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Reinforcement in nano-filled PAA hydrogels

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ABSTRACT

Presented experimental results bring an insight into the long-standing problem of the primary reinforcing mechanism in rubbery polymers filled with fine fillers. In this project the effect of silica nanoparticles on the linear viscoelastic response of model polyacrylamide (PAA) hydrogel systems was examined. Using water as a dispersion medium allowed for separating the effect of filler–filler and the filler–polymer interaction. Rheological data suggest that the primary mechanism of the nano-reinforcement in filled PAA hydrogels comes primarily from confinement to the PAA chains and bias of their conformational states in respect to their reference states. In hydrogels with very low concentration of PAA, the transition between the filler–filler and filler-induced conformational restriction mechanism of reinforcement was captured.

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1. Introduction

In spite of the fact that silica and carbon black nanoparticles have been used as reinforcing fillers in the rubber industry for many decades, the true physical mechanism of the linear elastic reinforcement still remains greatly controversial [1]. In principle, three major theories have been developed by scientists to explain this peculiar phenomenon. One of these theories tries to explain the filler-induced stiffening as a segmental immobilization phenomenon. Such a theoretical concept was based on the results obtained mainly from the pulsed NMR measurements [2] and assumes that the filler–polymer interaction causes significant slowing down of the segmental dynamics and creates a stiff glass-like interphase layer in close vicinity of the particle surfaces [3]. The engineering community often operates with the theory of particle agglomeration. This approach is based on the microscopy and the small-angle scattering experiments indicating that the filler nanoparticles form random assemblies with hierarchical structure percolating through the polymer matrix [4]. Such a percolated filler network is than assumed to possess stiffness sufficiently high to reinforce the rubbery polymer [5]. The third approach is based on the assumption that the filler nanoparticles interact with chains of the polymer matrix and such an interaction induces conformational restrictions to them [6]. In other words, the nano-filler particles cause stiff confinement to the chain molecules and bring

about retardation of their orientational dynamics. In spite of the fact that the first and the third concept are based on the assumption that the chains are immobilized, there are clear differences between them. The first concept assumes that the chains in the surface vicinity are not able to populate their conformational states with equilibrium probability. On the other hand, the approach provided by Sternstein et al. [1,6] works with the premise that the portion of such segments is negligible and the immobilization is on larger scale. In fact, the nanoparticles cause a confinement which is analogical to the tube constraint. However, large portion of the local interparticle constraints is assumed to be significantly shorter than the natural tube diameter. The reinforcement is then caused primarily by the constrained chain bridges connecting the filler nanoparticles. These bridging chains display bias in respect to their configurational reference states and, hence, are significantly stiffer [6].

In general terms, polymer chains in thermal equilibrium can adopt any orientation with equal probability. Thus the mean fractional extension $\langle \mathbf{r}/Nb \rangle = 0$ (where \mathbf{r} is the chain end-to-end vector and Nb represents the length of a fully extended chain). Fully equilibrated polymer melts or solutions do not possess elasticity due to the fully relaxed $\langle \mathbf{r}/Nb \rangle$ term [9]. This is satisfied when extremely long times or low frequencies of the perturbation field are used. Obviously, polymer melts composed of long chain molecules can easily be found in a state, where the mean fractional extension of the chain segments $\langle \mathbf{r}/Nb \rangle \neq 0$ due to various constraints imposed on them. The constraint can be caused by the covalent x-links, by the molecular uncrossability in a system of long chains, or by the specific interaction with filler surfaces [10]. In the last two cases, the chain fractional extension term relaxes gradually

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to zero due to the chain Brownian motion and, therefore, elasticity is considered to be a result of non-ergodic conditions.

In this project, the attention was focused on polymer hydrogels, where the topological interaction between chains was minimized. Hydrogels usually contain from 70 to 95wt% water and the rest is a swelled polymer network. Chain strands are in such a case conformationally homogeneous and the elastic free energy of a hydrogel is driven primarily by the configurational entropy term. In the case of presented investigation, a lightly x-linked polyacrylamide (PAA) network was used as a model polymer system, where water is an isotropic dispersion medium. Note that the water molecules and their clusters represent highly mobile entities causing strong plasticization of the PAA chains and, hence, the formation of a filler-induced glassy interphase layer in the nano-filled PAA hydrogel is not considered a relevant mechanism. Incorporating randomly agglomerated silica nanoparticles into the PAA network inevitably leads to the interaction of PAA chain strands with the silica surfaces. The sites of polymer adsorption behave as temporary x-links and cause confinement to the chains. This phenomenon is qualitatively distinct from the chemical x-links in the PAA network. While the chemical x-links can fluctuate in space, the adsorption sites have practically fixed positions and, hence, create a stiff confinement to the PAA chain strands. The hydrogel structure is schematically illustrated in Fig. 1. It is worth noting that the illustration in Fig. 1 is only an idealized scheme. As has been documented, based on the FTIR measurements, the interaction between SiO₂ and PAA chains takes place *via* H-bonding. This brings about significant stretching of the Si–O bonds in the substrate and the C=O bonds in PAA matrix [7]. One can then expect that this specific interaction can cause local conformational anisotropy at adsorption sites. Moreover, it is well known that even the silica or alumina surfaces possess sites of varying activity [8]. This work is focused primarily on studying the effect of non-local topological confinement on rheological response of PAA hydrogels.

2. Experimental

Chemicals: acrylamide – Alfa Aesar (USA), 2 wt% water solution of N,N'-methylenebisacrylamide – G-Biosciences (USA), ammonium persulfate – J. T. Baker (USA), and reverse osmotic (RO) water deoxygenized by the purging nitrogen prior any use, fumed silica with specific surface area $A_s = 390 \text{ m}^2/\text{g}$ and mean size of primary particles 7 nm – Cab-o-sil (USA). **Preparation of PAA hydrogels:** 10 g of AA + 0.01 g of APS (0.1 wt%) was dissolved in RO water so that 10 and 5 wt% solutions were obtained. Such solutions were then used for synthesis of hydrogel networks in a rheometer. N,N'-methylenebisacrylamide (Bis-AA) in form of 2 wt% solution was added into the prepared solutions of acrylamide using micropipette in a way that the molar ratios n_{AA}/n_{Bis-AA} were 10^3 , 10^4 , 10^5 . Corresponding concentrations of x-linker molecules v_x were then calculated.

Nano-filled samples were mixed with appropriate amount of fumed silica to achieve volume fractions $\phi = 0.002$, 0.004, and 0.006 and ultrasonicated for 5 min prior to the x-linking step. Such solutions were put on the Peltier plate in rheometer AR 2000 (TA Instruments) and appropriate truncation gap between the bottom plate and the upper cone was set up. A solvent trap was used to minimize the water evaporation during synthesis and consequent frequency sweep measurements. The PAA hydrogels were synthesized in-situ isothermally at 60 °C for 60 min through the free radical polymerization process. **Viscoelastic measurements:** Prior to each PAA network synthesis, a frequency sweep in the frequency range from 10^{-2} – 10^2 Hz and temperature 20 °C was carried out to obtain response of the silica nanoparticle network. In this measurement, a shear strain amplitude $\gamma = 0.005$ was used. This corresponded to the linear regime for all silica concentrations used in this work. The frequency sweep test was followed by the 1 h isothermal synthesis step at 60 °C. After cooling to 20 °C, another frequency sweep was carried out using a shear strain amplitude $\gamma = 0.0001$. This corresponded to the linear viscoelastic response in all investigated PAA hydrogel systems. Each viscoelastic measurement was repeated at least three times.

3. Results and discussion

In Fig. 2, a plot of the frequency dependent shear storage modulus is presented for the neat PAA hydrogel with polymer content $w_{PAA} = 5 \text{ wt\%}$, corresponding nano-filled hydrogel with filler volume fraction $\phi = 0.02$, and water-silica suspension with $\phi = 0.02$. The experimental data are supplemented with a theoretical calculation based on the Guth model, which takes into account only the micromechanical and particle size independent mechanisms of reinforcement: $G'_{composite} = G'_{matrix}(1 + 2.5\phi + 14.1\phi^2)$ [11]. The plot in Fig. 2 represents a very unique experimental result. First, the use of water as a dispersion medium allowed for measuring the shear storage modulus of nano-silica agglomerates. It is evident that such a colloidal solution exhibited a detectable shear elastic modulus with low dependence on the frequency of mechanical oscillations, which can resemble elasticity of rubbery networks. The most interesting result, however, represents the dependence measured for the nano-filled hydrogel. Note that in this particular case the synthesized PAA was more a branched polymer rather than an x-linked network, which is documented by clear terminal relaxation region (loss of elasticity in the low frequency region) in the plot in Fig. 2. On the other hand, this aspect was responsible for the observed transition from one reinforcing mechanism, operating at higher frequencies, to another, located beyond the terminal relaxation process of the neat PAA. The plot in Fig. 2 shows that the elastic response of the nano-filled PAA hydrogel was dictated by the filler network at low frequencies (at frequencies lower than the rate of the terminal relaxation

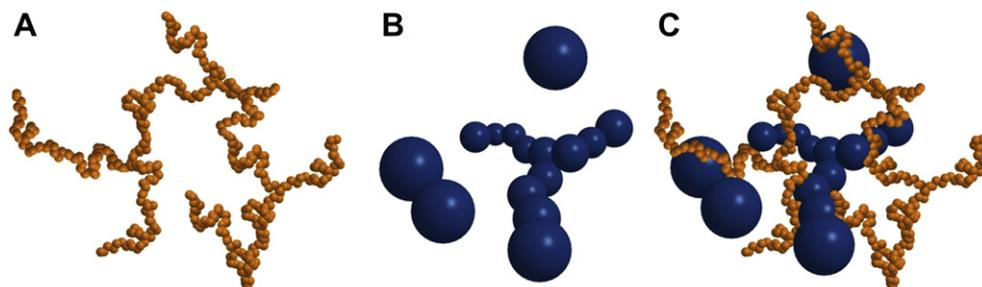


Fig. 1. A schematic illustration of model water-based systems studied in the presented investigation. (A) neat PAA hydrogel, (B) nano-filler suspension, and (C) nano-filled PAA hydrogel. Atomistic details were purposely omitted to provide a lucid illustration of differences between studied systems.

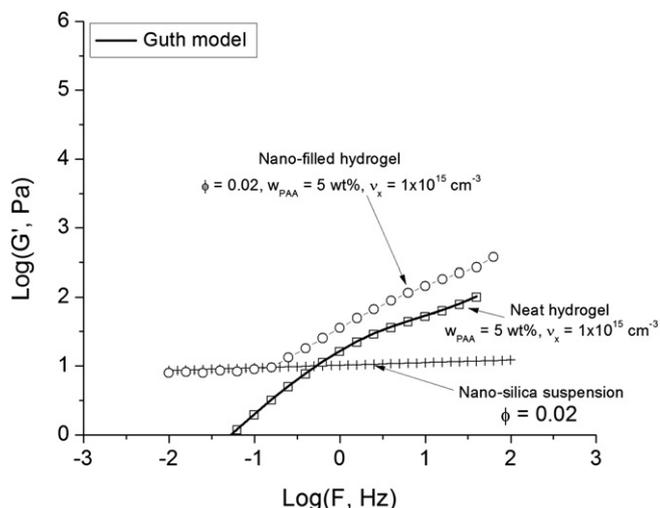


Fig. 2. Frequency dependent shear storage modulus for selected hydrogel system with $w_{PAA} = 5$ wt%. This plot illustratively depicts the transition from the immobilization to the filler network reinforcing mechanism. Neat PAA hydrogel undergoes terminal relaxation at frequencies below 1 Hz, where the elasticity gradually disappears under given conditions.

process). However, the frequency dependent shear storage modulus exhibited in the high-frequency region a behavior, which was clearly dictated by the polymer. One can also see that the nanocomposite linear elastic reinforcement was significantly higher than the micromechanical prediction and clearly uncorrelated to the response of filler agglomerates.

Corresponding experimental data for PAA hydrogel systems, $w_{PAA} = 5$ and 10 wt%, with different concentration of x-linking molecules are shown in Figs 3 and 4. One can recognize from these plots that the linear elastic response of the nano-filled hydrogel was dictated by the structure of the PAA network, not by the silica agglomerates. In other words, the linear elastic reinforcement as well as the relaxation spectrum is governed, within the particular frequency range, by the polymer itself and polymer–filler interaction, not by the filler agglomerated structure. This conclusion is in agreement with results and analysis provided recently by Sternstein et al. [1]

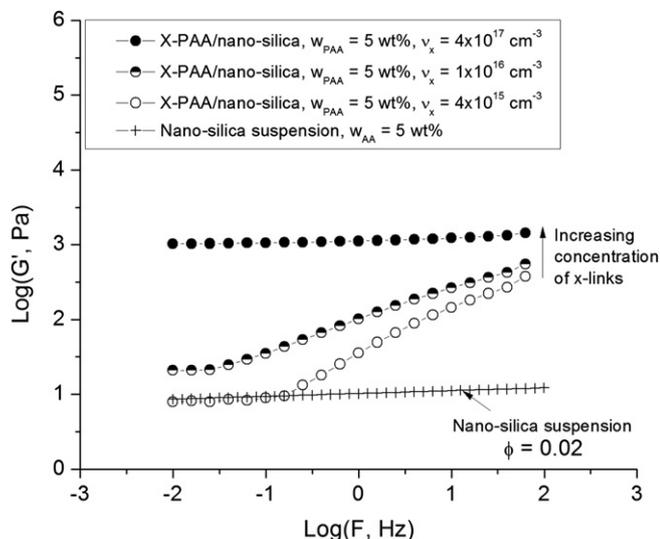


Fig. 3. Frequency dependent shear storage modulus of nano-silica suspension and corresponding PAA nanocomposite hydrogels, $w_{PAA} = 5$ wt%, with different concentration of x-links.

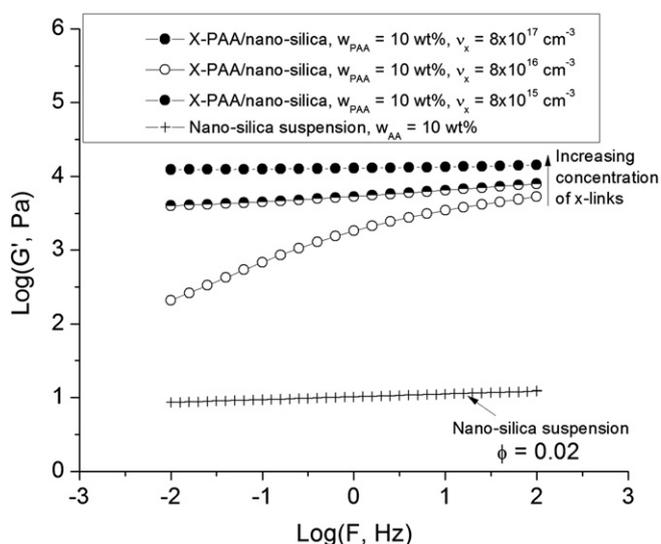


Fig. 4. Frequency dependent shear storage modulus of nano-silica suspension and corresponding PAA nanocomposite hydrogels, $w_{PAA} = 10$ wt%, with different concentration of x-links.

A closer analysis of all the measured linear viscoelastic data for systems with $w_{PAA} = 10$ wt% is shown in plots in Figs 5 and 6. First, the dependence of the linear elastic reinforcement, defined as $R = G'_{composite}/G'_{matrix}$, displays exponential behavior: $R = \exp(\phi/\psi)$ [1]. This result seems to be independent of the concentration of x-linking molecules, ν_x . The reinforcement efficiency was calculated according to Sternstein et al. [1] as the slope of the $\ln R - \phi$ dependence in the case of PAA nanocomposite with $w_{PAA} = 10$ wt% was found to be $1/\psi = 44.6$. In the case of nano-silica filled PVAc melts, this value of $1/\psi$ was approximately between 17–29 [1]. In the PVAc melt filled with PTFE nanoparticles, $1/\psi = 3.6$ [1]. Thus, the reinforcing effectiveness is considerably higher in the dilute PAA hydrogel compared to the dense PVAc nanocomposites above T_g . This is most probably due to the fact that significantly larger relative portion of the polymer system was involved in the trapped entanglement interaction in the hydrogel system. In the dense nano-filled melts, the natural entanglement and the trapped

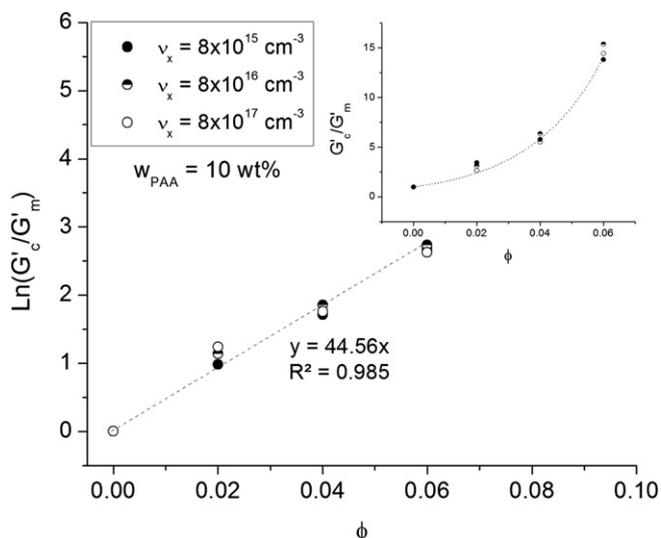


Fig. 5. Linear elastic reinforcement of nano-filled PAA hydrogel, $w_{PAA} = 10$ wt%. The inset is included to document the exponential character of the dependence.

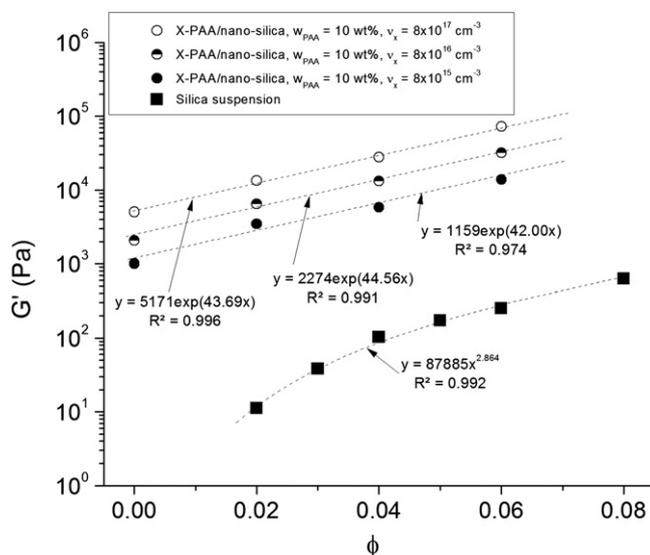


Fig. 6. Linear shear storage modulus dependence on silica nano-filler volume fraction for colloidal solution of silica in water containing 10 wt% of acrylamide monomer and corresponding nano-filled PAA hydrogel with $w_{\text{PAA}} = 10$ wt%.

entanglement constraint are simultaneously at work and, hence, the reinforcing effectiveness is correspondingly lower. Moreover, one can see in Fig. 6 that the PAA nanocomposite G' does not display any correlation to the elastic response of the filler network.

The data presented in this contribution can be explained using neither the Guth micromechanics model [11] nor the immobilized glassy interphase layer theory [3]. The Guth model provides too low values of R [12]. The filler network theory and the immobilized glassy layer concept, on the other hand, cannot explain the exponential behavior observed in various nano-filled systems [12]. Moreover, the formation of a glass-like interphase layer is not assumed to be active in a system containing 90–95 wt% of highly mobile molecules or molecular clusters of water. A theoretical concept explaining basic aspects of the trapped entanglement interaction will be provided in a foreseeable future.

4. Conclusions

It has been shown in this contribution that the theory of nanoreinforcement of rubbery polymers proposed by Sternstein et al. [1] is applicable even in hydrogel systems. More specifically, present data suggest that the primary contribution to the rubbery nanocomposite reinforcement is caused by the filler-induced conformational restriction mechanism. These restrictions cause bias of the reference configurational states of chains which makes them significantly stiffer. In systems which possess a terminal relaxation the transition to the regime dominated by the filler agglomerates can be expected. Moreover, the reinforcing effectiveness was found in dilute PAA systems considerably higher than in dense nano-filled melts and elastomers.

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