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Kinetics and Peculiarities of Polyamide Coatings Formation from Solutions

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Peculiarities of diffusion in 10 % methylolpolyamide (PFE) solution of various solvents (ethanol, butanol, water) and coatings formation were investigated. Dispersion and polar components of surface energy were determined ($\gamma_d = 21.6$ and $\gamma_p = 30.8$ mJ/m^2) together with polymer solubility index δ for which solvents absorption method was applied. Based on the laws of thermodynamics the surface energy of solvents was determined, components of which were used to determine interphase stresses in solution γ_{ij} between i and j components. Interphase stresses in their turn were used to calculate phase interaction changes when polymer solution is diluted using solvent, interaction of which with polymer solution is not known beforehand. Solvents diffusion coefficients were found and their dependences on solvent concentration were established for solvent diffusion in polymer solution. Stages of drying of the methylolpolyamide coating – free solvent evaporation, quasi-stationary and diffusion processes were established. The indices, application of which enables to forecast coating drying time, were found.

Keywords: polyamides, solvents, surface energy, phase interaction, kinetics of desorption.

INTRODUCTION

To form polymer coatings from solutions solvents mixtures are used which are chosen (mostly by testing) and mixed in proportions ensuring the formation of coatings with the best properties using simple technology [1 – 3]. Drying duration, internal stresses, adhesion and other coatings properties depend on a solvent type and on mixture proportions. Among polyamides, only few are known, which dissolve in organic solvents, mostly alcohols. Polyamide coatings are characterized by weak adhesion and their application is specific enough. They are suitable for the short-time metal surface protection (conservation), deactivation in "dry manner" and other purposes [4, 5]. These coatings can be easily peeled off also from other surfaces, for this reason they are widely used [6].

The objective of this work is to substantiate possibility of usage of solution mixtures for polyamide coatings formation and to investigate kinetics of the polyamide coatings formation.

APPLICATION OF THERMODYNAMIC INDICES FOR EVALUATION OF THE POLYMER-SOLVENT INTERACTION

Use of thermodynamic laws for research of polymers frequently is successful although without explaining the mechanism of the solvent action. The interface polymer-solvent does not match the classic phase concept as it forms between the polymer macromolecule and solvent molecules. If polymer has polar groups, the solvation of solvent polar groups is possible because of the donor-acceptor interaction. Solvation is also possible because of strong dispersion forces. The solubility of polymer is determined by cohesion energy difference of separate components. If polymer is dissolved in one solvent and second solvent is added, the first desorption condition [7, 8] is:

$$\gamma_{13} + \gamma_{23} - \gamma_{12} > 0 , \qquad (1)$$

where γ_{13}, γ_{23}, γ_{12} is the interaction energy between polymer (1) and solvents (2, 3) respectively.

Energy of the interphase interaction is evaluated, if for each component polar and dispersion constituents of surface energy are known. However, for most solvents they are unknown. They can be found from analytical link between the solvent surface energy and its solubility parameter. Hildebrand-Wood obtained following dependence [9]:

$$\gamma_i = 0.039 \cdot \delta_i^{2,3} \sqrt[3]{V_i} , \qquad (2)$$

here γ_i is the surface energy, δ_i is the solubility parameter, V_i is the molar volume.

The parameter δ_i of solvents may be resolved into components: dispersion (δ_d), polar (δ_p) and hydrogen bond (δ_h). Then it may be expressed through components by following dependence [10]:

$$\delta_i^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 . \qquad (3)$$

As the surface energy is additive quantity, from equations (2) and (3) we have:

$$\delta_i^{2,3} = \delta_d^{2,3} + \delta_p^{2,3} + \delta_h^{2,3} .$$

Thus, the equation (2) is not suitable for determination of γ_i components from δ_i components. From the lattice theory of liquids a linear dependence, linking δ_i^2 and γ_i, is obtained [11]:

$$\gamma_i = k\delta_i^2 \sqrt[3]{V_i} \big/ \sqrt[3]{N} , \qquad (4)$$

where k is the coefficient, N is the Avogadro Number.

After substitution of N the equation (4) can be written:

$$\gamma_i = 0.12k\delta_i^2 \sqrt[3]{V_i} = k_0\delta_i^2 \sqrt[3]{V_i} , \qquad (5)$$

where γ_i is measured in mN/m, δ_i^2 – MJ/m^3 and V_i – 10^{-6} m^3/mol respectively.

The coefficient k depends upon solvent molecular structure. For example, the coefficient k_0, calculated from

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the equation (5) for aliphatic alcohols using the values γ_i , δ_i taken from [10], depends upon the number of CH_2 groups in the molecule (Fig. 1).

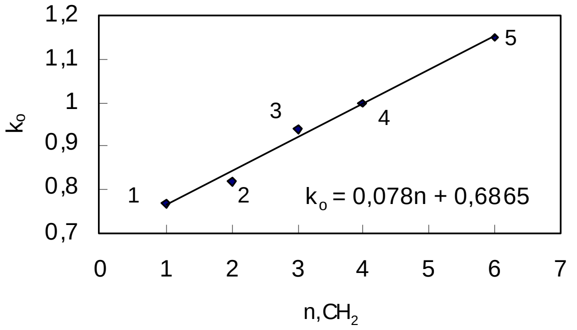

Fig. 1. Dependence of coefficient k_0 of aliphatic alcohols on CH_2 groups number in the molecule: 1 – methyl-, 2 – ethyl-, 3 – propyl-, 4 – butyl-, 5 – amyl- alcohols

Lately, the surface energy is more and more often treated as consisting from dispersion, Lifshitz-van der Vals (γ_i^{LW}) and acid-base (γ^{AB}) interaction [12, 13]. The acid-base interaction is actually acceptor-donor interaction of electrons. An example of such interaction is hydrogen bond between mobile hydrogen and oxygen atoms in alcohols and esters. Thus, γ^{AB} – component should be close to γ_h-component. For example, in case of water $\delta_h = 42.4$ $(MJ/m^3)^{1/2}$, $\gamma = 72.1$ mN/m, $k_0 = 1.23$ and calculated from eq.(5) $\gamma_h = 58.0$ mN/m. In some publications value $\gamma^{AB} = 51.0$ mN/m [14].

METHODS OF INVESTIGATION

Polymer 10 % methylolpolyamide (PFE) solutions in ethanol, butanol, their mixtures and ethanol-water mixtures were investigated. The mixture constituents are indicated by their volume part ratio. The mass losses and evaporation from polymers solutions rates were established using derivatograph made by the MOM firm (Hungary) from the forms of TG and DTG curves. Initial solution mas was 0.2 g and surface area was 4 cm^2.

Dispersion and polar components of the polymer surface energy are not known. They were found using the method of “droplet” by solving the two-equation system [7, 8]:

$$\frac{\gamma_2(1+\cos\theta)}{2\sqrt{\gamma_{2d}}} = \sqrt{\gamma_{1d}} + \sqrt{\gamma_{1p}} \cdot \sqrt{\frac{\gamma_{2p}}{\gamma_{2d}}} , \qquad (6)$$

where γ_2, γ_{2p}, γ_{2d} are common, polar and disperse components of the surface energy, γ_{1d}, γ_{1p} are dispersion and polar components of the surface energy of material investigated, θ is the wetting angle.

The droplets of water ($\gamma_d = 21.8$, $\gamma_p = 51.0$ mJ/m^2) and formamide ($\gamma_d = 39.0$, $\gamma_p = 18.9$ mJ/m^2) were used. It was found that for PFE $\gamma_d = 21.6$, $\gamma_p = 30.8$ mJ/m^2. The values of surface energy components are averaged values after measuring geometries of 10 sessile droplets for wetting angle θ calculations.

Interphase stresses in solution between i and j components were defined from the equation [7, 8]:

$$\gamma_{ij} = \left(\sqrt{\gamma_{id}} - \sqrt{\gamma_{jd}}\right)^2 + \left(\sqrt{\gamma_{ip}} - \sqrt{\gamma_{jp}}\right)^2 . \qquad (7)$$

The solubility index of methylolpolyamide was determined by solvents absorption method. It is equal to 26.3 $(MJ/m^3)^{1/2}$.

EXPERIMENTAL RESULTS AND DISCUSSION

Surface energy components of solvents, calculated for methylolpolyamide solutions using the equation (5), are presented in Table 1.

Using γ_d and γ_a values and the equation (7) the values of γ_{ij} were calculated, then using them and the equation (1) also value of the phase interaction change was found, when a polymer solution is diluted by a solvent, effect of which on the solution (aggregation or coagulation) is not known. Calculation results are presented in Table 2.

Following conclusions may be drawn considering results presented in Table 2:

- Polymer molecules will not absorb butanol only among other solvents being added to the ethanol PFE solution, while other solvents added tend to displace ethanol (because of thermal movement energy);
- Other solvents being added to butanol PFE solution will have a tendency to displace butanol, this would prolong coating drying duration;
- Interaction energies between polymer and solvents are different. The strongest interaction observed is between polyamide and water molecules (because of formation of hydrogen bonds).

It is not possible to define from the interaction of phases, which solvent causes macromolecular aggregation and to define critical in this sense concentrations. However, it is possible to indicate the solvents diluting with which will not cause any aggregation.

In Fig. 2 desorption from methylolpolyamide solution rate variation for some solvents, while the polymer film is formed, is presented. Shapes of these curves are not typical for diffusion process kinetics. For analysis of these shapes

Table 1. Thermodynamic indices of solvents

Solvent	δ_i , $(MJ/m^3)^{1/2}$ [10]	δ_d , $(MJ/m^3)^{1/2}$ [10]	V_i ,10^{-6} m^3/mol [10]	k_0	γ_d , mN/m	γ_a^* , mN/m	γ , mN/m [10]
Ethanol	26.36	15.78	58.50	0.82	7.96	14.36	22.32.
Butanol	23.05	15.93	98.80	0.93	11.56	13.81	24.57
Acetone	19.93	15.46	73.99	1.40	14.05	9.27	23.32
Butylacetate	17.30	15.65	132.50	1.65	20.61	4.59	25.20

$^*\gamma_a = \gamma - \gamma_d$

Table 2. Interaction change value for methylolpolymide solution (*j*) diluted using solvent (*k*), (mJ/m^2)

Main solvent (*j*)	Solvent (*k*)	$\gamma_{jk} + \gamma_{ik} - \gamma_{ij}$
Ethanol	Butanol	–1.2
-"-	Acetone	2.1
-"-	Butyl acetate	4.7
-"-	Water	10.7
Butanol	Butyl acetate	0.3
-"-	Acetone	3.4
-"-	Water	11.0
-"-	Ethanol	1.84

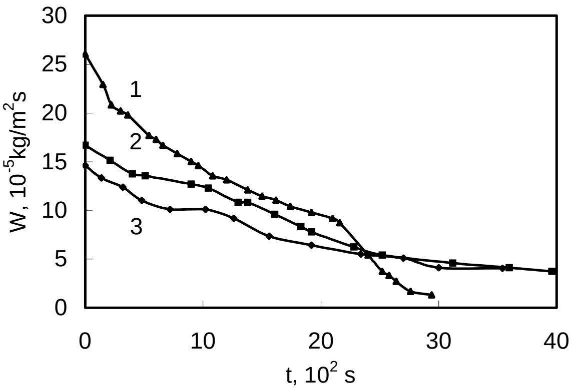

Fig. 2. Solvent desorption rate from 10 % methylolpolyamide solutions with evaporation of: ethanol (curve 1), ethanol and water (4:1) (curve 2) and ethanol + butanol (1:1) (curve 3) mixtures

we can divide the process into several stages: initial, rapid solvent evaporation, transitional and diffusive ones.

The first stage with duration of several to several tens of minutes is determined by the solvent evaporation from the surface, as in this case concentration gradient is equal to zero ($\partial c/\partial x = 0$). Apart from this, not all solvent molecules are linked to polymer molecules. Solvent concentration on the surface varies according to exponential dependence:

$$c(t) = c_0 \exp(-\beta t) \,, \tag{8}$$

where c_0 is the initial solvent concentration, β is the rate constant.

The evaporation rate of solvent is expressed:

$$W = -\frac{\partial c}{\partial t} = \beta c_0 \exp(-\beta t) = \beta c(t) \,. \tag{9}$$

$$\ln W = \ln \beta c_0 - \beta t \,. \tag{10}$$

The values of the evaporation rate constants are presented in Table 3.

Data in Table 3 indicate that application of solvents mixtures enables already in the first stage to vary solvents evaporation rate, drying time and desorption degree. During this period, on the surface of polymer solution a thin film with increased viscosity appears.

For polymer dissolved in solvents mixtures the evaporation rate is the sum of separate solvents evaporation rates $W = W_1 + W_2$. From the equation (9) and with condition $c(t) = c_1(t) + c_2(t)$ taken into consideration, we obtain:

$$\frac{c_1(t)}{c_2(t)} = \frac{\beta_2 - \beta}{\beta - \beta_1} \,, \tag{11}$$

where β, β_1 and β_2 are the evaporation rate constants of solvents mixture and its constituents correspondingly.

Table 3. Kinetic indices of the initial stage desorption of methylolpolyamide 10 % solutions

Solvent	β, 10^{-4} s^{-1}	Stage duration, min	Amount of solvent evaporated, %
Ethanol	5.30	25	55
Ethanol + butanol (4:1)	4.50	10	24
Ethanol + butanol (1:1)	4.66	8	21
Butanol	1.06	55	11
Ethanol + water (4:1)	5.20	7	20
Ethanol + water (3:1)	3.83	10	18

Considering that solvents differ little in density it may be stated that $c_1(t)/c_2(t) = \varphi_1/\varphi_2$ (φ is the solvent volume part in mixture). From the equation (11) and β values presented in Table 3 for polymer solution consisting of ethanol and butanol solvents with volume part ratio 1:1, it may be obtained that $c_1(t)/c_2(t) = 5.4$. When this ratio is 4:1, we have $c_1(t)/c_2(t) = 4.1$, corresponding to the ratio prepared. Considerable deviation in the first stage of solvent ratio from the initial value 1:1 may be explained by the weak interaction between ethanol and butanol molecules ($\gamma_{ij} = 0.34$ mN/m), and this weakens molecular interaction forces in solvent itself. As the evaporation rate of ethanol is about 5 times greater than one of butanol, their mixture β values are close to the β value of ethanol (see Table 3). The equation (11) presented is valid for cases when intermolecular action would be absent.

The transition period begins from the moment of stabilisation of evaporation rate of solvents with its subsequent slow decrease (see Fig. 2). The condition becomes a quasi-stationary one showing that solvent concentration $c = f(t)$ declines linearly. The process itself is analogous to stationary process of solvent permeability through polymer films. Further decrease is determined by the solvent diffusion from deeper layers to layers near the surface.

For quantitative evaluation of the third drying stage the diffusion kinetics equations were used. Concentration of solvent, which diffuses from the coating, varies according to law [15]:

$$c(x,t) = \frac{4c_o}{\pi} \sum_{i=0}^{\infty} \frac{1}{2i+1} \sin\frac{2i+1}{2} \cdot \frac{\pi}{x} \exp\left\{ -\left[(2i+1) \cdot \frac{\pi}{2h} \right]^2 Dt \right\} , \tag{12}$$

where x is the diffusion coordinate, h is the thickness of the coating, D is the diffusion coefficient.

If $c(x, t) \leq 0.8c_0$, then taking the first member only, introduces error less than 1 %. Then equation (12) assumes the form:

$$c(x,t) = \frac{4c_0}{\pi}\sin\frac{\pi}{2}\frac{x}{h}\exp\left(-\pi^2 Dt/4h^2\right). \quad (13)$$

The average solvent concentration in the film is:

$$\bar{c}(t) = \frac{1}{h}\int_0^h c(x,t)dx\,. \quad (14)$$

After integration of the equation (13) the equation (14) gives the average solvent concentration:

$$\bar{c}(t) = \frac{8c_0}{\pi^2}\exp\left(-\frac{\pi^2 Dt}{4h^2}\right). \quad (15)$$

The solvent desorption rate is:

$$W = -D\frac{\partial c(x,t)}{\partial x} = \frac{2c_0}{\pi}D\exp\left(-\pi^2 Dt/4h^2\right) = \frac{\pi^2}{4h}D\bar{c}(t)\cdot \quad (16)$$

The diffusion coefficients were calculated using this equation together with their dependencies on average solvent concentration in the coating (Fig. 3).

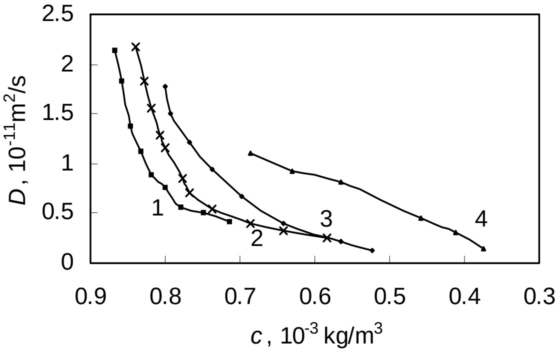

Fig. 3. Solvents diffusion coefficients as function of the concentration in polymer solution for solvents: 1 – ethanol and butanol (1:1), 2 – ethanol and water (4:1), 3 – ethanol and butanol (4:1), 4 – ethanol

These dependences in the coordinates ln$D$ = f(c) are linear (Fig. 4). Diffusion coefficient variation may be described using the empirical function:

$$D = D_0\exp\left(\alpha\bar{c}(t)\right), \quad (17)$$

here D_0, α are the coefficients.

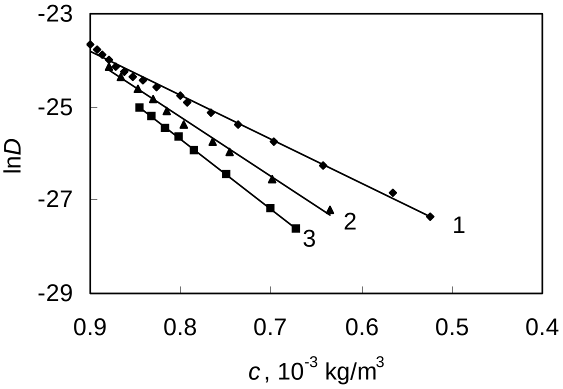

Fig. 4. ln$D$ of solvents as function of average solvents concentration in the coating. The curves:1 – ethanol and butanol (1:1), 2 – ethanol and water (3:1), 3 – ethanol and butanol (4:1)

The values of D_0 and α are presented in Table 4.

Table 4. Indices of the solvents diffusion from 10 % methylolpolyamide solutions

Solvents and their initial volume parts in mixtures	α, 10^3 m^3/kg	D_0, 10^{-14} m^2/s
Ethanol	13.5	0.97
Ethanol and butanol (4:1)	10.8	0.134
Ethanol and butanol (1:1)	9.4	0.96
Butanol	22.7	$1.73\cdot10^{-6}$
Ethanol and water (4:1)	17.2	$8.2\cdot10^{-4}$
Ethanol and water (4:1)	13.9	0.0153

The coefficient α depends on kind of solvent and its interaction with polymer. The greater α the greater is the rate of decrease of D value with $c(t)$ diminishing and the slower is drying process in the last stage. To define drying duration until certain given residual solvent concentration $c(t)$ is reached usage of the equation (15) is necessary while the diffusion coefficient is found from the equation (17). Only then, indices listed in Table 4 are used for polymer solution treated.

CONCLUSIONS

1. Using laws of thermodynamics, describing dependences of surface and cohesion energies and phase interactions, dispersion and polar solvent surface energy components and methylolpolyamide coatig solvents were established.The diffusion coefficients were cal
2. It was established that drying progression of the methylolpolyamide coating comprises three stages: free solvent evaporation, quasi-stationary and diffusion processes.
3. The analytical dependence of the solvents diffusion coefficients on solvents concentration in polymer was derived and indices enabling to forecast coating drying duration were specified.

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