

Full Length Research Paper

# Efficiency of densification process in preparation of carbon-carbon composites

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**Material balance of densification process was made to assess its efficiency in dependence on impregnation conditions. Theoretical values of apparent porosity, bulk density and apparent specific gravity were computed and compared with experimental ones. Densification efficiency was determined as the ratio of volume of added matrix to volume of pores.**

**Key Words:** Composites, Polymers, Structural behaviour, Porosity.

## INTRODUCTION

Properties of carbon-carbon composites (C-Cs) during I/CR process (impregnation, curing and re-carbonisation) are studied. Resin is liquefied by melting or dilution with ethanol and infiltrated into composite porous system (free of air and moisture), which causes increase of matrix volume. Composite is then cured and re-carbonised according to prescribed temperature regimes (Klučáková, 2004). Formation of gases and matrix shrinkage accompany these processes and cause re-opening of pores filled during impregnation. Volume content of matrix decreases, however its value is higher than that before I/CR process. The whole process can be repeated to achieve better pores filling.

Following properties of C-Cs significantly influence course of impregnation: porosity, size and shape of open pores, voids and cracks, properties of internal and external surfaces of C-Cs. These properties of C-Cs resulted from the process of their production (Klučáková, 2005), therefore they depend on properties of used materials and conditions of production before impregnation = on material history. It is assumed that fibers and original matrix (glass-like carbon) and its properties do not change during I/CR process or influence of impregnation is not important. Whole process is proceeding in porous system between fibers and original matrix and its course depends mainly on the properties of porous system and interfaces pore/fiber, pore/matrix.

## THEORY

In order to describe changes of C-Cs properties during I/CR process the following material balance for impregnation cycle  $i$  is assumed:

$$V_{f,i} + V_{m,i} + V_{p,i} = V_{tot,i} \Leftrightarrow \varphi_{f,i} + \varphi_{m,i} + P_i = 1 \quad (1)$$

where  $V_{f,i}$ ,  $V_{m,i}$ ,  $V_{p,i}$  and  $V_{tot,i}$  are volume of fibres, matrix and pores, and total external volume, respectively.  $\varphi_{f,i}$  and  $\varphi_{m,i}$  are appropriate volume fractions and  $P_i$  is porosity. Assuming that  $V_{tot,i}$  does not vary during I/CR process and fibres and matrix are incompressible materials we can define the volumetric densification efficiency  $VDE$  as the ratio between volume of added carbon matrix  $\Delta V_{m,i}$  and volume of open pores (in unit volume)  $P_{i-1}$ :

$$VDE = \frac{\Delta V_{m,i}}{P_{i-1}} = y_{carb} Y_i \frac{\rho_p}{\rho_{ap}} \quad (2)$$

where  $y_{carb}$ ,  $Y_i$ ,  $\rho_p$  and  $\rho_{ap}$  are carbon yield, impregnation efficiency in cycle  $i$ , density of liquid precursor and apparent specific gravity of carbonised precursor, respectively (Granda et al., 1998; Rellick, 1990).

If apparent specific gravity of added carbonised matrix  $\rho_{m,ap}$  is equal to the apparent specific gravity of carbonised precursor  $\rho_{ap}$  the efficiency of I/CR process (defined as the ratio of weight of added matrix  $\Delta m_{m,i}$  and theoretical value of weight of added matrix  $\Delta m_{m,th}$ )

$$Y_i = \frac{\Delta m_{m,i}}{\Delta m_{m,th}} = \frac{\rho_{m,ap}}{\rho_{ap}} \quad (3)$$

is equal to 1 ( $Y_i = 1$ ). The increase of weight of added matrix  $\Delta m_{m,i}$  is equal to increase of composite weight (in cycle  $i$ )  $\Delta m_{c,i}$ . If the increase of matrix volume after I/CR process ( $\Delta V_{m,i}$ ) is the ratio between weight of added matrix  $\Delta m_{m,i}$  and apparent specific gravity of carbonised precursor  $\rho_{ap}$

**Table 1.** Impregnation conditions

Sample number (chapter)	Mass fraction (-)	Temperature (°C)	External pressure (MPa)	Time (min)	Number of cycles (-)
4.1	0.25 - 1	90	0.4	60	1
4.2	0.65	30 – 90	0.4	60	1
4.3	0.35 - 1	90	0.4	20 – 180	1
4.4	0.65	90	0 – 0.5	60	1
4.5	0.65	90	0.4	60	1 - 4

$$\Delta V_{m,i} = \frac{\Delta m_{m,i}}{\rho_{ap}} \quad (4)$$

then porosity of C-Cs after cycle  $i$  can be expressed as

$$P_i = \frac{\rho_{b,i} P_{i-1}}{\Delta V_{m,i} \rho_c + \rho_{b,i-1}} = \frac{\rho_{b,i} P_{i-1}}{\Delta m_{m,i} + \rho_{b,i-1}} \quad (5)$$

and bulk density of C-Cs as

$$\rho_{b,i} = \rho_{b,i-1} + Y_i y_{carb} P_{i-1} \rho_p \quad (6)$$

On the basis of material balance following theoretical values for impregnation cycle  $i$  can be computed (assuming  $Y_i = 1$ ): theoretical volume of added matrix (in unit volume of C-Cs)

$$\Delta V_{i,th} = y_{carb} P_{i-1} \frac{\rho_p}{\rho_{ap}} = \frac{\Delta m_{th}}{\rho_{ap}} \quad (7)$$

theoretical porosity of C-Cs

$$P_{i,th} = P_{i-1} - \Delta V_{i,th} \quad (8)$$

theoretical bulk density of C-Cs

$$\rho_{b,th} = \rho_{b,i-1} + \Delta m_{m,i,th} \quad (9)$$

and theoretical apparent specific gravity of C-Cs (including closed pores)

$$\rho_{c,ap} = \frac{\rho_b}{1 - P_{i,th}} \quad (10)$$

Apparent porosity of C-Cs after cycle  $i$  of I/CR process can be expressed as

$$P_i = P_{i-1} (1 - VDE) \quad (11)$$

or by means of initial porosity (before impregnation)  $P_{0,comp}$

$$P_i = P_{0,comp} (1 - VDE_{aver})^z \quad (12)$$

where  $z$  is number of repeated cycles of I/CR process and  $VDE_{aver}$  is average value of volumetric densification efficiency. (Rellick, 1990; Oh and Park, 1996)

## EXPERIMENTAL

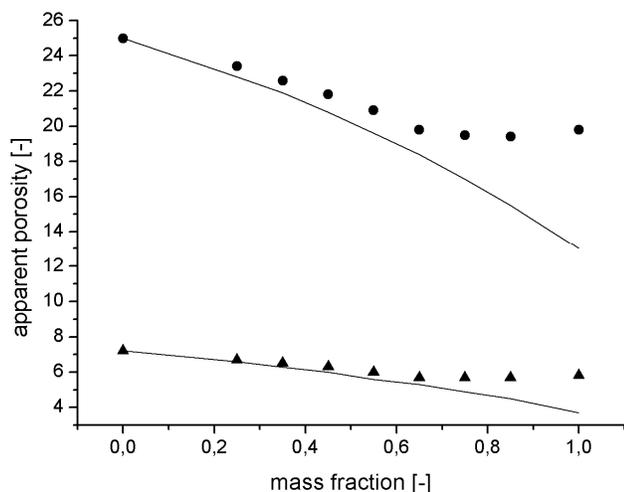
For experimental measurements two types of C-Cs were prepared: one-directionally reinforced C-Cs (UD) and C-Cs with cloth reinforcement (CT). Both of these types were prepared from carbon fibers T800H (Torayca) and phenolic resin (Umaform LE) using prepreg-technology (Fitzer, 1972; Fitzer, 1987). These C-Cs were dried (105 °C, 3 h) and impregnated under given conditions (see Table 1). The impregnation process consists of evacuation (10 min), tempering (30 min), and infiltration of precursor. The external pressure during impregnation was applied using (pressed) nitrogen. After impregnation, C-Cs were cured and carbonized according to regimes mentioned in ref. Klučáková, 2004. Prepared C-Cs were characterized by mercury porosimetry, image analysis of cross-sections and SAXS method in Klučáková, 2005; Weishauptová et al, 1996; Balík et al., 1996). Porosity, bulk density and apparent specific gravity of C-Cs in I/CR process were determined according to ASTM C20.

## RESULTS AND DISCUSSION

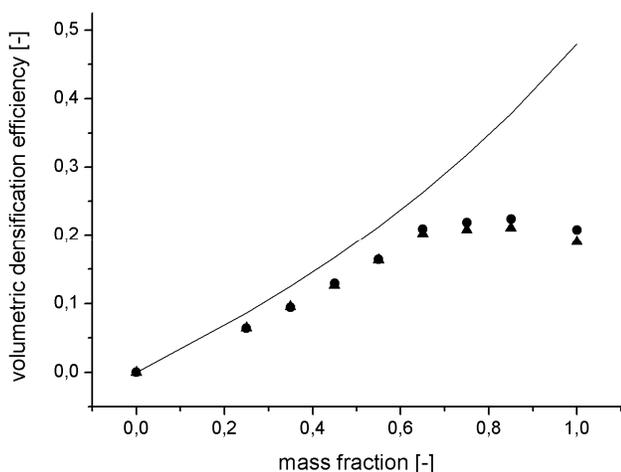
### Dependence of C-Cs properties on precursor concentration

Properties of C-Cs confirmed the conclusions obtained from viscosity measurements and mercury porosimetry (Klučáková, 2004; Klučáková, 2005). In Figure 1, the dependence of apparent porosity on the mass fraction of resin in matrix precursor is shown. We can see that experimental data correspond to theoretical values up to about  $w_{pol} = 0.65$  and then apparent porosity is approximately constant. Similar results were obtained for the measurements of bulk density and apparent specific gravity of C-Cs.

As it was mentioned in ref. Klučáková, 2004, while carbon yield of matrix precursor is directly proportional to the mass fraction of resin in precursor the dependence of viscosity on  $w_{pol}$  is exponential. For highly concentrated resin solutions the increase of carbon yield cannot compensate the increase of viscosity. Time dependence of viscosity probably also influenced its ability to penetrate into the porous system. Volumetric densification efficiency (VDE) swerves gradually with increase of  $w_{pol}$



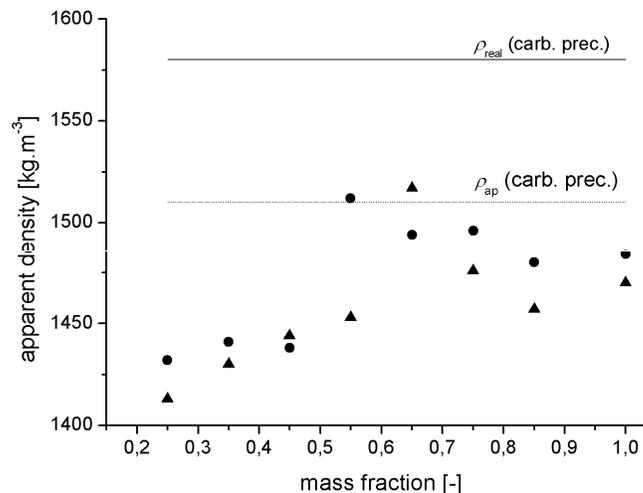
**Figure 1.** Apparent porosity of C-Cs impregnated after I/CR process in dependence on mass fraction of used precursor – comparison of theoretical (line) and measured values for CT (circles) and UD (triangles).



**Figure 2.** Volumetric densification efficiency of I/CR process in dependence on mass fraction of used precursor – comparison of theoretical (line) and measured values for CT (circles) and UD (triangles).

and for mass fraction  $w_{pol} > 0.65$  is also practically constant (see Figure 2).

In Figure 3 computed values of apparent density of added matrix in comparison with real density and apparent specific gravity of carbonised phenolic resin (Klučáková, 2004) are shown. Obtained curves have a maximum in range of mass fraction of resin in precursor  $w_{pol} = 0.5-0.6$  for CT and UD composites. For lower concentration of resin the high content of ethanol escaping during curing of C-Cs causes development of closed pores in formed matrix. On the other hand, escape of ethanol (and pyrolysing gases) is more difficult from more



**Figure 3.** Apparent density of added matrix in CT (circles) and UD (triangles) in comparison with real density  $\rho_{real}$  (line) and apparent specific gravity  $\rho_{ap}$  (dotted line) of carbonised precursor.

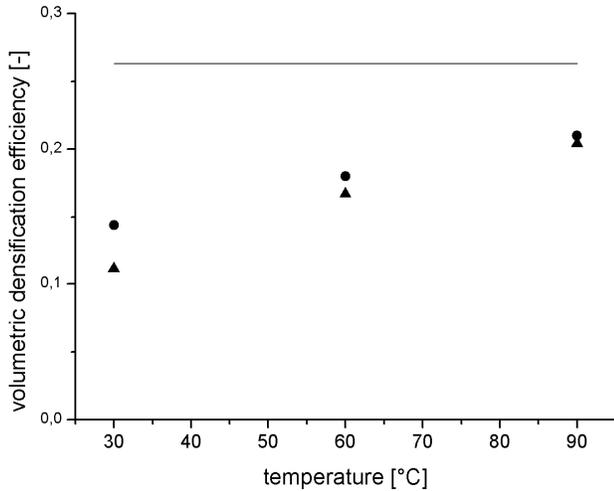
concentrated precursor solutions due to their unfavourable rheological behaviour and higher density. For precursor without ethanol ( $w_{pol} = 1$ ) apparent density of added matrix slightly increases (see Figure 3). Therefore the mass fraction  $w_{pol} = 0.65$  can be considered as the most suitable concentration of matrix precursor for impregnation of C-Cs to achieve the maximal efficiency of I/CR process.

### Dependence of C-Cs properties on temperature

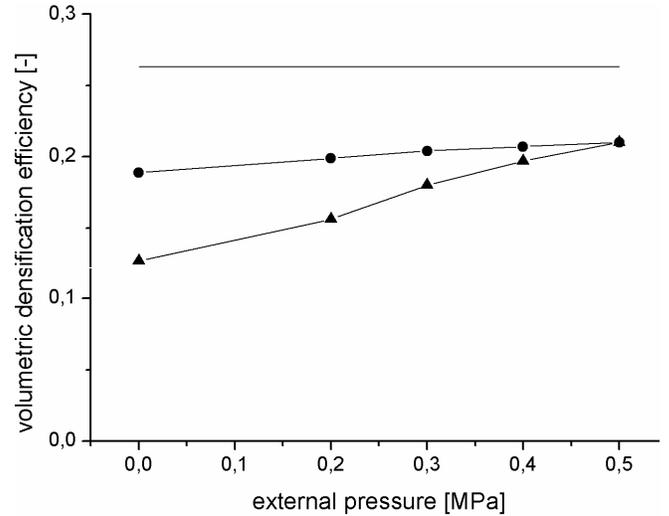
For impregnation at various temperatures precursor with  $w_{pol} = 0.65$  was used, therefore theoretical values of VDE and properties of C-Cs are constant (for all temperatures). As expected, increasing impregnation temperature improves efficiency of I/CR process and their final properties. Their values approach gradually to theoretical value of VDE with growth of temperature, therefore temperature 90 °C is considered as the most suitable, which corresponds with previous results (Klučáková 2004; Klučáková, 2005). The efficiency and properties of UD composites are closer to theoretical ones than these of CT (see Figure 4). This is logical consequence of lower initial porosity of UD composites and it is common for most of experimental data in this paper.

### Dependence of C-Cs properties on impregnation time

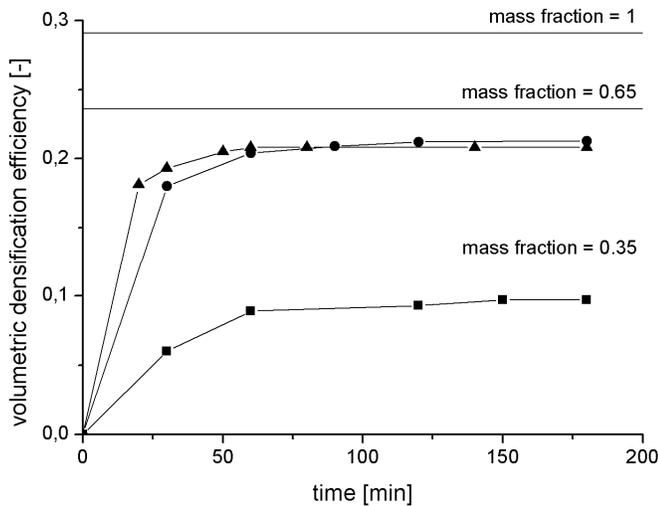
Three various values of precursor concentration were chosen for study of time dependence of impregnation efficiency and final composite properties. In Figure 5 the comparison of experimental and theoretical values of volumetric impregnation efficiency is shown. While experimental values for precursor with  $w_{pol} = 0.35$  or  $0.65$  are



**Figure 4.** Volumetric densification efficiency in dependence on impregnation temperature – comparison of theoretical (line) and measured values for CT (circles) and UD (triangles).



**Figure 6.** Volumetric densification efficiency in dependence on external impregnation pressure – comparison of theoretical (line) and measured values for CT (circles) and UD (triangles).



**Figure 5.** Volumetric densification efficiency in dependence on impregnation time – comparison of theoretical values (lines) with CT impregnated by precursor with mass fraction equal to 0.35 (squares), 0.65 (circles) and 1 (triangles).

more on less near to theoretical ones, real efficiency of impregnation with non-diluted resin ( $w_{pol} = 1$ ) is much lower than theoretical one and even lower than theoretical value for precursor with  $w_{pol} = 0.65$ , which is caused by increase of viscosity of non-diluted resin as a consequence of high rate of its cross-linking. Similar results were obtained from measurement of other C-Cs properties. Experimental values increase with time mainly in first 30 min and after 60 min vary only little. Therefore 60 min can be considered as optimal time for impregnation (except non-diluted resin).

### Dependence of C-Cs properties on external pressure

Because the maximal recommended pressure for used impregnation apparatus is 0.5 MPa, higher external impregnation pressure cannot be applied. The range of external pressure 0 - 0.5 MPa was used. In Figure 6 dependence of *VDE* on external pressure is presented. We can see that experimental values of *VDE* for CT are practically independent on used impregnation pressure. On the other hand *VDE* for UD is relatively strongly influenced by used external pressure. Because apparent density of added matrix is dependent on used pressure by similar way, the reason can be pores closing during I/CR process in case of CT composites. Therefore structure, size and shape of pores, voids and cracks in both used kinds of C-Cs have to be different.

### Dependence of C-Cs properties on number of I/CR cycles

Whole I/CR process was several times repeated and dependence of impregnation efficiency and C-Cs properties on number of impregnation cycles was studied. It was confirmed that *VDE* decreases with number of repeated impregnation cycles. The decline of *VDE* is connected with gradual closing of pores, which is proved by computed values of apparent density of added matrix. The apparent density of added matrix decreases with number of repeated impregnation cycles and after third cycle this value was lower than 1000 kg/m<sup>3</sup> (apparent specific gravity of carbonized precursor is equal to 1510 kg/m<sup>3</sup>). Similar results were obtained from the measurement of apparent porosity, bulk density and apparent specific gravity of C-Cs. Nevertheless, the repetition of

**Table 2.** Experimental data fitted by Eq. 12

	$P_{0,comp}$ (vol. %)	$P_{0,exp}$ (vol. %)	$VDE_{aver}$ (-)	$R^2$
CT	24.8	24.2	0.281	0.993
UD	8.1	8.2	0.208	0.999

I/CR process improves final properties of C-Cs. Probably the re-carbonisation of impregnated and cured composite causes partial re-opening of pores closed during infiltration of precursor and makes possible further impregnation cycle.

Eq. 12 was used for the description of the dependence of C-Cs apparent porosity on number of impregnation cycles. Obtained experimental parameters are listed in Table 2. It is evident that better agreement was achieved in the case of UD composites. However, Eq. 12 fits also values measured for CT sufficiently precisely.

## CONCLUSIONS

To assess the efficiency of densification process the material balance of was made in this paper.  $VDE$  of individual impregnation cycles was determined and compared with theoretical value. A variability of properties of C-Cs after I/CR process in dependence on impregnation conditions was also studied. It was confirmed that apparent porosity, bulk density and apparent specific gravity are improved by I/CR process. This effect is more marked in the case of CT composites due to their high initial porosity (before I/CR process). The repeating of I/CR process caused on the one hand subsequent improving of composite properties on the other hand the decrease of densification efficiency.

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