Nanofibre distribution in composites manufactured with epoxy reinforced with nanofibrillated cellulose: model prediction and verification

Yvonne Aitomäki¹, Mikael Westin¹, Jani Korpimäki² and Kristiina Oksman¹

¹Luleå University of Technology, 971 87 Luleå, Sweden,
²CSI Composites, 35700 Vilppula, Finland

Email: yvonne.aitomaki@ltu.se

Abstract. In this study a model based on simple scattering is developed and used to predict the distribution of nanofibrillated cellulose in composites manufactured by resin transfer moulding (RTM) where the resin contains nanofibres. The model is a Monte Carlo based simulation where nanofibres are randomly chosen from probability density functions for length, diameter and orientation. Their movements are then tracked as they advance through a random arrangement of fibres in defined fibre bundles. The results of the model show that the fabric filters the nanofibres within the first 20 µm unless clear inter-bundle channels are available. The volume fraction of the fabric fibres, flow velocity and size of nanofibre influence this to some extent. To verify the model, an epoxy with 0.5 wt.% Kraft Birch nanofibres was made through a solvent exchange route and stained with a colouring agent. This was infused into a glass fibre fabric using an RTM process. The experimental results confirmed the filtering of the nanofibres by the fibre bundles and their penetration in the fabric via the inter-bundle channels. Hence, the model is a useful tool for visualising the distribution of the nanofibres in composites in this manufacturing process.

1. Introduction
Nanofibres from different cellulose sources have been shown to reinforce polymers, even at low volume fractions [1], [2]. One possible way of exploiting this is reinforcing the matrix of a polymer composite with the aim of increasing the properties of the matrix and thus the properties of the entire composite. For such matrices to be used effectively, it is important to understand their behaviour when used in typical composite manufacturing methods so that appropriate processes can be found and modified if necessary. Resin transfer moulding (RTM) is a typical composite manufacturing method where a dry preform is held in a matched, closed mould and the resin is forced into the mould by pressurising the resin at the inlet. The advantages of this process are that it is a closed process, so chemicals are not released into the working environment, the pressure applied can be high to allow rapid impregnation, the volume fraction can be controlled by compressing the fibre mat into the mould and both surfaces of the part have a good finish. However, if a matrix reinforced with nanofibres is used in this process, the nanofibres are likely to be filtered by the fabric. This filtering will depend on a number of parameters such as the volume fraction and the size of the nanofibres. Numerical models that capture the complex particulate flow in RTM processes, and the result this has on the distribution of particles have been developed but requires complex modelling of the flow both in and between the
bundles [3], [4]. Evaluated here is whether a simple scattering model, that is easily modified, can be used as a visual aid to give a good initial understanding of the distribution of nanofibres when these types of particulate matrices are used in RTM. The proposed model is based on a Monte-Carlo model of photon transport in a scattering media [5] but modified substantially to reflect the movement of nanoparticles and their interaction with different surfaces.

The results of the model are a distribution of the nanofibres in the composite. Thus to verify these results a means of measuring this distribution is required. The proposed approach is to infuse a preform of glass fabric of known geometry and permeability with a resin containing stained nanofibres using RTM. The composite is then cut and the cross-section examined for the presence of nanofibres.

2. Method

2.1. Theory
The Monte-Carlo model has the following key elements:

• The geometry of the fabric to be impregnated can be modified to represent the fibre arrangement of the materials of interest.
• The nanofibres are randomly distributed across the resin inlet and the inlet can be adjusted to fill the whole surface of the composite.
• The length and width of the nanofibres are randomly selected from a probability density function (PDF) and these PDFs are the input parameters to the model.
• The nanofibres are randomly oriented.
• The nanofibres progress in the direction of the flow unless they encounter an obstacle. The nanofibres reflect off the surface of the obstacle at an angle based on the gradient of the surface at that point. The obstacles are the fibres in the fabric that is being impregnated.
• The gradient of the surface of the fabric fibres can be set to represent the hydrodynamic “surface”. Hence at slow speeds, the fabric fibres are set to a circular aspect whereas at higher flow velocities, the fibre is distorted to have an elliptical shape with the major axis aligned in the direction of the flow.

2.2. Implementation
The model has been implemented in Matlab (R2014b) and the fibres are represented as ellipses, randomly arranged in bundles (see Figure 1), hence the image represents a cross-section of the fibre mat. The markers show the position of different points on the nanofibres but are not drawn to scale so that their position can be seen even on the larger scale images. The size of the fibres, the major and minor axis of the ellipse, the number of fibres and the number of bundles are set as input parameters.

Figure 1. Nanofibres of width 70 nm and length of 3000 nm in a fabric where the single fibre diameter was 7 \( \mu \text{m} \) and the bundle size was 50\( \mu \text{m} \). (a) Shows the arrangement of fibres (black ellipses) within bundles (b) nanofibres hitting the surface of a single fabric fibre (c) a close up of a nanofibre showing it is made up in this case of 7 pixels representing 70 nm.
The fibres in the fabric are created as circles on an image using the equation of an ellipse such that
\[
\frac{x^2}{a^2} + \frac{z^2}{b^2} = r
\]  
where \(r\) is the radius, \(a\) and \(b\) are the radius fraction on the \(x\) and \(z\) axis respectively and \(x\) and \(z\) are the position on the image where the fibre is located. The centre for the fibre is randomly positioned on the image under the condition that the ellipse created does not overlap with another. The fibre bundles are created by simply using ellipses of larger size, superimposed over the image such that areas outside of the large ellipses are cleared of fibres. The radius is defined and the position of these bundles calculated based on this diameter and the gap between the fibre bundles. The size of the fibre bundles and the size of the fibres can be measured from the fabric or obtained from datasheets.

The positions of the nanofibres are randomly distributed across the image and represent the random distribution of the nanofibres across the upper surface of the composite. The current size of the image is set to 100 \(\mu m\). The fibre arrangement is produced at this scale then is enlarged by a scale currently set to 4 to allow the gradient at the point of contact of the nanofibres to be calculated with reasonable accuracy. This also allows a computationally efficient reproduction of a part of the fibre fabric. As stated earlier, the length and width of the nanofibres are randomly selected from a PDF. The currently implemented PDF is simply a normal distribution. The nanofibres are plotted on the image of the fabrics and a resolution is used such that each pixel represents 10 nm. A close up of a nanofibre on the surface of a fabric fibre is shown in Figure 1.

As well as being randomly positioned, the nanofibres are randomly oriented and this is implemented by calculating the shape of a nanofibre using vectors from a single point on its surface. The direction of the vector defines the orientation of the nanofibre.

The nanofibres move stepwise in the \(z\)-axis and their movement is defined by a directional vector associated with each nanofibre. The velocity of the flow is calculated based on a Darcian flow such that
\[
v_i = -\frac{K_{ij}}{\mu} \frac{\partial p}{\partial x_j}
\]
where \(v_i\) is the superficial velocity vector, \(K_{ij}\) the permeability tensor, \(\mu\) the dynamic viscosity, \(p\) the pressure and \(x\) are the coordinates. The subscripts \(i\) and \(j\) denote the free and summation indices, respectively. The superficial velocity is the local flow rate per unit area including both the solid and pore space and is thus related to the averaged interstitial velocity according to \(v = u_{int} \epsilon\) where \(\epsilon\) is the porosity. Hence for the one-dimensional case and assuming a constant pressure gradient and with \(L\) as the length of the flow path, the velocity is
\[
u_{int} = -\frac{K}{\epsilon \mu} \frac{\Delta p}{L}
\]

It is assumed that the nanoparticles move with this velocity in the \(z\)-direction. The repercussions of this assumption are that the particles undergo an increase in speed once a collision has occurred which is not possible. Issues surrounding this will be dealt with in later versions of the model, if deemed an important source of error. The velocity is not reflected directly in the current simulations although a timestamp for each point is calculated, thus it can be used to calculate position with respect to fill-time. The velocity is used indirectly to estimate the aspect ratio and thus the gradient of the surface from which the nanoparticles will be reflected.

As discussed earlier, the model was initially based on photon scattering, thus only representing the interaction with surfaces rather than of position throughout the fabric. The advantage with this is that it
rapidly gives the resulting distribution of nanofibres with little memory usage. However, to aid in the visualisation an additional function was added so that the progress of the nanofibres could be seen.

2.3. Experimental setup
The nanofibres used were fibrillated from Kraft Birch pulp, SCA, Munksund using an ultrafine grinder (Masuko Sangyo Co., Ltd., Japan). The dimensions of the nanofibres, as well the larger residual fibrous particles in the suspension were measured from dried samples using AFM (Veeco Multimode Scanning Probe, USA) and optical microscopy. The epoxy was Prime 20ULV (Gurit, UK) that has an initial viscosity of 139 mPas at 25°C. The procedure for the preparation of the stained nanofibre/epoxy is as follows: the colouring agent, Carmine, was added to the aqueous nanofibre suspension mixed and then a solvent exchange to acetone was done. In the process unbound carmine was removed. The mixture was then diluted to 1.5 wt.% nanofibres.

Epoxy/nanofibre resin was prepared by adding the now stained nanofibres to the epoxy such that final resin would contain 0.5 wt.% nanofibres. The nanofibre, epoxy and acetone mixture was thoroughly mixed and degassed after which the mixture was stirred and kept at a temperature of 60°C for 48 hours to remove the majority of the acetone. The residual acetone was estimated to be 5.1 wt.%.

Figure 2. (a) Photograph of the stained nanofibres (b) microscope image of stained nanofibres.

Figure 2 shows the stained nanofibres in epoxy. With the hardener, the epoxy system has a viscosity of 393 mPas at 25°C, making it suitable for processing via RTM. This resin was used to infuse a dry glass fibre preform of [0/90]_4 made up of two types of biaxial fabric, a core of weight 600 gm⁻² and outer layers of 450 gm⁻². The stack was placed in the mould and a release film and flow mesh was put on the top before the mould was closed. The nanofibre/epoxy resin was degassed for 10 min before injected into a heated mould (35°C). A pressure of 0.2 MPa was used at the inlet and a vacuum pressure was applied to the outlet. After 15 min, the outlet was clamped and the inlet pressure increased to 0.5 MPa for 90 min. The part was cured for 10 hours at 35°C then post cured at 70°C for a further 10 hours. The composite was then removed from the mould, trimmed and samples were cut and polished for evaluation under a zoom stereomicroscope (Nikon, Japan). The glass fibres and bundles sizes were measured from the polished surface of the composite.

3. Results
Table 1 shows the distribution of the size of particles in the nanofibrillated suspension. Although a large portion of the fibres lie in the 500nm class, this is thought to be due to the drying process in the AFM sample preparation and hence the aqueous suspension is more likely to be made up of nanofibre bundles in the class 18 nm. Reassigning 50% of group in the 500 nm to the 18 nm class, gives an average nanofibre size of 172 nm. This does not include the larger fibre sizes (25µm and 2µm) as their behaviour would be quite different. It is noted that a better approach would be to use a PDF for a binomial distribution of the fibres and nanofibre, instead of the normal distribution for the nanofibre sizes that is currently implemented.
Table 1. Distribution of size of particles in the dried samples of the nanofibrillated suspension.

| Diameter size class (µm) | Area of coverage (%) |
|--------------------------|----------------------|
| 25                       | 6                    |
| 2                        | 16                   |
| 0.5                      | 34                   |
| 0.018                    | 27                   |

The average glass fibres were 10±1 µm, the average fibre bundle was 1307±286 µm (n=5) in width and 212±13 nm (n=10) in height and the inter fibre bundle spacing was 210±66 µm (n=18). The volume fraction of the composite, $V_f$, was 40%.

Frames taken at different points in the video of a simulation are shown in Figure 3 when the option to trace the nanofibres is on. As can be seen, use is made of Matlab’s scaling feature that means the red circles indicate the position of the nanofibres and not their actual size. The random arrangement of the nanofibres on the top surface can be seen and their position at different time intervals. It can also be seen that these simulations do not capture a continuous flow of nanofibres but rather shows the final positions of all nanofibres injected into the area represented by the image.

Figure 3. Time sequenced frames from the video of the simulated flow of nanofibres through a fabric.

3.1. Simulation

The following selected scenarios were run in order to illustrate effects of changing different parameters and with this guide processing of nanofibre filled epoxy by RTM. In different scenarios, each time a simulation is run the position of the fibres in the fabric changes as well as the starting point of the nanofibres, their length, width and orientation. Running the simulations several times allows for a greater reliance on the results. Where stated, n represents the number of simulations run.

3.1.1. Scenario 1: Effect of increase flow velocity. When the flow velocity increases the nanofibres are more likely to be carried around the fibre by the flow. This behaviour is mimicked by decreasing the size of the fibres and increasing the gradient of the fibre surface that the nanofibres are reflecting off. Figure 4 show the resulting distributions of nanofibres in the glass fibre fabric. In Figure 4(a) an aspect ratio replicating the true geometry of the fabric fibres is used and in Figure 4(b) the aspect ratio is adjusted to $a = 0.7$ (Equation 1) in order to emulate the hydrodynamic shape of the fabric fibres.

Comparing Figure 4(a) to Figure 4(b) the predominating effect on the distribution is the differences in the number of fibres in any one area i.e. the fibre volume fraction. This was confirmed by running the simulation again whilst maintaining the same volume fraction, which showed there is little effect of the surface gradient on the nanofibre distribution.
3.1.2. Scenario 2: Effect of using shorter and thinner nanofibres. Nanofibres coming from different sources and isolated with different processing treatments have different geometries. Taking an extreme example, nanocrystals can be extracted from cellulose and are shorter and thinner e.g. 200nm in length and widths of 5-10 nm [6]. To see the effect of changing geometry, the simulation were run with nanofibres with a width of 10 nm and length of 200nm. We also test the effect of having more homogeneous distribution of nanofibres with widths of 70nm x 3000nm. The distribution of nanofibres in the glass fibre fabric resulting from the simulation of this scenario is shown in Figure 5(a) which can be compared to Figure 5(b) where the nanofibres are 3000 by 75 nm and to Figure 4(a) where the nanofibres were 3000 by 175 nm. The results show that the crystal sized particles can penetrate the bundles, even cross the entire simulated region (marked red in Figure 6(a)), however, a large proportion are still filtered out. Increasing the size to that of homogeneous nanofibre, reduced the depth of penetration to approximately < 40 μm in the bundles, which is similar to that achieved by the larger nanofibres modeled in Figure 4(a).

3.1.3. Scenario 3: Effect of inter-bundle channels. The effect of inter-bundle channels where simulated by using an inter-bundle channel width of 100μm rather than the actual 200 μm channels that are in the glass fibre mat. Since this channel width is much greater than the length of the nanofibres, this will not introduce a difference of behaviour and allows a more rapid simulation of the behaviour. Also tested is the effect of having smaller fibre bundles (400 μm) and channels (60 μm) but maintaining the same fibre to bundle ratio as in the glass fabric. The results for this scenario are shown in Figure 6(a) and it can be seen that nanofibres reach the end of the image, which represent a flow path of 100 μm.
The nanofibres are still however trapped in the upper part of the fabric when the flow path is through the fibre bundle. The results of having inter-bundle channels, suggest that this would allow good penetration of the nanofibres into the fabric though possibly results in a lack of homogeneity of the nanofibre distribution. Placement of several layers may however disrupt these channels.

![Figure 6](image)

Figure 6. Effect of inter-bundle channels on the nanofibre distribution (a) with large of 100 µm and (b) with narrow channels and fibre bundles.

The nanofibres form long tangled networks on the fabric fibres at the surface (inlet) and that this high concentration of nanofibre in the matrix will have a gradual transition to matrix without nanofibre in the main part of the composite plate. It is possible that this integrated layer would then provide good properties in terms of surface hardness and add rigidity to the composite. It is also clear that the impregnation should be made in the thickness direction to have any effect from the reinforcement in the resin on the composite since otherwise the nanofibres will be filtered out in the trim, before the composite part as been reached.

3.2. Experimental results

Microscope images of the polished cross-section of the composite are show in Figure 7(a) and (b) alongside a schematic of the glass fibre layup in Figure 7(c).

![Figure 7](image)

Figure 7. (a)Cross-section of composite showing nanofibres in the channels (b) higher magnification showing little impregnation the fibre bundles by the stained nanofibres and (c) schematic of the glass fibre layup.
The microscope images show that the nanofibres are concentrated in the channels and this is represented by the pink colour in the schematic diagram. Despite staining the nanofibres, due to their size, it is not possible to see individual or even low amounts of nanofibres. It is clear then that only low amounts nanofibre, if any, have penetrated the fibre bundles.

It is difficult to verify the model with precision but the overall result of the filtering effect of the nanofibres by the glass fibre is evident. Higher amounts of nanofibres can be seen in the sides of the bundles, which are not seen in the model. The most likely explanation for this is that the fibre volume fraction at these bundle edges is less than elsewhere as the fibre here can move into the inter-bundle space when compacted. The model shows that volume fraction has a large influence on penetration of nanofibres, and hence would support this explanation. The layer of fibres running perpendicular to the view direction (shown by the arrow in Figure 7(a)) appears to be pink. The likely cause of this is that the nanofibre/epoxy has filled the channel behind the transparent glass fibres (marked by the black arrow in Figure 7(c)). The model does not currently capture that behaviour as it does take into account transverse flow in these channels.

4. Conclusion

A simple scattering model has been developed and used to predict the location of nanofibres in a composite manufactured by RTM using a matrix reinforced with nanofibres. The results show clearly the effect of filtering by the fabric fibres and these are backed by the experimental results. Inter-bundle channels allow the nanofibres to penetrate the composite but are stopped by fibre bundles. The model shows that fibre volume concentration plays a major role in the penetration depth, and this is supported by penetration into the sides of the fibre bundles where the fibre volume fraction is lower. In conclusion, the model is a useful tool for showing the distribution of the nanofibres in composites though more work is needed to confirm the rest of the simulation results.

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