NANOCOMPOSITE BASED STRUCTURAL HEALTH MONITORING APPROACHES FOR FIBRE REINFORCED POLYMERS

ON DOORSTEP TO INDUSTRIAL RELEVANCE AFTER TWO DECADES OF INTENSE RESEARCH?

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ABSTRACT

Reliability and availability thus minimized cost-intensive downtime are mandatory for successful application of fibre reinforced polymer (FRP) structures in many industrial branches. Different approaches for Structural Health Monitoring (SHM) systems compete for industrial application. Nanoscale carbon particle filled polymer matrices exhibit good performance regarding structural integrity as well as spatial resolution to create functionally enhanced composites. Changes of electrical signal due to deformation of the modified polymer are used as corresponding piezoresistive signal (“Sensing”). Major drawbacks like incompatibility of implementation strategies into existing manufacturing processes or insufficient sensor properties anticipate propagating implementation of nanocomposite SHM approaches especially in large structures. Therefore fundamental material’s knowledge for property tailoring combined with well-thought-out implementation strategies are necessary. The present contribution offers an overview over today’s research on nanocomposite based SHM trials from nanoscale material level to promising implementation strategies.

KEYWORDS: Carbon-based nanocomposites, strain sensing, fibre reinforced composites, electrical properties, multiaxial load testing

INTRODUCTION

Increasing demands on lightweight and simultaneous highly reliable structures highlight the importance of fibre reinforced polymers (FRP) as material of choice. Excellent mechanical properties at low densities offer outstanding specific stiffness and strength. However, failure behaviour is more complex compared to isotropic materials and final fracture may occur abruptly. Accompanying with this fact, initial non-destructive testing (NDT) after production as well as for maintenance and repair reasons is still a highly challenging task to this day.

Against those odds, FRP structures find rapidly rising propagation in major industrial applications as for aircraft components or rotor blades in the spreading renewable energy sector. Both branches have large structural parts and, furthermore, their demand for maximal reliability in common. Failure scenarios with impact damage due to bird strike or lightning stroke are probable in aviation and wind power generation. Subsequent ongoing internal damage like inter-fibre failure, delamination or fibre failure may weaken the structure in inadmissible manner. Parallel to incalculable sudden damage or avoidance of catastrophic breakdown, economic demands require optimised down-times and long term product reliability. This is especially valid for products reaching the final stage of their calculated
lifetime. Thus, structural health monitoring (SHM) techniques for new built or retrofitted structures have gained importance in recent years and become mandatory for operating licence in some cases.

Since the first reports of strain sensitive electrical behaviour of Carbon Nanotube (CNT) polymer nanocomposites [1,2], numerous studies evaluated the potential as sensor material for strain and damage monitoring. Particularly with regard to FRP structures, carbon based polymer nanocomposites offer major advantages such as direct implementation as matrix material or integrity of structural implementation. Nevertheless, almost two decades of intense research have not lead to commercial application. One reason may lie in the large number of factors that have been determined to influence carbon based nanocomposites properties. We present an overview of the most dominant factors affecting nanocomposites electrical properties. Carbon filler material, filler content, matrix chemistry, dispersion state and processing route influence the nanocomposites capability to suit SHM requirements. This is mainly described in terms of conductivity to allow expanded sensor areas and sensitivity for early detection of changes. Furthermore, potential implementation strategies for economic large-scale applications are presented.

**CARBON BASED NANO_FILLERS**

Carbon black (CB) and CNT tend to form percolated networks within viscous matrices. Above the critical filler concentration, the so called percolation threshold, electrically conductive pathways are available for charge transfer within the composite material. Due to their high aspect ratio and good intrinsic electrical properties, CNT are preferentially used for matrix modification. Good electrical conductivity and high deformation sensitivity can be obtained at very low filler contents below 0.1 wt%. Tunneling of charge carriers between neighbouring particles limits the maximal composite conductivity obtainable and is the effect behind sensitivity against deformation. Tunneling resistance is exponentially dependent from inter-particle distance, plastic flow of matrix material during deformation in vicinity of particles affects this.

Figure 1 presents percolation curves for carbon nanoparticles in the low viscosity epoxy matrix system EPIKOTE RIM135 of Momentive, Columbus/USA regularly used for infusion of rotor blades. Initial low matrix viscosity is compulsory for dispersion of high filler contents as composite viscosity rises dramatically with increasing filler content. Formation of electrical conductivity in percolated, globular CB nanocomposites requires high filler content in the range of 6-12 wt%. It is shown that statistic percolation occurs earlier with increasing aspect ratio of the filler material. Commercial CB Printex 300 from Orion Engineered Carbons, Hanau/Germany exhibits globular (diameter ~13 nm) particle morphology without tendency of agglomeration formation. Inter-particle contact probability is thus very low and leads to high percolation threshold. Maximal composite conductivity is limited to 1E-3-1E-4 S/m which can be ascribed to predominant tunnelling compared to uninterrupted conduction within the graphitic structure. A strong tendency towards lower percolation thresholds is found with increasing aspect ratio. Commercially available CNT (C150P from Bayer Material Science, Leverkusen/Germany and NC7000 from Nanocyl, Sambreville/Belgium) exhibit aspect ratios from 66 to 150. Long, high crystallinity CNTs from an inhouse developed chemical vapour deposition process offers the possibility to obtain lengths up to 1000 µm at a mean diameter of 50 nm. Thus, aspect ratios of 2000 to 20000 yielding to early percolation at 0.01 wt% and comparably high conductivity of 1 S/m is observed. Furthermore an optimum in aspect ratio seems to exist as percolation behaviour is similar for 100 µm and 1000 µm CNT.
DISPERSION STATE

From an industrial, mass production point of view only multi-walled CNT (MWCNT) fulfil economic and technological requirements. Despite superior mechanical and electrical properties single wall CNT (SWCNT) are not of interest as price is far too high and large-scale availability is not given. The structure of MWCNT is theoretically described by a perfect tube with several graphite layers as walls, closed with fullerene caps. But, due to their high aspect ratio, their bendability and distortion (caused by lattice defects during growth) entanglement occurs. Additionally, CNTs exhibit outstanding high specific surface areas and tend to strong agglomeration caused by secondary bonding inter-particle interaction.

Aiming to homogenous CNT epoxy suspension, that are of special interest due to the wide industrial use of high performance formulated epoxy systems, dispersion technology is of great interest. For thermoset polymer matrices CNT are mostly dispersed by mechanical means. Stirring, ultrasonic treatment or three-roll milling are commonly applied for separation of primary particles and homogenous distribution within the viscous medium. Different dispersion qualities are schematically represented in figure 2. Good separation to single, primary particles and homogenous distribution is necessary for tailoring electrical properties of carbon nanocomposites for SHM application from the scratch. Only well-defined initial states offers the later possibility to influence the microstructure of the cured nanocomposite and thus sensitivity and conductivity. It has been shown that three-roll milling offers best dispersion quality at simultaneous low damage to the CNT primary structure and is thus preferred process method. Additional reactive dispersing additives like the well-known group of polyaminoamides, often used in highly filled bonding paste formulation, counteract the tendency towards reagglomeration.
Time and viscosity dependent reagglomeration, which is often called dynamic percolation, can be observed after dispersion in monomer. Furthermore addition of amine or anhydride curing agents induces strong reagglomeration due to drastically reduced viscosity and presence of functional groups. This makes it inevitable to carefully control polymerisation process conditions to perpetuate control about conductive network formation. Controlled reagglomeration of well dispersed CNTs is the key parameter to create defined conductive networks with tailored conductivity and sensitivity.

**PROCESSING CONDITIONS**

Dynamic percolation while subsequent processing of well-dispersed CNT epoxy nanocomposites highly affects final conductivity. Figure 3 depicts scanning electron microscopy images of low filler degree MWCNT/epoxy suspensions cured at different temperatures. Strong tendency to conductive network formation is observed with increasing temperature which can be ascribed to lower viscosity of the polymer matrix before gelation and thus higher mobility of the particles. Final conductivity is elevated of five magnitudes for high temperature cured nanocomposites. It should be mentioned that time for reagglomeration is simultaneously reduced due to increased curing kinetics. Thus an optimum has to be considered.

As final electrical composite conductivity is only one factor for the application of nanocomposites as SHM sensor, sensitivity and linearity are not to neglect. Improved linearity of sensor material and enhanced conductivity were obtained by particle network alignment through application of electrical AC fields while curing. Especially for long length inhouse MWCNT a high degree of entanglement can be observed in the nanocomposites. This leads to a drop of resistance after certain amount of elongation in tensile test. The effect observed can be explained by introduction of additional contacts of looped MWCNT. Figure 4 presents a stress-strain curve and corresponding resistance change for aligned and randomly orientated MWCNT/epoxy nanocomposites sensors. The resistance change
peak moves towards smaller strain levels with increasing primary particle length which is favoured in application because of superior conductivity and earlier percolation. However this limits operational range of the sensors and thus requires additional effort in terms of induced orientation to compensate this drawback.

Figure 4: Stress-strain diagram and resulting resistance change for 1000 µm inhouse MWCNT/epoxy nanocomposite: AC electrical field alignment of the particles while gelation of the polymer matrix lead to higher linearity of the piezoresistive response of the nanocomposites in cured state. Additionally, alignment decreased absolute resistance from 2E7 Ω to 9E6 Ω.

IMPLEMENTATION STRATEGIES

Damages of relevance have to be detected safely thus resolution limits and corresponding measuring signals are of great interest. Therefore we tested different implementation strategies for successful application as a reliable SHM solution on component scale. Restrictions from manufacturing process and monetary aspects do not allow complete matrix modification with carbon based fillers. Consequently semi-finished sensors like nanocomposite paints or CNT-modified prepregs are necessary for SHM integration. Both options deserve subsidiary recognition as retrofit of components advanced in years is of similar potential as new-builds with initial integration. Individual limits of each route are presented.

For early-integration application tests partially modified components of GFRP were manufactured to examine spatial resolution of damage detection. Based on different material combinations, prepregs were manufactured on pilot plant scale and processed to common laminates. Typical damages of FRP were produced e.g. with impacts and subsequent delaminations. Parallely conducted ultrasonic C-scans of the test coupons and electrical damage maps exhibit excellent comparability (Figure 5).
CONCLUSION

Intense research activity in the field of CNT based nanocomposites over the last two decades revealed the high complexity of particle-polymer interactions on nanoscale. Profound knowledge about the formation of electrically conductive networks within the curing, viscous thermoset matrix is available at this day. Detailed information about the carbon structure itself, the processing of the composite and the implementation strategy into fibre reinforced polymer structures enable today’s researcher to tailor CNT based sensor materials for implementation as structural health monitoring system. Economic pressure will generally emphasize the future application of SHM, unique obtainable spatial resolution and perfect structural integration possibility of nanocomposite based sensor make them an interesting option. Nevertheless it is not only the sensor material itself but a well-working, reliable system with distinct signals that decide about commercial application.

OUTLOOK

Spreading application of CNT based nanocomposite SHM systems for fibre reinforced polymer structures is only possible in the case of comprehensive research on system level. Fundamental understanding of fibre reinforced polymers degradation, tailored sensor materials, well adapted signal acquisition electronics and subsequent data processing will offer a promising method.

REFERENCES