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Nano-engineered joining employing surface modified graphite nanomaterials

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A new joining technique is reviewed where graphite nanomaterials are introduced at the interface to link the joining thermoplastic substrates and surfaces via massive interatomic bonds and other interactions followed by microwave irradiation. Replicated tests on the “nano-engineered” joints indicated improvement in energy absorption capacity, impact resistance, strength, ductility fatigue resistance of adhesive bonding as compared to conventional adhesive bonding. The demonstrated increase in mechanical properties, high efficiency in CNT-to-CNT and CNT-to-substrate joining and high level of replicability underline the potential for replacement of conventional adhesive bonding techniques with the technique presented.

Introduction

Since the discovery of carbon nanotube (CNT) in 1991 [1,2], CNTs have evolved into active fields of research with growing commercial applications [3–7]. CNTs and other nanomaterials provide distinct geometric, physical, chemical, and mechanical properties which enables developments of new materials with unprecedented balances of qualities [8–10]. The work presented herein uses CNTs at the interface of a thermoplastic materials for enhanced joint formation and highlights its contribution to the improvement of major mechanical properties.

Joints critically influence the performance of structures and other systems; ineffective and inefficient joining commonly undermines the gains in the performance or efficiency of structure which would be otherwise realized with advanced materials and structural systems [11,12]. The anisotropy, structural complexity and sensitivity of advanced materials increasingly challenge conventional joining techniques [13,14]. Modern designs push advanced materials (and structures) to new limits, challenging the capabilities of traditional joining methods [15–17]. Many advanced materials are also inherently sensitive to secondary processing during manufacturing; their microstructure and properties can thus be compromised during joining [18]. At the most fundamental level, all joining methods rely on mechanical, chemical and/or physical forces. These forces are currently used in the context of three principal joining methods: (i) mechanical fastening (and integral attachment) [19,20]; (ii) adhesive bonding [19,21]; and (iii) welding (including soldering, brazing) [20,22]. Nano-engineered joints are a new addition to this list and are becoming popular very rapidly [23–31]. Here we employ CNTs as an adhesive to a thermoplastic substrate using microwave radiation. The contribution of this technique to the mechanical properties, energy efficiency and replicability are thoroughly investigated.

The nano-engineered joints investigated in this study uses surface functionalized multiwalled CNTs (MWCNTs) to link the two surfaces. This joining mechanism is inspired by nature. Bacterial adhesion is an example; *Escherichia coli* [32,33] adheres to surfaces via nanofibers with $\sim$7 nm diameter and $\sim$1 μm length. The nanofiber tips are functionalized for effective bonding with carbohydrates. The helical structure of *E. coli* nanofibers yields a compliant behavior which leads to enhanced adhesion capacity by effectively resisting the fracture (peeling) modes of failure. Another bacterium, *Caulobacter crescentus* [34], which lives in rivers and streams, adheres to rocks via a slender stalk which culminates in functionalized nanotubes, This adhesion mechanism generates $\sim$70 MPa adhesion capacity, which is the highest

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observed so far in nature (and exceeds the adhesion capacities of most high-performance adhesives). Nanomaterial linkages are used by nature to establish structural (mechanical) as well as various functional continuities across discrete bodies (e.g., cells) [35].

The nano-engineered joints studied in this work use CNT as both the linking medium between the two surfaces and also as a processing aid. The role of CNT in processing relates to their high microwave energy absorption capability [23,36]. This feature enables local heating of surfaces at CNT contact points to enable joining of CNT with the surface. This mechanism is further described below after a brief introduction to microwave.

Microwaves represent a form of electromagnetic energy [37]. The microwave portion of the electromagnetic spectrum is characterized by wavelengths between 1 mm and 1 m, and corresponds to frequencies between 100 and 5000 MHz [38]. How materials behave in a microwave field depends not only on their chemical composition but also on their physical size and shape [39]. Microwave interaction with matter is characterized by a penetration depth [40]. Microwave heating of materials may be preferred in some applications over other alternative methods of heating, (e.g., those using plasmas, lasers or just oven) that heat the surface of materials. Conduction would then transfer the heat into the material, which is a very inefficient process for materials with low thermal conductivity. Microwave irradiation, on the other hand, heats the material at the molecular level, providing for volumetric heating. Because of this heating mechanism, microwave heating can be more selective, rapid, energy-efficient (consuming 10–100 times less energy) than conventional heating, lowering the heating cost 10- to 200-fold per unit volume of heated material [41]. Microwave absorbing materials could be classified into two major categories: dielectric and magnetic. The dielectric absorbers including MWCNT depend on the electronic polarization, ion polarization [42] and intrinsic electric dipolar polarization to realize microwave absorption [43,44]. Magnetic absorbers like Fe depend on the magnetic properties of a material, to absorb microwaves.

The joining process presented in this study relies on the role of CNTs as absorbers of microwave energy [45–47], with substrates being transparent to microwave. When CNTs are exposed to microwaves, they strongly absorb the microwave energy [48], producing intense heating, outgassing, and light emission. On the other hand, thermoplastics generally do not absorb the microwave energy [49,50], and thus do not experience a temperature rise when subjected to microwave irradiation. Thermoplastics soften when subjected to local heating at nano-contacts with nanotubes (noting that CNTs are good absorbers of microwave energy), which facilitates local penetration and anchorage of nanotubes. Therefore, microwave irradiation selectively heats CNTs, causing fusion of their nano-contacts with each other and local melting of thermoplastic substrates at nanotube contacts, leading to embedment of nanomaterials within substrates. These nano-contacts at the interfaces of nanotubes to substrate as well as nanotube to nanotube are further enhanced due to the surface functionalities of CNT's used in this investigation. Previous investigations have shown that introduction of a conductive material on a surface causes enhanced interfacial polarization due to the difference in the conductivity and dielectric constants of materials at the interface [51,52]. The introduction of CNTs at the interface thus enhances the microwave absorption at the joint, and enables selective (local) heating of joined surfaces. Selective heating of CNTs and their nanocontacts (interfaces) with substrates leads to welding of nano-contacts (Fig. 1); heated nanotubes also fuse at their nanocontacts with each other through reconstruction of atomic bonds [52]. Also, microwave irradiation induces covalent bond formation between nanotubes at their contact points [53,54].

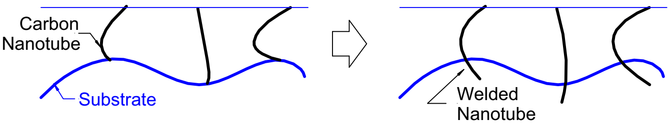

Fig. 1. Welding of nanotubes at nano-contacts with substrate.

Hence, when the joint assembly comprising of the joining materials with carbon nanotubes at the interface is subjected to simultaneous microwave irradiation and pressure, the structural joint is formed by welding of nanotubes to the substrate and fusion of nanotubes at their nano-contacts [55].

The joint structure with a fused nanotube mat at the interface is schematically depicted in Fig. 2a. The advantage of microwave welding over other conventional forms of welding is its capability to locally heat the substrate at the nanotube contact points (rather than heating the entire component). Joining via fusion and welding in microwave can be accomplished in a matter of minutes. This joint structure with a fused nanotube mat at the interface, when compared with the alternative of using an aligned array of nanotubes at the interface (Fig. 2b) is anticipated to provide more frequent and thorough contact/anchorage of nanotubes at the interface, greater conformability, ductility and energy absorption capacity.

In this study, nano-engineered joints were produced between thermoplastic substrates. This process involved: (1) spraying or depositing well-dispersed, COOH functionalized CNTs on thermoplastic plates, to produce self-assembled layers of functionalized CNTs; (2) pressing the surfaces against each other in such a way that functionalized CNT mats are facing each other; and (3) exposing the assembly to microwave radiation. This approach relies on the high microwave absorption of graphite nanomaterials to induce local heating of CNTs at the interface with the objective of embedding them at their contact points with thermoplastic surfaces, and forming of covalent bonds between nanotubes at their contact points. Fig. 3 schematically depicts the production process of nano-engineered joints. Performance of the resulted nano-engineered joints was evaluated through replicated shear, tension, impact, fatigue and thermal cycling tests.

Processing of the nano-engineered joints introduced above, relies on "surface melting" of nanomaterials, and allows for development of massive primary bonds without resorting to excessive temperatures. These nano-engineered joining process is energy-efficient because the process requires only selective heating at the nanotube-to-substrate and nanotube-to-nanotube contact points.

(a) The joint with nanotube mat at the interface

(b) The original joint with nanotube array at the interface

Fig. 2. Structure of joints with nanomaterials at the interface.

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