

# Reinforcing effect of MWCNT derivatives on glass/epoxy and carbon/epoxy composites perpendicular to the fiber direction

**Hamed NAZARPOUR-FARD**

Ph.D in polymer science, Department of Chemistry, Faculty of Sciences, Lorestan University, Khoram-Abad, Iran. His research interests include polymer characterization, composites and nanocomposites.

**Mohammad Hosain BEHESHTY**

Professor in polymer composites, Department of Composites, Iran Polymer and Petrochemical Institute, Tehran, Iran. His research interests include polymer composites, nanocomposites, resins and adhesive.

**HAMED NAZARPOUR-FARD** ▪ Department of Chemistry, Faculty of Sciences, Lorestan University, Khoram-Abad, Iran ▪ Nazarpour.ha@lu.ac.ir

**MOHAMMAD HOSAIN BEHESHTY** ▪ Department of Composites, Iran Polymer and Petrochemical Institute, Tehran, Iran

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## Abstract

In the current study, the nano-composites of unidirectional carbon and glass fiber reinforced-epoxy resin with multi-walled carbon nanotubes (MWCNTs) were separately prepared by hand lay-up and hot pressing of fiber epoxy prepregs. Three types of MWCNT derivatives (parent-CNT, low carboxylated CNT (LCCNT) and higher carboxylated CNT (HCCNT)) were dispersed into the epoxy resin/fiber composites. The improved mechanical properties observed in the three component composites could be attributed to the uniform dispersion of CNTs in epoxy/fiber matrices, nanosize of the additives and the improved interfacial interactions between the composite components. The COOH functional groups could also be effective in the increase of mechanical traits because they induce the amphiphilic nature into CNTs for better dispersion and to generate the better glass fiber/epoxy (E/G) and carbon fiber/epoxy (E/C) interactions. HCCNT led to the best mechanical properties among all the samples due to its higher carboxyl content. HCCNT also changed the curing peak of epoxy in DSC and improved its thermal stability. For instance, the final residual mass for E/HCCNT was 15.4% at 600 °C compared to 13.92% for the pure epoxy while the values of 17.55 and 16.48% were observed at 500 °C for E/HCCNT and epoxy, respectively. The observed effect of COOH functionality on the void formation within the composite and on the better CNT dispersion in the matrix can be considered as an important observation for investigating the E/C/CNTs nanocomposites.

Keywords: carbon fiber, glass fiber, multi-walled carbon nanotubes, epoxy resin, mechanical properties  
 Kulcsszavak: szénszál, üvegszál, többfalú szén nanocsövek, epoxi gyanta, mechanikai tulajdonságok

## 1. Introduction

Multi-component materials, especially polymer composites are usually prepared in order to improve the characteristics of materials or provide samples with unique properties for using in applications such as sensors [1]. Also, these types of composites have present interesting usages in the fields of bio-composites [2-3], recycling [4], and also the laminated materials such as fiber/epoxy composites [5].

Glass fiber composites are one of the layered composites that have industrial applications [6], such as their employment in the airplanes and the radar antennas [7]. Carbon fiber reinforced composites have also been employed in the usages, e.g., railway interior applications [8] and fuel tank of launch vehicles [9]. Nevertheless, the cryogenic aging of the tanks and the micro-cracks grown in the composite matrix due to the difference in the coefficients of thermal expansion of the composite components are from issues that accompany this composite type [10].

Despite the advantages of multi-layer composites, they have exhibited the weakness between layers, i.e., in perpendicular to the fiber direction [11] and also weak interlaminar shear resistance [12]. These mechanical issues can result in the important problems especially in the structural and construction applications. Thus, improve their transverse properties, for example by nano fillers can lead to the important development in these materials [13].

Carbon nanotubes (CNTs) due to their unique traits such as low coefficient of thermal expansion, have been widely used in recent years to strengthen the mechanical properties of various nanocomposites. Nevertheless, CNTs are still of interest for using in the various researches [14], and to improve the characteristics of fibrous composites [15]. Tendency to agglomeration in CNTs could result in unwanted stress concentrations that can be the starting point for failure during loading. The uniform dispersion of CNTs in the polymer matrix can be improved by growing the various functional groups on their surfaces [16]. Moreover, the good dispersion of CNTs into epoxy matrix can strongly affect the matrix-dominated mechanical properties *via* improving the interfacial stress transfer between the composite components by the bridging effect [17].

Incorporating the various nanoparticles into the epoxy resin and/or epoxy/fiber composite to enhance the characteristics of the polymer matrix is the typical method [18]. For example, Kim et al. [19] investigated the enhancement effect of MWCNTs on the crack growth resistance in the CNT/carbon/epoxy nanocomposites at a cryogenic temperature. Hossain et al. employed the XD-grade CNTs for reinforcing E/C composites [20]. Rana et al. developed reinforced E/C composites by adding single-walled CNTs into the epoxy matrix [21]. Taş and Soykok reported a remarkable improvement in the bending strength

by compositing CNTs with carbon fiber-based composites [22]. It is worthy of note that in our previous paper, the dynamic-mechanical properties of the laminar E/C composites were improved by adding the carboxylated CNTs to the E/C matrix [5].

On the basis of this introduction, we incorporated parent-CNT, LCCNT and HCCNT into the E/C and E/G composites separately in order to verify the impact of COOH functionalization and its content on the mechanical behavior of E/C composite in perpendicular to the fiber orientation. The hand laminating and compression molding methods were employed to prepare the E/fiber/CNT nanocomposites.

The present study is important, because strengthen the fiber/epoxy composites is the essential requirement in these materials. Also, studying the effect of COOH content in the CNT nanoparticles on E/C characteristics is a new study that could be developed to other functionalities such as amide, hydroxyl, silane, etc. Also, based on the requirement of polymer engineers to the high modulus but lightweight materials, E/C/HCCNT can be considered as the interesting composite for structural applications.

## 2. Materials and experiment

### 2.1 Materials

The unidirectional carbon fiber, UD T200 with the surface area of 200 gr m<sup>-2</sup> were supplied by PMP Co. (Tehran, Iran). The unidirectional glass fiber (L300E10C-0) with the surface area of 300 gr m<sup>-2</sup> was purchased from Metyx (Turkey). Bisphenol-A diglycidyl ether (Epikote 828) as the epoxy matrix was supplied by Momentive (USA) with epoxy group content of 5.34 mmol g<sup>-1</sup>. The dicyandiamide (DICY) curing agent with the melting point of 208-211 °C and average particle size of 150 μm was obtained from AlzChem Co. (Germany). 1-Methylimidazol (DY070) purchased from Huntsman company (Unaited States) was employed as a curing accelrator. Three kinds of MWCNTs as the nano reinforcement filler were supplied by American Elements Company, USA (see Table 1). The length and true density of CNTs were 10-30 μm and 2.1 g cm<sup>-3</sup>, respectively.

Nano particle	Special surface area (m <sup>2</sup> /g)	Outer diameter (nm)	COOH (wt%)
Parent-CNT	200	10-20	0
LCCNT	200	10-20	2
HCCNT	500	<8	3.86

Table 1 The specifications of the used MWCNTs derivatives  
1. táblázat A használt MWCNT-származékok specifikációi

### 2.2 Instrumentation

A homogenizer (Polytron, PT6100, Kinematica) was employed to strongly agitate the epoxy/CNT mixtures and achieve the homogeneous dispersion of CNT nanoparticles within the prepared mixtures. The ultrasonic bath (LBS2 series, FALC instruments) was applied for the better dispersion of the CNT nanoparticles in the mixtures. The viscosity determination of the mixtures was accomplished via Brookfield viscometer (RVDV-II+Pro model) based on the ASTM D 2196 standard method. For this purpose, a certain quantity of the desired mixture (around 3 to 7 cc) was poured into the chamber of the

device and the viscosity of the sample was measured at the desired temperature using Spindle 14. The curing behavior of the epoxy mixtures was analyzed via a differential scanning calorimetry (DSC) by using a NETZSCH DSC 200 F3 instrument. All experiments were conducted under a nitrogen flow of 50 mL min<sup>-1</sup> at the heating rate of 10 °C min<sup>-1</sup>. Thermogravimetry analysis (TGA) measurements of the cured epoxy mixtures were carried out on STA thermal analyzer (STA625 model) at the heating rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere. The gel time of the uncured epoxy mixtures was recorded on the basis of ASTM D4217 standard test method by using a 15SB-90FA bath (Italy) at three different temperatures of 110, 120 and 140 °C. WEGA/ TESCAN scanning electron microscope (Czech Republic) was employed to study the morphology of the nanocomposites and the MWCNs dispersion in the matrix. Before performing the microscopy analysis, the ready composites were coated with a thin film of gold under vacuum via sputter coater (K450X, EMITECH, England). 20 kV was chosen as a convenient voltage of SEM filament. The tensile tests were accomplished on the basis of the ASTM D3039 standard test method on a universal testing machine (UTM, 150 kN, Santam, Iran). The crosshead speed of the machine was constant at the rate of 2 mm min<sup>-1</sup>. The three point bending test was done according to ASTM D790-10 standard test method with sample dimensions of 60 × 13 × 3 mm<sup>3</sup> on the universal testing machine (UTM, 150 kN, Santam, Iran). The Izod notched impact test was carried out on the basis of the ASTM D 256 standard test by using Zwick impact tester, model 5102. For investigating the lap shear strength of the prepregs based on the ASTM D1002 standard test, aluminum plates series 5000 were employed with 2 mm thickness and the dimensions of 25 mm × 102 mm. Aluminum surface was treated with sand blasting paper no. 150, degreased with distilled water and acetone and then dried in oven for 2 h in order to better adherence of prepreg to the plate. Then, one ply of prepreg with the dimensions of 25 mm × 17 mm was cut and put on the treated part of aluminum with the overlap region of 13 mm × 25 mm. The samples were cured in a hot press at 140 °C and 25 bar for 45 min after which cooled to room temperature. Finally, the lap shear tests were carried out using a Santam tensile instrument (STM-150) with crosshead speed of 1.3 mm/min and load cell of 2000 kg. The lap shear strength was calculated by dividing the maximum force (to failure the sample) to the overlapping area. The hardness tests were carried out on Shore D hardness tester (GOTECH, GT-GS-MB).

For the fracture toughness measurements, the standard test method of ASTM D5045 was employed for providing the test requirements and the three-point single-edge notch bend (SENB) specimens. An initial crack (6 mm) was machined in the specimens and a natural crack was created by tapping on a fresh razor blade placed in the notch. The tests were accomplished in the flexure mode using a 150 kN Santam UTM instrument at a crosshead rate of 1.5 mm min<sup>-1</sup> at ambient temperature. The fracture toughness values were computed in the terms of plane strain critical stress intensity factor, K<sub>1C</sub>, by using the following equation [23]:

$$K_{1C} = \frac{P_Q}{BW^{\frac{3}{2}}} f(x) \tag{1}$$

where B and W are the thickness (cm) and the width (cm) of specimen, respectively,  $P_Q$  is the critical load to propagate the crack (kN), and  $f(x)$  is a non-dimensional shape factor calculated via the following relationship [23]:

$$f(x) = 6 \sqrt{x} \frac{1.99-x(1-x)(2.15-3.93x+2.7x^2)}{(1+2x)(1-x)^{\frac{2}{3}}} f(x) \quad (2)$$

where  $a$  is the crack length (cm) and  $x = \frac{a}{W}$ .

### 2.3 Preparation of the pure epoxy sample

A mixture of epoxy resin and the dicyandiamide (DICY) curing agent was obtained by mixing 7 phr of DICY with 100 phr of epoxy resin. Then, the prepared mixture was homogenized at 3000 rpm via a homogenizer for 60 min at room temperature. At the last 3 min of the homogenization process, 1-methylimidazol (0.6 phr) was added as an curing accelerator to the mixture. The contents of DICY and the 1-methylimidazol in the prepared composites were as the previously used in [5] and [23].

### 2.4 Preparing the mixtures of epoxy/MWCNT derivatives

DICY (7 phr) and the MWCNT (0.2 phr) were properly mixed with 100 phr of the epoxy resin by using a glass rod and then the sonication at 25 °C in an ultrasonic bath for 15 min. Afterward, the provided mixture was homogenized at 3000 rpm by a homogenizer for 60 min at ambient temperature. Then, 1-methylimidazole (0.6 phr) was added to the mixture and additionally homogenized for 3 minutes at the same rate. This final mixture was sonicated (60 kHz) at 25 °C for 15 min before being used for wetting the carbon fibre in order to providing the desirable preregs. The general protocol for preparation of the epoxy/MWCNT mixtures is shown in Fig. 1.

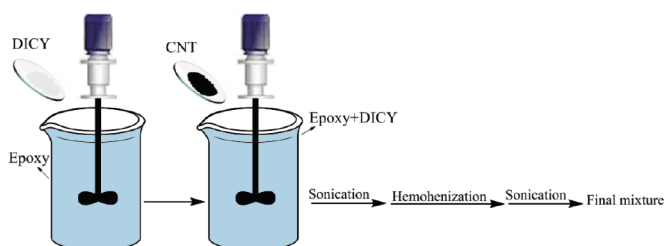


Fig. 1 Schematic representation of the procedure taken for the preparation of E/CNT mixtures

1. ábra Az E/CNT keverékek előállításánál alkalmazott eljárás sematikus ábrázolása

### 2.5 Preparation of the preregs

A sample of carbon fiber was impregnated with the pure epoxy resin or the mixture of epoxy/MWCNT, such that the ratio of fiber to resin was kept at  $50 \pm 2$  wt% to assure all the fibers are homogeneously impregnated with the resin mixture. The prepared prepreg (impregnated single layer of the carbon fiber) was provided for the next processing stages of lay-up and curing via the hot press to leave the final composite samples. The similar protocol was used to providing the glass fiber preregs.

### 2.6 Preparing the composite samples

The proper number of the carbon/epoxy preregs were laid up and the prepared hand lay up laminate was placed between

two layers of teflon film in an steel frame with the favorite thickness. The thickness of the frames used here were on the basis of the corresponding ASTM standard test method for each mechanical test. Then, the compression-molding of the hand lay up sample via hot pressing at 140 °C under 30 bar for 1.5 h left the final nanocomposites. After cooling the cured samples to ambient temperature, specimens with the certain dimensions were cut for using in the desired tests. The glass fiber reinforced samples were also prepared by the same methodology as used for the carbon fiber-incorporated composites.

### 2.7 Resin content of the preregs and the nanocomposites

Thermal pyrolysis method at the elevated temperature was used to determine the resin content of the glass fibers-based composites. In other words, the difference between the initial and final weights of the nanocomposite after completely burning of epoxy matrix, was designated as the resin content. Due to the thermal decomposition of carbon fiber at the elevated temperatures higher than 600 °C, acid digestion protocol was applied to evaluating the resin content of the E/C composites. In other words, the given amounts of the composite (initial weight) were soaked in sulphoric acid and after completely dissolving the resin,  $H_2O_2$  was slowly poured into the mixture. At the end, after washing the acid digested sample with deionized water and then drying it, the dried carbon fiber was weighed (final weight) and the difference between the final and initial weights was designated as the resin content.

### 2.8 Flow test

To determine the epoxy resin flowed from the fiber prepreg under the given pressure, the several samples of the prepreg (with known dimensions) were cut and placed under the hot press at 30 bar and 135 °C for 15 min. Then, after cooling the sample to room temperature, the weight loss of the initial prepreg was defined as the resin flow.

## 3. Results and discussion

### 3.1 Viscosity of the epoxy mixtures

The viscosity of the epoxy resin mixtures was obtained at three temperatures and the results were tabulated in Table 2. It was found that the MWCNTs and its derivatives led to the increased viscosity in the nanocomposites as compared to the pure epoxy resin. Whereas the significant differences were not observed between the viscosities of the CNT-contained epoxy mixtures.

Sample	Viscosity (cP)		
	30 °C	60 °C	90 °C
E	11660	375	75
E/Parent-CNT	~13300	~460	~112
E/LCCNT	~13400	~470	~114
E/HCCNT	~13450	~480	~115

Table 2 The viscosity results of the epoxy resin and its nanocomposites  
2. táblázat Az epoxigyanta és nanokompozitjainak viszkozitási eredményei

### 3.2 Resin content of the samples

After the resin content determination of the nanocomposites, the values of  $45\% \pm 2$  and  $40\% \pm 2$  were obtained for E/C and E/G samples, respectively. While, the flow test results showed that  $\sim 18\% \pm 1$  of the resin is flowed from the epoxy-wetted carbon and glass prepregs.

### 3.3 DSC analysis of the uncured epoxy

The DSC results of the different epoxy formulations can be observed in Fig. 2. It can be found that the curing peak of epoxy resin has been shifted to the lower temperatures after incorporating CNTs to the epoxy samples. It can be seen that the curing temperature range has decreased from  $\sim 120$ - $187^\circ\text{C}$  for the pure epoxy resin to  $\sim 115$ - $176^\circ\text{C}$  for the CNTs contained nanocomposites. This decrement of the curing temperatures can be related to the accelerating effect of CNT on the epoxy curing process due to its nanoscale size and COOH functional groups. It is worthy of mention that the heat of curing reaction ( $\text{mJ mg}^{-1}$ ) for the nanocomposites were  $\sim 1$  to 3.7% higher as compared to the pure epoxy showing the promoting effect of CNT on the epoxy curing.

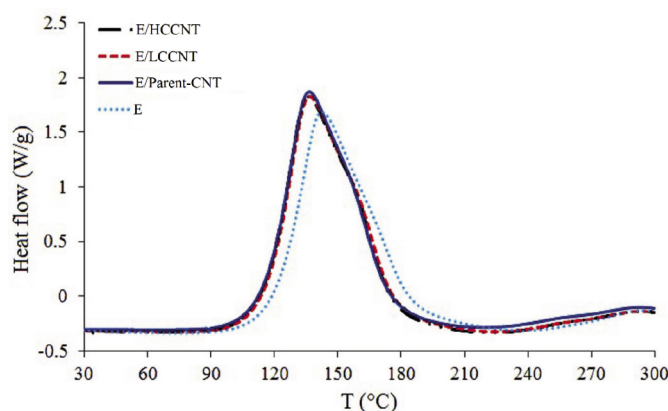


Fig. 2 DSC thermographs of the uncured epoxy resin and its mixtures with MWCNTs  
2. ábra A kikeményítetlen epoxigyanta és MWCNT-vel alkotott keverékeinek DSC termográfiája

### 3.4 Gel time determination of the epoxy resin mixtures

Gel time value is the essential parameter required to evaluating the optimized condition of the prepregs preparation. In other words, at the gel point, the prepregs processing and/or preparation could be difficult. On the other hand, the parameter implies the reactivity of the corresponding accelerator [35]. In this test, during the heating period, the samples were stirred continuously with a glass rod. The resin viscosity was firstly decreased due to the increased molecular movements and then was increased gradually that attributed to the crosslinks created between the epoxy chains. Afterward, it showed an elastic behavior (rubber like) and finally reached the gel state that at this point, the recorded time was designated as a gel time. The gel time of different samples was measured at the temperatures of 100, 120 and  $140^\circ\text{C}$  and the obtained data were tabulated at Table 3. It can be found that the gel time of the epoxy/CNTs mixtures is decreased at 100 and  $120^\circ\text{C}$  in comparison to the pure epoxy resin, while all the samples were gelled at  $\sim 3$  min

at  $140^\circ\text{C}$ . This can be attributed to the increasing effect of carbon nanotubes on viscosity and gelling process of epoxy. This reduce of gel time upon increasing temperature, is logical due to increasing the molecular movements after temperature increment.

Sample	Gel time (min)		
	100 °C	120 °C	140 °C
E/C	$\sim 37$	$\sim 12.0$	$\sim 3$
E/C/Parent-CNT	$\sim 25$	$\sim 11.6$	$\sim 3$
E/C/LCCNT	$\sim 24$	$\sim 11.0$	$\sim 3$
E/C/HCCNT	$\sim 22$	$\sim 10.2$	$\sim 3$

Table 3 The gel time values of the epoxy resin mixtures  
3. táblázat Az epoxigyantakeverékek gélesedési ideje

### 3.5 TGA analysis of the cured epoxy mixtures

TGA analysis results for the cured epoxy resin and its nanocomposites with Parent-CNT, LCCNT and HCCNT are shown in Fig. 3. It is obvious that CNT derivatives (0.2 phr) have not been caused the observable effect on the thermal degradation temperature of pure epoxy. While, pursuant to the residual content of the samples at various temperatures (e.g., 500 and  $600^\circ\text{C}$ ), it can be concluded that the carbon nanotube samples improve thermal stability of pure epoxy resin. On the other word, the solid content of the pure epoxy, E/parent-CNT, E/HCCNT and E/LCCNT were 16.48, 16.44, 16.76 and 17.55% at  $500^\circ\text{C}$  and 13.92, 14.3, 14.3 and 15.44% at  $600^\circ\text{C}$ , respectively. It is clear that HCCNT has been led to the highest thermal stability in the epoxy as compared to other nanoparticles, because it contains the more COOH content (and also the higher polarity) in comparison to other two CNTs.

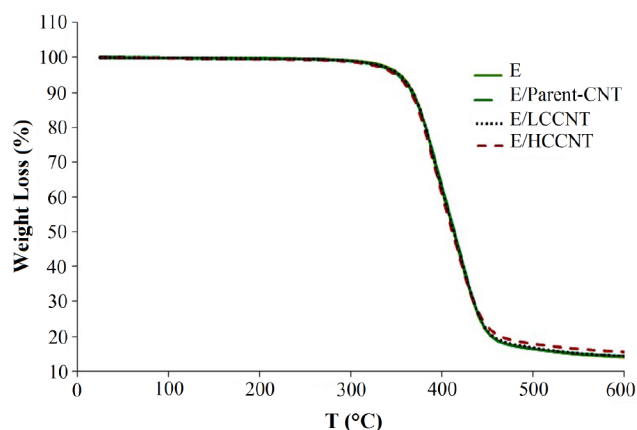


Fig. 3 TGA traces of the cured epoxy resin and its nanocomposites with MWCNTs  
3. ábra A kikeményedett epoxigyanta és nanokompozitjainak MWCNT-vel készült TGA nyomai

### 3.6 SEM microscopy

The SEM micrographs of E/C and its nanocomposites with MWCNT derivatives [9], were explained based on the voids appeared in the sample matrices and on the uniformities of the micrographs, as Seki interpreted the SEM images of polyester/jute fiber/epoxy composites on the basis of the holes observed between the fiber and resin [24]. The large holes in



the micrograph of the pure E/C composite indicate the weaker bondings between the epoxy and the fiber. These voids become even greater when the parent carbon nanotube is added to the E/C composite. The SEM micrographs of the nano-composites contained either LCCNTs or HCCNTs exhibited no remarkable holes/voids in the E/C interface indicating the enhanced bonding between the components. Additionally, the SEM micrograph of E/C/parent-CNT was found to be rougher in the surface than other nanocomposites maybe due to its tendency to agglomeration and inappropriate dispersion in comparison to E/C/LCCNT and E/C/HCCNT. On contrary, the micrographs of E/C/LCCNT and E/C/HCCNT demonstrate the enhanced smoothness and uniformity that can be attributed to fine dispersion of these CNTs into the polar epoxy matrix. The polar COOH groups remarkably participate in hydrogen bonding and also in dipole-dipole interactions consequently enhance the compatibility of these nanoparticles with epoxy resin. Here, the oxidized MWCNTs can be amphiphilic materials because of presence of the bearing polar COOH groups and the non-polar carbonaceous backbone. This amphiphilic nature allows them to having the  $\pi$ - $\pi$  and non-polar interactions with the carbon fibers and to create the dipole-dipole interactions in the same time with the polar segment of epoxy. Beside these stacking forces, the carboxylated CNTs can covalently link to the epoxy chains through reaction of epoxy rings with carboxyl groups. Further, the chemical bonding between epoxy and COOH groups can be accelerated by DICY curing agent (Fig. 4). Due to these interfacial interactions, LCCNT and HCCNT acquire the better dispersion into epoxy resin causing the smooth appearance and the better mechanical properties. Similar interfacial interactions were previously observed from SEM images by Ma et al., i.e., they demonstrated that silylated-CNTs are dispersed more uniform than pure CNT into epoxy matrix [25].

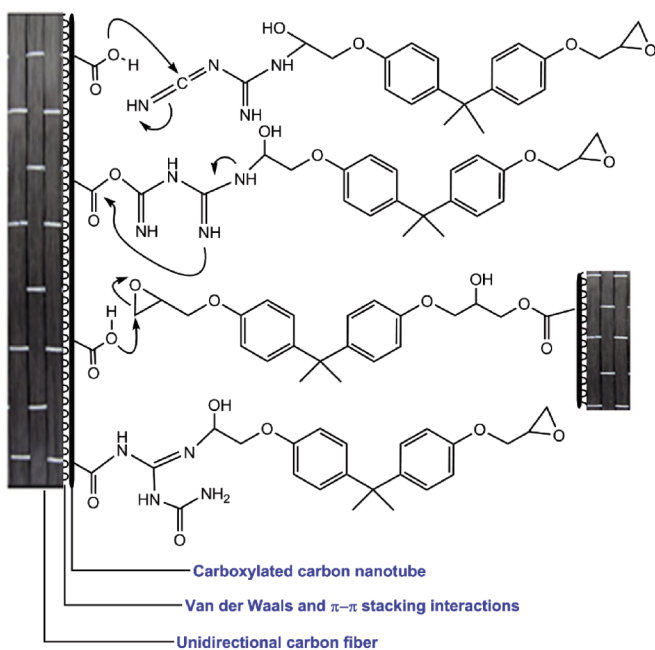


Fig. 4 The expected interactions between carboxylated CNTs and composite components

4. ábra A karboxilezett CNT-k és a kompozit komponensek várható kölcsönhatásai

SEM images for the E/G composites can be seen in Fig. 5. It can be seen that the image of the pure E/G composite is smoother and smoother than the prepared nanocomposites. After adding Parent-CNT into the composite bulk, its hydrophobicity could be led to create some voids between the resin and the fibers. As found for the carbon fiber-based nanocomposites, here, LCCNT and HCCNT also were found to be smoother in SEM image and better in dispersion as can be seen in the micrographs. In other words, the uniformity and smoothness of the microscopic images were as the order of HCCNT > LCCNT > Parent-CNT.

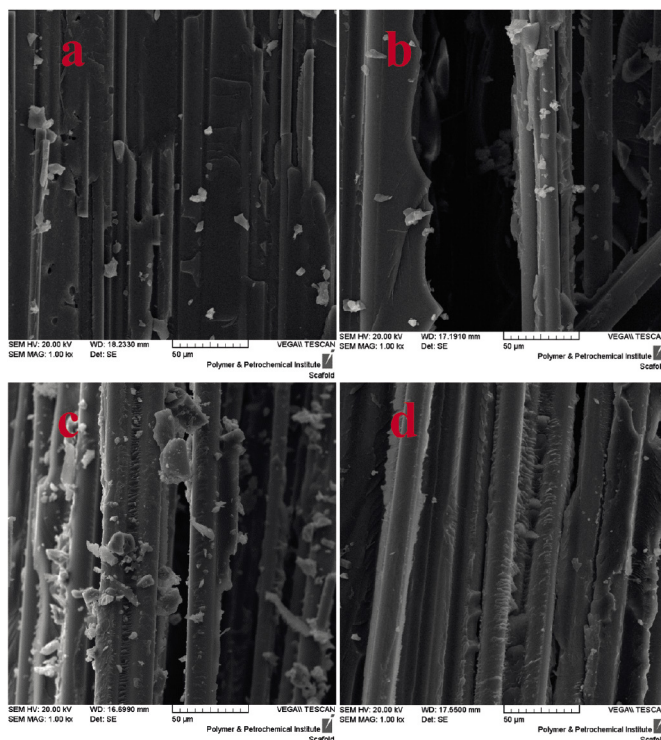


Fig. 5 SEM images of (a) E/G, (b) E/G/Parent-CNT, (c) E/G/LCCNT and (d) E/G/HCCNT

5. ábra (a) E/G, (b) E/G/Parent-CNT, (c) E/G/LCCNT és (d) E/G/HCCNT SEM-képei

### 3.7 Mechanical properties of E/C/CNT nanocomposites

The order of E/C < E/C/Parent-CNT < E/C/LCCNT < E/C/HCCNT was found for the flexural modulus values of the samples (Table 4). Among the samples, HCCNT showed the highest impact on the flexural modulus. It is worthy of note that the rising impact of CNTs on flexural modulus of E/C composite have also reported in [22]. The increasing order was found in the bending strength values similar to the flexural modulus data (Table 4). In this case, E/C/HCCNT with bending strength of  $85 \pm 8$  MPa was seen to be the strongest sample in the bending deformation among the samples. In the bending tests perpendicular to the UD fibers, the epoxy/fiber interface interactions are not dominant parameter on the mechanical characteristics. This can be attributed the fact that the fibers are distinct from each other in this direction, while the epoxy/CNT interactions are dominant and could influence on the mechanical characteristics of the UD fiber-based nanocomposites.

On the basis of the fracture toughness results (Table 4), it is obvious that the CNT samples have exhibited the improving effect on the fracture toughness values for the coresponding composites as obsrved in the bending analysis of the samples.

Impact resistance is defined as the material resistance to breaking under a shock loading or the fracture under the applied force at the high speed (low period of time) [26]. The growthing order of E/C < E/C/Parent-CNT < E/C/LCCNT < E/C/HCCNT was observed for the studied samples as appeared for othe mechanical characteristics. The enhancing effect of the pure MWCNT nanoparticles on the fracture toughness of the E/C composites have also been explained in [27] that can be useful for the better realization of the results in the present study.

The hardness of the samples was conducted based on Shore D hardness test. As can be seen in Table 4, the CNT samples led to the increasing effect on the hardness of the E/C composite that the maximum values were observed for E/C/HCCNT. It is interesting to mention that the similar Shore D values have been presented by Zakaria et al. [28] for other carbonous material (graphite) as a reinforcing filler.

The results of the lap shear test tabulated in Table 4, show the higher lab shear strength for E/C nanocomposites containing CNTs compared to the pure epoxy. This can be attributed to the better missibility/bondings between the nanoparticle and the E/C composites. HCCNT due to its higher polarity exhibited the more increasing effect on the values of the lap shear strength as compared to other two CNT samples. Also, CNTs and COOH functionality can lead to adhesive propertied of the prepregs to the aluminium plates as. For example of the effect of nanoparticles on the lap shear strngth, the lab shear strength values of the pure epoxy adhesive and its nancomposites with nanoalumina were found to be in the range of 4.39-6.83 MPa [29].

Generally, the same increasing order observed in all the mechanical tests for the samples can be assigned to the inherent reinforcing ability of the CNTs and also to the good interactions between the composite components thereby which the transfer of the impact energy between the phases of the composites can be improved. CNTs can form the interactions in the form of Van der Waals and  $\pi - \pi$  interactions with the E/C matrix. However, HCCNT and LCCNT can even form the conalant bonds with epoxy chains *via* their COOH functional groups. Moreover, the amphiphilic characteristic of HCCNT (COOHs interact with the epoxy segments, wherase the carbonous parts interact with the carbon fiber) could lead to the improvement effect on the E/C interface cohesion and the better stress transfer from epoxy to fiber and conversely, from fiber to epoxy. Also, the HCCNT polarity can be led to enhance its dispersion in the epoxy matrix (as seen in its uniform and free of void SEM micrograph) that the proper dispersion is very important to reaches the favorite

properties. Although the effects of LCCNT and HCCNT were more than that of Parent-CNT due to their amphiphilic nature and the higher COOH content as compared to the pure CNT. The better performances of LCCNT and HCCNT on comparison to Parent-CNT are expectable owing to their better bondings with the polar epoxy resin due to their COOH functionality. It can clearly that the values of E/C/LCCNT are higher than that of Parent-CNT, however the diameter of LCCNT and parent-CNT is equal to ~10-20 nm. Thus, it is concluded that the effect of COOH content on the fracture toughness values is remarkable and more predominant in comparison to the diameter of CNTs.

### 3.8 Mechanical properties of E/G/CNT nanocomposites

As shown in Table 5, the order of E/G/HCCNT > E/G/LCCNT > E/G/Parent-CNT > E/G was observed for the values of bending strength and flexural modulus of the E/G-based samples. This could be due to the inherent reinforcing properties of carbon nanotubes and different quantities of COOH functional group on the CNTs surfaces. In order to confirm the experimental data, the results were compared with the reported ones in literature, the results of the present study were in accordance to the ones published in literature. For instance, the improvement in modulus and bending strength of E/G composite was developed by adding CNTs into them [30-31].

Based on the results of the fracture toughness test (Table 5), Parent-CNT exhibits a higher fracture toughness than the E/C composite, which can be attributed to the small size of the nanoparticles and the intrinsic high modulus of CNTs that inherently strengthen the epoxy resin. While, the better performance of HCCNT and LCCNT than that of Parent-CNT can be due to their better interactions with the composite components. The enhancing effect of CNTs on fracture toughness of E/G composite have also been observed in [30].

Here, the increasing effects were laso found for CNTs on the impact test results of the glass fiber-based nanocomposites similira to other mechanical properties. The imrovment effect CNTs on the impact strength of E/G composites have also been reported by Zulfli et al. [30].

The similar changes were observed in the lap shear strength values of the samples (Table 5). This can be assigned to the improving effect of CNTs on the adherence between the glass prepreg and aluminum plates and also to their reinforcing effect on the fiber. The similar alterations were obsrved in the lap shear strength values of the samples (Table 5). It should be noted that the increases impacts on lap shear strength of epoxy material by CNTs have been reported in some studies [32-33].

In the hardness tests (Table 5), it was observed that Parent-CNT nanoparticles do not have a significant effect on the hardness of E/G composites, while the effects of LCCNT and

Sample	Hardness (Shore D)	Lap Shear Strength (MPa)	Impact Strength (J m <sup>-2</sup> )	Fracture Toughness (MPa m <sup>1/2</sup> )	Bending Strength (MPa)	Flexural Modulus (GPa)
E/C	64±1.2	10.7±0.8	86±1.2	6.4±0.37	45±5.5	5.4±250
E/C/Parent-CNT	65±1.0	11.0±0.8	96±8.0	6.9±0.39	47±6.0	5.8±300
E/C/LCCNT	69±0.7	11.4±0.5	97±5.0	10.9±0.6	70±6.0	6.5±150
E/C/HCCNT	73±1.7	12.0±0.7	100±6	11.1±0.4	85±8.0	8.3±300

Table 4 The mechanical characteristics of the carbon fiber-based samples  
4. táblázat A szénszál alapú minták mechanikai jellemzői

Sample	Hardness (Shore D)	Lap Shear Strength (MPa)	Impact Strength (J m <sup>-2</sup> )	Fracture Toughness (MPa m <sup>1/2</sup> )	Bending Strength (MPa)	Flexural Modulus (GPa)
E/G	1.5± 62.3	0.4± 10.5	10± 200	1.0± 19.0	11± 129	0.25± 8.2
E/G/Parent-CNT	1.0± 63.3	0.5± 10.9	11± 205	1.2± 19.4	14± 130	0.23± 8.7
E/G/LCCNT	1.5± 66.0	0.5± 11.4	9.0± 213	1.5± 20.5	10± 133	0.23± 9.1
E/G/HCCNT	2.0± 67.6	0.4± 11.8	14± 267	1.4± 23.6	13± 142	0.27± 9.5

Table 5 The mechanical characteristics of the glass fiber-based samples  
5. táblázat Az üvegszál alapú minták mechanikai jellemzői

HCCNT derivatives are more significant. This can be related to the increase of interfacial interactions in the nanocomposite and also to intrinsic reinforcing effect of CNTs. As a comparison with the reported studies, it was found that Mahadevaswamy et al. have also observed an increasing effect of MWCNTs on the hardness of E/G matrix [31].

It is clear that the presence of COOH functionality on the CNTs surface can play an important role on the mechanical properties of the prepared nanocomposites. These observations can be explained through the type of functional groups, the nature of glass fiber and epoxy resin, and the CNT distribution in nanocomposite bulk. It is expected that the COOH-functionalized CNTs exhibit stronger interactions with the fiber (containing SiO<sub>2</sub> units) and epoxy (containing OH and epoxide groups) than the parent-CNT. However, due to their weaker interactions with the composite bulk, the pure-CNT has revealed the less reinforcement in the E/G composites compared to the functionalized-CNTs. The properties can be a function of nanoparticle distribution in the texture of composites, the strength of E/G and nanoparticle/epoxy interactions, and the potential of nanoparticles to agglomerate. In general, fillers can strengthen polymers by four mechanisms, 1- inherent strength of the filler, 2- reducing the movements of polymer strands, 3- improving the interaction between composite ingredients and 4- interlayer stress transfer. Here, parent-CNT cannot create better interactions with epoxy fibers than LCCNT and HCCNT, thereby which the mechanical characteristics of E/G/Parent-CNT was found to be lower than the samples containing functionalized nanoparticles. Moreover, the imaginable accelerating effect of the functionalized CNTs on the curing process of epoxy (represented in Fig. 4) can also be occurred and effective in the case of E/G composites. The positive effect of pure carbon nanotubes on these mechanical property can be related to its inherent strength. But in the case of functionalized CNTs, the functionalization can affect on the CNT dispersion and E/G interactions as well as intrinsic reinforcing effect of CNTs.

#### 4. Conclusions

The multi wall carbon nanotube and its derivatives were successfully incorporated within the E/C and E/G composite separately via the hand lay up of the fiber prepregs and then compression moulding by using hot press. The SEM analysis confirmed the good dispersion of HCCNT and LCCNT samples into the epoxy/fiber matrices as compared to the Parent-CNT. The mechanical analyses showed the improving effects of the carbon nanotube samples on the epoxy/fiber matrices as the order of HCCNT > LCCNT > Parent-CNT. In other words, HCCNT considerably improves the mechanical characteristics of the nanocomposites in comparison to LCCNT and Parent-CNT.

This could be ascribed to its higher COOH content as compared to other CNTs. Undoubtedly, COOH functionality can induce amphiphilic nature into CNT and affect the CNT dispersion in the epoxy and its interactions with the composite components.

#### References

- [1] Khater, H. M., El Nagar, A. (2021) Evaluation of chloride resistance of silica fume and glass waste MWCNT-geopolymer composite. *Építőanyag-Journal of Silicate Based & Composite Materials*. Vol. 73, No. 2, pp. 44-53. <https://doi.org/10.14382/epitoanyag-jsbcm.2021.8>
- [2] Žižlavský, T., Vyšvařil, M., Rovnaníková, P. (2019) Rheology of natural hydraulic lime pastes modified by non-traditional biopolymeric admixtures. *Építőanyag-Journal of Silicate Based & Composite Materials*. Vol. 71, No. 6, pp. 204-209. <https://doi.org/10.14382/epitoanyag-jsbcm.2019.36>
- [3] Nazarpour-Fard, H. (2022) Composites of polyvinylpyrrolidone and polystyrene with rice husk ash as a bio and silica-rich material: thermal characteristics and water vapor absorption ability. *Építőanyag-Journal of Silicate Based & Composite Materials*. Vol. 74, No. 6, pp. 229-236. <https://doi.org/10.14382/epitoanyag-jsbcm.2022.33>
- [4] Shamsi, R., Asghari, G. H., Mir Mohamad Sadeghi, G., Nazarpour-Fard, H. (2018) The effect of multiwalled carbon nanotube and crosslinking degree on creep-recovery behavior of PET waste originated-polyurethanes and their nanocomposites. *Polymer Composites*. Vol. 39, No. S2, pp. E1013-E1024. <https://doi.org/10.1002/pc.24420>
- [5] Nazarpour-Fard, H., Rad-Moghadam, K., Shirini, F., Beheshty, M. H., Asghari, G. H. (2018) Reinforcement of epoxy resin/carbon fiber composites by carboxylated carbon nanotubes: a dynamic mechanical study. *Polimery*. Vol. 63, No. 4, pp. 253-263. <https://doi.org/10.14314/polimery.2018.4.1>
- [6] Dasari, S., Lohani, S., Prusty, R. K. (2022) An assessment of mechanical behavior of glass fiber/epoxy composites with secondary short carbon fiber reinforcements. *Journal of Applied Polymer Science*. Vol. 139, No. 12, pp. 51841. <https://doi.org/10.1002/app.51841>
- [7] Soethe, V. L., Nohara, E. L., Fontana, L. C., Rezende, M. C. (2011) Radar absorbing materials based on titanium thin film obtained by sputtering technique. *Journal of Aerospace Technology and Management*. Vol. 3, No. 3, pp. 279-286. <https://doi.org/10.5028/jatm.2011.03030511>
- [8] Jagadeesh, P., Puttegowda, M., Girijappa, Y. G. T., Rangappa, S. M., Siengchin, S. (2022) Carbon fiber reinforced areca/sisal hybrid composites for railway interior applications: Mechanical and morphological properties. *Polymer Composites*. Vol. 43, No. 1, pp. 160-172. <https://doi.org/10.1002/PC.26364>
- [9] Heydenreich, R. (1998) Cryotanks in future vehicles. *Cryogenics*. Vol. 38, pp. 125-130. [https://doi.org/10.1016/S0011-2275\(97\)00122-7](https://doi.org/10.1016/S0011-2275(97)00122-7)
- [10] Bechel, V. T., Camping, J. D., Kim, R. Y. (2005) Cryogenic/elevated temperature cycling induced leakage paths in PMCs. *Composites Part B: Engineering*. Vol. 36, No. 2, pp. 171-182. <https://doi.org/10.1016/j.compositesb.2004.03.001>
- [11] Yoshimura, A., Nakao, T., Yashiro, S., Takeda, N. (2008) Improvement on out-of-plane impact resistance of CFRP laminates due to through-the-thickness stitching. *Composites Part A: Applied Science and Manufacturing*. Vol. 39, No. 9, pp. 1370-1379. <https://doi.org/10.1016/j.compositesa.2008.04.019>
- [12] Ray, B. C. (2006) Temperature effect during humid ageing on interfaces of glass and carbon fibers reinforced epoxy composites.



- Journal of Colloid and Interface Science. Vol. 298, No. 1, pp. 111-117. <https://doi.org/10.1016/j.jcis.2005.12.023>
- [13] Rodriguez, A. J., Guzman, M. E., Lim, C. S., Minaie, B. (2011) Mechanical properties of carbon nanofiber/fiber-reinforced hierarchical polymer composites manufactured with multiscale-reinforcement fabrics. Carbon. Vol. 49, No. 3, pp. 937-948. <https://doi.org/10.1016/j.carbon.2010.10.057>
- [14] Vartak, D. A. (2022) Carbon nanotube composites to enhance thermal and electrical properties for space applications-a review. Journal of Environmental Nanotechnology. Vol. 11, No. 3, pp. 11-21. <https://doi.org/10.13074/jent.2022.09.223456>
- [15] Siddiqui, N. A., Khan, S. U., Ma, P. C., Li, C. Y., Kim, J. K. (2011) Manufacturing and characterization of carbon fibre/epoxy composite prepregs containing carbon nanotubes. Composites Part A: Applied Science and Manufacturing. Vol. 42, No. 10, pp.1412-1420. <https://doi.org/10.1016/j.compositesa.2011.06.005>
- [16] Yazid, A. F., Mukhtar, H., Nasir, R., Mohshim, D. F. (2022) Incorporating carbon nanotubes in nanocomposite mixed-matrix membranes for gas separation: a review. Membranes. Vol. 12, No. 6, pp. 589. <https://doi.org/10.3390/membranes12060589>
- [17] Tamayo-Vegas, S., Muhsan, A., Liu, C., Tarfaoui, M., Lafdi, K. (2022) The effect of agglomeration on the electrical and mechanical properties of polymer matrix nanocomposites reinforced with carbon nanotubes. Polymers. Vol. 14, Vol. 9, pp. 1842. <https://doi.org/10.3390/polym14091842>
- [18] Abobo, I. M., Rodriguez, L. D., Salvador, S. D., Siy, H. C., Penaloza, J. D. P. (2021) Effect of organoclay reinforcement on the mechanical and thermal properties of unsaturated polyester resin composites. Epitoanyag-Journal of Silicate Based & Composite Materials. Vol. 73, No. 2, pp. 63-67. <https://doi.org/10.14382/epitoanyag-jsbcm.2021.10>
- [19] Kim, M. G., Hong, J. S., Kang, S. G., Kim C. G. (2008) Enhancement of the crack growth resistance of a carbon/epoxy composite by adding multi-walled carbon nanotubes at a cryogenic temperature. Composites Part A: Applied Science and Manufacturing. Vol. 39, No. 4, pp. 647-654. <https://doi.org/10.1016/j.compositesa.2007.07.017>
- [20] Hossain, M. K., Chowdhury, M. M. R., Salam, M. B. A., Jahan, N., Malone, J., Hosur, M. V., Jeelani, S., Bolden, N. W. (2015) Enhanced mechanical properties of carbon fiber/epoxy composites by incorporating XD-grade carbon nanotube. Journal of Composite Materials. Vol. 49, No. 18, pp. 2251-2263. <https://doi.org/10.1177/0021998314545186>
- [21] Rana, S., Alagirusamy, R., Joshi, M. (2011) Single-walled carbon nanotube incorporated novel three phase carbon/epoxy composite with enhanced properties. Journal of Nanoscience and Nanotechnology. Vol. 11, No. 8, pp. 7033-7036. <https://doi.org/10.1166/jnn.2011.4226>
- [22] Taş, H., Soykok, I. F. (2019) Effects of carbon nanotube inclusion into the carbon fiber reinforced laminated composites on flexural stiffness: A numerical and theoretical study. Composites Part B: Engineering. Vol. 159, pp. 44-52. <https://doi.org/10.1016/j.compositesb.2018.09.055>
- [23] Niazi, M., Beheshty, M. H. (2019) A new latent accelerator and study of its effect on physical, mechanical and shelf-life of carbon fiber epoxy prepreg. Iranian Polymer Journal. Vol. 28, pp. 337-346. <https://doi.org/10.1007/s13726-019-00704-8>
- [24] Seki, Y. (2009) Innovative multifunctional siloxane treatment of jute fiber surface and its effect on the mechanical properties of jute/thermoset composites. Materials Science and Engineering A. Vol. 508, No. (1-2), pp. 247-252. <https://doi.org/10.1016/j.msea.2009.01.043>
- [25] Ma, P. C., Kim, J. K., Tang, B. Z. (2007) Effects of silane functionalization on the properties of carbon nanotube/epoxy nanocomposites. Composites Science and Technology. Vol. 67, No. 14, pp. 2965-2972. <https://doi.org/10.1016/j.compscitech.2007.05.006>
- [26] Srinivasa C. V., Bharath, K. N. (2011) Impact and hardness properties of arca fiber-epoxy reinforced composites. Journal of Materials and Environmental Science. Vol. 2, No. 4, pp. 351-356.
- [27] Bilisik, K., Erdogan, G., Sapanci, E., Gungor, S. (2019) Fracture toughness (mode-II) of nanostitched composites. Procedia Structural Integrity. Vol. 21, pp. 146-153. <https://doi.org/10.1016/j.prostr.2019.12.096>
- [28] Zakaria, M. Y., Sulong, A. B., Sahari, J., Suherman, H. (2015) Effect of the addition of milled carbon fiber as a secondary filler on the electrical conductivity of graphite/epoxy composites for electrical conductive material. Composites Part B: Engineering. Vol. 83, pp. 75-80. <https://doi.org/10.1016/j.compositesb.2015.08.034>
- [29] Gupta, S. K., Shukla, D. K., Kaustubh Ravindra, D. (2021) Effect of nanoalumina in epoxy adhesive on lap shear strength and fracture toughness of aluminium joints. Journal of Adhesion. Vol. 97, No. 2, pp. 117-39. <https://doi.org/10.1080/00218464.2019.1641088>
- [30] Zulfi, N. M., Bakar, A. A., Chow, W. S. (2013) Mechanical and water absorption behaviors of carbon nanotube reinforced epoxy/glass fiber laminates. Journal of Reinforced Plastics and Composites. Vol. 32, No. 22, pp.1715-1721. <https://doi.org/10.1177/0731684413501926>
- [31] Mahadevaswamy, M. B., Aradhya, R., Bhattacharya, S., Jagannathan S. R. Effect of hybrid carbon nanofillers at percolation on electrical and mechanical properties of glass fiber reinforced epoxy. Journal of Applied Polymer Science. Vol. 139, No. 26, pp. e52439 (2022). <https://doi.org/10.1002/app.52439>
- [32] Hsiao, K. T., Alms, J., Advani, S. G. (2003) Use of epoxy/multiwalled carbon nanotubes as adhesives to join graphite fibre reinforced polymer composites. Nanotechnology. Vol. 14, No. 7, 791-793. <https://doi.org/10.1088/0957-4484/14/7/316>
- [33] Srivastava, V. K. (2011) Effect of carbon nanotubes on the strength of adhesive lap joints of C/C and C/C-SiC ceramic fibre composites. International Journal of Adhesion and Adhesives. Vol. 31, No. 6, pp.486-489. <https://doi.org/10.1016/j.ijadhadh.2011.03.006>

Ref:

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