Fluid Phase Equilibria 471 (2018) 1–7

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

A new look at the semicrystalline polymer – liquid systems: Phase diagrams low-density polyethylene – n-alkanes

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ARTICLE INFO

Article history:
Received 21 February 2018
Received in revised form
20 April 2018
Accepted 22 April 2018
Available online 24 April 2018

Keywords:
Low-density polyethylene
n-alkane
Phase diagram
Lower critical solution temperature
Liquid–liquid binodal
Solubility curve

ABSTRACT

Experimental phase diagrams for the sealed systems low-density polyethylene (LDPE) – n-decane and low-density polyethylene – n-tridecane were plotted for the first time in a wide temperature-concentration range using an original optical method and gravimetry. Liquid-liquid phase separation of LDPE and n-decane with the lower critical solution temperature of 280 °C was detected. Two branches of the solubility curve were constructed, which describe the temperature dependence of the component ratios in the semicrystalline LDPE with absorbed n-decane and in the liquid n-decane containing extracted polymer. In the domain between the solubility curve and polymer full amorphization curve the system LDPE – alkane can be identified with a single-phase microheterogeneous gel with crystallites as physical crosslinks. Below the solubility curve the system is two-phase but the true equilibrium between the phases cannot be established without destroying polymer crystallites. An empirical approach based on analyzing the parameters of the polymer full amorphization curve was applied to find that n-decane is a slightly better solvent for LDPE than n-tridecane.

1. Introduction

Polyethylene, one of the most widely used commodity plastics, is insoluble in low molecular mass (LMM) alkanes under ambient conditions. The miscibility increases with the number of carbon atoms in an alkane molecule [1] or pressure [2]. Yet, studies on the thermal behavior of polyethylene (PE) – n-alkane compositions are relatively scarce. In the literature, there are only fragments of phase diagrams for PEs of various origins with n-alkanes that indicate an existence of the liquid-liquid equilibrium with lower critical solution temperature (LCST) or upper critical solution pressure (UCSP) well above the normal boiling point of an LMM component [3–13]. In these papers, the cloud point method was used to construct binodals for the blends of PE of various molar masses and n-alkanes containing 5 to 13 carbon atoms (pentane to tridecane). The binodals are located in the composition range with the polymer concentration not exceeding 10% by mass. If the molar masses of an n-alkane and polymer get closer, their LCST increases, which means that the molecular mixture of the components can exist in a wider temperature range.

The LCST values calculated using the Shultz-Flory method [4, 5], Sanchez–Lacombe equation of state [7-10], perturbed hard-sphere-chain equation of state [10, 11], statistical association fluid theory [12], or simplified generalized Flory dimer theory [13] are in a satisfactory agreement with the experimental values for the mixtures of polyethylene with n-pentane, n-hexane, n-heptane and n-octane. A more accurate Born-Green-Yvon approach [14] allowed finding LCST values that nearly coincide with the experimental data of ref. [4] for polyethylene mixtures with C_7–C_{13} n-alkanes.

Miscibility of high-density (HDPE), low-density (LDPE), and linear low-density polyethylene (LLDPE) with octadecane at lower temperatures was investigated in ref. [15] using AFM and DSC methods. It was shown that the miscibility of paraffin with polyethylene increases in the order of HDPE < LDPE < LLDPE. After homogenizing the mixtures at 150 °C for 2 min, the DSC melting curves were recorded from the crystallization temperature (70–100 °C) up to 150 °C. The Hoffman-Weeks method was applied to evaluate the equilibrium melting temperatures of polyethylenes in the presence of different amounts of paraffin. In particular, for the LDPE-octadecane system it was found that the polymer melting

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https://doi.org/10.1016/j.fluid.2018.04.023
0378-3812/

temperature, T_m, almost linearly decreases from 113 down to 92 °C with an increase in the initial octadecane mass fraction from zero to 90%.

In the present study, we apply an original optical method and gravimetry to describe the thermal behavior of not previously investigated LDPE mixtures with n-decane and n-tridecane in a wide temperature range. We plot a liquid-liquid binodal and such important boundaries as the solubility curves, one for n-alkane in the amorphous regions of LDPE, and another for the amorphous polymer fractions in a LMM component. Finally, we discuss the constructed experimental phase diagrams in the framework of our concept [16-18] treating semicrystalline polymers as metastable microheterogeneous liquids and compare the affinity of n-decane and n-tridecane with respect to LDPE. Note that throughout the paper by LMM we mean a substance with the molar mass much lower than that of the considered polymer but not necessarily low in its absolute value.

2. Experimental

2.1. Materials

Characteristics of the low-density polyethylene (PE 15803-020, Tomskneftekhim, Russia) sample are listed in Table 1. n-Decane (98 wt% by HPLC, Vekton, Russia) with the density $\rho = 0.73$ g cm^{-3} and refractive index $n = 1.412$ (measured on a IRF-454 B2M laboratory refractometer at 20 °C), n-tridecane (98 wt% by HPLC, Vekton, Russia) with $\rho = 0.76$ g cm^{-3} and $n = 1.441$ (at 17 °C), and toluene (99%, Khimmed, Russia) with $\rho = 0.87$ g cm^{-3} and $n = 1.496$ (at 20 °C) were used as LMM liquids.

Molar mass of the polymer was determined by GPC on a Waters 150C ALC/GPC system equipped with a refractometric detector and a Styragel HT 6E 5 μm 7.8 × 300 mm column, with 1,2,4-trichlorobenzene as an eluent (130 °C, flow rate of 1 mL min^{-1}). Prior to the experiments LDPE pellets were dissolved in 1,2,4-triclorobenzene at 130 °C for 30 min to obtain the polymer concentration of 0.7 g cm^{-3}. Calibration was performed with polystyrene standards (Waters, USA, $Đ = 1.03$).

Polymer density at 25°C and melting (full amorphization) temperature were found from the kinetic experiments on hydrostatic weighing using the method of quasi-equilibrium stepwise isothermal amorphization in the immersion liquid (polydimethylsiloxane PMS-20, Penta-91, Russia) [19]. Polymer crystallinity degree was found from the X-ray scattering studies on a DRON-3 diffractometer using CuKα radiation ($\lambda = 1.5418$ Å) in the scattering range (2θ) of 12–30° at room temperature. The data processing procedure is described in ref. [20].

2.2. Methods

For constructing phase diagrams of LDPE pseudobinary mixtures with n-decane and n-tridecane we implemented two methods, a rather laborious but well-established [18, 21–25] original optical method described in detail in ref. [26] and a gravimetric method.

The optical method implies using a horizontal microscope (cathetometer) for the observation of a binary system containg a polymer pellet and LMM crystals stepwise heated in a sealed ampoule. Based on the difference in the refractive indexes of coexisting phases, it allows one to determine, with an accuracy of ±0.5°C, the temperature values at which the state of an initially two-phase system is qualitatively changed during its heating from room temperature.

For polymer-enriched compositions we visually identified two events: (1) vanishing of a LMM compound as a result of its dissolution in the opalescent polymer and (2) transformation of a solid opalescent LDPE pellet into an optically transparent liquid. For alkane-enriched systems we observed three other events: (3) formation of an optically transparent two-phase system with a distinct horizontal boundary; (4) transformation of the above two-phase system into a single-phase one as a result of spontaneous mixing; (5) demixing of the latter homogeneous system into two transparent macroscopic phases. Note that the events 3 and 4 take place at the same temperature, whereas the event 5 occurs at a higher temperature.

The vapor pressure for n-decane at the highest temperature in our experiments (290°C) is close to 1 MPa [27], which cannot significantly change the liquid phase density and hence influence temperatures of the above events fixed by the optical method. Liquid-liquid phase separation (event 5) was observed for the mixtures with the polymer mass fraction falling into the range of $0.05 < w_2 < 0.16$. A simple estimate shows that under those conditions the mass of n-decane vapor was varied from 4 to 10% of the total amount of n-decane in our sealed ampoule. Accordingly, we did not introduce any corrections to the composition of the liquid mixtures when plotting the phase diagrams.

Unlike our previous studies [18, 21–25], we did not extract noncrystalline short macromolecules from polymer pellets via prolonged high-temperature treatment in a LMM liquid under stirring. Therefore, we can expect that during stepwise heating of a pseudobinary composition from room temperature up to the temperature of the event 3, such macromolecules possessing translational mobility will diffuse out of the pellet and form a polymer solution in the LMM component. Its concentration should increase with temperature according to the previously described scenario [16] of a semicrystalline polymer amorphization resulting from the simultaneous effect of elevated temperature and swelling pressure. Thus, at the time of the event 3 we observe coexisting solutions of alkane in fully amorphous LDPE and of extracted polymer fractions in the liquid alkane.

The cathetometer was also used to estimate the melting temperatures of n-alkanes in their mixtures with LDPE. Samples in ampoules were placed for 2 h into a freezer at −35 °C for n-decane and at−10 °C for n-tridecane. This time was enough for crystallization of n-alkanes. Then the compositions were stepwise heated by 1 °C being kept at each temperature for an hour, until melting of LMM crystals.

Gravimetric method was implemented to determine the mass of macromolecules extracted from an LDPE pellet into n-decane at 40–80 °C. Polymer pellets with a sevenfold excess of n-decane

Table 1
LDPE specification. Standard uncertainties in the measurements are $u(\rho) = 0.003$ g cm^{-3} and $u(T_m) = 0.4$ °C.

M_n /g mol^{-1}	M_w /g mol^{-1}	$Đ$[a]	Melt flow index[b]/ g/10 min	ρ[c] /g cm^{-3}	T_m /°C	Crystallinity degree α /%
26,000	114,000	4.4	1.32	0.915	111.6	42.1

[a] The dispersity $Đ$ replaces the obsolete term “polydispersity index (PDI)”.
[b] Measured at 190°C under a load of 2.16 kg (DIN EN ISO 1133:2005) with the standard uncertainty of 0.05 g/10 min.
[c] Determined pycnometrically at 25°C and 1 atm (DIN EN ISO 1183–1:2013).