



Keys to enhancing mechanical properties of silica nanoparticle composites hydrogels: The role of network structure and interfacial interactions



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ABSTRACT

Polymer nanocomposites have attracted an increasing interest by adding of trace amount of nano-scale fillers. The mechanical reinforcement of silica nanoparticle/poly(acrylamide) composites, which results in a homogeneous dispersion of small primary clusters in the matrix, is investigated based on a facile synthetic platform, and the structure–property relationship of the network structure is interpreted in this paper. The high grafting efficiency of polymer chains on silica nanoparticles surface pronouncedly confines the segmental motion of the chains, leading to a 6-time increase in toughness. The cluster network structure is observed by transmission electronic microscopy and mechanical response of the nanocomposites is studied by both small (oscillatory shear) and large (uniaxial tension) deformations as a function of silica particle volume fractions to demystify the effect of constrained region on the elastic properties. A constrained region model for nanocomposites is tentatively proposed and the result indicates that modulus enhancement of the nanocomposites is found to have good correlation with the volume of constrained region. This research reveals that the network structure–property relations relate to two main reinforcement effects, the filler network (filler–polymer matrix interaction) and filler mobility (energy dissipation), suggesting a need to reconsider the filler–polymer interaction and region of constraint polymer in forming a indirect “bridge network” among neighboring clusters.

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1. Introduction

The incorporation of nanoparticles into a variety of polymer matrix to fabricate nanocomposites has been broadly applied in an attempt to improve the physical, mechanical, and thermal properties [1–4]. While some fundamental progresses have been achieved, using nanoparticles is still an open challenge from both the industrial and academic points of view, and the resulting nanocomposites have yet to realize their full potential [5–7]. Among many inorganic nano-scale building blocks, including nanotubes [8], layered silicates (montmorillonite) [9], nanoparticles of metals (Au, Ag) [10,11], metal oxide (TiO₂) [12] and semiconductors (CdSe, ZnS) [13,14], silica nanoparticles (hereafter referred to as SNPs), with their nanometer size, high surface area, can function as structure and morphology directors to introduce efficient energy dissipation mechanism, leading to improved mechanical properties in various nanocomposites [15].

It is well documented that most rigid fillers could produce a remarkable increase in the modulus of composites compared to that of pristine polymer [16,17]. Nevertheless, this is always associated with a remarkable decline in the flexibility. Thus, an important issue for understanding the fundamental network structure and chain dynamics is to design nanocomposite structures and to predict macroscopic properties [2–4]. In the SNP loaded polymeric systems, the restrictive environment of the polymer chains among filler galleries dominates the molecular relaxation and mobility. The mechanical properties enhancement is partially attributed to the volume of constrained polymer chains at the well-dispersed filler surface, morphological changes induced by the SNP as well as interactions between filler and polymer matrix, which collectively attribute to an efficient energy dissipation mechanism under deformation [18]. For filled polymer nanocomposites, break initially occurs through the formation and propagation of crack, and crazing is a dominate deformation behavior, subsequently lead to the formation of cracks and collapse of materials [18]. Besides, the polymer nanocomposites fracture behavior is largely dependent on the type of polymer, size and morphology of filler, and

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interfacial interaction [19]. Thus, it is imperative to explore the fracture behavior of nanocomposites that possess attractive interfacial interactions and entanglement.

Although considerable work has been performed on SNP filled systems, a fundamental rationale describing the origin of such enhanced properties remains elusive. Therefore, this paper serves to demystify the keys of mechanical reinforcement, based on a facile silica nanoparticle/poly(acrylamide) (SNP/PAM) nanocomposites platform. The first one is linked to the filler network structure where in a further range of filler concentration the particles can form an interpenetrated network (percolation model). The second contribution is attributed to the interface between the filler and polymer matrix. Based on the classic rubber confinement theory, the polymer dynamics is found to be modified in the area that close to filler (termed as constrained layer), and the modulus enhancement of the nanocomposites is correlated to the volume of constrained region. Besides, the detailed fracture behavior during deformation is also examined. Finally, we would interpret the relationship between the network structures at the microscopic scale with the mechanical behavior of the nanocomposites at the macroscopic scale. The results indicate that the concept of nanoparticles mobility is still justified for reinforcing non-layered nanocomposite if the preconditions of good dispersion and favorable interactions between filler and matrix are guaranteed. Substantially, this system can be used as a model to interpret the underlying mechanism of nanocomposite reinforcement, and the obtained guidelines here are expected to shed some lights toward high mechanical performance in synthetic nanocomposites.

2. Experimental

2.1. Sample preparation

The colloidal solution containing silica nanoparticles (SNPs) was obtained by Stöber procedure through hydrolysis and condensation of tetraethyl orthosilicate in diluted alkaline solution [20]. In this solution, the native particles with an average radius of 30 nm determined from TEM micrographs, were electrostatically dispersed. The organosilane (γ -methacryloxypropyl trimethoxy silane, A174) was applied to graft polymer chains to SNP surface by “grafting-from” method [21] (Fig. 1(a)). Then a concentrated aqueous solution of acrylamide (AM, 20% w/v) was well mixed with a solution of SNP-A174 at various fractions, ranging from 0.022% to 0.22% w/v (corresponding to volume fraction of 0.01–0.1% v/v), while maintaining the matrix composition. The mixtures containing SNP-A174, acrylamide (AM), photo initiator (2, 2'-diethoxyacetophenone, 0.5% w/v) and water (25 mL) were stirred using a vortex mixer for 30 min, poured into appropriate molds, and subjected to UV radiation (365 nm) for 45 min (Fig. 1(b)). For all the samples, the yield was above 98% and the amount of extracted polymer chains analyzing by size exclusion chromatography (SEC), if observable, was less than 1 wt% of the total organic content. The disk-like samples (2.5 cm in diameter \times 0.1 cm in height) for the plate-plate oscillatory shear measurement, and rectangular sample (5 mm in height \times 40 mm in length \times 8 mm in width) for uniaxial deformation were prepared, respectively.

2.2. Characterization

Oscillatory shear tests, corresponding to low deformation levels (0.1%), were performed with a TA AR2000 rheometer equipped with a Peltier device for temperature control, in an angular frequency range from 0.1 to 100 Hz using 25 mm diameter parallel plates. Typically, three samples were analyzed and the repeatability of the measurements of the storage moduli and loss moduli

were usually within a range of 5%. Microscopic observation via transmission electron microscopy (TEM) analyses was performed using a JEM-1010 (JEOL) at an acceleration voltage of 80 kV. The thin samples were prepared using a microtome, ultrasonicated for 10 min and collected on copper grids for TEM observation. Fourier transform infrared (FTIR) spectroscopy was performed on an infrared spectrophotometer (Nicolet iN10-MX, Thermo Scientific). The spectra were obtained in an optical range of 600–4000 cm^{-1} using an average of 32 scans and a resolution of 4 cm^{-1} . Mechanical tests in tensile mode were conducted with a Zwick Z005 Materials Tester at 25 °C, imposing a cross speed of 30 mm/min. Raw data were recorded as force versus displacement, and they were converted to stress versus strain with respect to the initial sample dimensions (5 \times 8 mm^2). Five specimens for each batch were measured. Thermal gravimetric analysis (TGA) was carried out using a thermogravimetric analyzer (DTG-60, Shimadzu). The samples were ground into powder and about 5 mg of the powder was placed in an aluminum pan and heated from 25 to 550 °C at a rate of 10 °C/min under nitrogen atmosphere.

3. Results

3.1. Functionalization and morphology of silica nanoparticle/polymer composites

The covalent bonding of silylation and grafting efficiency were examined by FTIR and TGA spectroscopy. The FTIR spectra of SiO_2 , SiO_2 -A174 intermediate and PAM grafted SiO_2 are shown in Fig. 1(c). In comparison with pristine SiO_2 , where Si-OH vibration (3450 cm^{-1}) and Si-O-Si stretching (990 cm^{-1}), the SiO_2 -A174 shows a new band at 1630 cm^{-1} that can be assigned to the C=C stretching groups, implying A174 was grafted onto the surface of SiO_2 via silane bridges. After grafting with PAM macroradical, the adsorption peak of 1730 cm^{-1} for C=O stretching groups decreases, and primary amide (3340 and 1620 cm^{-1} for primary -NH₂ and 1642 cm^{-1} for C=O) and aliphatic acrylate backbone (2930 and 1450 cm^{-1} for -CH₂) of PAM are observed. The chemical reaction and the properties of A174 monolayer on silica fillers surface has been well described in the literature [22,23], and a mass loss of 8% (Fig. 1(d)) was found according to thermal gravimetric analysis which corresponded to grafting density of A174 onto the SNP amounts ca. 5 groups/ nm^2 .

Obtaining a uniform dispersion of nanoparticles in polymer matrix is a critical prerequisite to examine the mechanical properties of nanocomposites [3,4]. Based on the controlled synthesis and chemical treatment of fillers, uniform size and spatial distribution of SNPs in PAM matrix are achieved, and the individual particles are observed distinctly without significant aggregation (Fig. 2). This homogeneous dispersion of filler particles excludes the effect of aggregation on fracture properties of polymer nanocomposites. In fact, compared to organo-clay that can be intercalated or exfoliated by matrix polymer during compounding [24,25], the non-layered nanoparticles are easy to gather together due to their large surface area, leading to hard to be broken by usual mechanical treatment [5]. Therefore, weakening the interaction among nanofillers and enhancing the interaction between nanofiller and matrix are vital for providing certain nanoparticle mobility via network arrangements.

3.2. Stress–strain curves

The evolution of stress (σ) as a function of the elongation ratio (λ) for SNP volume fraction ranging from 0.02% to 0.1% v/v is shown in Fig. 3. There is a 6-time increase in the toughness of the nanocomposites as determined by area under the stress–strain curve.

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