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Sub-micrometer polyamide droplets dispersed in polyethylene: Dimensional stability above the melting point of polyethylene

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Abstract

Metallocene-catalyst polymerized ethylene-1-octene copolymers in which a polyamide 6 (PA6) is finely dispersed by means of a MA-grafted-polyethylene as compatibilizer show a non-conventional mechanical behavior at high temperatures. Once the ethylene-1-octene copolymer is melted the system still shows good mechanical properties and dimensional stability. Besides, due to the dispersed phase morphology of the system, so-called fractionated/homogeneous crystallization takes place (extra supercooling of around 50 °C compared to the bulk PA6 crystallization temperature) and the material can be processed in the same temperature range in which it later on will show good mechanical response. The explanation of this intriguing mechanical behavior is sought in the molecular architecture of the system and turns out to be related to the slower flow dynamics of the matrix chains in case of high enough molar mass. The slower dynamics is caused by an increase in entanglement density due to mixing/interactions between matrix chains and compatibilizer chains chemically attached to the droplets. The droplets thereby function as physical crosslinks.

Keywords: Ethylene-1-octene copolymers; Polyamide; Mechanical properties

1. Introduction

Polymer blending is a convenient way for obtaining new materials whose properties are better than just a simple superposition of those of the individual components. Because it is also cheaper and less time-consuming the method is more efficient than synthesis of new monomers or inventing new polymerization strategies. Miscible polymer blends are the exception rather than the rule and most polymeric blends are immiscible due to the positive values of the mixing Gibbs free energy. In many incompatible blends one of the components is dispersed as minor phase into the other that acts as matrix. As the adhesion between the two phases is crucial for the application envisaged, in most cases the system must be somehow compatibilized.

This work investigates the system obtained by dispersing a polyamide 6 (PA6), by means of a polyethylene-grafted-maleic anhydride (PE-*g*-MA) as compatibilizer in an ethylene-1-octene copolymer matrix. The special morphology of the system makes it interesting both from a fundamental and an applied perspective. From the fundamental point of view the system shows two outstanding characteristics, on the one hand the very fine dispersion of the PA6 droplets makes the system appropriate for studying the phenomenon of fractionated/homogeneous crystallization. On the other hand, the system shows a peculiar mechanical behavior at high temperatures: once the matrix has melted the sample still shows good mechanical properties [1]. This paper concerns mainly the last issue. It is precisely this intriguing mechanical phenomenon what makes the system attractive from the application point of view because it allows extending the use of ethylene-1-octene copolymers for applications where dimensional stability is required above their melting point. Moreover, due to the fractionated/homogeneous crystallization phenomenon the material can be processed at lower temperatures, in the same range in which it later on will show good mechanical properties.

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The mechanical behavior of polyethylene/PA6 incompatible blends has been extensively studied in the literature. Kudva et al. investigated blends in a broad range of compositions including the effect of the incorporation of PE-*g*-MA [2]. However, these authors focused on the improvement of the impact strength at moderate temperatures (below 80 °C). Impact strength and mechanical properties at room temperature have also been studied for this type of blend using different compatibilizers [3–12]. Minkova et al. studied blends of LDPE and PA6 with two types of functionalised polyethylene as compatibilizer, but focused on PA6 as the co-continuous phase and on the effect on microhardness at room temperature [13]. Bai et al. studied PP/PA6 blends employing PE-*g*-MA as compatibilizer. For PA6 contents from 0 to 40%, a dispersed phase morphology consisting of PA6 droplets was obtained. However, the mechanical properties were only studied below the melting temperature of the matrix [14]. Okada et al. studied the mechanical properties of blends of maleated ethylene–propylene rubber and PA6 at room temperature [15,16]. Tedesco et al. studied the system PP/PP-*g*-MA/PA6 in the ratio 63/7/30 (very close to the composition of our blends, see the Section 2) but they too did not consider the mechanical properties above the melting temperature of the matrix [17].

Many more references [18–26] describe the blending of PA with hydrocarbon elastomers and the effect of compatibilization through grafting of maleic anhydride on the polyethylene phase. However, the peculiar mechanical behavior of our system has not been previously reported for a blend with dispersed phase morphology.

In this work, we have dispersed the same percentage of PA6 in two ethylene-1-octene copolymers of different viscosities, i.e. different molar masses, using the same percentage of PE-*g*-MA as compatibilizer in each case. The two main goals of this paper are (i) to show and characterize for the first time a system with a dispersed droplet morphology that is able to keep good mechanical properties (modulus high enough as to maintain dimensional stability) above the melting point of the matrix, (ii) to explain the possible molecular origin of this phenomenon.

2. Experimental

2.1. Materials

The main characteristics of the polymers used in this work are listed in Table 1. Ethylene-1-octene copolymers (Exact® Plastomers 8201, 8210) with different melt flow index (MFI) were supplied by DEX-PLASTOMERS. These commercial available copolymers are homogeneous ones: the way the comonomer is incorporated during polymerization can be described by one single set of chain propagation probabilities of comonomer incorporation in the chain (P-set) per copolymer or, alternatively, by the combination of a single set of reactivity ratios (r-set) for all copolymers and a single monomer/comonomer ratio for each copolymer. Statistically there are no differences within and between the molecules (see [27] and references therein).

Table 1
Molecular characteristics of the materials

Material	MFI (dg/min)[a]	M_w (kg/mol)	$D^{23\ ^\circ\mathrm{C}}$ (kg/m^3)
Exact 8201	1	115	882
Exact 8210	10	72	882
PE-*g*-MA	–	65	–
PA6	–	24	–

Note. MMD for Exact grades calculated using universal calibration. MMD figures for PE-*g*-MA calculated using conventional calibration.

[a] Melt flow index 230 °C/5 kg.

Polyamide 6 (PA Akulon K123) was provided by DSM Engineering Plastics. Polyethylene grafted maleic anhydride (PE-*g*-MA) used as compatibilizer (Fusabond® N MO525D) was supplied by DuPont.

2.2. Blends preparation

Two different blends were prepared, keeping the same matrix/dispersed phase/compatibilizer ratio (62.5/30/7.5), while the characteristics of the matrix were changed. The matrix was in each case an ethylene-1-octene copolymer (Exact® 8201, 8210) with a different melt flow index, MFI, indicated by the two last numbers in the name (Table 1). Polyamide 6 was used as the dispersed phase. The compatibilizer agent was PE-*g*-MA. Blends were prepared on a Haake 60 cc batch mixer under polyamide 6 normal processing conditions. Before processing all materials were dried overnight at 80 °C under vacuum with a nitrogen flow leak. All blends were mixed at 240 °C at a screw speed of 80 rpm. During melt blending the mixing chamber was kept saturated with N_2 gas to avoid oxidative degradation.

The blends studied in this work using as matrix the above mentioned ethylene-1-octene copolymers 8201 and 8210 will be called B1 and B2, respectively.

2.3. Dissolution experiments

The morphology of the blends was analyzed by means of dissolution experiments to determine whether the extruded blends displayed a droplet/matrix or a co-continuous phase morphology. Small pieces of the samples were immersed in toluene (at 50 °C) and formic acid (at room temperature) under stirring conditions for several days. Formic acid is a solvent for PA6 and a non-solvent for the ethylene-1-octene copolymer. Toluene is a solvent for ethylene-1-octene copolymers and a non-solvent for PA6.

2.4. Transmission electron microscopy (TEM) and image analysis

TEM micrographs were made on a Philips CM10, operating at 80 kV. Sections of 100 nm were prepared with a diamond knife (Drukker, International) on a Leica Ultracut UCT microtome, equipped with a Leica EM FCS cryo unit. The temperature of the sample and knife was set to be −80 and −60 °C, respectively. The microtomed sections were collected