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Study of Cooperative Effects of Silanols on Modified Silica by Dielectric Relaxation Method

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SUMMARY: Two types of chemically modified silica gels with covalently bonded hydrophobic (alkyl, SiO_2-C_8) and hydrophilic (aminoalkyl, SiO_2-NH_2) groups were studied by dielectric relaxation method. For SiO_2-C_8 two relaxation maxima were detected at 140 and 238K. From comparison with bulk silica the lower temperature maximum was assigned to cooperative re-orientation of residual silanols and higher one to melting of physically adsorbed water. Both maxima are much weaker for SiO_2-C_8 then for bulk silica. In Arrhenius coordinates relaxation at 238K exhibits similar behavior as OH groups in polyvinyl alcohol and so it was assigned to mobility of orientation defects in mono-dimensional chain of physically adsorbed water. For SiO_2-NH_2 no low temperature relaxation effect was observed. Intensive relaxation was measured at 248 K only. Strong interaction between supramolecules of silanol groups, bonded aminogroups and adsorbed water was assumed.

Introduction

For last few years significant successes was achieved in study of surface topography of silica gel surface on atomic level. In particular, established that covalently bonded organic layer can have island-like structure 1). Direct proofs of such topography did not received yet. It was shown that thermal motion of silanol groups has complicated quantum-mechanical character but casual re-orientation of them dominate due to interaction with long wavelength surface acoustic phonons 2). The dipole moments of silanol groups are oriented in parallel to surface. They are in a potential profile with three possible equilibrium directions for re-orientation with potential barriers. Despite to absence of long-distance order in the system of surface groups micro ordering can be present. It leads to formation of supramolecular structure organized by silanols with similar orientation of dipoles 2,3). Investigation of dielectric relaxation in such materials enables us to determine existence of such supramolecular structures by means of monitoring molecular mobility of dipoles depending on surface nature and particularly depending on the bonded group nature 4).

The purpose of our work was investigation of cooperative effects related to mobility of polar groups on silica surface, chemically modified with hydrophobic (alkyl, SiO_2-C_8) and hydrophilic (aminoalkyl, SiO_2-NH_2) groups.

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Results

As a silica gel matrix spherical silica with particles size 7.5um was used (Silasorb Sph, Lachema). Direct measurements of highly dispersed systems (silica gels) reduce advances of high-precision technique of complex permeability. Polymeric composites (PC) with an inert polymeric matrix (polyethylene, PE) were used instead. Modified silicas were used as fillers. The filler was mixed with a powder of PE and then pressed in a vacuum at temperature 120°C and pressure 150 kg/cm^2. On similar manner samples of pure PE and polyvinilbutiral (PVB) were also received, as well as PC on the base of PVB with bulk silica gel. The investigation was performed in frequency range from 1 to 100 kHz at temperatures from 90 to 323 K. The volumetric concentration of silica in all investigated PC was identical (20%). It is higher than "percolation threshold" (16%). The experimental system enabled us to ensure heating speed in 1 K/min. In the experiment correlation between temperature and components of complex permeativity as well as dielectric loss factor were received at every 1-2K on four different fixed frequencies. It was found that the addition of silica gel to PE has no sufficient influences on thermal properties of PE. As it was expected no maxima were observed on the curve of dielectric losses (tg δ) from temperature for PE, Fig. 1. For PE filled with bulk silica gel two maxima were detected. One at low temperature (140 K) corresponds to the process of cooperative re-orientation of silanol groups 2). Significant increasing of dielectric losses from temperature higher then 248 K can be stipulated as melting of physically adsorbed water that definitely present on silica gel surface. It is known that concentration of silanol groups on silica gel with covalently bonded hydrophobic group is much less then on bulk silica but complete substitution of silanols with alkyl groups is impossible 1). Therefore presence of low-temperature maxima for the composite: PE + SiO_2-C8 was expected, Fig. 1. Certainly its intensity is much poor then for bulk silica. Identical temperature position of given maxima for both SiO_2 and SiO_2-C8 demonstrates identity of the mechanism of dielectric losses on these materials, and justify cooperative effects in re-orientation of silanol group dipoles on the surface of hydrophobic silica. In contrast to low-temperature part of the dependence tg δ – T it high-temperature part considerably differs for SiO_2-C_8 and bulk SiO_2. The reason is difference in macro properties of materials. Physically adsorbed water content on hydrophobic silica is small and week signal at 238 K was observed as a result. For the purpose of identification of the relaxation nature, correlation between the signal position and frequency range was studied and compare with relaxation process in polyvinyl alcohol and PVB. For last two polymers high-temperature maxima corresponds to mobility in orientation defects of one-dimensional chains of OH - groups [5]. From the identical behavior of the examined maximum for SiO_2-C8 and PVB at 238K in Arrhenius coordinates the same nature of the relaxation effects of all three materials can be suggested. Thus, on surface of the hydrophobic silica two supramolecular structures generated by mono-dimensional physically adsorbed water and two-dimensional residual silanol groups co-exist. Conclusion that follows from our experiment is one from few direct proofs of island-like distribution of surface bonded groups on alkyl-silica.

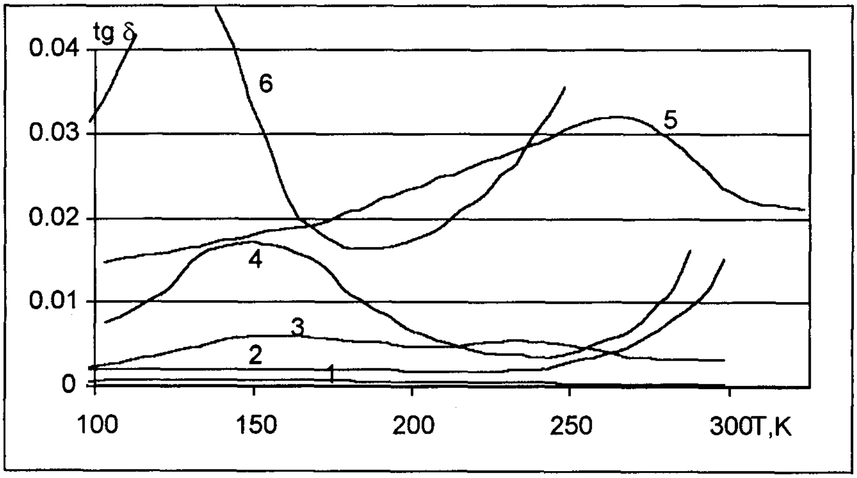

Fig. 1. Degree of dielectric loses (tgδ) from temperature (working friquency 10 kHz): 1)PE, 2)PE + SiO_2-NH_2, 3) PE + SiO_2-C_8, 4) PE + SiO_2, 5)PVB, 6) PVB + SiO_2.

Unexpected on the first sight behavior exhibits the correlation of dielectric losses form temperature for SiO_2-NH_2, Fig. 1. For this modified silica low-temperature effect of re-orientation for residual silanol groups was not observed. Intensive relaxation effect is observed only at temperature higher then 248 K. It indicates high concentration of physically adsorbed water on SiO_2-NH_2. Therefore it was unreasonable to assume deficiency of silanols on the aminosilica surface. We suggest other interpretation of this artifact. It is known that the covalently bonded aminogroups form hydrogen bonds with residual silanol groups on silica surface. From this it is possible to assume that supramolecular structure generated by fixed aminoalkyl groups promotes interaction between other two supramoleculars: residual silanols and adsorbed water and disorders orientation of silanol dipoles.

Conclusion

It has been shown that on surface of hydrophobic silica two supramolecular structures generated by mono-dimensional physically adsorbed water and two-dimensional residual silanol groups co-exist. In contrast to siilica with fixed alkyl groups, supramolecular associates of aminogroups interact with macromolecules formed by silanols and water and thus prevents disorder cooperative re-orientation of silanols.

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