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► **To cite this version:**

Julien Berriot, H el ene Montes, Fran ois Lequeux, Didier R. Long, Paul Sotta. Gradient of glass transition temperature in filled elastomers. EPL - Europhysics Letters, 2003, 64 (1), pp.50-56. 10.1209/epl/i2003-00124-7 . hal-02530630

HAL Id: hal-02530630

<https://hal.science/hal-02530630>

Submitted on 3 Apr 2020

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Gradient of glass transition temperature in filled elastomers

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PACS. 62.25.+g - .

PACS. 64.70.Pf - .

PACS. 68.15.+e - .

PACS. 61.41.+e - .

Abstract. – By studying model systems consisting of poly(ethyl acrylate) polymer chains covalently bound to silica particles, we show here how the temperature dependence of the modulus of filled elastomers can be explained by a long-ranged gradient of the polymer matrix glass transition temperature in the vicinity of the particles. We are lead to this conclusion by comparing NMR and mechanical data. We show thereby that the mechanisms of reinforcement are the same as those which lead to an increase of the glass transition temperature of strongly adsorbed thin polymer films. It allows us in particular to propose a new time-temperature superposition law for the filled elastomers viscoelasticity.

When considering a film deposited on a substrate with which the interactions are supposed to be very weak, Jones et al [1] have shown that the glass transition temperature can be reduced by as much as 25K for 100Å thick films. Numerous studies have confirmed this effect since then (see e.g. [2,3]). On the contrary many other experiments performed on strongly adsorbed films have shown that the glass transition temperature increases in this case [4,5], sometimes by as much as 60K for films 80Å thick. These T_g shifts are major effects if one considers molecular relaxation times, or viscoelastic properties. For instance -according to the usual WLF law- a shift of T_g of a few tens of Kelvins should result in an increase (or decrease) of relaxation times by several orders of magnitude at a given temperature T [6,7]. The same polymer film is therefore expected to have fundamentally different viscoelastic properties depending on the substrate on which it is deposited.

However, most measurements of T_g shifts have been performed either by dilatometry (ellipsometry) or by dielectric measurements and are somehow indirect as far as the mechanical properties are concerned. Mechanical measurements by Atomic Force Microscopy have been reported e.g. in [8–10], but brought conflicting results. Indeed, some studies have confirmed previous results [9,10] while another [8] failed to reveal corresponding changes in the viscoelastic properties. In order to gain insight of the dynamical and mechanical properties of polymer

layers in strong interaction with their substrate, we consider here the mechanical properties of filled elastomers. By studying model systems consisting of poly(ethyl acrylate) polymer chains covalently bound to monodisperse silica particles, we show here how the temperature dependence of the modulus in filled elastomers can be explained by a long-ranged gradient of glass transition temperature T_g of the polymer matrix in the vicinity of the particles. This effect results in a slowing down of the dynamics by several orders of magnitude at distances up to a few tens of nanometers. We combine NMR and mechanical measurements in order to relate the temperature variation of the glassy layer to reinforcement properties. Finally we argue that this long-ranged induced glass transition is key for the reinforcement mechanism of filled elastomers [11–14]. Note that it has been known for long that the presence of fillers modify the glass transition properties of the matrix [15–17], but the link to reinforcement was still missing.

The samples were prepared with spherical silica particles of radius $a = 25nm$, dispersed in a poly(ethyl acrylate) matrix to which they were grafted with a silane which copolymerizes with ethyl-acrylate monomers. The coverage corresponds to about 2 grafters per nm^2 . Flocculation of the silica particles was prevented as much as possible during the synthesis, using a method developed by Ford [18]. The samples were optically transparent, and we were not able to detect silica particle aggregation by S.A.N.S. [19]. The cross-linker density as detected by NMR did not vary with the filler concentration. Thus, the elastic modulus of the matrix as well as its bulk glass transition temperature are independent of the filler concentration. The maximum of the loss modulus at $\omega = 0.01Hz$ gives $T_g = 244 K$. Also, the cross-linker density is large enough so that the elastomer matrix may be considered as a continuous medium in between silica particles.

The polymer chain mobility was probed by static, solid state 1H NMR at 300 MHz on a Bruker ASX300 spectrometer. The magnetization relaxation (FID) was measured with a solid echo pulse sequence $((\pi/2)_x, \tau, (\pi/2)_{\pm y}, \tau, acq)$ with a pulse length $3\mu s$ and a delay $\tau = 8\mu s$. The FID is the sum of two, well separated components, a fast one corresponding to a rigid (glassy) fraction of monomers, and a slower one associated to mobile monomers. The fraction of glassy polymer was estimated quantitatively by fitting the whole FID (between 1 and $400\mu s$) with the superposition of a mobile and a solid contributions. The mobile contribution is taken of the form $M(t) = M_{liq} \exp(-\frac{t}{T_2} - \frac{qM_2 t^2}{2})$, where T_2 and qM_2 are two adjustable parameters determined independently by fitting the FID measured far above T_g in the pure matrix. These parameters do not significantly depend on T for $T \geq T_g + 50K$. The solid contribution is identical to the signal measured in a sample far below T_g . It is gaussian-like, with a typical relaxation time $70 \mu s$. The only adjustable parameter is thus the fraction of glassy polymer. The T_g value as measured in NMR was deduced from mechanical measurements on the matrix at 1 Hz, using the WLF relation with a shift in frequency of 50 kHz. The solid fraction of polymer is interpreted as a glassy layer around silica particles. Its thickness varies from 1.2 nm at $T_g + 140K$ to 3.5 nm at $T_g + 35K$ (see below).

The mechanical measurements were performed in simple shear flow in plate-plate geometry on a Rheometrics RDA II rheometer with disk samples glued on both rheometer plates. Both the elastic and loss moduli were measured as a fonction of frequency and temperature in the linear regime, from $T_g + 60K$ to $T_g + 140K$. The reinforcement $R(T, \Phi) = G_f(T, \Phi)/G_0(T)$ (where G_f and G_0 are the shear moduli of the filled and unfilled samples respectively) is plotted as a function of temperature in Fig.1, for two samples with different particle volume fractions Φ . It shows a pronounced maximum of up to ~ 60 at a temperature T_m . This temperature depends on the particles concentration and is higher but close to T_g . Moreover, the reinforcement exhibits also a slow decrease with temperature above T_m , that extends at

least up to $T_g + 100K$. Let us remark that these results are commonly observed in filled rubber systems. These classical observations are associated to the modification of the dynamic of the polymer in the vicinity of the particles (for review see e.g. [21]). We show here that these effects cannot be explained either by purely geometric effects, or by a short-ranged modification of the polymer dynamics close to the silica particles. Indeed, if the reinforcement was of purely geometric origin, it should write $R_0(\Phi) = 1 + \frac{5}{2}\Phi + F(g(r), \Phi)\Phi^2$ [22], where $g(r)$ is the pair correlation function of silica particles and F a fonctionnal difficult to estimate, and would be independent of temperature. The results presented in Fig.1 shows explicitly that the dynamics of the polymer is modified by the presence of particles. Moreover, the amplitude of the effect proves that the modification of the polymer matrix is long ranged, i.e. the range is comparable to the interparticle distance. According to the discussion above, we are thus led to the conclusion that the T_g shifts observed in thin polymer films in interaction with their substrate [4, 5] correspond to changes of the dynamics over the whole thickness of the film, and not only within a thin interfacial layer.

This is in agreement with the predictions of the slow units percolation model [23]. Recent observations [24–26] have shown that a crucial phenomena in glasses is the enormous spatial heterogeneity of the dynamics. Two of us proposed recently a model according to which the glass transition is controlled by the percolation of nanometric domains of very slow dynamics, which coexist with very fast nanometric domains close to T_g [23]. Thus, in this frame, an increase of the glass transition of a polymer film strongly anchored on a solid substrate can be predicted. In the vicinity of the solid substrate, the rigidity propagates into the sample on a distance equal to the correlation length of the percolation. Thus the rigidity of the polymer, and consequently its glass transition temperature depends on the distance to the substrate. As a consequence, this model predicts a shift of T_g at a distance z from a strongly adsorbing interface of the form $\frac{\Delta T_g(z)}{T_g} \approx +(\frac{\delta}{z})^{1/\nu}$ where $\nu \approx 0.88$ is the critical exponent of the correlation length in 3-D percolation and δ is of order one nanometer. In other words, a surface can induce a gradient of glass transition which decays as a power law of the distance to the interface. Note that this effect results in change of the dynamic properties by orders of magnitude, even at distances tens of nanometers to the interface.

Let us now consider the effect of the T_g gradient on a filled elastomer. In the vicinity of a particle, and at a temperature T above the T_g in bulk, three domains appear. First very near the particles, there is a shell of thickness e for which the elastic modulus is at least ten times the one of the elastomer in the bulk. Then, there is a small layer of thickness ξ , where the elastic modulus decreases from about ten times to about the value of the bulk elastic modulus. Lastly for a distance larger then $e + \xi$, the dynamics is nearly not modified by the vicinity of the particles. The thickness of the glassy shell e depends on the frequency ω of the measurement and is given by $e_g = \delta(\frac{T_g(\omega)}{T - T_g(\omega)})^\nu$. Very near T_g , the length ξ is large compared to the distance between the surface of neighboring particles. Thus, estimating the reinforcement requires to take into account the detailed spatial dependence of the elastic modulus. Within a lubrication picture, and using a "steepest descent method" approximation, one obtains for the reinforcement R :

$$\begin{aligned}
 \frac{R(\Phi, T, \omega)}{R_0(\Phi)} &= \frac{G_0(T - \Delta T_0, \omega)}{G_0(T, \omega)} \\
 &\times \frac{8}{3\pi^{1/2}} \left(\frac{\partial \ln G_0(T - \Delta T_0, \omega)}{\partial T} \Delta T_0 \right)^{-1/2}
 \end{aligned} \tag{1}$$

where ΔT_0 is the shift of T_g at half the typical distance h between two neighboring particles, related to the particle radius a and volume fraction Φ by $\frac{h+a}{a} = (\frac{\Phi_c}{\Phi})^{1/3}$ with $\Phi_c = 0.64$ the

random close packing volume fraction. This approximation however is valid in a narrow range of temperature, i.e. for temperatures around $T_g + 10K$. When increasing temperature, ξ decreases and becomes smaller than e and h . Thus we can make a coarse-grained approximation attributing to the local elastomer modulus either an infinite value - for distances to nearest surface smaller than e - or the bulk value at T - for distances to the surface larger than e . This leads to a first conclusion. In this approximation, typically valid for $T > T_g + 50K$ the reinforcement for a given sample R is a function of $\frac{T_g(\omega)}{T - T_g(\omega)}$. This is a new time-temperature superposition which specifically holds for filled elastomers [20].

$$R(\Phi, T, \omega) = f\left(\frac{T_g(\omega)}{T - T_g(\omega)}\right) \quad (2)$$

where f is a function that depends on the sample structure.

Comparison of sample of various particles volume fraction is more delicate, even in the frame of the coarse-grained approximation. A quantitative estimation would require the precise calculation of F , which is a nearly impossible task. We will thus limit ourselves to a very crude analysis, which consist in assuming that the reinforcement is a function only of the volume fraction Φ_{eff} of solid materials - particles plus glassy shell. This effective volume fraction depends both on temperature and frequency, and writes : $\Phi_{eff} = \Phi(1 + \frac{\delta}{a}(\frac{T_g(\omega)}{T - T_g(\omega)})^\nu)^3$,

In this crude approximation, the reinforcement is then given by :

$$R(\Phi, T, \omega) = R_0(\Phi(1 + \frac{\delta}{a}(\frac{T_g(\omega)}{T - T_g(\omega)})^\nu)^3) \quad (3)$$

Hence the concept of gradient of T_g has some consequences on the mechanical behavior of filled elastomers that can be tested experimentally.

Let us first test the time-temperature superposition (equation (2)) that we have suggested. In Fig.2, the reinforcement is plotted as a function of $T_g(\omega)/(T - T_g(\omega))$ for a sample with $\Phi = 0.161$. The value of $T_g(\omega)$ has been measured in the pure matrix, as the maximum of the loss modulus at the fixed frequency ω . All the data collapse on a master curve, within a window of three decades in frequency and 50 K in temperature. This shows that the modification of the dynamics of the polymer chains is governed by a glass transition process, and is in agreement with the concept of T_g gradient. However, it does not provide an estimation of the amplitude of the T_g gradient.

On the contrary, the effective volume fraction approximation could allow to estimate this variation. According to equation (2), plotting the reinforcement $R(\Phi, T, \omega)$ as a function of $\Phi_{eff}(\Phi, T, \omega)$ should give a master curve, by adjusting the parameter δ and the exponent ν . This is shown in Fig.3 for various samples with different volume fractions, at various frequencies and for temperatures varying from 343 K to 363 K. The optimal ν value is 1 ± 0.3 . We take $\nu = 1$ here. At high effective volume fraction, the superposition is surprisingly good. There is however some deviation from the master curve at lower volume fraction. Otherwise, in the vicinity of the maximum reinforcement -close to T_g -, Eq. 1 may give an estimate of the shift ΔT_0 . Results obtained for two different concentrations are summarized in Table I. A reasonable estimate of ΔT_0 is obtained. However, eq. 1 does not describe the precise form of the reinforcement R close to the maximum.

The temperature dependant thickness of the glassy shell are presented in Fig.4. It corresponds to the results of N.M.R., to the mechanical data near T_g presented in Table I, and from the building of master curve shown in Fig. 3. The slope on Fig. 4 - .83, is compatible with the one - -.88 - predicted in (-.88) [23]. We also underline the good agreement between the

thickness value deduced from the N.M.R. and the mechanical data far above T_g . The effective volume fraction approximation is probably correct because of the liquid-like structure of the solid particles in our systems, whatever the concentration [19]. However, the effective volume fraction rescaling is quite sensitive to the structure of the sample and this will be discussed in a further publication. Otherwise, the lubrication approximation provides also an estimate - close to T_g which is clearly in agreement with the other data obtained far from T_g . Moreover the order of magnitude of the gradient is similar to those observed in thin films with strong anchoring [5]. Finally all these results - both time-temperature superposition in Fig. 2 and temperature dependence of the glassy shell thickness Fig.4 - show that the modification of the dynamics of the polymer in filled elastomers is clearly due to a gradient of T_g induced by the solid particles. As the glassy thickness at $T_g + 5K$ is about 20 nm, these results confirm that the effect of the interface on the dynamical properties of the matrix are long-ranged. Our experiments thereby confirm that the T_g shifts measured on thin polymer films are not due to an average effect between a thin perturbed layer, but correspond to long-ranged effects, which take place on the whole thickness of the film. Moreover, the experiments described here allow for proposing a mechanism for the reinforcement of filled elastomers. Qualitative - or incomplete - interpretation of the polymer dynamics have been proposed for filled rubbers, referencing to the glassiness [17] of a polymer shell or of a gradient of mobility [21]. But here we show that a quantitative description of the complex dynamical behavior of these materials can be achieved using the concept of glass transition gradient. The behavior of filled elastomers is governed by various length scale, namely the thickness e of the glassy shell, but also the thickness ξ of the transient domain between solid and fluid, the distance between the particles, and also the characteristic size of the inclusions arrangement - in the case of aggregated systems. Finally, this abundance of length scales makes the richness of the mechanical behavior of filled rubbers.

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TABLE I – *The maximum reinforcement R_{meas} in two different samples. h : average distance between particles, R_0 : geometrical reinforcement*

Φ	h in nm	R_{meas}	R_0	ΔT_0 in K
9.16%	27	9.02	1.37	3
15.9%	18	58	2.5	6.1

*. – Table I

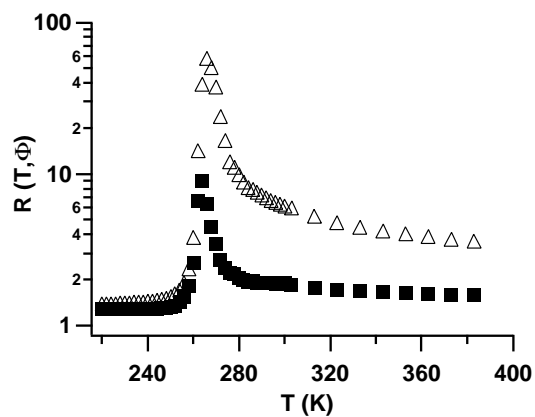


Fig. 1 – The reinforcement as a function of temperature at 0.1Hz. It shows a maximum 10 to 15K above the matrix glass transition temperature. \triangle : $\Phi = 16\%$; \blacksquare : $\Phi = 9.16\%$.

*. – Figure Captions

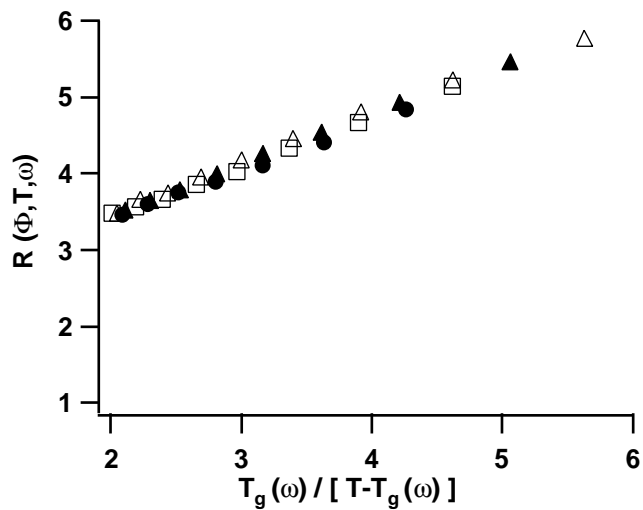


Fig. 2 – Reinforcement for the sample with a volume fraction 16.1% for temperatures varying from $T_g + 50K$ to $T_g + 100K$. as a function of $T_g(\omega) / (T - T_g(\omega))$ \square : 0.1 Hz, \circ : 0.01 Hz, \blacktriangle : 1 Hz, \blacksquare : 10 Hz.

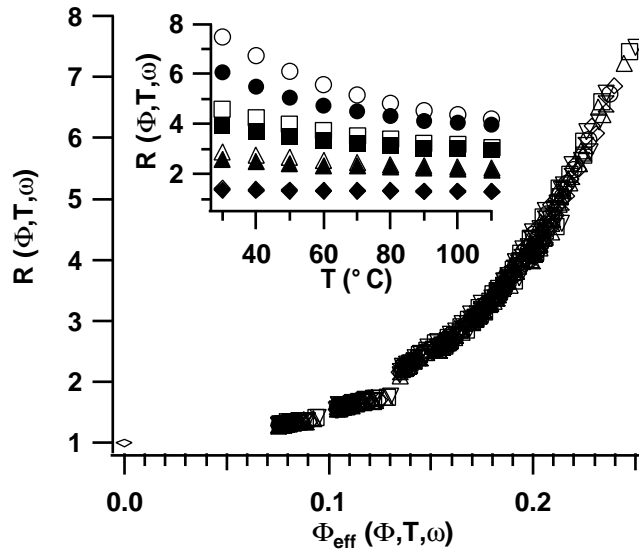


Fig. 3 – Master curve of the reinforcement as a function of the effective volume fraction Φ_{eff} , using eq. 3, for frequencies from 10^{-2} to 10 Hz, volume fraction Φ from 6.7% to 17.7% and temperature from $T_g + 50K$ to $T_g + 130K$. The solid curve is the purely geometrical reinforcement $R_{GG}(\Phi_{eff})$. Insert: Reinforcement as a function of temperature for volume fraction and frequencies respectively \circ : 17.7%, 10Hz, \bullet : 17.7%, 0.01Hz, \square : 15%, 10Hz \blacksquare : 15%, 0.01Hz \triangle : 12%, 10Hz \blacktriangle : 12%, 0.01Hz, \diamond : 6.7%, 10Hz, \blacklozenge : 6.7%, 0.01Hz.

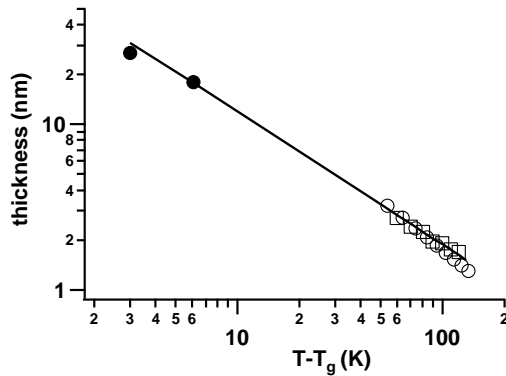


Fig. 4 – Glassy thickness e_g as a function of the temperature distance to the glass transition. Data obtained from: \square : NMR measurements, \circ : mechanical measurements at high temperature, \bullet : mechanical measurements close to the T_g of the matrix. The slope of the straight line is -0.83 .