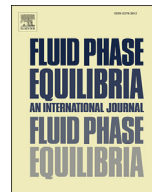




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Solubility of solvents in polyethylene below the melt temperature

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ABSTRACT

Polyethylene, the most ubiquitous polymer in use, is a semi-crystalline material. Solvents enter only the amorphous phase. The solubility in that phase, however, cannot be characterized by the amorphous solubility found above the melt temperature. The polymer chains that have ends attached to the crystalline structure but extend into the amorphous phase are referred to as tie chains, and they affect the overall solvent solubility. Six different polyethylenes covering a range of densities were studied. Below the melt temperature all the samples exhibited an increase in solubility with increasing temperature. The solubility of the penetrants, however, is not the same for different types of polyethylene. A model which incorporates an elasticity factor that accounts for the stress effects on the solubility in the tie chains was found to be valuable. When incorporated into a version of the UNIFAC free-volume model there was good correlation between of the solubilities. The present work indicates that the tie chain fraction, f , tends to increase with density.

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1. Introduction

Globally polyethylene (PE) is the most abundant polymer found in everyday life [1]. Some of the most common uses for PE included plastic bags, plastic film, bottles, and piping. Below its melting point polyethylene is a semi-crystalline polymer, i.e., some of the chains form an ordered dense crystalline phase while others are in an amorphous phase of lower density. In general, solvents are excluded from the crystalline phase [2]. To improve the ability of current models to predict the solubility in polyethylene the effect of the amount of crystallinity needs to be characterized.

The first type of polyethylene that was commercially produced was known as low-density polyethylene (LDPE) [3]. The production of this type of PE is done without the use of a catalyst. In the absence of a catalyst, the radical site can move from a location at the end of the chain to a more stable location in the middle of the chain. This causes a new ethylene monomer to polymerize at the radical site and form a branch in the middle of the PE chain. As this process continues a non-linear, highly branched PE chain is formed. In LDPE the large amount of chain branching prevents a portion of the chains from crystallizing [4]. Since the amorphous phase of PE has a much lower density than the crystalline phase, the reduction in crystallinity results in an overall product that has a lower density

than when the chains are completely linear.

Once catalysts were introduced into PE production high-density polyethylene (HDPE) was commercially produced. PE polymerization using a catalyst, such as a Zeigler-Natta or a metallocene catalyst, ensures that the radical site stays at the end of the PE chain, resulting in a final product that is a linear chain with little to no branching. These chains have a higher tendency to crystallize resulting in a high density PE [3].

Soon after the introduction of polymerization catalysts, longer α -olefins such as 1-butene, 1-hexene, and 1-octene were added to the polymerization process. This addition of a co-monomer results in a polyethylene chain that has a linear backbone with short side chains distributed along its length. As these side chains cannot be included in the crystal structure [2], they act to reduce the crystallinity of the polyethylene. The resulting linear low-density polyethylene is sometimes divided into subgroups: medium-density PE (MDPE) having a density between 0.94 and 0.926 g/cm³, linear-low-density PE (LLDPE) having a density between 0.926 and 0.915 g/cm³ and very-low-linear-density PE (VLLDPE) having a density below 0.915 g/cm³.

2. Semi-crystalline structure models

There are three common models in the literature used to describe the semi-crystalline structure of PE [5]. The first was Flory's switchboard model [6] which proposes that the majority of polyethylene chains leave the crystalline surface and cross over the

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amorphous region to a different crystalline surface rather than reenter the same crystal. The second is the adjacent reentry model of Hoffman and Lauritzen [7]. They propose two forms: a smooth surface in which almost all the chains that leave the crystalline surface immediately bend and reenter adjacent to where they exited, and a rough surface model in which the majority of chains still enter adjacent to where they exited the crystalline phase, but the fold length is not uniform. The third model was originally suggested by Stamm et al. [8] and later adapted by Strobl [9]. In either version crystallization from the melt occurs by formation of an aligned, long-range, ordered state, which then proceeds to develop into the long-range ordered crystalline phase.

In the past thirty years, numerous studies have been performed to study the effect of tie chains on the properties of semi-crystalline polymers. Most of these focus on mechanical properties [10,11]. A good review of the relationships between tie chains and mechanical properties in semi-crystalline polymers is provided by Seguela [12]. Only a few studies have focused on solvent solubility [13–16].

3. Solubility in PE

Unlike amorphous polymers, where the penetrant is evenly distributed throughout the polymer phase at equilibrium, semi-crystalline polymers, like PE, restrict the penetrant from entering the crystalline phase due to dense chain packing [2]. While the penetrant is not evenly distributed throughout the entire polymer domain, it is assumed to be evenly distributed within the amorphous domain of the polymer. Thus, when comparing the solubility between polyethylene samples with different crystallinity, the weight fraction of penetrant should be normalized in terms of the amount of penetrant in the amorphous phase of the polymer rather than on a total polymer basis. Above the melt temperature, where PE is entirely amorphous, models like the Group Contribution Lattice Fluid-Equation of State (GCLF-EoS) [17], UNIFAC-FV [18], and UNIFAC-vdw-FV [19] have been shown to accurately predict the solubility of solvents in PE [15]. Below the melt temperature application of these models to PE needs to be evaluated.

Michaels and Haussein [20] were one of the first to propose an explanation for the reduction in solubility in the amorphous phase in semi-crystalline polymers like PE. Their model, which was originally proposed in 1965, is still the most successful model. They postulated that the cause for the large temperature dependence in penetrant solubility in polyethylene is due to the tie chains. As the penetrant enters the amorphous phase these tie chains act like springs and apply an elastic force on the amorphous region which reduces the equilibrium concentration of penetrant within the amorphous phase. The most important assumptions of their derivation are:

- The amorphous phase is composed of two types of tie chains: elastically effected and inelastically effected chains. The elastically effected chains extend across the amorphous region, tethering two crystalline domains. The inelastic portion consists of chains which exit and reenter the same crystal phase, as well as chain ends and other short segments excluded from the crystal.
- The amount of tie chains is constant in the temperature range in which the polymer's crystalline structure does not change. Thus, the temperature dependent behavior of the tie chains is reversible as long as the crystalline structure does not change.
- The collective properties of the tie chains, such as length, can be accurately captured by an average of those properties.
- The deformation is uniform in all directions, i.e., isotropic.

By assuming that the force required to stretch the chains can be

approximated by Hooke's Law, the final expression lacked any terms that require the number of monomers in the tie chains, the length of the chains, or directly evaluating the Hookian spring constant. Dong and Ho [21] used Michaels and Haussein's expression for the chemical potential that the tie chains exert on the amorphous phase and converted it into an activity.

$$\ln a_1^{EL} = \frac{\left(\frac{\Delta H_f}{R}\right) \rho_a V_1 \left(\frac{1}{T} - \frac{1}{T_m}\right) - (\phi_1 - \chi \phi_1^2)}{\frac{3}{2f\phi_2} - 1} \quad (1)$$

Here the a_1^{EL} is elastic activity, ΔH_f is the heat of fusion for the semi crystalline polymer, ρ_a is the density of the amorphous phase, T_m is the melt temperature of the polymer, R is the gas constant, ϕ_i is the volume fraction of component i , χ is the Flory-Huggins interaction parameter, and f is the weight fraction of the elastically effected chains in the amorphous phase. This activity contribution was then added to the other contributions in the UNIFAC-FV model.

$$\ln a_1 = \ln a_1^C + \ln a_1^R + \ln a_1^{FV} + \ln a_1^{EL} \quad (2)$$

Here a_1^C , a_1^R , and a_1^{FV} are the combinatorial, residual, and free volume activities. The predictive methods of UNIFAC-vdw-FV, UNIFAC-FV and GCLF-EoS that have been modified by the inclusion of a_1^{EL} will be identified with the suffix MH.

The value of ΔH_f used was the experimentally determined value, 293 J/g [22]. The density of the amorphous phase was determined using an extrapolation of the amorphous density of PE above the melt via Tait's equation [23]. The value of χ was determined by both regressing the experimental data using the Flory-Huggins expression and by using the relationship between the UNIFAC residual and free volume activities as described by Dong and Ho:

$$\chi = \frac{\ln a_1^R + \ln a_1^{FV}}{\phi_2^2} \quad (3)$$

Even though the values of χ differed between the two methods, it had negligible effect on predicted activity even at the high experimental penetrant weight fractions.

4. Experimental

There were six different samples of PE on which solubility studies were performed. They were all produced with Ziegler-Natta catalyst and have crystallinities that range from 40.3 to 81.3%. One is an ethylene homopolymer (no co-monomer), three are ethylene-1-butene co-monomers, and two are ethylene-1-hexene copolymers. Table 1 provides the properties of these samples as supplied by the manufactures.

Three different methods were used to measure the solubilities: inverse gas chromatography using packed columns (PCIGC), quartz spring gravimetric, and pressure decay. Each of these methods has been described elsewhere (as referenced below) and only pertinent details will be repeated here. In the PCIGC method the solubility of granules is determined by analyzing the elution peak [24]. In the gravimetric approach the penetrant uptake is determined by measuring the extension of a calibrated quartz spring [25]. In the pressure decay method the solubility is determined by measuring the pressure drop in a constant temperature, constant volume chamber and converting that to mass by an equation of state [26,27].

The polyethylene samples in Table 1 were pressed into films by melting the samples and then slowly cooled at a rate of 10 °C/h.

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