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www.elsevier.com/locate/procedia**Euromembrane Conference 2012****[P1.021]****Correlation of gas diffusivity and local chain mobility in polycarbonate/POSS nanocomposites as determined by broadband dielectric relaxation spectroscopy**

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According to basic phenomenological models a connection between the diffusive transport of gas molecules in a polymeric matrix and the molecular mobility of the chain molecules on a certain length scale is in principle obvious.

Both phenomena depend on the molecular architecture of the polymer as well as on characteristics of amorphous chain packing, free volume and morphological features.

An important factor for these characteristics in polymer nanocomposites (PNC) is the influence of internal interfaces or interphases created upon addition of nanoparticles to the polymer matrix. The resulting dynamic behavior is determined by a complex interplay of local structural features. So the local interaction of the polymer matrix with a more or less rigid nanofiller interface may on the one hand lead to lower chain mobility due to partial adhesion, on the other hand to a looser chain packing and higher free volume – which in turn should facilitate the chain movement.

In such PNCs the resulting transport properties are often dominated or completely determined by the interphase behavior and thus subject to a range of new material design possibilities.

The investigation of PNCs with different nanofiller contents allows also the directed variation of these properties in order to study systematically the correlation of free volume, chain mobility and gas transport properties.

The molecular mobility in polymeric systems has been investigated by broadband dielectric relaxation spectroscopy (BDRS) sensitive to motions of molecular dipoles [1]. In polycarbonate besides the dynamic glass transitions (α -relaxation) a β -process at lower temperatures / higher frequencies corresponding to localized molecular fluctuations is observed. From the Arrhenius analysis of the temperature dependence of the relaxation rate, an activation energy E_A for this process can be estimated.

Complementary to that activation energies for the gas diffusion E_D have been determined from temperature dependence of diffusion coefficients obtained from time-lag measurements with different gases. In contrast to the diffusion coefficient itself, which depends in nanocomposite materials strongly on the tortuosity of the effective diffusion pathways, the corresponding activation energy reflects more closely the connection to the chain mobility.

The influence of the penetrant gases is usually discussed in terms of their kinetic diameter, which represents the smallest effective diameter of the gas molecules, taking into account also more complex geometries (in contrast to spherical equivalents based on the same volume or rotational modes).

For a series of nanocomposites of polyhedral oligomeric silsesquioxanes (POSS) in polycarbonate [2] a clear correlation of the activation energy of the β -relaxation E_A (from BDRS), representing local molecular motions, to the activation energy of diffusion E_D (from time-lag measurements) was found (see figure 1), where the resulting slope is related to the kinetic diameter of the gases investigated.

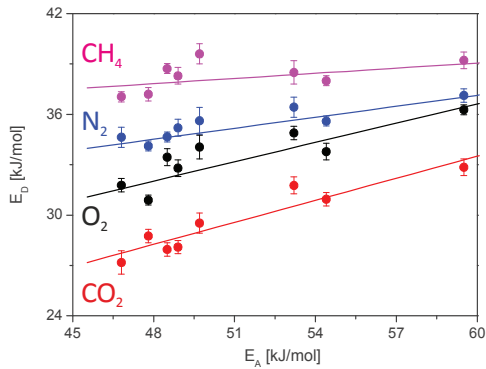


Figure 1. Correlation of the activation energy of diffusion E_D and the activation energy E_A of the β -relaxation for PC/POSS nanocomposites at POSS concentrations up to 40 wt.-% .

[1] F. Kremer, A. Schönhalz (Eds.), *Broadband Dielectric Spectroscopy*, Springer Berlin, Heidelberg, 2002

[2] N. Hao, M. Böhning, A. Schönhalz, CO₂ Gas Transport Properties of Nanocomposites Based on Polyhedral Oligomeric Phenethyl-Silsesquioxanes and Poly(bisphenol A carbonate), *Macromolecules* **43** (2010) 9417–9425

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