Available online at www.sciencedirect.com
ScienceDirect
Polymer 49 (2008) 303–316
polymer
www.elsevier.com/locate/polymer

Orientation of polyoxymethylene by rolling with side constraints

J. Mohanraj [a,1], J. Morawiec [b], A. Pawlak [b], D.C. Barton [a], A. Galeski [b,*], I.M. Ward [c]

[a] School of Mechanical Engineering, University of Leeds, Leeds LS2 9JT, UK
[b] Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland
[c] School of Physics and Astronomy, University of Leeds, Leeds LS2 9JT, UK

Received 4 July 2007; received in revised form 30 October 2007; accepted 6 November 2007
Available online 7 November 2007

Abstract

In this paper, we describe the application of the constrained rolling process to produce highly oriented polyacetal bars with enhanced mechanical properties. In this process, the heated polymer billet is deformed in a channel formed in the circumference of the bottom roll that provides lateral constraint to the material as it deforms. It is a process that has attracted interest due to its capability to produce thick cross-sectional oriented products continuously and at moderate production speeds. Here the focus is on two commercial grades of polyoxymethylene (a) Delrin® 100 and (b) Tarnoform® 300. Tarnoform®, unlike Delrin®, is a copolymer. The compression behaviour of these grades has been investigated in a plane strain channel die to determine the optimum constrained rolling conditions. Samples were then rolled to different reduction ratios close to but below the crystalline melting temperature of the two grades.

The modulus and strength increased almost linearly with reduction ratio. Rolled Delrin® exhibited higher modulus and strength than Tarnoform®. Under impact loading, with the initial notch perpendicular to the rolling direction, the fracture process was incomplete for both resins with the specimens exhibiting a hinge type break. Structural investigations of the rolled samples were carried out by wide and small angle X-ray diffraction. The structures produced were very similar to those produced in plane strain compression test. The pole figures from the (100) reflection suggest that the *c* axes of the POM crystals are oriented along the rolling direction while *ab* planes showed clustering of orientation of (100) normals in six directions. SAXS patterns from the rolled samples with the X-ray beam parallel to the force direction showed two-point patterns that suggest the transformation of the spherulitic morphology to a fibrillar structure in this direction. However, perpendicular to the rolling direction, four-point patterns were obtained that suggest cooperative kinking of the lamellae during deformation to produce a chevron-like structure. The enhancement in properties as a result of molecular orientation suggests that these materials can have major commercial applications.

Keywords: Polyoxymethylene; Rolling; Plane strain compression

1. Introduction

Molecular orientation in polymers greatly improves their mechanical and physical properties compared to the isotropic material [1–5]. Oriented polymers have found extensive applications in the production of fibres, films, pipes, sheets, etc. and recently more complex profiles have been manufactured.

Molecular orientation in polymers can be achieved by processing either in the melt or in the solid state. The enhancement of properties in the melt state is low due to the high temperature of the melt and the shaping device that increases the mobility of the molecular chains. However, in the solid-state processes, the molecular chains are essentially ‘‘frozen-in’’ leading to significant enhancements in the properties. In these processes, the polymers are processed below the crystalline melting temperature in the case of semi-crystalline polymer or near the glass transition temperature for amorphous polymer. Examples of solid-state orientation processes include tensile free drawing, die-drawing, hydrostatic extrusion, rolling, roll-drawing, constrained rolling process and equal

* Corresponding author. Tel.: +48 42 6803250; fax: +48 42 6803261.
E-mail address: andgal@bilbo.cbmm.lodz.pl (A. Galeski).
[1] Present address: Bridon, Carr Hill, Doncaster DN4 8DG, UK.

0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.11.008

channel extrusion process. A review of the above processes can be found in the literature [4–7].

The solid-state orientation processes can be broadly classified into two based on the stress state of the material in the shaping device. In the case of a tensile deformation process such as tensile free drawing and die-drawing, high production rates have been achieved [8]. However, the tensile nature of the processes causes structural damage in the material that lowers the fracture strength [9,10] of the oriented polymer. Fracture occurs when the flow stress, which increases with speed due to strain rate sensitivity, exceeds the fracture strength of the material. In the case of a compressive deformation process, the flow stress increases with strain and also due to the increased effect of the hydrostatic component of stress [11], which is counterproductive in terms of production speed. However, structural defects are minimised due to the compressive nature of the stresses in the material induced by the shaping device and this enhances the strength of the oriented polymer.

In this work the focus is on polyoxymethylene (POM), a polymer which has previously been oriented in the solid state by different routes and significant enhancements in modulus and strength have been obtained [9,12–14]. For example, a modulus of 58 GPa and strength as high as 2 GPa have been achieved by solid-state deformation of the polymer under hydrostatic pressure [9]. Oriented POM also offers superior resistance to creep [15], low coefficient of thermal expansion [16], heat shrinkage [17] and offers good chemical resistance [18]. Previous research has shown that this material in the oriented form is susceptible to structural damage such as voids [10,19,20], the extent of which has been shown to be influenced by the total plastic strain and the strain rate [21].

In this paper, we report the structure and properties of two commercial grades of polyoxymethylene oriented by the constrained rolling process. Polyoxymethylene has previously only been oriented by the conventional rolling process. Rolling thick cross-section polymer close to the melt temperature without side constraints can cause unnecessary transverse deformation and can lead to edge defects in the rolled material like fissures, edge cracking, warping, etc. [22]. This limits the conventional rolling process essentially to thin and wide strips of the material. In the constrained rolling process, the heated polymer billet is deformed in the channel formed between the circumference of the bottom-grooved roll and the top roll as schematically shown in Fig. 1. The channel in the bottom-grooved roll provides lateral constraint to the material as it deforms, which prevents transverse deformation and hence the formation of edge defects in the material. The top roll is of the same width as the channel and acts in effect as a plunger. The advantage of this process is its ability to orient relatively thick cross-section material continuously. This process has previously been used to orient a number of polymers [23–26]. Significant improvements in the modulus, strength and impact properties over the isotropic material have been reported for both polyethylene [24,25] and polypropylene [26]. However, no such studies have been reported for polyoxymethylene.

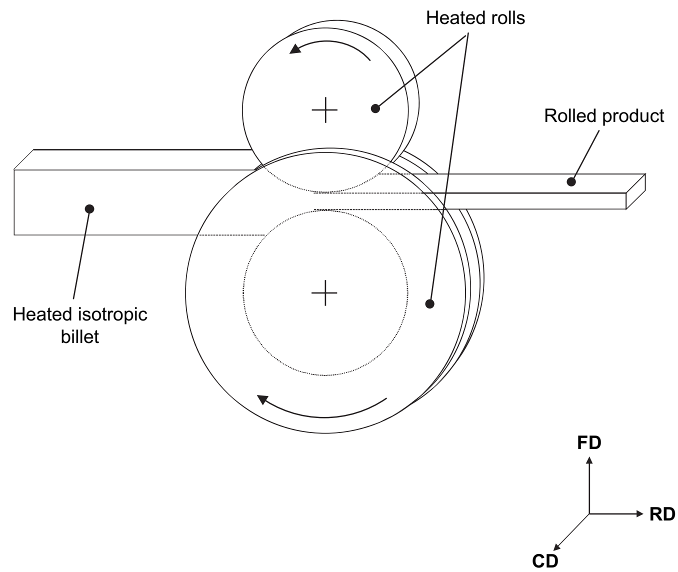

Fig. 1. Schematic of the constrained rolling process.

2. Experimental procedures

2.1. Materials

Two materials were used in this study. They are (a) Delrin® 100 by DuPont Engineering Polymers and (b) Tarnoform® 300 by Zaklady Azotowe Tarnow (Poland). Tarnoform®, unlike Delrin®, which is a homopolymer, is a copolymer produced by polymerisation of trioxane and copolymerized with 2–3% of dioxolane, which acts as a stabiliser in the resin. The density, melt flow index of the materials used in this study are given in Table 1. The materials were supplied as extruded sheets of thickness 16 mm and were cut into billets 1 m long and with varied width.

2.2. Thermal characterization

The melting behaviour of the extruded Delrin® and Tarnoform samples was studied out using a TA 2920 (Thermal Analysis, New Castle, DE) analyser. Indium was used to calibrate the temperature and enthalpy. The crystalline melting temperature was determined at a heating rate of 10 °C/min under nitrogen atmosphere using a sample weight of 5–8 mg. The melting temperature reported here is an average from 5 scans.

2.3. Plane strain compression tests

It has been shown in the case of polypropylene and HDPE that the deformation behaviour of the material in the constrained rolling process matches the Plane Strain Compression (PSC)

Table 1
Details of the materials used in this study

Material	Density, g/cm^3	Melt flow index (190 °C; 2.16 kg)
Delrin® 100	1.427	3.9
Tarnoform® 300	1.41	5.68