Flow induced crystallization prevents melt fracture of HDPE in uniaxial extensional flow

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This work concerns extension induced crystallization of a commercial high density polyethylene above the equilibrium melting temperature. We compare the nonlinear response during uniaxial elongation to the morphology obtained in the quenched fibers after cessation of the flow at a Hencky strain of 5. At 12°C above the melting temperature, the samples undergo brittle fracture. Samples stretched at 2 and 6°C above the melting temperature remain intact throughout the entire course of deformation and exhibit a strain hardening behavior that does not follow time temperature superposition. We propose that stabilization of the filament at lower temperatures, as well as the failure of time temperature superposition, is caused by flow-induced nucleation and growth of shish structures oriented along the flow direction. Further justification obtained from small-angle X-ray scattering performed on quenched filament showing an increased formation of shish with increase in deformation rate. We find the critical Hencky strain for the onset of shish formation to be between 0 and 0.6, which is significantly lower than the values reported in the existing literature. We model the influence of shish nucleation on the rheological response in extension using the hierarchical multimode stress function, which is modified to include the stretched network assumption.

I. INTRODUCTION

It has long been known that deformation enhances the tendency for polymers to crystallize. Flory [1] used equilibrium thermodynamics to explain the effect for cross-linked networks in terms of equilibrium thermodynamics. Basically the reduction in entropy upon stretching of the polymer chains lowers the entropic penalty in passing to the crystalline state. For flowing polymer melts, the mechanism of formation of crystalline structures is a more complicated problem, that has yet to be fully understood [2]. Some aspects of the problem have been resolved. Combined rheology and in-situ scattering methods have revealed that stretching of the high-molecular-weight fraction upon the application of flow causes the formation of needlelike nuclei [3, 4]. These nuclei grow into shish structures and only at a much later stage does the overgrowth of kebabs occur [5]. These needlelike nuclei are believed to be caused by threadlike precursors [6, 7]. However, the nature of these precursors, the mechanism of their formation and transition into nuclei in the flow remain to be resolved. For threadlike precursors to arise, some degree of chain deformation is necessary. The extent of deformation needed, however, is debated as well [8] along with considerations on how to interpret a melt containing precursors. Recent experimental studies suggest that considering the nucleating melt as a stretched network [8–11] yields a better description than the traditional coil-stretch transition proposed by Keller and Kolnar [4].

Resolving these questions is important, as flow-induced shish-kebab structures tremendously enhance the mechanical properties of the final material [12]. What is not so often emphasized, however, is the fact that these structures influence the mechanical properties of the melt, too. Recently, Li and co-workers found that after an extensional step strain is imposed on an iPP melt, flow-induced shish prevent the sample from necking. Necking is the result of a flow instability that arises in uncontrolled extension [13–15]. While the failure caused by necking is an interesting and relevant problem, it does not reveal insights into the true strength of the material and the reinforcement upon shish formation. A true fracture experiment can reveal the strength of a melt in extension, as well as the mechanism of failure, as performed by Huang et al. on amorphous systems [16, 17]. The fracture mechanics of semicrystalline systems undergoing flow-induced crystallization (FIC) has yet to be studied in controlled extension.

In this work, we study a commercial HDPE subjected to controlled uniaxial extensional flow above the melting temperature. We study the reinforcement of the filaments by shish nucleation and growth and its ability to prevent brittle fracture. Using a filament stretch rheometer combined with high-speed imaging, we study the fila-
ments and their extensional response during deformation. Ex-situ small-angle X-ray scattering (SAXS) reveals the morphology of the filaments after the cessation of the flow. In addition we attempt to model the rheological response using the hypothesis that a nucleating melt behaves like a cross-linked network.

II. MATERIALS AND METHODS

We investigated a commercial HDPE (CP00416-021 from Chevron Philips), referred to as "PE-460k" with 0.2 short-chain branches/1000 backbone carbons. The molecular weight distribution was characterized in a Polymer Laboratories GPC220 instrument with 2*30cm PlOlexis columns and a PlOlexis guard column operated at 160 °C with 1, 2, 4 trichlorobenzene as eluent and 200 ppm BHT as antioxidant. The measurements are shown in Figure 1a, from which \( M_w = 460\) kg/mol and PDI = 2.7, were determined. (Note: the values of \( M_w \) given by the supplier were slightly higher at 530 kg/mol and 3.0, respectively.)

Differential scanning calorimetry (DSC) measurements were performed on a Discovery DSC from TA Instruments in a nitrogen atmosphere with a heating and cooling rate of 10 °C min\(^{-1}\) from 50 to 200 °C. The samples weighed approximately 2-5 mg. The melting temperature 138.0 °C was obtained from an endothermic peak in the second heating process.

Samples for all rheological characterizations where molded into discs of diameter 8-9 mm and height 0.5-2.5 mm. Molding was carried out either in a hot press (165 °C, 30 min) or a vacuum mould (150 °C, 15 min). These conditions where found sufficient for erasing the thermo-mechanical history as annealing for longer (up to 48 h) in a vacuum oven at 160 °C or in the rheometer at 150 °C did not change the results (i.e. fracture, rheology or FIC).

The linear rheology was characterized in SAOS using an Ares G2 (TA Instruments) with 8 mm parallel plate geometry and creep using an MCR702 (Anton Paar). The creep data obtained at 150 °C was inverted initially to storage and loss compliance [18] and then to storage and loss moduli as described in Wingstrand et al. [19] (see also Münstedt and co workers [20, 21]). Inverted creep data and the frequency sweeps from SAOS obtained at 140-190 °C were combined using the time temperature superposition principle (TTS) to obtain mastercurves of dynamic moduli over a wide range of frequencies. Because of the very high molecular weight tail, the terminal regime at which \( G’ \) and \( G'' \) reach a slope of 2 and 1, respectively, was inaccessible experimentally, even in creep. In fact the shoulder at low frequencies appears consistent with a tail of about 5.000 kg/mol and the 3.4 scaling law, starting from the crossover, which is assigned to 530 kg/mol. The horizontal shift factors \( \alpha_T \) and an Arrhenius fit are shown in the inset of Figure 1b. The linear response was fitted by a multi-mode Maxwell model

\[
G(s) = \sum_i g_i \exp(-s/\tau_i).
\]  

The moduli \( g_i \) and time constants \( \tau_i \) of the nine modes are given in Table I, see also Figure 1b.

We conducted uniaxial extensional experiments at con-
stant Hencky strain rates \( \dot{\varepsilon} \). The instrument used was a filament stretch type rheometer (VADER 1000 from RheoFilament). It allows for on-line control of the true Hencky strain given by \( \varepsilon = -2 \ln(D/D_0) \) where \( D \) and \( D_0 \) is the current and initial diameter respectively [22–25]. The true stress of the material during deformation is in its simplest form given by \( \sigma_{zz} = \sigma_{rr} = (F - \frac{1}{2}mg)/(\frac{\pi}{4}D^2) \) where \( F \) is the measured axial force, \( m \) the mass of the filament and \( g \) the gravitational acceleration. Correction for initial shearing contribution is described elsewhere [26]. The experiments were performed at three different temperatures (140°C, 144°C and 150°C) and terminated by quenching to room temperature at a Hencky strain \( \varepsilon = 5 \). We used shift factors determined from SAOS (see inset in Figure 1b) to adjust the Hencky strain rates such that all samples where stretched at the same relative rates \( \alpha_T \dot{\varepsilon} \) irrespective of temperature. For selected samples the filament deformation was recorded using a high speed camera (FASTCAM Mini UX100 from Photron) with a LED light source placed either on the same side or opposite the camera.

Small angle X-ray scattering (SAXS) of the quenched filaments was performed using a Rigaku S-MAX 3000 system with a Gabriel design Multiwire, gas-filled proportional type detector (resolution: 200 microns). The sample-to-detector distance was 1525 mm and the exposure time for each pattern was 15–30 min. Patterns were collected from the mid-filament plane of the samples.

III. RESULTS AND DISCUSSION OF UNIAXIAL EXTENSION EXPERIMENTS

Figure 2 shows the rheological response of PE-460k in uniaxial extensional flow at three different temperatures: 140, 144 and 150°C. The results are given in terms of extensional stress versus Hencky strain at the same values of \( \alpha_T \dot{\varepsilon} \) which eliminates further need for TTS shifting. At low deformation rates \( \alpha_T \dot{\varepsilon} = 0.01 \) and \( 0.03 \text{s}^{-1} \), the start up responses at all three temperatures overlap including the apparent steady flow condition reached at \( \varepsilon \geq 4 \). The overlap implies that the nature of the response is independent of temperature and therefore, that TTS applies at low deformation rates. At high deformation rates \( \alpha_T \dot{\varepsilon} \geq 0.1 \text{s}^{-1} \), TTS breaks down and the response becomes highly temperature dependent. At 150°C, the sample undergoes brittle fracture at strains \( \varepsilon < 1 \). At 140°C and 144°C, PE-460k can be stretched beyond \( \varepsilon = 1 \) without undergoing fracture, but the rheological response at the two temperatures differs. The strain hardening at 140°C is significantly more pronounced than at 144°C. As the response of PE-460k at 140°C and 144°C do not overlap for \( \alpha_T \dot{\varepsilon} \geq 0.1 \text{s}^{-1} \), TTS do not apply in this region. The break down of TTS indicates that a flow induced phenomenon occurs with a characteristic time that does not scale with regular chain dynamics. We argue in the following, that the phenomenon in question is flow induced crystallization (FIC) that furthermore reinforces the filament and prevents fracture.

The observations from Figure 2 can be grouped in three regimes as illustrated in Figure 4. 1) The TTS-regime where the response is independent of temperature, 2) The fracture regime in which stretching to \( \varepsilon = 5 \) is impossible due to failure of the filament and 3) The FIC-regime where strain hardening due to FIC prevents the filament from fracturing.

Figures 3a and b show the difference between stretch experiments performed within FIC and fracture-regimes, respectively. Figure 3b shows a wedge-like edge fracture that separates the filament into two parts with flat surfaces as shown in the inset. By contrast, in the FIC-regime (Figure 3a), the filament remains intact with a smooth surface throughout the entire stretch. In the following, the two regimes will be analyzed in more detail.

A. The fracture regime

This section solely focuses on the fracture regime from Figure 4 where all stretch experiments results in brittle fracture. Figure 5 shows time resolved images of the filament during fracture. Multiple cracks propagate simultaneously [16] and influence the profiles of adjacent cracks. We use the early stages of the crack propagation, where the profile is less perturbed by adjacent cracks, to further analyse the fracture mechanics.

Time-resolved images similar to those shown in Figure 5 allow us to plot the crack opening at several different times in a common coordinate system as shown in Figure 6A. Here 0 ms, arbitrarily indicates the time for the first clear detection of a crack profile while 29 ms indicates the surface 29 ms later and so on. For each time, the coordinate system is shifted to have origin at the crack.
FIG. 3. Images of PE-460k in elongational flow stretched at $\dot{\varepsilon} = 0.18 \text{s}^{-1}$. a) at $T = 140^\circ \text{C}$ b) at $T = 150^\circ \text{C}$. The inset shows the filament after fracture. All images are obtained with camera and light source on the same side. Bright spots on the filament and top plate surface are reflections from the light source. The yellow dashed lines indicate vertical positions of sample-plate boundaries.

FIG. 4. Diagram delineating three types of dynamic behavior of PE-460k in uniaxial extension for combinations of reduced stretch rate (abscissa) and temperature in Centigrade (ordinate): the TTS-region where the melt satisfies the Time-Temperature Superposition principle, the Fracture-region where the melt fractures before reaching $\varepsilon = 5$ and the FIC-region where FIC occurs and prevents the filament from fracturing.

Hencky strain unit, we may compare the deformation rates from Figure 6A with the LVE spectrum in Figure 1. For $0.5 \text{rad/s} < \omega < 10^2 \text{rad/s}$ the loss tangent $\tan \delta = G''/G' \leq 1$ indicating primarily solid like behavior. This is in agreement with the parabolic trend [27] in Figure 6A.

It remains to rationalize the crack velocity. For an incompressible purely elastic material the crack velocity is limited by the speed of the shear wave $v_s = \sqrt{G/\rho}$ where $G$ is the shear modulus [27, 28]. For a viscoelastic liquid, the corresponding expression is $v_s = \sqrt{G'/\rho(1 + \frac{3}{8} \tan^2 \delta + \cdots)}$ ([29], the ratio $\omega/\beta$ in Example 5.4-1 expanded for small $\tan \delta$ so a small amount of dissipation does not alter the shear wave velocity materially. Since both expressions give shear wave speeds orders of magnitude greater than the measured crack velocity (of order $1 \text{mm/s}$) we conclude that inertia is not the limiting effect for the crack speed. Even with the parabolic trend in Figure 6A, we suggest therefore that dissipation is an important effect in the fracture process. For a single mode Maxwell model of time constant $\tau$ de Gennes [30] suggests that the parabolic crack profile close to the crack tip opens up in a trumpet-like profile for distances larger than $v_s \tau$. While the present PE-460k is far from a single mode material, one might argue that the dissipation is visible by the small tendency to a trumpet-like opening of the crack profile [16, 17] for distances more than about $0.2 \text{mm}$. Thus we arrive at a fracture regime with primarily elastic edge fractures albeit with crack speeds influenced by dissipation.
FIG. 5. Development of multiple cracks in the midfilament region for PE-460k stretched at $\dot{\varepsilon} = 0.18\,s^{-1}$ and $T = 150^\circ$C. Yellow, blue and red indicate regions where cracks are developing. $t = 0$ s is defined as the time at which the crack indicated by the blue circle is initiated.

FIG. 6. Fracture analysis for PE-460k stretched at $\dot{\varepsilon} = 0.18\,s^{-1}$ and $T = 150^\circ$C. a) Fracture profiles showing the initial development of the crack propagation. b) Crack length for three cracks. Red and blue symbols correspond to the cracks lengths observed for fractures indicated by blue and red circles, respectively in fig. 5. Black symbols show the crack length for the fracture in a) with black line being the best linear fit yielding a crack tip velocity of $V = 0.92\,mm/s$

B. The FIC-regime

This section focuses on the FIC-regime from Figure 4. In this regime brittle fracture is believed to be suppressed by reinforcement of the filament due to FIC even though experiments are carried out above $T_m$. Previous studies have shown that FIC in polyethylene subjected to strong flows is indeed possible above $T_m$ [31–33] due to a flow induced transition from the folded chain crystals that make up spherulites and kebabs to the considerably more stable extended chain crystals found in shish having a higher $T_m$.

Evidence of flow-induced crystallization during flow is present both in the nonlinear extensional rheology and ex-situ scattering patterns. The signs of FIC in the extensional rheology (Figure 2) are first of all absence of steady flow for stretch experiments within the FIC-region. Second, for experiments conducted at 140°C at the highest rates ($\dot{\varepsilon} = 0.3$ and 0.54 s$^{-1}$) a rate-independent response is observed at $\varepsilon > 4$. Third, break down of TTS. The first two characteristics suggest that the sample un-
The flow direction angle between the normal of the kebab-planes and the direction. We determine \( F \) in the crystalline domains and a given macroscopic deformation. The orientation for all filaments, irrespective of the presence of FIC (i.e. crystallization occurred only after cessation of flow) have found a one-to-one relation between the orientation factor \( F_{H,max} = 1 \) (perfect unidirectional orientation). Thus, \( F_{H} \) cannot keep increasing and a plateau region in which \( F_{H,max} = 1 \) is expected for the ideal case. Polymers are far from ideal. In fact, for PE-460k the maximum orientation factor appears to be around 0.7.

### IV. MODELLING EXTENSIONAL RHEOLOGY

We use the hierarchical multi mode stress function (HMMSF) formulated by Narimessa and Wagner as a base for modelling the nonlinear extensional behavior of PE-460k [38, 39]. Any other nonlinear models using a discrete spectrum of relaxation times, e.g. the Rolie-Poly, could be used as well [40].

The HMMSF model calculates the total stress tensor \( \sigma \) as a sum of stress contributions \( \sigma_i \) from each Maxwell mode:

\[
\sigma = \sum_i \sigma_i
\]

where \( \sigma_i \) is given by:

\[
\sigma_i(t) = -\frac{g_i}{\tau_i} \int_{-\infty}^t e^{-(t-t')/\tau_i} S_{DE}^A(t,t') f_i^2(t,t') dt'
\]

Here \( S_{DE}^A \) is the Doi-Edwards orientation tensor using the independent alignment approximation [41–43] and \( f_i \) is the segmental chain stretch of mode \( i \). Detailed descriptions of the model along with definition of \( S_{DE}^A \) and \( f_i \) can be found elsewhere [19, 38]. The HMMSF model contains one fitting parameter \( G_D \), the dynamic dilution modulus. It is a point along the relaxation modulus that separates permanently diluted chain segments from dynamically diluted chain segments.

Figure 10 shows the HMMSF prediction using \( G_D = 600 \) Pa and the Multimode Maxwell spectrum given in Table I compared with experimental data. At \( \varepsilon < 3 \) the measured response is relatively well captured by the HMMSF model for all deformation rates. However, as the model does not consider FIC, it does not capture the strain hardening due to FIC observed at \( \varepsilon > 3 \) for experiments conducted in the FIC regime (i.e. \( \alpha_T \varepsilon \geq 0.1 \)). Several studies use the onset of discrepancy between the nonlinear model and data to define the onset of crystallization [33, 44]. In the following sections we propose an alternative and in our opinion more accurate way to detect the onset of crystallization.

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\( \langle \cos^2 \phi \rangle = \frac{3}{2} \)

\[ F_H = 3 \langle \cos^2 \phi \rangle - 1 \]

---

\( T \)

---

\( \sigma \)

---

\( \tau \)

---

\( \varepsilon \)

---

\( \alpha \)

---

\( \varepsilon_{\text{crit}} \)

---

\( \sigma_{\text{crit}} \)

---

\( T_m \)

---

\( T_g \)

---

\( F \)

---

\( F_{H,max} \)

---

\( G_D \)

---

\( S_{DE}^A \)

---

\( f_i \)

---

\( \langle \rangle \)

---

\( \alpha_T \)

---

\( \alpha \)

---

\( \varepsilon \)

---

\( \alpha_T \)

---

\( \varepsilon \)
FIG. 8. SAXS patterns of PE-460k filaments at room temperature after uniaxial stretch above $T_m$ and quench at $\varepsilon = 5$. The stretching direction is vertical. The red, blue and black outlines indicate the boundaries for the TTS-region, the FIC-region and the Fracture-region.

FIG. 9. Herman’s orientation in quenched filaments versus the stress at quench. Symbols indicate filaments stretched at 140°C (black), 144°C (red), and 150°C (blue). The solid line is a guide to the eye showing two regions: one with a slope of 2/5 followed by a plateau region. The dashed line shows the linear relation observed in amorphous systems.

A. Incorporating FIC into the HMMSF model

In this section we incorporate the effect of crystallization into the HMMSF model. Several approaches to modelling FIC exist [45–48]. In this study, we consider the nucleating melt as a stretched network as illustrated in Figure 11 where we use the non-dimensional extension rate $Wi_R = \dot{\varepsilon} R$ based on the time constant for molecu-
lar stretch relaxation $\tau_R$. Crystalline nuclei are assumed to trap several chain segments in a nucleus and thus effectively act as a cross-link. The idea was originally introduced by Penning and co-workers [49] and in recent years experimental studies [8–11, 50, 51] seem to prefer the stretched network idea over the coil-stretch transition proposed by Keller and Kolnar [4].

We incorporate the stretched network assumption into the HMMSF model by modifying the relaxation time spectrum - not the model itself. If just a few nuclei exist, effectively the melt is weakly cross-linked, and therefore only the slowest modes are effected. If the density of nuclei is high, the relaxation of faster modes are effected as well. The modes effected by cross-links are set to have a relaxation time $\tau = \infty$. In the following, these modes are referred to as locked modes. Modes with a finite relaxation time are referred to as free modes. The modes are hierarchically locked meaning that a fast mode $i$ cannot lock unless all modes slower than $i$ are locked, as well. The effect of locking modes on the relaxation modulus is illustrated in Figure 11b. We assume that the cross-linking density is constant throughout the stretch, and hence, that the number of locked modes during a given stretch is constant. The model as implemented here assumes that very fast modes are not affected by crystallization. Of course this is not totally correct because when the nuclei are formed, also a lot of long and short dangling chains are formed. The motion of such dangling chains would also contribute to change the spectrum in the region of the faster modes. In fact, the number of locked modes also serves as a fitting parameter which could be eliminated by incorporating a kinetic model for FIC. In addition, we neglect latent heat released by crystallization, changes in density caused by crystallization and any influence from the spatial size of the nuclei. These assumptions are expected to be valid only during the initial stage of crystallization, when the sizes of crystalline domains are small and hence, the degree of crystallinity limited.

Figures 12a and b show the results of the modelling for 140 and 144 °C, respectively. This approach, indeed, enables the influence of shish formation on the extensional rheology to be captured. Note in particular that at 140 °C and $a_T \dot{\varepsilon} \geq 0.3$ the stress becomes independent of the stretch rate once $\dot{\varepsilon} \geq 4$. Even this behavior, normally associated with solids, is taken into account in the model.

B. Considerations on the onset of FIC

As previously mentioned several studies use the onset of discrepancy between measured extensional response and the nonlinear model prediction without crystallization as the onset of crystallization [33, 44]. To investigate if indeed this discrepancy is a sensitive indicator of the onset of FIC we compare in Figure 13 the effect of locking modes versus leaving them free for $a_T \dot{\varepsilon} = 0.3$ and 0.1 s$^{-1}$, respectively. It shows that evidence of FIC in the rheology appears at $\dot{\varepsilon} > 3$ (red dashed lines in Figure 13). The onset of crystallization may, never the less, have occurred any where between $\dot{\varepsilon} = 0$ and 3. In fact comparing experiments from the FIC-region with experiments conducted in the fracture region (Figure 4) enables a more accurate determination of the onset of crystallization. We hypothesize that nucleation and growth of shish in the FIC-region (i.e. 140 and 144 °C) reinforce the filament and enables extensional flow without failure caused by brittle fracture. In order for FIC at a given $a_T \dot{\varepsilon}$ to prevent brittle fracture, the onset must occur prior to the fracture strain observed in the fracture region for the same $a_T \dot{\varepsilon}$. The fracture strain for $a_T \dot{\varepsilon} = 0.1$ to 0.3 s$^{-1}$ is $\approx 0.6$ for all rates at 150 °C. Consequently the onset of crystallization at 140 and 144 °C must have been between $\dot{\varepsilon} = 0$ and 0.6. That is assuming that the fracture mechanics is independent of temperature from 140 to 150 °C. The new span of $\dot{\varepsilon}$ for the onset of crystallization is much smaller than the one obtained from the rheology and the values are surprisingly low. It suggests that initiation of shish nucleation does not require large deformations. A moderate deformation of just $\dot{\varepsilon} = 0.6$ is sufficient. This value is quite low compared to previously reported values [8, 33, 44] as a result of a more sensitive approach in detecting the onset of crystallization.

V. CONCLUSION

We have shown that flow-induced shish nucleation and growth in uniaxial extension above $T_m$ can stabilize filaments and prevent true fracture. We find the critical strain for the onset of shish formation to be $\leq 0.6$, which is quite low compared to previously reported values. We have shown that under the conditions tested here, the qualitative influence of crystallization on the extensional rheology can be captured by incorporating the stretched network assumption into the HMMSF model. The modelling suggests that while the locking of chains between nuclei is introduced at low Hencky strain, the effect remains invisible to rheology until much higher Hencky strains. The number of locked modes is a fitting parameter. More work will be needed to arrive at a fully predictive model including locking of the modes.

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FIG. 11. Stretched network assumption principle and effect on relaxation modulus. a) Illustration of the principle behind the stretched network assumption during uniaxial deformation and the effect. Top row show flow induced nuclei (red) imbedded in an amorphous polymer matrix (blue) going from low $Wi_R$ (left) to high $Wi_R$ (right). Bottom row shows how the effect of flow induced nuclei is modelled by substituting flow induced nuclei with effective cross-links. Flow direction is horizontal. b) Shows the effect of locking modes on the relaxation modulus. A lock mode $i = 7$ means that the 7th, 8th and 9th mode have $\tau_i = \infty$.

FIG. 12. Comparison of the measured extensional stress (symbols) and HMMSF predicted extensional stress using locked modes (lines) of PE-460k (A) at $T = 140^\circ C$ and (B) $T = 144^\circ C$. The value of nonlinear fit parameter $G_D = 600$ Pa, and nine Maxwell modes are used in the modelling. Depending on the stretch rate $\dot{\varepsilon} [1/s]$ the following modes are locked: For A) 0.54 and 0.30: modes 7, 8 and 9; 0.18: modes 8 and 9; 0.10: mode 9; 0.030 and 0.010: no locked modes. For B) 0.30: modes 8 and 9; 0.18: mode 9; 0.10, 0.030 and 0.010: no locked modes. A locked mode $i$ has $\tau_i = \infty$.

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FIG. 13. Comparison of the basic HMMSF model (dashed lines) and the HMMSF model including stretched network (solid lines). Black lines indicate the total stress colored lines indicated contributions from selected modes. a) for $\dot{\varepsilon}_T = 0.3 \text{ s}^{-1}$ and b) for $\dot{\varepsilon}_T = 0.1 \text{ s}^{-1}$. Vertical red dashed lines indicate the point at which the total stress is influenced by FIC.