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Material properties

Thermo-mechanical properties of β-nucleated polypropylene multilayers

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ABSTRACT

With the aid of a layer-multiplying coextrusion technique, polymer composites comprising up to 128 uniform alternating layers of polypropylene random copolymer (PPR) and β-nucleated PPR were produced. Crystallization, melting behavior and mechanical properties (bending, tensile and impact characteristics) were investigated. The results not only show an increasing amount of β-crystals, but also improved mechanical properties. In particular, the temperature dependence of the bending modulus reveals that a high number of layers leads to an increase in stiffness across a wide range of temperatures. For each layer composition, a distinct temperature can be determined that marks the upper limit of this synergistic effect.

1. Introduction

Polypropylene (PP) is one of the most important thermoplastic materials due to its relatively low cost, high chemical resistance and ease of fabrication. Copolymerization of propylene with other olefins is often used to improve the impact properties. In particular, copolymers with low ethylene content are commercially important [1]. For isotactic polypropylene, different crystalline modifications are known and were investigated in this study: While the α-modification is monoclinic, β-PP crystallizes in a hexagonal form. Since the main effect of hexagonal crystals is a shift in the ductile/brittle transition temperature, the impact properties can be further improved using specific β-nucleation agents [2].

Mixing of fluids is an important process in many industrial operations and devices. Highly viscous fluids such as polymer melts are mixed most efficiently when the so-called baker's transformation is applied [3]: a fluid is successively stretched, cut and stacked in the same way a baker rolls and folds dough. The baker's transformation can be realized in a continuous process, for instance, by using a multiflux static mixer. In the channel of this device, several “mixing elements” are present, in each of which the flow undergoes a baker's transformation. The geometry of the multiflux static mixer was first described by Sluijters [4].

Numerous researchers have reported on how layer-multiplying devices permit two polymers of widely dissimilar solid-state properties to be combined into unique microlayer structures. If the layers are sufficiently thin, the properties of the constituents can combine to synergistic effect. Micromechanical properties of two different polymers within microlayer compositions were investigated by Kerns et al. [5], Im and Schrenk [6], Gregory et al. [7], Ebeling et al. [8], Sharma et al. [9], Ivan'kova et al. [10], Shen et al. [11], and Lin et al. [12], focusing especially on microlayer systems consisting of alternating layers of macroscopically brittle (PS, PMMA, SAN) and ductile (PE,

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PPO, PC) polymers. The observed improvements in toughness are attributed to a fundamental change in the micromechanical deformation mode of the brittle component when its layer thickness is reduced to the micron range. Normally, brittle polymers exhibit crazing prior to yielding and, subsequently, fracture at low strains. In microlayers, these components yield after shear bands from the ductile layers propagate into the brittles layers.

Microlayer coextrusion can also be an effective research tool, because the unique structures obtained consist of a high number of interfaces. Thus, they are ideal for fundamental studies of phenomena such as interdiffusion and adhesion. Nazarenko, Pollock and Haderski [13–15] concentrated on crystallization and interdiffusion in nanolayers of two miscible polymers, i.e., polycarbonate and a copolyester. Initially, two glass transition temperatures can be observed by differential scanning calorimetry (DSC) that lie between the glass transition temperatures of the pure components. On annealing, the glass transition temperatures shift closer together, reflecting the extent to which interdiffusion has occurred. Furthermore, it was demonstrated that the formation of spherulites is strongly affected by diffusion of PC into the polyester layers, as nucleation is reduced and spherulite density decreases. Bernal-Lara et al. [16] showed that, in HDPE nanolayers (≤100 nm), crystallinity decreases significantly and, as a result, oxygen permeability increases by a factor of 3. Heating films above the melting temperature of HDPE resulted in fractionated crystallization initiated by layer instability and breakup. Pan et al. [17] investigated the crystalline structures of PE nanolayers by transmission electron microscopy (TEM), small angle x-ray scattering (SAXS) and wide angle x-ray scattering (WAXS), and revealed that at the molecular scale lamellae are oriented with the long axes perpendicular to the extrusion direction in a row-nucleated morphology.

Motivated by these studies, we investigated the influence of the layer structure on both the crystallization behavior and the mechanical properties of coextruded PPR/β-PPR samples.

2. Experimental

A Borealis RA130E polypropylene random copolymer (PPR) intended for plumbing and heating applications was used as the first component and combined with a β-nucleated Borealis RA7050. The melt flow rate (MFR) of both polymers was about 0.3 g/10 min in accordance with ISO 1133 standard (230°C, 2.16 kg). Plates with a nominal thickness of 4 mm were prepared using the layer-multiplying process described elsewhere [18]. They were fabricated into samples with 2, 8, 32 and 128 layers with a volume ratio of 50:50. For comparison, monolayer plates were prepared by coextruding two batches of RA130E or RA7050. Our coextrusion setup produced multilayers with straight interfaces and layers with similar thickness, as shown in Fig. 1.

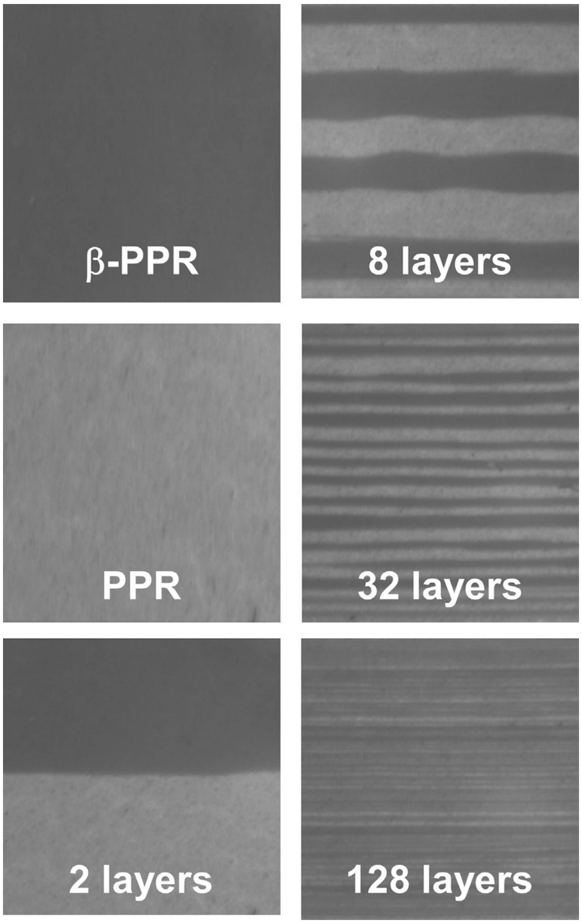

Fig. 1. Optical micrographs of the PPR/β-PPR multilayers produced.

A METTLER Toledo differential scanning calorimeter with nitrogen as purge gas was used to investigate the effect of the layer structure on the crystallization behavior. The samples (about 15 mg) were prepared by cutting the extruded plates along the entire cross-section. In addition, PPR and β-PPR granules were hot-pressed at 180°C for 1 min to produce 1 mm thick platelets. The specimens were heated to 235°C at a rate of 10°C/min and then cooled to −5°C at a rate of 10 °C/min. The samples were kept at −5° for 5 min to destroy anisotropy. The melting peaks were obtained after heating the samples again to 235°C at a rate of 10°C/min. Both thermal and crystallization parameters were obtained from the heating and cooling scans. T_m was considered to be the maximum of the endothermic melting peak from the second heating scans, and T_c that of the exothermic peak of the crystallization from the cooling scans. The heat of fusion (ΔH_f) and crystallization heats (ΔH_c) were determined from the areas of melting peaks and crystallization peaks.

The mechanical properties of the multilayer PPR/β-PPR samples were also examined. The extruded plates were subsequently cut into Charpy impact specimens with dimensions 80 mm × 10 mm × 4 mm. For tensile testing, “shouldered” test bars (dumbbell shaped) with a total length of 180 mm were used. All specimens were prepared using an automatic, microprocessor-controlled CNC specimen milling machine (Karg Industrietechnik, Germany). The centrally located notch tip was 2 mm from the struck