European Polymer Journal 89 (2017) 138–149

Contents lists available at ScienceDirect

European Polymer Journal

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

Crystallization of polypropylene in multilayered spaces: Controllable morphologies and properties

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ARTICLE INFO

Keywords:
Multilayer structure
Morphology
Polypropylene
Ethylene vinyl acetate copolymer

ABSTRACT

In this work, multilayer materials containing alternating layers of polypropylene (PP) and ethylene vinyl acetate copolymer (EVA) were fabricated through layer-assembly coextrusion. With increasing the number of layers, the growth of spherulites distributed in PP layers was gradually confined along the thickness direction leading to the slowdown of crystallization rate. Owing to the formation of the anisotropic spherulitic morphology, its influence on mechanical and optical behaviors of the multilayer specimens was investigated, respectively. Results revealed that the layer multiplication induced the increase of yielding strength and promoted the propagation of necking zone in a stretching process. When a beam of light passed through the specimen with more layers, a higher transmittance could be directly collected along the incident direction. It was recognized that the confined spherulites with high aspect ratios played a crucial role in weakening the light deflection, which provided a potential route to massively fabricate the transparent PP without filling nucleating agents.

1. Introduction

As one of commercial semicrystalline polymers, isotactic polypropylene (PP) has been widely applied in various fields. It is well known that its physical performances are strongly related to crystal forms [1–3], size [4–6], contents [7–9], and morphologies [10–12], which can be controlled by filling nucleating agents [13–15], changing heat treating conditions [16–18] and applying one or more special force fields [19–21]. Recent years, with the development of fabricating technologies, the crystallization in confined spaces has attracted increasing attentions which is recognized as another promising strategy to tailor the final performances of neat polymers.

Among various confining forms, the simplest is one-dimensional (1D) confinement within the lamellar geometry where the crystallization behaviors can be readily tailored by changing the thickness of the confined space [22–24]. It has been revealed that if the film thickness is less than the spherulitic dimension, lamellae tends to be organized into flattened spherulites or “discoids” [25]. However, the 1D confinement is commonly achieved with a spin-coated thin layer on a substrate [26], with a block copolymer that contains at least one crystallizable block [27], or with a patterned substrate [28]. In most instances, these techniques are solvent-required and the inconvenient morphological manipulation makes the correlation between the crystalline morphologies and physical performances seldom concerned. Thus, a novel manufacturing technology is eagerly required for efficiently fabricating the materials with controllable 1D-confined spaces.

As a specific melt-processing technology, layer-assembly extrusion has been increasingly applied to achieve multilayer materials by combining an assembly of layer-multiplying elements (LMEs) with two extruders (Fig. 1). The number of layers can be multiplied

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http://dx.doi.org/10.1016/j.eurpolymj.2017.02.013
Received 5 August 2016; Received in revised form 16 January 2017; Accepted 7 February 2017
Available online 12 February 2017

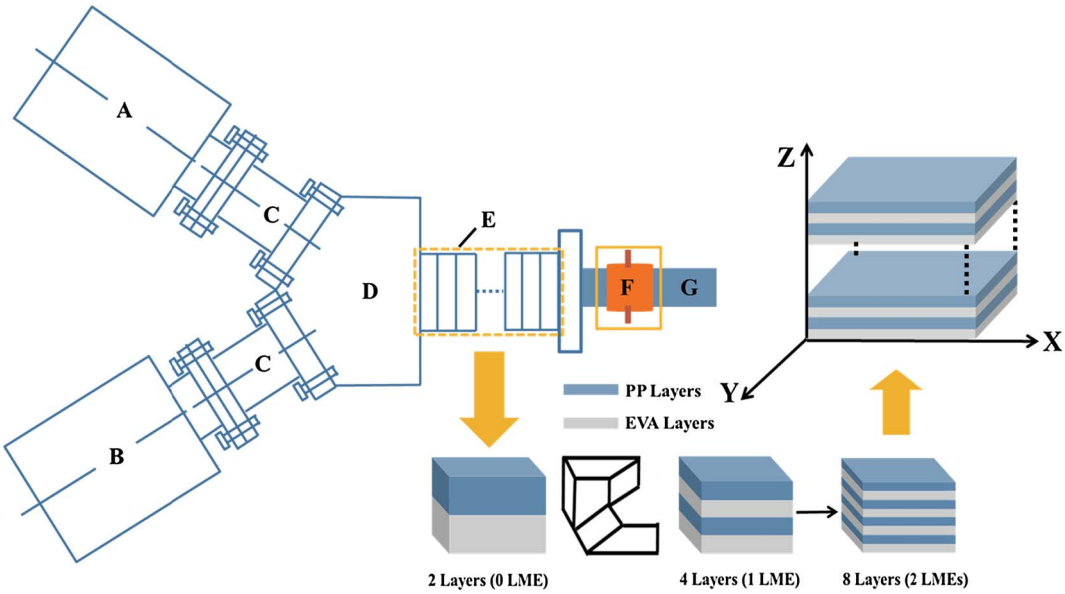

Fig. 1. Schematic of layer-assembly extrusion system: (A and B) single screw extruder; (C) connector; (D) coextrusion block; (E) layer-multiplying elements (LMEs); (F) rolling and cooling block; (G) extrudate.

by applying a different number of LMEs, without changing the overall thickness of the whole material. Previous work has presented that the thickness of each layer can be proportionally reduced by multiplying layer numbers, which offers an efficient and controllable approach to fabricate 1D-confined spaces [29–36]. For example, Jin et al. demonstrated that stacking lamellae could be obtained in nanoscale PP layers which were separated by polystyrene layers [33]. Wang et al. further found that highly orientated single lamellae could form in poly (ethylene oxide) layers when the thickness of each layer reached 20 nm, and such high aspect ratio in-plane lamellae could make the permeation pathway of oxygen more tortuous leading to a remarkable increase of oxygen barrier [34]. However, compared to that occurring in nanoscale spaces as reported before, the structural development in microscale layers and its influence on macroscopic properties have not been emphasized enough.

In this study, PP/ethylene-vinyl acetate copolymer (EVA) multilayer materials were prepared through the layer-assembly extrusion. By changing the number of layers, the spherulitic morphology was observed in PP spaces confined between EVA layers, and corresponding crystallization mechanism was proposed. Additionally, the influence of anisotropic morphology formed in the 1D confined spaces on the yielding behaviors along X direction (parallel to layer interfaces) and the optical properties along Z direction (vertical to layer interfaces) were also investigated.

2. Experimental

2.1. Materials

The isotactic PP (F401), with a density of 0.90 g/cm^3, a melt index of 3.0 g/10 min (230 °C, 2.16 kg) and a refractive index of 1.4900, was provided by Yangzi Petrochemical Company Ltd. (China). EVA (18J3), with a density of 0.94 g/cm^3, a melt index of 2.8 g/10 min (190 °C, 2.16 kg) and a refractive index of 1.4845, was obtained from Yanshan Petrochemical Company (China). The vinyl acetate content is 18 mol%. These materials were used as received.

2.2. Specimen preparation

PP and EVA were dried in an oven at 80 and 60 °C for 24 h prior to melt processing, respectively. 2-, 8-, 16-, 32-, 64- and 128-layer PP/EVA multilayer materials were fabricated through the layer-assembly extrusion technology, the details of which were described in other literatures [29–31]. By controlling the extruding speed, the total thickness of each extrudate was about 1.5 mm. The multilayer structure is schematically illustrated in Fig. 1 and the reference directions are designated: X, Y and Z denote the extruding, width and thickness directions of an extrudate, respectively.

2.3. Morphological observation

Polarized optical microscopy (POM, Olympus BX51) equipped with a heating cell was used to visualize the multilayer structure and crystalline morphology. A thin slice about 15 μm in thickness was cut from an extrudate parallel to the XZ plane by using a microtome. For recording the morphological development of spherulites, each slice was heated from 20 to 200 °C at a rate of 10 °C/