

HIGH PRESSURE IMPREGNATION - A SUSTAINABLE WAY OF PRODUCING ADVANCED MATERIALS

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The discussion of sustainability and climatic change shows, that a process of rethinking has begun. Today, the energy efficiency of a process and the functionalization of materials are very important. An alternative way of processing desired by industry for all groups of synthetic and native polymers is high pressure processing. For years companies have been forced to create innovative products. A lot of companies already create and produce innovative products by sustainable technologies being one key factor for their success in a global market. These new products can be produced with a reduced amount of chemicals, energy and water.

This article focuses on scCO₂-impregnation of polymers and biopolymers like leather. ScCO₂ is used because it is low-priced, well-accepted in industry and public, non-flammable, non-corrosive, harmless and easy to handle.

In a lot of applications the term impregnation means to superimpose a fluid on a matrix. Using high pressure impregnation, the term impregnation means to bring a fluid into a matrix. For this technique it is possible to use supercritical carbon dioxide because it combines the advantages of gases and liquids. It shows a high density and high uptake for certain substances, similar to liquids, by keeping a low viscosity, similar to gases. It can be dosed through spongy and porous material and may cause swelling of several matrices. There are different possibilities to use carbon dioxide for impregnation. CO₂ can be used to dissolve a substance and bring it into a matrix. Alternatively it may widen solid matrices for a better diffusion of substances into the matrix. In this case CO₂ acts as an “opener” for impregnating substances, which are not soluble in CO₂.

In this article a brief overview on some results of the impregnation research at Fraunhofer UMSICHT will be given. The research was done applying the mentioned mechanism for producing leather and impregnating polymers in environmentally friendly and sustainable way. The results of tanning leather under the influence of compressed CO₂ showed that it is possible to save time (reduction from 30h to 5h) and water (about 50%). This research was done by using 100 bar CO₂ pressure and standard tanning agents. Furthermore, the impregnation of polymeric matrices will be described using a new diffusion model. For this purpose different polymers were impregnated using various pressure, time and temperature conditions.

INTRODUCTION

The impregnation of polymers and biopolymers using compressed carbon dioxide is an efficient way to modify materials and to influence a technical process positively. For the results presented carbon dioxide was used to impregnate leather and polymers in two different ways. These two techniques will be explained and are demonstrated in figure 1.

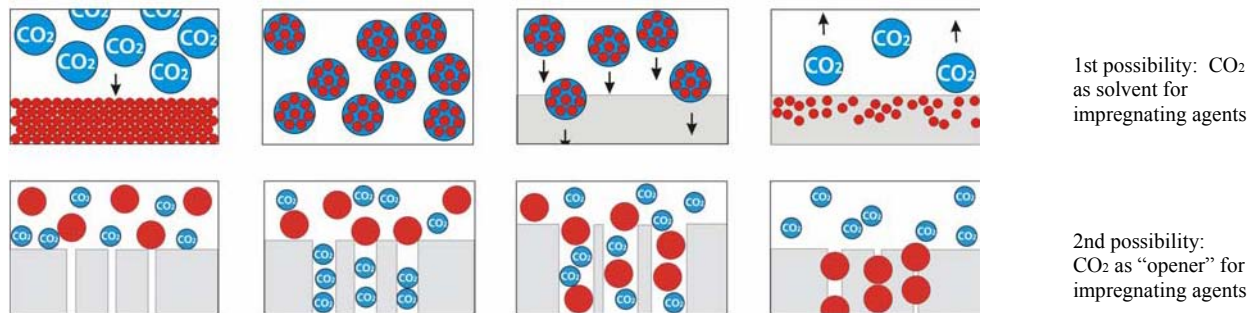


Figure 1: Impregnation techniques

1st CO₂ impregnation technique, CO₂ as solvent for impregnating agents

The first technique uses CO₂ as a solvent for impregnating agent(s). This principle is exercised when the impregnating agent is soluble in carbon dioxide. In the first step the impregnating agent is filled into an autoclave. Subsequently the autoclave is flooded with CO₂ and the impregnating agent dissolves in it. The solution can be pumped into a second autoclave which contains the matrix material. The solution of CO₂ and impregnating agent is diffuses through the material’s surface into the bulk. The longer the time the deeper is the impregnation. After reaching the intended concentration of impregnating agent the autoclave can be depressurized. The CO₂ loses its solvent power and the impregnating agent remains in the solid substrate.

2nd CO₂ impregnation technique, CO₂ as “opener” of impregnating agents

The second principle of using CO₂ is as an “opener” for impregnating agents. Therefore, a matrix sample (e.g. a polymer) is put into an autoclave and the impregnating agent (for example a liquid mixture) is filled in. Subsequently CO₂ is pumped into the autoclave up to the desired pressure. The matrix may swell under CO₂ pressure and the pores are widened, facilitating the filling of the pores with the impregnating agent. When reaching the desired result, the autoclave can be depressurized. The CO₂ diffuses out of the matrix and the impregnating agent may be left in the solid structure. .

Example for the 1st CO₂ impregnation technique:

Foaming of injection molded parts

The first principle should be used to transport for example thermo-unstable impregnating agents (e.g. pigments or pharmaceutical ingredients) into injection molded parts. First results show a good possibility for diffusion of CO₂ in different polymers at low temperatures (< 60°C). Important comparable works in the field of swelling and diffusion of CO₂ in polymers were e.g. presented by von Schnitzler [1], Prausnitz [2], Kazarian [3], Wissinger [4] and Berens [5].

Figure 1 shows a foamed polymer. After two hours of diffusion time the pressure was released suddenly. The carbon dioxide cannot diffuse out of the matrix in that short time. The result is a foamed polymer with a lot of CO₂ bubbles. In the next step an impregnating agent is to be inserted into the matrix.



Figure 1: Foamed injection molded part

The first step of this research is a model for defining diffusion coefficients in a polymeric matrix. Using a high pressure view cell the swelling of a polymeric sphere (Ø 2 cm) under CO₂ pressure is to be dedicated. With a magnetic suspension balance the weight increase of a polymer under the influence of CO₂ should be measured. Knowing these data, it is possible to define diffusion coefficients using the first level of a new diffusion model.

Instationary diffusion model for a sphere with changing volume

The sphere shows variant volume conditions under the influence of compressed carbon dioxide (Figure 1). For the first model of diffusion in a sphere the sphere is divided in a number of shells with boundaries at $r_{i+1/2}$ and $r_{i-1/2}$. The idea of the model is to look at the fluxes over the boundaries to describe the molar mass and volume changes in the shell and thereby the moving of the shell boundaries.

To calculate the concentration in a shell of the sphere, a volume change law is assumed as follows:

$$\frac{dV_i}{dt} = k \frac{dN_i}{dt} \quad (1)$$

This means, that change in volume of a shell i depends linearly on a change in molar mass in shell i . The change in volume of a spherical shell is given by

$$\frac{dV_i}{dt} = 4\pi \left(r_{i+1/2}^2 \frac{dr_{i+1/2}}{dt} - r_{i-1/2}^2 \frac{dr_{i-1/2}}{dt} \right) \quad (2)$$

and the change in molar mass by

$$\frac{dN_i}{dt} = A_{i+1/2} \left(j_{i+1/2} + \varphi \varepsilon_{i+1} c_{i+1} \frac{dr_{i+1/2}}{dt} \right) - A_{i-1/2} \left(j_{i-1/2} + \varphi \varepsilon_i c_i \frac{dr_{i-1/2}}{dt} \right) \quad (3)$$

The parameter φ describes the fraction of convection caused by moving of a boundary in the radial direction. Diffusional flux can be calculated from Fick's law as

$$j_{i+1/2} = \varepsilon_{i+1/2} D_{i+1/2} \left. \frac{dc}{dr} \right|_{i+1/2}, \quad j_{i-1/2} = \varepsilon_{i-1/2} D_{i-1/2} \left. \frac{dc}{dr} \right|_{i-1/2} \quad (4)$$

Hereby the moving law for the shell boundaries at $r_{i+1/2}$ and $r_{i-1/2}$ is given by

$$(1 - \varphi k \varepsilon_{i+1} c_{i+1}) \frac{dr_{i+1/2}}{dt} = \left(\frac{r_{i-1/2}}{r_{i+1/2}} \right)^2 (1 - \varphi k \varepsilon_i c_i) \frac{dr_{i-1/2}}{dt} + k \left(j_{i+1/2} - \left(\frac{r_{i-1/2}}{r_{i+1/2}} \right)^2 j_{i-1/2} \right) \quad (5)$$

The diffusion fluxes $j_{i+1/2}$ and $j_{i-1/2}$ over the shell boundaries must be calculated from a molar balance for the spherical shell volume,

$$eV_i \frac{dc_i}{dt} = -c_i \frac{dV_i}{dt} + \frac{dN_i}{dt} \quad (6)$$

and thereby with the terms given above

$$\frac{dc_i}{dt} = -\frac{c_i}{\varepsilon_i V_i} \frac{dV_i}{dt} + \frac{4\pi r_{i+1/2}^2}{\varepsilon_i V_i} \left[j_{i+1/2} - \left(\frac{r_{i-1/2}}{r_{i+1/2}} \right)^2 j_{i-1/2} + \varphi \left(\varepsilon_{i+1} c_{i+1} \frac{dr_{i+1/2}}{dt} - \left(\frac{r_{i-1/2}}{r_{i+1/2}} \right)^2 \varepsilon_i c_i \frac{dr_{i-1/2}}{dt} \right) \right] \quad (7)$$

Diffusional flux is then calculated numerically from concentration in neighbouring shells with finite difference approximation. Equations given above define an initial value problem, which can be solved numerically with known initial and boundary values. First calculations for $\varphi=1$ and $\varphi=0$ are shown in figure 2.

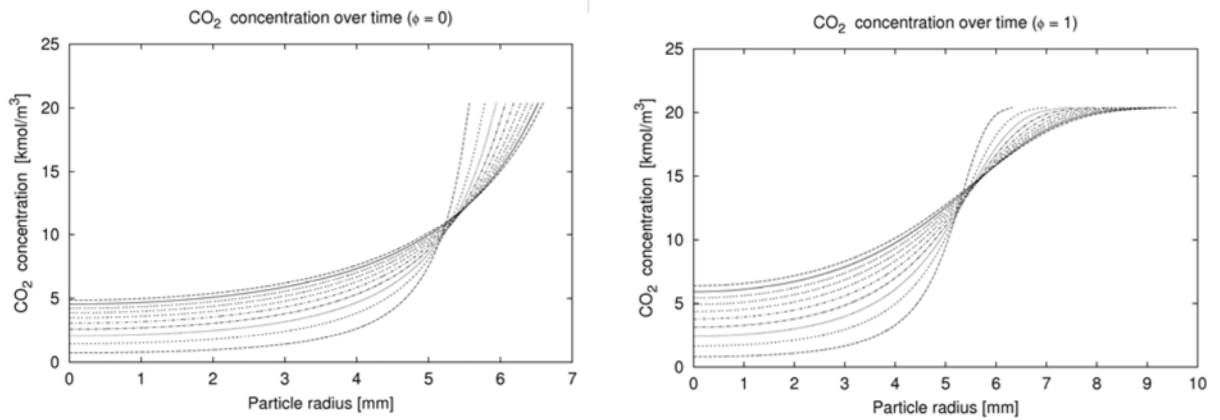


Figure 2: Diffusion model for $\varphi=1$ and $\varphi=0$ (φ : convective flow in polymer pores)

Adopted simulation data: Starting radius $R_0 = 5$ mm
 Border concentration $20,454$ kmol/m³
 Factor of change in volume $k = 0.0488$ m³/kmol
 Starting porosity $\varepsilon_{s0} = 0.01$ m³_{solid}/m³_{total}
 Diffusion coefficient $D = 5 \cdot 10^{-9}$ m²/s

Hier fehlt eine Erklärung was man in Fig 2 sieht und wie das hilft den Diffusionsvorgang zu verstehen. Soweit ich mich erinnere haben andere auch schon Diffusionsmodelle vorgeschlagen, wie passt unser Modell zu deren. Werden vergleichbare Ergebnisse erzielt. Oder ist unseres neu?

The second principle offers an interesting perspective because a lot of impregnating agents are not soluble in CO₂. This technique was used for an intensification of the traditional production process of leather.

Example for the 2nd CO₂ impregnation technique:

Impregnation of leather

The leather producing industry transforms untreated hides that may rot under wet conditions and are brittle under dry conditions into durable, imperishable leather by processes which incorporate tanning agents into hides. The major steps are curing, soaking, flesh removal, hair removal, scudding, deliming, tanning, dyeing, rolling and finishing [6]. High quality leathers (i. e. boil-proofness) can nowadays only be generated by impregnation with chrome [7] and [8]. One of the most time consuming steps is the tanning step. Conventional tanning takes approximately 24 to 35 hours [9] and [10]. With the usage of carbon dioxide the tanning time is to be shortened. The swelling of the matrix offers a better diffusion possibility for the tanning agents into it.

Traditional tanning

At first hide was tanned in lab scale in the traditional way; i.e. without CO₂. This was necessary to develop a standardized method and procedure, that later on allows generating comparable results with CO₂. The hide samples had a diameter of 2 cm and were tanned in an aqueous chrome solution (8 wt.-% Cr). The mass ratio between hide and tanning solution was 1:10.

Carbon dioxide tanning

The tanning of leather under the influence of CO₂ was realized in a high pressure view cell. The cell has a volume of 63 ml. Hide and tanning solution was put into the cell. Afterwards the cell was pressurized with CO₂ up to 100 bar. During the process the stirrer was in the solution and stirred at low rotary speed. A maximum of 7 hours tanning time was applied. The mass ratio between hide and tanning solution was equal to the traditional tanning.

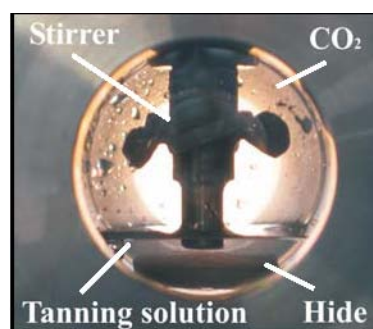


Figure 3: CO₂ tanning in lab scale

Analysis

In industry the leather quality is assessed by optic and haptic properties of the leather by a professional tanner. A quantitative indication for a good leather quality according to [11] is 3 wt.-% Cr in hide. Therefore, the collected tanning solution (after the impregnation) was diluted with water and measurements of an ICP gave the information on the chrome content

in the remaining solution. From this data the chrome content in the treated leather can be calculated and furthermore this content can be related for reaching 3 wt.-% of Cr in leather.

RESULTS

Results comparing traditional tanning with CO₂-pressurized tanning are shown in figure 3. 40% of the 3 wt.-% criterion is fulfilled after 1 h when using CO₂. Using traditional methods 3 h are necessary. 80 to 90% are reached after 4 or 24 h, respectively. The 3 wt.-% criterion is fulfilled after 4 to 5 h when using CO₂ as auxiliary substance and after up to 30 h when using traditional tanning methods. The time saving is significant. Nearly 75% of tanning time can be saved (**factor 6**).

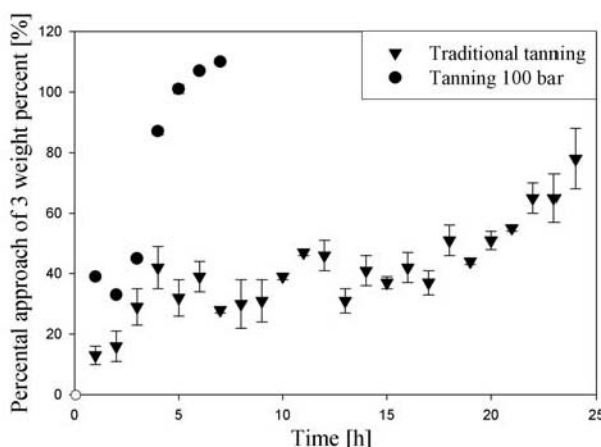


Figure 4: Comparison of the 3 wt.-% criterion

It is not expected that the chemical mechanism of chrome binding on hide collagen is influenced by compressed carbon dioxide. The most important parameters (viscosity, density, surface tension, etc.) that are influenced by CO₂ also do not seem to be responsible for a shortening of the tanning time. It is assumed, that the acceleration may be ascribed to the swelling of the matrix caused by CO₂. Some possible mechanisms are described in the section “2nd impregnation technique”. The swelling of the hide may give cause for a faster diffusion of tanning agents into the leather matrix. More Cr tanning solution can get to the reactive groups of the hide collagen and a fast binding and a shortened leather production is possible.

CONCLUSIONS

First results of the research regarding the first impregnation technique showed that a diffusion of carbon dioxide into different polymeric matrices is possible. This behavior can be used to impregnate polymers and to produce graduated materials with new structures [12]. Examples are microporous surfaces of polymers and foamed polymers (figure 1). For the characterization of the process the first level of a new diffusion model is shown. The usage of carbon dioxide as an “opener” for substances is shown for leather. A shortening of tanning time from 30 to 5 hours is realized.

The modeling of transport processes is necessary for understanding and production of new materials or for the creation of more effective processes. The aim of future research is an entrainer impregnation of polymers. If this is possible polymers could be impregnated with a great number of exciting substances (CO₂ insoluble pigments, thermo unstable substances, etc.).

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