



Mechanical properties and stress-induced polymorphic transformations of blends of random isotactic propylene-1-hexene copolymers



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ABSTRACT

The mechanical properties of binary blends of propylene-1-hexene random copolymers (with 11 and 21 mol% 1-hexene) are studied in parallel with polymorphic transformations under uniaxial tensile deformation. The modulus, yield stress, and draw ratio of the pure PH copolymers decrease with increasing 1-hexene content, while for the blends the change of mechanical properties with composition is highly non-linear. The addition of just 10 wt % PH11 to PH21 doubles the elastic modulus and yield strength of the blends in reference to the value of PH21, reaching for all blends values close to the performance of pure PH11. The elongation at break and the ultimate tensile strength increase more gradually with content of PH11. On tensile deformation, pure components and blends undergo morphological and polymorphic transformations, such as a reversible lamellar to fibrillar transformation of trigonal PH21, or an irreversible α crystal to mesophase in pure PH11 and the blends. In blends and neat PH11, a fibrillar trigonal morphology that develops under deformation is stabilized by the transformation of α to mesophase, and remains after removing the load, explaining the lower elastic recovery of the blends compared to PH21. The formation of stress-induced trigonal crystallites in PH11 and blends after strains >150% is explained as a decrease of the free energy barrier for nucleation of a phase that requires short iPP sequences.

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1. Introduction

Incorporation of stereo defects and low molecular weight α -olefins such as ethylene and 1-butene in the chain of isotactic polypropylene (iPP) using metallocene catalysts has been effectively utilized to change the mechanical properties of iPP from a rigid thermoplastic to elasto-plastomeric and to elastomeric behavior [1–10]. Adding defects or a comonomer to the iPP macromolecule decreases the crystallizable sequence length in the chain, and hence the degree of crystallinity decreases. The iPP polymorphic behavior also changes with type and defect content as amply studied in the last two decades [11–24]. Conversely, blending different types of iPPs, iPP with iPP-based copolymers, or blending different iPP-based copolymers is also an avenue for engineering mechanical properties. Compared to the synthetic approach, iPP blends are often a cost-effective path to change the

material properties. Blends of propylene-ethylene (PE) and propylene-1-butene (PB) copolymers have been studied extensively, and some of these blends are produced commercially for packaging applications [25,26]. However, the mechanical behavior of blends of iPP copolymers based on higher α -olefin comonomers such as 1-hexene and 1-octene is less known [27,28].

Recently, we reported a study of melt miscibility, crystallization kinetics and polymorphic behavior of binary blends of isotactic propylene and 1-hexene random copolymers with 11 (PH11) and 21 (PH21) mol% 1-hexene [29,30]. Blends of iPP and PH11, and blends of PH11 and PH21 are miscible in the melt, while blends of iPP and PH21 are immiscible. Furthermore, a detailed study of the crystallization kinetics of blends of PH11 and PH21 revealed that the blends form two populations of crystallites. The PH11 component crystallizes in a first stage in the monoclinic phase with the 1-hexene co-units rejected from the crystallites. PH21 crystallizes in a second stage in trigonal crystallites with the 1-hexene count participating in the trigonal unit cell. Due to the rejection of the 1-hexene count in the first crystallization stage, the crystallization kinetics of trigonal crystals in the blends increase in reference to

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the crystallization kinetics of pure PH21 [30]. In the present work, we expand these studies to investigating the mechanical properties of blends of these two PH copolymers which as individual constituents form different crystallographic phases, monoclinic (α) for PH11 and trigonal (δ) in PH21.

The mechanical properties of neat PH copolymers have been studied as a function of content of 1-hexene up to ~26 mol% [19,31–33]. With increasing content of 1-hexene, the level of crystallinity decreases, accordingly, the modulus and yield stress decrease while tensile elongation increases, the necking region becomes more diffuse [32], and the impact strength is significantly improved [33]. It was also observed that the yield stress decreases logarithmically with 1-hexene for PH with <10 mol% 1-hexene [19], a behavior also observed in propylene 1-octene copolymers (PO) [19]. Even at low contents of 1-hexene (~1 mol%), PH copolymers are thermoplastic materials with high flexibility [32]. In the range of 15–30 mol%, PH copolymers crystallize in the trigonal phase which changes significantly their mechanical properties; the strain hardening and tensile strength decrease compared to copolymers with lower comonomer content [32]. Due to the formation of trigonal crystals, in PH copolymers with >13 mol% 1-hexene, the yield stress is higher than for PO copolymers with matched comonomer content [19].

De Rosa et al. carried out a parallel study of the tensile behavior and strain-induced polymorphic transformations of PH copolymers under uniaxial deformation [32]. For copolymers with 1-hexene content <9 mol%, a transformation of α to mesophase was observed at relatively low elongations (100–200%). They explained that mechanical melting of the original α crystals was followed by reorganization of the chains that are pulled out of the lamellae during mechanical melting into mesomorphic longitudinally oriented bundles with low lateral order [32]. Copolymers with 1-hexene > 9 mol% behave differently, the characteristic reflections of the α phase disappear during deformation and reflections of the trigonal phase appear in addition to reflections associated with the mesophase. It was then concluded that the initial α phase crystals transform partly into trigonal and partly into mesophase for these copolymers [32]. No polymorphic transformation during deformation was observed for PH copolymers with 1-hexene content higher than 18 mol% which originally crystallize in the trigonal phase [32].

Unlike monoclinic crystallites, PH trigonal crystallites orient but do not transform to the mesophase under elongation, therefore, it was concluded that the trigonal phase was more stable under deformation [31]. On this basis, the formation of trigonal crystallites in PH11/PH21 blends, even at low levels of PH21 should influence their mechanical properties. Trigonal crystals that develop between the lamellae of monoclinic crystallites in the blends are expected to reinforce the mechanical strength making the materials more resilient to deformation. This behavior is tested in the present work by analyzing the mechanical properties under tensile deformation of PH11/PH21 blends, and collecting parallel 2D WAXD patterns to follow possible crystal transformations in the whole range of blend composition.

2. Experimental section

2.1. Materials

The isotactic propylene 1-hexene random copolymers used, PH11 and PH21, are experimental samples synthesized by Exxon-Mobil using a single-site metallocene catalyst. The copolymers have 11 and 21 mol% 1-hexene, a $M_w = 160 \text{ K} \pm 5 \text{ K g/mol}$ and $PDI = 2.03$ as described in prior works [14,29]. Blends of PH11/PH21 were prepared in solution dissolving weighed proportional masses of

each component in xylene at $125 \pm 1 \text{ }^\circ\text{C}$ in a concentration of 0.5 g blend/100 ml solvent and stirred for 15 min. The solution was further poured in methanol at $-10 \text{ }^\circ\text{C}$. The crystals were filtered, washed with methanol and dried overnight at $60 \text{ }^\circ\text{C}$ in vacuum until constant mass. The pure components were also subjected to the same solvent procedure. Blends are labeled by B followed by mass percent of PH11/mass percent of PH21. For example, B25/75 is the blend with 25% by mass of PH11 and 75% PH21. Films, ~250 μm thick, of each blend were prepared by melt compression molding at $200 \text{ }^\circ\text{C}$ and quenched to room temperature ($23 \pm 1 \text{ }^\circ\text{C}$). The films were kept at room temperature for at least two weeks prior to any testing.

2.2. Stress-strain measurements

Dumbbell shape samples were cut from the original films with a neck width of 2 mm, gauge length of 5.5 mm and thickness of 0.25 mm. Stress-strain curves were obtained at a drawing rate of 25 mm/min using a Thümler tensile test machine model TH 2730. Two bench marks were drawn in the neck region to follow the elongation. The engineering strain (ϵ) was obtained as $\epsilon = (l - l_0)/l_0$ with l_0 as the initial marked gauge length and l the distance between marks during deformation. The engineering stress (σ) is the force per initial cross sectional area. The elastic modulus (E) was obtained from the slope of the linear region at low deformation. The yield stress, σ_y , is taken at the point where $d\sigma/d\epsilon \approx 0$ after the region of linear deformation. The tensile strength, σ_b , and elongation at break, ϵ_b , were obtained from the values of stress and strain at breaking point. The intensity of strain-hardening was characterized by the slope of the stress-strain region at high elongations, those close to break, and by the difference between tensile and yield strengths, $\sigma_b - \sigma_y$. The recovered strain after break, r_b , was also recorded as it is a measure of the elastomeric behavior of pure components and blends. r_b was measured about two weeks after break as, $(l_b - l_f)/l_b$ where l_b is the length of the specimen at break and l_f the length after break. All reported values are averages over five independent stress-strain experiments for each sample.

2.3. Polymorphic transformations under tensile deformation

To study changes in crystal structure under deformation, a house-made stretching device was built to be able to deform the copolymers and blends inside the sample compartment of the Bruker Nanostar diffractometer. The dumbbell-shaped sample was stretched to a specific strain and WAXD and SAXS collected simultaneously while under tension. In order to reduce the effect of air scattering, vacuum of ~3 mbar was applied to the sample compartment. After collecting the patterns, the vacuum was released and the WAXD plate (Fuji Film image plate) was scanned using a Fuji FLA-7000 scanner to obtain the 2D WAXD pattern. The sample was stretched then to a higher strain and this procedure continued up to the breaking strain of the sample.

2.4. DSC melting

The melting of non-stretched samples, aged two weeks at room temperature was obtained using a TA DSC Q2000 instrument connected to an intercooler. The instrument operates under dry nitrogen and was calibrated for temperature and heat flow with indium. The aged samples were heated from -50 to $200 \text{ }^\circ\text{C}$ at the rate of $10 \text{ }^\circ\text{C/min}$. Melting was also obtained for stretched samples after breaking in order to study thermal stability of stress-induced crystallites. For the latter, the fibrous region close to the breaking point was encapsulated to record melting also at a heating rate of $10 \text{ }^\circ\text{C/min}$.

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