



INSTITUT DE FRANCE
Académie des sciences

Comptes Rendus

Physique

Helene Montes and Francois Lequeux

Relation between mechanical response of reinforced elastomers and dynamics of confined polymer chains

Volume 22, issue S5 (2021), p. 33-50

<<https://doi.org/10.5802/crphys.96>>

Part of the Special Issue: Prizes of the French Academy of Sciences 2020

© Académie des sciences, Paris and the authors, 2021.
Some rights reserved.

 This article is licensed under the
CREATIVE COMMONS ATTRIBUTION 4.0 INTERNATIONAL LICENSE.
<http://creativecommons.org/licenses/by/4.0/>



*Les Comptes Rendus. Physique sont membres du
Centre Mersenne pour l'édition scientifique ouverte*
www.centre-mersenne.org



Prizes of the French Academy of Sciences 2020 / *Prix 2020 de l'Académie des sciences*

Relation between mechanical response of reinforced elastomers and dynamics of confined polymer chains

Relation entre la réponse mécanique des élastomères renforcés et la dynamique des chaînes polymères confinées

Helene Montes[Ⓢ] ^a and Francois Lequeux[Ⓢ] ^{*, a}

^a Sciences et Ingénierie de la Matière Molle, UMR 7615, ESPCI Paris, Université PSL, CNRS, Sorbonne Université, 75005 Paris, France

E-mails: helene.montes@espci.fr (H. Montes), francois.lequeux@espci.fr (F. Lequeux)

Dedicated to the memory of Aurélie Papon, our brightest student, who unfortunately left us too soon.

Abstract. Elastomers used in everyday life are always reinforced with rigid nanoparticles (carbon black or silica). The addition of rigid nanoparticles to an elastomer gives it very specific viscoelastic properties. In this article, we discuss the current understanding of mechanical properties of a polymer matrix around its glass transition, focusing on the situation of polymers confined between two rigid surfaces with a nanometric gap. Then, we will explain how the properties of the matrix can help to understand the properties of filled or reinforced elastomers. We will then explain that in reinforced rubbers, the mechanical properties are dominated by stress propagation between neighboring aggregates through a nanometric polymer gap, thus by confined polymer bridges. We will discuss how knowledge of the dynamics of confined polymers allows us to understand the temperature dependence, the pressure dependence and the non-linearities observed for strain below 0.1 of reinforced elastomers.

Résumé. Les élastomères utilisés dans la vie courante sont toujours renforcés avec des nanoparticules rigides (noir de carbone, ou silice). L'ajout de nanoparticules rigides dans un élastomère leur confère des propriétés mécaniques très spécifiques. Dans cet article, nous rappelons d'abord ce que l'on connaît aujourd'hui des propriétés mécaniques d'un élastomère autour de sa transition vitreuse, et en particulier lorsqu'il est confiné entre deux surfaces solides proche de quelques nanomètres. Puis nous expliquerons comment ces propriétés peuvent aider à la compréhension de celles des élastomères renforcés. En effet nous montrons que dans les élastomères renforcés, les propriétés mécaniques sont dominées par la propagation de la contrainte entre nanoparticules par des ponts de polymère confinés. Nous discuterons comment la connaissance de

* Corresponding author.

la dynamique des polymères confinés permet de comprendre les effets de température, de pression et les non-linéarités précoces de la mécanique des élastomères renforcés.

Keywords. Glass transition, Polymer physics, Mechanical properties, Reinforced elastomers, Confinement, Nanoparticles, Pressure.

Mots-clés. Transition vitreuse, Physique des polymères, Propriétés mécaniques, Élastomères renforcés, Confinement, Nanoparticules, Pression.

Note. Francois Lequeux is the 2020 recipient of the « Grand prix de la fondation Michelin – Académie des sciences ».

Available online 2nd May 2022

1. Introduction

Glassy polymers (glassy polystyrene, polymethylmetacrylate (PMMA), and epoxies) and semicrystalline polymers (most of the polyolefins) are generally used without reinforcing with solid fillers. However, most of elastomers—crosslinked polymer above their glass transitions, such as those used in shoe soles, car tires, gaskets, and plastic nipples, are mixed and reinforced with solid fillers. The fillers used are generally carbon black or silica nanoparticles. A representation of a typical reinforced elastomer is shown in Figure 1. It consists of solid particles (typically 100 nm in size) of various shapes that are embedded in a matrix of crosslinked polymer chains. From an industrial point of view, fillers are added to achieve the two following objectives. The first is simply that fillers are less expensive than elastomers; hence, adding fillers reduces the price of the products. The second is at the heart of this work, is that the presence of inorganic nanoparticles considerably modifies and reinforces the mechanical properties of elastomers. Their addition increases the elastic modulus and the wear resistance as well as toughness. However, at small strain amplitudes (above 0.1%), the addition of fillers causes elastic nonlinearities (strain softening) that result in a dissipation mechanism crucial for applications, such as car tires and mechanical dampers.

Understanding the microscopic origin of the mechanical properties of reinforced rubbers has been challenging for scientists. The question of why rigid nanoparticles increase the elastic modulus of the filled sample and generate a complex mechanical response remains unsolved. The first possible answer, which appeared in the material science community fifty years ago [1], is that polymer dynamics is modified by the presence of rigid nanoparticles. However, the nature and physical origin of such a modification of polymer dynamics by the fillers has remained unclear since 2000. Similarly the question of how dynamics of polymer chains precisely affect the mechanical properties of reinforced elastomers remains a challenging question that we have addressed over the past twenty years [2–4].

Payne in 1962 [5] identified that the mechanics of reinforced rubber is controlled by hard and soft zones corresponding to various dynamical states of the polymers, which have different mechanical properties. In a seminal paper on the mechanics of filled elastomers, Payne has wrote “*We may assume that the proportion of hard and soft zones is determined by the type and concentration of (carbon) black (nanoparticles), the details of processing, here exemplified by the effect of heat treatment, the temperature and, of course the immediate preceding strain history.*” However, the nature of these hard and soft zones has not been made clear up to now. We propose in the present study that hard and soft zones, which correspond to the zones at which polymers connect to the rigid fillers, are in glassy and rubber states, respectively. This finding was inspired by experiments that revealed the possible modification of glass transition in the vicinity of solid surfaces. The idea that the dynamical response of polymers near their glass transition is modified in the vicinity of surfaces emerged in the physics community in 1995. The study conducted

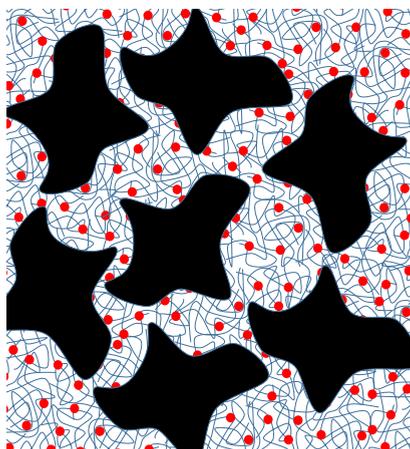


Figure 1. A schematic of a filled elastomer. Solid nanoparticles (in black) are embedded in cross-linked polymer chains (red dots). Possibly, the polymers can also be covalently connected to the particle surfaces.

by Keddie *et al.* [6] was one of the first to identify that the measured glass transition temperature of a thin layer of polymer was different from that of the bulk polymer. The effect of surface proximity on the polymer dynamics has been confirmed by several researchers and has been reported in numerous publications in the past decades [7, 8]. Thus, it has been suggested that the glass transition temperature near rigid boundaries is shifted compared to that in bulk polymers. Furthermore, Wang [9] was the first to propose that modification of the mechanical response of polymer chains near nanoparticle surfaces, which is similar to the shift of the glass transition temperature observed in thin films, can explain the mechanics of filled elastomers. However, other mechanisms have been proposed to explain some features of the mechanical behavior of filled elastomers: the possible adsorption–desorption of polymer chains under mechanical solicitations [10] and changes in polymer structure near a solid surface [11]. Both these mechanisms have a temperature dependence which is different from that of polymers near their glass transition. Lastly, other mechanisms have been proposed, such as the modification of reptation and the Rouse dynamics of polymer chains near the surface [12, 13]. We will see that the temperature dependence of the mechanical properties of filled elastomers, which follows the time–temperature law of pure polymers [14], unambiguously reveals that modification of the dynamics occurring locally in the vicinity of nanoparticle surface is the main origin of the linear and weak-nonlinear viscoelastic behavior.

In this paper, we therefore focus on the dynamical features of polymer chains near solid surfaces and their influence on the mechanical properties of filled elastomers. The objective of this paper is to summarize the effect of the modification of local polymer mechanical properties, which is induced by the presence of solid particles, on the macroscopic mechanical properties of filled elastomers.

This paper is organized as follows.

First, we briefly recall the mechanical properties of a pure elastomer matrix (without fillers) near the glass transition temperature in bulk polymers. We show that the concept of dynamical heterogeneities, which were discovered nearly 20 years ago, helps us to understand the origin of the width of the glass transition domain as well as the onset of yielding.

Second, we discuss the polymer dynamics in a confined geometry. The concept of dynamical

heterogeneities provides a physical interpretation of the mechanical properties of a polymer chain confined between two surfaces.

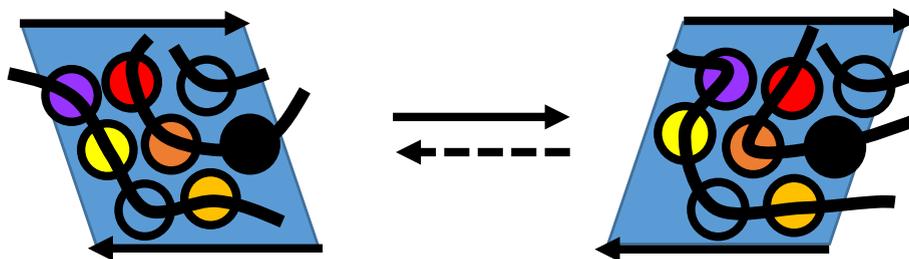


Figure 2. Schematic cage motions. Monomer (in orange) is trapped by its neighbors. The neighbors constitute the cage. Under sufficient stress (or thermal activation), the monomer escapes from the cage and the system reaches a new configuration: a new cage is formed. At a mesoscopic scale, this corresponds to a change in strain.

Third, we discuss the effect of polymer confinement on three macroscopic mechanical properties of filled elastomers, i.e., the linear viscoelasticity, variation of elasticity as a function of pressure, and nonlinear viscoelastic response observed at small amplitude known as “Payne’s” effect.

2. Bulk polymer mechanics near the glass transition

First, we briefly present the physical origin of polymer mechanical response near the glass transition. We schematically distinguish two regimes: the glassy and rubber states.

(a) The glassy state corresponds to low temperatures, where the chain dynamic is very slow compared to the duration of experiments. In the glassy state, the thermal motions of the monomers are slow and, in practice, restricted to distances smaller than 0.1 nm, i.e., smaller than the monomer. A consequence of the restricted motions is that any macroscopic deformation in the linear regime results in a tiny variation in the distance between neighboring monomers. Hence, the shear modulus originates from the intramolecular forces—mostly Van der Waals interactions [15]—between monomers and is of the order of the bulk modulus, which is typically 1 GPa.

Sufficiently large stress (50 MPa) or strain (0.05) may induce however irreversible motions (typically nanometric) of monomers known in the literature as “cage motions,” “plastic events,” or “hops” [16, 17]. These motions correspond to a modification of the structure with a change of the nearest neighbors of a given monomer (see for instance in Figure 2, the monomer in orange which has as first neighbors, before the application of the stress, monomers in blue, red and black and after the application of shear stress, monomers in violet, red and black).

Macroscopically, the phenomenon just mentioned corresponds to yielding. The yield strain originates from the monomer packing geometry. All glassy polymers yield above a given stress of typically a few tens of MegaPascals or when the deformation exceeds about 3–5%.

(b) In the rubbery state, the monomer motions are fast, corresponding to high temperatures, i.e., $T \gg T_g$, where the monomer dynamics are very fast compared to the duration of experiments. The monomers then experience fluctuations at the scale of the chains or more precisely at the scale of the distance between crosslinks and entanglements, typically over tens of nanometers. At this length scale, each chain may exhibit many configurations. In the rubber state, under macroscopic deformation, the entropy contribution to free energy dominates. The entropy modification of chains under elongation leads to a stress opposite to deformation, as depicted in Figure 3. The shear modulus resulting from this mechanism is of the order of 1 MPa in practice. The precise origin of the elastic response of crosslinked elastomers is well known, as it originates from



Figure 3. Chains connected to the network by crosslinks may be stretched by a few hundred of % while keeping their integrity. The elongation decreases the entropy and generates a force on the crosslinks.

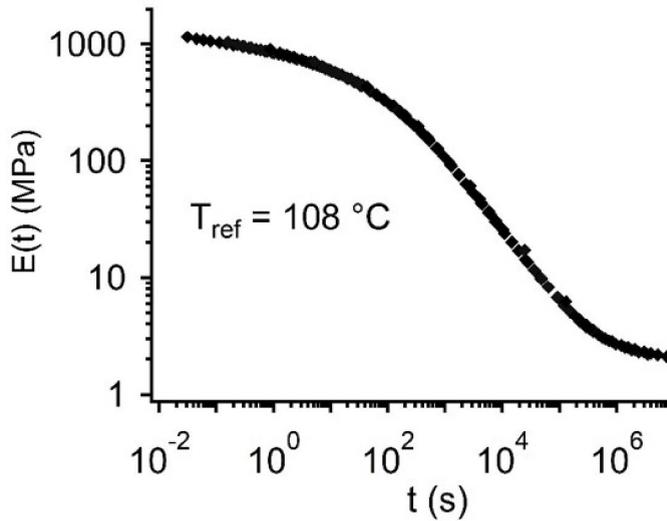


Figure 4. Relaxation modulus—or stress relaxation after a strain step divided by the step amplitude—of a crosslinked PolyMethylMethAcrylate (PMMA) matrix across the glass transition. The modulus is approximately 1 GPa before the cage hops (Van der Waals regime) and decreases progressively to approximately 1 MPa (entropic regime). Measurements were performed at a temperature of 108 °C. The WLF law was used to build the entire master curve, giving the modulus relaxation over 9 decades [16].

entropy modifications of a network under topological constraints caused by crosslinks and entanglements [18]. At a macroscopic scale, the deformation can produce reversible changes of a few tens of %.

At the crossover between the two regimes just mentioned, the monomer dynamics is of the order of the measurement time. It is governed by cage hops, which are similar to those induced by strain (Figure 2) but occurring spontaneously under the simple effect of thermal activation. The average lifetime of cages varies strikingly but continuously with temperature. By varying the temperature between the glassy and molten states, a sharp but continuous variation is observed in the elastic modulus from 1 GPa to 1 MPa at a given time scale (Figure 4). This phenomenon is called the glass transition [19]. In polymer science, the glass transition temperature T_g is usually defined as the temperature at which the average lifetime of the cages is 1 s.

Nearly all polymers exhibit a similar variation in their dynamics with temperature. This variation is in general described by the following empirical law for the mean monomer relaxation time, which is known as WLF law [14]

$$\ln\left(\frac{\tau}{\tau_0}\right) = \frac{-C_1(T - T_g)}{C_2 + T - T_g}, \quad (1)$$

where the mean monomer relaxation time τ_0 at T_g is chosen equal to 1 s. The WLF coefficients C_1 and C_2 weakly depend on the chemical nature of the polymer, with typical values of $C_1 \approx 17$ and $C_2 \approx 50$ K. The above empirical formula exhibits a divergence in the relaxation time for $T = T_g - C_2$. This divergence has been discussed in detail (see [20] for instance) and it appears not to have any physical meaning, because it cannot be reached experimentally. Indeed, measuring the relaxation time at temperatures below T_g by 10 K is very difficult because the relaxation times are very large, typically months or years.

The properties of a polymer material around its glass transition are described as viscoelastic. The viscoelastic modulus is the ratio of the stress over the strain, under a sinusoidal strain solicitation, using a complex number. For an elastic material, the stress and strain are in phase and the viscoelastic modulus is real, but it is complex for a polymer around the glass transition because of the relaxation. The viscoelastic modulus depends on both frequency and temperature. Equation (1) can be used to superimpose the frequency viscoelastic modulus at various temperature. At least in a time window of about 3 decades, over more than 50 K, the viscoelastic modulus appears to follow the time/temperature superposition law given by (1) [14]. Thus, WLF's law allows a measurement of the viscoelastic spectrum at a given frequency for various temperatures and to deduce the viscoelastic spectrum at other frequencies and temperatures, which considerably broadens the frequency window for polymer experimentation. For instance in Figure 4, the relaxation modulus is shown. The relaxation modulus is the stress relaxation of the material, as a function of the time, after a step of strain, divided by the strain test amplitude. It can be shown that it is also the Fourier transform of the frequency dependent viscoelastic modulus. Using the time rescaling of (1), the relaxation modulus spans over 10 decades of time. But it results from the superimposition of relaxation modulus measured over three decades of time over a temperature window of 50 Kelvin by applying (1).

WLF's relation gives a very good description of the temperature dependence of the characteristic relaxation time of polymers, but it does not describe the width of the glass transition at all. In the previous figure, it is implicitly assumed that all the cages have similar lifetimes, but recent measurements have shown that this is not at all the case. Near the glass transition, polymer materials exhibit "dynamical heterogeneities [10]." The term "dynamical heterogeneities" means that the lifetimes of the cages are distributed over more than 4 decades, and the correlation length of these rearrangements, i.e., the size of the cages is approximately 5 nm. These dynamical heterogeneities have been the subject of several vast studies of the glass transition, beyond polymers [21]. The mechanical consequences of these dynamical heterogeneities are considered and a step strain solicitation is applied to the crosslinked matrix in its glassy state. Each domain of the polymer matrix accumulates some stress. As time progresses, each domain will undergo a cage rearrangement that will cause a decrease in stress, as depicted in Figure 2. The stress of a given domain will relax over a time equal to the cage lifetime. Thus, the lifetime that is widely distributed leads to a non exponential slow decay of the stress relaxation. A full description of this is the following: from a mechanical point of view, a polymer can be considered as an ensemble of 5-nm domains, each with its own stress relaxation time, which is distributed over many decades over the entire material.

We have shown that these dynamical heterogeneities can be mimicked with the model shown in Figure 5. Following this model, the bulk is divided into 5-nm-wide domains, each exhibiting the following mechanical behavior: a glassy branch that corresponds to the intermolecular attraction contribution with a shear modulus of approximately 1 GPa and a specific relaxation time τ_i that mimics cage lifetime, in parallel with a 1-MPa branch that corresponds to the entropic contribution.

The distribution of lifetimes of the domains presents as a log-normal law, which reflects a Gaussian distribution of the energy barrier involved in cages hops, but it can be based on more

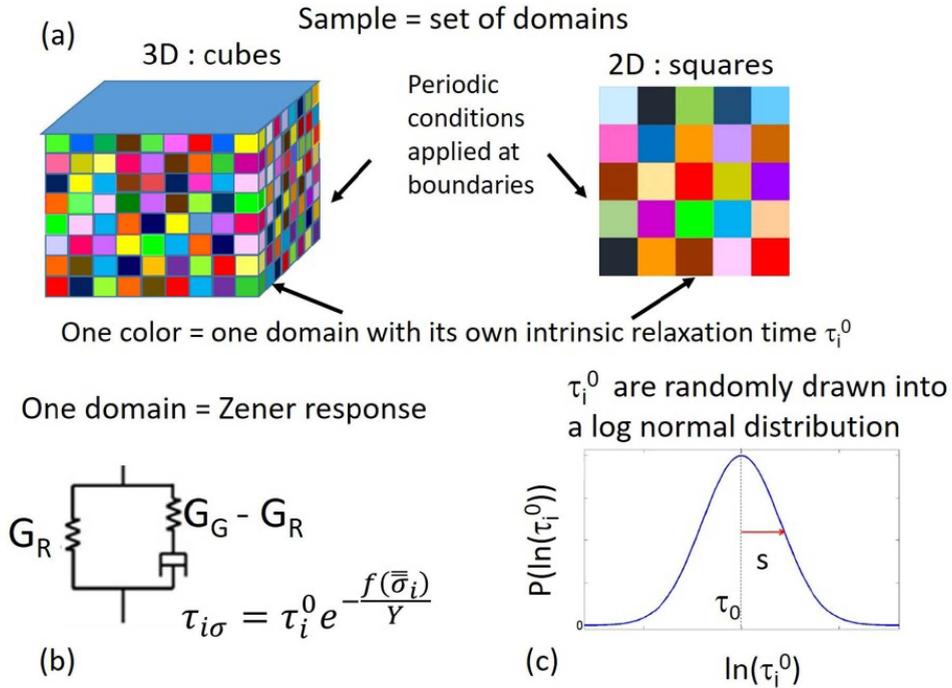


Figure 5. Mechanical simulations of polymer mechanics. Each domain possesses a rubber branch and a glassy branch in parallel. The latter is in series with a damper to have its own relaxation time. The relaxation time is drawn randomly from a log-normal distribution and may be affected by the local stress.

microscopic arguments (see Long and collaborator's work, for instance in [22, 23]). To a good approximation, we can write the lifetime distribution as follows:

$$P(\ln(\tau_i^0)) = \frac{1}{\sqrt{2\pi}s} \exp\left(-\ln\left(\frac{\tau_i^0}{\tau_0}\right) / 2s^2\right). \quad (2)$$

Where s is the width of the time distribution, and τ_0 a characteristic time. The width s depends on the polymer, but is typically around 4.5 for an homopolymer [24]. We then numerically solved the model [25], which appears to describe very precisely the viscoelastic modulus of polymer glasses in their linear regime [24], as shown in Figure 6 for two systems.

Therefore, including nonlinear mechanical properties in this model is easy. As explained in Section 2, the application of stress can induce cage rearrangements similar to that induced by thermal activation. The relaxation of domains under macroscopic stress has been measured in previous studies [26], and the results have been discussed recently by Long [27], and have been confirmed experimentally by us very recently [28]. The cage lifetime, and the time for the modulus decay from 1 GPa to 1 MPa, depends on the local stress applied. For the sake of simplicity, we write it in a scalar form in $\tau = \tau_0 e^{\sigma^2/Y^2}$, where σ is the local stress, Y is typically 10 MPa, and τ_0 is the cage lifetime in the absence of stress. This law describes how thermal hopping is modified by stress. Therefore, the mechanical properties of a polymer matrix near its glass transition can be satisfactorily described by including the local relaxation times from the previous model as follows:

$$\tau_i = \tau_i^0 e^{\sigma^2/Y^2}, \quad (3)$$

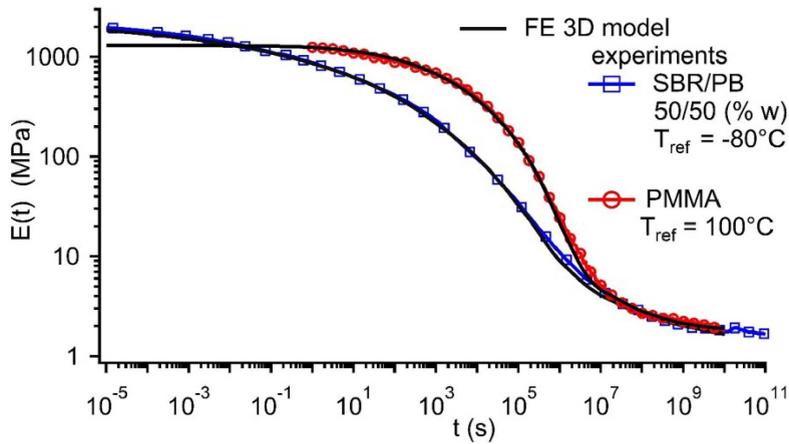


Figure 6. Relaxation modulus for crosslinked PMMA and crosslinked blends of poly butadiene. Continuous lines are results of the model presented in Figure 5. Details can be found in previous studies [13].

where the cage lifetime of domain $i\tau_i^0$ is randomly drawn over a log-normal distribution of many decades width (2), and σ is the local stress. This type of model has been proven to very efficiently describe the polymer mechanics both in the linear (as explained in the previous sentences) and nonlinear regimes in the glass–rubber crossover regime.

Once the physical origin of the polymer viscoelastic responses near the glass transition is established, including recent findings on the so-called dynamical heterogeneities, we will now explore how mechanical behavior is modified in confined geometries.

3. Confinement effects on polymer dynamics

We will now show that the model representing a polymer bulk as a collection of dynamical heterogeneous domains can explain confinement effects and thus the shift of glass transition temperature observed in thin polymer films. For a few decades, it has been observed that the polymer dynamics should be modified at the surface of solid particles in filled elastomers. These modifications have been correlated with some mechanical properties of filled rubbers [9]. More recently, motivated by the developments of nanotechnologies, the mechanical properties of thin-polymer film coatings on solid substrates have been studied, revealing that the dynamics of polymer films may be different from the those of bulk materials [8].

The recent literature unanimously agrees that the dynamics of polymers near their glass transition is modified by the presence of hard or soft boundaries [8]. We will now consider a situation of interest for reinforced elastomers: a polymer is confined between two solid walls with a strong anchoring between the walls and polymer (see Figure 7). This situation mimics the behavior of a polymer confined between two neighboring solid particles in a filled rubber and reveals size dependent mechanical properties discussed below [29].

First, let us assume that the thickness of the layer is approximately 5 nm and that hundreds of domains constitute the polymer bridge between particles. These have random relaxation times that span many decades, as explained above. We apply a step strain to this bridge and separately consider the slowest domain compared to other domains. When all other domains have relaxed their stress, the two solid walls remain mechanically connected only by the slowest domain, which has a modulus of 1 GPa, whereas other domains exhibit a modulus of 1 MPa. Thus, the

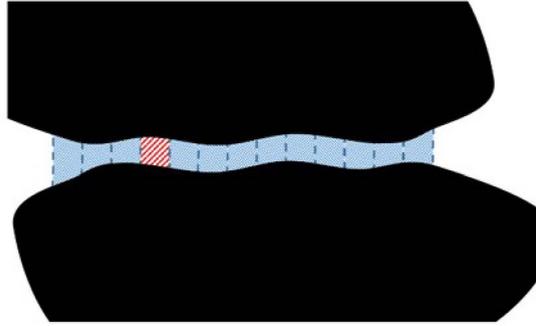


Figure 7. Polymer bridges between two particle surfaces, constituted by several domains. The slowest domains, which are 10^3 fold more rigid than the others at the end of the relaxation, controls the stress transmission.

stress is carried by the slowest domain, which provides an apparent modulus of about 10 MPa to the bridge. Therefore, the slowest domain dominates the mechanical response of the polymer connection between the walls. Thus, the rigidity of the polymer bridge is dominated by the one percent of slowest domains.

This situation is very different from the case of a bulk polymer. In that case, the slowest domains must at least form a percolation network to dominate the macroscopic mechanical response. Thus, in bulk polymers, the slowest domains that dominate the stress have to be more than in a film (typically more than 10% in bulk as compared to less than 1% in nanometric films).

Because polymer samples near T_g exhibit a large width in local relaxation times, their mechanical response will strongly depend on the geometry of the mechanical solicitation. A length over which the mechanical properties propagate may thus be introduced. This length has to be related to the dynamical heterogeneities. In a naive view, the change in mechanical transmission can be described as a shift of the glass transition temperature of polymer chains in the vicinity of a solid surface. In this frame, we show that a good approximation of the dependence of the glass transition temperature as a function of the distance z from the surface can be written as follows:

$$T_g(z) = T_g^\infty \cdot \left(1 + \frac{\delta}{z}\right), \quad (4)$$

where z is the distance to the surface, δ an atomic length, and T_g^∞ the glass transition of the matrix at an infinite distance from any surfaces, or in bulk. A more complete analysis of the mechanical behavior of a polymer thin film between two solid surfaces has been performed using the aforementioned model. Figure 8 shows that the mechanical response is shifted toward lower frequencies (or higher temperatures) under confinement. Furthermore, the glass transition domain is broadened. The simulation has been satisfactorily compared to the experimental results of filled elastomers. Introducing a clear mechanical criterion for the glass transition—e.g., the temperature at which the macroscopic modulus of a confined polymer film has a given value—Equation (4) can appear to be a satisfactory approximation. Hence we see that dynamical heterogeneities—that are considered as mechanical heterogeneities—induce an apparent shift of the glass transition of polymer chains confined between solids walls.

The slowing down of polymer dynamics has been the object of various interpretations. Note that effects other than the effect just mentioned may also contribute to a slowing down of the polymer mechanical response near surfaces. First, at a monomeric scale, the modification of the structure and of the dynamics induced by the change in structure may also contribute to

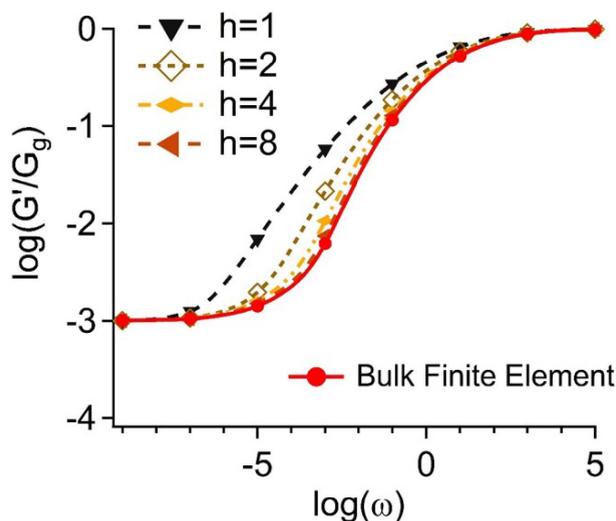


Figure 8. Real part of the apparent visco-elastic modulus of confined polymer in thin films versus frequency predicted by the aforementioned model for a film thickness h equal to 1, 2, 4 and 8 domains, as well as for the bulk finite element. The relaxation in thin films extends to lower frequencies as compared to the one in bulk polymers and broadens with increasing confinement [30].

slow the dynamics down. However, in that case, a shift in the dynamics is not expected to follow the frequency–temperature WLF’s law, in contrast to what is observed subsequently [2, 3]. The shift in dynamic caused by structural modification appears more like a rigid shell around the particles [31]. Second, the mechanism of adsorption/desorption under mechanical solicitation is involved when describing modifications of the dynamics near nanoparticle surfaces [10]. There is however no reason why these mechanisms would follow the frequency–temperature WLF law, while experimental results do. Finally, the polymer chain dynamics (Rouse motions and reptation) are modified near the surfaces, but these last contributions typically induce a shift in time relaxations of a factor of two, whereas the confinement effect leads to a shift of two decades.

The effect of confinement on the mechanical response of polymers is crucial because of dynamical heterogeneities. The mechanical behavior of elastomers will indeed reveal this effect, as explained in the next section.

4. Filled elastomer mechanics

In industrial filled elastomers, the amount of nanoparticles is optimized such that the average distance between nanoparticle surfaces is of the order of a few nanometers. The adjustment of nanoparticle concentration is in fact a compromise. A small distance between nanoparticles surfaces leads to the system becoming very rigid and brittle, whereas a large distance will cause the fillers to have a negligible effect on the mechanics. In the optimal situation, from an engineering point of view, the stress in filled rubbers originates mostly in the forces transmitted between nanoparticles through a thin layer of polymer. This peculiar mode of stress transmission is described in the literature as “particles network” [32] (see Figure 9). These effects of confinement are crucial in the stress transmission within the filled elastomers because they ensure the

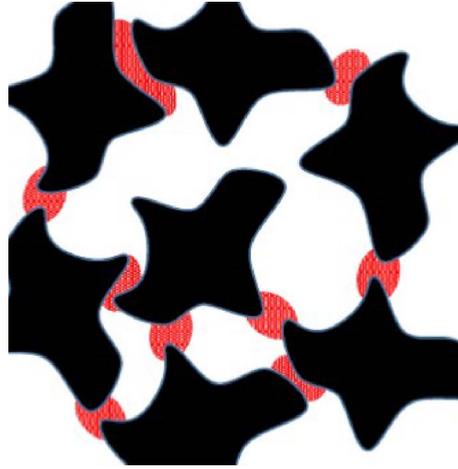


Figure 9. A schematic view of a particles network connected by polymer bridges (in red).

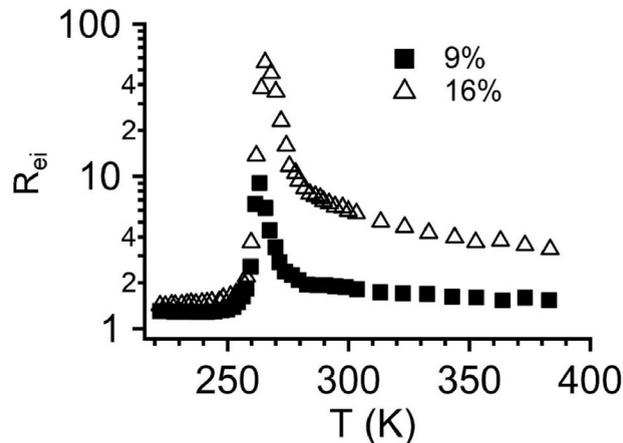


Figure 10. Ratio between the elastic modulus of filled elastomers versus the pure matrix for two spherical nanoparticle volume fractions (9% and 16%). Samples described in [2]. This ratio exhibits a maximum in the glass transition domain, and the modulus of the pure matrix simply decreases with temperature in this temperature range, as shown in Figure 4. This reveals that the filled rubbers have slower temperature decay than that of the matrix. Thus, the width of the glass transition domain of the bridges is on average larger than that of the matrix. The slow decay of R_e indicates that the glass transition domain of the bridges spans more than 100 K.

stress transmission between nanoparticles. We refer to the confined polymer between particles as “polymer bridges”.

The effect of stress transmission through the particle network can be quantified by the reinforcement coefficient R_{ei} , which is equal to the ratio between the elastic modulus in the presence of nanofillers divided by the elastic modulus of the pure matrix. R_{ei} depends obviously on the nanoparticle volume fraction. Moreover, R_{ei} decreases with increasing temperature, even at a few tens of Kelvins greater than the glass transition temperature of the matrix. Precisely, R_{ei} exhibits a bell-shaped dependence on temperature, as shown in Figure 10.

This phenomenon can be understood as follows. At low temperatures, both the matrix and bridges are glassy, and the reinforcement is weak. Similarly, at high temperatures, both the matrix and bridges are in the rubber state and the reinforcement is weak. Thus, the bell-shaped curve reveals that the mechanical difference between the elastic modulus of the bridges and that of the matrix is at maximum a few tens of Kelvins above the glass transition temperature. This reveals that there is a shift between the temperature dependence of the elastic modulus of the polymer bridges and that of the matrix, which agrees with the shift in the glass transition temperature measured directly for the confined polymers (or polymer bridges), as discussed in the previous sections.

Polymer bridges can thus be glassy or not, depending on the temperature and the gap thickness. For mechanical behaviour, the distribution of distances between neighboring particle surfaces is crucial. In practice, because filled elastomers are prepared by mechanical mixing, the distance between neighboring particles, or the thickness of the glassy bridges, is distributed. It is indeed possible to vary the distribution of distance with the same amount of filler in a model, filled elastomer prepared according to a nonindustrial process [33]. We observed that a change in the bridge thickness distribution strongly modifies the shape of the temperature dependence of the modulus. Thus, bridge thickness distribution is a key parameter for the mechanical response of filled elastomers.

Simple laws can be deduced from this remark. Let us consider that each bridge has its own gap d , and its distribution we will call $p(d)$. The glass transition of the bridge, which originates from the shift in T_g induced by the two surfaces, at a distance $d/2$ of the surface that can be estimated using the following relation [15]:

$$T_g(d) = T_g^\infty \cdot \left(1 + 4 \frac{\delta}{d}\right). \quad (5)$$

Thus, at temperature T , the bridges with a glass transition temperature $T_g(d)$ larger than T will be glassy, and the others will be rubber-like. For the most part, the bridges that really participate in the stress transmission across the sample are the glassy ones. Their fraction X is given as follows:

$$X = \int_0^{d_c} p(x) dx, \quad (6)$$

where the upper boundary of the integral is related to the room temperature and the glass transition temperature of the matrix:

$$d_c = 4\delta \frac{T_g^\infty}{T - T_g^\infty}. \quad (7)$$

Thus, it is expected that R_{ei} depends exclusively on the fraction X . This naïve view appears to efficiently predict frequency–temperature superposition behavior. As explained above, the definition of glass transition temperature depends on the choice of a characteristic time, meaning that T_g^∞ depends on the frequency of the measurements, which can be written as $T_g^\infty(\omega)$. Therefore, changing the frequency and temperature such that d_c remains constant must not modify the value of R_{ei} . This is indeed observed in our experiments [2], confirming that the shift in glass transition temperature is the most crucial factor that controls the mechanics of filled elastomers.

If the distribution p is smooth, increasing the temperature will lead to a decrease in X and may be somehow equivalent to a decrease in the filler volume fraction. As a result, in samples with “good” dispersion, a volume fraction/temperature superposition behavior is observed [3].

This qualitatively explains why different distributions (as measured with neutron scattering) lead to different temperature dependences in similar systems [33]. Furthermore, it can predict the pressure–temperature superposition law specific to filled elastomers, as explained in the next section.

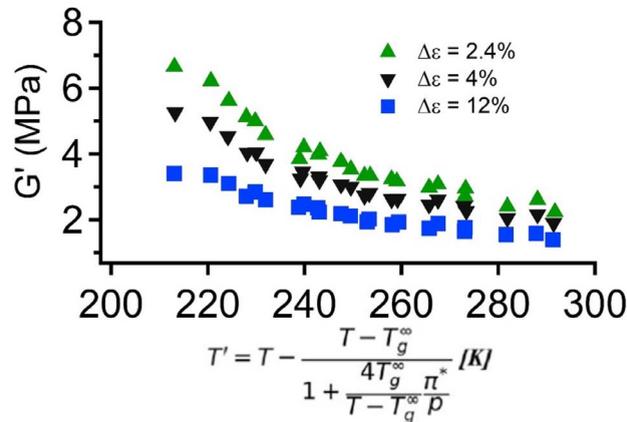


Figure 11. Temperature–pressure modulus master curves obtained for poly(dimethylsiloxane-co-diphenylsiloxane) elastomers filled with silica particles at 27% volume and applying sinusoidal strain of various amplitudes ($\Delta\varepsilon = 2.4\%$, $\Delta\varepsilon = 4\%$, and $\Delta\varepsilon = 12\%$). Master curves were obtained by taking $T_g^\infty = 158$ K and $\pi^* = 2.2$ MPa [23]. Pressure varies from 0 to 3.1 MPa.

5. Pressure effect

One of the consequences of the presence of glassy bridge connection particles is the effect of pressure on the mechanical properties of filled elastomers.

For bulk polymers, applying pressure is known to result in an increase in the glass transition temperature [14]. A basic picture is given by the free volume model. In this model, the dynamics of the chains are related to the amount of unoccupied volume, the free volume, in the system. As explained above, monomers are trapped in cages by their neighbors. There are periodic changes in density over time and space owing to thermal activation fluctuations in density. Once the density is weak enough at a given location, the cage can rearrange. According to the free volume theory, density is the key parameter that controls the polymer chain dynamics. Under pressure, density increases and thus free volume decreases, causing a slowing down of the dynamics and causing increase of the glass transition temperature. This basic image obviously has some limitations, but it is relatively correct. Experimentally, for pure elastomers, one observes typical increase in T_g of 0.5 K for a change in amplitude of the pressure is around 1 MPa.

In the case of reinforced elastomers, pressure causes an increase in the elastic modulus, which can similarly be expressed in terms of an increase in the glass transition temperature. However, the increase in amplitude of the T_g is approximately 50 K/MPa, two orders of magnitude larger than the one measured for a pure elastomer [34]. Under pressure, the density increases. This decreases the length of the glassy bridges, leading to a stronger confinement of the polymer chains in the glassy bridges. The dominant mechanism is not the variation in the free volume of the elastomer itself, but a decrease in the glassy bridge thickness. Because their rigidity considerably depends on the gap between bridges and the glassy bridges sustain most of the stress, the macroscopic modulus considerably increases under pressure.

We can easily quantify this effect. For the sake of simplicity, we assume that under pressure the sample undergoes uniform contraction. If R is the radius of the particles, the variation in distance δd between neighboring particle surfaces under pressure can be written as follows:

$$\frac{\delta d}{d + 2R} = -\frac{P}{K}, \quad (8)$$

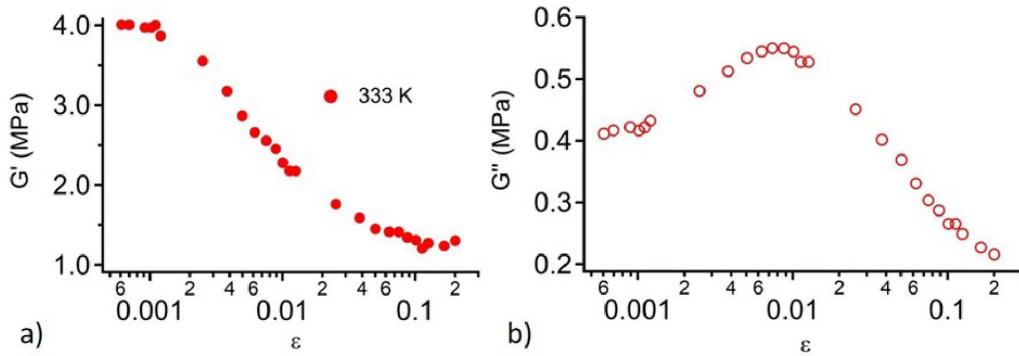


Figure 12. Typical apparent elastic and loss modulus as a function of strain amplitude ε of a poly(dimethylsiloxane-co-diphenylsiloxane) elastomer filled with silica particles at 27% volume at 333 K and 1 Hz.

where P is the applied pressure, K the compression modulus (typically 1 GPa), and V the volume of the sample. Thus, the fraction of bridges that are glassy is given by (6), but with the upper bound d_c shown as follows:

$$d_c = 4\delta \frac{T_g^\infty}{T - T_g^\infty} + \frac{P}{K} 2R, \quad (9)$$

with $R \gg d$. Under two pressure–temperature (P, T) and $(0, T_0)$ conditions, such that they lead to the same value of d_c , the same bridges will transmit the stress across the sample, and thus we expect to have the same mechanical behavior. This gives the pressure/temperature superposition law as follows:

$$T_0 = T - \frac{T - T_g^\infty}{1 + \frac{4T_g^\infty}{T - T_g^\infty} \frac{\pi^*}{P}}, \quad (10)$$

where $\pi^* = (K\delta)/(2R)$.

This is exactly what we observed experimentally in industrial samples as shown in Figure 11 [34]. Experimentally, π^* is of the order of a few MPa, which is in good agreement with the aforementioned estimation. Thus, in the mechanical modeling of filled elastomers, pressure effects should be taken into consideration as soon as the stress exceeds 1 MPa. To conclude, pressure effects reveal the strength of the glassy bridge approach.

6. Payne's effect

Compared to pure elastomers, reinforced elastomers exhibit a precocious nonlinear response [35, 36]. When submitted to oscillatory strain, the apparent elastic modulus typically begins to decrease at strain amplitudes larger than 1%, whereas the apparent loss modulus exhibits a maximum. Typical behavior of the apparent elastic and loss moduli as a function of strain amplitude is shown in Figure 12.

This is known as Payne's effect, and it is very important in industrial applications.

Payne's effect corresponds to a strong but nonlinear mechanical dissipation in filled elastomers. At the same temperature and strain amplitude, the matrix is purely elastic. In industry, because dissipation has to be controlled, particularly in car tires and filled rubber dampers, Payne's effect has been the object of numerous discussions. As a result, it is mainly described

as the progressive destruction of the particle network under increasing strain and at large amplitudes, the effect of a particle network disappears. We can quantitatively discuss the effect of strain on bridges.

Under strain, two effects may be considered: the modification of bridge thickness and strain softening of glassy bridges.

- (a) As explained in the previous section devoted to pressure effect, the distance between fillers is modified by strain. For a given bridge, depending on the respective positions of the fillers, compared to strain orientation, the distance between fillers may increase or decrease. However, on average, the distance increases with strain (at the second order), resulting in a decrease in the average glass transition temperature of the bridges. We estimate the effect of strain on the shift in the glass transition temperature of the bridges. Under a strain of amplitude ε , the mean distance averaged over all directions increases by a factor of $\varepsilon^2/3$. The average bridge thickness changes under a strain of approximately $2R\varepsilon^2$. According to (4), a T_g shift of approximately $(\Delta T_g)/(T_g^\infty) \approx -(8\delta R\varepsilon^2)/(3d^2)$ is expected.
- (b) The stress in the bridges decreases the relaxation times, as written in (3). Because the stress is transmitted by the glassy bridges, the stress concentrates in these glassy bridges: the local stress to consider has to be taken to be larger than the macroscopic stress by a factor equal to the particle section πR^2 divided by the bridge section, which can be estimated as $\pi R d$. Therefore, the local stress in the bridge is of the order of $((E_r R_{ei} R)/d)\varepsilon$. This corresponds to a shift in cage lifetime, as given by (3), which corresponds to (1) to a shift in glass transition temperature of $(\Delta T_g)/(T_g^\infty) \approx -(C_2)/(T_g^\infty C_1)((E_r R_{ei} R)/(Yd))^2$ using (1).

After quantifying all these relations, the second effect (b) typically dominates the first effect (a) by a factor of 100. Thus, Payne's effect is expected to be controlled by the strain softening of glassy bridges. Indeed, quantifying strain softening gives a good estimate of the strain at which the decrease of the elastic modulus and the increase of dissipation begins to be significant—more than 10% for a strain of about 1% typically. Moreover, the frequency–temperature equivalence can be observed for the viscoelastic non linear response associated to Payne's effect, similar to the one observed for the linear elastic modulus. A detailed analysis of Payne's effect has been made possible by all the tools developed in the recent past on the physics of glassy polymers. However, new tools must be developed to provide a stochastic and tensorial description of the bridges to the community.

7. Conclusion

Recent advances in the physical origin of the mechanics of amorphous polymers thus provided a renewed understanding of the mechanics of filled rubbers, a subject that is of great importance in the transportation sector, which is increasingly demanding in terms of high-level technology. To understand the mechanics of filled rubbers, one needs to combine the effect of dynamical heterogeneities on the dynamics of confined polymers and the yielding on polymer matrix mechanical response with the image of the particles network. Indeed, polymer bridges that mechanically connect the rigid particles dominate the mechanics of filled rubbers. More precisely, three effects on the viscoelastic modulus can be discussed precisely using the concepts of glassy bridge and confined polymer properties; the effect of pressure—that decreases the thickness of glassy bridges, the effect of temperature—that controls the rigidity of the glassy bridges, and the effect of strain amplitude—that controls their strain-softening.

Conflicts of interest

Authors have no conflict of interest to declare.

Acknowledgements

All the results presented in the article were obtained during the theses of five students who have worked since 1999 on the mechanical properties of filled elastomers: Julien Berriot, Thomas Chaussée, Aurélie Papon, Davide Colombo and Jonathan Champagne. The authors gratefully acknowledge their contribution as well as financial support from the companies Rhodia (now Solvay) and Hutchinson. Francois Lequeux acknowledges the 2020 award from the Académie des Sciences and the Michelin foundation.

References

- [1] S. Kaufman, W. P. Slichter, D. D. Davis, "Nuclear magnetic resonance study of rubber-carbon black interactions", *J. Polym. Sci. B Polym. Phys.* **9** (1971), p. 829-839.
- [2] J. Berriot, H. Montes, F. Lequeux, D. Long, P. Sotta, "Evidence for the shift of the glass transition near the particles in silica-filled elastomers", *Macromolecules* **35** (2002), p. 9756-9762.
- [3] J. Berriot, H. Montes, F. Lequeux, D. Long, P. Sotta, "Gradient of glass transition temperature in filled elastomers", *Europhys. Lett.* **64** (2003), p. 50-56.
- [4] A. Papon, H. Montes, M. Hanafi, F. Lequeux, L. Guy, K. Saalwächter, "Glass-transition temperature gradient in nanocomposites: evidence from nuclear magnetic resonance and differential scanning calorimetry", *Phys. Rev. Lett.* **108** (2012), article no. 065702.
- [5] A. R. Payne, "The dynamic properties of carbon black-loaded natural rubber vulcanizates. Part I", *J. Appl. Polym. Sci.* **6** (1962), p. 57-63.
- [6] J. L. Keddie, R. A. L. Jones, "Glass transition behavior in ultra-thin polystyrene films", *Isr. J. Chem.* **35** (1995), p. 21-26.
- [7] D. S. Fryer, P. F. Nealey, J. J. de Pablo, "Thermal probe measurements of the glass transition temperature for ultrathin polymer films as a function of thickness", *Macromolecules* **33** (2000), p. 6439-6447.
- [8] B. D. Vogt, "Mechanical and viscoelastic properties of confined amorphous polymers", *J. Polym. Sci. B Polym. Phys.* **56** (2018), p. 9-30.
- [9] M.-J. Wang, "Effect of polymer-filler and filler-filler interactions on dynamic properties of filled vulcanizates", *Rubber Chem. Technol.* **71** (1998), p. 520-589.
- [10] S. S. Sternstein, A.-J. Zhu, "Reinforcement mechanism of nanofilled polymer melts as elucidated by nonlinear viscoelastic behavior", *Macromolecules* **35** (2002), p. 7262-7273.
- [11] J.-L. Barrat, J. Baschnagel, A. Lyulin, "Molecular dynamics simulations of glassy polymers", *Soft Matter* **6** (2010), p. 3430-3446.
- [12] N. A. García, J.-L. Barrat, "Entanglement reduction induced by geometrical confinement in polymer thin films", *Macromolecules* **51** (2018), p. 9850-9860.
- [13] M. Vladkov, J.-L. Barrat, "Local dynamics and primitive path analysis for a model polymer melt near a surface", *Macromolecules* **40** (2007), p. 3797-3804.
- [14] J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, USA, 1980.
- [15] D. Long, F. Lequeux, "Heterogeneous dynamics at the glass transition in van der Waals liquids, in the bulk and in thin films", *Eur. Phys. J. E* **4** (2001), p. 371-387.
- [16] J. Perez, *Physics and Mechanics of Amorphous Polymers*, Routledge, London, UK, 1998.
- [17] J. S. Langer, "Shear-transformation-zone theory of plastic deformation near the glass transition", *Phys. Rev. E* **77** (2008), article no. 021502.
- [18] M. Rubinstein, S. Panyukov, "Elasticity of polymer networks", *Macromolecules* **35** (2002), p. 6670-6686.
- [19] G. R. Strobl, *The Physics of Polymers: Concepts for Understanding Their Structures and Behavior*, Springer-Verlag, Berlin, Heidelberg, 2007, e-books.
- [20] G. B. McKenna, S. L. Simon, "50th anniversary perspective: challenges in the dynamics and kinetics of glass-forming polymers", *Macromolecules* **50** (2017), p. 6333-6361.
- [21] L. Berthier, G. Biroli, "Theoretical perspective on the glass transition and amorphous materials", *Rev. Mod. Phys.* **83** (2011), p. 587-645.
- [22] S. Merabia, D. Long, "Heterogeneous dynamics at the glass transition in van der Waals liquids: Determination of the characteristic scale", *Eur. Phys. J. E* **9** (2002), p. 195-206.

- [23] A. Dequidt *et al.*, “Heterogeneous dynamics and polymer plasticity”, *Macromolecules* **49** (2016), p. 9148-9162.
- [24] H. Montes, A. Belguise, S. Cantournet, F. Lequeux, “Modeling the mechanics of amorphous polymer in the glass transition”, in *Mechanics and Physics of Solids at Micro- and Nano-Scales* (I. R. Ionescu, S. Queyreau, C. R. Picu, O. U. Salman, eds.), Wiley, London, UK, 2019, Ch. 9, p. 231-262.
- [25] R. J. Masurel *et al.*, “Role of dynamical heterogeneities on the viscoelastic spectrum of polymers: a stochastic continuum mechanics model”, *Macromolecules* **48** (2015), p. 6690-6702.
- [26] H.-N. Lee, R. A. Riggleman, J. J. de Pablo, M. D. Ediger, “Deformation-induced mobility in polymer glasses during multistep creep experiments and simulations”, *Macromolecules* **42** (2009), p. 4328-4336.
- [27] D. R. Long, L. Conca, P. Sotta, “Dynamics in glassy polymers: The Eyring model revisited”, *Phys. Rev. Mater.* **2** (2018), article no. 105601.
- [28] A. Belguise, S. Cantournet, F. Lequeux, H. Montes, “Weak nonlinearities in viscoelastic mechanical properties of polymers near their glass transition: Local versus macroscopic laws for stress-induced acceleration of the mechanical response”, *Phys. Rev. Mater.* **5** (2021), article no. 033601.
- [29] A. Dequidt, D. R. Long, P. Sotta, O. Sanséau, “Mechanical properties of thin confined polymer films close to the glass transition in the linear regime of deformation: theory and simulations”, *Eur. Phys. J. E* **35** (2012), article no. 61.
- [30] R. J. Masurel *et al.*, “Role of dynamical heterogeneities on the mechanical response of confined polymer”, *Phys. Rev. Lett.* **118** (2017), article no. 047801.
- [31] A. P. Holt *et al.*, “Dynamics at the polymer/nanoparticle interface in poly(2-vinylpyridine)/silica nanocomposites”, *Macromolecules* **47** (2014), p. 1837-1843.
- [32] J. G. Meier, M. Klüppel, “Carbon black networking in elastomers monitored by dynamic mechanical and dielectric spectroscopy”, *Macromol. Mater. Eng.* **293** (2008), p. 12-38.
- [33] H. Montes, T. Chaussée, A. Papon, F. Lequeux, L. Guy, “Particles in model filled rubber: Dispersion and mechanical properties”, *Eur. Phys. J. E* **31** (2010), p. 263-268.
- [34] J. Champagne *et al.*, “Role of glassy bridges on the mechanics of filled rubbers under pressure”, *Macromolecules* **53** (2020), p. 3728-3737.
- [35] A. D. Drozdov, A. Dorfmann, “The payne effect for particle-reinforced elastomers”, *Polym. Eng. Sci.* **42** (2002), p. 591-604.
- [36] H. Montes, F. Lequeux, J. Berriot, “Influence of the glass transition temperature gradient on the nonlinear viscoelastic behavior in reinforced elastomers”, *Macromolecules* **36** (2003), p. 8107-8118.