



Mechanical reinforcement in model elastomer nanocomposites with tuned microstructure and interactions

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ARTICLE INFO

Article history:

Received 27 October 2012

Received in revised form

27 December 2012

Accepted 5 January 2013

Available online 17 January 2013

Keywords:

Nanocomposite

Filler dispersion

Elastomer

ABSTRACT

Nanocomposites made of a crosslinked polydimethylsiloxane matrix filled with silica beads were prepared by solvent-casting. The nanoparticle dispersion was tuned by changing the solvent. Three types of surface properties are investigated for the nanoparticles through surface grafting. Hydrophilic (unmodified), hydrophobic or carboxylic acid functionalized (allowing particle-PDMS covalent bonding) nanoparticles were thus added to the PDMS with various degree of dispersion (isolated, aggregated or percolating). Nanocomposite microstructures were analyzed by SAXS and TEM while DMA experiments highlighted the viscoelastic behavior and the mechanical reinforcement in the rubbery state. At low silica loading ($\phi_{\text{SiO}_2} < 10$ vol.%) the mechanical properties were found to be independent on the microstructure and the interactions. At higher ϕ_{SiO_2} , two types of behavior are observed when increasing ϕ_{SiO_2} . For strong interactions, a percolation phenomenon occurred, leading to a high reinforcement level (driven by interparticle contacts and aggregate morphology) whereas a simple linear modulus augmentation is observed, independently of the aggregation state, for softer interactions.

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1. Introduction

Because of their outstanding mechanical and physical properties, when compared to pure polymers or conventional microcomposites, elastomeric nanocomposites are widely used for industrial applications (e.g. car tires or food packing) and are still of interest for fundamental studies. The improvement of their mechanical properties is known to be intimately related to three main parameters: the intrinsic mechanical properties, shape and size of the fillers; the microstructure (dispersion of the fillers within the matrix); and the strength of the interactions involved at the filler–matrix and filler–filler interfaces [1–6]. Several recent studies focused on the preparation of model nanocomposites and the investigation of the role played by these microstructure and interfacial interactions on the mechanical behavior.

From a general point of view, a more efficient mechanical reinforcement (increase in Young's modulus) is obtained when a rigid percolating filler network (involving stiff interparticle contacts) is created within the soft polymer matrix [7–13]. By contrast, when interparticle contacts are weakened or hindered, either by changing the nanoparticle surface [14–16] or by processing conditions [7–9],

a lower reinforcement level is reached. Nevertheless, modifying particle–particle interactions usually induces a change in dispersion and implies different polymer–particle interfaces; thus, limiting the interpretations.

Several studies have recently developed strategies to modulate the nanoparticle dispersion without changing the interfacial properties. Sen et al. [17] obtained various states of dispersion of silica beads in polystyrene by tuning the quality of the solvent and the evaporation rate. The kinetic of the solvent evaporation appeared to affect the interface structure since no T_g variation was observed for the polystyrene filled with highly dispersed nanoparticles, whereas T_g decreased for an agglomerated structure. Oberdisse et al. [11] investigated the influence of the aggregation state on the mechanical reinforcement in latex-silica nanocomposites. The aggregation number, N_{agg} , in the material was driven by the pH of the pristine suspension. For unmodified silica nanoparticle, as N_{agg} increases, a higher reinforcement was found and a more pronounced exponential increase with the silica content was observed. An analytical modeling approach which accounts for the occluded polymer volume inside the aggregates and their compacity was proposed. On the other hand, polystyrene-grafted nanoparticles lead to significantly lower N_{agg} values and a weaker reinforcement factor [11,18]. In 2002, Berriot et al. [19–21] initiated a wide study dealing with the microstructural (by SANS, small angle neutron scattering), mechanical and dynamical (by

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solid state nuclear magnetic resonance, NMR) properties of nanocomposites prepared from grafted silica nanoparticles and a poly(ethyl acrylate) (PEA) matrix. They mainly focused their discussions on two types of systems that consist either in well-dispersed nanoparticles covalently linked with the PEA chains (where only few small fractal aggregates were observed by SANS) or in aggregated hydrophobic nanoparticles (with large agglomerates). In their case, the in-situ polymerization has been shown to induce aggregation because of depletion forces; this phenomenon being more pronounced when no covalent bond is created between the nanoparticles and the matrix. Thus, the only interparticle attractive interactions result in this case from steric effects in the materials filled with hydrophobic nanoparticles. By looking at the temperature dependence of the reinforcement, by direct NMR analysis or, later on, by DSC [22], they proved the presence of a glass transition gradient in the vicinity of the silica particles. They analyzed the influence of this glassy layer on the mechanical behavior of the filled elastomers and showed that it depends both on the layer thickness (which increases with the strength of the interfacial interactions [19]) and on the spatial dispersion of the particles.

Thereby, in nanocomposites, the microstructure and filler–filler or filler–matrix interactions involve interdependent parameters very difficult to de-correlate and to discuss separately. The understanding of the mechanical reinforcement mechanisms in nanocomposite therefore remains an open question.

Among other materials, nanocomposites made of a crosslinked polydimethylsiloxane (PDMS) matrix reinforced with silica beads are commercially relevant systems, very convenient to investigate these parameters [1,4,23–25]. In previous studies, silica nanoparticles have been introduced in PDMS in a variety of ways: in-situ generation via a “sol–gel” method [4,25,26], blending [23,25] or solvent-casting [24]. Several types of microstructures were thus obtained: well-dispersed nanoparticles [4,26], aggregates or percolating network [23,24]. Furthermore, surface properties can be tuned by grafting functional groups [27–31] or polymer chains [32,33] onto the particle surface. Strong PDMS–ungrafted silica interactions are ensured through the hydrogen bonds between the silanols on the silica surface and the oxygen atoms of the PDMS chains. Aranguren et al. [28] showed that a maximum amount of adsorbed chains is obtained for untreated silica particles. From broad-band dielectric spectroscopy Kirst et al. [34] assumed the presence of a reduced mobility layer (1–2.5 nm thick, depending on the PDMS molecular weight) on neat nanoparticles unlike hydrophobized ones. Later on, Litvinov et al. [33] confirmed by NMR spectroscopy and DSC that the grafted PDMS layer consists in about four immobilized chain units at the PDMS–silica interface and mobile chains outside the interface.

The present study aims at preparing, by solvent-casting, dedicated model PDMS–silica nanocomposites with controlled microstructure and interfacial properties. We therefore considered a wide range of systems involving three types of PDMS/nanoparticle and interparticle interactions: stiff hydrogen bonding, weak adsorption or covalent linking, with two states of dispersion. To this end, from the same batch of silica beads, three types of surface properties are investigated: hydrophilic unmodified nanoparticles; grafted with hydrophobic alkyl groups or PDMS–silica covalent linking. Notably, the use of ungrafted nanoparticles will allow creating stiff interparticle contacts through hydrogen bonding whereas soft interactions will be involved between hydrophobic nanoparticles. Then, we propose to tune the nanoparticle dispersion in the PDMS matrix by changing the solvent employed for the material processing.

We finally highlight the influence of both the dispersion and the interactions by discussing the viscoelastic behavior and the mechanical reinforcement in the rubbery state for all materials from

dynamic mechanical analysis. In particular, we will address the question whether the concept of a T_g gradient at the nanoparticle interfaces proposed by Berriot et al. [19–21] and Papon et al. [22] is generalizable to all types of polymeric nanocomposites even very far from the T_g .

2. Experimental section

2.1. Materials

Succinic anhydride, aminopropyl-trimethoxysilane (APTS), octyltrimethoxysilane (OTS), dibutyltin oxide and a 35 wt% aqueous suspension of silica nanoparticles were purchased from Sigma–Aldrich and used as received. α,ω -Dihydroxy polydimethylsiloxane (PDMS–OH: $M_w = 1000 \text{ g mol}^{-1}$ PDI = 1.35) and tris(2-methyl-1-aziridinyl)phosphine oxide (MAPO) were purchased from ABCR and used as received. The different solvents were analytical grade.

2.2. Nanoparticle functionalization

In order to graft organic groups on silica nanoparticles, the aqueous initial suspension of non-functionalized nanoparticles (NF NPs) was diluted in ethanol up to a concentration of 5 wt%. In a first batch (H NPs), octyl groups were grafted following procedures already described [29,30]. 4 mL of OTS was added dropwise to 400 g of the ethanolic silica suspension (silane to silica ratio of 0.18) and the mixture was stirred for 18 h before dialysis against ethanol (molecular weight cut-off 3500). 10 dialysis were necessary to remove all the OTS excess. In a second batch (HA NPs), carboxylic acid functions were additionally grafted on the H NPs previously obtained. The grafting agent was firstly prepared by reaction of succinic anhydride with APTS [27,31]. 0.4 g of APTS was solubilized into 15 mL of anhydrous dioxane under N_2 . Then, one equivalent of succinic anhydride (0.25 g) was added to the solution and the mixture was stirred for 4 h. The mixture was slightly heated ($\sim 35^\circ\text{C}$) up to the reaction beginning. After elimination of dioxane by rotary evaporation at room temperature, 0.27 g of the obtained grafting agent was dissolved into 5 mL of ethanol and added dropwise to 200 g of H NPs suspension with a silane to silica weight ratio of 0.03. The mixture was stirred for 18 h before 10 dialysis against ethanol.

The reaction scheme of the nanoparticle functionalization is given Fig. 1.

2.3. Nanocomposite processing

PDMS–OH was firstly functionalized with succinic anhydride in order to obtain a telechelic α,ω -dicarboxylic acid polydimethylsiloxane PDMS (PDMS–COOH). A solvent-free reaction was performed by adding under argon two equivalents of succinic anhydride (4.2 g) into 10 g of PDMS–OH with 0.02 g of dibutyltin oxide as a catalyst [35]. The mixture was stirred for 24 h at 110°C , dissolved into pentane and filtrated in order to eliminate the excess of succinic anhydride. After pentane elimination, the obtained PDMS–COOH was characterized by ^1H NMR. Analysis of the spectrum (Fig. S1 in SI) indicates a complete reaction without changing in the average molecular weight. We note that this processing way was chosen in the goal of comparing, in an upcoming study under preparation, chemical with physical crosslinking (through electrostatic interactions by exchanging the proton from the COOH groups with different metallic cations).

For the nanocomposite processing, two different solvents were used: dimethylacetamide (DMAc) and ethanol (EtOH). The different EtOH nanoparticle suspensions were obtained as previously described, and the DMAc nanoparticle suspensions were obtained

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