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Review

Advanced silica/polymer composites: Materials and applications

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ABSTRACT

Recent advance on the silica/polymer composite materials combining the unique properties of the inorganic fillers and the organic polymers have widely been achieved in academic and industrial fields. Especially nanotechnology approaches to hybrid materials gives new opportunities in the development of advanced inorganic–organic hybrid composites to improve them in the overall properties of the system and to understand the interfacial interaction and nanosized level-hybridization of organic polymers and silica fillers. In this review, the scope of "advanced silica/polymer composites: materials and applications" includes the synthesis and characterizations of the composite materials and their applications such as uptakes for organic compounds and heavy metal ions, functional coatings, bioapplications.

Contents

Introduction

Over the past few decades, organic polymer–inorganic oxide filler composites have replaced a lot of the conventional polymers in application fields. These composites show unique properties combining the advantages of the inorganic fillers like the rigidity, high thermal stability, and mechanical property with the processability, flexibility, and ductility of the organic polymers [1]. Recently, nanotechnology approaches to hybrid materials gives new opportunities in the development of advanced inorganic–organic hybrid composites. A new understanding of the hybrid properties of such composites could make a broad

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impact because they are applicable in mostly industrial fields [1,2]. A characteristic of polymer composite with the nanosized inorganic filler is a dramatic increment in interfacial area compared with traditional one. This interfacial area related closely to a volume fraction of interfacial polymer. The properties of the composites even at low loadings are significantly different from that of the bulk polymer [1]. Inorganic oxide fillers like silica and alumina can be used as building blocks in nanocomposites. There are some nanoscale inorganic building blocks including spherical silica particles, layered silicates (e.g. montmorillonite), and nanotubes. Among inorganic oxide fillers, the silica particles have received much attention due to their well-defined ordered structure, high surface area, cost-effective production, and the ease surface modification [3–6]. In the polymer composition withsilica, silica particles can improve their thermal properties and self-sustaining ability under working environmental conditions. The modification of silica particles lead to better hydrophobic interactions with the polymer and unusual unique properties when compared with unmodified hydrophilic fillers [7,8]. There are some review articles reported recently in the area of silica/polymer nanocomposites: the recent trend of transparent polymer nanocomposites with functional inorganic nanofillers by Althues et al. in 2007 [9], the broad polymer/silica nanocomposites including the preparation, characterization, properties, and applications by Zou et al. in 2008 [1], and then the sol–gel method to silica-based materials and recent applications by Ciriminna et al. in 2013 [4]. This review focuses on more recent trend in the development of silica/polymer composites: materials and applications" including the synthesis and characterizations of polymer/silica composites and their applications such as up take for organic compounds and heavy metal ions, protective coatings, and bioapplications.

Modification of silica

The silica particles, which are prepared by wet (silica gel, precipitated silica) and thermal (pyrogenic silica) routes starting from silica precursors [6], and by the extraction from plants [9–12], have lots of hydroxyl groups on the surface, the so-called silanols. Such silanols are hydrophilic and reactive sites, and furthermore can be altered into other useful functionalities. Functional groups on the surface of silica particles play a critical role in the specific properties of composite materials such as hydrophilic, hydrophobicity, chemical binding ability, etc. [7,13,14]. The modification typically involves tailoring the surface properties of oxide fillers. Nanofillers such as the spherical and porous silica particles are usually obtained by a sol–gel process [6]. Especially the nanosized inorganic particles with hydrophilic hydroxyl groups can easily adhere to each other through hydrogen bonding network leading to irregular agglomerations [15]. Therefore it is difficult to disperse the inorganic oxide fillers into the polymers very well and does not process good compatibility with organic polymer. Meanwhile the inorganic fillers can be aggregated to form a porous networked structure in the composition process and liquid polymer can be filled into the voids of inter-aggregated fillers, thereby influencing the rheology of the composite with inner void filled and affording a substantial rise in the viscosity as the loading amount of silica filler increases [15]. The best performance of polymer composites can be achieved when the silica fillers are uniformly dispersed in the polymer matrix. Preparing homogenous mixtures creates new challengeable properties of composites. Silica commodities have been produced over 1 mill. ton/year and especially spherical nanosilica for composite with synthetic rubber is most commonly used for tire treads. The modification of hydrophilic surface of silica fillers can be changed to be hydrophobic property into hydrophobic and reactive. Therefore, the efficient dispersion of nanosized silica fillers in a polymer matrix is an art in technology [16]. Generally the silanols on the surfaces of silica fillers are altered with organic functionality either physically (by physisorption) or chemically by covalent bonding [9,17] as shown in Fig. 1. The drawbacks of physisorbed modification method are thermally and solvolytically unstable due to the relatively weak hydrogen bonding or van der Waals forces interaction between two phases, sometime anchoring them to their surface [18]. Alternatively, the composition of organic polymer and silica filler can be formed by the condensation reaction in sol–gel process between the functionalized prepolymers and alkoxysilane precursors, leading to the formation of a chemical bond between the polymer and the silica filler. These covalent grafting methods are preferred to maximize an interfacial stability between the silica fillers with polymers [7,19]. There are two methods for the modification of silica fillers for composition with polymers as followings:

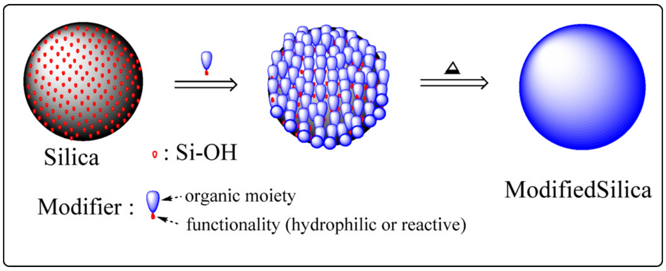

Fig. 1. Functionalization on the surface of silica particle with modifier.

Physical interaction

On the basis of physical interaction, the surface modification of silica fillers is usually performed with heteroatom containing macromolecules like surfactants adsorbing onto the silica surface [20]. The principle of such macromolecules treatment is the preferential adsorption of a polar group of a macromolecule to the surface of silica through hydrogen-bonding or electrostatic interaction [21]. A surfactant can reduce the interaction between the silica nanofillers through reducing the physical attraction and can easily be incorporated into a polymer matrix. For example, silica nanoparticles were treated with fatty acids such as stearic acid [22,23], and oleic acid [24–26] and with cationic salt like cetyltrimethylammonium bromide [27,28] to improve their dispersity and the interaction between the polymer and silica fillers [9]. Such surface-modified hydrophobic silica particles can be well-dispersed in polymer matrix. It was reported by Reculusa that the treatment of silica surface with ethylene oxide unit-containing macromonomer provides their surface with amphiphilic property due to the presence of ethylene oxide units, which are able to form hydrogen bond with hydroxyl groups existed onthe silica surface [29]. In the cases of the reactive organic functional group substituted at one of the terminal sites of modifier (containing alkoxysilyl units), there are some examples molecules containing polymerizable group such as a methacrylate group for the later polymerization reaction. The sunflower-like inorganic–organic polymer composites consisting of spherical silica and smaller conductive polypyrrole (PPy) particles were synthesized by a sol–gel reaction with silane precursors and an in situ self-assembly polymerization. When a chitosan was selected as a physically binding agent on silica surface, also they could be functioned as an adsorbent. The acetylamino group at chitosan can form hydrogen bonding with the amino unit of PPy on silica particles [30].

Chemical reaction

Generally the silylation of hydroxyl groups on silica fillers using organosilane coupling agents such as organoalkoxysilanes and