STRATEGIES TO COMBINE NANOCOMPOSITE AND ADDITIVE LAYER MANUFACTURING TECHNIQUES TO BUILD MATERIALS AND STRUCTURES SIMULTANEOUSLY

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Abstract

Developments in metallic materials for additive manufacturing (AM), such as EADS Scalmalloy®, have shown opportunity to tailor specific material concepts to good effect for improved properites. Developments in polymer composites for AM have, however, significantly lagged behind. In parallel, developments in continuous fibre polymer composite technologies are exploiting nano-materials by means of nano-augmented, nano-engineered and nano-enabled approaches. The nano-enabled approach provides an opportunity to make joint developments with AM to realise new materials which can be processed in net-shape and with a high degree of control over morphology. Strategies for net-shape layer-by-layer AM of composite materials are described, and it is shown that partial wetting of polymer materials through the thickness of carbon nanotube (CNT) forests and patterning of forest arrays, are two key development steps. Investigation of the wetting of aligned CNT forests have shown that the interaction of the polymer is non-uniform in cross section. This has prompted speculation for improved strategies to produce composites with a higher volume fraction of reinforcements and with controllable intra- and inter-layer orientation.

1 Introduction

1.1 Additive manufacturing

Additive manufacturing (AM) [1] has enjoyed an explosion of interest recently as the technologies the term encapsulates are moving from producing prototype models and parts to realising series production of functional parts. The most obvious *motivation* for the adoption of additive manufacturing technologies is the exploitation of the high degree of geometrical freedom that the technology can realise. Just as importantly, however, *justification* for changing to additive manufacturing can be secured on the basis of cost and weight, particularly for parts with a poor ‘buy-to-fly’ ratio requiring lengthy machining or expensive tooling for casting or forging. Polymer parts made by additive manufacturing have seen application seen low-demand components for aerospace and defence applications. For example air-conditioning ducting in Eurocopter rotary wing aircraft have been in series production since the mid-2000’s. More recently AM with metals have seen advances into series production, firstly in the medical device field, and now in demanding applications in aerospace and defence. Indeed, 2011 saw a Ti6Al4V part manufactured by Powder Bed Fusion fly on a satellite manufactured by Astrium.

Recent developments in AM-specific metallic materials have shown for the first time that material property combinations that improve on the state-of-the-art achievable by conventional means of manufacturing (precision casting, forging or maching of sheet or billet materials) can be combined with unprecedented levels of geometric complexity. The best example is a new aluminium-magnesium-scandium alloy, Scalmalloy®, developed by EADS Innovation Works [15]. Scalmalloy® exploits the extremely high cooling rates found in laser-based Powder Bed Fusion technologies to hold a high proportion of Sc in solid solution before performing a precipitation hardening heat treatment. The result is an extremely fine precipitation of 2-4 nm Al_3Sc-rich core within a Zr shell which provides grain boundary and dislocation pinning [16]. Such a material can be considered as a metal matrix composite of $Al_3(Sc,Zr)$ reinforcements in a continuous aluminium matrix. A comparision of mechanical properties to state-of-the-art aerospace-type aluminium alloys and a Powder Bed Fusion altnerative is shown in Figure1.

Alloy [temper] + process	Ultimate strength (MPa)	Yield strength (MPa)	Elongation (%)	Geometric freedom (low - moderate - high)
7050 [T7651] + milling [L]	524	455	7	moderate
AC42200 [T6] + casting	320	240	6	moderate
AlSi10Mg + LAM	340	275	8	high
Scalmalloy RP0,66-4,5[325°C/4h] + LAM	530	520	14	high

Figure 1 Mechanical property comparison of Scalmalloy® + Laser Additive Manufacturing (LAM) versus alternatives [16].

Development of polymer materials for additive manufacturing, where PA-11 and PA-12 are market leading, is lagging behind that of metals. In order to secure use in demanding engineering applications, such as aerospace and defence, materials with a sufficiently high glass transition temperature in hot/wet conditions in combination with high stiffness, strength and damage tolerance are required. The means to process by Powder Bed Fusion of polyaryletherketones has recently become available commercial from EOS GmbH. EOS PEEK HP3 material has a glass transition of 143 °C, a tensile strength of 90 MPa and Young modulus of 4250 MPa [2]. Presently, however, there is no reinforced format of polaryletherketone available for processing by Powder Bed Fusion. Other reinforced polymers for Photopolymer Vat and Powder Bed Fusion process are available and a table of glass transition temperature and mechanical properties is shown Figure 2. It is apparent from this list that the glass transition temperature of these reinforced materials is significantly below that of polaryletherketone whilst the improvement of mechanical properties characterized by compress strength, is only modestly effective.

Material	Thermoplastic/ Thermoset	Reinforcement	Tg Onset/°C (Average)		Compressive Yield Strength (MPa)		Ultimate Compressive Strength (MPa)	
			Unconditioned	Hot/Wet	Mean	SD	Mean	SD
Duraform GF (horizontal)	Thermoplastic	Glass	36.32	29.83	52.4	0.8	-	-
Duraform GF (vertical)	Thermoplastic	Glass	35.83	-	56.5	1.6	-	-
Duraform AF	Thermoplastic	Aluminium	37.34	25.76	59.4	2.3	76.4	2.1
Duraform	Thermoplastic	None	37.34	35.9	53.3	1	-	-
EOS SSC PA 2200	Thermoplastic	None	38.13	33.16	56.2	6	64.7	6.6
Windform XT	Thermoplastic	Carbon fibre	38.73	31.58	73.9	4.3	89.1	4.2
Bluestone (vertical)	Thermoset	None	48.17	31.16				
120°C Post Cured Bluestone (vertical)	Thermoset	None	56.69	37.41	112.6	9.2	233	14.1
NanoForm 15120	Thermoset	Nanoparticle	56.09	45.04				
120°C Post Cured NanoForm 15120	Thermoset	Nanoparticle	67.67	-	115.1	3	430.4	25.4
170°C Post Cured NanoForm 15120	Thermoset	Nanoparticle	96.77	64.3	-	-	-	-
FDM PPSF	Thermoplastic	None	135.83	120+	67.6	1.8	105.5	7.4

Figure 2 Comparison of thermoset and thermoplastic materials for photopolymer vat and powder bed fusion processes respectively (source: EADS).

1.2 Composite materials

The latest generation of large civil aircraft, such as the Boeing 787 and Airbus A350XWB feature >50% of the airframe by weight (including landing gear) of composite materials. These materials, as shown in Figure 3, can be considered as third generation materials and exploit interleaf thermoplastic toughening technologies. In order to be competive developments for future composite aircraft will require further have high acoustic attenuation, be suitable for rapid deposition and be cured under vacuum-only. One of the enablers foreseen to achieve this is the use of nanomaterials as reinforcements. Indeed, feasibility studies have shown nanomaterials, and in particular carbon nanotubes (CNTs), to impart improvements to laminate mechanical and physical properties [3]. This is achieved by mixing the nanomaterial into the resin at some stage during the processing resulting in a random dispersion and alignment of nanoreinforcements. This is refered to as *nano-augmentation* as the nanomaterial provides some modification to the laminates properties, which are in the main, still driven by the presence of the primary reinforcing micro-fibres [3].

An improved approach is to incorporate the nanomaterials into the laminate in controlled positions and can be achieved by adding aligned arrays of CNT forests between plies of prepreg (interlaminar reinforcement) or by growing or adding radial arrays of CNTs to the surface of the primary reinforcing fibre (intralaminar reinforcement). Known as *nano-engineered* it has been shown that particular mechanical properties, such as interlaminar shear strength, can be improved by this approach [4]. The ultimate aim is, however, to fully exploit the impressive mechanical and functional properties of nanomaterials by reinforcing with nanomaterials only. Known as *nano-enabled* there are a number of approaches proposed to achieve this. One such approach is the spinning of CNTs yarns [5]. This approach, however, would still require today's cumbersome composite processing technologies. The intention of this step-wise advancement is summarised in a quote from Professor Alan Windle *"…we need to make materials containing a high volume fraction of nanotubes which are both straight and very well aligned. It will mean an approach radically different to simply stirring (or sonicating) CNTs into a polymer melt or resin, as if they were the ultimate magic filler*" [6].

1.3 Motivation for work

In addition to the low glass transition temperatures, the main factors influencing the poor performance of the materials listed in Figure 2 are that reinforcements a) have a low aspect ratio, b) have poor control over alignment or are randomly aligned and c) are incorporated at a low volume-fraction. When considered against the quotation above it is apparent these materials can be improved in every respect. *Aspect ratio:*- It is not practical to further increase the aspect ratio from the maximum in the materials lists (Windform XT) as longer (carbon) fibre materials interfere with the effectiveness of the layer-by-layer recoating process in photopolymer vat and powder bed fusion processes if current layer thickness (~ 100 μm) is maintained. The only alternative to achieve an increased aspect ratio is to decrease the diameter of the reinforcements. As such nanotubes, especially those of carbon, are obvious candidates. *Alignment:*- In order to achieve a high degree of alignment it will either be the case that feedstock materials would contain aligned reinforcements and that this alignment would be maintained during layer-by-layer processing, or that reinforcement would be introduced in aligned arrays layer-by-layer. *Volume fraction:*- Efficiencies of packing means that aligned reinforcements are more amenable to increased volume fraction either by means of using high volume fraction feedstock or by in-process densification.

It is therefore logical to apply *nano-enabled* approaches to improve the state-the-art materials available for additive manufacturing in order to better exploit the geometric freedoms with materials that are competitive to those available for 'conventional' manufacturing. Such an aspiration is summarized in Figure 3 (ii). Furthermore, it would be attractive if a morphology freedom (control of alignment and volume fraction) could be identified analogously to the geometric freedom offered by additive manufacturing.

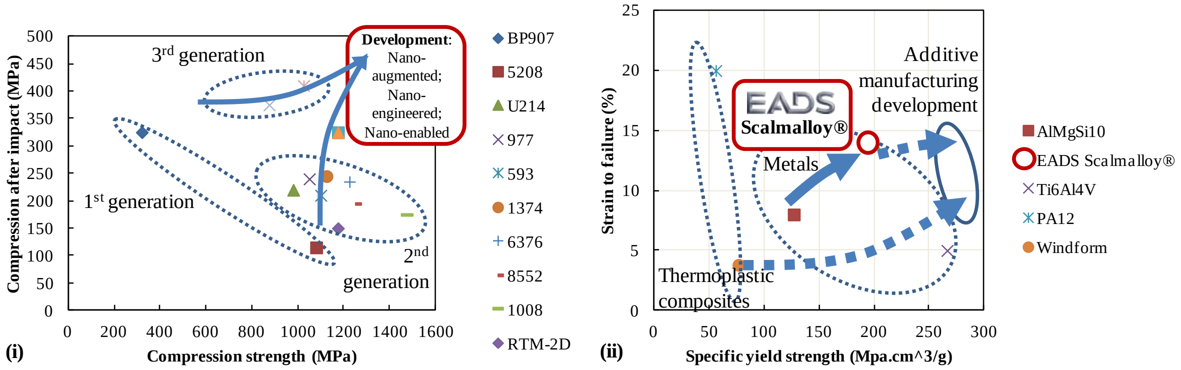

Figure 3 (i) Mechanical property comparison of various composite materials (trade names shown) and indication of desired future properties. **(ii)** Comparison of mechanical properties resulting from Powder Bed Fusion AM processes. The solid arrow indicates the improvement in specific strength and strain to failure (indicative of toughness) resulting from the design of the material specifically for AM. The dashed arrows indicate future developments for aluminium alloys (near-term) and thermoplastic composite (long-term) properties.

2 Approach

2.1 Filled polymer particle approach – challenges, expectations

It has been proposed that an improved thermoplastic polymer composite material and process could be conceived by the processing scheme shown in Figure 4 [7]. Although simple in concept, the challenge to realise such a process is the manufacture of a thermoplastic powder containing aligned high aspect reinforcements with a magnetic moment. This is the subject of current development at EADS Innovation Works and as such is not further elaborated here.

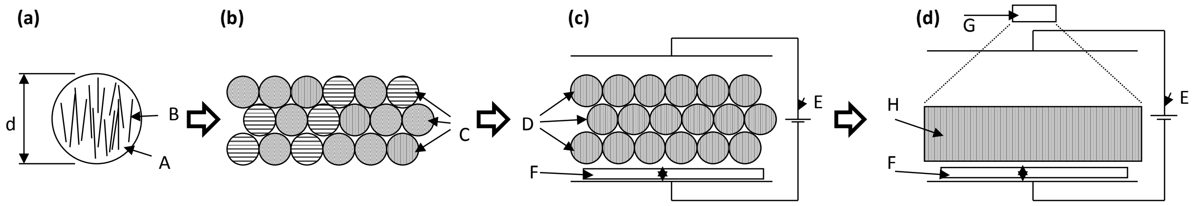

Figure 4 (a) High Tg thermoplastic particle, A, containing aligned high aspect ratio nanomaterial with a magnetic moment (CNT); **(b)** feedstock powder material (C) with random alignment between particles; **(c)** fluidized powder bed by application of an ultrasonic energy (F) and strong electromagnetic field (E) causes the reinforcing elements to globally align (D) ; **(d)** alignment is fixed (H) when an energy source (G) is applied melting the thermoplastic material. The process as described would repeat in a layer-by-layer fashion according to the definition of Powder Bed Fusion [7].

2.2 In-situ approach

An alternative to incorporating aligned reinforcements directly into thermoplastic feedstock powder is to introduce high aspect ratio reinforcements layer-by-layer during the process. An approach is outlined in Figure 5 where reinforcements are grown in arrays specific to each layer of reinforcement in order to match the pattern of nanotubes with the cross-section of the part being manufactured in net-shape [8].

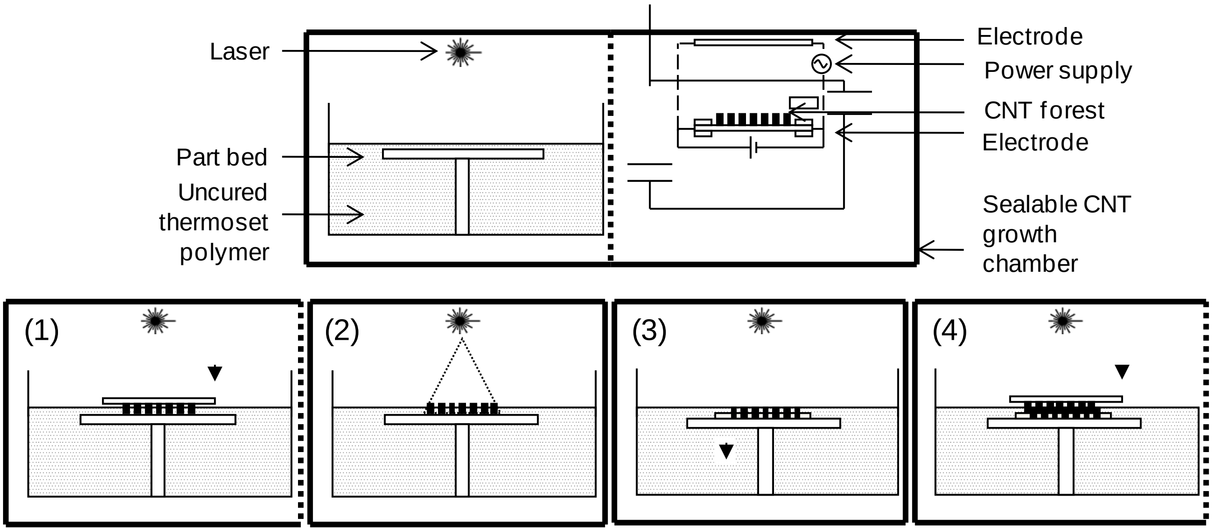

Figure 5 A schematic of the apparatus required for the in-situ growth of CNTs during additive layer manufacturing, allowing the net-shape growth of a component with CNT reinforcements produced ex-situ with variable volume fraction and alignment layer-by-layer. The part bed is vertically positioned so that it is covered by a thin layer of UV curable thermosetting polymer; (1) an array of CNTs grown ex-situ is lowered into the resin towards the part bed; the CNTs are anchored either by the interfacial forces resultant from contact with the resin or by locally curing the resin by heat conducted through the CNTs from a resistively heated substrate; (2) a desired cross section of resin is cured by a rastering of the laser; (3) the part bed is dropped so that a thin layer of uncured liquid resin forms on the surface; (4) a further layer of CNT reinforcement is introduced into the uncured resin before the process repeats [8].

2.2.1. Key steps

For such a process to be feasible there are two factors which need to be mastered to ensure through-thickness continuity, summarized below and in the schematic in Figure 6: *Through thickness partial wetting of CNT forests* - allowing for a layer of reinforcements to be fixed at their base in cured matrix before being wet from above to allow for fixing of the next layer of reinforcements. *Strategies for patterning of CNT forests* - as the ends of as-grown CNTs forests `are an entangled ‘spaghetti-like’ structure intimately passing CNTs past each other is not possible. It is therefore necessary to have patterned arrays so that forest pillars can be passed past each other.

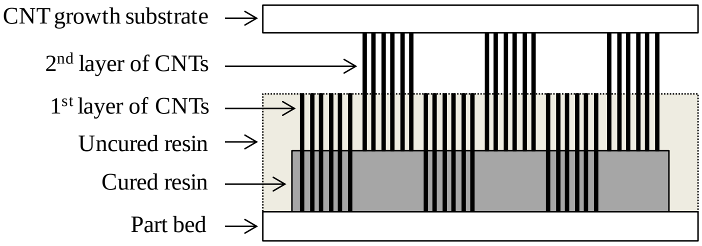

Figure 6 Critical features for a successful process.

3 Experimental, Results & Discussion

3.1 Growth of suitable carbon nanotube forests

A Sabretube chemical vapour deposition (CVD) system was used to synthesise aligned arrays of CNT ‘forests’[9]. Typical morphologies are shown in Figure 7.

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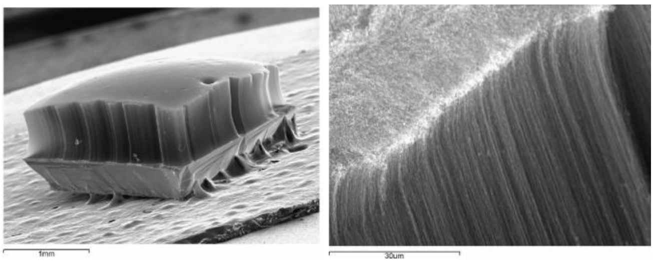

Figure 7 Typical CNT growth morphologies observed.

3.2 Down selection of wetting approaches

In order to check the assumption that pushing two forests together through their thickness would not be to successful to achieve intimate interleaving of multiple layers a simple manufacturing and test cell was created. The full results of this are reported by Beard et al where this assumption was confirmed **(10)**. To facilitate interleaving of CNT layers it was therefore clear that a patterned array would indeed be required; and further, that partial wetting through the thickness of the CNTs is needed to ensure through thickness continuity. An alternative approach of 'dipping' CNT forests in matrix materials was then trialed. Farmer et al [10] reported that thermoset resins appeared to be successful to partially wet through the thickness of a forest, until the point at which the resin viscosity dropped during curing resulting in complete wetting. An approach of limiting the available resin had the effect of causing the wetted areas of CNTs to spontaneously break-up into island pillars. Thermoplastic materials, which do not require a curing heating cycle to harden, did however seem to produce the desired partial wetting effect. These observations are summarised in Figure 8. One challenge remained, however, to confirm without reasonable doubt that a partial wetting effect was indeed in operation throughout the whole cross section of the sample. Furthermore, it would be desirable to identify a process window which could provide partial wetting with both thermoplastic and thermoset matrix materials.

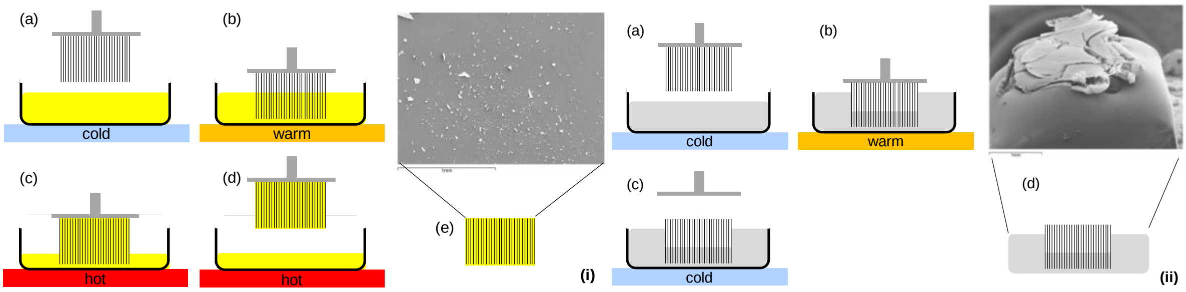

Figure 8(i) Partial wetting with Hexcel HexFlow RTM6 was possible when the resin bath was heated to a moderate temperature. However, when the temperature was subsequently raised to facilitate curing, strong capillary action caused wicking of the resin through the thickness of the CNT forest. **(ii)** Insertion of the CNT forest into a moderately heated low molecular weight thermoplastic appeared to result in successful partial wetting, although a heavy meniscus was present around the CNT forest sample.

3.3 Means to confirm partial wetting

Computed tomography (CT) has been explored as a technique to establish the position of the thermoplastic matrix material through the thickness of the CNT forests and is presented in detail by Allen et al [11]. The thermoplastic used was the co-polymer Ethylene Vinyl Acetate (EVA) with a 40wt% vinyl acetate composition and a molecular weight of around 22,000. One of the key observations of this work is the formation of columns of resin in the longitudinal (through thickness) direction of the CNT forests. This suggests a non-uniform interaction of the resin with the CNT array and the likely movement of the CNTs to bundle together. Such bundling would be initiated at sites of varying forrest areal density and height, which naturally occur as a result of the CNT growth process.

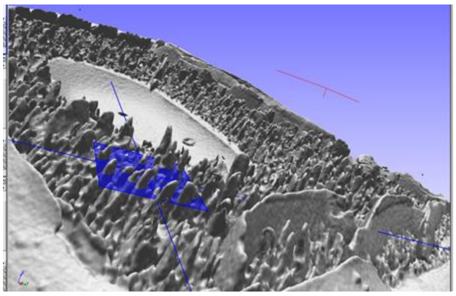

Figure 9 CT image showing the penetration of EVA matrix through the thickness of a CNT forest and resulting pillar structure of matrix in CNTs (CNTs not visible in CT).

Movement of discrete CNT forest pillars as been studied by De Volder et al [12]. In this work a solvent is condensed onto CNT forests pillars of a particular cross section. The capillary forces acting during evaporation of this solvent cause the CNT forest pillars to densify and deflect in a predictable manner. It is therefore apparent that not only does patterning of CNT forest pillars required to overcome the problem of entangled ends but also to turn the inevitable movement of the CNT forests from a problem to an opportunity.

3.4 Patterning strategies

The effects reported by De Volder et al can therefore be considered in a manner to facilitate improved multi-layer CNT polymer composites fabricated on a layer-by-layer basis. Such an approach has been proposed in modification to the method described in Figure 5 to facilitate an increase in volume fraction of reinforcements and for a simple method of controlling the alignment of reinforcements both intra- and inter-layer. A method for densification of reinforcements and subsequent processing strategy for a composite with increased volume fraction is shown in Figure 10 [13]. A modification of this method where orientation control would be possible on an intra- and inter-layer basis is shown in Figure 11 [14]. These approaches are the focus of research activities currently being initiated.

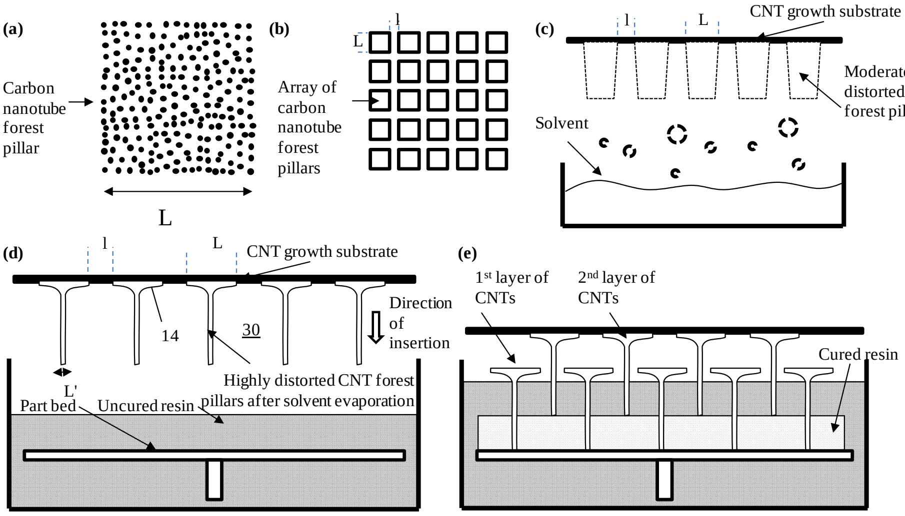

Figure 10 (a) Plan view of individual CNTs grown via a patterned catalyst in a square cross section. **(b)** Plan view of an array of square cross section CNT forest pillars. **(c)** Side-view of solvent being condensed into the CNT forest pillars where a moderate distortion takes place as a result of capillary forces. **(d)** Evaporation of the solvent results in a high distrortion of the CNT forest pillars resulting in a local desification. These pillars are introduced into an un-cured matrix material so that they are partially embedded. **(e)** The matrix in the partially embedded CNT layer is cured via ultraviolet light in a desired cross section before a further layer of matrix is 're-coated' into which a second layer of CNTs are partially embedded through the interstices of the 1st layer. The process then repeats [13].

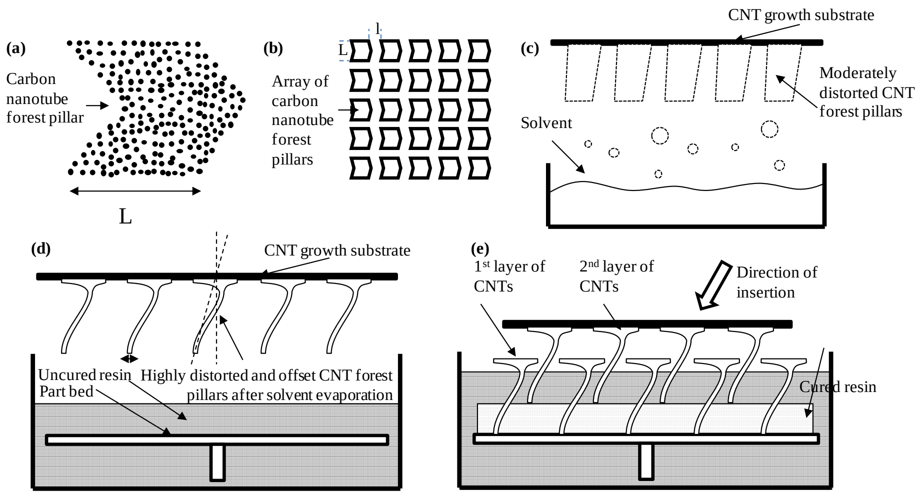

Figure 11 **(a)** Plan view of individual CNTs grown via a patterned catalyst in a chevron cross section (mirror symmetry). **(b)** Plan view of an array of square cross section CNT forest pillars. **(c)** Side-view of solvent being condensed into the CNT forest pillars where an off-axis moderate distortion takes place as a result of capillary forces. **(d)** Evaporation of the solvent results in a high distrortion of the CNT forest pillars resulting in a local desification and re-orientation of the CNT axis. These pillars are introduced into an un-cured matrix material so that they are partially embedded. **(e)** The matrix in the partially embedded CNT layer is cured via ultraviolet light in a desired cross section before a further layer of matrix is 're-coated' into which a second layer of CNTs are partially embedded through the interstices of the 1st layer. The process then repeats [14].

5 Conclusions

The direction of developments for nano-enabled materials concepts marry very well to the development needs for composite materials for additive manufacturing. Various strategies to realise such materials have been proposed. One approach was to introduce arrays of CNTs on a layer-by-layer basis during photopolymer vat processing. It has been established that for this to be successful a means of partially wetting the matrix material through the thickness of the CNT forests is required, together with a means of patterning the CNT forests to facilitate the nesting of multi-layers. A matrix material is now sought with an appropriate viscosity profile and surface energy combination and first work on patterning strategies is getting underway.

References

[1] ASTM F2792 - 12a Standard Terminology for Additive Manufacturing Technologies. 2012.
[2] EOS GmbH,Cited: April 28th, 2012. http://www.eos.info/en/products/materials/materials-for-plastic-systems/eos-peek-hp3.html.
[3] Farmer B.L., Beard M.A., Ghita O., Allen R., Evans K.E. *MRS Proceedings*, 2011. p. 1304 . mrsf10-1304-z03-04 doi:10.1557/opl.2011.602.
[4] Wicks S. S., Guzman de Villoria R., Wardle, B.L. *Composites Science and Technology*, 2010, Vol. 70, pp. 20–28.
[5] Li Y., Kinloch I.A., Windle A.H. *Science*, 2004, Vol. 304, pp. 276-278.
[6] Windle, A.H. *Composites Science and Technology*, 2007, Vol. 67, pp. 929-930.
[7] Farmer, B.L., Johns, D.M. *WO 2009/022167 A2* 2007. International Patent Application.
[8] Farmer, B.L., Johns, D.M. *WO 2009/019510 A1* 2007. International Patent Application.
[9] Laake L.V., Hart A.J., Slocum A. H. 2007 *Review of Scientific Instruments* p. 083901.
[10] Beard M.A., Ghita O., Farmer B.L., Johns D.M., Evans K.E. *14th European Conference on Composite Materials*, Budapest, Hungary, 2012. Paper ID: 841-ECCM14.
[11] Allen, R.A, Ghita, O., Farmer, B.L., Beard, M., Evans, K.E.*15th European Conference on Composite Materials*, Venice 2012.
[12] De Volder M., Tawfick S.H., Park S.J., Copic D., Zhao Z., Lu W., Hart A.J. *Advanced Materials*, 2010, Vol. 22, pp. 4384-4289.
[13] Farmer, B.L. *1104130.8* 2011. UK Patent Filing.
[14] Farmer, B.L. *1104131.6* 2011. UK Patent Filing.
[15] Palm, F., DE 10 2007 018 123 B4 German Patent.
[16] Schmidtke, K., Palm, F., Hawkins, A., Emmelmann, C., *Physics Procedia*, 2011, Vol. 12, pp. 369–374.