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VOLUME AND ENTHALPY RELAXATION RESPONSE AFTER COMBINED TEMPERATURE HISTORY IN POLYCARBONATE

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Volume and enthalpy relaxation in polycarbonate subjected to double temperature jumps in the T_g region has been analysed. It concerns both initial $T_{\text{down-jump}}$ from equilibrium above T_g to consolidation temperature below T_g and fina1 $T_{\text{up-jump}}$ to relaxation temperature, also below T_g. The measured H and V data after $T_{\text{up-jump}}$ were compared with respect to aging time calculating (dH/dV) ratio denoted as aging bulk modulus, K_a. According this new methodology H and V relaxation response after $T_{\text{up-jump}}$ demonstrates differences in relaxation responses.

Keywords: *enthalpy relaxation, memory effect, physical aging, polycarbonate, volume relaxation*

Introduction

Amorphous solids materials are in a non-equilibrium state below its glass transition temperature, T_g, as can be proved by the time-dependent character of material properties in glassy state at isothermal conditions. This phenomenon is usually called physical aging. The relaxation changes are frequently determined by the evolution of sample volume or enthalpy [1, 2].

Volume relaxation isotherms cover both directions of relaxation changes i.e. contraction and expansion of material. Volume contraction is initiated by a decrease in temperature, sample expansion by its increase. Analogically, during enthalpy relaxation energy is released from the sample, or is sucked from its vicinity (volume contraction or expansion, respectively) [3–5]. The methods of the process initiation by changes in temperature are usually called temperature down and up-jumps.

After a temperature up-jump definite behavior will be observed only in the case when the temperature increase is applied onto material in thermodynamic equilibrium. However, both sample expansion and compression appear together as a consequence of combined temperature history. It manifests itself as the memory effect during relaxation in both volume and enthalpy [3–5].

Volume and enthalpy relaxation responses were intensively studied in respect to their similarities [3, 5–12]. Overall, researchers conclude that both responses are very similar, nearly identical. For example Málek [6, 7], comparing different glass forming materials (amorphous polymers and inorganic glasses) and employing fictive relaxation rate, found that within the experimental error the volume and enthalpy relaxations are very similar. Simon *et al*. concluded that normalized volume and enthalpy responses slightly differ in the shape and time of reaching equilibrium, measured for polystyrene [8]. Further, Adachi and Kotaka [3], studying memory effect, found out that the relaxation curve for volume reaches the maximum at a slightly longer time-scale than for enthalpy.

Several papers can also illustrate the similarity in both responses through dH/dV ratio, which is constant during aging [3, 5, 8–12]. According to some of these authors the slope of the $dH(dV)$ dependence constructed in respect to the aging time gives the value which expresses the energy of new free volume formation or disappearance in the case of sample expansion or contraction, respectively, with the physical unit of J m^{-3} [3], or a kind of internal pressure directed outwards (in the case of sample contraction) and inwards (in expansion) with the unit of GPa [3, 10]. Overall, such calculations give for amorphous polymers values of about 1–2 J m^{-3} or GPa, after both temperature down and up-jumps [3, 5, 8–10, 12]. However, according to the results presented in [10] for polystyrene, the slope for the sample expansion (temperature up-jumps) was found to be about 30% higher than for contraction, i.e., there is some asymmetry in the processes. Our recent papers [5, 12] suggest that the changes in enthalpy relative to those in volume could be recognized as aging bulk modulus, K_a. Its values were found to be close to bulk modulus measured by direct compression for both polymeric glasses and inorganic glass formers. For polymers close to it gives the value of about 2 GPa, and for inorganic glass such as amorphous selenium around 4 GPa [12]. In [5] we concluded that the ratio calculated after a tempera-

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ture double jumps in PMMA increases with longer consolidation time, i.e. when the temperature up-jump is applied to a better-equalized structure.

In the present work enthalpy and volume relaxations for PC after a two-step temperature jump are researched. In the first stage the volume and enthalpy samples were exposed to an initial temperature down-jump which was followed, after some consolidation period, by another temperature up-jump. The main aim is to determine suitable conditions for experiments providing both expansion and compression parts of the relaxation curve in a sufficient length so that the (dH/dV) ratio during both expansion and compression part of relaxation isotherm can be calculated. Special attention is paid to the course of K_a in the vicinity of the maximum H and V on the relaxation curves.

Experimental

Material

Polycarbonate, PC, polymer for injection molding of compact discs, density 1.13 g cm^{-3}, enthalpy T_g=145°C (determined as midpoint measured at cooling/heating cycle 10 K min^{-1}).

Aging procedure

Both volume and enthalpy relaxation measurements were performed as double-step temperature jumps. In the first step, the material was maintained at the temperature T_i, well above T_g, to erase any previous thermal or mechanical histories. Then the temperature down-jump to the consolidation temperature, T_{a1} lying below T_g, was done. Finally, after some time at this temperature, temperature up-jump was carried out to temperature T_{a2} (also selected to be below T_g). After this procedure the relaxation measurements were performed as a function of elapsed time, t_{a2}, from the second temperature jump. The temperature program can be schematically described as follows:

$$T_i>T_g>T_{a2}>T_{a1}$$

Two types of temperature program (denoted I and II) were used. They are summarised bellow:

- annealing at T_i=150°C for 20 min
- I) temperature down-jump by jump to different consolidation temperatures T_{a1} (115, 120, 125, 127.5°C) pre-annealing for time t_{a1} 7 days
  II) temperature down-jump by cooling of 1 K min^{-1} to consolidation temperature T_{a1}=115°C and pre-annealing for different times t_{a1} 1, 7, 28 and 75 days
- I) temperature up-jump by jump to relaxation temperature T_{a2}=130°C and relaxation for time t_{a2} (up to 7 days)
  II) temperature up-jump by heating of 1 K min^{-1} to relaxation temperature T_{a2}=130°C and relaxation for time t_{a2} (up to 7 days)

Volume relaxation measurements

Mercury-in-Glass Dilatometer according to ASTM Standard D 864-52 was employed for volume relaxation measurements. The dilatometer capillary diameter was 0.63 mm. The sample was cut out of a compression-molded platelet in the form of bar with the cross-section of 6×6 mm and volume 1.75 cm^3. Two thermostatic baths filled with silicon oil were used for conditioning of the dilatometer. The first was GRAND W14 with temperature stability ±0.004°C and the other Julabo HP-14 with the stability ±0.01°C. Temperature jumps were performed by manual transferring of the dilatometer from the first bath to the other. Cooling/heating/isothermal stages in case of procedure II were done by programming of second thermostatic bath.

Enthalpy relaxation measurements

A set of samples for DSC analysis was prepared, each sample of the mass of ca. 6 mg. The temperature programme was carried out by a technique similar to the dilatometric part. The samples were covered in aluminium foil and placed into thermostatic bath in a strainer basket. Final calorimetric measurements were carried out using Perkin-Elmer DSC 1 Pyris analyser. The temperature scans of samples relaxed for time t_{a2} were performed on DSC at the heating rate of 10 K min^{-1} from 120 to 170°C.

Comparison pvT bulk modulus measurement

The bulk modulus values were extracted from volume-temperature isobars recorded at 500–2000 bars. The temperature range was from 100 to 220°C and the isobaric cooling rate was 2 K min^{-1}. The device used in these measurements was a piston-die type (PVT 100 analyzer, SWO Polymertechnik GmbH, Krefeld, Germany) working in the isobaric mode.

Results

Figure 1 presents volume (a) and enthalpy (b) relaxation isotherms at T_{a2} after a temperature up-jump following one week consolidation at different consolidation temperatures T_{a1} varying from 115 to 127.5°C (temperature program I, Experimental). The volume relaxation isotherms demonstrate well-pronounced phenomenon of the memory effect. In the first stage of the curve the sample expansion occurs, then it passes through a maximum, and finally decreases (sample compression) reaching equilibrium in the same way as after a single temperature down-jump. In the case when a temperature up-jump is applied onto material in equilibrium, only a simple expansion curve will be observed, in our case for 127.5°C. A similar dependence was found in enthalpy relaxation experiments Fig. 1b. In the initial stage of relaxation an endothermic change appears when material sucks energy from its vicinity, but after some time of relaxation the process becomes exothermic and energy escapes from the sample. Also in this case no memory effect was observed at a temperature jump from 127.5°C. Comparing *H* and *V* relaxation responses according to the shape and time to reach the maximum and equilibrium, one can find that they are very similar. Aging bulk modulus, K_a, (d*H*/d*V*) was calculated for expansion parts, up-to the curves maxima with the following results: for consolidation at 115°C→1.31±0.24 GPa, 120°C→1.18±0.23 GPa, 125°C→1.46±0.29 GPa, 127.5°C→1.49±0.62 GPa. In the compression part the values are around 3 GPa with unsatisfactory scatter of data.

The first set of measurement presented in Fig. 1 was carried out to find suitable experimental conditions of both enthalpy and volume tests. The findings were used to set-up experimental conditions in the second part of measurements represented by procedure II (Experimental). Further measurements were especially focused on the determination of K_a behavior in the inversion point of the relaxation isotherm, when its direction changes from expansion to compression. The temperature of 115°C and preannealing time t_{a1}=7 days were selected because approximately the same amount of relaxation changes occurs in both expansion and compression part of the relaxation isotherm. Further, this temperature provides a reasonably large experimental window, represented by logarithm of elapsed time (for expansion from approximately log*t*/min=0.12 to the maximum at 2.52, and for the contraction from the maximum to equilibrium at approx. log*t*/min=4.12). The data measured under condition II is presented in Fig. 2. Both enthalpy and volume preserve the same behavior as described above in Fig. 1, with additional finding that the memory effect is less pronounced as a consequence of longer time of pre-annealing. This effect diminishes for up-jump after 75 days of consolidation. The trend of both *H* and *V* responses in respect to the time-scale, and the time of curve maximums were found to be very similar. However, careful compare of *H* and *V* data reveals

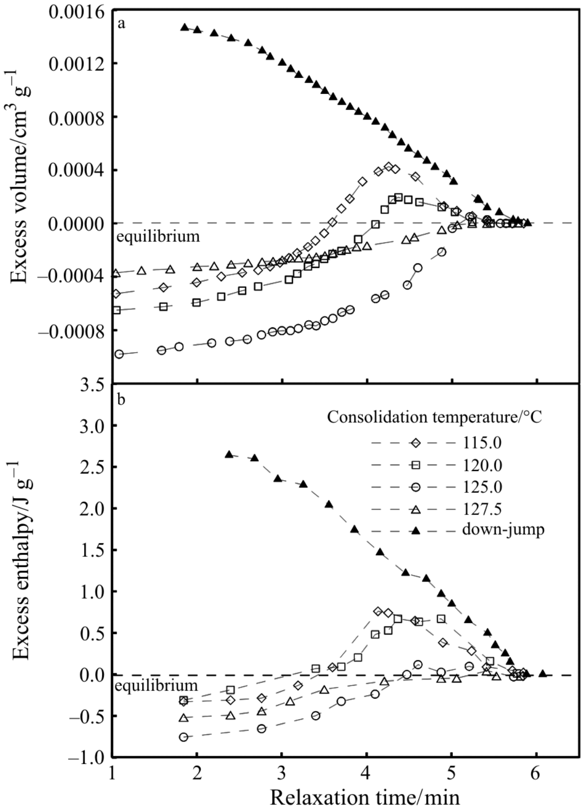

Fig. 1 a – Volume and b – enthalpy relaxation curves for PC after temperature up-jumps, relaxation temperature T_{a2}=130°C, consolidation temperatures T_{a1} indicated, consolidation time 7 days, temperature changes done by program I

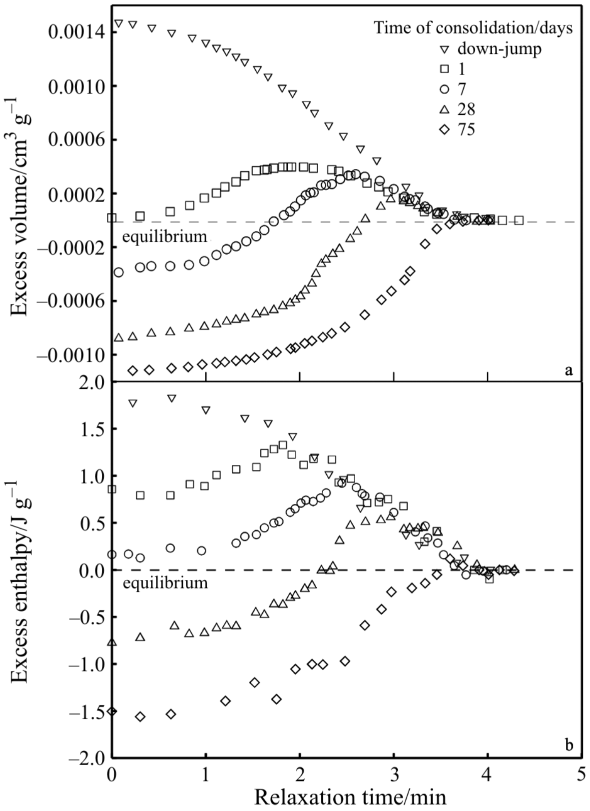

Fig. 2 a – Volume and b – enthalpy relaxation curves for PC after temperature up-jumps, relaxation temperature T_{a2}=130°C, consolidation temperature T_{a1}=115°C, consolidation times indicated, temperature changes done by cooling/heating cycle 1 K min^{-1} (program II)

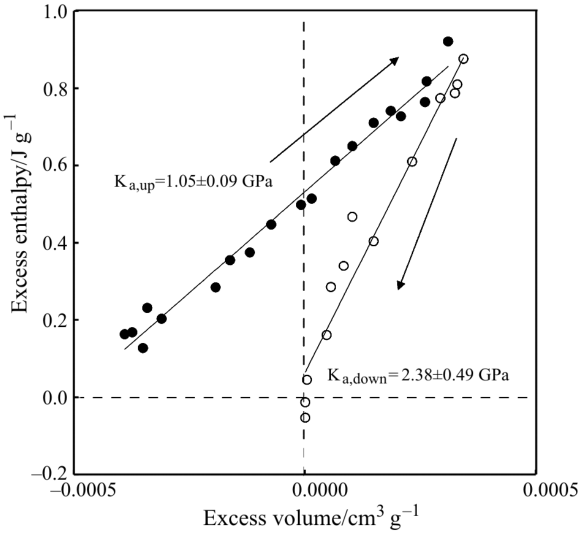

Fig. 3 dH(dV) dependence after a temperature up-jump to T_{a2}=130°C, constructed from the data of Fig. 2, consolidation time 7 days at T_{a1}=115°C. Arrows indicate relaxation time increase (program II)

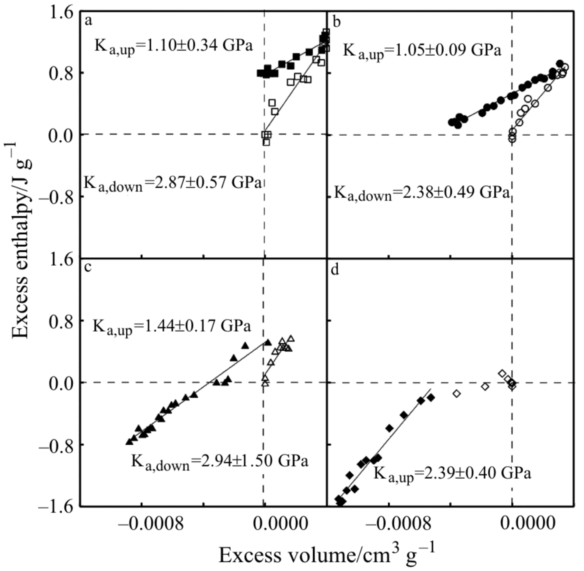

Fig. 4 dH(dV) dependence after a temperature up-jump to T_{a2}=130°C, constructed from the data of Fig. 2. Parts a to d represent 1, 7, 28 and 75 days of consolidation at T_{a1}=115°C (program II)

differences in initial values of properties. For example, for 1 day and 7 days consolidation the enthalpy curves starts above equilibrium in contrary to those of volume.

Aging bulk moduli calculated from data in Fig. 2 are presented in Figs 3 and 4. Except for compression data after 75 days, for each other data satisfactory (dH/dV) ratio can be calculated. The full symbols in Figs 3 and 4 represents the data for expansion and the empty ones are for compression. It can be noted that K_a is different for both directions and there was found reversal point on dH(dV) dependency situated around H and V curves maximum. For temperature up-jump after 7 days of consolidation, Fig. 3, K_a value is approximately twice lower during expansion than during the final compression. A similar situation can be observed in Fig. 4a–c. The values for expansion seem to increase with time of consolidation at 115°C, reaching the maximum value for up-jump after 75 days. The similar results were found for PMMA in an identical type of experiments [5]. The values for compression seem to be the same for each time of consolidation in this experiment. In Fig. 4d discrepancy was found in the data close to equilibrium. Overall, the calculated K_a moduli are close to bulk moduli in glass transition region measured by direct compression (presented in Fig. 5).

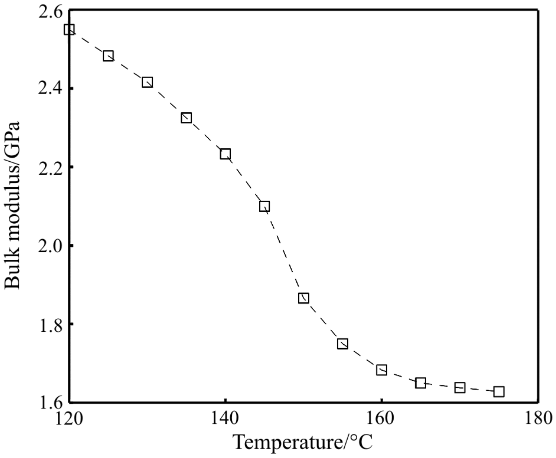

Fig. 5 Temperature dependence of PC bulk modulus measured by direct compression in the T_g region

Discussion

First of all, it is necessary to stress out that both H and V responses were measured under the same experimental conditions. It means the same temperatures and heating/cooling rates were researched by conditioning the dilatometer and also DSC samples in the same thermostatic bath. The only differences were in the different method of evaluating relaxation changes; in case of volume it was done by direct measurement of V changes in real time of process. On the other hand, relaxed enthalpy changes were determined indirectly as the amount of enthalpy elapsed from the sample during relaxation at DSC up-scan of the aged sample. Comparing both responses, an agreement is found in the position of the peak and time-scale of both processes. The aim of simultaneous enthalpy and volume relaxation measurements was to compare this both relaxation responses with the help of the (dH/dV) ratio. Performing the calculation of K_a moduli from dH(dV) dependency constructed in respect to aging time we found two regions where satisfactory interpolation of the data by a straight line can be done. In these regions the contributions from enthalpy and volume during relaxation are constant. A sharp inversion point was found, where ratio (d*H*/d*V*) changes its value and direction. This reversal point directly belongs to the maximum in enthalpy and volume data. The course of relaxation changes should be clear from the direction of the added arrows, which shows elapsing of relaxation time, Fig. 3. The expansion and contraction parts, however, are not symmetric, as can be seen from the K_a values. During sample expansion the contribution of enthalpy is less significant than in contraction, giving smaller values of aging moduli. Another important aspect of such non-uniform behaviour of *H* and *V* quantities according (d*H*/d*V*) ratio is that it does not go through the beginning of the coordinate system, as can be seen in Figs 3 and 4. The dependency goes from the left side and after the reversal point is reached, the line is directed to coordinates origin by sample contraction. According to this, one can say that *H* and *V* relaxation responses reveal some differences compared to relaxation curves after a single temperature up-jump presenting the memory effect. It can be caused by different relaxation kinetics of both expansion and contraction. For example at the same relaxation time the matter does not reach the appropriate state in *H* and *V*. This can be demonstrated by different initial values after an up-jump, when in cases of 1 and 7 days of consolidation at 115°C the enthalpy is above its equilibrium value contrary to volume. Further, also different kinetics of *H* and *V* responses during expansion can be taken into account. Finally, it is necessary to announce that such discrepancy can also arise from different experimental set-ups of both techniques, when one quantity is measured indirectly compared to the other, which is determined in real time of process.

Conclusions

Volume and enthalpy relaxation measurements on PC have revealed the existence of the memory effect, which diminishes with the increasing consolidation time. From the dependence of relaxed enthalpy in respect to simultaneous changes in specific volume changes, the aging bulk modulus, K_a, was calculated. Its values were found to be close to the value of bulk modulus measured by direct compression. An obvious inversion point was found in d*H*(d*V*) dependency around the maximum of the original data yielding two different values of K_a. Further, d*H*(d*V*) dependency does not cross the beginning of the coordinate system during expansion. The method tested in this paper was found to be capable of comparing *H* and *V* relaxation data and in our case the method has revealed that *H* and *V* relaxation responses after double step temperature initiation are not fully identical.

Acknowledgments

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