Polymer 122 (2017) 12–21

Contents lists available at ScienceDirect

Polymer

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

The influences of a novel shear layer-spherulites layer alternated structure on the mechanical properties of injection-molded isotactic polypropylene

FengYi Hou, DaShan Mi, Man Zhou, Jie Zhang*

College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu, 610065, China

ARTICLE INFO

Article history:
Received 21 April 2017
Received in revised form
12 June 2017
Accepted 17 June 2017
Available online 17 June 2017

Keywords:
Alternated multilayer structure
Multi-flow vibration injection molding
Shish-kebab

ABSTRACT

In general, the strength of injection molded objects increases with shear layer thickness or shish-kebab content. However, the effect of the change of the position of shear layer and spherulites layer on the mechanical properties is still unclear, when their thickness are fixed. To answer this question, a novel multilayer structure in which the shear layer mainly containing shish-kebab structure and spherulites layer consisted of spherulites stack alternatively was prepared by a self-designed multi-flow vibration injection molding (MFVIM) device. The results demonstrate that the impact strength can be enhanced significantly by such alternating structure, possibly because this structure is benefit for crack deflection and consequently induces more plastic deformation regions, through altering stress transfer direction and stress distribution. The tensile strength, however, is only affected little by such structure.
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1. Introduction

Extensive researches have been carried out on the flow-induced polymer crystallization due to both theoretical and practical requirements [1–4]. Under external flow including shear and elongation flow, some highly oriented structures (such as shish-kebab, cylindrites and transcrystallization) can be formed [5–7]. Among these oriented structures, shish-kebab structure has been drawn much attention in the past [8–12]. Its central position is mainly consisted of long and stretched chains (shish) led by external flow, which play a role of nucleating site for the lateral epitaxial growth of folded chains (kebab). Understandably, if such structure can be introduced into industrial products, their strength, stiffness and modulus would be effectively improved, since polymer chains in this structure aligned along the flow direction can withstand greater loading. Some succeed research works of introducing high content of oriented structure for enhancing materials' strength have been reported [13–19]. In general the more content of shish-kebab structure formed the higher strength and stiffness of material are. Mi [20] quantificationally investigated the effect of shish-kebab structure content on the mechanical properties of iPP by tuning the shear layer thickness. The result revealed that both tensile and impact strength are increased exponentially with the shish-kebab content.

Injection molding is one of the most common and important way for manufacturing polymeric materials. Product manufactured by this method exhibits an inhomogeneous skin/core structure, in consequence of the gradient distribution in thermal-mechanical fields (i.e. shear, temperature and pressure field) away from the mold wall [21,22]. The thin skin and shear layer nearing the cold mold wall and subjected to high shear stress and fast melt cooling rate mainly contain highly oriented structures. While, the weak shear stress and low melt cooling rate in thick core layer is benefit for chain relaxation and the generation of spherulites.

It is well accepted that material's macroscopic properties closely relate to its microstructures. Because spherulites and shish kebab structure are very different, the influence of shear layer and spherulites layer on the mechanical properties should also be varied. Actually, although the relationship between shish-kebab content and mechanical properties has been investigated, there is still an unclear question that when shear layer and spherulites layer thickness are fixed, what different effect would it have on the mechanical properties that if the position of shear layer and spherulites layer are changed?

Based on the conventional injection molding, our laboratory developed a MFVIM technology which can be applied for changing

* Corresponding author.
E-mail address: zhangjie@scu.edu.cn (J. Zhang).

http://dx.doi.org/10.1016/j.polymer.2017.06.035
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the arrangement and thickness of shear layer and spherulites layer. Before filling stage no difference exits between conventional injection molding and MFVIM. After filling stage, however, the notable difference from conventional injection molding is that several times of shear flow can be imposed by MFVIM on the melt in the mold cavity. Specific description of the unique features of MFVIM is follow: (1) after the finish of filing stage of the first polymer melt flow, an extra sheared polymer melt (the second melt flow) provided by vibration pressure penetrates the first one, which will increase the shear effect and induce the formation of highly oriented structures. Actually, the MFVIM machine is able to provide such melt flow for several times after the finish of filling stage. (2) to increase the shear effect of the second melt flow, in the mold cavity a flash groove is designed for the spilling of second melt during packing stage [20], which facilitates the flow of the second melt and increases its flow rate. (3) The time interval between two times of vibration can be controlled. Its operating principle is described in Fig. 1. If there is no extra melt flow imposed, typical skin/core structure can be formed (Fig. 1(a)). This process is the same with the conventional injection molding. After the finish of filing stage, however, if the second melt flow is exerted, a new shear layer with highly oriented structures will be formed (Fig. 1(b)). As a result, the whole shear layer thickness is increased. If the second melt flow is imposed with a relative long interval time after the finish of filing stage, a spherulites layer will be generated between two shear layers (Fig. 1(c)) in consequence of the two effects of the frozen of melt and chains relaxation. In this case, a multilayer structure with alternating arrangement of shear layer and sphrulites layer can be formed. According to above describing about the principles of MFVIM, it is easy to understand that the first two features are to strengthen the shear stress of second melt flow which can be applied for the formation of shear layer and increasing the whole shear layer thickness. While the last one plays a role for controlling the distribution of shear layer and spherulites layer.

To figure out the question that what effects it would have on the mechanical properties that if shear layer and spherulites layer stack alternatively but their thickness are fixed, in present work, a novel multilayer structure with alternating arrangement of shear layer and spherulites layer was obtained via a homemade MFVIM device. IPP was selected for the following reasons: (1) many attempts have been made to study the microstructure and modification of iPP in the past for its comprehensive properties and low manufacturing cost [23–29]; (2) under external flow field, highly oriented structures can be easy formed in iPP melt [30,31]. Additionally, for comparison a sample whose shear layer thickness is similar with that in the sample having a shear layer-spherulites layer alternating structure was also prepared by MFVIM. The results indicate that this alternating structure is in favor of the improvement of impact strength of iPP, whereas there is little influence of such structure on the tensile strength of iPP.

2. Experiment

2.1. Materials

IPP (trademark of T30S) with melt flow index (MFI) of 2.6 g/10min (230°C/2.16 Kg) and density of 0.91 g/cm^3 was purchased from Dushanzi petroleum chemical Co., China.

2.2. Sample preparation

Pellets of iPP were injected by a MFVIM machine. The mold temperature was fixed at 50 °C and the barrel temperature was limited within 160°C–200 °C from hopper to die. The thickness and distribution of both shear layer and spherulites layer were controlled by tuning the MFVIM processing parameters, including interval time and pressure. For brief, the sample manufactured by conventional injection molding was named CIM. Meanwhile, samples prepared by MFVIM were designated as A_1, A_2, B_1 and B_2. For example, sample A_1 represents the sample has an alternated structure, while sample A_2 as a control sample of sample A_1 has the same shear layer thickness with sample A_1. The naming for sample B_1 and B_2 is the same with sample A_1 and A_2 respectively, except the shear layer thickness in sample A_x and B_x is different.

2.3. Characterizations

2.3.1. Polarization light microscopy (PLM)

Thin slice with about 30 μm thickness was cut along the ND-MD plane(see Fig. 2) via a microtome and observed by a PLM of DX-1 (JiangXi Phoenix Optical Co., China) with a Nikon 500D digit camera.

2.3.2. Differential scanning calorimetry (DSC)

A DSC (TA Q200) device was used for analyzing thermal behavior of different samples. All measurements were carried out under dry nitrogen atmosphere. Samples about 5–10 mg cut along the ND-MD plane were heated from 40 °C to 200 °C at heating rate of 10 °C/min. The following equation was utilized for calculating the total crystallinity X_c of each sample:

$$X_c = \frac{\Delta Hm}{\varDelta H_m^0} \quad (1)$$

where $\varDelta Hm$ represents the measured value of the enthalpy of fusion. ΔH_m^0 means the fusion enthalpy of completely crystallized iPP. Here, the value of ΔH_m^0 of iPP was selected as 207 J/g [32].

2.3.3. Mechanical test

The standard dumbbell bar was made for tensile strength test conducted by an Instron testing machine (model 5569) with the across head speed of 50 mm/min at room temperature. The izod

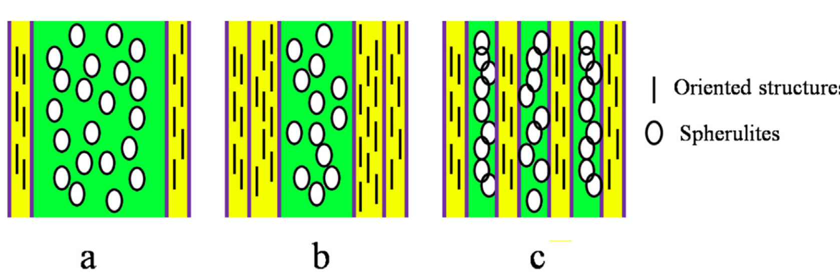

Fig. 1. Schematic diagram for the operating principle of MFVIM: (a) typical skin/core structure; (b) a new skin/core structure with increased shear layer thickness. (c) a shear layer-spherulites layer alternated structure.

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