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Swelling of EPDM rubbers for oil-well applications as influenced by medium composition and temperature Part III. Final experiments and conclusions

The paper focusses on time and temperature dependencies of swelling of crosslinked EPDM in three various solvents: *o*-xylene, cyclooctane and dodecane and their blends at 22 °C, 40 °C or 60 °C, mimicking the conditions in oil-wells. Sorption experiments of solvents in elastomers provide valuable information on the transport characteristics of the polymer composite, i.e. at what rate the liquid diffuses into the polymer matrix. The rates of the solvent swelling of a crosslinked EPDM sample have been measured in 16 organic solvents at various temperatures. The solvents mass uptake changed in order of: cycloalkanes > aromatic hydrocarbons > alkanes. A better way to determine the solubility parameter of the rubber from swelling in a single solvent, is observation of its swelling behaviour in mixtures of different solvents. In a mixture of solvents, with similar and different molar volumes, the respective components are absorbed by the rubber in the same volume concentration ratio as they were mixed. By mixing two solvents with different interactions towards the EPDM-rubber it is possible to shift the average solubility parameter of the mixture closer to the rubber and then get higher solvent mass uptake than for the pure components. The results show that the extents of the swelling for the pure solvents are nearly independent of temperature within the range studied here (20–80 °C), whereas in case of solvent mixtures at higher temperature, the solubility parameter becomes lower for the EPDM rubber. The interaction between rubber and solvent is the most sensitive and valuable parameter, which determines most prominently the swelling ratio. For the three classes of solvents investigated the solubility parameter approach that of the EPDM rubber, the higher their molar volumes, and consequently the degree of swelling increases.

Keywords: EPDM rubber, equilibrium swelling, organic solvents, temperature.

Wpływ składu oleju i temperatury na pęcznienie gumy EPDM do zastosowań w szybach naftowych Cz. III. Badania końcowe i wnioski

W artykule skupiono się na problemie zależności pęcznienia wulkanizatów EPDM od czasu, w trzech różnych rozpuszczalnikach: *o*-ksylenie, cyklooktanie i dodekanie lub ich mieszaninach, w temperaturach 22 °C, 40 °C lub 60 °C, naśladując warunki panujące w szybach wiertniczych. Wyniki badań sorpcji rozpuszczalników przez wulkanizaty dostarczają cennych informacji na temat charakteru ich transportu w kompozycie polimerowym, tj. szybkości, z jaką rozpuszczalnik dyfunduje w matrycy polimerowej. Zmierzono szybkości pęcznienia usieciowanych próbek kauczuku EPDM w 16 rozpuszczalnikach organicznych, w różnej temperaturze. Wzrost masy próbki następuje w następującym porządku: cykloalkany > węglowodory aromatyczne > alkany. Lepszym, od pęcznienia w jednym roztworze, sposobem oznaczania parametru rozpuszczalności gumy jest obserwacja jej zachowania się w mieszaninie różnych rozpuszczalników. Jeżeli składniki takiej mieszaniny mają taką samą objętość molową, są absorbowane przez gumę w takiej samej proporcji, w jakiej były zmieszane. Natomiast mieszanina dwóch roztworów o różnej objętości molowej pozwala przesunąć średni parametr rozpuszczalności układu w kierunku parametru rozpuszczalności kauczuku EPDM i uzyskać większą wartość pęcznienia równowagowego polimeru w porównaniu z jego pęcznieniem w roztworach składowych. Uzyskane wyniki wskazują, że pęcznienie wulkanizatów w „czystych” rozpuszczalnikach prawie nie zależy od temperatury w badanym zakresie (20–80 °C), natomiast parametr rozpuszczalności kauczuku EPDM w mieszaninie roztworów maleje w podwyższonej temperaturze. Oddziaływanie polimer–rozpuszczalnik są najbardziej czułym i ważnym parametrem z punktu widzenia oznaczania szybkości pęcznienia wulkanizatów. Z przeprowadzonych badań EPDM, przy użyciu trzech rodzajów rozpuszczalników wynika, że im większa objętość molowa rozpuszczalnika, tym większy stopień pęcznienia wulkanizatów.

Słowa kluczowe: kauczuk EPDM, pęcznienie równowagowe, rozpuszczalniki organiczne, temperatura.

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Introduction

This is the third and concluding manuscript of a series of three, covering the use of EPDM rubbers for swelling applications in oil-well packers. The first covered the theoretical background of swelling of rubbers in various media and has been published in an earlier issue of *Elastomery* journal [1]. The second one focused mainly on the determination of the solubility parameter of EPDM rubber and how it influences the equilibrium swelling of crosslinked EPDM in various solvents. It has been published as well in an earlier issue of *Elastomery* journal [2]. This last manuscript focusses on time and temperature dependencies of swelling of crosslinked EPDM in various solvents and their blends, mimicking the conditions in oil-wells.

4. Experimental continued

5.5. Time and temperature dependence of swelling of EPDM elastomer

The protocol for measuring the time and temperature dependence of swelling was described in section 4.4.1 of the second manuscript of this series. The swelling data obtained on the crosslinked EPDM test pieces in three basic solvent *o*-xylene, cyclooctane and dodecane at different temperatures of 22 °C, 40 °C, 60 °C and 80 °C are plotted in Figures 16–18 as percentage change in mass of the elastomer versus time of immersion in the solvents. In the pure swelling solvents, the EPDM attains a maximum increase in

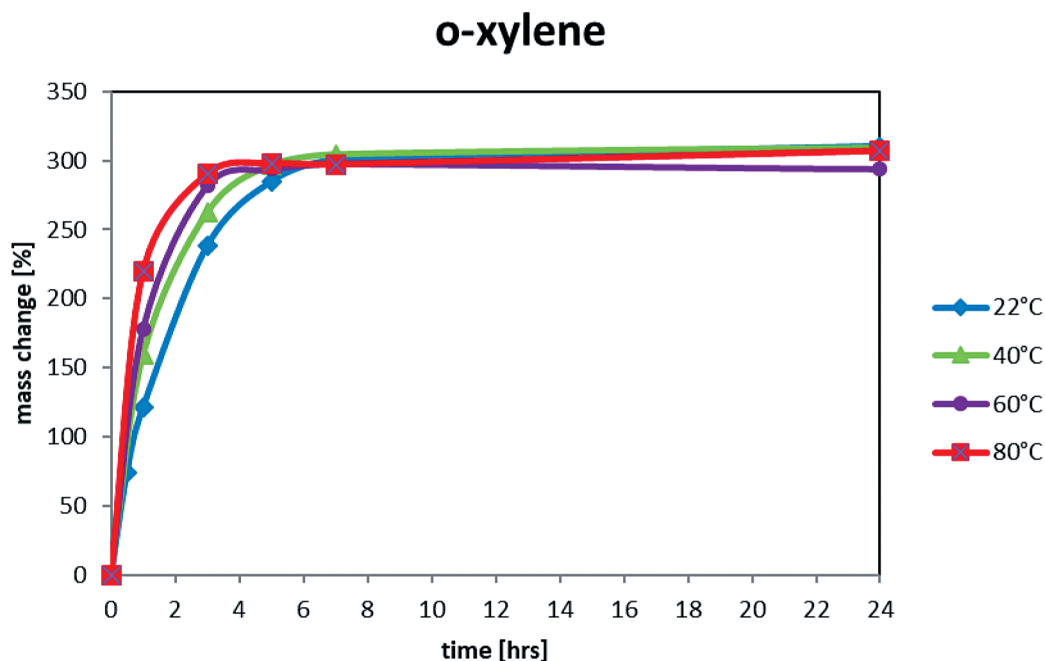


Figure 16. % change in mass vs. time of immersion of rubber sample in *o*-xylene at different temperature

Rys. 16. Procentowy wzrost masy próbki kauczuku w funkcji czasu zanurzenia jej w *o*-ksylenie, w różnej temperaturze

mass in about 24 hours, followed by fluctuations around constant magnitude. No significant differences in solvent mass uptake at equilibrium in the pure solvents was observed for the various temperatures. There are slight differences in the speed of mass change between the three solvents.

Increase in temperature has a clear influence on the speed of reaching equilibrium. At higher temperatures

equilibrium is reached earlier than at room temperature for each solvent, as was anticipated beforehand and commonly seen [3]. It can be explained by the solvent-absorption speed dependence on temperature - its speed increases with increasing temperature, because of faster movements of molecules between the elastomer chains at higher temperatures and so speed-up of the whole process of swelling [3].

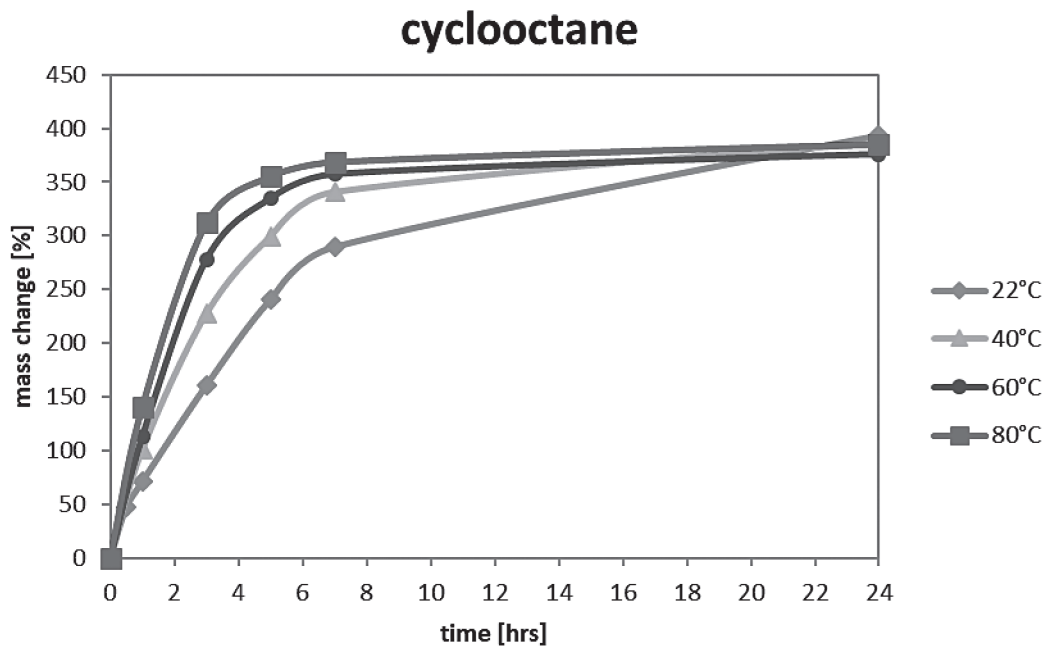


Figure 17. % change in mass vs. time of immersion of rubber sample in cyclooctane at different temperature

Rys. 17. Procentowy wzrost masy próbki kauczuku w funkcji czasu zanurzenia jej w cyklooktanie, w różnej temperaturze

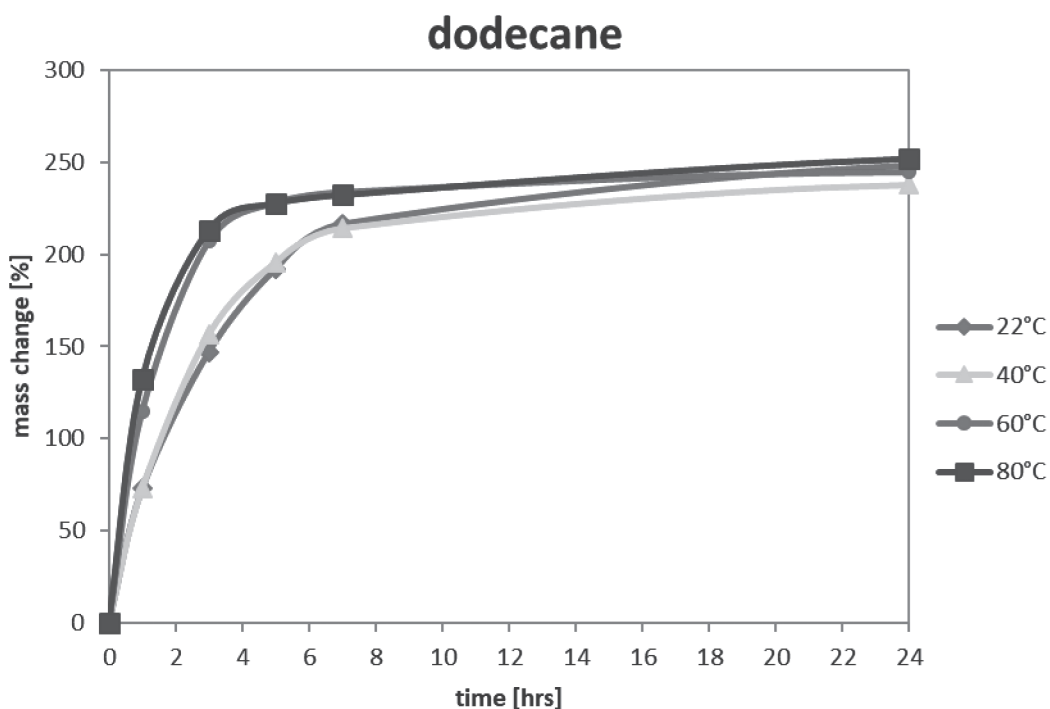


Figure 18. % change in mass vs. time of immersion of rubber sample in dodecane at different temperature

Rys. 18. Procentowy wzrost masy próbki kauczuku w funkcji czasu zanurzenia jej w dodekanie, w różnej temperaturze

To understand the mechanism of a solvent adsorption, the diffusion model for the interpretation of swelling of elastomers in different fluids should be considered. The diffusion coefficient, D , can in general be calculated using the equation:

$$\frac{Q_t}{Q_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \left[\frac{1}{(2n+1)^2} \right] \exp \left[-\frac{D(2n+1)^2 \pi^2 t}{h_0^2} \right] \quad (34)$$

Where, Q_t and Q_∞ are defined as the fractional change in mass at time t relative to $t = \infty$ for Q_∞ (saturation) and h_0 is the thickness of the elastomer.

For short initial times, the diffusion of a fluid in an elastomer of thickness h_0 follows the equation:

$$D = \pi \left(h_0 \cdot \frac{\theta}{4Q_\infty} \right)^2 \quad (35)$$

Where, θ is the slope of the nearly linear portion of the plot of Q_t vs. $t^{1/2}$ (minutes^{1/2}) before attaining 50% of the equilibrium swelling. This allows determination of D for a given solvent and elastomer.

As shown in Table 16, in each system the value of the diffusion constant D increases with temperature. The increase of diffusion with temperature invariably points towards activation of the diffusion process at higher temperature.

5.6. Swelling in a mixture of solvents as function of temperature

As shown in Table 6 in part II of this series, swelling in mixtures with different concentrations of *o*-xylene, cyclooctane and dodecane at 4 temperatures were carried out to establish the influence of mixed solvents on the swelling and eventually preferential adsorption. Keeping in mind that, when mixtures of two solvents of variable composition have solubility parameters, δ_{s1} and δ_{s2} , larger or smaller than the solubility parameter of the polymer ($\delta_{s2} > \delta_{s1} > \delta_r$ or then $\delta_r > \delta_{s2} > \delta_{s1}$), the solvents can be considered as non-symmetric liquids. In the present study

Table 16. Diffusion coefficients of polymer-solvent systems at different temperature

Tabela 16. Współczynniki dyfuzji dla układu polimer-rozpuszczalnik, w różnej temperaturze

Diffusion coefficient $D \cdot 10^{-5}$ [cm ² /s]				
T [°C]	22	40	60	80
<i>o</i> -xylene	1.48	2.75	8.88	9.06
cyclooctane	0.31	3.14	4.85	6.56
dodecane	0.46	4.25	5.07	7.41

o-xylene as component in binary solvent at 22°C

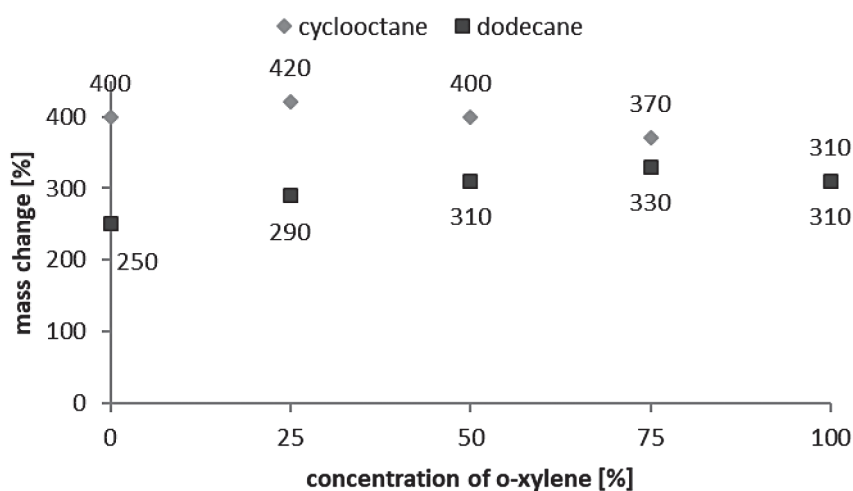


Figure 19. Results of equilibrium swelling tests for EPDM in binary solvents of *o*-xylene with respectively cyclooctane and dodecane at 22 °C

Rys. 19. Wyniki badań pęcznienia równowagowego kauczuku EPDM w dwuskładnikowej mieszaninie rozpuszczalników: *o*-ksylenu z odpowiednio cyklooktanem i dodekanem, w temperaturze 22 °C

a symmetric liquid occurs when the polymer is mixed with two solvents, of which the solubility parameter of the first δ_{s1} is smaller, respectively the solubility parameter δ_{s2} of the other liquid is larger than the solubility parameter of the polymer δ_r . As shown in

Figure 19, at room temperature a maximum value of swelling is a function of binary solvent composition, what is characteristic of a symmetric liquid. Those changes are related to the shift in solubility parameter: Table 6 in Part II, and according to Equation (23) in

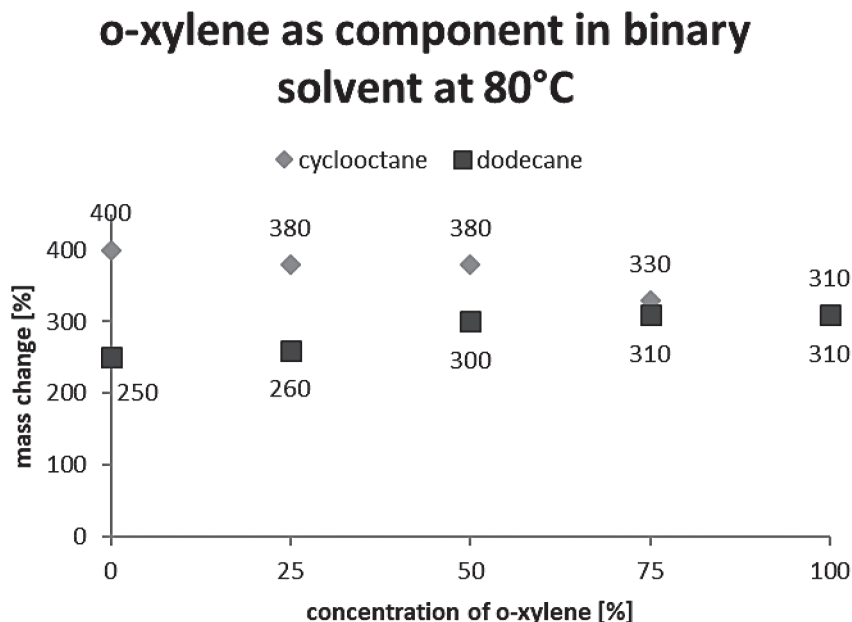


Figure 20. Results of equilibrium swelling tests for EPDM in binary solvents of *o*-xylene with respectively cyclooctane and dodecane at 80 °C

Rys. 20. Wyniki badań pęcznienia równowagowego kauczuku EPDM w dwuskładnikowej mieszaninie rozpuszczalników: *o*-ksylenu z odpowiednio cyklooktanem i dodekanem, w temperaturze 80 °C

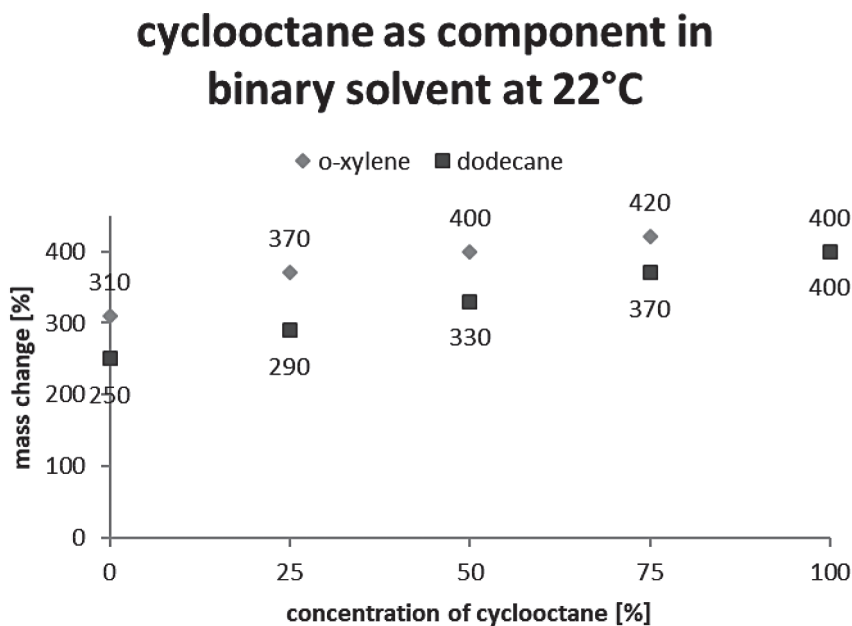


Figure 21. Results of equilibrium swelling tests for EPDM in binary solvents of cyclooctane with respectively *o*-xylene and dodecane at 22 °C

Rys. 21. Wyniki badań pęcznienia równowagowego kauczuku EPDM w dwuskładnikowej mieszaninie rozpuszczalników: cyklooktanu z odpowiednio *o*-ksylenem i dodekanem, w temperaturze 22 °C

cyclooctane in binary solvent at 80 °C

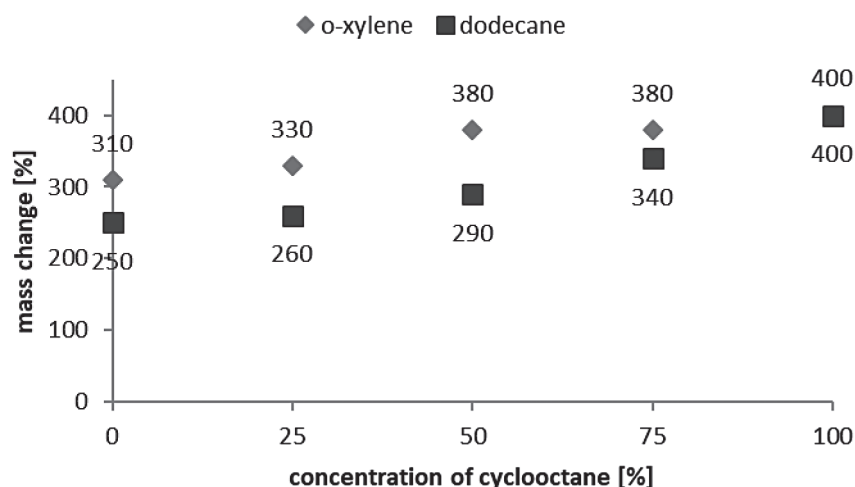


Figure 22. Results of equilibrium swelling tests for EPDM in binary solvents of cyclooctane with respectively *o*-xylene and dodecane at 80 °C

Rys. 22. Wyniki badań pęcznienia równowagowego kauczuku EPDM w dwuskładnikowej mieszaninie rozpuszczalników: cyklooctanu z odpowiednio *o*-ksylenem i dodekanem, w temperaturze 80 °C

Part I of this series, which states that the solubility parameter of a mixture is the sum of products of the volume fraction and the solubility parameter of the respective components. With increase of the *o*-xylene content in the mixture with cyclooctane or dodecane: Figure 19, at 22 °C the equilibrium swelling reaches a maximum for the mixture of 25% of *o*-xylene and 75% of cyclooctane. In the case of the mixtures of *o*-xylene with dodecane, the maximum in swelling occurs at 75% of *o*-xylene, because the solubility parameter of dodecane is much lower than that of the EPDM elastomer ($\delta_r = 17.65$ MPa, $\delta_{\text{dodecane}} = 16.0$ MPa). Mixtures of *o*-xylene with respectively cyclooctane and dodecane therefore represent symmetric liquids vs. the EPDM elastomer, as manifested by the presence of maxima in the equilibrium swelling.

As shown in Figure 20, at 80 °C no significant differences in mass uptake at equilibrium between the temperatures in the pure solvents occurs, as seen before, but in the mixture of *o*-xylene and cyclooctane now a linear change dependency is observed, without reaching a maximum peak. This change occurs because at higher temperatures the solubility parameters of the solvents and EPDM-rubber decreases, but at different speeds.

In case of mixtures of cyclooctane with dodecane at 22 °C and 80 °C, Figures 21 and 22 represent non-symmetric mixtures, and consequently the

changes in mass of solvent uptake are linear and shifted to the larger concentration of cyclooctane.

5.6.1. Headspace gas chromatographic results

To determine whether the shifts in degree of swelling at equilibrium, present in the swelling results for the mixtures of solvents are related to preferential absorption of one of the solvents, headspace gas chromatography was conducted applied according to the procedure described in Chapter 4.4.3 in part II of this series. As shown in Figures 23–26 green points (diamonds) represent the calibration line obtained for headspace gas generated by mixtures of the pure solvents in the vial. The red points (squares) correspond to the signal from the headspace gas phase formed by organic volatiles which came from the swollen rubber samples. In each case the data derived from the swollen rubber samples and the calibration line have a good fit, meaning that in the mixture of solvents the individual components are absorbed by the rubber in the same volume concentration as they were mixed. This information implies changes in solubility parameter of the given systems of solvents, due to differences in solubility parameter of the specific components of the mixtures.

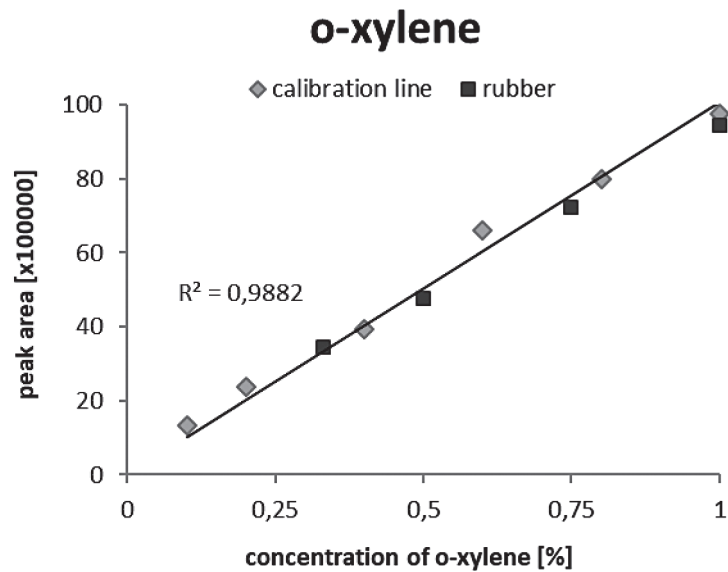


Figure 23. Concentration of *o*-xylene found in binary mixture with cyclooctane, for pure solvents and in swollen rubber samples as determined with HGC

Rys. 23. Zawartość *o*-ksylenu w dwuskładnikowej mieszaninie z cyklooktanem oraz w spęcznionym kauczuku EPDM, na podstawie pomiarów chromatograficznych metodą HGC

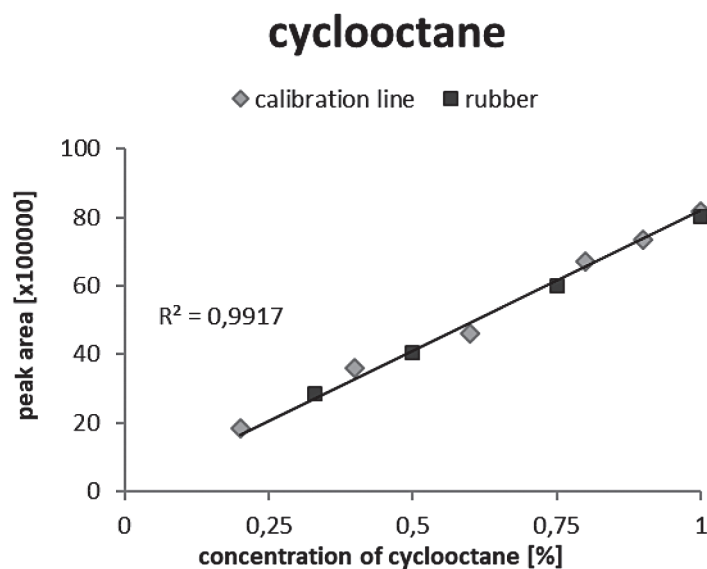


Figure 24. Concentration of cyclooctane found in binary mixture with *o*-xylene, for pure solvents and in swollen rubber samples as determined with HGC

Rys. 24. Zawartość cyklooktanu w dwuskładnikowej mieszaninie z *o*-ksylenem oraz w spęcznionym kauczuku EPDM, na podstawie pomiarów chromatograficznych metodą HGC

dodecane

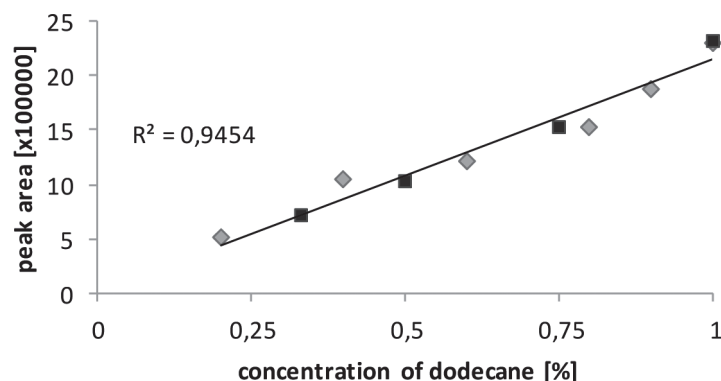


Figure 25. Concentration of dodecane found in binary mixture with *o*-xylene, for pure solvents and in swollen rubber samples as determined with HGC

Rys. 25. Zawartość dodekanu w dwuskładnikowej mieszaninie z *o*-ksylenem oraz w spęcznionym kauczuku EPDM, na podstawie pomiarów chromatograficznych metodą HGC

dodecane II

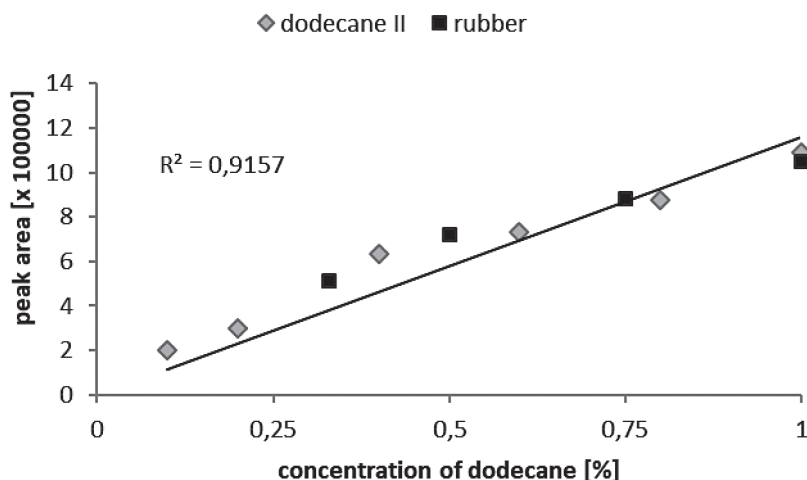


Figure 26. Concentration of dodecane found in binary mixture with cyclooctane, for pure solvents and in swollen rubber samples as determined with HGC

Rys. 26. Zawartość dodekanu w dwuskładnikowej mieszaninie z cyklooktanem oraz w spęcznionym kauczuku EPDM, na podstawie pomiarów chromatograficznych metodą HGC

5.6.2. Calculated solubility parameters related to swelling at higher temperatures

Using Equations (18–20) for solvents, with thermal expansion coefficients α taken from Table 10 and

Equation (15) for rubber with $\alpha = 1,6 \cdot 10^{-4} \text{K}^{-1}$ (Chapter 3.4 of paper I of this series) solubility parameters of solvents at higher temperatures were obtained as shown in Table 17.

In Table 17 it is shown that the solubility parameter decreases as temperature increases, because of the decrease of cohesive energy density which occurs at higher temperature.

Table 17. Solubility parameter of rubber δ_r and solvents at different temperature calculated from Equations (14) and (15)**Tabela 17.** Parametry rozpuszczalności dla kauczuku δ_r i rozpuszczalników w różnej temperaturze, obliczone na podstawie równań (14) i (15)

T [°C]	δ_{EPDM} [MPa ^{1/2}]	$\delta_{o\text{-xylene}}$ [MPa ^{1/2}]	$\delta_{cyclooctane}$ [MPa ^{1/2}]	$\delta_{dodecane}$ [MPa ^{1/2}]
22	17.65	18.10	17.50	16.00
40	17.60	17.66	17.38	15.89
60	17.54	17.20	17.23	15.75
80	17.49	16.70	17.08	15.60

As shown in Table 18, mass changes from swelling tests of *o*-xylene, cyclooctane and dodecane mixtures were compared with those calculated from swelling data for the pure components, as follows:

$$\%m_{\text{change - calculated}} = \nu_{s1} \cdot 310\% + \nu_{s2} \cdot 400\% + \nu_{s3} \cdot 250\% \quad (36)$$

Table 18. Mass changes and volume fractions of EPDM polymer in swollen mass ν_r from swelling tests, and calculated mass changes based on swelling data from pure solvents and dodecane with calculated χ Flory-Huggins interaction parameters, at equilibrium of swelling for 3 pure representatives components *o*-xylene, cyclooctane and dodecane and their mixtures at 20 °C**Tabela 18.** Zmiana masy i objętości frakcji polimerowej EPDM w spęcznionej próbce ν_r na podstawie wyników pęcznienia równowagowego i zmiana masy obliczona na podstawie wyników pęcznienia w „czystych” rozpuszczalnikach i dodekanie z obliczonymi parametrami oddziaływań χ Flory’ego–Hugginsa w warunkach równowagowych dla *o*-ksylenu, cyklooktanu i dodekanu oraz ich mieszanin, w temperaturze 20 °C

Mixture number	<i>o</i> -xylene [%]	Cyclooctane [%]	Dodecane [%]	mass change [%] from swelling test	ν_r at 22 °C	Calculated mass change [%]	HSP ν_s at 20 °C	Calculated χ at 20 °C
I	100	0	0	310	0.23		18.10	0.35
II	0	100	0	400	0.18		17.50	0.34
III	0	0	100	250	0.25		16.00	0.59
IV	33	33	33	330	0.21	320	17.03	0.37
V	75	25	0	370	0.20	330	17.95	0.34
VI	75	0	25	330	0.22	300	17.58	0.34
VII	50	50	0	400	0.19	360	17.80	0.34
VIII	50	0	50	310	0.22	280	17.05	0.37
IX	0	50	50	330	0.21	330	16.75	0.40
X	25	75	0	420	0.18	380	17.65	0.34
XI	25	0	75	290	0.23	270	16.53	0.44
XII	0	75	25	370	0.19	360	17.13	0.36
XIII	0	25	75	290	0.23	290	16.38	0.48
XIV	50	25	25	360	0.20	320	17.43	0.34
XV	25	50	25	350	0.20	340	17.28	0.35
XVI	25	25	50	320	0.21	310	16.90	0.38

where v_{s1} , v_{s2} , v_{s3} are the volume fractions of *o*-xylene, cyclooctane and dodecane, respectively. It is seen that in almost each system, the experimental mass changes are higher than that those expected from the calculation and these differences are up to 11% of the entire amount of swelling.

A similar situation occurs for swelling tests at 80 °C as shown in Table 19. There can be 2 reasons for that: (1) preferential adsorption of one of the components of the mixture; or (2) measurement error due to non-homogeneity of the vulcanized rubber sheets. Because the headspace gas chromatography results show that in the mixtures of solvents the various components are adsorbed by the rubber in the same volume fractions as they were mixed, the differences are probably the effect of the second option: differences in the crosslink density of the vulcanized rubber sheets.

The temperature effects on the swelling in the range of 20–80 °C are very small. There is a systematic trend for almost all solvents, to give slightly lower mass uptake at higher temperatures. Viewing the Flory–Rehner equation and solubility parameter changes as a function

of temperature, it can be seen that at higher temperature the differences between the solubility parameters of the EPDM-rubber and of the solvents increase, what leads to a lower swelling ratio. At 80 °C the solubility parameter of EPDM is $\delta_{EPDM}^{80} = 17.49 \text{ MPa}^{1/2}$, higher than for all solvents and mixtures thereof. As shown in Table 19, the highest values of the solubility parameter of solvents occur for solvents number II, VII and X and for these the mass change is the highest, as expected. Indeed, the closer the solubility parameters of the solvent and EPDM rubber, the higher the swelling.

5.7. Effect of molar volume of solvent on swelling

To determine the dependence of swelling of the EPDM elastomer on the molecular size of the solvents, additional swelling in various hydrocarbons was investigated. As shown in Table 20, these solvents molecules derive from the same homologous series of

Table 19. Mass changes and volume fractions of EPDM polymer in swollen mass v_r from swelling tests, and calculated mass changes based on swelling data from pure solvents and dodecane with calculated χ -Flory-Huggins interaction parameters, at equilibrium of swelling for 3 pure representatives components *o*-xylene, cyclooctane and dodecane and their mixtures at 80 °C

Tabela 19. Zmiana masy i objętości frakcji polimerowej EPDM w spęcznionej próbce v_r na podstawie wyników pęcznienia równowagowego i zmiana masy obliczona na podstawie wyników pęcznienia w „czystych” rozpuszczalnikach i dodekanie, z obliczonymi parametrami oddziaływań χ Flory’ego–Hugginsa w warunkach równowagowych dla *o*-ksylenu, cyklooktanu i dodekanu oraz ich mieszanin, w temperaturze 80 °C

Mixture number	<i>o</i> -xylene [%]	Cyclooctane [%]	Dodecane [%]	mass change [%] from swelling test	v_r at 80 °C	Calculated mass change [%]	HSP δ_s at 80 °C	Calculated χ at 80 °C
I	100	0	0	310	0,23		16.70	0.37
II	0	100	0	400	0.18		17.08	0.35
III	0	0	100	250	0.24		15.60	0.63
IV	33	33	33	320	0.21	320	16.30	0.42
V	75	25	0	330	0.22	330	16.81	0.36
VI	75	0	25	310	0.22	300	16.44	0.40
VII	50	50	0	380	0.19	360	16.90	0.36
VIII	50	0	50	300	0.22	280	16.16	0.45
IX	0	50	50	290	0.22	320	16.34	0.43
X	25	75	0	380	0.19	380	16.99	0.35
XI	25	0	75	260	0.23	270	15.88	0.53
XII	0	75	25	340	0.16	360	16.71	0.37
XIII	0	25	75	260	0.23	290	15.97	0.51
XIV	50	25	25	330	0,21	320	16.53	0.39
XV	25	50	25	350	0.20	340	16.62	0.38
XVI	25	25	50	300	0.22	300	16.25	0.44

aromatic, naphthenic and paraffinic species, but with increasing size and volume. In Table 20, the relevant parameters for the solvents are listed along with the measured maximum changes in swollen mass for the EPDM elastomer. The maximum changes in mass are the largest for the EPDM-samples immersed in cyclo-compounds. The mass changes for the *n*-alkanes are the lowest, and smaller even than for the aromatics.











Within each group of solvents, the swelling ratio increases as the molar volume of the solvent molecule increases. All compounds are hydrocarbon molecules and so have strong chemical interaction with an elastomer such as EPDM. In previous investigations [4–6] it was suggested that the swelling decreases as the molar volume of the solvent molecule increases, because larger molecules cannot diffuse into the network that easily. As shown in Table 20, not only the molecular size is an important factor in the swelling equilibrium behavior, but

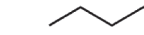
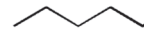
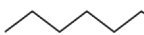
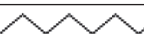
also the solubility parameter of rubber and liquid contribute to the observed swelling of the elastomer.

Because the results are therefore unexpected in comparison with previous interpretations taken from literature [4–6], in order to understand the influence of molar volume on the absorption and equilibrium swelling, the swelling curves for the 3 classes of solvents are given in Figures 27–29. It is seen during the first hours of swelling, that the molar volume of the solvents has a clear influence, i.e. the smaller the molecules, the faster the swelling equilibrium is reached. However, the ultimate equilibrium degrees of swelling are not necessarily related. In the present study the crosslink density is not a variable, so ν_E is constant, whichever solvent was used for the swelling experiment. If the amounts of swelling then vary, this must be the result of differences in the Flory-Huggins interaction parameter χ and/or of the molar volumes of the solvents, V_s .

Table 20. Comparison of molar mass, density, molar volume, solubility parameter of solvents and the maximum % changes in mass and volume of EPDM rubber

Tabela 20. Porównanie masy molowej, gęstości, objętości molowej, parametrów rozpuszczalności w rozpuszczalnikach oraz maksymalnych % zmian masy i objętości kauczuku EPDM

Fluid	Molar mass [g/mol]	Density [g/cm ³]	Molar volume [cm ³ /mol]	Structure	MOSCED δ_s [8] [MPa ^{1/2}]	HSP δ_s [9] [MPa ^{1/2}]	mass change [%] (own results)
benzene	78.11	0.874	89.37		17.91	18.51	185
toluene	92.14	0.867	106.27		17.80	18.16	264
<i>o</i> -xylene	106.16	0.879	120.77		18.10	18.10	314
<i>p</i> -xylene	106.15	0.861	123.29		17.80	17.70	306
cumene	120.19	0.864	139.11		17.90	17.95	244
1,2,4-trimethylbenzene	120.19	0.876	137.20		–	18.06	330
cyclopentane	70.10	0.751	93.34		16.40	16.50	340
cyclohexane	84.16	0.779	108.04		16.80	16.80	360
cyclooctane	112.21	0.834	134.54		17.50	17.50	404
<i>n</i> -pentane	72.15	0.630	114.52		15.30	14.40	164

<i>n</i> -hexane	86.18	0.659	130.77		15.70	14.90	206
<i>n</i> -heptane	100.21	0.683	146.72		16.00	15.30	223
<i>n</i> -decane	142.29	0.730	194.92		16.50	15.70	229
<i>n</i> -dodecane	170.33	0.750	227.11		16.70	16.00	253

Considering the Flory–Rehner Equation (10) in Chapter 3.3 in part I of this series, and changing χ as per Equation (22) in Chapter 3.5 in part I, after some

rearrangement we may compare both sides of the equation in the following form:

$$V_s \cdot \left[\left(v_r^{1/3} - \frac{v_r}{2} \right) + \frac{(\delta_s - \delta_r)^2 v_r^2}{RT} \right] = - \left[\ln(1 - v_r) + v_r + 0,34v_r^2 \right] \quad (37)$$

Table 22. Calculated volume fraction of polymer in swollen mass for given molar volume, which balances Equation (37)
Tabela 22. Zawartość frakcji polimerowej w spęcznionej próbce, obliczona na podstawie równania (37)

V_s	v_r
130	0.18
120	0.175
110	0.17
100	0.16
90	0.15

Table 22 then presents values of v_r , which balance both sides of Equation (37) for various given molar volumes and assuming $(\delta_s - \delta_r)$ to be constant.

Table 22 shows that the larger V_s , the lower the amount of swelling (the higher v_r , the lower the swelling). This is opposite to what was observed in the present study, a very surprising result. It must be, that differences between the solubility parameters of solvent

and rubber overrule the molar volume effects of the solvents. As it turns out, the higher the molar volume of the solvents, the closer is their value of the Hansen solubility parameter to that of the EPDM rubber studied here: 16.54 [MPa], either coming from above or below, depending on the class of solvents. This seems to be an accidental circumstance. It is worth to investigate this in more depth.

Swelling of EPDM in alkanes

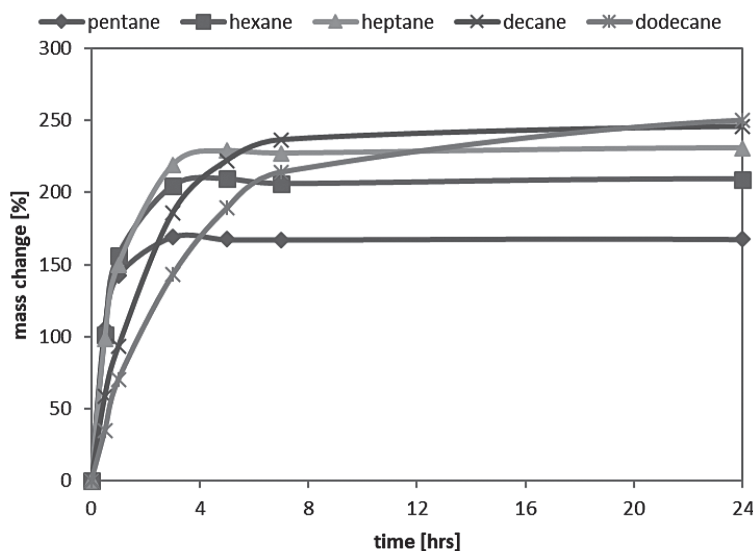


Figure 27. Changes in mass vs. time for immersion of EPDM-rubber in alkanes
Rys. 27. Zmiana masy EPDM w czasie, na skutek zanurzenia próbki w alkanach

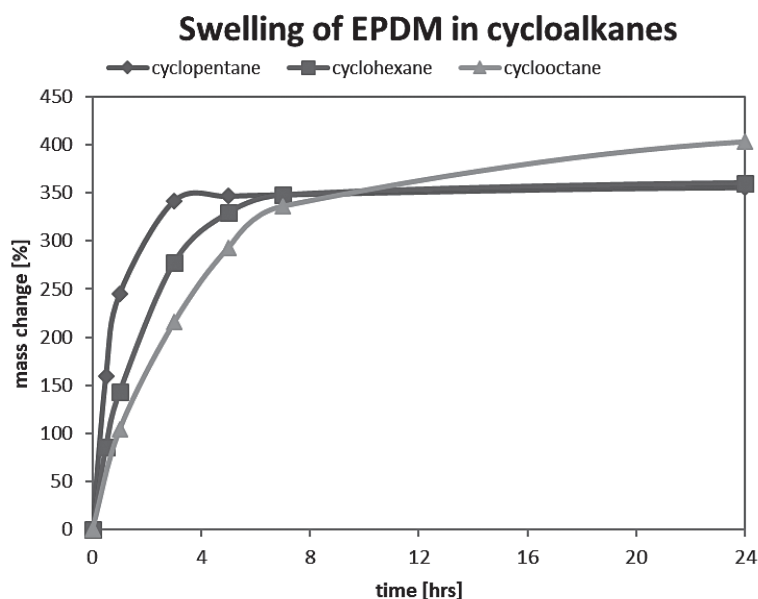


Figure 28. Changes in mass vs. time for immersion of EPDM-rubber in cycloalkanes
Rys. 28. Zmiana masy EPDM w czasie na skutek zanurzenia próbki w cykloalkanach

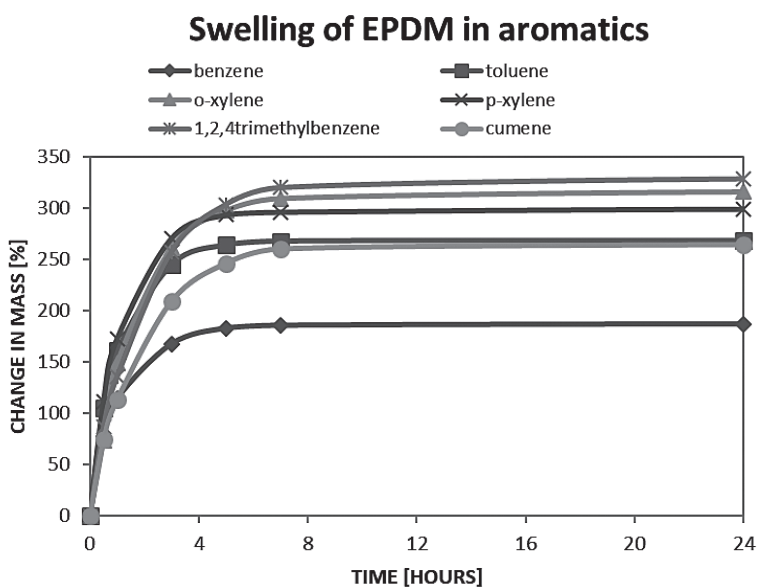


Figure 29. Changes in mass vs. time for immersion of EPDM-rubber in aromatics
Rys. 29. Zmiana masy EPDM w czasie, na skutek zanurzenia próbki w węglowodorach aromatycznych

Table 23. Hansen solubility parameter values for 3 representative solvents, their molar volumes and mass changes in swelling
Tabela 23. Parametry rozpuszczalności Hansena dla 3 reprezentatywnych rozpuszczalników, ich objętości molowe i zmiany masy próbek w wyniku pęcznienia

	δ_{HSP} [MPa ^{1/2}]	δ_d	δ_p	δ_h	V_s [cm ³ /mol]	Mass change [%]
cyclooctane	17.50	17.50	0	0	134.54	404
o-xylene	18.10	17.80	1.0	3.1	120.77	314
n-dodecane	16.00	16.00	0	0	227.11	253

N-alkanes, which are puckered in nature, present larger surface area than cycloalkanes or aromatics, the latter planar in shape. Hence it is more difficult for linear alkanes to penetrate a composite than annular

compounds with the result that the solvent uptake is less for alkanes. Differences between aromatics and cycloalkanes, which have almost the same sizes can be ascribed to the components of the Hansen solubility

parameter, which contains the energy from dispersion, polar, and hydrogen bonding interactions, as described in Chapter 3.4 in part I of this series, as shown in Table 23 for three representative solvents.

Regarding the aromatic molecules, the effects of polar and hydrogen bonding interaction need to be considered, which can counteract swelling (in comparison with cycloalkanes) in the case of the non-polar EPDM elastomer.

6. Conclusions

Sorption experiments of solvents in elastomers provide valuable information on the transport characteristics of the polymer composite, i.e. at what rate the liquid diffuses into the polymer matrix. The rates of the solvent swelling of a crosslinked EPDM sample have been measured in 16 organic solvents at various temperatures. The solvents mass uptake changed in order of:

cycloalkanes > aromatics > alkanes.

Alkanes and cycloalkanes are the least polar – no hydrogen bonding, electronegative atoms, polarizability and the net dipole moment is small at best, in comparison with aromatic molecules, what influences the interaction with the EPDM rubber and then its swelling behavior.

Application of the Flory–Rehner equation for the determination of the solubility parameter of EPDM-rubber is rather uncertain, because this method is very sensitive to changes in the molar volume of the various solvents employed. A better way to determine the solubility parameter of the rubber is observation of its swelling behavior in mixtures of different solvents.

In a mixture of solvents, with similar and different molar volumes, the respective components are absorbed by the rubber in the same volume concentration ratio as they were mixed. So, no preferential adsorption of one of the respective solvents occurs, as seen in the headspace gas chromatography investigation.

By mixing two solvents with different interactions towards the EPDM-rubber it is possible to shift the average solubility parameter of the mixture closer to the rubber and then get higher solvent mass uptake than for the pure components. This is observed in this study in case of the symmetric mixture of 25% of *o*-xylene and 75% of cyclooctane at 22 °C, where the value of equilibrium swelling reaches a maximum.

The results show that the extents of the swelling for the pure solvents are nearly independent of temperature within the range studied here (20–80 °C). Thermodynamically this requires that equilibrium swelling occurs with a near-zero enthalpy, as generally required for absence of a temperature effect on equilibrium. This conclusion is consistent with other results [7]. In case of solvent mixtures at higher temperature, the solubility parameter becomes lower, but also that of the rubber, which only has a small effect on the swelling volume.

As temperature increases, the solvent molecules can move faster and therefore, the speed of diffusion and swelling will increase. On the other hand, molecules can move also faster when their molar volume is smaller. However, concerning the equilibrium swelling the effect of the molar volume is different in comparison with previous investigations, i.e. the higher the molar volume, the higher the solvent mass uptake. On considering the Flory–Rehner equation, for a higher molar volume a lower amount of solvent adsorption will be observed, if differences in solubility parameters are neglected. But as seen in this study, the interaction between rubber and solvent is the most sensitive and valuable parameter, which determines most prominently the swelling ratio. For the three classes of solvents investigated the solubility parameter approach that of the EPDM-elastomer, the higher their molar volumes, and consequently the degree of swelling increases. Whether this is a coincidental effect of the choice of solvents in the present study is worth closer consideration.

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