Abstract

While chemically similar, it has long been known that polyethylene (PE) and polypropylene (PP) are immiscible and suffer poor interfacial adhesion when processed as layered films or blends. In this paper we present an examination of the effect that processing conditions, such as extrusion residence time and post-extrusion take-up, have on the interfacial adhesion between PE and PP.

Introduction

Owing to their diverse range of applications, commodity polyolefins, such as polyethylene (PE) and polypropylene (PP), account for a significant share of the plastics market worldwide [1]. In 2014, PE alone captured 35% of the US market share [2]. Polyolefins have found use in markets ranging from food packaging to medical devices, with a range of synthetic schemes and processing methods to tailor their properties to their targeted applications [1]. Although PE and PP are chemically similar, it is well-known that these two polymers are also immiscible [3, 4]. Three major avenues currently exist to improve interfacial adhesion between immiscible PE and PP, including: catalyst selection, incorporation of compatibilizers, and varying process parameters [5-7].

In 2000, Chaffin et al. demonstrated ~20-fold increase in PP/PE interfacial adhesion when they replaced Ziegler-Natta polymers with metallocene catalyzed PP and PE. This increase was attributed to the elimination of low-molecular weight oligomers at the PP/PE interface that resulted from a narrower molecular weight distribution [5]. Chaffin et al. also demonstrated in subsequent work that the inclusion of an ethylene-propylene copolymer (EPC) to act as a compatibilizer provided anchored interfacial entanglements to further improve PP/PE adhesion. This compatibilization effect resulted in an increase in tensile properties at low temperature [6]. This concept of compatibilization can be extended to reactive interfaces, where chemical bonds are formed across the interface of immiscible polymers via functional moieties included in the polymer backbone [8]. Song et al. investigated the role of processing parameters, such as take-up speed, on the interfacial adhesion between Ziegler-Natta catalyzed PP and PE and showed that faster take-up speeds improved interfacial adhesion ~5-fold [7]. The focus of this work is to utilize computational simulations to understand the role of interfacial crystallization resulting from coextrusion of a metallocene PP/PE bilayer film.

Experimental

Bilayers of metallocene catalyzed PP (mPP, MFI 25, 0.905 g cm$^{-3}$, $T_m = 154 \, ^\circ C$) and metallocene catalyzed PE (mPE, MI 4, 0.94 g cm$^{-3}$, $T_m = 133 \, ^\circ C$) were fabricated at 180 °C using three different techniques. First, mPP/mPE laminates were formed by melt pressing individual sheets of mPP and mPE at 180 °C and 1.1 MPa for 300 sec. The individual films were rinsed with CHCl$_3$ (Sigma Aldrich) to remove residue from the Teflon sheets used during compression molding. The films were then laminated at 180 °C and 1.1 MPa for 45 sec before ambient cooling as shown in Figure 1.

Second, a series of bilayers were fabricated utilizing a novel small-scale coextrusion adapter on a capillary rheometer, shown schematically in Figure 2 [9]. By varying the rheometer piston speed, the melt contact time of mPP/mPE bilayers was varied between 2.8 sec and 630 sec at 180 °C during capillary coextrusion before ambient cooling, allowing us to probe the role of melt contact time on interfacial crystallization.

Finally, a series of mPP/mPE bilayers was fabricated using a lab-scale continuous coextrusion process at 180 °C similar to the equipment described by Song et al. and
shown in Figure 3 [7, 8]. The overall volumetric flow was kept constant at ~32 cm$^3$ min$^{-1}$, resulting in approximately uniform melt contact times of ~45 sec. The left extruder in Figure 3b is a single screw extruder, which melted and conveyed molten mPE to the corresponding gear pump. The right extruder in Figure 3b was a twin screw extruder which melted and conveyed mPP to the corresponding gear pump. Varying the revolution speed of each gear pump allowed us to vary the volumetric ratio of mPP/mPE in the bilayer films ranging from 50/50 to 15/85. The molten bilayer stream was then passed through an exit die before being quenched on symmetric chilled nip rollers. This enabled us to probe the effect of shear stress in the exit die during coextrusion and also the role of interfacial crystallization time during take-up on the nip rollers. For all three fabrication methods, overall bilayer film thickness was kept constant at ~0.8 mm.

**Results & Discussion**

The individual heat capacity profiles and crystallization temperature range of mPP and mPE were determined using differential scanning calorimetry at a cooling rate of 10 °C min$^{-1}$. The cooling profiles of each bilayer system were modelled using a non-linear transient thermal analysis in ANSYS 17.0 software. Using ambient convective heat transfer in air for the laminates and all the capillary coextruded samples, the crystallization time was ~5 sec. However, the interfacial crystallization time of the lab-scale coextrusion technique employing chilled nip rollers was determined to be highly dependent upon the offset volume composition. In the case of the 50/50 volume composition films, interfacial crystallization occurred in ~4.4 sec. This crystallization time was comparable to the bilayer films cooled under ambient conditions from the lamination technique and capillary coextrusion technique. As the mPP/mPE interface migrated to the edge of the bilayer film by shifting volume composition, interfacial crystallization time decreased significantly.

T-peel tests were conducted using a uniaxial tensile film fixture on an RSA rheometer (TA Instruments) as shown in Figure 4. The peeling rate was set to 5 mm min$^{-1}$ and samples were cut to an average width of 15 mm. Peel force was taken as the force plateau over 30 mm of each of 5 individual T-peel samples.

To examine the effect of processing technique, the laminated mPP/mPE films, capillary coextruded mPP/mPE films (with melt contact time ~41 sec) and 50/50 lab-scale coextruded mPP/mPE films were compared. These samples were chosen for their similarity in melt contact time and interfacial crystallization time. No significant difference in interfacial adhesion was found comparing these three techniques, as shown in Figure 4. An especially gratifying result showed no statistical difference between capillary coextrusion, which required less than 10 g material, and lab-scale coextrusion, validating use of this technique when limited quantities of materials are available.

Use of the twin bore capillary coextrusion technique allowed us to probe the effect of melt contact time over the range 2.8 sec to 630 sec, which was not possible with the
lab-scale multilayer coextrusion technique. As melt contact time increased to 630 sec, an observed increase in adhesion between mPP and mPE of ~2.2-fold was observed, when compared with samples having melt contact times less than 41 sec. Probing the effect of interfacial crystallization time, revealed a substantial increase of ~6-fold in adhesion between mPE and mPP layers as interfacial crystallization time decreased.

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Figure 4. T-peel test adhesion strength measurements of mPP/mPE bilayers prepared via lamination, capillary coextrusion, and lab-scale coextrusion.

Conclusions

In conclusion, these results highlight the interplay between processing parameters such as melt contact time and interfacial cooling in determining interfacial adhesive strength of immiscible polyolefin bilayers. These results can be extended to investigate the role of polymer processing on the properties of immiscible polyolefin blends without expensive block copolymer compatibilizers.

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References