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Reinforcing mechanisms in amorphous polymer nanocomposites

Jan Kalfus\*, Josef Jancar

Institute of Materials Chemistry (IMC), School of Chemistry, Brno University of Technology, Czech Republic, 118 Purkynova, Brno, 61200, Czech Republic

\*Corresponding author, e-mail: [kalfus@fch.vutbr.cz](mailto:kalfus@fch.vutbr.cz), Phone: 00420 541 149 491, Fax: 00420 541 149 361, web: <http://www.fch.vutbr.cz/cs/laboratore/kompozity.html>

## ABSTRACT

Despite the large volume of experimental data on the peculiarities of the deformation response of polymer nano-composites published over the last 20 years, models addressing the principal physical reinforcing mechanisms taking into account the appropriate length and time-scales are scarce and not generally accepted. The characteristic length and time scales in polymer nano-composites are also strongly temperature dependent, which further complicates the theoretical treatment due to principal differences in the behavior of polymers below and above their  $T_g$ . In addition, the chain mobility above  $T_g$  also affects nano-composite response below  $T_g$  due to effects of segmental immobilization on the formation of polymer structure during solidification. It seems evident that the principal reinforcing mechanism above the  $T_g$  is related to the chain immobilization induced by the presence of rigid high specific surface area inclusions. As a result, the length scale limits of validity of size independent continuum mechanics should be determined since the discrete nature of the matter at the nano-scale prohibits simple scaling down the micro-mechanics models. In

this contribution, the existing reinforcing mechanisms are briefly analyzed in the view of the characteristic length and volume scales in polymers with nano-scale heterogeneities. The results are used to provide a conceptual framework for selecting a suitable molecular dynamics model accounting for molecular details relevant for deformation response of true nano-composites and an identification of possible bridging law between the micro- and nano-length scales.

Keywords: nano composites, elastic properties, dynamic mechanical thermal analysis (DMTA)

Considerable volume of literature has been published on the experimental observations of the deformation response of amorphous polymer composites with rigid nano-scale inclusions. Their mechanical response deviates substantially from that observed for polymers filled with micrometer sized inclusions [1, 2]. Presence of rigid particles results in enhancement of the elastic modulus of polymer composite compared to that of the neat polymer. The reinforcement can be caused in principle by one of the three main mechanisms: (i) the stress transfer from matrix to the non-isometric particles [3], (ii) the partial substitution of soft matrix with stiffer filler [3] and (iii) the segmental immobilization caused by the interaction of polymer chains with filler surface [2]. The stress transfer mechanism depends on the inclusion aspect ratio, its orientation to the applied load, the strength of adhesion and, thus, it is considered as size independent contribution for the case of sufficiently flexible matrix chains. The second mechanism is independent of particle size as well. On the other hand, the segmental immobilization mechanism contributes to the overall composite reinforcement with the extent primarily

affected by the size of the inclusions, becoming important for submicron particles with large surface to volume ratio.

As shown in Figure 1, the reinforcement in nanocomposite is very temperature sensitive variable and two principal temperature regions can be identified [4]. Below the  $T_g$ , the concentration dependence of the relative storage modulus,  $E_r$ , only small deviations from the prediction based on the simple Kerner-Nielsen substitution model were observed [3]. At temperatures above matrix  $T_g$ , the  $E_r$  increased well above the continuum micromechanics prediction suggesting that the segmental immobilization is the primary mechanism responsible for the polymer reinforcement. It has been proposed that the filler surface area per unit weight of nano-composite is the most suitable structure variable in modeling compositional dependence of elastic moduli of polymer nano-composites. This phenomenon has not been observed in the case of polymers filled with micrometer-sized fillers due to their small surface to volume ratios [1]. In these systems, the observed deviations were attributed to the change in Poisson's ratio or relief of internal stresses upon heating [3].

At low filler content, the main reinforcing mechanism in polymers, above their  $T_g$ , filled with high specific surface area nanoparticles results from processes occurring in the large interphase matrix surrounding nano-inclusions. In order to derive a suitable conceptual framework to describe the chain immobilization based reinforcing mechanisms active in the nanocomposites, basic physical principles governing molecular mobility in amorphous polymers have to be outlined. Entangled amorphous polymers are unique systems with macroscopic viscoelastic response driven by the relaxation processes on the molecular level [5]. These relaxation processes represent specific motions of a portion of chains occurring within some characteristic volume,  $V_c$ ,

at various temperatures. The characteristic volume varies from  $10^{-3} \text{ nm}^3$  for localized bond vibrations to  $10^6 \text{ nm}^3$  for the non-local normal mode relaxation (Figure 1). In the later case, the characteristic volume is the boundary value still displaying strong dependence on the chain size,  $V_c \sim R^3 \propto N^{3/2}$ , where  $R$  is the chain end-to-end distance and  $N$  is the number of monomer units in a chain. The characteristic time,  $\tau_c$ , for each particular relaxation process varies from  $10^{-14} \text{ s}$  for bond vibrations to the infinitely long times for the chain diffusive motion below  $T_g$ . Thus, the macroscopic viscoelastic response is a manifestation of a range of molecular relaxations localized in a characteristic volume and the relaxation rate is indirectly proportional to its localization.

The individual relaxations are a consequence of thermal agitation of chain sub-units. One may consider the polymer chain as a set of linearly linked Brownian particles executing thermally activated motion primarily *via* the torsion around the single bonds. Due to the intra- and inter-chain potential field, kinetic energy of a Brownian particle must be sufficient to overcome the energy barrier caused by the torsion potential. Thus, particular activation energy,  $E_A$ , can be ascribed to each particular relaxation mode. In general, neglecting any secondary process being of Arrhenius nature, the relaxation times typical for the  $\alpha$ -relaxation (glass transition) and normal mode are persistence times displaying temperature dependence well described by the Vogel-Fulcher-Tamann equation in the approximate form [5]:

$$\tau \approx \tau^* \exp\left(\frac{E_A}{k_B(T - T_0)}\right). \quad (1)$$

In. Eq. (1),  $\tau^*$  is the time characteristic of torsion vibration,  $k_B$  is the Boltzmann constant and  $T_0$  is Vogel temperature typically some  $50^\circ\text{C}$  bellow the experimentally measured  $T_g$ . Note that the torsion vibrations represent very localized relaxation. The

time characteristic of torsion vibrations does not manifest such a strong temperature dependence compared to the other microscopic motions, and  $\tau^* \approx (k_B T)^{-1/2}$  [6].

Considering the hypothesis put forward above, one can see that the characteristic time, temperature and volume represent variables correlated to each other (Figure 2). At low temperatures, the microscopic modes are too slow compared to the time scale considered unable to maintain equilibrium values of the extensive thermodynamic quantities. Glassy chains can relax only due to extremely rare conformation transitions of low-mobility chain segments trapped in the energy landscape. Hence, the glassy polymer response is principally energy driven and the torsion vibrations with  $V_e$  of value about  $10^{-3} \text{ nm}^3$  are the primary microscopic motion governing response of a majority of polymer units in a glassy solid. Polymer glass is composed of individually vibrating chain segments; rotational isomeric state (RIS) jumps represent rare cooperative events very sensitive to the local density of monomer units. Consequently, one may express the modulus of elasticity,  $G_{glass}$ , of the glassy polymer in the approximate form:

$$G_{glass} = \gamma^*/V_e, \quad (2)$$

where  $\gamma^*$  is the single bond torsion force constant of the order  $\gamma^* = 10^{-19} - 10^{-20} \text{ J}$  [7].

At higher temperature, when the log-time sufficiently advanced the enormous frequency of the chain conformational changes results in normal mode fluctuations able to completely relieve the applied load. Thus, the characteristic volume increased from  $V_e \sim 10^{-3} \text{ nm}^3$  to the value typical of random coil dimensions,  $V_c \approx 10^5 \div 10^6 \text{ nm}^3$ . In high molecular weight polymers the rubbery plateau can be detected. The rubbery region exhibits primarily entropy driven behavior and the elastic modulus,  $G_{rubber}$ , in entangled polymers can be approximated as [8]:

$$G_{rubber} = 4\rho RT/5M_e. \quad (3)$$

Because the characteristic volume of the entangled network,  $V_c$ , can be expressed as:

$$V_c = (M_e C_N b^2 / M_0)^{3/2} \pi / 6, \quad (4)$$

the modulus of elasticity may be then written in the form:

$$G_{rubber} = 4\rho R T C_N b^2 / 5 M_0 (6 V_c^{ent} / \pi)^{2/3}, \quad (5)$$

where  $M_e$  is the entanglement strand molecular weight,  $M_0$  is the monomer unit molecular weight,  $C_N$  is the chain characteristic ratio,  $b$  is the bond length,  $\rho$  is the rubber density and  $R$  is the universal gas constant.

Let us compare the molecular characteristic volumes with those of filler inclusions (Figure 3). In the glassy polymer filled with micrometer-sized particles, the ratio  $r_v = V_p / V_c$  ( $V_p$  is the particle volume) is of the order of  $10^{15}$  (Table 1). Obviously, the rubber ( $T > T_g$ ) filled with micrometer-sized inclusions exhibits  $r_v$  equal to the ratio characterizing the glassy polymer ( $T < T_g$ ) filled with nanometer-sized inclusions. On the other hand, the rubbery matrix filled with nano-inclusions represents a unique system specific by the very low value of  $r_v$ , which means that the volume characteristic of the relaxation process is considerably larger compared to the stiff nano-inclusion (Table 1). At high  $r_v$ , matrix characteristic structural unit in which relaxation mode occurs is small enough being negligible compared to the inclusion size. At higher temperatures, the  $r_v$  decreases suggesting that the matrix loses its continuum character under given conditions.

In addition, the physical reasons for the breakdown of continuum elasticity on the nano-scale include increasing importance of surface energy due to appreciable surface to volume ratio [9], the discrete molecular nature of the polymer matrix discussed above [10], presence of the nano-scale inclusions [11, 12] and the internal



strain due to molecular motion within a non-primitive lattice [13, 14]. Quantum confinement effects can also play a role inducing a strain gradient on the nano-scale without presence of any external loading, however, its importance is limited to the size range below 2 nm [15] and it is not considered here. Heterogeneity of the polymer structure at the nano-scale resulting from the long chain nature of the molecules is further complicated by adding stiff nano-sized filler particles.

In order to estimate the length scale at which the classical elasticity becomes non-valid, the molecular dynamics on a model amorphous polyethylene-like chain was performed under periodic boundary conditions at 50K [16]. The corresponding length scales for the longitudinal and transverse directions were 1.85 and 3.81 nm, respectively. Nikolov et al. [17] estimated that rubbers above their  $T_g$  should have non-local length scale approximately 5 nm. The high non-locality in polymers most probably stems from a cooperative behavior of large number of chain segments characteristic for entangled polymers. As a result, parts of the material system may undergo considerable non-affine deformation associated with occurrence of high moment stresses. Consequently, for such systems, taking strain-gradient effects into account while investigating nano-scale elastic phenomena may impart significant size-dependent corrections to the results obtained from classical continuum elasticity [10, 16].

Although the immobilization is a reasonable reinforcing mechanism and its molecular origin has been well documented in literature [18-21], precise prediction or simulation of its extent for various composite systems under changing external conditions still represents intriguing problem unresolved yet. This contribution attempted to set the reinforcing mechanism responsible for the observed peculiarities of the mechanical response of polymer nano-composites, under given conditions, into a

conceptual physical framework. The emphasis was put on the estimation of the boundary between length scales where the continuum mechanics is still valid and the length scales, where the discrete molecular structure has to be taken into account resulting in the need to apply molecular dynamics models. It was shown that the boundary does not represent a simple constant characteristic of a given composite system; however, it can change under varying test conditions such as time, temperature or strain. It seems that combining the strain gradient continuum elasticity with the molecular dynamics could provide suitable bridging law capable of transforming the peculiarities of the nano-scale effects into the behavior of continuous matter at larger length scales.

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Tables:

Table 1: Ratios of the particle volume/polymer characteristic volume,  $r_v$ , and particle diameter/polymer characteristic length,  $r_l$ , for microcomposite and nanocomposite below and above the glass transition.

Figures:

Figure 1: Temperature dependence of relative storage modulus for the poly(vinylacetate)/hydroxyapatite nano-composite; nanocomposite storage modulus was related to the value of neat matrix at each temperature. Experimentally measured data were complemented with the Kerner-Nielsen micromechanics model [4].

Figure 2: Microscopic relaxation processes on the background of the time, temperature and characteristic volume scale.

Figure 3: Contrast between the filler particle size and volume characteristic of given microscopic relaxation mode.

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	<b>Filled glass</b>	<b>Filled rubber</b>
Microcomposite (d = 10 $\mu\text{m}$ )	$r_v = 10^{15}, r_l = 10^5$	$r_v = 10^6, r_l = 10^2$
Nanocomposite (d = 10 nm)	$r_v = 10^6, r_l = 10^2$	$r_v = 10^{-3}, r_l = 10^{-1}$

Figure 1

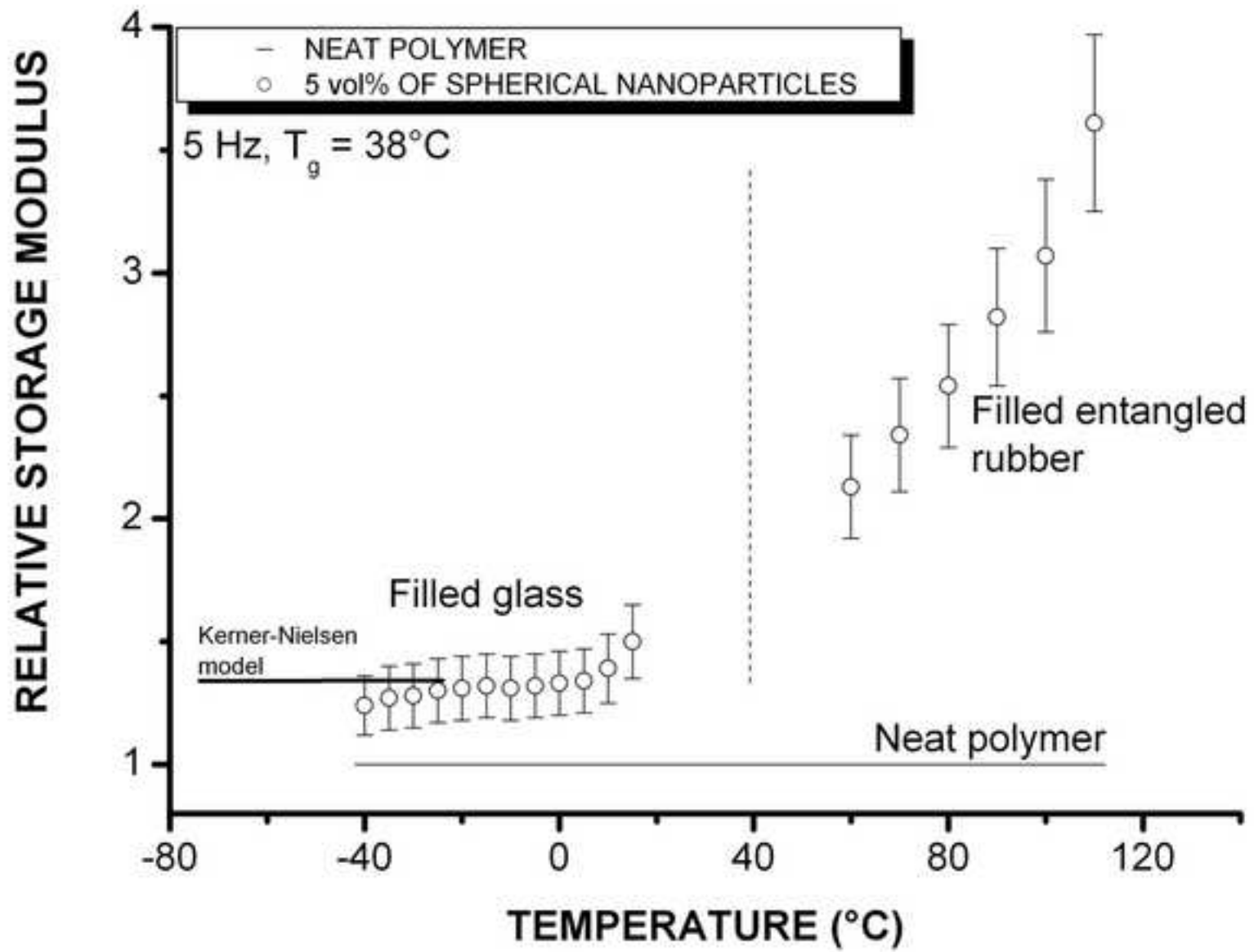
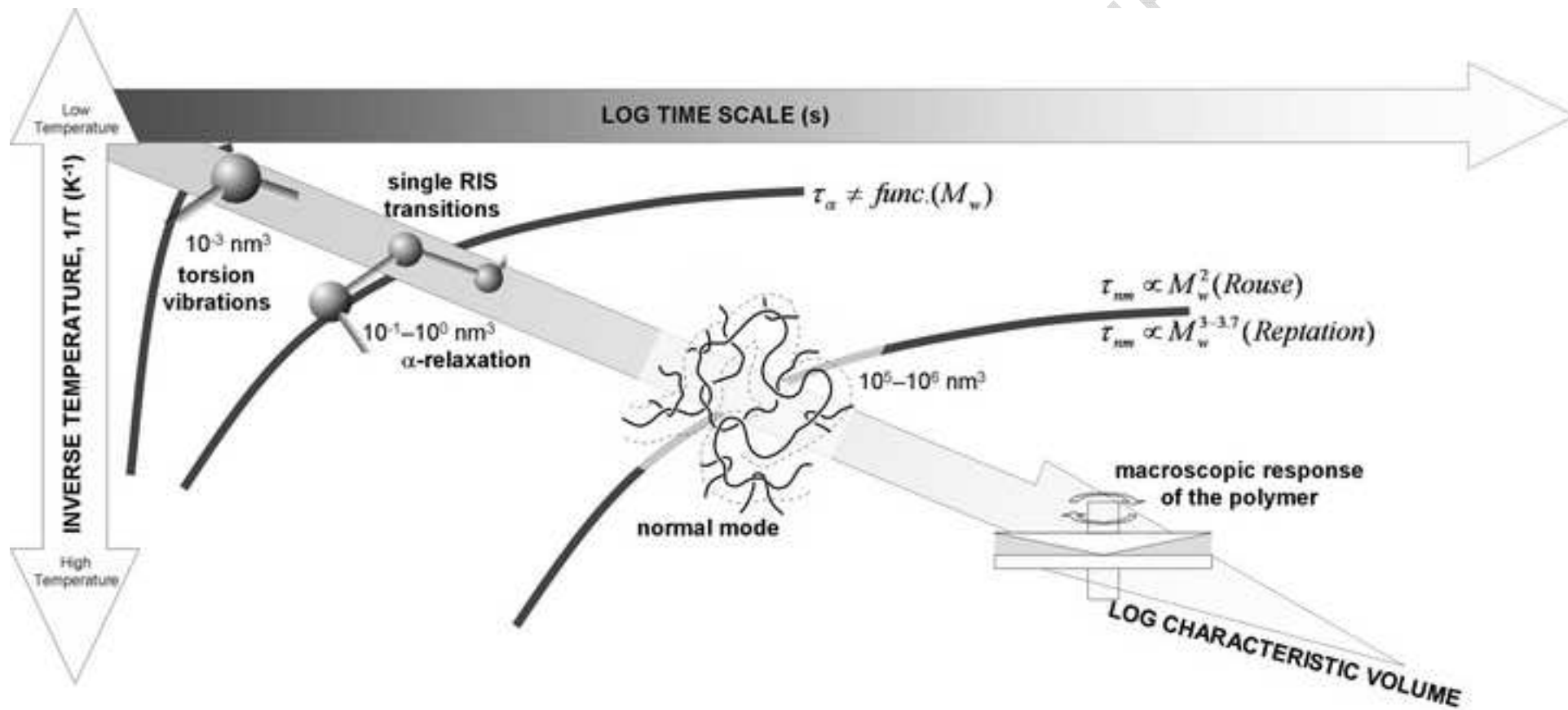


Figure 2



AC

