Chapter 9
Multifunctional Microwire Composites: Concept, Design and Fabrication

With microwires fully discussed in the previous chapters, we now divert our attention to innovative microwire-based materials, i.e. advanced microwire multifunctional composites, which have attracted much attention [1] due to the multitude of their properties and the associated broad range of engineering applications, from structural health monitoring to electromagnetic interference shielding. From this chapter on, we will focus on the design, fabrication, and characterisation of microwire composites. In order to provide the readers with a comprehensive picture of this novel kind of composite, both the art of application-oriented design of versatile microwire composites and the fundamental physics will be fully discussed.

9.1 Concept of Multifunctional Composites

First of all, we need to understand the basic concept of multifunctional composites. A multifunctional composite conventionally refers to a composite material that, beyond the primary structural function, possesses other functionalities as well, achieved by constituent components in an optimised structure [2, 3]. Gibson [4] divided multifunctional composites into three types: (i) multiple structural functions, (ii) non-structural functions plus structural functions, and (iii) both. This is a classification of multifunctionalities in a broad sense. In view of the recent development and the trend of multifunctional composites, our discussion has been limited to type (ii), which we deem to be a judicious and strict definition. Therefore, two points are underscored in this definition: (i) the composite must have multiple functions, and (ii) they are enabled by the constitutive materials. Such logic may lead one to a picture of a complicated composite structure consisting of any specific materials according to the recipe of intended functionalities, without regard to the compatibility of these materials. However, the architecture design of the composite will be a huge issue to tackle. It will also be difficult to predict the properties of the resultant composite from those of the constitutive materials insofar as the physical and chemical interactions

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between them are concerned. The brilliant idea of multifunctionalities is then tarnished by the high cost of manufacturing and maintenance. It appears that the making of this kind of composites remains far from ideal, as demonstrated by a wide spectrum of so-called multifunctional composites in the literature, inasmuch as they merely show a plus functionality at the expense, typically, of the mechanical performance. Strictly speaking, they are closer to multifunctional structures or systems rather than materials. To address these issues, the following should be realised: (i) an omnipotent functional filler is essential, in that it will ensure the achievement of multifunctionalities and a relatively simple composite architecture. This does not necessarily mean that all the functionalities must be exceptional. But the versatility thus obtained warrants no increase of cost, weight, and complexity [5]; (ii) a homogeneous material is a great priority for structural integrity and implementation, which can be approached in two ways: chemical intimacy between the fillers and matrix and extremely low loading of fillers that permits physical perturbations only. It is therefore reasonable to consider these standards as implicit behind the term of multifunctionalities, based on which the concept of truly multifunctional composites is initiated. To approach this concept, a couple of aspects are of major concern: (i) the functional fillers as described above and (ii) the topological arrangements of these fillers. To sum up, in realising the multifunctionalities, the filler answers the question of yes or no and the filler topology answers the question of how good it can be.

In line with this philosophy of multifunctional composites, microwires are certainly an ideal filler to be pursued in realising such composite materials in light of their following merits: (i) they are fine fillers with excellent mechanical properties. A typical glass-coated microwire fabricated by the Taylor-wire technique has a diameter of 1–30 μm, which can well match the size of reinforcing fibres such as carbon fibre and glass fibre. As such, they can retain, if not improve, the mechanical properties of structural matrix. (ii) They have superior GMI and GSI effects, rendering them useful inclusions into polymer matrices to realise microwave field-tunable composites and self-sensing smart composites. (iii) They have outstanding soft magnetic properties and good conductive properties, suggesting that they can be easily excited by the electromagnetic waves to realise many useful microwave behaviours such as absorption and negative refractive index. (iv) They are inexpensive and have strong market potential in the energy and aerospace engineering sectors, which have an increasing demand for multifunctional composites. In this context, multifunctional microwire composites have been developed to meet both the trend and the need.

9.2 Design and Preparation of Microwire Composites

9.2.1 General Design Strategy

As the microwire composites are expected to be applied in many different areas, their design should follow different criteria set by the application specifications.

The design of microwire composites mainly involves the following tasks: (1) **Choice of matrix**. This is relatively easy in the microwire composite case, as it is not required to have any special functional properties. But special polymers such as conjugated polymers can be a plus for some applications such as shielding; (2) **Choice of wires**. It has taken us seven chapters to discuss the close relationship between the wires' properties and numerous influencing factors such as geometry, composition, and post-processing conditions. When it comes to embedding microwires into polymer, these factors should also be considered, as the composite behaviour is very much dependent on the properties of the microwires embedded; and (3) **Mesostructure**, i.e. the topological arrangement of fillers. For this kind of two-phase heterogeneous composites, the mesostructure is believed to be the most crucial factor that dominates the composite behaviour [6]. In the case of microwire composites, the mesostructure is parametrised by the interwire spacing or concentration.

This subject will be treated from two categories of composites: continuous-wire composites and short-wire composites. Short-wire composites can also be subdivided into two categories according to whether the wires are randomly dispersed or periodically arranged. The design of microwire composites appears to be a complicated task, inasmuch as all the aforementioned relevant parameters may need to be varied to meet different application requirements. Without a full knowledge of these multiple functionalities, especially in terms of their relations with the composite structure, it is not possible to fulfil this task. Therefore, we attempt here just to outline the general principles, although more details are given in the later sections when individual cases are examined.

Generally speaking, to meet the basic structural requirement, a proper matrix should be adopted with either large strength or ductility. The wires should have a fine size and good mechanical properties. When it comes to the mesostructure, the long continuous wires should be aligned regularly and short wires are preferably homogeneously dispersed in the matrix, and a good interfacial bonding is always desirable. On the other hand, to realise various functionalities, some particular design of mesostructure is essential. Specifically, to realise a negative refractive index, a periodical arrangement of long continuous wires with proper interwire spacing is required. To obtain large magnetic field tunability, proper wire diameter and interwire spacing are needed to obtain the large relaxation parameters associated with the skin effect in a continuous-wire composite [7], while in the case of short-wire composites, the length and concentration of the microwires have to be fully considered [8]. For absorption purposes at a certain frequency, the relative permittivity and permeability play key roles, so the wire diameter, microstructure, and domain structure need to be carefully devised [9]. It is worth mentioning that, as there are conflicts arising from the requirement for different functionalities, it may be necessary to prioritise the need for target functionality but compromise on other, conflicting, functionalities. For example, at the same frequency, the absorption and metacomposite behaviours demand opposite characteristics of scattering spectra; this will be discussed in later sections.

Loosely defined, a microwire composite can be any form of material consisting of wires and a matrix material, although in engineering parlance, microwire composites conforming to the above definition may not be able to serve general structural purposes and hence cannot be categorised as composite materials. In this book, the scope will be extended to any form of microwire composite, with a particular note of its application range. The emphasis is placed on the microwire composites that meet the quest for both functional and structural use.

9.2.2 Microwires–Epoxy

Epoxy is believed to be the most extensively used matrix material for all kinds of composites and coatings for engineering applications. Zhang et al. [10] prepared a microwire composite coating on the surface of aluminium plate using polyamine dissolved by alcohol. The resultant composite and microwires arrangement are shown in Fig. 9.1. Liu et al. [11] also used epoxy to cast the toroidal samples for microwave characterisation. Starostenko and Rozanov [12] fabricated a composite mat by coprecipitation of glass fibre and wire pieces in a dilute solution of polystyrene. It should be noted that the wire pieces used in these works are in the range of 5–10 mm. If the wires are too long, it will be challenging to realise a good dispersion of wire pieces and receive the 2D plane-isotropic composite. If the wires are too short, the demagnetising effect will be too strong and ruin the overall electromagnetic properties of the microwire composite. The type of composite thus made is suitable for microwave absorption or shielding as a functional coating layer.

9.2.3 Microwires–Elastomers

Compared to epoxy, elastomers usually have much smaller Young's modulus (2 MPa) and hence will strain appropriately when subject to even a relatively small

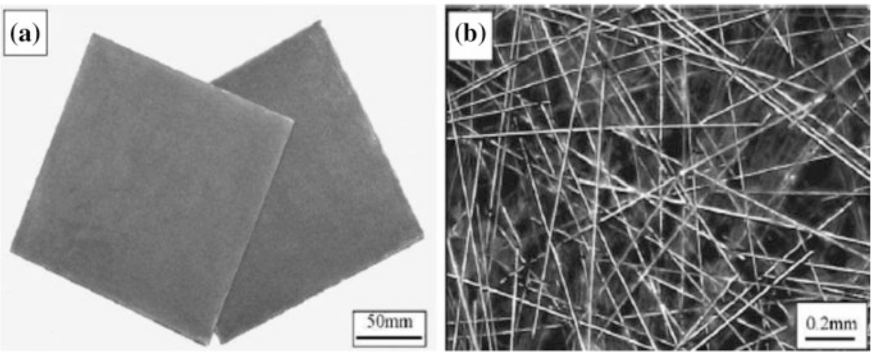

Fig. 9.1 Morphology of polymer composite plate sample (**a**) and arrangement of the short-cut microwires in it (**b**). Reprinted with permission from [10], copyright 2010 Elsevier

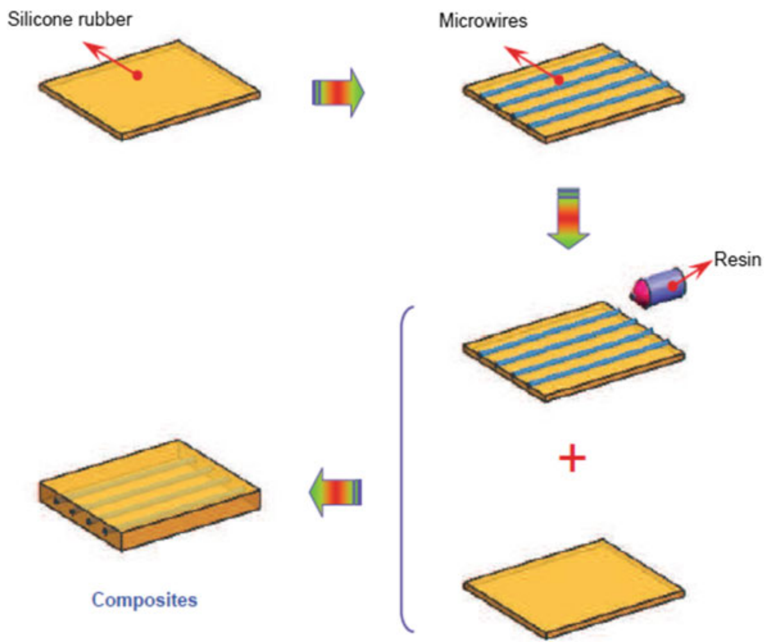

Fig. 9.2 Schematic of the preparation of continuous-wire composites based on silicone rubber for freespace measurements; the final dimensions of the resultant composite are 520 × 500 × 1.5 mm

force. Thus, rubber-based composites can then be exploited as high-performance stress self-sensing composites.

Qin et al. [13, 14] used two pieces of transparent silicone rubber sheets to prepare planar composites with periodically arranged continuous wires. The procedure schematically shown in Fig. 9.2 is as follows:

(1) 500-mm-long microwires were laid out in a periodical manner with a fixed wire spacing on the white sheet.
(2) Around 80 g of thoroughly stirred and vacuumed liquid silicone rubber/hardener mixture was uniformly cast on the surface as the adhesion layer, which was followed by covering the transparent layer right on top. An aluminium plate and heavy weights were then placed on top of the preform to assist the curing process in the ambient air.
(3) After 24 h, when the resin was cured, four surface-roughed glass fibre tabs of 10 mm × 500 mm with two drilled holes of diameter 6.35 mm were attached on both sides normal to the longitudinal direction of the sheet. The holes were designed for load bearing.
(4) The sample was then sent to an oven to cure the resin used for gluing the tabs at 70 °C for 1 h. As a final step, the holes in the tabs were further pierced through the sample, and strings were passed through the holes for fastening the weights for the study of the stress-tunable effect.

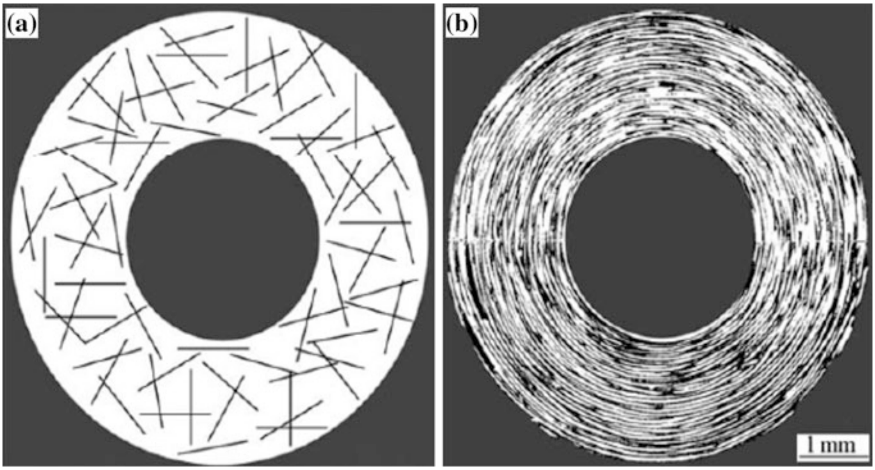

Fig. 9.3 Schematic structure of toroidal composites: **a** isotropic samples; **b** anisotropic sample. Reprinted with permission from [16], copyright 2007 Nonferrous Metals Society of China

For the case of short-wire composites, Marin et al. [15] dispersed 40 g of 1 mm Fe-rich microwires into silicon resin to receive a composite sheet for microwave absorption application. Di et al. [16] and Zhang et al. [10] used rubber dissolved by acetone to prepare composite of a toroidal ring shape, such that it could fit the specific sample holder used for the measurement by a vector network analyser. The wire arrangement can be made either regular or random, as shown in Fig. 9.3, which determines whether the composite is isotropic or anisotropic. Yet this kind of composite (inner diameter of 3 mm, outer diameter of 7 mm, height of 3.5 mm) is very small and has limited application.

9.2.4 Microwire E-glass Prepregs

E-glass prepregs have been widely used in industry and are themselves excellent structural composites. Naturally, using these as a matrix to make microwire composite secures the structural function even with a very small amount of microwires.

Reference [17] detailed the preparation of short-wire composites and continuous-wire composites with E-glass prepregs as matrices. For example, the preparation work of the short-wire composite was done in the following steps:

(1) 5-cm wire pieces were laid out at the zero degree along the glass fibre direction between the two layers of prepregs with in-plane size of 50 cm × 50 cm (the size may vary to fit different measurements). The wire spacing was controlled at fixed values of the order of centimetres (comparable to the wavelength at gigahertz range) in perpendicular and parallel directions as shown in Fig. 9.4

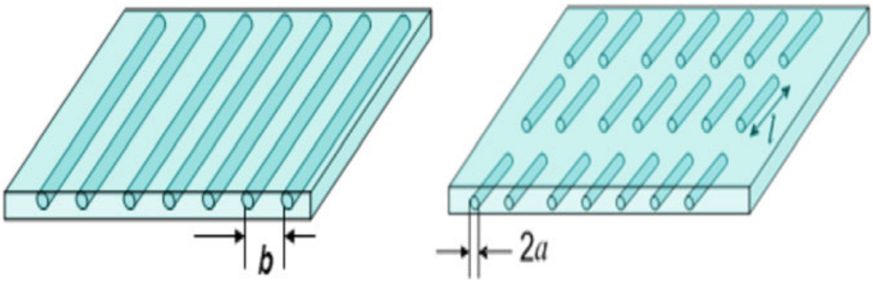

Fig. 9.4 Schematic of the continuous-wire composite, where *b* is the interwire spacing (*left-panel*) and short-wire composites (*right panel*), in which *a* denotes the wire radius and *l* denotes the wire length

(right panel). Note that the wire length and spacing are selected within the resolution range of the microwave measurements at gigahertz.

(2) Another two layers were laid up on the top and bottom of the wire-embedded layers in the same direction, giving a lay-up of four prepreg layers containing short wires.

(3) After bagging the composite on an aluminium plate with air sucked out to the required vacuum of 94.6–104.7 kPa, the material was cured in an autoclave. The curing conditions are as follows: the temperature was raised at a rate of 2 °C/min to 127 °C and kept for 80 min before cooling down naturally to room temperature. At a rate of 69 kPa/min, the pressure was increased to 206.7 kPa (30 psi) and kept at this level for 30 s and then 690 kPa for 600 min before decreasing at a rate of 20.7 kPa/min.

With the same procedure, one can also prepare the continuous-wire composite and fishnet-structured composites. These will be especially useful for realising metacomposites characteristics. In comparison with the short-wire composites, they are much easier to fabricate and hence have a better application perspective.

A typical in-plane view of prepreg-based wire composite is shown in Fig. 9.5a. On the exterior surface, one can see several ridges of different colours from other regions (indicated by arrows), which is attributed to a non-uniform distribution of the resin and glass fibre in the prepregs, as revealed in the scanning electron microscope image of the cross section (Fig. 9.5b). It is the microwire, which is slightly larger than the glass fibres in diameter, that results in the non-uniform distribution of the resin in the region close to it. However, this influence of the microwires is limited to the near-wire region only and is comparable to the inherent defects in the prepregs.

Besides, since the wire composite is intended to contain a very small number of wires that are separated by spacings of a few millimetres to a few centimetres, which is 3–4 orders of magnitude higher than the diameter of the microwires, the disruption of microwires to the composite integrity is minimal.

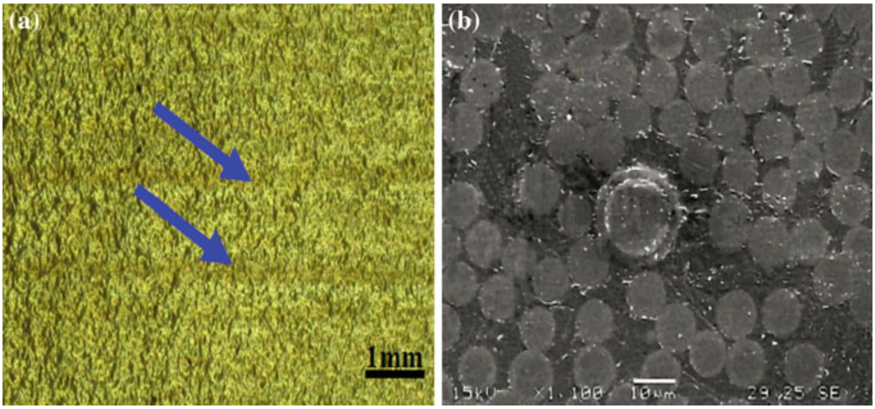

Fig. 9.5 **a** In-plane view optical micrograph of composite surface and **b** a cross-sectional SEM image of the composite where the single metal wire with both glass coating and glass fibres in the composite is shown. Reprinted with permission from [18], copyright 2010 Elsevier

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