論 文 内 容 の 要 旨

Fiber-reinforced polymer composites (FRPs) are widely used in various fields of application including aerospace, automobile, marine, and structural applications due to their exceptional mechanical properties, good resistance of corrosion, and low density. However, damages, such as interfacial debonding, micro-cracks, and delamination, may occur in FRPs. Recently, cellulose nanofibers (CNFs) have been added as a nano modifier in FRP composites thanks to its outstanding mechanical properties, environmentally friendly, recyclability, low cost, and low density. CNF is an attractive material for improving the mechanical properties of composite materials. Mixing CNFs with epoxy resin can improve both fiber/matrix interfacial strength and the matrix toughness. Due to its hydrophilicity, CNF may require additional surface treatment prior to its use in FRPs. Thus, can result in increasing the resin viscosity making it difficult to impregnate the reinforcing fibers. The performance of fiber-reinforced polymer composites is highly dependent on the fiber/matrix interface bonding. In this study, a new approach by vacuum impregnating glass fibers (GF) with CNFs was proposed to improve the interfacial strength, and avoid processing high viscosity resin or the formation of aggregations in the matrix.

In the first part, different concentrations of CNFs were prepared by ultrasonication and then applied to the surface of glass fibers to improve mechanical properties of glass fiber-reinforced epoxy (GF/EP) composites. In order to evaluate the effect of CNFs on the interfacial shear strength (IFSS), single GF was pull out from glass fabric, and immersed into CNF solutions. After few seconds, the GF was taken out, and then dried to remove the moisture before the formation of epoxy resin. Microdroplet tests were conducted to determine the glass fiber/epoxy (GF/EP) adhesion by calculating the IFSS. As for the macromechanical effect of CNFs on GF/EP composites, vacuum assisted resin transfer molding (VaRTM) technique was used to incorporate CNFs into woven glass fiber laminates. CNFs were successfully grafted onto GF surfaces, and the treated laminate (GF-CNFs) were then used to manufacture GFRP composites. Two composite laminate systems (untreated: GF/EP and CNFs-treated: GF-CNFs/EP composites) were manufactured using VaRTM process. Flexural strength of the composite laminate was determined by three-point bending tests. Scanning electron microscope was used to characterize the morphology of the GF surface treated with CNFs, and eventually to determine the strengthening mechanisms. The surface of CNF-treated GF indicated a rougher than that of untreated GF. The results from the mechanical tests indicated that the mechanical properties improved with the increase of CNF concentrations. A maximum increase of 78% in the IFSS was obtained at with the optimum CNF concentration (10 ppm wt%), while a 20 % enhancement was found the flexural strength of the modified GF-CNF/EP composites, with respect to the unmodified GF/EP composite. The improvement in IFSS was attributed to the web-like thin thickness layer of about 279 nm grafted onto GF surface allowing a good impregnation of GF with the resin. The roughness of the reinforcing fiber surface in the GF-CNF/EP composites played also an important role in this result. From the quantitative evaluation, it was found that this CNFs layer became thicker with increasing the CNF content leading to a decrease of the IFSS of GF-CNF/EP composites. The mechanisms behind the improvement in flexural strength and flexural fatigue were considered as mechanical interlocking, and matrix toughness from CNF bridging between neighboring fibers. The results suggested that grafting a low quantity of CNF onto glass fiber can significantly improve the interfacial strength of glass fiber/epoxy composites.

In the second part, the influence of CNFs on fatigue properties of GFRP composite was investigated. However, VaRTM process was improved to avoid the irregular surface of one side of laminated composite

by replacing peel ply with an aluminum plate. Successfully, flatter and smoother surfaces of manufactured composites were obtained. Thus, the flexural strength and flexural fatigue of the GF/EP and GF-CNF/EP composites were evaluated after three-point bending tests. The fatigue tests were conducted under low cycle stress at a stress ratio R = 0.1, and a frequency of 5 Hz. The low frequency was selected because the use of high frequency may cause internal heating in the specimen, and then leads to decreasing the fatigue properties. A field-emission scanning electron microscope was used to characterize the strengthening mechanisms. The flexural modulus remained constant in all CNF concentrations except 0.5 wt% while the flexural strength increased slightly with increasing the CNF concentration. An improvement of 6% (from 429 MPa to 454 MPa) was observed in the GF-CNF/EP composite at 0.1wt% in comparison with the neat GF/epoxy composite. Although this result is lower than that obtained in the previous experiment, it has been found to be more reliable due to the improvement in the surface of the composite. However, for the same CNF concentration, the fatigue life increased by five times higher than the GF/EP composite. At 0.5 wt%, the flexural modulus and strength decreased due to the CNF clusters formed onto glass fiber resulting in hindering the impregnation of GF with EP resin. The low number of cycles found can be attributed to the high stress level used during the fatigue tests. The fracture surface indicated that the presence of CNFs on the GF surface increased the interfacial bonding between GFs and EP resulting in improving the fatigue life.

Finally, cellulose nanofibers (CNFs) were used to improve the fracture toughness of glass fiber reinforced epoxy composites (GFRPs). Although, grafting CNFs onto GFs by vacuum impregnation has shown to be a potential method to improve flexural strength and fatigue life of GFRP composite, this method may be limited for improving interlaminar fracture toughness. Because, with this method CNFs were more present on the outer layers of GF laminate than those in the middle. Therefore, in this section different CNF suspensions (0.05, 0.075 and 0.1 wt%) were prepared and sprayed onto the surface of glass fiber laminates at the mid-plane. The vacuum resin transfer molding (VaRTM) process was used to manufacture the GFRP composite laminates. End notched flexure tests were conducted to evaluate the effect of CNFs on the critical energy release rate in mode II fracture toughness GIIC. The interlaminar fracture toughness GIIC was improved by 28% with the addition of 0.05 wt% of CNFs to GF/epoxy composites, whereas with 0.1 wt% of CNFs content it a degradation was observed due to the uncomplete impregnation of GF with epoxy resin resulting from thickening of CNF layer at the interfacial laminates. The toughening mechanism for this improvement was investigated using a field-emission electron microscope. Shear hackles and large epoxy deformations were found to be the predominant mechanisms for improving the interfacial strength of GF-CNF / EP composites.