



Melt strain hardening of polymeric systems filled with solid particles: review and supplementary experimental results

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Abstract

Melt strain hardening is an interesting characteristic property of the elongational flow of polymers. While strain hardening of many unmodified polymer melts has been widely discussed, a comprehensive presentation of the influence of particles on this property is missing. Using literature data and own measurements, the effects of solid particles of various geometries are compared. Micro-sized particles generally reduce melt strain hardening and may even lead to strain thinning. This behavior is postulated to be due to shear flow components around the particles and resulting shear thinning of the polymer matrices that reduces the resistance to flow. More complex is the influence of nano-sized fillers and layered silicate nanoparticles, in particular. Weakly exfoliated particles show effects similar to micro-fillers, but for strongly exfoliated silicates distinct strain hardening is observed that increases with decreasing elongational rate. This behavior is particularly pronounced for polymers modified with maleic anhydrides and thought to be related to electrostatic forces between exfoliated platelets of the silicates and polymer molecules hindering molecular motions.

Keywords Melt strain hardening · Rate dependence · Polymer melts · Solid fillers · Filler-polymer interactions

Introduction

The increase of the elongational viscosity of polymeric materials as a function of time or elongation above the relation valid in the linear range of deformation is called melt strain hardening. This property of polymer melts is interesting insofar as it is a challenging test for any constitutive equation and molecular model. Moreover, strain hardening has attained some importance with respect to applications because its occurrence has been shown to support the geometrical uniformity of items from processing operations where the extensional deformation of the polymer melt comes into play (e.g., Münstedt (2018)).

Strain hardening depends on the molecular structure of a polymeric material and experimental parameters as well. Thus, it is widely known from the literature that long-chain branching or high molar mass components induce strain hardening, while for a great number of polypropylenes

and some linear polyethylenes, strain hardening was not observed at least within the range of elongational rates experimentally applicable. The features become still more complex by the existence of samples exhibiting strain hardening either increasing or decreasing with elongational rate. This behavior interesting from a processing point of view is not understood up to now and raises many fundamental questions. A review of relevant experimental results is given by Münstedt (2023).

Furthermore, the influence of particles on strain hardening of a matrix is of interest from a fundamental and a processing point of view. Thus, own results and those from the literature are presented here and discussed with respect to a deeper understanding of the molecular processes underlying the elongational behavior.

Fillers are widely used for modifying polymeric materials, and their rheological properties in shear have intensively been studied. Results can be found, for example, in books by Shenoy (1999) and Leblanc (2010). Characterizations in elongational flow are scarce in the literature, however. Fillers cover a large variety of composition and geometrical structure. In the following, elongational properties of polymer melts are discussed according to filler content, size, and geometry.

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Microfillers

Particles with small aspect ratios

Widely used particles of sizes in the range from μm to mm with an aspect ratio of one are glass beads. Their effect on elongational viscosity is reported for an HDPE by Kobayashi et al. (1996a) and for an LDPE by Takahashi et al. (1999), for example. The LDPE shows the typical behavior of this class of material with strain hardening being pronounced at higher rates and disappearing at lower ones. The addition of 20 vol. % glass beads with an average diameter of $30\ \mu\text{m}$ slightly increases the linear viscosity but depresses the strain hardening.

The unfilled HDPE studied by Kobayashi et al. (1996a) exhibits a special feature insofar as strain hardening is stronger at smaller rates. Such a behavior found for several linear polyethylenes is discussed in more detail by Münsterd (2023). Reduction of the strain hardening of the HDPE was obtained by the addition of glass beads with $18\ \mu\text{m}$ in diameter, and this effect became more pronounced with an increase of filler content chosen between 5 and 20 vol. %.

Detailed studies of the influence of the concentration of glass beads with an average diameter of $19\ \mu\text{m}$ on the elongational viscosity of a strain hardening LDPE are presented in Fig. 1, where the time-dependent elongational viscosity

$$\mu(t) = \sigma(t)/\dot{\epsilon} \quad (1)$$

is plotted for various elongational rates $\dot{\epsilon}$.

The unfilled LDPE exhibits strain hardening becoming more pronounced with increasing elongational rate typical of this type of long-chain branched polyethylenes. For all samples, the envelopes to the curves of elongational viscosity correspond to three times the shear viscosity measured at low shear rates. That means the Trouton rule is valid for the unfilled and filled LDPE samples studied. This agreement gives a hint to the reliability of the tensile experiments. All the samples were stretched up to the same total elongation of around $\epsilon = 3$ enabling the direct comparison of strain hardening at this strain. Obviously, strain hardening compared at the same elongational rates decreases with filler loading and is not seen, anymore, at the lowest elongational rates for 30 vol. % glass beads.

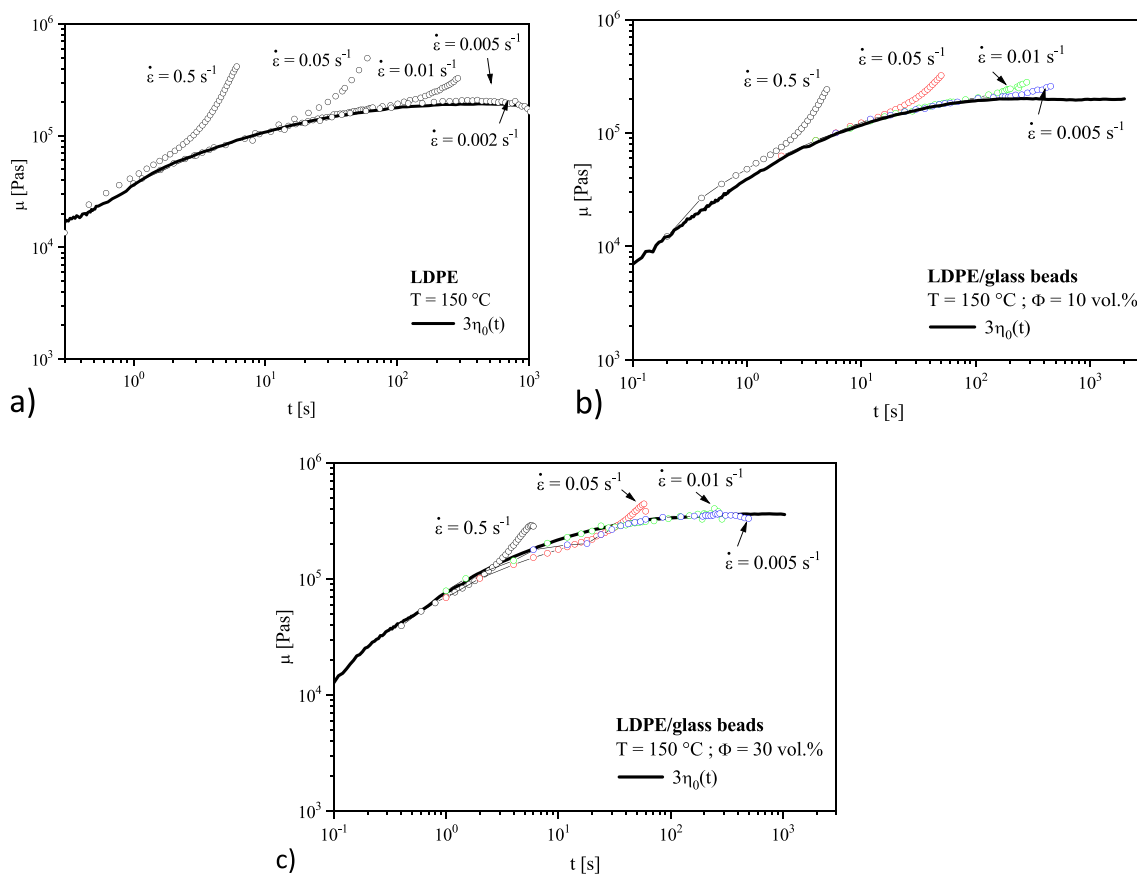


Fig. 1 Elongational viscosity μ as a function of time t at different elongational rates $\dot{\epsilon}$. a) LDPE of the density $\rho = 0.918\ \text{g/cm}^3$, b) LDPE filled with 10 vol. % glass beads, c) LDPE with 30 vol. % glass

beads. The average bead diameter was $19\ \mu\text{m}$. The full lines describe three times the time-dependent linear shear viscosities $\eta_0(t)$ (Schmidt (2000))

A very important precondition for the reliability of elongational experiments on polymer melts is the uniformity of sample deformation. The measurements above were performed with the MTR, the basic features of which are described by Münstedt and Schwarzl (2014), for example. In this rheometer, the sample is stretched in a liquid the density of which is adapted to that of the melt as accurately as possible to avoid its deformation under gravity or buoyancy. At any stage of elongation, the sample can be frozen by moving down the liquid-filled vessel, and its uniformity determined outside the rheometer. In Fig. 2, examples are shown for the diameters along the sample length up to 50 cm. Starting from an initial length of 2.5 cm, this elongation corresponds to the Hencky strain of about 3 attained by the samples in Fig. 1. For minimizing sagging during the elongational measurements, the sample of the unfilled LDPE was stretched in silicone oil and the filled samples were elongated in glycerol to compensate the different gravities by buoyancy. The diameter of the LDPE is relatively uniform along the sample length (full line) and only somewhat below the value of 1.12 mm calculated under the assumption of a constant volume during a uniform elongation. For the two filled samples presented, the uniformity is obviously worse than that of the neat LDPE. Along a part in the middle the measured diameter of the sample filled with 25 vol. % glass beads, it is in reasonable agreement with its value corresponding to a uniform deformation, but to the sample ends the deviations become stronger, approaching about 20%. Therefore, elongational experiments of that kind showing a reduced uniformity should be used for qualitative conclusions, only. For example, within the accuracy of the measurements, the sample geometries are not distinguishable

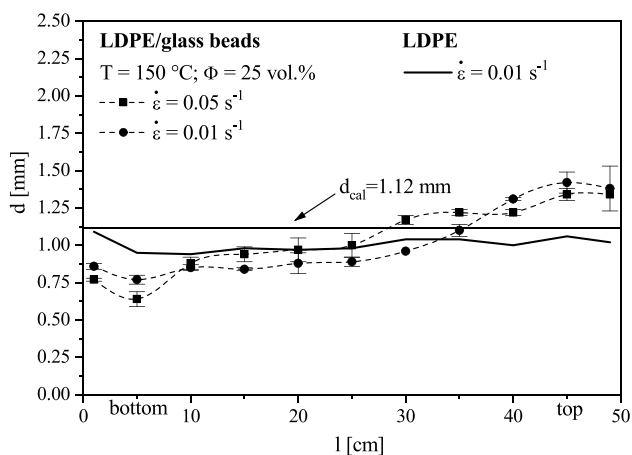


Fig. 2 Sample diameter d along the sample length l for the LDPE matrix (full line) and two samples filled with 25 vol. % glass beads stretched up to the Hencky strain 3 at 150°C and two elongational rates. The faint line stands for the diameter expected from a uniform sample deformation at constant volume and the dotted lines are drawn to guide the eye (Schmidt (2000))

at the two elongational rates, and this finding supports the conclusion that the disappearance of strain hardening at the lower rate being obvious from Fig. 1 c) is not due to a non-uniformity of deformation.

A more quantitative assessment of the influence of the glass beads on the strain hardening of the LDPE is obtained from Fig. 3, which shows the strain hardening coefficient

$$SH = \mu(\dot{\epsilon}, t) / \mu(t) \tag{2}$$

as a function of the bead volume concentration Φ for different elongations at the elongational rate of 0.5 s^{-1} . For the three strains chosen, SH linearly decreases with ϕ , whereby the filler effect becomes more pronounced at higher elongation. The measured strain hardening coefficient is less than that assessed by the assumption of a simple mixing rule for the reduction of strain hardening according to the content of the rigid filler. This result points to processes due to the fillers that reduce the averaged tensile stresses within the matrix and, subsequently, strain hardening.

Experiments with glass beads of a smaller diameter of 7 μm , corresponding to a larger specific surface area did not show a stronger effect on the strain hardening of the LDPE matrix than the 19 μm particles within the accuracy of the measurements, if compared at the same filler content. But nothing is known about the distributions of the glass beads in the melt, and thus, their effective surface area that could be reduced by agglomerations.

The role of surface area for interactions in a filled polymeric system is supported by another experimental finding of Takahashi et al. (1999). At the same concentration of 20 vol. %, the strain hardening of an LDPE was reduced more efficiently by talc of 1.7 μm in size and the aspect ratio of 1.7 than by glass beads of 30 μm in diameter with the aspect ratio of 1.

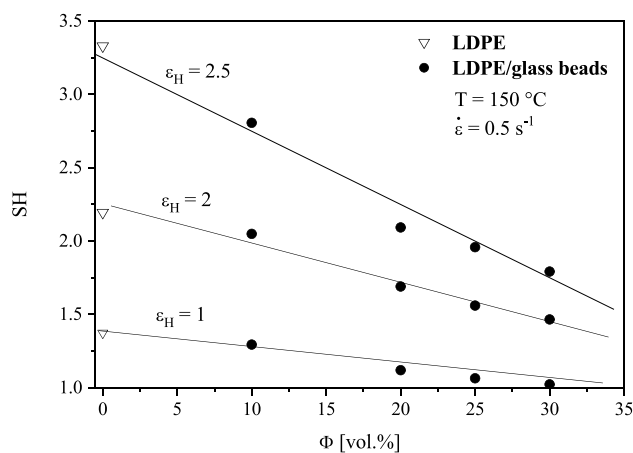


Fig. 3 Strain hardening coefficient SH as a function of the volume concentration Φ of the glass beads with 19 μm diameter for three Hencky strains ϵ_H at the elongational rate $\dot{\epsilon} = 0.5 \text{ s}^{-1}$ (Schmidt (2000))

Rather early elongational experiments on filled polystyrenes were performed by Tanaka and White (1980). They used calcium carbonate, titanium dioxide, and carbon black as fillers in concentrations of 10, 20 and 30 vol. %. The filler sizes decreased from calcium carbonate to titanium dioxide and then further to carbon black, but nothing was said about their states of agglomeration. In all cases, they found an increase of the linear elongational viscosity with filler content and distinct shear thinning effects. The steady-state viscosities obtained decreased with growing elongational rate. The influence of particle size on strain thinning could not be quantified, because sample uniformities during the measurements were not discussed and various pretreatments not specified.

A distinct effect of particle size on strain hardening is reported by Le Meins et al. (2003). They studied the influence of monodisperse polystyrene spheres with diameters of 0.18, 0.70, 1.4, and 2.7 μm on the elongational behavior of a commercial polyisobutylene at ambient temperature at which the PS is far below its glass transition. The matrix and the samples with concentrations up to 25 vol. % showed strain hardening increasing with strain and elongational rate. However, the addition of PS particles to the PIB reduced the amount of strain hardening. The data exhibit some experimental scatter, but the tendency of this reduction becomes more pronounced the smaller the particle size at a distinct concentration. At an elongational rate of 2 s^{-1} and a concentration of 15 vol. %, strain hardening became smaller with decreasing particle size and was found to be negligible for the smallest particles of 0.18 μm in diameter. At the higher rate of 5 s^{-1} , this size effect could not be clearly derived, due to the scatter of the data. Nevertheless, these results point to the role of the specific surface area of particles for their influence on strain hardening

Particles with larger aspect ratios

Results from the literature

A distinct thinning effect by the addition of 20 vol. % glass fibers with a mean diameter of 13 μm and an aspect ratio of 23 to an LDPE was reported by Takahashi et al. (1999). Strain thinning was more pronounced the larger the elongational rate. Similar results were found for 11 wt. % glass fibers with aspect ratios between 15 and 20 in a polypropylene matrix by Ferec et al. (2009) and in an earlier paper by Kamal et al. (1984) for an injection grade PP with glass fibers up to aspect ratios of 30 and concentrations between 4 and 18 vol. %.

Mewis and Metzner (1974) found an increase of the elongational viscosity of a Newtonian matrix with growing aspect ratios of glass fibers.

For other inorganic fibril fillers, comparable features with respect to strain hardening were obtained. Kobayashi et al.

(1996b) investigated the influence of commercial potassium titanate whiskers with diameters of 0.2 to 0.5 μm and aspect ratios up to 100 on the elongational flow of a polystyrene. Five vol. % of the whiskers reduced the weak strain hardening of the PS used, and 10 vol. % suppressed it completely. Moreover, it was found that the fiber orientation only marginally affected the elongational viscosity.

Of the not very numerous studies of the elongational behavior of glass-fiber filled polymer melts in the literature, most of them suffer from the deficiency that the uniformity of the deformation is not discussed, and thus, conclusions from the experimental results have to be considered with some caution.

For the matter of completion, measurements on organic fibers should be mentioned, the results of which are reported to be totally different from those with glass fibers. Hong et al. (2005) generated filled systems in situ by extruding three HDPEs of different viscosities filled with 1 or 5 wt. % PP. Depending on the viscosity ratio, droplet or fiber morphologies were obtained. The fibers had diameters of around 10 μm , and aspect ratios were not reported. While the HDPE matrices and the samples with spherical morphology showed weak increases of elongational viscosities with time, distinct strain hardening effects were found at 150°C for the fibril structures being more pronounced at the higher volume content. Various elongational rates were not applied, and thus, no conclusions concerning the interesting questions on the rate dependence of strain hardening discussed by Münsted (2023) can be derived. Furthermore, the morphology studies leave several questions open with respect to the definite dimensions of the dispersed fibers and their distributions. Nevertheless, it has to be stated that the addition of organic fibers leads to strain hardening in contrast to the strain thinning effects of inorganic fibers described above. Fibril networks as the source of strain hardening were excluded due to the low concentrations chosen.

Detailed experiments on glass-fiber filled LDPE

To broaden the experimental base on the elongational behavior of fiber-filled polymer melts by well-characterized samples, the same LDPE as used for the studies above on the influence of glass beads was modified by various amounts of glass fibers of the mean diameter $D = 16\text{ }\mu\text{m}$ and the aspect ratio $L/D = 7$ with L being the average fiber length. The sample uniformity during elongation in the MTR was worse than in case of the glass beads, and thus, the total strains had to be restricted. To keep the deviations of the diameters along the length of the elongated sample within $\pm 10\%$, for 10 vol. % glass fibers, a maximum Hencky strain of 2.5 could be applied, and this strain decreased to 2 for 20 vol. % glass fibers.

Figure 4 exemplarily shows measurements of the elongational viscosity as a function of time at various elongation

rates for LDPE with 20 vol. % glass fibers performed with the MTR. The curve at $\dot{\epsilon} = 0.005 \text{ s}^{-1}$ comes to lie on $\mu(t) = 18 \eta(t)$, with $\eta(t)$ representing the shear viscosity at the shear rate $\dot{\gamma} = 0.01 \text{ s}^{-1}$. At higher elongational rates, the elongational viscosities are found to deviate from this curve and reach plateau values distinctly below the envelope typical of shear thinning materials. The deviations occur at shorter times and become more pronounced with increasing elongational rate. The plateau values have a high degree of reliability, because they are reached at Hencky strains at which a good uniformity of sample deformation was shown.

Interesting is the finding that the time dependencies of shear and elongational viscosities in the linear range are the same, but somewhat surprising is the factor 18 between shear and elongational viscosity instead of three following from the Trouton relation experimentally verified for various unfilled polymer melts. An explanation of this result is still open.

The reduction of strain hardening is more pronounced for glass fibers than for glass beads as becomes obvious from a comparison of Fig. 1 and Fig. 4. While 20 vol. % of fibers totally suppress the strain hardening of LDPE and even lead to strain thinning, for the same concentration of glass beads, strain hardening is still observable but at a level distinctly lower than that of the matrix.

Discussion of the results on microparticle composites

Two papers published many years ago by Batchelor (1971) and Goddard (1978) are often cited when it comes to the question how the effect of fibers on elongational viscosity could be explained. The authors assess the additional stress generated by straining motion around elongated particles. But none of the theories is able to quantitatively describe experimental observations.

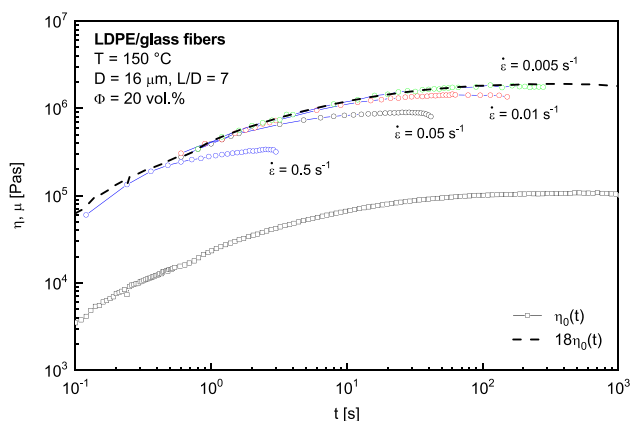


Fig. 4 Elongational viscosity μ as a function of time t at various elongational rates $\dot{\epsilon}$ for an LDPE filled with 20 vol. % glass fibers of the mean diameter $D = 16 \mu\text{m}$ and the mean aspect ratio $L/D = 7$. Additionally, the shear viscosity $\eta(t)$ at the shear rate $\dot{\gamma} = 0.01 \text{ s}^{-1}$ is displayed together with the envelope to the elongational curves $\mu(t) = 18 \eta(t)$

As reported by Goddard (1978), no agreement could be found between theoretical and experimental data for the steady-state viscosities of a HDPE filled with 20 and 40 wt. % glass fibers. Thus, a quantitative description of the strain thinning effect of glass fibers in polymer melts has not been possible up to now.

Nevertheless, a qualitative interpretation is based on shear fields existing around slender particles as theoretically derived by Goddard (1976). He argued that for matrices with a pronounced shear thinning behavior, the contribution of slender particles to tensile stress is reduced in comparison to a Newtonian fluid. Takahashi (1996) and Takahashi et al. (1998) visualized by a simple hand-driven tearing test that shear components may also occur around a sphere during a macroscopic tensile deformation. As well known, many polymer melts and, in particular, the LDPE underlying the results of Fig. 1 and Fig. 4 show strong shear thinning, and this behavior around the fillers can be considered to overlay the strain hardening found for the pure matrix material. The effect may become more dominant the larger the particle content and, thus, the overall amount of shear deformation. Furthermore, shear thinning typically becomes more pronounced with shear rate, and this dependency would explain that strain thinning is found to be stronger at higher elongational rates.

The existence of a complex flow near polystyrene beads and between them is also assumed by Le Meins et al. (2003) for their explanation of the strain hardening decrease of the PIB matrix found by the addition of the polymer particles.

The stronger reduction of strain hardening for fibers in comparison to beads resulting in distinct strain thinning effects may be explained by a more pronounced shear deformation around slender particles.

The model of shear thinning cannot be applied to the results of strain hardening found for PP fibers in a HDPE matrix (Hong et al. (2005)). Their decisive difference to inorganic fibers is the thermoplastic behavior at the measuring temperatures allowing some kind of deformation. The authors assume that a fiber is stretched according to its rigidity. Obviously, the stretching is zero for a solid fiber, but the fiber may extend with the applied tensile stress at temperatures above the melting point leading to an increase of the aspect ratio with ongoing sample elongation. The authors provided an at least qualitative interpretation of the strain hardening observed for their polymeric fibers by discussing results published by Mewis and Metzner (1974). These authors found an increase of the elongational viscosity of a Newtonian matrix with growing aspect ratios of glass fibers.

Nanofillers

Nanofillers are widely used today for modifications of polymeric materials. Various layered silicates and compact SiO_2 particles play a dominant role in this field. The latter show

simple basic geometrical structures, which are relatively stable with respect to compounding. It may be challenging, however, to homogeneously distribute them in polymer melts because of their tendency to agglomeration. Layered silicates, however, are more complex because they can be modified to allow the intercalation of matrix molecules or even to get exfoliated to various degrees. Shear properties of polymer melts filled with nanoparticles have been extensively studied, but investigations of the elongational behavior are not very numerous, particularly, with respect to strain hardening.

SiO₂ particles

The effect of SiO₂ fillers on the elongational behavior of polymer melts can be rather complex because of various possible interactions between the particles and matrix molecules and those between the particles themselves. Such interactions are dependent on properties of the filler surfaces and of the polymer molecules as well. An example how the strain hardening of a polymer melt may be influenced by special surface characteristics of SiO₂ is given in the following.

Kakuda et al. (2006) studied the elongational behavior of a poly (methylmethacrylate) filled with 5 wt. % hydrophobic or hydrophilic SiO₂ particles with a mean diameter of 16 nm at elongational rates between 0.01 and 0.5 s⁻¹. The PMMA matrix showed a slight strain hardening becoming more pronounced with increasing elongational rate. The strain hardening was suppressed by adding the hydrophilic particles, and the elongational viscosities followed the linear curve derived from shear measurements in good approximation. The addition of the hydrophobic particles showed different results insofar as strain hardening was found to become more pronounced with decreasing elongational rate. The authors hypothesized that the hydrophilic particles agglomerate and, thus, show the strain hardening reducing effect of larger particles like glass beads, for example, on the elongational behavior, whereas the hydrophobic ones remained dispersed to a great deal and interacted with the PMMA molecules. But neither morphological studies were provided nor ideas on the physical nature of the interactions presented.

Interesting results on the influence of SiO₂ nanoparticles on elongational properties of another polymer melt were published by Sun et al. (2020). They studied the effect of directly generated SiO₂ particles of a mean diameter of 12 nm on the elongational viscosity of a poly(2-vinyl pyridine) (P2VP) with a weight average molar mass of 100 kg/mol and a polydispersity index of 1.07. Uniform particle distributions could be obtained as proven exemplarily by transmission electron microscopy of a sample filled with 4 vol. % SiO₂. For the PVP matrix, viscosities gradually becoming smaller with decreasing elongational rate and approaching the linear behavior were found as is known for many other polymer

melts. For the P2VP filled with 5 vol. % SiO₂, the elongational viscosity as a function of time at various elongational rates is shown in Fig. 5.

As can be seen from a comparison of the envelope to the elongational viscosity curves and the time-dependent linear viscosity obtained from dynamic-mechanical measurements, the Trouton relation is fulfilled. This agreement is an indication of the reliability of the extensional experiments performed. The time dependence of the elongational viscosity or its strain dependence, respectively, shows a surprising feature insofar as it first becomes less pronounced with decreasing Weissenberg number approaching the linear curve similar to the behavior reported for the matrix material, but then increases again. That means, the P2VP/ 5 vol. % SiO₂ compound exhibits strain hardening decreasing with rate in the range of lower and just the opposite behavior at higher elongational rates. A similar feature is reported for other SiO₂ contents ranging from 4 to 8 vol. % by Sun et al. (2020). Such a behavior has not been found in the literature up to now for any other polymeric system. It is discussed below in more detail.

The authors interpret their findings by the assumption of a deformation-induced network formation by the nanoparticles, giving rise to a yielding feature at low rates or stresses, respectively. With increasing rate, the network becomes more and more destroyed, leading to a reduced resistance to flow and, subsequently, to a lower viscosity. At higher rates, the elongational behavior is governed by interactions of the matrix molecules resulting in strain hardening getting more

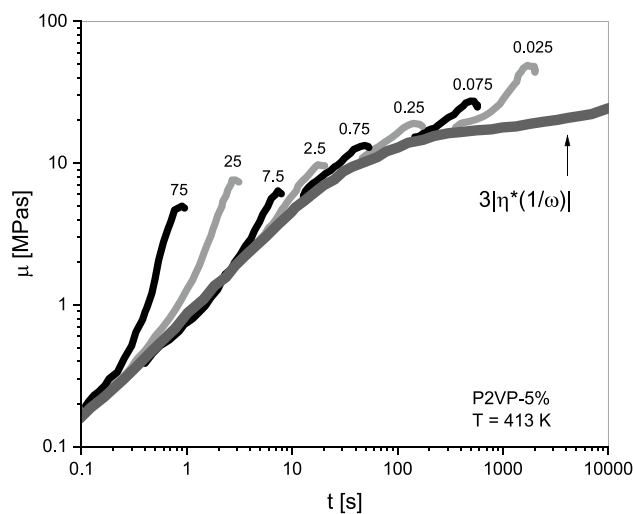


Fig. 5 Elongational viscosity μ as a function of time t for the P2VP filled with 5 vol. % SiO₂ of the mean diameter 12 nm at various Weissenberg numbers indicated at each curve. The full line represents $3|\eta^*(1/\omega)|$ obtained from dynamic-mechanical experiments in the linear range of deformation (Sun et al. (2020)). The elongational rates corresponding to the Weissenberg numbers are difficult to derive from the paper, but they were chosen between 10⁻³ and 6 s⁻¹ according to the authors

pronounced with rate as found for several polymer melts. Information on the network formation was derived from small-angle X-ray scattering of the polymer nanocomposites frozen at various states of sample extension.

This interpretation raises some questions, however. Firstly, a network formation at particle contents of 5 vol. % is hard to imagine. Moreover, micrographs giving hints to ordered particle structures under elongation are not available. Secondly, the hypothesis of a particle network developing with elongation does not explain the increase of the storage modulus above that of the matrix in the linear range of deformation for samples with a uniform particle distribution shown by electron micrographs (Sun et al. (2020)). But the results on the moduli point to some kind of interactions between the fillers and the matrix molecules.

Studies on elongational properties of SiO₂ filled polymer melts are very scarce in the literature, and thus, a broad experimental base supporting a fundamental understanding is missing. Measurements of rheological properties in shear of polymethylmethacrylate (PMMA) with SiO₂ nanoparticles of a mean diameter of 12 nm were performed by Münstedt et al. (2010). They found an increase of elastic properties with the addition of fillers measured by the recoverable creep compliance in the linear range of deformation at small particle contents up to 2 vol. % that was related to the existence of longer relaxation times due to interactions of matrix molecules with the particle surface. Such an interaction could occur by hydrogen bonding between the OH⁻ moieties of silanol groups on the surface of the SiO₂ particles and the PMMA molecules as discussed by Kulkeratiyut et al. (2006). The bond strength in the molten state has to be assumed to be weak, however, because it was shown by Münstedt et al. (2010) that a shear stress of 50 Pa reduces the elasticity of the filled system to that of the matrix.

Nevertheless, the interaction between PMMA molecules and SiO₂ particles postulated could give a hint to an explanation of the strain hardening increasing with decreasing elongational rate as described above for the PMMA with hydrophobic SiO₂ fillers.

Keeping these considerations in mind, it could be assumed that the distinct strain hardening of P2VP/SiO₂ found at small elongational rates is due to bonding forces between the silanol groups on the SiO₂ surface and the nitrogen within the pyridine ring of the matrix molecules. It is well-known that the nitrogen is strongly electronegative and, thus, could support bond formation via an electrophilic reaction. However, it remains an open question whether these bonds are strong enough to withstand tensile stresses around several thousand Pa at melt temperatures around 140°C, at which a resistance to flow is still pronounced according to Fig. 5. This assumption of some kind of hydrogen bonding could explain the decrease of elongational viscosity with

increasing rate, however, as the detachment of more and more bonds with the related stress enhancement is plausible.

Layered silicates

Layered silicates are more complex in comparison to spherical SiO₂ particles, but they play a more important role in practical applications. They consist of stacks of thin layers of two to three atoms, and the spaces between these layers can be widened by intercalation with various species up to an extent that the stacks become exfoliated and form a more or less uniform distribution of thin platelets within a polymer matrix (e.g., Espindola et al. (2023)). Nanoclays are a natural mineral of the montmorillonite type.

Polyolefinic matrices

Extensional experiments on a polypropylene modified with 0.2 wt. % maleic anhydride and filled with 4 wt. % montmorillonite are reported by Okamoto et al. (2001). The montmorillonite was intercalated with stearyl ammonium ions. For this compound, the authors found a distinct strain hardening in comparison to the non-strain hardening PP matrix. Because the total strains at the various elongational rates are different and the linear behavior is not well defined, the rate dependence of strain hardening is difficult to determine, however. From electron micrographs of samples taken at different stages of elongation, they found well-dispersed silicate platelets, surprisingly orientated perpendicularly to the stretching direction.

The influence of a maleic anhydride modified polypropylene (MAPP) on rheological properties of a commercial polypropylene filled with 5 wt. % nanoclay based on dimethyl hydrogenated-tallow ammonium was studied by Park et al. (2006). Using small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM), it was shown that an exfoliation of the nanoclay could be obtained in an internal mixer by adding MAPP to the PP. For the samples with the exfoliated nanoclay, a distinct strain hardening with the tendency of increasing with decreasing elongational rate was found. This result can be interpreted by an interaction between the extended layer surfaces and the polypropylene molecules of the matrix due the MAPP acting as a compatibilizer. The effect is still more pronounced for the pure MAPP with nanoclay pointing to the role of the polar maleic anhydride for a coupling to the layers reducing the molecular mobility. These interactions enhance the resistance of the matrix molecules to flow and can be considered as the source of strain hardening. From this assumption, it is obvious that with increasing elongational rate or stress, respectively, more and more molecules get detached from the silicate layer and the strain hardening becomes less pronounced.

Extensional experiments on another commercial isotactic polypropylene filled with nanoclay were performed by Lee et al. (2007). The organoclay was a natural montmorillonite modified with a quaternary ammonium salt via exchange reaction. A maleic anhydride grafted polypropylene was used as a compatibilizer. Using SAXS, it was shown that exfoliation of the layered silicates was obtained by melt compounding in a twin-screw extruder.

Although the experiments show some scatter, certain conclusions can be drawn from the results presented. The authors do not see strain hardening for the polypropylene matrix and the blend with 5 wt. % nanoclay. Adding 5 wt. % of the maleic anhydride modified polypropylene, leads to distinct strain-hardening that could be interpreted by assuming the bonding of matrix molecules to the exfoliated silicate layers by the compatibilizer. Such a mechanism increases the resistance to flow and enhances the stresses necessary for molecule motions. Nothing is said, however, about the uniformity of sample deformation and the reason for the stress maxima measured.

Extensional data of an ethylene-vinyl acetate copolymer (EVA) filled with the layered silicate nanocomposite sodium-bentonite was published by Gupta et al. (2005). The hydrophilic clay was rendered organophilic using cetyl-dimethyl-ethyl-ammonium bromide. Blends with filler contents between 1.5 and 10 wt. % were obtained by melt mixing in a twin-screw extruder. Predominantly exfoliated nanolayers were verified by X-ray and electron microscopic characterizations. Besides shear rheological properties, some few elongational experiments were performed that are of special interest with respect to the topic of this paper. Strain hardening becoming more pronounced with increasing elongational rates between 0.1 and 1 s⁻¹ was found for the EVA matrix polymer. The compound with 5 wt. % nanoclay showed the same rate dependence of strain hardening at a somewhat reduced intensity, however. This result is in contrast to the above findings on the nanoclay-filled polypropylene with maleic anhydride modified polypropylene (MAPP) as compatibilizer that the addition of nanoclay induced strain hardening decreasing with increasing rate. The various behavior could be explained by the absence of electrostatic interactions between the EVA molecules and the exfoliated bentonite nanolayers. Then, the silicate layers could be considered as non-reactive fillers, reducing strain hardening of the matrix similar to the mechanism of the inert glass beads discussed above.

Other matrices

Rheological experiments on a polyamide (PA 6) filled with dimethyl hydrogenated-tallow ammonium modified montmorillonite (MMT) (Cloisite 93A) are reported by Seong et al. (2005). For the compounding of PA 6, montmorillonite,

and the organic modifier, a twin-screw extruder was used. The exfoliation of the particles was shown by X-ray diffraction and transmission electron microscopy. Although not of a high standard, it can be concluded from the measurements that the PA 6 matrix exhibits a tendency of strain thinning. The absence of strain hardening is known from linear polymers with short Rouse times like polypropylene and high density polyethylene (e.g., Münstedt (2023)). However, distinct strain-hardening effects are seen for a PA sample with 5 wt. % exfoliated nanoclay. Strain hardening increases with decreasing elongational rate at least between 0.5 and 0.03 s⁻¹ and up to the measured Hencky strains around 2. Such a strain-hardening effect was not observed for a compound of PA 6 and 5 wt. % of the unmodified MMT (Cloisite Na⁺).

The influence of the modification of MMT on strain hardening points to an interaction between the modifier and the polyamide molecules with their hydrophilic amide groups as the source of strain hardening. At small stresses or elongational rates, respectively, these molecular interactions effect a resistance to flow that gradually decreases with the increase of the detachment of molecules at growing stresses.

Rheological properties of polymethylmethacrylate (PMMA) containing 3.3 and 5.0 wt. % smectite clay modified with a paraffin-like organic chloride of a somewhat complex chemical structure are reported by Kotsilkova (2002). Two parts of the modifier were added to one part of the clay leading to laminate structures of several hundred layers within the directly polymerized PMMA. The pure PMMA exhibited a minor strain hardening at the elongational rate of 1 s⁻¹ up to Hencky strains of around 3 that became smaller with decreasing rate. The filled samples showed a distinctly more pronounced strain hardening with qualitatively the same rate dependence as the matrix. This result is surprising because the rate dependence is just opposite to that of the polypropylene with the modified nanoclay. This could possibly be due to the lack of exfoliation of the particles added to the PMMA. But then an effect of strain-hardening reduction should be found similar to the polymer melts filled with unmodified particles like glass beads or glass fibers as reported above. The findings on PMMA/nanoclay are tried to be explained by the author assuming nanoclay domains, which resist the deformation of the elongational flow applied. This interpretation is not very specific, however, and leaves some questions open, particularly, with respect to other results from the literature on PMMA/nanoclay discussed in the following.

Katsikis et al. (2007) studied the elongational behavior of a PMMA filled with a commercial nanoclay the primary cations of which were already exchanged by ammonium salts with alkyl chain side groups. The compounds were prepared by a two-step process. A master batch with 30 wt. % clay was prepared in a PMMA solution. The dried material was melt-mixed then in a kneader with the pure material to

obtain compounds with different filler contents. The clay is well dispersed, but exfoliated only to a minute extent, as can be seen from transmission electron micrographs. Platelets with smallest dimensions around several nm and various aspect ratios up to around ten can be distinguished. Intercalation of matrix molecules was proven by X-ray scattering.

As Fig. 6 shows, the PMMA matrix exhibits negligibly small strain hardening in the range of elongational rates between 0.005 and 0.1 s^{-1} up to the total Hencky strain 2 measured. All data come to lie on one curve in good approximation, which increases with time first and then reaches a distinct time-independent plateau indicating a steady-state viscosity independent of rate within the range chosen corresponding to a Newtonian behavior. For all filled samples, however, the viscosity curves are lower at higher strain rates, but their features are very similar. After an increase they attain plateau values decreasing with rate. Such behavior is typical of strain-thinning materials. The thinning effect was found to become more pronounced with the amounts of nanoclay chosen between 3.2 and 8.9 vol. % as can be seen from Fig. 6. The viscosity plateaus increase with filler

content, and this growth is more pronounced the smaller the elongational rate.

In addition to the measurements at constant elongational rates, creep experiments in extension on samples with various nanoclay contents were performed (Katsikis et al. (2007)). The steady-state elongational viscosities obtained from the two different methods are in good agreement, and this finding demonstrates the reliability of the results.

The extensional behavior of PMMA with nanoclay obtained by the two authors above is obviously different showing strain hardening in one case and strain thinning in the other. The reason for these differences may be seen in the particle morphologies. The nanoclay used by Kotsilkova (2002) was modified with a large amount of an organic chloride resulting in agglomerates, whereas for the samples of Katsikis et al. (2007), mainly non-exfoliated clay particles distinctly separated from each other were observed. The flow behavior of the matrix molecules around these particles with high ratios of lateral dimensions to thickness may be comparable to that of glass fibers with large aspect ratios and, consequently, some kind of shear flow around the edges

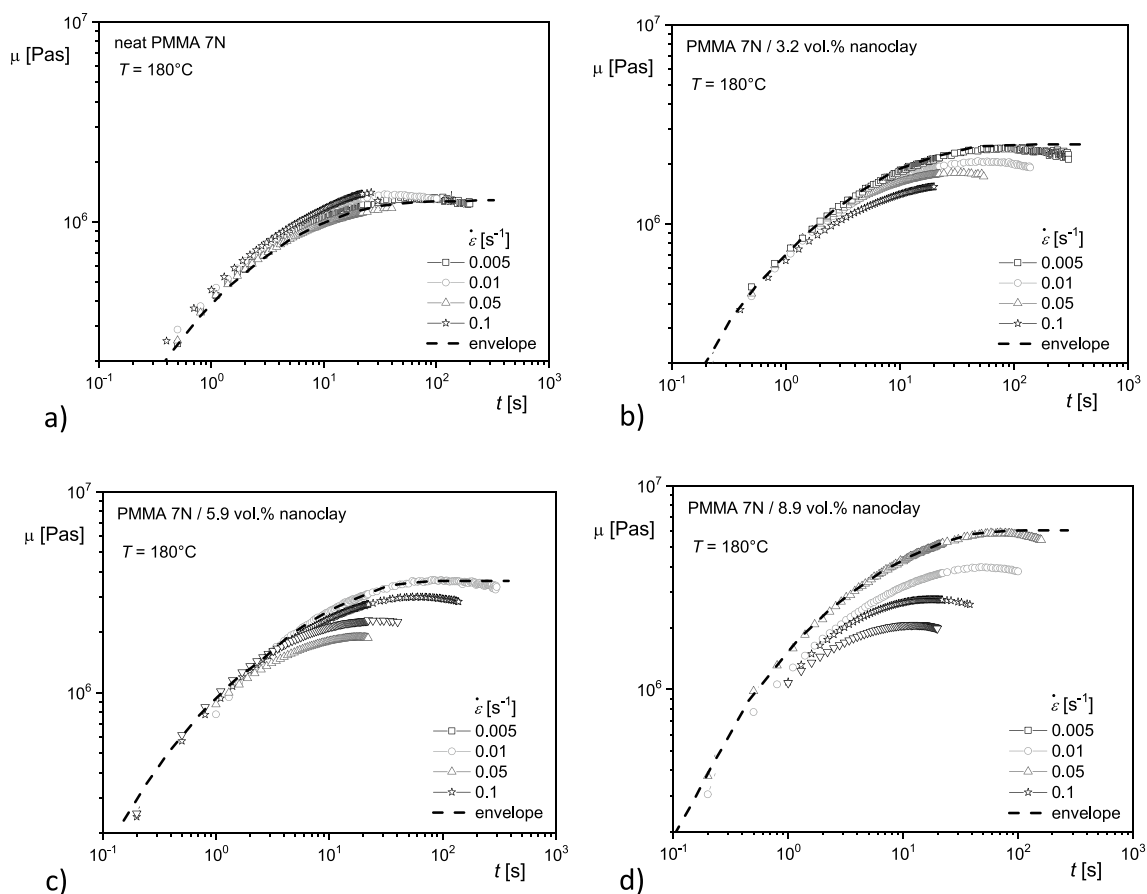


Fig. 6 Elongational viscosity as a function of time at 180°C and various elongational rates for a) neat PMMA b) PMMA with 3.2 vol. %, c) PMMA with 5.9 vol. %, d) PMMA with 8.9 vol. % nanoclay (Katsikis et al. (2007))

could be postulated that initiates shear thinning reducing the resistance to flow as discussed above. These effects are expected to be more efficient the higher the filler content as long as agglomeration does not take place, and just this feature can be seen in Fig. 6.

However, the results on the PMMA filled with the two different nanoclays leave some questions open, that probably could be addressed to some extent, if information on the morphology were available.

Conclusions

Glass beads reduce strain hardening and even generate strain thinning in case of non-strain hardening polymers. This effect is more pronounced the larger the aspect ratio of the filler and was found to be particularly obvious for glass fibers and non-exfoliated nanoclay. These features are qualitatively explained in the literature by assuming the occurrence of shear flow components around the solid particles and a shear thinning effect that reduces the resistance to flow of the polymer matrix (Takahashi et al. (1999), for example). It should be mentioned, however, that the uniaxial deformation of particle-filled polymer melts may comprise other kinds of flow like compression and biaxial deformation the general influence of which is difficult to assess.

The dependence of the reduced strain hardening of filled samples on elongational rate follows that of the matrix material and becomes smaller with decreasing rate. Strain thinning due to the introduction of particles gets more pronounced with increasing elongational rate. Both tendencies, the reduction of strain hardening or strain thinning have a negative effect on the uniformity of sample deformation that is essentially determined by strain hardening and make processing operations, at which elongational flow comes into play, more challenging for polymer systems filled with beads and fibers than for the matrix material.

Additionally, many facets of nanoparticles influence the elongational behavior of polymer melts due to their various properties and states. Their large specific surface areas are predestinated for interactions with matrix molecules. Whenever strong binding forces of matrix molecules to particle surfaces could be achieved, strain hardening at small elongational rates was observed that decreased with increasing rates. Such behavior could be related to distinct hydrogen bonding either existent according to the chemical structures of polymer molecule and filler or generated by polymer modifiers like maleic anhydride as demonstrated in the case of polypropylene filled with montmorillonite. Binding and its effect on the resistance to elongational flow decrease with the number of detached polymer molecules that may become smaller with increasing tensile stress or elongational rate, respectively.

A special role among nanoparticles play layered silicates, because they may exist as dense packages of a great number of thin sheets, as arrays of sheets intercalated by matrix molecules or even in a more or less exfoliated state offering a large surface area for molecular interactions. These may lead to strain hardening effects becoming more pronounced with decreasing elongational rate as was shown for filled PP and PA the matrices of which did not exhibited strain hardening in the range of rates experimentally available. Hydrogen bonding can be assumed as a binding force between silicate layers and matrix molecules often modified with maleic anhydride.

The overall efficiency of such interactions depends on their strength and the particle surface area available for attachments. But publications on the effects of these structural elements of filled polymeric systems on rheological properties being of some fundamental and practical interest are rare. Studies of strain hardening at small elongational rates could contribute to a better understanding of fundamental interactions. Such insights could contribute to an optimization of product developments with respect to processing operations involving elongational flow.

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Declarations

Conflict of Interest The author declares no competing interests.

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References

- Batchelor GK (1971) The stress generated in a non-dilute suspension of elongated particles by pure straining motion. *J Fluid Mech* 46:813–829
- Espindola SP, Zlopasa J, Picken SJ (2023) Systematic study of the nanostructures of exfoliated polymer nanocomposites. *Macromolecules* 56(18):7579–7586
- Ferec J, Heuzey MC, Perez- GJ, de Vargas L, Ausias G, Carreau PJ (2009) Investigation of the rheological properties of short

- glass fiber-filled polypropylene in extensional flow. *Rheol Acta* 48:59–72
- Goddard JD (1976) The stress field of slender particles oriented by a non-Newtonian extensional flow. *J Fluid Mech* 78:177–206
- Goddard JD (1978) Tensile behavior of power-law fluids containing oriented slender fibers. *J Rheol* 22:615–622
- Gupta RK, Pisanovic-Zujo V, Bhattacharya SN (2005) Shear and extensional rheology of EVA/layered silicate-nanocomposites. *J Non-Newtonian Fluid Mech* 128:116–125
- Hong JS, Ahn KH, Lee SJ (2005) Strain hardening behavior of polymer blends with fibril morphology. *Rheol Acta* 45:202–208
- Kakuda M, Takahashi T, Koyama K (2006) Elongational viscosity of polymer composite including hydrophilic or hydrophobic silica nano-particles. *Nihon Reoroji Gakkaishi* 34:181–184
- Kamal MR, Mutel AT, Utracki LA (1984) Elongational behavior of short glass fiber reinforced polypropylene melts. *Polym Comp* 5:289–298
- Katsikis N, Königer T, Münstedt H (2007) Elongational viscosities of polymethylmethacrylate/nano-clay composites. *Appl Rheol* 17(52751):1–9
- Kobayashi M, Takahashi T, Takimoto J, Koyama K (1996a) Influence of glass beads on the elongational viscosity of polyethylene with anomalous strain rate dependence of strain-hardening. *Polymer* 37:3745–3747
- Kobayashi M, Takahashi T, Takimoto J, Koyama K (1996b) Flow induced whisker orientation and viscosity for molten composite systems in a uniaxial elongational flow field. *Polymer* 36:3927–3933
- Kotsilkova R (2002) Rheology-structure relationship of polymer/layered silicate hybrids. *Mech Time-Depend Mat* 6:283–300
- Kulkeratiyut S, Kulkeratiyut S, Blum FD (2006) Bound carbonyls in PMMA adsorbed on silica using transmission FTIR. *J Polym Sci B* 44:2071–2078
- Le Meins JF, Moldenaers P, Mewis J (2003) Suspensions of monodisperse spheres in polymer melts: particle size effects in extensional flow. *Rheol. Acta* 42:184–190
- Leblanc H (2010) Filled polymers: science and industrial applications. Taylor and Francis Group, Boca Raton, USA
- Lee SH, Cho ENR, Youn JR (2007) Rheological behavior of polypropylene/layered silica nanocomposites prepared by melt compounding in shear and elongational flows. *J Appl Polym Sci* 103:30506–33525
- Mewis J, Metzner AB (1974) The rheological properties of suspensions of fibers in Newtonian fluids subjected to extensional deformations. *J Fluid Mech* 62:593–602
- Münstedt H (2018) Extensional rheology and processing of polymeric materials. *Intern Polymer Process* 33:594–618
- Münstedt H (2023) Various features of melt strain hardening of polymeric materials in uniaxial extension and their relation to molecular structure: review of experimental results and their interpretation. *Rheol Acta* 62:333–363
- Münstedt H, Köppl T, Triebel C (2010) Viscous and elastic properties of poly (methyl methacrylate) melts filled with silica nanoparticles. *Polymer* 51:185–191
- Münstedt H, Schwarzl FR (2014) Deformation and Flow of Polymeric Materials. Springer, Heidelberg
- Okamoto M, Nam PH, Maiti P, Kotaka T, Hasegawa N, Usuki A (2001) A house of card structure in polypropylene/clay nanocomposites under elongational flow. *Nano Letters* 1:295–298
- Park JU, Kim JL, Kim DH, Ahn KH, Lee SJ (2006) Rheological behavior of polymer/layered silicate nanocomposites under uniaxial extensional flow. *Macromolecular res* 14:318–323
- Schmidt M (2000) Scher- und dehnreologische Untersuchungen an Suspensionen auf der Basis sphärischer Füllstoffe (Rheological studies in shear and elongation of suspensions with spherical fillers), Doctoral Thesis, Friedrich-Alexander-Universität Erlangen-Nürnberg
- Seong DG, Kang TJ, Youn FR (2005) Rheological characterization of polymer-based nanocomposites with different nanoscale dispersions. *e-Polymers* 005:1–14
- Shenoy AV (1999) Rheology of filled polymer systems. Kluwer Academic Publisher, Dordrecht
- Sun R, Melton M, Zuo X, Cheng S (2020) Non-monotonic strain rate dependence on the strain hardening of polymer nanocomposites. *ACS Macro Lett* 9:1224–1229
- Takahashi T (1996) Studies on the effect of molecular chain structure on elongational rheology, Ph.D. Thesis. University of Yamagata, Japan
- Takahashi T, Nakajima H, Masubuchi Y, Takimoto J, Koyama K (1998) Strain-hardening property and internal deformation of polymer composite melts under uniaxial elongation. *Sen-i Gakkaishi* 54:538–543
- Takahashi T, Takimoto J, Koyama K (1999) Uniaxial elongational viscosity of various molten polymer composites. *Polymer Composites* 20:357–367
- Tanaka H, White JL (1980) Experimental investigations of shear and elongational flow properties of polystyrene melts reinforced with calcium carbonate, titanium dioxide, and carbon black. *Polym Engng Sci* 20:949–956

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