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# Influence of amino-functionalized carbon nanotubes and acrylic triblock copolymer on lap shear and butt joint strength of high viscosity epoxy at room and elevated temperatures



Jojibabu Panta<sup>a</sup>, Andrew N. Rider<sup>b</sup>, John Wang<sup>b</sup>, Richard (Chunhui) Yang<sup>a</sup>, R. Hugh Stone<sup>c</sup>, Ambrose C. Taylor<sup>d</sup>, Scott Cheevers<sup>e</sup>, Ashleigh L. Farnsworth<sup>b</sup>, Y.X. Zhang<sup>a,\*</sup>

<sup>a</sup> Centre for Advanced Manufacturing Technology, School of Engineering, Design and Built Environment, Western Sydney University, Sydney, NSW, 2751, Australia

<sup>b</sup> Platforms Division, Defence Science and Technology Group, Melbourne, VIC, 3207, Australia

<sup>c</sup> Airbus Australia Pacific, Richmond, NSW, 2755, Australia

<sup>d</sup> Department of Mechanical Engineering, Imperial College London, South Kensington Campus, London, SW7 2AZ, United Kingdom

<sup>e</sup> Metrologi Pty Ltd, NSW, 2155, Australia

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# ABSTRACT

This study investigates the effectiveness of incorporating different amino-functionalized carbon nanotubes (CNTs) and acrylic triblock copolymer (BCP) into an aerospace-grade relatively high-viscosity epoxy (EA9396) resin to enhance the lap shear and tensile butt-joint strength at room and elevated temperatures (90 °C). To address the common issue of nanoparticle agglomeration in epoxy resin, which is exacerbated by its relatively high viscosity, a novel processing method was developed. This method involves ozone oxidation followed by functionalization with either polyethyleneimine (P + oz-CNTs) or a polyamine hardener (H + oz-CNTs). The functionalization not only ensures uniform dispersion of carbon nanotubes (CNTs) but also enhances their chemical reactivity with both the epoxy and block copolymer (BCP) matrix. The bonding performance of the epoxy, incorporating functionalized CNTs and BCP, was evaluated using single lap shear and tensile butt-joint tests. The results emphasize the substantial enhancement of both lap shear and butt-joint strength in the BCPmodified epoxy with the incorporation of functionalized CNTs (P + oz-CNTs and H + oz-CNTs), evident at both room temperature and 90 °C. At ambient conditions, the lap shear strength of the nanocomposite adhesives (P + oz-CNT + BCP/EA9396 and H + oz-CNT + BCP/EA9396) exhibited significant improvements of 40 % and 48 % respectively. At 90 °C, both formulations demonstrated a 20 % increase in lap shear strength. Furthermore, considerable advancements were observed in butt joint strength, with enhancements of 22 % (P + oz-CNT + BCP/EA9396) and 28 % (H + oz-CNT + BCP/EA9396) at room temperature. Importantly, compared to the unmodified epoxy, the butt joint strength displayed even more remarkable improvements of 49 % (P + oz-CNT + BCP/EA9396) and 42 % (H + oz-CNT + BCP/EA9396) at 90 °C. The analysis of fracture studies showed that introducing amine functionalization resulted in a more consistent dispersion of CNTs and enhanced the ability of the BCP/EA9396 to undergo plastic deformation. The study further demonstrates that functionalization with PEI and amine hardener reduces CNT pull-out, which enhances energy dissipation mechanisms and increases lap shear and butt joint strengths.

### 1. Introduction

Adhesive bonding has become ubiquitous in the production of structural joints and bonded reinforcements across diverse engineering disciplines, ranging from aerospace to electronics [1–3]. Epoxy resin is recognized for its outstanding chemical stability, excellent adhesion,

and corrosion resistance [4–6], and it is commonly utilized as both a matrix in filler-reinforced composite materials and as an adhesive. Upon curing, epoxy transitions into an amorphous state and forms a highly cross-linked structure, characteristic of thermosetting polymers. The design of epoxy adhesive joints in engineering applications requires careful consideration of the effect of temperature on their strength.

\* Corresponding author. E-mail address: sarah.zhang@westernsydney.edu.au (Y.X. Zhang).

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Various factors, such as cure shrinkage, coefficients of thermal expansion, and adhesive material properties at different temperatures, significantly affect the adhesive strength [7–9]. The commercially available epoxies exhibit a substantial reduction in bond strength due to the glassy-to-rubbery state transition within the temperature of 20-80 °C [10].

EA9396 epoxy is widely utilized in the aerospace industry due to its strong bond strength at room temperature and retains its strength well at elevated temperatures, thanks to its tetraglycidyl diaminodiphenylmethane (TGDDM) composition with a high glass transition temperature of 149 °C [11]. Despite its higher viscosity, EA9396 can still be employed in wet layup repairs, though achieving precise control over porosity and bondline thickness may be challenging without experienced practitioners. However, its lower fracture toughness may lead to debonding or delamination failures, limiting its use in structural applications [12,13]. Therefore, there is a need for a high-performance paste adhesive material that can be cured at room or moderate temperatures, offering enhanced bond strength and toughness to expand repair applications, particularly in environments with limited infrastructure and ensure their suitability for demanding engineering applications [14].

Experimental studies examining the performance of structural adhesives as a function of temperature typically demonstrate a reduction in strength as temperature increases. Houjou et al. [15] conducted a study investigating the effect of different testing temperatures spanning from -20 °C to 135 °C on the epoxy lap shear strength. Their findings revealed a gradual decrease in lap shear strength, declining from approximately 32 MPa–15 MPa. Banea and da Silva [16] assessed the strength of adhesive joints at -40 °C, room temperature, and 80 °C, and their findings indicated a reduction of approximately 30 % in the epoxy lap shear strength at 80 °C compared to those tested at room temperature and by approximately 10 % at -40 °C.

Carbon nanotubes (CNTs) exhibit exceptional mechanical, thermal, and electrical properties, making them promising candidates for reinforcing materials and creating innovative opportunities for the advancement of new composite materials [17-23]. Extensive research has been dedicated to incorporating CNTs into epoxy systems to enhance their mechanical properties and revealed many complex chemical and mechanical interactions that take place at the nanoscale [24]. However, improvements are typically limited due to the notorious issue of CNT agglomeration within the epoxy, resulting in the formation of areas with concentrated stress under load, ultimately resulting in premature fracture [25]. Proper fine dispersion of nanomaterials in epoxy of relatively high viscosity, such as EA9396, exacerbates this problem. A significant focus of research has been directed toward developing approaches to enhance CNT dispersion and facilitating higher loadings to realize the potential benefits offered by the nanomaterial. In addition, as the interphase between CNTs and the epoxy matrix significantly influences the mechanical performance of the nanocomposite epoxies, extensive research efforts have been dedicated to enhancing the interfacial characteristics [26-28]. Generally, as untreated CNT disperse poorly, research has examined processes that aid the incorporation of functional groups which can improve the chemical interaction with the polymer matrix and reduce agglomeration [29-31]. The mechanical properties of nanocomposite adhesives can be effectively enhanced through the surface functionalization of CNTs, creating a strong CNT/matrix interface [32–34]. Furthermore, surface functionalization plays an important role in preventing CNT agglomeration and facilitating their dispersion within the polymer matrix. The selection of an appropriate functional group grafted to the CNT that bonds to the epoxy matrix is critical for mechanical property enhancement. Polyamines offer a good candidate for functionalization as they are often used as curing agents in epoxy resin systems. During the curing process, the amine groups react with the epoxy groups and create a three-dimensional network of cross-linked polymer chains. The presence of amine groups, capable of both participating in the curing of epoxy resin and modifying CNTs, have the potential to create a good bridge and establish a strong interfacial bonding between CNTs and the epoxy matrix. Furthermore, it has been stated that functionalizing CNTs with amine groups can significantly enhance the CNT dispersion [35–37]. Chen et al. [38] have reported that incorporating 0.4 wt% of tannic acid (TA) and polyethyleneimine (PEI) treated CNTs (TA-PEI/CNTs) into the epoxy composite resulted in a significant enhancement in impact strength and tensile strength, reaching 41 kJ/m<sup>2</sup> and 81 MPa, respectively. This represents a remarkable improvement of 154 % and 148 % when compared to pristine CNTs/epoxy composites.

Despite the existing research focus on the influence of individual CNTs and different copolymers on the mechanical properties of epoxy, there is insufficient research published on the concurrent influence of functionalized CNTs and BCP on the bonding performance of epoxy at elevated temperatures within the available literature. In addition, due to the difficulty of achieving good dispersion of nanoparticles in epoxy, most of the research reported has focused on epoxy resins with low viscosity and very little research has examined epoxy with relatively high viscosity.

In this study, we demonstrate the viability of utilizing functionalized CNTs and BCP to enhance the lap shear and tensile butt joint strength of the relatively high viscosity EA9396 epoxy adhesive both at room temperature and 90 °C. BCP was composed of a polystyrene (PS) block, central poly(butyl acrylate) (PBuA) block, and poly(methyl methacrylate) (PMMA) block. The addition of BCP produces a dispersion of elastomeric domains that toughens the epoxy matrix by enhancing plastic deformation [39-42]. To achieve uniform dispersion and establish a suitable amine-rich interface for interaction with the epoxy, the CNTs underwent a functionalization process. This process involved both ozone treatment and subsequent grafting with either PEI dendrimer or a polyamine hardener [35,43]. To assess the functionalized CNTs effect on the bond behaviour of the epoxy, the CNTs were incorporated up to 1 wt % using the 3-roll milling technique. Lap shear and tensile butt joint testings were conducted at both room temperature and 90 °C to investigate the bonding strength of the nanocomposite epoxy. The matrix structural changes in the cured nanocomposites were observed using Fourier transform infrared (FTIR) spectroscopy. Furthermore, the thermal stability of the nanocomposites was studied using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). FESEM analysis was conducted on the fractured surfaces of the nanocomposite adhesive joints to identify the active strengthening mechanisms.

This study presents a novel approach to enhancing the bonding performance of high-viscosity EA9396 epoxy adhesive at both room temperature and elevated temperatures by utilizing functionalized CNTs and BCP. Additionally, this study addresses the challenge of achieving nanoparticle dispersion in high-viscosity epoxy, which has been largely overlooked in existing research. By employing a functionalization process involving ozone treatment and subsequent grafting with PEI dendrimer or a polyamine hardener, this study achieves uniform dispersion of CNTs and establishes an amine-rich interface for interaction with the epoxy matrix. The incorporation of BCP further enhances the epoxy matrix by promoting plastic deformation through elastomeric domain dispersion. This work thus contributes to advancing the understanding of nanocomposite adhesive behaviour and offers insights into optimizing bonding strength in high-viscosity epoxy systems under varying temperature conditions.

### 2. Experimental programs

### 2.1. Materials

An aerospace-grade EA9396 epoxy resin and a polyamine hardener were obtained from Aerospace Materials, Australia. BCP (Nanostrength® E21, Arkema, France) was used to enhance the toughness of the epoxy. CNTs with a diameter ranging from 10 to 15 nm and a length of 10–20  $\mu$ m were procured from Hanwha Chemicals, South Korea. PEI

# (M<sub>w</sub>, 25,000 g/mol) was obtained from Sigma-Aldrich, Australia.

### 2.2. Functionalization of CNTs

The CNTs were subjected to ozone treatment for 16 h which yields oz-CNTs, the full details of CNT ozone treatment were presented in our previous study [44]. The oz-CNTs were coated with either PEI or a polyamine hardener by mixing with an aqueous oz-CNTs solution at a 1:1 ratio, followed by ultrasonication for 4 h and stirring for 12 h. After the PEI/hardener treatment, the resulting dispersion was dried using a spray dryer (BUCHI B-290, Switzerland). The PEI and hardener-treated CNTs were named as P + oz-CNTs, and H + oz-CNTs respectively.

### 2.3. Nanocomposite adhesive preparation

To prepare BCP/EA9396, 10 wt% of BCP was first dissolved in dichloromethane solvent. The resulting solution was blended with the epoxy resin and stirred at 120 °C. The residual solvent was then evaporated through vacuum degassing at 120 °C. Untreated or functionalized CNTs were then uniformly dispersed in a BCP/EA9396 mixture up to 1.0 wt% using a laboratory THINKYMIXER (ARV-310P, Japan) and EXAKT 80E 3-roll mill (Germany) [44]. Finally, the hardener was added at a 100:30 wt ratio and mixed for 10 min at 1000 rpm using a laboratory THINKYMIXER. Fig. 1 shows a schematic representation of nano-composite adhesive preparation.

# 2.4. Adhesive joint manufacturing and testing

Single lap shear and tensile butt joints were manufactured by bonding aluminium alloy 7075 plates and aluminium 2024-T3 rods, respectively. Before the joint preparation, the aluminium surfaces were solvent degreased using MEK solvent, abraded with Scotch-Brite<sup>TM</sup> 7447 and dried at 80 °C for 20 min. The abraded aluminium surfaces were subsequently grit blasted with 50 µm alumina grit using dry nitrogen as a propellent at a pressure of 450 kPa. The substrates were then immersed in 1 % aqueous solution of  $\gamma$ -glycidoxypropyltrimethoxysilane for 20 min and dried at 110 °C for 1 h [45].

For both single lap shear and butt joints, a consistent 0.15 mm bondline thickness was carefully maintained to attain the highest possible joint strength. For the single lap shear joints, the bondline thickness was maintained by keeping the shim as a spacer between the aluminium plates, while the butt joints bondline thickness was maintained by mixing 0.15 mm diameter of glass beads in the adhesives. Both lap shear and butt joints were allowed to cure in a conventional oven at 25 °C for 24 h, and post-curing at 80 °C for 4 h.

### 2.4.1. Single lap shear joints

Single lap shear joints were fabricated in accordance with the ASTM D1002 standard by bonding aluminium alloy 7075-T6 plates as shown in Fig. 2. A critical consideration in the use of adhesive joints is their temperature sensitivity, particularly the bond interface performance at varying service temperatures. The interfacial bond strength and adhesive stiffness can be substantially compromised at elevated temperatures exceeding 80 °C. To address this concern, the developed nanocomposite adhesives were evaluated both at room temperature (25  $^{\circ}$ C,  $\sim$ 55 % Relative humidity) and 90 °C (in a conventional oven) with a loading rate of 1.3 mm/min. This testing aimed to assess the effectiveness of incorporating functionalized CNTs in maintaining bonding strength both at ambient and elevated temperature conditions. Understanding how these functionalized CNTs enhance the thermal stability and mechanical properties of the adhesive joints is crucial for determining their suitability for applications requiring reliable performance in elevated temperature environments. For measuring the lap shear strength of the adhesive joints, at least four samples were tested for each material.

# 2.4.2. Tensile butt joint testing

Tensile-butt joint specimens were manufactured as per ASTM 2095



Fig. 2. Single lap shear joint according to ASTM D1002. (Note: the dimensions are in mm).



Fig. 1. Schematic of EA9396 nanocomposite adhesive preparation.

by joining AA 2024 T3 rods using optimized nanocomposite adhesives derived from the lap shear tests (Fig. 3). The dimensions of the butt-joint specimens were slightly changed to ensure reliable tensile property measurements [2,20]. The joints were fabricated by utilizing a specialized fixture with a pressure of ~20 kPa applied to ensure uniform thickness across the bonded area. Following the curing process, the butt joints were tested at room temperature (25 °C, ~55 % relative humidity) and 90 °C (in a conventional oven) with a loading rate of 1.3 mm/min. For measuring the butt joint strength of the adhesive joints, at least 4 samples were tested for each material.

# 2.5. Characterizations

The morphology of both untreated and functionalized CNTs was examined using a FESEM (Thermo Fisher Scientific, Australia). Thermal gravimetric analysis (TGA) of functionalized CNTs was recorded on a thermogravimeter (Netzsch TGA 209 Libra) over a temperature ranging from 30 to 400 °C at 10 °C/min heating rate under a helium environment. Attenuated total reflection (ATR-FTIR) of nanocomposites was obtained using a Nicolet 5700 equipped with an ATR system. The glass transition (Tg) and degradation temperatures of nanocomposite adhesives were determined by employing the DSC Q100 TA instrument and TGA (Netzsch TGA Libra) analyzer, respectively. These analyses were performed under a nitrogen atmosphere, with a consistent heating rate of 10 °C/min. The failure surfaces of the single lap shear joints were observed using a FESEM.

### 3. Results and discussions

# 3.1. Morphological characteristics of functionalized CNTs

Fig. 4 illustrates the morphological characteristics of the CNTs before and after functionalization. The diameter of the CNTs was approximately 15 nm and the appearance of the CNTs did not change significantly (Fig. 4b) after ozone treatment. However, after functionalization with PEI and hardener, the morphology of the ozonized CNTs underwent a significant transformation. Fig. 4c and d clearly show the presence of PEI and hardener film coatings on CNTs, respectively. It is anticipated



that the amine groups present in the PEI and hardener molecules should form a covalent bond with the CNT surface.

Fig. 5 displays the TGA results of untreated and functionalized CNTs. After 400 °C, the untreated CNTs exhibited a mass loss of ~2 %. In contrast, oz-CNTs experienced a significant mass loss, measuring 14 % due to the hydroxyl or carboxyl groups on the CNT surface. After amino functionalization, a mass loss of 33 % was observed for P + oz-CNTs, whereas 41 % was noticed for H + oz-CNTs. The difference in the mass loss of PEI and hardener-functionalized CNTs is ascribed to the NH<sub>2</sub> groups on the surface of CNTs. This observation aligns with the decomposition of PEI and hardener as shown in Fig. 5.

### 3.2. FTIR analysis of unmodified EA9396 and nanocomposites

The FTIR spectra of the unmodified EA9396 and nanocomposite adhesives are presented in Fig. 6. In unmodified EA9396, the peak observed at 2900 cm<sup>-1</sup> is indicative of the -CH<sub>2</sub> stretching vibrations. The peaks at 1612 and 1520 cm<sup>-1</sup> correspond to the C-C bond stretchings in the aromatic ring. Furthermore, the peaks at 1224, 1035 and 698  $\text{cm}^{-1}$  can be attributed to C–N. C–O–C and C=C bonds. respectively [46]. The appearance of a new ester peak at 1728 cm<sup>-1</sup> in BCP/EA9396 is attributed to the presence of acrylate carboxyl groups of BCP. These groups participate in a chemical reaction with the epoxy groups, leading to the formation of C=O bonds [47]. In oz-CNT + BCP/EA9396 composite, a possible reaction mechanism could entail the breaking of epoxide rings as a result of their interaction with the -OH groups present on the CNTs [48]. In the spectra of PEI and polyamine hardener, a peak observed at 1595 cm<sup>-1</sup> corresponds to the deformation vibration of N-H bonds. Additionally, the 2820 cm<sup>-1</sup> and 2940 cm<sup>-1</sup> bands correspond to -CH2 and -CH3 stretching vibrations of the aliphatic propyl chain, respectively. In P + oz-CNT/EA9396, and H + oz-CNT/EA9396, the peak initially associated with N-H deformation vibration at 1595 cm<sup>-1</sup> exhibited a noticeable shift to 1612 cm<sup>-1</sup> in addition to an increased peak intensity. This change is indicative of a chemical reaction occurring between the amine groups of PEI/hardener and the epoxy groups [49, 50].

# 3.3. Thermal stability of the nanocomposites

Fig. 7 illustrates the DSC curves of the EA9396 and nanocomposites, while Table 1 presents the corresponding values. The EA9396 epoxy initially exhibited a single glass transition temperature ( $T_g$ ) at 149 °C. However, upon the addition of BCP to EA9396, two distinct  $T_g$  values became evident: one at 85.6 °C (attributed to BCP) and another at 147.2 °C (associated with EA9396). The second  $T_g$  value exhibited a slight reduction due to the existence of the soft BCP in the EA9396. In the nanocomposites, the addition of functionalized CNTs did not impact the  $T_g$ . Nonetheless, the first  $T_g$  identified in BCP/EA9396 was retained in the CNT nanocomposites, and this can be attributed to the presence of softer BCP phase.

TGA results also showed no significant change in the onset decomposition temperature ( $T_{onset}$ ) for BCP/EA9396 and CNT nanocomposite adhesives (Fig. 8 and Table 1) suggesting that the degradation temperature of the EA9396 was not compromised by the incorporation of soft phase BCP and the functionalized CNTs.

### 3.4. Lap shear performance of nanocomposite adhesives

Fig. 9 shows the impact of BCP and functionalized CNTs on the lap shear strength at room temperature and 90 °C. Unmodified EA9396 had a lap shear strength of 35.6 and 21.8 MPa at room temperature and 90 °C, respectively. The addition of BCP into EA9396 led to an increase in strength both at room temperature and 90 °C by 21 % and 16 % respectively.

For the nanocomposites, as the content of untreated CNTs increased, the lap shear strength decreased most likely due to localised



Fig. 4. Morphology of the CNTs before and after functionalization a) CNTs, b) oz-CNTs, c) P + oz-CNTs, and d) H + oz-CNTs.



Fig. 5. TGA curves of untreated and functionalized CNTs.

agglomerations. However, oz-CNTs, P+ oz-CNTs, and H+ oz-CNTs demonstrated a substantial enhancement in lap shear strength compared to those unmodified EA9396 and untreated CNT at equivalent filler content.

At room temperature, the highest lap shear strengths of 50.0 and 52.7 MPa were observed for both 0.5 % P + oz-CNT + BCP/EA9396 and 0.5 % H + oz-CNT + BCP/EA9396 which are 40 % and 48 % higher than the EA9396. CNTs that have been functionalized with PEI or hardener resulted in an increased lap shear strength that exceeds the enhancements seen with untreated CNTs by 35 % and 44 %, respectively. This suggests a beneficial interaction between functionalized CNTs and epoxy matrix, leading to enhanced lap shear strength. This phenomenon



Fig. 6. FTIR spectra of the cured EA9396 and nanocomposites.

can be attributed to two key factors. Firstly, the higher surface area of CNTs enables greater contact with the surrounding matrix. Secondly, the functionalization of CNTs with PEI/hardener creates strong interfacial bonds between the matrix and CNTs, which in turn facilitates efficient load transfer between them. The superior effectiveness of H + oz-CNTs, in comparison to P + oz-CNTs, is due to the higher amounts of amine functionalization, as evidenced by the DSC results in section 3.1, may lead to a larger interphase region between the CNTs and the epoxy matrix. Consequently, this enhanced interphase may lead to a higher lap shear strength.

At higher temperatures (90 °C), the lap shear strength was



Fig. 7. DSC curves of unmodified EA9396 and nanocomposites.

Table 1
$\Gamma_{\rm g}$ and $T_{\rm onset}$ temperatures of unmodified and EA9396 and nanocomposites from
DSC and TGA curves.

Material	T <sub>g</sub> (°C)		T <sub>onset</sub> (°C)
	1st T <sub>g</sub>	2nd T <sub>g</sub>	
EA9396	_	$149.2\pm0.3$	$\textbf{338.4} \pm \textbf{0.7}$
BCP	$\textbf{85.6} \pm \textbf{0.7}$	-	-
BCP/EA9396	$\textbf{85.3} \pm \textbf{0.3}$	$147.2\pm0.1$	$\textbf{337.5} \pm \textbf{0.8}$
0.5%oz-CNT + BCP/EA9396	$\textbf{85.5} \pm \textbf{0.4}$	$147.3\pm0.3$	$338. \pm 0.3$
0.5%P + oz-CNT + BCP/EA9396	$\textbf{85.9} \pm \textbf{0.2}$	$147.4\pm0.1$	$\textbf{338.1} \pm \textbf{0.2}$
0.5%H + oz-CNT + BCP/EA9396	$\textbf{85.8} \pm \textbf{0.1}$	$147.7\pm0.5$	$\textbf{338.7} \pm \textbf{0.3}$



Fig. 8. TGA curves of unmodified and nanocomposite epoxy adhesives.

marginally increased for both 0.5 % P + oz-CNT + BCP/EA9396 and 0.5 % P + oz-CNT + BCP/EA9396 CNTs, which is 22 % higher than the EA9396. In lap shear joints, the primary load-bearing mechanism involves shear forces acting parallel to the adhesive bond line. From the DSC results, we observed that the initial T<sub>g</sub> of the BCP/EA9396 occurred at ~85 °C. Beyond this temperature, the epoxy matrix undergoes a transition to a more ductile state, which can lead to less resistance to





Fig. 9. Lap shear strength of the EA9396 and nanocomposite adhesives a) at room temperature and b) at 90  $^\circ C$  (Black horizontal line represents EA9396 lap shear strength).

shearing forces. Additionally, the CNTs effectiveness in load transfer under shear conditions might diminish at elevated temperatures, contributing to the lower level of improvement in lap shear strength compared to room temperature testing.

# 3.5. Tensile but joint performance of nanocomposite adhesives

The tensile butt joint strength of the unmodified and optimized nanocomposite adhesives is shown in Fig. 10. At room temperature, the unmodified EA9396 joints exhibited a butt joint strength of ~56 MPa, whereas this strength decreased to ~25 MPa at 90 °C. Upon incorporating BCP, a notable enhancement in joint strength was realized, reaching ~64 MPa at room temperature and ~28 MPa at 90 °C. These improvements correspond to a 15 % increase in strength at room temperature and a 10 % increase at elevated temperatures, respectively. Moreover, the butt joint strength experienced a significant improvement with the incorporation of functionalized CNTs into BCP/EA9396. In particular, the joint strength reached approximately 68 MPa for the 0.5 % P + oz-CNT + BCP/EA9396 joints, marking a 22 % increase compared to the unmodified EA9396. Additionally, the 0.5 % H + oz-CNT + BCP/



Fig. 10. Butt joint test results of the unmodified EA9396 and nanocomposite adhesives at room temperature and 90  $^\circ \rm C.$ 

EA9396 joint exhibited 28 % enhancement under room temperature test conditions. At 90  $^{\circ}$ C, both 0.5 % P + oz-CNT + BCP/EA9396 and 0.5 % H + oz-CNT + BCP/EA9396 exhibited substantial improvements in butt joint strength, with increases of 42 % and 49 %, respectively, when compared to unmodified EA9396 joints. These enhancements in joint strength highlight the positive impact of functionalized CNTs on the tensile performance of the nanocomposite adhesive joints, particularly in different temperature conditions. In the tensile butt joint configurations, the primary load-bearing mechanism involves tensile forces acting perpendicular to the bond line. The enhanced tensile butt joint strength could be attributed to the CNTs ability to maintain their load-carrying capabilities under tensile loads even at higher temperatures, thereby leading to increased strength in this configuration. Jen et al. [51] reported that the polymer matrix's softening at elevated temperatures facilitates the alignment of nano-fillers in a direction favourable for load transfer, consequently enhancing both the stiffness and strength of the nanocomposites. In the present study, it is evident that the use of functionalized CNTs significantly enhances the butt joint strength of the BCP/EA9396 adhesive, both at room temperature and at 90 °C. Additionally, the incorporation of these functionalized CNTs mitigates the bondline's susceptibility to defects and porosity caused by the change in rheological properties resulting from the introduction of nano-additives [20].

# 3.6. Fractography

Fig. 11 depicts the SEM images of fractured unmodified EA9396 and nanocomposite and lap shear joints. The unmodified EA9396 exhibits a characteristic brittle fracture surface with river lines (Fig. 11a). The introduction of BCP results in a more rough fracture surface, signifying an enhancement in plastic deformation. In Fig. 11b, there are observable indications of BCP debonding and cavitation leading to shear yielding on the fracture surface, thereby facilitating the absorption of fracture energy [4,52]. For the CNT + BCP/EA9396 adhesive (Fig. 11c), the presence of CNT pull-outs indicated weak interfacial adhesion between the untreated CNTs and the matrix which reduced the strength of the adhesive joints. The oz-CNT + BCP/EA9396 composite demonstrated that the ozonated CNTs appeared to be well integrated into the BCP/epoxy matrix. However, oz-CNTs still experienced pull-outs (Fig. 11d), suggesting that localized stress regions during fracture could potentially exceed the interface strength.

combination of P + oz-CNT + BCP. The presence of carbonyl groups on the oz-CNTs enabled them to bond effectively with the amine groups of PEI, promoting excellent dispersion and interaction within the matrix, especially at higher loadings (0.5 %). Furthermore, the rapid reaction of BCP/EA9396 near the CNT surface played a role in preserving the highly dispersed nanocomposite structure that formed during the mixing phase, preventing CNT re-agglomeration. In addition, the reactive NH<sub>2</sub> groups found in hyperbranched PEI had the potential to engage in the epoxy-curing reaction, resulting in the formation of strong oz-CNTs + BCP networks [50,53]. These networks, in turn, contributed to the development of a tougher interphase region, thereby improving the fracture resistance of the nanocomposites.

In the case of the 0.5 % H + oz-CNT + BCP/EA9396 nanocomposite adhesive (Fig. 11f), the fracture surfaces demonstrate that the H + oz-CNTs are well incorporated into the epoxy matrix, significantly enhancing both lap shear and butt joint strength. After oz-CNTs are subjected to functionalization with the polyamine hardener, amine groups are incorporated onto the CNTs. These nitrogen-functional groups can undergo reactions that are comparable to those of PEI [54]. It is important to highlight that the variations in fracture surface microstructures between PEI and the polyamine hardener functionalized CNT nanocomposites can be attributed to differences in the extent of chemical reaction and the structure of the functional groups involved.

Fig. 12 illustrates the strengthening mechanisms observed in nanocomposite EA9396 adhesives modified with functionalized CNTs. In each scenario, the cavitation and debonding of the BCP results in the formation of stress concentrations (Fig. 12a-d), leading to increased plastic deformation. However, the existence of CNT pull-outs limits the joint strength of CNT + BCP/EA9396 (Fig. 12a). Conversely, in the cases of oz-CNT + BCP/EA9396, P + oz-CNT + BCP/EA9396, and H + oz-CNT + BCP/EA9396, the functional groups within the CNTs facilitate a stronger interaction with the epoxy matrix. The incorporation of functionalized CNTs resulted in an enhanced effectiveness of BCP/EA9396 by increasing the modulus and strength of the EA9396, consequently leading to improvements in both lap shear and butt joint strengths [20]. Therefore, crack pinning, crack deflection and crack bridging are regarded as active strengthening mechanisms for the nanocomposite adhesives (Fig. 12b–d). Moreover, the P + oz-CNTs/H + oz-CNTs and BCP interface play a vital role in strength enhancement due to the improved interfacial bonding.

### 4. Conclusions

In this research, the effectiveness of incorporating aminofunctionalized CNTs and BCP into high-viscosity EA9396 adhesive on the bonding performance was investigated both at room and elevated temperatures. Incorporating amino-functionalized CNTs and BCP into high-viscosity EA9396 adhesive led to significant improvements in bonding performance. The key findings are summarized below.

- At room temperature, both nanocomposite adhesives (P + oz-CNT + BCP/EA9396 and H + oz-CNT + BCP/EA9396) showed remarkable enhancements in lap shear strength, with increases of 40 % and 48 %, respectively.
- At 90 °C, both nanocomposites (P + oz-CNT + BCP/EA9396 and H + oz-CNT + BCP/EA9396) exhibited a 20 % increase in lap shear strength compared to that of EA9396 adhesive.
- The butt joint strength exhibited significant improvements of 28 % for (H + oz-CNT + BCP/EA9396) and 22 % for (P + oz-CNT + BCP/EA9396). These enhancements were even more pronounced at 90 °C, with increases of 49 % and 42 %, respectively.
- FTIR, DSC and TGA results showed that the amino-functionalized CNTs and BCPs were well bonded with epoxy resin without compromising other properties such as  $T_g$  and thermal decomposition temperature.



Fig. 11. SEM images of a) EA9396, b) BCP/EA9396, c) CNT + BCP/EA9396, d) oz-CNT + BCP/EA9396, d) P + oz-CNT + BCP/EA9396, and f) H + oz-CNT + BCP/EA9396.

- Functionalization with PEI and hardener significantly enhanced energy dissipation mechanisms and increased both lap shear and butt strength of the CNT-based nanocomposite adhesives.
- The hardener-functionalized CNTs exhibited a higher level of effectiveness when compared to the PEI-functionalized CNTs.
- SEM images of fractured joints revealed the mechanisms behind the enhanced strength, including crack pinning, deflection, and bridging, facilitated by the presence of functionalized CNTs and BCP. These mechanisms contributed to the overall improvement in joint strength.

This study demonstrated that amino-functionalized CNTs, when incorporated into EA9396 adhesive with BCP, effectively improved both lap shear and tensile butt joint strength, offering potential applications in aerospace and other high-performance industries. The enhanced properties were attributed to improved interfacial bonding and active strengthening mechanisms facilitated by the functionalized CNTs and BCP.

### CRediT authorship contribution statement

Jojibabu Panta: Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. Andrew N. Rider: Writing – review & editing, Validation, Supervision, Funding acquisition. John Wang: Writing – review & editing, Validation, Supervision, Funding acquisition. Richard (Chunhui) Yang: Writing – review & editing, Validation, Funding acquisition. R. Hugh Stone: Writing – review & editing, Validation. Ambrose C. Taylor: Writing – review & editing, Validation. Scott Cheevers: Writing – review & editing, Validation. Ashleigh L. Farnsworth: Writing – review & editing, Investigation. Y. X. Zhang: Writing – review & editing, Supervision, Project administration, Funding acquisition.

# Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence



Fig. 12. Strengthening mechanisms of a) CNT + BCP/EA9396, b) oz-CNT + BCP/EA9396, c) P + oz-CNT + BCP/EA9396, and d) H + oz-CNT + BCP/EA9396.

the work reported in this paper.

### Data availability

The authors do not have permission to share data.

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