MICRO-SCALE MEASUREMENTS ON EPOXY USING IN-SITU MICROSCOPIC TECHNIQUES

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Abstract: *Fiber reinforced composite materials are typically comprised of two phases, e.g. the reinforcing fibers and a surrounding matrix. As a result, the matrix phase in unidirectional composites is composed of many interconnected, microscale (1 – 200 µm), tube-like volumes confined by the reinforcing aligned fiber bundles. Only very little is known on the micromechanical behavior of these small epoxy. Here, we show that the microscale behavior is clearly different and has extreme ductility not observed in the bulk scale brittle behavior. The confined microsize epoxy volumes have a plastic deformation behavior resulting in a substantially higher ultimate tensile strength (up to 380 MPa) and strain at break (up to 130 %) compared to their bulk counterpart (68 MPa and 8%). Polarized light microscopy confirmed the internal epoxy network structure rearrangement during loading. This work thus provides novel insights on the epoxy material behavior at the confined microscale as present in fiber reinforced composite materials.*

Keywords: Scanning Electron Microscopy (SEM); micromechanical testing; yielding; plasticity

1. Introduction

The specific build-up of fibre reinforced polymer composites where individual fibres are surrounded by matrix material, results in the presence of very small zones of matrix material (order of µm) in between the individual fibres. These micro volumes of matrix material tend to have different properties than is expected from standard testing of bulk scale specimens. This has important consequences towards the deformation behaviour and especially the microscale modelling of composite materials, where the current material models are still lacking.

Several researchers pointed out that these microscaled resin regions may have different mechanical properties than their macroscopic/bulk counterpart [1–4]. This has important consequences towards understanding the deformation behavior of fiber reinforced polymer composites. For example, microscale modelling of composites [5] is done very frequently to predict and optimize a composite material without the requirement of expensive time-consuming experimental trial-and-error. Yet, this requires accurate input of the material behavior at the microscale [6]. Nevertheless, most characterization of composites is performed at the bulk scale, typically using the prescribed standardized test methods such as ASTM D638 or ISO 527, while the research into microscale matrix properties is still very limited [1,2,4].

In this respect, a better understanding of epoxy at the microscale is of utmost importance as it is the most used matrix material in composites. Yet, for thermoset materials such as epoxies only a handful of studies are available [1–4]. Hobbiebrunken et al. introduced a production method which enabled the production of microfibers from epoxy resin that have a similar volume as the volumes present in composite materials (fiber diameters between 22 and 52 µm) [1]. Such microfibers indeed offer a good model for the pillar like matrix zones in between the

reinforcing fibers. An increase in ultimate tensile strength and strain showed that microscale fibers have a higher strength than larger bulk scale specimens. Misumi et al. expanded the research by also studying the yield strength and stiffness in addition to the ultimate tensile strength for five different epoxy systems [3]. They observed an increase in both yield and ultimate tensile strength for all systems. Recently, Sui et al. conducted a study over a broader range of microfiber diameters to compare the mechanical properties at the microscale with those at the bulk scale [4]. Again a decrease in diameter resulted in an increase in ultimate strength and strain.

Overall, it is clear that the mechanical behavior of epoxies may change depending on its size. However, there is currently no agreement whether these changes are induced by a size-effect (related to the amount of defects inside the material), by a difference in microstructure (e.g. orientation of polymer chains) and/or by the production method of the specimens (e.g. a difference in conversion degree). While several researchers describe necking and ductility of the epoxy microfibers, only post-mortem observations are currently available. Furthermore, the amount of tested samples is limited and there is a large variability reported in the results.

Therefore, we studied the deformation behavior of microscale epoxy fibers through tensile testing, thermal analysis (study of glass transition temperature and conversion) and in-situ (electron) microscopy (observation of necking behaviour). The combination of these techniques allows a deeper analysis of the epoxy behavior. In addition, polarized light optical microscopy enabled to study possible rearrangements in the internal network structure of the microscale epoxy samples due to deformation since this was only briefly discussed up till now.

2. Materials and methods

Fine epoxy fibers were made via an optimized method based on the work of Hobbiebrunken et al. [1] by drawing fibers from a vitrifying degassed epoxy mixture. For the specific system used in this paper, the resin was first cured 24h at room temperature in an acclimatized room. This was followed by heating up the resin to 80°C. After 7 minutes this led to the possibility of drawing fibers out of the resin. Fibers were drawn from the resin using an in-house developed automated dip-coater at a constant speed of 10 mm/s (Figure 1-a). The produced fibers are placed on a rack and put in an electrically heated oven at 80°C for 15 hours to complete the curing cycle (Figure 1-b). The complete cured fibers are glued onto paper supports with a two-component 5-minute epoxy glue (Figure 1-c). In total, 42 microfibers were produced with a diameter ranging from 30 to 400 µm and a standard deviation of less than 10%.

Both bulk and microscaled epoxy specimens were produced using the same curing conditions to minimize any change in properties induced by a difference in conversion. This was confirmed by Modulated Differential Scanning Calorimetry (TA instrument Q2000 DSC, heating rate of 3°C/min, modulation of 0.5°C/min, scan from 0°C to 150°C). The glass transition temperature (Tg) of bulk scale and microscale specimens was 86.8 ± 1 °C and 87.3 ± 3 °C respectively. As the Tg is directly linked to the conversion degree [7], this shows that both bulk and microscale specimens have a similar conversion degree. In addition, no additional exothermic peak was measured above the Tg for both types of specimens.

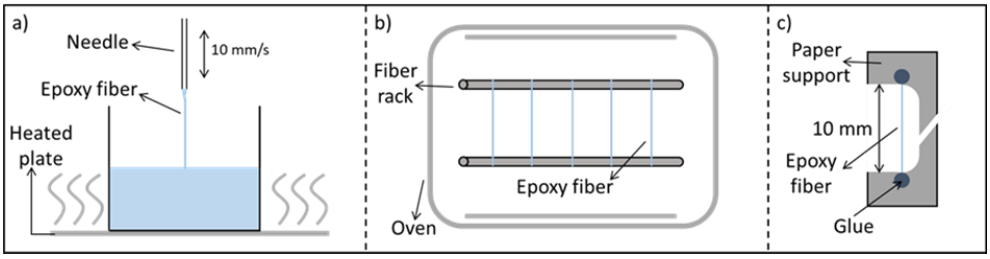

Figure 1 Production method. (a) Epoxy fibers are drawn from the vitrifying resin. (b) The produced fibers are cured at 80°C in an oven for 15h. (c) The final fibers are glued on paper supports, ready to be tested.

The tensile properties of the fibers were determined through tensile tests that agreed both with the ISO 527-1 (strain rate) and ISO 11566 standard (specimen geometry, strain rate), for bulk and fiber materials respectively, utilizing a dedicated fiber testing machine (Textechno Favimat™, force resolution 0.01 mN). The fiber is placed between the clamps at the glued points, the gauge length is 10 mm for all tests. A constant strain rate of 10%/min was selected. Mechanical data for the bulk scale was reused from previous research obtained in our group as published by Allaer et al. [8].

An Olympus BX-51 optical microscope with polarized light was used to inspect all fibers before and after testing. At least 5 pictures were used to measure the diameter of the fibers over the complete gauge length. In addition to the tensile experiments, several specimens were mechanically tested while observed with a Scanning Electron Microscope (SEM, Phenom XL, FEI). Here, a dedicated tensile stage was used (Tensile Sample Holder for Phenom XL, 150N load cell) that could be controlled during SEM imaging.

3. Results and discussion

Mechanical analysis of the microfiber epoxy samples revealed a high overall ductility with nominal strains reaching over 100%, this in contrast to bulk epoxy samples with the same conversion rate. A representative force-displacement curve for a microfiber epoxy sample, Figure 2, illustrates linear elasticity (zone I) followed by plastic deformation (zone II). For bulk scale samples this almost immediately leads to fracture, as only minor plastic deformation before failure is encountered for the majority of epoxy systems used in composites. On the other hand, the microfibers sustain this local decrease in diameter leading to a stable necking process and fracture is only encountered in a much later stage. Generally the microfibers show a lower stiffness and yield stress compared to the bulk samples (figure 3). The necking proceeds throughout the whole microfiber resulting in a large plateau in the force - displacement curve, resulting in an extreme ductility of the microfiber specimens (zone III, drawing of the microfibers). Finally, an increase in stress is observed (zone IV) and brittle fracture occurs. The increase in stress is likely related to strain hardening occurring during the necking of the microfiber.

An increase in E-modulus can be observed with decreasing microfiber diameter, the smaller the fibers become the stiffer they are (Figure 3a). This is probably due to a more perfect network structure with very few or no defects. Yet, the presence of small defects will have a large influence on the fibers resulting in more variability of the reported values compared to their bulk counterparts [3,4]. It has to be noted that for the microscale tests, the crosshead displacement of the tensile stage was used to determine the strain. This likely leads to an

underestimation of the E-modulus since any fixture compliance (e.g. slippage, backlash, …) results in an artificially increased strain. It can thus explain why the bulk scale modulus, which was accurately measured through DIC and clip-on extensometers, is higher than those of the microfibers. Indeed, one would expect that the more perfected network structure of the microfibers would result in a higher stiffness.

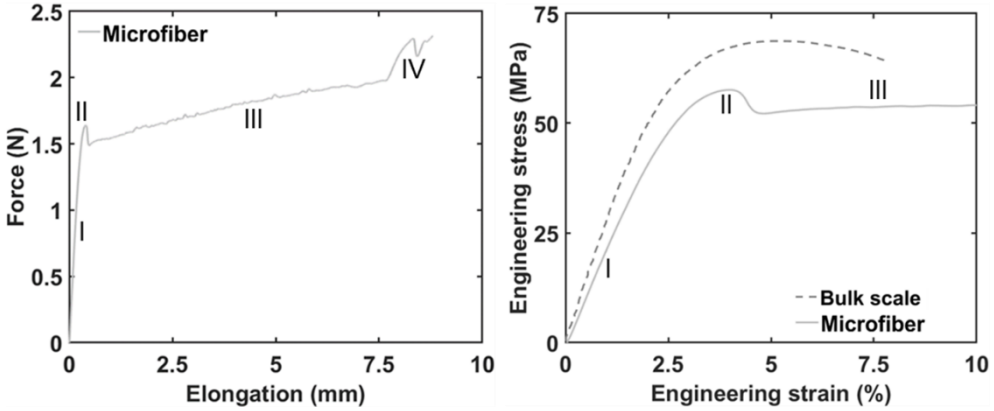

Figure 2 Stress-strain curve of a microfiber and bulk scale (the latter adapted from previous work. [23]). Representative force - displacement curve of a microfiber. Four zones can be observed: I - linear elastic zone, II - necking formation III - constant necking IV - strain hardening.

The microfibers show a similar yielding behavior over the full tested diameter range. In general the observed yield stress is somewhat lower than the values obtained for the bulk sample, while the yield strain is similar to the bulk values (Figure 3c and 3d). The latter can likely again be attributed due to the strain being based on crosshead displacements.

After yielding, the microfibers start to deform plastically resulting in necking. Similar to the yield stress, the necking stress and strain remain relatively unaffected by the diameter range tested here. The necking stress of the microfibers averages around 55 – 60 MPa (Figure 3e) while the necking strain averages around 4.5% of strain (Figure 3f). This indicates that for the microscale specimens there is somewhat less restriction for the epoxy network to deform and network chains possibly slip over one another resulting in reorientation of the chains in the internal network [4,9], somewhat similar to the deformation behavior of thermoplastics.

A drastic increase in ultimate tensile strength is observed as well. Whereas the bulk material has a ultimate tensile strength of around 68 MPa the fibers show a ultimate tensile strength up to 380 MPa. Moreover, an increasing trend in the ultimate tensile stress is observed for decreasing fiber diameters (Figure 3h). Similarly to the ultimate tensile strength, the strain at break increases drastically for all of the microfibers, with values going up to 130% (the bulk material has a strain at break of 8%).

Not all fibers reach these very high ultimate tensile strains as some fracture earlier during the necking process (zone III) which may be attributed to the presence of voids or defects. Due to the small volume, the chance of a void or defect being present is low which results in higher possible strengths [1]. Yet, if a void is present this will largely influence the mechanical behavior of the microfiber, resulting for example in early failure.

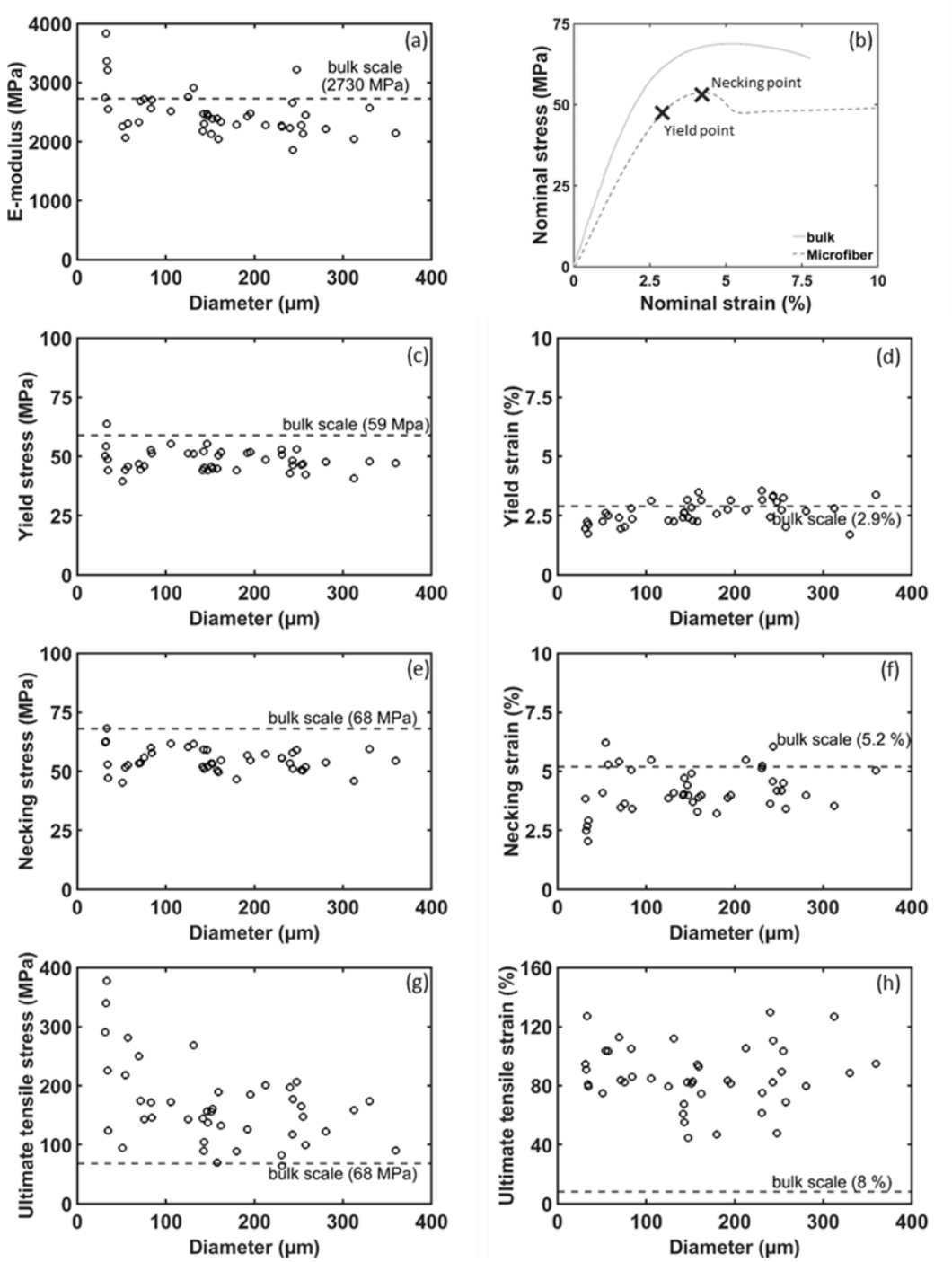

Figure 3 Representation of all mechanical data (a) E-modulus (b) engineering stress – engineering strain curve of representative microfiber tensile test with indication of necking and yield point (c) yield stress (d) yield strain (e) necking stress (f) necking strain (g) ultimate tensile stress and (h) ultimate tensile strain.

Figure 4 schematically illustrates the change in network structure during the deformation of the microfiber specimens, resulting in an oriented network structure after necking. Initially, the epoxy network is similar to that of a bulk material and can be considered random. During necking, the network has the possibility to align itself in the tensile direction by sliding and reorientation of the network chain segments, explaining the sudden and relatively large decrease in cross-sectional area. This reorientation is indeed confirmed by the sharp increase in

stress once the necking has proceeded completely through the gauge area of the fiber. (Figure 2, zone IV). This (local) strain hardening effect can be explained by a more oriented state of the molecular network. After this reorientation, the stress increases and the epoxy network finally fractures via the rupture of chains (chain scission) as it cannot accommodate the increasing tensile strain anymore.

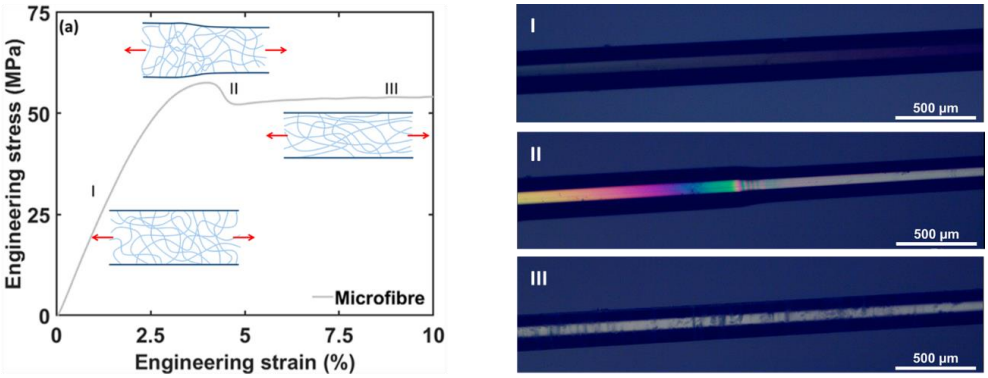

Figure 4 Schematic representation of the rearrangement of the epoxy network under tensile stress. Polarized optical microscopy confirms an oriented molecular microstructure in the necked zone of the specimens.

Polarized optical microscopy of tested fibers further confirm the change in orientation of the molecular network in the necked zone (Figure 4). Before stress is applied, the sample barely interacts with the light, resulting in a low amount of light passing through the second polarizer and thus a dark zone. Once stress is applied on the sample it starts to interact with the polarized light due to straining of the network structure. Around the necking zone, the network starts to orient. The oriented network interacts with the polarized light resulting in a bright zone showing a difference in internal structure with the unnecked zone. This confirms that a random network is present with no preference for any direction before necking, while a reorientation at molecular level occurs during necking.

To have a better view of the necking behavior several microfibers were mechanically tested with in-situ scanning electron microscopy. Via the obtained SEM pictures the diameter of the fiber is accurately measured which gives the possibility to calculate the change in diameter due to necking and the corresponding change in length (Eq. 1). Assuming a constant volume (v = 0.5, plasticity), the strain in the fiber direction can be calculated from the diameter variation via Equation 1:

$$Tensile\ strain = \frac{(D_1^2 - D_2^2)}{D_2^2} \quad (1)$$

Where D_1 and D_2 are the diameter just in front of the neck and just behind the neck (Figure 5).

The necking process that takes place during the plastic deformation of the microfibers can be clearly seen in Figure 5. All tested microfibers showed a decrease in diameter between 16 and 20%, with an average value of 18.3%, corresponding to a strain in the fiber direction ranging from 40 to almost 60% (average of 49.9%). Note the measured contraction is only due to the necking process, the tensile strain developed in the linear elastic zone or after necking of the fiber is not considered here.

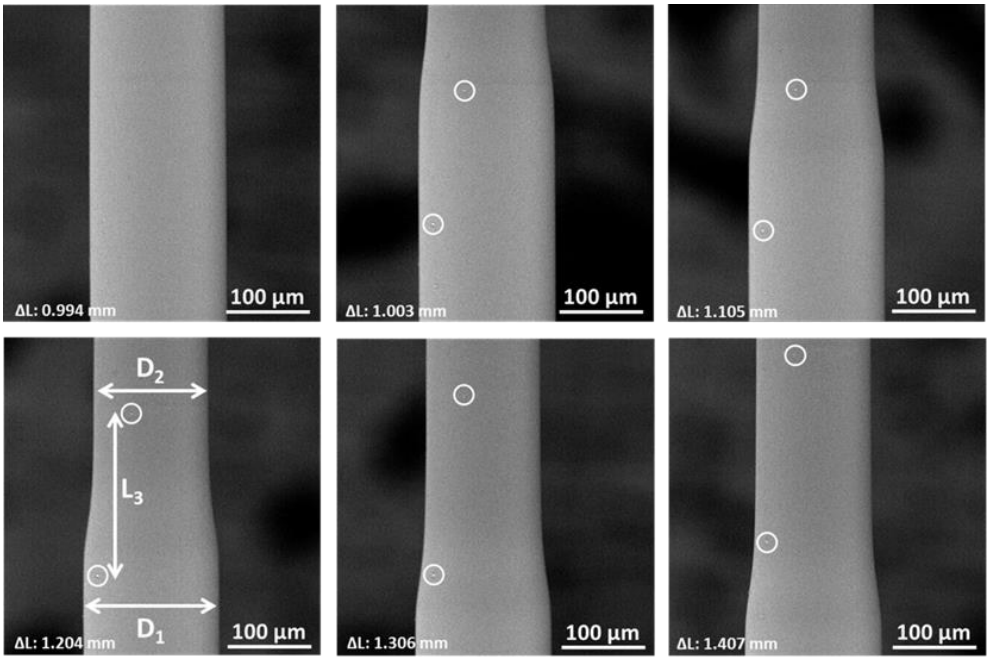

Figure 5 Sequential SEM images of necking in a microfiber. ΔL indicates the displacement of the clamps.

In addition to calculating the strain according to Eq. (1), the idea of video-extensometry is proposed as well to directly measure the increase in tensile strain after necking. We therefore deliberately handled a couple of specimens without gloves, resulting in small contamination onto the surface of the specimens that are ideal as surface markers, see Figure 5. These surface markers allowed to directly calculate the tensile strain. The results are listed Table 1 and confirm that the values obtained through Eq. (1) are correct.

Table 1 Comparison of the strain calculated based on the diameter reduction and the surface markers.

	Calculated strain via diameter (%)	Strain (%)
Microfiber 1	50.1	52.5
Microfiber 2	52.1	53.7
Microfiber 3	41.8	41.0

4. Conclusion

A set of microfibers was produced and studied via standard tensile testing. The deformation behavior of the confined microfiber epoxy samples was substantially different compared to bulk epoxy behavior, while thermal analysis confirmed a similar conversion rate of the epoxy in both the microfiber and the bulk state. During both linear elastic deformation and yielding, the microfibers behaved very similar to bulk samples. Yet, after necking, the behavior of the microscale and the bulk scale samples is very different. Indeed, the bulk scale samples show fracture shortly after yielding, whereas the microfiber specimens showed a large plastic deformation via the formation of a necked zone that extended throughout the fiber. As a result, much higher strains at break (up to 130% vs. 8% for bulk) and ultimate tensile strengths (up to 380 MPa vs. 68 MPa for bulk) were observed for these confined microfibers.

This high plastic deformation is attributed to a rearrangement of the epoxy network structure in the microfibers, as confirmed by polarized optical microscopy and the occurrence of strain hardening. In-situ electron microscopy moreover allowed to accurately observe the deformation behavior of these microfibers and measure tensile strains and diameter contractions during loading. An increase in length of around 50% was observed due to necking only.

The remarkable difference between the deformation behavior of epoxy resin at the micro- and macroscale clearly illustrates the need of microscale testing. Indeed, the resin pockets in fiber reinforced polymer composites are confined microsized regions as well that cannot be accurately characterized via bulk testing. Especially for predictive modelling tools, such as micromechanical modelling, this necessitates the use of microscale measured properties to obtain correct data and insights.

5. References

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