論 文 の 内 容 の 要 旨
Thesis Summary

論文題目　Development of Polyaniline (PANI)-Based Conductive Thermosetting Matrix for FRPs and Their Structural Applications
(導電性ポリアニリンを用いたFRP用熱硬化型樹脂の開発と構造部材への適用)

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In the recent years, aerospace industry has seen a gradual shift from metallic structures to the Carbon Fiber Reinforced Plastics (CFRPs) in structural applications. CFRPs have shown remarkable properties in many structural areas but, there are still some issues which need to be addressed in the near future. One of them is the loss of the electrical properties of carbon fibers in thickness and longitudinal directions in epoxy based CFRPs. This loss of electrical conductivity of the composites can be attributed to the insulating behavior of the resin matrix. To improve the electrical properties of the composites many researchers have tried to add conductive filler into the insulating matrix. Adding CNT, carbon black, graphene etc. into the insulating matrices is the most common methodology employed. However, using this methodology, very high electrical properties have not yet been realized, especially in case of thermosetting composites. Recently, researchers have tried many other alternative ways and have also shown great interest in conductive polymer based composites. A highly conductive composite material with good mechanical properties is the need of the hour in present industrial and academic fields. Therefore, a thermoset conductive composite with high mechanical and electrical properties has been tried to be developed in this work and its application have been investigated especially structural applications of conductive CFRPs.

Since the discovery of intrinsically conductive polymers (ICPs), they have attracted tremendous attention of researchers. Conductive polymer based composites have been researched extensively due to their outstanding properties and vast applications. Polypyrrole (PPY), ploy (3, 4-ethylenedioxythiophene) (PEDOT) and polyaniline (PANI) are the most studied conductive polymers. PANI has a special status among all the conducting polymers. PANI has been the center

of research due to its ease in availability, ability to tune electrical conductivity and remarkable optical properties. It is well known that, emeraldine base form of PANI can be rendered conductive by doping with a protonic acid. In the present work dodecylebenzenesulfonic acid (DBSA) has been used as a dopant for PANI due to its surfactant properties which improves the solubility of the PANI-DBSA complex in the matrix i.e. DVB.

A unique one-step synthesis process of PANI-DBSA/DVB composite has been demonstrated in this work while choosing divinylbenzene (DVB) as the matrix. It is demonstrated that a PANI-DBSA/DVB composite has very high electrical and good mechanical properties after curing. However, due to the low environmental stability (early start of curing at room temperature) of this matrix, a parametric study has been done to optimize the present system. Roll-milling process and control doping process of PANI have been introduced for the mass production of this thermosetting conductive resin system. High electrical & mechanical properties with good environmental stability were aimed in the final composite. To improve electrical conductivity and mechanical properties of the system, additional conductive filler VGCF was also used. With addition of additional conductive filler VGCF-H, higher electrical conductivity and better mechanical properties have been achieved. The idea of using additional conductive fillers was derived by the hypothesis that PANI-DBSA agglomerates are the conductive islands in the insulating DVB matrix. Therefore, additional conductive fillers can be used as the conductive connecting bridge between those islands, simultaneously improving the mechanical properties. Different combinations of dopant ratios and conductive fillers were tried with the main PANI-DBSA/DVB matrix and their effects on composite properties have been investigated.

Prepared composite has been characterized using various techniques like; Fourier transform infra-red spectroscopy (FTIR), ultra violet-visible-near infrared red spectroscopy (UV-vis-NIR), thermogravimetric analysis (TGA), thermal optical microscopy, electromagnetic interference (EMI) shielding measurements and four-probe electrical conductivity. The effect of dispersion on electrical and mechanical properties has also been elaborated using scanning electron microscope (SEM) micrographs.

Applications of this composite system have been investigated. This conductive resin system was used to impregnate FRPs to prepare highly conductive FRPs. Carbon fiber reinforced composite prepared by using PANI-based thermosetting resin (CF/PANI) has shown approximately 36 times higher electrical conductivity as compared to epoxy based CFRPs (CF/Epoxy) in the direction of thickness and approximately 6 times higher in the direction of fiber.

It is observed that high electric and dielectric properties contribute to the high EMI shielding efficiency. Therefore, this composite find its application in EMI shielding technology as well. The composite with VGCF-H as additional conductive filler has shown 73 dB shielding effectiveness at 13.2 GHz with the composition of 5 wt. % VGCF, 45 wt. % PANI-DBSA and 50 wt. % DVB in the composite. Electrical conductivity up to 1.97 S/cm with the addition of 5 wt. % VGCF-H and flexural modulus up to 1.71 GPa with 3 wt. % of VGCF-H have also been achieved. These results confirmed that a polymer thermoset conductive composite with improved electrical, mechanical and very high EMI shielding effectiveness has been successfully prepared.

These outstanding results make the PANI-DBSA/DVB composite a potential candidate for light strike protection (LSP), structural capacitor and EMI shielding material. This work gives a start towards unravelling the new horizon of applications of Structural Conductive Composites.