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Magnetic and Dynamic Mechanical Properties of Nd-Fe-B Composite Materials with Polymer Matrix

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1. Introduction

At the end of the last century whole variety of technical-technological achievements occurred. Cars overflow the streets, air-conditions coated the facades, everyday life became unimaginable without computers and cell phones; kitchens are filled with assorted appliances, and industry has been improved and enforced by high technology in order to achieve higher manufacturing products, with less energy and manpower consumption. If a deeper look is taken, behind modern design exteriors, inside all of these appliances, it is noticeable that one of the key roles in their performance is engaged by permanent magnets. These materials have very important role as functional components within the wider spectra of contemporary devices in different industrial branches, as well as in the wider consumption. One of the most important applications of the permanent magnets are: spare parts in AC and DC engines production (Slusarek & Dudzikowski, 2002), as well as synchronized motors, transformers, actuators, magnetic buffers, stationary fields, etc. (Gutfleisch et al., 2011). Information storage (hard discs), communications, medical appliances and scanners, automobile and aircrafts industries, could also be emphasized as important applications (Matsuura, 2006; Brown et al., 2002).

The nanocrystalline Nd-Fe-B alloys are one of the most superior magnetic materials with high value of maximum energy production (app 50 MGOe) (Herbst, 1991). Besides their high values of the remanence and coercivity, as well as relatively high Curie temperatures (app 312 °C) (Sagawa et al., 1984) this type of magnetic alloys are identified suitable for research and further development of magnetic composite materials with polymer matrix, so called bonded magnets (Brown et al., 2006; Ma et al., 2002). Contemporary research in the field of magnetic composite materials on the basis of Nd-Fe-B alloys are directed into four basic directions: increase of magnetic energy, meaning optimisation of magnetic capacities; improving corrosion resistance; optimisation production process of process parameters; and reduction of the subtle rare earth content (Nd), targeting decreasing the price of the final magnetic material, keeping high values of the maximum magnetic energy. Application of
various process techniques in the production process of bonded magnets, gives the possibility for utilisation of various magnetic powder in combination with different polymeric materials as binding agent. Development of bonded technology, exploring the possibility of applications of various types of magnetic powder and polymeric matrices, testing of their influence, as well as the influence of the process parameters, to achieve optimal mechanical and magnetic capacities are in research focus during the last few years (Garrell et al., 2003; Lahelin et al., 2009). Research trend is reflected in development of bonded hybrid magnetic composite materials with improved dynamic mechanical capacities and noticeably lower cost due to the replacement of the expensive Nd-Fe-B magnetic powder with cheaper ferrite magnetic materials, achieving satisfying values of the maximum magnetic energy.

The objective of this chapter is to give more insight on the role of Nd-Fe-B particles on dynamic mechanical, thermal and magnetic properties of Nd-Fe-B/epoxy resin composite materials. Replacing one fraction of Nd-Fe-B with barium ferrite the hybrid composite materials with upgraded dynamic mechanical properties is produced. Interactions between employed magnetic powders and interactions between magnetic powders and polymer binder are considered. The advantage of DMA technique compared to the standard mechanical test methods is demonstrated. In addition, predictive mathematical models are employed to evaluate behaviour of composite. Results obtained with proposed mathematical models are in very good agreement with experimental values.

2. Synthesis of Nd-Fe-B / epoxy resin composite materials

There are several different process routes for bonded magnet production (Hamano, 1995; Gronefeld, 2002). The compression moulding is the most common technique utilized for materials with thermosetting polymer matrices. Composites with varied content of Nd-Fe-B particles in epoxy matrix from 15 to 95 wt% are produced by compression moulding under a pressure of 4MPa at room temperature, using a lab scale compression moulding press. Also, Nd-Fe-B/barium ferrite/epoxy resin composites as well as pure epoxy samples are obtained. The moulded samples are then allowed to cure under a moulding pressure for about 24 hours. The synthesis is carried out under conditions that avoid air bubbles in the mixture. No external magnetic field is used during the cure.

2.1 Polymer binder

As polymer matrix thermosetting epoxy system that is a combination of liquid mixture of Bisphenol A and Bisphenol F resins and cross linking agent (hardener), which cures fully at room temperature, is used. In terms of manufacture, the curing time of the matrix must be long enough for the polymer and magnetic alloy to be properly mixed, but shorter than required for the gravitational settling of the Nd–Fe–B particles. During curing, shrinkage should be minimal, and the thermal expansion of both polymer matrix and Nd–Fe–B should be comparable. Applying these criteria, the medium hard epoxy resin has the following properties: tensile strength ~ 58 MPa, elongation ~ 2.8%, compression strength ~ 96 MPa, flexural strength ~ 78 MPa and density ~ 1.2 g/cm$^3$, is selected.

2.2 Magnetic materials

The rapid quenched Nd$_{11.7}$(Fe$_{68.5}$Co)$_{30.8}$B$_{8.3}$ magnetic powder obtained by melt spinning method with particle size from 74 to 177 μm is employed as a magnetic filler for polymer composite
magnets manufacturing. Hybrid magnetic composites are produced by replacing the part of Nd-(Fe,Co)-B particles with spherical barium ferrite (BaFe$_{12}$O$_{19}$) agglomerates. The magnetic properties of started magnetic materials are presented in Table 1.

<table>
<thead>
<tr>
<th>Material</th>
<th>Chemical Formula</th>
<th>$B_r$ [kG]</th>
<th>$H_{cb}$ [kOe]</th>
<th>$H_{cj}$ [kOe]</th>
<th>$(BH)_{max}$ [MGOe]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neodymium Iron Boron</td>
<td>Nd$<em>{11.7}$(Fe$</em>{0.5}$Co$<em>{0.5}$)$</em>{88.3}$</td>
<td>8.2</td>
<td>6.0</td>
<td>8.7</td>
<td>13.1</td>
</tr>
<tr>
<td>Barium Ferrite</td>
<td>BaFe$<em>{12}$O$</em>{19}$</td>
<td>2.3</td>
<td>1.9</td>
<td>3.6</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Table 1. Magnetic properties of started magnetic materials

The chemical composition of the starting Nd-Fe-B alloy is Nd: 21-25 wt%, Co: 3-5 wt%, B<1.5 wt%, Zr: 3-5 wt%, Fe: balance.

2.3 Measurements

The structure and morphology of fracture surfaces of synthesized composite materials are observed by JEOL JSM-5800 Scanning Electron Microscope (SEM), with an accelerating voltage of 20 kV. After tensile tests at room temperature, fracture sample surfaces are sputtered with gold using a POLARON SC 502 sputter coater for enhanced conductivity.

Thermal analysis of investigated magnetic composites, as well as pure epoxy material are performed by SDT Q600, TA Instruments equipment for simultaneous DSC/DTA/TGA measurements. The samples are heated at a rate of 5 °C/min in a nitrogen environment with a temperature range of ambient temperature up to 600 °C.

A TA Instruments DMA Q800 is used to obtain dynamic mechanical data of investigated magnetic composites and pure epoxy sample. Storage modulus, loss modulus, and tan delta are recorded as a function of temperature. The samples are tested using three-point bend clamp with a 20 mm span width and rectangular-edge probe, at a frequency of 1 Hz and displacement amplitude of 20 μm. A displacement control mode is used to maintain deflection through glass transition temperature $T_g$; a Force Track setting of 125% is used, i.e. an applied static force was 25% higher than the dynamic force. Samples are placed on a platform located on top of the three-point bend fixture so that no sample deflection could occur during annealing. Testing is done over a temperature range from 25 °C to 100 °C with a temperature ramp of 3 °C/min.

The Nd-Fe-B/epoxy composites and pure epoxy polymer samples are machined into tensile and flexural specimens, which are then tested at ambient temperature. The tensile specimen is dumbbell shaped, as required by ASTM D 3039-00 (American Society for Testing and Materials [ASTM], 2000), with a cross-section of 40 x 5 mm in the gauge length. The specimens for flexural tests are rectangular plates 100 x 10 x 2 mm as required by ASTM D 790-03 (ASTM, 2003). At least five specimens are tested in tests consisting of both composite and pure epoxy specimen. The dumbbell-shaped tensile specimens of pure epoxy resin are fabricated by casting the resin into the rubber moulds and following the recommended curing cycle from the material manufacturer. Flexural tests are performed using three point bend kit. A universal material testing machine (Schenck TREBEL RM 100) is used for mechanical tests. The moduli of elasticity are derived from the linear portion of the stress-strain curves obtained by both tensile and flexural tests.

The examination of macroscopic magnetic properties is tested using Superconducting Quantum Interference Device (SQUID) magnetometer. During the measurements at ambient temperature (300 K), magnetic field strength $\mu_0H$ is varied from -5 to 5 T. Sample preparation
and experimental procedures have been conditioned such that the demagnetization factor can be neglected. While the SQUID magnetometer is a very sensitive device, a magnetic field strength from $10^{-12}$ up to $10^3$ A/m$^2$ can be measured with accuracy of 0.1 %.

3. Nd-Fe-B / epoxy composite magnetic materials – bonded magnets

The Nd-Fe-B bonded magnets have been commonly used in various fields, such as electric appliances, automobile parts (Brown et al., 2002; Li et al., 2006), sensing elements (Radojević et al., 2007), electronic, communication and micro-electro-mechanical system (MEMS) applications (Chin, 2000; Hono & Ping, 2001). Advantages of the using bonded composite materials include their simple technology, possibility of forming their final properties, lowering manufacturing costs because of no costly finishing and lowering of material losses resulting from the possibility of forming any shape (Dobrzanski et al. 2007). The amount of Nd-Fe-B powder in the bonded magnet plays a crucial role in determining magnetic properties. A higher content of Nd-Fe-B powder usually results in a higher remanence magnetization ($B_r$) and maximum energy product ($B_H$)$_{max}$ and therefore, it is desirable from the magnetic perspectives. However, a higher content of magnetic filler may change the rheology of polymer melt during the process, subsequently, impact the mechanical strength of bonded magnets. Nevertheless, the balance between magnetic properties and corresponding dynamic mechanical behaviour is an important issue for bonded magnet applications (Garrell et al., 2003b). The presented study is undertaken with the intention to understand the effect of different filler contents on the thermal, dynamic mechanical and magnetic properties of the Nd-Fe-B/epoxy magnetic composite materials.

3.1 Structure and morphology

Uniform particle distribution and good adhesion between Nd-Fe-B particles and a polymer matrix are essential for the quality of composites, especially at temperatures above the glass transition temperature ($T_g$) of the polymer. The particle size of magnetic powder plays an important role in determining powder to binder ratio, degree of particle alignment and, magnetic and mechanical properties (Kokabi et al., 2005). Generally speaking, the plate-like particles would result in higher packing density under the optimal compression conditions (Rodrigues et al., 1996; Zhang et al., 2009). SEM micrographs of fracture surface morphology of Nd-Fe-B/epoxy composites are presented in Fig.1.

Fig. 1. SEM micrographs of fracture surface of composite material with a) 50 wt% and b) 95 wt% of Nd-Fe-B filler observed by JEOL JSM-5800 Scanning Electron Microscope
The Nd–Fe–B particles are shown as light grey and the epoxy matrix is shown as dark. The darkest gray parts represent the holes ensued by dragging the Nd-Fe-B particles during the mechanical breaking (tension). Although Nd–Fe–B particles are of variable size and shape, they seem to be attached rather well to the matrix.

3.2 Thermal properties

Using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), different phase transformations caused by decomposition, oxidation, dehydration, etc. can be detected. Also, materials can be analysed in different experimental environments. Increasing the heating rate temperature of transformation can be moved to higher values because a temperature lag between the heater and the specimen occurs (Withaeger, 2001). The DSC and TG curves for Nd-Fe-B/epoxy composite are shown in Fig. 2. Thermogravimetric experiments (Fig. 2a) were carried out to determine the degradation temperatures \( T_d \) of magnetic composite materials i.e. the temperature corresponding to the highest rate of weight loss. The results of thermal degradation studies clearly show that the samples with higher amounts of magnetic filler have a lower temperature of thermal degradation and a lower degradation rate in regard to the pure epoxy resin. The results obtained by DSC are in accordance with TG measurements.

DSC curves show an exothermal effect which appears between 300 °C and 380 °C refers to the reaction of thermal degradation or decomposition of the composite materials. The change of enthalpy which occurred during this process is decreased with a decrease in the amount of epoxy matrix in the composites. Small endothermic effects in temperature range between 47 °C and 50 °C are referring to glass transitions in the investigated composite materials (Maity et al., 2007). The quantitative values of degradation temperatures and the corresponding changes in enthalpy are presented in Table 2.

Fig. 2. TG and DSC curves for the pure epoxy resin and Nd-Fe-B composites

The quantitative values of glass transition temperatures \( T_g \) obtained by DSC are presented with DMA results in section 3.3 (Table 3.). Due to negligible thermal effects i.e. enthalpy change, for the sample with 95 wt% Nd-Fe-B, the corresponding DSC curve is not included in the Fig. 2b. All investigated samples have very close values of glass transition temperatures which is confirmed by DMA measurements (Fig. 3).
<table>
<thead>
<tr>
<th>Sample (Composite)</th>
<th>TG</th>
<th>DSC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_d$, °C</td>
<td>$T_d$, °C</td>
</tr>
<tr>
<td>Pure epoxy resin</td>
<td>354.7</td>
<td>344.6</td>
</tr>
<tr>
<td>15 wt% Nd-Fe-B</td>
<td>352.5</td>
<td>338.8</td>
</tr>
<tr>
<td>50 wt% Nd-Fe-B</td>
<td>349.7</td>
<td>333.5</td>
</tr>
<tr>
<td>75 wt% Nd-Fe-B</td>
<td>342.2</td>
<td>330.3</td>
</tr>
<tr>
<td>85 wt% Nd-Fe-B</td>
<td>341.3</td>
<td>329.2</td>
</tr>
<tr>
<td>95 wt% Nd-Fe-B</td>
<td>324.4</td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Degradation temperatures and corresponding change of enthalpy obtained from TG and DSC curves

3.3 Dynamic mechanical properties

Dynamic mechanical analysis (DMA) is probably the most sensitive single technique available for characterizing and interpreting the mechanical and curing behaviour of polymers and polymer composites. This sensitivity allows the DMA to detect the glass transition temperature, $T_g$, of highly crosslinked thermosetting polymers or of thin coatings. (Menard, 1999). DMA can be simply described as applying an oscillating force to a sample and analyzing the material’s response to that force. The technique separates the viscoelasticity of a material into the two components of complex modulus ($E^*$), a real part which is the elastic modulus ($E'$) and an imaginary part which is the damping or viscous component ($E''$), and is expressed $E^* = E' + iE''$ (Ferry, 1980). These properties are often described as the ability to lose energy as heat (damping) and the ability to recover from deformation (elasticity). Due to the viscoelastic nature of polymer composites, their dynamic and thermal behaviour significantly depends on strain, frequency and temperature. For composite materials, particle shape and size, uniform particle distribution, and good adhesion between Nd-Fe-B and polymer, are important parameters which have significant impact on microstructure and stiffness of the final magnetic material (Guschl et al., 2002).

The dynamic mechanical properties of the pure epoxy polymer and the Nd-Fe-B/epoxy magnetic composite materials are examined as a function of temperature, from the glassy to the rubbery state. Applied three-point bending oscillatory testing is considered as a “pure” mode of deformation and is recommended for stiff materials. The results presented in Fig. 3 show a considerable improvement in the storage modulus (elastic component) caused by the presence of the Nd-Fe-B magnetic filler.

![Fig. 3. DMA curves of storage modulus $E'$ and $\tan\delta$, for the pure epoxy resin and the composites with different Nd-Fe-B filler content versus temperature](www.intechopen.com)
In the glassy region (around 25 °C), modulus of the pure polymer, modulus of the filler, and concentrations of both, as well as the adhesion factor between the filler and polymer, have direct influence on the total dynamic modulus of composites (Payne, 1965; Wang, 1999; Alves et al., 2004). The addition of 15 wt% and 50 wt% Nd-Fe-B powder into epoxy matrix induce an increase of roughly 6 % and 75 % in the storage modulus of pure epoxy polymer, respectively. Thus, magnetic composites with 75 wt% and 85 wt% of magnetic filler were found to have 3.2 and 5.8 times higher storage modulus than the pure epoxy sample, respectively. At the other end of temperature range, the storage modulus decreases with the temperature to the lower values in the rubbery state (Deng et al., 2007). In this region, approximately above 75 °C, the dynamic storage modulus is a function of the hydrodynamic effect, well-known to be dependent on the shape of the filler particles or agglomerates, on the concentration of the filler, and on the fillers interactions with polymer. Comparing to pure epoxy sample values for storage modulus these are 1.7, 2.9, 9.1 and 40 times higher for composites with 15 wt%, 50 wt%, 75 wt% and 85 wt% of Nd-Fe-B, respectively, which is a significant improvement of storage modulus (Grujič et al., 2010a). DMA tests for highly filled Nd-Fe-B/epoxy polymer composite (95 wt% of Nd-Fe-B) showed an 11 times higher storage modulus values at ambient temperature and up to 87 times higher at 75 °C (in rubbery state), compared with the polymer matrix. The significant enhancement of the storage modulus in the rubbery region could be explained by the variable size and shape of Nd–Fe–B particles resulting in higher packing density, good particle to particle interaction and attachment to the epoxy matrix (Payne, 1965). When comparing material properties, a material with a higher storage modulus would be stiffer and harder to deform than one with a lower $E’$. Besides the elastic component, a material also has a viscous component called the loss modulus ($E’’$). This viscous component relates to the materials ability to lose energy. The material’s $\tan \delta$ designates the material’s ratio of viscous to elastic components ($E’’ / E’$) and it is sometimes called the materials damping ability (Menard, 1999). A composite material with a higher $\tan \delta$ ($\approx 0.7$ for composite with 15 wt% of Nd-Fe-B filler) has a higher viscous percentage than one with a lower $\tan \delta$ ($\approx 0.6$ for composite with 95 wt% of Nd-Fe-B filler). Therefore the material would be more likely to absorb a vibration or impact, and disperse it throughout the material without failure. DMA results presented in Fig. 3b show that glass transition temperatures ($T_g$) obtained from $\tan \delta$ curves for all investigated magnetic composites were found to lay in the same temperature region (around 54 °C). This could be a consequence of the use of Nd-Fe-B powders with similar particle size distribution and without particle surface modification (uncoated) (Otaigbe et al., 1999). The quantitative values of glass transition temperatures obtained by different methods are presented in Table 3.

<table>
<thead>
<tr>
<th>Sample (Composite)</th>
<th>Glass Transition Temperature ($T_g$, °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DSC</td>
</tr>
<tr>
<td></td>
<td>onset</td>
</tr>
<tr>
<td>Pure epoxy resin</td>
<td>46.8</td>
</tr>
<tr>
<td>15 wt% Nd-Fe-B</td>
<td>45.3</td>
</tr>
<tr>
<td>50 wt% Nd-Fe-B</td>
<td>44.4</td>
</tr>
<tr>
<td>75 wt% Nd-Fe-B</td>
<td>46.7</td>
</tr>
<tr>
<td>85 wt% Nd-Fe-B</td>
<td>47.0</td>
</tr>
<tr>
<td>95 wt% Nd-Fe-B</td>
<td>55.3</td>
</tr>
</tbody>
</table>

Table 3. Glass transition temperatures obtained by DSC and DMA

www.intechopen.com
The difference in $T_g$ value for each composite obtained from DSC and DMA arises due to the difference in the method of measurement and the variations in the definition of transition temperature used (Maity et al., 2007).

### 3.4 Tensile and flexural properties

In order to determine the in-plane tensile and flexural properties of the polymer matrix composite materials reinforced by the Nd-Fe-B magnetic particles, standard test tensile and flexural methods are used (ASTM, 2000, 2003). The ultimate tensile stress $\sigma_m$ of the investigated magnetic composite materials is calculated using:

$$\sigma_m = \frac{F_{\text{max}}}{b \cdot d}$$

(1)

Where:
- $\sigma_m$ – ultimate tensile stress, MPa;
- $F_{\text{max}}$ – maximal load before failure, N;
- $b$ – sample width, mm; and
- $d$ – sample thickness, mm.

The values of ultimate tensile stress, elongation and modulus of elasticity have been taken from obtained stress-strain diagrams for all investigated composites, and presented as a function of the Nd-Fe-B content in the epoxy matrix respectively (Fig.4. & Fig.6.). The elastic modulus $E$ of investigated magnetic composite materials was calculated using:

$$E = \frac{\Delta \sigma}{\Delta \varepsilon} = \frac{\Delta F}{\Delta e \cdot b \cdot d}$$

(2)

Where the ratio $\Delta \sigma/\Delta \varepsilon$ is determined by linear regression method. From the linear portion of stress-strain curves i.e. in the Hookean region.

With a decreasing quantity of the thermosetting epoxy polymer in the composites i.e. with an increasing content of the Nd-Fe-B filler, the values of tensile stress and elongation are decreasing (Fig. 4.). In addition, composite materials become more brittle, and less ductile (Hemrick et al., 2004; Grujić et al., 2010b).

![Fig. 4. a) Ultimate tensile stress, and b) strain in function of Nd-Fe-B content](https://www.intechopen.com)
break or that do not fail in the outer surface of the test specimen within a 5.0% strain limit of these test methods. When a homogeneous elastic material is tested in flexure as a simple beam supported at two points and loaded at the midpoint, the maximum stress in the outer surface of the test specimen occurs at the midpoint. This stress may be calculated for any point on the load-deflection curve by means of the following equation:

\[ \sigma_f = \frac{3F \cdot L}{2b \cdot d^2} \]  

(3)

where: \( \sigma_f \) – stress in the outer surface at midpoint, MPa; F - load at a given point on the load-deflection curve, N; L - support span, mm; b - width of beam tested, mm, and d - depth of beam tested, mm.

Deformation caused by flexural test \( \varepsilon_f \) is fractional change in the length of an element of the outer surface of specimen at middle point, where stress is maximal, and it can be calculated using the following equation:

\[ \varepsilon_f = \frac{6D \cdot d}{L^2} \]  

(4)

where: \( \varepsilon_f \) - strain at outer (opposite) surface, mm/mm; D – maximal deflection in middle point of specimen, mm, L – support span, mm; and d – thickness of the specimen, mm.

The tangent flexural modulus of elasticity represents the ratio of stress to corresponding strain in the range of elastic behaviour of materials. The flexural modulus of elasticity is calculated by drawing a tangent to the steepest initial straight-line portion of the load-deflection curve. Similar to tensile test results, the flexural stress and elongation are decrease with increasing content of Nd-Fe-B filler (Fig. 5).

Fig. 5. Ultimate flexural stress and strain as the function of Nd-Fe-B content

Moduli of elasticity obtained by both tensile and flexural tests are increase with higher quantities of magnetic filler. This is crucial in analysis of possible use of the investigated magnetic composite materials as functional material (Fig. 6.). This means that material with higher amounts of Nd-Fe-B filler, subject to equal stress levels (ballast), tolerate 2 to 3.5 times lower deformation.

The modulus of elasticity is a very important parameter for analysis of the composite materials behaviour under discontinuous load conditions. The values of elastic modulus,
obtained by tensile and flexural tests, upswing with an increasing amount of Nd-Fe-B powder from 50 wt% achieve 9.2 and 7.1 GPa, respectively. Within the narrow region, up to 20 wt% content of Nd-Fe-B, where the modulus of elasticity is practically constant according to tensile and flexural tests, dynamic-mechanical analysis could be applied to acquire additional information’s related to mechanical behaviour about transitions in polymer composites (Maity et al., 2007; Almagableh et al., 2008).

Fig. 6. Comparative view of the changes in the modulus of elasticity at 25 °C
The values of storage modulus observed by DMA were compared with elastic modulus obtained by tensile and flexural tests (Fig. 6.). In contrast to Deng, S. et al. (Deng et al., 2007) mechanical properties at temperatures higher than ambient are not compared with DMA results observed using two different clamps. It seems that observing the elastic modulus of composites by tensile, flexural and DMA tests at room temperature in the present study gives a better look at the increasing trend of elastic component of materials with increasing Nd-Fe-B filler content in the polymer matrix.

3.5 Mathematical prediction of Nd-Fe-B / epoxy composite behaviour
The strong influence of relatively small amounts of filler particles on the dynamic mechanical properties of polymers has significantly contributed to increased use of polymer materials in many commercial applications (Bergstrom & Boyce, 1999). The incorporation of filler particles is known to increase the stiffness of the material and alter time dependent aspects of material behaviour such as hysteresis and stress relaxation. Even at strains sufficiently large for the structure to have been eliminated, the storage modulus is greater than that of the pure polymer and, greater than the amount which can be predicted due to hydrodynamic interaction of the filler particles.

Ideally, in an attempt to reduce laboratory cost, one would like to make a prediction of a new material’s behaviour by numerical simulation, with the primary goal being to accelerate trial and error experimental testing. The recent dramatic increase in computational power available for mathematical modelling and simulation raises the possibility that modern numerical methods can play a significant role in the analysis of heterogeneous microstructures. This section is devoted to the mathematical prediction of storage modulus of observed composite. The focus is on analytical models, due to fact that they are simple to use and required input data are only properties of individual constituents of composite and
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their fraction. The several proposed analytical models are tested versus experimental data as it is illustrated in following text. Some of applied models agree very well with experimental data, whilst others deviate significantly.

There have been several attempts to derive formulas giving the apparent modulus due to a dispersion of particles in polymer (Donnet, 1998). The earliest of these attempts was by Smallwood using the analogy to Einstein’s viscosity equation:

$$E_{\text{comp}} = E_{\text{matrix}} (1 + 2.5c)$$  \hspace{1cm} (5)

where: $E_{\text{comp}}$ - storage modulus of composite (Pa), $E_{\text{matrix}}$ - storage modulus of matrix (Pa), and $c$ – volume faction of particle in composite

Smallwood’s estimate is only good at very low filler concentrations. A number of attempts have been made to incorporate interactions between neighbouring particles to allow prediction at higher volume fractions. Most of these models add one or more terms to a polynomial series expansion. One of the most cited model of this class is the Guth-Gold (Guth & Gold, 1938):

$$E_{\text{comp}} = E_{\text{matrix}} (1 + 2.5c + 14.1c^2)$$  \hspace{1cm} (6)

Later Guth extended the Guth-Gold model to include impact of particle shape on properties. Guth introduced a shape factor $f$ (ratio of diameter to width of particle) and proposed a new equation (Guth, 1945):

$$E_{\text{comp}} = E_{\text{matrix}} (1 + 0.67f \cdot c + 1.62f^2 \cdot c^2)$$  \hspace{1cm} (7)

Budiansky developed a model, for the special case of rigid particles in an incompressible matrix written as (Budiansky, 1965):

$$E_{\text{comp}} = \frac{E_{\text{matrix}}}{1 - 2.5c}$$  \hspace{1cm} (8)

Ponte Castaneda has proposed a different self-consistent estimate for rigid particles in a neo-Hookean matrix (Ponte Castaneda, 1989):

$$E_{\text{comp}} = \frac{E_{\text{matrix}}}{1 - 3c}$$  \hspace{1cm} (9)

Later Govindjee and Simo proposed the novel model, for the case of rigid particles in a neo-Hookean matrix written (Govindjee & Simo, 1991):

$$E_{\text{comp}} = E_{\text{matrix}} \frac{1-c / 2}{1-c}$$  \hspace{1cm} (10)

In addition, it is worth to mention the empirical formula suggested by Brinkmann (Brinkman, 1952):

$$E_{\text{comp}} = E_{\text{matrix}} (1 - c)^{5/2}$$  \hspace{1cm} (11)
Major characteristics of all aforementioned theoretical models are: they neglect the impact of filler properties and assume that the medium wets the filler particles, but they do not chemically react with the filler surface. Mori-Tanaka proposed a model, which takes into consideration the impact of filler properties on overall composite properties (Mori & Tanaka, 1973). The Mori-Tanaka model for spherical particles isotropically dispersed in an elastic matrix can be written as:

\[
K_{\text{comp}} = K_{\text{matrix}} + \frac{c(K_{\text{particle}} - K_{\text{matrix}})K_{\text{matrix}}}{3K_{\text{matrix}}(1 - c)(K_{\text{particle}} - K_{\text{matrix}})} + K_{\text{matrix}}
\]

\[
G_{\text{comp}} = G_{\text{matrix}} + \frac{c(G_{\text{particle}} - G_{\text{matrix}})G_{\text{matrix}}}{(1 - c)(G_{\text{particle}} - G_{\text{matrix}})6\left(K_{\text{matrix}} + 2G_{\text{matrix}}\right)} + G_{\text{matrix}}
\]

\[
E_{\text{comp}} = \frac{9K_{\text{comp}}G_{\text{comp}}}{3K_{\text{comp}} + 2G_{\text{comp}}}
\]

where: \(K_{\text{comp}}, K_{\text{matrix}}, K_{\text{particle}}\) are bulk modulus of composite, matrix and particle, respectively (Pa), and \(G_{\text{comp}}, G_{\text{matrix}}, G_{\text{particle}}\) are shear modulus of composite, matrix and particle, respectively.

The experimentally obtained values of storage modulus are compared with analytical models discussed above and presented in Fig. 7. Predictions of models proposed by Budiansky, Ponte Castaneda and Govindjee-Simo give inadequate estimation so they are not included in Fig. 7.

![Fig. 7. Models predictions against experimental data](image)

From Fig. 7 one may notice that all models included in analysis give very good predictions of storage modulus at lower particles concentrations (till 50%). This suggests that in this concentration range, the interactions between neighbouring particles have very low
intensity. At higher concentrations, interactions become high intensity, this is why the Smallwood’s model starts to show significant deviation from experimental results. Mori-Tanaka’s model follows the trend of experimental results, but it gives poor predictions. Brinkman’s model gives good predictions at high concentrations, but at very high concentrations of particles, it extensively overpredicts the storage modulus. The Guth and Guth-Gold models are in very good agreement with experimental results. The explanation for this behaviour lies in the fact that both models take into consideration interactions between neighbouring particles.

3.6 Magnetic properties
Characteristic of all magnetic materials is a manifestation of the hysteresis phenomena. The hard magnetic materials have the greater values of hysteresis (Goll & Kronmüller, 2000). A word of Greek derivation, hysteresis describes magnetic materials as highly nonlinear, meaning that their response to a stimulus lags behind in a repeatable manner. The stimulus in this case is an applied magnetic field and the material’s response is the magnetization or induction (Trout, 2000). Magnetic properties of magnetic composite materials (bonded magnets) are affected by the magnetic properties of the magnetic powder and weight (volume) ratio of the powder. It is known that bonded magnets have inferior magnetic characteristics compared to magnetic material obtained by conventional methods (sintering for example), because in bonded technology maximal density of magnetic powder can not be achieved (Zhang et al., 2009). One of the most important characteristics of the used type of Nd-Fe-B rare-earth magnetic material is high values of remanence and coercivity, which have a direct influence on high values of maximum energy product (Gutfleisch 2000; Chen et al., 2004). The results of magnetic measurements i.e. complete hysteresis loops for bonded Nd-Fe-B/epoxy type magnets with different content of functional magnetic particles are presented in Fig. 8a. It is obvious that the largest hysteresis loop correspond to the magnetic composite with the highest amount of magnetic component.

Fig. 8. a) Hysteresis loops of magnetic composites, b) magnetic properties of the composites as the function of the Nd-Fe-B filler content

On the basis of these results corresponded B-H diagrams are constructed and the changes of remanence ($B_r$), coercivity ($H_{cb}$) and maximum energy product ($BH_{max}$) with an increasing content of Nd-Fe-B in the epoxy matrix are taken and presented in Fig. 8b. The presented graph illustrates the upswing of three magnetic parameters of composite materials with increasing amounts of Nd-Fe-B particles in the epoxy matrix. For example, the maximum
energy product for composite with 95 wt% Nd-Fe-B is around 8 MGOe, which is two times higher than for composite with the 85 wt% Nd-Fe-B case. For composites with Nd-Fe-B content higher than 75 wt%, \((BH)_{\text{max}}\) rapidly increase i.e. for the highly filled composites even a small addition of magnetic medium have a strong influence on magnetic properties of bonded magnets. Also, the maximum energy product \((BH)_{\text{max}}\) of Nd-Fe-B bonded magnets can be simulated using a mathematical model, and choosing appropriate parameters for the magnetic texture and the magnetic coupling micro-grains, one can increase the value of \((BH)_{\text{max}}\) (Vuong et al., 2003, Xiao et al., 2000).

4. Hybrid magnetic materials

One way of improving some physical properties of the bonded magnets is to produce the hybrid magnets prepared from a mixture of two powders with different properties, e.g. the Nd–Fe–B powders with barium ferrite (Plusa et al., 2006). The addition of ferrite to the Nd–Fe–B powder decreases the temperature coefficient of coercivity (commonly known as \(\beta\) [%/°C]), which means that this type of bonded magnet can work under elevated temperatures. Also, for example, the bonded magnet has improved the mechanical properties with addition of iron powder (Dobrzanski & Drak, 2008). Further benefits of adding ferrite or iron would be cost reduction and ease of magnetization. The synthesized hybrid magnetic composite materials correspond to a mixture of Nd-Fe-B and barium ferrite in different ratio. More precisely, this type of composite can be observed as a substitution of a part of Nd-Fe-B particles with barium ferrite. A better insight into the effect of added barium ferrite to the final characteristics of hybrid composite materials are examined for a constant quantity of the polymer matrix. SEM micrographs of hybrid magnetic composite materials are presented in Fig. 9.

Fig. 9. SEM micrographs of hybrid magnetic composite materials

Since the crumbled ferrite agglomerates are incorporated between bigger particles of ferrite and Nd-Fe-B, they contribute to the improved dynamic mechanical properties of composite. The results of DMA are presented in Fig. 10. For different types of composites, the values of storage modulus and \(\tan \delta\) are compared. All composites have improved storage modulus compared to pure epoxy resin, while the hybrid Nd-Fe-B/barium ferrite/epoxy resin type composite has the highest value (Fig. 10a). The peaks of \(\tan \delta\) curves lie in a temperature region between 45-50 °C and indicate glass transition temperatures.
This phenomenon is continuously investigated using composites with different ratios of magnetic particles and for various types of polymer matrices. For this purpose, injection bonded magnets are produced using thermoplastic poly (methyl methacrylate) (PMMA) as a matrix and Nd-Fe-B and barium ferrite as a functional magnetic component, in order to investigate the dynamic mechanical properties of hybrid composite materials. The results presented in Fig. 11 show the same tendency of increasing the storage modulus as for composites with epoxy matrix. Hybrid magnetic composite has improved elastic properties compared to the pure PMMA matrix, Nd-Fe-B/PMMA and barium ferrite/PMMA composite materials. 

Fig. 10. Nd-Fe-B/epoxy composites: a) storage modulus, and b) $\tan\delta$ as the function of temperature

Fig. 11. Nd-Fe-B/PMMA composites: a) storage modulus, and b) $\tan\delta$ as the function of temperature

Magnetic properties of started magnetic powders and hybrid composite materials are investigated and corresponding SQUID hysteresis loops are presented in Fig. 12a. The shape of barium ferrites hysteresis loop illustrates that magnetic saturation ($M_s$) is achieved at 70 emu/g. The coercivity, remanence and consecutively maximum energy product values are less significant as for Nd-Fe-B powder (Goll & Kronmüller, 2002). The saturation magnetization Nd-Fe-B alloy is about 3 times higher than barium ferrite. The values presented in Fig. 12a should be taken as approximate because the field strength of SQUID magnetometer (5 T) is not sufficient for full saturation of Nd-Fe-B powders. It can be seen in the first quadrant, the horizontal end of the hysteresis loop of barium ferrite indicates that this magnetic powder achieves complete saturation, as opposed to Nd-Fe-B alloy.
It is obvious from Fig. 12a that the hysteresis loops becomes more constricted as the quantity of barium ferrite increases, which is consistent with the investigations of D. Plusa et al. (Plusa et al., 2006). With an increasing content of barium ferrite in the hybrid composites, the value of magnetic remanence, coercive force, and the maximum magnetic energy decreases. Change of magnetic properties, is practically linear in relation to the magnetic powders ratio (Nd-Fe-B to barium ferrite) in hybrid composites. The magnetic properties of hybrid magnetic composites are taken from obtained hysteresis loops and used for constructing the diagram presented on Fig. 12b.

Fig. 12. a) SQUID hysteresis loops of starting magnetic powders and hybrid magnetic materials and b) magnetic properties as the function of Nd-Fe-B and barium ferrite content

5. Conclusion

The results of this study show that addition of plate shape Nd-Fe-B particles to the polymer affect the rheological properties the polymer matrix via internal structural changes and, subsequently, the impact the mechanical strength of bonded magnets. Moreover, the stability of composite materials at elevated temperatures is a crucial property has a major impact on their utilization. There is a wide range of polymers and magnetic powders that may be used for production of magnetic composites. It seems that the mixture of Nd-Fe-B particles and epoxy resin is suitable for bonded magnet applications due to good adhesion, homogeneity, mechanical and magnetic properties. One of the characteristics of this type of materials is that the degradation temperature rises as the content of epoxy increases. The thermal experiments DSC/TGA reveals that the addition of a high quantity of Nd-Fe-B particles results in a reduction of the composite thermal decomposition enthalpy. On the other side, glass transition temperatures evaluated by DSC and DMA disclose that concentration of particles have no impact on glass transition temperature. This result could be a consequence of applied micro size particles without coupling agents or additives. Moreover, DMA data show that the value storage modulus amplifies in glassy, as well as in rubbery state, as the concentration of filler in composite rises. The tensile and flexural tests at ambient temperature show enhancement of modulus of elasticity with quantity of magnetic filler, which is a crucial parameter for analysis of composite materials behaviour. Information extracted from tensile and flexural tests are consistent with results evaluated by DMA. As expected, magnetic properties are drastically improved with higher quantities of Nd-Fe-B magnetic powder, especially for highly filled composites. These results provide information
about the Nd-Fe-B/epoxy composites which could be of importance in cases where the relatively brittle metallic permanent magnets are not useable.

Hybrid materials development and utilization are economically motivated, due to fact that these materials can be produced at low cost. For example, replacing one fraction of Nd-Fe-B with less expensive barium ferrite creates a new hybrid composite. This hybrid composite shows lower intensity of magnetic property comparing to the original composite, but on the other side shows improved dynamic mechanical properties. In view of aforementioned facts on the subject of hybrid materials, it could be said that hybrid materials could replace existing composite materials in numerous applications.

For better insight into viscoelastic behaviour of composites, beside experiments, a theory that explicitly takes the particle distribution, shape factor, particle-particle interactions as well as particle-polymer matrix interactions into account is required. Considering the increasing interest in polymer composites and advanced analytical tools, the present study provides a useful basis and motivation for future experiments and theory development for the multifunctional components and commercially important polymer bonded magnets.

Further work has been focused on researching and developing bonded Nd-Fe-B composite materials with thermoplastic or rubber matrix using the injection or extrusion methods. Design of the composites with improved dynamic mechanical and optical properties can be realized by assembling magnetic powders and fibres blends. Also, corrosion resistance is one of the potential goals in further research activities.

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7. References


Magnetic and Dynamic Mechanical Properties of Nd-Fe-B Composite Materials with Polymer Matrix


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Composite materials, often shortened to composites, are engineered or naturally occurring materials made from two or more constituent materials with significantly different physical or chemical properties which remain separate and distinct at the macroscopic or microscopic scale within the finished structure. The aim of this book is to provide comprehensive reference and text on composite materials and structures. This book will cover aspects of design, production, manufacturing, exploitation and maintenance of composite materials. The scope of the book covers scientific, technological and practical concepts concerning research, development and realization of composites.

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