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# How polymers lose memory with age

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## Abstract

Uniquely in the world of materials, polymers deformed at high temperature and subsequently quenched to low temperature, memorize the temperature at which they have been processed. Polymers can even memorize multiple temperatures. This temperature memory is reflected by a maximum of residual stress restored at the temperature of initial processing. It has been speculated that this capability could arise from the presence of dynamical heterogeneities in glassy domains of polymers. Processing the material at a given temperature would result in the selection of certain heterogeneities that participate to the storage of mechanical stress. But because dynamical heterogeneities are associated to particular relaxation times, temperature memory of polymers should depend on time such as the glass transition temperature depends on the frequency. The first experimental study of temporal effects on the temperature memory of polymers is presently reported. It is found that aging at high temperature shifts the maximum of residual stress towards greater temperatures. The corresponding loss of memory is explained by the relaxation of dynamical heterogeneities with short characteristic times. The present results clarify the origin of the temperature memory and provide insights for its efficient exploitation in applications.

## Introduction

The properties of most solid materials depend on their processing and thermal history. Quench hardening of steel for example is used for centuries to make materials with improved properties. Thermal treatments coupled to mechanical deformations affect the structures of materials and allow non-equilibrium states to be quenched. Generally the resultant variations of properties and memorization of temperature remain qualitative. But quite uniquely in the world of condensed matter, glassy and semi-crystalline polymers have been recently shown to exhibit an accurate memory of the temperature at which they have been processed prior a thermal quench. This memorization was performed in the frame of studies of shape memory polymers. Shape memory polymers (SMPs) are intensively investigated for applications such as packaging, heat shrink tubing, deployable structures, smart textiles, morphing composites and biomedical applications [1-11]. SMPs are first mechanically deformed at a given temperature before being quenched to a fixed state at low temperature. Shape recovery is triggered in a second stage by heating the material. The treatments

of the first stage are defined as the programming process. SMPs are programmed at a high temperature  $T_d$  which is generally above the glass transition temperature  $T_g$  of the polymer. A temporary shape is fixed by cooling down the material under fixed strain. Mechanical energy is stored by polymer chains which are frozen in unstable conformations. Heating the material at high temperature, above  $T_g$ , allows the polymer chains to gain mobility and to revert towards more stable conformations. The material either generates a mechanical stress if its strain is kept fixed during heating or reverts towards its original shape in absence of applied load. The shape memory behavior of polymers can be tuned by the programming process in a surprisingly accurate way. Indeed, even simple polymers exhibit a so-called “temperature memory effect” (TME) [5, 12-20]. This effect refers to the ability of a polymer to memorize the deformation temperature  $T_d$  even after having been cooled down to an arbitrary temperature. Polymers actually exhibit a peak of generated stress at a temperature  $T_s$  when the material is reheated in conditions of fixed strain. The generation of stress corresponds to the relaxation of the stress stored during the programming process. The temperature  $T_s$  was found to be nearly equal to  $T_d$ . An inflexion of the strain recovery rate at  $T_s=T_d$  was also reported in free strain experiments [12]. More recently, it was observed that polymers have also the capability to memorize multiple temporary shapes [21-28] in a single shape memory cycle in free strain conditions [25]. This effect called “multiple shape memory” reflects the exceptional ability of polymers at memorizing complex programming processes and different temperatures. The possibility to control the shape memory behavior of polymers by changing the programming process provides routes toward new applications of SMPs without changing their chemical compositions. Exciting examples of possible applications have been recently reported [14, 18] and many others are expected to emerge. Nevertheless, in spite of a fast growing interest in the TME, the origin of this phenomenon remains elusive. It has been speculated that TME and multi-shape memory effects could be due to the intrinsic broadness of the glass transition [12]. This transition is a dynamical phenomenon which involves dynamical heterogeneities of the polymer material [29-32]. Dynamical heterogeneities are associated to different relaxation times [29-32]. Time and aging are therefore expected to play an important role in the memory of polymers. Heating and deformations rates have been actually shown to alter the response of shape memory polymers [33, 34]. The observed effects were described using the phenomenological concepts of temperature dependent visco-elastic properties of the materials. But the influence of kinetics factors on the TME remains to be established.

We report in this work an experimental study of shape memory effects in different kinetic conditions of programming. Neat polyamide 12 (PA12) and polyamide micro-fibers loaded with carbon nanotubes (CNTs) are used in the present study. These materials allow temporal effects as well as double-shape memory effects in conditions of fixed strain to be explored. It is found that the temperature memory is lost when the materials are slowly deformed during the programming process. In addition, the sequence order of programming temperatures and draw ratio are essential to achieve responses that reflect a multi-temperature programming process. The present findings are discussed by considering the mechanical energy supplied during the programming process and the relaxation of dynamical heterogeneities at different temperatures. From a more applied point of view, the present results show how to optimize the processing of polymers to achieve accurate temperature and multi-shape memories. It is concluded that fast temperature quenches are needed to achieve an accurate TME. A fast quench prevents dynamical heterogeneities with short characteristic times from relaxing. Polymer domains associated to these heterogeneities can thereby

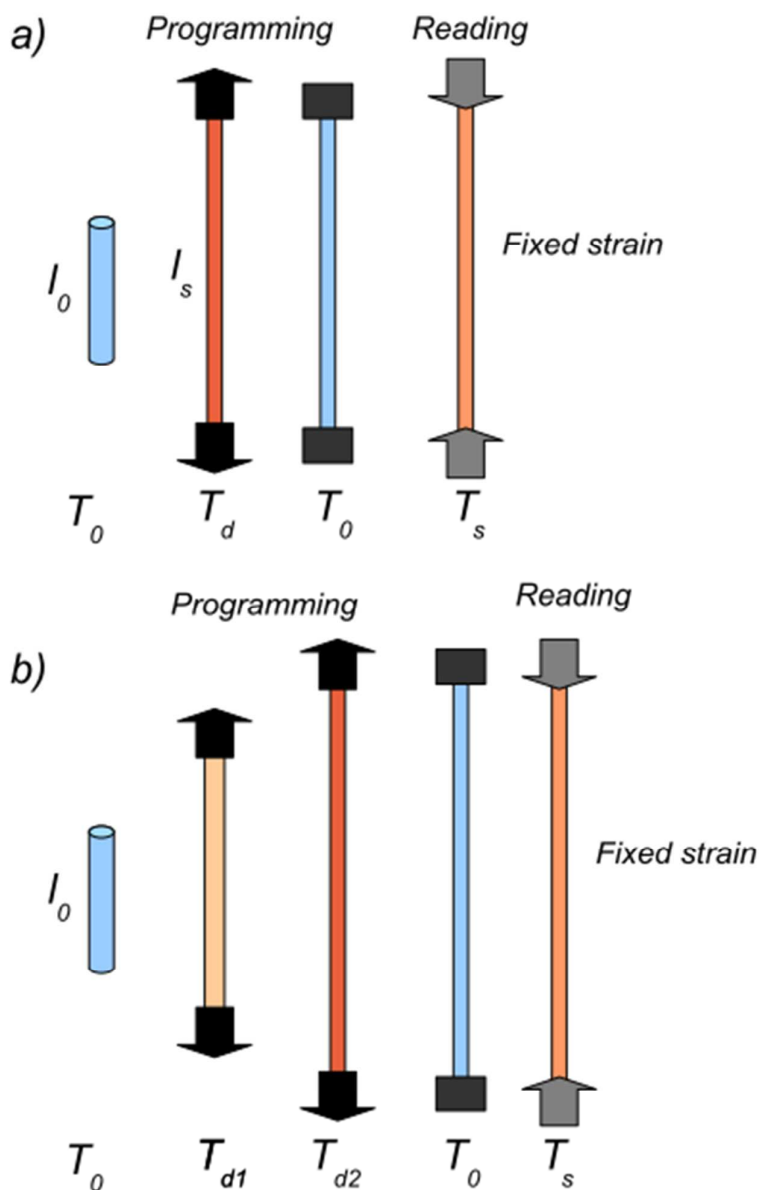
store mechanical energy and contribute to the shape memory behavior. Even though recent studies on distinct polymers suggest that TME is a general phenomenon, the present results clarify why temperature memory effects could be easily evidenced with polymer micro-fibers loaded with carbon nanotubes. Because of their small volume and enhanced thermal conductivity such materials can indeed be quickly quenched to low temperature. It is possible that the relatively late discovery of the TME in spite of extensive studies of shape memory polymers in the past was due to slow temperature quenches and/or to the large dimensions of the investigated samples.

## Experimental

Neat and composite fibers (Figure S1) made of polyamide 12 (AMNO TLD-grade Arkema) and multiwall carbon nanotubes (C100- Graphistrength Arkema) produced by a catalyzed chemical vapor deposition process were used throughout the study. The glass and melting temperatures of the polymer respectively are 55°C (Figure S2) and 180°C. The nanotubes have an average external diameter of 10-15nm and a length of a few hundreds of nanometers. The fibers have been spun by a melt spinning process already described in the literature [35, 36]. The composite fiber contains 7 wt% of CNT. Before processing, neat PA12 or PA12-CNT blends (Figure S3) were dried overnight at 80°C in vacuum. The dried materials were introduced in a Scamex single screw extruder (Figure S4) and heated up to 250°C, a temperature well above the melting temperature of the polymer. The molten polymer was forced through a cylindrical spinneret with a 0.5 mm diameter. The screw extruder velocity was set to 30 rpm to control the supply rate of polymer. The extruded filament was wound up around the rolls of a drawing bench at a constant take-up velocity (Figure S4). The linear velocity of the collecting roll was set to 27.5 m/min. The diameter of the resultant fibers is about 200  $\mu\text{m}$ . Mechanical and thermomechanical properties have been characterized using a Zwick BTC-2.5TN.D09 tensile test machine and a temperature controlled chamber, as detailed in [12]. A piece of fiber of length  $l_0$  is stretched at a temperature  $T_d$ , or at two different temperatures  $T_{d1}$  and  $T_{d2}$  for double shape memory experiments, and then cooled down to room temperature under fixed strain. Samples with a length  $l_0$  of 10 mm have been used throughout the present study. The samples are heated up to  $T_d$  in a few minutes typically. This time is not controlled but has no influence on the performed experiments. The fibers are treated only when the temperature has reached  $T_d$  (or  $T_{d1}$  and  $T_{d2}$ ). They are not deformed while heating. Programming processes are characterized through the measurements of stress vs strain curves. The computed stress is the true stress. The force is normalized by the section of the stretched fiber. The section is deduced from the original section and by considering that the volume of the fiber remains constant during stretching. A first series of experiments is performed to assess the temperature memory of neat PA12 and nanocomposites. The materials are deformed at either  $T_d=60^\circ\text{C}$  or  $T_d=120^\circ\text{C}$ . The heated fibers are then quickly cooled down to room temperature after having been stretched up to 200% at a rate of 20mm/min. Fast cooling is achieved by switching off the heater of the controlled temperature chamber and by opening its door. The rate of heating was then varied to study temporal effects. In particular, in a second set of experiments, CNT-PA12 fibers are programmed at the same temperature 100°C and at the same level of strain of 200%. But the fibers are stretched at different rates from 0.056mm/min up to 100mm/min. The corresponding stress vs strain curves are shown in Figure S5. In other series of experiments the fibers have been kept a given time  $t_h$  at high temperature before being cooled down to room temperature. In the last series of experiments, fibers have been stretched in two

stages. They are first stretched at 140°C and at 20mm/min to a length  $l_{s1}$  that corresponds to a strain deformation of 80%. The fibers are then cooled down to 60°C at fixed strain and then further stretched at the same speed to a length  $l_{s2}$  so that the total strain deformation reaches 180%. Control fibers have been stretched in similar conditions but in a single stage at a single temperature.

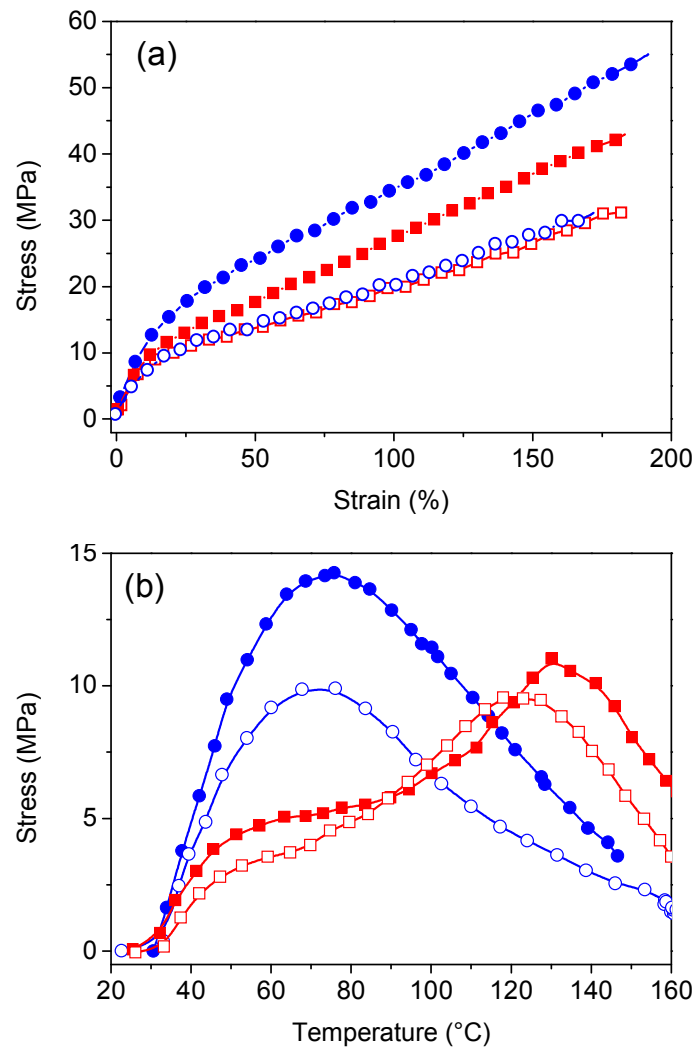
Shape memory effects have been characterized by re-heating the fibers under fixed strain. The length  $l$  of the stretched fiber was kept constant after the programming process. The stress generated by the fiber was monitored by the force sensor of the tensile test machine. The stress is deduced from the generated force normalized by the section of the stretched fiber. The strain  $\varepsilon$  is defined by  $\varepsilon = \frac{l-l_0}{l_0}$ . The rate of heating during recovery experiments is set to 5°C/min. This rate allows a clear manifestation of temperature memory effects. It is expected that this factor should have an influence on the recovery behavior but is kept constant to achieve comparable results in the present different series of experiments.



**Figure 1:** (a) Experimental method to characterize thermomechanical properties of polymer materials. A fiber sample of length  $l_0$  is stretched at a temperature  $T_d$  to a length  $l_s$ . The sample is then cooled down to room temperature  $T_0$  under fixed strain. In the last reading stage, the fiber is heated and its propensity to contract is reflected by the generation of a force under fixed strain. Different series of experiments are performed by changing the stretching rate or the time during which the samples are kept at high temperature before cooling. (b) A similar approach is used to study double shape memory effects. In this case the fiber is first stretched to a length  $l_{s1}$  at a temperature  $T_{d1}$  and then stretched further to a length  $l_{s2}$  at another temperature  $T_{d2}$ . The sample is then cooled down and reheated in a last reading stage.

## Results

The stress vs strain curves of the programming process of fibers deformed at  $T_d=60^\circ\text{C}$  or  $T_d=120^\circ\text{C}$  are shown in Figure 2a. It is observed that fibers loaded with CNTs exhibit a greater Young's modulus than neat PA12.



**Figure 2:** **a)** True stress vs strain curves of neat PA12 (open symbols) and CNT-PA12 (filled symbols) composite fibers drawn at either  $60^\circ\text{C}$  (blue circles) and  $120^\circ\text{C}$  (red squares). The area under each curve represents the energy absorbed by the fibers. **b)** Stress generated by neat PA12 (open symbols) and CNT-PA12 (filled symbols) fibers programmed at different temperatures at either  $60^\circ$  (blue circles) and  $120^\circ\text{C}$  (red squares). The stress is measured as the temperature is raised from  $20$  to  $160^\circ\text{C}$  at a rate of  $5^\circ\text{C}/\text{min}$ .

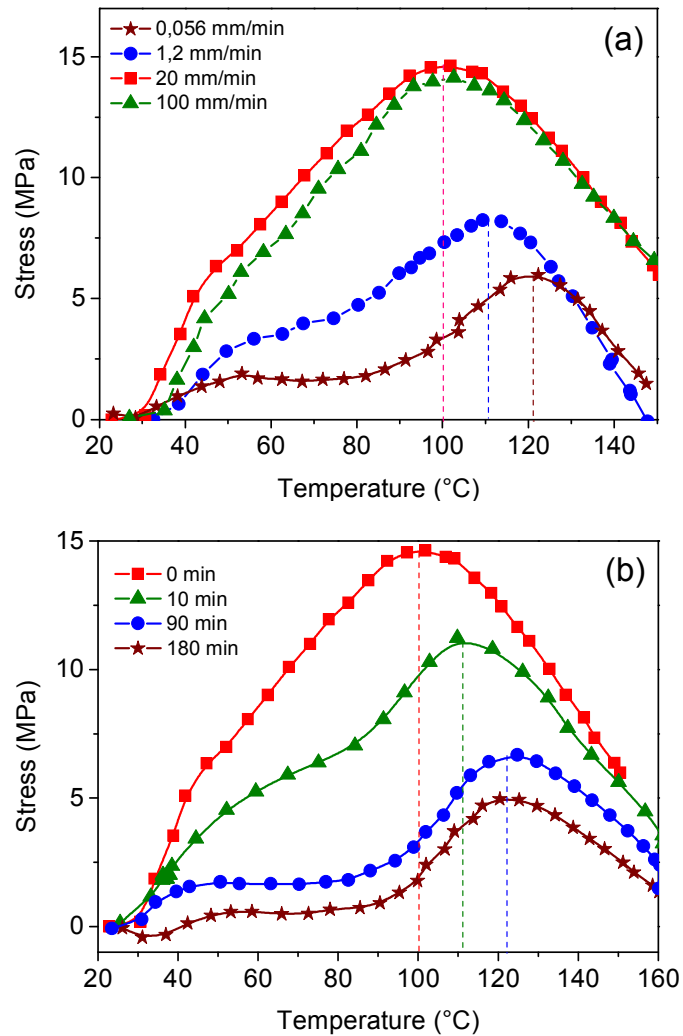
The heated fibers are then quickly cooled down to room temperature after having been stretched as indicated in the experimental section. The stress generated during reheating at fixed strain is shown in Figure 2b.

The conventional temperature memory effect (TME) is well observed. Indeed the generated stress for both samples exhibits a peak at a temperature that is close to the temperature of programming. Fibers programmed at 60°C exhibit a peak at 75°C whereas fibers programmed at 120°C exhibit a peak at 130°C. It is also observed that the stress generated by CNT-PA12 fibers is greater than that generated by neat PA12 fibers. This can be understood by considering that CNT-PA12 fibers have absorbed more energy during the programming and display a greater Young's modulus. It can also be noted that the generated stress is greater for fibers treated at 60°C compared to fibers treated at 120°C. Actually this is in agreement with earlier studies showing that the generated stress decreases with increasing temperature [12]. The TME could in principle be observed at higher temperatures. But such experiments would result in a still lower generated stress and in a less clear manifestation of the effect.

In the second set of experiments, the fibers are stretched at different rates from 0.056mm/min up to 100mm/min. As in previous experiments, the fibers are quickly cooled down to room temperature before the reading step. The stress generated by the fibers upon reheating is shown in Figure 3a. It appears that fibers programmed at a high drawing speed exhibit an accurate TME. Indeed the stress generated by such fibers shows a peak at the temperature of pre-deformation. Fibers that have been slowly deformed also exhibit a peak of generated stress. Surprisingly this peak is shifted towards temperatures well above the programming temperature. The difference of  $T_s$  from  $T_d$  increases with lowering the speed of drawing. Fibers that have been drawn at low speed have actually spent a greater time at high temperature before cooling. One can thus wonder if the loss of TME is due to the long time spent at high temperature for fibers that have been slowly stretched. Indeed the total time required to draw the fibers is on the order of 6 hours for fibers drawn at 0.056mm/min whereas it is only of about 12 sec for fibers stretched at 100mm/min.

In order to answer this question, CNT-PA12 composite fibers have been drawn at the same temperature of 100°C and at the same drawing speed of 20mm/min. But the fibers have been kept a different time  $t_h$  at 100°C at the end of the drawing process before being cooled down to room temperature. The aging time  $t_h$  was varied from 0 sec (direct quench as soon as stretching was completed) to 180 min. The stress generated by the treated fibers upon re-heating is shown in Figure 3b.

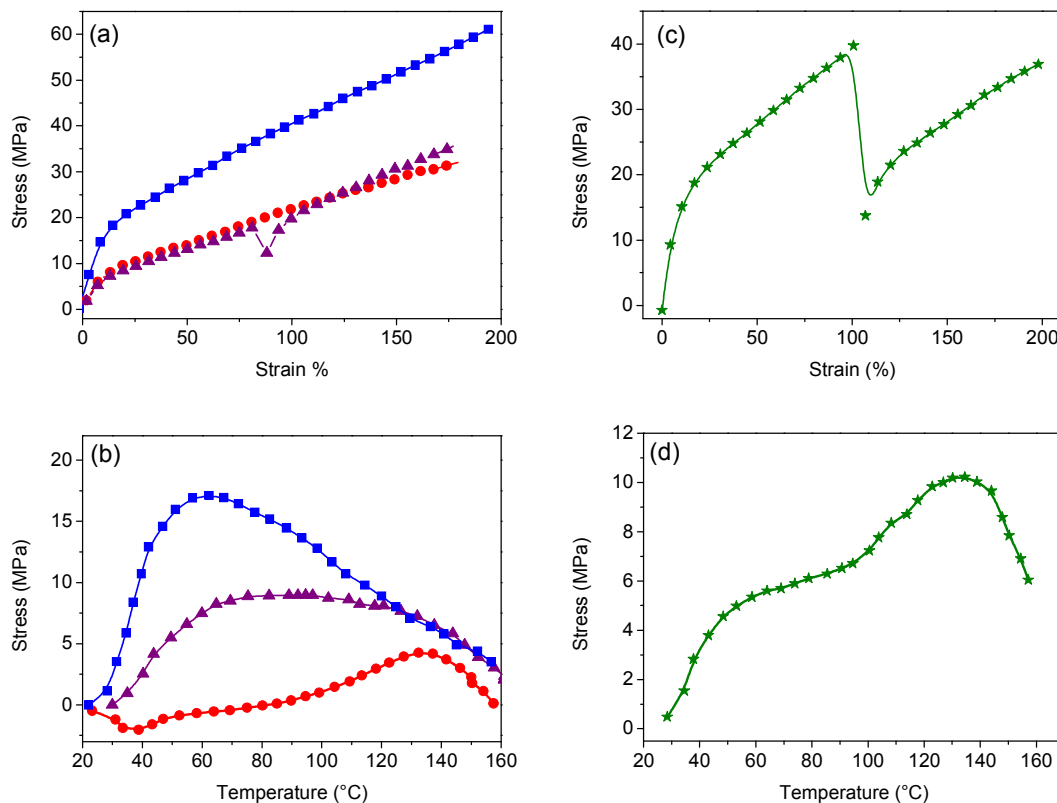




**Figure 3:** **a)** Stress generated by CNT-PA12 fibers programmed at 100°C but stretched at different speeds from 0.056mm/min up to 100mm/min. The stress is measured as a function of temperature. The temperature is raised at a rate of 5°C/min. **b)** Stress generated by CNT-PA12 fibers programmed at 100°C but kept a certain time  $t_h$  at 100°C before being cooled down to room temperature.  $t_h$  was varied from 0 to 180min. The stress is measured as a function of temperature. The temperature is raised at a rate of 5°C/min.

Here again a surprising loss of TME is observed when the material ages for a long time at high temperature. However materials that have been quenched instantly or shortly after the programming stage exhibit an accurate TME. It is also important to note that the loss of TME is associated to a decrease of generated stress. This is observed both for fibers stretched at different velocities and fibers kept at high temperature during different times.

In the last series of experiments, fibers have been programmed by stretching the samples in two stages as indicated in the experimental section. Control fibers have been stretched in similar conditions but in a single stage at a single temperature. The corresponding stress vs strain curves are shown in Figure 4a.



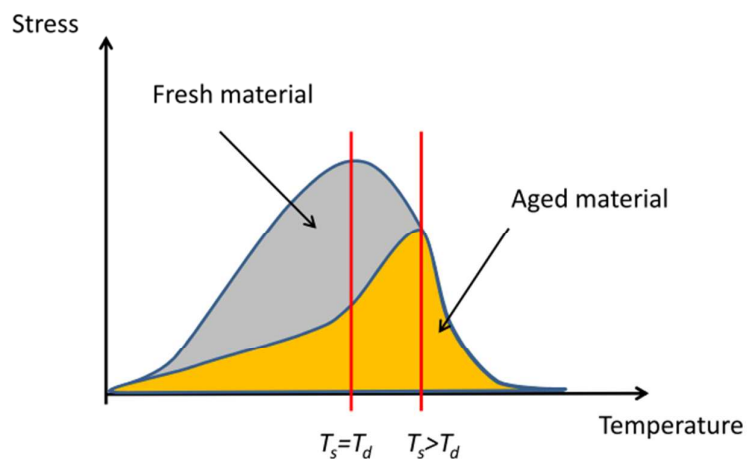
**Figure 4:** **a)** True-stress vs strain curves of CNT-PA12 fibers stretched either in a single step at 60°C (blue squares) or 140°C (red circles) or in a double steps process (purple triangles) with a first stretching at 140°C and a second stretching at 60°C. **b)** Stress generated by the fibers programmed in conditions used in Figure 4a. The stress is measured as a function of temperature. The temperature is raised at a rate of 5°C/min. **c)** True stress vs strain curve of a fiber stretched at 60°C to a strain of 100% and subsequently at 140°C to a total strain of 200% (green stars). **d)** Stress generated by the fiber programmed in conditions used in Figure 4b. The stress is measured as a function of temperature. The temperature is raised at a rate of 5°C/min.

The memory of such materials is evaluated by using the same reading procedure as above. The curves of generated stress at fixed strain are shown in Figure 4b. Curves of the control materials treated at a single temperature reflect the conventional TME observed in other materials with a peak of generated stress at a temperature  $T_s$  nearly equal to  $T_d$ . By contrast, the curve for fibers treated at two temperatures doesn't exhibit a sharp and well defined peak. Instead, it exhibits a broad peak that could result from a convolution of peaks at 60°C and 140°C. This shows for the first time a signature of a multi-shape memory effects in conditions of fixed strain. The programming sequence has been inverted in a subsequent experiment. Samples have been first stretched to 100% at 60°C and then up to 200% at 140°C. The corresponding stress vs strain curve is shown in Figure 4c. Stretching was performed at 20mm/min. The stress generated by such fibers after quench and upon

reheating is shown in Figure 4d. The curve differs markedly from the curve shown in Figure 4b. Indeed, the generated stress now exhibits a main peak of maximum stress at 140°C. But the signature of the treatment at 60°C is much less pronounced. Actually the curve in Figure 4d is closely reminiscent of curves shown in Figure 3 and 2, which are curves for materials treated at a single temperature. It seems therefore that the first step of the processing has been erased by the second treatment at high temperature. This observation highlights the critical importance of the programming process in the shape memory properties of polymers.

## Discussion

The above results can be understood in a single and general framework by considering fundamental concepts of the glass transition and the importance of dynamical heterogeneities in glassy materials. Dynamical heterogeneities are associated to distinct characteristic relaxation times. Relaxation time distributions are shifted to faster characteristic times with increasing temperature. When the material is stretched at a given temperature  $T_d$ , fractions of polymers which exhibit short characteristic times at  $T_d$  relax quickly and do not store mechanical energy before completion of the programming process. This is why such fractions of polymers are not expected to contribute to the shape memory behavior. By contrast fractions that have a long relaxation time at  $T_d$  remain deformed and store mechanical energy after completion of the programming process. Upon reheating, most of the mechanical energy is restored at the temperature of pre-deformation because the time scales of the programming and reading experiments are on the same order of magnitude. These arguments have been already speculated in the literature to explain the temperature memory effect [12]. Nevertheless, these speculations were only based on the observation of the TME and were not supported by any other experimental facts. The present results which include kinetic effects and double shape memory effects provide a strong support to the above scenario. Indeed, it is observed that a slow deformation or the storage of deformed polymer at high temperature induces a loss of the TME. This loss is associated to a decrease of generated stress at low temperature. This results in an apparent shift temperature of the peak of generated stress towards higher temperature, as schematized in Figure 5.



**Figure 5:** *Fresh materials exhibit a good temperature memory with a peak of generated stress at  $T_s \sim T_d$ . During aging at high temperature dynamical heterogeneities with short characteristic times associated to low temperatures relax in first place. The contribution of energy storage at low temperature is therefore lost with aging. This lost contribution appears in grey in the schematics. Only dynamical heterogeneities with long relaxation times at high temperatures contribute in aged materials. The peak of generated stress thus artificially appears at a temperature  $T_s$  greater than  $T_d$ . The material loses memory with age.*

The loss of generated stress at low temperature arises from the fact that dynamical heterogeneities with short relaxation times have ample time to relax if the material is too slowly deformed or kept a long time at high temperature before quenching. Only fractions with long relaxation times associated to high temperatures store mechanical energy in these conditions. These fractions restore energy when the temperature is sufficiently high during the reading process. Time plays therefore a critical role in the shape memory behavior, exactly as in the glass transition where the interplay of time and temperature is often described by the so-called time-temperature superposition principle. Double and multi-shape memory effects can be understood in the same framework. Indeed, only fractions of polymers with long relaxation times would be involved in the storage of mechanical energy if the material is first rapidly deformed at a high temperature. Fractions of polymers that exhibit slow relaxation times become highly deformable only at high temperature. These slow fractions don't have time to relax. In a second step, when the material is stretched at low temperature, fractions of polymers with short relaxation times come into play. But fractions, which have responded only at high temperature, are not expected to be substantially affected by further quenches at low temperature. The material after programming is composed of fractions deformed at different temperatures and draw ratio. The response of the polymer in reading experiments naturally reflects this particular state resultant from effects of dynamical heterogeneities stimulated at distinct temperatures. Now let's consider a programming process in which the material is first deformed at low temperature. In these conditions, only fractions of polymers with short relaxation times are affected. Fractions of polymer with longer relaxation times have to be heated to greater temperatures to be involved. In the second step of the process, which corresponds to a deformation at a greater temperature, these slow polymer fractions are actually stimulated. But at the same time the fractions with short relaxation times associated to lower temperatures have ample time to relax. This is why the first programming steps at low temperatures are literally erased by the last treatment at high temperature.

The present results also provide guidance for optimization of temperature memorization and clarify why TME is not systematically observed in all shape memory polymers. Indeed, as presently observed a clear memorization is associated to a fast cooling quench. Such a fast cooling is more easily achieved in samples of small dimensions such as micro-fibers. In addition, cooling can be accelerated with an improved thermal conductivity of the material [37]. The addition of carbon nanotubes, or other stiff solid fillers, to polymers increases their thermal conductivity. This is why such an addition can help in improving the memory of the material, in particular for large specimens. Indeed, large samples that exhibit a low thermal conductivity are not expected to display an accurate temperature memory because of the long time needed to cool them. This can explain why TME was not observed in some past studies of shape memory polymers. Even though it is difficult to quickly cool down materials of large dimensions, large structures with TME can still be envisioned. Microfibers can indeed be assembled into large cables, belts or textile structures. Such assemblies could therefore be

used as materials smarter than conventional shape memory materials that respond uniquely at a given temperature. Here macroscopic structures made from micro-sized materials could exhibit temperature and multi-shape memory phenomena otherwise not achievable on large scale.

## Conclusion

In conclusion, the thermo-mechanical memory of polymers strongly depends on kinetic factors. The deformation speed of processing is important as it determines the time spent by the material at high temperature. Polymers exhibit a TME if this time is kept sufficiently short. But they lose memory with age because of the relaxation of dynamical heterogeneities with time. The shown experiments therefore strongly support that temperature and multi-shape memory effects arise from the broadness of the glass transition; the latter being associated to dynamical heterogeneities with a large distribution of relaxation times. From a more technological point of view, the present results provide also a guidance to optimize shape memory effects with temperature or deformation at different temperatures. It is in particular critical to perform fast quenches in order to avoid the relaxations of dynamical heterogeneities associated to short relaxation times. This is why small samples that exhibit good thermal conduction are ideal candidates for the manifestation of such phenomena. Larger scale structures may be developed by assembling micro-sized samples. Work is currently in progress with the development of textiles that exhibit porosity changes at a single well defined temperature or at different temperatures based on temperature and multi-shape memories of polymer microfibers.

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