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A new semi-phenomenological approach to predict the stress relaxation behavior of thermoplastic elastomers

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Abstract

In this paper we report on a new semi-phenomenological approach to predict the stress relaxation behavior of thermoplastic elastomers at long times. This approach relies on the method of Gurtovenko and Gotlib [J Chem Phys 115 (2001) 6785], which has originally been conceived to describe the relaxation dynamics of inhomogeneously crosslinked polymers forming agglomerations of crosslinks. In this work we demonstrate that the method can be extended to predict the stretched exponential stress decay of homogeneously crosslinked thermoplastic elastomers, which are subjected to an extensional strain pertaining to the nonlinear regime of mechanical properties. In our approach thermal fluctuations induce fluctuations in size of domains of crosslinks via a chain-pullout mechanism. We compare our theoretical predictions to the experimental measurements of Hotta et al. [Macromolecules 35 (2002) 271] performed on poly(styrene-isoprene-styrene) triblock copolymers, which are composed of hard domains of polystyrene embedded in a rubbery polyisoprene matrix. Our study confirm the importance of the chain-pullout mechanism in the stress relaxation process and demonstrates the involvement of multiple time- and structural-length-scales.

Keywords: Stress relaxation of thermoplastic elastomers; Size fluctuations of crosslink domains; Chain-pullout mechanism

1. Introduction

Thermoplastic elastomers are high performance elastomers engineered to enhance the performance capabilities of a wide spectrum of end products and applications. For example, the poly(styrene-isoprene-styrene) (SIS) triblock copolymers are generally used for pressure sensitive applications, where durability and elasticity are important. For high molecular weights and at low temperatures the two endblocks composed of polystyrene (PS) are thermodynamically incompatible with the midblock composed of polyisoprene (PI). This causes the system to microphase separate into soft and hard domains both being rich in either one of the components. Depending on the volume fraction of one block, the microphase separated structure may be periodically arranged in spherical or cylindrical domains of one component in a continuous matrix of the other component or it may be arranged in a lamellar structure in which the two components alternate [1]. As a consequence of the emergence of new high-performance catalysts many more exciting morphologies have been discovered recently [2–5]. It appears, however, that testing all novel materials for all their properties is a very time-consuming and cost-intensive task. Therefore, new theoretical approaches, which can explain and reliably predict their properties, are of inestimable interest and can open new perspectives for many new technological innovations [6–8].

Among many challenges, the prediction and understanding of the stress relaxation behavior is of particular importance, because it provides informations about the molecular mechanisms affecting the macroscopic properties of the material. The stress relaxation behavior of thermoplastic elastomers at long times has been studied in several experimental investigations [9]. Chasset and Thirion [10] recognized that an excellent representation of their data at

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long times $t \gg \tau_p$ is given by a power-law equation of the type

$$E(t) \approx E_{t\to\infty}[1 + (t/\tau_p)^{-\gamma}] \tag{1}$$

where $E(t)$ is the isothermal relaxation modulus. The parameter $E_{t\to\infty}$ is the equilibrium modulus, while γ and τ_p are material parameters. In later investigations it has been established that $E_{t\to\infty}$ and τ_p depend on the temperature and crosslink density of the material [11,12], while γ does not [13]. Ferry [11] has speculated that the molecular processes associated with the power-law decay are related to the relaxation of loops and free dangling chains attached to the hard domains in the polymer network. He assumed that their relaxation is slow because of the presence of entanglements, which act as topological constraints. This picture has been confirmed by the studies of Curro and Pincus [11,12]. However, from stress relaxation experiments on several thermoplastic elastomers it is well-known that above a characteristic temperature deviations from power-law behavior do occur [9,14]. Smith [9] concluded from his experiments on a poly(styrene-butadiene-styrene) (SBS) triblock copolymer that the deviations are due to plastic flow and breakup of the domains, which he presumed to be relatively soft at these temperatures. Hotta et al. [14] deduced from their experimental investigations that their SIS copolymers undergo a stretched exponential stress relaxation of the type

$$E(t) \approx E_{\tau_s\to\infty} \exp[-(t/\tau_s)^{\beta}] \tag{2}$$

where $0 < \beta < 1$ and $E(t)$ is the time-dependent effective extensional modulus defined through the stress–strain convolution integral

$$\sigma(t) = \int E(t-t')\frac{\mathrm{d}\varepsilon(t')}{\mathrm{d}t'}\mathrm{d}t' \tag{3}$$

with $E_{\tau_s\to\infty}$ as the modulus for $\tau_s \to \infty$. They suggested that the stretched exponential decay might be the result of a readjustment of the network, taking place through a chain-pullout mechanism.

Relaxation phenomena obeying a stretched exponential decay behavior have been found in several relaxation processes, such as, e.g. in the relaxation of glasses, polymers and gels [15]. Their occurrence is generally attributed to the existence of a disorder or/and strong interactions in the system, which cause a superposition of different exponential processes or a superposition of intrinsically non-exponential processes. For example, in Ngai's approach [16] the relevant network units relax independently obeying an exponential relaxation at times $t < t_c$, where t_c represents a characteristic crossover time. At $t > t_c$ these units undergo a transition to a stretched exponential-type relaxation due to strong interactions with neighboring units, causing a constrained motion and therefore a slowing down of the relaxation. In a recent paper Gurtovenko and Gotlib [15] demonstrated that a stretched exponential decay in an inhomogeneously crosslinked network may also be caused by a broad size distribution of non-interacting network regions each composed of a certain number of relaxing elements (crosslinks, polydisperse chains, etc.). According to their approach the behavior is a consequence of structural heterogeneities in the polymer network, which cause a superposition of the relaxation processes of the different domains in the network. These inhomogeneities may, e.g. occur by applying a mechanical deformation on polymer films or gels [17,18]. In such cases agglomerations of crosslinks are created, whose number of relaxing elements (crosslinks) determine the contribution to the overall modulus of the relaxation process.

In this paper we investigate the possibility of a stretched exponential decay behavior of the relaxation modulus in a homogeneously crosslinked network with transient crosslinks, which forms domains of different number of relaxing elements if subjected to a nonlinear extensional deformation. These domains are created through thermal fluctuations inducing themselves fluctuations in the domain sizes via a chain-pullout mechanism. The domain sizes obey a probability distribution derived from the equilibrium fluctuation theorem [19]. We compare our theoretical predictions to the experimental measurements of Hotta et al. [14] performed on SIS triblock copolymers with either a spherical or cylindrical arrangement of PS hard domains in a rubbery PI matrix. Experimental evidences for the readjustment of the transient network under deformation are in particular the persistent change in the sample dimensions after unloading and the recovery of the original sample shape at long times and/or upon annealing [14,20]. Hotta et al. explained this phenomenon by the assumption of a chain-pullout mechanism.

Our paper is structured in the following way. In Section 2 we introduce the theoretical approach employed in this work, followed in Section 3 by a brief recall of the stress relaxation experiments performed by Hotta et al. with the different SIS morphologies. Afterwards, in Section 4 we derive the probability distribution of the domain sizes using the equilibrium fluctuation theorem, while in Section 5 we present the results of our theoretical investigation in comparison to the experimental measurements mentioned previously. Finally, we end the paper by conclusions and a brief outlook.

2. Theoretical model

2.1. Relaxation of domains of crosslinks

We start with the introduction of the domain-model approach of Gurtovenko and Gotlib, which describes the relaxation dynamics of polymer network structures embedded in an effective viscous medium. To this end, let us consider a crosslinked polymer as an ensemble of network regions (domains) each having a finite number of crosslinks (relaxing elements). All the domains possess a homogeneous internal network structure and consist of n relaxing elements connected with each other in an arbitrary way. In Fig. 1, we show a sketch of the domain model in case of a SIS copolymer. We see that the system forms domains of crosslinks via a chain-pullout mechanism. Inside the domains the network consists of a regular homogeneous arrangement of spherical PS micelles, which are interconnected by bridging chains of PI. This property permits to treat the polymer inside the domains as a network composed of regularly arranged junctions connected by coarse-grained effective chains. On the junctions free dangling chains and loops are attached, responsible for the slow power-law decay inside the domains. We emphasize that the model can easily be generalized to other phase morphologies, like, e.g. the hexagonally packed cylinders of PS embedded in a PI matrix. Now, let us focus on the long-time viscoelastic properties of our crosslinked polymer by determining the dynamic behavior of such an ensemble of network domains at long times. The domains distinguish themselves only by their different number of relaxing elements. Moreover, they are embedded in an effective viscous medium, which is common for all the domains and takes into account the stochastic character of contacts of the chain segments not explicitly included in the model. Next, we suppose that there are enough relaxing elements inside the domains and that, under a nonlinear deformation and upon thermal activation, our single-domain system splits reversibly into a broad size distribution of domains and undergoes fluctuations in the domain sizes via a permanent network readjustment. These domain size fluctuations are induced by thermal fluctuations causing fluctuations of stresses on a local scale. Regarded from a molecular perspective, the forces on a particular bridging chain decrease the activation barrier of the process of pulling the chain out of the PS hard domains it connects. Depending on the local concentration of the physical entanglements in the PI matrix, the pullout process propagates in a fracture-like fashion at low entanglement concentration or, if the propagation is hindered, manifests itself in form of readjustments by partially pulling the chains out of the PS hard domains. Both dynamical processes cause that the copolymer reversibly splits into several domains of different size. The copolymer under the imposed tensile strain is driven in a new equilibrium state under the influence of the external perturbation. The dynamical equilibrium ensures that the system remains homogeneous and does not crack, while allowing an efficient stress relaxation. In the following we further assume in a first approximation that the different domains relax independently of each other with characteristic relaxation times and boundaries determined by the network fluctuations [21]. We suppose that these fluctuations essentially occur at the PS–PI interfaces, as has recently been observed by Alig et al. by investigating SIS copolymers with lamellar morphology employing dielectric spectroscopy [22]. The viscoelastic response of such an ensemble of domains to an external perturbation can be reproduced by the response of a number of Maxwell elements connected in parallel [23]. As a consequence, the overall modulus $E(t)$ of the relaxation process, given through the stress–strain convolution integral in Eq. (3), is the result of the superposition of the relaxation moduli of the different network domains, relaxing independently of each other. Gurtovenko and Gotlib demonstrated that the size distributions of the network domains in polymers generally obey particular probability distributions [15,21]. We will show in the following that, to describe equilibrium fluctuations in the domain sizes, the Gaussian distribution is a reasonable assumption. Moreover, we will see that in the terminal relaxation zone all the domains have relaxed, excepting the one with the maximal amount of relaxing elements. This causes that in this regime no superposition is possible anymore, and the domain with the largest amount of relaxing elements entirely determines the final relaxation behavior.

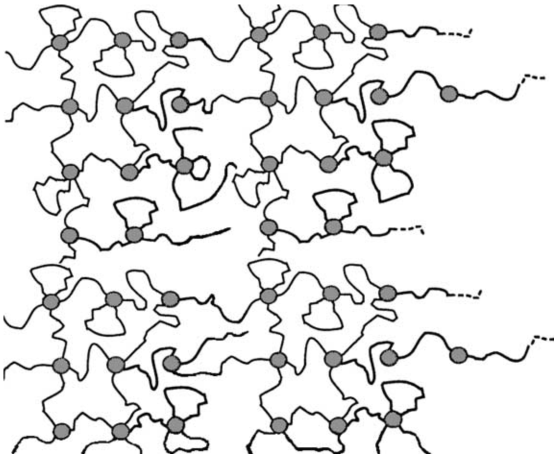

Fig. 1. Domains formed in a SIS copolymer under nonlinear tensile deformation and at temperatures above the characteristic temperature T^*.

2.2. Relaxation inside the domains at short and long times

Let us now suppose that our thermoplastic elastomer at low temperatures is an elastic solid and obeys a classical rubber-like power-law relaxation. With growing temperature the material approaches the glass transition temperature of the PS hard domains at which the system transforms from a rubbery solid to a viscous liquid [18]. Above this temperature the PS hard domains go over in the melt state, but they remain interconnected by the PI chains. In the transition region the mechanical properties of the polymer network are intermediate of the two states and the material behaves as a critical gel [24,25]. With further increase of the temperature the material undergoes an additional phase transformation known as the order–disorder transition, above which the copolymer chains are randomly distributed in the system. In this work we are essentially interested in the regime below the order–disorder transition, where the chains are phase separated, and we can assume that the internal relaxation of the domains of crosslinks is due to the dangling chains and loops attached to the PS crosslinks [11, 12,14]. In these domains we can suppose a power-law internal relaxation of the type

$$E(t,T) = E_{t\to\infty}(T)\left[1 + \left(\frac{t}{\tau_0(T)}\right)^{-\gamma}\right] \tag{4}$$

where $\tau_0(T)$ characterizes the minimal relaxation time of the domain which is a function of the temperature T [11]. The parameter $\gamma > 0$ is the power-law exponent. Since all the domains of crosslinks consist of the same type of relaxing elements and have identical internal architecture, the minimal relaxation time at a given temperature can be considered to be similar for all the domains.

Alternatively, the viscoelastic properties of a polymer network can also be described in terms of the relaxation spectrum $H(\tau)$, representing the distribution function of relaxation times τ on a logarithmic scale. The quantity is related to the relaxation modulus $E(t)$ via the formula [26]

$$E(t) = E_{t\to\infty} + \int_{-\infty}^{\infty} H(\tau)\exp[-t/\tau]\mathrm{d}\ln\tau \tag{5}$$

Let us now consider the relaxation spectrum $H(\tau, T, n)$ of a domain of n number of crosslinks at a temperature T. Since each domain has a finite size, it can be characterized by a maximal relaxation time $\tau_{\max}(n)$, and we can accordingly write for the relaxation modulus of the domain

$$E(t,T,n) \approx E_{t\to\infty}(T) + \int_{-\infty}^{\ln\tau_{\max}(n)} H(\tau,T,n)\exp[-t/\tau]\mathrm{d}\ln\tau \tag{6}$$

The maximum relaxation time $\tau_{\max}(n)$ represents a specific time of the network domain, characterizing the maximum relaxation time of a dangling chain (or loop) surrounded by the neighboring crosslinks [27]. It separates contributions of network motions of different length-scales. The intra-chain and crosslink motions have characteristic times smaller and greater than $\tau_{\max}(n)$, respectively. The intra-chain motions, responsible for the power-law relaxation at $t < \tau_{\max}(n)$, are generally attributed to the slow diffusion of the dangling chains by arm retraction in the presence of topological constraints in the surrounding medium [11,12]. At times $t > \tau_{\max}(n)$ and scales of network motions larger than the average distances between the crosslinks, the large-scale collective crosslink motions are excited and their contribution to the overall relaxation modulus becomes predominant. It is worth noting that the motions of the bridging chains (inter-chain motions) should be excited at earlier times than the collective crosslink motions and should appear on an intermediate branch of the relaxation spectrum. However, their contribution is expected to be negligible due to the regularity of the network, which is taken into consideration by the concept of effective chains. It is also worth pointing out that at times around $\tau_{\max}(n)$ the intra-chain relaxation process begins to provide only a constant contribution proportional to $E_{t\to\infty}(T)$, which is independent of time [27]. To derive an explicit expression for the maximum relaxation time $\tau_{\max}(n)$, we suppose that all the domains possess a sufficiently large number of crosslinks, i.e. $n \gg 1$. In such cases the relaxation times τ and the distribution of eigenvalues λ inside a network domain can be assumed to be a function of the continuous variable ξ, numbering internal relaxation modes. It can easily be shown that the relaxation time $\tau(\xi, n, T)$ of a specific mode ξ in a domain of size n is related to the minimum relaxation time $\tau_0(T)$ through the formula (see derivation in Appendix A)

$$\tau(\xi,n,T) \approx \tau_0(T)\left(\frac{n}{\xi}\right)^{1/\gamma} \tag{7}$$

Now, if we suppose that at $\xi = 1$ all the modes of the domain have relaxed, we get the maximum relaxation time of the domain as

$$\tau_{\max}(n,T) = \tau(\xi = 1,n,T) \approx \tau_0(T)n^{1/\gamma} \tag{8}$$

We see that, because $\gamma > 0$, the maximum relaxation time of a domain increases with the number of relaxing elements. To derive the relaxation modulus of the domain at times $t > \tau_{\max}(n)$, we express the relaxation spectrum H in terms of the continuous variable ξ, which gives

$$H(\tau,T,n) = -E_{t\to\infty}(T)\frac{1}{n}\frac{\mathrm{d}\xi}{\mathrm{d}\ln\tau} \tag{9}$$

in the limit of large number of crosslinks in the domain [15, 28]. Next, inserting Eqs. (9) and (7) in Eq. (6), we obtain

$$E(t,T,n) \approx E_{t\to\infty}(T) - \frac{E_{t\to\infty}(T)}{n} \times \int_0^1 \exp\left[-\left(\frac{t}{\tau_0(T)n^{1/\gamma}}\right)\xi^{1/\gamma}\right]\mathrm{d}\xi \tag{10}$$

which can easily be shown to give

$$E(t,T,n) \approx E_{t\to\infty}(T)\left(1 + \frac{\gamma}{n}\left(\frac{\tau_{\max}(n,T)}{t}\right)\exp\left[-\left(\frac{t}{\tau_{\max}(n,T)}\right)\right]\right) \tag{11}$$

where $\tau_{\max}(n, T)$ is defined by Eq. (8). In conclusion, we deduce from the result in Eq. (11) that at times $t > \tau_{\max}(n, T)$ the relaxation modulus of a domain with n crosslinks is composed of a product of slow power-law and fast exponential relaxation. Such a type of time behavior of the relaxation modulus is caused by the cutoff the relaxation spectrum of the given domain and is a consequence of its finite size. Moreover, we see that at long times $t \gg \tau_{\max}(n, T)$ the main contribution to the relaxation modulus of a domain is provided by the exponential term in Eq. (11).

2.3. Relaxation of the ensemble of network domains

Next, we derive the overall relaxation modulus $E(t, T)$ of a polymer network of the type introduced in the previous sections, which is composed of an ensemble of network domains. As already mentioned, the quantity is a consequence of the superposition of the relaxation moduli of all the domains forming the network, which only differ through their size. In other words, each domain provides its specific contribution to the total modulus, whose amount depends on the number of relaxing elements n in the domain. Following the approach of Gurtovenko and Gotlib, we suppose that the domain sizes are distributed according to a normalized distribution function of the following form [15]:

$$p(n) = \frac{n^\sigma \exp[-an^\delta]}{\int_0^\infty n^\sigma \exp[-an^\delta]\, \mathrm{d}n} \tag{12}$$

where δ and σ are parameters characteristic for the type of network motion under consideration, while a is a parameter related to the average number of crosslinks in the domains $\langle n\rangle$ [15]. Next, using the number distribution function in Eq. (12) for averaging over all the domains, we obtain the relaxation modulus of the network ensemble in the time interval $t \gg \tau_0(T)$.

$$\begin{aligned} E(t,T)|_{t\gg\tau_0(T)} &\approx \int_0^\infty p(n)E(t,T,n)|_{t\gg\tau_{\max}(n,T)}\mathrm{d}n \\ &= E_{t\to\infty}(T)\int_0^\infty \frac{n^\sigma \exp[-an^\delta]}{\int_0^\infty n^\sigma \exp[-an^\delta]\,\mathrm{d}n} \\ &\quad \times \left[1 + \frac{\gamma}{n}\left(\frac{\tau_{\max}(n,T)}{t}\right)\exp\left(-\frac{t}{\tau_{\max}(n,T)}\right)\right]\mathrm{d}n \end{aligned} \tag{13}$$

Now, by taking into account the dependence of $\tau_{\max}(n,T)$ on the number of crosslinks, Eq. (8), and using the saddle-point procedure for large times $t \gg \tau_0(T)$, to evaluate the integral in Eq. (13), we finally obtain

$$\begin{aligned} E(t,T) &\approx E_{t\to\infty}(T) \\ &\times \left[1 + \frac{C_1}{\langle n\rangle}\left(\frac{t}{\tau^*(T)}\right)^{(\sigma-3\delta/2)/(1/\gamma+\delta)} \exp\left(-\left(\frac{t}{\tau^*(T)}\right)^{\delta/(1/\gamma+\delta)}\right)\right] \end{aligned} \tag{14}$$

where τ^* is a characteristic relaxation time determining the stretched exponential decay and C_1 is a constant. It can easily be shown that τ^* is proportional to the maximum relaxation time of the domain realized with maximal probability $\tau_{\max}(\langle n\rangle,T)$, i.e. [15]

$$\tau^*(\langle n\rangle, T) = C_2\tau_{\max}(\langle n\rangle, T) = C_2\tau_0(T)\langle n\rangle^{1/\gamma} \tag{15}$$

where C_2 represents a constant. In conclusion, we deduce from Eqs. (14) and (15) that the decay behavior of the overall relaxation modulus at long times is controlled by the relaxation time τ^*, which depends on the temperature T and the average domain size $\langle n\rangle$.

3. Tensile stress relaxation experiments

In Ref. [14] one of us (A. Hotta) reported on tensile stress relaxation measurements at different temperatures using SIS copolymers with a PS weight fraction of 14 and 17%, respectively. These copolymers form microphase separated structures, where either spherical or cylindrical hard domains of PS are embedded in a rubbery PI matrix. Both copolymers have been provided by Aldrich Chemical Corporation. The total molecular weight was 245,000 g/mol for the SIS copolymer of 14% PS and 160,000 g/mol for the SIS copolymer of 17% PS, which implies a molecular weight of 17,150 and 13,600 g/mol for each terminal PS block, respectively. The glass transition temperatures T_g of the PS and PI phases in both SIS copolymers were measured by differential scanning calorimetry. Hereby, the T_g of PI and the T_g of PS were measured at −50 and 65 °C for the SIS copolymer of 14% PS and −55 and 72 °C for the SIS copolymer of 17% PS, respectively. The test samples were homogeneous and transparent, indicating no sign of degradation. The samples were extended to 125% of their original length at temperatures between 4 and 90 °C. The force on the sample and the temperature were measured as a function of time for 2 days after the deformation.

In these experiments Hotta et al. observed that, below a characteristic temperature of $T^* \sim 30$ °C, the curves of the relaxation modulus of both SIS copolymers obey a power-law decay, which was interpreted as the typical mechanical response of a permanently crosslinked rubber. In contrast, they noticed that above T^* the relaxation curves show a faster than power-law decay, which could best be reproduced by a stretched exponential functional form. In this regime an apparently non-recoverable change of sample length at constant crosslink density after a long period of deformation was observed. In later experiments on similar materials Dair et al. [20] discovered that, even if the original sample length is not recovered immediately upon unloading, it is recovered at long times and/or high temperatures. The reversibility of the deformation process implies long-time viscoelasticity and excludes the implication of plastic flow or breakage of the PS hard domains, which typically cause permanent irreversible deformations [20]. The phenomenon has been explained with the existence of transient crosslinks, which allow under force the pulling out of the bridging chains from the crosslink aggregates. Based on differential scanning calorimetry measurements, no evidence for a structural phase transformation at T^* could be found, which is in support of a unique underlying mechanism.

The equations, that were determined to fit the experimental curves optimally, are recalled in the following. Below T^*, the best fit to the experimental relaxation curves of the SIS copolymer with 14% PS was obtained using the following power-law equation:

$$E(t) \approx E_{t\to\infty}(1 + 1.6t^{-0.12}) \tag{16}$$

while above T^* the best fit was determined to be a stretched exponential of the form

$$E(t) \approx 835 \exp\left[-\left(\frac{t}{\tau^*}\right)^{0.2}\right] \tag{17}$$

Similarly, the experimental data of the SIS copolymer with 17% PS was best fitted below T^* with the power-law equation

$$E(t) \approx E_{t\to\infty}(1 + 2.2t^{-0.15}) \tag{18}$$

while above T^* the best fit to the experimental relaxation curves was obtained using a stretched exponential of the type

$$E(t) \approx 1088 \exp\left[-\left(\frac{t}{\tau^*}\right)^{0.2}\right] \tag{19}$$

4. Distribution of domain sizes

To derive an expression for the distribution of domain sizes in the polymer networks under consideration, we assume that at long times and above a certain temperature T^* the domains are formed via a chain-pullout mechanism, induced by network fluctuations on scales larger than the average distance between the crosslinks. These domains differ only in their respective number of relaxing elements, which fluctuates around the average value $\langle n\rangle$. Using the fluctuation theorem, it can easily be shown that this number obeys a Gaussian distribution (see Appendix B)

$$p(n) \propto \exp\left[\frac{(n-\langle n\rangle)^2}{2\Lambda^2}\right] \tag{20}$$

which can be reexpressed in the form

$$p(n) \propto g(n) \exp\left[-\frac{n^2}{2\Lambda^2}\right] \tag{21}$$

where Λ is the standard deviation and $g(n) = \exp(n\langle n\rangle/\Lambda^2)$. As the relaxation of the system progresses in time, the contribution of the domains with large number of crosslinks, i.e. $n \gg \langle n\rangle$, becomes more significant with regard to the smaller domains and determine the long-time relaxation behavior. This can easily be made clear by considering the relaxation function $E(t,T,n)$ of a single domain given in Eq. (11), which describes its relaxation behavior at times $t > \tau_{\max}(n,T) \approx \tau_0(T)n^{1/\gamma}$. The size dependence of $\tau_{\max}(n,T)$ in the exponential causes that the small domains relax earlier than the larger ones and, thus, provide a decreasing contribution as the relaxation progresses. The effect is amplified with increasing temperature in the system. In this situation we must expect a flattening and broadening of the distribution (20), because the probability of a domain of average size $\langle n\rangle$ decreases while the standard deviation Λ increases. Since in this work we are primarily interested in the long-time regime, we take into account that $n \gg \langle n\rangle$ and approximate $g(n)$ by an as yet undetermined polynomial in n. This leads then to the following normalized distribution function of the domains sizes

$$p(n) \approx \frac{n^\sigma \exp\left[-\frac{n^2}{2\Lambda^2}\right]}{\int_0^\infty n^\sigma \exp\left[-\frac{n^2}{2\Lambda^2}\right] \mathrm{d}n} \tag{22}$$

Comparing Eq. (22) to the general form of the distribution function in Eq. (12), we deduce that the parameter $\delta = 2$. The parameter σ is suitably chosen so that the theoretical curves reproduce the power-law decay of the SIS copolymers below T^*, measured in the experiments described in the previous section. This condition provides for the spherical and cylindrical morphology $\sigma = 1.76$ and 1.7, respectively. In this context, it also worth emphasizing that the choice of σ does not affect the stretched exponential index $\delta/(1/\gamma + \delta)$ in Eq. (14), which determines the long-time relaxation above T^* [29]. Finally, the γ-indices, characterizing the relaxation inside the domains at times $t < \tau_{\max}$, are obtained from the Eqs. (16) and (18).

5. Results and discussion

Inserting the previously determined δ-, σ- and γ-indices for the respective morphologies into Eq. (14), we obtain for the overall effective relaxation modulus of the 14% PS copolymer in the time interval $\tau_0 \ll t < \tau_{\max}(n_{\max})$

$$E(t,T) \approx E_{t\to\infty}(T)\left\{1 + C_{\mathrm{sph}}\left(\frac{t}{\tau_0(T)}\right)^{-0.12} \exp\left[-\left(\frac{t}{\tau^*(T)}\right)^{0.19}\right]\right\} \tag{23}$$

and for the overall effective modulus of the 17% PS copolymer

$$E(t,T) \approx E_{t\to\infty}(T)\left\{1 + C_{\mathrm{cyl}}\left(\frac{t}{\tau_0(T)}\right)^{-0.15} \exp\left[-\left(\frac{t}{\tau^*(T)}\right)^{0.23}\right]\right\} \tag{24}$$

where C_{sph} and C_{cyl} are prefactors containing the constants C_1 and C_2 of the spherical and cylindrical morphology, respectively. In the terminal relaxation zone $t > \tau_{\max}(n_{\max})$ we get for both copolymers

$$E(t,T) \approx E_{t\to\infty}(T)\left[1 + C_{\mathrm{tm}}\left(\frac{t}{\tau_0(T)}\right)^{-1} \exp\left(-\frac{t}{\tau_{\max}(n_{\max})}\right)\right] \tag{25}$$

where C_{tm} is the prefactor of either the spherical or cylindrical morphology in the terminal relaxation zone. In Fig. 2 we show the theoretically and experimentally

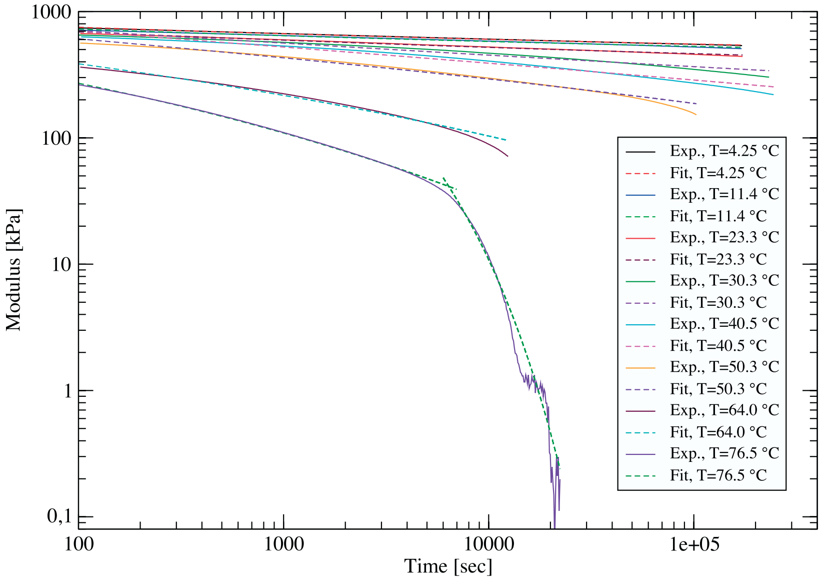

Fig. 2. Experimentally and theoretically determined effective extensional modulus versus time at different temperatures of the SIS copolymer with 14% PS, where spherical PS micelles with cubic phase symmetry are embedded in a PI matrix.

determined curves of the overall effective extensional modulus versus time obtained for the SIS copolymer with spherical morphology at different temperatures. We see that the functional form (23) derived with our domain-model approach reproduces qualitatively correctly the experimental curves at all temperatures in the time interval $\tau_0 \ll t < \tau_{\max}(n_{\max})$. In this regime the relaxation moduli of the different domains, obeying an exponential decay, superimpose and provide an overall stretched exponential relaxation. The deviations observed at longer times announce the beginning of the terminal relaxation zone suitably described by the exponential given in Eq. (25). In this regime only the single domain remains, which possesses the largest number of relaxing elements and, thus, the longest relaxation time $\tau_{\max}(n_{\max})$. As a consequence, the contribution of the largest domain determines the final relaxation behavior, and the overall relaxation modulus decays exponentially to zero, since at this stage no superposition is possible anymore. In Fig. 3 we show the corresponding fitting parameters as a function of temperature obtained with the Levenberg–Marquardt procedure and a tolerance of 10^{-7}. We observe that the quantity $E_{t\to\infty}(T)$ as well as $\tau^*(T)$ continuously decrease with increasing temperature, while $C_{\mathrm{sph}}\tau_0^{0.12}(T)$ increases instead. This clearly demonstrates that with growing temperature the stretched exponential relaxation mechanism through domain formation becomes more important with respect to the power-law relaxation mechanism, involving the relaxation of dangling chains and loops. Next, in Fig. 4 we plot the theoretically and experimentally determined overall effective extensional modulus versus time of the cylindrical SIS morphology at different temperatures. In analogy to the spherical case we see that the functional form of Eq. (24), obtained with our domain-model approach in the time interval $\tau_0 \ll t < \tau_{\max}(n_{\max})$, reproduces well the experimental curves at all temperatures using the fitting parameters visualized in Fig. 5. Again, we observe deviations at longer times, which announce the beginning of the terminal relaxation zone suitably described by the exponential given in Eq. (25). To demonstrate this, we fit the functional form of Eq. (25) to the tail of the long-time record available at $T = 59.9$ °C. At this temperature the system is well-below the glass transition of the PS cylinders, which has experimentally been determined to be at 72 °C. In the same way we fit the functional form (25) to the tail of the relaxation curve of the long-time record available for the spherical SIS morphology and show the fit in Fig. 2. The temperature of $T = 76.5$ °C is slightly above the glass transition temperature of the PS micelles $T_g(\mathrm{PS}) = 65.0$ °C. In this regime the SIS copolymer forms a phase-separated morphology, where the PS micelles are in the melt state and are loosely interconnected by the PI chains. Under these conditions the SIS copolymer forms an elastic network, which behaves as a thermoreversible gel [18]. The noise observed experimentally relates to the small stresses encountered in the terminal relaxation zone and are caused by background fluctuations. The problem of measuring small fluctuating signals in the terminal relaxation zone is a typical difficulty encountered in long-time relaxation experiments [30].

Next, let us investigate how our domain model approach allows us to successfully describe the power-law and stretched-exponential regime in an unified framework. By analyzing the Eqs. (23) and (24), we notice that the theoretical equations succeed in describing the relaxation behavior below and above T^* through the $\langle n\rangle$-dependence of the relaxation time τ^*. Since from Eq. (15) we know that $\tau^* \propto \langle n\rangle^{1/\gamma}$ with $\gamma > 0$, we can conclude that if the system is

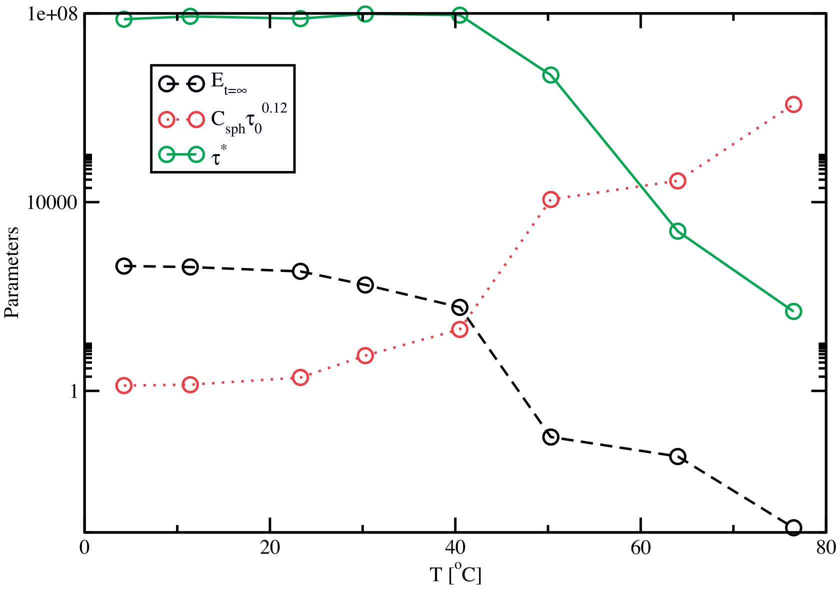

Fig. 3. Parameters versus temperature resulting from the fit to equation $E(t,T)=E_{t\to\infty}(T)[1+C_{\mathrm{sph}}\tau_0^{0.12}(T)t^{-0.12}\exp(-(t/\tau^*(T))^{0.19})]$ of the SIS copolymer with 14% PS, where spherical PS micelles with cubic phase symmetry are embedded in a PI matrix.

macroscopically large, i.e. $\langle n\rangle\to\infty$, and it is only composed of a single domain, the relaxation time $\tau^*\to\infty$. Subsequently, applying this limit to the Eqs. (23) and (24), we see that the theoretical equations predict a power-law relaxation, which is consistent with the experimental observations for both SIS copolymers in the regime below T^*. Therefore, the slow power-law decay of the overall relaxation modulus is caused by the intra-chain relaxation of loops and dangling chains in a single macroscopically large domain. At temperatures $T>T^*$ and under a nonlinear strain, the system is subjected to increasing collective network fluctuations and forms domains of different sizes via a chain-pullout mechanism. In this regime different length-scales come into play, which are characterized by their respective relaxing elements. As already mentioned, the stretched exponential relaxation behavior is observed on length-scales larger than the average distance of the crosslinks and is due to the superposition of the contributions of domains of different size. Inside the domains, the stress is found to relax according to a power-law at times $t<\tau_{\max}(n)$, while at times $t>\tau_{\max}(n)$ it is found to relax according to the exponential decay given by Eq. (11). The relaxation behavior inside the domains is governed by the maximum relaxation time $\tau_{\max}(n)$, which separates the contributions of network motions on length-scales smaller and larger than the average distance of the crosslinks. At

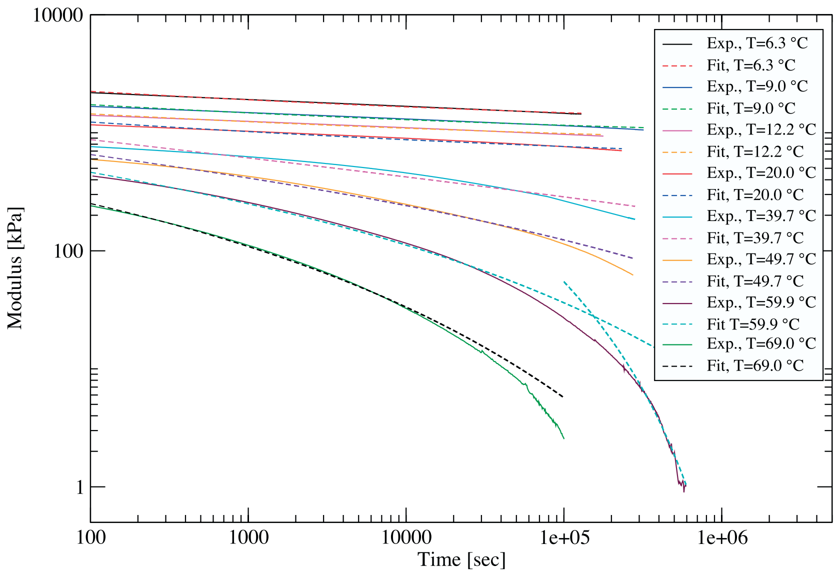

Fig. 4. Experimentally and theoretically determined effective extensional modulus versus time at different temperatures of the SIS copolymer with 17% PS, where hexagonally packed PS cylinders are embedded in a PI matrix.

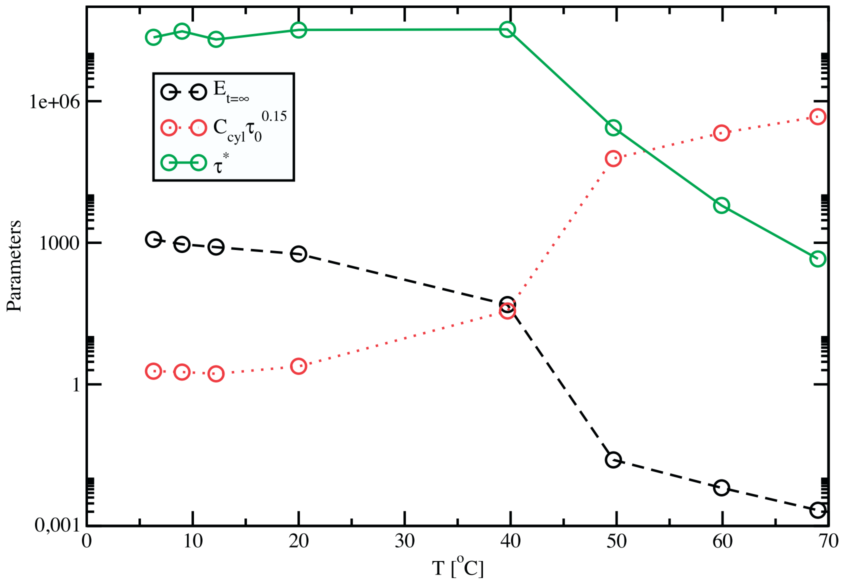

Fig. 5. Parameters versus temperature resulting from the fit to equation $E(t,T)=E_{t\to\infty}(T)[1+C_{\rm cyl}\tau_0^{0.15}(T)t^{-0.15}\exp(-(t/\tau^*(T))^{0.23})]$ of the SIS copolymer with 17% PS, where hexagonally packed PS cylinders are embedded in a PI matrix.

low temperatures the fluctuations in the system are reduced and, consequently, the size of the domains are very large. Therefore, only a power-law decay behavior is observed on experimental accessible time-scales. Moreover, we recognize that the stress relaxation of the SIS copolymers under nonlinear deformation and upon thermal activation is influenced by the implication of different time-scales. Below T^*, the fast but inefficient stress relaxation of loops and dangling chains is the dominant relaxation mechanism, while at temperatures above T^* and at longer times the relaxation through crosslink-domain formation enables an efficient stress relief. The efficiency of the latter mechanism becomes more significant with increasing temperature, because the higher kinetic energy in the network increases the frequency of the pullout events. This leads to the formation of a larger number of domains of smaller size. Since $\tau^*\propto\langle n\rangle^{1/\gamma}$, the stress relaxation through crosslink-domain formation becomes faster with increasing temperature, which is in consistency with the experimental observations of Hotta et al. [14]. To conclude, we emphasize that the thermoreversible mechanism of chain-pullout also explains the reversibility of the deformation process at long times and/or high temperatures observed experimentally [20], and is also likely to be mainly responsible for the strain-rate- and temperature-dependence of the mechanical properties of these materials.

6. Conclusions

In summary, we have shown in this paper that our extended domain-model approach, originally conceived by Gurtovenko and Gotlib to describe the relaxation dynamics of inhomogeneously crosslinked polymers, is also useful to describe the stress relaxation behavior at long times of homogeneously crosslinked poly(styrene-isoprene-styrene) copolymers, subjected to a non-linear deformation. Our approach correctly predicts the power-law decay behavior, experimentally observed by Hotta et al. below a characteristic temperature T^*, by assuming a macroscopically large single-domain system of crosslinks. With increasing temperature thermal fluctuations induce fluctuations in size of domains of crosslinks, either by a full detachment or by a partial pulling of the bridging chains out of the PS hard domains. The process becomes faster and more probable as the forces on the bridging chains increase. We correctly predict the experimentally determined index of the stretched exponential, which governs the decay behavior of the overall effective extensional modulus above T^*. This result confirms the relaxation mechanism through domain formation and the importance of the underlying chain-pullout mechanism in the relaxation process. However, our conclusions are in opposition to theoretical interpretations of previous works, which explained the deviations in the long-time behavior as a direct consequence of plastic flow and breakup of the PS hard domains. In our view the copolymer under the imposed tensile strain is driven in a new dynamical equilibrium. Finally, it is also worth emphasizing that the dynamical process of chain-pullout, which is primarily responsible for the long-time behavior of the mechanical properties, is likely to play an important role in the fracture, healing and aging processes of these materials. To conclude, we point out that our theoretical investigation also demonstrates that the mechanical properties of thermoplastic elastomers are strongly influenced by multiple length- and time-scales. Thus, our future research will focus on the development of new theoretical approaches that allow a reliable prediction and understanding of their contribution.

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Appendix A. Maximal relaxation time of a domain

To derive an explicit expression for the maximal relaxation time of a large domain ($n \gg 1$), we consider that its relaxation spectrum H can be expressed as

$$H(\tau(\xi,n,T),T) \approx -E_{t\to\infty}(T)\frac{1}{n}\frac{\mathrm{d}\xi}{\mathrm{d}\ln\tau(\xi,n,T)} \tag{A1}$$

where $\tau(\xi,n,T)$ denotes the relaxation time and ξ the continuous relaxation mode variable. On the other hand, a rather slow power-law decay of $E(t,T)$ inside the domains permits to apply Alfrey's approximation [15,26] on Eq. (4) and to find the approximate behavior of the relaxation spectrum

$$aH(\tau(\xi,n,T),T) \approx -\frac{\mathrm{d}E(t,T)}{\mathrm{d}\ln t}\Big|_{t=\tau(\xi,n,T)}$$
$$= E_{t\to\infty}(T)\gamma\left(\frac{\tau(\xi,n,T)}{\tau_0(T)}\right)^{-\gamma} \tag{A2}$$

From Eq. (A2), we conclude that inside the domains the relaxation spectrum obeys a power-law decay. Since the domains of crosslinks have finite sizes, they each possess an individual maximal relaxation time $\tau_{\max}$. One can easily show this by setting Eq. (A1) equal to Eq. (A2) and, subsequently after variable separation, integrating from $\xi=0$ to ξ and $\tau=\infty$ to $\tau(\xi)$, respectively. This leads then to the following relation between the relaxation times:

$$\tau(\xi,n,T) \approx \tau_0(T)\left(\frac{n}{\xi}\right)^{1/\gamma} \tag{A3}$$

Now, inserting $\xi=1$ in Eq. (A3), immediately provides the maximal relaxation time as

$$\tau_{\max}(n,T) = \tau(\xi=1,n,T) \approx \tau_0(T)n^{1/\gamma} \tag{A4}$$

where the exponent $\gamma > 0$. From Eq. (A4), we deduce that the maximum relaxation time of a domain indeed depends on the number of elements n in the domain and goes to infinity as $n \to \infty$.

Appendix B. General theory of fluctuations

Let us consider a non-insulated subsystem of n crosslinks inside a large homogeneously network system in equilibrium. The state of the subsystem can be characterized by some value n fluctuating in equilibrium around the average size $\langle n\rangle$. According to the fluctuation theorem the probability of a fluctuation is [19]

$$p(n) \propto \exp\left[-\frac{R_{\min}(n)}{k_B T}\right] \tag{B1}$$

where $R_{\min}$ is the minimal work to create the fluctuation. The minimal work has two components

$$R_{\min} = R_{\mathrm{int}} + R_{\mathrm{ext}} \tag{B2}$$

where R_{int} is the internal work resulting from the fluctuation itself and R_{ext} the external work caused by the environment. Let us now expand R_{int} in series around $\langle n\rangle$

$$R_{\mathrm{int}}(n) \approx R_{\mathrm{int}}(\langle n\rangle) + (n-\langle n\rangle)k_B TN + \frac{1}{2}k_B T\frac{\partial N}{\partial n}(n-\langle n\rangle)^2 \tag{B3}$$

where

$$N = \frac{1}{k_B T}\frac{\partial R_{\mathrm{int}}}{\partial n}\Big|_{n=\langle n\rangle} \tag{B4}$$

is the thermodynamic force. The external work R_{ext} must be proportional to n-$\langle n\rangle$ and thus gives

$$R_{\mathrm{ext}} = -(n-\langle n\rangle)k_B TN \tag{B5}$$

Inserting Eqs. (B3) and (B5) in Eq. (B1) using Eq. (B2), we obtain for the probability of creating a fluctuation of size n

$$p(n) \propto \exp\left[-\frac{1}{2}\frac{\partial N}{\partial n}(n-\langle n\rangle)^2\right] \tag{B6}$$

Thus, we see that the probability of fluctuations in size of the domains of crosslinks follows a Gaussian distribution of the form

$$p(n) \propto \exp\left[-\frac{(n-\langle n\rangle)^2}{2\Lambda^2}\right] \tag{B7}$$

with the standard deviation

$$\Lambda = \left(\frac{\partial N}{\partial n}\right)^{-1/2} = \sqrt{\langle(n-\langle n\rangle)^2\rangle} \tag{B8}$$

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