Polymer 83 (2016) 116–128

Contents lists available at ScienceDirect

Polymer

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

The prediction of mechanical performance of isotactic polypropylene on the basis of processing conditions

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ARTICLE INFO

Article history:
Received 30 September 2015
Received in revised form
30 November 2015
Accepted 1 December 2015
Available online 18 December 2015

Keywords:
Semi-crystalline polymer
Structure-property relations
Lamellar thickness
Yield stress

ABSTRACT

A strategy is presented to predict the yield kinetics following from different thermomechanical histories experienced during processing in non-isothermal quiescent conditions. This strategy deals with three main parts, i.e. processing, structure and properties. In the first part the applied cooling conditions are combined with the crystallization kinetics and the cooling history of the material is calculated. From this history the lamellar thickness distributions are predicted in the second part. Finally, in the third part these distributions are used to predict yield stresses. Experimental validation is carried out for all the different parts of the strategy. In situ temperature measurements, lamellar thickness distributions from SAXS experiments and yield stresses measured in uniaxial tensile deformation are performed for validation purposes. The versatility is investigated by applying this procedure on two different iPP grades. The yield stress predictions show good agreement with the experimentally obtained results in two separate deformation mechanisms, and only a few parameters are dependent on the specific iPP grades that were used here. Moreover, it is shown that the average lamellar thickness is sufficient to predict the yield stress, and that the width of lamellar thickness distributions does not have to be taken into account.

1. Introduction

Polymers are used in a wide spectrum of applications ranging from packaging to structural engineering. Polyolefins, specifically polyethylene and polypropylene, form a substantial part of the synthetic polymers used because of their low costs, ease of manufacturing and versatility. To illustrate, these materials are used in extrusion processes (pipes), film blowing processes (packaging) and injection molding processes (structural applications). Within this specific class of materials multiple variants of polypropylene exist, e.g. isotactic-, syndiotactic-, atactic polypropylene and many copolymers. Their properties are related to the chemical structure, in particular the presence of regularity [1], since it allows polypropylene (iPP and sPP) to partially crystallize upon cooling. Due to the ability to crystallize the solidification takes place at higher temperatures as compared to aPP, largely affecting the mechanical properties. Other important aspects dominating the morphology and thereby the mechanical properties, are the processing conditions. Flow and cooling conditions are known to largely affect the morphology and therewith the yield kinetics and overall mechanical response [2,3]. Since changes of these processing conditions throughout a product may therefore result in strong spatial variations of mechanical performance [4], an undesired consequence is that weak spots are typically present. In this work a first attempt is made to relate the mechanical properties to the morphology resulting from well-defined processing conditions.

The solid crystalline parts, present in iPP, are connected by chains surpassing the amorphous regions [5,6]. Some general findings on the relation between the crystals and the mechanical properties follow from several studies performed in the past. First, the Young's modulus increases with the degree of crystallinity, whereas the impact performance and the toughness decrease [7,8]. Furthermore, the yield stress appears to be strongly correlated to lamellar thickness [9–14]. This relation was rationally based on the nucleation and propagation of screw dislocations [12] in the crystalline lamellae and thus on the lamellar thickness.

Besides the variations in the thickness of the crystalline domains (lamellae), multiple crystallographic structures can be present. In iPP, monoclinic α, pseudo-hexagonal β, orthorhombic γ and mesomorphic unit cell structures [15,16] can be formed with alternating amorphous and rigid amorphous regions in between

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http://dx.doi.org/10.1016/j.polymer.2015.12.001
0032-3861/

[17], affecting the mechanical properties as well. The presence of these regions together with the polymorphism makes it complicated to reveal the relationship between mechanical properties observed on a macroscopic scale to morphologies present at a microscopic or even smaller nanometer scale [18].

The crystallization process is kinetically controlled and therefore local thermo-mechanical conditions experienced by the polymer during processing can have pronounced effects on the lamellar morphology that forms, as well as on the polymorphism within the crystals [19–21,4]. Structure development under processing conditions has been subject of substantial research carried out in the past [22–24]. When we focus on conditions imposed during a compression molding process, i.e. moderate non-isothermal quiescent conditions, it is found that in the case of neat iPP typically α crystals develop [25]. Depending on the applied cooling rate, the crystallinity as well as the number and size of spherulites varies. Furthermore, this unavoidably results in variations of the lateral size of the crystal sheet-like domains, but more important for the yield kinetics, differences in the thickness will appear. The lamellar thickness is determined by the undercooling during the crystallization process [26] and, therefore, directly related to the cooling rate. Van Erp et al. [3] specified this effect of cooling rate to investigate the structure property relation for iPP. On the other hand, several studies have been devoted to the development of model frameworks capable of quantitatively predicting the processing dependent crystal structures as a result of processing [25,27–30].

The main aim of this work was to make a coupling between the processing-structure and structure-property relation in a predictive way. The strategy chosen to accomplish this goal is schematically shown in Fig. 1 and is divided into three main blocks. Different processing histories are obtained in terms of variable cooling rates. In the first block the processing dependent crystallization kinetics are predicted as a function of time and temperature. The time-temperature history follows from the heat equation, which is used in combination with the crystallization model proposed by van Drongelen et al. [25] to account for latent heat release. Temperature and pressure dependent growth rate and nucleation density are the most important parameters governing the crystallization process, whereas the boundary conditions together with the thermal contact resistance determine the temperature evolution. In the second block the obtained evolution of crystal volume as a function of temperature is used in combination with the Lauritzen-Hoffman equation [26] to determine the lamellar thickness distributions resulting from the different cooling rates. Also the dependency of the molecular properties of the iPP chain on the crystallization temperature and lamellar thickness is determined. Finally, in block three, the lamellar thickness is used to get the yield kinetics by making use of an empirical relation reported by van Erp et al. [3].

In the present study we will first give more detailed background information on 1) the crystallization model and the simplifications that are used, 2) the coupling to a structural feature, in this case lamellar thickness and 3) the relation between the lamellar thickness and the yield kinetics. Subsequently these three distinct parts are coupled and used to predict yield stresses resulting from well defined thermo-mechanical histories. The validity of this approach is experimentally shown for two iPP grades.

2. Experimental

2.1. Materials

Two isotactic polypropylene homopolymer grades were used: iPP-1 (Borealis HD234CF) with a weight averaged molar weight Mw = 310 kg/mol and a polydispersity Mw/Mn = 3.4, and iPP-2 (Borealis HD601CF) with Mw = 365 kg/mol and Mw/Mn = 5.4. These two materials were chosen because they were used in several other crystallization studies in our group [25,31].

2.2. Sample preparation

To obtain samples with different thermal histories, sheet material with a thickness of 1 mm was compression molded from both the iPP-1 an iPP-2 grade. A mold, sample surface area of 100 cm^2, was sandwiched in between stainless steel sheets (0.5 mm) and placed in a hot press, see Fig. 2. The stack was subsequently heated to 230 °C and a force of 100 kN was applied stepwise. The sheets were kept under these conditions for 3 min to erase previous thermo-mechanical history. The solidification was induced by putting the stack in a cold press for 3 min, at temperatures varying from 20 °C to 90 °C (steps of 10 °C). To monitor the temperature

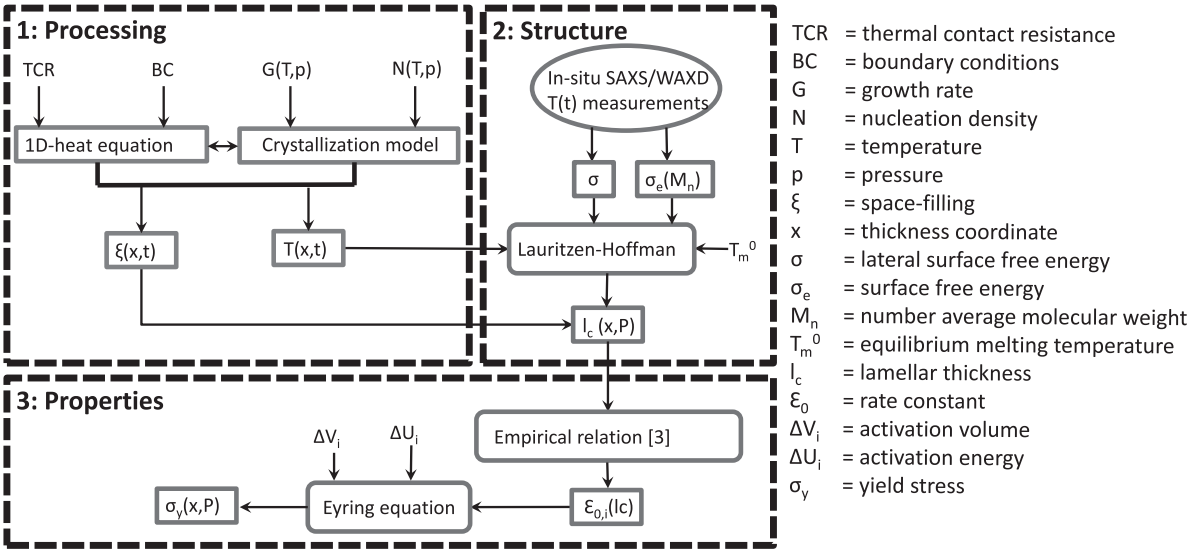

Fig. 1. Strategy to predict the yield stress directly from processing conditions.