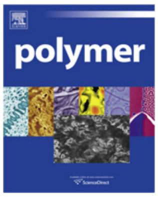
Polymer 52 (2011) 4562–4570

Contents lists available at ScienceDirect

Polymer

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



Constraints in semicrystalline polymers: Using quasi-isothermal analysis to investigate the mechanisms of formation and loss of the rigid amorphous fraction

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ARTICLE INFO

Article history:
Received 27 June 2011
Received in revised form
29 July 2011
Accepted 4 August 2011
Available online 9 August 2011

Keywords:
Poly(trimethylene terephthalate)
Quasi-isothermal calorimetry
Constrained amorphous phase

ABSTRACT

The nanoscale phase behavior of a semicrystalline polymer is important for mechanical, thermal, optical and other macroscopic properties and can be analyzed well by thermal methods. Using quasi-isothermal (QI) heat capacity measurements, we investigate the formation behavior of the crystalline, mobile amorphous, and rigid amorphous fractions in poly(trimethylene terephthalate), PTT. The crystal and rigid amorphous phases comprise the total solid fraction in PTT at temperatures above T_g, the glass transition temperature of the mobile amorphous fraction. PTT was quasi-isothermally cooled step-wise from the melt which causes its crystalline fraction to be fixed below 451 K. Between the high temperature fulfillment of the T_g step and 451 K, the temperature dependent rigid amorphous fraction (RAF) is completely determined. For PTT, most of the RAF vitrifies between 451 K and T_g step by step during QI cooling after the crystals have formed. The constraints imposed by the crystal surfaces reduce the mobility of the highly entangled polymer chains. We suggest the vitrification of RAF proceeds outward away from the lamellar surfaces in a step by step manner during QI cooling. Upon reheating, devitrification of RAF occurs at a temperature above its previous vitrification temperature, due to the effects of densification brought by physical aging during the long period of quasi-isothermal treatment. Finally, we consider recent concepts related to jamming, which have been suggested to apply to filled polymer systems, and may also be applicable in describing constraints exerted by crystal lamellae upon the RAF.

1. Introduction

Semicrystalline polymers constitute the largest group of commercially useful polymers. These polymers exist as viscous liquids at temperatures above the melting point of the crystals. Upon cooling, crystals nucleate and grow to fill the available volume. The reason these materials are called “semicrystalline” is that some fraction of the polymer remains un-crystallized, or amorphous, when the polymer is cooled to the solid state. The amorphous polymer chains become trapped between the growing crystals, inside or outside lamellar stacks. As a result of the highly entangled nature of the polymer chains, the movement of the amorphous polymer chains becomes restricted. The conception of a third phase, termed the “rigid amorphous fraction” (RAF), was introduced to explain the constraints exerted by the crystals upon the mobility of the amorphous phase [1–9]. RAF is characterized as a nanoscale interfacial region between crystalline (C) and mobile amorphous (MAF) phases induced by tie molecules [8,9]. RAF represents the fraction of the amorphous phase that does not contribute to the heat capacity increment at the glass transition, T_g. RAF also has no contribution to the heat of fusion of the crystals. It was suggested that RAF contains molecules whose mobility is inhibited in the presence of crystallinity [10].

The purpose of the present work is to determine whether some of the unusual aspects of the vitrification and devitrification of RAF, reported in our prior work [11] on poly(ethylene terephthalate), PET, are more general phenomena. We choose a related polymer for study, poly(trimethylene terephthalate), PTT, having an odd number of methylene groups. By using the technique of quasi-isothermal (QI) cooling, we are able carefully to control the degree of crystallinity so that all three fractions (C, MAF, and RAF) are determined through quantitative heat capacity analysis. In our previous work on PET [11], we found that: 1. vitrification of most of the RAF occurred during quasi-isothermal cooling after secondary crystallization was completed; 2. at certain temperatures, there was a greater amount of RAF (larger solid fraction) found during QI-reheating than during QI cooling; and, 3. most of the RAF devitrified before the start of observable melting in PET during step-wise

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doi:10.1016/j.polymer.2011.08.006

heating. In PTT, an increased solid fraction during QI heating compared to QI cooling is also observed, when the same temperature is compared. Even though the rigid amorphous phase has been studied widely, so far no one has suggested any detailed explanation of how it forms. Here, the mismatch between the solid fractions during QI cooling and reheating is explained by the effects of densification brought by physical aging which causes the devitrification temperature of RAF to be higher than its previous vitrification temperature. In the last section of discussion, we suggest relationships between the effects seen here in the formation behavior of RAF, and recent concepts related to jamming that have been suggested in polymer nanocomposites.

2. Experimental section

2.1. Materials

PTT pellets were supplied by Shell Chemical Company with an intrinsic viscosity of 0.9 dl/g, measured in a 50/50 mixture of methylene chloride and trifluoroacetic acid at 30 °C according to the supplier.

2.2. Wide angle X-ray scattering (WAXS)

Real-time WAXS was performed in transmission at Brookhaven National Laboratory's National Synchrotron Light Source at the X27C beam line. Wavelength wave, λ, was 0.1371 nm and the scattering vector q, (where $q = 4\pi\sin\theta/\lambda$, for θ the half-scattering angle) was calibrated using aluminum oxide (Al_2O_3) standard. The sample-to-detector distance for WAXS was 132.7 mm. A MAR CCD X-ray detector (MARUSA) was employed for detection of 2D-WAXS images, having a resolution of 1024×1024 pixels (pixel size = 0.158 mm). All scattering/diffraction signals were corrected for detector linearity, sample absorption effect, background transmission due to air scattering, and possible changes in incident beam intensity during real-time data collection.

The sample (PTT after QI cooling) was heated inside a Mettler FP90 hot stage, and the X-ray beam passed through the viewing port of the hot stage. Intensity was accumulated every 45 s as the sample was heated from 303 K to 451 K at a rate of 10 °C/min and then cooled from 451 K to room temperature at the same cooling rate.

WAXS data were also collected in our laboratory, using a Bruker AXS at wavelength = 0.1542 nm. The scan range of two-theta is from 5° to 30° and the power was set at 40 kV, 20 ma. Scattered intensity was collected for 15 min, and was corrected for air background. The two-dimensional isotropic pattern was converted to a one-dimensional pattern by integrating over a sector.

2.3. Differential scanning calorimetry (DSC)

Thermal analysis studies were carried out using a TA Instruments temperature modulated DSC (TA Q100). The instrument was calibrated with indium for the heat flow and temperature, while the heat capacity was evaluated using sapphire standard. Nitrogen gas was purged into the DSC cell at a flow of 50 ml/min. Two modes were adopted in the study, quasi-isothermal TMDSC mode and standard mode.

Quasi-isothermal cooling and heating tests were performed with temperature modulation amplitude of 0.5 K and period, $p = 60$ s. The temperature increases or decreases with a step of 2–5 K, depending on the change anticipated in the sample response. The sample was held for 20 min at each temperature, during which the first 10 min was ignored and only data of the last 10 min were collected. Previous work demonstrated that 20 min holding time at each step was sufficient for the calorimeter to approach steady state conditions for PTT samples [12]. The reversing heat capacity C_p is obtained using

$$C_p = [A_\Phi / A_T \omega] K' \tag{1}$$

where A_Φ is the amplitude of the modulated heat flow rate, A_T is the amplitude of the temperature modulation with frequency $\omega(\omega = 2\pi/p)$, and K' is the calibration factor at the given conditions of the measurement. K' is determined as a function of temperature from the standard sapphire calibration. Note that the term "reversing" is used for C_P since it may include enthalpy changes due to slow evolution or absorption of latent heat and the true reversibility has not been established [13,14].

Standard DSC scans on cooling and heating were carried out at 5 K/min. A three-run method is adopted to obtain the specific heat capacity. The first run is empty Al sample pan vs. empty Al reference pan to obtain baseline correction. The second run is sapphire standard vs. empty Al reference pan to calibrate heat flow amplitude. The third run is sample vs. the empty reference pan. The sample mass was kept around 8 mg. The Al reference pan is slightly lighter than the sample pan with an error ±0.01 mg.

3. Results

The basic thermal analysis of melt-crystallized PTT is illustrated in Fig. 1a. Non-isothermal cooling (curve 1) shows a single exotherm, which is completed by about 450 K. The reheating curve (curve 2) shows an exothermic peak (at about 489 K) followed immediately by a single endothermic peak at 499 K. Reheating after QI cooling (curve 3), results in a double-melting endotherm with peaks at 493 K and 502 K. The degree of crystallinity, ϕ_C, is determined by measuring the endothermic area using a sigmoidal baseline [15] from:

$$\phi_C = \Delta H_{\text{means}} / \Delta H_f \tag{2}$$

where ΔH_{means} is the measured heat of fusion of the semicrystalline polymer while $\Delta H_f = 145.5$ J/g (30 J/mol) is the heat fusion of 100% crystalline PTT [12,14]. A very slight increase in crystallinity occurs in the PTT cooled quasi-isothermally, and the major melting peak shifts to higher temperature, indicating more perfect crystal was formed during QI cooling. After QI cooling, $\phi_C = 0.400$, while after non-isothermal cooling, $\phi_C = 0.385$.

Room temperature WAXS data for PTT are shown in Fig. 1b for samples treated by non-isothermal cooling (curve 1), or quasi-isothermal cooling (curve 2). For comparison, the molten amorphous sample is shown at $T = 553$ K (curve 3). The quasi-isothermally cooled sample has greater crystal perfection.

The specific reversing heat capacities of quasi-isothermal cooling (red filled circles) and subsequent reheating (black filled circles) are displayed in Fig. 2. The glass transition step occurs at about 360 K, and the solid state is achieved during cooling once temperature decreases below about 313 K. Upon quasi-isothermal reheating (black filled circles), the solid state reversing heat capacity is expressed until the glass transition temperature step occurs. During QI-reheating, the heat capacity step associated with the glass transition is reduced in amplitude and occurs at slightly higher temperature than during QI cooling. Comparing the reversing heat capacity at equal temperatures, we see that the heat capacity during quasi-isothermal heating falls below that of the cooling data, from the start of the glass transition step up to about 413 K. The variation between the heating and cooling data is outside the limit of experimental error. The reversing heat capacity during heating then crosses the cooling data, and remains slightly above the cooling data up to 471 K. From 413 K to 471 K, the