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Influence of the Quenching Temperature on the Dynamic Mechanical Property of Poly(Vinyl Chloride)

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ABSTRACT: In this paper, we report the dynamic mechanical behavior of amorphous poly(vinyl chloride) (PVC) samples that have received three different thermal treatments: (**a**) quenched from a temperature near calorimetric T_g, 80 °C; (**b**) quenched from a temperature above T_g, 90 °C; and (**c**) quenched from a temperature well above T_g, 130 °C. Dynamic mechanical measurements have been done at a heating process from about 50 to 115 °C, and from each run, we obtained tan ϕ and the storage modulus as functions of temperature for two frequencies, 10 and 1 Hz. The results clearly show that the quenching temperature has dramatic effects on the dynamic mechanical behavior of amorphous PVC and the range of physical aging is not limited to below the α-relaxation peak temperature (T_α).

Introduction

There has been significant experimental and theoretical effort recently aimed at the influence of thermal histories on the properties of glassy polymers. On the experimental side, a number of properties, including volumetric, thermal, mechanical, dynamic mechanical, and dielectric, have been studied. These studies have clearly shown the nonequilibrium nature of the glassy state by demonstrating, for example, an increase in density and a decrease in loss tangent, as a glassy material is annealed below the glass transition temperature, T_g, after quenching from above T_g.[1−8]

Moreover, these effects are mainly observed in the zone between T_g and the secondary relaxation peak, T_β.[2] As for the region above T_g, glass-forming polymeric systems are assumed to behave as thermodynamic metastable equilibrium systems for convenience, to distinguish them from nonequilibrium glassy systems.[6] Therefore, in the above studies about the effects of thermal histories on the properties of glassy polymers, to erase previous thermal histories and achieve a reproducible standard initial thermodynamic equilibrium state, samples were kept a short time at a temperature about $T_g + 15$ °C.

However, the difference between the small molecular and polymeric glass-forming systems has to be considered. When polymers are heated through the glass transition, they do not go directly over to Newtonian fluids but rather go to a viscoelastic “rubbery plateau”.[9−12] An interesting question then arises: can quenching a glass-forming polymeric sample from different temperatures above T_g exert some different influence on its dynamic mechanical properties?

In this work, we report the first study of the influence of the quenching temperature (i.e., a temperature at which the sample was annealed before quenching) on the dynamic mechanical property in glass-forming polymeric systems. We choose amorphous poly(vinyl chloride) (PVC) for this study. This glass-forming polymeric system has the advantage that it does not crystallize, allowing us to experiment at a wide temperature range above T_g.

Experimental Section

Samples of PVC were obtained from a PVC resin (Trovidur, Dynamit Nobel), dry-blended with 2% stearate and extruded at 175 °C, followed by annealing for 2 h at 100 °C and then slowly cooling to room temperature. Its calorimetric glass transition temperature is 77 °C, measured at a heating rate of 20 °C/min; M_w is 1.07×10^5 and M_n is 5.6×10^4, obtained by gel-permeation chromatography.

Dynamic mechanical testing was conducted in tension with an Imass Corp. Dynastat instrument. Some specifications of the instrument are shown as follows: the frequency range (optional) is 0.01−99.99 Hz, and absolute accuracy is ±0.1% of the setting; the absolute accuracy of the temperature is ±0.1 °C; the range of loss tangent measurement is from 0.001 to 19.999. Sample sizes were about $2 \times 10 \times 15$ mm^3. Before starting the tests, each sample (the sample was well wrapped by a thin tin foil to avoid contamination by water during the following quenching process) was annealed for more than 2 h at the quenching temperature selected and then quenched by the mixture of ice and water. After these thermal treatments, dynamic mechanical measurement was done during a stepwise heating process from about 50 to 115 °C. At each step, the temperature was raised by about 1 °C. As a result, the average heating rate was about 2.3 °C/min. From each run, we obtained tan ϕ and the storage modulus as functions of temperature for two frequencies, 10 and 1 Hz.

All of the results described were found to be readily reproducible. The variation in loss tangent between the supposedly identical samples was about ±0.003, and the storage modulus was about ±0.005. During the measurements, the states of the samples achieved after the different quenching histories changed gradually and spontaneously, to the extent allowed by the heating at a rate of 2.3 K/min, but this extent remained the same for all samples. Thus, the features of the curves in Figure 1 can be directly compared. It should finally be mentioned that we did not use liquid nitrogen for quenching, just for the same reason as Struik[2] has pointed: rapid quenching from above T_g can be the origin of thermal stress.

Results and Discussion

The effect of quenching temperatures on the dynamic mechanical properties for amorphous PVC is shown in Figure 1:

(1) For the samples quenched from 90 and 80 °C, the height of the α-relaxation peak, measured during the heating process for 10 and 1 Hz, does not change with

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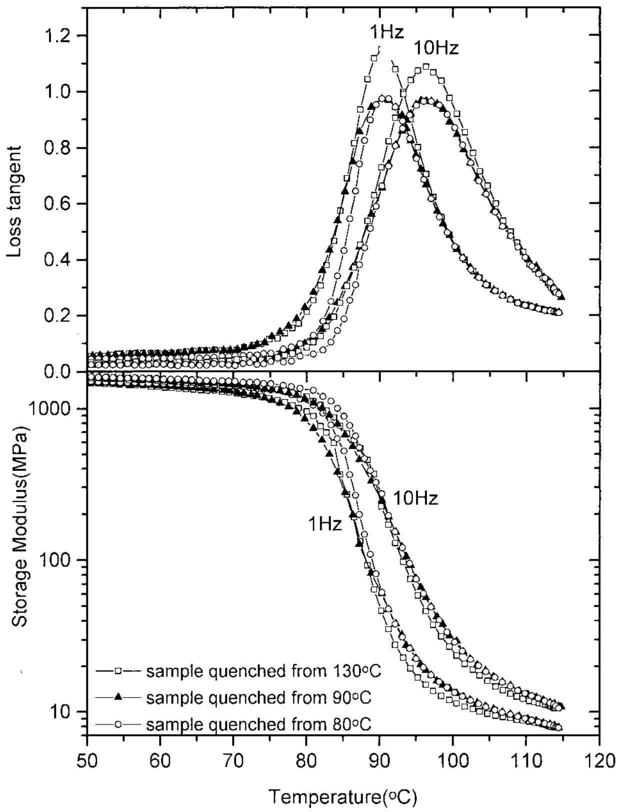

Figure 1. Mechanical loss tangent and logarithm storage modulus against temperature after different quenching processes for PVC. Samples were annealed for more than 2 h at 130, 90, and 80 °C, respectively, and then quenched by the mixture of ice and water. Tests were done during a stepwise heating process.

the frequencies. At the temperatures above 90 °C, the damping behavior of these two samples is not affected by its thermal histories; only at the lower side of the α peak does the one quenched from 90 °C shows a higher loss tangent value than the one from 80 °C.

(2) For the sample quenched from 130 °C, during the same heating process as above, the height of the α-relaxation peak measured for 1 Hz is higher than that measured for 10 Hz, and the height of the α-relaxation peak in this sample is higher than that of the samples quenched from 90 and 80 °C. Figure 1 also shows that, at temperatures above about 98 °C, the value of tan ϕ for the three samples is identical when the frequency is fixed on 1 Hz, and when the frequency measured is 10 Hz, the temperatures are above about 107 °C.

(3) Near the α loss tangent peak temperature, the storage modulus is not as the sensitive as loss tangent to the effects of thermal histories. However, in a logarithm scale, this characteristic can also be clearly shown in the plots of the storage modulus. Just as expected, a higher loss tangent corresponds to a lower storage modulus.

The above results clearly show that the annealing temperature before quenching dramatically affects the dynamic mechanical behavior of amorphous PVC, and the range of physical aging is not limited to below the α-relaxation peak temperature (T_α).

Analogous dynamic mechanical measurements of poly(vinyl chloride) by Roche[13] clearly showed that, for a sample quenched from 120 °C by liquid nitrogen and then annealed at 40 °C, the height of the loss modulus or the loss tangent peak decreased with annealing time, while the author's main attention was focused on a sub-T_g peak exhibited in the loss modulus function. The measurements[13] were finished by means of a DuPont 981 DMA, in which the frequency decreased from 20 Hz at −80 °C to 5 Hz near T_g. But from a study of poly(methyl methacrylate) by an inverted forced torsional oscillation pendulum, Muzeau et al.[14] showed that the thermal history only affects the dynamic mechanical behavior of the sample below calorimetric T_g. They inferred that the effect mentioned above is entirely because, above the calorimetric glass transition temperature range, glass-forming polymeric systems are in a thermodynamically metastable equilibrium state; therefore, thermal history only affects the dynamic mechanical behavior of the sample below calorimetric T_g. However, their view could not give a reasonable explanation to our result 2 above. If the samples are in the thermodynamically metastable equilibrium state in the region above the calorimetric T_g, then the annealing temperatures should not have dramatic effects on the dynamic mechanical behavior of amorphous PVC. Maybe Muzeau et al.'s results[14] and our result 1 above, that thermal history does not affect the higher side of α peaks, is because the annealing temperature before quenching occurred near the α peak temperature.

To well understand the above results, it is desirable to recall the difference between the small molecular and polymeric glass-forming systems. As mentioned in the Introduction, glass-forming polymeric systems are more complex than small molecule glass-forming systems, due to the fact that the glass−liquid transition is spread out into the glass−rubber−liquid transition. For small molecular glass-forming systems, it can be readily accepted that the systems are in the thermodynamic equilibrium state in the temperature range above T_g. However, for glass-forming polymeric systems, the T_g generally used actually denotes the glass−rubber transition temperature; thus, whether the systems in the rubbery state above T_g can be considered to be a thermodynamic equilibrium state is not quite clear. The results of this paper seem to show that, even above the glass transition temperature, polymers never are truly in a thermodynamic equilibrium state.

By the way, the observations of this study possibly can present some useful information to the following question. During recent years, a great deal of experimental effort has been made in the studies of the dynamics of glass-forming systems above their glass transition temperature range, and this behavior is directly related to the dynamics of such systems in the supercooled liquidlike equilibrium state.[11] However, almost nothing is known about whether the α process could appear in the nonequilibrium state. As shown in Figure 1, for the sample quenched from 130 °C, measured at 10 or 1 Hz, the α loss tangent did appear in the nonequilibrium state.

Recently, by a thermally stimulated depolarization current (TSDC) technique, Colmenero[11] studied the relaxation behavior of glass-forming systems at a fixed temperature below T_g. In this experimental procedure, the sample was polarized above T_g and, without removing the polarization field, cooled at a constant rate (10 K) until the measurement temperature was reached. Then, after a waiting time, t_w, the electric field was removed and the depolarization current was measured as a function of time. The results showed that the dielectric relaxation corresponding to the α relaxation was not completely arrested just above the glass transition; it can also appear just below T_g.[11] Thus, Colmenero's results also show that the dielectric relaxation corresponding to the α relaxation could appear in the nonequilibrium state.

In addition to the above implications, the observations reported here may shed light on the overall understanding of how thermal history affects the physical properties of synthetic polymers. A detailed theoretical analysis of these observations and their implications along with further measurements of the dynamic mechanical behavior of other polymers is currently being carried out in our laboratory.

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