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About Models of Polymer Matrices Impregnation with Functional Additives in Supercritical Carbon Dioxide

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Abstract

The article discusses the impregnation models of a polymer matrix with organometallic complexes in supercritical carbon dioxide.

Keywords: Anomalous impregnation; Cyclopentadienyl manganese tricarbonyl; SC CO_2; Functional additive; Fick's law

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Introduction

The term "impregnation" is formulated in modern literature, dedicated to "green chemistry" as a diffusion of functional additive in carbon dioxide solution into polymer matrix not dissolved but swelled in it. The impregnation is a main method of functional material making by supercritical (SC) technologies. The catalytic, magnetic, luminescent, conductive, antifriction, materials for medicine and many others. The impregnation is complicated multy-factor process and concentration of functional additive (FA) in a polymer matrix depends on FA and a matrix chemical nature, on their compatibility, on solubility of FA in supercritical solvent (SCS), on the temperature, pressure, and duration of an experiment. Therefore, predictive estimates of the structure and composition of composites are not very accurate. To increase the accuracy of forecasting, in 1997 the first phenomenological model of this process was developed by the example of the impregnation of a polyester based on tere/isophthalic acid and bisphenol A (polyarylate DV) with the chemical formula

$$\left[-O-C_6H_4-C\left(CH_3\right)_2-C_6H_4-O-C\left(O\right)-C_6H_4-C\left(O\right)-\right]_n$$

with the organometallic complex cyclopentadienyl manganese tricarbonyl $CpMn\ (CO)_3$ (cymanthrene) in SC carbon dioxide (SC CO_2) [1] and it was found that the impregnation coefficient $K=\pi D/h^2$ (where D is the diffusion coefficient and h is the film thickness) is directly proportional to temperature and inversely proportional to pressure. The increase in cymantrene concentration in the polyarylate film was monitored in a band 2020 cm^{-1} in IR spectra with preliminary calibration by plotting $D_{2020}\ cm^{-1}=f(C)$, where $D_{2020}\ cm^{-1}$ is the optical density at 2020 cm^{-1}, C is the concentration of FA in the film.

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The kinetic curves of FA accumulation in the matrix increased linearly with a gradual reaching a plateau, which corresponded to normal diffusion according to Fick's law. However more careful the process investigation has shown that a diffusion in SC medium (SCM) has more complicate character and FA concentration after the maximum begins to decrease, reaching a certain minimum and again monotonously increases with reaching a plateau, after which it again falls. The new analytical model was developed soon. The model analyzes the curve including the plateau. The nature of the kinetic dependence in the model is explained as follows: the substance flow to the film surface and further to the depth arising due to the concentration gradient in the SC CO_2 solution and in the film is conventionally divided into two flows: diffusion due to the cymanthrene concentration gradient and drift-SC CO_2 flow with the dissolved complex due to the concentration gradient of SC CO_2. Since the diffusion coefficient of SC CO_2 ($\sim 10^{-7} cm^2 s^{-1}$) is much larger than that of cytanthrene ($\sim 10^{-10} cm^2 s^{-1}$), then the second flow in the polymer is always much larger than the first. Introducing into the polymer, SC CO_2 rapidly moves from all sides to the center, while cymanthrene accumulates in the surface layer. Having reached the middle of the film, the flow ceases and at the same time ceases accumulation of the FA in surface layer, the concentration of which at this moment is maximum and excess compared to equilibrium (Figure 1). Therefore, the cimanthrene layer then begins to dissolve and diffuses both inward and outward [2,3]. This process corresponds to the falling section of the kinetic curve. The decrease in concentration occurs to a certain minimum value, determined by the competition of diffusion and relaxation of the matrix structure. At minimum point, there is already a new relaxed structure with its own characteristic sorption ability and, as a result, the absorption of the FA solution begins to increase again, gradually reaching a plateau, after which the whole picture of sorption is likely to repeat at a new relaxation level. This is the so-called "oscillating diffusion", which is associated with the competition of the rates of diffusion and relaxation of the film structure. The model determines the mathematical expression for the concentration of FA at the extreme points of the kinetic curve and the time to reach the minimum point t_{min} and the plateau t_3. It was found that these times are proportional to h^2, but at the same time $t\ min \sim C_0$, and $t_3 \neq f\ (C_0)$. Minimum initial solute concentration when it is still possible a formation of the surface layer with an excess concentration of the substance is determined by the formula $C_{min} = \left(\frac{C_s}{C_1}\right)\left(\frac{D_1}{D_2}\right)^{1/2}$. The equilibrium amount of the impregnated substance, the normalized initial value does not depend on C_0 and h, while the minimum value $W_{min} \sim 2\left(\frac{k}{\pi}\right)^{1/2} = 2\left(\frac{C_s}{C_m}\pi\right)^{1/2}$.

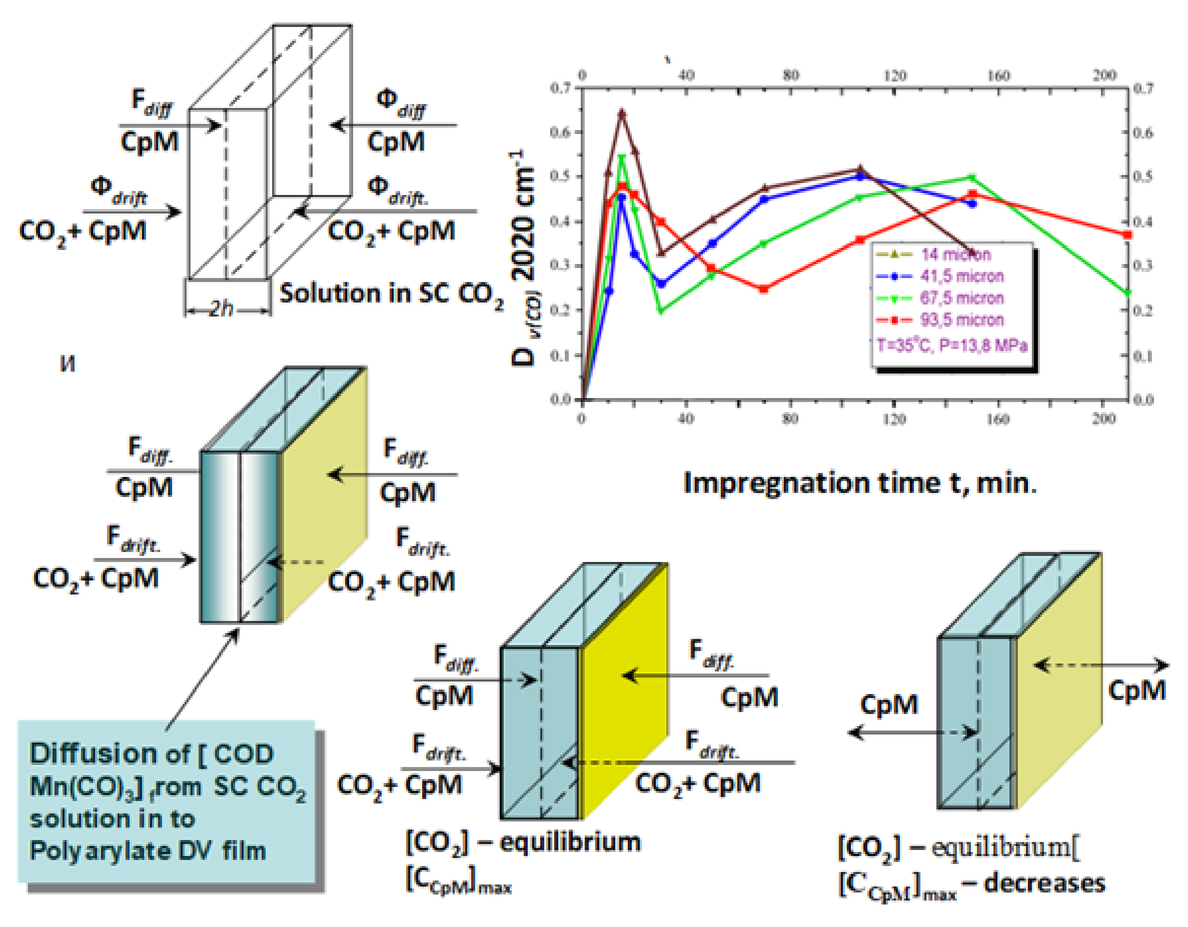

Figure 1: Kinetics of unsteady-state diffusion of CpMn $(CO)_3$ in SC CO_2 solution into polyarylate film and images of impregnation stages. F_{diff}-diffusional flow, F_{drift} -drift flow, CpM-CpMn $(CO)_3$.

The absolute value of the impregnated FA A~h, also depends on the initial concentration as $(C_0)^{3/2}$ at $t=t_{min}$ and $\sim C_0$ at the plateau level ($t>t_3$). K^{-1} is the degree of supersaturation of the surface layer relative to Cs, the equilibrium concentration of FA in the film. C_m is the concentration of FA in the surface layer, h is the film thickness, l is the thickness of the surface layer, D_1 is the diffusion coefficient of $CpMn(CO)_3$ in the film in the presence of SCM, D_2 is the diffusion coefficient of SCM in the film, C_0 is the concentration of FA in the SCM solution, C_1 is the maximum weight concentration of CO_2 in the polymer. The concentration of FA on the plateau matches ~Cs.

The ratio $\frac{1}{h}=\frac{C_0C_1}{C_m}$. An important conclusion follows from the model: non-stationary diffusion is observed only at high solubility of FA in SCM. At low solubility (10^{-4}-10^{-6} mol/L), there is no maximum at the beginning of the curve (since there is a lack of equilibrium concentration of FA in the solution to create an excess concentration in the surface layer of the film and the kinetic curve is monotonous. This conclusion we tested and confirmed during the impregnation of Red13 dye into a DV polyarylate film [4]. The concentration boundary of the transition from one type of impregnation to another is currently unknown and requires a special definition for each FA. Since the first maximum on the kinetic curve is reached in 15-20 minutes, it is possible by repeated impregnation for 20 minutes followed by rapid decompression to create a large concentration of FA in the surface layer.

Conclusion

The described model, despite its shortcomings (it does not take into account matrix swelling in SCM), is by far the most detailed mathematical representation of FA impregnating process (on the example of an organometallic complex) into a polymer matrix and can be used after experimental verification of the main conclusions and additional modernization for quantitative forecasting of the impregnation process. In the future, it can serve as the basis for the transfer of impregnation in SCM from art to technology. Therefore, it would be extremely important to experimentally verify all the quantitative conclusions of the model. This work would stimulate the solution of the most important problem - the development of industrial impregnation processes in SC CO_2 and more generally in SCM.

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