Ageing effects around the glass and melting transitions in poly(dimethylsiloxane) visualized by resistance measurements
Brom, H.B.; Romijn, I.G.; Magis, J.G.; van der Vleuten, M.; Michels, M.A.J.

Published in:
Proceedings of the XVth International Conference on Gas Discharges and their Applications, 5-10 September, 2004, Toulouse, France

Published: 01/01/2004

Document Version
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:
• A submitted manuscript is the author's version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

Citation for published version (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.
• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain.
• You may freely distribute the URL identifying the publication in the public portal.

Take down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.
The properties of amorphous polymers (AP) often change in time below the rubber-glass transition temperature $T_g$ (1). For $T < T_g$ the material can be regarded as a solidified supercooled liquid of which the volume, enthalpy and entropy are larger than in the equilibrium state (2, 3). The gradual approach to equilibrium affects various properties of the system (not only mechanical, like elasticity, creep- and stress-relaxation rates, but also dielectric and optical (4)), and is called physical ageing to distinguish it from chemical influences. For many plastics or rubbers the ageing range includes the temperatures for practical application. The same processes are playing a role in semi-crystalline polymers (SCP), like poly(dimethyl siloxane) (PDMS), but in addition the presence of very thin crystal lamellae makes them inhomogeneous, giving a strong resemblance to composites (3). But unlike the amorphous rubbers, semi-crystalline polymers turn out to age at temperatures above their $T_g$. Usually these changes are monitored via mechanical probes (elasticity measurements), or in case of polar constituents also spectroscopically. For non-conducting non-polar crystalline and amorphous polymers addition of Carbon-Black (CB) particles has been used to make these material conducting, and the conductivity and noise data were shown to have marked relaxation effects (5). Here we revisit this approach and demonstrate that properly dispersed small amounts of conducting CB particles form a fractal network through the polymer, of which the conductivity properties can be well understood (6). The CB particles do not influence the rubber and glass transition in an essential way and hence the time evolution of the conductivity is representative for changes in the polymer itself. We illustrate the method for PDMS. The data turn out to be not only a very sensitive detector for subtle changes due to the rubber and glass transitions as found previously (5), but also demonstrate that continuous monitoring of the resistance gives insight in the long time constants of the aging process.

PDMS has a $T_g$ of the amorphous phase around 150 K and a melting transition temperature $T_m$ of the crystalline phase at 222 K (1, 7). This difference of 70 K makes the material very convenient to study the influence of both transitions on the polymer structure below room temperature. The PDMS chains have a typical length of hundred repeat units, i.e. about 100 nm, and are crosslinked at the end points only. As conducting filler material CB is attractive as it is known to form fractal distributions (8) with percolation thresholds of the order of a few tenths of a percent or lower in volume fraction, when dispersed under the proper circumstances (6). The CB (Printex XE-2 from Degussa, Probst) in the present study is quite similar to the Ketjenblacks used previously (6). The primary particles are hollow half spheres with a typical diameter of 30 nm, which in the gas phase have formed aggregates of 100 nm. The sample quality was checked by confocal scanning and optical microscopy.
As shown by Struik [4], in most of its aspects ageing in AP and SCP can be explained in a straightforward way from free-volume concepts (\(V_f\)), see Fig. 1. The segmental mobility of the polymer chains in a dense system is primarily determined by the free volume, and above a critical degree of packing steeply falls to zero.

Below the glass temperature, the AP and SCP will behave similarly, but as mentioned already, unlike AP the SCP turn out to age above their \(T_g\), for the following reason. Let us consider a SCP above \(T_g\). Since the amorphous polymer chains are connected to the crystallites, the segmental mobility near the particle surface will be reduced. Only far away from the crystallites, the mobility and other properties of the rubber matrix will be equal to those of the amorphous rubber. The glass transition of a SCP will be broadened on the high temperature side. By ageing, which will now occur in a wide range of temperatures above \(T_g\), the amorphous regions will become quite rigid. In between these two temperatures the rubber has the possibility of (re)crystallization and especially the crystallization will crucially depend on the thermal history.

The electrical conduction in systems with a low concentration of conducting particles dispersed in a nonconducting matrix, is well documented and occurs via Mott variable-range hopping. The \(T\)-dependent conductivity can be written as \(\sigma = \sigma_0 \exp\left[-\left(T_0/T\right)^\gamma\right]\), where the value of \(\gamma\) depends on details of the filler distribution, the filler density of states, and the importance of Coulomb interactions [6, 8].

We performed two kinds of measurements: temperature scans (dependence of the resistance \(R\) on \(T\) and cooling/warming rate \(dT/dt\)) and time scans (time evolution of \(R\) at constant \(T\)). In the latter we compared results of a ‘down-quench’ \(T_{room} \downarrow T\) with those of a ‘down-up-quench’ \(T_{room} \downarrow 10\ \text{K} \uparrow T\), where we discriminate between three regimes for the final temperature: \(T < T_g\), \(T_g < T < T_m\) and \(T_m < T\). The (4-points) data were also taken with pulsed fields with different field strengths to check for ohmic behavior while avoiding possible heating. Data taken at room temperature as function of filler volume fractions are well represented by \(\sigma(p) = \sigma_0(p - p_c)^t\) with \(t = 2.3 \pm 0.2\) and \(p_c = 0.0033 \pm 0.0004\). In Figs. 4 and 6 we show the resistivity as function of temperature \(T\).

\(R\) as function of \(T\). When we compare cooling-down and warming-up curves, the data only merge below 80 K and above 320 K, and show strong hysteresis in between. Apparently the region between 320 K and 80 K is affected by the melting and rubber-glass transitions, which from Differential Scanning Calorimetry data for all studied rubbers were found to be around 220 K and 160 K respectively, in agreement with the literature [1]. Dynamical Mechanical Analysis (DMA) of the same systems revealed the rubber-glass transition as a peak in \(\tan \delta\) at 154 K and the melting temperature around 220 K by a loss in viscosity. Especially because the resistance data show the same pattern independent of CB filler fractions, we conclude that at these small concentrations the CB particles do not change the polymer properties in an essential way and the aging effects in \(\sigma\), which are in general due to subtle changes in the particle network, are caused by the polymer matrix. As in previous CB samples [4], sufficiently far below the glass transition the conductivity is well described by \(\sigma = \sigma_0 \exp\left[-\left(T_0/T\right)^\gamma\right]\). From fits to \(\sigma\) between 20 and 80 K for the 1.5 % sample we find \(\gamma = 0.68\) and \(T_0 = 50 \pm 7\) K. For the interpretation we refer to Ref. 6, where these values (which can be seen as a measure for the quality of the dispersion) were argued to be characteristic for percolation on a fractal carbon network.

\(R\) as function of time \(t\). For \(T_m < T < 300\) K, the resistance after a down-quench remained constant (measured up to \(10^5\) s, not shown). The same is true for \(T < T_g\). Strong time dependences where seen for \(T_g < T < T_m\), for which a typical result is shown in Fig. 5b. Down-up-quench results with a final temperature below \(T_g\) do not show noticeable changes, which is also the case for the down-quench data. For \(T > T_m\) the similarity between the two kinds of measurements is absent and long-time tails become visible after heating, see Fig. 5. In the region \(T_g < T < T_m\) the time constants are again quite long, see Fig. 6.

How can we explain the overall features of the resistivity versus temperature and what is their connection with the melting and glass transition?

The increase in \(R\) with cooling is a general feature for hopping transport, where the available phonon energy plays an important role. The melting point remains almost unnoticed upon cooling the sample (typical cooling rate of 1-3 K per minute). This is likely because formation of crystallites is delayed and hence does not affect the distances in the percolation path. Things change around 190 K, where crystallization seems to nucleate and starts to change the CB distances and the segmental

![Fig. 2](image_url)
mobility. By this process some amorphous regions might even pass through the glass transition (see also below), by which the structural reorganization process will be slowed down appreciably. The $R$ versus $T$ curves below 80 K can be explained in the same way as in Ref. [2].

During heating from about 10 K the warming-up resistance curves remains rather smooth above 80 K, deviating strongly from the cooling down data. Some reorganization seems to occur, a process that becomes more important between $T_g$ and $T_m$. Because of the increase in chain mobility further crystallization is possible which leads to more free volume, etc. We believe that this process is at the heart of the resistance anomaly around the melting temperature of 220 K. Above $T_m$ the crystals melt and the whole polymer system becomes amorphous. Note that, in contrast, in the DMA data mainly the rubber-glass transition shows up during warming up. This phenomenon might find its explanation in the specific character of the conductance data, which are very sensitive to changes on small (atomic) length scales, while DMA and other methods that are applied from outside probe mean values where longer distances are involved.

What can we learn more by looking at the time dependence of $R$? The fact that after a down-quench to $T$ above $T_m$ the resistance remains stable, is no surprise as no isothermal volume relaxation or crystallization is expected: the system is still in thermodynamic equilibrium. The effect of the down-quench to 205 K is remarkable (Fig. 4). First the resistance grows and thereafter it decreases with a much longer time constant. It also appears that the closer we go to the melting temperature the longer the initial time constant becomes. Most likely the increase in resistance is due to the formation of crystalline regions. This process will redistribute the CB particles and create some longer distances and hence so called "hard hops" in the percolation path through the sample, which will increase the resistance. In the neighborhood of the crystalline material the chain mobility is reduced - some amorphous regions are passing through their glass transition and therefore we are now in the broadened $T_g$ regime, with slow isothermal volume relaxation. The removal of free volume will bring the CB particles closer together and lead to a decrease in $R$.

In summary, dispersing small amounts of CB particles in a fractal network in non-conducting rubbers opens a convenient way for continuously monitoring the structural changes on small length scales due to ageing. Even above the melting temperature we observe long time constants in the relaxation and therefore have to conclude that the sample is still not in thermal equilibrium. Only by waiting for several days, the hysteresis loop seems to close again.

We acknowledge Océ Technologies for providing the samples and hospitality (MvV), and Sander Smit and Julian Hulea for participation in the measurements. The work of I.G.R. forms part of the research programme of FOM-NWO.

References


[9] At the same time, although $\sigma$ is due to the CB-particles, its changes are driven by the polymer matrix.