Received: 16 February 2023 | Revised: 12 May 2023 | Accepted: 8 June 2023

DOI: 10.1002/pc.27504

RESEARCH ARTICLE

spe INSPIRING PLASTICS PROFESSIONALS Polymer COMPOSITES WILEY

Experimental evaluation on the synergistic effect of PC/ABS/DGEBA blend in fracture toughness enhancement of CFRP composites at cryogenic temperatures

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Funding information
AICTE National Doctoral Fellowship (NDF) Scheme 2018

Abstract

The current study confirms that modified carbon fiber reinforced polymer (CFRP) composites have higher fracture toughness than unmodified CFRP composites achieved by exploiting the synergistic effect of a polycarbonate (PC)/acrylonitrile butadiene styrene (ABS) blend in toughening the diglycidyl ether of bisphenol A (DGEBA) epoxy resin. The CFRP composite specimens are tested at near cryogenic temperatures using TMA, DMA, and microcrack analysis to determine the best-suited concentration of ABS in the PC/ABS blend. TMA and DMA results, as well as microcrack analysis at cryogenic temperatures (CT), confirm that the blend 90/10 is effective in reducing the brittle nature of DGEBA resin and increasing bond strength, resulting in the fracture toughness enhancement of CFRP specimens at CT. Further investigation of 90/10 modified CFRP (90/10 m-CFRP) and unmodified CFRP specimens using Mode II fracture using ENF test and SEM analysis reveal significant reduction in brittle characteristics of matrix with increase in elongation at failure and fracture surface morphologies confirm nano web-like structures bridging the CF layers, proving to improve fiber/matrix bond strength. This study concludes the effectiveness of hybrid PC/ABS blend in synergistically-modifying DGEBA resin for improved fracture toughness of CFRP laminates across a wide temperature range (−150°C to 150°C).

KEYWORDS

CFRP, cryogenic temperature, fracture toughness, immiscible polymer blends, thermal expansion coefficient

Highlights

- Synergistic effect of PC/ABS blend proves to be more effective in enhancing fracture toughness of CFRPs.
- 90/10 composition of PC/ABS blend exhibits overall performance in enhancing thermos-mechanical properties.
- 10% ABS content in PC/ABS proves to reduce the CTE of modified CFRPs by 20% compared to PC-modified DGEBA-based CFRPs.
- The Mode II interlaminar fracture toughness values exhibits 146.8% enhancement in results compared to unmodified CFRPs.
- PC/ABS blend-modified DGEBA shows better adhesion with carbon fibers compared to unmodified DGEBA.

1 | INTRODUCTION

CFRP laminates are used in many applications where high specific strength materials are required.[1–4] The brittle nature of the thermoset epoxy matrix inherited by CFRPs and the high chances of delamination in laminate layers of composite[5] limits its use in many applications, particularly those requiring cryogenic performance.[6,7] Fiber/matrix modifications improve fracture toughness,[8] reduce delamination[9] and brittleness, and increase resistance to microcracks,[10,11] pushing the use of CFRPs even further. Various thermoset (TS), nanofillers,[12–18] and thermoplastic (TP) based modifiers[10,19–21] and surface coating techniques[22] have been reported to improve CFRP interlaminar fracture toughness (IFT). Improving the IFT of composite laminates is regarded as the most effective method for increasing their resistance to delamination, thereby elevating their significance for broader applications.[23]

Among the various preferred toughening techniques, direct resin modification is considered to the simplest, direct and cost-effective way.[24] The techniques involving the modification of epoxy resin using solvent or melt mixing are the most preferred among the various modification techniques due to their ease of processability. However, with solvent mixing, there is a risk of void formation within the matrix after curing due to the removal of any remaining solvents,[25] which can result in unexpected failures, making it less desirable. The melt-mixing of modifiers into epoxy, on the other hand, ensures easy blending of modifiers with the epoxy resin. Furthermore, the void formation that is common with solvent mixing can be easily avoided. The system is also not completely reliable in the melt-mixed case due to the uncontrollable rise in viscosity after resin modifications.[6] Modified epoxy resins with high modifier thermoplastic concentrations will have much higher viscosity values incompatible for resin infusion. Limiting the modifier concentrations used in melt-mixing can be used to control the rise in viscosity of modified resins. Low modifier concentrations (1.5–2.5 wt%) have been reported to limit the high rise in viscosity after modification, making it suitable for use in resin infusion methods for the development of CFRP composites. Furthermore, 1.5 wt% thermoplastic content in epoxy resin has been shown to effectively increase fracture toughness and resist microcracks in CFRP composites under cryogenic conditions.[10]

Many studies have been conducted to assess the effectiveness of various thermoplastics such as polyetherimide (PEI),[26] poly-acrylonitrile butadiene styrene (pABS),[25,27,28] polyaryletherketone (PAEK),[29] polyethersulfone,[30] polycarbonate (PC),[10,31,32] polybutylene terephthalate (PBT),[10] and others.[33,34] Ductile characteristics are inherited by the TS resin by incorporating a TP modifier,[19,20] resulting in a reduced brittle characteristic, as observed in reported research works over the past years. It has been reported that TS/TP have a synergistic effect in improving the thermal,[8,35] mechanical,[36] and thermo-mechanical properties[37] of CFRPs. All of these works report a threshold value of modifier concentration above which increasing the modifier concentration has a weakening effect in the composites prepared.[10,37] According to reports, the use of TP materials as modifiers in TS matrix increases the fracture toughness of modified CFRPs by imparting ductility to the matrix. Consequently, the hardening of CFRPs can be ensured by a single or multiple schemes, such as bridging, deflecting, deviation, or deformation of crack paths. This will also result in several unfavorable outcomes, including decreased strength, stiffness, and delamination risk in prepared CFRP composites. To ensure a positive synergistic effect after modification, it is essential to choose a TP modifier that is appropriate for the selected TS system. The chemical structure similarity, availability, cost, melting point, and viscosity of the TP modifier with respect to the selected TS resin are among the most important factors to consider before selecting the most suitable TP modifier for the TS resin.

TP hybrid blends can impart synergistic effects that improve thermal and mechanical properties beyond the range of their individual components.[38] Due to their numerous advantages over their individual selves, the synergism effect of two or more types of thermoplastics has been extensively studied. One major example is the widely used industrially preferred PC and ABS plastics. The synergism resulting from PC/ABS for various blend combinations has been thoroughly investigated earlier.[39] It should be noted that PC/ABS blend compositions can produce high mechanical and thermal properties with improved morphologies when compared to their pure states.[40–42] This effectiveness of PC/ABS hybrid blend compositions can be utilized to improve the fracture toughness of epoxy resins by melt-mixing small amounts of TP (<5 wt%) into epoxy. By doing so, the uncontrollable rise in viscosity resulting from high content of TP in epoxy can be controlled to the desired levels and can be made possible for vacuum infusion applications.

It should be noted that the effect of two or more types of TP modifiers on the toughening of epoxy resin at near cryogenic temperatures are rarely investigated and reported. The presence of PC/ABS hybrid blend is expected to act as an agent in enhancing the fiber/matrix interfacial layer toughness at cryogenic temperatures while keeping the viscosity rise as minimum as possible. The current study is a continuation of our previous research work in which we have explored the synergistic effectiveness of hybrid blends of PC/ABS to be used with diglycidyl ether of bisphenol-A (DGEBA) in enhancing the thermal and mechanical properties of CFRP laminates at room conditions. Specifically speaking, this paper investigates the cryogenic toughening capabilities of modified CFRP composites resulting from the synergistic effect of PC/ABS/DGEBA (1.5 wt% of TP in TS) blend with CF fabric. The results along with the results obtained on the thermal characteristics[35] can be used for the development of inner materials for cryogen storage units by exploiting low-concentration cost-effective resin modification process.

2 | MATERIALS AND METHODS

2.1 | Materials

The current work is based on the use of TP modifiers such as PC and/or ABS to modify the TS resin (DGEBA) via a method known as melt-mixing. Virgin quality TPs are purchased to correlate the effect of specified modifications with the DGEBA matrix. Commercially available virgin quality PC and ABS were purchased for the current work from the industries of Makrolon, Germany, and Cycolac, Saudi Arabia, both of which have centres in India. The DGEBA resin, which has an epoxide equivalent weight (EEW) of 185–194 g/eq and is known as YD-128, was purchased from Reliance Industries Ltd. in India. The fiber reinforcement used in this project is a 3K genuine, 220 g/m^2, 2 × 2 Twill Weave carbon fiber (CF) fabric, Manufacturer (Part No. CBC24030), Carbon black Composites, India.

2.2 | Processing method and characterization

The CF fabrics are cut into 150 × 150 mm^2 pieces. Each CF fabric is wiped with acetone and heated in an 80°C vacuum chamber for 1 h as recommended by the supplier. The heated CF fabric is cooled to room temperature before being stacked in 15 layers for vacuum assisted resin infusion (VARI). The layup sequence (−45, 45, 0, 45, −45, 90, 45, 0, −45, 90, 0, −45, 45, 0, 45) was selected and kept similar for all vacuum infused samples. We are currently using DGEBA (YD-128) resin with a viscosity of 3.73 Pa s (at 30°C) as the reference for the resin system. The maximum weight concentration (wt%) set for modifying the DGEBA resin was 1.5 wt% of the resin used for vacuum infusion. This is consistent with Yuxin et al. findings, which confirm 1.5 wt% as the best suitable concentration of TP modifier in DGEBA resin for exhibiting maximum improvement in mechanical and thermal properties for cryogenic applications. As mentioned in our previous research, the DGEBA resin is modified using PC and/or ABS via melt-mixing at 200°C in this work. When the temperature is raised above 200°C, the DGEBA resin begins to show color change and begins to boil within a few seconds. As a result, it is critical to note that, a constant temperature of 200°C must be maintained throughout the processing time. It is also observed that PC takes longer to dissolve into DGEBA than ABS, which may be due to PC's higher melting point than ABS. The modified DGEBA resin with ABS content turns slight yellow[37] compared to DGEBA and PC-modified DGEBA. The modifications include 1.5 wt% TP content, which can be PC, ABS, or a combination of the two. The viscosity versus temperature characteristics for the unmodified and modified resins were determined from Anton Paar Modular Compact Rheometer (MCT102) at National Institute of Technology, Calicut. Table 1 shows the modified resin compositions, and melt-mixing time and temperature and viscosity of uncured resins at 30°C. From the viscosity values at 30°C, it is clear that the modified resin comprising of blend composition 90/10 exhibits the minimum rise in viscosity compared to other modifications. The unmodified and modified resins are mixed with a modified cycloaliphatic amine (TH7301) hardener in a 2:1 weight ratio (suggested by the manufacturer) prior to vacuum infusion into the 15-layer CF fabric

TABLE 1 Data table comprising of resin composition and process parameters.

		Composition (1.5 wt % DGEBA)		Melt-Mixing		
Sample Name	DGEBA (g)	PC (g)	ABS (g)	Temperature (°C)	Time (min)	Viscosity at 30°C (Pa s)
Unmodified DGEBA	200	–	–	–	–	3.730
PC 100 m-DGEBA	200	3	–	200	45	6.191
ABS 100 m-DGEBA	200	–	3		30	8.738
PC/ABS (90/10) m-DGEBA	200	2.7	0.3		45	5.837
PC/ABS (10/90) m-DGEBA	200	0.3	2.7		45	8.998

layup to produce 3 mm thick CFRP composite laminates. After infusion, the laminates are left to cure under vacuum at room temperature for 24 hours, followed by an additional 36 hours of curing before being ready for testing. CFRP specimens are cut from 150 × 150 mm^2 laminate sheets according to ASTM standards for characterization. The current study aims to determine the extent to which a PC/ABS blend has a synergistic effect on the thermo-mechanical properties of CFRP composites at cryogenic temperatures. The specimens are tested over −150°C to 150°C temperature range using thermo-mechanical analysis (TMA) and dynamic mechanical analysis (DMA). The test conditions for TMA are 0.1 N force and at 10°C/min. A dual-cantilever clamp setup with a constant frequency input of 0.5 Hz and at 2°C/min heating rate is used for DMA analysis. After 5 min of maintaining an isothermal condition at −150°C, the specimens are tested. The polished surface of modified and unmodified CFRP is laser scanned at 10× magnification after cryo-cycling for 5 cycles to determine the effect of modification under cryogenic temperatures (CT). Cryo-cycling is a thermal cycle treatment process in which a specimen at 20°C is immersed in a cryo-fluid such as liquid nitrogen (LN_2) to achieve a temperature of −194°C. The specimen is returned to 20°C after reaching −194°C. Before laser scanning, this process is repeated 5 times (5× cryo-cycled). By comparing before and after laser scanned surface morphology images, the surface roughness characteristics of modified and unmodified CFRP, as well as before and after cryo-cycling, can be determined.

The best performing synergistic composition is then selected for Mode II fracture toughness analysis using end-notch flexure (ENF) test as shown in Figure 1. For Mode II analysis, CFRP laminates were manufactured using the VARI method. Ten layers of CF fabric were stacked in the warp direction and a 30-μm-thick PTFE

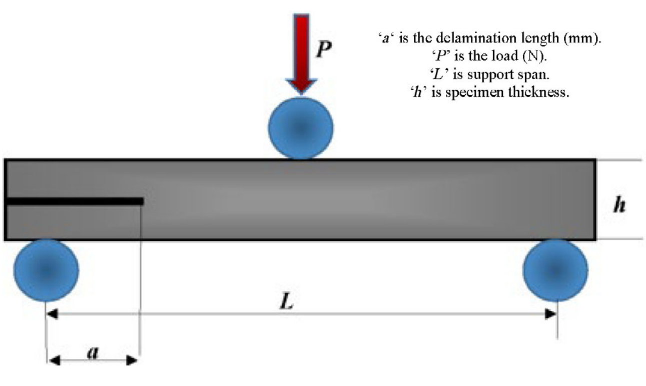

FIGURE 1 Schematic representation of CFRP specimen prepared for end-notched flexure test to perform Mode II Fracture analysis.

non-stick film was inserted between plies #5 and #6 to serve as a crack initiator.[43] The degassed epoxy resin was then infused at 35°C under vacuum. In order to promote fiber impregnation, the test panels were kept at this temperature overnight after infusion. Under the same conditions, a control panel containing no modifications was also prepared. The modified and unmodified CFRP specimens are prepared as per ASTM D6671 standards for ENF testing. The critical energy release rate for Mode II (G_{IIC}) was determined using Equation (1).[43]

$$G_{IIC} = \frac{9P\delta a^2}{2B(2L^3 + 3a^3)} \quad (1)$$

where P, δ, B, a, and $2L$ corresponds to load (N), cross head displacement in the load point (mm), specimen width (mm), delamination length (mm), and span length (mm), respectively, as mentioned in previous research work.[44]

3 | RESULTS AND DISCUSSION

3.1 | Effect of PC/ABS on storage modulus characteristics of modified CFRP using DMA

The stiffness and overall loadbearing capacity of CFRP laminates are determined by the storage modulus value. In our current study, samples are kept in an isothermal state at −150°C for 5 min before testing. As Yuxin previously stated,[10] if the storage modulus values increase at CT, the modification is referred to as bringing cryogenic toughening to the system. In Figure 2A, the storage modulus characteristics tend to decrease in value as the temperature increases from −150°C to 150°C, representing the transition of CFRP characteristics from elastic to visco-elastic state as mentioned in previous works. In our current work, −150°C to 50°C represents a glassy region, followed by a transition region between 50°C and 70°C, and finally a rubbery region beyond 70°C. Because the CF fabrics are unaltered and the layup sequence for all specimens is the same, the variation in storage modulus can be attributed solely to the TP-modified TS resin matrix in the CFRP laminates. It is observed that minor differences in storage modulus values are observed after PC and/or ABS are blended with the DGEBA resin system. Notably, when compared to ABS, modified DGEBA resins with a high PC content exhibit the greatest improvement in storage modulus values (4% increase over unmodified CFRP) as observed earlier.[10,39] The high ABS concentration in DGEBA may cause a coalescence

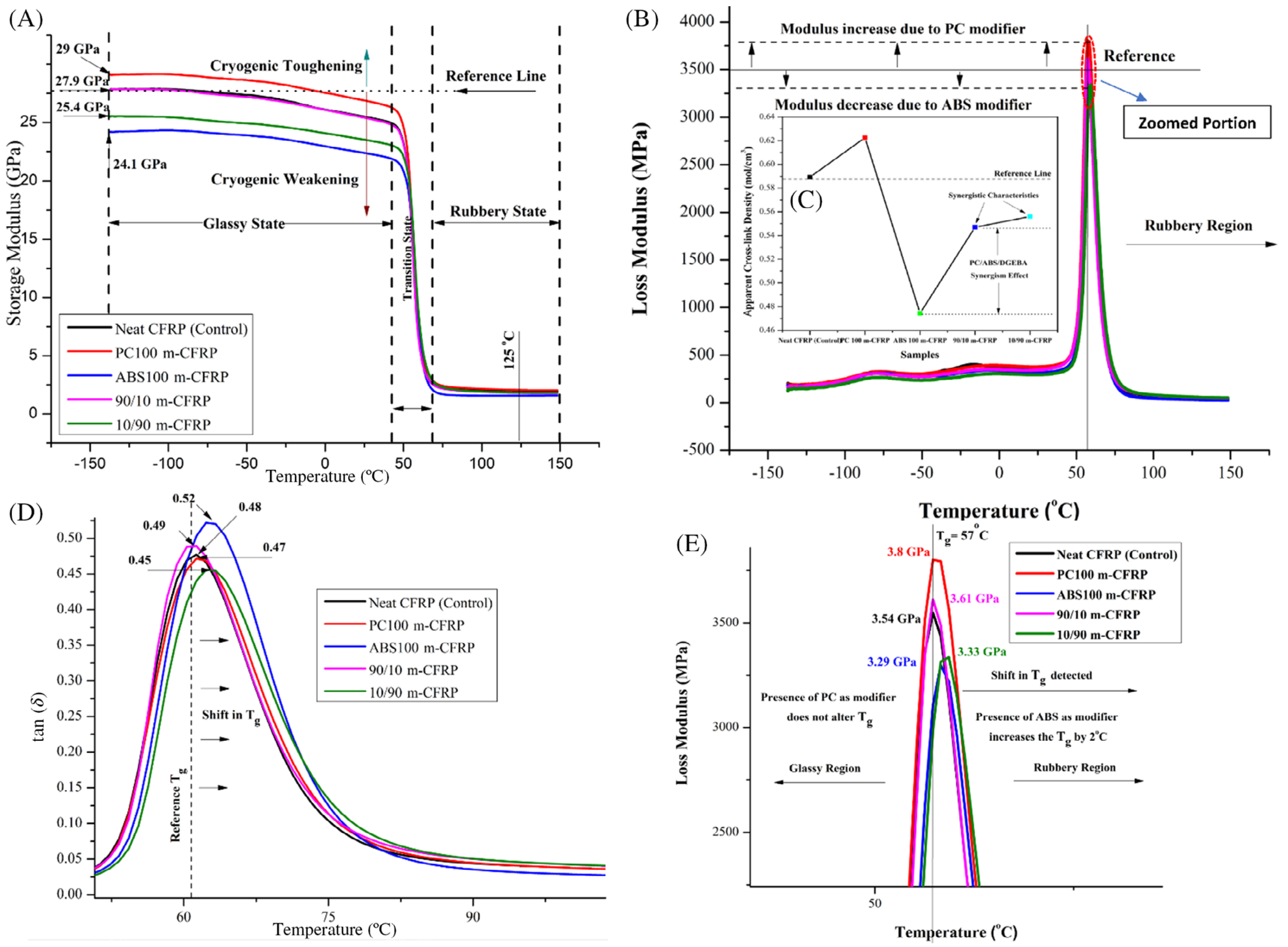

FIGURE 2 DMA curves of unmodified (neat) and modified CFRP laminates (A) storage modulus versus temperature curve, (B) loss modulus versus temperature curve, (C) apparent cross-link density of unmodified (neat) and modified CFRP laminates, (D) tan (δ) versus temperature characteristic curve and (E) zoomed portion of peak characteristics of loss modulus curve.

effect, resulting in void formation within the matrix.[37] As shown in Figure 2A, this can result in lower storage modulus values, resulting in cryogenic weakening. As a result, lower ABS concentrations, such as 10% in this case, are recommended for modifying DGEBA resins. It should also be noted that PC, despite its superior ability to maximize storage modulus, falls short in some areas due to their induced brittleness after −40°C.[10] This can be avoided further by blending PC with low concentrations of ABS, where the rubbery content in ABS ensures that the brittle characteristics of PC at CT are reduced, as confirmed by our previous findings.[8] To confirm this effect, the apparent cross-link density for modified CFRPS was compared to unmodified CFRP, as shown in Figure 2C, where it is clear that at 100% concentration of PC modification, the cross-link density increases, potentially resulting in lower fracture toughness values.[45] This can eventually lead to the expected brittle properties of individual PC-modified CFRPs at CT. Figure 2C also shows that as the ABS concentration in the PC/ABS blend increases, the apparent cross-link density decreases from 0.56 to 0.47 mol/cm^3. The PC/ABS blend composition, which contains 90% PC and 10% ABS, has a moderate cross-link density value[45] compared to other cases. This could lead to higher fracture toughness values when compared to unmodified and other modified CFRP laminates.

The loss modulus also tends to increase in value as the temperature rises from −150°C, reaching peak points at glass transition temperature (Tg) for the composite material as defined by ASTM D4065 and then declining due to viscosity rise, as observed in Figure 2B. The rightward shift observed in peak values of loss modulus shown in Figure 2E indicates higher temperature, which could be due to better fiber/matrix adhesion.[46] It should also be noted that DGEBA with 100% PC modifier has the best performance, followed by 90% PC and 10% ABS blend (90/10). As the concentration of ABS in the

PC/ABS exceeds 10%, the peak loss modulus falls below the reference, represented in Figure 2B.

As shown in Figure 2E, the peak values of the loss modulus curve for 100% ABS concentration (3.29 GPa) were the lowest, followed by 90% ABS concentration (3.33 GPa). However, the blend 90/10, with its synergistic effect, exhibits promising fracture toughness due to the rubber content provided by the blend's 10% ABS concentration.[37] Thus, the presence of lower concentrations of ABS (less than 10%) in PC/ABS can improve fiber/matrix adhesion as well as CFRP load carrying capacity under cryogenic conditions. The additional toughness imparted by the ABS component to the PC prominent blend as a result of PC/ABS synergism may result in improved performance of PC-modified DGEBA under cryogenic conditions. Tan delta (tan (δ)), the mechanical loss factor or the ratio of loss modulus to storage modulus represents the damping properties of a material.[46] Figure 2D depicts the fiber/matrix interface effect and polymeric chain mobility. The peak values of the tan (δ) curve represent the degree of fiber cross-linkage in CFRP composites. The decrease in polymer chain mobility is represented by the rightward shift in the tan (δ) peak.[46]

We can see from Figure 2D that polymer chain mobility increases only for the 90/10 modified CFRP, while it decreases in all other cases. This confirms that as the concentration of ABS in the composition increases, the polymer chain mobility is restricted more. As a result, the 90/10 PC/ABS blend with combined effect of shear yielding capability of PC followed by rubber toughening mechanism of ABS enables it to better perform.[39] When considering load carrying capacity, stiffness, fiber/matrix adhesion and fiber linkage, 90/10 blend modification exhibits more promising characteristics compared to other modifications.

3.2 | Linear thermal expansion characteristics of PC/ABS-modified CFRP composites

Over the temperature range of −150°C to 150°C, under a constant load of 0.1 N, the effect of PC/ABS modifier on the linear change in dimension of modified CFRP relative to unmodified CFRP is investigated. Figure 3A depicts the characteristic curves of modified CFRP with respect to changes in dimension and temperature. As a result of the presence of CF reinforcement, which accounts for 58% of the prepared CFRP composites, the change in dimensions for all samples is negative at −150°C and increases gradually with rise in temperature. Previously, it was observed that TP-modified DGEBA resins undergo much less dimension change at −150°C than unmodified DGEBA.[10] The PC-modified DGEBA exhibits the greatest degree of dimension change at −150°C among these TPs. From Figure 3A, a very similar trend can be observed, in which the CFRP with PC 100% modified DGEBA (PC 100) exhibits the highest levels of dimension change at −150°C.

By adding 10% ABS to PC (90/10 blend), the dimension change of CFRP at −150°C can be reduced by 21.5% in comparison to PC 100 m-CFRP composites. The improved interfacial bonding between CF and modified matrix caused by the low ABS concentrations in the

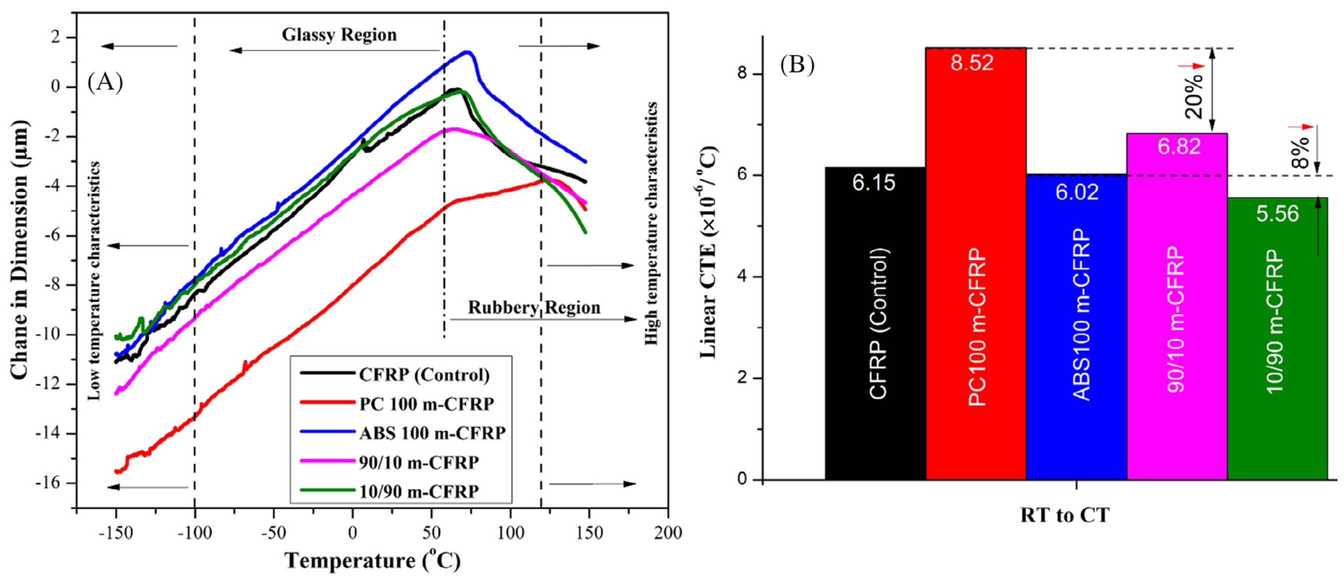

FIGURE 3 (A) TMA characteristic curve from −150°C to 150°C and (B) linear thermal expansion coefficient of unmodified (control) and modified CFRP laminates.

PC/ABS blend can be the reason. As previously reported, DGEBA with low concentrations of ABS exhibits improved fracture toughness as a result of the droplet/matrix morphology that is prevalent in low concentration modified resins. But in the case of ABS 100% and PC/ABS with a 10/90 blend composition, the change in dimension at −150°C is negligible compared to DGEBA-based CFRP composites that have not been modified (control). As the temperature increases from −150°C to Tg, the dimension change of unmodified and modified resins tends to increase linearly. Due to the presence of TPs, such as PC and/or ABS, in the DGEBA resin, the Tg values display a slight shift to the right. This shift in Tg values for modified DGEBA is approximately 2–3°C higher than for unmodified DGEBA resin. In the case of PC 100 modified DGEBA-based CFRP, the change in dimension curve exhibits a slight hump after 56°C (the Tg of unmodified DGEBA) and then follows a linear trend until 140°C, which is very close to the Tg value of PC. PC with a structure similar to DGEBA is partially miscible in DGEBA, which may be the cause of this property. All of the samples exhibit the same characteristics, including a hump in the curve at Tg, where the residual stresses accumulated during curing tend to balance out as a result of increased chain mobility, resulting in a greater change in dimension. After equilibrium is reached through the release of residual stresses, the negative thermal expansion of CF dominates the system, resulting in a further diminution of the change in size.

Figure 3B illustrates the linear coefficient of thermal expansion (CTE) for modified and unmodified DGEBA-based CFRP composites at −150°C. Below Tg values, the CTE values of CFRPs are measured. The unmodified CFRP composites (control) exhibit a linear CTE of 6.15×10^{-6}/ °C as the temperature decreases from room temperature (RT) to near cryogenic temperatures (CT). As previously stated, it is known that the CF have a negative CTE.[11] Since all composites are manufactured with the same orientation of CF, the variation in CTE can be attributed solely to the modified matrix. From Figure 3B, we can confirm that, compared to unmodified CFRP, the CTE of CFRP composites with DGEBA modified using PC 100 composition, as shown in Table 1, tends to increase by 38.2%, whereas the CTE of ABS 100 composites decreases by 2.1%. Reducing CTE values improves the durability of materials for use in applications characterized by extreme thermal cycling environments. Consequently, we can see that in the present case, the ABS 100 composition in DGEBA exhibits promising characteristics for reducing the CTE of CFRPs at temperatures close to cryogenic. Utilizing the synergy of PC/ABS blends, 90/10 and 10/90 blend compositions as shown in Table 1, it is possible to observe a further decrease in CTE values. 10% ABS content in PC/ABS blend reduces CTE values in modified CFRP by 20% compared to PC100 m-CFRP, as shown in Figure 3B whereas 10% PC content in PC/ABS led to an additional 8% reduction in CTE values when compared to ABS100 m-CFRP. The results indicate that the synergy resulting from the PC/ABS blend is superior for modifying CFRP composites with more promising CTE values than the unmodified as well as PC100 and ABS100 composition modified CFRP composites.

3.3 | Surface roughness and microcrack characteristics of modified CFRP

This experiment explains the effect of cryogenic liquid nitrogen (LN2) on the surface morphology of unmodified and modified CFRP composites. Before analysis, the surfaces of the CFRP composites are polished with progressively finer grades of emery paper (Grade 80 to 220). Before cryo-cycling, all polished surfaces were scanned with a laser scanning profilometer for reference. Cryo-cycling is the technique employed here to implement extreme temperature fluctuations on CFRP composites. In order to achieve this, polished CFRP specimens at RT

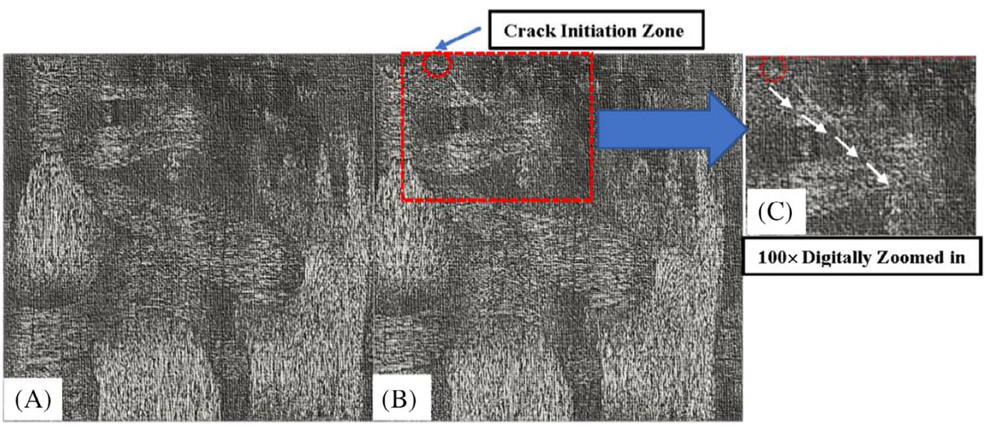

FIGURE 4 Laser scanned image of unmodified CFRP laminates (A) before cryo-cycling, (B) after 5 cryo-cycles and (C) 100× digitally zoomed portion of microcrack region detected after 5 cryo-cycles.

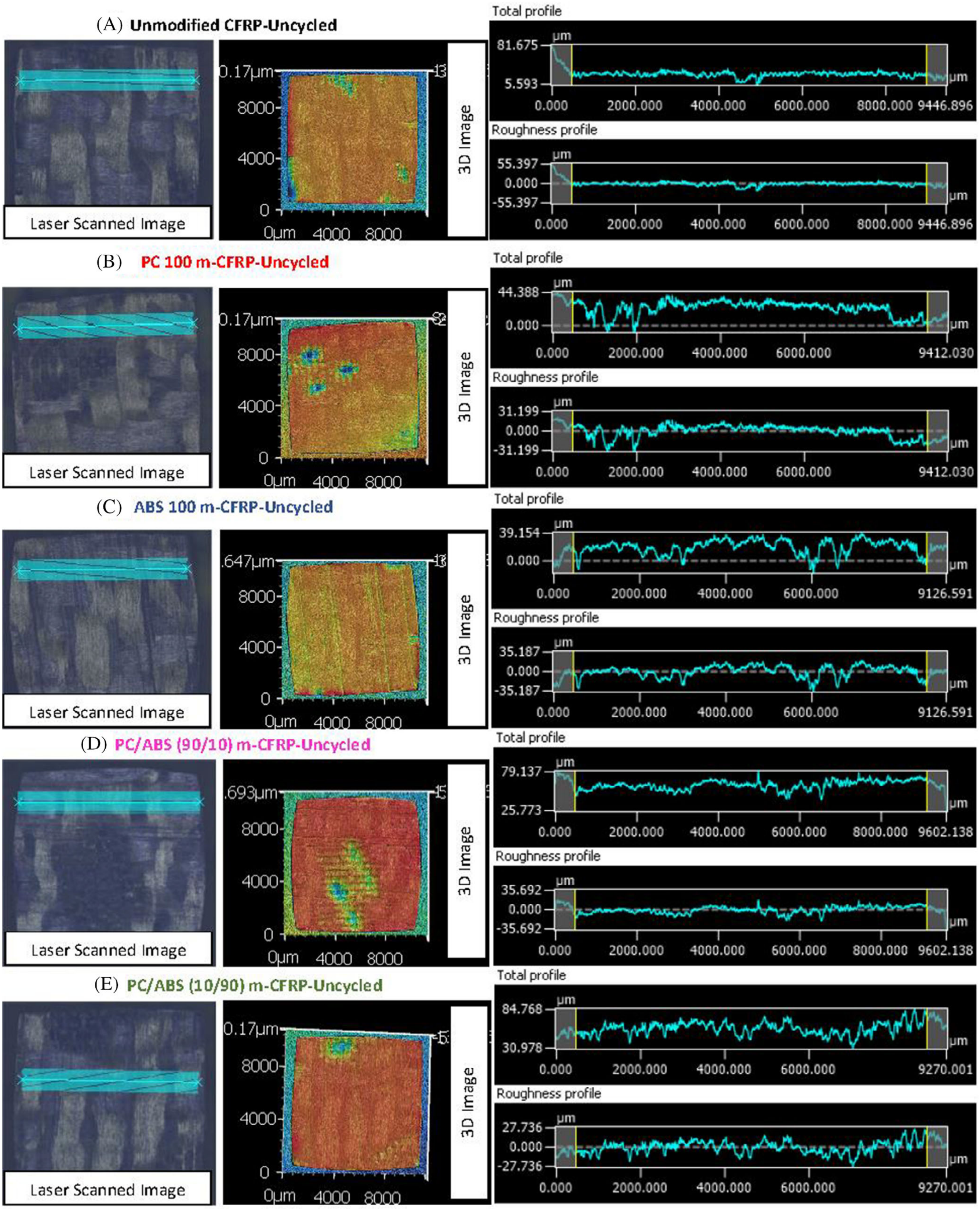

FIGURE 5 CFRP specimens (A) Unmodified CFRP, (B) PC 100 m-CFRP, (C) ABS 100 m-CFRP, (D) PC/ABS (90/10) m-CFRP, and (E) PC/ABS (10/90) m-CFRP laser scanned before cryo-cycling.

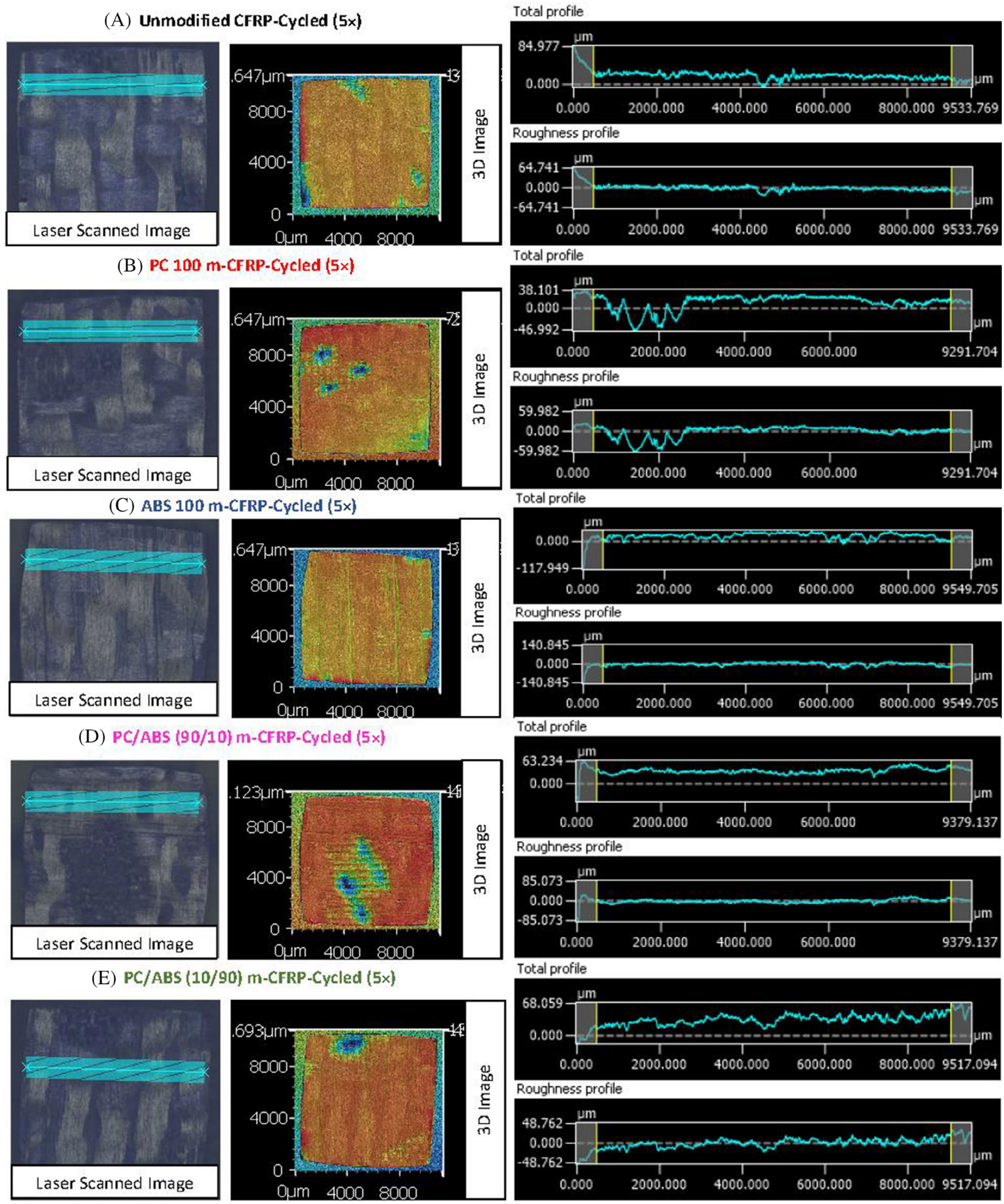

FIGURE 6 CFRP specimens (A) Unmodified CFRP, (B) PC 100 m-CFRP, (C) ABS 100 m-CFRP, (D) PC/ABS (90/10) m-CFRP, and (E) PC/ABS (10/90) m-CFRP laser scanned after cryo-cycled (5×) using liquid nitrogen (LN_2).

are immersed in LN2 and then returned to RT. This is repeated five times before being scanned with a laser. During cryo-cycling, after 5 cycles, a slight crack can be seen on the surface of unmodified CFRP composite as shown in Figure 4. The brittle characteristics of DGEBA matrix fails to restrict microcracks during cryo-cycling as

TABLE 2 Arithmetic average roughness (R_a) values measured using Laser Scanning Profilometer for unmodified and modified CFRP composites before and after cryo-cycling with 90/10 m-CFRP exhibiting reduction in R_a.

	Arithmetic average roughness (R_a)		% Change (↑↓)	
Sample tested	Uncycled	5× cryo-cycled	After modification	After cryo-cycled
Unmodified CFRP	5.239	6.076	–	15.9 ↑
PC100 m-CFRP	10.343	14.415	97.4 ↑	39.4 ↑
ABS100 m-CFRP	8.630	8.750	64.7 ↑	1.40 ↑
PC/ABS (90/10) m-CFRP	5.489	5.193	4.80 ↑	5.40 ↓
PC/ABS (10/90) m-CFRP	6.548	7.568	24.9 ↑	15.6 ↑

shown in Figure 4B. As a result, the microcracks propagate along the matrix as shown in Figure 4C. As shown in Figures 5 and 6, the arithmetic average roughness (R_a) values of unmodified and modified samples before and after cryo-cycling are recorded and analyzed, respectively. As shown in Table 2, the R_a values of DGEBA modified with individual compositions of PC (PC100) and ABS (ABS100) are increased by approximately 97% and 65%, respectively, compared to unmodified CFRP. Incorporating the synergism between PC/ABS blends, the R_a values for 90/10 and 10/90 PC/ABS compositions are reduced to 4.8% and 24.9%, respectively, compared to unmodified CFRP as shown in Table 2. For this reason, we can confirm that the PC/ABS blend compositions 90/10 and 10/90 tend to reduce R_a values by 46.9% and 24.0%, respectively, compared to PC100 and ABS100 compositions. In addition, the effect of cryo-cycling leads to an increase in R_a values exhibiting brittle matrix characteristics at CT.[47]

After cryo-cycling, CFRPs exhibit a slight increase in R_a characteristics relative to all other compositions except the 90/10 blend system. The PC100 composition exhibits the highest levels of brittleness, followed by the ABS100 composition and the 10/90 blend. Surprisingly, the R_a value of the 90/10 blend has decreased when compared to its original uncycled state. This can be attributed to the successful inheritance of plastic properties from the 90/10 PC/ABS blend by the DGEBA matrix, resulting in a reduction of brittle properties at CT. The high levels of fracture toughness for co-continuous thermoplastic phase observed in the 90/10 PC/ABS blend and the droplet/matrix heterogeneous morphology imparted by the 90/10 blend system with DGEBA may account for the decreased brittleness of the 90/10 m-CFRP following cryo-cycling. As stated in previous research, R_a values are comparable to the material's brittleness percentage.[47] Based on the information presented in Table 2, modifier compositions with a predominant PC content tend to exhibit the most brittle properties compared to ABS-dominant compositions. Compared to unmodified CFRP, surface roughness values for CFRP with a PC/ABS blend of 90/10 show only a slight increase.

After cryo-cycling, the 90/10 mixture is the only composition that successfully reduces R_a values. Importantly, the 90/10 composition of DGEBA enables the matrix to have a synergistic effect, resulting in a 5.4% decrease in R_a values after cryo-cycling. Consequently, the overall brittle percentage of the surface decreases, rendering the modified CFRP more plastic. Based on these results, we can conclude that 10% ABS can successfully reduce the brittleness of PC below −40°C.

3.4 | ENF (Mode II Fracture Analysis) of modified CFRP

The end notch flexure test is used to compare the fracture toughness of 90/10 m-CFRP to that of unmodified CFRP in order to verify this property (ENF). Due to the brittle nature of unmodified DGEBA matrix, adhesion between the CF and matrix interface is poor. This reduces the interlaminar fracture toughness of CFRPs, thereby limiting their applicability. In the ENF test, a three-point bending load was applied to analyze the Mode II fracture toughness (G_{IIC}) of unmodified and 90/10 modified CFRP test specimens. Due to the development of cracks with unstable propagation patterns, only one load cycle was applied. Figure 7A,B depicts the load and displacement characteristics curves obtained for the unmodified and 90/10 m-CFRP, respectively. With a 76.7% increase in ultimate load, the 90/10 composition of DGEBA results in improved fracture toughness characteristics compared to unmodified DGEBA. Note that the displacement shifts to the right from 7 mm to 9.8 mm, as shown in Figure 7A,B, respectively. This shift in displacement at ultimate load might be resulting from the induced plastic characteristics of 90/10 blend by the DGEBA matrix. This will also improve matrix/CF bonding, resulting in increased fracture toughness. After ENF testing, the G_{IIC} values for 90/10 m-CFRP indicate a 148.6% improvement

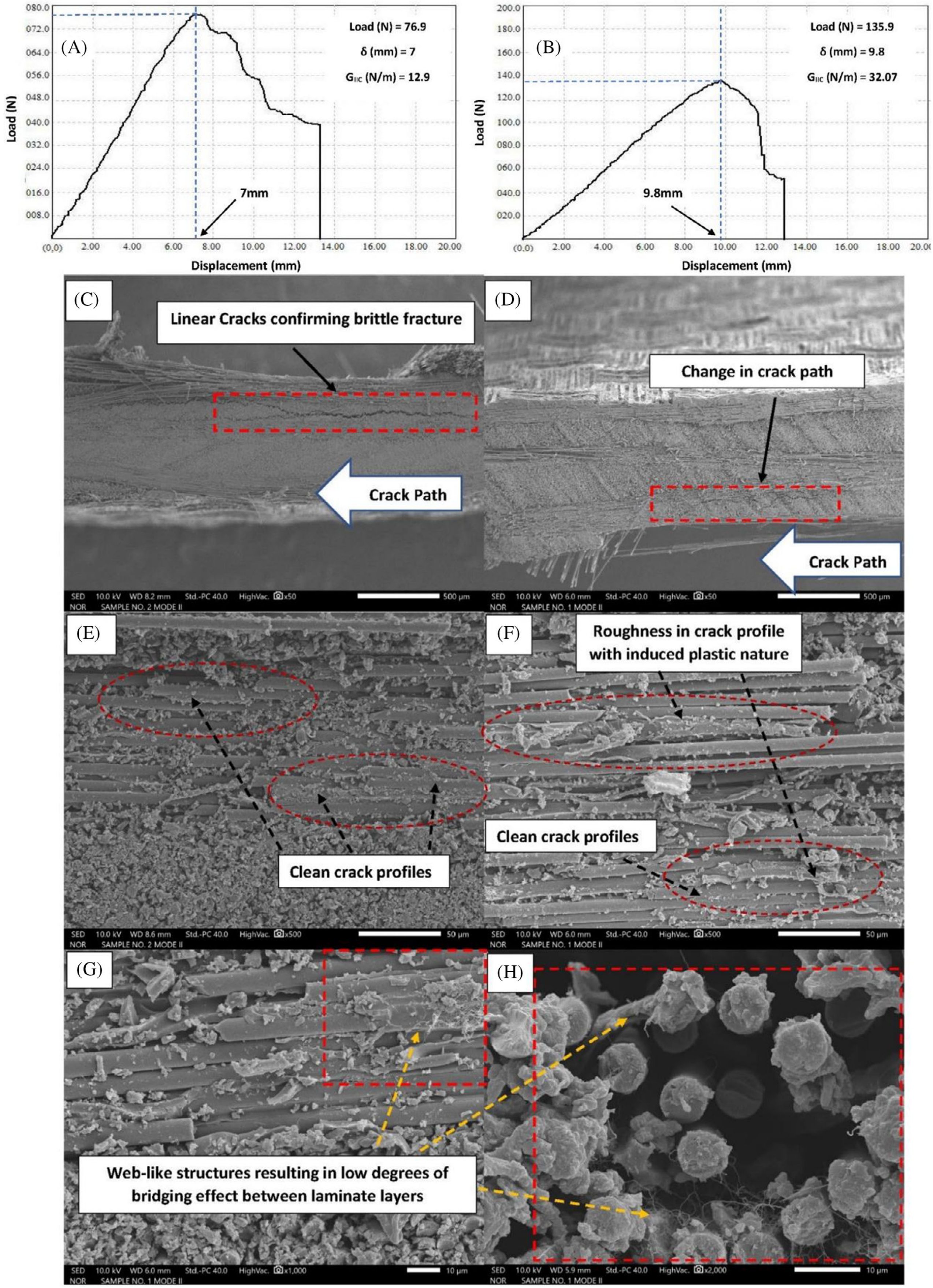

FIGURE 7 Legend on next page.

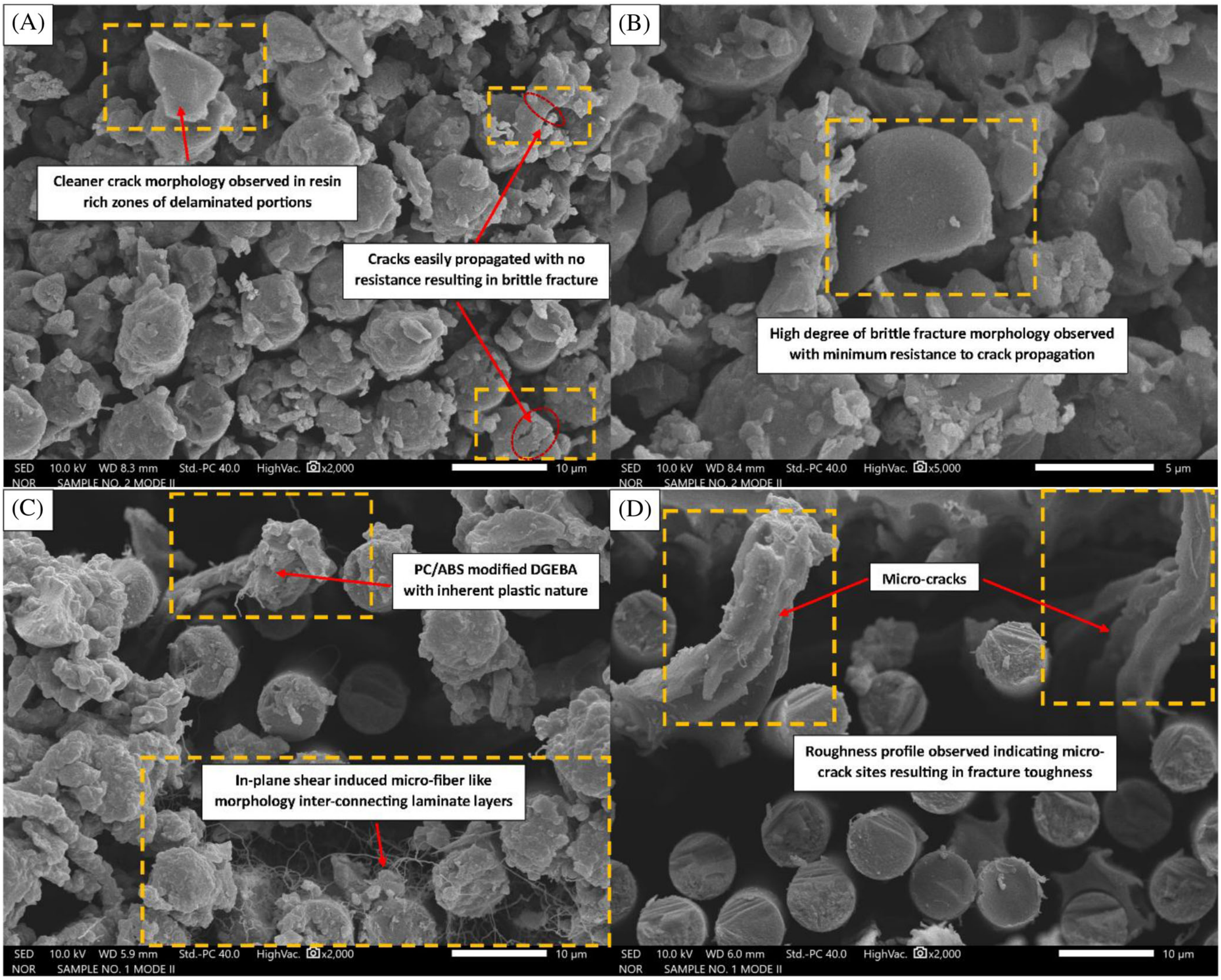

FIGURE 8 Fracture toughness investigation on fracture morphologies after Mode II analysis (A) 2000× magnified, (B) 5000× magnified fracture regions of unmodified CFRP, and (C) and (D) 2000× magnified fracture regions of PC/ABS (90/10) m-CFFRP.

over unmodified CFRP. The fracture toughness confirmation resulting from the synergistic effect of dispersed PC/ABS blend in DGEBA matrix can be investigated from the fracture morphologies from ENF test as shown in Figures 7 and 8. Figure 7C–H illustrates the fracture surface morphologies derived from SEM images. By comparing Figure 7C,D, we can see that unmodified CFRP displays crack propagation without deviation, whereas 90/10 m-CFP displays deviated crack paths. This deviation in crack paths may be caused by the DGEBA matrix's induced plasticity, which restricts crack propagation. Figure 7E–H depicts enlarged SEM images that are used to further confirm the cause of this trend. Figure 7E demonstrates clean crack profiles with less matrix adhesion to CF, confirming high brittleness, whereas Figure 7F displays a mixture of clean and rough crack profiles. The presence of PC/ABS in DGEBA induces portions of plastic properties in the predominately brittle matrix, resulting in roughness in crack profiles. Also, the ENF test reveals greater adhesion between the CF and matrix, resulting in increased fracture toughness. The fracture morphologies at 1000× and 2000×

FIGURE 7 Load versus displacement curve characteristics of (A) unmodified and (B) 90/10 modified CFRP laminates obtained after end-notched flexure (ENF) test, SEM images of fracture surface representing (A) 50× magnified unmodified CFRP, (B) 50× magnified PC/ABS (90/10) m-CFFRP, (C) 500× magnified unmodified CFRP, (D) 500× magnified PC/ABS (90/10) m-CFFRP, (E) 1000× magnified PC/ABS (90/10) m-CFFRP and (F) 2000× magnified PC/ABS (90/10) m-CFFRP after ENF test.

magnification were analyzed to further investigate the reason for the enhanced fracture toughness of 90/10 m-CFRP. Higher magnification images of 90/10 m-CFRP fracture surfaces demonstrate the presence of web-like textures.

During the ENF test, these can form as a result of plastic deformation of the ductile characteristics of PC/ABS dispersed phase in the DGEBA matrix. The 2000× magnified SEM images clearly depict the web-like pattern formed between the CF layers, which resulted in high fracture toughness values during ENF test.

Fiber bridging is the most frequently observed toughening mechanism for CFRPs when twill-woven carbon fiber reinforcement is utilized. Figure 7A,B demonstrates that in the case of TP-modified DGEBA-based CFRPs with twill weave CF reinforcement, matrix toughening schemes such as crack bridging, deviation and/or deflection, and ductile tearing occur, resulting in improved Mode II fracture toughness of 90/10 m-CFRPs over u-CFRPs. The TP tougheners, PC and ABS in a composition of 90/10 work synergistically to toughen the brittle DGEBA matrix. This is accomplished due to the ductile nature of the PC/ABS content melt-mixed into the DGEBA matrix, which tends to undergo ductile tearing and deformation, as depicted in Figure 8C,D, with the formation of multiple microcracks. The more ductile nature of PC/ABS compared to DGEBA resin also permits the formation of elongated microweb-like structures between laminate layers to prevent further crack propagation in CFRPs, thereby achieving fracture toughness. The fracture morphology of 90/10 m-CFRPs, depicted in Figure 8C, reveals this clearly. The combination of ductile tearing and crack bridging validates the efficacy of the 90/10 modifier as a direct toughening agent for the DGEBA matrix for developing high performance polymer-based composites.

Enhancing the fracture toughness of CFRP composites at CT can be accomplished by achieving strong resin/CF interfaces with a 90/10 blend of modified DGEBA resin matrix. SEM micrographs confirm the formation of multiple microcrack sites within the resin-rich zones of CFRP composites based on a critical evaluation of fracture morphologies after ENF testing. As depicted in Figure 8C,D, this can lead to crack deflection by off-plane force, generating new sites of fracture surfaces and resulting in higher strain energy for fracture propagation. Figure 8C,D confirms the tortuous crack propagation morphology that is frequently observed in the case of CFRPs where DGEBA resin/CF exhibits better adhesion, resulting in the brittle resin matrix's inherent plastic properties. As shown in Figure 8A,B, the unmodified DGEBA resin/CF interface clearly demonstrates lower interlaminar fracture toughness. Resin-rich regions exhibit clean fracture surfaces without the presence of microcrack formations, indicating high brittle nature and poor adhesion characteristics with CF. As a result, we observe lower fracture load values in the ENF test, as depicted in Figure 7A. In addition to the formation of microcracks, we observe microweb-like structures connecting the CF laminate layers as shown in high resolution fracture morphologies of 90/10 modified CFRP composites (Figure 8C,D), which may be the result of a tensile load experienced by the cured resin portions in the CFRP composite laminates. This further verifies the inherited plastic nature of the PC/ABS blend by the brittle DGEBA resin, which acts as crack path deviators and contributes to the resin/CF interface's fracture toughness. The resultant toughening effect can be summed up as the inherent effect of tough and ductile PC/ABS in DGEBA matrix and improved adhesion with CF laminates following the scheme of ductile tearing, crack bridging and deviation. Based on the observed results, it is evident that synergism arising from PC/ABS/DGEBA modified resin systems can be utilized to improve the fracture toughness of CFRP composite laminates compared to individual PC or ABS-modified resin systems without significantly increasing the viscosity of the modified resins.

4 | CONCLUSION

This article investigates the effect of PC/ABS synergism on the modification of DGEBA resins for the development of high-performance CFRPs. The research compares the degree of modification of PC/ABS blends to their individual cases. Data from DMA, TMA, and surface roughness analyses indicate that the PC/ABS blend with a 90/10 composition performs the best among the selected compositions. It is a promising material for cryogenic applications because the 90/10 synergy with DGEBA reduces the brittleness of CFRPs after cryocycling even further. Thus, the displacement at ultimate load for 90/10 m-CFRP is 40% greater than that of unmodified CFRP. By incorporating 10% ABS, the PC's induced brittleness at below −40°C can be eliminated. The fracture toughness analysis reveals a 146.7% increase in interlaminar fracture toughness values for 90/10 m-CFRP compared to unmodified CFRP, confirming the efficiency of PC/ABS blend in modifying DGEBA resins for high performance applications. The fracture surface morphologies demonstrate the formation of web-like structures following crack bridging scheme as a result of the PC/ABS-induced plasticity on the brittle DGEBA matrix. The web-like structure formed between the CF layers and the droplet/matrix heterogeneous morphology of the 90/10 modified DGEBA increased the fracture toughness of 90/10 m-CFRP, allowing it to be utilized in high performance industrial applications. The present study along with the thermal characteristics data observed in our earlier published work might help in better understanding of PC/ABS-modified DGEBA systems for developing inner materials for cryogenic storage applications.

ACKNOWLEDGMENTS

It is to be mentioned that the facility helps provided by Cornell Center for Materials Research (CCMR), Cornell University, USA, supported through the NSF MRSEC program (DMR-1719875). National Institute of Technology, Calicut and FAN Services, Maharashtra, India, along with the funding from AICTE National Doctoral Fellowship (NDF) Scheme 2018 at the time of COVID-19 pandemic is the most essential element in the successful completion of this research work. The entire synthesis and fabrication of specimens were performed at Space Technology Laboratory, Department of Mechanical Engineering, TKMCE, Kollam, Kerala, India with the assistance from APJ Abdul Kalam Technological University, Thiruvananthapuram, India.

DATA AVAILABILITY STATEMENT

Data available on request from the authors.

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How to cite this article: Jayarajan A, Krishnan Kutty Elsy Bai RR. Experimental evaluation on the synergistic effect of PC/ABS/DGEBA blend in fracture toughness enhancement of CFRP composites at cryogenic temperatures. *Polym Compos*. 2023;44(9):5499-5513. doi:10.1002/pc.27504