Thermochimica Acta 614 (2015) 207–212

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Short Communication

Heating scans of stretched polystyrene films with stable baselines: Preparation method of samples for thermal analysis

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ARTICLE INFO

Article history:
Received 7 May 2015
Received in revised form 22 June 2015
Accepted 28 June 2015
Available online 30 June 2015

Keywords:
Differential scanning calorimetry (DSC)
Sample preparation
Polystyrene
Characterization
Thermal analysis
Baseline stability

ABSTRACT

Differential scanning calorimetry (DSC) examinations were carried out for stretched polystyrene (PS) films. A specific sample preparation technique was developed to overcome the entropic shrinkage, which makes DSC baselines unstable and divergent with each other. As a result, the data were acquired for stretched PS film with stable baselines overlayable below and above glass transition temperature shoulder. This method enables us to observe shoulder shift and evaluate the area bounded by two heat flow curves with and without both thermal ageing and stretching.

1. Introduction

The structural relaxation behavior studies of polymers are currently increasing to seek for entirely appropriate descriptions of phenomenological models because of their flexible representations of basic relaxation features, such as hysteresis, non-linearity, non-exponentiality, and thermorheological simplicity/complexity. The structural relaxation study is concerned with the slow evolution of thermodynamic properties toward the equilibrium, where the effect of physical ageing is frequently observed using differential scanning calorimetry (DSC) technique with the measurement of enthalpy variation as an actual thermodynamic quantity. Polymers with confined or constrained situations have recently attracted considerable attention regarding the physical ageing; including, layered glassy films [1,2], composites with nanoparticle [3,4], and polymer networks with different degrees of cross-linking [5].

With this background, we investigated and reported the enthalpy recovery for a polystyrene (PS) film sample with a mild stretching ratio in comparison with a film without stretching [6]. In the experiment, it is necessary to conduct the heating measurement for a sample after the stretching. It is also required that DSC heating curves are overlayable in baselines before and after the glass transition temperature (T_g) shoulder for samples with and without stretching so that the recovered enthalpy can be calculated from the area bounded by the resulting two DSC curves.

In general, it is preferable to fill a DSC cup with powdered sample. Alternatively, DSC curves of the second run or even the third run are used for the analyses when sampling a bulk, resin, gel, or any other form of likely inhomogeneous polymers [7]. These methods may be assumed as semi-empirical to acquire DSC data with stable baselines. Whereas, DSC data are likely unstable and not overlayable in baseline through loading a solid film sample into DSC cup. Destabilization is mainly attributed to movements of the samples, namely shrinkage, inside the pans on DSC heating. The movements can cause frictional heat as well as volume change, which are included in DSC curve and thus even in the quantities determined from the curve. Moreover, the heat transfer coefficient between sample and pan surface is changed by the sample movements, which causes the shift of the baseline. In order to overcome the problem of baseline destabilization, we attempted data acquisition with looking for an appropriate condition in crimping DSC pan. In this paper, the repeat of the improvement for the loading of DSC cups is described to reach the suitable sampling method for PS film.

2. Experimental

2.1. Materials and examination methods

Polystyrene film was fabricated using hot press machine at pressure of approximately 20 MPa with thickness of 0.5–2 mm.

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http://dx.doi.org/10.1016/j.tca.2015.06.031
0040-6031/

Polystyrene pellet of G120K (Lot.1F1606) was kindly supplied by Nippon Polystyrene. The specimen with the size of 90 × 15 mm was cut out from the film and used for thermal ageing experiment with placing line markers for determining the stretch ratio ($d = L/L_0$), where L_0 and L are the distances between two markers before and after stretching. Polystyrene powder was prepared from G120K pellets via precipitation with methanol from solution in tetrahydrofuran.

Fig. 1(a) shows the experimental steps, including thermal ageing, stretching, and DSC examination. Film chucks and the chuck holder, on which the specimen lies, were used to stretch the specimen with a handle stretcher while performing the ageing process. The handle stretcher was placed in the oven at 84 °C of the ageing temperature (T_A). The specimen was heated to 200 °C before the thermal ageing, as shown in the period [I] in Fig. 1(a), to eliminate thermal history of the sample. Afterwards, it was moved from the oven of 200 °C and fixed to the stretcher while removing the chuck holder in the period [II], and then kept at T_A condition for the ageing process. We also checked the temperature variation of the chuck holder without removing it from the stretcher. The results are shown in Fig. 1(b). Consequently, it was verified that the temperature decreased at a constant rate to 84 °C. From this observation, the start of the thermal ageing (the start of ageing time (t_A)) was determined as 10 min after the specimen was taken out of the oven of 200 °C, shown as dashed line in Fig. 1(b). Subsequent to thermal ageing and stretching processes, the specimen was quenched and stored in a freezer at −28 °C.

Immediately before the measurement, the specimen was taken from the freezer, cut into pieces and was placed in a DSC cup to be used for DSC examination from the room temperature to 200 °C with a rate of 5 °C min^{-1}. The DSC examinations were conducted with Seiko DSC 200 instrument.

2.2. DSC sample preparation

In loading the DSC pan with the sample, sufficiently stable baselines were achieved through carrying on several improvements concerning the sample preparation, summarized in Table 1 as Methods 1–6. Two kinds of aluminum open sample pans of tall (5 mm in height) and short (2.5 mm in height) were used. An uncrimped reference pan was used when the sample pan was uncrimped and a crimped reference pan was used when the sample pan was crimped. Before conducting the DSC scan, the stored specimen was cut using a regular scissors or a paper cutter into small pieces, which shapes were also observed and roughly classified as hexagonal and rectangle. Rough sketches are also shown in Table 1 for loading the DSC pans.

3. Results and discussion

3.1. Sample storage

The specimens were stored in a freezer at −28 °C after thermal ageing. The effect of the storage period on the enthalpy relaxation was examined for the samples without ageing ($t_A = 0$) and without stretching. Fig. 2 shows DSC thermograms of the sample kept for various storage periods while the sample weight (w) was carefully controlled to be constant. The insignificant differences among the thermograms can indicate that the storage at −28 °C has no progress in enthalpy decrease even after 96 h in the freezer.

3.2. DSC observations

Samples with d ratios of 1.0, 2.0, and 2.1 were used in Method 1 with the uncrimped DSC tall pan, which was the first try to acquire the DSC thermograms for film samples. While the DSC thermogram for sample with d of 1.0 shows a stable baseline at

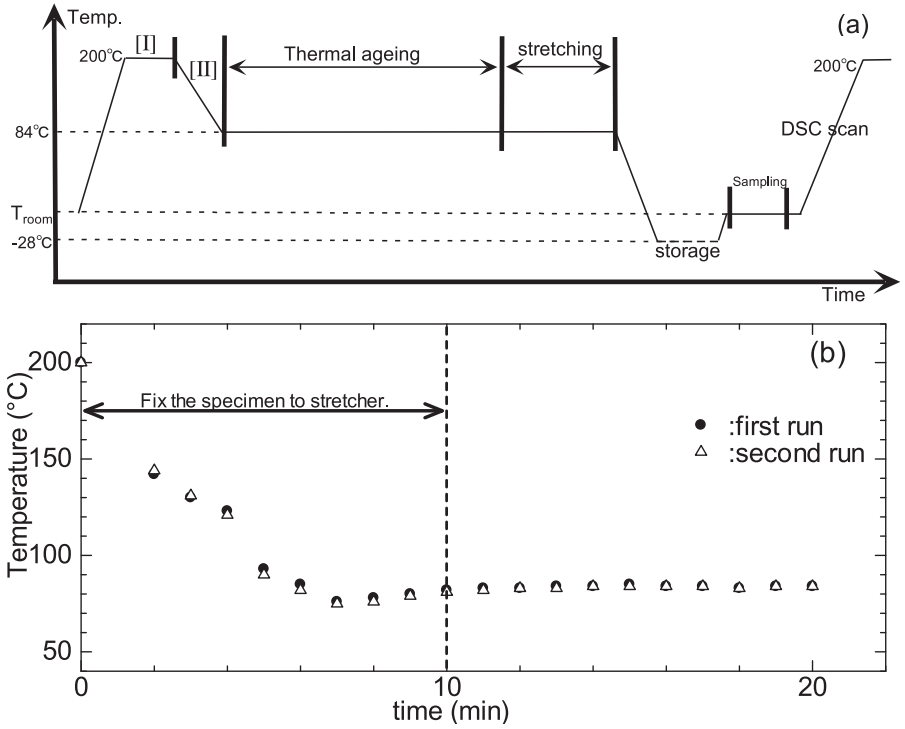

Fig. 1. (a) Schematic diagram for temperature program to acquire DSC data of stretched film samples. The thermal history in the sample was removed in the period [I]. While the temperature of the specimen decreased with a constant rate in the period [II], the specimen was fixed to the stretcher placed in an oven at T_A of 84 °C. (b) Temperature profiles of the chuck holder in the period [II]. The specimen was moved at t of 0 from an oven of 200 °C to another oven of 84 °C.