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Impregnation of polycarbonate with copper nanoparticles using supercritical CO_2

Relatore: Prof. Alberto Bertucco
Correlatore: Prof. Thomas Gamse

Laureando: SIMONE SCHIAVO

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Abstract

The supercritical impregnation of polycarbonate pellets with copper has been investigated in this study. The aim was to produce a nano composite polymer with enhanced electrical or biological properties. In this work the 2-step process previously developed by the Graz research group was studied. The method consists of 2 distinct and sequential stages; in the first one the pellets are impregnated with dithizone and in the second one the polymer is loaded with copper. Both steps were carried out in supercritical carbon dioxide media, with and without the addition of ethanol as modifier. Impregnation was performed in a range of 100–250 bar and 40–50 °C. The dithizone and the copper load were analysed by UV-spectroscopy and ICP-OES techniques, respectively. SEM coupled with an EDX detector was used to investigate the presence and the deepness of the copper particles in the polymer. The impregnation of polycarbonate pellets with dithizone was achieved and the method was successful also by using pure $scCO_2$ as carrier. Dithizone proved to be soluble in $scCO_2$, a result not reported in the literature yet. A maximum copper load of 131±103 mg/kg was reached. The samples produced with the studied process were highly inhomogeneous and a big standard deviation between pellets of the same sample was recorded. The reason of this phenomenon was investigated and a possible explanation of the process dynamic was proposed. The high standard deviation problem could not be solved with the available experimental apparatus. Copper clusters between 5–400 nm were found in the polymer matrix; the impregnation resulted deep and homogeneous inside the pellet. The impregnation depth achieved in this work resulted relevantly higher than the studies on the topic found in the literature. Eventually, an industrial process and plant has been proposed, however, before scaling it up, more studies have to be performed.

Riassunto

Questo lavoro di tesi è stato svolto presso “Graz University of Technology”, nell’istituto “Institute of Chemical Engineering and Environmental Technology”, durante un periodo di scambio di 5 mesi nell’ambito del programma Erasmus+. Il progetto è stato supervisionato dal Prof. Thomas Gamse.

I polimeri nanocompositi sono considerati molto promettenti in un grande numero di applicazioni. Le nanoparticelle infatti, possono modificare notevolmente le caratteristiche della matrice polimerica; le proprietà particolari che il materiale può acquisire sono svariate: catalitiche, elettrochimiche, meccaniche, magnetiche, ottiche e biologiche. L’impregnazione supercritica è uno dei metodi utilizzabili per caricare il polimero con nanoparticelle metalliche. Tale processo, applicato anche a tessuti, aerogels, fibre e legno, risulta conveniente sia per quanto riguarda il consumo energetico, sia per gli impatti ambientali generati.

In questo progetto è stata studiata l’impregnazione supercritica di rame in policarbonato sotto forma di pellet. Lo scopo del lavoro era la produzione di un polimero nanocomposito con migliorate proprietà elettriche o biologiche. Un nuovo processo a due stadi (*2-step impregnation*) è stato sviluppato dal gruppo di ricerca, e l’obiettivo dello studio è stato di comprendere e migliorare questo nuovo metodo. Il procedimento consiste in due impregnazioni consecutive, tutte e due eseguite con anidride carbonica (CO_2) pura o con l’aggiunta di etanolo come modificatore. Nel primo step, i pellet di policarbonato sono impregnati con dithizone, un composto molto reattivo con gli ioni metallici, utilizzato per la loro analisi e separazione da soluzioni acquose. Successivamente, nel polimero impregnato vengono assorbiti direttamente ioni rame (Cu^{2+}) con due metodologie diverse. Il processo a fase singola utilizza una miscela di CO_2 ed etanolo come carrier, mentre il processo a doppia fase comprende una fase supercritica ed una soluzione acquosa all’equilibrio. Il processo a doppia fase si è dimostrato più promettente ed è stato approfondito e studiato in maniera molto maggiore.

Il policarbonato in forma di pellet è stato procurato da Saudi Arabian Basic Industries Corporation (SABIC, LEXAN 121 resin) mentre l’anidride carbonica (purezza 99.5%) è stata fornita da Linde Gas GmbH; il Dithizone, i sali di rame e altri prodotti chimici sono stati ordinati, invece, presso Sigma-Aldrich Austria. Gli esperimenti sono stati eseguiti in un contenitore per alta pressione variando le condizioni operative negli intervalli tra 100–250 bar e 40–50 °C. Nell’ambito dello studio tre diversi riempimenti del contenitore sono stati utilizzati, in modo da modificare il volume del sistema ed il miscelamento interno secondo le esigenze.

Il contenuto di dithizone è stato misurato tramite spettroscopia UV, mentre il carico di rame è stato determinato con una tecnica ad emissione atomica (ICP-OES). La presenza, la forma e la

profondità di assorbimento del rame sono state valutate tramite un SEM (*Scanning Electron Microscope*) equipaggiato con un detector EDX, che è stato utilizzato per determinare la composizione atomica delle particelle trovate.

L'impregnazione dei pellet di policarbonato con il dithizone è stata ottenuta con successo anche utilizzando l'anidride carbonica senza modificatori. Il dithizone è risultato solubile in $scCO_2$, fatto non ancora riportato in letteratura. Sono state proposte osservazioni sulla cristallizzazione del policarbonato in presenza di CO_2 supercritica con e senza l'aggiunta di etanolo come modificatore. I materiali così ottenuti possono essere sviluppati come sensori ed adsorber selettivi per soluzioni contenenti ioni metallici.

Il massimo contenuto di rame misurato è di 131±103 mg/kg; ma i risultati ottenuti sono soggetti ad una grande deviazione standard, che è causata da una distribuzione disomogenea del rame nei diversi pellet dello stesso campione. Queste variazioni nel prodotto finale costituiscono un problema significativo, che è stato approfondito. Come possibile spiegazione è stato proposto il mescolamento insufficiente all'interno del contenitore. Tuttavia, non è stato possibile ottenere un carico di rame omogeneo nei pellet con l'apparato sperimentale a disposizione. È stato anche dimostrato che il primo step, l'impregnazione con il dithizone, fa aumentare il contenuto di rame ottenuto con il secondo step, ma la funzione del composto nel meccanismo non è ancora nota. Con lo stesso metodo è stata eseguita con successo un'impregnazione con zinco, a conferma della flessibilità del processo e della possibilità di estenderlo anche ad altri ioni metallici.

Tramite l'analisi con il SEM sono state trovate particelle di rame della grandezza di 5–400 nm, distribuite omogeneamente ed in profondità nei pellet. La profondità dell'impregnazione risulta essere molto alta rispetto agli esempi trovati in letteratura, dove gli studi inerenti all'impregnazioni di metalli interessano, il più delle volte, film di polimero molto fini (25-39 µm).

Infine, a completamento dello studio, è stato proposto lo schema di un impianto industriale, considerando gli impianti di impregnazione con CO_2 supercritica già esistenti. Tuttavia, prima di applicare il processo su larga scala, ulteriori studi devono essere condotti sia sulle proprietà del materiale prodotto sia, in particolare, per risolvere il problema della grande deviazione standard nella qualità dell'impregnazione.

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Introduction

Nowadays, many economic, environmental and political factors force the market to move towards sustainable processes. The main goal, in fact, is to reduce the overall impact (on the society, the environment and the economy) of products and organizations. Due to their unique intermediate and tuneable properties between gasses and liquids, supercritical fluids are considered a promising tool to decrease the energy consumption and to design new ‘green’ processes. This technology has been studied and applied recently in many fields, not only to replace conventional solvents, but also as a reprocessing technique to produce particles and foams [1].

Nanoscale composite polymers have a very high potential in a wide range of applications. The original matrix can be modified with nanoparticles to gain many unique properties such as catalytical, electrochemical, mechanical, magnetical, optical and biological ones [2]. One sustainable way to produce these materials is by supercritical impregnation. This process is convenient, energy efficient and environmentally friendly and it is widely applied to polymers, textiles, aerogels, fibers and wood.

The aim of this work is to successfully impregnate polycarbonate pellets with copper nanoparticles using supercritical carbon dioxide (CO_2) as medium. Particularly the goal was to study the 2-step impregnation method with which the Graz research group had already achieved some good results. The studied process consists in a dithizone impregnation of the pellets and a second copper impregnation carried out with a copper salt instead of a metallic-organic compound (detailed description in paragraph 1.5).

This document is composed by five chapters. In the first one, a brief presentation on supercritical fluids and the CO_2-polycarbonate interaction is reported. The standard metal impregnation of polymers along with the state of the art is also described.

The second chapter contains the materials description plus the experimental and the analytical methods used in the study.

The third and the fourth chapters report, respectively, the study performed on the dithizone and the copper impregnation steps. The fourth describes also the proposed 2-step impregnation process dynamic.

In the fifth chapter, the existing impregnation industrial plants are analysed and a plant layout for the studied 2-step process is proposed.

This study was carried out at “Graz University of Technology” at the Institute of Chemical Engineering and Environmental Technology during an Erasmus+ exchange period of five months. The work was supported by the PhD student Varga Dániel under the supervision of the Prof. Thomas Gamse.

A special thank is due to both Prof. Thomas Gamse and Dániel Varga: Prof. Gamse for the possibility to come to Graz and to improve the knowledge on the high pressure technology topic; Varga Dániel for his great help, suggestions and support given during all part of the study.

Chapter 1

State of the art

1.1 Supercritical Fluid Impregnation

Impregnation in general is the process of incorporating a solute with a solid matrix. The purpose of this process is to modify the properties of the material upon impregnation. A medium is needed to carry the material (the solute) inside the solid matrix; organic solvents, water and supercritical solvents are usually used to this scope. In order to carry out a successful impregnation the substance has to be soluble in the medium.

In this study we focus on supercritical fluid impregnation processes. There are many possible applications of these processes, and for that reason, a wide range of matrixes could be used, however the most commonly ones are polymers, wood and aerogels.

A substance becomes supercritical above its critical temperature and pressure where there is no more distinction between liquid and gas phase [3]. Starting from 1970's, they have been applied for many processes due to their unique properties [4].

The interest in supercritical fluids arises because they have intermediate properties between those of typical gases and liquids. Compared with liquids, they have lower density and viscosity but the diffusivity is greater. Another important factor is that by changing their temperature and pressure the properties of the phase (like density, viscosity etc.) also change in a significant manner. Therefore, this additional degree of freedom can be used to optimize the process conditions [3]. The behaviour of the fluid and its solvent power can be tuned by adding small quantity of cosolvent which change its polarity. For example, strongly non-polar supercritical CO_2 can be a good solvent for slightly polar compounds.

Supercritical CO_2 ($scCO_2$) is the most used supercritical fluid and it is convenient, environmentally friendly, relatively cheap and not toxic. Due to its relatively low critical pressure and temperature (73.9 bar and 31.1°C, see figure 1.1), the usage of $scCO_2$ does not require very special equipment and extraordinary security regulations [3]. In addition, CO_2 is a by-product of many processes so there is no need of extra CO_2 production for a new process. Considering all these factors it is easy to understand why it is studied in so many applications.

Figure 1.1 shows the phase diagram of the CO_2.

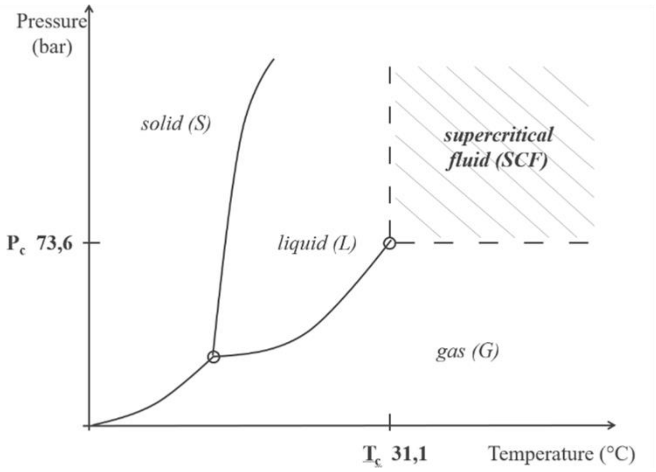


Figure 1.1. *Schematic phase diagram of carbon dioxide.*

One of the problems of the conventional impregnation methods carried out by organic solvents is the removal of the solvent residue from the impregnated material, which is really energy consuming. Hence it is quite hard to completely remove an organic solvent and this can be a big issue particularly in the pharmaceutical field. Using, instead, $scCO_2$ as an impregnation media, a complete separation can be achieved by simply depressurizing the system as CO_2 leaves in gas form. In several cases this CO_2 can be cleaned and recycled, to be used again for the same process.

1.1.1 Supercritical impregnation of polymers

A lot of factors can influence the process of supercritical impregnation of polymers.

The impregnation is feasible when the active substance (the solute) is soluble in the supercritical fluid, the polymer is swollen by the supercritical solution and the partition coefficient (that is the ratio between the concentration of the solute in the polymer and its concentration in the fluid phase) is favourable enough to allow the matrix to be charged with enough solute. [5]

A supercritical impregnation can be classified on the base of the following criteria [5]:

1. The solubility of the solute in the supercritical fluid.
2. The solute modification inside the polymer matrix.

For the first criterion two mechanisms can be identified. The first one is simply a deposition of the solute inside the polymer matrix upon depressurization. The substance can be trapped inside the matrix even if there is low affinity between the solute and the polymer. In this case a crucial factor is the solubility of the solute in the supercritical fluid. The second mechanism takes advantage of a high partition coefficient of the solute between the fluid phase and the polymer.

The second criterion distinguishes between solutes that are not modified and to those that undergo a modification within the polymer. In the first group we can find drugs and dyes molecules, in the second one there is the majority of the organometallic complexes.

1.2 Polycarbonate-scCO$_2$ interaction

1.2.1 Polymer-Supercritical fluid general interactions

When impregnating polymers it is important to take in account the polymer-supercritical fluid interaction. In fact the fluid can diffuse into the polymer modifying its properties. Depending on the chemical composition and their structures (crystalline, glassy, rubbery) the polymers behave differently when contacted with scCO$_2$. Three phenomena can occur:

1. Sorption of the supercritical fluid in the polymer phase
2. Polymer swelling caused by sorption
3. Polymer's glass transition temperature (T_g) reduction

The sorption time to reach the equilibrium and the amount of swelling are usually higher in rubbery polymers, but there are some exceptions. For example, in PMMA, a glassy polymer, scCO$_2$ has a larger sorption than in certain rubbery polymers. This is probably due to the chemical composition of the PMMA and its strong interaction with the CO$_2$ [6]. Another effect of the supercritical fluid is to decrease the glass transition temperature of the polymer. In fact the fluid molecules inside the polymer act like a lubricant that facilitates the sliding of the polymer chains.

These phenomena are very relevant to the impregnation process because they increase the free volume of the polymer allowing the solute to enter deep into the matrix. Also the time needed for the process is decreased by the increase of the diffusion coefficient of the solute inside the matrix.

1.2.2 Sorption, Swelling and T_g depression effect

To perform an impregnation it is important to state and understand the polymer-supercritical fluid interaction. Many authors studied the polycarbonate-scCO$_2$ behaviour.

The CO$_2$ solubility in polycarbonate was studied by Sun *et al.* [7] and by Tang *et al.* [8] at different temperature ranges. In both studies, it was shown that a saturation concentration is reached and that the amount of CO$_2$ inside the polymer increases with increasing pressure and decreasing temperature.

Figure 1.2 shows the swelling percentage measured by Schnitzler at 100 and 300 bar and in a range from 40 to 120°C [9]. It can be seen that PC swelling is relatively higher compared with PET swelling. From 40 to 60°C a decrease of the swelling percentage with the temperature is observed. This is due to the temperature effect on CO_2 density, in fact with a lower fluid density we observe less CO_2 sorption in the polymer.

At higher temperature, other factors become dominant and an increase of the swelling percentage is observed. This can be related to a higher mobility of the polymer chains due to the temperature effect in the polymer [9].

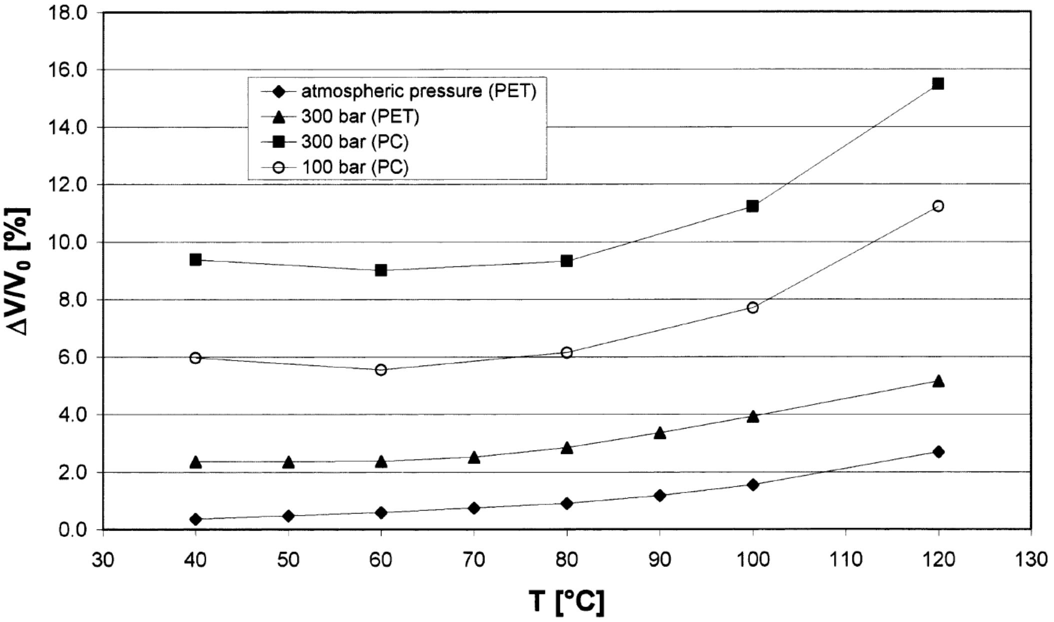


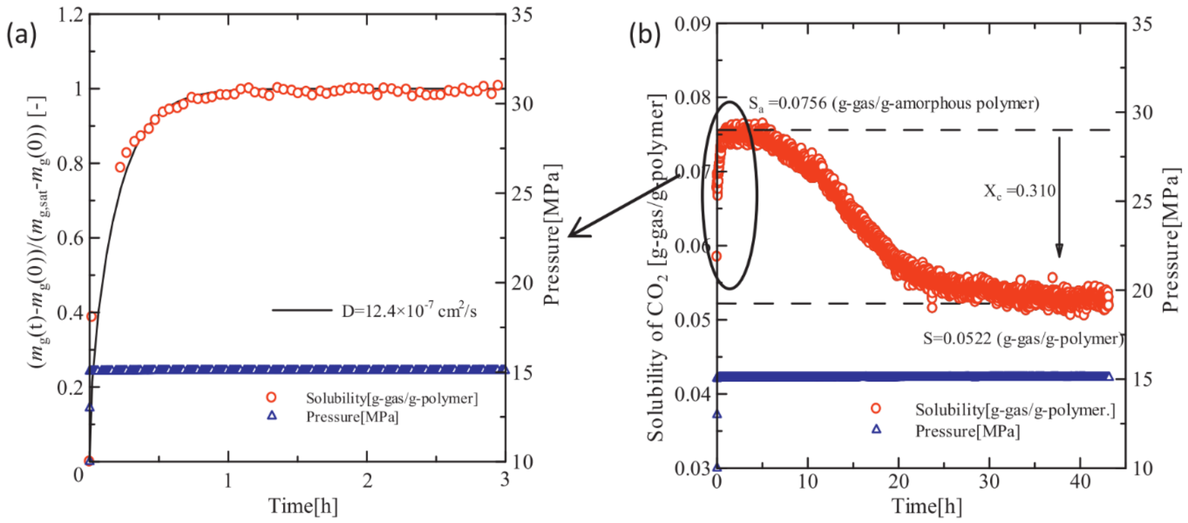
Figure 1.2. *Swelling percentage measured by Schnitzler et al.[9] for PET and PC. The swelling is measured by* $\Delta V/V_o$ *where* V_o *is the volume of the polymer at the experiment temperature.*

Concerning the T_g depression, Schnitzler [9] shows that at 300 bar the depressed T_g of PC should be around 70°C. Zhang *et al.* [10] reported data below 100 bar and he showed that the glass transition temperature decreases with an increase of pressure. However, according to Beckman [11], T_g versus CO_2 pressure should pass through a minimum. Beckman indicates also that such a minimum should be between 100 and 250 bar and over that point T_g should increase by 5°C/100bar (however there is not a direct measurement about this fact).

1.2.3 Supercritical CO_2 inducted crystallization and foaming

Polycarbonate shows also additional interaction with $scCO_2$. In its commercial form, PC is transparent and glassy; however, it can become semi-crystalline if it is contacted with $scCO_2$ for some time. This is probably due to the plasticizing effect of the supercritical fluid that allows the polymer chains to slide and rearrange.

Sun *et al*. [7] studied and modelled this phenomenon; Figure 1.3a-b shows the time dependence of the CO_2 sorption at 100°C and 15MPa.



(a) ***(b)***

Figure 1.3a-b. *Solubility of CO_2 in PC.* ***Figure a.*** *CO_2 sorption in a short time interval.* ***Figure b.*** *Effect of crystallization on CO_2 sorption. (Sun et al. [7])*

It can be seen that, after a couple of hours, the glassy polymer saturation sorption is reached. Increasing the experiment time, crystallization is observed and the CO_2 concentration decreases because the crystalline regions cannot dissolve the same amount of fluid. After a longer period, a new plateau for the semi-crystalline polymer is reached (Figure 1.3b).

This phenomenon is reported to happen after a certain induction time when the difference between the working temperature and the depressed T_g is above 40°C [7].

Another $scCO_2$ dependant polymer modification can occur during the depressurization stage. When the polymer is subjected to high-pressure gas and the pressure is suddenly decreased, the gas will escape from the polymer rapidly. This fast gas release can cause the nucleation and growth of bubbles within the polymer. Once a significant amount of gas has left, the T_g of the polymer drops and, thus, “freezing” the foamed structure [4]. Data has not been found in the literature about the limiting depressurization rate for foaming to occur; Mascia *et al*. [12] obtained foaming in polycarbonate depressurising at 5MPa/min. Liao *et al*.[13] did not report any foaming depressurizing in 1.5 hours from 3.6 MPa (0.4MPa/min).

1.2.4 Diffusion in the polymer

The diffusion of CO_2 in the polymer is a critical step for impregnation processes. Many authors [7], [14] and [8] obtained good results along the diffusion of the CO_2 inside the polymer using the Fickian model. Solving the equation 1.1 (second Fick's law), the effective diffusion coefficient D can be determined fitting the experimental data.

$$\frac{\partial \Phi}{\partial t} = D \frac{\partial^2 \Phi}{\partial x^2} \qquad (1.1)$$

Where Φ = concentration of the substance [amount/volume], x = position [distance], t = time and D = Diffusion coefficient [Area/time] (usually m^2/s).

In particular two diffusion coefficient can be calculated, one measured during absorption experiments (D_s) and another one during desorption experiments (D_d). It was observed that D_s increases when increasing the pressure due to the plasticizing effect of the supercritical fluid, and D_d increases when the initial CO_2 adsorbed amount increases.

A different dependence in temperature was found. In fact, increasing the temperature, an increase in D_s and a decrease in D_d were observed [8][14]. At least at low temperature D_d is higher than D_s. It is assumed that during the sorption process, the polymer substrate is rigid, so that the infusion of carbon dioxide has to overcome larger resistance due to lower chain mobility of polymer substrate. During the desorption process, however, the polymer substrate has already been swollen and plasticized, therefore the exudation of carbon dioxide suffers less resistance due to higher chain mobility of the polymer substrate [8].

In a semi-crystalline polycarbonate, a lower D_s was observed [7] and that is one of the reasons why CO_2-induced polymer crystallization should be avoided.

Regarding the diffusion of the solute inside the polymer matrix, no useful data for this study can be found in literature. This is due to the fact that each solute has its own diffusion coefficient. Berens *et al.* [15] reported the effect of high pressure CO_2 on the diffusion coefficient of different compounds in plasticized and in non-plasticized polymers. It was proven that $scCO_2$ sorption by the polymer can results in orders-of-magnitude increase of diffusion coefficient of the solute [16].

1.3 Nanoparticle modified polymers

A nanoscale composite material is defined as a material that has a structure where at least one of its phases has one or more dimensions (length, width or thickness) in the nanometer size range [17].

Polymer nanocomposites are one of the most promising composite materials. Different nanometric scale compounds can enhance the properties and expand the applications of given polymers [2]. When such nanoparticles are homogeneously distributed inside the polymeric matrix, the properties of nanocomposite material are superior to that of the single nanoparticles or the single polymer. Polymers can be modified with nanoparticles to gain many unique properties such as catalytical, electrochemical, mechanical, magnetical, optical and biological ones [2]. All these characteristics make nanoparticles modified polymers interesting in wide range of applications.

1.3.1 Polymer nanocomposites production

Various preparation methods have been used to synthesize these types of materials. The most commons involve the polymerization process. In fact, in this case the aim is to form the matrix directly around the nanoparticles. The conventional methods are: the sol-gel method, the one-pot synthesis method, the emulsion polymerization method, the hot press method, the in situ polymerization method and the oxidative polymerization method, however, other newer procedures can be found in the literature as well [2].

The main problem of these processes is the control of size, loading and distribution of the particles within the polymer. For example concerning the sol-gel method, the metallic precursors in solution can interfere with the polymerization, generating a material with undesirable properties [17].

This study intends to focus on the nanocomposite modification of raw polymers.

The dispersion of such nanoparticles can be achieved by a simple mixing process by melting the polymer or during the extrusion process. However, this technology is characterized by serious problems of particle aggregation and uniformity of the distribution. In addition, the conditions needed to melt the polymer can degrade any temperature-sensible compounds. A way to produce nanocomposites films is the solvent casting procedure. The main drawbacks of this process are the high amount of organic solvent needed and the consequent solvent removal step required.

Impregnation can be performed not only with conventional organic solvents but also with supercritical fluids. Due to the attractive properties of the supercritical impregnation discussed above and in order to overcome the drawbacks of recent techniques; this study is focused on nanoparticle modified polymers production by the use of $scCO_2$.

1.4 Standard metallic compound impregnation procedure

The production of metallopolymer nanocomposites through supercritical impregnation is carried out by a 3-step process. First the synthesis of an organometallic complex (metallic precursor) is needed. The aim is to produce a compound soluble in a supercritical fluid. This stage could be very expensive due to the high cost of the reactants and for the difficult purification of the final complex. Nevertheless, these syntheses can often be realized with a low yield. The impregnation step is already discussed in this chapter and the resulting product consists in an organometallic complex impregnated polymer.

After this stage the metallic precursor have to be converted into metal nanoparticle. This can be done through three different reduction steps [17]:

- Chemical reduction in the supercritical fluid (SCF) with a reducing agent, such as hydrogen or an alcohol;
- Thermal reduction in the SCF
- Thermal decomposition in an inert atmosphere or chemical conversion with hydrogen or air after depressurization.

The reduction step, especially the thermal one, can cause a degradation in the polymer with the consequent loss of mechanical properties. Figure 1.4 summarizes the process steps.

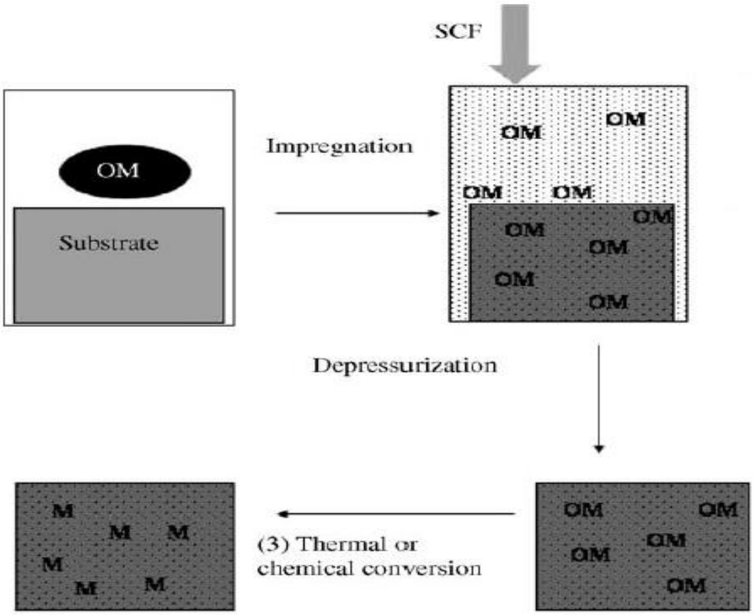


Figure 1.4. *[17] Supercritical fluid impregnation steps after the metallic precursor synthesis. In this process the reduction is not carried out in SCF atmosphere.*

The advantages of the process have been discussed by Kazarian *et al.* [5]:

- $ScCO_2$ shows high penetration into polymers.
- The matrix tends to prevent an agglomeration of metal particles.
- It is possible to control the solvent power and the impregnation rate and, therefore, to control the composition and morphology of the obtained composite.
- The final product does not require special drying.
- Low surface tension allows impregnation even of such barrier polymers as Teflon or obtaining of a continuous metal layer on their surface.

There are also some possible drawbacks; the most important is the depth of impregnation that can be reached. In fact the majority of the supercritical impregnation studies found in literature are carried out on very thin polymer support samples, thick 39µm [18] and 25 µm [19]. In addition, the depth of impregnation is not investigated in these papers.

The only study found that investigates this phenomena in polycarbonate is the one by Hasell *et al.* [20]. A silver complex impregnation was carried out and it was reported a nanoparticle depth was only 6.5 µm even after 24 hours in contact with the supercritical environment.

It is noteworthy that Nikitin *et at.* [18], with this method, obtained a maximum copper load in polyarylate of 6.3 % wt.

1.5 Aim of the work

The aim of the work is to achieve a successful supercritical impregnation of copper nanoparticles in polycarbonate. In addition, the impregnation of zinc in the same polymer is studied. The goal is to enhance the properties of polycarbonate in particular the electrical ones. No examples of this material and this process were found in literature and for this reason, the new material behaviour needs to be investigated.

An improvement also on the biological properties of the polycarbonate can be achieved according to some authors. It has been demonstrated by Borkov *et al.* [21] the broad-spectrum anti-bacterial, anti-viral, anti-fungal, and anti-mite activities of copper impregnated polyester fibres. Other authors report only the anti-bacterial activity but specifically for copper and zinc impregnated polycarbonate [22].

In the research group at the Graz university of technology [23], the copper impregnation effectiveness with $scCO_2$ in polycarbonate of three different complexes has already been investigated by using: $Cu(hfac)_2*xH_2O$ copper hexafluoroacetylacetonate hydrate, $Cu(HDz)_2$ primary copper dithizonate and Cu(Dz) secondary copper dithizonate. The results were unsatisfying; all the samples were below or slightly above the detection limit of the ICP-OES (4ppm). By using $Cu(hfac)_2$ it is believed that the unsuccessful impregnation was due to the relatively high solubility of the complex in the $scCO_2$, i.e. its low partition coefficient between the polymer and the fluid phase. Unlike CuDz, $Cu(HDz)_2$ was found to be soluble in $scCO_2$ according to our observations carried out in a high pressure view cell. However, impregnation by using $Cu(HDz)_2$ was not successful, as presumably the high molecular weight or size of the complex limited the impregnation.

However, a successful impregnation was performed by a 2-step process. First a dithizone impregnated polycarbonate (DPC) was produced with both $scCO_2$ alone and ethanol-CO_2 mixture in supercritical conditions. A concentration between 0.0055 and 0.1786 mg/g of dithizone in the polymer was reached. Only preliminary experiments were carried out on the dithizone impregnation in that work. Therefore, the impregnation efficiency of dithizone has been investigated in the first part of the study.

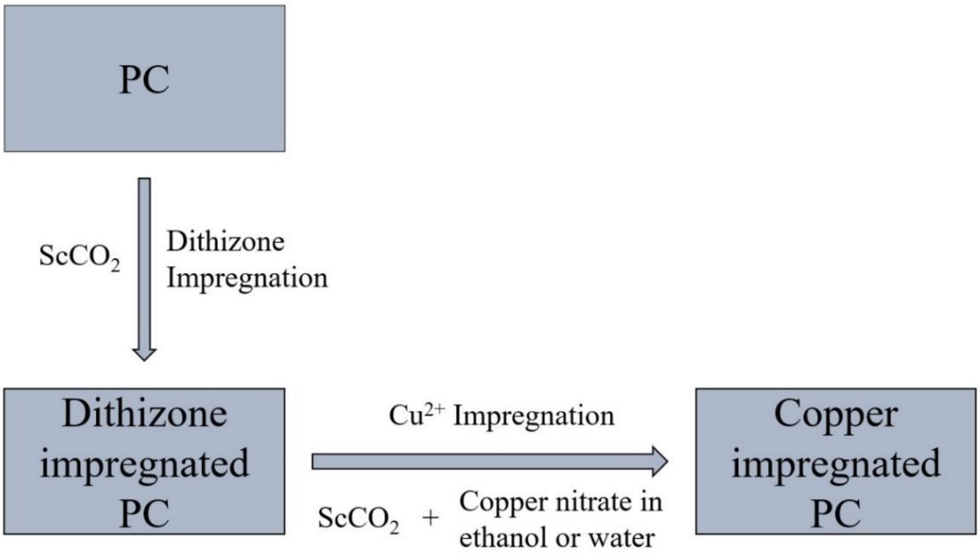


Figure 1.5. *Process steps of the new impregnation method*

The second step was an impregnation of the DPC with copper ions dissolved in water or in ethanol, in $scCO_2$ environment. Figure 1.5 shows the 2 process steps of the impregnation method newly proposed. The aim was to carry out the complexation between copper and dithizone inside the polymer matrix. Three copper salts were investigated: copper nitrate trihydrate $Cu(NO_3)_2{*}3H_2O$, copper sulphate $CuSO_4$ and copper Chloride $CuCl_2$, meanwhile the pH of the solution was also varied adding KOH or HNO_3 to the system.

Copper ions are not soluble in $scCO_2$ but the impregnation was successful anyway. A similar result was achieved and patented by Perman *et al.* [24]. It was discovered that even additives that are substantially insoluble in a supercritical fluid can be impregnated in the polymer even if there is not compatibility with the substrate. This was achieved by contacting the polymer with a liquid carrier (where the addictive is soluble) and in the presence of the supercritical fluid. It is supposed that sorption and the swelling induced by the fluid in the polymer allows the addictive to penetrate the matrix.

The best result, obtained by the Graz research group with a basic solution and with $Cu(NO_3)_2*3H_2O$ dissolved in water, was of 109±3 ppm of copper in the polymer matrix. The sample was analysed by scanning electron microscopy that determined an almost equal impregnation through the entire polymer pellet and a variable particle size between 5 and 400 nm.

The aim of this study is to optimize this technology to increase the copper load in the polymer matrix and to investigate the possible applicability of different metal ions in the process.

Dithizone containing matrices have high importance. Gupta *et al.* [25] developed a Zn^{2+} selective potentiometric designing a PVC membrane containing dithizone. Yu *et al.*[26] produced a dithizone immobilized silica gel useful to the adsorption of trace amount of copper. For this reason, the kinetics for the dithizone uptake of polycarbonate has also been studied.

Chapter 2

Materials and methods

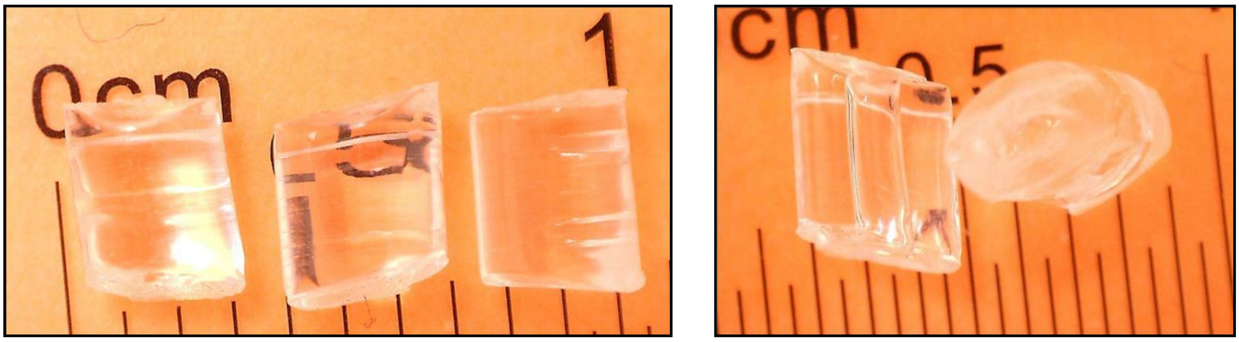
2.1 Materials

Bisphenol A polycarbonate (PC) samples (LEXAN 121 resin) were provided by Saudi Arabian Basic Industries Corporation (SABIC) in pelletized form. Properties:

- T_g = 147 °C,
- Melt Flow Rate, 300 °C/1.2 kg = 17.5 g/10 min,
- Density (ρ) = 1200–1220 kg/m^3.

The samples appear transparent and they are completely amorphous. The pellets have cylindrical shape with a diameter of 2.80±0.10 mm and a height of 3.50±0.10 mm.

As the aim is to treat the polymer directly after the extrusion process, for this reason the pellets are not perfectly identical on shape and dimensions. Figure 2.1a highlights the slightly different pellets shape. Figure 2.1b shows a pellet with a cylindrical hole, as some pellets in the sample had this shape.



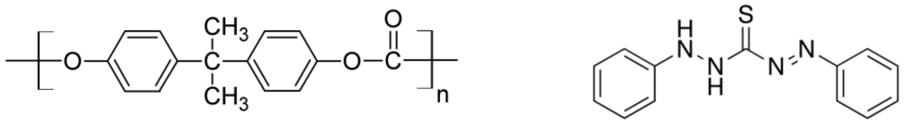
(a) **(b)**

Figure 2.1a-b. *Different pellet in the sample.* ***Figure a****. Pellets with different shape.* ***Figure b****. Pellets with long cylindrical hole*

Carbon dioxide (purity > 99.5%) was supplied by Linde Gas GmbH.

Dithizone (IUPAC name = (1E)-3-anilino-1-phenylimino-thiourea, MW = 256.33 g/mol) was provided by Sigma-Aldrich Austria. Dithizone, at ambient conditions, appears to be like a black powder; it is soluble in ethanol and aqueous solutions with a basic pH. This compound is highly reactive with metal ions and is used to separate and analyse ions like copper, silver, mercury, zinc, nickel, cadmium, lead and other heavy metals. The chemical structure of polycarbonate and dithizone is shown in Figure 2.2a-b.

Metal ions combine with dithizone in basic solutions to yield nonpolar coloured complexes whose colours differ significantly from the dithizone one [27]. These nonpolar complexes can be extracted from the aqueous solution with an organic solvent and their concentration can be measured by a spectrophotometer sensor.



(a) *(b)*

Figure 2.2a-b. ***Figure a***. *Chemical structure bisphenol A polycarbonate.* ***Figure b***. *Dithizone chemical structure*

Copper nitrate trihydrated $(Cu(NO_3)_2*3H_2O$ was ordered from Sigma-Aldrich Austria. Properties: MW= 241.60 g/mol, density = 2320 kg/m^3. This salt has a very high solubility in water 3.81 g/mL at 40 °C [28].

High purity ethanol 99.99%, potassium hydroxide, washing ethanol, nitric acid, copper salts and other chemicals were provided by Sigma-Aldrich Austria.

2.2 Experimental Apparatus

Impregnation experiments were carried out in a batch mode using a high pressure vessel (R-01). Figure 2.3 shows the experimental apparatus scheme.

The pump P-01 (Haskel ASF 100, USA) is a pneumatic liquid pump which allows to reach the experimental pressure. To maintain the CO_2 liquid during compression, the pump is cooled by a recirculation cooling bath that maintains it below 5°C. The device is equipped with a pressure transmitter and a rupture disk (not reported in the figure) for safety reasons.

The high pressure vessel R-01 is placed inside a thermostated heating chamber (H-01, Spe-ed SFE, Applied Separations, USA) which controls the temperature of the experiment. It can reach a maximum temperature of 250°C.

A pressure control system is installed (PC-01, PT-01) and is used during the depressurization to achieve the desired pressure profile. The pressure data measured by PT-01 are recorded automatically by a computer. The control system is connected to a fail-open metering valve (V-06, Kämmer Typ KA, Flowserve ltd, Germany).

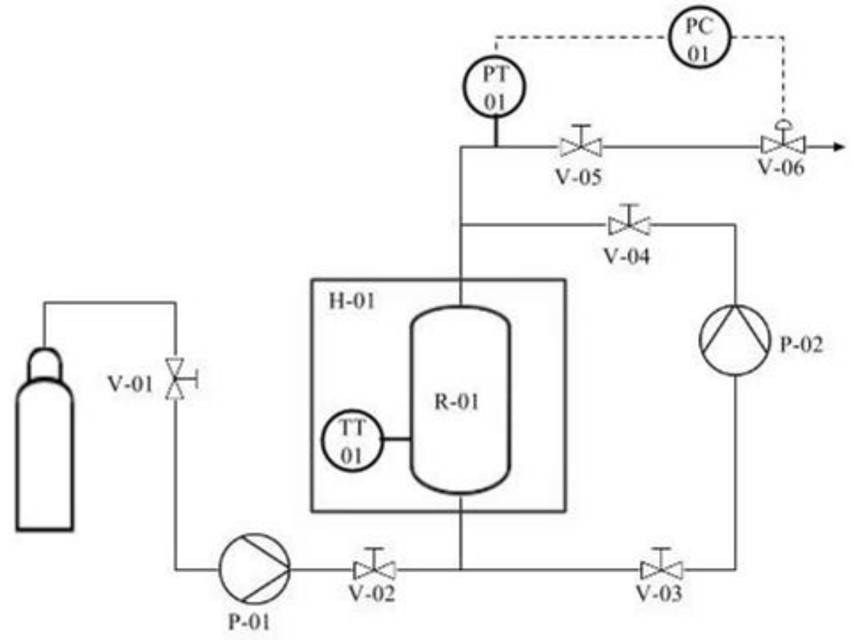


Figure 2.3. *The figure shows the P&I Diagram for the experimental equipment.*

High pressure tubes, fittings and valves were obtained from SITEC and Nova Swiss, Switzerland. The gear pump (P-02) was designed and custom manufactured at ETH Zurich, Switzerland. It is used to mix the vessel when the experiment is running and to avoid overheating problems, the pump is set to run 5 minutes every 15 minutes of experiment.

2.2.1 High pressure vessel

The high pressure vessel (R-01) was supplied by Thar design Inc. The maximum specification for pressure is set to 690 bar (10000 psi). Figure 2.3 shows the pieces and the assembled vessel. The equipment is a cylinder with an internal volume of 300 ml. The vessel can be opened from the top and from the bottom by two relatively big screw type closures. The sealing used are two carbon-filled PTFE groove rings. The bottom and the top closure are connected to the experimental apparatus by 1/16” pipe (Nova Swiss, Switzerland). The lower part can be closed with a conical joint, the upper one can be closed easily by hand with a special connection from Applied Separations (USA). To record the temperature, the vessel is equipped with a thermocouple (TT-01); the sensor is fixed on the lateral wall and it is protected from the environmental temperature by a PTFE cylindrical coating.

To reduce the internal volume and to modify the behaviour of the fluid, some stainless steel fillers are introduced in the high pressure vessel. In this study, three vessel setups were used (Figure 2.4). For all the experiments the equipment was kept in vertical position (like it can be seen in Figure 2.3 and in Figure 2.4)

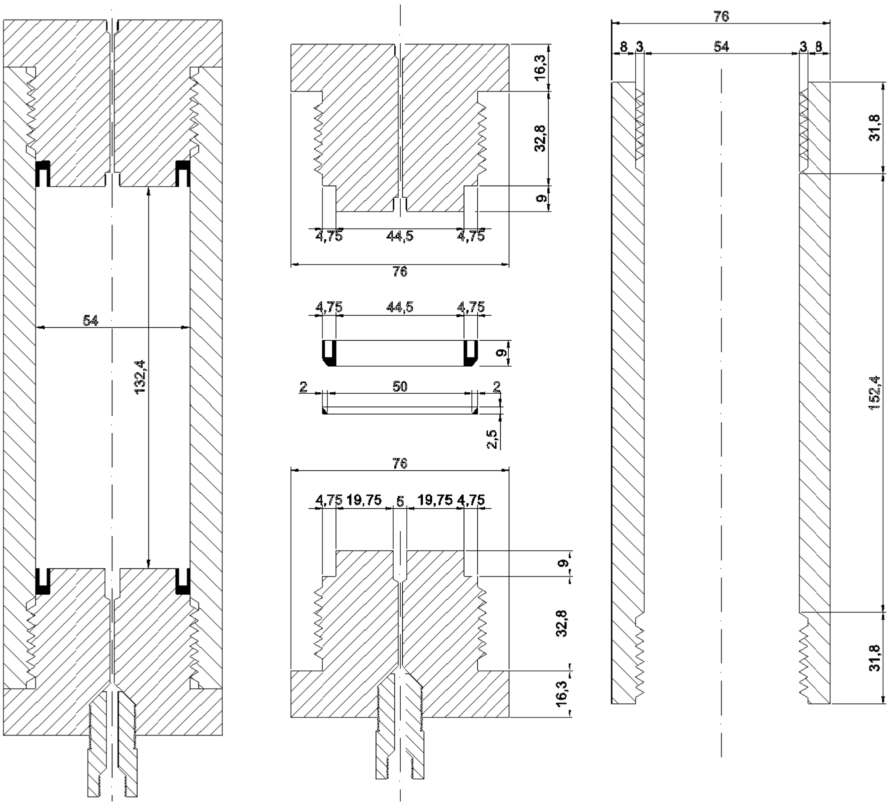
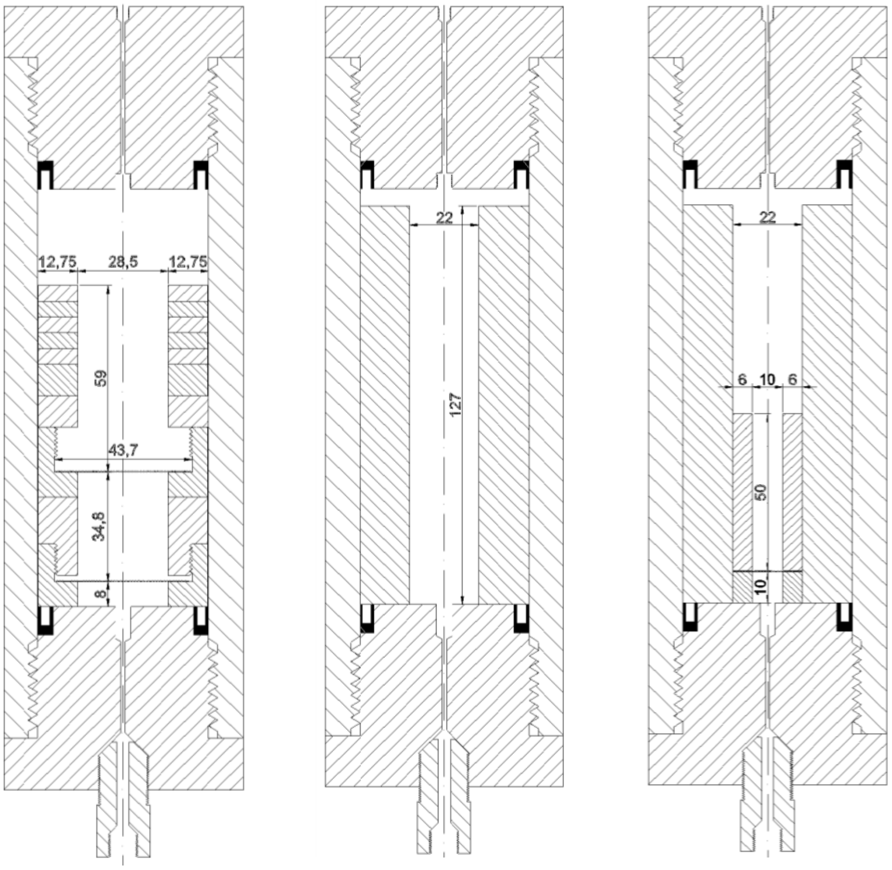


Figure 2.3. *Assembled vessel (on the left) and vessel pieces (on the right) cross section.*


Setup A

Setup B

Setup C

Figure 2.4. *Cross section drawing for the three vessel setups used. Setup A (on the left), Setup B (on the center) Setup C (on the left)*

Setup A (Figure 2.4a) was used only for the dithizone impregnation of polycarbonate carried out only with $scCO_2$ (without addition of ethanol). This configuration is adopted to obtain comparable results with the previous impregnation data of the Graz research group. The setup consists in various rings placed one over the other.

Two screwed rings are laid at the bottom; they hold 2 sieves at two different levels. During the experiment the dithizone powder is placed on the lower sieve and the polymer pellets are placed on the one above.

Setup B (Figure 2.4b) is used for the dithizone impregnation with $scCO_2$ and ethanol and for the copper with both ethanol and water. A cylindrical pipe-shape filler is placed inside the vessel. This feature is mainly used to reduce the volume; the polymer pellets were simply laid on the vessel bottom.

Setup C (Figure 2.4c) was used only for a few copper impregnation experiments. This configuration was developed to improve the mixing action of the gear pump (P-02). A two pipe shape cylinders are inserted inside the filler used for Setup B. The polymer is placed inside this narrow channel on a sieve located 10 mm above from the bottom of the vessel.

The calculated effective volumes for the various setups are reported in table 2.1.

Table 2.1. *Calculated volumes for the high pressure vessel, the system with the mixing equipment excluded and the system with the running mixing for the 3 setups.*

	Fluid volume in the vessel [ml]	Fluid volume mixing equipment excluded [ml]	Fluid volume mixing equipment included [ml]
Setup A	144.3	147.2	157.7
Setup B	58.6	61.6	72.0
Setup C	42.6	45.5	56.0

2.3 Experimental methods

2.3.1 Impregnation with Dithizone

First the material is weighted with an analytical balance (Sartorius, ± 0.0001 g) then the vessel is filled with the ingredients needed for the impregnation: polycarbonate pellets, dithizone powder and eventually 10.0 mL of high purity ethanol (>99.99%). The amount of polymer charged in the vessel varies between 2.0 g (for the dithizone impregnation study) and 6.0 g (for the dithizone impregnated polycarbonate production). The amount of dithizone chosen for these experiments was 0.06 g.

The vessel is sealed, connected to the system and placed in the thermostated heating chamber (H-01), where it is heated up to the desired temperature. Once the temperature is reached, the pressure data recorder is switched on and the system is pressurized in 1–2 minutes. There is no indication from the literature where pressurizing rate is reported to be critical when using polymers for the impregnation. Successively the vessel is isolated from the pump P-01 by closing the valve V-02 and the mixing is started by switching on the gear pump (P-02). During the experiment pressure and temperature are maintained at ± 3.0 bar and ± 0.5 °C, respectively. The sorption time is measured from the moment which the desired pressure is reached until the depressurization is started.

To start depressurization, the control system is switched on and valve V-05 is opened. The set-point function is chosen to have, for all the range, a linear pressure decrease. In the dithizone impregnation experiment a depressurization time of 30 min is chosen.

At the end, the polymer pellets and the vessel are washed with ethanol and dried in air at ambient temperature.

2.3.2 Impregnation with Copper

The copper impregnation procedure is similar to the dithizone one. The amount of polymer chosen for these experiment is between 1.75 g and 2.0 g. The amount of copper salt, water, ethanol, KOH, HNO_3 was varied. Once the vessel is filled the same procedure as the dithizone impregnation is carried out. For this impregnation, a depressurization time of 60 min was chosen to obtain comparable results with the Graz research group previous experiment in the topic.

During the impregnation experiment carried out with water, copper salt and KOH, copper hydroxide ($Cu(OH)_2$) precipitated in the solution. For this reason, the samples were washed for one minute with a sulphuric acid aqueous solution (about 9%) to be sure to remove all the copper hydroxide from the polymer surface before the analysis.

2.4 Analytical methods

2.4.1 UV analysis

The dithizone content in the polymer was measured by UV spectroscopy. The equipment is: a double beam UV-Vis spectrophotometer (UV-1800, SHIMADZU Handels GesmbH, Austria) and 1.00 ml quartz vials were used. To use this technique various dichloromethane-dithizone solutions with different concentrations were prepared to calibrate the measure.

To carry out the analysis the highest peak (that is, the adsorption maximum) within the analysed range (300–800nm) on the absorbance plot was chosen as reference with the aim to find a relationship between the concentration and the absorbance through the Lambert-Beer law.

It was possible to use pure dichloromethane as reference because dissolving untreated PC pellets in dichloromethane does not change the absorbance in the wavelength range of interest. The highest value of the absorbance for dithizone in dichloromethane was found at a wavelength of 609 nm. Figure 2.5 shows the measured and calculated calibration line.

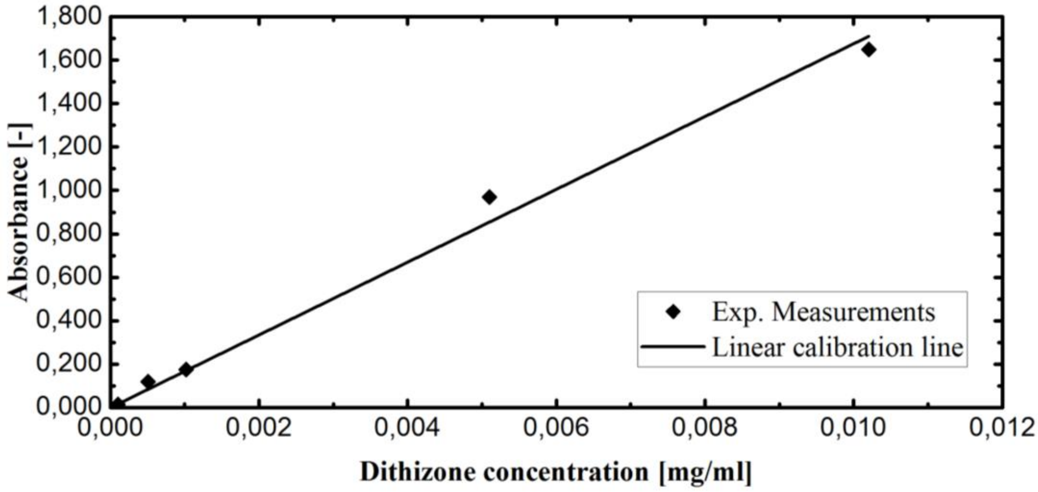


Figure 2.5. *Experimental data and obtained calibration line for the dithizone content analysis*.

From the plot of Figure 2.4 it was possible to determine the coefficient for the Lambert-Beer law (linear relation between absorbance and dithizone concentration) for the studied system (relation shown in equation 2.1).

$$C = A/167{,}58 \tag{2.1}$$

With: C = Dithizone concentration in dichloromethane [mg/ml]
A = Absorbance [-]

To measure the dithizone content in the impregnated polymer, 3 groups of 4–8 pellets each (depending on the dithizone concentration) are taken (4 pellets weight between 75 and 90 mg of polycarbonate). The 4 pellets are weighted and put into a vial. After the addition of 2.000 mL of dichloromethane, the vial was closed and left for 1-2 hours until the polycarbonate was completely dissolved.

After dissolution the sample was analysed with the UV device between 300 and 800 nm; the absorbance and the wave length of the highest peak were recorded. From the absorbance value, with the equation 2.1, it is possible to calculate the concentration of the dichloromethane solution and thus determine the dithizone content of the polymer.

This procedure means 3 parallel measurements for each sample; in this way it is also possible to have an indication of the homogeneity of each impregnation. The average was calculated on the three values.

Dithizone is very reactive with metallic ions and even traces of metals can lead to a slightly different absorbance spectrum and errors in the measurement. For this reason, the analysis was carried out paying attention to all the possible contamination sources.

2.4.2 ICP-OES/MS analysis

It was not possible to perform the analysis at the Institute of Chemical Engineering and Environmental Technology so it was carried out externally. The copper load in the polymer was measured by Helmar Wiltsche and by IKEMA d.o.o. (Lovrenc na Dravskem polju, Slovenia) with the ICP-OES technique. The same procedure is followed by the two laboratories. The digestion step was carried out with closed ceramic crucibles; 100 mg of sample (5-6 pellets) are taken and 6 ml of aqua regia (4 ml of HNO3 and 2 ml of HCl) was added. Then the sample was brought at the temperature of 240°C in 20 min. The increase of the temperature causes the system to reach a pressure of 40 bar. The system was left at the conditions for 15 min; the digestion was aided with microwaves (Anton Paar Multiwave 3000 SOLV, Austria). The resulting solution was diluted to 50 ml and then it is measured by the ICP-OES. In the equipment used (Spectro Ciros Vision EOP, 1350 W power, Spectro, Kleve, Germany), λ = 324.754 nm was applied for copper determination.

2.4.3 Scanning electron microscope investigation

Copper impregnation was studied with a Scanning Electron Microscope. A single pellet from the sample was cut with a diamond knife (Leica Ultracut UCT, Diatome) and the surface was coated with graphite to ensure surface conductivity. The sample was then measured with SEM (Zeiss Ultra 55). A backscattered electron detector (BsE) was also used to make easier the individuation of metallic particles into the polymer matrix; this is done increasing the contrast between the two solid phases. To analyse the elemental compositions an Electron Dispersive X-ray Spectroscopy (EDX) detector was used. EDX was measured by applying 5 and 20 kV accelerating voltage.

2.4.4 X-ray photoelectron spectroscopy investigation

The X-ray photoelectron spectroscopy (XPS) technique was applied to determine the oxidation state of copper in the polycarbonate matrix. To perform the measure inside the matrix a pellet was cut. The spectrophotometer (PHI 5700) worked with X-ray radiation from two types of Al K_α source (1486.6 eV), standard and monochromatic. The base pressure in the equipment was $2*10^{-10}$ mbar. To analyse the energy of the emitted photoelectron a hemispherical electron analyser operating at pass energies of 29.3 eV and 58.7 eV for high-resolution spectra and 187.8 eV for survey spectra was used. The take-off angles of 5°, 20°, 45°, and 90° with respect to the sample surface were scanned during the analysis to evaluate the polymer at different depth. In the performed analysis the depth (90° take-off angle) was in a range of 1.5 – 5 nm. The analysed area had a radius of 0.4 mm. The accuracy of the binding energy scale is estimated to be 0.2 eV. In the XPS spectra the pure core-level transitions (Cu 2p, C 1s, O 1s, N 1s, and S 2p) were analysed.

Chapter 3

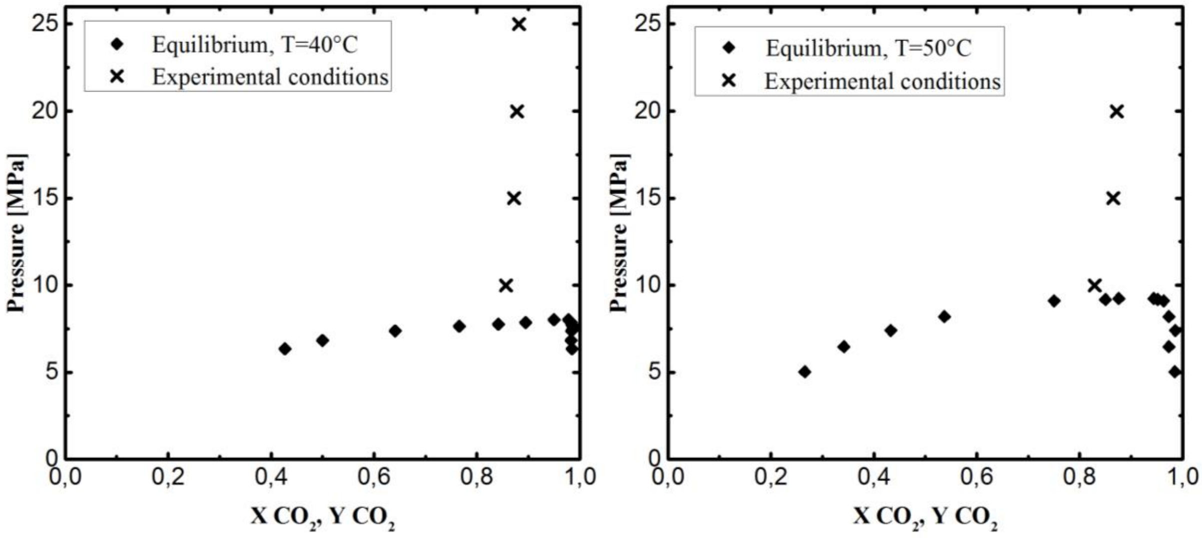
Dithizone impregnation

3.1 Impregnation with CO_2 and Ethanol

The dithizone impregnation of polycarbonate in $scCO_2$ (first step of the process investigated) was studied both with pure $scCO_2$ and with ethanol as a modifier. In this paragraph the results of the impregnation carried out with the addition of 10 ml of EtOH in the vessel are reported. The high pressure vessel configuration used is Setup B; for all the experiments the valves V-03 and V-04 (Figure 2.3) were open and the gear pump was running. The entire volume for this configuration (included pipes and fitting) was calculated as 72.0 ml (Table 2.1).

3.1.1 $ScCO_2$-Ethanol equilibrium

The aim of this part of the study is to perform a dithizone impregnation with the mixture of $scCO_2$-EtOH. The equilibrium of CO_2-ethanol system was checked to avoid the presence of two separate phases. Figure 3.1 reports the data by Lim et *al.* [29] for the mixture and the experimental conditions studied at 40 and 50°C.



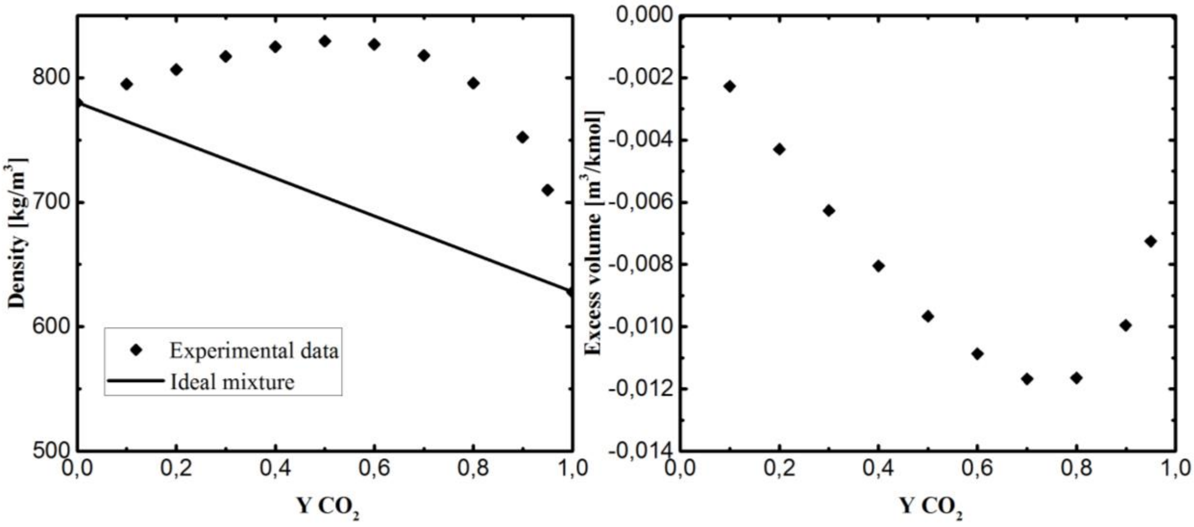
(a) (b)

Figure 3.1a-b. *Equilibrium and experimental conditions points for CO_2- Ethanol system at 40 °C (a) and at 50 °C (b). Data by Lim et al. [29]*

Figure 3.1 proves the presence of a single fluid phase in the experimental apparatus; particularly at the working pressures, the CO_2-EtOH system results to be a single phase for all ethanol compositions. The experimental ethanol concentration, reported in Figure 3.1a-b, was determined with the method described in paragraph 3.1.2.

3.1.2 ScCO$_2$-Ethanol density calculation

As already reported in this chapter, for every experiment 10 mL of ethanol are loaded in the vessel and then the system is pressurized. For this reason, the ethanol concentration is not known in advance and it has to be calculated. Besides, information on the excess volume of the system is needed. Unfortunately, the only data on the mixture at 40 °C available in the literature are recorded at 100 bar, and information at higher pressure are missing. For this reason, an extrapolation is needed to have an estimation on the behaviour at 15 0, 200 and 250 bar.



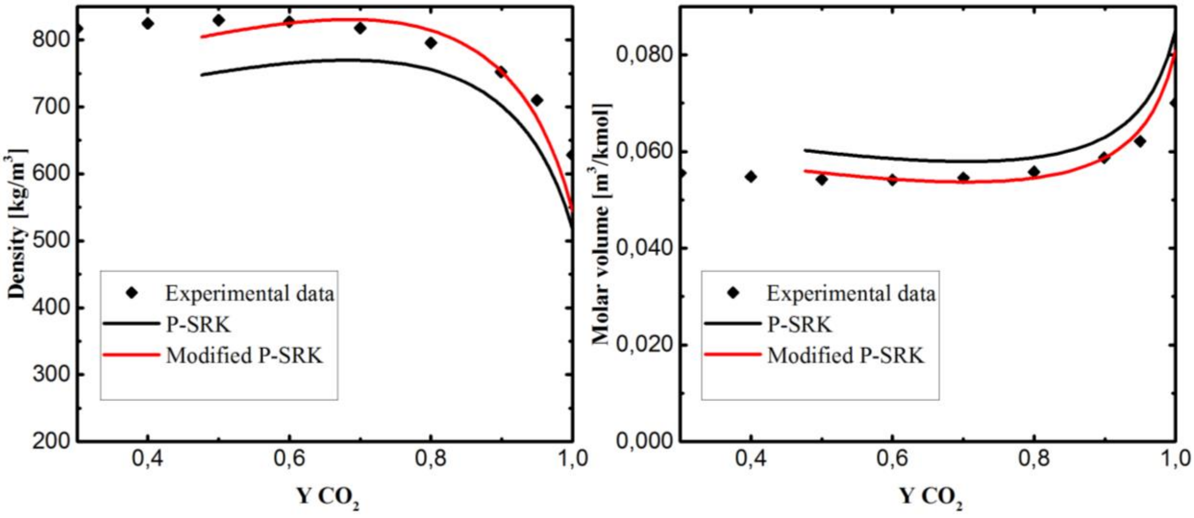
(a) **(b)**

Figure 3.2a-b. *Data by Kato et al.* [30]. ***Figure a.*** *Experimental density for CO_2- Ethanol system at 40 °C and 100 bar.* ***Figure b.*** *Excess volume calculated for the system*

Figure 3.2b shows a relevant excess volume for the mixture and by consequence the ideal mixture cannot be assumed. To model the system, it has been decided to use a cubic equation of state; however, with these models, the determination of the density near the critical point is inaccurate. For this reason, the volume shift proposed by Peneloux *et al.* [31] has been applied. Between the models investigated, the predictive Soave-Redlich-Kwong equation of state (P-SRK) was chosen because it fits better the experimental data. Equation 3.1 reports the Soave-Redlich-Kwong model with Peneloux volume shift correction (additional parameter *c*).

$$P = \frac{RT}{v+c-b} - \frac{a\,\alpha(T)}{(v+c)(v+c+b)} \tag{3.1}$$

The volume shift was calculated by taking into account the difference on the calculated and the experimental molar volume for an ethanol molar fraction (Y_{Eth}) of 0.1. This choice was made to improve the accuracy in the studied range (Y_{Eth} = 0.05–0.15). Figure 3.3a-b reports the experimental data and the model before and after the Penelux correction.



(a) ***(b)***

Figure 3.3a-b. *Experimental points, P-SRK and Peneloux modified P-SRK. Experimental data by Kato et al.* [30]. ***Figure a.*** *Density.* ***Figure b.*** *Molar volume.*

With the calculated volume shift (0.00424 m^3/kmol) it was possible to reach a good accuracy in the studied range of compositions. This model was then used to calculate the ethanol molar fraction in the various experimental pressures. The results obtained with this method are reported in Table 3.2.

The data from Pöhler *et al.* [32] were used to calculate the compositions at 50 °C; the publication reports data at different pressures for various concentrations. The same equation of state (P-SRK with Peneloux volume shifting) was chosen to model the system. Also, in this case, a reference concentration has been selected to determine the volume shift. To assure a good accuracy the correction was calculated considering the closest data (in terms of concentration and pressure) to the impregnation experimental conditions. The chosen conditions and the calculated volume shifts are reported in Table 3.1. The calculated ethanol molar fractions are reported in Table 3.2. All the calculations have been made using the software SimSci ProII process simulator.

Table 3.1. *Conditions and data used to determine the volume shift, calculated volume shift. Experimental data by Pöhler* et al. *[32].*

T [°C]	P [bar]	Y_{Eth} [-]	ρ [kg/m³]	V. shift [m³/kmol]
50	100.6	0.193	630	-0.00793
50	156.9	0.096	764	0.00456
50	193.5	0.096	805	0.00458

Table 3.2. *Calculated molar volume and ethanol molar fraction at the experimental conditions.*

T [°C]	P [bar]	YEth	Mixture molar volume [m^3/kmol]
40	100	0.144	0.0566
40	150	0.128	0.0535
40	200	0.122	0.0513
40	250	0.118	0.0495
50	100	0.170	0.0715
50	150	0.135	0.0566
50	200	0.128	0.0537

The concentrations reported in Table 3.2 are displayed graphically in Figure 3.1a-b.

3.1.3 Reproducibility

While studying the copper impregnation step, it was important to maintain the same starting conditions. So, to obtain comparable results, polymer samples with the same dithizone content needed to be produced. For that reason, many experiments at the same conditions were performed and, in this way, it was possible to check the reproducibility of the process. The chosen conditions are: 100 bar, 40°C and 2 hours of impregnation time. The external mixing was running 5 min every 15 min (5 min ON, 10 min OFF). Table 3.3 reports the results obtained in all the experiments; Figure 3.4 displays them graphically.

Table 3.3. *Dithizone content measured for 4 different experiments carried out at the same conditions*

P [bar]	T [°C]	Ethanol amount	Impregn. Time [h]	Depress. Time [h]	Gear pump Mixing schedule	Dithizone load [mg/g]
100	40	10 ml	2.0	0.5	5min ON, 10min OFF	**0.1085**
100	40	10 ml	2.0	0.5	5min ON, 10min OFF	**0.1151**
100	40	10 ml	2.0	0.5	5min ON, 10min OFF	**0.1122**
100	40	10 ml	2.0	0.5	5min ON, 10min OFF	**0.0970**

Three different groups of pellets were analysed for each experiment. Since the difference on the measurements was minimal, the dithizone was assumed to be equally distributed through the sample. Due to the relatively low standard deviation shown in Figure 3.4, the process was considered to be reproducible. Starting from these results, the average and then the standard deviation was calculated. The standard deviation calculated is mg/g (7.4%); the value of this parameter can be related with the process itself but also with the analytical method. In fact, dithizone is very reactive with metallic ions and even traces of metals can lead to a slightly different absorbance spectrum and errors in the measurement.

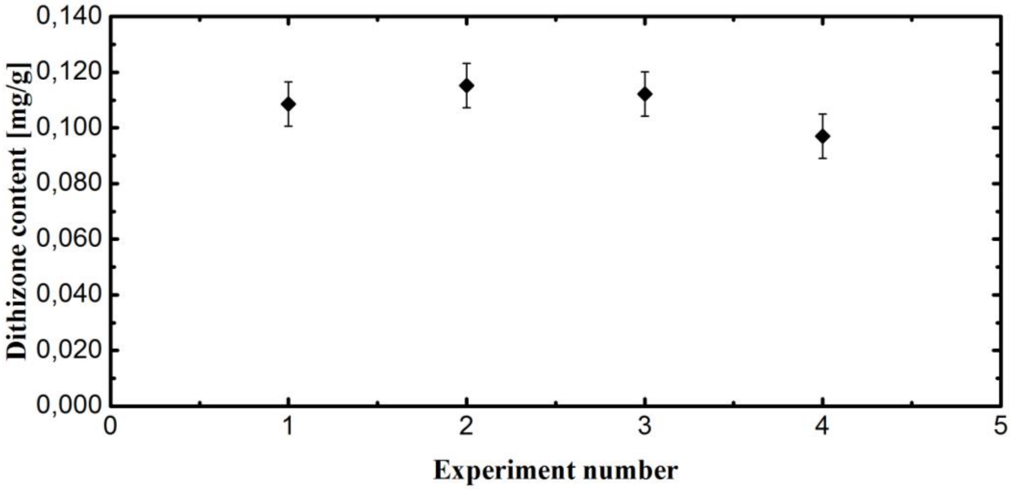
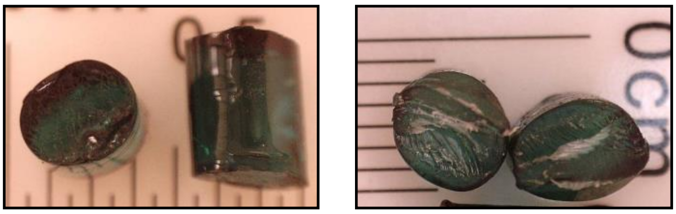


Figure 3.4. *Dithizone content measured for 4 different experiments carried out at the same conditions (100 bar, 40°C and 2 hours). The calculated standard deviation for the process is displayed.*

The dithizone impregnated polycarbonate obtained with this process had a dark green colour and it looked transparent. Cutting a pellet in a half, the impregnation visually appears homogeneous and no gradient on the colour was noticeable. Figure 3.5a-b shows some pellets (entire and cut) obtained with the reported process.



(a) ***(b)***

Figure 3.5a-b. *Dithizone impregnated polycarbonate pellet obtained with $scCO_2$ and ethanol.* ***Figure a.*** *Entire pellets in different position.* ***Figure b.*** *Cut pellet.*

3.1.4 Time dependence

The dependence on the impregnation time was investigated for the same conditions of the reproducibility study (100 bar and 40°C); the aim was to determine if higher concentrations can be reached, and eventually the maximum uptake. The results obtained for an impregnation time of 1, 2 and 3 hours are reported in Table 3.4 and displayed in Figure 3.6.

Table 3.4. *Results for the dithizone impregnation with ethanol at different impregnation.*

P [bar]	T [°C]	Ethanol amount	Impregn Time [h]	Depress. Time [h]	Gear pump Mixing schedule	Dithizone load [mg/g]
100	40	10 ml	1.0	0.5	5min ON, 10min OFF	**0.0711**
100	40	10 ml	2.0	0.5	5min ON, 10min OFF	**0.1122**
100	40	10 ml	3.0	0.5	5min ON, 10min OFF	**0.1199**

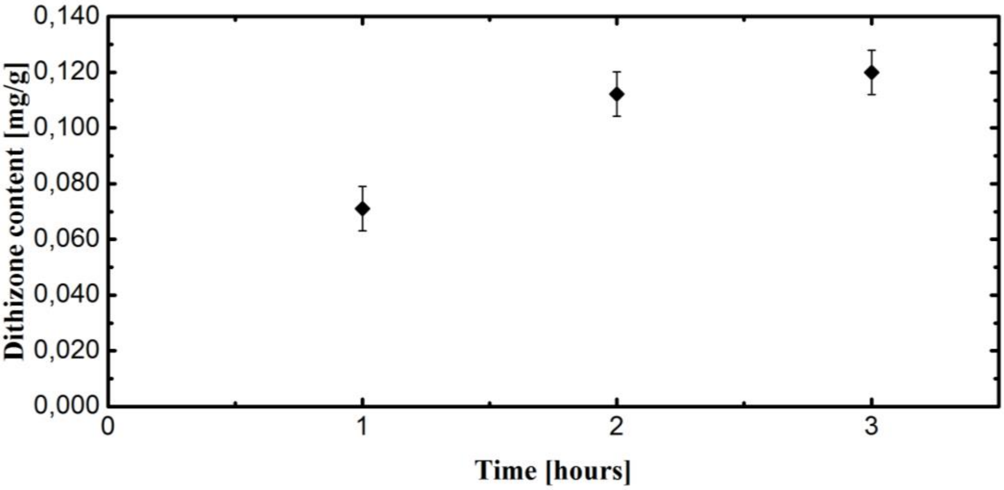


Figure 3.6. *Results for the dithizone impregnation with ethanol at different impregnation time for the conditions: 100 bar, 40°C.*

These results show that the concentration increases at higher times; however, the results obtained at 2 and 3 hours are close to each other, so that, looking at the standard deviations the equilibrium can be assumed.

3.1.5 Temperature and pressure dependence

To study the impregnation, the experimental conditions were changed. The temperatures investigated were 40 and 50°C; it was not further increased in order to avoid the $scCO_2$ induced polycarbonate crystallization. The experimental pressure at 40°C was between 100 and 250 bar, whereas at the 50°C ones the investigation was stopped at 200 bar because the crystallization was noted. The results obtained are summarized in Table 3.5 and displayed in Figure 3.7.

From Figure 3.7, an unusual pressure dependence is observed at 40 °C. Except for some fluctuation, the dithizone content results to be more or less independent of pressure and consequentially of the supercritical phase density. The data were explained with some consideration on the ethanol effect. Comparing the results with the ones shown in paragraph

3.2 (impregnation without ethanol), it is possible to state the big improvement on the dithizone content thanks to ethanol addition. For each experiment the same amount of ethanol was used (10 ml) and this entails a different EtOH concentration in the vessel at different pressure. The consequence of this experimental method is that the concentration (and the partial density) of the ethanol inside the apparatus remains constant, a fact which may explain the pressure independence result.

Table 3.5. *Results for dithizone impregnation experiments carried out at different temperature and pressure.*

P [bar]	T [°C]	Ethanol amount	Impregn. Time [h]	Depress. Time [h]	Gear pump Mixing schedule	Dithizone load [mg/g]
100	40	10 ml	2.0	0.5	5min ON, 10min OFF	**0.1122**
150	40	10 ml	2.0	0.5	5min ON, 10min OFF	**0.0918**
200	40	10 ml	2.0	0.5	5min ON, 10min OFF	**0.0908**
250	40	10 ml	2.0	0.5	5min ON, 10min OFF	**0.1179**
100	50	10 ml	2.0	0.5	5min ON, 10min OFF	**0.2056**
150	50	10 ml	2.0	0.5	5min ON, 10min OFF	**0.2480**
200	50	10 ml	2.0	0.5	5min ON, 10min OFF	**0.2130**

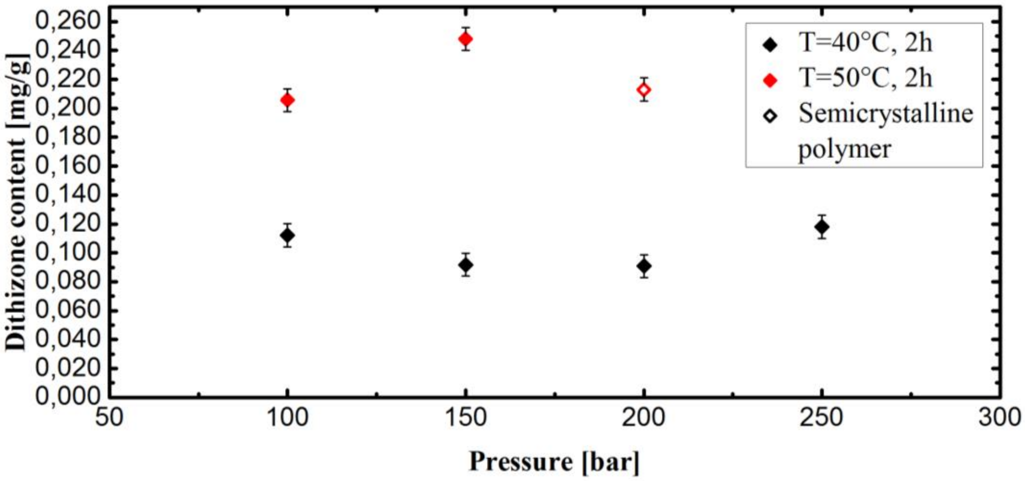


Figure 3.7. *Results for dithizone impregnation experiments carried out at different temperature and pressure. The impregnation time was kept constant at 2 hours. The semicrystalline samples are highlighted in the plot.*

The impregnation values obtained at 50 °C are relevantly higher than the one at 40 °C. Indeed, even if the CO_2-EtOH density is lower, an increase of temperature enhances the dithizone solubility and increases the chain mobility in the polymer. The dithizone content increases when the pressure is brought from 100 to 150 bar. The decrement on the experiment at 200 bar is probably due to polycarbonate crystallization; in fact, the amorphous structure is easier to penetrate than the crystalline one that is characterized by a relevantly lower diffusion. The crystallinity was not measured by DSC but it was clearly visible. The comparison between an amorphous impregnated pellet and a semicrystalline one is displayed in Figure 3.8.

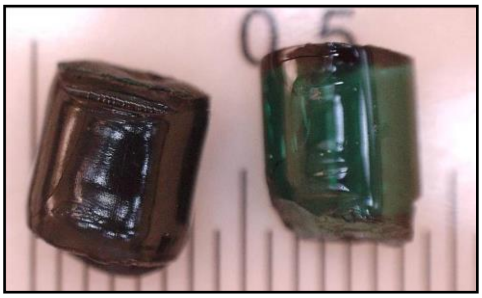


Figure 3.8. *Opaque semicrystalline pellet (on the left), amorphous pellet (on the right).*

Due to the fact that crystallization was detected at 200 bar, the impregnation study at this temperature was stopped and the experiment at 250 bar was not carried out.

3.2 Impregnation with $scCO_2$

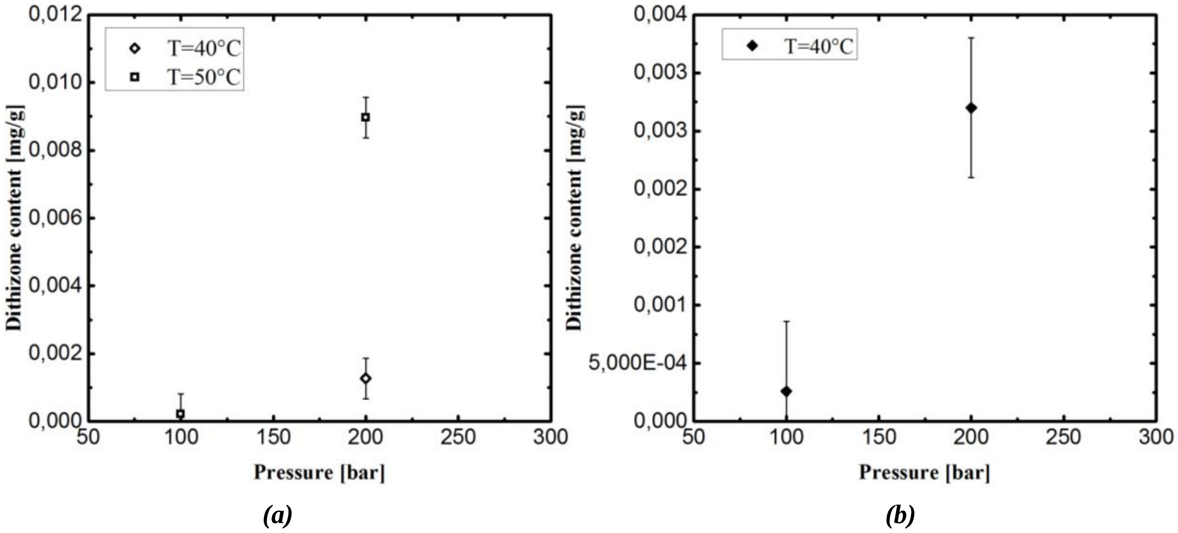
The impregnation carried out without the addition of ethanol as modifier was studied. The dithizone content achieved with this technique resulted of an order of magnitude lower than the one described in the previous paragraph. This impregnation was studied to obtain a product with less dithizone concentration but also to improve the process itself. Without ethanol it is possible to maximize the advantages of supercritical CO_2 and to design an environmentally friendly process completely free of organic solvents. No investigation on the reproducibility were made for this specific process, however, comparing a result of this study to an old result of the Graz research group, a standard deviation of 0.0006 mg/g has been calculated. The standard deviation has been reported in the plots (Figure 3.9a-b, Figure 3.11, Figure 3.12).

3.2.1 Temperature and pressure dependence

To understand the effect of the operating variables on the process, experiments were carried out varying pressure (100–200 bar), temperature (40–50 °C) and impregnation time (3–6 hours). Table 3.6 and Figure 3.9a-b report and display the results obtained.

Table 3.6. *Dithizone content reached with impregnations at different conditions*

P [bar]	T [°C]	Impregn. Time [h]	Depress. Time [h]	Gear pump Mixing schedule	Dithizone load [mg/g]
100	40	6.0	0.5	5min ON, 10min OFF	**0.0003**
200	40	3.0	0.5	5min ON, 10min OFF	**0.0013**
200	40	6.0	0.5	5min ON, 10min OFF	**0.0027**
100	50	3.0	0.5	5min ON, 10min OFF	**0.0002**
200	50	3.0	0.5	5min ON, 10min OFF	**0.0090**
200	50	6.0	0.5	5min ON, 10min OFF	**Crystalline, Not analyzed**



(a) ***(b)***

Figure 3.9a-b. *Results for the condition dependence experiments.* ***Figure a.*** *Results obtained for 3 hours of impregnation time.* ***Figure b.*** *Results obtained at 40 °C for 6 hours of impregnation time.*

The data on Figure 3.7a-b show the really low concentration reached when impregnation is carried out at 100 bar. This fact is probably due to a really low solubility of dithizone at this pressure; based on this results, it was decided to move to 200 bar to achieve better ones.

The highest dithizone content was reached in the experiment at 50 °C, 200 bar and 3 hours. Unfortunately, when increasing the experimental time at these conditions a crystallization problem was encountered. Impregnating the sample for 6 hours, the pellets displayed in Figure 3.10 were obtained. Due to the sample crystallinity the dithizone content was not measured.

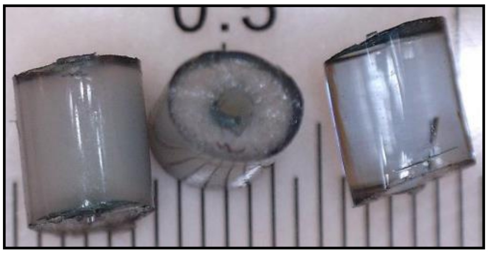


Figure 3.10. *Crystalline pellets obtained at 50 °C, 200 bar and 6 hours of impregnation time.*

As in the experiments with ethanol as modifier (paragraph 3.1.3) crystalline pellets were encountered after only two hours of impregnation, it was concluded that the presence of ethanol accelerates the crystallization phenomenon; no literature reference was found on this fact. Therefore, it was decided to perform the study on the impregnation time dependence at the conditions: 40 °C and 200 bar to avoid crystallinity.

3.2.2 Time dependence

The dithizone impregnation has been studied for the conditions: 40 °C and 200 bar, varying the process duration. Table 3.7 and Figure 3.11 report the results obtained in these experiments.

Table 3.7. *Results for experiments carried out at different impregnation time.*

P [bar]	T [°C]	Impregn. Time [h]	Depress. Time [h]	Gear pump Mixing schedule	Dithizone load [mg/g]
200	40	1.5	0.5	5min ON, 10min OFF	**0.0002**
200	40	3.0	0.5	5min ON, 10min OFF	**0.0013**
200	40	6.0	0.5	5min ON, 10min OFF	**0.0027**
200	40	15.5	0.5	5min ON, 10min OFF	**0.0048**
200	40	24.0	0.5	5min ON, 10min OFF	**0.0052**

From the plot in Figure 3.11 it can be noted that the impregnation needs a certain time to start; in fact, the CO_2 needs to be sorbed by the polymer (at least at the surface) and the dithizone powder has to be dissolved in the supercritical phase. Even after 24 hours of impregnation time the equilibrium concentration cannot be assumed; it is suggested that this is due to the relatively high polycarbonate pellet thickness.

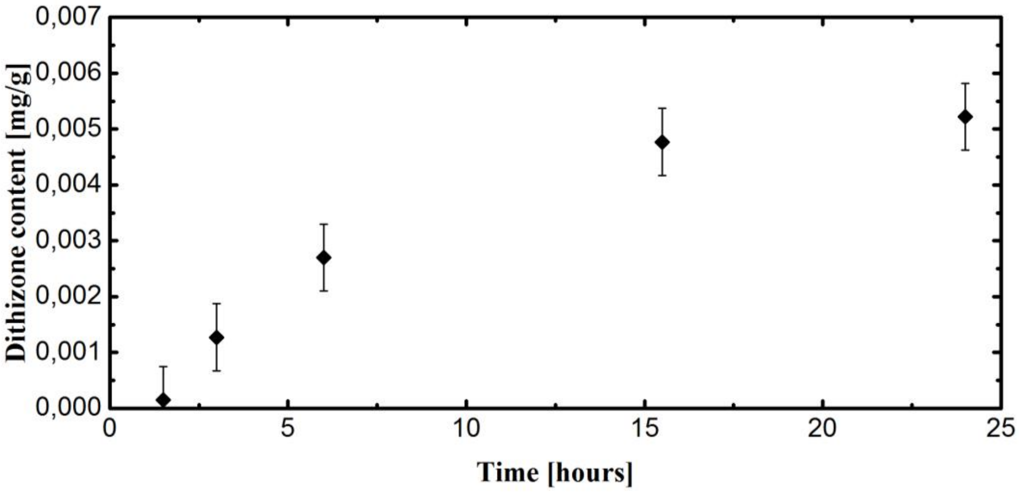


Figure 3.11. *Results for experiments carried out at 40 °C and 200 bar at different impregnation time.*

3.2.3 Diffusion coefficient estimation

The diffusion coefficient of dithizone molecules in the polycarbonate matrix under supercritical CO_2 has been estimated. To do this, the equation derived by Fu *et al.* [33] was used. The relation, initially developed for drug release system, is the Fick diffusion model for cylindrical geometries. Equation 3.2 calculates the amount of dithizone transferred across the cylinder (pellet) surfaces.

$$\frac{M(t)}{M(\infty)} = 1 - \frac{8}{l^2 a^2} \sum_{m=1}^{\infty} \frac{\exp(-D {\alpha_m}^2 t)}{{\alpha_m}^2} \, x \sum_{n=0}^{\infty} \frac{\exp\left(-D {\beta_n}^2 t\right)}{{\beta_n}^2} \tag{3.2}$$

With:

- $\beta_n = \frac{(n+1)*\pi}{l}$
- α_m = roots of $J_o(a\alpha) = 0$ (J_o is a zero order Bessel function)
- a = pellet radius [mm]
- $2l$ = pellet length [mm]
- D = diffusion coefficient of dithizone [mm^2/sec]
- t = time [sec]
- M(t) = dithizone uptake in function on time [mg/g]
- $M(\infty)$ = dithizone uptake for t = ∞ [mg/g]

The equation has been used under some assumptions:

- Diffusion coefficient independent on time
- Perfectly cylindrical and identical pellets

The diffusion coefficient has been determined fitting the experimental data in Table 3.5 (Figure 3.11). The calculation was carried out using the software Matlab (MathWorks®). The diffusion coefficient, the equilibrium concentration and an induction time (D, $M(\infty)$, t_o respectively) were chosen as fitting parameters. The induction time was introduced in the equation to take into account the time that the process needs to be triggered (polymer swelling, dithizone solubilisation). To compute the equation 3.1 numerically, the two series terms were cut at m,n =25. The analysis of samples with higher dithizone concentration was considered more accurate; for this reason, into the fitting calculations, it was decided to factor with a double weight the values obtained with an impregnation time of 15.5 and 24 hours.

The parameters obtained from the fitting are listed in Table 3.8.

Table 3.8. *Calculated values for the fitting parameters*

D	1.88E-06	mm^2/sec
$M(\infty)$	0.0081	mg/g
t_o	5478	sec

The value estimated for the diffusion coefficient is one order of magnitude less than the one reported by Tang *et al.* [8] for the CO_2 into polycarbonate at the same conditions (1.22×10^{-5} mm^2/s). This difference is due to the different size of the dithizone and the CO_2 molecules that allows carbon dioxide to diffuse much faster between the polymer chains. For all these reasons, the calculated value for the diffusion coefficient was considered realistic. Figure 3.12 displays the experimental data and the calculated curve.

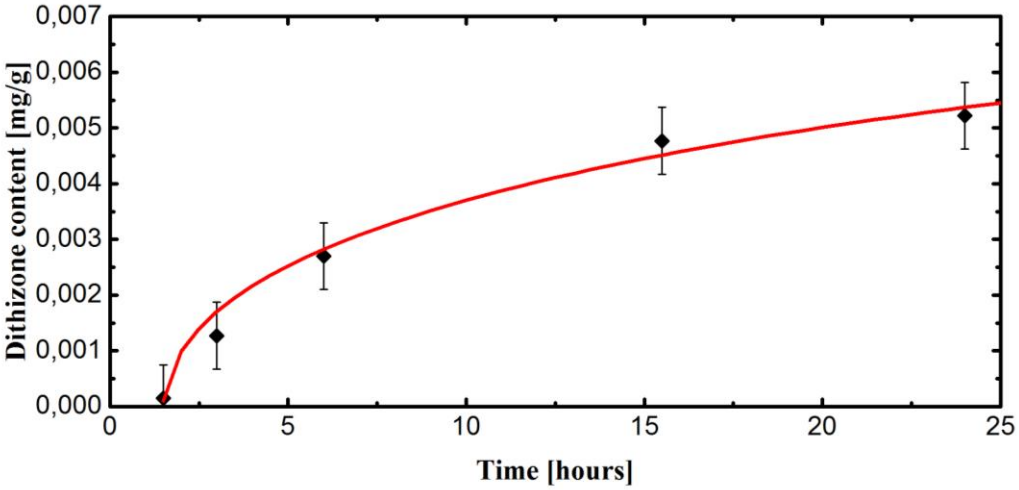


Figure 3.12. *Plot of the experimental results and the curve resulted from the fitting.*

The value calculated for the dithizone equilibrium concentration in polycarbonate, and in general the parameters of the fitting, should be taken only as a first estimate. The results have been obtained only through five experimental data; to obtain more reliable results more experiments need to be carried out.

3.3 Conclusively remarks

The dithizone impregnation of polycarbonate pellet has been studied both with and without ethanol as a modifier and the crystallization phenomenon has been observed and reported.

The investigation of the dithizone impregnated polycarbonate as a product is not the final aim of this study. However, as already reported in the first chapter, some dithizone containing material has already been developed as a potentiometric sensor and a solid adsorber [25] [26]. Probably, to use this polymer, it is necessary to make some modification in the polymer structure to gain, for example a membrane or a porous structure. Also for this reason the diffusion coefficient (for the conditions that does not lead to crystallinity) has been estimated; in this way the application on other polymer shape/structures results easier.

Chapter 4

Copper impregnation

4.1 Single phase process

The second stage of the 2-step process consists in copper impregnation. As already stated in the first chapter two different methods were applied. The single phase process was performed with a mixture of ethanol and $scCO_2$, the aim was to solubilize the copper salt ($Cu(NO_3)_2$) in the mixture to obtain a standard impregnation. Due to the supposed absence of solubility of inorganic salts, no experiments were carried out in $scCO_2$ only.

The single phase copper impregnation was successful during the preliminary experiment carried out by the Graz research group, but the measured copper load resulted lower than the 2 phases process (see details in paragraph 4.2). The presence of the single fluid phase in the vessel can be proved looking at the CO_2-EtOH equilibrium data (reported in paragraph 3.1.1). The results of these preliminary experiments are shown in Table 4.1.

Table 4.1. *Results of the preliminary single phase copper load experiments [23].*

P [bar]	T [°C]	Dithizone content [mg/g]	EtOH amount [ml]	Calculated EtOH molar fraction	Impregn. Time [h]	Depress. Time [h]	Gear pump Mixing schedule	Copper load [mg/Kg]
100	40	0.0055	10.0	0.1367	2.2	1.0	1x15 min	**45±2**
100	40	0.1785	10.0	0.1367	2.0	1.0	2x15 min	**10.9±0.3**

From the values in Table 4.1, it seems that the copper load decreases when increasing the dithizone concentration. However, starting from commercial polycarbonate (not dithizone impregnated) no impregnation could be achieved. Due to the fact that, from the beginning, the 2 phases process was more promising, only a few experiments with ethanol were carried out. Table 4.2 reports the results obtained.

Table 4.2. *Results obtained for single phase copper impregnation experiments.*

P [bar]	T [°C]	Dithizone content [mg/g]	EtOH amount [ml]	Calculated EtOH molar fraction	Impregn. Time [h]	Depress. Time [h]	Gear pump Mixing schedule	Copper load [mg/Kg]
100	40	/	10.0	0.1367	2.0	1.0	5min ON, 10min OFF	15.49±1
100	40	0.1122	10.0	0.1367	2.2	1.0	5min ON, 10min OFF	25.09±15.4

In the latest experiments the copper load was significantly lower compared to the preliminary experiment and the dithizone content effect seems to be the opposite. The low amount of experiments carried out do not allow to state the reproducibility of the process and to define the dithizone content dependence. The high standard deviation measured in the second sample can be caused by a number of factors: the mixing performance, the dithizone distribution through the polymer, an error in the experimental procedure and others.

Due to the different results and to the data inconsistency, it was decided to focus on the more promising 2 phase process.

4.2 Two phase process

In the 2 phases process the polymer is contacted with an aqueous solution of copper and with the supercritical CO_2 phase. A similar impregnation was carried out and patented by Perman *et al.* [24], but this patent lacks in details about the procedure. The 2 phases process results to have a complicated dynamic, which is still unclear. Later on, in this chapter is reported a possible explanation of the process mechanics made after the results analysis.

For this impregnation the preliminary results were really promising; a copper load of 109±3 mg/kg was reached. Table 4.3 reports the preliminary results for the experiment carried out by the Graz research group.

From Table 4.3, where many results are reported, some general remarks on the process can be obtained. However, the data are too few to have certain information. As can be seen various copper salts were studied; the best results were achieved with copper nitrate. For this reason, the following experiments were all carried out using this salt.

The preliminary experiment carried out on commercial polycarbonate (without the dithizone impregnation step) turned out to be unsuccessful. This proved that the first impregnation step induced the increase on the copper load; the improvement seems not to be influenced by the dithizone content. In fact, a similar result was achieved with a difference of a couple of order of magnitude on the dithizone load (0.0055 to 0.1785 mg/g).

Table 4.3. *Results of the preliminary experiments for the 2 phases process [23].*

P [bar]	**T [°C]**	**Dithizone content [mg/g]**	**Aqueous phase composition**	**Impregn Time [h]**	**Depress. Time [h]**	**Gear pump Mixing schedule**	**Copper salt**	**Copper salt amount [g]**	**Copper load [mg/Kg]**
100	40	/	8ml H2O + 2ml KOH 0.1M	2.0	1.0	2x15 min	$Cu(NO_3)_2$* $3H_2O$	0.440	**4±1**
100	40	0.0055	8ml H2O + 2ml KOH 0.1M	2.3	1.0	2x15 min	$Cu(NO_3)_2$* $3H_2O$	0.290	**109±3**
100	40	0.1785	8ml H2O + 2ml KOH 0.1M	2.0	1.0	3x15 min	$Cu(NO_3)_2$* $3H_2O$	0.468	**90±3**
100	40	0.0970	8ml H2O + 2ml KOH 0.1M	2.2	1.0	5min ON, 10min OFF	$Cu(NO_3)_2$* $3H_2O$	0.317	**43+11**
100	40	0.1100	8ml H2O + 2ml KOH 0.1M	2.3	1.0	15 min only at the beginning	$Cu(NO_3)_2$* $3H_2O$	0.267	**< LOQ**
100	40	0.1100	8ml H2O + 2ml KOH 0.1M	2.0	1.0	3x15 min	$CuCl_2$	0.278	**9.2±0.3**
100	40	0.1100	8ml H2O + 2ml KOH 0.1M	2.0	1.0	2x15 min	$CuSO_2$*$5H_2O$	0.476	**15±7**

A lot of different experiments were carried out and it seems too confusing to report them all together. Therefore, it was decided to divide the results in order to better analyse and understand dependences and characteristics of the process.

4.2.1 ScCO2-Water equilibrium

Differently from the $scCO_2$-Ethanol system, at the studied conditions, the $scCO_2$-water mixture results to be two phase one. Figure 4.1 reports the data at 40°C of the solubility of water in $scCO_2$ published by King et *al.* [34].

As can be seen from Figure 4.1, the molar fraction of water in $scCO_2$ is really low, so that the amount of water in the supercritical phase results to be negligible. It has been calculated that, for the high pressure vessel used, only 0.08g (at 100 bar and 40°C) of water are in the CO_2 phase. Considering all the experimental conditions (pressure and vessel setup) used, the amount of water in the supercritical phase is 0.13g at maximum.

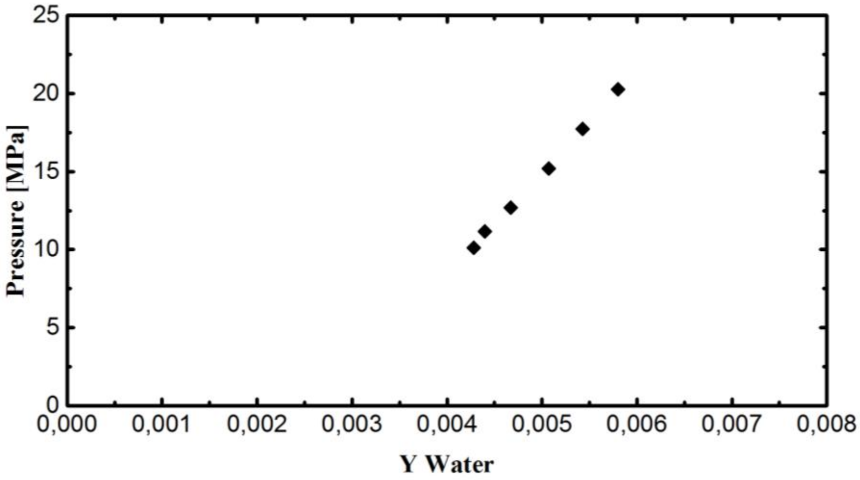


Figure 4.1. *Data of solubility of water in scCO$_2$ at 40°C* [34].

The studied system involves an aqueous solution of salts instead of pure water, and it is assumed that the salts do not relevantly modify the equilibrium, so that presence of the two phases can be assured.

4.2.2 Reproducibility and pressure effect

The first information that needed to continue the study is about the reproducibility of the process. In fact, if the impregnation is not reproducible no further experiment should be carried out before modifying and fixing the procedure.

To check the reproducibility two equivalent experiments are carried out and the results are compared. This procedure was made twice at two different pressures. Table 4.4 reports the results obtained for the 2 experiment sets.

From the data reported in Table 4.4 the process seems reproducible; the results for the two experimental sets are similar and can be overlapped. However, the values for the copper load suffers from a huge standard deviation, that indicates an inhomogeneous impregnation occurring in the various pellets in the same sample.

A high value of standard deviation is a significant problem for a research study. These big variations on the final results make the data not comparable and the analysis itself is influenced by randomness. A huge difference on the values, in fact, can be obtained only choosing different pellets to analyse. Comparing the data of two equivalent experiments (81±75 and 131±103 mg/Kg, reported on Table 4.4), it is impossible to say if the average copper load of the two samples is similar or not.

Table 4.4. *Results for the reproducibility experiments.*

P [bar]	T [°C]	Dithizone content [mg/g]	Aqueous phase composition	Impregn Time [h]	Depress. Time [h]	Gear pump Mixing schedule	$Cu(NO_3)_2$ amount [g]	Copper load [mg/Kg]
100	40	0.0643	8ml H2O + 2ml KOH 0.1M	2.0	1.0	5min ON, 10min OFF	0.3200	**81±75**
100	40	0.0643	8ml H2O + 2ml KOH 0.1M	2.0	1.0	5min ON, 10min OFF	0.3195	**131±103**
200	40	0.1151	8ml H2O + 2ml KOH 0.1M	2.0	1.0	5min ON, 10min OFF	0.3260	**10,65±3,5**
200	40	0.1151	8ml H2O + 2ml KOH 0.1M	2.0	1.0	5min ON, 10min OFF	0.3230	**14.37±2.7**

A remarkable effort was made in this study to reduce the standard deviation and to understand the causes of it. Possible explanations supported by experimental results are reported later on in this chapter.

Results for experiments carried out at different pressure can be seen in Table 4.4. The reason of the lower copper load for experiments at higher pressure is unknown and it was not studied in depth. The hypothesis is that the modification of the density and the viscosity of the $scCO_2$ due to the higher pressure influences the circulation of the aqueous solution. The influence of the solution circulation and the mixing in the vessel is discussed in paragraph 4.3.5.

4.2.3 Effect of the acid/basic solution

The process was studied changing the amount and the composition of the aqueous solution. Particularly, the solution pH was varied adding nitric acid or potassium hydroxide. Table 4.5 compares the results for the experiments carried out modifying these two additives amounts.

The data in Table 4.5 show that all the experiments performed with an acid and a neutral solution were unsuccessful. It was found that KOH is needed to achieve the impregnation however the KOH addition does not lead necessary to a significant increase of the solution pH. In fact, a reaction takes place between the copper and the OH^- ions and the copper hydroxide ($Cu(OH)_2$) precipitates. $Cu(OH)_2$ has a really low solubility in water so that the majority of the hydroxide ions, come from the KOH, precipitates with the copper (this is also due to the fact that, in our conditions, the OH^- ions are the limiting reactant).

Table 4.5. *Results for the experiments performed varying the solution pH.*

P [bar]	T [°C]	Dithizone content [mg/g]	Aqueous phase composition	Impregn Time [h]	Depress. Time [h]	Gear pump Mixing schedule	Cu(NO3)2 amount [g]	Copper load [mg/Kg]
100	40	0.0033	9ml H2O + 1ml HNO3 65%	2.4	1.0	5min ON, 10min OFF	0.3260	**< LOQ**
100	40	0.0970	10ml H2O	2.0	1.0	5min ON, 10min OFF	0.3684	**< LOQ**
100	40	0.0033	1ml H2O	2.0	1.0	5min ON, 10min OFF	0.3210	**11.6±2.3**
100	40	0.0055	15ml H2O + 1.5ml KOH 0.1M	2.0	1.0	5min ON, 10min OFF	1.5409	**25±8**
100	40	0.0643	8ml H2O + 2ml KOH 0.1M	2.0	1.0	5min ON, 10min OFF	0.3195	**131±103**
100	40	between 0.0013 and 0.0055	10ml H2O + 5ml KOH 0.1M	2.0	1.0	5min ON, 10min OFF	0.3141	**98±7**

The amount of KOH in the solution does not seem to be a key parameter for this process, and increasing its concentration leads only to a higher amount of solids in the vessel. However, the experimental data show that the impregnation results to be less effective when the ratio between the KOH and the copper ions is too low.

4.2.4 Dithizone content effect

To understand the dithizone effect on the impregnation some experiments were carried out starting with polymer pellets with a different dithizone content. Table 4.6 reports some of the results obtained.

Table 4.6. *Results for the experiments performed varying the dithizone content of the starting polymer.*

P [bar]	T [°C]	Dithizone content [mg/g]	Aqueous phase composition	Impr. Time [h]	Depress. Time [h]	Gear pump Mixing schedule	Cu(NO3)2 amount [g]	Copper load [mg/Kg]
100	40	/	8ml H2O + 2ml KOH 0.1M	2.0	1.0	5min ON, 10min OFF	0.3194	**26±8**
100	40	between 0.0013 and 0.0055	10ml H2O + 5ml KOH 0.1M	2.0	1.0	5min ON, 10min OFF	0.3141	**98±7**
100	40	0.0643	8ml H2O + 2ml KOH 0.1M	2.0	1.0	5min ON, 10min OFF	0.3195	**131±103**

It was found that the dithizone enhances copper impregnation. With the first impregnation step significantly higher results are achieved. Surprisingly, similar and comparable copper loads were reached with a difference of one order of magnitude on the dithizone concentration in the polymer. However, it was preferred to carry out most of the experiments with a constant dithizone content of 0.1080±0.0080 mg/g (see paragraph 3.1.2) to be sure of producing comparable data.

The mechanism of copper absorption by dithizone has been studied by Yu *et al.* [26]. Figure 4.2 displays the reaction reported in that paper.

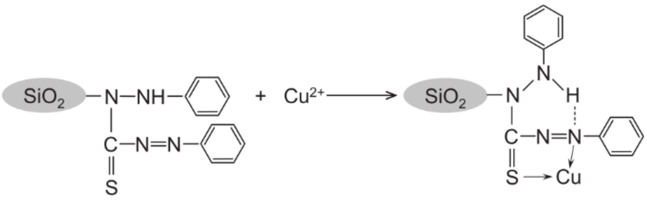


Figure 4.2. *Dithizone role on copper absorption proposed by Yu et al. [26].*

In the study, dithizone molecules are bound on the silica gel to improve the sorption efficiency with respect of copper ions. The described mechanism consists in a bond formation between a molecule of dithizone and a single copper ion. In this work, the reported reaction has been excluded because of the copper load achieved. From the experimental data obtained, it was calculated that the impregnated copper ions ($1.54*10^3$ mmol/g) are 4 to 70 times higher than the dithizone molecules (from $2.13*10^5$ to $3.91*10^4$ mmol/g).

The role of dithizone in the process is still unknown. Due to the small dependence on the concentration, it is assumed to have a catalytical-like function acting on the transportation of the copper inside the matrix.

4.2.5 Effect of mixing

The external mixing in the high pressure vessel resulted to be a key parameter in this study. Table 4.7 reports the results obtained changing the 2 phases recirculation in the vessel. The recirculation can be modified by changing the experimental setup, the pump action and the aqueous solution amount.

The data in Table 4.7 report that the experiment carried out with the gear pump circuit closed was unsuccessful; the copper load reached is one of the lowest achieved. During this experiment the polycarbonate pellets were completely under water and no polymer was in contact with the supercritical phase. Another experiment reported in the paragraph 4.3.3 (1ml water) shows that the simple contact with the scCO$_2$ phase, even with water as modifier, is not enough to achieve impregnation.

Table 4.7. *Results for the different 2 phases recirculation in the vessel.*

P [bar]	T [°C]	Dithizone content [mg/g]	Aqueous phase composition	Impregn Time [h]	Depress Time [h]	Gear pump Mixing schedule	Cu(NO3)2 amount [g]	Vessel Setup	Copper load [mg/Kg]
100	40	0.0643	13.5ml H2O + 1.5ml KOH 0.1M	2.0	1.0	**No mixing**	0.463	**B**	**4±1**
100	40	0.0643	8ml H2O + 2ml KOH 0.1M	2.0	1.0	5min ON, 10min OFF	0.320	**B**	**81±75**
100	40	0.0643	8ml H2O + 2ml KOH 0.1M	2.0	1.0	5min ON, 10min OFF	0.320	**B**	**131±103**
100	40	0.0033	18ml H2O + 2ml KOH 0.1M	2.0	1.0	5min ON, 10min OFF	0.606	**B**	**15,57**
100	40	0.1122	8ml H2O + 2ml KOH 0.1M	2.0	1.0	5min ON, 10min OFF	0.326	**C**	**10±4**
100	40	/	8ml H2O + 2ml KOH 0.1M	2.0	1.0	5min ON, 10min OFF	0.326	**C**	**5±2**
100	40	0.1122	8ml H2O + 2ml KOH 0.1M	2.0	1.0	5min ON, 10min OFF **Inverted**	0.320	**C**	**5±2**

These results prove that the polymer should be in contact with both the supercritical phase and the aqueous solution. For this reason, the high standard deviation of the successful results is probably related to an inhomogeneous mixing. In the studied system, it is really difficult to circulate the two phases in a way they can contact all the polymer pellets; particularly some pellets can remain in contact only with the $scCO_2$ or the aqueous solution during all the impregnation time. Consequently, not all the pellets would result to be impregnated and the high standard deviation is generated.

To improve the process, the amount of the solution was changed from 10 ml to 15 and to 20 ml. The results obtained were similar to the previous ones and the standard deviation problem was not solved.

The high pressure vessel setup was changed to ensure that all the pellets were homogeneously contacted by the 2 phases. Setup C (Figure 2.4) was developed but a copper load comparable with the previous experiments was not achieved (lower rows, Table 4.7). It was not possible to give a certain explanation to these results, probably the solution path in the vessel was not the expected one. The vessel C setup is designed to have the solution droplets coming from the top and fall directly in the 1cm diameter polymer container. It can be imagined that the droplets descent is not in the centre, in this way it would be possible for the solution to reach the bottom moving by the wall without efficiently contacting the polymer. This could be due to the inlet of the solution (top of the vessel) that deviates the droplets or, alternatively, to an imperfect vertical positioning of the vessel.

To improve the mixing, another attempt was made changing the direction of the circulation, in this way the $scCO_2$ was bubbled through the aqueous solution. With this setup the impregnation was unsuccessful as well.

4.2.6 Zinc impregnation

A preliminary experiment on the two phases process has been carried out with zinc. The aim was to better understand the procedure and to state if the method could be useful to other metals impregnation. Zinc nitrate hydrate ($Zn(NO_3)_2*6H_2O$) has been used as salt. The result and the same conditions of 100 bar and 40°C are reported in Table 4.8.

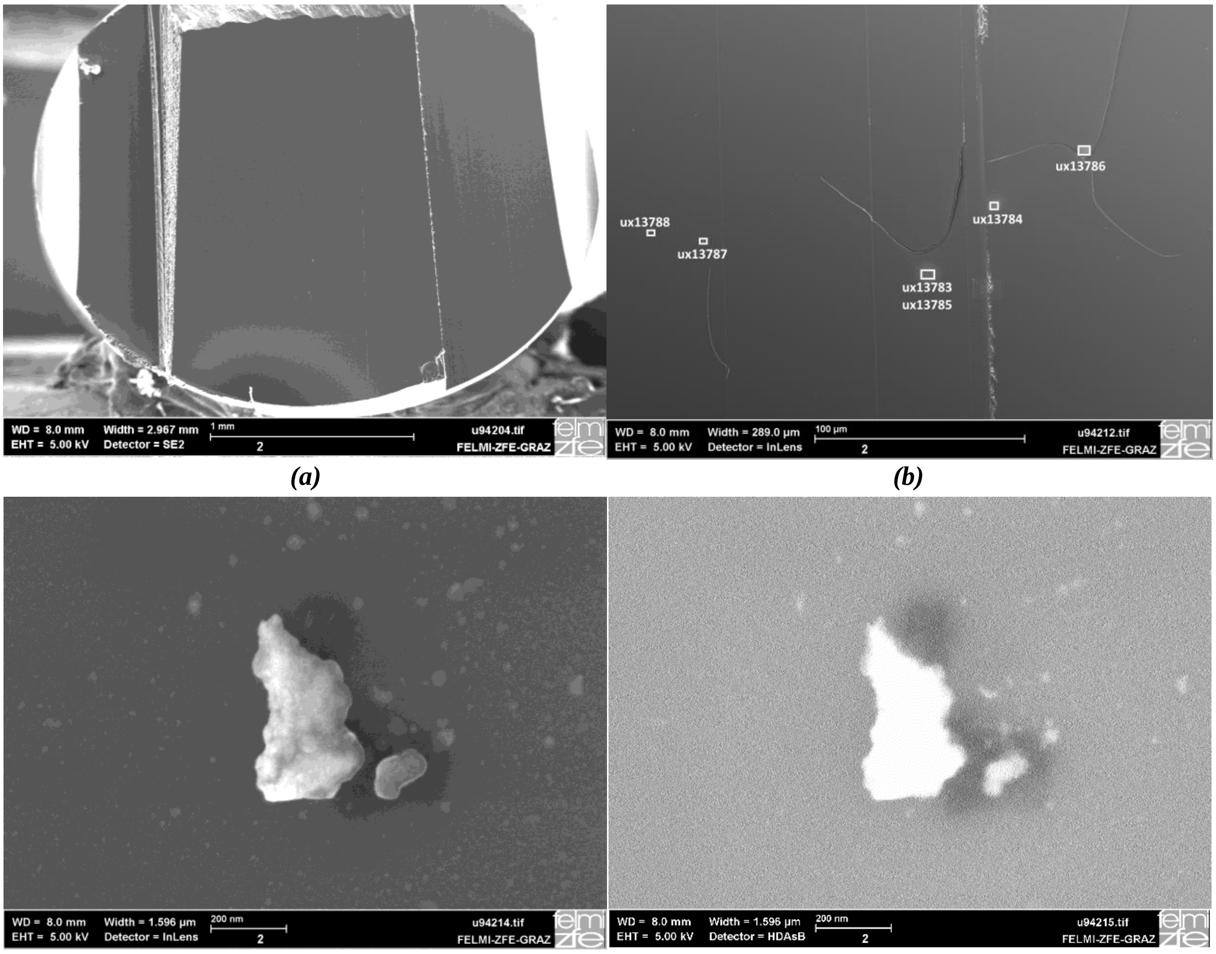
Table 4.8. *Result for the Zinc impregnation*

P [bar]	T [°C]	Dithizone content [mg/g]	Aqueous phase composition	Impregn Time [h]	Depress. Time [h]	Gear pump Mixing schedule	$Zn(NO_3)_2*6H_2O$ amount [g]	Copper load [mg/Kg]
100	40	0.1085	8ml H2O + 2ml KOH 0.1M	2.0	1.0	5min ON, 10min OFF	0.4047	201±145

The experiment was successful and a relatively high zinc load was reached. A really high standard deviation is observed also in this case. So, the main reason why this process is considered promising is that it can be extended to other systems and for other metals.

4.3 Scanning electron microscope investigation

The impregnation was assessed using a SEM. A sample obtained with the 2 phases process with relatively high copper load (109±3 mg/kg) was measured. The pictures and the results are shown in Figure 4.3a-b-c-d and in Figure 4.4a-b.



(a) *(b)*

(c) *(d)*

Figure 4.3a-b-c-d. *Results obtained with the SEM investigation.* ***Figure a.*** *polycarbonate pellet cut and coated.* ***Figure b.*** *highlight of the particles occurred in the polymer matrix.* ***Figure c.*** *picture of a single copper particle.* ***Figure d.*** *picture of the particle obtained with the backscattered electron detector*

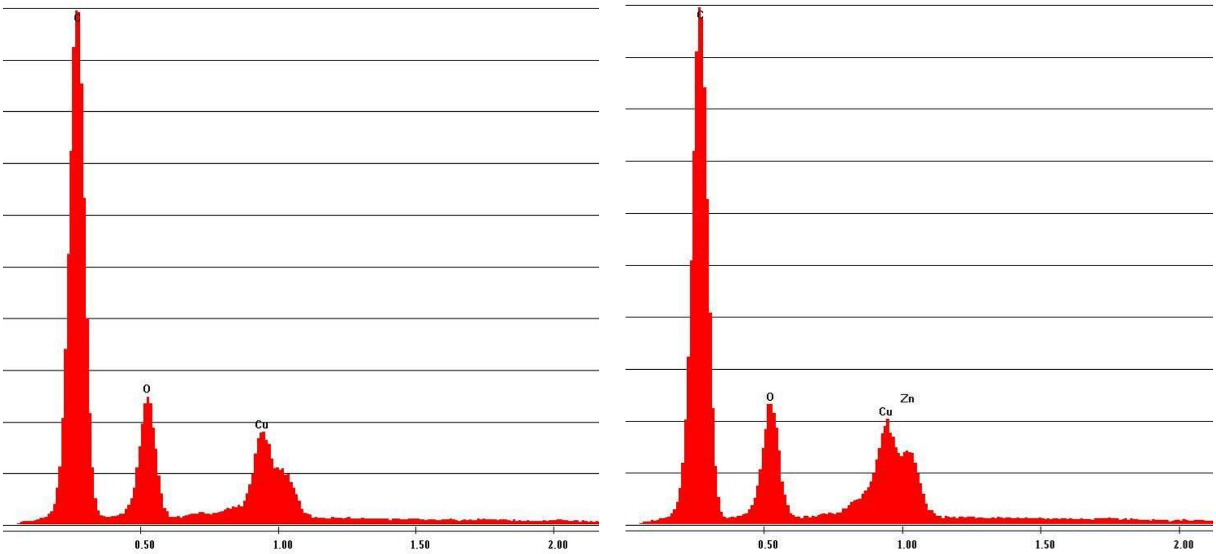


Figure 4.4a-b. *Plots obtained with the EDX detector measuring the spots of two different particles found in the matrix.*

These results give a good information on the final impregnation achieved. Deep inside the polycarbonate pellet copper was found in the form of relatively big clusters (in the order of 200-400 nm) surrounded by a lot of smaller particles (Figure 4.3c). The EDX detector confirmed that the particles were made of copper (Figure 4.4a-b).

With this technique, it was found that a deep impregnation has been achieved (not only a surface deposition) and information on the copper particles size and their distribution were obtained.

4.4 XPS analysis

A XPS technique was used to determine the oxidation state of the copper inside the polymer matrix. This measurement was performed to understand how this process works. The same sample investigated with SEM was analysed. The determination of the oxidation state is done evaluating the spectra obtained; particularly, the pure core-level transition is assessed. Figure 4.5 shows the theoretical binding energy plot (Cu 2p) for the three oxidation states of copper.

Looking and evaluating the sample binding energy plot between 960 and 930 eV is possible to determine the oxidation state of the copper into the polymer matrix. Figure 4.6 report the complete binding energy plot; Figure 4.7 focus on section between 960 and 910 eV.

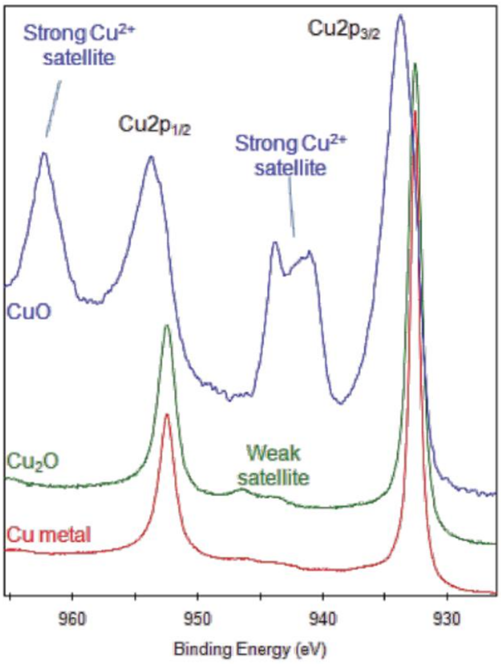


Figure 4.5. *Comparison of the three oxidation state of copper theoretical binding energy plot for the pure core-level transition Cu 2p* [35].

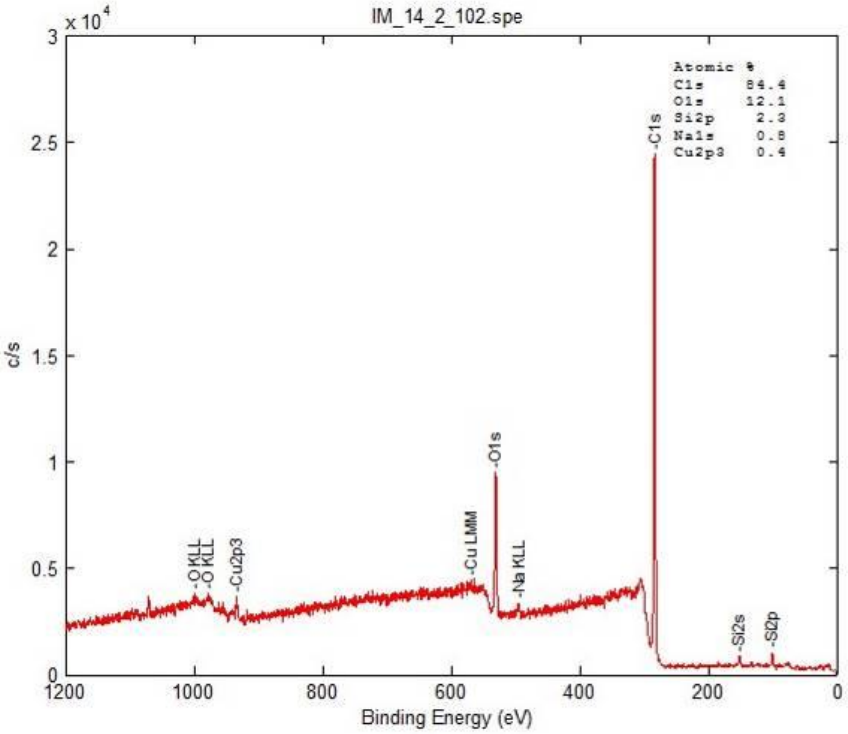


Figure 4.6. *Complete binding energy plot measured*

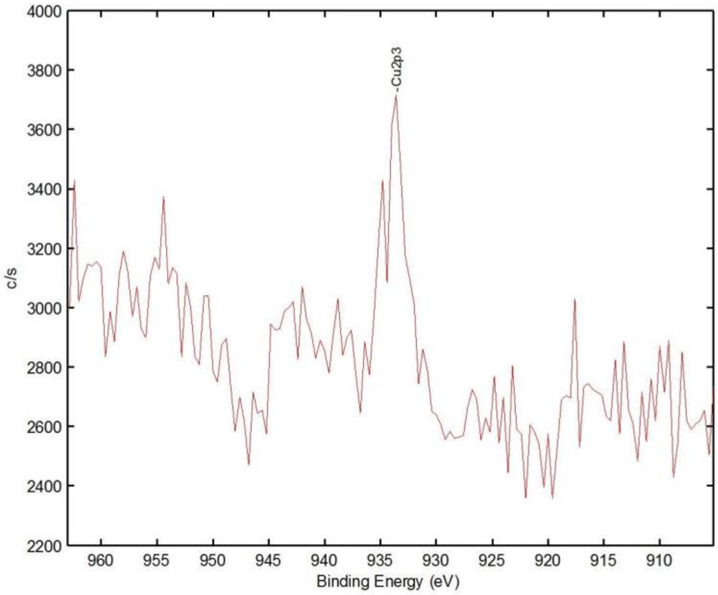


Figure 4.7. *Section between 960 and 910 eV for copper determination.*

The copper peak in the plot (Figure 4.6) results to be really small; this is probably due to the low copper load in the polymer and to the small analysed depth with the polymer surface. For this reason, the signal in Figure 4.7 appears really noisy and the fluctuations are somehow comparable with the height of the peaks studied. The noise of the measurement causes the impossibility to make a round hypothesis on the oxidation state of the copper.

However, an idea on the oxidation state can be proposed overlapping Figure 4.7 with the theoretical binding energy plot (Figure 4.5). Looking at the general shape of the measured signal and at the position of the main peak, the Cu^{2+} oxidation state results to be the most probable copper state in the matrix.

4.5 Possible explanation of the process dynamic

To explain the experimental results, an assumption on the 2 phase-process dynamic is proposed. The high pressure vessel is charged with the polycarbonate pellets, water, the KOH solution and the copper nitrate hydrate; suddenly the copper hydroxide is produced and due to its low solubility it precipitates immediately. Once the vessel is pressurized, some of the CO_2 is solubilized in the aqueous phase and a little amount of water passes into the supercritical phase. At the end of the pressurization step, four phases are in the vessel: the aqueous solution, the supercritical phase, the polycarbonate pellets and the solid copper hydroxide.

A key factor for the process is the acid behaviour of the CO_2 in water. In fact, when CO_2 dissolves an important reaction takes place modifying the pH of the solution.

$$CO_{2(aq)} + OH^{-}{}_{(aq)} \leftrightarrows HCO_3{}^{-}{}_{(aq)} \tag{4.1}$$

The pH as function of temperature and pressure for the water-CO_2 binary system was measured by Meyssami *et al.* [36]. These authors report an equilibrium pH close to 3.20 for the studied conditions (100bar and 40°C). In our work, it is assumed that the acid behaviour of the CO_2 allows the copper hydroxide to be solubilize, at least in part, in the aqueous solution. The solubility equilibrium, in fact, is highly dependent on the hydroxide ions concentration in the solution. Equation 4.2 reports the reaction that leads to the copper hydroxide formation.

$$Cu^{2+}{}_{(aq)} + 2OH^{-}{}_{(aq)} \leftrightarrows Cu(OH)_{2(s)} \tag{4.2}$$

Also the polymer-CO_2 interaction plays an important role in the process. In paragraph 4.3.5 the necessity of contacting the polymer with both the aqueous and the supercritical phase has been discussed, suggesting that the $scCO_2$ has to penetrate inside the pellets, inducing the swelling and the T_g depression. The solution, when in contact with the swollen polymer, can partially diffuse inside the matrix.

During the depressurization step, CO_2 leaves gradually the water phase making the copper hydroxide precipitate again. Some of the copper is trapped inside the matrix and forms the particles seen at the microscope.

This theory might explain our experimental results, like the mixing effect and the KOH role in the process. The dithizone function in the impregnation is still unknown. It is suggested that it is able to improve the transportation of the aqueous solution into the polymer matrix.

It has to be noted that this possible explanation of the impregnation dynamic is just a speculation. Many factors of the process are still unknown and to state something more certain more experimental data have to be collected and analysed.

4.6 Conclusively remarks

A new process for copper impregnation of polycarbonate pellets was proposed and tested. The procedure is promising manly for the depth of the impregnation and the possibility to be applied for other metal ions. However, a better understanding of the dynamic is needed and the standard deviation problem needs to be solved.

The aim of the work was to modify the properties of the polycarbonate pellets, especially the electrical ones, however the produced material has not been investigated yet. Moreno *et al.* [37] increased the polycarbonate conductivity up to 6 order of magnitude (from 10^{-10} S/cm to 10^{-4} S/cm) introducing only 400 mg/Kg of silver nanowires. The highest concentration reached in this study (131±103 mg/Kg) can be sufficient to modify this kind of properties but also the particles shape (spherical instead of wire-like) and the oxidation state of the copper (unknown) play an important role.

An alternative and promising application for this polymer could be in the biological field, as already explained in the first chapter. The material, with the achieved copper load, can be used, for example, to reduce the number of bacteria and viruses in aqueous streams or to prevent the growth of microorganism in medical applications.

Chapter 5

Supercritical impregnation and industrial plants

5.1 Existing plants

The supercritical impregnation technique of solid materials is currently studied by many research groups, all over the world, for its promising features, as already described in chapter 1. Even if this technology has a lot of possible applications, only few industrial plants have been built so far. This fact is probably due to the high initial investment cost that makes the process somehow unappetizing for investors.

The first plant of this type, for wood impregnation plant, was built by FLS miljø (Valby, Denmark) through a new joint venture company named Supertræ (Superwood). The plant was developed with an annual capacity of 40–60.000 m^3 and is situated in Hampen, Denmark. The plant started operation in March 2002 [38]. The supercritical carbon dioxide penetrates inside the microcapillary network in the wood and carries the organic fungicide deep in the matrix. In this way the wood is protected against rot and decay.

Another supercritical dyeing process was developed by DyeCoo to dye textiles. A plant was built in Taipei (Taiwan) in 2014. The company NIKE Inc. utilises already this technology through its Taiwanese contract manufacturer Far Eastern New Century Corp (FENC). This process allows a water-free textile dyeing with a lot of environmental benefits and unprecedented colouring quality achieved [39].

5.1.1 Plants characteristic

Probably due to the relatively new process, not much information of the existing plants was found. The reported scheme and the plant operation are described taking into account the data found and the probable analogies with the supercritical extraction plants. Iversen *et al.* reported a schematic visualization of the process for the wood impregnation [38] (Figure 5.1). A patent by Schollmeyer *et al.* [40] describes more in details a similar plant also for the supercritical dyeing.

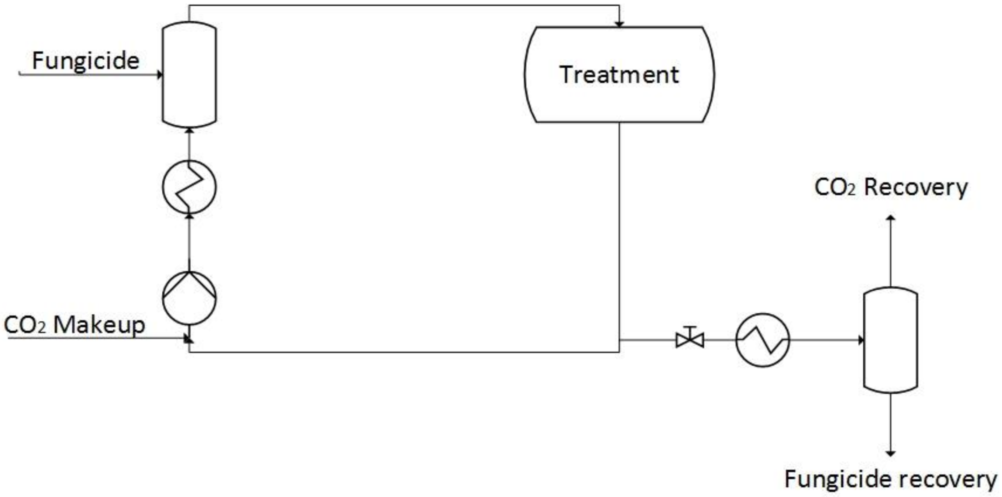


Figure 5.1. *Plant scheme for wood impregnation reported by Iversen et al.* [38]

In the reported processes (Figure 5.1, [38]), the wood and the organic fungicide are charged in the vessel and the system is pressurized. A pump pressurizes and recirculates the CO_2 in the system. The fungicide is dissolved in the supercritical phase, then it is transported through the wood where the impregnation takes place. At the end of the process the system (or only the wood vessel) is depressurized through a lamination valve and all the components (CO_2, fungicide not absorbed) are recovered. The treated wood is discharged and raw wood is loaded to start a new cycle. The charging and the discharging of the wood are carried out automatically by some carriages to reduce the manual work and to decrease the cycle time (Figure 5.2).

Figure 5.2. *Automatic charging of the wood in the impregnation vessel. The 3 vessels can be seen.* [41]

Considering the evidences found, the existing industrial plants do not include a single impregnation vessel. The wood impregnation description [38] indicates the presence of 3 different wood impregnation vessels. His corresponds also in the pictures found for the for the wood and the dyeing plant (Figure 5.2 and 5.3).

Figure 5.3. *Impregnation vessels of the supercritical dyeing plant* [39]

For this reason, successively it is reported the suggested (wood and dyeing) plant layout. It has been chosen to display in Figure 5.4 and Figure 5.5a-b only the wood impregnation plant, because the two schemes are practically the same. The plant layout is proposed taking into account the supercritical extraction process which has a lot of similarities with the impregnation [42]. Figure 5.4 displays the suggested plant layout.

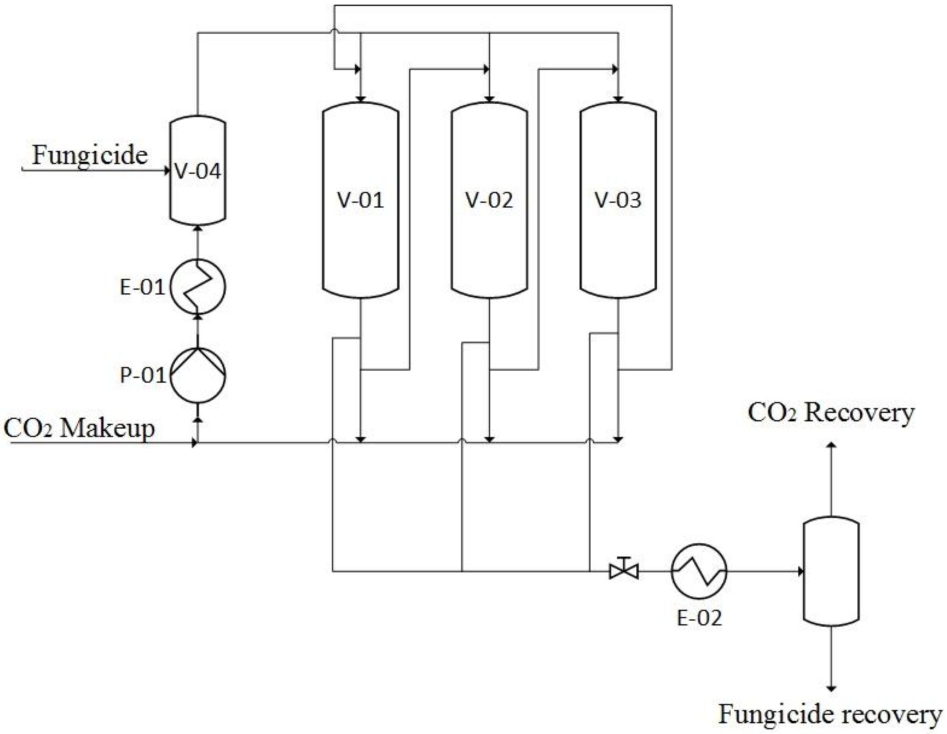
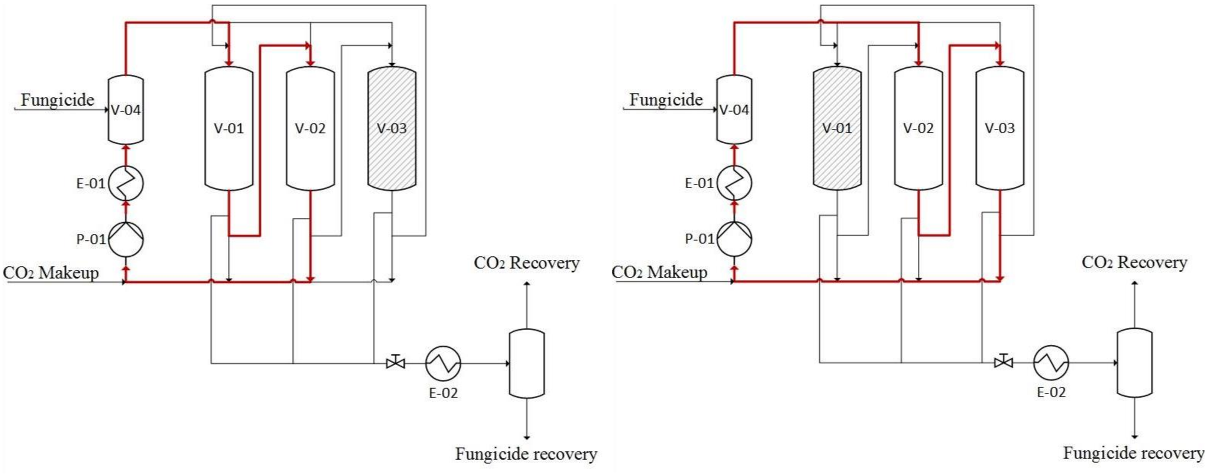


Figure 5.4. *Industrial wood impregnation plant layout proposed.*

In Figure 5.4, three impregnation vessels can be pressurized and depressurized independently. The proposed plant operation is described with the help of Figure 5.5a-b. The system is designed in a way that only two vessels are working while the other is involved by the discharging and charging operations. In Figure 5.5a, the impregnation takes place only in vessels V-01 and V-02, while vessel V-03 is not under pressure. When vessel V-03 is charged and ready, vessel 1 is depressurized and the CO_2 path is changed like shown in Figure 5.5b. The CO_2, passing through the vessel V-04, is enriched with the fungicide (or the dye); then the supercritical phase is sent to two of the treatment vessels where impregnation occurs. These two vessels are operated in series in a way that the one with the raw wood (or the textile) (vessel V-03) is downstream with respect of the other vessel (V-02). This is due to the fact that there is a slight decrease on the fungicide amount between the two equipment and it is preferable to have the higher concentration for the 'final' treatment of the wood (this allows to keep the driving force of the process as high as possible).



(a) *(b)*

Figure 5.5a-b. *Suggested plant layout with the CO_2 path highlighted at different moments.* ***Figure a****. Plant operation with vessel V-03 in the charging/discharging phase.* ***Figure b****. Plant operation with vessel V-01 in the charging/discharging phase.*

The plant reported in Figure 5.4 has some benefits with respect of the one in Figure 5.1. The proposed plant results to be semi-continuous instead of the completely discontinuous one. The new configuration permits a constant operation of the recirculation pump and, then a smaller pressurization pump can be used. The proposed layout allows easier and quicker charging-discharging operations.

5.2 Proposed plant layout

The process studied in this thesis is a two-step impregnation and for this reason the plant has to be different from the one described in the previous paragraph. Therefore, it is suggested a plant similar to the wood impregnation one, but it integrates additional inlet and outlet to the impregnation vessels to allow the aqueous solution recirculation. Figure 5.6 displays the proposed plant layout.

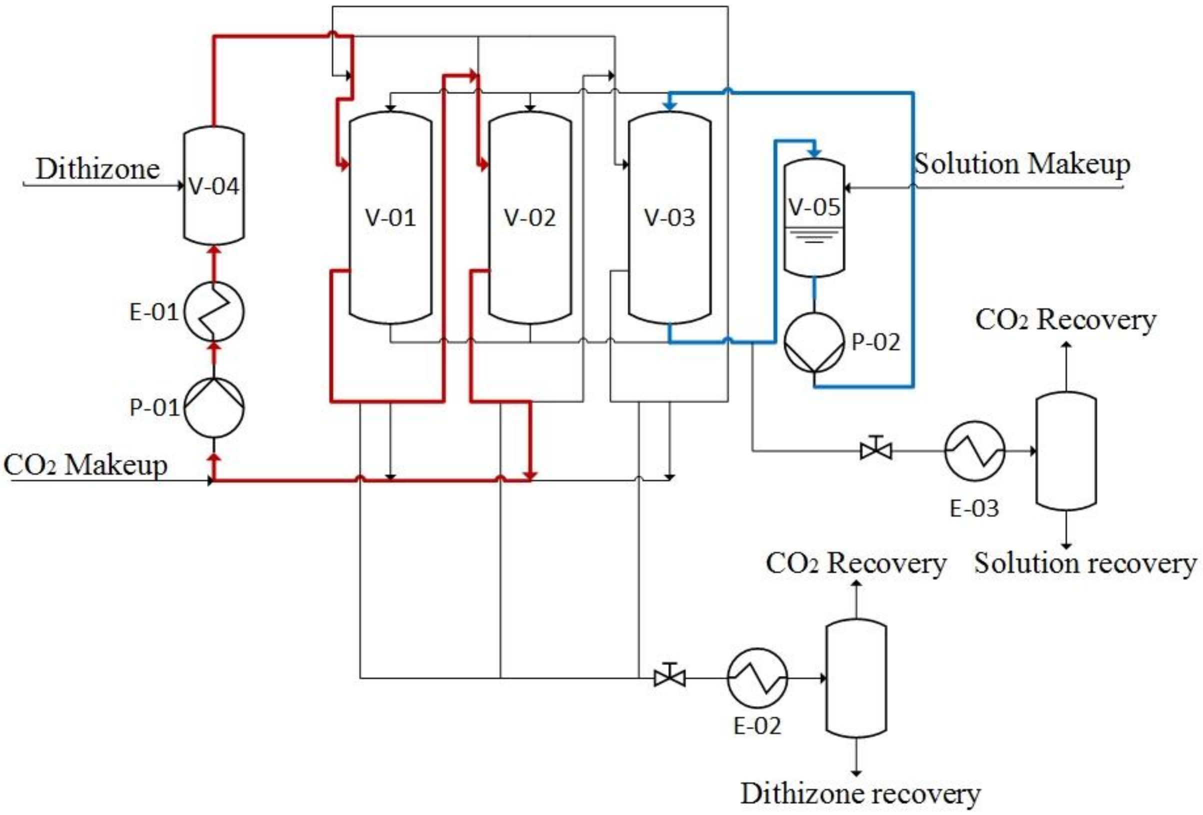


Figure 5.6. *Proposed industrial plant for the 2-step impregnation process.*

Considering the fact that a similar copper load was reached also without adding to the supercritical phase ethanol as modifier, it was chosen to carry out the first impregnation using pure $scCO_2$. In this way, a 'green' process, completely free of organic solvents, is designed. The recovery of the dithizone from the supercritical phase results easier because it can be achieved by a simple depressurization. It was considered to carry out the first step at 200 bar, 40 °C and 6 hours to achieve a good dithizone content and to avoid any crystallization problem.

The impregnation vessels shown in Figure 5.2 and 5.3 are designed respectively for wood and textile. Due to their shape and characteristic, these materials are easy to transport and charge in the reactor. The polycarbonate used in this process is on pelletized form and, due to its powder-like behaviour, a different vessel structure is needed to allow a fast operation (charging or discharging). Two different solutions are available in the market for this type of material and both require a vertical impregnation vessel. The first option is used for supercritical extraction of rice; this technology has been applied to minimize plant-protective agents and fatty oils from the product and, therefore, achieve substantial quality improvements [42]. This vessel consists of a gate that separates the bottom closure from the rice itself; in this way it is possible to charge the material from the top and then discharge everything by gravity (Figure 5.7a). The second solution, used in most of the extractions, consists of an internal container where the material is charged (Figure 5.7b); when the vessel is open it is sufficient to remove the basket with the product and to insert a new one with the raw material.

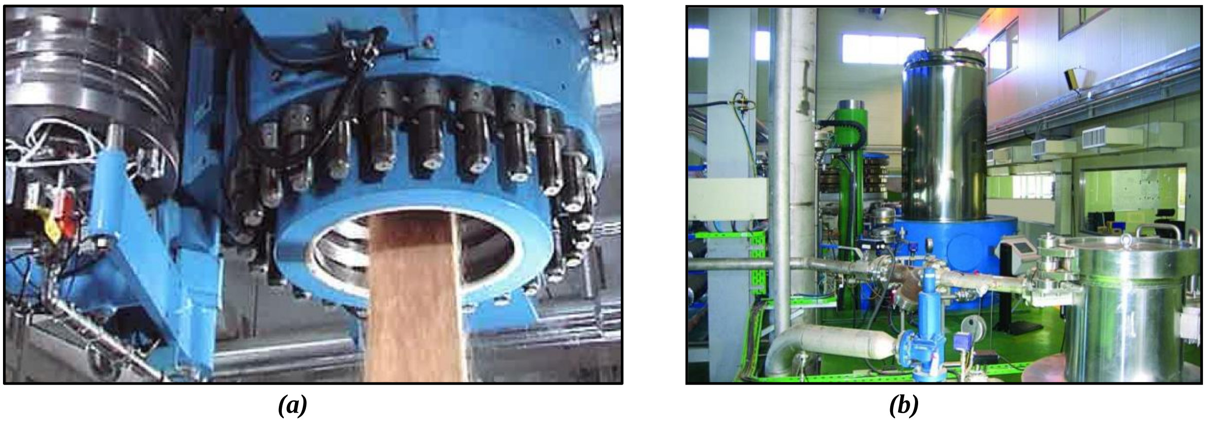

(a) (b)

Figure 5.7a-b. *Different types of impregnation vessels.* ***Figure a.*** *Rice treatment vessel.* ***Figure b****. Impregnation vessel with the material container.* [42]

The vessel proposed here is the "basket configuration" (Figure 5.7b). This choice is linked to the second impregnation step of the studied process. The solid copper hydroxide in the aqueous solution can cause fouling accumulation in the system; this, through the various cycles, can lead to a complexation between the dithizone and the copper outside the polymer matrix. The internal container, in the chosen configuration, can separate the water from the vessel itself; in this way it is possible to clean the container only without stopping the plant.

5.2.1 Impregnation vessels sizing and operation

Taking into account the condition chosen for the industrial process, (200 bar, 40 °C, 6 hours for the dithizone impregnation and 100 bar, 40 °C, 2 hours for the second step) the sizing of the impregnation vessels has been carried out. The three vessels plant configuration showed in Figure 5.6 has been considered, and the calculations have been made fixing an annual productivity of 5000 tons of copper-nanoparticles impregnated polycarbonate.

To size the vessels correctly, a more specific process schedule needs to be defined. With the conditions chosen, the single vessel operation shown in Figure 5.8 is proposed.

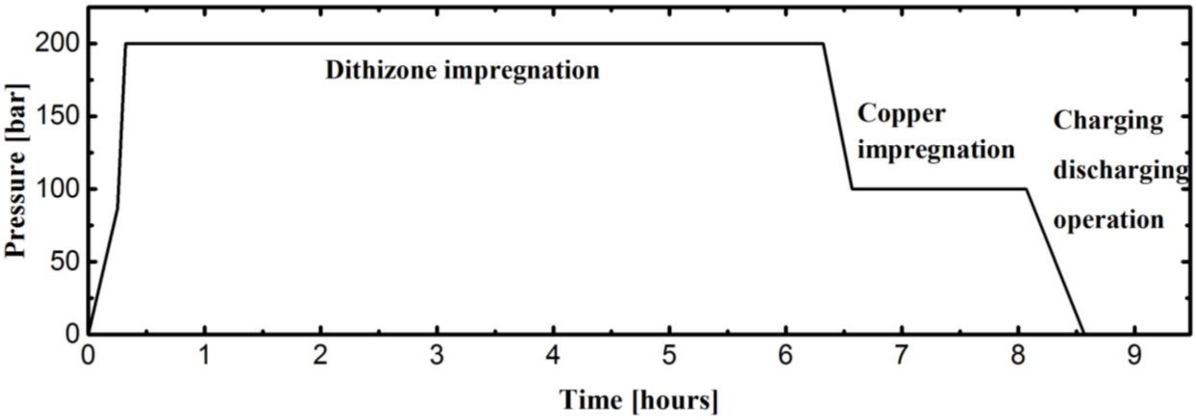


Figure 5.8. *Proposed pressure profile inside an impregnation vessel.*

Figure 5.8 reports a copper-nanoparticles impregnation time of 1.5 hours, instead of 2. The time was reduced by taking into account the differences between the industrial application and the laboratory study. In fact, during the research, the experiments start from the atmospheric conditions, and additional time is needed for the CO_2 to penetrate inside the polymer. Instead, in the industrial application the polymer has already been swollen at the time it gets in contact with the copper solution. Unfortunately, no experiment has been carried out to quantify this phenomenon; however, a shorter or longer impregnation time can be implemented easily in the proposed process operation without changing the cycle duration. Slightly less than one hour (55 minutes) has been assigned to the charging and discharging operations. Figure 5.9 reports the pressure profile for the three impregnation vessels simultaneously and shows better the overall plant operation. The proposed operation allows to discharge/charge a vessel every 190 minutes.

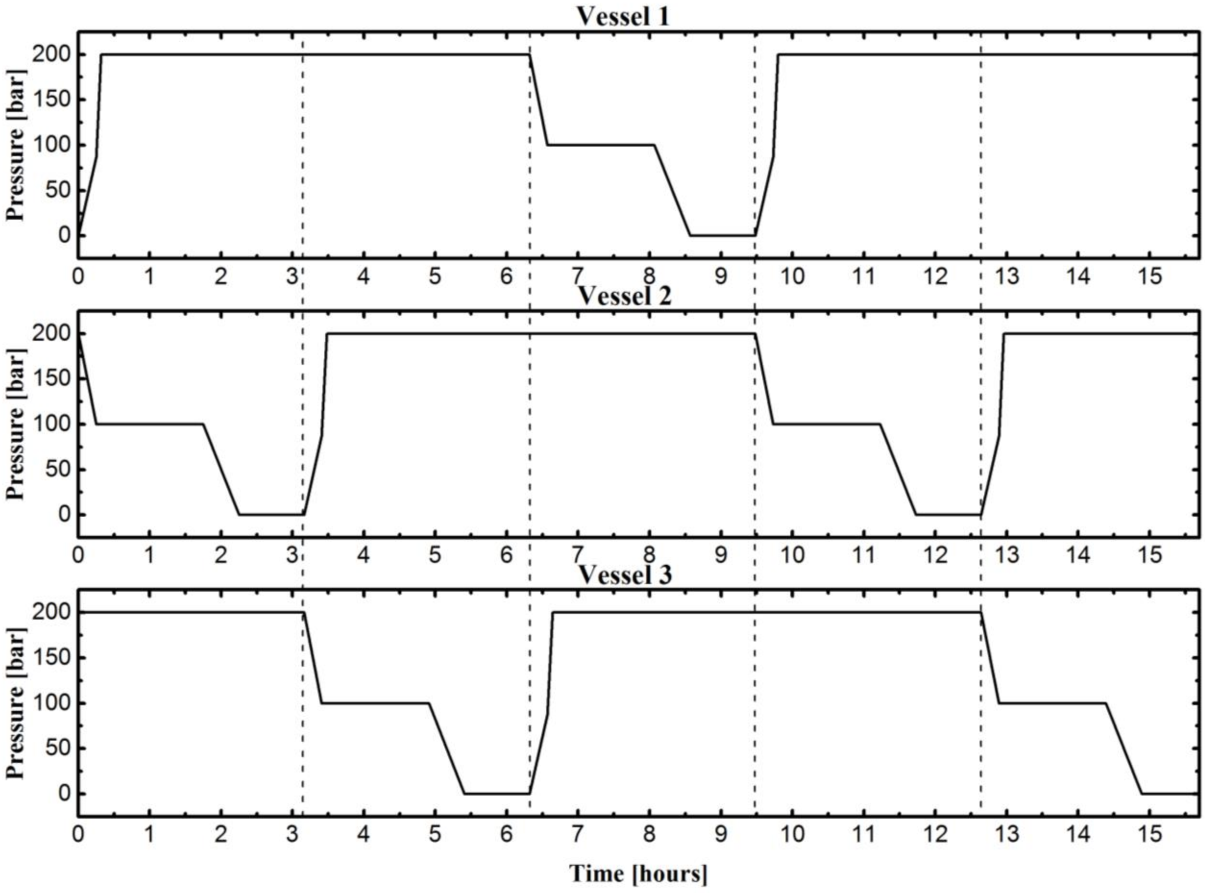


Figure 5.9. *Pressure profiles in the 3 impregnation vessels with respect of the time.*

The sizing has been made considering the plant to operate 24 hours per day and 351 days per year. The measured pellets bed porosity of 47% has been used to determine the three vessels volume. Table 5.1 reports the values calculated for the three vessels.

Table 5.1. *Productivity, vessels specifications and consumption estimation for the proposed plant.*

Productivity	5000	ton / year
Polymer treated every 190 min.	1876	kg
Polymer volume	2.92	m^3
Vessel diameter	1.25	m
Vessel height	3.00	m
CO_2 consumption	115063	kg/year
Minimum Dithizone consumption	13.5	kg/year

Both for the dyeing and the wood impregnation, a CO_2 recovery higher than 95% has been reported. The same value was assumed for the proposed plant. The total dithizone consumption was not determined because its solubility data in $scCO_2$ were not available; for this reason, it was impossible to calculate the amount loss in the recovery. Table 5.1, in fact, reports only the amount of dithizone loaded in the polycarbonate matrix. In the same way it was impossible to determine how much of the aqueous solution makeup is needed. The copper impregnation step is a new process and the information needed for the liquid phase cannot be assumed a priori.

Conclusions

The aim of the study was to impregnate polycarbonate pellets with copper nanoparticles by a supercritical fluid technology. In this work the 2-step process developed by the Graz research group was studied. The method consists of 2 sequential stages; in the first one the pellets are impregnated with dithizone and, in the second one, the polymer is loaded with copper. Both steps were carried out in supercritical carbon dioxide media, with and without the addition of ethanol as modifier.

The proposed method allows to avoid the expensive organometallic complex synthesis and uses a cheap salt as a copper source, thus reduce significantly the operative cost of the process.

The experiments were carried out in a high pressure vessel in the range of 100–250 bar and 40–50 °C. The samples were analysed with an UV-spectroscopy technique to determine the dithizone content reached after the first impregnation. After the second step, the overall metal load was measured by ICP-OES. The impregnation was studied and evaluated with a SEM and with an EDX detector to determine the atomic composition of the metal clusters in the polymer matrix.

The impregnation of polycarbonate pellets with dithizone was successful by using pure $scCO_2$ as carrier, but adding ethanol as modifier it was possible to reach a load of one order of magnitude higher. Dithizone proved to be soluble in $scCO_2$, fact that was not reported yet in the literature. Observation on the polycarbonate crystallization under supercritical CO_2 and an estimation of the observed diffusion coefficient have been reported.

In the second process step, copper nanoparticles were encapsulated in the dithizone containing polymer. The maximum copper load reached with this process was 131±103 mg/kg; the high standard deviation is caused by an inhomogeneous distribution of copper in the pellets of the same sample. The reason of this result was investigated and a possible explanation of the process dynamic was proposed, in which the poor mixing in the vessel has been suggested as the main cause of the standard deviation. It was also demonstrated that, the presence of dithizone increases the copper load reached in the second step, even if its role is still unclear. A successful zinc impregnation was carried out simply by changing the salt used; the results suggests the possibility to extend the methods also for other metals ions.

Through SEM analysis, copper clusters in a range of 5–400 nm were found deep and homogeneously distributed inside the polymer pellet. The high impregnation depth reached is interesting because the studies found in the literature are mostly carried out on thin polymer support samples (39µm [18] and 25 µm [19]).

Eventually, an industrial plant layout has been proposed for the studied process, however before scaling it up, more experiments have to be carried out.

In summary, this process has great potentials thanks to its lower cost and to its high flexibility.

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