Research Article

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PVDF green nanofibers as potential carriers for improving self-healing and mechanical properties of carbon fiber/epoxy prepregs

Abstract: The novel aligned polyvinylidene fluoride (PVDF) green core–shell nanofibers were reinforced to carbon fiber/epoxy prepregs and were manufactured through the vacuum bagging technique. Aligned nanofibers were achieved by suspending a grounded needle between the nozzle and the collector of electrospinning. The self-healing properties were tested through a periodic three-point bending test at an interval of 24 h at room temperature. The healing behavior was further confirmed through field-emission scanning electron microscopy coupled with dispersion X-ray spectroscopy (EDX) and an electrical conductivity test. The self-healing prepregs (1038.42 MPa) regained 66% of their original strength (1577.85 MPa) after the initial damage. EDX analysis confirmed the elements of the resin (VE (C, O)) and hardener (MEKP (C, O), CN (C, O, Co)) from the ruptured healing carriers. The damaged carbon prepregs healed by showing electrical conductivity of around 83%. The mechanical properties of self-healing composites were tested by tensile, flexural, and Izod impact tests and showed an increment in both flexural (7–12%) and impact strength (5–7%) with the addition of nanofibers. Overall, the research findings provided a design of eco-friendly carriers for carbon fiber-reinforced composites to obtain decent self-healing properties without deteriorating the mechanical strength.

Keywords: aligned nanofibers, carbon prepreg, vacuum bagging, self-healing composites, mechanical properties

1 Introduction

Carbon fiber-reinforced polymer (CFRP) composites are the most popular that are being used in many applications due to their high specific strength, low density, corrosion resistance, and low thermal expansion coefficient [1–4]. In general, CFRP composites experience damage on the surface and inside the composite in their service life with variable loads that may not be visible, which affects the structural integrity and durability [5–7]. Even though the formed cracks are of nano/micro size due to vibrations and dynamic loads or thermal loads, they will propagate with time and lead to significant damage [8,9]. Such microcracks on the surface or within the composites are critical to examine, which leads with the time to the major damage. Even though various non-destructive inspection methods, including micro-CT, ultrasonic test, C-scan, acoustic emission testing, and electromagnetic interference, are available to inspect the nano/microcracks on composite materials [10–13], these techniques have limitations to use for detecting the damages in real-time performance and complicated testing procedures [14].

Nanohealing carriers played a vital role in self-healing applications due to their more advantages and also overcame few limitations of microcapsules such as the absence of resin-filled capsules at the damaged place and non-homogeneous distribution of microcapsules in the composites [15,16]. Nanofibers are the most used nanohealing carriers in self-healing composites, which can be synthesized by an electrospinning process. The electrospinning process is very simple in which nanofibers can be prepared from thermoplastic polymers with controlled morphology and compositions; the process utilizes the electrostatic repulsion to stretch charged precursor polymer solution into a fiber [17]. The nanofibers produced through the electrospinning process are generally multi-oriented and not in an aligned manner; an additional setup is fixed to increase the electrical conductivity to synthesize aligned nanofibers. Aligned nanofibers have the main advantages...
compared with unaligned nanofibers of being utilized as a nanocarrier as the mechanical properties of resulting self-healing composites make the vertical movement of the resin possible during the VARTM process, thereby interlocking the nanofibers in the composites. In addition, the uniformity and distribution throughout the composites could be achieved with aligned nano fibers for obtaining healing process entire the composites. Similarly, a co-axial nozzle is used to prepare core–shell nanofibers in which two types of solutions for both the core and shell were guided through the electrospinning method [18]. Incorporation of nanofibers into composites is a challenging task, and several research groups have worked on the effective interlaying of nanofibers between the reinforcement fabrics to not affect the mechanical properties of the composites. Directly laying nanofibers on the fabrics and reinforcing in the matrix and placing nanofiber mats in between the layers of the reinforcement and fabricating composites are the generally used methods for preparing self-healing composites with reinforcement/core–shell nanofibers [19–21]. The vacuum bagging method is a well-known and very flexible process for consolidating fiber-reinforced polymer laminates; it is a friendly method used to fabricate composites with carbon prepreg [22].

Many research groups have studied the mechanical and self-healing properties of coatings and composites by incorporating nanofibers between reinforcement layers and in polymers. Few works are also published on the fabrication of self-healing composites including core–shell nanofibers. Neisiany et al. incorporated SAN core–shell nanofibers that contain a healing agent (epoxy and curing agent) between reinforcement fabrics and fabricated a self-healing carbon fiber–epoxy composite, and the mechanical properties and curing behaviors both showed that incorporation of nanofibers into carbon layers can impart the conventional carbon/epoxy composite with a self-healing ability, allowing it to repair itself to restore its mechanical properties for up to three cycles at room temperature in the absence of any external driving force [23]. Lee et al. developed PAN self-healing nanofibers and tested their mechanical and self-healing properties through periodic tensile testing; later, they directly embedded the core–shell nanofibers into PDMS and detected that the PDMS-impregnated composites with PRC show good self-healing properties [24]. The results showed that the resin monomer and curing agent were released from the cores of PAN–resin-curing agent (PRC) nanofiber mats that were damaged by tensile tests and up to 15% strain accompanied by irreversible plastic deformation. Neisiany et al. fabricated carbon/epoxy self-healing composites by incorporating PAN core–shell nanofibers as healing carriers and showed a greater improvement in tensile, flexural, and short beam shear strengths. The healing properties were tested with a three-point bending test and confirmed a 96% recovery of strength after 24 h of initial bending fracture [25].

However, this is the first research work, to the best of our knowledge, on green nano-carriers by blending thermostatic starch with PVDF and preparing aligned TPS/PVDF core–shell nano fibers. In addition, the prepared core–shell nano-carriers were incorporated into carbon fiber/epoxy prepregs and their self-healing and mechanical properties were studied. Hence, the above-stated novelty of the research was taken into consideration, and the current study synthesized aligned TPS/PVDF core–shell nanofibers by the electrospinning technique using an additional grounded needle that improves electrical conductivity. The prepared nanofibers were incorporated into carbon fiber/epoxy prepregs by fabricating self-healing composites using vacuum bagging method. Three types of composites were manufactured, such as carbon fiber/epoxy prepregs (CPC), nanofiber-inserted CPC (NCPC), and core–shell nanofiber-inserted CPC (CNPC). The mechanical properties, such as tensile, flexural and impact strengths, of the fabricated prepregs were tested. The self-healing properties of the prepregs were evaluated by a three-point bending test and further confirmed through field-emission scanning electron microscopy coupled with dispersion X-ray spectroscopy (FESEM-EDX) analyses and electrical conductivity tests.

2 Materials and methods

2.1 Materials

Unidirectional carbon fiber/epoxy prepregs (USN125B; thickness: 0.12 mm) were purchased from SK Chemical, Korea. PVDF and glycerol (ACS reagent ≥99.5%) were procured from Samchun Chemicals, South Korea. Cornstarch (72% amylopectin and 28% amylose) was supplied by Samyang Corporation Ltd., South Korea. Cobalt naphthalene (accelerator), methyl ethyl ketone peroxide (MEKP) (catalyst), and vinyl ester (VE) (viscosity = 150 cps and specific gravity = 1.03) were received from CCP Composites, Korea.

2.2 Synthesis of aligned nanofibers

The synthesis of nanofibers was performed by using an electrospinning machine (model: NSI NanoSpinner electrospinning
The polymer solution used for fabricating the nanofibers was prepared by adding 18 wt% PVDF to a 1:3 (w/w) acetone/dimethylformamide mixture and stirring at 80°C for 8 h. Later, 10 wt% TPS (combination of corn starch, glycerol, and DI water) was mixed with the PVDF solution and stirred for 6 h at 80°C. Two different core–shell nanofibers were synthesized by placing VE-CN and MEKP in the core of TPS/PVDF shell nanofibers as described in our previous study [26]. A small modification had been done in the electrospinning machine by suspending a grounded needle between the nozzle and the collector, as shown in Figure 1, to form self-bundling of polymer nanofibers in an aligned manner applicable to both the normal and core–shell nanofibers [27].

2.3 Fabrication of self-healing composites

The composites were manufactured via the vacuum bagging method by using unidirectional carbon prepregs as a reinforcement. Three types of composites were manufactured such as CPC, NCPC, and CNCPC. The fabrication of CPC composite as follows: First, a Teflon sheet was attached onto an aluminum mold and the carbon prepregs were arranged in the laminate sequence (0°/90°/90°/0°), the prepregs were covered with a peel ply, and then a layer of breather was placed over the peel ply to avoid excess resin in the composite. A double-sided sealant tape was attached around the laid prepregs and finally the total setup was sealed with a vacuumed bag by placing an output connected to a vacuum pump. Then, the setup was vacuumized by a vacuum pump and placed in a composite curing oven at a temperature of 120°C for 2 h. A similar process was used to fabricate NCPC and CNCPC composites by placing nanofibers between the carbon/epoxy prepregs, as shown in Figure 1.

2.4 Testing and characterization

The tensile and flexural tests were carried out on a UTM machine (10-ton load, R&B Inc., South Korea) at a crosshead speed of 2 mm/min. The tensile test specimens were prepared (250 mm × 25 mm) by following ASTM D-3039, and the flexural test specimens were sized into 63 mm ×
12.7 mm as per ASTM D-790 with a span length of 16 times the specimen thickness. The Izod impact test was performed on an Izod impact tester (model QC-639F [Cometech, Korea]) of 22 J capacity, and the specimens were prepared (63.5 mm × 12.7 mm with a notch of 2 mm) as per the ASTM D256 standard. The electrical conductivity test was conducted using an electrical conductivity meter (METEX, ME-3200).

Surface and cross-sectional morphologies of fractured specimens were observed by scanning electron microscopy (FESEM, LYRA3xm, Czech Republic) and energy-dispersive X-ray (EDX) spectroscopy at an accelerated voltage of 5–30 kV, and the samples were sputter-coated with gold using an automated fine coater (JEOL JFC-1600).

The self-healing efficiency was evaluated by following the procedure as per our recently published research [26]. Briefly, the periodic flexural tests on the self-healing composites proceeded at an interval of 24 h. The specimens were first tested until their initial damage, and the damaged specimen was left undisturbed for 24 h to get healed and retain its strength, as the VE-CN and MEKP that were present in the core–shell nanofibers required time to come out of ruptured nanofibers, flow through the cracks of the fractured surface, and get solidify by combining each other, which is already discussed in our previous research article.

3 Results and discussion

3.1 Mechanical properties of self-healing composites

3.1.1 Tensile behavior

The tensile test results of CPC, NCPC, and CNCPC composites are presented in Figure 2 and Table 1. The tensile strengths were found to be 668.39, 646.49, and 629.28 MPa, respectively, as shown in Table1. The stress–strain graphs of the three composites are shown in Figure 2(a), indicating that
and modulus of NCPC composites. In contrast, the CPC curve showed higher strength and higher tensile failure elongation and maintained a smooth curve. It showed that the composites containing nanofibers have low tensile strength than the control composites. The decrement of the strength in NCPC and CNCPC composites is due to the presence of nanofibers between the layers of carbon prepregs that act as foreign material and weaken the composites, as shown in Figure 2(d), whereas such voids are not present in CPC composites, as shown in Figure 2(c). The tensile strength acts on the cross section of the specimens and the low-strength resin layers with nanofibers in the cross section lead to the decrease in tensile strength [28].

The tensile modulus values of the composites also follow the same trend as tensile strength and show a reduction in modulus with the addition of nanofibers, as shown in Figure 2(b). The tensile moduli of CPC, NCPC, and CNCPC composites are 35.75, 35.36, and 34.56, respectively. The tensile modulus is a measure of the stiffness of the components present in the composites. As the nanofibers have less stiffness than the carbon fibers, they cannot bear the tensile load and reduces the modulus of the whole composite. Thus, the presence of nanofibers in NCPC and CNCPC reduces the modulus compared to that of the CPC composite. The core–shell nanofibers present in CNCPC are weaker than the solid nanofibers, which reduce the strength and modulus of CNCPC composites compared to those of NCPC composites. The presence of a liquid core inside the nanofibers still weakens and reduces the strength and modulus of NCPC composites.

### 3.1.2 Flexural behavior

The flexural test is conducted to know the bending strength of the composites with the insertion of nanofibers and the flexural stress–strain curves of the composites, as shown in Figure 3(a). The stress–strain curve shows high strength and high percentage of elongation in NCPC and CNCPC composites and has less elongation for CPC composites. The flexural strengths of CPC, NCPC, and CNCPC composites are 1459.29, 1628.95, and 1574.86 MPa, respectively, as tabulated in Table 1. The strong bonding of nanofibers to the matrix can be attributed to the much higher specific surface area of nanofibers. The nanofibers will also break and detach from the matrix when the flexural load is applied on the surface of the composite, and it delays the crack propagation throughout the path of the cracks. Thus, the strengths of NCPC and CNCPC are higher than that of CPC composites.

Additionally, the presence of carbon fibers on the top and bottom layers of the composite initially opposes the load in the concentric load areas, and the effect of load passes through the depth of the composite in which the nanofibers opposes the crack propagation easily. Due to the absence of nanofibers in CPC composites, the cracks will propagate quicker than in the composites with nanofibers. The flexural strength of CNCPC is less than that of NCPC due to the presence of core–shell nanofibers, which contain liquid in their cores and weaken the strength of nanofibers. Due to the presence of weak nanofibers that cannot withstand much load the strength is reduced in NCPC composites, as shown in Figure 3(c and d).

The flexural moduli of CPC, NCPC, and CNCPC composites are 98.38, 102.83, and 99.56 GPa, respectively, as shown in Table 1. The flexural moduli of NCPC and CNCPC composites are higher than that of the CPC composite and can be observed in Figure 3(b). The increment in the moduli of NCPC and CNCPC composites is due to the increase in thickness of the composites with the addition of nanofibers, and the liquid solution in the core–shell nanofibers present in the CNCPC composite as shown in Figure 3(d) is responsible for the reduction in strength compared to that of NCPC composites.

### 3.1.3 Impact behavior

The Izod impact strengths of CPC, NCPC, and CNCPC composites are 0.376, 0.406, and 0.398 J/mm², respectively, as shown in Table 1. The strengths of NCPC and CNCPC composites are higher than that of the control composites, as shown in Figure 4(a). The presence of

### Table 1: Mechanical properties of CPC, NCPC, and CNCPC composites

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Tensile strength (MPa)</th>
<th>Tensile modulus (GPa)</th>
<th>Flexural strength (MPa)</th>
<th>Flexural modulus (GPa)</th>
<th>Impact strength (J/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPC</td>
<td>668.39</td>
<td>35.75</td>
<td>1459.29</td>
<td>98.38</td>
<td>0.376</td>
</tr>
<tr>
<td>NCPC</td>
<td>646.49</td>
<td>35.36</td>
<td>1628.95</td>
<td>102.83</td>
<td>0.406</td>
</tr>
<tr>
<td>CNCPC</td>
<td>629.28</td>
<td>34.56</td>
<td>1574.86</td>
<td>99.56</td>
<td>0.398</td>
</tr>
</tbody>
</table>
nanofibers at the center of carbon preregs opposes the impact of the pendulum and resists the damage to the composite, which helps in the increment of strength, whereas the control composite does not contain such opposition force to show higher strengths. This improvement in Izod impact strength is similarly accredited to nanofibers obstructing crack propagation and supporting the distribution of the applied load, thereby allowing more energy to be absorbed prior to failure. Thus, the strength of control composite is low compared to that of the nanofiber-reinforced composites.

Figure 4(b) shows the total variation of the overall mechanical properties of composites with nanofibers (NCPC and CNCPC). The tensile strengths are decreased by 3 and 6% with the addition of nanofibers in NCPC and CNCPC composites, respectively. Contradictory to tensile properties, the flexural strengths have increased by 12 and 7% for NCPC and CNCPC composites, respectively, compared to that for CPC composites. The Izod impact strengths are increased by 7 and 5% with the addition of nanofibers in NCPC and CNCPC composites, respectively.

3.2 Self-healing properties

3.2.1 Confirmation through mechanical testing

To evaluate the self-healing properties through mechanical testing, a periodic flexural test was conducted on CPC and CNCP composites. The flexural load was applied on CPC and CNCP until initial damage occurred to the specimen and the results were noted. Figure 5 shows the stress–strain graphs of CPC and CNCP composites, and the flexural strengths of both the composites at 0 h
(initial stage) are 1441.73 and 1577.85 MPa, respectively. After 24 h, both composites (CPC and CNCPC) were tested again by the flexural test to know the strength regained after healing. The CNCPC composite retained 66% of its strength and showed a strength of 1038.42 MPa, as shown in Figure 5(b), which confirms the healing ability due to the presence of healing carriers. In contrast, the CPC composite could not retain its energy and showed only 20% of strength after 24 h, which is 292.78 MPa, as shown in Figure 5(a), as there were no healing carriers in the composite. These results of periodic flexural tests confirmed the healing ability of CNCPC composites due to the healing of damaged portions via healing carriers (core–shell nanofibers) [29]. The self-healing efficiency of the CNCPC composites after 24 h is 66% as mentioned in Figure 5(b).

3.2.2 Confirmation through morphology and EDS analysis

The healing phenomenon of the composites is confirmed by FESEM images of the fractured surfaces of self-healing composites (CNCPC composites), as shown in Figure 6. Figure 6(a and b) clearly shows the ruptured nanofibers on the surface of the fractured composites, and the pull-

![Figure 4: (a) Izod impact strengths of CPC, NCPC, and CNCPC composites and (b) % variation in mechanical properties with the addition of nanofibers.](image)

![Figure 5: Flexural stress–strain curves of (a) CPC and (b) CNCPC composites at 24 h interval.](image)
**Figure 6:** (a and c) FESEM images of the fractured surface of CNCPC composites (b and d) Higher magnification of (a) and (c).

**Figure 7:** EDX mapping for the fracture surface of CNCPC composites.
out core–shell nanofibers can also be observed in the figure. The flow of VE-CN and MEKP from the ruptured nanofibers is observed at the yellow pointed places. The holes formed due to the pulling out of nanofibers can be seen in Figure 6(c and d), and the liquid discharging from the damaged nanofibers inside the holes flows and mixes to solidify and can be clearly observed at red marked places.

The flow of the healing agent from core–shell nanofibers is further confirmed through EDS analysis, as shown in Figure 7. To confirm that the spill-out liquid is VE-CN and MEKP, the solidified part in the healed surface of the composite is observed by elemental analysis. Figure 7 shows the elemental analysis of the solidified resin in the fractured surface of CNCPC composites and shows all the elements present in VE (C, O), MEKP (C, O), CN (C, O, Co), and TPS/PVDF (C, O, F). Due to the presence of all elements present in all the components used for core–shell nanofibers and also the liquid in the core, it can be confirmed that the liquid resin comes out and solidifies from the ruptured nanofibers at the time of composite damage.

3.2.3 Confirmation through electrical conductivity

Considering an electric circuit in which the CNCPC composite sample was placed as a conductor and an electric bulb as an indicator, the self-healing process was tested, as shown in Figure 8. The CNCPC specimen and the electric bulb were connected through copper tape and a voltage of 10 V was applied as shown in the figure and also connected to a digital multimeter to read the voltage passing through the circuit. When the circuit was tested with the original specimen as the conductor, the bulb glowed and a voltage of 9.31 V could be observed, as shown in Figure 8(a), which states that the sample is acting as a good conductor. Later, the bulb turned off when the specimen was cut into two pieces and no passage of electricity through the circuit with 0 V in the electrical conductivity meter was observed, as shown in Figure 8(b). The total setup was left undisturbed for 24 h; then, the healing took place due to the resin inside the carriers, and again the specimen acted as a conductor, allowing the bulb to glow and a voltage of 7.88 V was observed in the conductivity meter which is clearly seen in Figure 8(c). This demonstrated that the conductivity of the specimen is recovered and confirmed the healing of the specimen. The decrease of voltage for the second time was due to the obstacle formation of healed resin between the damaged carbon prepregs, and the specimen could regain 83% of electrical conductivity even after total partition, which also confirms the healing process.

4 Conclusion

In this study, a high-strength, self-healing carbon prepreg composite incorporating green PVDF core–shell nanofibers was introduced. The core–shell nanofibers were synthesized successfully in an aligned manner by overhanging a grounded needle. The composites were fabricated by stocking carbon prepregs and nanofibers according to the design proposed via a vacuum bagging method. The major research findings are as follows: the flexural strength increased to 1574.86 MPa with the incorporation of core–shell nanofibers compared to that of CPC (1459.29 MPa), which is almost 7–12%. A similar trend was followed by Izod impact results by improving the strength to 0.398 J/mm² (CNCPC) from 0.376 J/mm² (CPC). However, the tensile results
showed a strength reduction of 3–6% with the incorporation of nanofibers. The self-healing efficiency was calculated with periodic flexural tests over a span of 24 h, and a healing efficiency of 66% was acquired. The fabricated composites have the ability to heal themselves at room temperature without any external efforts. The healing phenomena were confirmed by FESEM and EDS analyses, in which the leakage of the liquid resin (VE-CN) and hardener (MEKP) was observed that flowed through the cracks in damaged specimens. In addition, an electrical conductivity test was performed for further confirmation of the healing phenomena in the self-healing composites considering the self-healing sample as an electric conductor. Therefore, the results strengthened the idea that using core–shell nanofibers as healing carriers has the potential to cure the damage caused to a composite. The prepared self-healing composites can be used in various applications where self-healing of the components is highly required, like mobile phone pouches, tennis rackets, small components in automobiles, and so on.

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