SL 11.5

Qualitative and Quantitative Measurements of PDMS Adsorption on Silica by Flow Micro-calorimetry Technique

R. Al-Akoum, B. Haidar, A. Vidal
Institut de Chimie des Surfaces et Interfaces (ICSI), CNRS-UHA
B.P. 2488, 68057 Mulhouse Cedex, France

Polymer reinforcement by fillers is mainly determined by an important polymer/solid surface-contact. Yet, polymer/solid interactions, solid/solid interactions, solid arrangement in the polymer matrices, surface accessibility, polymer conformation… are just a few of numerous factors affecting the development of the interphase and thus the overall macroscopic behavior. It is commonly admitted that surface modification is an inevitable and neat tool generally used to control these factors, nevertheless, the adjustments of such modifications continue to require a better understanding. Such understanding is considered essential in order to, primarily, establish a comprehensive structure/properties relationship of reinforced polymer, but also, to improve our ability to monitor both structural architecture (density and conformation of adsorbed polymer, distribution and de-agglomeration of particles) and polymer/filler attraction forces (adhesion, adsorption enthalpy,...).
In the present work a series of six chlrorosilane-modified and unmodified fumed silicas with increasing both degree of modification and particle size (surface area ranging from 50 to 400 m^2/g) was selected. Morphologies, surface areas (S) as well as surface energies (γ_{sd}) were determined by electron microscopy, nitrogen adsorption and inverse gas chromatography, respectively. The adsorption of a series of PDMS with different and narrow-distributed molecular weights (MW) was performed in the dry state. It was determined after an extensive extraction of the un-adsorbed polymer by a good solvent. Scaling laws relating the amount of adsorbed polymer to MW and S were proposed, polymer chain conformation was deduced and the relationship between surface accessibility and MW was established.
Three parameters are identified as pertinent factors in the determination of polymer chain adsorption and conformation on filler particles: 1) sterical, governing the relation between the dimension of surface irregularities and the size of the approaching molecule; 2) physico-chemical, controlling the affinity of the approaching molecule to the surface and 3) particles organization, enhancing intra- or inter-particle adsorption and its relation to MW.
However, this current paper is specially dedicated to the effect of the chemical modification of above mentioned silicas on the adsorption enthalpies of a series of PDMS with different and narrow-distributed molecular weights (MW in the 4 000 to 420 000g/mol range) as determined by flow micro-calorimetry (FMC).