Journal of Thermal Analysis and Calorimetry, Vol. 72 (2003) 667–674

ISOMETRIC CRYSTALLIZATION OF STRETCHED POLY(ε-CAPROLACTONE) SHEETS FOR MEDICAL APPLICATIONS

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Abstract

Low melting temperature thermoplastic sheets based on poly(ε-caprolactone) (PCL) can be formed directly on the patient and are used as immobilization device (mask) in the radiation therapy. The immobilization mask is allowed to harden in isometric conditions on the body at room temperature.

A new method for isometric crystallization kinetics of thermoplastic polymer sheets is developed using a tensile-strength instrument. The isometric crystallization method allows investigating the shrinkage force on time of crystallization of stretched samples of thermoplastic polymer sheets or immobilization medical devices. The dependence of the shrinkage force on time is described by Avrami equation and the kinetics parameters of isometric crystallization are calculated.

Keywords: Avrami equation, immobilization medical devices, isometric crystallization, poly(ε-caprolactone), shrinkage force

Introduction

It is known that low melting temperature thermoplastic sheets based on poly(ε-caprolactone) (PCL) can be formed directly on the patient and are used as orthopaedic splints and immobilization devices (masks) in the radiation therapy. The immobilization mask is allowed to harden (crystallize) in a fixed isometric condition on the patient body at room temperature for relatively short period of time (5–10 min). Subsequently, the mask is removed and stored at room temperature until the moment of next use in the radiation therapy, which may be, for instance, a few days or weeks later. It is therefore desired to have polymer masks with a low contraction during this storage time, such that the mask is still fitting on the patient at the moment of therapy.

A wide variety of methods is known to obtain information about crystallization kinetics of polymer materials under different non-isothermal and isothermal conditions, such as for instance dilatometry [1], density and micro hardness measurements [2], hot stage light microscopy [3], differential scanning calorimetry (DSC) [3–7], X-ray diffraction [1, 5, 7, 8], time-resolve Fourier transform infrared (FTIR) spectrophotometry [9], and nuclear magnetic resonance (NMR) [7, 10]. The disadvantage of

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1388–6150/2003/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

these known methods and instruments is that they are all designed for relatively small sized samples and cannot be used to measure the kinetics of crystallization of large samples or real size polymer articles.

The objectives of this study is to develope a new method for crystallization kinetics at isometric conditions of industrial samples of stretched thermoplastic polymer sheets and to evaluate the hardening (contraction) kinetics of thermoplastic immobilization devices for medical applications.

If the polymer sheet sample is stretched faster to the certain elongation in the molten state, fixed in a stretched position, and let it crystallize at isometric conditions at certain temperature, the internal shrinkage force due to the volume contraction of the sample during crystallization can be measure incessantly. The plot of the shrinkage force data against the time can be used to evaluate the kinetics of isometric crystallization of the polymers.

Experimental

Materials and instruments

The specimens (150×30×2.4 mm) from extruded polymer sheets of PCL were used. The PCL sheets were partially cross-linked to increase the melt strength.

Three different commercially available thermoplastic head immobilization masks UON™ (Orfit Industries, Belgium), Uni-frame™ (Med-Tec, USA) and U-frame™ (WFR, USA), based on partially cross-linked PCL are used to evaluate the contraction of the mask after moulding on the model.

The shrinkage force of stretched PCL samples is measured by means of Lloyd Instruments materials testing machine (LRX Plus).

A water bath (70°C) is used to heat the thermoplastic samples and head immobilization masks and a conditioned room (21°C) is used for air cooling of the PCL samples during crystallization.

The non-isothermal crystallization has been studied using TA Instruments DSC at different cooling rates (1.5, 5 and 10°C min^{-1}).

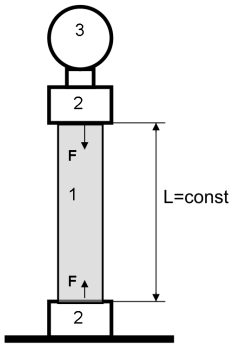

Fig. 1 Isometric crystallization of polymer flat sheet sample: 1 – sample; 2 – clamps; 3 – load measuring cell; F – shrinking force

Test setup

Isometric crystallization of stretched PCL sheet samples (Fig. 1)

A specimen (150×30×2.4 mm) is cut from a PCL sheet. It is heated 3 min in a water bath at 70°C. The sample is taken out of the water bath and it is fixed between the grips of the Lloyd Instruments testing machine. The sample is stretch (1000 mm min^{-1}) to a particular extension – usually of 50% and it is kept in this position at room temperature (21°C). All data of shrinkage force at constant length of the sample are recorded continuously *vs.* the time of crystallization.

Hardening contraction of thermoplastic head immobilization mask

The dummy head is attached to the force measuring cell of Lloyd testing instrument (Fig. 2). The immobilization mask is heated 3 min at 70°C in a water bath and it is pulled over the dummy head. The mask is allowed to air-cool (conditioned room 21°C) on the dummy head for 10 min and all data of shrinkage force are recorded. The mask is removed from the dummy head and it is stored at room temperature. The mask is placed back on the dummy head for 10 min and all data of shrinkage force are recorded continuously at various time intervals.

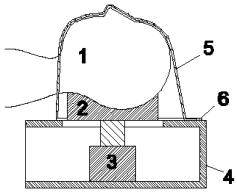

Fig. 2 Isometric crystallization of a thermoplastic immobilization mask; 1 – plastic dummy head; 2 – head support; 3 – load measuring cell; 4 – supporting box with clamps; 5 – thermoplastic mask; 6 – frame of the thermoplastic mask

Isometric isothermal crystallization kinetics

The crystallization kinetics of the materials generally is described as the transformation of the fraction of the materials from melt to solid *vs.* the time.

The isothermal crystallization kinetics of bulk polymers is usually interpreted in terms of Avrami equation [11, 12]:

$$\alpha(t)=1-\exp(-zt^n) \quad (1)$$

where: $\alpha(t)$ is a mass fraction of polymer transformed from melt to solid at time t, n is an exponent, who contains contributions related to the crystal growth geometry and the time dependency of the nucleation rate, z is an overall crystallization rate constant including contribution from crystal growth and nucleation.

As mentioned above different methods can be used to measure the fraction of the polymer $\alpha(t)$ that is transformed from melt to solid at time t. It is known that a crystalline polymer sharply decreases the volume (ΔV) during cooling at crystallization temperature T_c (first order transition):

$$\Delta V_{T_c} = V_{melt} - V_{crystal} \quad (2)$$

This phenomenon is used to measure the kinetics of crystallization by dilatometry techniques [1].

If the sample is held tightly in one direction and the size of the sample is kept constant in the same direction, the contraction of the sample during crystallization will create the induced internal force (F) in the same direction:

$$F(t) \sim \Delta V(t) \sim \alpha(t) \tag{3}$$

The increase of the internal stress due to a solidification contraction of the sample is measured with the time of crystallization.

Results and discussion

Kinetics of isometric crystallization of stretched PCL sheets

A partially cross-linked PCL sheet sample is heated at 70°C and stretched in the molten state with a high speed (1000 mm min^{-1}) to 50% elongation and fixed in a stretched position (L_{end}=const) during an air cooling crystallization at room temperature (21°C). The stretching allows to preload the samples and therefore to measure the initial internal shrinkage force data in the beginning of the crystallization process. A lower stretching ratio (less than 5%) can be used only to compensate the samples own mass. A higher stretching ratio depends on the required stretching conditions for the application of the industrial polymer materials. The internal shrinkage force (F) due to the volume contraction (ΔV) is measured continuously with a load cell of a material testing instrument (Fig. 1).

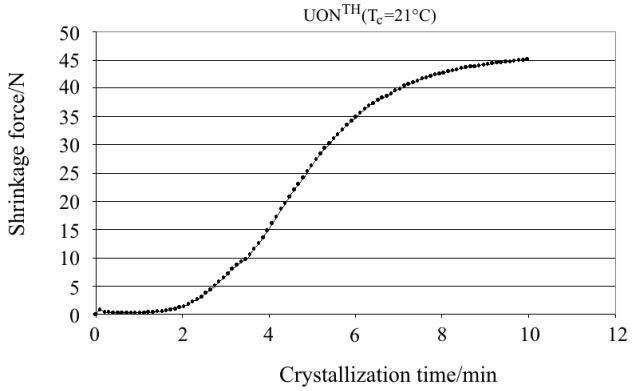

Fig. 3 Dependence of the shrinkage force F_i of PCL sheet (UON$^{TM)}$ on time of isometric crystallization at 21°C. Stretched ratio ε=50%

The time dependence of the shrinkage force which is presented in Fig. 3 can be interpreted in terms of modifying Avrami equation (4):

$$\alpha(t)=F_i/F_n=1-\exp(-zt^n) \tag{4}$$

where F_i is the value of the shrinkage force at time t_i, F_n is the value of the shrinkage force at the end of the crystallization time.

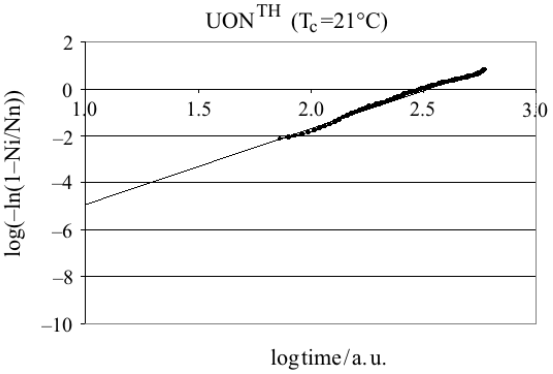

Fig. 4 Avrami log plot for the shrinkage force F_i

The logarithmic plot of Avrami equation (5) is a straight line (Fig. 4), which means a good fitting of experimental data by this equation:

$$\log(-\ln(1-F_i/F_n))=\log z+n\log t \quad (5)$$

The intercept of this line is equal to log$z$ and the slope to n.

Application of the Avrami equation on the isometric contraction force data for PCL sheet at 21°C gives for the overall crystallization rate constant $z=6.76\cdot10^{-9}$ and for n value 3.2. This value of the parameter n means a spherulite type of crystallization of the stretched PCL sheet sample at isometric conditions. The half time of crystallization $\tau_{0.5}$ ($\tau_{0.5}=(\ln(2)/z)^{1/n}$) is 297 s.

The kinetics parameters of isometric crystallization of PCL sheets are comparable with the kinetics parameters of isothermal crystallization of PCL determined by DSC [6]. Therefore the new method for isometric crystallization enables to evaluate the crystallization kinetics of stretched industrial polymer samples at isothermal isometric conditions.

Kinetics of isometric crystallization of stretched thermoplastic head immobilization masks

The isometric crystallization method is applied to measure the contraction of different, commercially available polymer masks for head immobilization, based on partially cross-linked PCL (UON™ from Orfit Industries, Uni-frame™ from Med-Tec and U-frame™ from WFR).

The contraction force of the immobilization mask is measured by means of a particularly modified tensile-stress instrument (Fig. 2) and all data of shrinkage force are recorded continuously (Fig. 5).

The application of the Avrami equation on the isometric contraction force data for UON™ immobilization mask at 21°C gives for the overall crystallization rate constant $z=1.65\cdot10^{-4}$ and for the half time of crystallization $\tau_{0.5}=103$ s; for Uni-frame™ immobilization mask – gives for the overall crystallization rate constant $z=6.08\cdot10^{-4}$ and for the half time of crystallization $\tau_{0.5}=130$ s.

Therefore the UON™ immobilization mask crystallizes (hardens) faster than the Uni-frame™ immobilization mask.

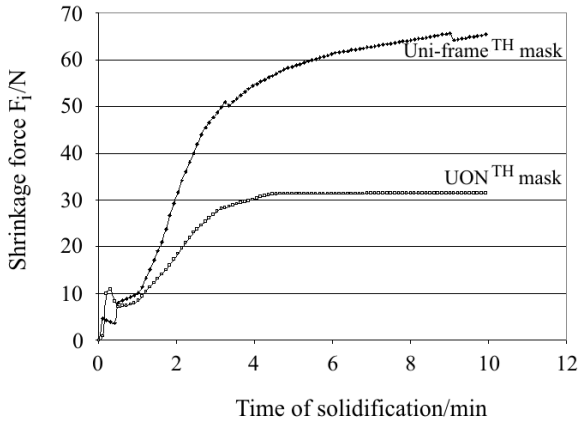

Fig. 5 Dependence of the shrinkage force of different thermoplastic immobilization masks (UON^{TM} and Uni-frame^{TM}) on time of isometric solidification

Contraction of thermoplastic head immobilization masks during storage at room temperature

The DSC results show that the final crystallization temperature of PCL is lower than the room temperature (about 11–15°C) at a cooling rate of 10°C min^{-1} (Fig. 6). Therefore, it is possible to expect the complete crystallization of the PCL sheets and immobilization devices to go on for a long time by storing at room temperature.

To investigate the time of complete hardening (crystallizing) the immobilization mask is removed from the dummy head and it is stored at room temperature 21°C. After that the mask is placed back on the dummy head and the data of shrinkage force are recorded at various time intervals.

The shrinking force increases during the storage time of the head immobilization mask and keeps relatively constant after 24 h (Fig. 7). The value of the shrinkage force of UON^{TM} is approximately two times less than the shrinkage force of the other two types immobilization masks.

The non-isothermal crystallization of different PCL samples was studied by DSC at different cooling rates from 1.5 to 10°C min^{-1}. The UON^{TM} shows faster crystallization by cooling from 70 to –20°C compare with Uni-frame^{TM} (Fig. 6). The crystallization temperature of UON^{TM} is higher than the crystallization temperature of Uni-frame^{TM}.

Accordingly, the present study provides an effective method by which the tensile-strain materials testing machine (load measuring instrument) can be used as an instrument to measure the kinetics of isometric crystallization of polymer sheets or real size polymer products such as immobilization mask for radiation therapy. This method also allows to investigate the kinetics of solidification of other types of polymer materials during cooling from melt temperature to different crystallization temperatures at isometric conditions using a thermostatic camera.

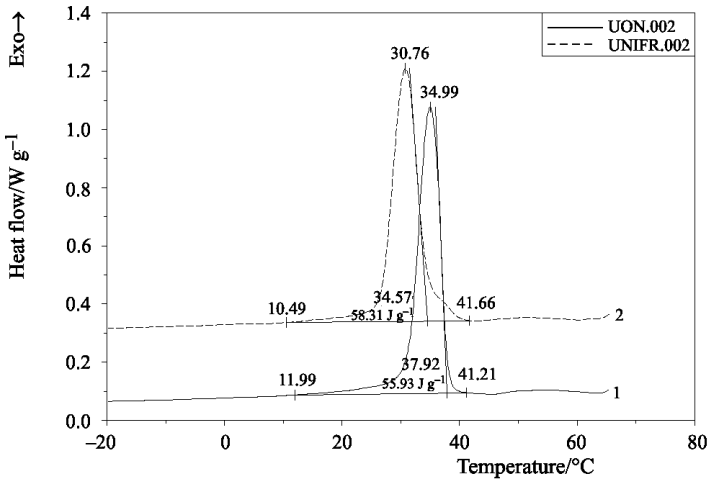

Fig. 6 DSC crystallization curves of UON^{TM} (curve – 1) and Uni-frame^{TM} (curve – 2) PCL immobilization masks; cooling rate 5°C min^{-1}

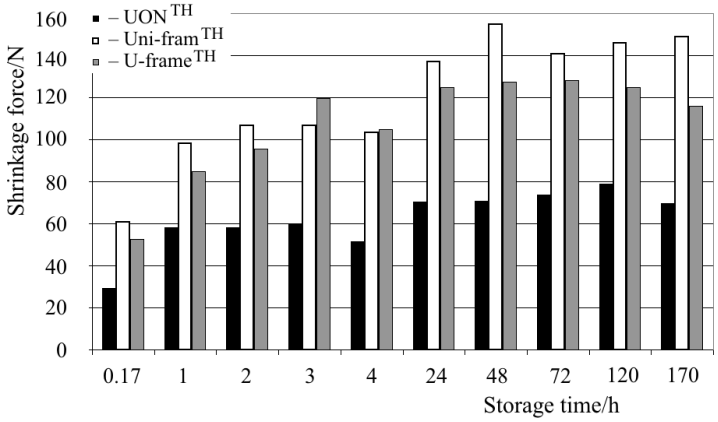

Fig. 7 Dependence of the shrinkage force of different PCL thermoplastic immobilization masks (UON^{TM}, Uni-frame^{TM} and U-frame^{TM}) on storage time at 21°C

Conclusions

A new method for isometric crystallization kinetics of industrial polymer sheets is developed. It is comprised of an incessant measurement of an internal shrinkage force of polymer sheet that is fixed in a stretched position during the solidification of the polymer at crystallization temperature.

The plot of the shrinkage force data, measured by means of tensile – strain instrument, against the time at constant temperature (21°C) are described in terms of Avrami equation and is used to evaluate the kinetic parameters of isometric crystallization of large polymers samples.

The isometric crystallization method allows to evaluate the kinetics of solidification of thermoplastic immobilization devices with a medical application.

The contraction of UON™ is less than the contraction of Uni-frame™ and U-frame™ head immobilization masks due to the higher crystallization speed of UON™ by air cooling at room temperature.

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