Fabrication of lightweight and high-strength carbon fiber-reinforced poly(ethylene-2,6-naphthalene) solid and foam composites

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Abstract
Poly(ethylene-2,6-naphthalene) (PEN) is one of the most important engineering polymers with high performance. However, the effects and foaming behavior of carbon fiber (CF)-reinforced PEN (CFRPEN) remain to be explored. In this study, PEN was used as the matrix for CF-reinforced composites, and its foaming behavior and mechanical properties were investigated. High mechanical properties can be evaluated through comparison with other similar CF-reinforced thermoplastic composites. A fabrication method to generate lightweight and high-strength CFRPEN composites is hence proposed.

Keywords
poly(ethylene-2,6-naphthalene) (PEN), carbon fiber (CF), foaming, injection molding, polymeric composites

Introduction
Carbon fiber-reinforced composites (CFRCs) are increasingly utilized in a wide variety of fields such as aerospace, automotive, marine, and wind energy sectors, partially due to the excellent and unique properties of CFs such as lightweight, higher specific strength, and corrosion and environmental resistance.¹⁻⁵ However, the essential properties of CFRCs are often limited by the intrinsically poor properties of the matrices. To maximize the function of CF, the selection of the matrix is indispensable and highly important. Compared with traditional thermosetting resins, thermoplastic matrices are somewhat beneficial to recycle, reuse, and protect the environment, which encourage trends of increasing applications.⁶⁻¹¹ However, the heat resistance and mechanical properties of common thermoplastic matrices are often reported to be not competitive enough, which may limit the increasingly restrictive requirements of practical applications. These disadvantages can be partially made up by the use of new materials with improved heat and mechanical properties. For example, poly(ether-ether-ketone) (PEEK), a thermoplastic resin with good heat resistance and high mechanical properties, can be viewed as a successful representative.¹² However, the processability of PEEK is somewhat difficult, owing to its high melting temperature.¹³ In this respect, poly(ethylene 2,6-naphthalate) (PEN) may become an ideal matrix of CFRCs owing to its favorable processing conditions and excellent performance.

PEN is a popular aromatic polyester having a similar chemical structure to poly(ethylene terephthalate) (PET).¹⁴,¹⁵ Compared with the weaker interactions between the molecules of PET, which mainly consists of benzene rings, the interaction between the naphthalene

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rings in PEN is stronger, resulting in higher heat resistance and improved mechanical properties.\textsuperscript{16,17} Advantages of PEN also include excellent stability, outstanding chemical resistance, and barrier properties in comparison with most of the other thermoplastic resins\textsuperscript{18,19} which makes it quite attractive as a candidate for CFRC thermoplastic matrices. However, there have been only a few investigations on CF-reinforced PEN (CFRPEN) composites. Furthermore, as one of the main means of satisfying the requirements of lightweight composites, foam processing\textsuperscript{20–23} has a wide range of applications especially in the aerospace and automotive fields. Unfortunately, there is obviously a lack of research that explores PEN foam processing.

To explore the feasibility of PEN resin applied as a CF-reinforced polymer matrix, CFRPEN composites were fabricated using the conventional impregnation method. The obtained CFRPEN pellets were then injection molded with or without a blowing agent. The results demonstrate that the CFRPEN composites have good processability and foamability, suggesting that the CFRPEN composites are potential lightweight and high-strength materials. In addition, injection molding (IM), which is a versatile technique to manufacture parts with complex geometries at a high production rate as well as utilization of fiber-reinforced materials in particles directly, can be used for CFRPEN preparation. The mechanical strength of CFRPEN foamed products can be retained along with the maximum degree of weight loss.

Experiment

The PEN (TN8085S, melt flow index (MFI): 5.0 g/cm3) and the sized CF (polyacrylonitrile (PAN-based) T700, 12K) used in this study were commercial products. A modified product of 5-phenyltetrazole (5PT) was used as a blowing agent, and which can generate nitrogen at 220°C. The original CFs bundle and the single CF pulled out from the PEN matrix are shown in Figure 1(b), an average cell radius of 97 m and a foam density of 105 cells/cm3 indicate that the processability of PEN is good and is very similar to other kinds of neat polymers such as PET and polycarbonate (PC), although its melt temperature is the highest. The morphological characterization of neat PEN in the molded solid sample is shown in Figure 1(a), which has almost no obvious differences from the neat PET and PC when observed from SEM images. Furthermore, as shown in Figure 1(b), an average cell radius of 97 µm and a foaming density of $1.38 \times 10^5$ cells/cm$^3$ indicate that the foaming effect of neat PEN seems to be not effective enough. However, it is still within the acceptable range considering the foaming conditions used for polymer processing, that is different from the ideal quiescent state used in batch forming.\textsuperscript{22} The foaming density of neat PEN in IM exceeds that of neat PC and PET using the same conventional machine.\textsuperscript{27,28}

The prevalence of CF undoubtedly influences the processability of PEN, which was also reflected by the morphological features. The original CFs bundle and the single CF pulled out from the PEN matrix are shown in
Figure 1(c) and (d), respectively. Although the surface of CFs appears to be smooth (Figure 1(c)), the surface of the pulled CF has many grooves as shown in Figure 1(d). This indicates that an excellent interfacial bonding between CF and PEN matrix existed, which can lead to high mechanical strength. The effects of CFs on the morphology of PEN can be further observed from the solid and foamed samples shown in Figure 1(e) and (f), respectively. The CFs are uniformly dispersed in the PEN matrix, as shown in Figure 1(e), indicating that PEN is completely compatible to be the matrix of CFs. In addition, Figure 1(f) indicates that the CFRPEN composites have a better foaming effect than neat PEN as evidenced by a decrease in the average radius of the cells to 24 μm and an increase of the foaming density to $7.62 \times 10^5$ cells/cm$^3$, which is attributed to the heterogeneous nucleating effect of the existing CFs.$^{24,25}$

The mechanical properties of the solid and foamed IM CFRPEN composites were examined and are shown in Figure 2. The neat PEN sample had a tensile strength of 70.79 MPa and a modulus of 1694.3 MPa, which exceeds most of the engineering plastics such as PC and PET resins.$^{28,29}$ It is expected that the engineering value of tensile strength decreases with the decrease in weight owing to the foam structure. The foamed sample shows an average tensile strength of 61.68 MPa and a modulus of 1688.9 MPa. The decreasing range of mechanical properties and foaming degree basically appear to be
equivalent. Therefore, it is acceptable that the existence of foamed cells did not significantly deteriorate the mechanical properties of products. An addition of 20-wt% CFs was found to improve the tensile strength of PEN to 145.45 MPa and the modulus to 5840.6 MPa, indicating that the reinforcing effect is very remarkable and good interfacial interaction between CFs and PEN exists. Most interestingly, the foamed CFRPEN sample had a tensile strength as high as 146.64 MPa, which is even higher than that of the solid sample, although the modulus of 5489.4 MPa was lower. This indicates that the CF reinforcement effect of the foamed sample is more effective and is possibly attributed to the excellent foaming effect as shown in Figure 1(f). Further investigation of the mechanism is still ongoing.

Figure 3 shows the impact strength of the solid and foamed CFRPEN samples. For the solid samples, a low impact strength PEN sample was obtained first, indicating the matrix with low strength existed. The foaming process can improve the impact strength, as evidence by a high value of the foamed PEN sample compared to that of the solid one. The addition of CF can drastically improve the impact strength of both the solid and foamed samples, suggesting furtherly a good reinforcement effect of CFs.

Nevertheless, it can be concluded that PEN is truly a good CFRC matrix based on the facts that the solid and foamed CFRPEN composites can be easily manufactured by IM method and both have satisfying mechanical properties. Therefore, the fabrication method of lightweight and high-strength CFRPEN composites presented in this work can be thought to be as feasible and reasonable.

Conclusion

Herein, PEN is proposed to be used as a matrix of CFRCs. The feasibility of CFRPEN composite manufacturing was verified in this study. The investigation of processability and foamability using the solid and foamed IM suggest that PEN is a good candidate to be used as a CFRC matrix. It was demonstrated that the CFRPEN composite is an ideal lightweight and high-strength material. This work enriches the research of CFRCs and provides a path for the practical application of CFRC materials.

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