Investigating the effect of pH on the surface chemistry of an amino silane treated nano silica

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Abstract

Purpose – The purpose of this paper is to investigate the effect of different pHs on the surface chemistry of fumed silica treated with aminopropyltrimethoxysilane (APTMS).

Design/methodology/approach – The reaction conditions involved variation of pH ranging from acidic to alkaline. Different analytical techniques including FT-IR spectroscopy, thermogravimetric analysis (TGA), CHN and Zeta potential analyses were employed to investigate the surface chemistry of treated particles. In addition, the stability of silanised silica dispersions were studied using turbidimetric and rheometric measurements.

Findings – It was revealed that in all conditions silica was more or less chemically grafted by the silane. When the pH of treating bath was adjusted to 1-2 prior and during the reaction, 58 percent grafting was observed, as obtained by CHN and TGA analyses. At very alkaline conditions, however, the grafting content declined to 29 percent. The variations in grafting were dependent on the silane hydrolysis and its further condensation with the silica surface. Zeta potential measurements showed a drastic change from −7.1 mv to +18.01 mv (at pH 7) for the untreated particle and the one with the highest grafting, respectively. The dispersion stability of differently treated particles varied in solvents with different Hansen solubility parameters (HSP). Moreover, due to the variations of surface chemistry of particles, their rheological behaviours were significantly influenced.

Originality/value – The results obtained in this work showed that the surface chemistry of fume silica could be tuned with treating method. The highest content of grafting led to a better dispersion in solvents having greater hydrogen bonding component and to an inferior dispersion in solvents with higher polar component.

Keywords Surface treatment, Surface chemistry, Rheology, Silica, Wettability

Paper type Research paper

Introduction

Fumed silicas, due to their very fine particle size and high specific surface area, have shown to be one of the most important reinforcing fillers for polymers and coatings (Roberts and Bergna, 2006; Sun et al., 2005). Apart from the geometry, surface chemistry of silica also greatly affects the degree of reinforcement. As silica contains a large number of silanol groups on its surface in the form of vicinal, geminal and isolated, it can be considered highly polar (Chen et al., 2005). Therefore, it is less compatible in non-polar media (Jesionowski and Kkrysztafkiewicz, 2001). Moreover, the surface silanol groups have a great affinity to form hydrogen bonding with each other, resulting in a strong filler-filler interaction (Chen et al., 2005; Jesionowski and Kkrysztafkiewicz, 2001; Jiang et al., 2007). This can be prevented by the aid of coupling agents, thereby modifying the hydrophilic nature of silica surface. Such a surface modification not only improves the wettability of silica in organic media, but also functionalises the particle to interact chemically with coating media. The formation of chemical bonds between the inorganic and organic is expected to guarantee a durable interaction between the two incompatible phases. For the modification of silica surfaces, organosilanes are most commonly used (Chen et al., 2005; Sun et al., 2005).

Recently, much attention has been given to the use of these materials which are able, to some extent, to couple filler to an organic media (Jesionowski and Kkrysztafkiewicz, 2001; Jiang et al., 2007; Iijima et al., 2007; Wieczorek et al., 2004). Generally, silane coupling agents may possess two functional active groups, i.e. an alkoxy group capable of reacting with surface silanol, and an organic functionality, generally having amino, epoxy and acrylic groups in its structure. These may participate in the curing system leading to a possible strong linkage between the silica and the polymer (Jiang et al., 2007). Consequently, a silane coupling agent can function as a bridge between silica and polymer, thereby enhancing interaction between these two. Many types of silane coupling agents, varying in chemistry and reactivity are available, of which amino silanes are among those usually used for silica modification (Chen et al., 2007; Jesionowski and Kkrysztafkiewicz, 2001; Wieczorek et al., 2004).

The action of alkoxy silanes starts with hydrolysis. The rate of hydrolysis significantly depends on the pH as well as on the type of organo- and silicon-functional groups (Roberts and Bergna, 2006; Xhanthos, 2005). Different factors can affect the reaction of silica with inorganic particles, among which, the natural pH of the silane, isoelectric point of the particle, ratio of water to silane as well as the pH of the reaction media, and the method of dispersion can be considered as the more important ones (Xhanthos, 2005). At high and very low pH values, the rate of hydrolysis is higher than that of the silane natural pH, at which silanes are most stable. For example,