

“Surface Modification of Fumed Silica with PEO-Silanes”

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

Transport of lithium ions occurs through the amorphous phase of polyethylene oxide (PEO), and short chain polyethylene glycols (PEGs) have been attached as branches or copolymerized with other polymers to enhance their ionic mobility. Recently, inorganic fillers such as fumed silica (SiO_2) have been shown to suppress crystallization of high molecular weight PEO in the presence of lithium salt and thus increase room temperature conductivity. We have prepared inorganic-organic hybrid materials from fumed silica ($380\text{m}^2/\text{g}$, 7nm primary particle size) silanated with PEG silanes ($(\text{CH}_3\text{CH}_2\text{O})_3\text{Si}-\text{CH}_2\text{CH}_2-\text{O}-(\text{CH}_2\text{CH}_2\text{O})_n\text{CH}_3$, where the average molar mass of the PEO segment is 450 and 5000[PEG(450)-silane and PEG(5000)-silane], and have blended them with linear PEO's. These materials have applications as components in polymer electrolytes for lithium ion batteries.

The amount of covalently attached silane was determined by thermogravimetric analysis (TGA), and the transition temperatures and enthalpies (ΔH) by differential scanning calorimetry (DSC). For the PEG(450)-silane silanated silica [referred to as PEG(450)- SiO_2], and their blends, DSC data were also obtained in the presence of LiClO_4 [O/Li ratio = 8/1]. Table I presents the glass transition (T_g) and melt (T_m) temperatures, as well as ΔH_m for the these systems and select model compounds.

Low molecular weight polyethylene glycol dimethyl ethers (PEGDME) do not exhibit a T_g ; they are predominantly crystalline and have a molecular weight dependent T_m . High molecular weight PEO is semicrystalline and thus exhibits both a T_g and T_m . The PEO(450)-silane is also semicrystalline, with a T_g , T_m and ΔH_m lower than PEG or PEO. When attached the PEO(450)-silane is gelled, through condensation of the ethoxy groups, there is an increase in T_g , presumably due to restriction in chain mobility, and a decrease in ΔH_m . Attachment of the PEO(450) to SiO_2 results in almost complete suppression of the crystallinity, and an increase in T_g to that comparable to high molecular weight PEO.

Blends of PEO(450)- SiO_2 with low molecular weight PEO(1000) or PEO(600,000) were prepared by first dispersing/dissolving the components in acetonitrile. The resultant T_g was characteristic of the matrix, and the composite had a ΔH_m that depended on its composition.

Addition of LiClO_4 in a O/Li ratio of 8/1 resulted in an increase in T_g of $\sim 25^\circ\text{C}$ and a suppression of crystallization for all the materials.

A silane with a 5000 molar mass PEO segment [PEO(5000)-silane] was also attached to A380-fumed silica using toluene as the grafting solvent; the samples were rinsed with both toluene and methanol. The maximum amount of silane that could be covalently attached to the fumed silica was about 38%. For comparison, the melting behavior of a comparable molar mass PEO dimethyl ether, PEO(4600) was investigated. The results of the calorimetric investigation are presented in Table II. The ΔH_c were similar to ΔH_m^2 and are not

reported. Subsequent scans gave similar T_m^2 , T_c^2 , and ΔH_m . None of the materials exhibited a T_g . Compared with the PEO(4600), the PEO(5000)-silane showed similar T_m s but lower enthalpies of melting. When attached to silica at concentrations below $\sim 10\%$, neither a T_g nor a T_m was observed. With increasing wt% PEO(5000)-silane attached to silica, the T_m , T_c and ΔH_m increased, but were below those obtained for the neat PEO(5000)-silane. The values of ΔH_m were normalized to the weight percent PEO in the PEO(5000)- SiO_2 obtained from TGA data. These results indicate that when attached to the silica surface, the PEO is prevented from crystallizing completely, and forms smaller, less perfect crystals.

Table I-PEG (450)

Sample	T_g ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	ΔH_m (J/g)
PEGDME ⁺ (500)	none	13.5	120
PEO(600,000)	-55.5	60	99.5
PEG(450)silane	-90	-1.8	73.2
PEG(450)gel	-66	-8.0	44.9
PEG(450)- SiO_2	-54	none	
PEO(450)- SiO_2 / PEGDME(1000)	-69	35.3	60.4
PEG(450)- SiO_2 / LiClO_4^*	-27	none	
PEG(450)- SiO_2 / PEGDME(1000)/ LiClO_4^*	-46.9	none	
PEG(450)- SiO_2 / PEO(600,000)/ LiClO_4^*	-28	none	

⁺ PEGDME = PEG dimethyl ether *O/Li ratio = 8/1

Table II-PEO (5000)

Sample	T_m^1 ($^\circ\text{C}$)	ΔH_m^1 (J/g)	T_c^1 ($^\circ\text{C}$)	T_m^2 ($^\circ\text{C}$)	ΔH_m^2 (J/g)
PEO(4600)	57.5	188.0	37ch	59.9	180.9
PEO(5000)- silane	57.4	166.7	37.7	59.6	150.6
PEO(5000)- silane/ SiO_2 10% silane	none	none	none	none	none
20% silane	15.5	15.3	-38	22.5	19.7
25% silane	28.8	44.5	-28	39.8	53.4
37 %silane	48.2	81.2	+7.2	52.1	78.0
38% silane	48.1	92.2	+16.0	50.6	96.0

Superscripts (1,2) indicate results of (first, second) DSC scans. Subscripts (m,c) indicates (melting, crystallization)