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An Electric Criterion to Evaluate Glass Transition Temperature: Dielectric Relaxation Measurements

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Summary: In this contribution, a dielectric measurement technique for the evaluation of phase transition temperature and the study of physical aging on polymeric thin films is considered. This kind of measurement provides the possibility of displaying phase transitions with a high degree of precision. Furthermore, it can be considered alternatively to techniques not applicable in the case of thin films, such as Differential Scanning Calorimetry (DSC). In this work, owing to the high sensitivity of the utilized experimental set-up, a glass transition T_G of 156 K, with a precision equal to 0.3%, and a melting $T_M = 220$ K have been assessed for 4 μm thick Polydimethylsiloxane (PDMS) films. Performing measurement as a function of time, it was possible to monitor physical aging phenomena, mainly consisting in a change of dielectric properties. As expected, the time evolution of the aging phenomena can be described by a simple logarithmic law.

Keywords: A.C. measurements; dielectric relaxation; glass transition; physical aging; Universal Dielectric Response

I. Introduction

The growing worldwide interest for organic electronics is justified by the possibility to fabricate low cost devices, which can be easily integrated with large area and flexible substrates, unlike the more traditional silicon based devices.[1,2] In this regard, the study of the properties exhibited by polymers grown as thin films, used as substrates or active layers, is very important in order to optimize their electrical behavior and investigate the real application perspectives.[3]

In particular, concerning their structural properties, it is well known that amorphous polymers undergo both a glass, T_G, and a melting, T_M, transitions, producing the change of the mechanical properties. Furthermore, polymers display also a physical aging which can be responsible for device performance degradation.

About the experimental evaluation of T_G, it should be observed that its value can be strongly affected by the conditions of the performed experiment. Indeed, it is widely reported in literature that the T_G value depends on the film thickness and on the interactions between the film and the substrate.[4,5] Due to this dependence, T_G value can change of many tens of degrees. Usually, T_G is determined by performing thermo-mechanical measurements, such as Differential Scanning Calorimetry (DSC),[6] requiring very thick specimens.[7] A more refined version of this technique, the so called Ultrasensitive Differential Scanning Calorimetry[8] can be used also on thin films, but it operates only in particular and restrictive conditions. More recently, T_G has been evaluated on thin PDMS films by means of electrical measurements; in particular R(T) measurements can highlight the glass transition but, unfortunately, these measurements require a doping procedure.[9] Actually, it is clear that by this

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technique the T_G value can be modified by the presence of dopants and by their concentration.[10,11]

An alternative electrical tool for the evaluation of glass transition temperature in polymeric films is represented by dielectric relaxation measurements, consisting in the visualization of both the dielectric permittivity ε_r and the a.c. conductivity $\sigma_{a.c.}$ (i.e. dielectric losses).[12] Such measurements allow to study the local and cooperative chain dynamics of polymers, both in the liquid and solid state, across an extremely wide range of frequencies (10^{-2}–10^{10} Hz). In particular, the segmental dynamics, which is referred to as the α-relaxation (in the low and middle frequency regions, up to 10^5 Hz), reflects the dynamic glass transition. In this scenario, the temperature dependence of the dielectric function $\varepsilon(T,\omega)$ (where $\varepsilon(T,\omega) = \varepsilon^{|}(T,\omega)\text{-}i\varepsilon^{||}(T,\omega)$, with $\varepsilon^{|}(T,\omega) = \varepsilon_r(T,\omega)$ and $\varepsilon^{||}(T,\omega)^{*}\omega^{*}\varepsilon_0 = \sigma_{a.c.}(T,\omega)$), for a fixed frequency ω belonging to the above mentioned range, allows to display the phase transition and consequently to evaluate qualitatively the value of T_G. By this measurement procedure, the precision of the extracted T_G value is strictly related to the high degree of cleanliness that can be reached. Furthermore, the permittivity ε_r allows also to monitor the Physical Aging coming from the modification of dielectric properties, since the degradation is related to the cooperative motion of chains too.[13] In this paper, we report on the evaluation of T_G and T_M of PDMS (Poly-dimethylsiloxane) thin films, by using a dielectric measurement technique. A first analysis of Physical Aging undergone by the same material has been reported too. The choice of PDMS is due to the fact that it is one of the most known Semi-Crystalline Polymers. Its simple chemical constituent (Fig. 1) is a backbone $[SiO(CH_3)_2]_n$ arranged in a network-like structure, where the Si–O bonds give a considerable flexibility to the polymeric backbone. PDMS is widely studied both for its mechanical and unusual rheological properties, which render its applications interesting in several fields, such as microfluidics.[14] In addition, it is believed that due to its low dielectric constant value, it is also a good candidate for microelectronics,[15] in particular for Organic FET applications.[16]

Further developments of such technique, concerning its application to different organic materials with T_G between 300 and 400K, will be reported elsewhere.

Moreover, we are going to analyze the opportunity of describing the T_G behavior as a function of the a.c. electrical field frequency according to a logarithmic behavior related to relaxation phenomena in supercooled liquids.[17]

II. Experimental Details: Samples Preparation and Experimental Setup

The starting point of our analysis was the fabrication of simple parallel plane plate capacitors, filled with PDMS dielectric films (Fig. 1).

Usually, such devices are employed to study and characterize the dielectric and conducting properties of many materials by the determination of the permittivity, ε_r, and the a.c. conductivity, σ, as a function of frequency, temperature and d.c. bias. These quantities can be simply extracted from a measurement of the capacitance C and conductance G by the formulas:

$$\varepsilon_r = \frac{C * d}{\varepsilon_0 * S}; \quad \sigma = \frac{G * d}{S} \tag{1}$$

where ε_0 is the vacuum permittivity, S is the surface of the metallic plates and d the thickness of the material filling the capacitor. In our work, the PDMS films were sandwiched between an Ag bottom electrode (S about 9 mm^2), deposited by sputtering on glass substrates, and an Al top electrode, deposited on the top of the PDMS by thermal evaporation technique in high vacuum conditions (10^{-6} mbar).

PDMS thin films, Sylgard 184 purchased by Dow Corning, were spin coated in a clean room on the above mentioned metallic plates; in detail, Sylgard 184 is a

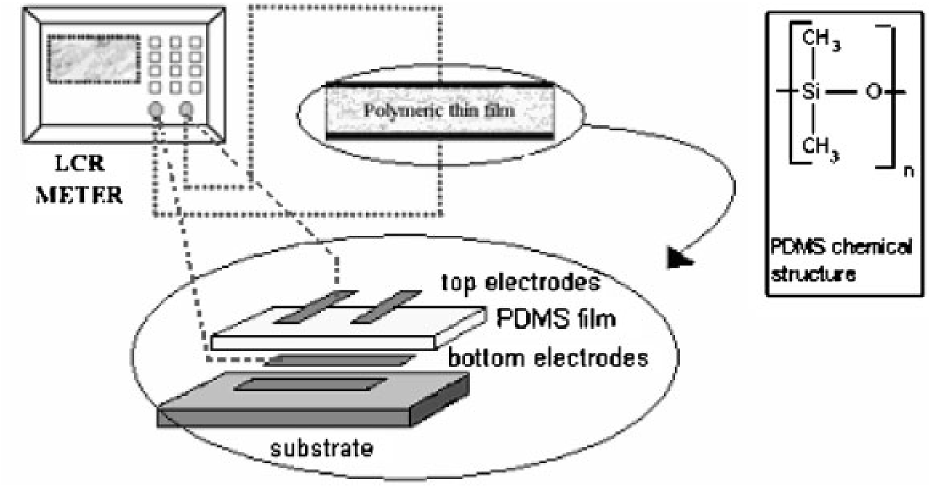

Figure 1.
Layout of the experimental set up and geometry of the manufactured capacitor. In the inset, the chemical structure of PDMS monomer is displayed.

two-component heat-curing system and consists of one part of curing agent and ten parts of base (by weight). The base and the curing agent were mixed in a plastic cup using a plastic spoon for at least a few minutes, depending on the amount of material. After the mixing, the silicone mixture needed to be degassed in vacuum in order to remove air bubbles incorporated during the mixing phase. When the silicone was completely clear and transparent it was ready to be spinned. After spinning, the samples were annealed for one hour at 100 °C. Capacitance and conductance were measured in vacuum both as a function of frequency and temperature by an Agilent LCR meter (Fig. 1). To this end, the sample was mounted in a cryogenerator which allows to perform measurements in a temperature range between 40–340 K. For higher temperatures, a vacuum probe station, already described in ref. [18], can be used. The cryogenerator, furnished with an antivibrating support, was then connected to the LCR meter by means of SMA connectors. The experimental resolution for the capacitance and conductance measurements is equal to 10^{-1} pF and 10^{-10} S, respectively. The electrical connections on the sample inside the cryogenerator were made mainly by spot weldings and, sometimes, by silver paste, avoiding contacts between the silver paste solvent and the polymer.

The analysis here reported has been performed in a temperature range starting from room temperature down to 40 K, with a cooling rate of 5K/min, and subsequently by warming up the samples with an heating rate, slower than 2 K/min. In this way, it is possible to evidence the differences induced on phase transitions by different cooling-warming rates.[19] Finally, temperature was monitored accurately with two different thermometers.

III Experimental Results: Phase Transitions and Physical Aging

As described above, the experimental set up allows to perform a complete analysis of the dielectric response as a function of temperature, frequency and applied d.c. bias. However, here, our analysis has been focused on the detection of the phase transitions and on the study of the aging effects by measurements mainly performed as a function of temperature and time. A more complete analysis, including the dielectric response dependence on frequency and d.c. bias will be reported elsewhere, also considering different sample geometries.

Phase Transition

In Fig. 2, typical capacitance (Fig. 2.a) and conductance (Fig. 2.b) measurements, performed as a function of temperature, are reported. These measurements were carried out at a frequency of 1 KHz and with an a.c. voltage V = 0.1 Volt. No significant changes have been observed by increasing the a.c. voltage level up to 10 Volts.

As expected, at room temperature, the permittivity value for PDMS extracted by the formula (1) is about 2.4, while the d.c. conductance results to be limited by the experimental set-up, since as expected from the data reported in literature it is lower than 10^{-10} S.[20]

Focusing the attention on the curves displayed in Fig. 2a, the experimental measurements well agree with the predictions of the Free Volume Theory.

Below T_G, the available specific volume (where polymeric chains present a non null segmental mobility) reduces to its minimum value, so the rotation of the bonds doesn't occur any more (the material becomes hard). As a consequence, ε_r is constant and increases only approaching T_G. On the contrary, above T_G in the temperature range corresponding to the

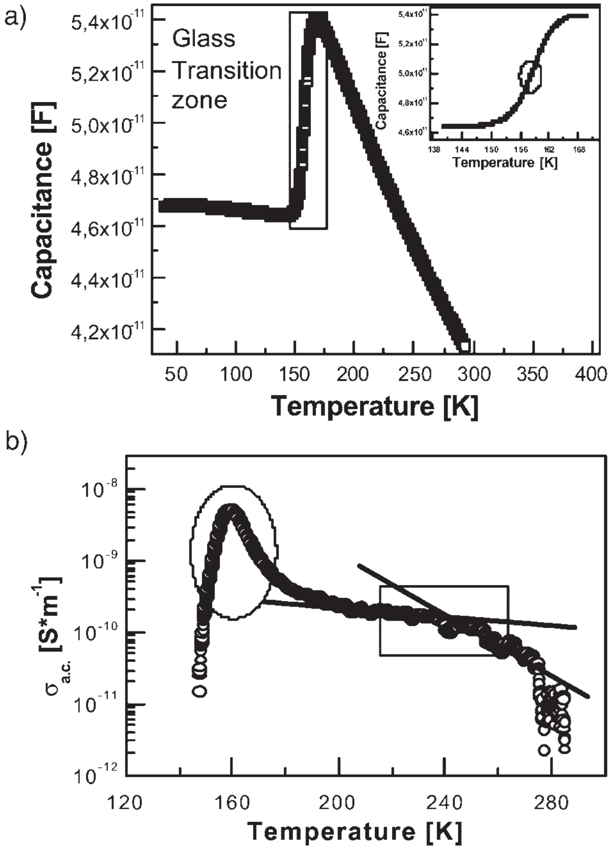

Figure 2.

Capacitance (a) and Conductivity (b) as a function of temperature measured at f = 1 KHz. The glass and melting transition regions are circled. T_G value corresponds to the maximum of the conductivity or to the inflection point of the capacitance curve. The glass transition region is magnified in the inset. T_M corresponds to the slope change in the conductivity curve (Fig. 2.b).

rubber-like phase, the regained thermal expansion of the polymeric film, frozen in the glassy phase, increases the thickness of the material, decreasing capacitance.

Here, T_G corresponds to the inflection point in the left side of the peaks evaluated by computing with ORIGIN software the second derivative (not reported).

As far as the a.c. conductivity is concerned (see Fig. 2.b), its maximum value (maximum of the losses in the material) corresponds to the T_G value. Moreover, it is noteworthy that the $\sigma_{a.c.}(T)$ shows obviously both the phase transitions occurring in the material. Indeed, one can retain that T_M corresponds to the change in slope of conductivity, as indicated in Fig. 2.b.

The frequency dependence of measurements shows that T_G undergoes a shift towards higher values of temperatures if the frequency of the applied field increases (Figs. 3, 4). As a consequence, the static value of T_G is obtained by considering the limit of the frequency towards zero (d.c. limit), as indicated in Fig. 3 with a black line.

Since the ε_r (T) curves are nearly indistinguishable at lower frequencies (Fig. 3), the quasi-static value of T_G has been extrapolated from the curve recorded at 300 Hz. Such value is equal to 156 K, in good agreement with the values reported in literature. The high degree of precision presented by our measurements is directly related to the good sensitivity of the experimental set-up, with a tolerance of about 0.3%. Finally, as shown in Fig. 4, the melting transition occurs around 220 ÷ 230 K. In this case, it is believed that the melting temperature for an applied frequency of 1KHz or 100 KHz can be deduced from the slope changes occurred in the conductivity curve carried out as a function of temperature.

Physical Aging

Since the glassy phase is out of the thermodynamic equilibrium, the properties of glassy materials exhibit a time dependence, or Physical Aging, consisting in a molecular rearrangement inside the structure of the polymeric material. As a consequence, physical aging results in a modification of some physical parameters, such as permittivity.[13] Hence, physical aging in PDMS is here displayed by performing the above described permittivity measurements as a function of time. It is worth to remember that the study of aging permittivity is fundamental for possible applications based on the use of PDMS films (such as dielectric barrier in FET devices, packaging, Lab on chip applications).

About our measurements, they started 6 hours after the end of the sample

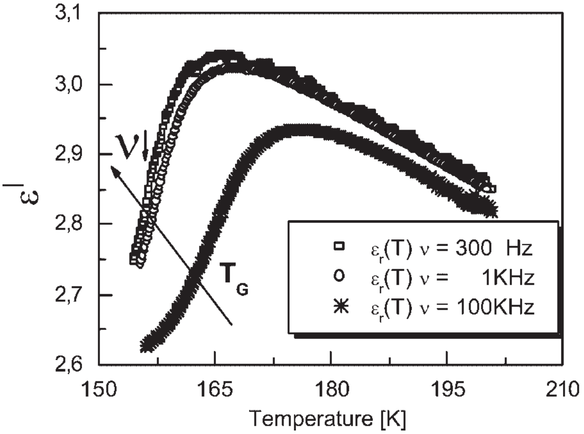

Figure 3.
Permittivity versus Temperature at different fixed values of the a.c. field frequency. T_G depends on the frequency values, as indicated by the black arrow.

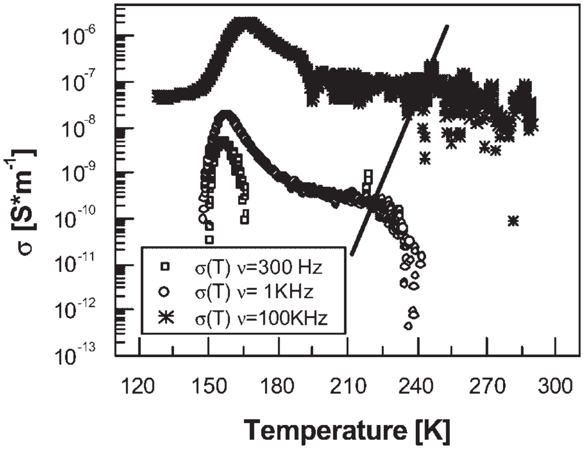

Figure 4.
Conductivity versus Temperature at different fixed values of the a.c. field frequency. TM increases by increasing the frequency of the applied field (black line).

preparation, taking care of keeping them in vacuum as long as possible. The measurements were performed at 1 KHz, in agreement with the IEEE standards,[21] during a range of 7 days, in which the sample underwent a recycling from room temperature to 40 K, always under vacuum.

Fig. 5 reports the $\varepsilon_r(t)$ measurement, normalized to its initial value, at four different temperatures: T = 200 K and T = 75 K are deeply inside the melting and glassy phases, respectively, while T = 170 K and T = 145 K represent the region where the material is partially glassy or crystalline.

The expected trend, consisting in the ε_r lowering as a function of time, is confirmed. The observed aging is less than 0.1%, confirming the high resolution of the technique.

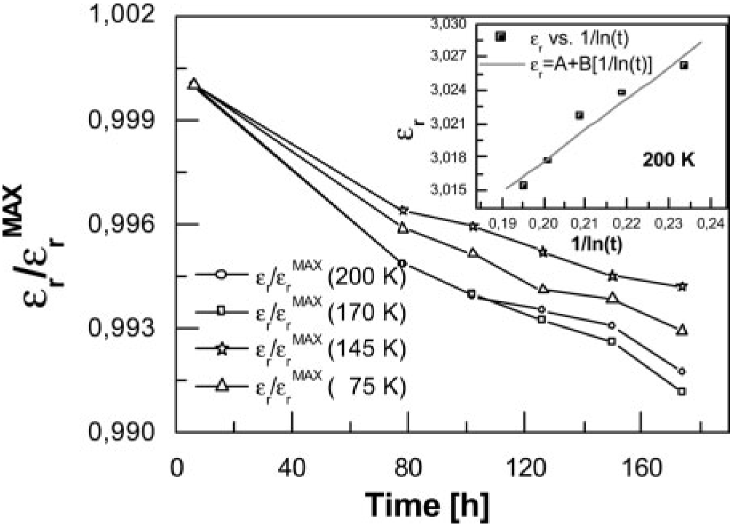

Figure 5.
Permittivity versus time, normalized to its initial value εrMAX, for different temperatures. The aging in the heart of glassy phase (75 K) is slower than that occurred in crystalline phase (200 K).

It is also shown that the aging is slower below T_G, where relaxation mechanisms are less fast, due to the lack of available free volume for the segmental mobility of macromolecules. The time dependent lowering of ε_r follows a typical logarithmic behavior:[22] $\varepsilon_r \approx \frac{1}{\ln(t)}$. To this purpose, in the inset of Fig. 5 it is shown that the predicted behavior fits the curve recorded at 200 K, plotted by linearizing the logarithmic form above mentioned. A more complete study, as a function of frequency in presence of d.c. bias, is under analysis and it will be reported later.

Conclusions

Dielectric measurements represent a simple and powerful tool for the visualization of phase transitions and physical aging in polymeric thin films. In the present work, we have employed such technique on PDMS thin films in order to visualize phase transitions and measure T_G and T_M with a high degree of precision. The extracted values of T_G, equal to 156 K, and T_M, about 220 K, are in very good agreement with those reported in literature.

As far as the physical aging is concerned, we have investigated the lowering of the dielectric constant in four different zones keeping the sample under vacuum for one week. The lowering is slower in the glassy phase, where the rearrangement of macromolecules is frozen. The technique allows to measure aging less than 0,1%.

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