

EXAMINATION OF POLYOLEFINS–ORGANIC COMPOUNDS INTERACTIONS BY INVERSE GAS CHROMATOGRAPHY

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The investigations of interactions between polyolefins and test solutes at temperatures 58–122°C were carried out in the work. The test solutes were intentionally selected as representatives of the most important groups of compounds occurring in technological oils, which may be used as additives in conditions of industrial decomposition of polyolefins in Poland. For this purpose both the Flory–Huggins theory and inverse gas chromatography (IGC) were used. On the basis of retention data the values of both interaction and solubility parameters of analyzed polymers were determined. Solubility parameter δ and interaction parameter χ are related to some heat quantities e.g. excess free energy of mixing. It was observed influence of molecular mass and existence of chain branches on the values of the parameters. The obtained values allowed determination of influence of composition change of typical technological oils on their interactions with polymers and, at the same time, on course of charge preparation in these processes.

Keywords: Flory–Huggins interaction parameter, oils, polyolefins, solubility parameter

Introduction

Processes of thermal and thermocatalytic decomposition, especially of polyolefins, gain more significance as a recycling method leading to production of valuable materials of energetic or chemical significance [1–4]. Liquid products at room temperature obtained this way with yield of ca. 90% [5–7] may then be applicable, e.g. after distillation, as crude fuel fractions. High requirements made for this kind of products still impose necessity of their parameters modification in order to satisfy imposed standards. One of the crucial inconveniences is very high non-saturated hydrocarbons content, usually ca. 40–60%. Hence, one proposes their hydrogenation [7, 8] or decomposition of polymers–solvents systems [9–12], called technological oils. The second solution, besides possibility of obtained products modification, allows mitigating conditions of the process and increase its yield, but sometimes it is connected with sulfur compounds introduction. Hence, investigation of interactions between polymers and oils became extremely important. These interactions have vital influence on course of mutual dissolution of both substances before their thermal decomposition. Mixtures of polyolefins (mainly PE and PP) in industrial conditions are soluted in different technological oils in temperature 150–170°C (for LDPE – 120°C and for PP – 150–170°C) [13]. The change of reactor charge structure, may have significant influence on course of further thermodestruction of the charge, and investigations at temperature conditions lower than technological make possible optimization of the process.

Aim of the work

The main aim of investigations was utilization of Flory–Huggins theory for analysis of interactions between polymers and test solutes, which were intentionally chosen as representatives of the most important groups of compounds occurring in technological oils, which can be used in conditions of industrial decomposition of polyolefins in Poland. For this purpose the inverse gas chromatography (IGC) was used. Solubility parameter δ and interaction parameter χ are related to some heat quantities e.g. excess free energy of mixing. Values of both interaction parameter and solubility parameter of analyzed polymers were determined on the basis of test solutes retention data. Basing on changes of said parameters one may determine the influence of oil composition on polymer–oil interactions, and thereby the selection of its optimal composition and process conditions. Interactions between polymers–organic compounds mixtures and test solutes are not frequently studied, but it is very important problem in new technology of decomposition of polyolefins with technological oils, due to its influence on the process.

Theory

Solubility parameter δ_i for any compound is defined from Hildebrand–Scatchard solution theory as:

$$\delta_i \equiv \left(\frac{\Delta E^{\text{coh}}}{V_i^0} \right)^{1/2} \quad [(\text{J m}^{-3})^{1/2}] \text{ or } [\text{Pa}^{1/2}] \quad (1)$$

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where E^{coh} – cohesion energy, J mol^{-1} , V_i^0 – substance molar volume, $\text{m}^3 \text{mol}^{-1}$, i.e., as the square root of the cohesive energy density, which is itself defined as the ratio of the energy of vaporisation to the molar volume, both referred to the same temperature [14]. Cohesive energy is identified with standard energy of vaporization at given temperature [15]:

$$E^{\text{coh}} = \Delta U_v^0 = \Delta H_v^0 - RT \quad [\text{J mol}^{-1}] \quad (2)$$

where ΔU_v^0 – standard energy of vaporization, J mol^{-1} , ΔH_v^0 – standard enthalpy of vaporization, J mol^{-1} , R – gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, T – temperature, K .

Hence, for volatile substances (in case of present work – solvents) solubility parameter is calculated from relationship:

$$\delta_1 = \left(\frac{\Delta H_v^0 - RT}{V_1^0} \right)^{1/2} \quad [\text{Pa}^{1/2}] \quad (3)$$

Solubility theory gives energy of mixing of two liquids at constant volume, ΔE_m , as follows:

$$\frac{\Delta E_m}{x_1 x_2} = V_m (\delta_1 - \delta_2)^2 \quad (4)$$

where x_1, x_2 – volume fractions of the components, V_m – average molar volume based on the mole fractions, $\text{m}^3 \text{mol}^{-1}$, δ_1, δ_2 – solubility parameter of the liquids, $\text{Pa}^{1/2}$.

The theory has been particularly successful in describing thermodynamic properties of dilute solutions, especially when the component liquids are non-polar.

The Flory–Huggins interaction parameter is the key parameter in modelling the solubility of a liquid and vapour in polymer. In order to calculate interaction parameters one can use the Van Laar–Hildebrand equation [16]:

$$\chi_{1,2} = \frac{V_1^0}{RT} (\delta_1 - \delta_2)^2 + \beta \quad (5)$$

where $\chi_{1,2}$ – Flory–Huggins interaction parameter, β – constant, which accounts for entropic effects (it is often approximated by 0.34).

Flory–Huggins interaction parameter $\chi_{1,2}^\infty$ and solubility parameter for non-volatile substances are often determined by IGC [14, 17] with the use of equation:

$$\chi_{1,2}^\infty = \ln \left(\frac{273.15R}{p_1^0 V_g M_1} \right) - \frac{p_1^0}{RT} (B_{11} - V_1^0) + \ln \left(\frac{\rho_1}{\rho_m} \right) - \left(1 - \frac{V_1^0}{V_2^0} \right) \quad (6)$$

where subscript 1 relates to solvent, while subscript 2 – to investigated substance (polyolefins), M_1 – molar mass of solvent, kg mol^{-1} , p_1^0 – saturated vapour pressure of solvent in given temperature, Pa , B_{11} – second virial coefficient of solvent, $\text{m}^3 \text{mol}^{-1}$, V_g – retention volume, m^3 , ρ_i – substance density, kg m^{-3} .

In case of mixture of two polymer substances, relation (6) takes on form [18]:

$$\chi_{1,2}^\infty = \ln \left(\frac{273.15R}{p_1^0 V_g M_1} \right) - \frac{p_1^0}{RT} (B_{11} - V_1^0) + \ln \left(\frac{\rho_1}{\rho_m} \right) - \left(1 - \frac{V_1^0}{V_2^0} \right) x_2 - \left(1 - \frac{V_1^0}{V_3^0} \right) x_3 \quad (7)$$

where ρ_m – mixture density, kg m^{-3} , V_1^0, V_2^0 – molar volumes of components, $\text{m}^3 \text{mol}^{-1}$, x_2, x_3 – volume fractions of mixture components, x_1 – volume fraction of test solute.

On the basis of values $-\infty < \chi_{1,2}^\infty < +\infty$ calculated from Eqs (6) and (7) and δ_i of test solutes calculated from Eq. (3) one can determine solubility parameter of investigated substance δ_2 from slope of line plotted in coordinate system: left-side of Eq. (8) vs. δ_{1i} :

$$\frac{\delta_{1i}^2}{RT} - \frac{\chi_{(1,2)i}^\infty}{V_1^0} = \frac{2\delta_2}{RT} \delta_{1i} - \left(\frac{\delta_2^2}{RT} + \frac{\chi_s^\infty}{V_1^0} \right) \quad (8)$$

where χ_s^∞ – entropic component of interaction parameter.

Two quantities were chosen for characterization of investigated substances and their interactions: Flory–Huggins interaction parameter $\chi_{1,2}^\infty$ and solubility parameter δ_i . Similar values of parameter δ_i for different substances indicate existence of strong interactions between them. It is accepted that difference in δ_i values below $2 \text{ MPa}^{1/2}$ indicates good mutual solubility of investigated systems [19]. In case of interaction parameter $\chi_{1,2}^\infty$, the lower its value indicates the stronger interactions between substances. Change of interaction parameter sign often tells about change of interactions character.

Experimental

Materials

Substrates for investigations were: isotactic polypropylene (PP), low density polyethylene (LDPE), as well as nonadecane (Fluka) as a compound of structure similar to average molecule of paraffin oil. The latter is the most often used additive in industrial processes of polymer decomposition in Poland (paraffin oil: $M_{\text{av}}=295 \text{ g mol}^{-1}$; iodine number $5 \text{ gJ}_2/100 \text{ g}$; $t_b=69-362^\circ\text{C}$).

The following samples were investigated:

- LDPE sample No. I
- PP sample No. II
- LDPE+n-nonadecane (1:1) sample No. III
- LDPE+n-nonadecane (1:3) sample No. IV
- PP+n-nonadecane (1:1) sample No. V
- PP+n-nonadecane (1:3) sample No. VI

As the test solutes the following ones were used: pentane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, 2,3-dimethylpentane, heptane, 2-methylhexane, 1-heptene, 2,2-dimethylhexane, benzene, toluene (POCh, Gliwice, Poland).

Deposition of analyzed systems on support consisted in dissolution of weighed amounts of components (polyolefins and nonadecane) in adequate solvents, introduction of carrier into solution and evaporation of solvent during continuous mixing. Content of the stationary phase on carrier was investigated with the use of thermogravimetric method (TG), basing on difference between masses of both sample and carrier in 800°C. The measurements were carried out in MOM OD-103 derivatograph in following conditions: Pt crucible, sample mass: 50 mg, final temperature: 800°C, heating rate $q=10 \text{ K min}^{-1}$, inert atmosphere of nitrogen (gas flow rate $12 \text{ cm}^3 \text{ min}^{-1}$).

IGC experiments

All investigated systems were deposited on chromatographic support Chromosorb G DMCS 60–80 mesh (Johns-Mansville, USA) in amounts ca. 5% of mass. The measurements were carried out in Chrom 5 chromatograph equipped with flame-ionization detector (FID) in following conditions: steel column: $1.2 \text{ m} \times 4 \text{ mm}$, column temperature: 58–122°C, injector temperature: 150°C, detector temperature: 200°C, carrier gas: nitrogen (flow rate $20\text{--}24 \text{ cm}^3 \text{ min}^{-1}$), sample volume: 0.1 μL .

Values of the second virial coefficient B_{11} were calculated according to procedures included in work [20]. Parameter δ_1 was determined from Eq. (3), parameter $\chi_{1,2}^\infty$ from relationship (6) (in analyses of interactions between polyolefins-test solutes) and (7) (for systems polyolefins+nonadecane). δ_2 was determined from slope of straight-line plotted in coordinate system: left side of Eq. (8) vs. δ_1 .

Results and discussion

On the basis of measurements made with the use of IGC method the values of both interaction parameter $\chi_{1,2}^\infty$ (Table 1, for temperature 86°C) and solubility parameter δ_2 (Table 2) were determined for particular polymers.

From data presented in Tables 1 and 2 follows that temperature increase is accompanied by increase of interactions between polymers and test solutes, what is manifested by decrease of interaction parameter $\chi_{1,2}^\infty$. There are positive values of $\chi_{1,2}^\infty$ observed for almost all test solutes in temperature 86°C, what means existence of not so strong interactions. At the same time the difference in $\chi_{1,2}^\infty$ values for LDPE and PP is clearly visible. The higher values of $\chi_{1,2}^\infty$ are observed in case of PP, which is characterized by higher

Table 1 Values of Flory–Huggins parameter $\chi_{1,2}^\infty$ for examined polyolefin – test solute pairs (exemplary data at 86°C)

| Test solute | $\chi_{1,2}^\infty$ | |
|---------------------|---------------------|---------|
| | LDPE | PP |
| | I | II |
| heptane | 0.5120 | 0.7572 |
| octane | 0.3845 | 0.8466 |
| nonane | 0.4407 | 0.5248 |
| decane | 0.6093 | 0.9834 |
| isooctane | 1.0572 | 0.9418 |
| 2,3-dimethylbutane | –0.4436 | –0.4703 |
| 2-methylhexane | 0.1784 | 0.0670 |
| 2,3-dimethylpentane | 0.1444 | 0.1348 |
| 2,2-dimethylhexane | 0.3377 | 0.2566 |
| 1-heptene | 0.2150 | 0.1452 |
| 1-decene | 0.6042 | 0.7569 |
| cyclohexane | 0.1005 | 0.4119 |
| benzene | 0.3257 | 0.6131 |
| toluene | 0.4181 | 0.8266 |

Table 2 Values of solubility parameter δ_2 for examined polyolefins

| Polymer | $\delta_2/\text{MPa}^{1/2}$ | | |
|---------|-----------------------------|-------|-------|
| | 86°C | 102°C | 122°C |
| LDPE | 15.69 | 14.70 | 14.93 |
| PP | 14.36 | 14.54 | 13.94 |

melting point (ca. 150°C from DSC data), what represents existence of weaker interactions. It is clearly visible that there is lack of regularities of changes of δ_2 together with temperature changes for particular polyolefins. In turn, this effect appeared in further part of investigation, which concerned polyolefins–nonadecane systems. Analysis of influence of test solute constitution on existing interactions will be presented in next part of the present work.

The next stage of investigations was analysis of interactions between mixtures of polyolefins and nonadecane with test solutes. The chosen results are presented in Table 3 – interaction parameter $\chi_{1,2}^\infty$ and Table 4 – solubility parameter δ_2 .

Similarly to previous case, temperature increase was accompanied by increase of interactions between polymers and test solutes, what is manifested by decrease of interaction parameter $\chi_{1,2}^\infty$. From data presented in Tables 3 and 4 follows that in case of polyolefins–nonadecane systems the decrease of $\chi_{1,2}^\infty$ value is clearly visible comparing to adequate polyolefins. The fact proves existence of stronger interactions already in lower temperatures (58°C). Decrease of solubility parameter δ_2 (Fig. 1) is also clearly visible

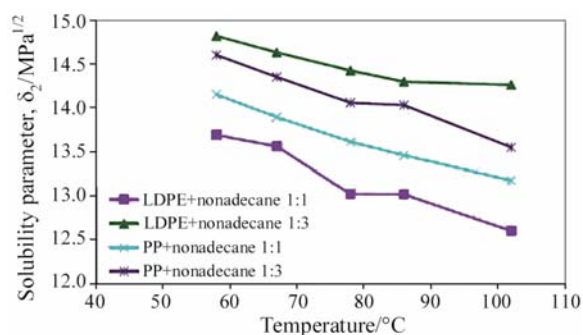


Fig. 1 Temperature influence on solubility parameter δ_2 for analyzed samples of polyolefins mixtures and nonadecane

ble, what causes its approaching to δ_1 of solvents and, in addition, confirms the conclusion about interaction increase. According to Flory–Huggins theory about improvement of mutual miscibility of two substances one may conclude from decrease of $\chi_{1,2}^\infty$ from one side, and from decrease of difference between δ_i of said substances from the other side. In case of analyzed aromatic hydrocarbons (benzene and toluene) the difference $\Delta\delta_i$ is ca. $3 \text{ MPa}^{1/2}$ and it reaches quite high values, especially in case of systems III, IV, V and VI, comparing to the other test solutes. It is surprising that, on the basis of analyzed criteria, aromatic compounds do not represent expected quality, although solubility properties of these systems are generally known and they consist in fast and easy dissolution of many polymers.

The relationship between molecular structure of solvents and their interactions with investigated systems was proved. Considering rectilinear relationships (4) for particular systems, it is clearly visible that analyzed test organic compounds (benzene and toluene) were located in total different place on the plot comparing to other substances (Fig. 2). This clearly tells about existence of interactions of different nature (with greater contribution of polar interactions), what is the result of different molecular structure. It was noticed that increase of molecular mass of solvents is accompanied by decrease of interaction force (increase of interaction parameter value, $\chi_{1,2}^\infty$ – Fig. 3).

It was also proved that existence of chain branches in aliphatic hydrocarbons influences $\chi_{1,2}^\infty$ value (on the example of heptane, 2-methylhexane and 2,3-dimethylpentane – Fig. 4). Branched hydrocarbons, having at the same time identical molecular mass, represent better miscibility (decrease of interaction parameter $\chi_{1,2}^\infty$) in comparison to non-branched ones. The effect is even more visible, while number of branches increases.

The influence of branch position on miscibility of model substances with investigated systems (comparison of 2-methylpentane with 3-methylpentane – Fig. 5) is also observed. The position of methyl group at carbon in position 3 causes improvement of miscibility in comparison to isomer with methyl group having carbon in position 2.

Table 3 Values of Flory–Huggins parameter $\chi_{1,2}^\infty$ for different examined mixtures – test solute pairs (exemplary data at 86°C)

| Test solute | $\chi_{1,2}^\infty$ | | | |
|---------------------|---------------------|---------|---------|---------|
| | III | IV | V | VI |
| pentane | -1.0215 | -0.3687 | -0.5544 | -0.2954 |
| 2-methylpentane | -0.7757 | -0.1275 | -0.3042 | 0.0174 |
| 3-methylpentane | -0.8782 | -0.2581 | -0.4088 | -0.0117 |
| 2,3-dimethylbutane | -0.9482 | -0.3227 | -0.4945 | -0.1768 |
| heptane | -0.7552 | -0.0834 | -0.2128 | 0.0952 |
| 2-methylhexane | -0.7629 | -0.1212 | -0.2494 | 0.0562 |
| 2,3-dimethylpentane | -0.7973 | -0.1551 | -0.2722 | 0.0377 |
| 1-heptene | -0.7338 | -0.0843 | -0.2054 | -0.0142 |
| 2,2-dimethylhexane | -0.7696 | -0.0935 | -0.2250 | 0.0848 |
| benzene | -0.4635 | 0.1688 | 0.0602 | 0.3784 |
| toluene | -0.5218 | 0.2037 | 0.1022 | 0.4287 |

Table 4 Values of solubility parameter δ_2 for different examined mixtures

| Polymer | Sample No. | Polymer amount/% | $\delta_2/\text{MPa}^{1/2}$ | | | | |
|-----------------|------------|------------------|-----------------------------|-------|-------|-------|-------|
| | | | 58°C | 67°C | 78°C | 86°C | 102°C |
| LDPE+nonadecane | III | 50 | 14.82 | 14.63 | 14.43 | 14.30 | 14.26 |
| | IV | 25 | 14.15 | 13.89 | 13.61 | 13.46 | 13.18 |
| PP+nonadecane | V | 50 | 13.91 | 13.92 | 13.52 | 13.41 | 13.01 |
| | VI | 25 | 13.69 | 13.56 | 13.02 | 13.02 | 12.60 |

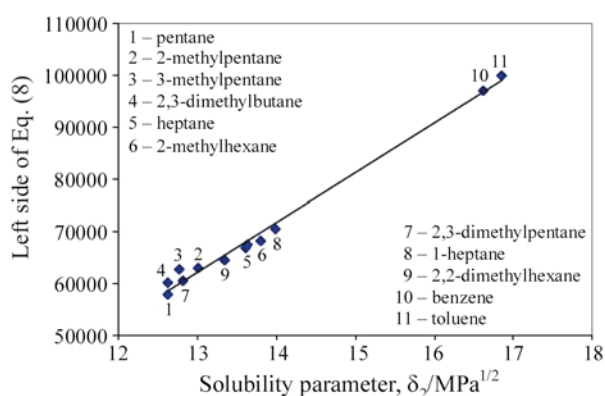


Fig. 2 Graphical presentation of Eq. (8) for sample No. III (LDPE+nonadecane) at temperature 86°C

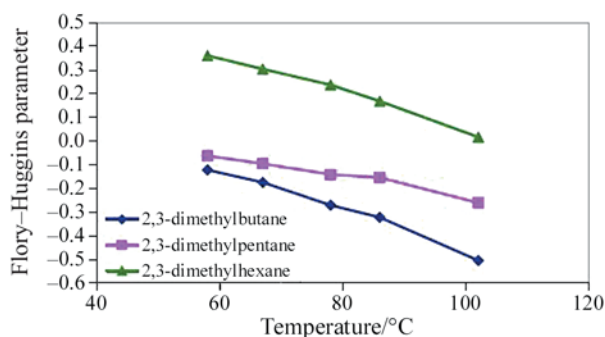


Fig. 3 The influence of test solute chain length on $\chi_{1,2}^{\infty}$ value

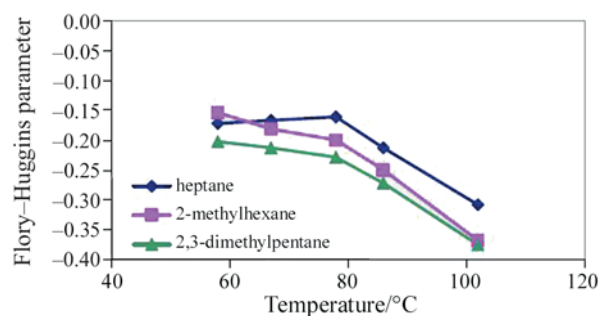


Fig. 4 The influence of side chains existence in test solutes on $\chi_{1,2}^{\infty}$ value

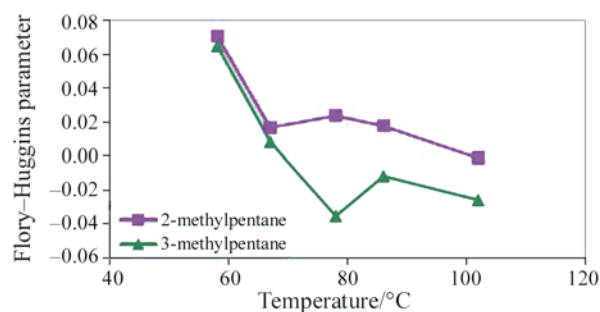


Fig. 5 The influence of side chain position on $\chi_{1,2}^{\infty}$ value

On the basis of results obtained during investigations of applied solvents one can draw the conclusion that decrease of molecular mass of technological oils (or average molecular mass, in case when oil is a mixture of different compounds) beneficially influences mutual dissolution process. It was also proved that increase of branched hydrocarbons content gives similar results. At the same time the position of side chains is not meaningless (very close position to the end of a chain is unfavorable). The investigations of course require broadening for other groups of chemical compounds, but on the basis of analyses already carried out it is possible to select the best technological oils from point of view of dissolution process.

As it was proved above, the strongest interactions are for branched hydrocarbons with low molecular mass. However, in industrial practice molecular mass cannot be excessively lowered for the sake of both oil vapor pressure in temperature of dissolution process (ca. 150–170°C) before decomposition and, at the same time, necessity of construction of vapor condensation system. Therefore, the proper balance between these factors is necessary. However, the investigation carried out allowed describing the relationships between oil composition and its interactions with analyzed polyolefins. In industrial practice, it will allow to select the best technological oil of these available one the market.

Conclusions

It was found that for technological oils containing mainly saturated hydrocarbons (paraffin oil) decrease of molecular mass causes increase of interaction force (lower $\chi_{1,2}^{\infty}$ values) and easier mutual dissolution. It was also proved that existence of branches in aliphatic hydrocarbons influences $\chi_{1,2}^{\infty}$ value (on the example of heptane, 2-methylhexane and 2,3-dimethylpentane). Branched hydrocarbons, having at the same time identical molar mass, present better miscibility (decrease of interaction parameter $\chi_{1,2}^{\infty}$) comparing to non-branched ones. When the number of branches increases, the effect is even more visible. The influence of branches position on miscibility of model substances with investigated systems is also visible – comparison of both 2-methylpentane and 3-methylpentane. The position of methyl group at carbon in position 3 causes improvement of miscibility in comparison to isomer with methyl group having carbon in position 2.

On this basis, one can say that the strongest interactions are for branched hydrocarbons with low molecular mass. However, in industrial practice the said mass cannot be excessively lowered for the sake of both oil vapor pressure at temperature of the pro-

cess (ca. 150–170°C) and, at the same time, necessity of construction of complicated systems of vapor condensation or fuel fractions collection. Therefore, the proper balance between these factors is necessary. However, the investigation carried out allowed describing the relationships between oil composition and its interactions with analyzed polyolefins. In industrial practice, it will allow to select the best technological oil of these available one the market.

At the same time, one can notice that within analyzed temperature range dissolution of LDPE runs much easier than of PP. From analysis of systems: polyolefins–nonadecane follows that dissolution of polyolefins in this aliphatic hydrocarbon results in decrease of solubility parameter $\Delta\delta_2=0.5\text{--}1.4\text{ MPa}^{1/2}$ and also significantly influences interaction parameter $\chi_{1,2}^\infty$. It means that there are much stronger interactions between investigated system and test solutes. In this case, it is also observed that for saturated hydrocarbons the decrease of molecular mass of test solute is accompanied by decrease of $\chi_{1,2}^\infty$ value and, at the same time, by increase of interaction forces.

Surprisingly, on the basis of analyzed criteria (Flory–Huggins interaction parameter $\chi_{1,2}^\infty$ and difference between solubility of polymers and aromatic compounds ($\Delta\delta_1\approx 3\text{ MPa}^{1/2}$) aromatic compounds do not represent expected quality, though solubility properties of these systems are generally known and the properties consist in fast and easy dissolution of many polymers. Probably this effect can change at higher temperatures.

Thus, the presented investigations make valuable completion and broadening of hitherto carried out analyses in laboratory scale and as well thermogravimetric analyses (TG) as differential scanning calorimetry (DSC) [9, 10]. They allow both evaluation of influence of technological oils compositions used in soaking process and selection of process conditions.

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