



## Short communication

## Size-dependent linear rheology of silica filled poly(2-vinylpyridine)



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## ABSTRACT

Nanoparticles reinforcement of polymers has been of great interest to researchers for the better part of a century. However, researchers are in confusion in describing the role of filler network. Herein we report a framework to solve both reinforcement and dissipation of nanocomposites with respect to strain amplification effect of dynamically retarded bulk polymer phase and jamming of nanoparticles in the filler phase, disclosing a new mechanism differing from previously established ones. We show how the viscoelastic filler phase impacts on the terminal flow of the matrix. Our finding, which counters the conventional understandings of nanoparticles reinforcement, provides a unique description of linear rheology of nanocomposites comprised by fillers of different sizes and polymers of different molecular weights.

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Nanocomposites unexceptionally demonstrate a liquid-to-solid (LTS) transition with increasing filler volume fraction ( $\phi$ ), sharing many similarities to colloidal glass transition, gelation and aggregation [1–8]. This transition may proceed via direct nanoparticles flocculation or mediation by bound layer [9,10] and/or chain bridges [2,11], which has been investigated in many (percolation, jamming, soft glass, gelation) theories, but with great conceptual conflict and experimental discrepancy [6,7].

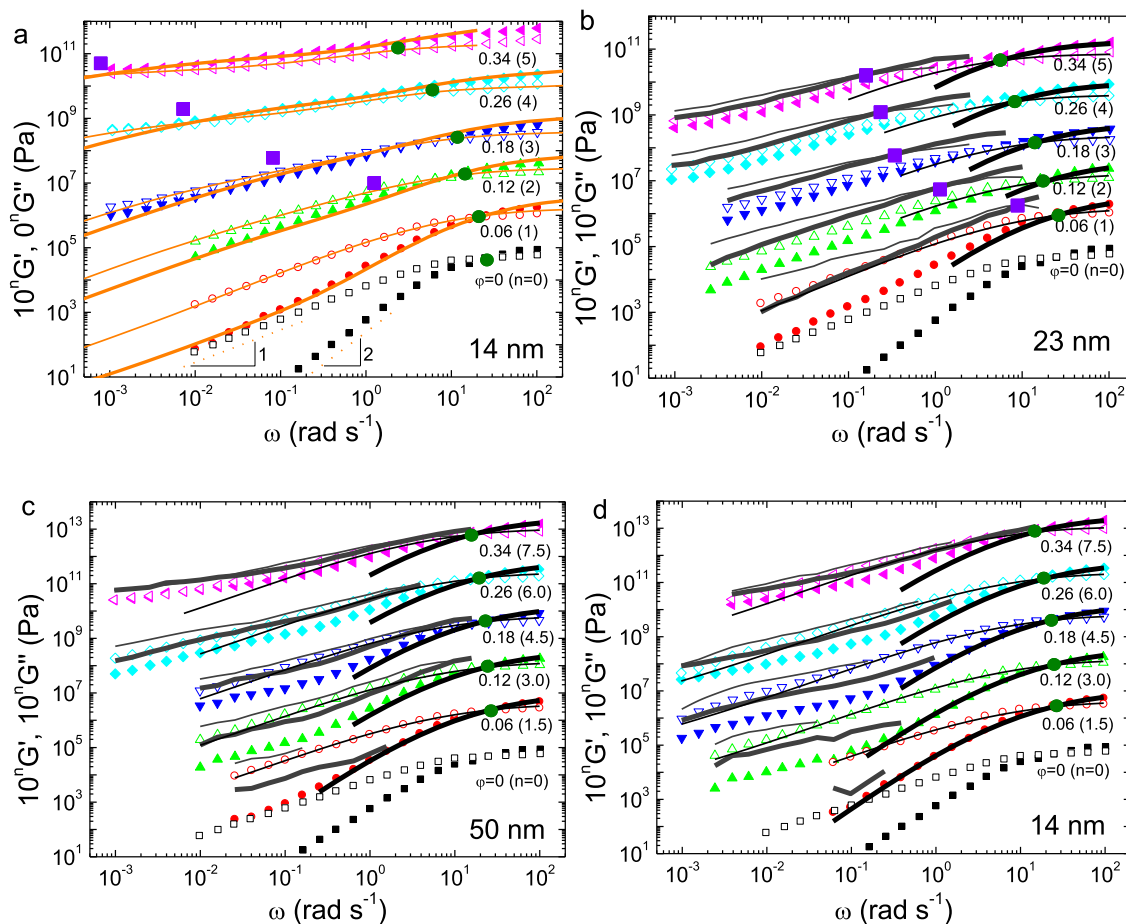
Nanocomposites have been conceptualized as a two-phase system consisting of a bulk matrix and a filler network that interact through the filler-polymer interface. On the one hand, the importance of filler network is disclosed by creating time-concentration superposition (TCS) master curves of linear rheology of the nanocomposites at  $\phi$  above a threshold value ( $\phi_c$ ) or by subtracting the rheological contributions of totally free polymers from the linear rheology of nanocomposites [6,7,12–20]. On the other hand, the rheological contributions of dynamically retarded chains (reversibly) adsorbed on the filler surface are illuminated in constitutive models [21,22]. In the nanocomposites, the confined dynamics of the chains can translate into the bulk phase through topological interactions [23]. Recent investigations reveal that the retarded diffusion of chains in the bulk phase rather than interfacial layer provides the major mechanism of reinforcement and dissipation in the hydrodynamic regime [24,25] and the TCS principle is

able to account for the hydrodynamic-to-non-hydrodynamic transition with respect to  $\phi$  and frequency ( $\omega$ ) [26–28]. These advances pose a significant challenge of traditional investigations of the reinforcement effect at arbitrary  $\phi$  and  $\omega$  [6,7,13,29,30].

The nanocomposites' rheology is sensitive to filler size [1,31–33] and polymer molecular weight [2,24,34–36]. Herein linear rheology of model nanocomposites formed by silica nanospheres well dispersed in monodisperse, entangled poly(2-vinylpyridine) (P2VP) [1,2], with clearly known thickness of glassy layer [9], is analyzed for evaluating the contributions of filler structure and polymer dynamics and their dependences on diameter of silica ( $R$ ) [1,9] and number-averaged molecular weight ( $M_n$ ) of P2VP [1,2]. Experiments report on different changes in glass transition temperature and segmental mobility [2,9,37–39], a controversial and hot topic that is not considered here. Nevertheless, it is generally accepted that nanoparticles do not markedly influence the  $\alpha$ -relaxation of the bulk phase due to the screening effect of the bound layer [37]. As shown in Fig. 1, the nanocomposites at given  $M_n$  ( $97 \text{ kg mol}^{-1}$ ) undergo the LTS transition with increasing  $\phi$ , as identified from appearance of plateaus of storage and loss moduli [ $G'(\omega, \phi)$  and  $G''(\omega, \phi)$ ] in the low- $\omega$  side where P2VP exhibits the terminal flow characteristic ( $G' \sim \omega^2$ ,  $G'' \sim \omega^1$ ) [6,7]. A clear solid-like behavior [ $G'(\omega, \phi) > G''(\omega, \phi)$  in the low- $\omega$  side] is only demonstrated by the nanocomposite ( $R = 14 \text{ nm}$ ) at  $\phi = 0.34$ . The liquid-like dynamics at low  $\phi$ , with slightly elevated  $G'(\omega, \phi)$  and  $G''(\omega, \phi)$ , are ascribed to the increased friction arising from the favorable filler-polymer interactions [1,2,40]. On the other hand, the LTS transition is ascribed to the networking of nanoparticles

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**Fig. 1.** Linear rheology of silica/P2VP ( $97 \text{ kg mol}^{-1}$ ) nanocomposites at  $180 \text{ }^\circ\text{C}$ . a-d,  $G'$  (solid symbols) and  $G''$  (hollow symbols) for the nanocomposites with  $R = 14$  (a),  $23$  (b),  $50$  (c), and  $100$  nm (d), respectively. In (a), the model predicted  $G'$  (thick) and  $G''$  (thin) curves well describe the measured data. In (b–d), the high- and low- $\omega$  rheological responses are determined by  $G'$  (black thick curves) and  $G''$  (black thin curves) of dynamically retarded bulk polymer phase and those of filler phase ( $G'$ : gray thick curve;  $G''$ : gray thin curves), respectively, and the crossover frequency of the filler phase (large square) is considerably lower than that of the bulk phase (large circle). The measured  $G'$  and  $G''$  data taken from Chen et al. [1] are shifted vertically by a factor of  $10^n$  with  $n$  indicated for each volume fraction  $\phi$ .

interconnected by flexible and glassy bridges at intermediate and high  $\phi$ , respectively [1,2,41–44].

As far as linear rheology is concerned, the “two-phase” models [1,6,15–20,30,45] are constructive. Complex modulus of the nanocomposites,  $G^*(\omega, \phi)$ , is formulated as a sum of those from the matrix,  $G_m^*(\omega)$ , and the filler phase. To account for the retarded terminal dynamics of chains in the bulk phase and the role of “dead” bound layer surrounding nanoparticles, terminal relaxation time of the bulk phase,  $\tau(\phi_{\text{eff}})$ , and effective volume fraction of filler,  $\phi_{\text{eff}}$ , should be introduced, yielding  $G^*(\omega, \phi_{\text{eff}}) = (1 - \phi_{\text{eff}})A_f(\phi_{\text{eff}})G_m^*(\omega\tau(\phi_{\text{eff}})/\tau_m) + \phi_{\text{eff}}G_f^*(\omega, \phi_{\text{eff}})$  [24–28]. Here,  $A_f(\phi)$  is referred to as a strain amplification factor, and  $\tau_m$  is terminal relaxation time of the pure matrix identified as reciprocal of  $G_m^*(\omega) - G_m''(\omega)$  crossover frequency. Accordingly, rheological curves in the high- $\omega$  hydrodynamic regime are established following a two-step shifting protocol (Fig. 2a) [46,47]. In the first step, the  $\tan\delta$  curve of nanocomposites is shifted horizontally by a factor of  $\tau(\phi_{\text{eff}})/\tau_m$  so as to superimpose on that of the matrix (not shown). In the second step, the  $G'(\omega, \phi)$  and  $G''(\omega, \phi)$  curves are shifted vertically by a factor of  $1/[(1 - \phi_{\text{eff}})A_f(\phi_{\text{eff}})]$  so as to superimpose on those of the matrix. The superposition is excellent in the high- $\omega$  region, as demonstrated for silica ( $R = 14$  nm) filled P2VP of three different  $M_n$  by plotting reduced moduli  $G_r^*(\omega, \phi_{\text{eff}}) = G^*(\omega, \phi_{\text{eff}})/[(1 - \phi_{\text{eff}})A_f(\phi_{\text{eff}})]$  and  $G_r''(\omega, \phi_{\text{eff}}) = G''(\omega, \phi_{\text{eff}})/[(1 - \phi_{\text{eff}})A_f(\phi_{\text{eff}})]$  against  $\omega\tau(\phi_{\text{eff}})/\tau_m$  (Fig. 2b). In the meantime, though, the superposition fails in the low- $\omega$

region, indicative of the impact of the filler phase. The same situation is testified in P2VP ( $M_n = 97 \text{ kg mol}^{-1}$ ) filled with larger ( $R = 23, 50$  and  $100$  nm) silica. The results reveal that, despite of the wide ranges of  $M_n$  (and thus  $\tau_m$ ; inset in Fig. 2b) and  $R$ , the reinforcement and dissipation of the nanocomposites in the hydrodynamic regime are exclusively determined by the retarded relaxation of chains in the bulk phase and the strain amplification effect to this phase.

It is instructive to make a comparison of the present attempt with others. Cluster-cluster aggregation model and jamming and percolation theories are extensively used for description of “small-strain modulus” as a function of  $\phi$  [6,7] while they could neither address any roles of the polymer molecular weight [36] and filler size [48] nor account for  $G''$ . In the meantime, many constitutive network models and filler structure reorganization models that disregard the role of free chains usually overemphasize the interfacial behavior [6,7]. Furthermore, many experimental studies by measuring “small-strain modulus” do not care the dynamics of chains in the bulk phase. In the present approach, both  $A_f(\phi_{\text{eff}})$  and  $\tau(\phi_{\text{eff}})/\tau_m$  are  $\omega$ -independent, allowing for adequate inspections of the roles played by the bulk polymer, the filler phase, and their interplay. In all cases,  $A_f(\phi_{\text{eff}})$  could be approximated by cluster-cluster aggregation model  $A_f(\phi_{\text{eff}}) \sim \phi_{\text{eff}}^{3.5}$  at  $\phi_{\text{eff}}$  above its threshold  $\phi_{\text{effc}}$ . Thus plotting  $A_f(\phi_{\text{eff}})$  and  $\tau(\phi_{\text{eff}})/\tau_m$  against  $\phi_{\text{eff}}/\phi_{\text{effc}}$  allows normalization of the data from the nanocomposites of varying  $M_n$

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