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Impact of the acetone/DMSO binary solvent on porosity of epoxy polymer films

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Effect of mixed acetone/dimethyl sulfoxide solvent composition on morphology of porous epoxy polymer films obtained by chemical solution deposition method was studied. Total and surface porosity of the polymer films as well as the size of open pores were determined using FTIR spectroscopy and SEM techniques. It was revealed that the choice of the solvent composition is a key factor affecting the porosity of the polymer films. It was shown how varying the composition of the binary acetone/dimethyl sulfoxide solvent in a wide range of concentrations affects the rheology and characteristics of the porous polymer films. The obtained results allow to influence both the overall porosity of the polymer films and the size of the formed pores.

Keywords: porosity, epoxy polymer, mixed acetone/DMSO solvent, thermodynamic affinity, polymer film.

Вплив бінарного розчинника ацетон/ДМСО на пористість епоксидних полімерних плівок. *А.Дунаєва, Д.Мішуров, С.Дукаров, О.Рошаль*

Досліджено вплив складу змішаного розчинника ацетон — ДМСО на морфологію пористих полімерних плівок на основі епоксидного полимеру, створених методом хімічного осадження з розчину. Загальну та поверхневу пористість полімерних плівок, а також розмір відкритих пор визначали за допомогою спектроскопії FTIR та SEM. Було встановлено, що вибір розчинника є ключовим фактором, що впливає на пористість полімерних плівок. Показано, як варіювання складу бінарного ацетон — ДМСО розчинника в широкому діапазоні концентрацій впливає на реологію та характеристики пористих полімерних плівок. Отримані закономірності дають можливість впливати як на загальну пористість полімерних плівок, так і на розмір утворених пор.

1. Introduction

In recent decades, the popularity of porous thin-film materials has grown rapidly. Thin porous polymer films are widely used as various functional applications [1–5]. Despite the fact that such materials have been developed quite a long time ago, research on synthesis of the new porous polymeric films with a set of specific properties, as well as the search for the new areas of such film application is being actively conducted today.

Polymer porous films with nano-size pores, are among the most promising materials. They are widely used due to their effective functional and mechanical characteristics, and low thickness compared to the porous systems composed of inorganic substances. That explains the key role of such film materials usage in the high-tech industry. Besides, the application of these materials is also an effective way to solve the problem of miniaturization and to reduce the material consumption for devices of various purposes. That is why, one of the top priority in this research area is the search for an optimal method for obtaining

the polymer porous films, that allows to control effectively the number and size of the pores in the films. The control of these parameters, in turn, can result in increase the films functionality during their use.

At present, various methods to obtain the thin polymer porous films are developed [6–8]. These methods allow to create the porous film materials of different permeability, common porosity, bulk structure, and having various sizes of the pores, physico-mechanical and chemical properties. The film properties are influenced by many factors depending on some technological parameters [9–11] that must be taken into account when the new polymer porous systems are developing.

One of the most effective way for the polymer porous films obtaining is the chemical solution deposition (CSD) method. CSD method is relatively simple and may be carried out at ambient temperatures. In this method, the control of the porous structure of the formed polymer films is performed by selecting a certain individual or mixed solvent [10, 12]. The choice of one or another solvent or solvents mixture is based on its thermodynamic affinity to the polymer that can be characterized by the Hansen solubility parameters (HSP) [13].

The HSP is a very useful experimental tool allowing to affect the porosity of the polymer films obtained using the CSD method [14, 15]. Varying the HSP parameters of a binary solvent by changes in a ratio of its components over a wide range, one is able to control the size and number of pores in the polymer films [10]. The purpose of the present work is to study the features of the formation of the supramolecular and porous structure of films based on an epoxy polymer using a binary solvent containing different ratios of acetone and dimethyl sulfoxide (DMSO).

2. Experimental

2.1. Materials

Bisphenol A liquid diglycidyl ether (DGEBA) was used to prepare epoxy polymer (520 epoxy, Spolchemie, with epoxy equivalent weight of 184). Diethylenetriamine (DETA, Dow Chemical) was used as a hardener. Commercial acetone and dimethyl sulfoxide (DMSO) — components of the binary solvent were purified before use.

2.2. Polymer films preparation

Thin films for the study were obtained by chemical deposition method from DGEBA solution in binary solvent DMSO:acetone with ratios of components (v/v): 10:90; 20:80; 30:70; 40:60; 50:50. First, 0.1 g/mL DGEBA solutions in all the binary solvent with mentioned DMSO:acetone ratios were obtained. Then, DETA was added into each solution to achieve a stoichiometric ratio of DGEBA/DETA equaled to 10:1 w/w.

Glass microscope coverslips of 170 mm thickness used as a substrate for the polymer films were cleaned by sonication in detergent solution for about 10 min. Then, they were rinsed in deionized water and boiling ethanol, and finally dried at 90°C for 10 min.

Thereafter, the thin films were spin-coated onto the pre-cleaned coverslips at 1000 rpm for 0.5 min and cured at the room temperature for 24 h in vacuum. To remove residual acetone, the polymer films were then annealed for 3 h at 100°C [16]. To remove residual DMSO, the polymer films were washed in distilled water for 72 hours at 25°C using a magnetic stirrer. Presence of the residual solvents traces in the polymer films was monitored using FTIR spectroscopy. Quantification of the residual solvent was based on the values of optical density at 1710 cm^{-1} [16] and 1130 cm^{-1} in the absorption band maximum of acetone carbonyl group stretching and S=O group in DMSO, respectively. The thickness of the obtained polymer films was 1.0 mm.

2.3. Polymer films characterization

FTIR spectra were registered by a Spectrum One (Perkin Elmer) Spectrophotometer in the range of 400–4000 cm^{-1}. Photomicrographs of the polymer film surfaces were obtained using scanning electronic microscopy (JSM JEOL Model 840) with operating voltage of 20 kV. Since the polymer films under investigations are dielectrics, the preliminary vacuum deposition of electrically conducting chrome layer of 100 nm thickness on the films surfaces was made. The obtained experimental data are presented in Table 1. The thickness of the polymer films was measured using a Linnik type interference microscope MII-4. The Linnik interferometer configuration (a kind of Michelson configuration) was described in [17].

3. Results and discussion

3.1. Determination of thermodynamic affinity of mixed solvent acetone-DMSO and epoxy polymer using Hansen solubility parameter

As noted above, one of the most common methods for porous thin polymer films obtaining is techniques for the polymer deposition from solutions containing solvents of various nature. In this case, the solubility of the polymer plays a decisive role [18].

Table 1. Hansen solubility parameters for mixed acetone/DMSO solvent

Ratio of co-solvents, v/v		dD_S, MPa$^{1/2}$	dP_S, MPa$^{1/2}$	dH_S, MPa$^{1/2}$	R_a	RED
acetone	DMSO					
100	0	15.5	10.4	7.0	4.3	0.86
90	10	15.8	11.0	7.3	3.7	0.73
80	20	16.1	11.6	7.6	3.2	0.63
70	30	16.4	12.2	8.0	2.8	0.56
60	40	16.7	12.8	8.3	2.8	0.56
50	50	16.9	13.4	8.6	3.1	0.62
40	60	17.2	14.0	8.9	3.5	0.70
30	70	17.5	14.6	9.2	4.1	0.82
0	100	18.4	16.4	10.2	6.3	1.27

The formation of a polymer phase during the monomer polymerization first leads to phase separation in the polymer-solvent system, and consequent removal of the solvent causes the formation of micropores in the polymer film formed [19].

Obviously, a necessary condition of tuning the size and number of pores in the polymer films is the possibility to change in the polymer solubility, which is easy to achieve using mixed solvents consisting of "good" and "bad" components in different ratios.

In the previous section, we noted that synthesis of the thin epoxy polymer films was carried out in two-component mixtures containing acetone (as a "good" solvent) and dimethyl sulfoxide (as a "bad" solvent).

In our opinion, the most important step responsible for micropores formation is a first stage of the polymer synthesis, when forming the aggregates of macromolecules, and appearing the polymer phase in the solution. The aggregation level and structure of the aggregates formed depend on the solubility of the polymer in the mixed solvent used.

Following curing the polymer phase leads to cross-linking the macromolecules and their further aggregation. Following washing and drying of the films results in removal of the components of the mixed solvent from the pores. This last stage of the polymer film formation is unlikely to significantly affect the rheology of the polymer phase.

Solubility of the epoxy polymer in the mixed solvent containing various ratios of acetone and DMSO, as well as the subsequent establishment of a relationship between the composition of the mixed solvent and the porosity of the resulting films were evaluated using the Hansen solubility parameters [20].

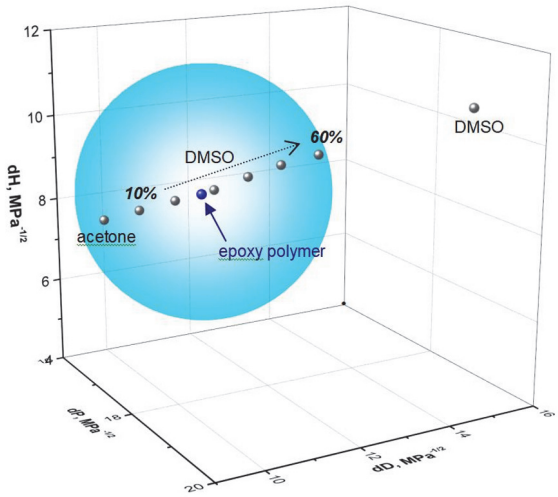

Fig. 1. Hansen space positions for epoxy polymer (blue bullet) and solvents (grey bullets) in coordinates dD (dispersion parameter), dP (dipole-dipole polar interaction parameter), dH (hydrogen bonding parameter). The radius of a blue sphere corresponds to R_0 parameter for the epoxy polymer.

As is known, any solute and solvent can be characterized by the four empirical Hansen parameters. Three of them — dD, dP and dH describe, respectively, an influence of dispersion, dipole-dipole interactions and hydrogen bonding. The differences in corresponding parameters for two substances characterize their physical affinity and, accordingly, their mutual miscibility or solubility. In a graphical interpretation, dD, dP and dH values are coordinates of the point in the 3D so-called Hansen space. The fourth empirical parameter, R_0, is the radius of the sphere centered at that point. A greater overlap of the spheres of the components indicates their greater affinity and, accordingly, solubility [18].

Figure 1 shows the relative position of the sphere, whose position and size correspond to dD_P, dP_P, dH_P and R_0 parameters of the epoxy polymer (of uncrosslinked structure) [18]. Points with coordinates dD_S, dP_S, dH_S for acetone and dimethyl sulfoxide and their mixtures are also presented in Fig. 1.

Mathematically the miscibility can be characterized with a solute/solvent affinity parameter R_a calculated according to the equation [15]:

$$R_a = \sqrt{4(dD_S - dD_P)^2 - (dP_S - dP_P)^2 - (dH_S - dH_P)^2},$$

For the solubility estimation, the value RED can be used [15]:

$$RED = \frac{R_a}{R_0}.$$

When $RED > 0$, the solvent is classified as "bad", when $RED < 0$ — as "good".

The values of the Hansen parameters dD_P, dP_P, dH_P and R_0 for epoxy resin based on DGEBA were taken from [15, 21, 22], and equal, correspondingly, to 17.4 $MPa^{1/2}$; 10.5 $MPa^{1/2}$; 9.0 $MPa^{1/2}$ and 5.0 $MPa^{1/2}$. Similar parameters for the mixed solvent were calculated according to the algorithm published in [23]. They are listed in Table 1.

The analysis of the RED values shows that epoxy resin has the best solubility in the mixed solvents containing from 20 % to 50 % vol. of DMSO. In pure acetone, the affinity of the polymer to the solvent is lower than that in the mixtures. At the same time, pure DMSO can be classified as a "bad" solvent for epoxy resins.

The similar conclusion can be formulated from Fig. 1. It can be seen that the point corresponding to DMSO is out of the affinity sphere that allows to classify DMSO as a "bad" solvent for epoxy resin [20], where the solubility of the latter is lower than in the acetone/DMSO mixtures. It is worth to note that pure acetone also does not demonstrate a high affinity to the polymer, and the maximal solubility is typical for the mixed solvent containing 30–40 % vol. of DMSO.

The relationship between polymer solubility in the binary acetone/DMSO solvent and porosity of the obtained films is discussed in the following sections.

3.2. Determination of total porosity and pores size of polymer films by FTIR spectroscopy

The relative porosity of the obtained films was estimated using IR spectroscopy by the changes in the optical density of the samples. According to previously described methods [4–26], one carries out measurements in bands with minimal transmittance. Therefore, for the studied samples, the transmittance values were determined at 1250 cm^{-1} that corresponds to the characteristic band of the C–O–C ether group valence vibrations. IR spectra of the polymer films obtained from the solutions with different ratios of acetone and DMSO are shown in Fig. 2.

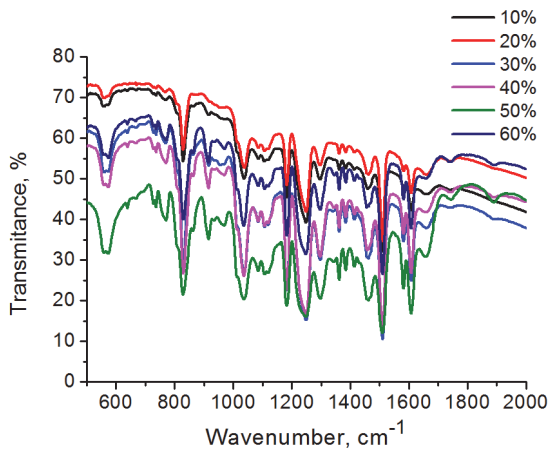

Fig. 2. FTIR spectra of epoxy polymer films obtained from mixed solvent acetone/DMSO with different DMSO concentrations.

On the one hand, the presence of pores leads to a decrease in the bulk density of the films and, as a consequence, to a decrease in the volume concentration of IR-absorbing groups of the polymer. The last, in turn, results in a decrease in optical density of the samples [24]. Thus, an increase in porosity should lead to an increase in the transmittance of the films and a decrease in the intensity of mentioned absorption band.

However, on the other hand, the increase in porosity should also lead to the opposite optical effect: a growth in optical density due to increased scattering of the IR beam in the polymer layer. Therefore, in contrast to works [24–26], we previously separated two mentioned effects using the baseline method, for which we additionally measured the transmission values in the regions of maximum transparency of the films: at 700 cm^{-1} and 2000 cm^{-1} — T^b_{700} and T^b_{2000}.

Considering the baseline in the IR range to be linear, we calculated the background transmittance at 1250 cm^{-1} (T^b_{1250}) using the least squares method, and the resulting value (responsible for light absorption due to dispersion effect) was subtracted from the experimental transmittances measured at 1250 cm^{-1}. According to [24] transmittance

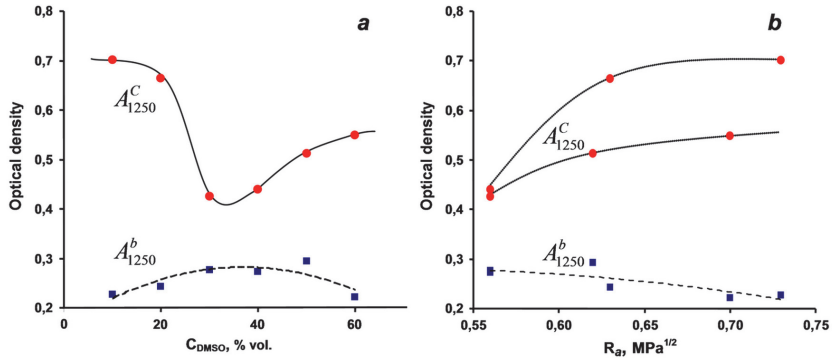

Fig. 3. Dependence of optical density due to ether absorption A^C_{1250} and due to light A^B_{1250} dispersion on volume concentration of DMSO in acetone — CDMSO (a), and on Hansen parameter R_a (b).

values should be transformed to extinction coefficients. However, since the layer width of all the studied films was always 1 μm, the corrected transmission value was converted further to optical density.

Plots of the optical density in the absorption band of the ether fragment A^C_{1250}) and background optical density (A^B_{1250}) against mixed solvent composition are depicted in Fig. 3a.

As can be seen, the weakest absorption of the ether groups and, accordingly, the maximal porosity of the polymer film are observed when obtaining the epoxy resin in the solvent containing 30–40 % vol. of DMSO. With a further increase or decrease in the DMSO concentration, the porosity of the film decreased. Minimal porosity is typical for polymer films obtained from mixtures containing low concentrations of a "bad" solvent.

A dotted curve in Fig. 3b shows that the values of the background optical density due to scattering are maximal when using the mixed solvent with 30–50 % vol. of DMSO. Thus, the maximum light scattering and, accordingly, the maximum porosity, estimated from background optical densities, demonstrate approximately the same results as those obtained from the absorption of ether groups.

The parameter α used as a measure of relative porosity was calculated according to the equation:

$$\alpha = \frac{A^{\max}{}_{1250} - A^C{}_{1250}}{A^{\max}{}_{1250}},$$

where $A^{\max}{}_{1250}$ is the optical absorption of a film of minimal porosity, $A^C{}_{1250}$ optical absorption of films obtained from binary solvent with different ratio of components.

As $A^{\max}{}_{1250}$ value for α calculations the optical density of the film obtained from the solvent containing 10 % vol. DMSO was used. The plot of α aginst binary solvent composition is depicted in Fig. 4a. It can be seen that a maximal porosity about 40 % is typical for the mixed solvent containing 30–35 % vol. DMSO.

The dependence of the polymer film absorbance $A^C{}_{1250}$ on the Hansen parameter R_a depicted in Fig. 3b shows a general trend towards increase in the porosity of the obtained films with increase in the affinity of the solvent to the polymer. However, as can be seen from the figure, the experimental points form two separate dependences for binary solvent with high and low DMSO content. This suggests that the affinity between the polymer and the binary solvent, characterized by the parameter R_a, is not the only factor affecting the porosity of the obtained samples.

The same conclusion can be made for a plot in Fig. 4b demonstrating the interplay between the relative porosity α and the R_a parameter. It can be seen that the porosity of the polymer films decreases with the decrease in solvent-polymer affinity, however this effect is more dramatic for the binary solvent with low DMSO content.

In our opinion, the observed dependency of polymer porosity on the binary solvent composition and the Hansen parameter Ra is due to at least two main reasons. The first one, already mentioned above, is the level of affinity of the binary solvent to the polymer when obtaining the latter.

It is obviously that with increase in average molecular weight of a polymer during its synthesis, the solubility of this polymer decreases. The rate of the solubility fall depends on the affinity between solvent and solute.

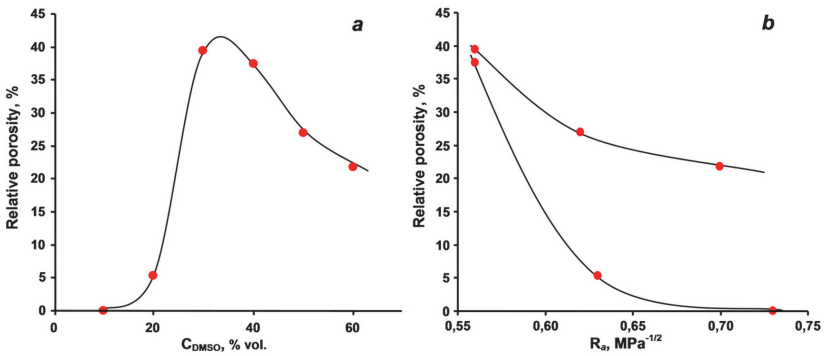

Figure 4. Dependence of relative porosity on volume concentration of DMSO in acetone ›– C_{DMSO} (a), and on the Hansen parameter R_a (b).

In the solvents with lower affinity to the polymer, the solubility decreases faster, and the formation of the polymer phase begins at low polymer concentrations. In this case, by the end of the synthesis, macromolecules form large aggregates with a small surface area and a narrow solvation shell that explains the formation of a dense network when cross-linking at high-temperature curing.

In solvents with the high affinity to the polymer, where the latter has a higher solubility, the aggregates form at later stages of synthesis. When finishing the reaction, such aggregates have a smaller size, a larger surface area, and consequently a solvate shell of larger volume. In this case, the resulting polymer is less cross-linked and the polymer phase must contain a larger amount of the solvent, after removal of which a greater number of pores is formed.

We can see that the maximal porosity is typical for the polymer, when it was obtained in the binary solvent containing 30–40 % vol. of DMSO and having the affinity to the epoxide polymer with $R_a = 0.56$.

The second reason explaining the observed dependency of the polymer porosity on the binary solvent composition is peculiarities of the solvent removing from the polymer phase. When curing the polymer films at 100°C, acetone (T_b = 56°C) diffuses and evaporates from the polymer phase. A high boiling DMSO (T_b = 189°C), which has low affinity to the epoxy polymer remains there as a separate solvent phase. After formation of the polymer films, DMSO is extracted by water freeing additional pores. This explains why the polymer films obtained from the binary solvent of similar R_a — with 20 % vol. and 50 % vol. of DMSO have different porosity, the higher one in the latter case.

3.3 Determination of open pores distribution in polymer films using SEM method

Another important characteristic of porous materials is the size of open pores, i.e., pores which are in contact with the polymer film surface. The number and size of the pores determine the surface area, which directly affects the functionality of the polymer films (for example, when they used as contact polymer sensors or catalysts). Surface porosity analysis was carried out using SEM microscopy. The resulting micrographs are shown in Fig. 5. As seen from the microphotographs, a change in the ratio of acetone and DMSO in the binary solvent drastically affects the distribution and parameters of the pores.

The parameters of the open pores, such as their average transverse area, average diameter and number of the pores per unit area of the polymer film, are listed in Table 2.

Graph plots of the porosity characteristics of the polymer films and the average pore parameters against the composition of the binary solvent are depicted in Fig. 6.

As shown in Fig. 6a, the number of the pores on the surface of the films increases sharply when the polymer is obtained from the binary solvent having maximal affinity to the polymer and containing 30–40 % vol. DMSO. This conclusion is in a good agreement with the results obtained by IR analysis of the film porosity.

The dependence of the pore concentration on the Hansen affinity parameter R_a (Fig. 6b) can be described by a power function that demonstrates sharp increase of porosity with increasing of the solvent-polymer affinity. In the case of low affinity, the polymer films demonstrate always the low porosity regardless the composition of the binary solvent.

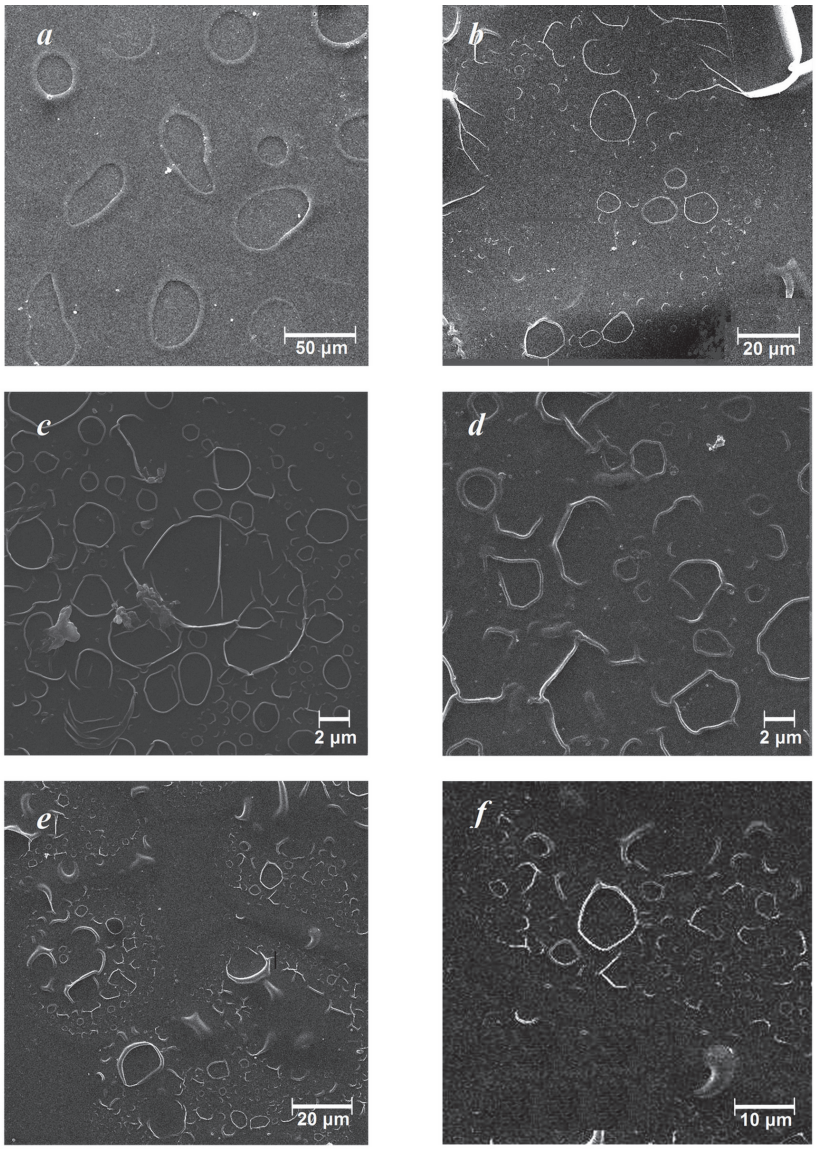

Fig. 5. Microphotographs of polymer films obtained from binary solvent acetone/DMSO containing a — 10 % vol., b — 20 % vol., c — 30 % vol., d — 40 % vol., e — 50 % vol., f — 60% vol. of DMSO.

Table 2. Geometrical parameters and surface distribution of the open pores in polymer films obtained from binary solvent with different ratios of acetone and DMSO

DMSO content, % vol.	Number of pores per 10^3 μm^2 of the film	Total transverse pore area relative to the entire film area (S_R), %	Average cross-sectional pore area, μm^2	Average pore diameter, μm
10	0.2	14.2	1181.6	38.8
20	5.2	15.2	29.4	6.1
30	42.3	28.9	6.8	3.0
40	50.2	28.3	5.7	2.7
50	6.5	11.2	15.6	4.5
60	2.5	9.1	36.8	6.8

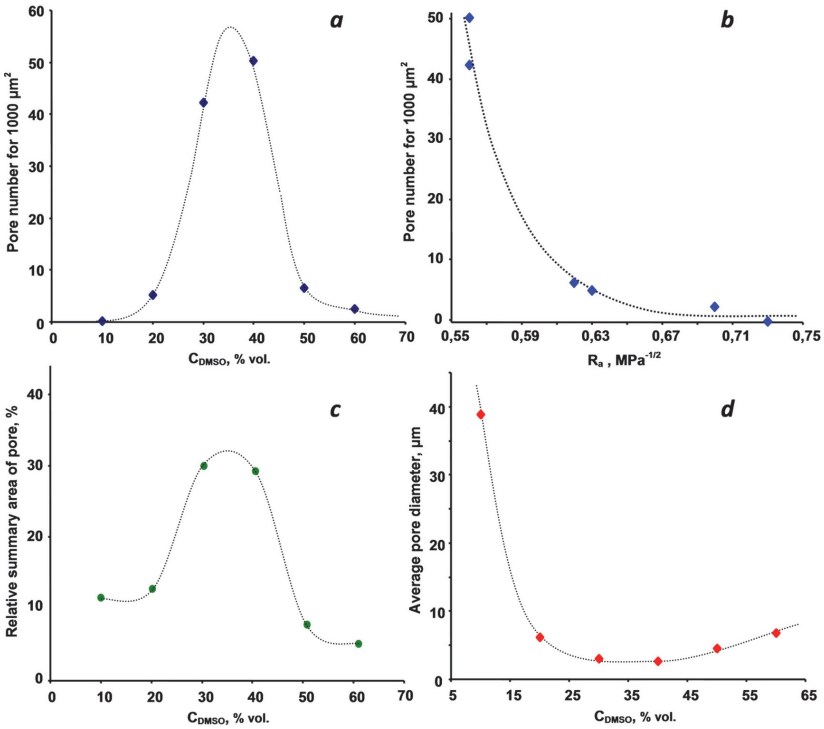

Fig. 6. Dependencies of the polymer films porosity parameters obtained by microscopic method on solvent composition. a and b — number of pores for 10^3 μm^2 of surface against DMSO content and R_a Hansen parameter, correspondingly; c and d — relative total transverse pore area (SR) and average pore diameter against DMSO content, correspondingly.

Another parameter characterizing the porosity of the films is the relative total transverse pore area — S_R, which is the ratio of the total transverse pore area to the total surface area of the film (or the area of the site on which the number of pores and their geometrical parameters were counted). As shown in Fig. 6c, the obtained dependence of S on solvent composition basically repeats that in Fig. 6a, that indicates a relationship between the S_R parameter and the pores number. The linear correlation coefficient between these parameters reaches 0.95 that is possible only at approximately the same average pore diameter. As shown in Fig. 6d, in most cases, the pore size does not change significantly with the solvent composition, ranging from 3 to 7 μm.

Some indirect conclusions about the pores structure can be made when comparing the surface concentration of the open pores obtained by SEM microscopy and the total porosity α calculated from their IR spectra. The first parameter is related to the pore diameter, while the second one depends on its volume.

For the binary solvent containing from 10 to 40 % vol. of DMSO, there is a strict linear relationship ($R = 0.997$) between the total porosity of the films (Table 1) and the surface concentration of the open pores (Table 2). This indicates the similarity of the pore geometry in all the films obtained. However, the films obtained from the mixed solvent with 50–60 % vol. of DMSO the porosity (in bulk) remains quite substantial in spite of a dramatic decrease in concentration of the open pores on the film surface. This can evidence the changes in the pores geometry, particularly the increase in the pores length at simultaneous decrease in their cross-section diameter.

4. Conclusion

The studies performed have shown that the use of binary acetone/DMSO solvent with different affinity to the polymer is an effective way to control the porosity of epoxy polymer films and, accordingly, to tune their physico-chemical properties. The dependence of the polymer porosity on composition of the solvent, in which the polymer forms, is mostly determinates by different solubility of the polymer. By this way, the solvent governs the formation rate of the polymer phase, which, in turn, affects the sizes of aggregates formed at the final stage of the synthesis.

The ability to use the solubility Hansen parameters to adjust the polymer films porosity not only opens a simple way for optimizing the physico-chemical properties of the porous polymer materials, but also provides a rational and generalized way of the design and obtaining the new materials for wide applications with the fully tunable functionality.

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