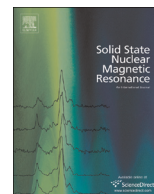




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Solid State Nuclear Magnetic Resonance

journal homepage: www.elsevier.com/locate/ssnmrSolid-state ^{13}C NMR and synchrotron SAXS/WAXS studies of uniaxially-oriented polyethyleneMobae Afeworki^{a,*}, Pat Brant^b, Arnold Lustiger^a, Alexander Norman^b^a Corporate Strategic Research, ExxonMobil Research and Engineering Company, Clinton, NJ 08801, USA^b ExxonMobil Chemical Co., Baytown Technology and Engineering Complex, Baytown, TX 77520, USA

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ABSTRACT

We report solid-state ^{13}C NMR and synchrotron wide- and small-angle X-ray scattering experiments (WAXS, SAXS) on metallocene linear low density polyethylene films (e.g., Exceed™ 1018 mLLDPE; nominally 1 MI, 0.918 density ethylene-hexene metallocene copolymer) as a function of uniaxial draw ratio, λ . Combined, these experiments provide an unambiguous, quantitative molecular view of the orientation of both the crystalline and amorphous phases in the samples as a function of draw. Together with previously reported differential scanning calorimetry (DSC), gas transport measurements, transmission electron microscopy (TEM), optical birefringence, small angle X-ray scattering (SAXS) as well as other characterization techniques, this study of the state of orientation in both phases provides insight concerning the development of unusually high barrier properties of the most oriented samples ($\lambda=10$). In this work, static (non-spinning) solid-state NMR measurements indicate that in the drawn Exceed™ films both the crystalline and amorphous regions are highly oriented. In particular, chemical shift data show the amorphous phase is comprised increasingly of so-called “taut tie chains” (or tie chains under any state of tautness) in the mLLDPE with increasing draw ratio – the resonance lines associated with the amorphous phase shift to where the crystalline peaks are observed. In the sample with highest total draw ($\lambda=10$), virtually all of the chains in the non-crystalline region have responded and aligned in the machine (draw) direction. Both monoclinic and orthorhombic crystalline peaks are observed in high-resolution, solid-state magic-angle spinning (MAS) NMR measurements of the oriented PE films. The orientation is comparable to that obtained for ultra-high molecular weight HDPE fibers described as “ultra-oriented” in the literature. Furthermore, the presence of a monoclinic peak in cold-drawn samples suggests that there is an appreciable internal stress associated with the LLDPE. The results are confirmed and independently quantified by Herman’s Orientation Function values derived from the WAXS measurements. The degree of orientation approaches theoretically perfect alignment of chains along the draw direction. We deduce from this observation that a high fraction of the non-crystalline chains are either tie chains that directly connect adjacent lamellae or are interlocking loops from adjacent lamellae. In either case, the chains are load-bearing and are consistent with the idea of “taut tie chains”. We note that transmission electron micrographs recorded for the ultra-oriented Exceed showed the lamellae are often appreciably thinner and shorter than they are for cast or blown Exceed 1018. Combined with higher crystallinity, the thinner lamellae statistically favor more tie chains. Finally, the remarkably large decrease in permeability of the $\lambda=10$ film is primarily attributed to the high degree of orientation (and loss of entropy) of the amorphous phase.

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1. Introduction

We have previously examined the properties of uniaxially-oriented cast films made from a metallocene Linear Low Density Polyethylene (mLLDPE; 1 MI, 0.918 g/cc) × [1]. The films were drawn in the machine direction in two sequential carefully controlled steps from an essentially isotropic cast sheet (as shown by

very low birefringence) to form ultra-oriented films. Films drawn once to $5\times$ are moderately oriented (optical birefringence) and display block-shear type chevron morphology. During the second draw ($1.95\text{--}2\times$) of the already $5\times$ drawn film for a total draw of $\sim 10\times$, the films whiten (become translucent), and display a fine crystalline morphology. The whitening is due to trapped voids formed in the film. These ultraoriented films exhibit a sharp drop in their permeability [2]. The transport behavior (coefficients of permeability, diffusion, and solubility; P, D, and S, respectively) of the films to various gases (H_2 , He, CH_4 , N_2 , O_2 , CO_2) was studied, and the

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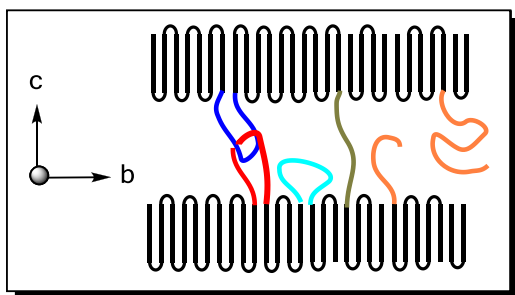


Fig. 1. Schematic of types of chains found in semi-crystalline PE. Schematic of types of chains found in semicrystalline polymers: looped or knotted tie chains, interlamellar tie chains, loops, dangling chains.

sharp decreases in P, D, and S with increasing orientation were attributed, in part, to an increase in the degree of crystallinity and increase in tortuosity due to the blocky crystalline morphology. It was proposed that the decreases in P, D, and S are also due to an unspecified increase in the amorphous phase density.

To better understand and quantify the relative contribution of the amorphous phase to the enhanced barrier properties of the oriented and ultra-oriented films, we have undertaken solid-state NMR and detailed X-ray orientation measurements of the films. Both methods enable simultaneous interrogation of the crystalline and amorphous regions of the films. In particular, solid-state NMR offers the unique opportunity to examine quantitatively the chemical state of both the crystalline and amorphous region as a function of draw ratio.

In general, the amorphous region is comprised of dangling chains, loops, bridges (tie chains), and untethered chains as illustrated in Fig. 1. Loops can be topologically constrained to produce pseudo-tie chains. Under our drawing conditions, the fraction of amorphous chains that is anchored to adjacent crystals, either through direct inter-chain trajectory or through entangled loops, should also become highly oriented. Such chains have been denoted as “taut tie chains” [3,4] and have been associated with highly drawn fibers of ultra-high molecular weight (UHMW) HDPE. In the current work we describe solid-state NMR and X-ray scattering experiments designed to better quantify especially the chemical state of the amorphous region as a function of orientation.

Prior to draw the structure of the original polymer is roughly isotropic, as are its mechanical properties. Uniaxially-drawn polymers exhibit properties that are a direct function of the drawing. Properties such as the permeability, diffusion coefficient, tensile strength, stiffness, and crystallinity are affected by drawing. Although the morphology of the isotropic state has been studied extensively, the structure of the polymer in the drawn state remains in large part a mystery. Indeed, the very mechanism of how the isotropic polymer transforms into the oriented fibril morphology has been a source of great controversy over the last 50 years [5,6].

Several analytical techniques, including solid-state NMR, have been used to characterize the orientation of polymers. Solid-state NMR powder line shapes for a non-axially symmetric and axially symmetric (where $\sigma_{11} = \sigma_{22} = \sigma_{\parallel}$; $\sigma_{33} = \sigma_{\perp}$) chemical shift interactions with the principal tensor components, σ_{11} , σ_{22} , and σ_{33} relative to the direction of the external magnetic field, \mathbf{B}_0 , and the corresponding ^{13}C chemical shifts for a linear polymeric alkane, relative to an external TMS standard have been reported by VanderHart workers [7]. VanderHart's NMR measurements showed that chain segments in the crystalline phase are not completely rigid and are termed as constrained crystalline interphase [8] by some workers. These chains are reported to have T_1 C's that are a couple of orders of magnitude shorter than the bulk crystalline

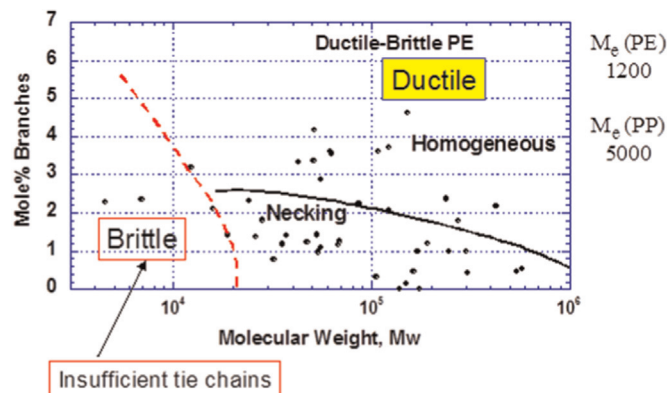


Fig. 2. Effect of incorporation of branches on polymer properties. Summary of data from Popli and Mandelkern [38] showing the effect of incorporating branching on polymer properties as a function of molecular weight.

phase T_1 C's. For instance, in a model ethylene-1-butene copolymer of molecular weight 100,000 and NMR-determined crystallinity of 41%, the ethyl branches in the crystalline region were only about a tenth of those in the amorphous region. [9] As the length of the branch is increased from ethyl to butyl to hexyl to decyl, by copolymerizing ethylene with 1-hexene, 1-octene and 1-dodecene, respectively, the incorporation of the branches in the crystalline phase is expected to decrease—likely going to zero for butyl and longer branches.

The solid-state NMR measurements focused on structure-property investigations, including measurements of amorphous, crystalline, exchanges between crystalline and amorphous regions, fibers, annealed polymers, and some included variable-temperature NMR [10–31]. Physical properties such as gas barrier and spectroscopic investigations using infra-red and Raman are also noted [32–37].

The importance of tie chains to mechanical and failure properties is captured in Fig. 2 where we plot the tensile behavior recorded by Popli and Mandelkern [38] for polyethylene as a function of molecular weight and the number of branches (defects) in the chains. The data show low tensile strength below around 10–20 kMW, depending on branch content. The brittle–ductile transition occurs at lower MW with increasing branch content because branches promote chain rejection from the crystal and, therefore, the probability of tie chain formation.

In this report we extend our study of the ultra-drawn films to solid-state NMR and we re-visit the morphology by SAXS, and WAXS. The solid state NMR experiments provide direct evidence for a change in the state of the amorphous region, perhaps reflecting the presence of so-called “taut tie chains” – that is, chains which exist in the amorphous region but are substantially in an all *trans* configuration [39–41].

Semi-crystalline polymers are described by either a two-phase (amorphous and crystalline) or a three-phase (amorphous, amorphous–crystalline interface, and crystalline) model. Polyethylene, one of the simplest polymers has one of the most complex relaxation properties and the controversy of whether PE is composed of two or three and more phases is apparently yet to be resolved in the literature [42–44]. The three-phase model is described with an interfacial region comprised of a small (few weight percent) to a substantial fraction (up to 50%, according to some researchers) of the structure. Polyethylene's relative molecular simplicity allows the study of the amorphous region to be more accessible and NMR is one of the few techniques that can probe the structure of the amorphous region independent of the crystalline region, unlike, for example, infrared dichroism, in which dichroic peaks are associated with crystalline orientation

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