論 文 の 内 容 の 要 旨

論文題目　Development of conductive polymer composites using curable dopants
（硬化型ドーパントを用いた導電性ポリマー複合材料の開発）

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Aerospace engineering needs constant upgradation through continuous research and multidisciplinary development. This research work is such an example in which the author tried to apply the emerging field of conducting polymers into the fabrication of CFRP panels for application in aircraft industries. CFRP with its high strength and low weight is one of the most critical material for the 21st century. Owing to the high mechanical strength, low weight CFRP has made its way into various sectors like aerospace, automobiles, space vehicles, etc. Additionally, CFRPs also provide exceptional durability and low thermal expansion. This makes it an attractive material for shipbuilding and other externally exposed materials. . Conventional CFRPs are fabricated from Carbon fibres impregnated with an insulating resin like epoxy. The conductivity of such panels comes only from the conducting carbon fibres resulting in non-isotropic and non-uniform conductivity as compared to the metallic counterparts. This dielectric nature of the resin results in numerous limitations of the CFRP like limited lightning strike resistance. Lightning strike is a very prominent and frequent danger for the aircrafts. They can not only damage the structural integrity of the plane and hamper the radio system, but also sometimes severe attacks can cause fatal accidents due to fuel vapour ignition. Aircrafts companies generally use an efficient and sophisticated Lightning strike protection (LSP) system, which is a multilayer technology to provide metallic conductive path for the lightning current to pass and hence protect the aircraft from damages. However, this strategy does not aid in the goal of a lightweight aircraft plan. This technology not only adds money to the overall cost but also adds weight to the overall aircraft. Researchers have attempted to incorporate conducting nanoparticles like graphene and carbon nanotubes into epoxy, but that comes with its own limitations of agglomerations and percolation threshold . Conducting polymers　are a promising way to accomplish a successful solution to this problem and providing in-built LSP. Polyaniline (PANI) is a hotspot for scientists in various fields owing to its many attractive properties like easy and economical availability , tunable conductivity. Our research team has been working on PANI and developed a PANI/DBSA-DVB based resin that has accomplished to be effective against lightning strike. This resin based CFRP has high conductivity and toughness, however the resin lacks stability and demonstrated compromised mechanical properties. This is due to a lack of connectivity between the three distinct and functionally dissimilar materials which constitute the resin system. Therefore, this thesis attempts to introduce the new concept of curable dopants. These are the class of dopants which can not only provide conductivity to the resin through PANI, but also cure to form a mechanically strengthened composite. P-2M is a methacrylate containing acid which is predicted to behave like a curable dopant. This thesis efforts to verify that by detailed characterisation by using Thermal microscopy, UV-Vis spectroscopy , FTIR, Differential Scanning Calorimetry (DSC) to confirm the functionality of P-2M as a curable dopant to PANI. All these techniques were used to characterize and confirm the functionality of P-2M as a curable dopant. The doping was qualitatively confirmed by Thermal microscopy, UV-Vis spectroscopy and FTIR spectroscopy. The curing was confirmed by the structural changes shown in the FTIR analysis. Further using DSC, we estimated the exact amount of time for doping the complex of PANI-P-2M. After the positive results, a conductive thermoset resin was synthesized after thorough optimisation and analysis of the activation and curing energy . The activation energy was evaluated by using both Kissinger’ s method and Barret’ s method. This is the first work on the cure kinetics analysis of a PANI based conductive resin material. Thereby the curing profile was obtained by estimating the curing energy. The amount of heat was provided in terms of curing temperature, duration of heating, applied pressure in the hot press and the post curing temperature and duration. The PANI/P-2M resin was cured to obtain an electrical conductivity of 0.5 S/m in the resin with 20 wt. % of PANI. The flexural modulus didn’ t show quite a small variation (2.5-3.2 GPa). This can be ascribed to the fact that P-2M is a bi-functional material which is being used for both conductivity and strength, however by two quite different mechanisms and hence employing two different functional groups. The rheological analysis of the resin showed a highly stable steady-state viscosity (1500 mPa.s for the 20 wt. % PANI resin) which is quite favourable for CFRP fabrication. , the strength of the material is not immensely affected by the addition of PANI or doping complex in the resin. This mechanical property is comparable with epoxy resin. The uncured neat resin showed Newtonian behaviour and for the resin with PANI added we observed shear thinning properties owing to the good dispersion and de-agglomeration of the resin with higher shear rates. Hence, this resin can be used to develop prepregs to fabricate CFRPs using this PANI-P-2M resin.

Further the resin was used to fabricate CFRPs by using the technique of previously impregnated and stored carbon fibres i. e. prepregs. This is the first report of a CFRP fabricated using the prepreg technique for a PANI based conducting thermoset resin. The stability of the prepreg was studied in detail. The PANI/P-2M resin remains shining and maintains its phase and state for a very long period even at room temperature. As compared to the previous resin of PANI/DBSA ,which hardened within hours of synthesis, this new resin remains completely in the state of liquid . This ability aids in the prepregs synthesis, industrial storage, transportation of the resin. Further, the DSC of the resin was also monitored from time to time and the heat of reaction was estimated . The viscosity of these resins was varied from room temperature (25 ^{o}C) to higher temperature (55 ^{o}C). epoxy resin also shows similar response with temperature , the viscosity initially decreases with increasing temperature and then it starts increasing as the resin approaches towards curing. The resin shows steady state viscosity in a favourable range , thereby successful CFRP fabrication is achieved through prepreg stacking technique. The prepregs were studied for a span of 80 days. The resin viscosity remained almost same at ~1500 mPa.s. the morphology also showed how the resin shows a shiny texture even after hours of synthesis, whereas the previous resin hardens sooner. In order to understand the resin reactivity, we also studied the resin viscosity with temperature and like epoxy resin, the PANI/P-2M resin shows initial drop in the viscosity and subsequently hardening of the resin as it goes towards curing. The prepregs stacked for 80 days also showed similar texture as day 0. Thus, the attempt to apply prepreg technique with long storage time to PANI based conductive resin is achieved successfully. The CFRPs showed flexural modulus 45 ± 1 GPa and the conductivity of 0.14 ±0.02 S/cm for the sample with 10 wt. % PANI. The samples were morphologically analysed to study the damage development and the effect of the amount of PANI. In the next step, another methacrylate group based material called TMP was introduced into the resin to enhance its mechanical properties. Although TMP could enhance the mechanical strength of the sample, but the modulus remained unchanged at any significant level. Therefore TMP is reported as a strength enhancer and doesn’t aid in the conductivity of the samples. As part of a very basic analysis, the CFRP samples were tested under simulated lightning strike conditions to verify the resin effectiveness against lightning strikes. Simulated lightning strike was applied to the specimens using an impulse current generator (developed by Otowa electric Co., Ltd., owned by National Composite Centre Japan at Nagoya University). Physical examination shows that unlike epoxy there was no burning of the sample. However, owing to the high impact the panel suffered from delamination . The NDI results demonstrate that the impact is only in the first layer and the internal layers seem intact. Therefore the Lightning strike test applied on the samples showed that the CF/PANI-P-2M is effective at a preliminary stage test and confirmed lower damage as compared to CF/Epoxy samples. Further, the detailed analysis of the sample constitution for achieving the maximum lightning strike effectiveness can be studied further.

Polyaniline has been very well studied as a component of the conductive resin material for the CFRPs . This thesis also introduces a new concept of curable dopants for PANI. However, no work has been reported yet about the theoretical analysis on the PANI based resin. This research also attempts to predict the material properties of the PANI based resin using molecular dynamics simulations. The study is to predict the modulus of the resin as we change the amount of PANI using MD simulations through JOCTA software. COGNAC is a general purpose molecular dynamics program developed to handle various coarse grained and atomistic models. It can be used to study higher order structure and physical properties of polymeric materials. Here we have used it to study the mechanical properties of the polymeric materials like Youngs modulus and the stress strain curve. The COGNAC models of the 3D cell boxes were subjected uniaxial deformation using NVT (constant number of atoms, volume and temperature) simulation and the constant strain was applied along z-direction. The stress-strain curves of the simulated resin under longitudinal loading direction were also calculated. The elastic modulus was computed from the linear regime of the stress-strain curve. This thesis gives a qualitative comparison between the results obtained by experimental analysis and MD simuations. The trend is similar in both of them , however the difference between the exact values can be reduced when the detailed quantitative analysis is done.

In conclusion, this research introduces a concept of curable dopant for PANI to synthesize conductive structural composites to be used as an aircraft CFRP. This research also attempts to predict the mechanical properties of the resin using MD simulations.