



Effect of the rigid core of the filler on the properties of melt-mixed polystyrene/core–shell particle nanocomposites



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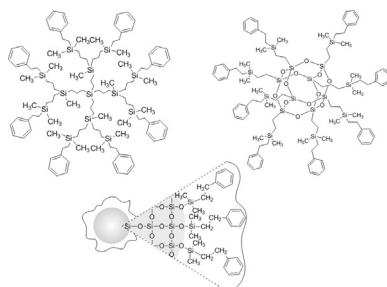
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HIGHLIGHTS

- We investigated PS mixtures with hybrid nanoparticles with different core rigidity.
- The organic surface layer of particles acts as a “solvent” in the matrix polymer.
- The rigid core of the filler is manifested as a dimensional effect in nanocomposites.

GRAPHICAL ABSTRACT



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ABSTRACT

This research investigates polystyrene mixtures with nanosized surface-modified particles, i.e., molecular silicasol, silsesquioxane, and first-generation carbosilane dendrimer. Three types of similarly sized particles with the same type of surface layer possess different chemical structures and rigidities of the cores. The latter is defined not by the numerical value of the elastic modulus but is based on the concept of molecular mobility of the chemical bonds that form the core. The phase and rheological behaviour as well as the relaxation and dielectric properties of the systems were investigated. The viscosity and the glass transition temperature of the systems decrease with increasing filler content but do not depend on the core rigidity of the particles. However, the molecular structure of the core of a hybrid nanoparticle defines both its own elastic modulus and the elastic modulus of the whole composite as well as affects the rate and activation energy of the segmental motion in the polymer. The characteristics of the composite depend on the core rigidity of the nanoparticles if the correlation radius of the physical characteristic is comparable to or less than the nanoparticle radius. The organic surface layer of nanoparticles serves both as a compatibilizer of the polymer-nanoparticle system and as a peculiar type of a “solvent” in the polymer matrix.

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1. Introduction

Polymer nanocomposites are advanced materials that can be

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used in the development of new devices and functional materials for various applications. Applied and fundamental interest in these materials is spurred by the possibility of implementing new properties and improving the performance of polymers via the introduction of small amount of nanosized filler (such as optical, mechanical, electrical, magnetic, rheological, gas-barrier and flame-retardant properties) [1–4]. Wide industrial use of nanocomposites is limited by problems that occur in mixing of nanosized particles with polymer; in particular, particle aggregation and uneven distribution in the polymer matrix and the need for special methods and additional equipment [4–6]. Currently, experiments have proven that nanoparticle aggregation essentially decreases the effectiveness of their introduction and quite often makes it impossible to obtain composites with the desired properties [4,5,7]. Development of common approaches for solving this problem would be a crucial step in the transition from an empirical to a science-based approach to preparation of nanocomposites with given properties. One of the options for solving this problem is the use of “core–shell”-type organo-inorganic hybrid nanoparticles as a filler [8–12]. With good affinity for the matrix polymer, this material prevents aggregation of the filler and increases the compatibility between particles and the matrix until their mutual dissolution.

Currently, it is difficult to predict resulting material properties and the role of nanoparticles in material structure and behaviour because approaches and models previously developed for description and forecasting of the properties of composites containing microparticles appeared to be ineffective when applied to nanocomposites [13–15]. Although the factors that determine the properties of microparticle-filled systems are the volume fraction, shape and size of microparticles, filler–matrix interaction level, and structure of polymer–particle interface layer, with the transition to nanosized fillers, the contribution of each factor becomes less obvious, and the criteria for optimisation of nanocomposite properties are not easy to formulate. This problem is primarily related to qualitative changes in the relative sizes of macromolecules and filler particles, the steep increase in the contact surface, and the decrease in the thickness of the polymer layer between particles. Consequently, in the presence of nanosized fillers, the molecular dynamics of macromolecules are altered, and the relaxation, rheological, and mechanical properties of composite are largely determined by the degree of polymer chain “perturbation” caused by the presence of nanoparticles [8,9,15–22]. Apparently, the polymer chain mobility near a nanosized inclusion surface considerably depends on the notably large free energy of the nanoparticles with high surface area, which predetermines the adsorption interaction of macromolecules with the dispersed phase surface on which is imposed the specific interaction between the macromolecule functional groups and nanoparticle surfaces (chemisorption) [3,8,16,18,20–24]. Therefore, the surface layer of a hybrid nanoparticle affects the polymer matrix conformations, and particularly, the glass transition temperature of the nanocomposite [25].

Analytical approaches and computer modelling of the molecular dynamics of polymer nanocomposites use simplified models of polymer chain – nanoparticle surface interactions in which the nanoparticle is considered as a rigid inclusion [16,18–20,26]. In terms of microcomposites, the elastic modulus of a particle is assumed to be essentially greater than that of a polymer matrix. In this approximation, the nanoparticle properties (i.e., mobility of the chemical bond and structural fragments), which are substantially lower than those of polymer, can be neglected.

The dependence of the mechanical and relaxation properties of nanocomposites on the type of nanoparticles introduced into the polymer has been experimentally determined in previous work

[27,28]. However, the literature data obtained in research on various systems do not make it possible to access the effect of the nanoparticle inner structure and its surface layer on composite properties in general. Therefore, proper model systems are required to solve this problem.

In the current research an impact of the core rigidity of hybrid nanosized particles on the properties of nanocomposites based on polystyrene (PS) is studied. The key point of the study is to investigate what properties of the nanocomposite and why depend on the particle morphology.

Macromolecular nanoparticles [29] were used as model fillers. Three types of hybrid nanoparticles were chosen with similar sizes but with different architectures. The first type is molecular silicasol, i.e., a solvent-borne silica with [dimethyl(2-phenylethyl)silyl] groups on the surface layer [29–31]. In these hybrid nanoparticles, a core based on hyperbranched polyethoxysiloxane acts as filler, and an organic shell minimises the “rejection” of nano-inclusions by the polymer matrix, and by PS in particular, thus reducing the potential filler aggregation. The second type is octasilsesquioxane with grafted [dimethyl(2-phenylethyl)silyl]ethyl groups. This particle core, which is nearly a perfect “cube” in shape, cannot practically change its shape or deform due to the low mobility of the chemical bonds [32,33]. The third type is a first generation carbosilane dendrimer with [dimethyl(2-phenylethyl)silyl]propyl groups in the external layer. According to existing concepts, dendrimers with acyclic structures can be described as soft elastic spheres [9,29,34,35]. Thus, three types of similarly sized particles with the same type of surface layer possess different chemical structures and rigidities of the cores. The latter is defined not by the numerical value of the elastic modulus but is based on the concept of molecular mobility of the chemical bonds that form the core. The phase behaviour as well as rheological, relaxation and dielectric properties of the composites prepared from PS and macromolecular nanoparticles are investigated systematically in the current study.

2. Experimental section

2.1. Materials

Macromolecular objects representing hybrid particles with a “core–shell” structure were selected as research objects. The cores consist of silicasol, first-generation carbosilane dendrimers, or octasilsesquioxane. The external surface layer of these particles is formed by [dimethyl(2-phenylethyl)silyl] (silicasol), [dimethyl(2-phenylethyl)silyl]ethyl (silsesquioxane), or [dimethyl(2-phenylethyl)silyl]propyl (dendrimer) end groups.

2.1.1. Synthesis of nanoparticles

A general scheme for synthesis of hybrid nanoparticles is shown in Fig. 1.

All the manipulations were carried out under an atmosphere of argon. Toluene was dried and distilled over CaH₂, tetrahydrofuran (THF) – over LiAlH₄. Dimethylchlorosilane (DMCS) was distilled prior to use. Styrene was distilled under reduced pressure in the presence of an inhibitor (2,4-dimethyl-6-tert-butylphenol). Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution in xylene (2.1–2.4%) was used as a catalyst (PC072 zero-valency platinum Karstedt catalyst, Aldrich).

Synthesis of the first-generation poly(allyl)carbosilane dendrimer and octavinyl octasilsesquioxane was performed according to the technique published elsewhere [36–38].

[Dimethyl(2-phenylethyl)silyl]ethyl octasilsesquioxane was obtained by hydrosilylation of octavinyl octasilsesquioxane. Dimethyl(2-phenylethyl)silane (2.9 g, 17.4 mmol) and platinum

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