Effects of Surface Area and Surface Functionality of Fumed Silica on the Crystallization of PEO

Jiang Ding, Prithwiraj Maitra, and Stephanie L. Wunder
Department of Chemistry 016-00, Temple University
Philadelphia, PA 19122

Inorganic fillers such as SiO_2, TiO_2, and Al_2O_3 have been shown to suppress the crystallization of polyethylene oxide(PEO)/lithium salt polymer electrolytes and thus increase their room temperature conductivity[1, 2]. Although slow, the process of crystallization can still occur. The mechanism of the conductivity enhancement is not completely understood. In the present work, the interaction of PEO with fumed silica is investigated, using hydrophilic and a hydrophobically modified fumed silica, as well as a system in which a PEO-silane is covalently attached to the silica.

In particular, the effects of surface area and surface properties on the crystallization of polyethylene oxide (PEO-with a molecular weight of 4600g/mol) were investigated using fumed silica (nanoparticle SiO_2 from DeGussa). Physical mixtures of fumed silica and PEO were prepared in the absence of Li salt, at varying SiO_2/PEO wt ratios. The PEO and SiO_2 were dissolved or dispersed, respectively, in methanol or toluene until uniform, and the solvent then removed under vacuum. Fumed silicas having nominal surface areas of $380m^2/g$ (A380), $200m^2/g$ (A200) and $50m^2/g$ (OX50), as well as a material functionalized with methyl groups ($220m^2/g$ R812s) were used. Native fumed silica has a surface consisting of Si-O-Si (hydrophobic) and Si-OH (hydrophilic) groups. The surface can be modified by reaction of the surface silanols with silanes. A PEO silane $(CH_3CH_2O)_3$-Si-PEO, with a PEO molar mass of 5000g/mol, was attached to A380 fumed silica at different weight ratios, and its crystallization properties compared with the physical mixtures of fumed silica and PEO. The grafted PEO-silane was rinsed extensively with methanol and toluene to remove material not covalently attached to the silica.

The samples were characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The weight loss observed by TGA for the physical mixtures of PEO and SiO_2 agreed with that expected based on the relative weights added in the solutions. In the case of the PEO-silane, the amount grafted was less than that added in the solution, and a maximum of 38% by weight could be covalently attached. The initial melt temperatures, T_m^1 , and enthalpies, ΔH_m^1 and the crystallization and melt (T_c, ΔH_c and T_m^2, ΔH_m^2, respectively) on subsequent cooling and heating cycles obtained by DSC showed rearrangement of the PEO in the presence of the silica. ΔH_m and ΔH_c were used as a measure of the degree of crystallinity of the PEO.

For example, Figures 1 and 2 show DSC traces of 30%PEO/70%SiO_2 for A380 and R812s, respectively. The melting temperatures and ΔH_m are higher for PEO adsorbed onto the silica with methyl groups (59°C) compared with silanol groups (55°C); T_m^1 of neat PEO occurs at 60°C. Crystallization exotherms are observed at 30°C for both A380 and R812s, the same temperature as for neat PEO. A second crystallization peak is observed at –30°C in the case of PEO on A380, and is attributed to PEO segments in closer proximity to and interacting with the silica surface. The second heat for PEO adsorbed onto A380 shows endotherms of approximately equal magnitude near 22°C and 55°C, also suggesting that the PEO in close contact with the silica has a lower T_m. In contrast T_m^2 for the second heat of PEO adsorbed on the methyl silanated silica occurs at the same temperature as T_m^1.

Several other interesting trends were observed: (i) for native fumed silica (i.e. with surface OH groups), suppression of the crystallization of PEO was more effective the higher the surface area, i.e. A380 > A200 > OX50; (ii) for comparable surface areas, the native silanol surface was much more effective in suppressing crystallization than a surface modified with methyl groups; (iii) for physical mixtures of PEO and SiO_2, T_m and ΔH_m decreased upon thermal cycling, whereas T_m and ΔH_m increased for PEO grafted onto silica; (iv) two (and sometimes three) T_ms and T_cs were observed for PEO adsorbed or attached to the fumed silica.

Figure 1. DSC trace of PEO(4600)/A380(surface OH groups) fumed silica blend in 30/70 wt ratio

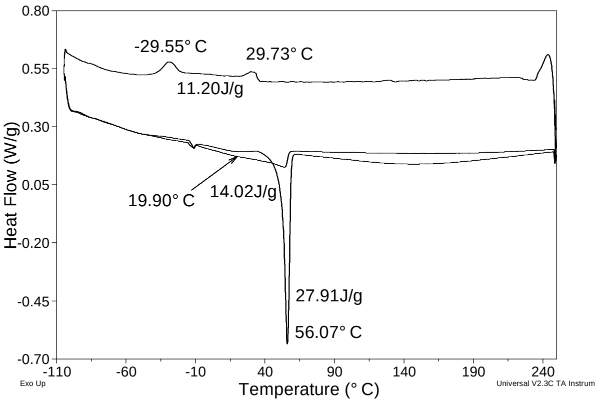
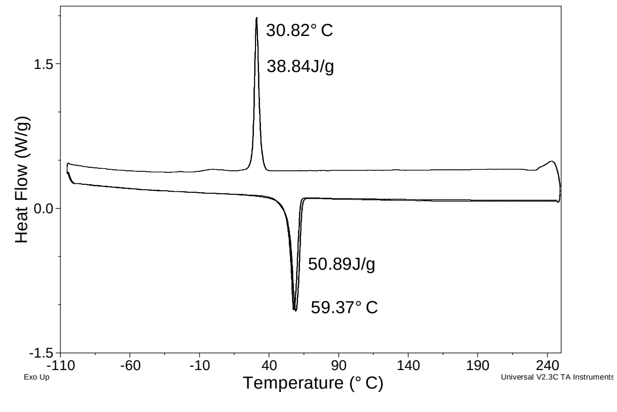


Figure 2. DSC trace of PEO(4600)/R812s(surface methyl groups) fumed silica blend in 30/70 wt ratio



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