

Impregnation of Polymers with Colors and Nanoscale Particles

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To generate the best characteristics for diverse applications, polymers are colored, functionalized and additives are employed. Relevant functionalizations are coloring, UV stabilizing, antistatic effects, scratch stability etc. There are two main conventional processes to achieve this: One way is compounding polymers, for example with colors. Normally this is done by admixing pigments or precolored masterbatches. Assets are resistance against scratches, easy processing and accuracy of fit. Drawbacks are low material efficiency of additives and high temperatures, which make a usage of thermolabile additives impossible. The other way is to coat polymers. Assets are easy change of additives like colors, material efficiency and low temperatures. Drawbacks are low scratch resistance, removal of solvents and pretreatment of polymers, which is necessary as the adhesion on „pure“ polymers is mostly too low. Several methods like applying primers, surface grinding etc. are employed to increase the adhesion between polymer and coating.

A possibility to combine the assets of compounding and coating is the impregnation of polymers using high-density carbon dioxide. Our work is focused on deep impregnation of surfaces in a range between 10 and 1 000 µm. The impregnation shows high material efficiency, good penetration characteristics, scratch resistance and regular distribution. The lecture will give an overview of the results for different polymers (polypropylene, nylon, thermoplastic polyurethane and polycarbonate), used parameters like pressure, temperature and time and depths of penetration. The possibility of colorization will be discussed by comparing new results with results given in literature. One new application is the colorization of powders for laser sintering. A complete penetration of nylon particles could be shown and future fields of application will be discussed. The possibility to bring nanoscale particles into dense polymers in solid state will also be presented and examples will be given for amorphous and semi-crystalline matrices.

1. INTRODUCTION

Articles made of plastics have to withstand exposure to heat, light, and humidity without changes in appearance and mechanical performance. Furthermore neat polymers in most cases do not show satisfactory properties regarding e. g. color, surface touch or flammability. Regarding optimization of mechanical performance, appearance and functionality a broad variety of different additives and fillers is used.

The total global production of plastics grew to 260 million tonnes in 2007 [1]. The average use of additives in plastics is 5 to 7 % by weight which corresponds to a global annual additive consumption of 13 to 18 million tonnes a year.

Important groups of additives and fillers used in plastics modification are antioxidants, stabilizers, lubricants, slipping and antifogging aids, flame retardants, blowing agents, crosslinkers, colorants and whitener, reinforcing fillers and coupling agents.

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Typically additives and fillers are incorporated into the neat polymer by means of melt mixing (compounding). Machines used for compounding are kneaders, single and co- or counter-rotating twin screw extruders. The additives and fillers are solved or dispersed into the polymer matrix at temperatures between 100 °C and 400 °C under high shear forces. During melt mixing the additives and fillers are equally distributed over the whole volume of the plastic part.

Since most of the effects addressed by additives are surface functionalities (tribological, visual and haptic effects) huge amounts of chemicals are wasted.

The wall thickness of plastic articles is limited by the forming process and typically ranges from several ten micrometers (packaging) to some millimeters (automotive, consumer electronics, construction). Nevertheless surface functionalities are generated by the chemical composition of surface near regions only. Depending on the addressed effect the relevant depth covers some few molecular layers (wetting) to some micrometer thickness (color). Therefore up to 99 % of the additives addressing surface modification could be saved with a technique to bring the additives in near surface regions only. High pressure impregnation using compressed carbon dioxide could be a technical opportunity capable to activate this potential.

A further advantage of high pressure impregnation is the possibility to process additives at lower temperatures (compared to melt mixing). This may be of interest when dealing with high polymers that possess melting temperatures between 250 and 400 °C or when the modifiers are sensitive to shear and temperature e. g. pharmaceuticals.

Moreover an impregnation process carried out after shaping the product enables the realization of a customer or application oriented tailoring of color or other functionalities like antimicrobial effects, haptics etc. This may be of big importance e. g. in rapid manufacturing.

Assuming the above mentioned savings and the large annual additive consumption super critical impregnation is promising a high potential for sustainable technology development. In this article examples are given on the colorization of different amorphous and semicrystalline thermoplastic polymers as well as an outlook on polymer modification by impregnating them with nanoparticles.

2. STATE OF THE ART

2.1 Surface Modification of Polymers

As mentioned in the first chapter the most widely used route to plastic modification is melt mixing. A well established alternative to melt mixing is surface modification by coating or electroplating of plastic parts. Even though some interesting functionalities and a noble appearance is achieved by coating or electroplating there are severe disadvantages caused by lack in scratch resistance or adhesion.

In contrast to compounding and coating impregnation techniques have hardly been used in the polymer processing industry until now. Two rather new processes have been published recently: the Bayer-Aura-Color-Infusion-Technology (WO2007025579A3) and the Essilor impregnation-process of optical lenses (DE069713509T2).

The Bayer-Aura-Color-Infusion-Technology is a new approach to colorize already shaped parts of polycarbonate. Transparent bodies of polycarbonate are dipped into a bath for several

seconds. The immersion bath has a temperature of 100 °C and is composed of water, ethylene glycol butylether, diethylene glycol and colorants. Further additives can be used when they are soluble in the solvent system. After dipping the parts are dried and the solvent has to be recovered. The achieved depth of impregnation is typically around 20 µm. The process is well suited for small batches or customer tailored colorization.

The colorization of lenses composed of polycarbonate has been patented by Essilor GmbH. In a first step the polycarbonate is degraded by exposure to UV-radiation (320 nm, 48 J/cm²) for some minutes. Afterwards the colorization is conducted in a solvent bath containing the dyes. The temperatures needed are about 100 °C and the dipping time is more than one hour. After colouring the lenses are dried and stabilized at 140 °C for two hours.

A major drawback of the two processes is the utilization of hazardous solvents which requires several measures regarding safety and environmental protection during processing and application. Further disadvantages are the long drying times and the degradation of the polycarbonate which decreases the mechanical properties of the lens surface.

2.2 Processing of polymers in solid state assisted by highly compressed carbon dioxide

CO₂ is distinguished from conventional solvents because its solvent properties may be varied by adjusting the density of the fluid between that of a liquid and that of a gas through pressure and temperature regulation. This density ‘tuning’ may be exploited when control over the diffusion of additives impregnated from a scCO₂ solution is performed as a result of polymer free volume and solvating power control [2]. Furthermore CO₂ molecules weakly interact with basic sites along macromolecular chains, resulting in the plasticisation of amorphous domains in glassy and semi-crystalline polymers [3]. A survey on carbon dioxide assisted polymer impregnation is given by Tomasko et al. [4].

3.1 Experimental set-up

High pressure impregnation was accomplished in laboratory scale using a highpressure viewing cell, a high pressure vessel and a technical scale pilot plant with a rotary basket.

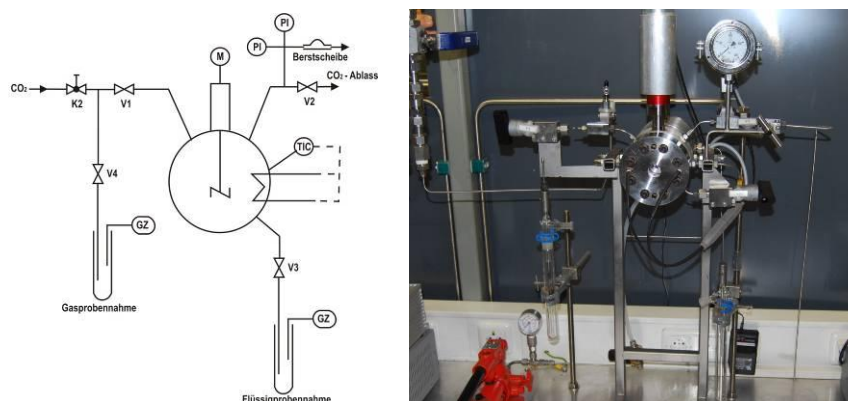


Figure 1: Design and photograph of the high-pressure viewing cell system (63 mL, 350 bar, 250 °C)

The high pressure viewing cell has an internal volume of 63 cm³ and a maximum operating range of up to 350 bar at 250 °C. Figure 1 shows the set-up of the equipment used. The pressure is built up by means of a pump by continuously injecting CO₂. Two heating elements integrated in the outer wall of the container heat the viewing cell. The interior of the cell can

be observed via two windows on the front and rear sides. A stirrer is mounted on the top of the viewing cell.

For the impregnation of larger amounts of powder a high pressure vessel was used (Fig. 2). The vessel has an internal volume of 1.5 L and a maximum operating range up to 200 bar at 300 °C. The vessel jacket is electrically heated. The maximum number of revolutions of the stirrer is 1 000 min⁻¹. For the impregnation in pilot scale, a new system was built up (Fig. 3). It consists of a rotating basket placed within a 20 litre autoclave which allows pressures up to 300 bar at 80 °C and numbers of revolution up to 20 min⁻¹.



Figure 2: High pressure vessel with 1.5 L, 200 bar, 300 °C

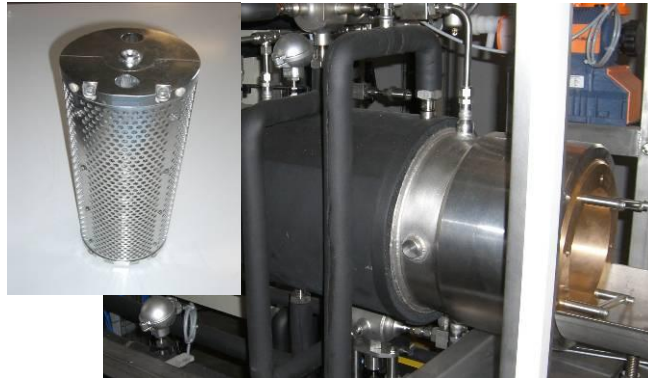


Figure 3: Pilot scale impregnation equipment with 20 L, 300 bar, 80 °C

3.2 Materials

The materials that were impregnated are amorphous thermoplastic polyurethane (TPU) and polycarbonate (PC) as well as semicrystalline polyamide 11 and 12 (PA 11, PA 12) and polypropylene (PP) (Table 1). The polymers are investigated as parts of injection molded test specimens (TPU, PC, PP, PA 12), in powder form (PA 11, PA 12) and as a laser sintered body (PA 12). The glass transition temperatures of TPU and PP are much lower and that of PA 11 and PA 12 are little lower than that of the chosen processing temperatures (60 to 110 °C). The glass transition temperature of PC is much higher. Hardness and tensile modulus of the polymers are in a narrow range, except for TPU. TPU is a much softer elastomeric material.

Two commercial dyes are used for colorization: a mixture of anthraquinone and azo dyes and a nitro dye preparation.

The nano-Ag-dispersion for further impregnation experiments is prepared using ethanol, nanosilver with purity of 99.5 % and particle size of 35 nm and three dispersing agent based on block copolymers differing in molecular weight and number of acidic or basic groups.

Table 1: Investigated Polymers

type of polymer	hard-ness (Shore A/D)	tensile-modulus	glass transition temperature
thermopl. polyurethane	78 (A)	5 MPa	-45 °C
polycarbonate	n. a.	2400 MPa	147 °C
polyamide 12	70 (D)	1100 MPa	46 °C
polyamide 12 (powder, laser sintered part)	73 (D)	1586 MPa	46 °C
polyamide 11 (powder)	72 (D)	1300 MPa	37 °C
polypropylene	72 (D)	1520 MPa	-10 °C

4 TEST PROCEDURES AND RESULTS

4.1 Effect of scCO₂ on polymerstructure

Depressurization strongly affects the microstructure of the polymers to be impregnated with supercritical carbon dioxide. Figure 4 shows a thermoplastic polyurethane which was placed for two hours in carbon dioxide at 200 bar, 60 °C and afterwards fastly depressurized with > 6 bar/s to ambient conditions. The polyurethane originally transparent turned into white, volumetric swelling exceeded > 300 % and dimensional stability was poor. Nevertheless the resulting foam structure was permanently stable, so a process combining modification and foaming could be a possible field of future research. The microstructure shows microbubbles from 10 to 70 µm within the bulk, however, in the surface near regions (< 150 µm) no bubbles are visible. The latter may result from the dense and lamellar structure with low permeability that develops during injection moulding as a consequence of melt flow regimes in near wall regions.

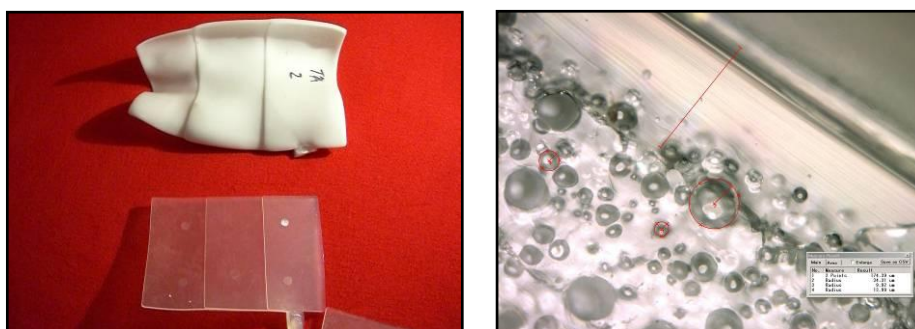


Figure 4: TPU sample before and after high pressure impregnation with depressurization rate > 6 bar/s (left), foam microstructure of the TPU (right)

After a supercritical impregnation for 10 min at 230 bar and 90 °C, choosing a depressurization rate of 2 bar/s the semicrystalline polymers (except for PA 12 powder) exhibited an increase in crystallinity (determined by DSC measurement with 10 K/min under N₂

atmosphere). The increase in crystallinity occurs because of the carbon dioxide acting as a temporary plasticizer which increases chain mobility and thus allows further crystallization even at low temperatures. In opposition to the other semicrystalline polymers the PA 12 powder shows a decrease in crystallinity. This is caused by the fact that the powder is a not fully condensed polyamide. It may contain crystalline regions of low molecular weight fractions which are soluble in supercritical CO₂ and further polycondensate during impregnation without subsequent re-crystallization. While semicrystalline polymers show an increase in crystallinity the amorphous polymers remain amorphous.

Table 2: Change in crystallinity as a consequence of supercritical impregnation (230 bar, 90 °C, 2 bar/s depressurization rate)

Polymer	Crystallinity before impregnation	Increase in crystallinity
TPU	Amorphous	0
PC	Amorphous	0
PA 12	31.9 %	+ 4.0 %
PA 12 (powder)	47.3 %	- 16.7 %
PA 11 (powder)	34.3 %	+ 12.8 %
PP	37.6 %	+ 9.6 %

4.2 Colorization of polymer parts

In preliminary tests pressure, temperature, weights of dye and polymer as well as stirrer rate were investigated to find optimal working conditions. Good results with respect to the black colorant were obtained at 230 bar and 90 °C. In each trial a part of a polymer test specimen and 0.05 g of dye were placed into the cell, the cell was sealed and set under carbon dioxide pressure at a rate of 5 bar/s. At these conditions a saturated supercritical solution was prepared containing 0.13 % of dye. Once the desired pressure was reached, the valves were closed and the stirrer inside the viewing cell was set to 50 min⁻¹. Impregnation times were chosen from 1 to 20 minutes, afterwards depressurization took place with a rate of < 2 bar/s. The resulting samples were washed with water and dried until mass constance.

Figure 5 gives an overview on the impregnation results using the black colorant. At 230 bar and 90 °C the two amorphous materials showed considerable and uniform colorization even at short times. The results for PA 12 and PP were less successful.

The mass uptake after 20 minutes attains 1.5 % for TPU and 0.4 % for PC (Figure 6). During the first 2 minutes the increase in weight is very fast, which may happen due to surface adsorption of the dye. Afterwards it shows linear increase with time. Which means that not only Fickian diffusion but also relaxation behavior contributes to mass transport kinetics. In the case of TPU the mass uptake slows down after 10 minutes, with PC there is no change in the slope during the investigated time range.

Nevertheless volumetric swelling occurred and exceeded:

- TPU: 9.4 % (2 min) and 197.4 % (20 min)
- PC: 2.2 % (2 min) and 3.8 % (20 min)

The variation in swelling of the two materials results from the big difference in their glass transition temperatures and therefore diffusivity of scCO_2 .

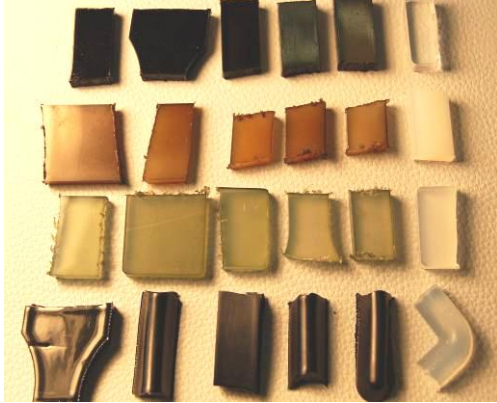


Figure 5: Impregnated parts of PC, PA 12, PP, TPU (from top to bottom), the duration of impregnation increases from 0 to 10 min (from right to left)

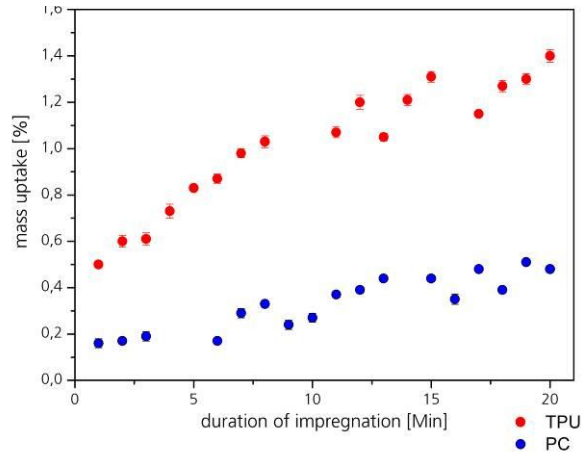


Figure 6: Increase in weight as a function of duration of impregnation (230 bar, 90 °C)

A large increase in penetration depth for PC after 15 min can be observed, which may be a result of relaxation behaviour (Figure 7). The penetration depth of TPU increases linearly with time.

The micrographs of the surface near regions (Figure 8) show an increase in penetration depth with impregnation time. While the polycarbonate exhibits a homogenous and dense penetration region, thermoplastic polyurethane shows lots of microbubbles whose amount increases during time while the size of the bubble increases with the distance to the surface.

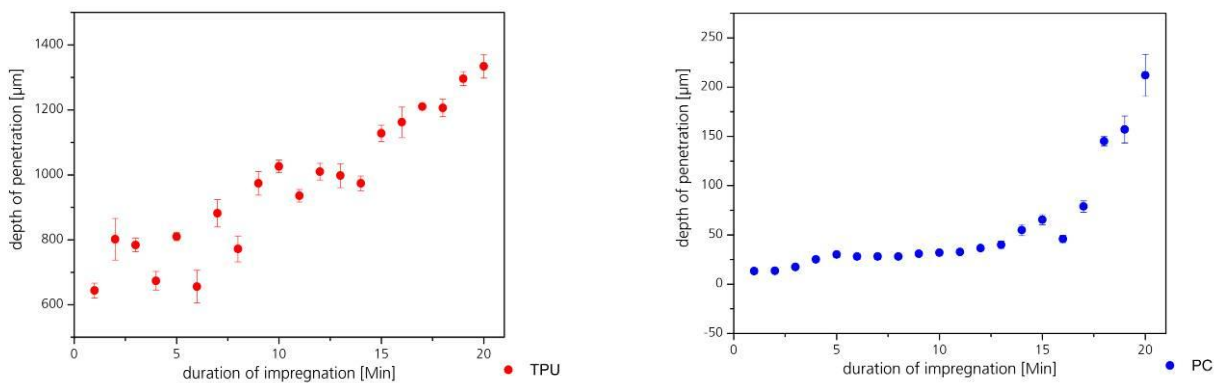


Figure 7: Depth of penetration as a function of duration (230 bar, 90 °C, left: TPU, right: PC)

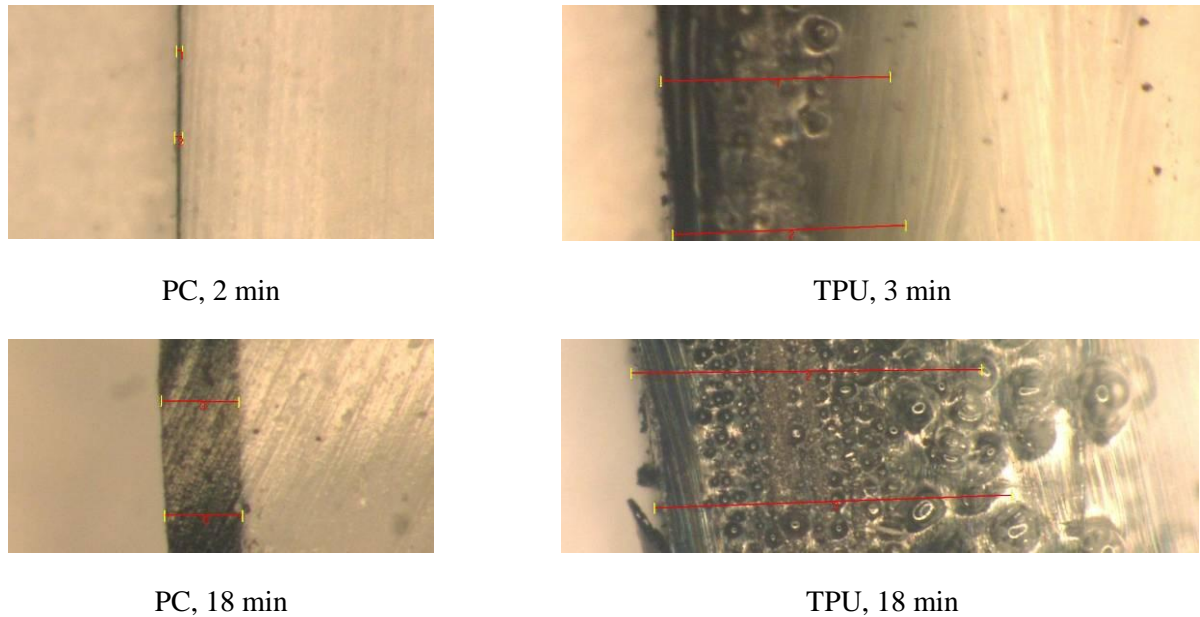


Figure 8: Micrographs of the penetration depth as a function of polymer and time (in each picture the outer surface of the polymer part is on the left side)

4.3 Colorization of Polymer Powders and Lasersintered Parts

Selective laser sintering is a process gaining increasingly in importance in rapid manufacturing. Compared to conventional technologies like injection molding its mold-free shaping procedure is a costeffective way of manufacturing, especially for customer tailored products or small batches. Nevertheless until now there is only a small range of materials available for this process. Mainly PA 12 powders are used which possess a very high sphericity. Supercritical impregnation could be used for the modification of available powders in two ways: a) impregnation of the powders before laser sintering or b) impregnation of the lasersintered bodies.

Due to the fact that the impregnation results for PA 12 at 230 bar, 90 °C and a duration of up to 20 minutes were not satisfying, a second parameter study was carried out. For the yellow dye trials at 225 bar, 110 °C, an impregnation time of 25 min and a depressurization rate of 3 bar/s showed good results. The colorization was homogeneous, stable during washing in water at 70°C and after drying a homogeneous powder was yielded (Figure 9). No bubbles were visible inside the particles and the shape of the particles remained spherical (Figure 10). Therefore, the powder allows a good flowability, which is a key parameter in application.

Figure 11 shows a laser sintered propeller before and after impregnation using the same conditions which were chosen for the powder. Impregnation was complete over the whole surface with no defects.



Figure 9: High pressure colored laser sinter powder

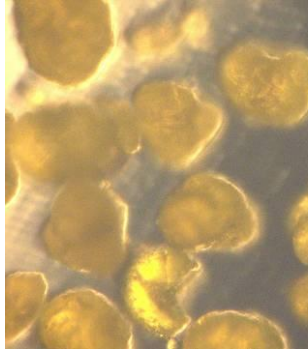


Figure 10: Colored lasersinter powder showing high sphericity



Figure 11: High pressure colored laser-sinter body before and after impregnation with yellow dye

4.4 Impregnation with Nanoparticles

Ag-nanoparticles for the antimicrobial modification of plastics nowadays become increasingly important. Therefore trials were carried out on the same TPU and PC used for colorization with ethanol based silver dispersion containing 1.0 to 2.0 % nano-Ag. Dispersants were used with a weight rate of 2 to 3 related to the nano-Ag. The nanoparticles had sizes from 30 to 300 nm (Figure 12).

The impregnation was carried out in a similar way as the colorization. Pressure was varied between 1 and 230 bar, temperature was hold constant at 70 °C and the time of impregnation changed in the range of 2 to 10 min.

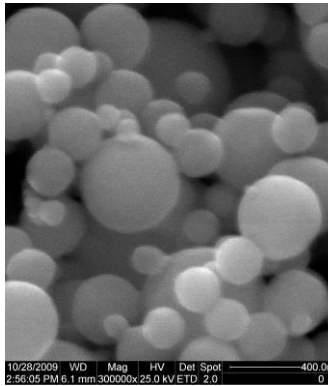


Figure 12: Ag-nanoparticles

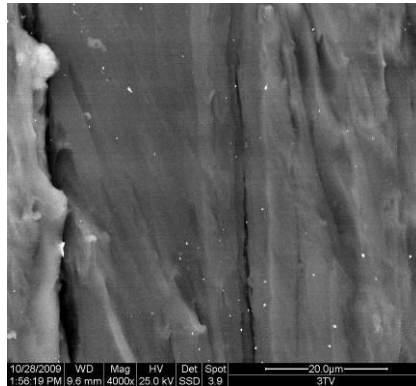


Figure 13: SEM of TPU surface after impregnation with Ag-nanoparticles (white spots indicate Ag)

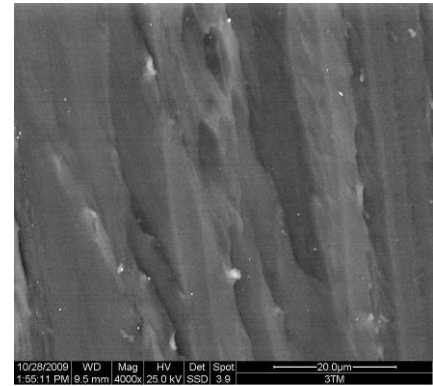


Figure 14: SEM of TPU in a depth of a few millimetres after impregnation with Ag-nanoparticles (white spots indicate Ag)

There was no mass-uptake at ambient pressure even at long times. At pressures over 200 bar the mass-uptake became much higher while in the range from 100 to 200 bar the influence of pressure was low. After an impregnation time of two minutes the increase in weight slowed down in every trial.

The dispersant showed the highest mass-uptake in combination with lowest volumetric swelling. The resulting increases in weight were 1.5 % for TPU and 0.3 % for PC. In SEM the white spots in the pictures detected by backscattered secondary electrons (BSH) indicate Ag-nanoparticles at the surface (Figure 13) and in lower concentration even in a depth of a few millimeters (Figure 14).

5. CONCLUSIONS AND OUTLOOK

Compared to conventional compounding, coating or solvent based impregnation has some advantages. High pressure impregnation based on supercritical carbon dioxide is a solvent free process, no subsequent drying is required and surface additives are implemented in surface-near regions only: It is applicable to different polymer matrices and since it is possible to process plastic bodies in solid state it is well suited for customer tailored production.

With respect to a global market for plastics additives which exceeded more than 36.2 billion \$ in 2008 [5] high pressure impregnation therefore is a promising technology for the plastic processing industry.

Within a follow-up project a impregnation pilot plant will be built up in industrial scale at Fraunhofer UMSICHT. In late 2010 it will be possible to impregnate bodies and powders in a 1 400 litre high-pressure system. The system is intended to show how efficiently impregnation can be realised. It will also be possible for potential users to test the new technology with their products and thus implementation in the industry will be significantly facilitated.

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