a function of temperature at low equivalent frequencies of 10^{-2}-10^{-4} Hz.[6] The method allows for a quick characterization of the overall dielectric behavior of the materials and is characterized by high sensitivity and high resolving power. A home-made TSDC equipment was used for measurements in the range -175 to 30 °C.[5, 6] The samples were discs of about 1 mm thickness and a diameter of 30 mm for DRS and 13 mm for TSDC. In addition to these techniques, the results were combined with results from small and wide angle X-ray scattering (SAXS and WAXS), differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) measurements.

Results and Discussion

It is well known that PUs are amorphous materials with weak degree of microphase separation in hard and soft blocks.[7] This degree decreases by increasing the molecular weight of OPG, due to the decrease of concentration of the rigid blocks. It is also known that the composites have a more heterogeneous structure, compared to the structure of the polymer matrix, due to the presence of the crystalline phase of the inorganic component. SAXS and WAXS measurements showed that the size of these heterogeneities varies in the range 8-11 nm and that this size decreases with increasing the molecular weight of the OPG used.[8]

In Fig. 1 TSDC thermograms for the samples 1052 and 3603 (pure and filled with 20 % wt. NaSi) are presented. Two distinct peaks are clearly observed. The peak at low temperatures is assigned to the main, or segmental, α-relaxation, associated to the glass transition of the polyurethane matrix. The temperature of the TSDC α-peak, T_α, is a good measure of the glass transition temperature, T_g,[9] at the equivalent frequency of 1.6 mHz. The latter corresponds to a dielectric relaxation time: τ=100 sec.[6] At higher temperatures (~ -20 °C), a peak, tentatively attributed to the interfacial Maxwell-Wagner-Sillars polarization, is observed. In some cases, the α-peak is masked by the larger MWS peak, reflected also to DRS measurements.

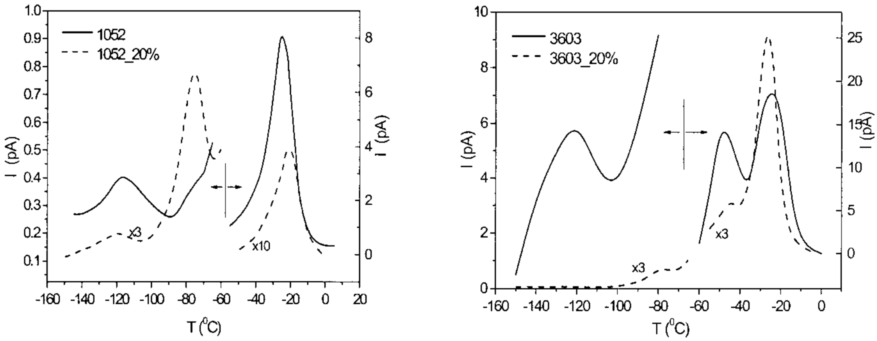

Figure 1. TSDC thermograms for the samples of series 1052 (left) and 3603 (right). Solid lines are for the pure PU matrices, while dashed lines are for the composites filled with 20 % wt. NaSi.

In the composites, the glass transition relaxation shifts to higher temperatures. The glass transition temperature is -25 and -20 °C for the 1052 and 1052-20 samples, respectively. For the samples of 3603 serie, the glass transition temperatures are considerably lower (-48 °C for the 3603 matrix and -44 °C for the same PU filled with 20 % wt. NaSi). It should be mentioned that results of DSC and DMTA measurements show the contrary effect. These techniques indicate that the composites with 20 % wt. NaSi have lower glass transition temperatures, compared to the pure matrices (1052 and 3603). This may be explained by the presence of the MWS relaxation, which has high magnitude, located at high temperatures and masks the α-relaxation. The values of the glass transition temperatures, as obtained from the various techniques used, for all the samples studied are listed in Table 1.

The most interesting result in Fig. 1 is that molecular mobility, as measured by the magnitude of the depolarization current, increases in the composites.[10] This result is in agreement with DRS measurements, to be presented later.

Table I. The glass transition temperatures (°C) for the samples studied as obtained by the various experimental techniques used. T_α is the temperature of the TSDC α-peak.

Sample	T_α	T_g^{DSC}	T_g^{DMTA}
1052	-25	-18	-15
1052-20	-20	-19	-18
3603	-48	-48	-40
3603-20	-44	-47	-40

DRS measurements show that the relaxation spectra of OIPCs are changed with varying the composition and the temperature. Fig. 2 presents comparative plots of dielectric permittivity, ε', and dielectric losses, ε", as a function of frequency, at room temperature for the samples of 1052 serie. Similar results were obtained for the other OIPCs, too. As it is seen, the filled samples have higher values of ε' and ε", compared to the pure PU matrix. It means that the overall molecular mobility of the composites increases, in agreement with TSDC results.[10] The higher values of dielectric losses for the composites, means also that the filled samples are more conductive, compared to the pure matrices. This result will be discussed in details later.

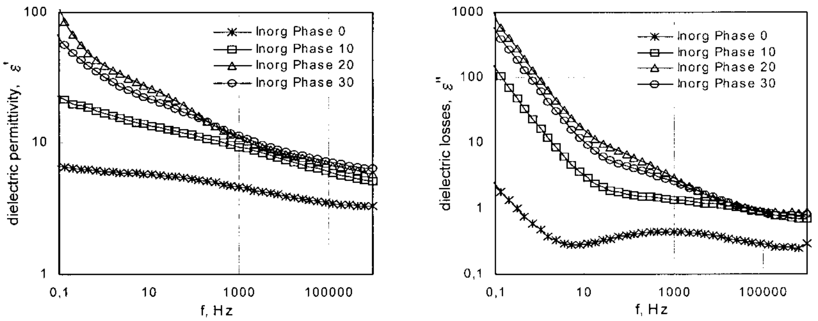

Figure 2. Real, ε', and imaginary, ε", part of the complex dielectric permitivity as a function of frequency, f, for the samples of 1052 serie at room temperature.

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. The broad relaxation observed at about 1 kHz is for the pure PU matrix is attributed to the glass transition. This peak is also present in the composites, but it is masked by a larger peak at lower frequencies, attributed to the interfacial MWS polarization.

It is also interesting to mention that the overall dielectric response of the composites with 20 and 30 % wt. inorganic phase is very similar, suggesting a kind of saturation. This result is in agreement with TSDC measurements.

Fig. 3 shows $\epsilon''(f)$ plot for the sample 3603 filled with 20 % wt. inorganic phase at various temperatures. The change of the dielectric response, which is observed for temperatures higher than -40 °C, is associated to the glass transition. The α-loss peak shifts to higher frequencies with increasing temperature. At high temperatures/low frequencies high values of dielectric losses are measured, related to conductivity effects.

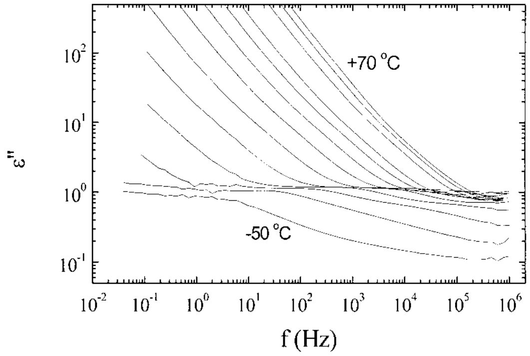

Figure 3. Dielectric losses as a function of frequency for the sample 3603 filled with 20 % wt. inorganic phase and for temperatures from -50 up to +70 °C in steps of 10 °C. The lines connect the data to guide the eye.

The DRS data, measured isothermally, have been replotted and analyzed in isochronal (at constant frequency) plots against temperature, to compare with TSDC and DMTA results. An example for the pure PU 3603 is given in Fig. 4. In this figure, ϵ' and ϵ'' are presented as a function of temperature for various frequencies. The glass transition peak, at about -20 °C (for frequency equal to 100 Hz), is clearly observed, as well as the conductivity relaxation at higher temperatures. With increasing frequency, the α-loss peak shifts to higher temperatures. Conductivity effects are more intense for the lower frequencies/higher temperatures. Similar results have also been obtained for the other OIPCs.

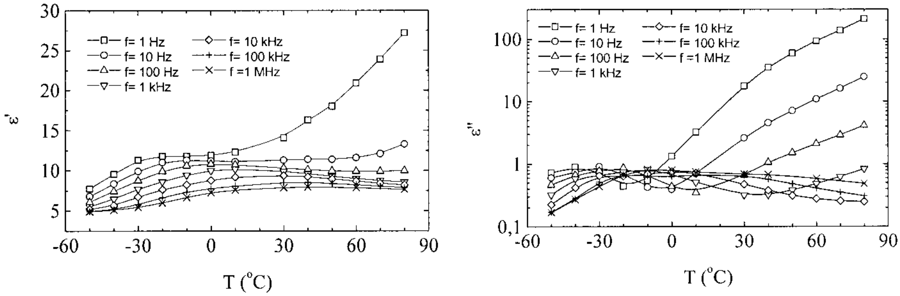

Figure 4. Isochronal plots of ε' and ε'' for the sample 3603 at several frequencies indicated on the plots.

Fig. 5 presents the Arrhenius plots (activation diagrams) of the glass transition mechanism for the samples 3603 and 3603 filled with 20 % wt. NaSi. In these plots, the maximum frequency of the α-relaxation peak is plotted as function of reciprocal temperature. The most striking result in this plot is that the glass transition mechanism becomes faster (moves to higher frequencies) for all the filled samples studied.

The data in Fig. 5 have been fitted by the Vogel-Tammann-Fulcher-Hesse (VTFH) equation:[11]

$$f_{\max} = A\exp\left(-\frac{B}{T-T_0}\right) \tag{1}$$

where A, B and T_0 (Vogel, or ideal, glass transition temperature) are temperature independent empirical constants. For all the composites, the fittings are good with reasonable values of the fitting parameters, which, however, will be discussed elsewhere.

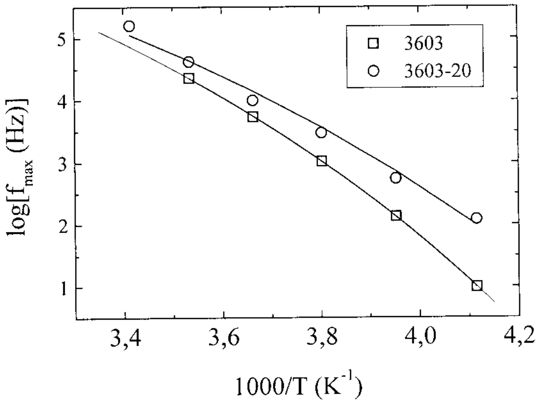

Figure 5. Arrhenius plots (activation diagrams) of the α-relaxation for the 3603 (squares) and 3603 filled with 20 % wt. NaSi samples (circles). The lines are the best fitting of Eq. (1) to the experimental data.

The electrical conductivity of the samples was calculated by the equation: $\sigma = i\omega\varepsilon_0\varepsilon''$, where ϵ_0 is the vacuum dielectric permitivity and ω is the angular frequency. In the low frequency region, where ϵ'' takes high values (Figs. 2 and 3), the conductivity is frequency independent, ie. taking the dc conductivity value (not presented here).

The dependence of conductivity on the temperature for the 3603 and 3603-20 samples is shown in Fig. 6. As it is seen, the filled composites are more conductive than the unfilled PU matrix. With increasing the inorganic phase content, the conductivity increases 2-3 orders of magnitude (depending on the filler content, see also Fig. 2). The experimental data were fitted by the VTFH equation, too. It was also found that the electrical conductivity of the OIPCs depends on the molecular weight of OPG used, too. With increasing the molecular weight of OPG, the conductivity increases about two orders of magnitude. Probably the increase of molecular chain length facilitates the charge transport through the chain.

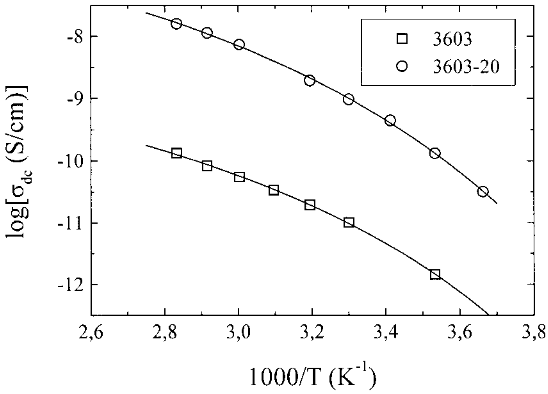

Figure 6. Comparative Arrhenious plot of the conductivity relaxation for 3603 (squares) and 3603-20 (circles) samples. The lines are the best fitting according to the VTFH equation.

Finally, all complementary experimental techniques employed indicate that the results are more intense for the composites based on the polyurethane with lower molecular weight (OPG-1052, in this work). Probably, the addition of inorganic phase influences more drastically the shorter chains of the organic matrix.

Conclusions

In this work the dielectric properties of organic/inorganic polymer composites, which consist of polyurethane (PU) and sodium silicate (NaSi), were investigated. PUs with various molecular weights and different functionalities were studied. The weight content of the inorganic phase was also varied. Broadband dielectric relaxation spectroscopy and thermally stimulated depolarization current techniques were employed to investigate molecular mobility, glass transition mechanism and conductivity relaxation. Both techniques indicate that the overall molecular mobility increases in the composites. The glass transition temperature shifts to lower temperatures/higher frequencies with the addition of inorganic phase. Electrical conductivity increases with increasing the inorganic phase content, or the molecular weight of the polyurethane used. The results are more intense for the composites based on the PU with low molecular weight.

Acknowledgements

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[1] E.F. de Sousa, C.C. Bezerra, F. Galembeck, *Polymer* **1997**, *38*, 6285.
[2] E.V. Lebedev, S.S. Ischenko, A.B. Pridatko, *Compos. Polym. Mater.* **1999**, *21*, 3.
[3] S.S. Ischenko, V.F. Rosovitskii, A.B. Pridatko, N.Y. Babkina, E.V. Lebedev, *J. Appl. Chem.* **1998**, *11*, 1929.
[4] S.S. Ischenko, E.V. Lebedev, *Ukr. Chem. J.* **2001**, *67*, 116.
[5] G. Georgoussis, A. Kyritsis, V.A. Bershtein, A.M. Fainleib, P. Pissis, *J. Polym. Sci.: Part B: Polymer Physics* **2000**, *38*, 3073.
[6] P. Pissis, A. Anagnostopoulou-Konsta, L. Apekis, D. Daoukaki-Diamanti, C. Chistodoulides, *J. Non-Crystalline Solids* **1991**, *131-133*, 1174.
[7] P. Pissis, A. Kanapitsas, Yu. Savelyev, E.R. Akhranovich, E.G. Privalko, V.P. Privalko, *Polymer* **1998**, *39*, 3431.
[8] Ye. P. Mamunya et al., unpublished results
[9] A.S. Vatalis, C.G. Delides, O.P. Grigorieva, L.M. Sergeeva, A.A. Brovko, O.N. Zimich, V.I. Shtompel, G. Georgoussis, P. Pissis, *Polym. Eng. Sci.* **2000**, *40*, 2072.
[10] A. Kanapitsas, P. Pissis R. Kotsilkova, *J. Non-Crystalline Solids* **2002**, *305*, 204.
[11] E. Donth "*Relaxation and thermodynamics in polymers*", Akademie Publisher, Berlin **1992**.