Complex Dielectric Relaxation Behaviour of Highly Crosslinked PDMS Networks in the Glass Transition Region: an experimental study

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Dielectric relaxation studies were carried out on unfilled and silica particle filled highly crosslinked PDMS samples, at temperatures above the calorimetric glass transition temperature. Our experiments suggest that the main α relaxation peak is preceded by a pre - α relaxation one, whose characteristics are not dependent in their nature on the presence of the reinforcing silica particles. This suggests that its presence may be characteristic of the high crosslink density PDMS.

Keywords: highly crosslinked siloxane elastomers, silica filler, dielectric relaxation in the glass transition region, a-relaxation

The study of relaxation processes for crosslinked polymer networks usually can be probed by more than one kind of spectroscopy [1, 2]. One of the most common and conventional methods to obtain melt and glassy polymer viscoelastic relaxation spectra is mechanical spectrometry, e.g. rheometry, ultrasonic attenuation, etc. However, as it was formulated [3], the linear response theory for memory systems does not apply uniquely to mechanical relaxation, but to a rather wide family of physical relaxation types, each type corresponding to a particular external excitation (generalized force), e.g. mechanical forces, electro – magnetic forces, etc. We note that direct comparison between different physical types of experimental data is possible through the spectral decomposition of the response functions.

In the recent past, there has been an increasing interest in comparative relaxation studies in the linear domain using different experimental techniques such as shear rheometry and dielectric spectroscopy [4 - 11]. The aim of most of these studies was to get a deeper understanding of the α (main glassy) and of the secondary (a.k.a. Johari – Goldstein) glassy relaxation processes [12 - 14, 15]. Although a complete description of the glassy polymer molecular dynamics is not available due to the great complexity of these systems, it is generally accepted that the glassy α process is related to the relaxation of the main chain segments. The secondary β relaxation may be related to relaxation type motions of the side parts (when present) or to localized motions of the flexible parts in the case of main chain polymers. In order to explain the complex behavior of the α relaxation process, several models have been proposed. Among the most authoritative we mention the coupling model of relaxation developed by Ngai, Plazek Roland and co-workers [16 - 20].

A survey of the recent literature has revealed that most comparative relaxation studies were focused on non-entangled or entangled polymer systems. Generally these studies have revealed the existence of a high intensity α-peak, and of secondary, much lower intensity, β - , γ - , etc. relaxation processes, related to a broader relaxation time distribution than the α one. Crosslinked polymer networks have received less attention and it might be expected that crosslinking and the addition of solid filler particles to increase the degree of topological complexity that will result in a more complicated relaxation pattern. The aim of this communication is to explore the dielectric relaxation behavior at temperatures above the T_g for two series of unfilled and silica filled PDMS elastomers, the linear viscoelastic relaxation pattern of which is presented in [21].

Results and discussions

Two samples, unfilled and filled trimethylsiloxy terminated dimethylsiloxane, vinylmethylsiloxane copolymers, commercially named PS 424 and manufactured by United Chemical Technologies Inc., were used for this study. The molecular weight of the uncrosslinked polymer, determined by size exclusion chromatography technique, is M_w = 43200 daltons; since the critical molecular weight for PDMS is roughly 28000 daltons, the samples are in the entangled regime [2]. The unfilled samples were crosslinked primarily at the vinyl sites, through free radical reaction with tert-butyl peroxy-2-methylbenzoate as initiator. The filled samples were obtained by mixing first the polymer matrix with Cab-O-Sil silica particles (from Cabot Inc.) and then crosslinked following the same procedure as for the unfilled samples (for more details on processing see reference [21]. According to our previous study, this chemical procedure provides high crosslink density, estimation for the molecular weight between crosslinks being 750 daltons [21]. The calorimetric glass transition temperatures T_g were measured, using the differential scanning calorimetry technique, with a Perkin Elmer DSC7 instrument at a heating rate of 10^0C / min. The results are T_g = -121.7^{0}C for the unfilled PS 424, and T_g = –120.6^{0}C for the 20% wt. filler content PS 424. The dielectric measurements were carried out on a TDSS-1 spectrometer (Imass Inc.) using circular plate shaped samples (45 mm diameter and 2 mm thickness) for temperatures between –35^{0}C up to –95^{0}C. All measurements were performed under N_2 atmosphere; before starting the experiments, all samples were kept

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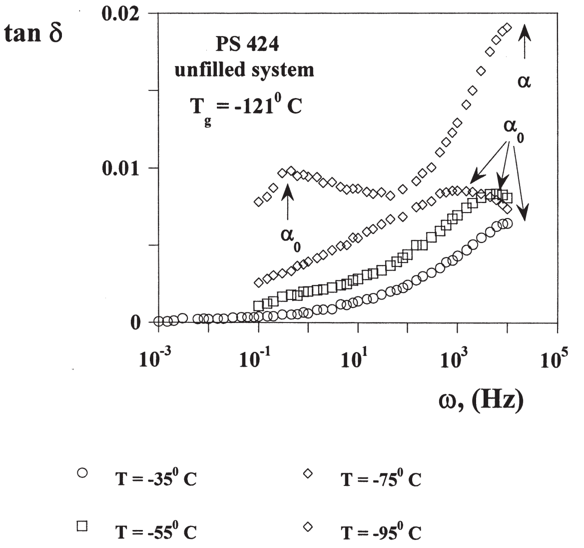

Fig. 1. Isothermal loss tangent curves plotted vs. frequency for the unfilled crosslinked system (for details see the text)

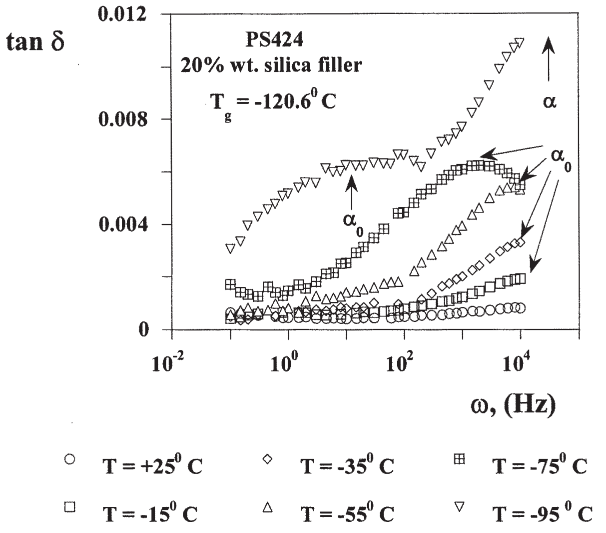

Fig. 2. Isothermal loss tangent curves plotted vs. frequency for the 20% wt. filled crosslinked system (for details see the text)

long enough in the dielectric cell to ensure a perfectly moisture free environment. According to the manufacturer data, the polymer matrix contains only a negligible amount of conductive impurities, thus their contribution to ε" data may be neglected. The raw time dependent experimental results were numerically transformed into the frequency domain using the FFT technique. The frequency range covered by this study is from 10^{-1} to 10^4 (Hz).

We present on figures 1 and 2 the (dimensionless) tan δ (= ε" / ε') plotted vs. the frequency, ω. Both plots reveal the following (unexpected) behaviour: the existence of a relative low intensity relaxation peak for temperatures above –95⁰C, and the possible existence of a higher intensity peak when approaching the T_g, at –95⁰C. Since the polymer is highly crosslinked, these resonance peaks can not be related to a terminal dispersion relaxation and must be interpreted as reflecting the softening dispersion. The first one, named α_0 on both figures, exhibits typical α relaxation pattern, i.e. as the temperature decreases it shifts to lower frequencies and increase in intensity. As expected, this behaviour shows the failure of the time temperature superposition principle in this temperature range, since the (discrete) modes of the isothermal relaxation spectra have different temperature dependencies (for more on the time temperature superposition principle see [22- 23]). By comparing the absolute values of the α_0 peak on both figures, we observe that in the case of the filled sample the peak intensity is two times lower when compared to the unfilled sample. This may be related to the presence of the silica filler particle in the polymer matrix: possible chemical interactions between polymer segments and the filler may result in a partial adsorption of the former to the particle surfaces, thus decreasing the degree of mobility.

The data measured at –95⁰C on both unfilled and filled samples show the presumable existence of a second peak, named α on the figures, located roughly four logarithmic decades toward higher frequencies. At this temperature, the dielectric window prevented us to measure a broader spectrum; on both figures the arrows point on the presumable location on the frequency scale of the curve maximum. The intensity of this α peak seems to be almost twice than that of the α_0 and, most important, can not be related to a classical secondary β relaxation. We recall here that it is generally admitted that, in the case of polymers, additional high frequency resonance peaks like the secondary β relaxation are at least one order of magnitude lower than that of the main α relaxation [13, 14, 24]. Here our data show the reverse situation: a high frequency peak is much more intense than the previously ones and lead to the conclusion that high crosslinked systems exhibit a pre – α relaxation, named here α_0. In this case, the α_0 seems not be influenced in its nature by the presence of the filler particle; however, if the filler would be conductive, the dielectric properties will be strongly affected [25].

Conclusions

Dielectric relaxation studies were carried out on unfilled and silica particle filled highly crosslinked PDMS samples, at temperatures above the calorimetric glass transition temperature. As is the case of many polymer systems studied in the literature, dielectric relaxation master curves can not be obtained using the time temperature superposition principle in this temperature range. Our data suggest the hypothesis that the main α relaxation is preceded by a pre – relaxation, named here α_0, whose characteristics are not dependent in their nature on the presence of the reinforcing silica particles. Its presence may be characteristic of the high crosslink density PDMS. Future studies will concentrate on other highly crosslinked polymers in order to elucidate its origin. In this study, because of technical limitations, it was not possible to investigate the properties of the high frequency (true) α peak, and this remains to be done in the future. It is hoped this experimental study will provide insight for models like the one given in [26] to also account for dielectric relaxation, and prove useful and inspiring when one investigates even more complex polymer systems, as it is the case in [27].

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