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J.M. Molina-Jordá

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Mesophase pitch

Mesophase pitch +
TiC nanoparticles

Rheology experiments

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viscosity, advancing contact angle, equilibrium contact angle

Insights into the flow behaviour of the AR24 mesophase pitch and nanoparticle-doped AR24 mesophase pitch during infiltration into particulate porous preforms

J.M. Molina-Jordá*

Instituto Universitario de Materiales de Alicante and Departamento de Química Inorgánica, Universidad de Alicante, Apdo. 99, E-03690, Alicante, Spain

Abstract

Synthetic mesophase pitches, extensively used as graphite precursors, manifest particular fluid-dynamic properties given their liquid crystal nature. Their recent use in infiltration processes to manufacture graphite-based monolithic and porous materials demands the study of their physical properties, mainly viscosity and contact angle, under dynamic conditions. In this work a new infiltration device was conceived and constructed to measure the infiltration kinetics of the AR24 naphthalene-based mesophase pitch and TiC nanoparticle-doped AR24 mesophase pitch into preforms of packed NaCl particles. The experiments allowed activation energies for viscosity to be obtained, along with pseudo-equilibrium and advancing contact angles.

1. Introduction

Aromatic-derived synthetic mesophase pitches have been extensively used for more than three decades as low-temperature precursors of graphitic materials. They are especially appealing in liquid-state manufacturing processes given their low softening point and good capability to wet the vast majority of solid substrates. In the liquid state they behave as discotic nematic liquid crystals with a planar molecular architecture that consists of aromatic oligomers, where aromatic planes stack approximately in parallel to one another [1-3]. Nowadays a wealth of monolithic and porous carbonaceous materials is fabricated by capillary imbibition (either spontaneous or forced) of mesophase pitches into non-fully densified preforms. Mesophase-derived carbon and graphitic phases are

* Corresponding author. E-mail: jmmj@ua.es. Tel: 965903400 (2055)

later obtained by controlled heat treatments at moderate (up to 1400°C) and high (above 2700°C) temperatures, respectively. Recent studies have proved that the presence of TiC nanoparticles in naphthalene-based mesophase pitches is beneficial for catalysing their graphitisation transformation [4].

In general, infiltration processes are rich phenomena that are far from being understood in-depth. Indeed the ability of a liquid to imbibe the open channels of a porous solid medium involves several intrinsic properties of the liquid, such as viscosity and surface tension, and of the liquid-solid interface, such as the contact angle, and also of the porous solid architecture, such as its permeability, pore volume fraction and pore size distribution [5]. Infiltration with molten mesophase pitches turns out to be an even more complicated phenomenon. On the one hand, there have been many studies into pitch rheology to demonstrate that viscosity is shear-dependent and molten mesophase pitches can behave as non-Newtonian fluids under certain conditions [1,2,6-8]. The liquid infiltration of the mesophase pitch, as well as traditional fibre spinning, is prone to be a framework where non-Newtonian behaviour may appear since either spontaneous or forced capillary imbibition imposes major shear stresses on the penetrating liquid. Whether some inertial effects due to viscoelasticity are reflected in the infiltration kinetics is still unclear. Actually, there is a large gap in knowledge on the fluid-behaviour of pitch under relevant infiltration processing conditions. On the other hand, another important and practical issue is that mesophase pitches suffer from swelling upon heating [9]. To overcome this drawback, the authors of [10] performed liquid pressure infiltrations of the mesophase pitch into particulate-packed preforms in pressure chambers, which allowed to first melt the mesophase pitch under pressurised conditions of argon gas at 4 bar and to then apply an infiltration pressure of 12 bar. These conditions were successful for preventing the pitch from swelling, but also evidenced another relevant issue: infiltrations could not be conducted along the entire length of preforms. The use of pressure instead of vacuum atmosphere before and during melting the pitch, along with the use of closed-bottomed crucibles to contain the packed preforms, causes that the movement of the infiltrant front during infiltration downwardly displaces the argon gas entrapped in the preform, which is gradually compressed. Once no differential pressure can be ascribed astride both sides of the infiltration front, infiltration is hindered. As a result, there is always a portion of the preform that remains uninfiltrated.

TiC nanoparticles embedded in the mesophase pitch may also strongly influence the infiltration kinetics since the presence of solid second phases can significantly increase the viscosity of liquid polymers [11,12]. For all these reasons, a thorough understanding of the underlying phenomenology of liquid mesophase pitch infiltration is intriguing and it is necessary in order to face emerging challenges in the manufacturing of technologically important carbon-based materials. Notwithstanding, no careful systematic studies on the important parameters that govern mesophase pitch infiltration have yet been presented.

This work addresses the study of the fluid-dynamic behaviour of the AR24 naphthalene-based mesophase pitch in NaCl particle-packed preforms under infiltration conditions. It includes pitch under two conditions: as received and doped with TiC nanoparticles. Here infiltration is conducted under both constant and variable pressure gradients to emulate the two standard experimental conditions of industrial- and laboratory-scale infiltrations.

2. Governing equations

The following general law governs the infiltration of a fluid into a porous medium:

$$z^2 = \frac{2K}{\phi} \int_0^t \frac{1}{\mu(\gamma)} \Delta P(t) dt \quad (1)$$

where z is the infiltrated distance, t is the infiltration time, K is the permeability tensor of the preform, $\Delta P(t)$ represents the pressure drop of the liquid between the entrance of the preform and just ahead of the infiltration front, ϕ is the void volume fraction (porosity of the preform) and $\mu(\gamma)$ is the shear-dependent apparent viscosity. This Equation is valid for Newtonian and non-Newtonian fluids under certain fluid-dynamics conditions (please see Supplementary Materials section for more information on the derivation and applicability of Equation (1)).

Much of the experimental work that pertains to non-Newtonian flow in porous media involves fluids that are shear thinning. A viscosity that decreases with the shear rate characterises these fluids. Nevertheless, many of these fluids, including mesophase pitches, generally manifest a Newtonian plateau at moderate shear rates. In this region, they can be characterised by a single viscosity value such that η does not depend on

the shear stress and follow the well-known Darcy's law. The general expression of Equation (1) can be used to rationalise the behaviour of viscous flows into porous preforms in two experimental cases of interest, which are herein discussed (Figure 1).

Figure 1 – (a-b): Schematics of infiltration for two cases of interest: a) infiltration in a two-sided open container – experiments E1; and b) infiltration in a closed-bottomed container – experiments E2; (c) is a drawing of an equivalent cylindrical pore being infiltrated by a wetting liquid. Legends: P_a : liquid applied pressure; P_g : gas pressure in the uninfiltred portion of the preform; P_i : liquid pressure just behind the infiltration front; P_e : liquid pressure just ahead of the infiltration front; θ : contact angle.

2.1 Infiltration in two-sided open containers – experiments E1

In this case the preform is retained in a container opened at two ends. The liquid is subjected to applied pressure P_a and the gas of the non-infiltrated preform ahead of the infiltration front is kept at pressure P_g , which we assume is constant over time for this particular configuration (Figure 1a). In this case, $\Delta P(t)$ takes the form:

$$\Delta P(t)_{E1} = P_a + \Delta P_c(t) - P_g \quad (2)$$

Where $\Delta P_c(t)$ is the capillary pressure at the infiltration front, defined as $\Delta P_c(t) = P_e - P_i$. P_g is taken as being negative since it opposes infiltration. ΔP_c can, in turn, be calculated by the following equation:

$$\Delta P_c(t) = S \rho_p \frac{V_p}{(1 - V_p)} \sigma \cos \theta \quad (3)$$

Where σ is the liquid surface tension, θ is the contact angle defined by the local interaction between the liquid and the solid substrate of the preform, S is the specific surface area and ρ_p (kg/m^3) is the density of the solid preform. In Equation (2), $\Delta P_c(t)$ is taken as being positive since θ is normally $<90^\circ$ for the mesophase pitches in the majority of substrates [13]. The dependence of ΔP on time comes through contact angle θ , which is considered to be dynamic throughout the infiltration process as the infiltration front moves at steadily decreasing velocities over time. The dynamic contact angle and velocity of the contact line are intrinsically related through the capillary number C_a [14]. A specific expression for the calculation of the dynamic contact angle is the empirical equation deduced by Joos et al. [15]:

$$\cos \theta = \cos \theta_{eq} - 2(1 + \cos \theta_{eq})C_a^{1/2} \quad (4)$$

Where θ is the advancing contact angle at a given time and θ_{eq} is the equilibrium contact angle (i.e. at an infinite time). C_a refers to the capillary number, calculated by the following expression;

$$C_a = \frac{v_o \cdot \mu(\gamma)}{\sigma} \quad (5)$$

A huge amount of experimental results exists on the infiltration of porous preforms by liquids (especially metals and polymers) for which ΔP_c has been found to be constant (i.e. the infiltration front advances at a constant contact angle). In practical terms, we call spontaneous infiltration to that infiltration that proceeds without external overpressure, by the sole action of the capillary pressure (hence, $P_a = P_g$). Alternatively, a forced infiltration proceeds when $P_a > P_g$.

2.2 Infiltration in closed-bottomed containers – experiments E2

Here we consider the case in which infiltration takes place in a container that is closed-bottomed (Figure 1b). In this case, the movement of the infiltration front displaces downwards the gas contained in the preform and the gas pressure increases over time, which hinders infiltration. In this case, $\Delta P(t)$ takes the form:

$$\Delta P(t)_{E2} = P_a + \Delta P_c(t) - P_g(t) \quad (6)$$

Where $P_g(t)$ is the gas pressure that opposes infiltration.

By assuming adiabatic infiltration and considering the equation of ideal gases (i.e. PV constant), $P_g(t)$ at a given temperature evolves as:

$$P_g(t) = P_g^o \frac{h'}{h' - z} \quad (7)$$

Where P_g^o is the initial gas pressure in the preform before the initiation of infiltration, h' denotes the total height of the preform and z , as usual in this text, is the infiltrated distance. In this case, Equation (1) cannot be integrated analytically and has to be solved numerically with the capillary pressure $\Delta P_c(t)$ calculated by Equations (3) and (4). In this case, spontaneous infiltration occurs for $P_a = P_g^o$ and forced infiltration takes place when $P_a > P_g^o$.

3. Experimental procedures

3.1 Materials

The AR24 naphthalene-based synthetic mesophase pitch was kindly supplied by Mitsubishi Gas Chemical Company Inc. (Tokyo, Japan) in the form of pellets, which were approximately 10 mm long and 3 mm in diameter. Its main characteristics are provided in Table 1. NaCl particles of analytical quality (purity > 99.5%), purchased from Sigma-Aldrich (Riedstr, Switzerland), were used in this study. These particles, originally of 30-400 μm , were ground and sieved to obtain fractions of narrower particle size distributions, from which those within the 100-150 μm range were selected. The volume fraction attained by NaCl particles compaction was 0.58 ± 0.02 (i.e., ϕ (porosity) = 0.42 ± 0.02). The specific surface area of these particles was $320 \text{ m}^2/\text{kg}$, based on gas adsorption measurements and an analysis by the Brunnauer, Emmet and Teller (BET) method. TiC nanoparticles were purchased from Sigma-Aldrich (Riedsth, Switzerland) as a titanium (IV) carbide (TiC) nanopowder <200 nm of high purity (>95%). A detailed examination under the TEM microscope shows that the average size of these particles is well below the maximum size indicated by the supplier. Micrographs of all the materials described can be found in the Supplementary Materials section (Figure S.1).

Table 1. Main characteristics of the AR24 mesophase pitch delivered by the Mitsubishi Gas Chemical Company (as indicated by the supplier, except for the softening point, which was measured in this work).

Element content (%)				Anisotropy (%)	Softening point (°C)
C	H	N	S		
93.9	5.23	0.38	0.06	100	244±2

3.2 Doping the mesophase pitch with TiC nanoparticles

Doping the mesophase pitch with TiC nanoparticles was achieved by dispersion with toluene following a procedure that involved five steps [4]: i) TiC nanoparticles are mixed with the mesophase pitch in solid state in the desired proportions in a reactor flask; ii) toluene is added in a 25:75 weight proportion of mesophase pitch:toluene; iii) the mixture is homogenised at room temperature by a mechanical blade-stirring system working at 400 rpm for 1 h; iv) while blade-stirring continues at 400 rpm for an additional 1 h, ultrasounds are applied to the reactor with a LT-100-PRO equipment working at 40 kHz; and v) toluene is evaporated by magnetic stirring at 75°C until a dried mixture is attained. In order to obtain a complete toluene-free mixture, an extra final step is added: the TiC-doped mesophase pitch is molten at 300°C under nitrogen atmosphere and mechanically blade-stirred for 1 h, after which it is solidified and subsequently ball-milled.

This method that combines mechanical stirring, partial dissolution in toluene and ultrasounds was first proposed in [4] for dispersion of TiC nanoparticles in the AR24 mesophase pitch. The AR24 mesophase pitch dissolves only partially in toluene – its solubility in toluene is as low as 21.9%, as reported in [16]. The possible chemical changes induced by the method proposed are discussed in detail further in this manuscript.

3.3 Preparation of particulate preforms

Preparation of porous preforms by packing of the NaCl particles into quartz tubes with either one or the two sides open is a delicate process that needs proper equipment and experimented personnel to achieve homogeneous porous architectures. The procedures and experimental details explained in [17-19] were followed. The tubes are of 99.9% fused quartz and 200 mm length, with an internal diameter of 5 mm and a wall thickness

of 1.5 mm. The particulate preforms with a volume fraction that deviated more than 2% from the average (0.58) were discarded (approximately 15% of the total number of prepared packed preforms were rejected for this reason).

3.4 Equipment for the infiltration experiments

The infiltration equipment was designed and conceived to have the necessary versatility required for the purpose of this work. A schematic diagram of the setup core of its two main conceptions can be seen in Figure 2. Both configurations are easily interconvertible and we only work with one of them each time. For safety reasons, the setup core is mounted inside a rectangular aluminium frame covered with 8 mm thick transparent protective plates made of polymethyl methacrylate. In a first conception (Figure 2a), conceived for experiments E1, the equipment basically consists of a quartz tube that is connected, through a shut-off valve on both ends, to a pressure transducer and to a pressurized argon supply. The tube, which contains a packed particulate preform (height 40 ± 1 mm) and the mesophase pitch, can be heated up to the desired temperature with the help of an electrical furnace, commanded by a Omron E5T temperature controller. This configuration allows infiltration by enabling a constant pressure gradient between the mesophase pitch and the preform. The preform is always kept at a constant argon pressure of 4 bar. Pressure transducers control the pressure on both ends of the tube with an accuracy of ± 0.05 bar.

In a second conception (Figure 2b), conceived for experiments E2, the tube is open only on one side and is connected through a shut-off valve to a pressure transducer, and also to a pressurized argon supply. A pressure of 4 bar is set with argon gas before the mesophase pitch is molten. Once it is in molten state, a pressure gradient is achieved by setting a constant pressure in the tube.

Infiltration experiments were carried out at three nominal temperatures, 330°C, 360°C and 385°C, selected to be representative in the manufacturing processes that involve this molten mesophase pitch. Two sets of experiments were performed for each configuration: i) spontaneous infiltrations, for which a zero pressure gradient was applied (hence $P_a = P_g = 4$ bar for either experiments E1 and experiments E2); ii) forced infiltrations, in which a certain pressure gradient was set between the mesophase pitch and the gas contained in the porous preform. Additional spontaneous infiltration experiments were carried out with polyethylene glycol under ambient conditions (25°C and 1 bar).

Figure 2 – Schematic diagram of the infiltration setup for the two conceptions: a) two-sided open container – for experiments E1; and b) closed-bottomed container – for experiments E2.

3.5 Measuring the viscosity of the AR24 mesophase pitch according to the shear rate

A RT 20 Haake rheometer was used to measure viscosity with a variable shear rate or temperature. The equipment has a plate-plate configuration with 20 mm diameters and a variable interplate distance. Prior to testing, adapted pellets were prepared with 0.35 g of the mesophase pitch and were moulded into a disk (13 mm diameter). The sample was placed in the interplate space and the oven was continuously purged with nitrogen to prevent sample oxidation at high temperatures. Temperature was controlled to $\pm 0.2^\circ\text{C}$. To eliminate transient phenomena, the sample was sheared for 80 seconds at a fixed shear rate before measuring each viscosity. Flow rates were obtained at three temperatures, 330°C , 360°C and 385°C , and shear rates within the $0.1\text{--}11\text{ s}^{-1}$ interval.

3.6 Contact angle of polyethylene glycol on NaCl substrates

Reliable wetting experiments were performed with polyethylene glycol (PEG) on the NaCl substrates at 25°C with the help of a contact angle goniometer SL150 series (USA KINO Industry Co. Ltd, Shanghai, China). PEG was of type 200 (polyethyleneglycol-200) with 99% purity, which was purchased from Panreac (Panreac, Química S.L.U, Barcelona, Spain). The NaCl substrates were prepared by mould casting liquid NaCl at 850°C into metal moulds (14 mm diameter). Slices of 5 mm were cut from the casted rods and were polished up to finish with diamond paste of 1 micron in Metcloth polishing clothes supplied by Buehler (Buehler, Illinois, USA). With the help of an optical profilometer (ZeGage 3D Optical Surface Profiler), the polished substrates were characterised to have an arithmetic average roughness of less than 5 nm ($R_a < 5\text{nm}$),

which is an acceptable value for contact angle measurements. The volume of the PEG droplets needed to ensure no deformation due to gravity effects was kept below 11 mm^3 , which roughly corresponds to a spherical droplet height of 2.75 mm.

3.7 Other characterization techniques

Infrared spectroscopy (BRUKER IFS 66 spectrometer with a resolution of 1 cm^{-1}) was used to characterise any chemical changes after the doping treatment followed to incorporate the TiC nanoparticles into the mesophase pitch. A thermomechanical analyser (TMA 2940, TA Instruments) was used to obtain the thermal response curves from which the softening points derived. Extra thermal characterizations were performed by thermogravimetry and differential scanning calorimetry; its main description and results can be found in the Supplementary Materials section.

4. Results and Discussion

4.1 Rheological behaviour of the AR24 mesophase pitch

Many research works in the literature on mesophase pitches are concerned about their rheological behaviour by measuring viscosity according to the steady shear rate to obtain the so-called flow curves [8,20-22]. Mesophase pitches are generally known to behave as non-Newtonian fluids under certain low shear stress conditions. Figure 3 shows the flow curves obtained in this work for the AR24 mesophase pitch at 330°C , 360°C and 385°C . The dependence of viscosity on shear stress follows the normal trend encountered for liquid crystal polymers (LCPs). Two domains of viscosity, below and above 3 s^{-1} , are clearly distinguished. At low shear rates below 3 s^{-1} (region I in Figure 3) viscosity linearly decreases with shear stress, with an approximate slope of -0.48 for all three temperatures. This value is consistent with both the model developed by Marucci [23] for LCPs, in which a slope of -0.5 was predicted for region I, and with the experimental results obtained for analogous naphthalene-based mesophase pitches [22]. This behaviour is known as shear thinning and is attributed to a stretching of crystalline domains. At higher shear rates above 3 s^{-1} (region II in Figure 3), viscosity remains constant, which allows the mesophase pitch to be considered Newtonian fluid. In this region crystalline domains are oriented in a structure on a small size scale that behaves as a polydomain structure [22]. At even higher shear rates (not explored herein, but documented in [24,25]), the viscosity of an AR24 mesophase pitch once again lowers

for shear stresses above roughly 4000 s^{-1} at 305°C and the polydomain structure transforms into a monodomain continuum.

The viscous flow in the molten mesophase pitch is a thermally activated process, and hence the following equation holds:

$$\mu = \mu_0 e^{\frac{Q}{RT}} \quad (8)$$

Where Q is activation energy, T is temperature, R is the molar gas constant and μ_0 is approximately a constant. Q can be calculated from a linear fitting of experimental data at different temperatures in the Newtonian region, conveniently represented in a $\ln(\mu)$ versus $1/T$ plot, as shown in Figure 3b. The encountered viscosity values in the Newtonian region are: $1.32 \text{ Pa}\cdot\text{s}$ at 330°C , $0.21 \text{ Pa}\cdot\text{s}$ at 360°C and $0.05 \text{ Pa}\cdot\text{s}$ at 385°C . The calculated activation energy for the AR24 mesophase pitch is 199 kJ/mol . The values found in literature for the activation energy of anisotropic naphthalene-based pitches fall within the $177\text{--}285 \text{ kJ/mol}$ range, which agrees with the value encountered in this work. Specifically, a value of 200 kJ/mol and comparable viscosity values has been found for the 5T14 methyl-naphthalene-based mesophase pitch in [8], for which a similar softening point of 242°C has been reported.

Figure 3 – (a) Flow curves for the AR24 mesophase pitch according to temperature – the plot displays two domains: region I (non-Newtonian regime) and region II (Newtonian regime); (b) plot of $\ln$ (viscosity in $\text{Pa}\cdot\text{s}$) versus the inverse of the absolute temperature for the AR24 mesophase pitch in the Newtonian region at the three temperatures of (a) - the straight line fitting the data is $\ln(\mu) = 2.40 \times 10^4 \cdot (1/T) + 3.85 \times 10^1$; the fitting coefficient R is > 0.99 .

Despite the viscosity values found for similar mesophase pitches being qualitatively compared, we must bear in mind that the singular encountered features from one pitch to another are indicative of the synthetic pitches being more specific for their molecular arrangements than those processed from natural feedstock [25].

4.2 Permeability of the packed NaCl particulate preforms from infiltrations with polyethylene glycol

Permeability, known in fluid mechanics as a measure of the ability of a porous medium to allow fluids to pass through it, is a key parameter to study infiltration kinetics. However, obtaining reliable permeability values for particulate-packed preforms is a difficult task, overcome in the present work by the careful preparation of the particulate preforms and the accurate control during the infiltration process. The permeability of the packed preforms of NaCl particles was obtained by performing infiltrations with polyethylene glycol (PEG) at ambient temperature (25°C). This procedure was demonstrated as being effective and appropriate for a large number of different packing particulates [17-19], provided that PEG properly wets the surface of particles and can hence spontaneously flow into the porous preform under its own capillary pressure. While all the infiltration experiments with PEG in the literature were performed under similar conditions to those defined herein for experiments E1, this work reports the results for the infiltrations from both experiments E1 and E2 types. The main physical characteristics of PEG at 25°C are found in Table 2. Data were either taken from the literature or measured in the present work.

Table 2. The main physical characteristics of polyethylene glycol at 25°C. ^a Panreac Products Catalogue; ^b measured in this work.

Density (kg/m ³)	Surface tension (mN/m)	Viscosity (mPa.s)	Equilibrium contact angle on NaCl
1130 ^a	42.5 ^a	60 ^a	9° ^b

A salient feature in Table 2 is the low measured equilibrium contact angle value (9°) of PEG on NaCl substrates, which is indicative of a highly wetting system. According to Trumble [26], contact angles lower than 90° are necessary, but not sufficient, to ensure spontaneous infiltration in particulate preforms. Specifically for densely packed particulate preforms, spontaneous infiltration requires the contact angle to be below

50.7°. Therefore, spontaneous infiltration can be expected for the PEG/NaCl system at hand.

The aforementioned equilibrium contact angle of PEG on NaCl was obtained from the experiments of spreading of PEG on a NaCl substrate (Figure 4a). The initial contact angle was 25°, which rapidly lowered to 9° in about 120 seconds. The experimental values were compared with the calculations done with Equation (4), and the linear velocity of the moving triple line on the NaCl substrate, calculated from the measurements done of the droplet radius evolution (calculated as $v = dD/2dt$, where D is the droplet diameter), is also shown in Figure 4a. The measured and calculated results reasonably agree with and validate the usefulness of Equation (4) to predict dynamic contact angles based on its value at equilibrium condition and the linear velocity of the wetting liquid.

Figure 4 – (a) contact angles in the PEG/NaCl system measured by the sessile drop method; spontaneous infiltration results for experiments E1 and E2: infiltrated distance versus time (b) and the square of the infiltrated distance versus time (c); (d) calculated contact angles in the PEG/NaCl system derived from infiltration experiments E1 and E2.

Spontaneous infiltration experiments were performed under the E1 and E2 conditions. The infiltrated distances with time are provided in Figure 4b. Replotting these data in terms of the square of the infiltrated distance vs. time allowed us to observe that the results for experiments E1 follow parabolic infiltration kinetics, as it can be found in the literature for a wide variety of non-wetting metal/ceramic and wetting polymer/ceramic systems [5,27]. Infiltration in experiments E2 did not further proceed after roughly 9 mm. The infiltrating liquid was initially driven into the porous preform by capillary pressure. As liquid moved in, it displaced the gas in the preforms so that its pressure continuously rose in the non-infiltrated portion of the preform by acting as a counter pressure and relented infiltration. After a certain time, both capillary and counter pressures equalled and infiltration stopped. Under the E2 conditions, it was not possible to find any linear relation between the square of the infiltrated distance and time (Figure 4c). Figure 4b and Figure 4c also contain the predictive results for the infiltration kinetics calculated with the help of Equations (1-7). To calculate the capillary pressure (ΔP_c), the contact angle was estimated with Equation (4). The results of the calculated contact angles with time are illustrated in Figure 4d, in which two broken lines, which correspond to the maximum and minimum measured contact angles of Figure 4a, are drawn. It is apparent that in experiments E2 the calculated contact angle for the low infiltration kinetics corresponded well with the 9° value measured under the equilibrium conditions by the sessile drop method. In experiments E1, such a low value was only expected after very long times, when the parabolic rate of infiltration would become low enough. However, the contact angle values came close to that of the equilibrium for the time scale used in the present infiltration experiments. These observations point to the fact that the contact angles obtained by direct measurements (i.e. sessile drop method) and the contact angles derived from finite time infiltration experiments can only be correlated when the time scales of both experiments are similar. The parabolic rates obtained in experiments E1 (Figure 4c) allowed the easy calculation of preforms permeability. By accounting for the fast spreading kinetics of the contact angle and the relatively long infiltration times, we can assume as a first approach that, during infiltration, the relevant contact angle was that of the equilibrium, and hence the capillary pressure was nearly constant during the embedment of PEG into the porous preform. Equation (1) can be used in combination with Equations (2) and (3) to give, for constant viscosity, the following expression in which we took $\theta = \theta_{eq}$:

$$z^2 = \frac{2Kt}{\mu\phi} (-S\rho_p \frac{V_p}{\phi} \gamma \cos \theta_{eq}) \quad (9)$$

Note that the applied pressure P_a in Equation (2) equals 4 bar under the spontaneous infiltration conditions, as well as P_g . Note also that the specific experimental conditions allow to take $\theta=\theta_{eq}$ in Equation (3). The slope of a linear fitting of z^2 vs. the t data for experiments E1 allows permeability to be calculated. By taking $\phi=0.42$ and $S=320$ m²/kg, permeability can be calculated to be $K=3.02\times 10^{-13}$ m², which is in accordance with other works in which particles of similar specific surface areas were packed by the same procedure [18]. This value represents the so-called intrinsic permeability since preforms are spontaneously wetted by a liquid with a small enough contact angle to insure full saturation [17,18].

If we now consider experiments E2 and Equations (1,4-7), the curve that best fits the experimental results (Figures 4b and 4c) is obtained for a permeability of 3.06×10^{-13} m², which well agrees with the former result for experiments E1.

4.3 Infiltration kinetics with the AR24 mesophase pitch

Experiments E1 and E2 under the spontaneous and forced infiltration conditions were carried out with the AR24 mesophase pitch used as an infiltrating liquid at three temperatures (330°C, 360°C and 385°C). Temperatures were selected according to the standard conditions employed to manufacture the mesophase pitch-derived materials. Figure 5 depicts images of the infiltrated samples under the spontaneous E1 and E2 conditions. In both sets of experiments, infiltration fronts are planar, which allows modelling the infiltration kinetics by taking measurements of the infiltrated heights. Discussion on the results obtained for both sets of experiments E1 and E2 is provided separately in this section. The surface tension of the AR24 mesophase pitch, needed for the calculations, is taken to be 27 mN/m at 325°C, in accordance with [13]. Temperature effects are considered by accounting for a temperature coefficient of 0.05 mN/mK, which is a typical value for polymer liquids, and a much smaller one than for simple liquids [28].

Figure 5 – Photographs of the infiltrated samples of packed NaCl particles with the AR24 mesophase pitch under the forced E1 (a) and E2 (b) conditions.

4.3.1 Experiments E1

The first set of experiments E1 was performed under the spontaneous infiltration conditions. The infiltration kinetics for the three temperatures are shown in Figure 6a. Figure 6b shows the linear profiles obtained when the square of the infiltrated height was plotted *versus* time. Both figures also report the respective calculated curves performed with Equations (1-5). The viscosity values, needed to obtain the best fittings to the experimental data, are reported in Table 3. For modelling, first it was necessary to calculate the shear stress to which the mesophase pitch was subjected in each infiltration step (Figure 6c). Shear stresses are enormously high in the first infiltration moments as a result of the high infiltration kinetics, and rapidly drop so that after a time of roughly 500 s, the calculated shear stress reaches a fairly constant value that is below 100 s^{-1} . Figure 6c also contains an inset of the results for the calculated contact angle over the infiltration time. In general, we can see that the contact angle behaves similarly to shear stress. The rapid entrance of the mesophase pitch in the preform characterises the very first stages of infiltration, in accordance with the parabolic law observed for experiments E1. The driving force for infiltration is the capillary pressure since pressures of 4 bar on both sides of the infiltration system are cancelled ($P_a=P_g=4 \text{ bar}$). Infiltration becomes progressively slower and the shear stresses that act on the mesophase pitch lower to values of 2% of the initial values, which causes the movement of the mesophase pitch in the preform to continuously slow down. For long infiltration times, capillary numbers C_a acquire minimum values, and hence contact angles approach the equilibrium contact values (the so-called pseudo-equilibrium contact angles). Table 3 collects the contact angle values calculated at the final stages of infiltration (final contact angles θ_f) for all the considered temperatures. As usual, the

contact angles are lower at high temperatures [29] since the van der Waals interactions between the infiltrant liquid and substrate are temperature-activated. Besides the fact that all the derived contact angles are clearly wetting angles, the value encountered at 330°C is slightly higher (51°) than that predicted by Trumble (50.7°) for the spontaneous infiltration of a liquid into densely packed particulate preforms. Somehow, the volume fraction attained in the NaCl packed preforms of this work (0.58) is not characteristic of dense packing since values of 0.65 can be reached for random spherical particle packing. In this sense the angular shape of the NaCl particles and a relatively wide size distribution may cause discrepancies. In any case, the low contact angle values derived here are comparable with those found in the literature from sessile drop measurements for mesophase pitches on different substrates [13].

Figures 6d, 6e and 6f depict the experimental and calculated results for the E1 infiltrations under forced conditions of $P_a=11$ bar. Except for the present faster infiltration kinetics, similar trends to those observed in the spontaneous infiltrations can be detected. The viscosities and contact angles that derive from these experiments are found in Table 3 and deserve some comments. In viscosity terms, we observe that the values closely agree with those obtained in experiments E1, and allow using the spontaneous or forced experiment conditions to obtain reliable viscosity data at each temperature. Regarding contact angles, the final values obtained in the forced infiltrations are slightly higher than those that derive from the spontaneous experiments. The forced movement of the mesophase pitch imposed by the presence of external pressure causes the shear stresses that act on the mesophase pitch to be higher (Figure 6f), and the same applies to the contact angle. The capillary pressure, which acts to facilitate infiltration, has a minimal influence on the infiltration kinetics because its value is much lower at all times than the external applied pressure.

Figure 6 – Results for the infiltrations with experiments E1 under the spontaneous (a-c) and forced ($P=11$ bar) conditions (d-f) at 330°C, 360°C and 385°C. (a) and (d) are the infiltration profiles; (b) and (e) are plots of the square of the infiltrated height versus time; (c) and (f) show the calculated shear rates and contact angles for different infiltration times.

Table 3. The results of derived viscosity μ (Pa·s), final contact angle θ_f (°), time t_{3s-1} (seconds) at which a shear rate of $3 s^{-1}$ is achieved and activation energy Q (kJ/mol) from experiments E1 and E2 under the spontaneous and forced infiltration conditions. The end of infiltration was taken after 3600 s.

		330°C	360°C	385°C
E1 spontaneous ($P_a=4$ bar)	μ	1.38	0.16	0.04
	θ_f	51	32	23
	t_{3s-1}	> 3600 s	> 3600 s	> 3600 s
	Q	213		
E1 assisted ($P_a=11$ bar)	μ	1.31	0.19	0.06
	θ_f	53	33	25
	t_{3s-1}	> 3600 s	> 3600 s	> 3600 s
	Q	186		
E2 spontaneous ($P_a=4$ bar)	μ	1.35	0.18	0.05
	θ_f	51	30	22
	t_{3s-1}	450	235	220

	Q	198		
E2 assisted ($P_a=11$ bar)	μ	1.40	0.17	0.04
	$\theta_{\square}$	50	30	22
	t_{3s-1}	> 3600	2815	809
	Q	214		

4.3.2 Experiments E2

The infiltrations performed under the spontaneous and forced E2 conditions led to much shorter infiltration distances than those found for experiments E1 (Figure 7). The spontaneous infiltration profiles (Figure 7a) show a marked temperature-dependent behaviour. At 330°C and after 3600 s, the mesophase pitch still continued to invade the porous preform. At 360°C and 385°C a plateau was easily distinguished in the infiltration profiles after 1000 s. As these are the experimental facts, it is worth mentioning that the calculated contact angles, along with the calculated shear rate, become constant and acquired their minimum value after roughly 1000 s for all the temperatures (Figure 7b).

The infiltrations under the forced conditions of 11 bar of applied pressure allowed longer infiltrated distances to be measured (Figure 7c), although the general trends for shear stress and contact angle (Figure 7d) are similar to those indicated for the spontaneous infiltrations. An important salient feature here is that the final contact angles that derived from the spontaneous and forced infiltrations remain equal, within error. This is indicative of a similar linear velocity of the infiltrant mesophase pitch in later infiltration stages, which is reasonable given that the counter pressure in experiments E2 slowed down infiltration as it progressed under both the spontaneous and forced conditions.

(a)

(b)

Figure 7 –Results for the infiltration with experiments E2 under the spontaneous (a-b) and forced ($P_a=11\text{bar}$) conditions (c-d) at 330°C, 360°C and 385°C. (a) and (c) are the infiltration profiles; (b) and (d) show the calculated shear rates and contact angles at different infiltration times.

Based on the contact angle values obtained for experiments E1 and E2, some issues are worth mentioning. The values encountered for the pressure-assisted E1 experiments shall be taken as advancing contact angles as the mesophase pitch maintains a quadratic rate of infiltration distance with time. In these experiments, the counter pressure imposed was constant and the infiltration rate slowly decreased, mainly because the pressure gradient in the mesophase pitch was imposed by only the capillary pressure or by both the capillary and the applied external pressure together, and it decreased as the infiltrated distance became longer. Conversely in experiments E2, the counter pressure increased quickly as the mesophase pitch progressively invaded the porous perform. Hence infiltration was rapidly hindered. The spontaneous E1 experiments also showed relatively low infiltrations kinetics. As a result, the final contact angles encountered for these conditions were considered pseudo-equilibrium contact angles and could be compared with those in the literature obtained by the sessile drop method. Unfortunately, reliable data on the equilibrium contact angles of the mesophase pitch on NaCl substrates are not available in the literature. In [13] a study is presented of the wetting behaviour of a naphthalene-based mesophase pitch on different substrates by the sessile drop method. Very low (wetting) contact angles are reported for the vast majority of systems.

A general comment about viscosity that derived from experiments E1 and E2 was that the values at the three different temperatures closely agreed with the steady values obtained from the rheological measurements, which indicates that the AR24 mesophase pitch behaved as a Newtonian fluid during its infiltration in the present packed

preforms. Another issue that is worth commenting is that in prolonged infiltrations such as those shown in this work, polymerization reactions or degradation of the mesophase pitch could eventually occur, especially at the high temperatures studied. These reactions could change the properties of the pitch and thus affect its kinetics of infiltration. To check this effect, the softening point of the remaining non-infiltrated pitch after infiltration experiments for 3600s was measured for six samples, corresponding to spontaneous infiltrations at the three studied temperatures (330°C, 360°C and 385°C) and the two conditions E1 and E2. The softening points were 243°C (330°C-E1), 244°C (330°C-E2), 245°C (360°C-E1), 244°C (360°C-E2), 245°C (385°C-E1) and 244°C (385°C-E2), all in perfect agreement with the value measured for the as-received mesophase pitch. The invariability in the softening point allows pointing out that the mesophase pitch did not undergo important reactions during the infiltration experiments. To further check this point, thermal characterizations by TG/DTG in the 25-925°C range and DSC in the 50-450°C range were performed for the as-received pitch (namely AR in plots of Figure S.2 and Figure S.3 in the Supplementary Materials section). The TG results show that the AR mesophase pitch starts losing significant weight at a temperature of 401°C. Below this temperature a total weight loss of roughly 1.5% is registered, most probably caused by volatilization of low molecular weight species from the pitch. It must be born in mind that during infiltrations this weight loss may not occur, given the high pressures applied to the pitch to avoid swelling. The DSC profiles show two main thermal transitions in the 50-450°C temperature range. The first one is an endothermic process at around 242°C, which assigns to the softening point (in clear agreement with the results obtained by the thermomechanical analyser). The second transition occurs at temperatures above 400°C and can be ascribed to decomposition of the pitch (these results are in line with those found by Lee et al. [30] for the same type of mesophase pitch). All these experimental facts, besides that the kinetics of infiltration can be justified with a single viscosity value, allow thinking that there were no reactions occurring during the infiltration of the pitch or that the extension of these reactions were so small that they have minimal effects on either the softening point or the kinetics of infiltration.

4.4 Slug-flow assumption: saturation over an infiltrated distance

Equations (1-7) are valid under the slug-flow hypothesis, which assumes a fully saturated flow in the porous preform, and hence constant permeability K along preform

length. Let's recall at this point that saturation in this context refers to the amount of mesophase pitch that has invaded the preform in respect to the total amount of mesophase pitch necessary to completely fill the porous space of that portion of the preform. In other words, a fully saturated flow means that the fluid leaves no pores remaining in the preform. The slug-flow assumption has proven a practical assumption for many infiltration systems, and has been often justified if the system displays wetting behaviour or if the external applied pressure is high enough compared to the capillary pressure in non-wetting systems. Curves that confer saturation *versus* either applied pressure or infiltrated distance are often obtained in soil science or reservoir engineering, and allow the validity of slug-flow hypothesis to be confirmed. Such curves are shown in Figure 8 for experiments E1 and E2 under forced infiltrations of the AR24 mesophase pitch into NaCl packed preforms. Optical microstructures of the infiltrated samples at close distances to either the pitch entrance or the infiltration front are provided in Figure 9. Given that saturation approximately defined a step-function, which equalled 0 in the non-infiltrated region and 100% in the infiltrated part, the slug-flow assumption was confirmed. Hence the use of Equations (1-7) were soundly justified.

Figure 8 – The AR24 mesophase pitch saturation versus the distance from the pitch entrance for the NaCl-packed preforms infiltrated with experiments E1 and E2 under the forced infiltration conditions at 330°C.

Figure 9 – Optical micrographs of the infiltrated samples taken at portions close to either the pitch entrance (a) or the infiltration front (b).

4.5 Infiltration kinetics with the AR24 mesophase pitch doped with TiC nanoparticles

The incorporation of TiC nanoparticles into the mesophase pitch has been demonstrated to have intrinsic benefits given its catalytic effect during graphitisation [4]. However, presence of TiC nanoparticles may pose augmented viscosity drawbacks in infiltration processes, which would transfer to reduced infiltration kinetics. The mesophase pitch with low TiC nanoparticles concentrations can be treated as a nanofluid, comparable to those already studied in the literature based on polymer matrices that contain nanoparticles of different natures [11,12,31]. This constitutes the framework of the present study.

The procedure to incorporate TiC nanoparticles into the mesophase pitch consists of a first step of partial dissolution in toluene and posterior heat treatments to release the solvent. These treatments are likely to cause chemical changes in the mesophase pitch that might alter its main physical properties, which are relevant in infiltration (i.e. viscosity and softening point). To check this possible effect, a portion of mesophase pitch was subjected to the whole protocol of treatments used to incorporate TiC nanoparticles and was analysed by Infrared Spectroscopy (IR). For comparison purposes, Figure 10a shows the IR spectra of the as-received AR24 mesophase pitch (AR) and the AR24 mesophase pitch subjected to the treatments to incorporate nanoparticles (AR0TiC). The IR spectrum of AR24 exhibits characteristic vibrational bands of aromatic C–H bonds (at 3048 and 700–900 cm^{-1}) and aliphatic C–H bonds (at 2850–2920 and 1385–1440 cm^{-1}). Bands due to bending vibrations of the polyaromatic C=C structures (at 1595–1610 cm^{-1}) are also observed. In the region with higher frequencies, a broad band appears at 3200–4000 cm^{-1} , which corresponds mainly to the

stretching vibrations of the bound and unbound hydrogen bonds in the NH group; this band can offer marginal contributions from the stretching vibrations of the OH group due to the pitch's given surface functionality. However, it is not possible to distinguish any clear band at either 1697 cm^{-1} or 1240 cm^{-1} , which correspond to the C=O vibrations in arylketones or arylaldehydes, and also to the asymmetric vibrations of the etheric C–O–C groups respectively, given that the amount of oxygen in the present pitches was very restricted.

Figure 10 – (a) The infrared (IR) spectra of the mesophase pitch in the as-received condition (AR) and after the treatments to incorporate TiC nanoparticles (AR0TiC); (b) is a magnification of (a) in the region of frequencies of $2500\text{--}4000\text{ cm}^{-1}$.

The clearest difference encountered between the two IR spectra stands for the bands at $2850\text{--}2920\text{ cm}^{-1}$ and 3048 cm^{-1} , with a lower intensity in AR0TiC (see Figure 10b for an amplified superposition in the region of frequencies of $2500\text{--}4000\text{ cm}^{-1}$). In line with this, the bands at $700\text{--}900$ and at $1385\text{--}1440\text{ cm}^{-1}$ also had diminished intensity, but on this occasion the change was less apparent. This was most probably caused by the evaporation of part of the most volatile species (low-molecular-weight units) in the mesophase pitch during the treatments for solvent release while incorporating nanoparticles. This gave smaller amounts of both the C–H aromatic and aliphatic groups. The removal of a considerable fraction of small molecular species can reduce, or even remove, pitch fusibility [1]. Additionally, the broad band at $3200\text{--}4000\text{ cm}^{-1}$ was still there, but was slightly less intense. Reduced intensity could be caused by the surface defunctionalisation of the pitch, which could alter the amount of the O–H groups. Extra experiments of thermal characterization allowed corroborating the ideas extracted from the infrared analysis. In thermogravimetry experiments (Figure S.2 in the

Supplementary Materials section) it can be observed that the profile of the untreated pitch (AR) goes slightly below the profiles of the treated pitches (AR0TiC, AR1TiC and AR4TiC) over the 25-400°C range, pointing out that the treatment for TiC incorporation eliminates a fraction of weight corresponding most likely to low molecular weight species. Besides this, the differences in the TG profiles in the interval of the infiltration temperatures are very slight. At high temperatures (around 600°C), however, it can be seen that the curves for AR0TiC, AR1TiC and AR4TiC are overlapping (once the profiles have been corrected to eliminate the mass effect of the TiC nanoparticles) and generate a greater stabilization of the pitch, because their total weight loss is much less than for the AR untreated pitch.

We expected that the aforementioned chemical modifications could consequently cause changes in the mesophase pitch's physical properties. Figure 11a shows a granule of a 4%TiC-containing mesophase pitch obtained after grinding large pieces of the doped material. The microstructure in Figure 11b was obtained by the infiltration with AR4%TiC of a packed bed of NaCl particles, once these had been dissolved in water towards a better characterisation. Overall, the two images evidence quite a good distribution of the nanoparticles in both materials. The infiltration kinetics was determined with experiments E2 under the forced infiltration conditions. The experimental results, along with the calculated curves, are shown in Figures 11c-11f for the 0%, 1%, 2% and 4% of TiC nanoparticles contents, respectively. Table 4 includes the viscosity values derived for all three temperatures considered herein.

(a)

(b)

Figure 11 – (a) micrograph of a granule of the mesophase pitch that contained 4% of TiC nanoparticles; (b) a microstructure that derived from the infiltration of a packed bed of NaCl particles with the material in (a) after the water dissolution of NaCl particles; (c-f) the infiltration profiles obtained with experiments E2 under the forced ($P_a=11\text{bar}$) conditions for AR0TiC (c), AR1TiC (d), AR2TiC (e) and AR4TiC (f) at three temperatures each (330°C, 360°C and 385°C).

Table 4. Viscosity μ (Pa.s) derived from experiments E2 under the forced infiltration conditions and softening point of the AR24 mesophase pitch that contained 0% (AR0TiC), 1% (AR1TiC), 2% (AR2TiC) and 4% (AR4TiC) TiC nanoparticles. Although sample AR0TiC was free of TiC nanoparticles, it was subjected to the same heat treatments as the others.

		AR0TiC	AR1TiC	AR2TiC	AR4TiC
Softening point (°C)		256 ± 2	259 ± 2	258 ± 2	257 ± 2
μ (Pa.s)	330°C	3.20	5.50	6.80	8.30
	360°C	0.45	0.90	1.60	2.20
	385°C	0.12	0.26	0.47	0.80

It was generally observed that the heat treatments applied to incorporate nanoparticles significantly affected the mesophase pitch's viscosity for all three temperatures

explored herein, most probably caused by elimination of low molecular weight species, as commented above (compare the values of AR0TiC with those in Table 4 for the as-received mesophase pitch). While the curves at 330°C all illustrate low infiltration kinetics, the shape of the curves that correspond to 360°C and 385°C vastly vary when passing from the rapid infiltration kinetics that correspond to low TiC nanoparticles contents to the slow infiltration kinetics of the mesophase pitch that contain the 4% volume of TiC nanoparticles. Working with the TiC nanoparticles-containing mesophase pitch consequently present the disadvantage of having viscosity values that increase with TiC content. One important partial conclusion at this point is drawn from the fact that each set of experimental infiltration data, defined by a certain TiC content and temperature, admits being fitted with a single viscosity value, which allows us to state that the mesophase pitch at any of the TiC volume concentrations explored herein exhibits Newtonian behaviour during infiltration into NaCl packed preforms.

The softening points, which derived from the thermomechanical analysis, show no clear dependence on TiC content (see Table 4). To accurately determine the softening point values, the first and second derivatives were calculated from the rough curve provided by the thermomechanical analyser (Figure 12), and the softening point was established by crossing the second derivative with the abscissa axis. The values of softening point collected in Table 4 are in close agreement with those derived from Differential Scanning Calorimetry (DSC) experiments (Figure S.3 and Table S.1 in the Supplementary Materials section). Since the presence of different contents of TiC nanoparticles is not accounted for by essentially different thermal profiles (Figure S.2 and Figure S.3 in the Supplementary Materials section), it can be drawn that the apparent changes in viscosity are exclusively ascribed to fluid-dynamic effects caused by the presence of TiC nanoparticles in the mesophase pitch. The presence of dispersed nanoparticles in fluids has demonstrated to significantly affect their transport (e.g. viscosity) and thermal properties (e.g. surface tension) under certain particle sizes and concentrations [11,12,31].

Figure 12 – (a) the rough curve from the thermomechanical analyser, and the first and second derivatives (b) for the AR24 mesophase pitch.

In order to establish a proper correlation among viscosity, the TiC nanoparticle volume percentage and the mesophase temperature, we followed the procedure of Namburu et al. [31]. These authors showed that a careful statistical analysis of many experimental data of Newtonian nanofluids with polymeric and water-based base fluids concluded that the exponential model given by the following Equation (10) can be considered:

$$\text{Log}(\mu_s) = Ae^{-BT} \quad (10)$$

Where, in the present context, μ_s is the TiC-containing mesophase viscosity in centipoise (cP) (the author prefers to fully respect the original notation and units given in [31]), T is the temperature in K, and A , B are nanoparticle volume percentage functions (Θ).

The experimental data presented in Table 4 can then be easily evaluated with a linearization of Equation (10) by plotting the natural logarithm of $\log(\mu_s)$ versus temperature T , as illustrated in Figure 13a. The corresponding A and B values were calculated from the linear fittings, and are offered in Table 5.

Figure 13 – (a) The natural logarithm of $\log(\mu_s)$ versus absolute temperature – the fitting parameters are provided in Table 5 and (b) viscosity μ_s versus the temperature-containing calculated curves with Equation (10) based on the modelling procedure of Namburu et al. [31].

Table 5. Values of parameters A and B from the fittings with Equation (10) of AR24 mesophase viscosity versus the temperature for the different TiC nanoparticles contents.

	AR0TiC	AR1TiC	AR2TiC	AR4TiC
A	1043	444	195	103
B	0.0095	0.0080	0.0065	0.0054

Coefficients A and B are related with the volume percentage of nanoparticles (Θ) as:

$$A = -27.74(\Theta)^3 + 261.8(\Theta)^2 - 839.9(\Theta) + 1050 \quad (11)$$

$$B = 5.583(\Theta)^3 - 1.025(\Theta)^2 - 1.493(\Theta) + 0.0095 \quad (12)$$

for Θ that ranged from 0% to 4%. Equations (11) and (12), in combination with Equation (10), can be used to calculate the viscosity for any Θ value within the 0-4% range. Figure 13.b depicts the experimental data and the calculated curves for the different samples at hand. Therefore, the empirical correlation proposed in [31] for the polymeric and water-based base fluids, expressed in Equation (10), also holds for the mesophase pitch that contains TiC nanoparticles, which can be consequently treated as a nanofluid with Newtonian fluid transport.

5. Conclusions

From the present study, the following conclusions about the AR24 mesophase pitch fluid-dynamic behaviour, both with and without TiC nanoparticles in its infiltration in the 330°C-385°C range into NaCl particle-packed porous performs, can be reached:

- Planar infiltration fronts were encountered during the invasion of the NaCl particle-packed porous preforms by the mesophase pitch under the pressure and pressureless infiltration experiments performed in two-sided open tubes (experiments E1) or closed-bottomed tubes (experiments E2), provided that a minimum pressure of 4 bar was used to prevent the mesophase pitch from swelling.
- The slug flow hypothesis, usually not obeyed in the vast majority of non-wetting liquid-solid infiltrating systems, is fulfilled in all infiltrations of the mesophase pitch under conditions E1 and E2, either spontaneous or forced, which is indicative of strong wetting interactions with the porous preform.
- The infiltration profiles obtained under conditions E1 are parabolic with time while those obtained for E2 conditions show much smaller infiltration kinetics since the presence of a steadily increasing counter pressure slows down the advance of the infiltration front.
- The contact angles derived from the pressure-assisted (fast-kinetics) E1 experiments can be considered as advancing contact angles while those derived from the (low-kinetics) E2 experiments and the spontaneous E1 experiments can be taken as pseudo-equilibrium contact angles, comparable with those found in the scarce literature from sessile-drop experiments; in any case the values of contact angle encountered are low, indicating strong interactions between the mesophase pitch and the porous preform, in accordance with the slug-flow hypothesis and the presence of planar fronts.
- The values of viscosity derived during the infiltration conditions imposed by experiments E1 and E2, either spontaneous or forced, are coincident with those measured with accurate rheometers under Newtonian regimes (at shear rates roughly above 3s^{-1}).
- The non-Newtonian behaviour of the mesophase pitch might be manifested only at very high shear rates, characteristic of the early stages of infiltration. Nevertheless, the infiltration curves (profiles of infiltrated distance over time) obtained under standard infiltration conditions can be well characterized by a single viscosity value.
- Very late infiltration stages would be prone to show non-Newtonian behaviour of the mesophase pitch given that shear rates are calculated as being low. However, the advance of the mesophase invading the preform is also slow and any change in viscosity is not transferred to the measurable changes in the infiltrated distance.
- The incorporation of TiC nanoparticles into the mesophase pitch by partial dissolution in toluene and use of combined blade stirring and ultrasounds generates slight changes

in the physical properties of the mesophase pitch that can be explained by chemical modifications generated by the volatilization of low molecular weight species.

- The mesophase pitch with TiC nanoparticles shows increased viscosity which depends on the TiC concentration, being able to be studied under the consideration of Newtonian nanofluids.

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