EFFECT OF HIGH PRESSURE ON THE MELTING, CRYSTLIZATION AND MOPHOLOGY OF LINEAR POLYESTERS

David Rohindra, Keiichi Kuboyama and Toshiaki Ougizawa

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, 2-12-1-S8-33, Ookayama, Meguro-ku, Tokyo 152-8552, Japan.

Introduction

Industrial molding processes of polymeric materials are often done under elevated pressures and fast cooling rates. These processing conditions influence the crystallization kinetics and morphology of the final product. Therefore, information on Pressure–Volume –Temperature (PVT) behavior of polymers are essential to predict the processing conditions because physical properties of the polymers depend on the crystalline morphology of the material. Although many investigations have been conducted on polymers that cover a wide pressure range using confining fluid dilatometers, limitations of the apparatus such as slow cooling rate, exact melting or crystallization temperatures not known and use of bulk materials that have temperature gradients across the sample, restricts the usefulness of the generated data in mimicking the processing conditions[1]. However, only a few experiments have been performed under fast cooling rates[2] using modified pressure apparatuses. Moreover, the majority of the studies under high pressure have concentrated on one polymer, polyethylene, dealing with the formation of extended chain crystals under isothermal conditions.

Over the years the demand for polymeric materials has increased and so have the environmental problems associated with the disposal methods. The solid waste management crisis has generated a need for environmental friendly materials to replace the conventional plastics. Polyesters of the succinate group are promising materials to be used as general purpose plastic substitute. Although these polyesters have low melting temperatures, they have high thermal stability similar to aromatic polyesters. Poly(tetramethylene succinate) (PTMS) derived from butanediol and succinic acid has excellent biodegradability and has been commercialized under the trade name Bionolle due to its good processing ability. It has a fast crystallization rate which makes it possible to perform experiments under various conditions. As the application of this polymer finds new areas in the near future, other processing conditions may be used to obtain materials for different purposes. Therefore, knowledge in thermal and morphological properties under elevated pressures and varying cooling rates are important for the design of new products with desired properties.

Due to the limitations of the conventional confining fluid dilatometers, high-pressure Differential Thermal Analysis (DTA) is a useful technique that can generate data comparable to the processing conditions provided the heating and cooling rate could be controlled precisely and the sensitivity in recording the thermal changes of the sample is high. Since the DTA sample cells were not commercially available, we designed the cells from aluminum in our laboratory which gave very high sensitivity with minimal noise.

In this study, we investigated the non-isothermal crystallization behavior of PTMS under hydrostatic pressure using a high-pressure DTA at different cooling rates. The effects of pressure and cooling rates on crystallinity and morphology of the crystals are presented.

Experimental

Materials.

PTMS was kindly provided by Showa High Polymers with a melt flow rate of 39g/10 min at 190 °C with a trade name of Bionolle. The average molecular weight and PDI was measured by a Shodex DU-H7000 GPC system against polystyrene standards attached to a Shodex RI-71S refractive index detector at 30°C. Properties of PTMS are given in Table 1. The chemical structure is shown in Fig 1.

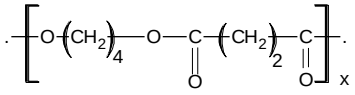


Figure 1. Chemical structure of PTMS

The polymer was purified by dissolving in chloroform and precipitating in methanol and vacuum dried for several days at 80 °C before analysis.

Table 1. Polymer Properties

Mw	PDI	T_m(°C)	T_g(°C)	η(melt) (Pa.s)
7.8×10^4	1.78	113	-38	150

Instrumentation.

High pressure Differential Thermal Analysis. High-pressure DTA was carried out with an inner heater type DTA cell. The temperature range was from 20 - 220 °C and the heating and cooling rates were controlled by a PID controller to ± 0.1 °C. Pressure measurements were performed up to 500 MPa and were controlled using a Heise gauge within ± 1MPa. Low viscosity silicone oil (KF-96-100CS; Shinetsu Chemicals) was used as the pressure transmitting fluid. The temperature scan was recorded with a two channel recorder.

High pressure crystallization. PTMS of dimension (10 x 5 x 1 mm) was wrapped tightly in aluminum foil and coated with epoxy resin to protect the sample from direct contact with the pressure transmitting oil. The sample was placed in the high pressure vessel and the temperature and pressure was varied according to experimental requirements.

Results and Discussion

Crystallization behavior under high pressure.

Figure 2 shows the cooling curves at different pressures at a cooling rate of 5 °C/min. The peak profiles showed a single exothermic peak. Similar curve profiles were obtained at different cooling rates. With increasing pressure the crystallization peak shifted to higher temperatures while with increasing cooling rate the peak shifted to lower temperatures. The peak profiles from atmospheric pressure up to 200 MPa were relatively similar but above this pressure, the peak became broader which indicated that crystallization process was affected by pressure.

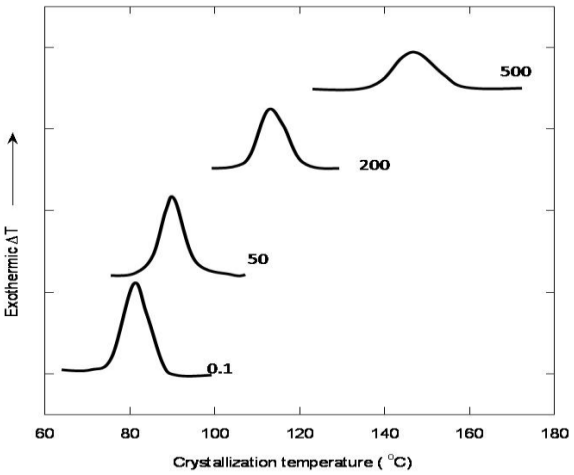


Figure 2. Cooling curve profiles of PTMS obtained at 5 °C/min at different pressures. Pressure in MPa is indicated next to the curve.

Detailed crystallization kinetic analysis showed no significant changes in the crystallization up to 200 MPa. The evolution of relative crystallinity as a function of temperature at various cooling rates and different pressures all showed an *S-type* curve which was consistent for a nucleation and growth process. A comprehensive analysis using the OZAWA model[3] was also preformed to test the validity of the equations under high pressure.

Atmospheric pressure crystallized samples were flexible regardless of the cooling rate where as above 200 MPa all samples became brittle. Brittleness can be caused by either increase in crystallinity, change in crystal form or increase in the spherulite size. The degree of crystallinity obtained from DSC and density measurements for samples crystallized under 500MPa at different cooling rates are given in Table 2. Determining crystallinity by DSC for PTMS became troublesome because of the melting and recrystallization process during the heating scan and due to the cold crystallization peak just prior to melting.

However, crystallinity measured from density, (X_m) also showed no significant change between atmospheric and 500 MPa pressure at a cooling rate of 10 °C despite the high-pressure crystallized sample being brittle. Increased crystallinity was not the cause of brittleness.

Table 2. Degree of crystallinity in samples crystallized under 500 MPa at different cooling rates.

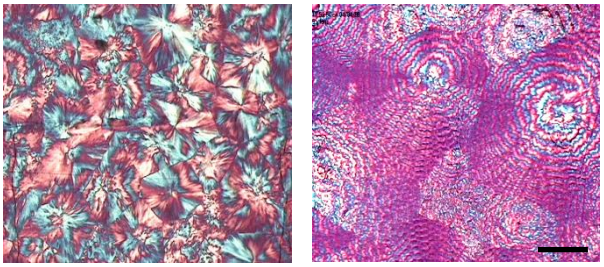
Cooling rate (°C/min)	Density (g/cm^3)	X_m (%)	DSC (%)
2	1.28	65	34
5	1.27	59	32
10	1.26	54	32
20	1.26	53	31
0.1MPa (10 °C/min)	1.26	53	31

Morphology observation.

The crystallized samples were microtomed and observed under the polarized optical microscope. The spherulitic form was the common crystal morphology of the crystallized samples. Figure 3 shows the optical micrographs of bulk samples crystallized at atmospheric and 500 MPa pressure at a cooling rate of 10 °C/min. From atmospheric pressure up to 200 MPa no noticeable change occurred in the morphology. The same was also observed for different cooling rates. However, at higher pressures, nucleation density was significantly reduced and was manifested with increasing cooling rates. Large spherulites were formed with well-developed extinction rings, which caused the samples to become brittle. These observations are explained on the basis of the chain transport mechanism. When pressure is applied to the polymer melt, the viscosity increases and subsequently reduces the chain mobility. The growth rate equation in the dynamic mode[4] is given by

$$\frac{dx}{dt} = \frac{G_o}{\emptyset} \exp\left(-\frac{U}{R(T-T_c)}\right) \exp\left(-\frac{K_g(T_m - T_c)}{2T_c^2(T_m - T_c)}\right)$$

According to this equation, the temperature difference, (T_m-T_c), and the activation energy influences the nucleation and growth rate. Generally, at low supercooling, the nucleation and growth rate are both slow. In this experiment, at atmospheric pressure, (T_m-T_c), was found to be 40°C, at 200 MPa 47 °C and at 500 MPa it increased to 66.6°C. Secondly, the activation energy related to the transport of the chains to the growth site (secondary nucleation) may also be a contributing factor. At high temperature of 200 °C the polymer is completely in the melt state with no thermal history present. Nucleation is assumed to be heterogeneous. Two regions can be clearly seen in fig. 3B, one is the large banded spherulites and the other marked by an arrow enclosed between the large spherulites, which is thought to be formed during crystallization by the impingement of the large spherulites. As crystallization proceeded, there was a build up of negative pressure in this enclosed space because of the low specific volumes of the crystallized material. Beyond a certain negative pressure, cavitation occurred which eventually ruptured into small nucleation sites giving rise to small spherulites. This phenomenon has been reported in poly(methylene oxide)[5] and isotactic polypropylene[6] but under isothermal conditions and atmospheric pressure.



A B

Figure 3. *Optical Micrographs at (A) 0.1 MPa and (B) 500 MPa at a cooling rate of 10°C/min.(Scale bar:20μm)*

The SEM micrographs showed the lamellar morphology to be rough at high pressure and fast cooling rate.

The melting behavior of the high pressure crystallized samples did not show any new peaks or shifting of the peaks to high temperatures indicating no formation of new crystal or lamellar thickening.

Wide-angle X-ray measurement performed on samples crystallized at different pressures and cooling rates showed similar diffraction pattern to that obtained at ambient pressure. With increasing pressure and decreasing cooling rate, diffraction peaks became sharp, indicating improvement of crystal order. The results indicate that only one crystal structure existed regardless of pressure and cooling rates.

Conclusion

In this work the design of the sample cell in the high pressure DTA enabled us to study the non-isothermal crystallization behavior of PTMS under hydrostatic pressure at varying cooling rates. The crystallization curve from atmospheric pressure up to 200 MPa remained relatively similar suggesting that the crystallization kinetics was not affected up to this pressure. Above 200 MPa peak broadening was observed and analysis of crystallization kinetic data showed the crystallization process was affected.

Optical micrographs and secondary electron images showed that the spherulitic form was the common crystal morphology. The number of spherulites per unit area decreased above 200 MPa indicating the nucleation and growth process was hindered because of the high melt viscosity. Large spherulites were formed with well-developed extinction rings, which caused the samples to become brittle. X-ray diffraction pattern of the high pressure crystallized samples showed no crystal modification.

From the crystallization kinetic data and morphological observations, it can be clearly demonstrated that if processing conditions are kept around or below 200 MPa, the magnitude of morphological changes in PTMS is minimal similar to atmospheric pressure.

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David Rohindra
Department of Organic and Polymeric Materials, Tokyo Institute of Technology,
2-12-1-S8-33 Ookayama, Meguro-ku,
Tokyo 152-8552, Japan
Phone: +81-3-5734-2439
Fax:+81-3-5734-2439
E-mail : rohindra.d.aa@m.titech.ac.jp

Personal Information
Nationality (Fiji Islander)
2006.10.1. Joined Ougizawa Lab.