Polymer Based Nanocomposites with PhenethylPOSS as Nanofiller Investigated by Dielectric Spectroscopy and Gas Transport Measurements

*N. Hao, M. Böhning, S. Wohlrab, A. Schönhals**

Summary: Polyhedral oligomeric silsesquioxane with phenethyl substituents (PhenethylPOSS) as nanofiller was incorporated within Poly(bisphenol A carbonate) (PBAC) as matrix. Dielectric spectroscopy proved an almost complete miscibility of PhenethylPOSS up to 7 wt. %. At higher concentrations phase separation yields composites with a PBAC-rich matrix and POSS-rich domains which posses well shaped interfaces. The nanocomposites were also investigated with respect to their gas transport behaviour. An increase of the gas permeability was found at higher PhenethylPOSS concentrations, which is due to the phase separated structure.

Keywords: dielectric measurements; nanocomposites; permeation; polycarbonates; polyhedral oligomeric silsesquioxanes

Introduction

One special interest in creating new organic-inorganic composite materials is to develop and to investigate new polymer based hybrids containing polyhedral oligomeric silsesquioxanes (POSS[1]). In the last years, a lot of different POSS species consisting of a molecularly defined inorganic silica core surrounded by an organic surface have been developed.[2,3] The organic substituents can be varied over a wide range in their chemical characteristics. Accordingly, POSS can either be incorporated within a polymeric backbone via reactive spacers[4,5] or mixed within a polymeric matrix using phase compatible side groups.[6–10]

In this work the latter possibility to incorporate phenethyl substituted POSS into PBAC was examined. Using dielectric spectroscopy measurements it was possible to investigate the miscibility behaviour of the filler. Accordingly, at high filler concentrations a phase separated structure was found. This morphology changes the permeability of gases like CO_2, which was determined using gas transport measurements.

Experimental Part

PhenethylPOSS was obtained from Hybrid Plastics®, Inc., as a viscous liquid at room temperature. MALDI-TOF mass spectroscopy shows that the purchased product is a mixture of octa-PhenethylPOSS (T8), deca-PhenethylPOSS (T10) and smaller amounts of POSS of larger cage sizes.[11] Poly(bisphenol A carbonate) (PBAC, $M_n = 2.2 \cdot 10^4$ g/mol, PDI = 1.23) was purchased from Sigma-Aldrich®.

To prepare nanocomposites, selected amounts of PhenethylPOSS were dissolved in parts of a dichloromethane stock solution containing 20 wt-% PBAC. The mixtures were treated by ultrasonification (Bandelin® Sonopuls, HD200/UW200 homogenizer equipped with KE76 titanium tapered tip) for at least 5 minutes and casted onto a glass substrate by a custom-made casting knife. To control the initial evaporation casting was performed in a closed chamber.

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After this first evaporation step, the films were depleted from the substrate. To remove the residual solvent the samples were dried in a second step in vacuum at 363 K for 24 h. By this procedure, pinhole free samples, 40 mm in diameter and 50 to 100 microns in thickness, were obtained. The concentration of PhenethylPOSS in the prepared nanocomposites was confirmed by FTIR spectroscopy.

Dielectric relaxation spectroscopy in the frequency range from 10^{-1} Hz to 10^{7} Hz was applied to investigate the nanocomposites. The complex dielectric function $\varepsilon^{*}(f) = \varepsilon'(f) - i\varepsilon''(f)$ (f- frequency, ε' and ε'' - real and imaginary part of the complex dielectric function) was measured by a high resolution ALPHA analyzer equipped with a Quadro cryo-system with a stability better than 0.1 K from Novocontrol® (Hundsangen, Germany).

To measure the permeability of the composites to permanent gases the time-lag method[12] was applied in the upstream pressure (p_1) range from 1.0 to 20 bar using a temperature controlled set-up. The samples were degassed prior to the measurements using a turbomolecular vacuum pump system ($<10^{-5}$ mbar) for at least 72 h. The pressure increase in the closed downstream volume (p_2) was determined by a temperature controlled MKS Baratron gauge in the range of 10 mbar.

Gas sorption was measured gravimetrically using an electronic high pressure microbalance (Sartorius 4406) placed in a temperature controlled air-bath equipped with a turbomolecular vacuum pump for degassing.

Dielectric Measurements

Nanocomposites with different component ratios, respectively the nanocomposite forming pure components, PhenetylPOSS and PBAC, were investigated with regard to the phase morphology using dielectric measurements as molecular probe for structure. Exemplary results are shown in Figure 1 where the dielectric loss ε'' is plotted at fixed frequency vs. temperature.

Pure PhenethylPOSS shows a single dielectric relaxation process indicated by a peak in the dielectric loss with a maximum at 264 K. The temperature dependence of the mean relaxation rate follows the Vogel-Fulcher-Tammann equation[13–15] characteristic for glassy dynamics. Therefore the relaxation process is assigned to the dynamic glass transition which was also proved by DSC measurements.

PBAC shows two relaxation processes which are characteristic for amorphous

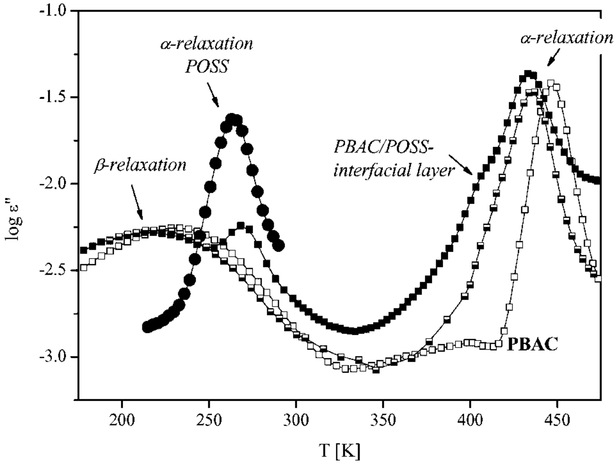

Figure 1.

Dielectric loss vs. temperature at a frequency of 10 kHz: □ - pure PBAC, ⬓ - 4.8 wt-% POSS, ■ - 28.6 wt-% POSS, ● - pure POSS. Lines are guides for the eyes.

polymers. Here a β-relaxation at lower (~232 K) and an α-relaxation (dynamic glass transition) at higher temperatures (~447 K) can be observed.

Nanocomposites consisting of low concentrations of POSS also show the β- and the α-process but shifted to lower temperatures (~222 K respectively ~435 K). For the dynamic glass transition this effect is known as plasticization. The appearance of only single peaks both, in the α-relaxation region and in the β-relaxation region, indicates that PhenethylPOSS is miscible within the PBAC matrix on a molecular level. Incorporation of such small amounts of PhenethylPOSS in PBAC leads to a decreased packing density of the surrounding matrix resulting in a local increase of the free volume and therefore in a decreased glass transition temperature due to enhanced molecular mobility. For a detailed discussion see ref. 11.

For higher concentrations of POSS the α-relaxation splits into two processes. The main peak at ~434 K has to be assigned to the glass transition of the PBAC-rich matrix in which PhenethylPOSS is dispersed on a molecular level. A shoulder at slightly lower temperatures becomes visible which suggests that this effect is also related to polycarbonate. The further temperature reduction compared to the main peak of the PBAC-rich matrix implies that more PhenethylPOSS molecules are involved than in the main process. In parallel, in the temperature region previously assigned to the glass transition of pure PhenethylPOSS, a third relaxation process is evident, indicated by an additional peak in ε''. This process has to be related to the dynamic glass transition of PhenethylPOSS-rich domains. At constant pressure and temperature the number of possible phases has to be two. For that reason process 2 is assigned to an interfacial layer between the POSS-rich domains and the PBAC-rich phase (see reference 11).

The appearance of these additional peaks has to be assigned to a phase separation which takes place in the nanocomposites with higher concentrations of PhenethylPOSS. Furthermore, a dielectric glass transition temperature T_g^{Diel} can be deduced from the temperature dependence of the relaxation rates. Figure 2 gives the thermal glass transition temperature T_g^{DSC} (DSC = differdifferential scanning calorimetry) and T_g^{Diel} of the POSS/PBAC nanocomposites vs. concentration of Phenethyl-POSS. The

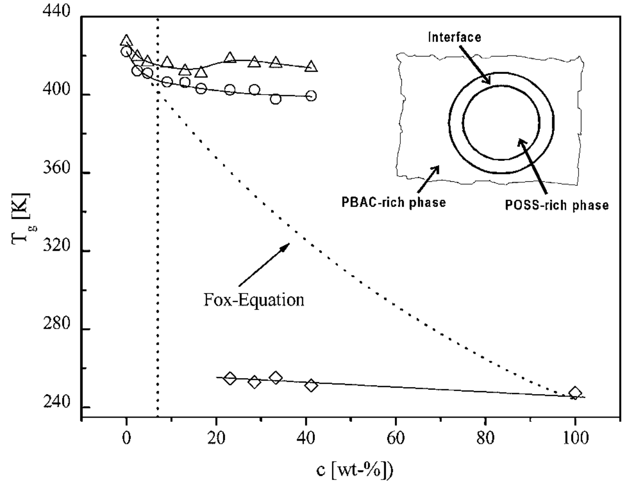

Figure 2.

Dependence of T_g^{DSC} (○) and T_g^{Diel} (△) for the PBAC-rich phase vs. concentration of POSS. ◇ gives T_g^{Diel} of the POSS-rich domains. Solid lines are guides for the eyes. (dashed line = miscibility limit; inset = sketch of the proposed structure).

prediction of the Fox-equation is included which is expected to be valid for a molecularly miscible system.

For 10 wt-% and higher concentrations of POSS the glass transition is much less dependent on concentration variation than predicted by the Fox-equation, indicating a strongly reduced miscibility of POSS in PBAC. This dependence levels off for high concentrations of POSS. For these concentrations PhenethylPOSS can no longer completely be dissolved in PBAC on a molecular level. In parallel the double peak for the dynamic glass transition is observed. Thus the maximum concentration for a molecular miscibility of PhenethylPOSS into PBAC is at about 7 wt. %.

Gas Transport Measurements

Figure 3 shows the permeability P of CO_2 versus upstream pressure p_1 and POSS concentration. As expected for glassy polymers with increasing p_1 the permeability decreases for a certain POSS concentration. At constant upstream pressure P is almost constant for lower concentrations of PhenethylPOSS but increases significantly at higher concentrations.

The CO_2-permeability shows no significant change in its concentration dependence at 7 wt-% but increases for concentration higher than 20 wt. %.

Using the time lag τ observed in the permeation experiments diffusion coefficients D_{eff} can be calculated. The POSS-concentration dependence of D_{eff} is similar to that of the permeability P. This leads to the conclusion that the concentration dependence of the permeability is due to changes of the diffusivity. PhenethylPOSS is a viscous liquid at room temperature. Keeping in mind that the nanocomposites have a nanophase separated structure the increase of the permeability can be understood by a faster diffusion of the gas molecules inside the POSS-rich domains because its molecular mobility is essentially higher than that of the surrounding polycarbonate-rich matrix. Because the critical concentration for phase separation is lower than that for the increase in the permeability it might be that the nanophase separated domains need to have a certain size and/or volume fraction in order to significantly influence the gas transport in the nanocomposite. Also their interconnectivity can be of importance.

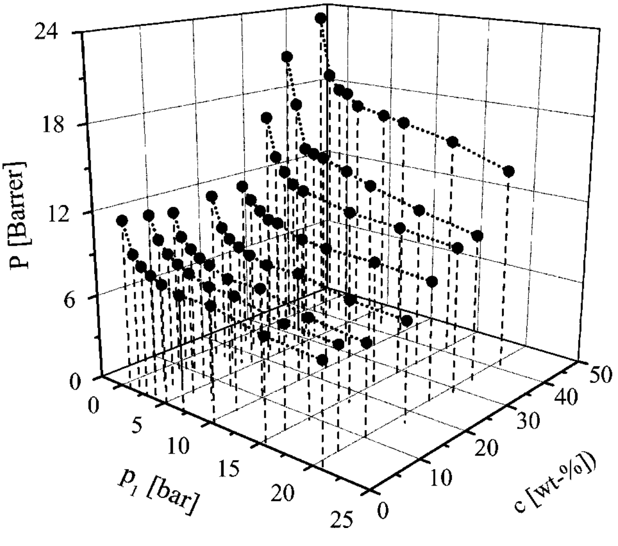

Figure 3.
CO_2-Permeability of the nanocomposites at T = 308 K vs. upstream pressure p_1 and POSS concentration (1 [Barrer] = 10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} cm Hg^{-1}).

According to the solution-diffusion mechanism describing the transport of small penetrant molecules through nonporous amorphous polymer layers permeability is given by $P = S * D$. The solubility S can therefore be estimated from permeation measurements. Here S decreases slightly with increasing POSS concentration. From sorption experiments measuring the mass uptake the concentration of the sorbed gas molecules this could be confirmed.

Conclusion

The miscibility of PhenethylPOSS within PBAC is limited to $\sim$7%, which could be shown using dielectric spectroscopy. Above this value PhenethylPOSS-rich domains have been detected which are responsible for a significant increase of gas permeability.

[1] POSS and PhenethylPOSS are trade marks for Polyhedral Oligomeric Silsesquioxane and phenethylsilsesquioxane (MS0870) of Hybrid Plastics, Inc. (Hattiesburg, MS, USA), respectively.

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