

High-performance carbon nanofiber reinforced epoxy-based nanocomposite adhesive materials modified with novel functionalization method and triblock copolymer

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Abstract

New high-performance epoxy-based nanocomposite adhesive materials were developed based on EA9396, a resin system with relatively high viscosity, with the innovative use of carbon nanofibers (CNF) by developing effective nanotechnology to achieve even CNF dispersion and significantly enhanced the bond strength, especially at elevated temperatures. The EA9396, a tetraglycidyl diaminodiphenylmethane (TGDDM) based aerospace-grade epoxy adhesive with a high glass transition temperature and viscosity was combined with functionalized CNFs and a phase-separated poly(styrene)-poly(butadiene)-poly(methyl methacrylate) triblock copolymer (SBM). The ozone-treated CNFs (OZ-CNFs) were functionalized with polyethyleneimine dendrimer (PEI+OZ-CNFs), or a polyamine hardener (H+OZ-CNFs) and

characterized using X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) to confirm the chemical reaction of the amine functional groups. Room temperature mechanical testing revealed the optimized nanocomposite adhesives containing SBM and CNFs functionalized with either PEI or hardener resulted in a 40% increase in lap shear strength (50 MPa) when compared to the unmodified epoxy (35.6 MPa). At the elevated temperature of 90 °C, a strength improvement of 35% and 38% (29.5 MPa and 30 MPa) was observed for the adhesives containing SBM and CNFs functionalized using PEI or hardener, respectively. SEM images showed that CNF functionalization provided a more uniform distribution in the adhesive and enhanced the SBM plastic deformation during crack propagation. The PEI and hardener functionalization also significantly reduced the level of CNF pull-out, which was believed to enhance the energy dissipation mechanisms responsible for the significant increase in the lap shear strength.

Keywords

Block copolymers, Carbon nanofibers, Epoxy, Functionalization, Lap shear strength

1. Introduction

Adhesive bonding has been widely used for producing structural joints and bonded repairs because of the advantages compared to traditional joining methods such as mechanical fastening [1, 2]. Adhesive joining offers the benefits of design flexibility, ease of fabrication and the capability of joining similar and dissimilar materials applied in various fields such as automotive, aerospace, and electronic engineering [3-5]. In addition, adhesive bonding can be used for the temporary modification of aircraft structural components or the battle-damage repair of military vehicles [6-8].

EA9396 epoxy is a popular adhesive material used in the aerospace industry with a relatively high viscosity compared to regular commercial epoxy systems. Whilst possessing high bond strength at room temperature, EA9396 also provides excellent strength retention at elevated temperatures [9], due in part to the tetraglycidyl diaminodiphenylmethane (TGDDM) composition providing a high glass transition temperature of 149 °C. Despite the higher viscosity, EA9396 may still be used in wet layup repairs, however, controlling the porosity and bondline thickness may be difficult without skilled practitioners. Due to the lower fracture toughness of the adhesive, debonding/delamination failure may occur, which limits their usage in structural applications [10, 11]. Thus, a high-performance paste adhesive material cured at room or moderate temperatures with enhanced bond strength and toughness could extend the application of repairs in environments where limited infrastructure exists [12].

One of the most frequently employed methods for enhancing the bond performance and fracture toughness of epoxy adhesives is by dispersion of tougheners where a range of crack energy dissipation mechanisms can be activated [13, 14]. Various types of tougheners such as reactive rubbers [13], thermoplastics [15, 16], inorganic fillers [17], as well as nanoparticles [18, 19], have been used with varying degrees of success in enhancing fracture toughness. However, toughness enhancements in most rubber-modified epoxies have resulted in a

significant decrease in the glass transition temperature (T_g) of the cured epoxies. Some of the thermoplastics such as polyethersulfone [20], polyetherimide, polycarbonates [21], and polyphenylene oxide [22] can enhance fracture toughness without sacrificing the T_g , strength and stiffness of the epoxy [23]. Furthermore, these thermoplastic-modified epoxies can only be processed and cured at high temperatures to attain the desired mechanical properties [24], which has limited application in wet layup and field repair applications. Recent studies have demonstrated that the addition of triblock copolymers (BCPs) has less impact on the matrix stiffness and thermal stability. These BCPs can be dissolved at relatively lower temperatures and the modified epoxies can be cured at room temperatures which is feasible for wet layup repair applications. Our recent research using the poly(styrene)-poly(butadiene)-poly(methyl methacrylate) (SBM) [18, 25] demonstrated that the effective toughening could enhance the mechanical and fracture performance of a commercially available diglycidyl ether of bisphenol A (DGEBA) based low viscous epoxy resin, without compromising the thermal stability.

The addition of a small weight fraction of nanoparticles is known as a highly effective means of enhancing bond performance and mechanical properties of epoxy [1, 26-28]. The excellent mechanical, thermal, and electrical properties of carbon nanofibers (CNFs) make them a suitable candidate for nanoreinforcement in polymer matrix composites [29-31]. The addition of nanoparticles to resin systems to improve mechanical properties has been researched extensively but has often failed to produce significant enhancement due to the inherent complexity of chemical and mechanical interactions occurring at the nanoscale [32, 33]. In addition, the notorious issue of effective nanoparticle dispersion becomes even more challenging when employing relatively high-viscosity materials like EA9396.

On the other hand, the benefit of BCPs and their nanostructures in improving the fracture performance of bulk epoxy systems have been established [34-36]. Despite the benefit offered by BCPs to epoxy resins, the use of these composite systems as adhesive materials is still

relatively underrepresented in the open literature [25, 33, 37]. In addition, most of the CNF/epoxy nanocomposite adhesive research in the open literature has focused on the diglycidyl ether of bisphenol A (DGEBA) epoxy resins tested at room temperatures [38-41] and very little attention has been paid to the TGDDM-based epoxy systems such as EA9396 due to difficulties in incorporating BCPs into these high viscosity and crosslink density resins. According to the knowledge of the authors, there is no prior research addressing the hybrid effect of CNFs and SBM incorporation on the adhesive properties of the TGDDM-based epoxy resins.

This study aims to develop a high-performance nanocomposite adhesive based on EA9396, TGDDM-based epoxy systems, in operating conditions at elevated temperatures via the hybrid effect of CNFs and SBM incorporation. This work studies the effect of functionalized CNFs and the phase-separated SBM nanostructures on the adhesive properties of the EA9396 epoxy adhesive. The CNFs were functionalized using ultrasonicated ozonolysis followed by grafting branched polyethyleneimine (PEI) dendrimer or polyamine hardener to enhance the uniform dispersion and to produce an amine-rich interface that is suitable for chemical reaction with the epoxy resin. The lap shear strength of the nanocomposite adhesives was measured both at room and elevated temperatures. The change in morphology of the composite adhesives after the addition of SBM and functionalized CNFs is correlated with the lap shear performance of the adhesive joints and the associated toughening mechanisms are also discussed. The developed adhesive materials could offer flexibility to be used in both composite and metallic airframes, either as a stand-alone adhesive or as a toughened resin system for composite structural repairs where laminating is required. It should be noted that the current study reports the optimization of toughening and nano-additions to provide the best lap shear strength over a broad temperature range, whereas most research typically only reports performance at room temperature. Another novel feature of this study is that the unmodified and nanocomposite

adhesives are cured at room temperature for 24 hours followed by post-curing at 80 °C for 4 hours which is significantly lower than temperatures reported in the literature where the high-temperature adhesives are usually cured well above 120 °C [42, 43]. The significant improvement in lap shear strength at higher temperatures with low curing temperatures can enhance the joint performance in the operating environment and extend the range and capability of repairs, ultimately making repairs more efficient and increasing airframe availability.

2. Experimental Programs

2.1. Materials

A commercially available two-part aerospace-grade epoxy adhesive, LOCTITE EA 9396 AEROPART A epoxy resin and, LOCTITE EA 9396 AERO PART B, a polyamine-based curing agent (mixture of tetraethylene pentaamine, N,N'-Bis(3-aminopropyl)piperazine and tetraazatetradecamethylenediamine) purchased from Aerospace Materials, Australia was used. An SBM triblock copolymer (Nanostrength® E21, Arkema, France) was used as a toughening agent. CNFs having a diameter of 30-150 nm and length of 50–200 μm (PR-19-XT-LHT, Pyrograph products, Applied Sciences, USA) were used as reinforcement material. Branched polyethyleneimine dendrimer (M_w of 25,000 g/mol) was obtained from Sigma-Aldrich, Australia. Dichloromethane (Sigma-Aldrich, Australia) was used (SBM : Dichloromethane ratio of 1:2 by weight) to dissolve SBM in the epoxy resin.

2.2. CNF surface functionalization

In this study, three different methods were used to functionalize the CNFs. In the first method, the CNFs were oxidized for 16 hours using the ultrasonicated ozonolysis (USO) process to produce OZ-CNFs. The pristine CNFs were first diluted in ultra-pure water (1.0 g/L) and ultrasonicated for 2 h using a 50 L ultrasonic bath (USB, Sonorex, Bandelin, Germany) at 35

kHz and 600 W. Moisture-free oxygen with a flow rate of 500 mL/min passed through an ozone generator (TG-20, Ozone Solutions, USA) and treated the aqueous-CNF solution cooled at 5 °C. During the ozone treatment, the solution was continuously stirred using a magnetic stirrer to avoid the settling of CNFs. After every 4 h of ozone treatment, the solution was ultrasonicated for 2 h.

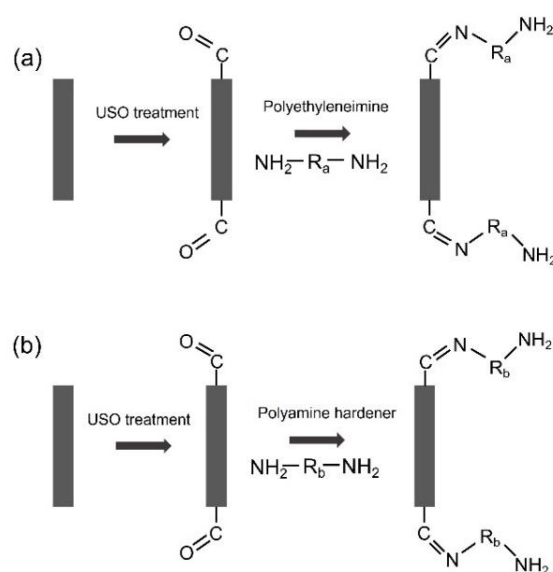


Fig. 1. Schematics of surface oxidation due to ultrasonicated ozonolysis (USO) treatment and amine-functionalization of CNFs, a) PEI+OZ-CNFs, and b) H+OZ-CNFs.

In the second method, PEI was added to the OZ-CNFs aqueous solution at OZ-CNF: PEI ratio of 1:1 and ultrasonicated for 4 hours, followed by 12 hours of mechanical stirring at room temperature. The dispersion was then spray dried (B-290 spray dryer, BÜCHI Labortechnik AG, Switzerland) with a 0.7 mm nozzle, an outlet drying temperature of 65°C, a pump feed rate of 30% and an inlet drying temperature of 200°C. The ozone and PEI-treated CNFs are designated PEI+OZ-CNFs. In the third method, PEI was replaced with the polyamine hardener used for curing the EA9396 to produce H+OZ-CNFs. The primary amine groups in the

PEI/polyamine can react with the carbonyl functional groups present on the OZ-CNFs through an amidation reaction to form a covalent bond, as shown in Fig. 1.

2.3. Characterization of functionalized CNFs

The morphology of the untreated and functionalized CNFs was studied by using a FESEM (Apreo S, Thermo Fisher Scientific, Australia).

The functionalized CNFs were characterized by using a Kratos AXIS Nova XPS with a monochromatized Al K α 1 (1486.6 eV) X-ray source operated at 150 W with 160 eV and 20 eV pass energies for survey and region spectra, respectively. All spectra were acquired using a 90° take-off angle to the sample surface. Spectra were quantified using Kratos XPS elemental sensitivity data after Shirley background subtraction. The data was processed using Casa XPS software.

FTIR spectra were determined using Smart iTR spectroscopy (Thermo Fisher, Massachusetts, USA) to study the functional groups attached to CNFs. The CNFs were pressed into a pellet with potassium bromide (KBr) and scanned from 4000-800 cm⁻¹.

TGA (Netzsch STA 449C Jupiter) was used to analyse the functionalized CNFs. Samples weighing ~5 mg were placed in alumina crucibles and heated from 30 to 400°C at a heating rate of 2 °C/min under helium with a flow rate of 25 mL/min.

2.4. Preparation and characterization of nanocomposite adhesives

For the fabrication of SBM-modified EA9396, the required quantity of SBM (2, 5 and 10 wt.% of epoxy resin) was dissolved in dichloromethane followed by mixing with epoxy resin. The obtained solution was then stirred at 120 °C to evaporate the dichloromethane. Any remaining traces of solvent were removed by degassing under a vacuum at 120 °C, before adding the hardener.

To prepare for the ternary nanocomposites, the untreated/functionalized CNFs (0.1, 0.3 and 0.5 wt.%) were added into the SBM+EA9396 mixture and pre-mixed using a planetary mixer (Thinky, ARV-310PCE, Japan) at 2000 rpm for 10 mins. The uniform dispersion of the CNFs in the SBM+EA9396 was obtained by using a 3-roll mill (EXACT 80E, Germany) at 180 rpm for 10 passes. The gap sizes between the 1st and 2nd roller, and 2nd and 3rd rollers were 20 μm and 5 μm , respectively. The hardener (100:30 ratio by weight) was then added to the final mixture and mixed for 10 minutes using a vacuum planetary mixer (Thinky, ARV-310PCE, Japan) at 1000 rpm.

The curing behaviour of the unmodified and nanocomposite adhesives resins was investigated using differential scanning calorimetry (DSC Q100). To measure the total heat of the reaction, dynamic scanning was undertaken under a nitrogen atmosphere at a flow rate of 50 mL/min with ~ 10 mg sample size in aluminium pans using a constant heating rate of 10 $^{\circ}\text{C}/\text{min}$ from 25 $^{\circ}\text{C}$ temperature to 175 $^{\circ}\text{C}$.

Optical microscopic images were then captured on a small droplet of the uncured CNF+SBM+EA9396 epoxy mixture placed on a microscope glass to examine the level of dispersion after each stage of mixing.

Attenuated total reflectance FTIR studies were performed on cured unmodified and nanocomposite adhesive samples, between 4000 and 400 cm^{-1} at a resolution of 4 cm^{-1} using a Nicolet 5700 FTIR in combination with an ATR accessory (Smart iTR, Thermo Fisher, Massachusetts, USA) to enable qualitative comparison in chemistry for the different adhesive mixtures.

The glass transition temperature (T_g) of the cured unmodified and nanocomposite epoxy adhesives was measured using DSC Q100 under a nitrogen atmosphere at a flow rate of 50 mL/min with 10 mg samples in aluminium pans using a constant heating rate of 10 $^{\circ}\text{C}/\text{min}$ from 25 $^{\circ}\text{C}$ temperature to 200 $^{\circ}\text{C}$. The thermal stability was studied using a TGA (Netzsch

STA 449C Jupiter) under a nitrogen atmosphere from 25 °C to 600 °C at a heating rate of 10 °C/min.

2.5. Lap shear joint preparation and testing

Single lap shear joints were prepared by bonding 3.2 mm thick aluminium alloy 7075-T6 substrates using unmodified and nanocomposite adhesives. The aluminium surface was wiped with methyl ethyl ketone (Bio strategy, Australia) and abraded with Scotch-Brite™ 7447 (3M, USA) followed by grit blasting using 50 µm size alumina grit (AccuBRADE-50, Coltronics, Australia) with a pressure of 450 kPa. The grit-blasted surfaces were then cleaned using dry nitrogen gas at a pressure of approximately 500 kPa. The cleaned grit-blasted adherends were then immersed in 1% γ -glycidoxypopyl trimethoxy silane (Sigma-Aldrich, Australia) aqueous solution, followed by drying at 110 °C for 1 hour [44]. The single lap shear joints were prepared as per the ASTM D1002 [25] standard with a bond area of $12.7 \times 25.4 \text{ mm}^2$. The dimensions and schematic of the single lap shear joint are shown in Fig. S1. The bondline thickness of 0.15 mm was maintained for all the joints by shim placement. The lap shear joints were then cured at room temperature for 24 hours followed by post-curing at 80 °C for 4 hours.

The lap shear strength of the unmodified and modified epoxy adhesive joints was measured both at room and elevated (90 °C) temperatures using a universal tensile testing machine (Mecmesin, MultiTest 25-i, 25 kN, United Kingdom) with a loading rate of 1.3 mm/min. For measuring the lap shear strength of the adhesive joints, at least four samples were tested for each combination.

Fracture surfaces of the lap shear joints and cross sections of the cryogenically fractured bulk samples were observed using a FESEM operating at 10 kV accelerating voltage with a 4 mm working distance. Samples were gold coated (~3 nm thick) using a sputter coater (Quorum, Q150R EA, England) to prevent sample charging.

3. Results and discussion

3.1. Morphology and surface functionalities on CNFs

The morphology of the untreated and functionalized CNFs was studied by SEM as shown in Fig. 2. The diameter of the CNFs was measured to be 30-150 nm. The smooth appearance of the untreated CNF (Fig. 2a) was unchanged after ozone treatment for the oz-CNF (Fig. 2b). However, the morphology of oz-CNT significantly changed after PEI and hardener functionalization. In Figures 2c and 2d, it is possible to verify the presence of PEI and hardener films surrounding the CNFs, respectively. The presence of amine groups in PEI and hardener is expected to be covalently bound to the CNF surface and was not eliminated during the spray drying process.

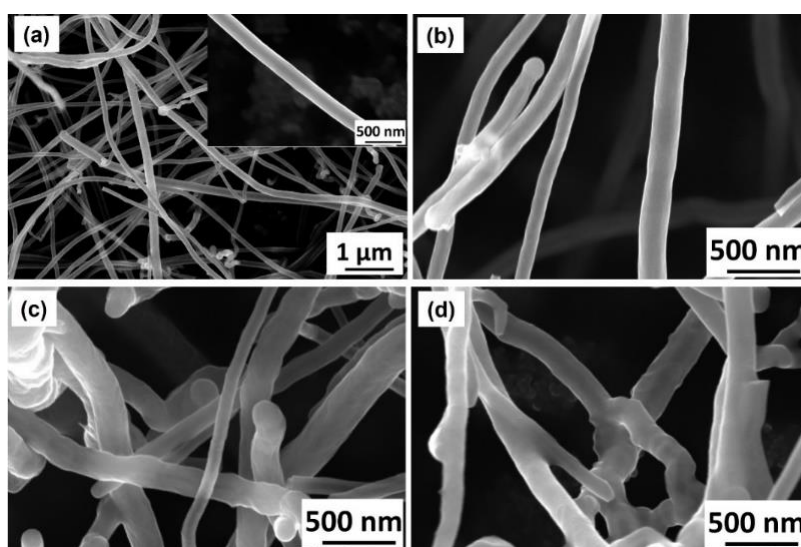


Fig. 2. SEM images of a) untreated CNF (inset shows the high magnification), b) oz-CNF, c) PEI+OZ-CNF and d) H+OZ-CNF

Fig. 3a shows the XPS survey spectra for the CNFs before and after USO treatment and following amino functionalization, with the elemental compositions summarized in Table 1. The binding energies at 285 eV and 532 eV attributed to the C1s and O1s, respectively [45], show an increase in oxygen content (~6 atomic%) after USO treatment due to the addition of

oxygen functional groups onto the CNF surface, consistent with previous studies [46, 47]. The increase in the 400-eV intensity, due to N1s, occurs for both the PEI+OZ-CNFs and H+OZ-CNFs, corresponding to the addition of polyamine molecules.

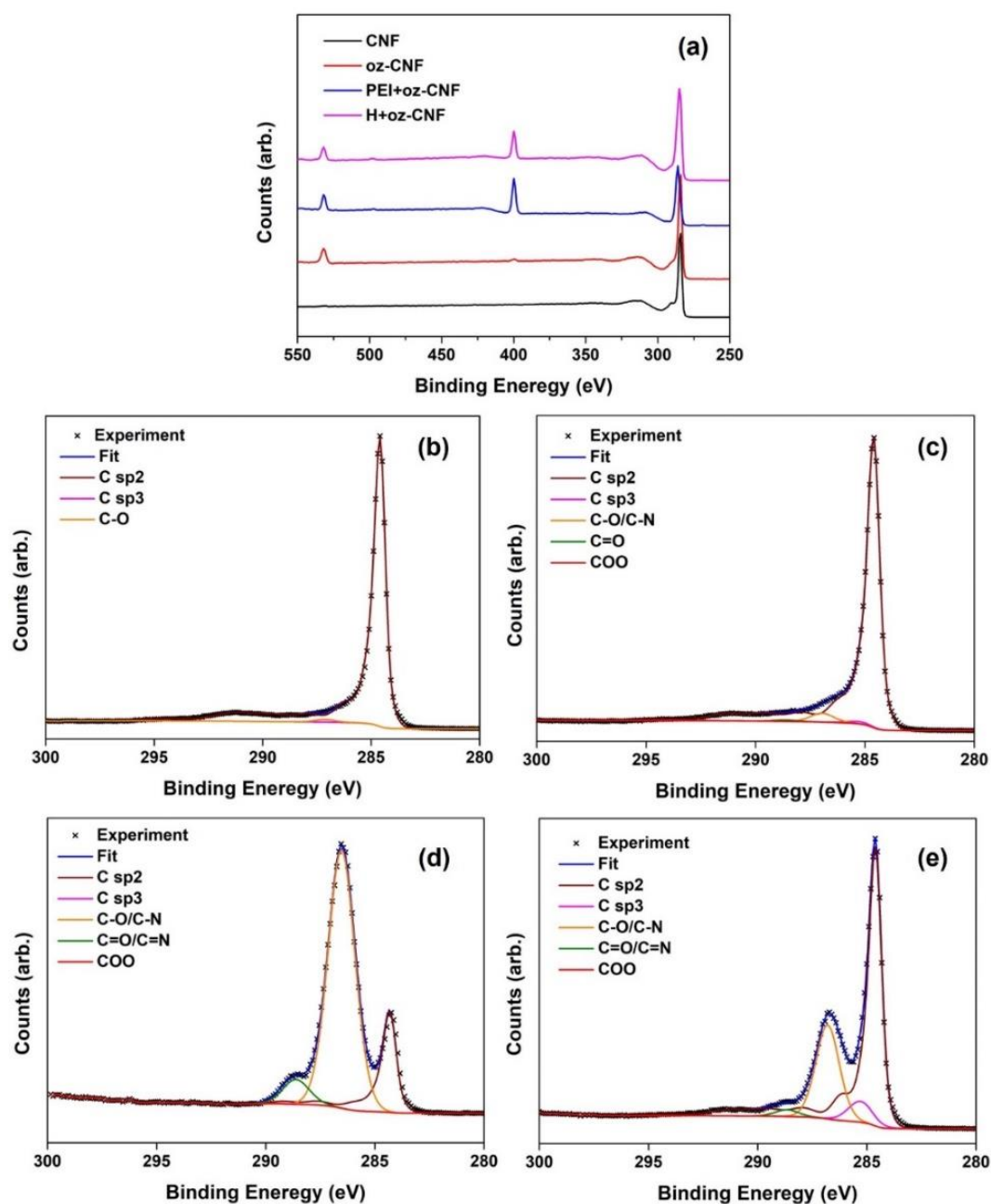


Fig. 3. XPS spectra for untreated and functionalized CNFs (a) Survey spectra indicating changes in elemental O, N and C levels and high-resolution C1s spectra: (b) CNF, (c) OZ-CNF, (d) PEI+OZ-CNF, and (e) H+OZ-CNF, indicating the fitted components.

To identify the chemical nature of the carbon species, high-resolution carbon (C1s) spectra are shown in Fig. 3b-e and the compositions are summarized in Table 2. To fit the C1s peaks in Table 2, a model consisting of a series of Gaussian Lorentzian peaks was developed to fit the C1s spectrum for an untreated CNF to consider the sp² and sp³ contributions. This model was then applied to the OZ-CNF, PEI+OZ-CNF and H+OZ-CNF samples. Additional peaks representative of the oxygen and nitrogen functionalities were then added to fit the spectra. The addition of these components is shown in Fig 3. The peak positions are consistent with literature values for these contributions [45, 48, 49]. Fig. 3b and 3c show the C1s spectra of the as-received and OZ-CNFs indicating the introduction of C-O and C=O species following treatment. The PEI and polyamine hardener-treated OZ-CNFs (Fig. 3d and 3e) show significant changes in the C1s spectrum due to the adsorption of the nitrogen-rich PEI and polyamines, attributed to amine and amide bonding. The presence of amine and amide functional groups was supported by fitting components at 286.7 eV (C-N) and 288.7 eV (C=N), respectively [45, 50]. Due to the attachment of PEI and polyamine molecules, a significant increase in the C-N contribution of ~22 atomic % (PEI+OZ-CNF) and ~11 atomic % (H+OZ-CNF) was observed, indicating increased surface coverage of the OZ-CNFs by the PEI and polyamine hardener, respectively.

Table 1. XPS quantification data for the CNF before and after USO and polyamine functionalization treatments (nd indicates not detected).

Treatment	Atomic Concentration (%)							
	Na1s	F1s	O1s	N1s	C1s	Cl2p	Si2p	S2p
CNF	nd	nd	0.4	nd	99.5	nd	nd	0.1
OZ-CNF	nd	nd	6.0	1.1	92.9	0.04	nd	nd
PEI+OZ-CNF	0.2	0.9	6.0	21.7	70.5	0.4	0.2	0.1
H+OZ-CNF	0.3	0.4	4.2	11.4	83.5	0.02	0.2	0.1

Table 2. XPS peak fitting data for the C 1s high-resolution spectra for the CNF before and after functionalization treatments, indicating the relative compositions of the fitted components.

Sample (BE/eV)	C 1s Composition (at%)				
	sp ² (284.6)	sp ³ (285.0)	C-O/C-N (286.7)	C=O/ C=N (288.7)	COO (289.5)
CNF	98.5	0.0	1.0	0.0	0.0
OZ-CNF	88.3	0.8	3.3	0.5	0.1
PEI+OZ-CNF	14.2	0.0	51.3	4.9	0.1
H+OZ-CNF	54.1	5.2	22.5	1.6	0.1

Fig. 4 shows the FT-IR spectra of CNFs obtained after ozone and PEI/hardener functionalization treatments. For untreated CNFs, the bands at 1058 and between 3300 and 3600 cm⁻¹ are attributed to the presence of hydroxyl groups (–OH) on the surface of CNFs, which are believed to result from both ambient atmospheric moistures bound to CNFs and oxidation, during purification of raw material. Another band at 1640 cm⁻¹ is assigned to the C=O stretching of quinone groups on the surface of CNFs. After ozone treatment, the increased peak intensity at 1640 cm⁻¹ is assigned to the C=O stretching mode of quinone groups, while the band at 1515 cm⁻¹ is assigned to C sp² bonds located near the newly formed oxygenated groups [51, 52]. The broad peak that appeared between 3300 and 3600 cm⁻¹ is attributed to stretching vibration bonds of the hydroxyl groups (O–H) consistent with the activation of oxygen functional groups on the CNF surface by ozone treatment and the XPS results in Fig. 3. In contrast to untreated CNFs and OZ-CNFs, the PEI+OZ-CNFs and H+OZ-CNFs both show the presence of amines molecules. The increase in peak intensities at the ranges of 1450–1650 cm⁻¹ and 3300–3400 cm⁻¹ are attributed to the –NH₂ bending and stretching vibration of the amine groups, respectively [53]. The peak at 1120 cm⁻¹, corresponding to C–N stretching vibrations, also supports the presence of amine functional groups on the CNFs.

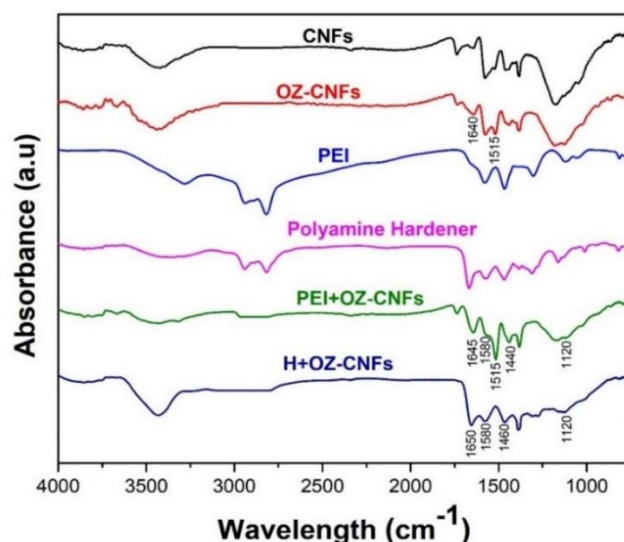


Fig. 4. FTIR spectra of untreated and functionalized CNFs.

TGA results of the untreated and functionalized CNFs are presented in Fig. S2. A mass loss of approximately 2% was observed for the untreated CNF at the end of TGA (at 400 °C) while ~16% mass loss was observed for oz-CNFs. The increase in mass loss is due to the oxidation of the CNF and the presence of organic functionalities on the CNF surface. The mass loss of 29% and 35% were observed for PEI+OZ-CNF and H+OZ-CNF respectively. The variation in the mass loss of PEI+OZ-CNF and H+OZ-CNF can be attributed to the grafted amine functional groups on the CNF surface, which agree with the degradation of PEI and hardener as shown in Fig. S2.

3.2. Dispersion of CNFs in the SBM-modified epoxy resins

The macroscopic images of the untreated and functionalized CNF dispersions in the aqueous solutions are presented in Fig. S3. Stable and homogeneous dispersions of functionalized CNFs were observed even after 7 days compared to the untreated CNFs. In addition, optical microscopic studies were carried out to observe the dispersion of untreated and functionalized CNFs in the SBM+EA9396 epoxy adhesive mixtures. The optical images of the nanocomposite

adhesives mixtures with untreated and functionalized CNFs at different levels of mixing are shown in Fig. 5. The CNF+SBM+EA9396 epoxy dispersions after pre-mixing by planetary mixer showed loosely packed aggregates of CNFs formed due to van der Waals attraction forces. However, the functionalized CNFs were homogeneously dispersed with only small aggregates even with the simple pre-mixing provided by the planetary mixer. The best CNF dispersion was achieved by employing a 3-roll milling machine. In the final mixing stage after 10 passes of 3-roll milling, the functionalized CNFs were well dispersed without any CNF aggregates. However, small CNF aggregates can be found in the CNF+SBM+EA9396 final mixture even after 10 passes. Therefore, the functionalization of CNFs not only facilitates the chemical reactivity of the CNF surface with the epoxy, but also enhances the dispersion efficiency in epoxy resins.

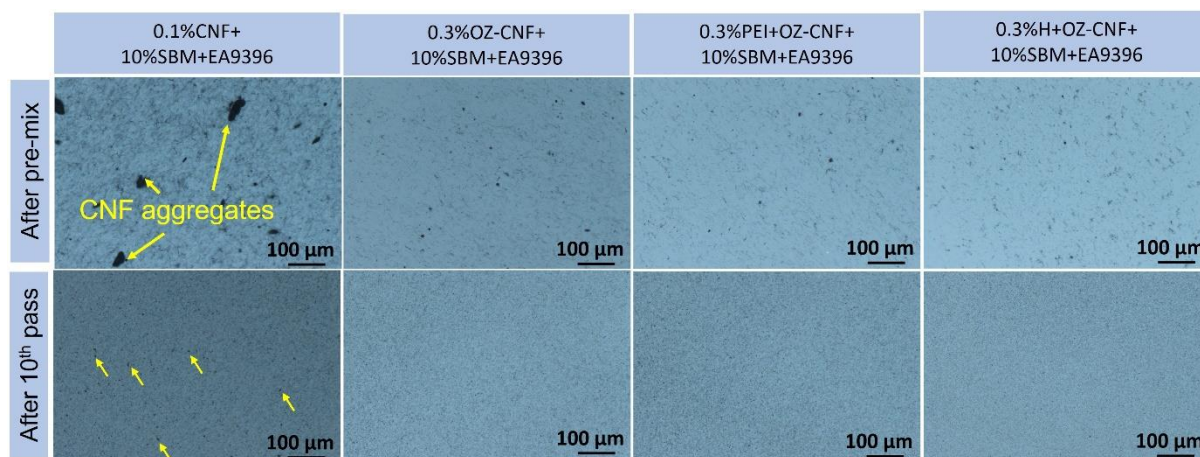


Fig. 5. Optical micrographs of untreated and functionalized CNF dispersions in SBM+EA9396 mixtures after pre-mix (planetary mixing) and 3-roll milling after the 10th pass

3.3. Curing behaviour of the nanocomposite adhesives

The influence of SBM and functionalized CNFs on the curing kinetics of EA9396 was confirmed by DSC analysis. Fig. S4 shows the DSC thermograms, the exothermic peak

temperatures (T_p) and the total heat of reaction values, which are summarized in Table 3. The results revealed that there was no change in exothermic peak temperature with the SBM and CNF addition. However, the incorporation of untreated CNFs and OZ-CNFs showed a slight decrease in total heat reaction [54]. This could be due to the physical hindrance of CNFs to the mobility of the epoxy monomers, leading to a slower cure reaction. But the addition of PEI+OZ-CNFs and H+OZ-CNFs increased the total heat of the reaction due to the presence of amine groups on the CNFs, which could participate in the curing reaction of epoxy.

Table 3. Exothermic peak temperatures (T_p) and total heat reaction (ΔH) of unmodified and nanocomposite adhesives

Material	Exothermic peak temperature, T_p ($^{\circ}\text{C}$)	Total heat reaction, ΔH (J/g)
EA9396	111.37	389.4
10%SBM+EA9396	111.91	392.3
0.1%CNF+10%SBM+EA9396	111.72	385.5
0.3 OZ-CNF+10%SBM+EA9396	111.15	383.0
0.5%PEI+OZ-CNF+10%SBM+EA9396	110.31	417.9
0.3%H+OZ-CNF+10%SBM+EA9396	111.60	405.7

3.4. Chemical structural analysis and thermal stability of the nanocomposite adhesives

Fig. 6 shows the FTIR spectra of the unmodified and nanocomposite adhesives. The EA9396 spectrum displays vibrations at 1510 cm^{-1} (phenyl structure), 1440 cm^{-1} (C-H), 1340 cm^{-1} (C-N), the 835 cm^{-1} (epoxy ring) and $2830\text{--}2920\text{ cm}^{-1}$ (C-H) expected for the epoxy molecular structure [55, 56]. The typical absorption peaks of SBM at 1728 cm^{-1} and 698 cm^{-1} correspond to the presence of acrylate carboxyl groups of poly(methyl methacrylate) and C-H out-of-plane

bending vibration due to the presence of poly(styrene) in SBM, respectively (Fig. 6b). The SBM peaks at 1728 cm^{-1} and 698 cm^{-1} observed in SBM+EA9396 (Fig. 6c), are due to the reaction with EA9396 [57]. In OZ-CNF+SBM+EA9396, a possible reaction mechanism would involve epoxide ring rupture due to a reaction with the hydroxyl (-OH) groups on the CNFs. The ozone treatment produces two distinct surface-bound functional groups, such as esters (at 1754 cm^{-1}) and quinones (at 1650 cm^{-1}) [58]. Hong et al. [59] reported that the formation of a new band 1754 cm^{-1} is evidence of good adhesion of the OZ-CNFs with the epoxy matrix by esterification. In the present study, the ester peak was shifted towards 1728 cm^{-1} in OZ-CNF+SBM+EA9396, which may suggest that the OZ-CNFs have reacted with the SBM+EA9396 matrix.

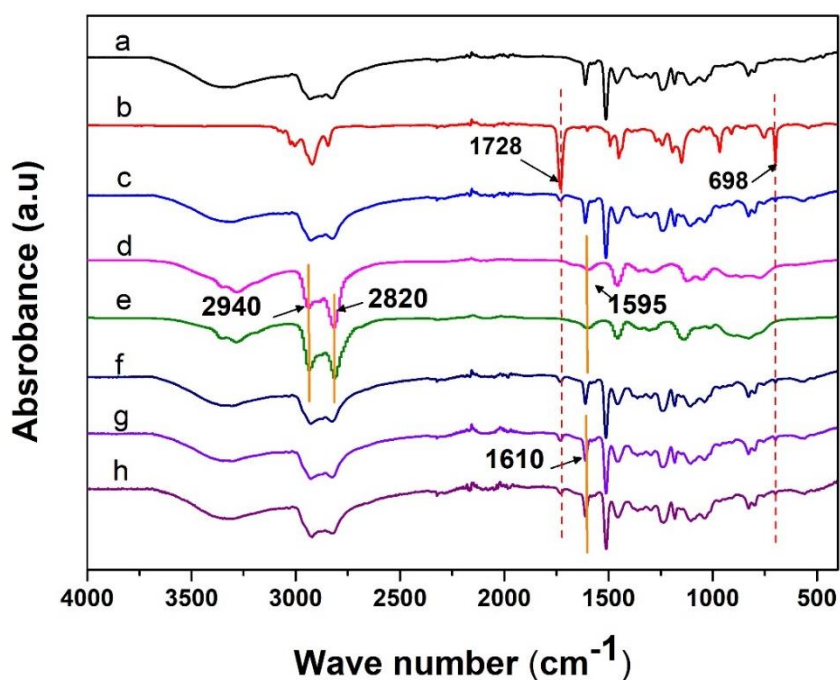


Fig. 6. FTIR spectra of unmodified and nanocomposite adhesives, a) EA9396, b) SBM, c) SBM+EA9396, d) PEI, e) Polyamine hardener, f) OZ-CNF+SBM+EA9396, g) PEI+OZ-CNF+EA9396, and h) H+OZ-CNF+EA9396.

In PEI dendrimer and polyamine hardener, the absorption peak that appeared at 1595 cm^{-1} is ascribed to the N-H deformation vibration bond and symmetrical and asymmetrical stretching bonds of aliphatic C-H are visible at 2820 and 2940 cm^{-1} respectively. In the ternary composites, the peak position corresponding to N-H deformation vibration (1595 cm^{-1}) was shifted to 1611 cm^{-1} and the increased peak intensity was observed due to the reaction between amine groups of PEI/hardener and epoxy functional groups [53, 60].

Thermal stability studies using DSC and TGA were performed to observe the effect of the incorporation of SBM and functionalized CNFs on the T_g and onset degradation temperatures of the EA9396 adhesive. The DSC thermograms of the EA9396 and nanocomposite epoxy adhesive are shown in Fig. S5, and the values are reported in Table 4.

Table 4. Glass transition and onset degradation temperatures of unmodified and nanocomposite adhesives.

Material	Glass transition temperature ($^{\circ}\text{C}$)		Onset degradation temperature ($^{\circ}\text{C}$)
	1 st T_g	2 nd T_g	
EA9396	-	149.2 ± 0.3	338.4 ± 0.7
SBM	85.6 ± 0.7	-	-
10%SBM+EA9396	85.3 ± 0.3	147.2 ± 0.1	337.5 ± 0.8
0.3%OZ-CNF+10 SBM+EA9396	85.5 ± 0.1	148.0 ± 0.3	339.4 ± 0.4
0.5%PEI+OZ-CNF+10%SBM+EA9396	86.2 ± 0.1	150.8 ± 0.5	341.5 ± 1.0
0.3%H+OZ-CNF+10%SBM+EA9396	86.5 ± 0.1	149.3 ± 0.3	339.7 ± 0.6

The unmodified EA9396 and SBM powder show the T_g of $149\text{ }^{\circ}\text{C}$ and $85.6\text{ }^{\circ}\text{C}$ respectively. In the binary composites, the addition of SBM into EA9396 resulted in two T_g 's at $85.6\text{ }^{\circ}\text{C}$ (corresponding to SBM) and $147.2\text{ }^{\circ}\text{C}$ (corresponding to EA9396) with a slight decrease in the

second T_g due to the soft phase of SBM. For the ternary nanocomposites, the functionalized CNFs helped to offset the slight decrease in the second T_g that arises with the SBM addition and led to similar values to the EA9396 adhesives. However, the first T_g still exists in the ternary composites due to the presence of the soft SBM phase.

The TGA results revealed that there was no change in thermal stability for the SBM+EA9396 (Fig. S6 and Table 4). In addition, the incorporation of functionalized CNFs showed a slight increase in onset degradation temperature, indicating that the functionalized CNFs do not degrade the thermal stability of the epoxy.

3.5. Lap shear strength and performance of the unmodified and nanocomposite adhesive joints

The effect of different weight fractions of SBM addition on the lap shear strength of the EA9396 at room and elevated temperature test conditions are shown in Table 5. The lap shear strength of unmodified EA9396 was shown to be 35.6 MPa at room temperature and 21.8 MPa at 90 °C. As the amount of SBM in the EA9396 increased, the lap shear strength increased at room temperature test conditions obtaining the maximum strength of 43.2 MPa, which was 21% higher than that of the unmodified EA9396. At a higher temperature (90 °C), the maximum lap shear strength of 26.6 MPa was obtained at a lower SBM content (2 wt.%), which was slightly reduced with higher SBM contents.

Our previous study [25] showed that the addition of 10% SBM into a diglycidyl ether of bisphenol A (DGEBA) based low viscous epoxy resin resulted in 93% (~11 MPa improvement) in lap shear strength at room temperature compared to the unmodified epoxy. Prolongo et al. [37] reported that the DGEBA epoxy resin was modified with 10 wt.% SBM showed an enhancement of 44% (~5 MPa improvement) in the lap shear strength. The variation of

improvement in lap shear strength in our present study is due to the higher viscosity and cross-linking density of the TGDDM epoxy which restricts the mobility of the polymer molecules. Hence, the diffusion growth of the SBM particles in the TGDDM epoxies during the phase separation process is slower compared to the DGEBA-based epoxies. This eventually led to different degrees of improvement in fracture toughness and lap shear strength. Ma et al. [61] reported that the thermoplastic particles in DGEBA-based epoxy blends showed a higher degree of plastic deformation which indicates a larger energy dissipation in crack propagation compared to the TGDDM epoxy blends. It was observed that 10 wt.% SBM+EA9396 composites are shown to provide the best compromise for use at both room and elevated temperatures. Thus, ternary nanocomposite adhesives were prepared based on the 10 wt.% SBM to observe the effect of untreated and functionalized CNFs.

Table 5. Lap shear strength of SBM+EA9396 adhesives at room and elevated temperature test conditions.

Material	Lap shear strength (MPa)	
	RT	90 °C
EA9396	35.6±1.1	21.8±1.1
2% SBM+EA9396	38.5±2.1	26.6±0.6
5% SBM+EA9396	42.9±2.9	24.8±1.0
10% SBM+EA9396	43.2±1.6	25.4±0.8

Figures 7 and 8 show the effect of different weight fractions of untreated and functionalized CNFs on the lap shear strength of the 10 wt.% SBM+EA9396 composites adhesives at room and elevated temperatures. It should be noted that the mechanical performance of a composite depends on the dispersion of CNFs and the interfacial interaction between CNF and surrounding epoxy. The ternary nanocomposite adhesives containing untreated CNFs resulted

in a reduction of lap shear strength with increasing CNF content due to the poor interfacial strength between the filler and matrix. The composites containing functionalized CNFs such as OZ-CNFs, PEI+OZ-CNFs and H+OZ-CNFs exhibited a significant increase in lap shear strength over the range of CNF weight fractions studied and showed a higher lap shear strength than the untreated CNF at the same filler content. The enhancement in lap shear strength is due to the combination of better CNF dispersion and stronger filler–matrix adhesion resulting from the functionalization. It should also be noted that the strength of nanocomposite adhesives containing untreated CNFs rapidly degraded with increasing content of CNFs after reaching a maximum at 0.1 wt.% of CNF content, while the strength of the nanocomposites containing functionalized CNFs continued to improve up to 0.3 wt.% for OZ-CNFs and H+OZ-CNFs and 0.5 wt.% for PEI+OZ-CNFs, which is clear evidence of the improved dispersion and interfacial interactions between the functionalized CNFs and the surrounding matrix. The composites containing H+OZ-CNFs and PEI+OZ-CNFs also exhibited higher lap shear strength than the of OZ-CNFs both at room and elevated temperatures.

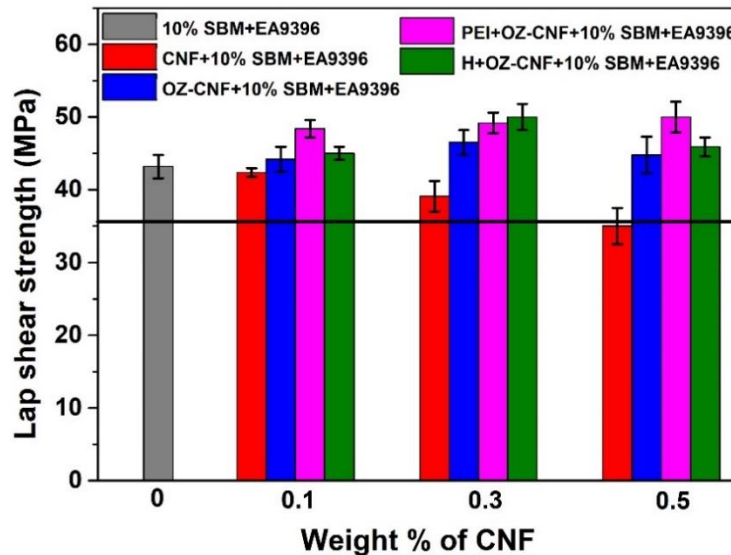


Fig. 7. Lap shear strength of CNF+10% SBM+EA9396 ternary nanocomposites adhesives at room temperature test condition. The horizontal line represents the lap shear strength of the unmodified epoxy.

At room temperature (Fig. 7), the maximum lap shear strength of 50 MPa was obtained for both 0.3 wt.% H+OZ-CNFs and 0.5 wt.% PEI+OZ-CNFs, which was 40% higher than that of the unmodified epoxy. These observations suggest that amino-CNFs are more effective in enhancing the lap shear strength of the nanocomposite adhesives, even at high CNF contents. At elevated temperatures (Fig. 8), an improvement of 35% was observed for 0.1 wt.% PEI+OZ-CNF+SBM+EA9396, while the 0.5 wt.% H+OZ-CNF+SBM+EA9396 adhesives resulted in a 38% enhancement. The high-temperature strength appears to decrease for the PEI treatments with higher CNF concentrations. Whilst the epoxy adhesive T_g doesn't appear to be sensitive to the PEI, as shown in Table 4, the interphase reaction between the CNF and SBM-modified epoxy may be affected by the PEI. As shown in Table 2, the PEI+OZ-CNFs exhibited a higher concentration of PEI molecules than that of H+OZ-CNFs. The difference in strength for the PEI and polyamine hardener functionalization, clearly suggests the high-temperature strength is very sensitive to interphase chemistry.

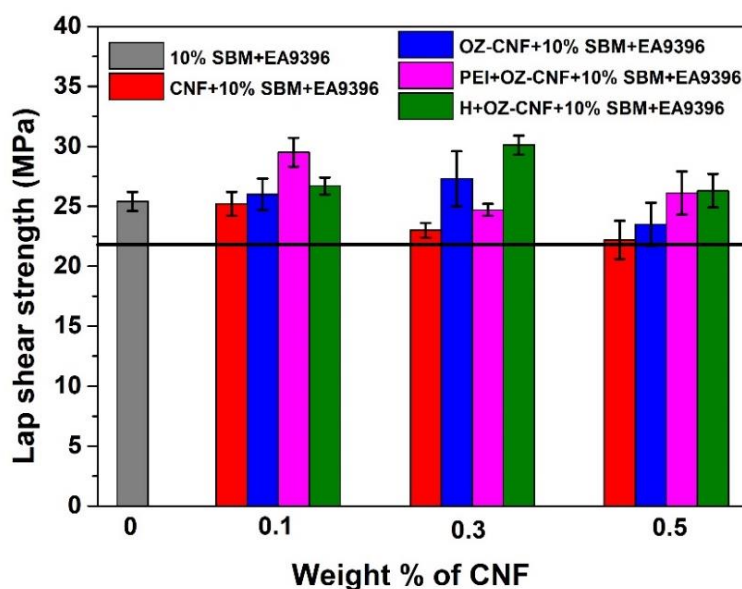


Fig. 8. Lap shear strength of CNF+10% SBM+EA9396 ternary nanocomposites adhesives at the elevated temperature (90 °C). The horizontal line represents the lap shear strength of the unmodified epoxy.

At higher weight fractions, the CNFs tend to form agglomerates after reaching their critical value. These agglomerates would be expected to act as localised stress concentrations within the adhesive and act as critical crack initiation sites that would reduce the ability of the adhesive performance to attain the same levels of plastic deformation observed in the more homogeneous nanocomposites with lower CNF weight fractions [26].

3.6. Fractography

The morphologies of the lap shear joint fracture surfaces of the unmodified and different weight percentage SBM+EA9396 nanocomposite adhesives are shown in Fig. 9. The failure surface morphology of the unmodified EA9396 (Fig. 9a) showed a typical brittle fracture with fracture lines revealing poor fracture resistance. In SBM+EA9396 fracture surfaces (Fig. 9b-d), the addition of SBM caused the fracture surfaces to appear rough, indicating more plastic deformation occurs before failure. All the SBM+EA9396 adhesives exhibit phase-separated structures but with different morphologies. As the weight fraction of SBM increased, the phase morphology was transformed from sea-island (2 wt.% in Fig. 8b) to the co-continuous (5 wt.% in Fig 9c), and finally to the continuous phase structure (10 wt.% in Fig 9d). For the 2 wt.% SBM adhesives, although the lap shear strength values were increased by adding SBM to the EA9396, the fracture surfaces of the modified samples still had a relatively brittle appearance with small SBM-rich domains evident as localised rough surface regions (Fig. 9b), surrounded by the continuous pure epoxy phase. The fracture surface of the 5 wt.% SBM adhesive showed more plastic deformation and a rougher surface (Fig. 9c) compared with the unmodified EA9396. The fracture surface of the 10 wt.% of SBM adhesive was considerably rougher than that of the 5 wt.% of SBM, which suggests that more plastic deformation occurred. This is consistent with the higher lap shear strength value of the 10 wt.% SBM adhesives, as shown in Table 5. The morphology of the composites with 10 wt.% of SBM in Fig. 9d displays SBM-rich continuous phase in the epoxy matrix.

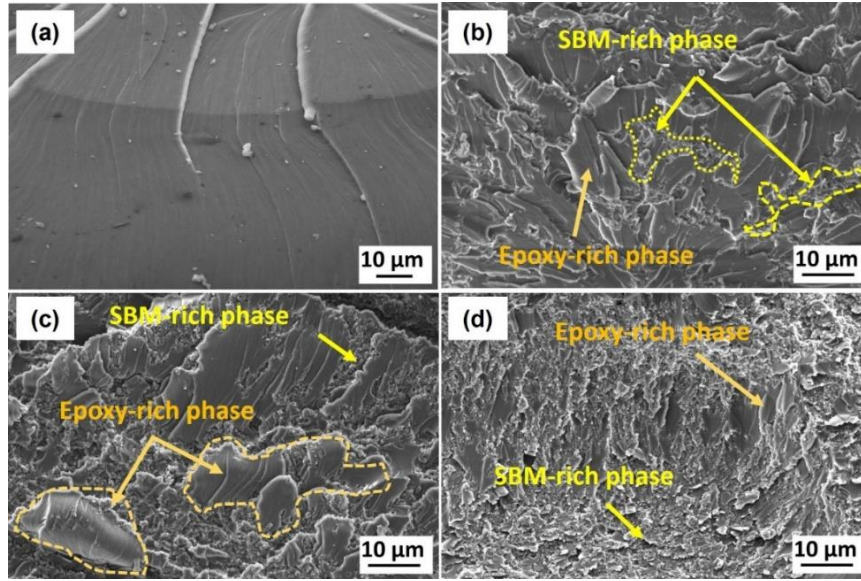


Fig. 9. Fracture surfaces of adhesive joints a) EA9396, b) 2wt.% SBM+EA9396, c) 5 wt.% SBM+EA9396, and d) 10 wt.% SBM+EA9396.

Fig. 10 shows the SEM images of the fracture surfaces of the SBM+EA9396 nanocomposite adhesive joints manufactured with untreated and functionalized CNFs. For the 0.1 wt.% CNF+SBM+EA9396, the presence of CNF pull-outs (Fig. 10a) indicates a lack of adhesion between the untreated CNF and the SBM+EA9396 matrix, confirming the necessity of the surface functionalization of CNFs. Fig. 10b shows the fracture surface of the 0.3 wt.% OZ-CNF+10 wt.% SBM+EA9396 joints, where the OZ-CNF pull-outs have been reduced due to the increased OZ-CNF/matrix interfacial adhesion, compared to the untreated CNF/matrix. The presence of rigid OZ-CNFs may resist the crack propagation that can occur in the epoxy matrix by increasing the crack length. The evidence of some OZ-CNF pull-out in Fig. 10b (inset) suggests that the interface strength between OZ-CNFs and SBM+EA9396 may still, however, be exceeded during fracture in localised stress regions.

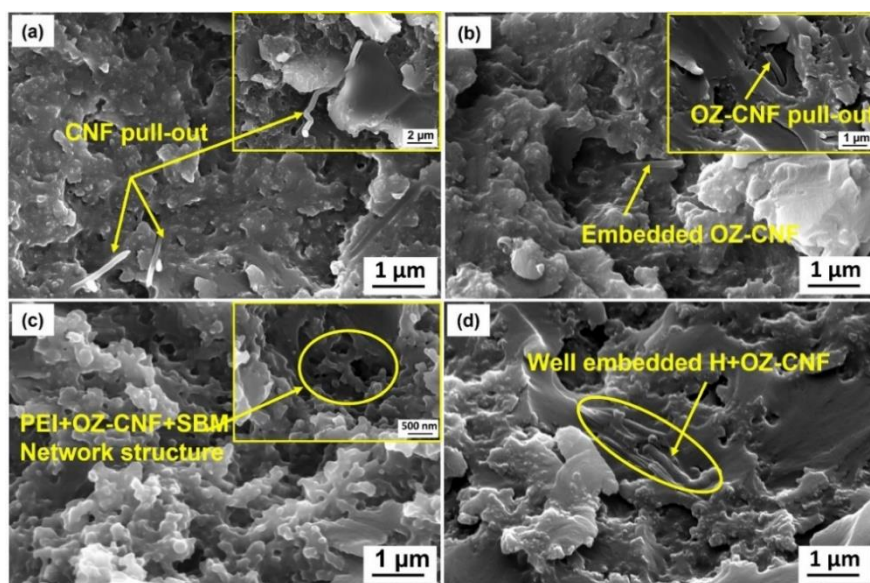


Fig. 10. Fracture surfaces of the hybrid nanocomposite adhesive joints a) 0.1 wt.% CNF+10 wt.% SBM+EA9396, b) 0.3 wt.% OZ-CNF+10wt.% SBM+EA9396, c) 0.5 wt.% PEI+OZ-CNF+10 wt.% SBM+EA9396, and d) 0.3 wt.% H+OZ-CNF+10 wt.% SBM+EA9396.

For the 0.5 wt.% PEI+OZ-CNF+10 wt.% SBM+EA9396, the fracture surface was the roughest among all the adhesives (Fig. 10c), due to the PEI+OZ-CNF+SBM network formation. Carbonyl groups present on the OZ-CNFs bond to the PEI amine groups, which in turn aids good dispersion and reaction of the CNFs in the epoxy matrix at the higher loadings (0.5 wt.%). Potentially, polyamine functional groups attached to CNF may affect the rheological behaviour of the epoxy interphase region. The possible rapid reaction of SBM+EA9396 in the region near the CNF surface could help to retain the highly dispersed nanocomposite created in the mixing phase and prevent CNF re-agglomeration. Additionally, active NH_2 groups of hyperbranched PEI dendrimers can participate in the curing reaction of epoxy [60], forming a strong PEI+OZ-CNF+SBM network and simultaneously forming a tough interphase zone that increases the fracture resistance of the nanoadhesive [62]. Fig. S7 reveals that the network formation was increased with the increased PEI+OZ-CNF content. The fracture surfaces of the 0.3 wt.%

H+OZ-CNF+10 wt.% SBM+EA9396 nanocomposite adhesive (Fig. 10d) show that the H+OZ-CNFs were well embedded in the epoxy matrix, which enhanced the lap shear strength significantly. After the functionalization of OZ-CNFs using polyamine hardener, amine groups are introduced onto the CNF surface (Fig. 2). These nitrogen-containing functional groups can react in a similar way to the PEI [47]. The PEI and polyamine hardener show subtle differences in fracture morphology that is expected to be related to differences in chemical reactivity and morphology of the functional groups present.

To observe the dispersion of functionalized CNFs and interfacial bonding with the surrounding SBM+EA9396 matrix, careful SEM characterization was carried out on cross-sections of cryogenically fractured bulk nanocomposite adhesives at different locations. Fig. 11 shows the low and high-magnification SEM images of the cryogenically fractured nanocomposite adhesives. The low magnification SEM image of 0.1 wt.% CNF+10 wt.% SBM+EA9396 (Fig. 11a) shows that the untreated CNFs formed agglomerates of about 3-5 μm size, which is the possible maximum agglomerate size using 3-roll milling with a 5 μm roller gap. The high magnification image (Fig. 11b) clearly shows the CNF pull-outs and the CNF surface appeared to be smooth with no epoxy traces on the untreated CNF surface, indicating the poor interfacial bonding between the CNF and the surrounding matrix. However, the functionalized CNFs showed uniform distribution and improved interfacial bonding with reduced CNF pull-outs as shown in Fig. 11c-h. The high magnification images of the 0.5 wt.% PEI+OZ-CNF+10 wt.% SBM+EA9396, and 0.3 wt.% H+OZ-CNF+10 wt.% SBM+EA9396 adhesives show that the PEI+OZ-CNFs and H+OZ-CNFs are encapsulated with the SBM+EA9396, which represents the improved interfacial bonding with the surrounding matrix.

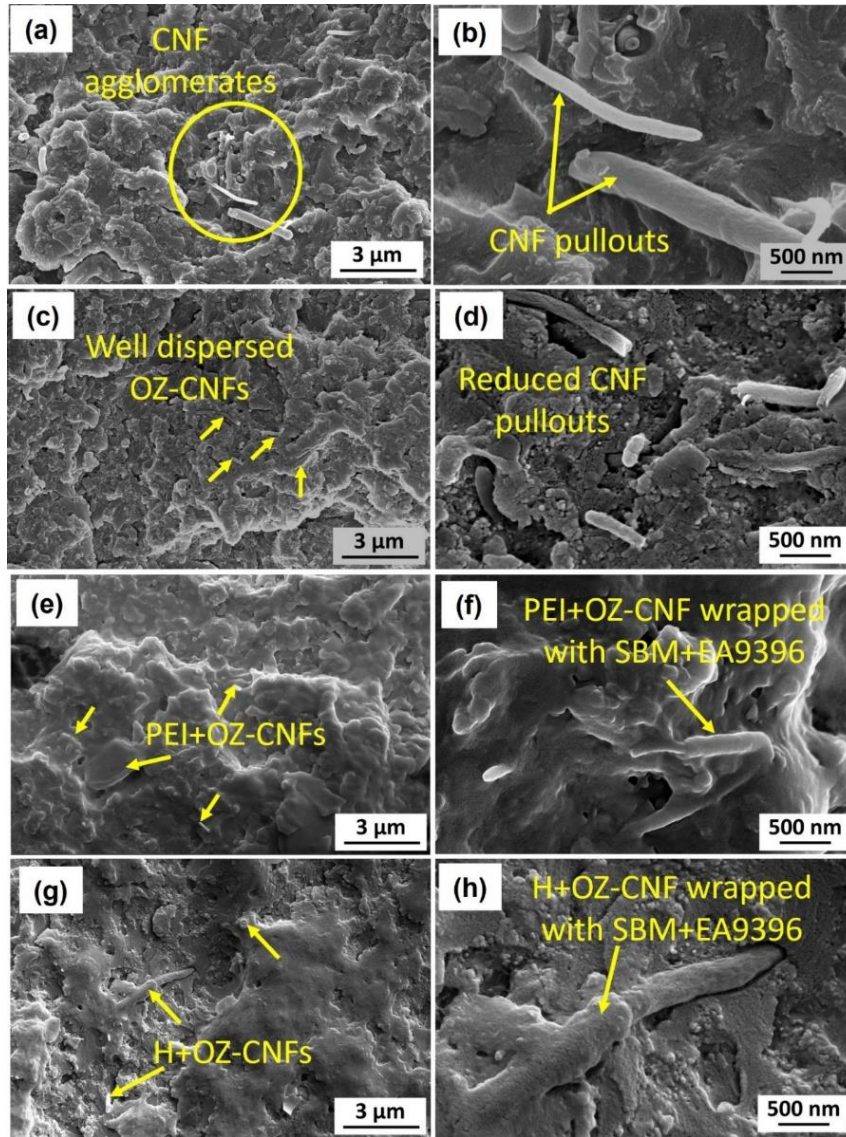


Fig. 11. Low and high magnification SEM images of the cryogenically fractured nanocomposite adhesive a, b) 0.1 wt.% CNF+10 wt.% SBM+EA9396, c, d) 0.3 wt.% OZ-CNF 10 wt.% SBM+EA9396, e, f) 0.5 wt.% PEI+OZ-CNF+10 wt.% SBM+EA9396, and g,h) 0.3 wt.% H+OZ-CNF+10 wt.% SBM+EA9396.

Fig.12 shows a schematic representation of associated toughening mechanisms for the ternary nanocomposite adhesives. In all the ternary nanocomposite adhesives, cavitation/debonding of the SBM creates a stress concentration around the SBM particles (Fig. 12a-12d), leading to matrix plastic deformation including plastic matrix dilation initiated from the debonded

regions. The presence of CNFs increased the SBM+EA9396 effectiveness by enhancing the stiffness and strength of the matrix which lead to the improvement in lap shear strength to some extent. However, with the presence of CNF pull-outs, the enhancement in lap shear strength was limited in CNF+SBM+EA9396 (Fig. 12a). On the other hand, in OZ-CNF+SBM+EA9396, PEI+OZ-CNF+SBM+EA9396 and H+OZ-CNF+SBM+EA9396 adhesives, the existence of functional groups increased the reaction with epoxy matrix. The associated toughening mechanisms (shown in Fig. 12b-12d) are crack bridging, crack pinning and crack deflection. PEI-OZ-CNFs/H+OZ-CNFs and SBM interface provided a significant effect on the lap shear strength, which is due to the enhanced interaction between the amine-functionalized particles and the surrounding SBM+EA9396 matrix.

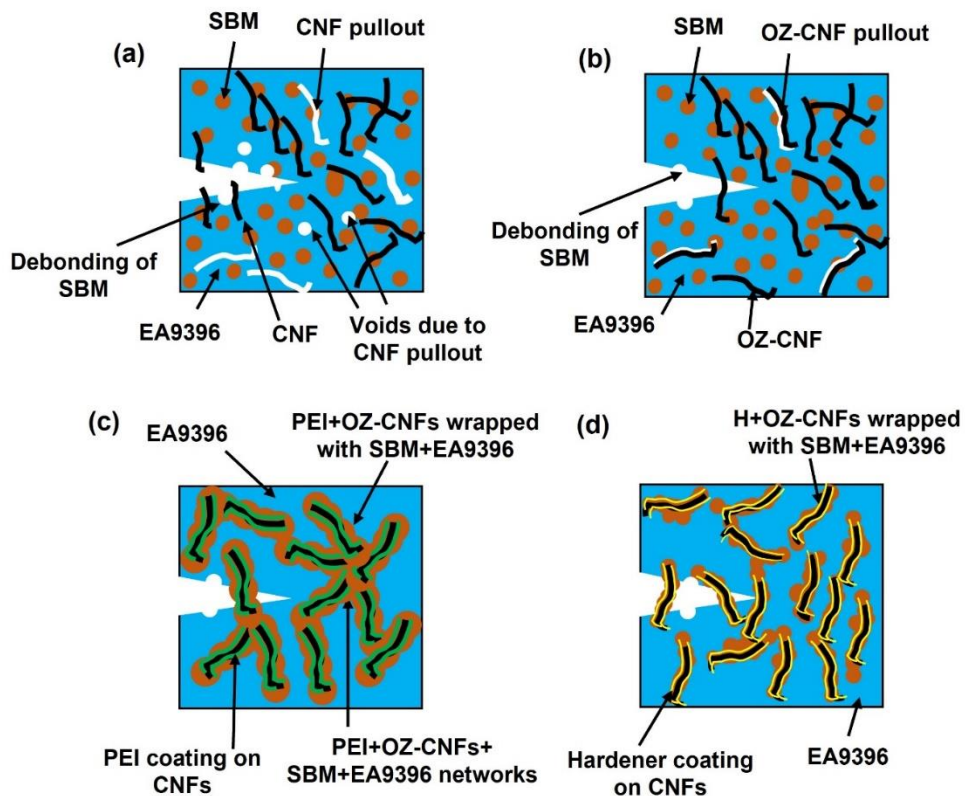


Fig. 12. Schematic of possible toughening mechanisms of the hybrid nanocomposite adhesives a) CNF+SBM+EA9396, b) OZ-CNF+SBM+EA9396, c) PEI+OZ-CNF+SBM+EA9396, and d) H+OZ-CNF+SBM+EA9396.

4. Conclusions

In this study, high-performance TGDDM-based epoxy nanocomposite adhesive materials were developed by incorporating functionalized CNFs and a phase-separated block copolymer. CNFs were effectively functionalized by incorporating functional groups using an ozone treatment followed by a reaction with a branched polyethyleneimine or polyamine hardener. The XPS and FTIR studies confirmed that the oxygen and nitrogen functional groups present on the CNF surface after ozone and amine functionalization treatments, respectively. The amine groups both enhanced CNF dispersion and chemical reactivity with the epoxy matrix. The optimized hybrid nanocomposite adhesives resulted in a 40% increase in lap shear strength when compared to the unmodified epoxy. At elevated temperatures, an improvement of 35 - 38% enhancement in lap shear strength was achieved. Failure surfaces of the toughened SBM+EA9396 revealed a change in fracture morphology from a sea-island structure (at low SBM contents) to a continuous phase-separated morphology (at higher SBM contents), which correlated with improved joint strength. The addition of amine-functionalized CNFs to the SBM+EA9396 led to even greater levels of plastic deformation during crack propagation, due to both improved CNF dispersion and enhanced adhesion with the epoxy matrix. Subtle differences in fracture morphology were observed between the PEI dendrimer and polyamine hardener. Whilst PEI functionalization resulted in the formation of a network structure with the surrounding SBM toughened epoxy matrix, the polyamine hardener did not produce any change in resin morphology. The current study has revealed that precise and repeatable experiments interrogating nanoscale interactions at the interphase of nanocomposites are required to accurately understand the critical factors affecting macro-scale mechanical properties of adhesive joints.

Acknowledgements

The financial support from the Small Business Innovation Research for Defence (SBIRD) Program under the Next Generation Defence Fund for this project is acknowledged. The authors would also like to acknowledge Dr Ashleigh Farnsworth (Defence Science and Technology Group) for helping with FTIR and thermal stability studies.

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