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# Effect of temperature, strain rate and particle size on the yield stresses and post-yield strain softening of PMMA and its composites



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#### ABSTRACT

The extent of strain softening controls strain localization and governs the character of the post-yield response of polymer glasses. In order to understand how solid particles affect strain softening in a common glassy polymer, we investigate the composition dependence of the upper ( $\sigma_v$ ), lower ( $\sigma_f$ ), and rejuvenated ( $\sigma_{vr}$ ) yield stresses of neat PMMA as well as glass microparticle (MP) and silica nanoparticle (NP) filled PMMA composites. All yield stresses increase with the filler volume fraction  $v_f$ , as expected; the extent of this enhancement increases with T, and is uniformly larger for NP- than for MP-filled systems. This trend cannot be interpreted using simple volume-replacement models; we interpret their breakdown as arising from NP-imposed alteration of segment-scale packing and dynamics at the filler-matrix interface. Furthermore, they vary qualitatively differently with temperature and strain rate, leading to disparate responses of two measures of strain softening ( $\Delta \sigma_{fl} = \sigma_v - \sigma_{fl}$  and  $\Delta \sigma_{vr} = \sigma_v - \sigma_{vr}$ ). We analyze these results in terms of recent microscopic and constitutive models. The strain rate dependence of  $\Delta \sigma_{fl}$  agrees well with predictions of the Chen-Schweizer PNLE model, while poorer agreement is found for temperature dependence. Finally, we extend the recently developed "three-region" picture of strain softening (van Breemen LCA, Engels TAP, Klompen ETJ, Senden DJA, Govaert LE, J Polym Sci Polym Phys 2012, 50, 1757) to composite systems. Our results should lead to an improved understanding of the factors controlling plastic deformation of polymer composites.

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# 1. Introduction

Polymer glasses deformed beyond yield undergo a drop in stress that is known as strain softening or yield-drop, corresponding to the onset of strain localization, and playing a critical role in controlling their ultimate mechanical properties [1–3]. Despite the tremendous industrial importance of having the ability to control this process, progress towards understanding it at a microscopic level remained slow until recent years [4–7]. Several recent developments including (e.g.) the Ediger group's discovery that segment-scale relaxation rates increase by orders of magnitude upon yield [4,5], the Govaert group's observation that long-term ductile failure under constant load is governed by the same process as short term ductile failure at constant strain rate [6], and Chen and Schweizer's development of the PNLE theory [7] for the mechanical response of polymer glasses, have led to an explosion of

interest in the field. Molecular simulations have also contributed significantly to our understanding of yielding, strain softening, and plastic flow [8–13].

Most studies of strain softening that have aimed to understand its microscopic fundamentals of the process in glassy polymers have focused on neat (single-component) systems. Highperformance plastics, however, are typically multicomponent systems with micro- or nano-scale inclusions dispersed in a polymer continuum. Rigid nanoscale fillers are known to strongly affect the segment scale ordering and relaxation dynamics of the surrounding polymeric matrix, producing property changes that are valuable for engineering applications, such as enhanced stiffness, strength and, in some cases, toughness [14-18]. Such fillers have been shown in many studies to produce stronger effects than micronsized particles at the same filler-particle volume fraction. However, the extent to which fillers affect the magnitude and microphysical mechanisms of strain softening has not yet been systematically investigated over a broad range of parameter space including variation of filler size and loading, strain rate, temperature, and sample preparation protocol. In this paper we do so by



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examining strain softening in a typical ductile glassy polymer filled with rigid nano- and/or micro-scale particles.

Theories, experiments and simulations have all shown that the segment-scale-dynamics (SSD) of neat polymer glasses are critical in controlling the macroscopic mechanical response. For example, strain softening is closely associated with post-yield acceleration of the  $\alpha$  relaxation [4.5.7.8]. Further, many studies have shown that SSD in melts above  $T_g$  are slowed by formation of a glassy layer at NP-polymer interfaces [19–22]. In contrast, an open question is: to what extent do NPs with variable interfacial energetics (i.e. variable filler-matrix interactions) affect mobility in, energy landscapes of, and consequently the mechanical response of actively deforming polymer composites? Here we use NPs as probes that alter the local SSD, and attempt to address the above mentioned question by varying parameters that can affect interfacial energetics, such as temperature, strain rate, and sample preparation protocol. A wellknown example of how the latter can affect mechanical response is that quenched systems occupy higher regions of their energy landscape, resulting in reduced yield stress and yield drop.

We recently performed an extensive study [23] analyzing the effects of composition and filler particle size on the plastic flow and strain hardening response of PMMA/SiO<sub>2</sub> (NP) and PMMA/glassbead (MP) composites. Our results on composition dependence of the rejuvenated yield stress ( $\sigma_{vr}$ ) and strain hardening modulus (G<sub>H</sub>) suggested that the above mentioned test variables substantially and qualitatively modify chain packing, segmental mobility, and the position of composites on their potential energy landscapes - and hence their large-strain mechanical response. The  $\sigma_{vr}$  used in this analysis was defined as the intercept of the stress-strain curve and the linear extension of the strain hardening region exhibiting neo-Hookean post yield behavior, and can be identified with the steady-state plastic flow stress that would be present in the absence of strain hardening [7]. Here, in order to gain insight into the molecular origin of yielding of glassy polymers and their composites, we investigate the effects of the above mentioned variables on a range of mechanical response not considered in Ref. [23], focusing on the upper  $(\sigma_v)$ , lower  $(\sigma_{fl})$  and rejuvenated  $(\sigma_{vr})$  yield stresses as well as two measures of the extent of postyield strain softening, i.e.,  $\Delta \sigma_{yf} = \sigma_y - \sigma_{fl}$  and  $\Delta \sigma_{yr} = \sigma_y - \sigma_{yr}$ . Specifically, we examine whether and how these scale with  $v_f$ , the specific interface area per unit volume of the composite S<sub>f</sub>, temperature, strain rate, and sample preparation protocol.

Van Breemen et al. [24] recently showed that the temperatureand deformation-rate dependence strain softening, defined as the difference between the upper and lower yield stress ( $\Delta \sigma_{vf}$ ), in the neat PMMA can be conveniently characterized by defining the three "regions" schematically depicted in Fig. 1. They showed that: (i) in region I (low strain rate, high temperature),  $\sigma_v$  and  $\sigma_{fl}$  are controlled by both  $\alpha$  and  $\beta$  processes; (ii) in region II,  $\sigma_y$  is still controlled by both  $\alpha$  and  $\beta$  processes but  $\sigma_{fl}$  is controlled only by the  $\alpha$  process; (iii) in region III (high strain rate, low temperature), both are controlled by the  $\alpha$  process. Note that if both  $\sigma_{\gamma}$  and  $\sigma_{fl}$  exhibit the same T and strain rate dependence, the difference  $\Delta \sigma_{yf}$  is independent of both T and strain rate. There are, however, intervals where  $\sigma_v$  and  $\sigma_{fl}$  exhibit different T and strain dependences resulting in dependence of the stress drop on testing conditions. Here we extend the picture developed in Ref. [24] to include composite systems. We show that  $\sigma_f$  and  $\sigma_{vr}$  exhibit different T and strain rate dependences that lead to corresponding differences between the strain softening responses. Those of  $\Delta \sigma_{yf}$  correspond to regions I and II, while those of  $\Delta \sigma_{yr}$  exhibit behavior corresponding under different conditions to each of the regions I, II and III.

We find, as expected for attractive interfacial interactions, that all three yield stresses increase monotonically with filler volume fraction  $v_f$ . Their rates of increase with  $v_f$  (at fixed T and strain rate) are always largest for  $\sigma_{yr}$  and smallest for  $\sigma_{y}$ , indicating that fillers' effects on composite mechanical response vary with increasing strain in a highly complex and perhaps nonmonotonic fashion. The extent of these enhancements increases with *T* and is always greater for NP compared to MP filled systems at identical  $v_f$ . The latter implies (and we show) that NP loading reduces the extent of strain softening (compared to neat PMMA) more effectively than MP loading; this effect strengthens monotonically with  $v_f$  and holds over the entire interval of T and  $\varepsilon/dt$  investigated. Thermal history dependence of all five stresses and yield drops is generally stronger for NP-filled than for MP-filled systems.

Simple (yet widely used) volume-replacement models [16,38–43] cannot account for these trends because they include only one parameter ( $v_f$ ) and do not treat alteration of the polymer matrix by filler particles. We show that the Turczanyi-Pukánszky model [25–27,45,46], which accounts for such alterations, provides a substantially superior description of the composition dependencies of the yield stresses. However, while phenomenological models like Refs. [25–27] can qualitatively explain the trends observed here, they cannot provide a microphysical interpretation for them. We attempt to provide such an interpretation in terms of effects such as filler-induced alterations of segmental dynamics and segment-particle coupling, and discuss potential ways in which our results can lead to improved theoretical models for glassy-polymernanocomposite mechanics.

#### 2. Materials and methods

Fumed silica nanoparticles (SiO<sub>2</sub>, Sigma Aldrich) with the specific surface area of 390 m<sup>2</sup>/g (BET, Quantachrome, USA) and primary particle diameter (TEM, Quanta, FEI CZ) of 10 nm and glass beads with average particle diameter (Zetasizer) of  $(10 \pm 4) \mu m$  and specific surface area (BET) of 0.3 m<sup>2</sup>/g were used as the fillers. The sample preparation protocol was identical for all the composites investigated. The PMMA used (Plexiglas 8N, Evonik, Germany) has  $M_n = 68$  kg. mol<sup>-1</sup>,  $M_w/M_n = 1.7$  and  $T_g = 376$  K (DMA, 1 Hz, 3 K/ min.).

The filler was mixed with the PMMA in 1:1 acetone: toluene solvent using an ultrasound dispersion tip. After vigorous mixing for 3 h to obtain uniform NP and MP dispersion [23], the mixture was cast into a film and dried at 80 °C in a vacuum oven. The dried films were milled under liquid nitrogen and the powders were compression molded at 180 °C into cylindrical specimens with height and diameter equal to 6 mm. The neat PMMA underwent the same sample preparation procedure.

The dispersion of particles in glassy matrices is known to play a critical role in polymer composite mechanics [28–36]. In our experiments, NPs form fragile, approximately 200 nm "string-like" structures consisting of primary NPs with high specific surface area, while MPs are well separated [23]. As before, and for simplicity, we therefore *hypothesize* in the below discussion that NP dispersion in undeformed samples is characterized by random positioning of individual NPs within the polymer matrix. The average interparticle distance normalized to the particle diameter,  $L_c/D$ , has been obtained from computer simulation using the model of Zidek et al. [53].

Prior to measurements, specimens were either annealed at  $T_{hi} = T_g - 20$  K for  $10^4$  s, followed by cooling to room temperature at the cooling rate of  $10^{-3}$  K<sup>-1</sup> (referred to as "annealed") or heated at  $T = T_g + 20$  K for  $4 \times 10^3$  s, followed by quenching to room temperature at the cooling rate of  $4 \times 10^{-1}$  K<sup>-1</sup> (referred to as "quenched"). Thus the annealed samples are also moderately *aged*, while quenched samples are not aged and show a closer-to-"intrinsic" response [3].



**Fig. 1.** Schematic representation of the three regions proposed by van Breemen at al [24]. Showing different temperature dependence of the  $\alpha$  and  $\beta$ -relaxation resulting in variation of the yield drop with strain rate (a) and temperature (b). Adapted from Ref. [24].

Uniaxial compression experiments were performed at constant true compressive strain rates ranging from  $10^{-4}$  to  $10^{-1}$  s<sup>-1</sup> and at temperatures ranging from  $T_{lo} = T_g - 80$  K (20 °C) to  $T_{hi} = T_g - 20$  K (80 °C). These experiments employed an Instron 5800 mechanical tensile and compression tester. Cylindrical samples with a surface to volume ratio of 1 were employed. Temperature effects on true stress–strain curves due to internal heat generation, reported in the literature [5] for samples with surface to volume ratios smaller than 1, are neglected in our work. To prevent barreling of the sample due to friction, a thin film of Teflon tape (3M 5480) was attached to the sample ends and the platens were lubricated with a silicon oil spray, dramatically reducing the friction between sample and platens. The instantaneous lateral sample dimension of the cylindrically symmetric sample as a function of compressive strain was calculated by assuming the PMMA is incompressible.

As illustrated in Fig. 2, all systems exhibit a linear-elastic response followed by yield, strain softening, plastic flow, and finally strain hardening. For each system, the yield and flow stresses,  $\sigma_{y}$ , and  $\sigma_{fl}$ , were respectively assigned to the first maximum and first minimum on the true stress-true strain curve. Values of  $\sigma_y$  and  $\sigma_f$  were calculated from an average of 5 independent measurements for every composition and test condition (T,  $d\epsilon/dt$ ,  $v_f$ ); standard deviations among these measurements were less than 15%. The mechanically rejuvenated yield stress ( $\sigma_{yr}$ ), determined assuming neo-Hookean post yield behavior [23,24], should



**Fig. 2.** Schematic of our data analysis procedure for determining the lower yield stress  $(\sigma_{fl})$ , rejuvenated yield stress  $(\sigma_{yr})$ , the upper yield stress  $(\sigma_y)$  and the respective strain softening amplitudes  $(\Delta \sigma_{yn} \ \Delta \sigma_{fl})$ .

only be weakly dependent on preparation protocol and can be identified with the steady-state plastic flow stress that would be present in the absence of strain hardening [7,23]. To capture the differences between the three yield stresses, in the below, we quantify the strain softening of PMMA with particle loading, temperature and strain rate in terms of the two quantities  $\Delta \sigma_{fl} = \sigma_y - \sigma_{fl}$  and  $\Delta \sigma_{vr} = \sigma_v - \sigma_{vr}$ .

We analyze the temperature dependence of our results in terms of distance from the glass transition temperature  $T_{g}$ . From the strong reduction of the strength of the temperature dependence of the loss modulus G' near  $T_g$  upon addition of the nanosized SiO<sub>2</sub> [23] one can conclude that the NPs significantly reduce the system fragility, analogous to antiplasticizers [37]. In contrast, the fragility of microfilled PMMA remains almost unaffected by increasing filler loading, suggesting that fragility alteration is controlled by the volume fraction of segments at the polymer-filler interface (i.e. proportional to the specific particle-PMMA interface area,  $S_f$ ). For the system investigated, adding up to 5 vol. % of fumed SiO<sub>2</sub> NPs results in only a slight reduction of  $T_g$  (~4 K) when compared to the neat PMMA [23]. We believe that this small shift produces only secondary effects for the measurements of primary interest in this study (made at temperatures at least 20 K below T<sub>g</sub> and focusing on  $\Delta \sigma_{yf} - \Delta \sigma_{yr} - \nu_f - L_c/D$  relationships). No measurable change in  $T_g$  was observed in the case of MP filled PMMA. We therefore make the approximation that  $T_g$  is independent of  $v_f$  for both MP and NP filled systems, and use the value for the neat PMMA (373 K) as a reference  $T_{\rm g}$  for measurements of temperature-dependent properties in the glassy state.

## 3. Results and discussion

Expecting a complex temperature, strain rate and composition depends of strain softening, we begin by discussing results for the individual yield stresses- $\sigma_y$ ,  $\sigma_{yn}$  and  $\sigma_{fl}$ -for all systems and test conditions. Values for neat PMMA are given in Table 1. In all cases, annealed systems show larger yield and plastic flow stresses than quenched systems. This is expected for yield stresses, and our reasoning for the larger flow stresses is that annealed systems are expected to possess "tighter" segmental packing that persists (at least) into the plastic flow regime [23]. Stress levels at  $T_{lo}$  are about five times larger than at  $T_{hi}$ , consistent with the expected roughly linear scaling with the distance from the glass transition. Values for the associated yield drops  $\Delta \sigma_{yr}$  and  $\Delta \sigma_{fl}$  are given in Table 2, and will be discussed extensively below.

Table 1				
Upper $(\sigma_n)$ lower $(\sigma_n)$ and rejuvenated $(\sigma_n)$ yield stresses of the neat PMMA	measured at $T_{lo} = T_{a}$	$-80$ K and $T_{15} = T_{\pi} - 1$	20 K at the compressive strain	rate of $10^{-3}$ s <sup>-1</sup>

T [K]	Annealed $\sigma_y$ [MPa]	Annealed $\sigma_{yr}$ [MPa]	Annealed $\sigma_{fl}$ [MPa]	Quenched $\sigma_y$ [MPa]	Quenched $\sigma_{yr}$ [MPa]	Quenched $\sigma_{fl}$ [MPa]
$T_{lo} = 293$ $T_{hi} = 353$	107 ± 5	60 ± 5	95 ± 5	87 ± 4	57 ± 6	81 ± 3
	19 ± 2	11 ± 3	17 ± 1	16 ± 1	9 ± 2	15 ± 2

#### Table 2

Extent of strain softening of the neat PMMA measured at  $T_{lo} = T_g - 80$  K and  $T_{Hi} = T_g - 20$  K at the compressive strain rate of  $10^{-3}$  s<sup>-1</sup>.

T [K]	Annealed $\Delta \sigma_{yr}$ [MPa]	Annealed Δσ <sub>fl</sub> [MPa]	Quenched $\Delta \sigma_{yr}$ [MPa]	Quenched ⊿σ <sub>fl</sub> [MPa]
$T_{lo} = 293$	40	12	30	6
$T_{hi} = 353$	8	2	7	1

Next we analyze the composition dependence of  $\sigma_y$ ,  $\sigma_{yr}$  and  $\sigma_{fl}$  at  $T_{lo}$  and  $T_{hi}$ . Results are summarized in Fig. 3. As expected, both the NP and the MP filler particles act to enhance all three yield stresses compared to those for neat PMMA; all increase monotonotically and roughly linearly with  $v_f$ . Thermal history affects the strength of the v<sub>f</sub>-dependences only negligibly for MP-filled systems, but systematically for NP-filled systems; yield stresses for quenched nanofilled composites exhibit uniformly weaker composition dependence than their annealed counterparts. When normalized to values of these characteristic stresses (i.e.  $\sigma_{yr}$ ,  $\sigma_{yr}$  and  $\sigma_{fl}$ ) for neat

PMMA, the increases are essentially equally strong for MP filled systems, while for NP filler systems they are uniformly largest for  $\sigma_{yr}$  and smallest for  $\sigma_y$  (Fig. 4). These results indicate that fillers' effects on composite mechanical response vary with increasing strain in a highly complex and perhaps nonmonotonic particle size dependent fashion.

Data in Figs. 3–4 also reinforce the point that temperature and sample preparation influence the mechanical response of our systems in nontrivial ways. For NP-filled PMMA, property enhancements at  $T_{lo}$  are greater for annealed systems, while for the quenched systems they are greater at  $T_{hi}$  (except for  $\sigma_{yr}$ , where the effect of thermal history observed at  $T_{hi}$  persists for temperatures down to  $T_{lo}$ ). Previously, we argued [23] that quenched systems at  $T_{lo}$  and annealed systems at  $T_{hi}$  occupy similar positions on their energy landscapes. Based on the new data reported here, the actual physics appears more complicated.

The larger effect of NPs on yield stresses is consistent with previous observations of the non-Newtonian rheological behavior of concentrated suspensions of spherical particles that exhibit



**Fig. 3.** Composition dependence of the three yield stresses measured at the strain rate of  $10^{-3} \text{ s}^{-1}$  at  $T_{lo}$  (blue symbols) and  $T_{hi}$  (red symbols). Panels (a) and (b) compare data for quenched (Q) and annealed (A) NP filled PMMA. Panels (c) and (d) compare data for annealed NP and MP filled PMMA. The lines (solid for annealed and/or NP filled, dashed for quenched and/or MP filled) serve as guides for the eyes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 4.** Composition dependence of the three yield stresses relative to that for the neat PMMA,  $\sigma_y^{rel}$ ,  $\sigma_y^{rel}$ 

yielding [41]. It also indicates that filler-particle-induced effects on yield stresses and strain softening cannot be properly understood using the simple one-parameter volume-replacement models [16,25,38–43] (typically of form  $\sigma_{yX}(v_f) = F(v_f)\sigma^0_{ym}$  for some composite yield stress  $\sigma_{yX}$  and neat matrix yield stress  $\sigma^0_{ym}$ ) commonly employed to describe the response of MP-filled systems. These models fail to describe the yielding behavior of PMMA nanocomposites at the loading fractions considered here because NPs significantly alter the segment-scale structure and dynamics of the matrix in ways that MPs do not. In other words, the yield stress of the neat matrix ( $\sigma^0_{ym}$ ) differs from its filler altered value for the matrix bulk in the composite ( $\sigma_{ym}(v_f)$ ).

To illustrate this point, we analyze our data in terms of more sophisticated (yet still continuum and phenomenological) models that account for the envisioned alteration of the polymer matrix in the vicinity of the filler-matrix interface. Introducing a  $v_f$  - dependent bulk matrix yield stress,  $\sigma_{ym}(v_f)$ , the Turczanyi model [25,44] predicts the composition dependence of the composite's yield stress ( $\sigma_{yc}$ ) to take the form:

$$\sigma_{yc} = \left[\frac{1 - v_f}{1 + \Omega v_f} \sigma_{ym}^0\right] \exp\left(B^* v_f\right),\tag{1}$$

where  $\sigma^0_{ym}$  is the yield stress of the neat polymer and  $(1 - v_f)/(1 + \Omega v_f)$  expresses the reduction of the matrix load bearing cross section (i.e. the stress concentration) arising from the presence of the non-deformable, non-load-bearing spherical filler particles. The parameter  $\Omega$  depends on the spatial arrangement of the filler particles and the maximum achievable filler volume fraction  $v_f^{max}$ . For random packing of monodisperse spheres,  $v_f^{max} = 0.637$  [41], and  $\Omega$  is estimated to be about 2.5 [25]. The dimensionless interfacial interaction parameter  $B^*$  takes the form [44–46]:

$$B^* = \left(1 + A_f \rho_f t\right) \ln \frac{\sigma_{yi}}{\sigma_{ym}^0}.$$
(2)

In Eq. (2),  $\sigma_{yi}$  is the yield stress in the interface immobilized segment layer,  $\rho_f$  is the filler density, and *t* is the immobilized layer's thickness. A<sub>f</sub> is the specific *surface* area of the filler, which is different from the specific *interfacial* area per unit composite volume, S<sub>f</sub> [50]. The temperature and strain rate dependence of  $\sigma_{yc}(v_f)$  arises from the *T* and *de/dt* dependences of  $\sigma_{ym}^0$  and that of the interaction parameter *B*<sup>\*</sup> which in turns arises primarily from *T* and

de/dt dependences of  $\sigma^0_{ym}$  and  $\sigma_{yi}$  [47,49]. However, only the  $\sigma_{yi}$  is related to the presence of filler particles and to the strength of interfacial interactions. The interaction parameter B<sup>\*</sup> is usually determined by data fitting [26,27,51]. Here, we determine B<sup>\*</sup> from the slope of the  $ln(\sigma_y^{norm})$  vs.  $v_f$  plot (Fig. 5(a–b)). Values for the two characteristic temperatures  $T_{lo}$  and  $T_{hi}$  are given in Table 3. Larger values of B<sup>\*</sup> are obtained for  $T_{hi}$  than for  $T_{lo}$  because the  $\sigma_{yi}$  exhibit weaker T dependence than the  $\sigma^0_{ym}$ . Thus, at least for the systems considered here, the interpretation of B<sup>\*</sup> seems more directly related to the different T dependences of  $\sigma_{yi}$  and  $\sigma^0_{ym}$  than to the strength of interfacial attraction as originally suggested [25,44].

For our systems, the  $v_f$ -dependence of the normalized yield stresses agrees with the pre-exponential functional form of Eq. (1). Thus it appears that filler-induced reduction of the matrix yield stress can be reasonably attributed to the enhancement of local stress concentrations that produce plastic flow at lower externally applied stress. However, the strength of this enhancement clearly depends on both filler size and temperature, neither of which are explicitly accounted for by (Eqs. (1)-(2)). It is important, therefore, to go beyond such simple continuum models [52]. We assume that the mean interparticle distance normalized by the particle diameter,  $L_c/D$ , is a reasonable microstructural parameter for the analysis of the vield stresses' composition dependence. For NP filled systems, this variable can be considered a measure of the extent of interparticle chain bridging and the spatial distribution of immobilized chains, while for MP filled systems, it is a measure of the overlap of filler-particles' stress fields [16]. Both variables are related to the mechanical response of polymer composites. Normalized yield stresses ( $\sigma_v^{norm}$ ) are plotted as a function of  $L_c/D$  (calculated for randomly packed monodisperse spheres [53]) in Fig. 6. All data can be fitted with a simple exponential of form:

$$\sigma_y^{norm} = 1 + A \exp\left(\frac{L_c}{\psi D}\right). \tag{3}$$

The pre-exponential parameter *A* increases with increasing *T* and decreasing filler size, while the parameter  $\Psi$  is almost independent of these variables and equal to about -0.5 for all analyzed systems (Table 4). The normalized yield stresses apparently scale with the logarithm of the shortest interparticle distance at both  $T_{lo}$  and  $T_{hi}$ . Thermal history seems to have only a weak effect on this scaling for both NP and MP filled PMMA (Fig. 6).



**Fig. 5.** (a) Composition dependence of chararacteristic yield stresses normalized by the pre-exponential function,  $\sigma_y^{norm}(v_f) = \sigma_{yc}(v_f)/[\sigma_{ym}^0(1-v_f)/(1+2.5v_f)]$ , (Eq. (2)). Panels: (a)  $ln(\sigma_y^{norm})$  as a function of  $v_f$  at  $T_{lo}$ : (b)  $ln(\sigma_y^{norm})$  as a function of  $v_f$  at  $T_{hi}$ . Lines are fits of the experimental data to Eq. (1).

Table 3
List of the interfacial interaction parameters, $B^*$ , determined from the slopes of the
$ln(\sigma_y^{norm})$ vs. $v_f$ plots at $T_{lo}$ and $T_{hi}$ (Fig. 5) for the upper, lower and rejuvenated yield
stresses.

Temperature [°C]	Filler	Quenched			Annealed		
		$\sigma_y$	$\sigma_{\rm fl}$	$\sigma_{yr}$	$\sigma_y$	$\sigma_{\rm fl}$	$\sigma_{yr}$
20	NP	5	6	7	7	6	7
	MP	_	_	_	4	4	4
80	NP	9	10	11	11	11	12
	MP	-	-	-	6	7	7

Simple phenomenological models like those discussed above (Eqs. (1)-(3)) do not account for microscopic dynamical phenomena such as the  $\alpha$ - and  $\beta$ -relaxations. More recent efforts such as the "three-region" analysis [24] discussed above, while still

phenomenological, do account for both of these, and have been applied to neat PMMA. Here, we first apply a three-region analysis to our neat systems (Fig. 7), for the purpose of extending the picture of vanBremen et al. [24]. to NP- and MP- filled composites (Fig. 8). Fig. 7 shows  $\Delta \sigma_{fl} = (\sigma_v - \sigma_{fl})$  and  $\Delta \sigma_{vr} = (\sigma_v - \sigma_{vr})$  for annealed and quenched neat PMMA as a function of temperature for the two limiting strain rates of  $10^{-1}$  and  $10^{-4}$  s<sup>-1</sup> (panels a-b), and of strain rate for all four temperatures (panels c-d). As expected, the yield drops are largest for annealed systems, low temperatures, and high strain rates. As temperature increases, annealed neat systems show a clear crossover in behavior between  $T_g - 40$  K and  $T_g - 20$  K as the glass transition is approached, consistent with expectations for systems in the crossover region II between regions I and III [24]. However, this crossover is much less dramatic in quenched systems, suggesting (as expected) that these occupy a gualitatively different, "higher and smoother" region of their respective energy landscapes [23].



**Fig. 6.** Normalized yield stresses plotted as a function of the  $L_d/D$  ratio for NP and MP filled PMMA. Panel (a): Comparison of the quenched (half left symbols) and annealed (filled symbols) NP filled PMMA at  $T_{lo}$  and  $T_{hi}$ . Panel (b): Comparison of the annealed NP (filled symbols) and MP (open symbols) filled PMMA at  $T_{lo}$  and  $T_{hi}$ .

Table 4			
Parameters A and $\Psi$ of	of Eq. (3) for all the sy	stems investigated a	at T <sub>lo</sub> and T <sub>h</sub>

NP, T <sub>lo</sub>		NP, T <sub>hi</sub>	NP, T <sub>hi</sub>		MP, <i>T</i> <sub>lo</sub> ,		MP, T <sub>hi</sub> ,	
	Quenched	Annealed	Quenched	Annealed	Annealed	Quenched	Annealed	Quenched
Α	1.4	1.4	3.2	3.2	0.8	0.8	1.4	1.4
Ψ	-0.46	-0.45	-0.45	-0.46	-0.49	-0.48	-0.45	-0.45



**Fig. 7.** Temperature dependences of (a)  $\Delta \sigma_{yf}$  and (b)  $\Delta \sigma_{yr}$  at 4 strain rates for annealed (filled symbols) and quenched (open symbols) neat PMMA, and the strain rate dependences of the (c)  $\Delta \sigma_{yf}$  and (d)  $\Delta \sigma_{yr}$  at 4 temperatures for annealed and quenched neat PMMA. Blue symbols are for  $T_{lo}$  (20 °C), red symbols are for  $T_{li}$  (80 °C), green symbols are for T = 40 °C and orange symbols for 60 °C. Lines serve as guides for the eyes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Panels (c-d) show that systems deformed at  $T_g - 60 K$  and  $T_g - 40 K$ show significant rheological complexity, again consistent with expectations for systems in region II [24]. *Quenched* systems at  $T_g - 20 K$ also appear to lie in region II even when the applied strain rate is as high as  $10^{-1}$  s<sup>-1</sup>, while annealed systems are rheologically simple at this temperature. This again supports our arguments that the controlling physics is different for the quenched and annealed systems. For example, the yield drops for systems at  $T_g - 80 K$  should be controlled by both the  $\alpha$  and  $\beta$  relaxations, whereas they should be controlled primarily by the  $\alpha$  relaxation at  $T_g - 20 K$ . A final significant result illustrated in Fig. 7 is that  $\Delta \sigma_{yr}$  is much larger than  $\Delta \sigma_{fl}$ . This indicates that incipient strain hardening exerts a significant influence on  $\sigma_{fl}$ . Van Breemen et al. [24] examined only  $\Delta \sigma_{fl}$  and  $\Delta \sigma_{yr}$ .

Fig. 8 shows the yield drops  $\Delta \sigma_{fl}$  and  $\Delta \sigma_{yr}$  as a function of temperature and strain rate for annealed NP and MP filled PMMA at the same  $v_f = 0.05$ . Again, the temperature dependence data (panels (a-b)) shows a crossover between T<sub>g</sub> - 40 K and T<sub>g</sub> - 20 K. Microcomposite and nanocomposites show similar trends, and both show considerably smaller stress drops than neat polymer. Nanocomposite systems show smaller drops than microcomposite systems at the same loading, reinforcing the point that matrixmodification effects (as opposed to just  $v_f$ ) play an important role in controlling strain softening.

These results are all consistent with the well-established idea that chains in the vicinity of attractive filler surfaces become less mobile [54] well above the bulk  $T_{g}$ . However, it is interesting to discuss them further in the context of the filler particles' surface structure. MD simulations of polymer melts near attractive surfaces [48] have attributed this immobilization to increased neighbour caging (arising from densification of polymer near the surfaces), which in turn leads to slower structural relaxation and increased dynamic heterogeneity within the densified layer. For flat structureless surfaces, this process resembles the behavior observed [48] for bulk polymer melts approaching  $T_{g}$ . For flat *structured* surfaces, simulations showed that the specific surface energy topography plays the pivotal role, with polymer segments caged in localized energy minima. Our filler particles may vary between the two limiting cases described above. On the segment length scale, MP surfaces resemble structureless flat surfaces, while NPs are more likely to exhibit surface energy variations [55]. Hence, the nature (and not only the extent) of the surface layers may differ. We suggest that the immobilized chains partly preserve their disordered structure (i.e. remain similar to chains in quenched neat PMMA) during vitrification and annealing. Further, since the volume occupied by these "surface quenched", segments is proportional to the specific interface area  $S_f$ , the effect is more pronounced for NP filled than for MP filled systems. As a result, the yield drop is always smaller for the NP filled compared to neat and MP filled PMMA, especially at  $T_{lo}$  (Figs. 8 and 9).

The strain rate dependence (Fig. 8, panels (c-d)) also shows a crossover between the lowest and highest strain rates. Values of the



**Fig. 8.** Temperature dependences of (a)  $\Delta \sigma_{fl}$  and (b)  $\Delta \sigma_{yr}$  at 4 strain rates, and strain rate dependences of  $\Delta \sigma_{yf}$  (c) and  $\Delta \sigma_{yr}$  (d) at 4 temperatures, for annealed NP (filled symbols) ( $v_f = 0.05$ ) and MP (half right filled symbols) ( $v_f = 0.05$ ) filled PMMA. Blue symbols are for  $T_{lo}$  (20 °C) and red symbols are for  $T_{hi}$  (80 °C), green symbols are for T = 40 °C and orange ones for T = 60 °C. Lines serve as guides for the eyes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

yield drops show an apparent inflection point at approximately  $10^{-3}$  s<sup>-1</sup>. This may be related to the strain rate crossing the inverse alpha relaxation time, and as in neat systems, is consistent with expectations for systems in region II [24]. Below, since the response of these systems at intermediate *T* and strain rates is particularly complex, we focus on contrasting behavior at the characteristic temperatures  $T_{lo} = T_g - 80$  K and  $T_{hi} = T_g - 20$  K at the strain rate  $10^{-3}$  s<sup>-1</sup>.

Finally, in the spirit of van Bremen et al.'s [24] approach, Fig. 9 summarizes the temperature dependence at two strain rates  $(10^{-4} \text{ and } 10^{-1} \text{ s}^{-1})$  and the strain rate dependence at two temperatures ( $T_{lo}$ ,  $T_{hi}$ ) of  $\Delta \sigma_{fl}$  and  $\Delta \sigma_{yr}$  for annealed neat, NP- and MPfilled PMMA (both at  $v_f = 0.05$ ). Adding filler always reduces both yield drops, but to different extents; the reductions are more pronounced for  $\Delta \sigma_{yf}$  compared to  $\Delta \sigma_{yr}$  at  $T_{lo}$  compared to  $T_{hi}$ , and for NP filled PMMA compared to MP filled systems.

To provide a link to microscopic physics-based theories, Fig. 10 compares our experimental data for  $\Delta \sigma_{fl}$  with the predictions made using the Chen-Schweizer PNLE model [7], which is currently the most complete segment-scale model of the non-linear mechanical response of polymer glasses. Our data for the temperature dependence of  $\Delta \sigma_{fl}$  (panel (a)) agree rather poorly with theoretical predictions for annealed neat PMMA [7], perhaps because the current version of PNLE accounts only for the  $\alpha$  (but not the  $\beta$ ) relaxation. Strain rate dependence, however, agrees quite well (panel (b)) with theory for annealed neat and composite systems.

The poorer agreement for quenched systems is presumably due to significant differences in the thermal and aging histories of our samples and those treated in Ref. [7], and is included only to illustrate the importance of preparation protocol.

We conclude our study by examining the composition dependencies of the yield drops. Fig. 11(a–b) shows  $\Delta \sigma_{fl}$  and its relative value  $\Delta \sigma_{fl}(v_f)/\Delta \sigma_{fl}(v_f = 0)$  for annealed and quenched NP and MP filled PMMA at  $T_{lo}$  and  $T_{hi}$ , measured at the strain rate  $10^{-3}$  s<sup>-1</sup>. In absolute terms, strain softening as measured by  $\Delta \sigma_{fl}$  weakens monotonically with increasing  $v_f$  for all systems. By comparing Fig. 11(a) with Fig. 3 it can be seen that while fillers increase both  $\sigma_v$ and  $\sigma_{fl}$ , they increase  $\sigma_{fl}$  more. This trend is consistent with fillers producing a greater mobilization of the dissipative plastic events necessary to maintain chain connectivity [12], perhaps driven by an increase in segmental mobility that weakens the increase in yield relative to flow stress. It could also be interpreted as arising from increased density fluctuations at NP surfaces; this latter interpretation is consistent with our hypothesis that the filler-surfaceimmobilized layer possesses enhanced liquid-like disorder and/or enhanced packing frustration at the interface between immobilized and bulk chains. We include the normalized data in panel (b) because both  $\sigma_v$  and  $\sigma_{fl}$  exhibit nontrivial filler size and loading dependence and considering absolute values of  $\Delta \sigma_{fl}$  can be confusing. At both  $T_{lo}$  and  $T_{hi}$ , annealed systems show stronger effects for NPs than for MPs, in agreement with previously published results [23]. The data are consistent with our above assumption



**Fig. 9.** Temperature dependences of (a)  $\Delta \sigma_{gl}$  and (b)  $\Delta \sigma_{yr}$  at 2 strain rates, and strain rate dependences of (c)  $\Delta \sigma_{yf}$  and (d)  $\Delta \sigma_{yr}$  at 2 temperatures, for neat annealed PMMA and NP and MP filled PMMA. The loading fraction is  $v_f = 0.05$ . Blue symbols are for  $T_{lo}$  (20 °C) and red symbols are for  $T_{hi}$  (80 °C). Lines serve as guides for the eyes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

that the chains immobilized at the surface, prior to vitrification (in the process of sample preparation), possess a more disordered structure than bulk chains. This would reduce the stress needed to enhance segmental mobility at large strains for interfacial compared to bulk chains. Notably, this effect is strongest in NPfilled systems, i.e. it strengthens with increasing  $S_f$  at fixed  $v_f$ . Next we discuss absolute and relative results for composition dependence of the rejuvenated stress drop,  $\Delta \sigma_{yr} = \sigma_y - \sigma_{yr}$ . As discussed above and illustrated in Fig. 8, absolute strain softening is much larger using this alternative measure since it removes the contribution of incipient strain hardening to the stress minimum. For the MP filled systems at  $T_{lo}$ , strain softening is almost



**Fig. 10.** Temperature (a) and log( $d\epsilon/dt$ ) (b) dependences of  $\Delta\sigma_{\rm fl}$  for annealed and quenched neat PMMA ((PMMA-A, PMMA-Q), PMMA filled with 5 vol.% of MP and/or NP. Experimental data are compared with theoretical predictions made by Chen and Schweizer [7] at  $d\epsilon/dt = 10^{-3} \text{ s}^{-1}$  for anneal and quench preparation protocol with annealing temperature  $T_g - 5$  K (panel (a) solid line) and at  $T_g - 30$  K for polymer glass aged for  $10^3$  s (panel (b) solid line).



**Fig. 11.** Panels (a–b): Composition dependence of (a) absolute values of  $\Delta \sigma_{fl}$  and (b) values relative to the neat matrix,  $\Delta \sigma_{fl}^{rel}$ , for annealed (filled symbols) and quenched (half left symbols). Squares indicate results for NP filled and circles indicate results MP filled systems at  $T_{lo}$  (blue symbols) and  $T_{hi}$  (red symbols) measured at the strain rate  $10^{-3} \text{ s}^{-1}$ . Panels (c–d): Composition dependence of the (c) absolute values of  $\Delta \sigma_{yr}$  and (d) the values relative to the neat matrix,  $\Delta \sigma_{yr}^{rel}$ , for annealed (filled symbols) and quenched (half left symbols) NP (squares) and MP (circles) filled PMMA at  $T_{lo}$  (blue symbols) and  $T_{hi}$  (red symbols) measured at the strain rate  $10^{-3} \text{ s}^{-1}$ . Lines serve as guides for the eyes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

independent of  $v_{f}$ , indicating that yield and "true" plastic flow stresses scale similarly with  $v_{f}$ , and presumably that both are controlled by similar mechanisms [13,56]. The NP filled systems show a systematic and non-linear decrease with increasing  $v_{f}$ ; this decrease arises primarily because  $\sigma_{yr}$  increases more than  $\sigma_{y}$ . Results for  $T_{hi}$  show greater difference between the NP and MP filled systems; the latter exhibit only a small increase in  $\Delta \sigma_{yr}$  at small  $v_{f}$ . All these differences between NP- and MP-filled systems are consistent with the idea that effects arising from chain immobilization at filler surfaces are several orders of magnitude larger for NPs, due to their correspondingly larger  $S_{f}$ .

The effect of thermal history consists of a vertical shift of the absolute values of both  $\Delta \sigma_{fl}$  and  $\Delta \sigma_{yr}$  (Fig. 11a and c) to lower values for quenched (half left filled symbols in Fig. 11) compared to annealed systems (filled symbols in Fig. 11). This seems consistent with our hypothesis that thermal quenching and interfacial chain immobilization both enhance the structural disorder of the polymer matrix in a similar manner. Thus both processes reduce the extent of the post-yield stress drop. Due to the non-equilibrium character of both processes and their strong dependence on the interfacial energetics, surface topology and composite preparation protocol, discovering the relation between these two processes poses a great challenge for future research in this field.

Fig. 12 shows results for the composition dependence of the normalized yield drops  $\Delta \sigma_{Jr}^{norm}$  and  $\Delta \sigma_{yr}^{norm}$ . Following the data reduction procedure used above, we normalized the absolute

values of  $\Delta \sigma_{fl}$  and  $\Delta \sigma_{yr}$  by  $[\Delta \sigma^0_{ym} (1-v_f)/(1+2.5v_f)]$  (Eq. (1)) in order to remove the effects brought about by particle induced local stress concentration and that of the neat (interface unaffected) matrix. The normalized data indicates that (as expected) alteration of segmental dynamics at the interface is much more pronounced at  $T_{hi}$ , especially for nanofilled systems.

Considering the complexity of the microscopic processes involved in the various yield stresses, composition dependences of both  $\Delta \sigma_{JI}^{norm}$  and  $\Delta \sigma_{yr}^{norm}$  exhibit remarkable similarity to each other at both  $T_{lo}$  and  $T_{hi}$ , especially for the NP filled PMMA. According to the Chen-Schweizer PNLE model [7], reduction of the yield drop at constant strain rate and temperature is related to the enhancement of the local amplitude of density fluctuations. This is consistent with our hypothesis that the chains immobilized near the fillersurface in the process of vitrification preserve their liquid state disordered packing.

A fully developed, microscopic theory of the mechanical response of polymer composites should explain the breakdown of volume-replacement models for nanofillers in terms of differences in filler-matrix interactions (in particular, segment-particle coupling [43]) that lead to differences in the strain-induced alteration of segmental dynamics, and hence the entire post-yield mechanical response. More specifically, any successful microscopic theory of the composition dependence of yield stress and strain softening must consider both (i) preparation-protocol-dependent chain packing near filler surfaces, and (ii) spatially heterogeneous



**Fig. 12.** Composition dependence of the characteristic yield stress drops normalized by the pre-exponential function of Eq. (1),  $\Delta \sigma_y^{norm}(v_f) = \Delta \sigma_{yc}(v_f)/[\Delta \sigma_{ym}^0 (1-v_f)/(1+2.5v_f)]$ , at  $T_{lo}$  (blue symbols) and at  $T_{hi}$  (red symbols). Lines serve as guides for the eyes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

dynamics. These should in principle be strongly related to (iii) the strength of interfacial interactions and the specific interface area per unit volume ( $S_f$ ) as well as (iv) details of NP dispersion (e.g. their spatial arrangement affects both chain bridging and filler–filler stress transfer.) However, to the best of our knowledge, spatially varying density fluctuations and dynamics at have not yet been experimentally resolved at scales smaller than 10 nm, and little is known about how (iii–iv) affect (i–ii). An example of how items (i-iv) might all fit together is: chains immobilized at nanofiller surfaces prior to vitrification (in the process of sample preparation) may better preserve the disordered structure of the PMMA melt than either their bulk counterparts or their surface counterparts in micro-filled systems. This increased disorder would then reduce the stress needed to enhance these chains' segmental mobility, thereby producing strain localization and causing yield.

## 4. Conclusions

We examined composition and test variable dependence of the upper, lower and rejuvenated yield stresses (respectively  $\sigma_v$ ,  $\sigma_{fl}$ , and  $\sigma_{yr})$  and the strain softening amplitudes  $\Delta\sigma_{fl}=\sigma_y-\sigma_{fl}$  and  $\Delta \sigma_{vr} = \sigma_v - \sigma_{vr}$ , of neat, NP-filled and MP-filled PMMA within temperature and strain rate domains corresponding to the regions I and II proposed by van Breemen et al. [24]. Under compressive loading, both nano- and micro-filler particles enhance all three yield stresses compared to those for neat PMMA. NPs produce a greater enhancement of these properties compared to MPs at the same  $v_{f}$ , indicating that the simple continuum-micromechanics models often used to describe the response of MP-filled systems cannot account for filler-size dependence. We argued that this failure occurs because filler particles at the loading fractions considered here significantly alter the character of the matrix, and that (especially for nanocomposites) this alteration depends on preparation protocol.

Our results provide data that should be useful in developing enhanced theoretical models. For example, a naive theoretical approach could run as follows; the relative importance of fillermatrix interactions should scale as  $S_f \sim v_f/D$ , while effects of the particle–particle interactions should scale as  $v_f$  and be only weakly dependent on D. Over the range of  $v_f$  investigated, we observed roughly linear dependence of  $\sigma_y$ ,  $\sigma_{fl}$  and  $\sigma_{yr}$  on  $v_f$ . However, attempts to correlate property enhancements with  $S_f$  were not successful, and we showed that the above approach is too simple. Specifically, our results suggest that those details of filler-matrix and particle—particle interactions which are generally different for NP and MP filled systems play a pivotal role.

Potential tools for investigating these outstanding issues include MD simulations<sup>REFs</sup> and future extensions of PNLE theory to nanocomposite systems [7]. The former is excellently suited to examining the mechanical consequences of filler rearrangement during deformation, which has recently been shown [57] to produce large effects in PMMA samples deformed *above*  $T_g$ . The latter could be especially useful in providing leads for analyzing the effects of nanofillers on strain softening by considering their effect on various mathematically well-defined structural variables in supercooled polymer liquids. However, it is important to point out that while both the  $\alpha$ - and  $\beta$ -relaxations are must be accounted for over the temperature and strain rate domains investigated in this work, current PNLE theory considers only the former.

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