

# Organic solvents effect on the physical and mechanical properties of polyethylene

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## ABSTRACT

Swelling of high-density polyethylene (PE) in organic solvents, orthodichlorobenzene and orthoxylene, was investigated. The swelling kinetics of the PE specimen was described by the first-order equation. For the first time, the PE specimen swelling rate constant was shown to decrease with increasing thickness of the specimens. The equilibrium swelling of the PE specimen was evaluated. It was found that equilibrium swelling is independent of the thickness of specimens. It was shown that storage of polyethylene specimens in organic solvents changes its mechanical properties (tensile strength, Young's modulus, and elongation-at-break) due to polymer plasticization. We have shown that the increase in flexibility and elongation-at-break after relatively short-term immersion of PE samples in these organic solvents is significant. However, the tensile strength of swollen specimens remains high enough. The interaction between polymer chains and solvent molecules was not detected. The results obtained are important for the design and operation of PE coatings and PE products, such as pipes, tanks, and other accessories exposed to oil products. **Polyolefins J (2022) 9: 25-31**

**Keywords:** High-density polyethylene; organic solvents; swelling; mechanical properties; FTIR spectroscopy.

## INTRODUCTION

Polyethylene (PE) is the most common polymer which is widely used for manufacturing containers, tanks, and pipes for storage and transport of oil, oil refining products, fuels, and aggressive liquids including organic solvents [1, 2]. Studies of chemical resistance and changes in the mechanical characteristics of items under their storage in organic solvents make it possible to predict their reliability and consistency at aggressive

liquid effects. In recent years, particular attention has been drawn to the study of the effect of aggressive media on the polymer behavior. PE is known to be insoluble in any solvent at room temperature, although it may swell in certain solvents [1]. The effect of toluene/methanol mixture [3], water solution of sulfuric acid and crude oil [4], isooctane/toluene mixture [5], cycloalkanes and aromatic hydrocarbon [6], diesel and

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biodiesel fuel [7] on the PE mechanical characteristics and its swelling behavior was detected. According to Refs. [3-7], the PE swelling capacity depends on the PE structure which is determined by the method and conditions of specimen preparing. The effects of temperature and the nature of solvents on the mobility of PE macromolecules were also reported [5, 7].

Considering the presence of aromatic hydrocarbons in crude oil, oil products, and gas condensate, the organic solvents, orthodichlorobenzene  $C_6H_4Cl_2$  (ODCB) and orthoxylene  $C_8H_{10}$  (OX), were chosen to simulate the effect of liquid hydrocarbons on PE items.

The goal of this work was to investigate the PE swelling kinetics in ODCB and OX and to detect the diversity of the PE mechanical properties upon swelling.

## EXPERIMENTAL

### Materials and sample preparation

The specimens were prepared using a 276-85 commercial grade of high-density polyethylene (Stavrolene, Russia) with a  $M_w$  of 170,000 g mol<sup>-1</sup>,  $M_w/M_n = 4-5$ , 65% degree of crystallinity and a melting point of 132°C.

In this study, three types of the specimens were used:

- The films with a thickness of 32 μm were obtained by PE melt extrusion through the slit die with a Scamia laboratory extruder (France).
- The extruded cylindrical rod with a diameter of 50 mm; it was afterwards cut for discs with a thickness of 5, 10, 15, and 20 mm.
- Flat dog bone specimens with a thickness of 4 mm (according to the ASTM D638 Standard Tensile Test, specimen type I [8]) were molded in a die with an IntEllect 50-110 Smart injection molding machine (Sumitomo Shi DEMAG, Germany-Japan).

The melting point and degree of crystallinity of the specimens obtained as detected with the differential scanning calorimetry (DSC) method were 131.8 ± 0.2°C and 65 ± 2 %, respectively.

### Characterization

The mechanical properties of original and swollen PE specimens were investigated upon their extension with

a 5966 Universal testing machine (Instron, Germany). Tensile strength, Young's modulus, and elongation-at-break were evaluated from the stress-strain curves. The average values of these characteristics were calculated using, at least, five individual measurements. Data spread did not exceed 5% of the average value. The studies of mechanical properties were carried out at room temperature and at an extension rate of 500 % min<sup>-1</sup>.

To investigate swelling processes, we placed the dog bone and disc specimens into an exsiccator filled with either ODCB or OX and kept them at 60°C for 35 days. Variation in the specimen mass with time was monitored by weighting with an accuracy of 0.1 mg. The swelling degree ( $\alpha$ ) was determined as follows:

$$\alpha = \frac{m - m_0}{m_0} \times 100\% \quad (1)$$

where  $m_0$  is the initial mass of the specimen, and  $m$  is the mass of the specimen after keeping in an organic solvent.

The swelling capacity of the PE specimens was characterized by the maximum (equilibrium) swelling degree ( $\alpha_{max}$ ). After reaching  $\alpha_{max}$ , the mass of the specimen placed in a solvent did not change over time. Fourier transform infrared (FTIR) spectroscopy was used to investigate the original and swollen PE films. The FTIR spectra were recorded with an IR-21 Prestige FTIR spectrometer (Shimadzu, Japan) in transmission regime. The spectra of original PE film and PE films swollen in the organic solvents were recorded in the range from 450 to 4000 cm<sup>-1</sup>, 100 scans were averaged at a resolution of 2 cm<sup>-1</sup> and analyzed with Shimadzu software.

## RESULTS AND DISCUSSION

Immersion of PE specimens in the organic solvents, ODCB and OX, causes their limited swelling. When we tested the samples of different size and shape (the discs of different thickness and flat dog bone specimens), we concluded that the equilibrium degree of swelling does not depend on the size and shape of the specimens and the values of 15.5 and 12.4% were

achieved for ODCB and OX, respectively. This conclusion is illustrated in Figure 1 for the PE disc samples. Significant solvent sorption is due to the fact that PE, being a non-polar polymer, shows a high affinity to non-polar aromatic and aliphatic hydrocarbons [5].

As ODCB and OX are adsorbed by PE specimens, there is an increase in their volume. The change in the disc specimen diameter was monitored. The diameter of the initial samples was 50.0 mm.

The discs swollen to equilibrium in ODCB and OX had a diameter of 52.5 mm and 52.0 mm, respectively. Thus, the diameter and the height of the swollen PE samples increased by 5% and 4% when they were swollen in ODCB and OX, respectively.

The swelling kinetics curves of the PE discs exhibit a typical growth for limited swelling (Figure 1(a) and (b)). As could be seen from Figure 1(a), the specimens with thickness of 5, 10, 15, and 20 mm were swollen in ODCB to equilibrium for about 9, 23, 35, and 46 days, respectively. The same specimens were swollen in OX to equilibrium for about 7, 21, 28, and 38 days, respectively (Figure 1(b)). The results demonstrate that the swelling rate is higher for PE specimens with a smaller thickness. This is because the swelling time is proportional to the ratio of the surface area of the specimen to its volume. A faster achievement of equilibrium swelling of PE specimens in OX compared to ODCB occurs since the swelling rate is proportional to the diffusion coefficient of the solvent into the polymer [9].

To describe the swelling kinetics, we used a first-order

equation [9]:

$$V = \frac{d\alpha}{dt} = K(\alpha_{\max} - \alpha) \quad (2)$$

where  $V$  is the swelling rate,  $K$  is the swelling rate constant,  $t$  is time, and  $\alpha_{\max}$  is the equilibrium swelling degree.

At the boundary conditions ( $\alpha = 0$  at  $t = 0$  and  $\alpha = \alpha_{\max}$  at  $t = \infty$ ), the solution of Equation (2) is obtained:

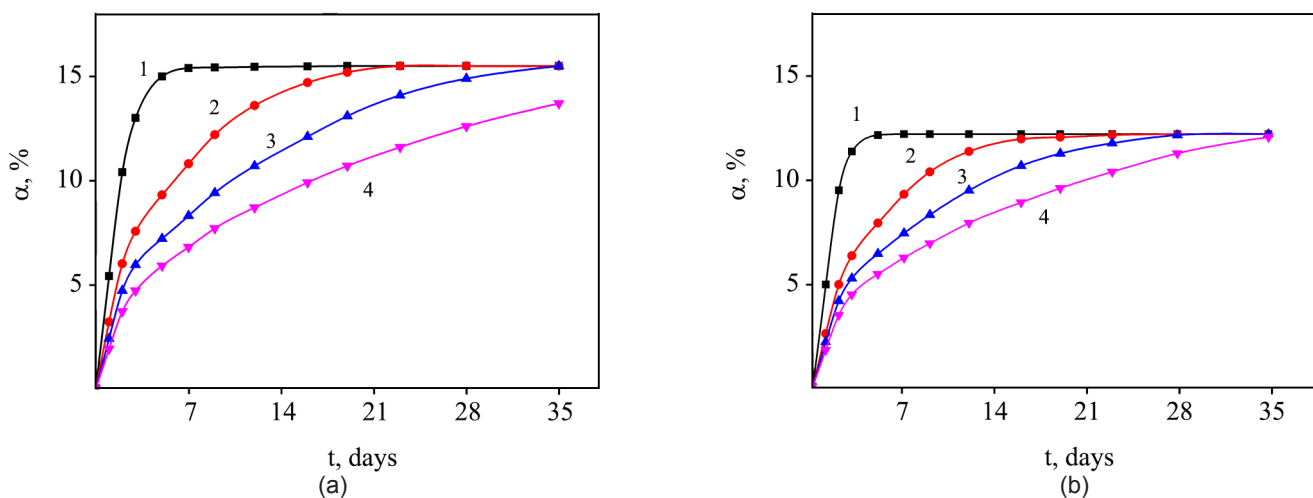
$$\alpha = \alpha_{\max} (1 - e^{-Kt}) \quad (3)$$

It follows from Equation (3) that the swelling rate constant can be calculated by the formula:

$$K = \frac{1}{t} \times \ln \frac{\alpha_{\max}}{\alpha_{\max} - \alpha} \quad (4)$$

As follows from Equation (4), the swelling rate constant  $K$  is inversely proportional to the characteristic time of swelling. Determination of the swelling rate constants derived from the swelling kinetics curves (Figure 1) is given in Figure 2(a) and 2(b). Table 1 shows the values of the kinetic constants depending on the specimen thickness. A comparison of the data presented in Table 1 shows that PE specimens swell 1.3 times faster in OX than in ODCB.

The PE swelling is, in fact, adsorption of the solvent molecules by PE specimens. Therefore, knowledge of the dimensions of solvent molecules and the PE free



**Figure 1.** Swelling kinetics curves of the PE discs with a thickness of (1) 5, (2) 10, (3) 15, and (4) 20 mm in (a) ODCB and (b) OX.

**Table 1.** Swelling rate constants (K) of PE specimens with different thicknesses (d) immersed into ODCB and OX.

Swelling media	K, day <sup>-1</sup>			
	d = 5 mm	d = 10 mm	d = 15 mm	d = 20 mm
ODCB	0.71	0.19	0.11	0.07
OX	0.95	0.23	0.15	0.09

volume holes in amorphous regions is essential for understanding molecular inclusions. The dimensions of the OX molecule have been reported to be equal to 3.834 and 7.269 Å, depending on direction [10], whereas a rough estimation of the dimensions of the ODCB molecule falls within the interval between 4 and 7 Å [11]. On the other hand, the holes volume fraction

in PE and the holes volume have been evaluated as 0.779% and 0.0902 nm<sup>3</sup>, respectively [12]. This finding allows estimating the PE hole size as ~5.6 Å. We can conclude that the dimensions of the adsorbate molecules allow their penetration into PE holes. However, for adsorption of polar molecules, the interaction between adsorbing molecules and PE molecules is a crucial factor. Thereupon, the Hildebrand solubility parameter  $\delta$  providing a numerical estimation of the degree of interaction between materials, particularly for nonpolar polymers, such as PE, should be taken into account [13, 14]. Materials with similar values of  $\delta$  are proposed to be miscible. The  $\delta$  values have been found to be 15.7, 17.8, and 20.5 (J cm<sup>-3</sup>)<sup>1/2</sup> for PE, OX, and ODCB, respectively [14], thus assuring PE swelling in the solvents used. According to the experimental results presented in Table 1, the smaller the difference in solubility parameters between the polymer and the solvent, the higher the swelling rate.

The engineering stress-strain curves were obtained for the dog bone specimens and for those swollen in organic solvents to the equilibrium (Figure 3). The values of engineering stress ( $\sigma_e$ ) are related to the cross-section of original specimens.

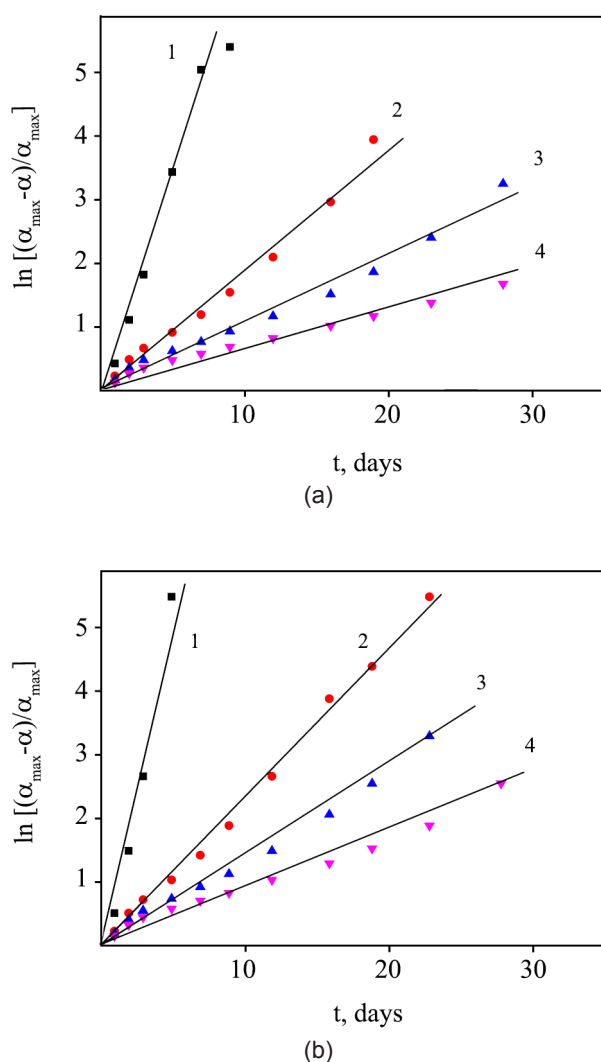
As could be seen from Figure 3(a), the elongation-at-break for the original PE specimens reaches 400 %, while the specimens swollen in ODCB and OX are characterized by deformation at failure exceeding 600% and 550%, respectively. Obviously, the cross-section area of specimens varies significantly during the extension process. To take these changes into account, the true stress values were calculated as follows [15]:

$$\sigma_{true} = \sigma_e (1 + \varepsilon) \quad (5)$$

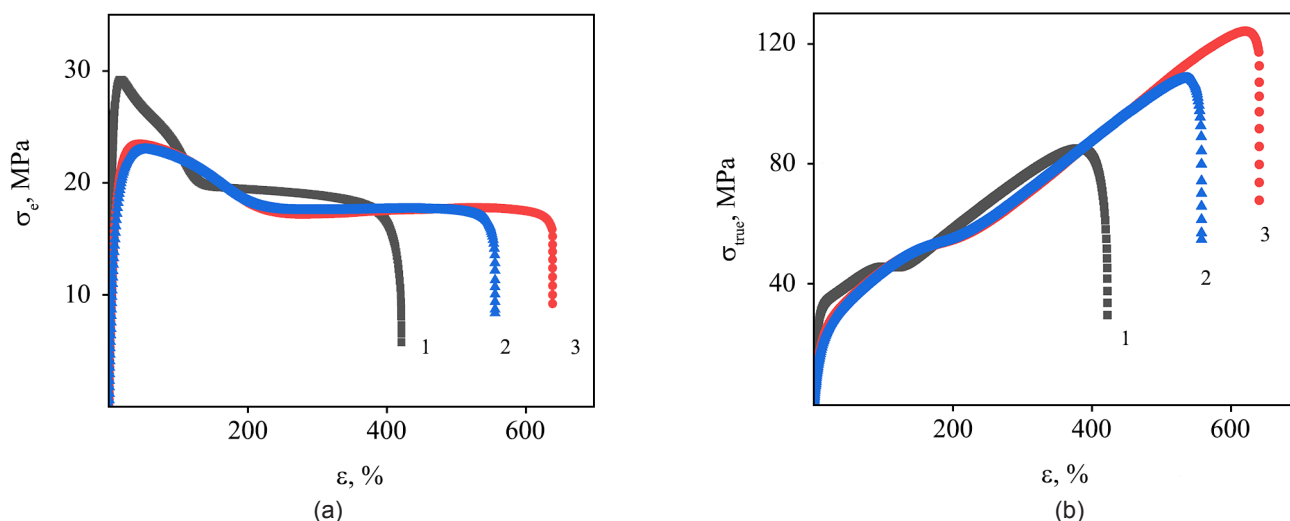
Where,  $\sigma_{true}$  is the true stress,  $\sigma_e$  is the engineering stress, and  $\varepsilon$  is the relative strain.

The true stress-strain curves (Figure 3(b)) were used to determine tensile strength, yield strength and Young's modulus. Table 2 shows the mechanical characteristics of the original PE specimens and those immersed into organic solvents for 1 day and up to their saturation. The swelling degree of the PE specimens after 1 day in ODCB and OX was 5.4 and 5.0%, respectively.

As could be seen from Table 2, the sorption of the



**Figure 2.** Graphical determination of the swelling rate constants in (a) ODCB and (b) OX for the PE discs with a thickness of (1) 5, (2) 10, (3) 15, and (4) 20 mm.



**Figure 3.** (a) Engineering and (b) true stress-strain curves at the extension of (1) initial specimens and those swollen to equilibrium in (2) ODCB and (3) OX.

organic solvents results in significant change in the PE mechanical characteristics. After one day of the PE swelling in ODCB and OX, a decrease in Young's modulus, an increase in elongation-at-break, and an increase in tensile strength of the specimens were observed. When the maximum (equilibrium) swelling degree is reached, the change in mechanical properties becomes even more pronounced. Higher strength values of the swollen samples are explained by facilitated orientation of PE macromolecules during extension. Thus, it can be proposed that the polymer is plasticized when it is immersed into organic solvents. Sorption of ODCB and OX by amorphous phase of PE improves macromolecules mobility, macromolecular segments slipping, and increases probability of coiled gauche (G)- into elongated trans (T)-isomers transition during specimens extension [4].

In order to clarify whether the PE chains interact with the solvent molecules, we studied both original and swollen PE films with FTIR spectroscopy. We chose two regions of the PE FTIR spectra: 705–735

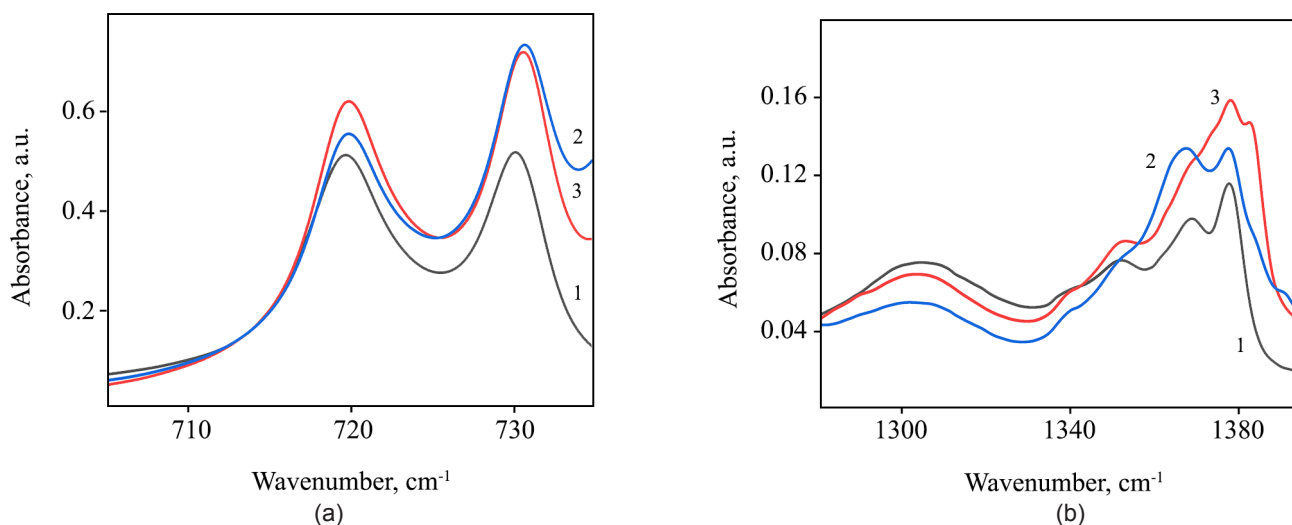
$\text{cm}^{-1}$  (Figure 4(a)) and 1280–1390  $\text{cm}^{-1}$  (Figure 4(b)), related to crystalline and amorphous regions of PE, respectively.

The bands at 720 and 730  $\text{cm}^{-1}$  correspond to the rocking vibrations of the  $\text{CH}_2$  groups in PE orthorhombic crystal lattice [16, 17]. As follows from Figure 4(a), the position of these bands after PE swelling in both ODCB and OX does not change. This means that there is no interaction between the PE chains in the crystalline regions and the solvent molecules.

In Figure 4(b), four absorbance bands at 1304, 1352, 1369, and 1378  $\text{cm}^{-1}$  could clearly be recognized. The bands with maxima at 1304, 1352, and 1369  $\text{cm}^{-1}$  correspond to the wagging vibrations of the  $\text{CH}_2$  groups in the GTG, GG, and GTG conformers of PE, whereas the band with maximum 1378  $\text{cm}^{-1}$  is associated with bending vibrations of the  $\text{CH}_3$  groups [16, 17]. Since their positions after swelling in the organic solvents do not change, we can conclude that there is no interaction between the polymer chains in the

**Table 2.** Mechanical characteristics of original and swollen PE specimens.

Specimen	Swelling degree, %	Tensile strength, MPa	Elongation-at-break, %	Young's modulus, MPa
Original	–	86	385	1051
Swollen for 1 day in:	ODCB	92	435	588
	OX	107	536	502
Swollen to equilibrium in:	ODCB	117	537	482
	OX	130	648	440



**Figure 4.** FTIR spectra at (a) 705 – 735  $\text{cm}^{-1}$  and (b) 1280 – 1390  $\text{cm}^{-1}$  of (1) original PE and PE swollen in (2) ODCB and (3) OX.

amorphous regions and the solvent molecules.

## CONCLUSION

The swelling of the PE specimens of different shape and thickness in the organic solvents, ODCB and OX, was investigated. It was shown that swelling leads to an increase in the mass and volume of specimens and a change in mechanical properties. Particularly, an increase in flexibility and elongation-at-break becomes noticeable after relatively short-term immersion into these organic solvents. The results obtained seem to be important for design and operation of PE coatings and PE products (pipes, tanks, etc.) that may have either long-term or short-term contacts with oil products.

## CONFLICT OF INTEREST

The Authors declare that there is no conflict of interest.

## SYMBOLS AND ABBREVIATIONS

DSC	differential scanning calorimetry
FTIR	Fourier transform infrared
ODCB	orthodichlorobenzene
OX	orthoxylyene
PE	polyethylene

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