

The Influence of Molecular Weight Distribution of Industrial Polystyrene on its Melt Extensional and Ultimate Properties

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We analyze the linear viscoelastic behavior and the strain-rate dependence of nonlinear viscoelastic as well as the ultimate extensional properties of industrially relevant linear polystyrene mixtures (PS). The studied materials comprise different miscible binary mixtures of a well entangled matrix and unentangled diluent resulting in bimodal molar mass distribution (MWD). We also analyze the effect of the diluent weight average molar mass (M_w) by comparison with a mixture having broad but monomodal MWD. We show that the dilution effect on linear rheological properties is in agreement with the theoretical value of unity for the dilution exponent. We further show that the processing window, expressed as the ability of the material to withstand a given load without loss of homogeneity during elongation or ultimate loss of cohesion, is affected differently depending on the diluent M_w and concentration. Finally, we conclude that the existence of strain hardening is not sufficient for complete characterization of extension dominated operations. Our results demonstrate that significant enhancement of strain hardening achieved by adding small- M_w diluents is often accompanied by trade-off with respect to failure behavior of these mixtures. POLYM. ENG. SCI., 56:1012–1020, 2016. © 2016 Society of Plastics Engineers

INTRODUCTION

In most processing operations, the polymer undergoes complex combinations of shear and elongation over a broad range of deformation amplitudes and rates. Understanding and predicting rheological properties during processing as well as the ability of the melt to undergo the applied stresses without catastrophic failure or instability is therefore of primary importance.

Generally, it is very challenging to mimic material behavior during complex processing operations using commercially available rheometric setups. However, some operations are dominated by a single type of deformation. This is, for instance, the case of fibre spinning, film tenting or film blowing, where the process is controlled by (nonisothermal) uniaxial or biaxial deformation. It is therefore crucial to understand the rate and temperature-dependent extensional properties of polymers to predict their behavior in processing operations.

Apart from unique custom built equipment utilizing lubricated squeezing flow [1–3] in a commercial scale true rheometers capable of controlling biaxial extension kinematics and measure the resulting stresses are practically unavailable. The

situation is fortunately different for uniaxial extension which is qualitatively related to biaxial extension. Indeed, since a few years, additional fixtures for measuring extensional viscosity at different strain rates are available for commercial rheometers.

Previous attempts to understand the link between the extensional properties of molten polymers and the characteristics of the corresponding end-products show that enhanced strain hardening and high strain-at-rupture in the melt provide better extensibility with more homogeneous morphology [4].

Strain hardening, also known as extensional thickening, can be described as the resistance of a polymer melt to stretching. It is observed as a steep increase of elongational viscosity at large strain, which deviates from the linear viscoelastic envelope. This material characteristic is related to the level of entanglements of the polymer and its resistance to disentangling under an applied strain at a given strain rate. The polymer properties affecting the resistance to disentanglement are molecular architecture (long-chain branching) [5–7], molecular-weight distribution (MWD) [8–10], and effective entanglement molecular weight [11, 12].

In references 5, 13, the authors study the extensional behavior of linear and branched polymers by comparing different structural characteristics of the final product. Results of their experimental correlation between uniaxial extension and biaxial extension dominated processes demonstrate that a linear polymer matrix exhibiting no strain hardening is also characterized by worse morphological characteristics in comparison with branched polymers with pronounced strain hardening.

On the other hand, Stange and Münstedt in Ref. 14 argue that different molecular structures characterized by similar strain hardening behavior lead to comparable extensional behavior. These authors also show that the existence of strain hardening itself is an important but not sufficient characteristic for extension dominated processes. Namely, the dominating factor is the correspondence between the characteristic processing strain rate and the strain rate at which hardening occurs. Moreover, the uniformity of deformation in the strain hardening phase is also a critical parameter.

This study builds on observations and predictions that dilution of an entangled polymer by an unentangled diluent can dramatically increase strain hardening. The extensional flow behavior of entangled and unentangled polymer solutions has been extensively studied in Refs. 8, 15–19. A recent study of the linear shear and nonlinear uniaxial elongational flow of concentrated polymer solutions by Huang et al. [11, 12] shows that while polymer melts and entangled solutions having the same number of entanglements are characterized by similar behavior under small angle oscillatory shear, the strain hardening of the

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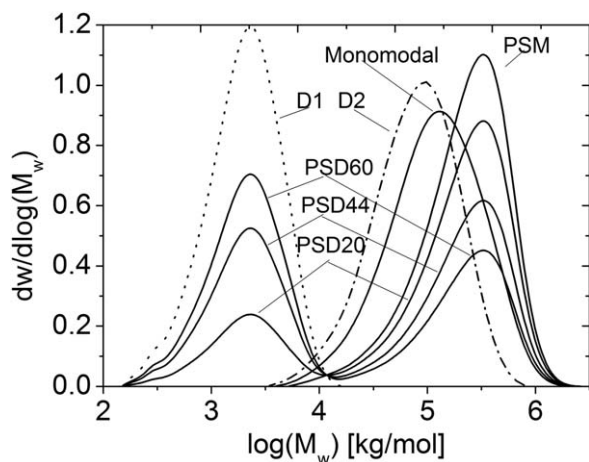


FIG. 1. Molecular weight distributions of the materials.

solutions is markedly enhanced as compared to the melts in strong extensional flow. This behavior is attributed in [12] to nematic interactions between polymer and diluent (solvent) that are negligible in the linear deformation regime but become significant under strong flow. The authors posit that reduced nematic interactions between a polymer and a low molar mass diluent can explain enhanced strain hardening compared to mixtures with higher molar mass diluents, which tend to become aligned with the neighboring chains.

In this paper, we also analyze the failure behavior of the samples under extension. Even though the subject remains poorly understood, there have been many attempts to advance in understanding the underlying physics of failure modes in startup uniaxial extension of entangled polymers. Since the pioneering works of Vinogradov and co-workers in the 1970s and 1980s, it has been recognized that polymers melt can fail either in a ductile or a brittle mode. A ductile-like behavior should be related to the ability of the polymer to rearrange its structure at large scale under flow. According to Ref. 19, the switch of the failure mode from yielding to elastic rupture is controlled by the Rouse Weissenberg number. Alternatively, Zhu and Wang [20] distinguish four different modes of failure behavior during startup uniaxial extension of entangled polymer melts: capillary, tensile decohesion, shear-yielding-induced necking, and rupture. The authors have also analysed origin of necking. They employ birefringence and particle-tracking velocimetric observations to reveal that localized shear yielding is a precursor to the nonuniform extension that finally leads to formation of a neck.

The specific objective of this study is inspired by the industrial relevance of improving strain hardening of polymer melts without compromising other mechanical properties. Thus we compare the effect of poorly entangled and unentangled diluents on the linear and nonlinear extensional viscoelastic properties and failure behavior of a well entangled linear polystyrene (PS) matrix. We will study the influence of diluent concentration and molar mass distributions of the mixture on those characteristics.

EXPERIMENTAL

Materials

We test mixtures having monomodal and bimodal molecular weight distributions. The bimodal systems are prepared by

mixing a well entangled PS matrix (PSM) with an unentangled styrenic diluent, referred to as “D1”. A monomodal mixture, labeled as “monomodal”, is prepared by mixing the same PS matrix with a fraction of poorly entangled PS referred to as “D2”.

We also analyze the effect of concentration of D1 in mixtures, referred to as “PSD20,” “PSD44,” and “PSD60” representing 20, 44, and 60 wt% diluent content, respectively. As we want to avoid significant reduction of T_g or phase separation upon dilution, the diluents (D1 and D2) have full miscibility with, and comparable with the matrix’s T_g .

All mixtures have been prepared by blending in a Brabender twin-screw extruder at $T = 220^\circ\text{C}$, which is a standard mixing protocol, utilized in industrial labs. This temperature may appear too high for the “safe” processing of polystyrene mixtures, therefore in order to verify that these conditions will not lead to the degradation of the mixture prior to blending, both components have been extruded and no changes in MFI have been detected. Moreover, a SEC-MALLS analysis presented in Fig. 1, shows no obvious trace of material degradation that could occur during mixing at 220°C . Such degradation should indeed be visible as a low molecular weight tailing of the SEC trace.

The glass transition temperatures are measured using Mettler Toledo DSC 821e at heating rate $10^\circ\text{C}/\text{min}$.

Table 1 summarizes the description of all materials used in this study.

Molecular Characterization

The characterization of the samples with respect to the molecular weight distribution is carried out using size-exclusion chromatography (SEC) coupled with a multiangle laser light scattering (MALLS) detector, and a refractive index detector. This method allows determination of the absolute mass average molecular weight of each SEC fraction.

SAOS Measurements

All measurements in small angle oscillatory shear are conducted using TA Instruments advanced rheometric expansion system (ARES). Parallel-plate fixtures of 25 and 8 mm were used for LVE measurements in a temperature range of $130\text{--}170^\circ\text{C}$ and a frequency range $0.01\text{--}100\text{ rad/s}$. All measurements are carried out within the linear regime as confirmed from strain sweep experiments. After loading and every temperature change the samples are equilibrated at constant

TABLE 1. Description of the materials.

Sample	Description
PSM	PS-matrix Pure PS matrix ($T_g \sim 105^\circ\text{C}$)
D1	Diluents Styrenic oligomer ($T_g \sim 95^\circ\text{C}$)
D2	Poorly entangled PS ($T_g \sim 102^\circ\text{C}$)
Monomodal	Effect of diluent’s M_w 65/35 D2/PSM ($T_g \sim 104^\circ\text{C}$)
PSD60 (bimodal)	60/40 D1/PSM ($T_g \sim 100^\circ\text{C}$)
PSD44	Effect of diluent concentration 44/56 D1/PSM ($T_g \sim 102.2^\circ\text{C}$)
PSD20	20/80 D1/PSM ($T_g \sim 103.0^\circ\text{C}$)

TABLE 2. Results from the SEC-MALLS analysis of all materials.

Sample	M_w (kg/mol)	PDI
PSM	306.5	2.45
Monomodal	182	2.64
PSD20	245.7	—
PSD44	172.8	—
PSD60	124	—
D2	116.7	2.22
D1	2.6	1.86

temperature during ~ 30 min until normal forces are completely relaxed. In the course of the measurements, the sample is kept under nitrogen protection to avoid thermal degradation.

We utilize time-temperature superposition principle (TTS) to extend measured frequency range of the dynamic storage, G' , and loss, G'' , modulus. The master curves are constructed using the same WLF shift factors: $C_1 = 8.57$, $C_2 = 73.35$ K at reference temperature $T_{\text{ref}} = 120^\circ\text{C}$. The temperature effect on density is taken into account according to the expression $G(T_0) = G(T)/b_T$, where $b_T = \frac{\rho(T)T}{\rho(T_0)T_0}$, as suggested in [21].

As mentioned above, both diluents are on purpose selected with their T_g approximately equal to that of the matrix. We can thus avoid applying iso-free-volume correction during construction of the master curves. Moreover, we argue that correcting experimental data for T_g differences can lead to misinterpretation of the effect of dilution on the polymer mechanical properties. However, solely for comparison with theoretical predictions of linear rheology, we compute horizontal shift factors using an extended WLF equation taking into account different T_g of the samples. Details will be presented in the results and discussion section.

Rheological Measurements in Elongation

We conduct measurements of nonlinear extensional properties using an ARES-rheometer equipped with an extensional viscosity fixture (EVF) at five strain rates: 0.01, 0.03, 0.1, 0.3, 1.0 s^{-1} and $T = 120^\circ\text{C}$.

All samples for the extensional rheology measurements are prepared from granular material using a hot press. Material granules are compressed during 25–30 min at 150°C . The long molding time is important to obtain stress-free equilibrated samples. Homogeneous rectangular plates made in this way are cut manually using a razor blade to produce strips with dimensions $[20 \text{ mm}(\text{length}) \times 3 \text{ mm}(\text{width}) \times 1 \text{ mm}(\text{thickness})]$ appropriate for uniaxial extension measurements.

We note that all measurements of extensional stress in this study are limited by the design features of the EVF fixture used. When strain reaches value of ~ 3.0 s.u. the sample starts to overlay on itself thus causing discontinuity of the measured data.

RESULTS AND DISCUSSION

Molecular Characterization

From the results of SEC-MALLS measurements presented in Fig. 1, two well-separated MWD corresponding to unentangled D1 (on the left) and well entangled matrix PSM (on the right) can be distinguished. It must be noted that the major fraction of

D1's molecular weight distribution is below entanglement molecular weight, which for PS is defined in the range of 13.16 kg/mol depending on level of description/type of the model used. On the other hand, the MWD of the sample labeled “monomodal” is obviously broader by comparison with that of PSM.

The weight average molar mass, M_w , and polydispersity index defined as $\text{PDI} = M_w/M_n$ are summarized in Table 2.

Linear Shear Rheology

As mentioned above, linear shear rheology measurements are conducted at different temperatures and later shifted according to TTS in order to construct master-curves at $T_{\text{ref}} = 120^\circ\text{C}$. The experimental linear dynamic moduli for all studied materials are presented in Fig. 2.

All systems analysed in this paper demonstrate broad terminal relaxation spectra typical for industrially relevant polymers. Therefore detection of the plateau modulus, G_N^0 , as well as exact determination of zero-shear viscosity, η_0 , is problematic, especially in the diluted samples. According to Ref. 22, approximate value of G_N^0 can be determined as the value of G' at a frequency corresponding to minimum value of $\tan \delta = G''/G'$, as illustrated in Fig. 2a.

In Fig. 3a and b we demonstrate the effect of dilution on G_N^0 and η_0 . The data suggests much stronger effect of dilution on the samples with bimodal distribution. Unfortunately, due to small number of data points, theoretical analysis of obtained G_N^0 as function of PSM fraction, assuming $G_N^0 \sim \phi^{1+d}$, does not provide unique value of the dilution exponent d . Instead, both previously reported values of $d = 1$ [15, 23, 24] and $4/3$ [25] seem to fit the same number of the points. On the other hand, the concentration dependence of zero-shear viscosity, determined from the same experimental data as $\eta_0 \approx \lim_{\omega \rightarrow 0} (G''(\omega)/\omega)$, and fitted as $\eta_0 \sim \phi^{1+2.4d}$ [26], is better with $d = 1$ (see Fig. 3b). We note, that obtained fit can barely be convincing as the number of data points is very small and also terminal relaxation zone of some of the measured $G^*(\omega)$ is not perfectly established. However, we will use $d = 1$ in the modeling section of this article and we will show that observed discrepancies have more fundamental origin that can not be fixed by solely adjusting value of d .

MODELLING ANALYSIS

In this section we present predictions of the dynamic complex modulus of our polymer mixtures. For this purpose we employ the state-of-the-art tube-based model BoB [27, 28].

This model has been reported to quantitatively predict both linear as well as nonlinear rheological properties of entangled branched polymers with industrial-level complexity [29]. However, to our knowledge, it has been poorly tested on linear polymers. Besides, due to the incomplete understanding of the constraint release effects, the state-of-the-art tube models are not capable to quantitatively predict the linear rheology of arbitrarily polydisperse systems without free adjustment of model parameters. Therefore modeling rheological characteristics of our polydisperse samples is a rather strong test for this model.

The following model parameters have been used in our predictions: molecular weights and PDI of each sample according to Table 2, monomer molar mass $M_0 = 104.15 \text{ g/mol}$, number of

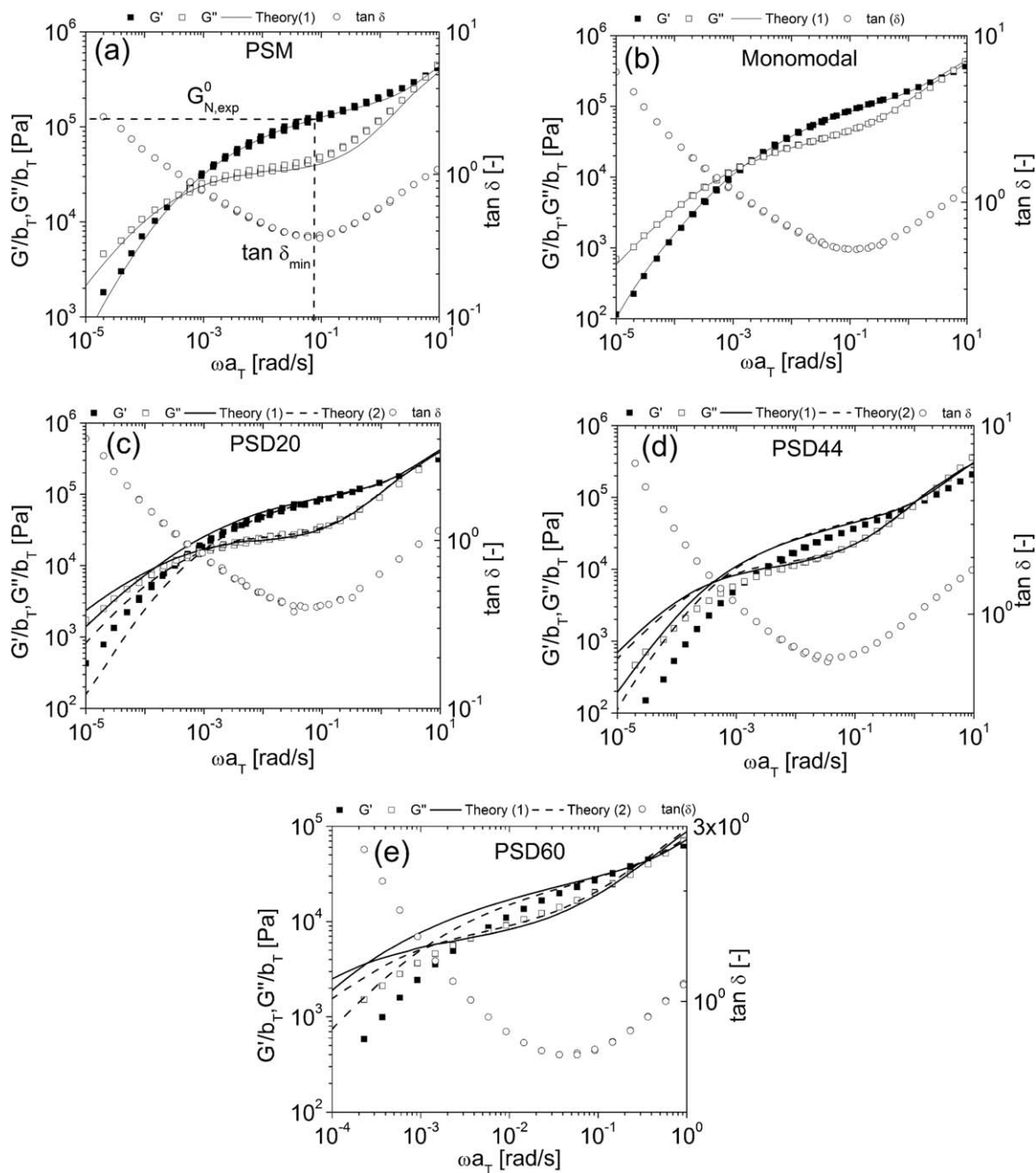


FIG. 2. Master curves of the viscoelastic storage G' , loss modulus G'' , and dissipation angle $\tan\delta$ confronted with the theoretical predictions obtained using BoB model ($M_e = 14$ kg/mol, $d = 1$, $N_c = 1000$). All master curves are constructed at reference temperature 120°C . Theory (1) demonstrates prediction of polymer chain reptating along the thin tube, whereas theory (2) corresponds to reptation along the current tube. The description and SEC-data of the samples are presented in Tables 1 and 2.

monomers in the entanglement strand $N_e = 134$, dilution exponent $d = 1$, number of chains for each component $N_c = 1,000$.

In our predictions we first attempt to use the recommended default set of settings for all systems. For example, in the default settings, chain reptation is modelled along the so-called “thin” tube composed of entanglements with polymer chains of any present molar masses.

For comparison with the experiments we horizontally shift the predicted curves according to the small differences in glass

transition temperatures of the samples (see Table 1). The shift factors are determined with respect to dynamic complex modulus of PSM [21]:

$$\log_{10} a_T = \frac{-C_1 (T_g^{PSM} - T_g)}{C_2 + T_g^{PSM} - T_g} \quad (1)$$

In the Fig. 2, we confront results of the theoretical predictions and the experimental data.

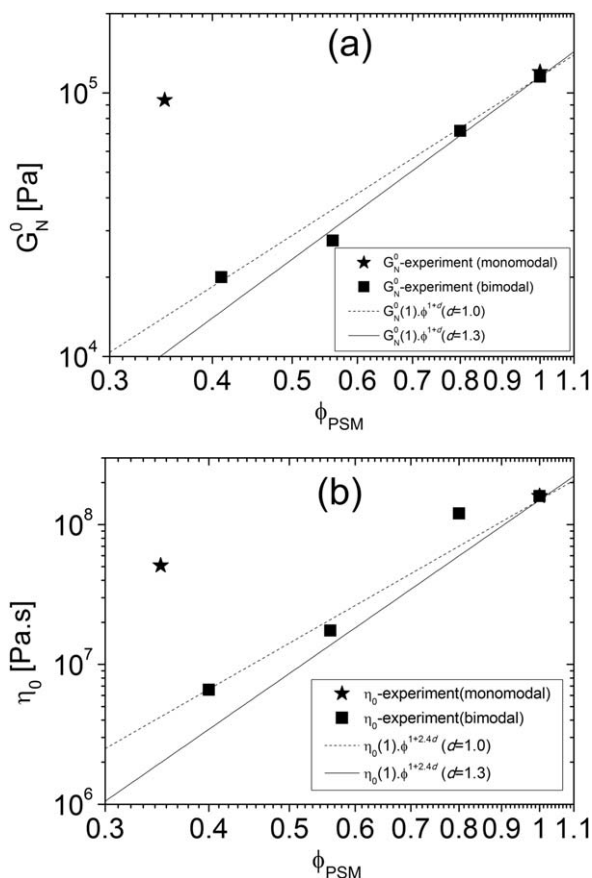


FIG. 3. Determination of the dilution exponent, d . The scaling of the sample's (a) plateau modulus G_N^0 and (b) zero shear viscosity η_0 as function of PSM fraction ϕ_{PSM} . The error bars are within size of the markers.

The comparison reveals that the model is capable of quantitatively good predictions of the monomodal mixtures (Fig. 2a and b). However, by increasing D1 fraction in the bimodal mixtures, the model predicts time-scale of the terminal zone somewhat larger than observed experimentally (Fig. 2c–e).

In our modeling all mixtures with D1 and D2 are presented as two-component blends with respective polydispersities. Alternatively, we tried to model bimodal blends as single component solutions of PSM with diluted in respective concentrations entanglement strands, $N_e(\phi) = N_{e,0}/\phi^d$, that is equivalent to 17.5, 12.3 and 8.8 effective entanglements of PSD20, PSD44 and PSD60, respectively. However, it did not improve quality of predictions. Therefore we assume that observed discrepancies could partially be attributed to the limited applicability of existing molecular models to poorly entangled systems [30, 31].

We have also analysed different “advanced settings” of the model by testing proposed “reptation schemes” which, in fact, represent different constraint release algorithms. In particular we have noticed that, as expected, the fastest relaxation corresponds to reptation Scheme 2, equivalent to Marucci's dynamic tube dilation algorithm [32], where the chain reptates along the tube with the time-dependent diameter. The slowest relaxation corresponds to the set by default Scheme 1, where the chain reptates along the thin tube (see Fig. 2c–e). There are also two modifications of Scheme 2, where user is proposed to choose at which moment tube dilation stops. The longest relaxation time

corresponding to these two options fall in the range between those predicted by Schemes 1 and 2.

Finally, we have tested this model by predicting transient elongation viscosity of our samples [28]. However, the obtained results do not reproduce the strain hardening behavior, that can possibly be explained by the model's primary applicability to branched polymer topologies.

Extensional Rheology

In this section we analyse the nonlinear elongational flow of our samples. Our primary interest is to observe and characterise their strain hardening behavior.

The strain hardening is typically observed if strain rate is higher than the inverse chain stretch relaxation time [25]. In case of undiluted melt, this time is identical to the Rouse time of the chain [26], which is $\tau_R = \tau_e Z^2$, where Z is the total number of entanglements per chain with weight-average degree of polymerization and τ_e is the Rouse relaxation time of a single entanglement segment. By using parameters from our BoB predictions of PSM: $\tau_e = 0.5$ s and $Z = M_w/M_e = 21.9$, where $M_w(\text{PSM}) = 306.5$ kg/mol and $M_e = N_e M_0 = 14$ kg/mol, we can compute $\tau_R = 240$ s. This suggests that even at the smallest strain rate of 0.01 s $^{-1}$ strain hardening can be observed. According to Auhl and co-workers [25], at small dilution characteristic stretch relaxation time increases in proportion to $\sim \phi^{-d}$. Therefore, the more diluted is the matrix the lower is the onset rate of its strain hardening.

In Fig. 4, results of the elongational behavior at different strain rates are presented as time-dependent stress growth coefficients. The stress growth coefficient is defined as $\eta_E^+(t) = \sigma_E(t)/\dot{\epsilon}_H$, where $\sigma_E(t)$ is the extensional stress and $\dot{\epsilon}_H = d \epsilon_H/dt$ is the Hencky strain rate. The Hencky strain is defined as $\epsilon_H = \ln(L(t)/L(0))$, where L is the length of the sample.

The linear extensional viscosity envelope is obtained from the respective complex shear modulus $G^*(\omega)$ decomposed into Maxwell modes:

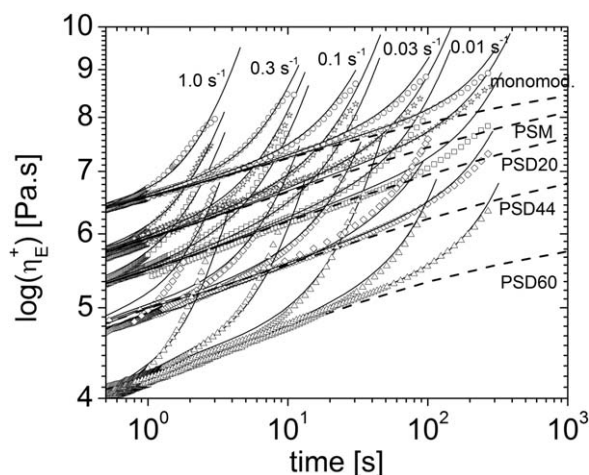


FIG. 4. Stress growth coefficient as function of time at different strain rates obtained at $T_{\text{ref}} = 120^\circ\text{C}$. Curves are shifted in vertical direction for a better visualization with the coefficients 4, 1, 1/2, 1/4, and 1/16 for monomodal, PSM, PSD, PSD44, and PSD60, respectively. Multimode Rolie-Poly fits (solid lines) and linear extensional viscosity envelopes (dashed lines) for every material are shown.

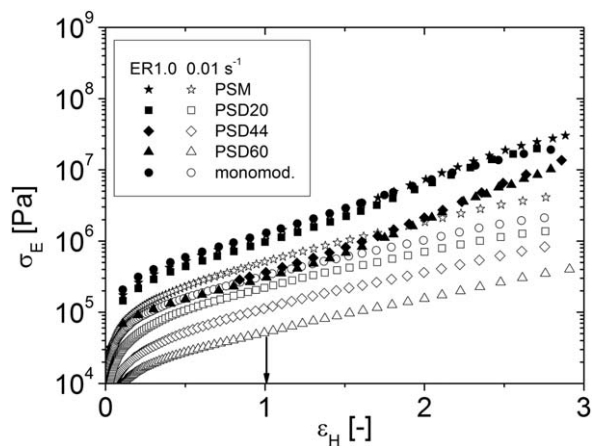


FIG. 5. Stress as function of applied strain ε_H as determined by uniaxial extension experiments at strain rates 1.0 s^{-1} (closed markers) and 0.01 s^{-1} (open markers). The arrow shows approximate value of strain at the onset of strain hardening.

$$\eta_{E,0}(t) = 3 \sum_i g_i \tau_i (1 - e^{-t/\tau_i}), \quad (2)$$

where g_i and τ_i are the modulus and relaxation time of the i^{th} Maxwell mode. We use the same modes in order to perform a multimode Rolie-Poly fit of the nonlinear data [33]. The figure demonstrates that all the elongational flow data is consistent with the independently measured linear rheology data. Besides that, as it was predicted, all studied materials are characterized by strain hardening behavior at every measured strain rate. This is clearly demonstrated by the divergence of the extensional viscosity from their respective linear viscosity envelopes.

In order to estimate the effect of dilution on the measured extensional stress, σ_E , and rate of strain hardening we demonstrate stress-strain curves of the samples (see Fig. 5). The data shows that despite enhanced strain hardening of the diluted samples the stress of pure PSM is higher than in all other mixtures. At strain rate 0.01 s^{-1} the stress is reduced proportionally to the fraction of oligomeric diluent (D1), however the effect of the higher molecular weight diluent (D2) is milder as suggested by comparison PSD60 with the “monomodal” sample. On the other hand, at the highest strain rate, measured stress seems less sensitive to the molecular weight and concentration of the diluent. The steeper slope of the curves at strain rate 1.0 s^{-1} , indicates higher rate of strain hardening. Using data in Fig. 4 we can estimate that at all probed strain rates divergence from the linear behavior occurs at ε_H of ~ 1 s.u.

In order to highlight differences between strain hardening of the materials in Fig. 6 we plot so-called strain hardening coefficients defined as:

$$X_E(t, \dot{\varepsilon}_H) = \eta_E^+(t, \dot{\varepsilon}_H) / \eta_{E,0}(t) \quad (3)$$

The data demonstrates that increasing the fraction of D1 leads to a steeper slope at the onset of strain hardening. This is especially clear at high strain rates (Fig. 6a); however, this difference ceases at lower rates. A similar conclusion can be made after comparison of the “monomodal” and corresponding bimodal sample as shown in Fig. 6b. The bimodal sample shows

slightly steeper slopes at the onset of strain hardening as compared to the “monomodal”.

As can be seen in Fig. 7, where only the maximum values of X_E are shown, in the limit of low strain rates ($< 0.1 \text{ s}^{-1}$), all materials demonstrate similar strain hardening behavior. At increasing rates, all diluted samples demonstrate remarkable growth of X_E as compared to pure PSM. Finally, a downturn is observed for PSD20 and PSD44 following its maximum values at 0.03 s^{-1} . In contrast, X_E of the most diluted bimodal sample PSD60 demonstrates a plateau at rates above 0.1 s^{-1} . An attempt to rationalize this observation will be made in the next section.

The strain hardening behavior of the “monomodal” sample is very similar to that of pure PSM.

By comparing PSD60 with the “monomodal” mixture, i.e. samples having similar diluent fractions but very different diluent molecular weights, it can be clearly seen that the molecular weight of the diluent dramatically affects the strain hardening behavior of the PS matrix in particular at high strain rates. This observation is in accordance with results presented in Ref. 12. According to Huang and co-workers, nematic interactions in the diluted polymer mixtures impose anisotropy in the system and thereby reduce their strain hardening. They argue that nematic

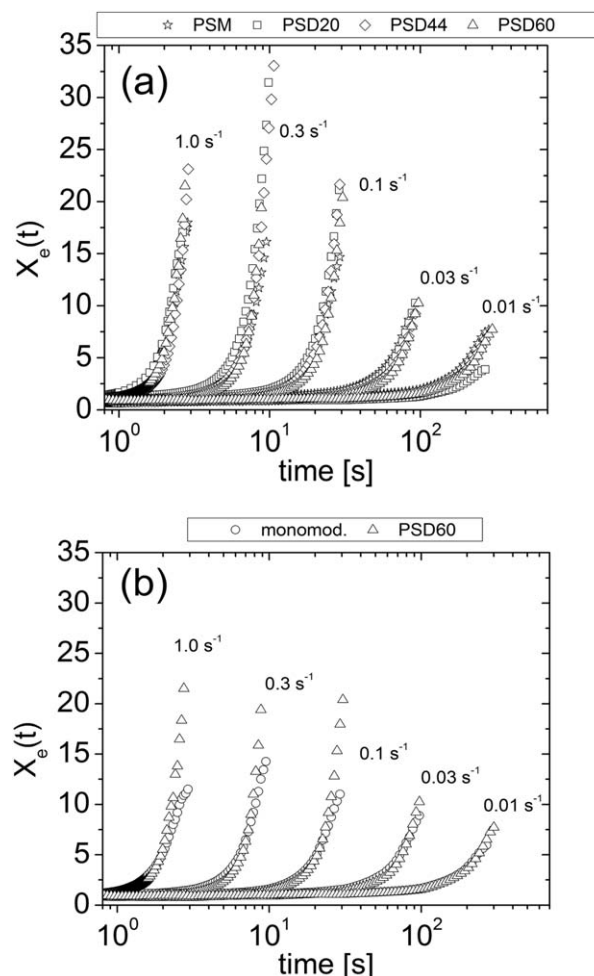


FIG. 6. Strain hardening coefficient X_E as a function of time at different strain rates, obtained at $T_{\text{ref}} = 120^\circ\text{C}$. (a) PSM mixed with various concentrations of D1; (b) Samples with monomodal and bimodal molar mass distribution with comparable fractions of the diluents.

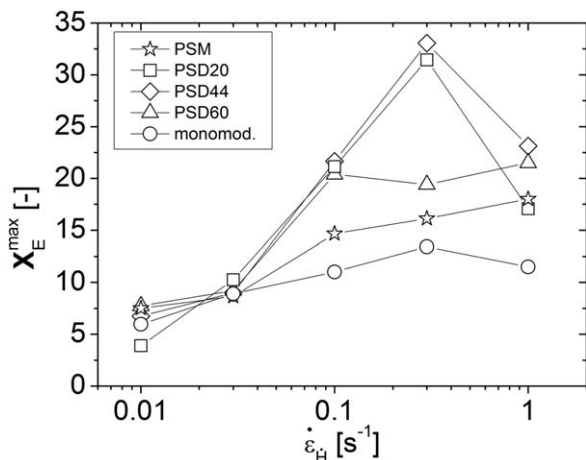


FIG. 7. Maximum strain hardening coefficient, $X_E^{\max}$, as function of strain rate, $\dot{\epsilon}_H$, obtained at $T_{\text{ref}} = 120^\circ\text{C}$. The error bars are within size of the markers. Lines are drawn for directing the reader's eye.

interactions between polymer matrix and diluents are proportional to the molar mass of the diluent and therefore mixtures with shorter diluents strain harden more.

Failure Behavior in Uniaxial Elongational Flow

Although the processability of polymeric materials is primarily governed by their viscoelastic properties, the processing parameters are also constrained by the ultimate load that can be handled by the polymer melt without loss of integrity. In this section, we analyze the failure behavior of the samples upon extension.

The dynamic instability referred throughout this paper as *failure* is indicated by the appearance of “necking” that progressively develops until complete breakage of the sample. This homogeneity limit can be predicted from the *Considère* condition [34, 35], which states that a viscoelastic material under transient extension is homogeneously deformed only if the engineering stress, σ_E (force/initial area) is an increasing function of extension.

$$\frac{d\sigma_E}{d\epsilon_H} \geq 0 \quad (4a)$$

Equivalently, this condition states that for homogeneous elongation, the Trouton ratio ($Tr = 3X_E$) should increase at least exponentially in order to overcome the exponential decrease of the cross section area:

$$\frac{d \ln Tr}{d\epsilon_H} \geq 1 \quad (4b)$$

In our experiments, we measure strain until the sample is completely separated in two parts (this is indicated by the measured torque decreasing below 0.001 N.m). We refer to this limiting strain as strain-at-rupture and we measure it at different $\dot{\epsilon}_H$.

Results presented in Fig. 8a demonstrate strain-at-failure at different strain rates. The dependence on strain rate is insignificant if one takes into account error bars. However, absolute values of strain-at-failure are localized between those of the

“monomodal” and PSD60. This is especially well pronounced at low and medium rates, whereas at the highest rates rupture often happens even before the onset of necking and thus difference between samples ceases.

In Fig. 8b the dependence of the strain-at-rupture on $\dot{\epsilon}_H$ is shown. The data points are better localized, as compared to Fig. 8a and clear step-like profile can be observed around a critical strain rate of 0.1 s^{-1} for all materials with bimodal molar mass distribution. This is characterized by an abrupt decrease (by $\sim 50\%$) of the ultimate Hencky strain from the maximum observed at lower $\dot{\epsilon}_H$. According to Ref. 36 this transition can be attributed to a change of the ultimate strain regime from viscoelastic or ductile at low rates (i.e., a direct consequence of necking) to brittle failure (i.e., solid-like crack propagating failure) characterized by lower limiting strains at high rates often occurring even before loss of homogeneity.

Interestingly, this transition is slightly smoother for materials with a lower fraction of D1 and especially the monomodal mixture. This is a surprising observation especially considering that the only difference between the monomodal mixture and PSM

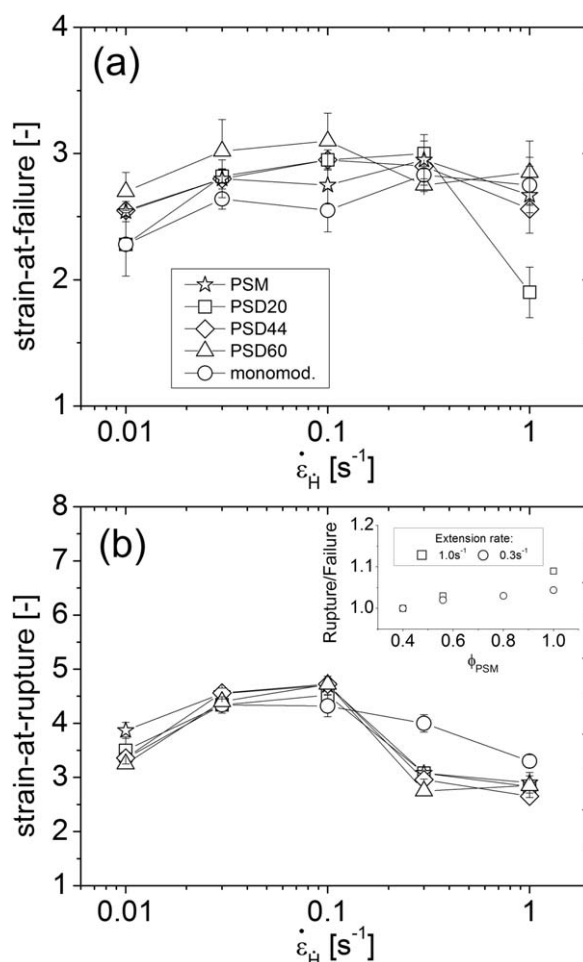


FIG. 8. (a) Dependence on strain rate of strain-at-failure, (b) strain-at-rupture measured at $T_{\text{ref}} = 120^\circ\text{C}$. Inset in (b) demonstrates ratio between average values of strain-at-rupture and strain-at-failure at strain rates 0.3 and 1.0 s^{-1} as function of PSM concentration. The error bars represent standard deviation from the average value obtained from 3 to 5 measurements. Not shown error bars are of the size of the markers. Lines are drawn for directing the reader's eye.

(which is also monomodal) is a slightly broader molar mass distribution of the former.

By comparing Fig. 8a and b, it can be concluded that the processing window, governed by the ability of the material to withstand a given load without loss of cohesion is affected differently by the diluents of different molecular weights. However, contrary to the strain-at-failure, no pronounced concentration effect D1 on the strain at decohesion is observed for all bimodal mixtures. In the inset of Fig. 8b we plot ratio between average values of strain-at-failure and strain-at-rupture of our bimodal samples at the two highest probed strain rates (0.3 s^{-1} and 1.0 s^{-1}). Ratio equal to unity shown by PSD60 at both rates, corresponds to the case when decohesion of the sample occurs before loss of homogeneity of deformation, that we attribute to elastic rupture. By reducing fraction of D1, we observe gradual change of the type of failure towards ductile-like, which occurs as a consequence of necking. Thus, at both strain rates we observe similar tendency, that failure mode of the sample can be slightly modified upon mixing with the unentangled diluent.

This plot explains the plateau observed at high strain rates of PSD60 in Fig. 7, where sample ruptures elastically at strain of ~ 3 s.u.

CONCLUSIONS

The goal of this study was to analyze the trade-off between improved strain hardening and ultimate mechanical properties for mixtures of entangled polymer and a diluent. We have studied the linear shear and nonlinear extensional behavior of industrially relevant linear PS. Tested materials comprised different binary mixtures of matrix and unentangled diluent with well separated M_w 's as well as a monomodal mixture with broad MWD.

Obtained results can be summarized as following:

- The dilution effect on G_N^0 and η_0 , induced by adding unentangled diluent, is found to be in agreement with the theoretical value of the dilution exponent d ($=1$).
- The effect of diluent molecular weight and concentration is clearly seen from the stress growth coefficients. Contrary to the monomodal diluted sample, mixtures with well separated M_w 's show pronounced buildup of X_e and a steeper slope at the onset of strain hardening proportionally to the diluent concentration at high strain rates.
- In relation to the ultimate behavior, we have demonstrated that the processing window, governed by the ability of the material to withstand a given load without loss of homogeneity during elongation and ultimate loss of cohesion, can be affected differently if blended with diluents of different molecular weights as well as concentrations. For example, we observed that dilution with D1 enhances limit of homogenous deformation of the sample, determined by Considère criterion, but at higher rates sample ruptures in an elastic manner at much lower strains even before the onset of necking.
- Conducted tube-based modeling using BoB model have demonstrated good agreement with linear rheology of the monomodal samples. However, the model is not able to obtain as good results for our bimodal linear samples. We have concluded that observed discrepancies should be addressed to the consequences of current incomplete understanding of constraint release effects and limitations of applying tube models

to poorly entangled components, rather than disadvantages of any specific tube-based model. We thereby hope that this work will further motivate theoreticians to develop a fully predictive tube model for industrially relevant linear polymers.

In summary, we have demonstrated that existence of strain hardening behavior is not sufficient for complete characterization of extension dominated operations. The results obtained in this study illustrate that the enhancement of strain hardening achieved by adding small- M_w diluents is often accompanied by a trade-off with respect to sample's ultimate properties.

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