氏名（本籍・生年月日）	王毅　（　中国・　西暦 1984 年 12　月 1　日）
学位の種類	博士（　工学　）
学位記番号	乙　第　227　号
学位授与の日付	平成 26 年 3 月 20 日
学位授与の要件	信州大学学位規程第５条第２項該当
学位論文題目	Development and characterization of nano functionally graded materials
論文審査委員	主査　教　授　倪 慶清
	教　授　鮑 力民
	教　授　村上　泰
	准教授　夏木　俊明
	教　授　邱　建輝　（秋田県立大学）

論　文　内　容　の　要　旨

In this work, Nanofiller employed and polymer based functionally graded materials (FGMs) have been developed using a centrifugal method, the exploration of fabricating nano FGM under different condition is conducted, also the properties of FGM is characterized.

As the matrix, polymer has unique advantage because of its excellent mechanical and electrical insulation properties, lightness, and low cost. Due to the limitation of processing methods for polymer FGMs, there are not so much application compared to ceramic or metal based FGMs.

Preparing FGMs with nano particle is a challenging work. Nano particle has its own problem of aggregation when disperse in the matrix. The dispersion have been always the main obstacle for the nanocomposites in industry application.

Under centrifugal environment, the density difference between the polymer and nanofiller become the main factor that influence movement of nanofiller in the polymer. In that case, proper nanofiller and polymer is very important. Detailed contents as follows:

(1)Vapor-grown carbon-fiber (VGCF)-incorporated polymer-based functionally graded materials (FGMs) were produced. Epoxy was used as the matrix, under relative high viscosity, the experiments were conducted at room temperature and the centrifugation speed was varied from 1000 rpm to 3000 rpm with a constant centrifugation time. In order to study the effect of centrifugation time on the VGCF distribution in the matrix, for each centrifugation speed, centrifugation times of 30 min and 60 min were used. The results confirmed that the volume content of VGCF in the epoxy substrate increased as a function of the normalized thickness along the centrifugal force direction, which caused a gradient. A uniform VGCF gradient in the composite can be observed using field-emission scanning electron microscopy. Along the centrifugal force, the friction coefficient of the middle part decreased to about 0.1, and the friction coefficient of the bottom slice decreased to 0.05, i.e., as the VGCF concentration increased to 1.6 vol%, the friction coefficient of the FGM decreased to 25% that of the original value. For the electrical conductivity, it was found that when the VGCF content reached 0.8 vol% in the composites, a significant decrease in the volume resistivity appeared as a result of the formation of conductive pathways in the nanocomposites at the percolation threshold. Microwave absorption varies from the different contents of VGCFs. The bottom of the FGMs exhibits the best microwave absorbing property. The minimum reflection loss of bottom sample is about -4 dB at 10 GHz when d= 2 mm represents the best absorbing porperty.

The results indicate that the grading process lead to a VGCF content change in dielectric, significantly affecting the microwave absorption behavior. Gradual VGCF incorporation within an epoxy resin effectively produced depth gradients in the fiber distribution, microstructure, mechanical, and electrical conductivities and microwave absorbing properties. This VGCF-grading capability indicated that it is possible to tailor desired gradient filler content distributions by careful selection of the processing parameters to control variations in the property and microstructure precisely.

(2) Functionally graded multiwalled carbon nanotube (MWCNT) reinforced epoxy matrix composites are fabricated. Under relative low viscosity of epoxy, aggregation of the MWCNTs during the epoxy curing process is prevented using a two-step aminosilane modification. In the first step, the surface of MWCNTs was oxidized using nitric acid. In the second step, the silane coupling agent was used to modify the surface of oxidized MWCNTs. Chemical interaction of the silane with the oxidized nanotube surface is confirmed using Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. Raman spectroscopy of acid-treated MWCNTs corroborates the formation of surface defects owing to the introduction of carboxyl groups.

With silane treatment to the MWCNTs, the MWCNT content in the epoxy matrix increased as a function of the normalized thickness along the direction of the centrifugation force. The storage modulus increased gradually with increasing MWCNT content in the whole range. The value of tan delta increased with MWCNT content and that T_g also increased with MWCNT content, which further confirmed the gradient in the properties of the materials. The mechanical and microwave absorption property gradients of the composites correspond with those produced via silane modification indicating potential application to microwave absorbing materials. The MWCNTs are better dispersed in the epoxy resin after the modification, making it possible for them become efficiently graded in the epoxy matrix.

(3) Functionally graded nano-TiO_2 epoxy matrix composites were successfully fabricated. In the preparation of the composite, under relative low viscosity, the aggregation of nano-TiO_2 occurred during curing, which had a negative effect on the composite performance. To solve this problem, we introduced a silane coupling agent to modify the surface of the nano-TiO_2, thereby improving the performance and mechanical properties simultaneously. Prior to application of the agent, 5 vol% pure water in ethanol was prepared, and then the silane coupling agent was diluted in the water/ethanol system to give a 1 wt% solution. The amounts of coupling agent (%) added were based on the weight percentage of the filler. The treated TiO_2 was then dried at 100 °C for 5 h to allow complete evaporation of ethanol. The modified nano-TiO_2 (s-TiO_2) had better dispersion in the epoxy resin, making it possible to produce depth gradients of the mechanical properties of functionally graded materials (FGMs). The s-TiO_2 was characterized with respect to functional groups, morphology, and chemical elements using transmission electron microscopy, X-ray photoelectron spectroscopy, and Fourier-transform infrared spectroscopy. Although the s-TiO_2 had been washed several times and sonicated in ethanol before the TEM measurements, a thin layer of thickness several nanometers was still attached to the surface of the TiO_2. The survey scans of the treated TiO_2 showed the presence of Ti, O, C, N, and Si, indicating that the TiO_2 surface was silanized. From top slice of the FGM to the bottom, the hardness increases 2.5-fold. Also the microwave absorption properties were characterized and discussed.

(4) The electromagnetic (EM) wave absorption performance of the FGMs and homogeneous material (HM) was compared and discussed. Through approximate calculation, FGMs displayed a better absorption property than HM in the whole range of frequency. Based on the analysis, we consider that the absorption properties of FGMs can be predicted by the calculation, in this case, prior to fabricating, the demanded absorbing ability of FGMs may designed in advance, which can be used to instruct the preparing. As a result, the graded structure design is suggested to used to fabricate the EM wave absorbing materials.