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User Report

Production of nanocomposites

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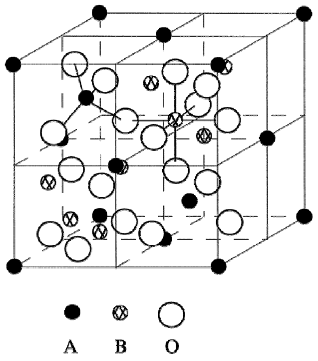

Corvette Visby, a low signature ship built almost entirely of polymer composite materials (Försvarets Bildbyrå/Peter Nilsson)

Crystal lattice of a spinel ferrite unit cell, a potential nanoparticle radar absorber

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Abstract (not more than 200 words)

This report summarises the work done during 2002 towards the production of polymer-based nanocomposite materials. Two other reports have been published during the year, and these present the work in more detail. References to these reports are given. In addition, a presentation was made at the International conference on Nanostructured Materials, July 2002.

During this year most emphasis has been placed on synthesis of ferrite nanoparticles with a range of compositions, and preliminary experiments have been made to integrate these into an acrylic polymer matrix. Most recently an apparatus for ultra-violet curing of polymers has been constructed, and this will be tested before the end of 2002. The focus next year will be to optimise the polymer matrix and functionalisation of the nanoparticle surfaces.

Initial measurements of the microwave properties of the samples produced have been made. The experiments were successful, but show that the properties of the materials made to date are not those desired.

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Tillverkning av nanokompositer

Sammanfattning (högst 200 ord)

Rapporten sammanfattar det arbete som utförts under 2002 gällande tillverkning av polymerbaserade nanokompositmaterialer. Två andra rapporter har publicerats under året och dessa presenterar arbetet mera utförligt. Hänvisningar finns till dessa rapporter. Dessutom har en presentation gjorts vid ”International Conference on Nanostructured Materials” i juli 2002.

Under året har tyngdpunkten lagts på syntes av ferritnanopartiklar med olika sammansättningar och preliminära experiment har utförts i syfte att integrera dessa i en akrylat polymermatris. Nyligen har en apparat för ultraviolett härdning av polymerer konstruerats, tester kommer att genomföras innan årets slut. Nästa år kommer vi att fokusera på att optimera polymermatriser och på funktionalisering av nanopartikelytorna.

Initiala mätningar på microvågsegenskaperna i de tillverkade materialproven har gjorts. Experimenten lyckades men visar att vi har ännu inte uppnått de önskade materialegenskaperna i de tillverkade materialen.

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4. **Research activities**

Introduction

This report summarises the work done during the period 1 January 2002 to 30 November 2002 in the project Nanocomposite Materials (Sv. Nanokomposit-material).

Since this project was started in January 2001 it has been divided (at the request of the client) into two parts:

Part 1 – Planning and preparations for a programme on "Nanotechnology in Defence Applications," which will be reported separately at the end of February 2003. An interim report [1] was published in June 2002.

Part 2 – Production and characterisation of multifunctional polymer nanocomposite materials, which is in collaboration with the project "Avancerade radarabsorbenter" at FOI and the departments of Polymer Technology and Materials Chemistry at the Royal Institute of Technology, Stockholm.

Part 2 will be briefly reported here. More details have been published in a status report [2] and a thesis [3]. A presentation was made at the International conference on Nanostructured Materials, July 2002 [4]

Objective

The objective of this work is to combine the functions of microwave (radar) absorption with a reasonable degree of mechanical load-bearing capacity. Presently used materials are one of two types:

a) load-carrying materials (e.g. carbon-fibre reinforced polymers) which have a limited degree of microwave absorption due to electrical losses in the carbon fibres. Further reduction in radar signature has been obtained by geometrical design of the object (aeroplane, surface ship, etc) to reflect radar away from enemy radar detectors. This approach has limited applicability due to the difficulty of reconciling the geometrical shapes with other essential functions such as streamlining, and will be less and less useful as bistatic radar systems become more widespread.

b) surface coatings containing magnetic lossy particles in a polymer matrix. Theses are applied to the object (aeroplane, vehicle, ship, etc) after the latter is manufactured, and contribute nothing to the load-carrying capacity of the structure. Instead these radar absorbing coatings represent parasitic weight (especially important in aerospace), and are often sensitive to degradation by normal weather conditions.

The rational behind this project is to incorporate magnetic lossy particles (possibly at a later date also electrical lossy fibres) into the polymer matrix which fills the spaces between the mechanical reinforcement of a conventional fibre reinforced composite. This polymer constitutes about 30 vol. percent of the composite and at present serves only to distribute mechanical loads from the structure to the fibre reinforcements. It is also a weak part of the material, as failure by delamination is a common problem in fibre reinforced composites. Such failures are difficult to detect, impossible to repair and may extend over areas much larger than an apparent damage to the surface.

It has been shown that addition of quite small levels of inorganic nanoparticles and nanofibres can greatly improve the chemical, physical and mechanical properties of all types of polymers, including thermosets (e.g. epoxies) and thermoplastics (e.g. polycarbonate). Additions of less than 5 vol. percent have been shown to greatly improve primary properties such as mechanical strength and elastic modulus and secondary properties such as fire resistance, thermal conductivity and heat softening temperature. It is important to note that comparable additions of conventional (micrometre) size particles will have little positive effect on mechanical properties and a considerable negative effect on properties such as toughness and damage tolerance.

The hypothesis to be tested in this work is that by making small additions of lossy nanoparticles a microwave absorbing function can be integrated into a polymer, which simultaneously will show comparable or improved mechanical properties.

Project organisation

This project is jointly financed by the two FOI projects: *Nanocomposite material* and *Advanced radar absorbers*.

The project is conducted in collaboration between FOI and two research departments at the Royal Institute of Technology, department of Polymer Technology. Professor Ulf Gedde is responsible for developing the process technology to integrate magnetic nanoparticles into the polymer matrix. At the department of Materials Chemistry, Professor Mamoun Mohammed is responsible for synthesis of the magnetic nanoparticles.

A doctoral student is employed at KTH and is “shared” between the two departments. In addition, the student has the possibility to participate in measurements made at FOI.

FOI is responsible for measurement and interpretation of the microwave properties of the materials produced.

Due to the original student (Andrew Horvath, employed from 1 August 2001 to 31 September 2002) resigning from the project a new doctoral student was employed from 15 September 2002). Otherwise, the project continues as planned, although the personnel changes have naturally caused some slight delays.

At the request of the client this project is extended by one year, and will now be completed in December 2004.

Research activities

Much of what has been done within the project to date has already been reported [3], [2] and will therefore only be summarised here.

The project is treated in three parts:

1) synthesis of spinel ferrite nanoparticles and studies of their electromagnetic properties
2) selection of suitable polymer matrices and development of methods to integrate the ferrite nanoparticles into the polymer matrix
3) microwave studies of the resulting nanocomposites

These parts cannot be treated independently, and some overlap is actively encouraged, e.g. some experiments to integrate ferrite nanoparticles into a thermosetting (acrylic) polymer have already been made under Part 1.

Part 1

Ferrites are considered as promising materials for microwave absorbers, and are used in existing materials for this purpose. They have a wide range of magnetic properties, which can be tuned by varying the composition. In the present application it is necessary to optimise the composition for *maximum* magnetic loss. It can be noted that as the Curie temperature of these types of materials is often high, and they are stable to high temperatures, spinel ferrites may have some potential as high temperature microwave absorbers. In such applications the matrix must of course also be temperature resistant. High temperature polymers (some of which are capable of use at temperatures up to 200-300 °C) may be used, or for even higher temperatures ceramic matrices may be necessary. Relatively large (micron-size) particles are used at present, dispersed in polymer and rubber matrices. Such large particles are detrimental to the material's mechanical properties.

Ferrites have been and are being studied intensively, as they have important potential for use in various electronic applications. There also seems to be interest in these materials as drug carriers and contrast agents in medical treatments. The crystal structure of ferrites is complex, as shown in figure 1 below.

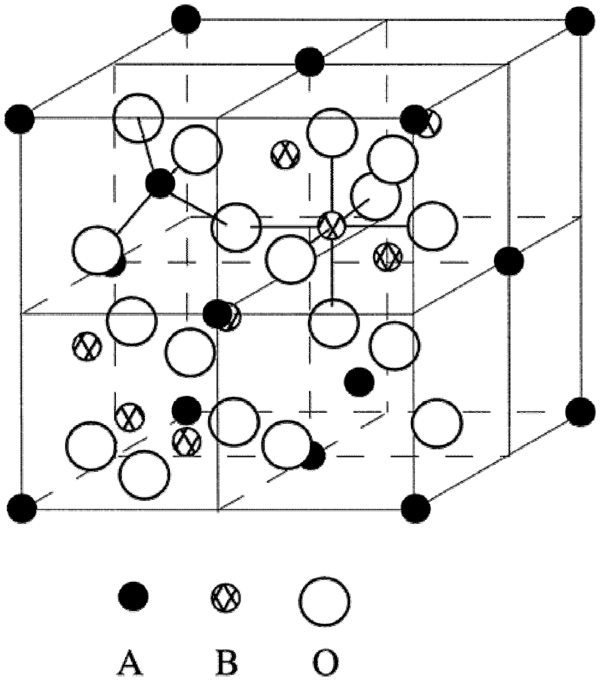

Figure 1. Structure of a spinel ferrite

The atoms A and B can be one of several divalent transition metal ions (e.g. Ni, Zn, Mn, Co, Cu), which gives considerable flexibility to modify and optimise the composition, and therefore the magnetic and electronic properties. It has also been noted in this work that depending on the method of synthesis, the positions of the A and B transition metal ions may vary. Several methods have been studied, as described by [2].

Valin has used chemical precipitation to prepare ferrite nanoparticles with a typical size of 16 nm and composition $Ni_{0.5}Zn_{0.4}Cu_{0.1}Fe_2O_4$. The system was modelled thermodynamically to obtain the optimum conditions of concentration and pH. These nanoparticles were examined by transmission electron microscopy (TEM), x-ray diffraction (XRD), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). Despite the relatively high temperature of the precipitation reaction (80 °C) it was found that heat treatment of the ferrite nanoparticles at various temperatures after precipitation could lead to improved crystallinity.

Some preliminary attempts were made to mix the ferrite nanoparticles produced with a conventional thermosetting acrylic polymer. This was done by mixing the nanoparticles with acrylic powder, followed by hot-pressing. Acrylic was chosen as a convenient and readily available matrix, and is not optimised for microwave absorption applications.

Nanoparticles have a great tendency to agglomerate, due to Van der Vaals forces between the particles, and their high surface energy. De-agglomeration before admixture with the acrylic is essential. This is a complex subject, and requires that the surfaces of the nanoparticles be functionalised by bonding with molecules which are compatible with both the inorganic surface of the nanoparticle itself, the organic polymer matrix and other demands for thermal stability, etc.

Functionalisation can be done as part of the nanoparticle synthesis process, which is perhaps preferable when all other parameters have been optimized or at a later stage which is simpler. In the present case a simple functionalisation, involving attachment of an organosilane compound to the nanoparticles was chosen. The molecule used was 3-(aminopropyl)-trimethoxysilane (APTMS). The organic (aminopropyl) functional group will attach itself to the organic matrix, and the trimethoxysilane functional group to the inorganic ferrite nanoparticle surface. This will enable chemical bonding between the nanoparticle and the matrix, and simultaneously help to de-agglomerate the nanoparticles by preventing them from coming in contact with each other (shown schematically in figure 2 below.

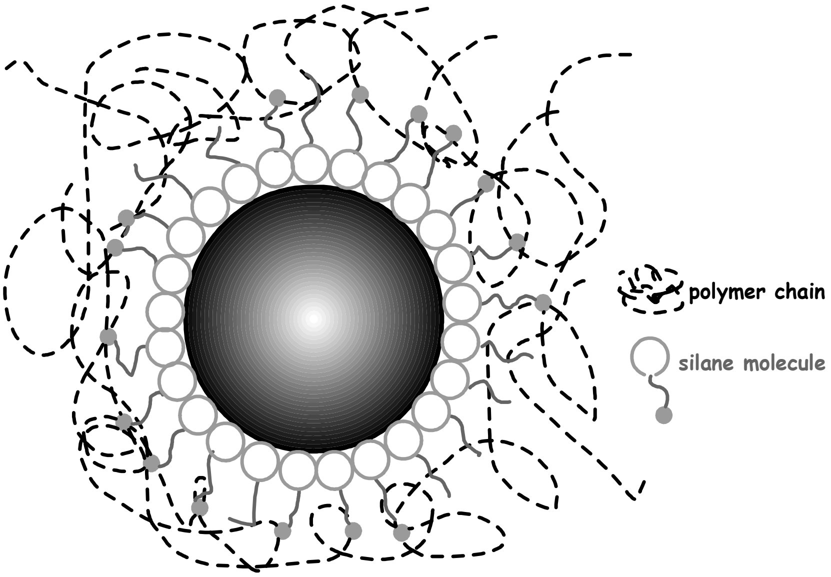

Figure 2. Schematic representation of the chemical coupling between the $Ni_{0.5}Zn_{0.4}Cu_{0.1}Fe_2O_4$ ferrite particle and the acrylic matrix via silane molecule

It is important that the correct amount of the silane surfactant is used – sufficient to cover the nanoparticle surface, but not an excess. This requires a knowledge of the surface area, measured by the Braun-Emmett-Taylor (BET) method.

A number of experiments were made to integrate the nanoparticles, both with and without functionalisation into the acrylic matrix.

Following the nanocomposite production, preliminary microwave absorption measurements were made on hot-pressed samples containing 5, 20 and 50 wt% nanoparticle additions to the matrix. Measurements were made in X-band (8.2 – 12.4 GHz) and P-band (12.4 – 18 GHz). Further measurements were not possible due to limitations on the amount of material available at that time. Details of the microwave measurement results are given in [3] and will not be repeated here. It should be noted that these are preliminary results from measurements on non-optimised samples.

Part 2

The main emphasis of the project at present and for the next year is selection of appropriate polymer matrices, and methods to integrate ferrite nanoparticles into these matrices.

Various approaches are possible, including separate synthesis of nanoparticles followed by integration into the polymer, or by in-situ nanoparticle synthesis. Although in-situ synthesis would appear to be optimal, this method is of limited flexibility with respect to composition of the nanoparticles and any subsequent heat treatment of the same. It has therefore been decided to concentrate on separate synthesis of nanoparticles, followed by functionalisation and incorporation into the matrix by either melt blending or in-situ polymerisation. Melt blending, while commonly used in industry is only applicable to thermoplastic polymers (which are certainly of interest in the present project) may be difficult to apply for mixing nanoparticles into the polymer. The very small particles sizes demand very high hydrodynamic shear forces for effective blending, which may not be available from existing equipment.

Mixing the nanoparticles with a monomer, followed by polymerisation may be a more feasible approach (although at this stage we have not decided against also studying the melt blending method). This method is applicable for both thermoplastic and thermosetting polymers, including commonly used plastics such as polycarbonate, epoxies and vinyl esters.

Epoxies are widely used in defence applications, as are ester-based polymers. Conventional hardening by adding chemical (peroxide) catalysts has been used for many years, but has several disadvantages, including the need for highly reactive and environmentally undesirable chemicals. Furthermore, once the catalyst has been added there is a limited time available before the polymerisation reaction starts and the viscosity increases to the point where further moulding is impossible. The final product also often contains small amounts of porosity (resulting from the catalyst) which are detrimental to the damage tolerance and other mechanical properties.

For these reasons, ultra-violet (UV) curing has been investigated as a potential alternative for hardening the polymers used. UV curing (“cure on demand”) has several advantages, including:

- Unlimited time before curing is initiated
- Very rapid (seconds-minutes) curing once UV exposure started
- No residual porosity from the curing initiator
- There are also a number of other advantages directly related to the use of UV curing in production, including less stringent environmental requirements.

To use UV curing on a laboratory scale to produce nanoparticle containing (nano)composites a small scale apparatus has been built, and will be tested during December 2002. This is shown in figure 3 below. The monomer/nanoparticle mixture to be cured is placed in the vertical mould in the centre of the apparatus, and illuminated from above by a UV lamp. UV light is reflected into the sample through the sides of the mould.

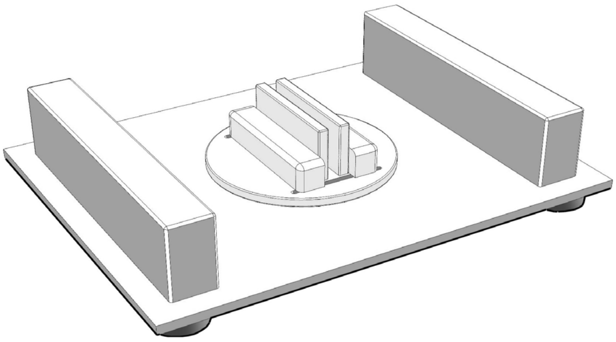

Figure 3. Nanocomposites will be cured in the vertical sample holder, seen in the centre. Bars by the sides are to illustrate the source of a magnetic field. UV radiation will originate from above, and be reflected into the sample through the mould sides.

Functionalisation of the nanoparticle surfaces is an intricate problem, where the functionalisation is dependent on many factor such as temperature, pH, surfactant concentration and type, solvent, and the nanoparticle surface itself.

Some preliminary experiments have been made, but much remains to be done in order to effectively and homogeneously distribute the nanoparticles in a polymer matrix. This will be done concurrently with development of techniques to mix the nanoparticles and monomers before UV curing.

The possibility to apply a magnetic field across the sample, thereby orienting the ferrite particles before UV curing has also been built into the apparatus. This will be used to produce anisotropic samples.

Continued experimental work during 2003

Testing and optimisation of the UV curing apparatus
Further work on synthesis of ferrite nanoparticles
Development of functionalisation procedures for the nanoparticles
Production of nanocomposites with varying concentrations of ferrite nanoparticle additions
Microwave property characterisation of the nanocomposites produced

Conclusions

Much has been learnt about synthesis of ferrite nanoparticles, and how their properties such as size and shape are influenced by the synthesis conditions.

An apparatus for production of small samples of nanoferrite polymer composites has been built.

Initial studies into suitable polymer systems have been made, and preliminary experiments made.

Preliminary microwave measurements have been made on composite materials, and found to be not more difficult than on conventional materials

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