

POLYMER NANOCOMPOSITES FOR LOAD-BEARING MRI-COMPATIBLE IMPLANTS

Pierre-François Köver, Heiko Zerlik, Jörg Mayer,
Karl-Ludwig Eckert and Erich Wintermantel

*Biocompatible Materials Science and Engineering, Department of Materials
Swiss Federal Institute of Technology Zurich, Wagistrasse 23, 8952 Schlieren, Switzerland*

SUMMARY: Polymeric nanocomposites are potential materials for the manufacturing of magnetic resonance imaging (MRI) compatible and repeatedly sterilisable minimally invasive surgical instruments, e.g. endoscopes. The low increase of viscosity due to the incorporation of nano-reinforcing agents into polymeric matrices makes nanocomposites suitable for injection moulding of thin-walled instruments. However, knowledge is scarce regarding the preparation of nanocomposites based on technical polymeric matrices such as polyetheretherketone (PEEK). The aim of this study was evaluate the potential of manufacturing nanocomposites by direct melt intercalation with shear. It has been demonstrated that this approach is a suitable method to compound nanocomposites of technical polymers. Tensile testing was used to compare the manufactured nanocomposites to fibre-reinforced microcomposites and showed that for low reinforcing agent fractions nano-reinforced composites can compete with fibre-reinforced composites.

KEYWORDS: Nanocomposites, Thermoplastics, Polyetheretherketone, Silicate, Sodium-Bentonite, Mechanical Properties

INTRODUCTION

Since its introduction, magnetic resonance imaging (MRI) has become one of the most valuable visualising methods, showing an outstanding contrast for soft tissues. The MRI method requires static magnetic fields with a strength of 0.5 to 2.5 Tesla. With the introduction of interventional magnetic resonance imaging (iMRI) allowing access to the patient during the imaging process and on-line localisation of instruments and implants in the body, it became obvious that while iMRI systems are produced in series, there is still a lack of adequate surgical instruments able to exhaust the full potential of this new diagnostic tool. The aim of this work is to develop a new biomaterial not interfering with iMRI and capable of transmitting loads for applications such as surgical instruments or implants.

Nanocomposites are a new category of materials characterised by phase dimensions in the nanometer range. Nanocomposites with layered silicates as reinforcing additives are used in various industrial and scientific applications such as transportation and food packaging. They exhibit a favourable combination of stiffness, strength and weight [1-8]. Nanocomposites can

be manufactured either by intercalation of a monomer followed by polymerisation or by polymer intercalation from a solution. However, in many cases none of these approaches is satisfactory because neither a suitable monomer nor an adequate solvent for the polymer can be found. Recently, a third approach based on direct melt intercalation was presented [6]. The polymer-silicate mixture was heated up above the softening point of the polymer, either statically or under shear using an extruder. This method was demonstrated on polymers like polyamides where an increase in tensile modulus of 90 % was obtained. In this study, evidence was made that this approach can be applied to high-performance polymers like polyetheretherketone (PEEK).

MATERIALS AND METHODS

An organosilicate reinforcing additive (organobentonite, OB) was prepared by modifying substituted sodium bentonite (Ibeco, Germany) with octadecylamine (Fluka, Switzerland) according to [3]. This organobentonite was then incorporated into PEEK 450 G (Cellpack, Switzerland) at a fraction of 4 wt-%. The incorporation was carried out using direct incorporation of dry organobentonite into dry PEEK under shear in an extruder above the melting point of the polymer. The structure of the modified and unmodified reinforcing agents was investigated using TEM. Silicium-titanium-carbide fibres (UBE Industries, Japan), exhibiting mechanical properties similar to T300 standard carbon fibres, and unmodified sodium bentonite were also incorporated at 4 wt-% into PEEK in order to evaluate the mechanical performance in comparison to other nanocomposites and to fibre-reinforced microcomposites. Compounding of the materials was carried out on a Brabender segmented corotating twin-screw extruder using the following parameters (Table 1):

Table 1 Compounding parameters for the extrusion of premixed and directly incorporated nanocomposites.

Parameter	Value
Screw diameter	25 mm
Screw aspect ratio	22
Inlet temperature	370 °C
Screw temperature 1	380 °C
Screw temperature 2	390 °C
Nozzle temperature	400 °C
Injection pressure	33 b
Revolutions	15 rpm

The compound was the injection moulded to double-shoulder test bars using a Ferromatik Milacron K40/80V injection moulding system with a screw diameter of 25 mm. The parameters below were used (Table 2):

Table 2 Parameters for the injection moulding of double shoulder test bars.

Parameter	Value
Hopper temperature	370 °C
Screw temperature 1	380 °C
Screw temperature 2	390 °C
Nozzle temperature	395 °C
Mould temperature, edge	170 °C
Mould temperature, centre	160 °C
Injection pressure	75 b
Back pressure	95 b

Tensile testing of the injection moulded double shoulder bars was carried out on a Zwick 1456 Universal Testing Machine. At least 5 bars were tested each time, in order to perform a statistical analysis. Testing was carried out using extensometers for strain measurements. The samples were clamped into the testing machine with a proofing distance of 40 mm. The extensometers were symmetrically placed in the middle of the proofing distance, exhibiting a measuring distance of 20 mm. The testing speed was 5 mm/min, observing a pre-load of 10 N. The tensile modulus was determined between 20 and 50 % of the maximum stress.

Impact strength experiments were carried out on a Zwick 5113 pendulum-striking machine with digital data display using a 4 J swing hammer. An Izod test procedure was developed, allowing a relative comparison of the sample materials. The proofing distance was 30 mm; the samples had a height of 5 mm and a width of 3 mm. The swing was carried out over the width. Five samples were tested for each material in order to get statistical results.

RESULTS AND DISCUSSION

The viscosities of the investigated nanocomposites at processing the temperature of 380 °C are shown in Fig. 1. It appears that the organobentonite nanocomposite 450 G OB4 exhibits a lower viscosity especially at higher shear rates compared to a fibre-reinforced nanocomposite (450 G SiTiC4).

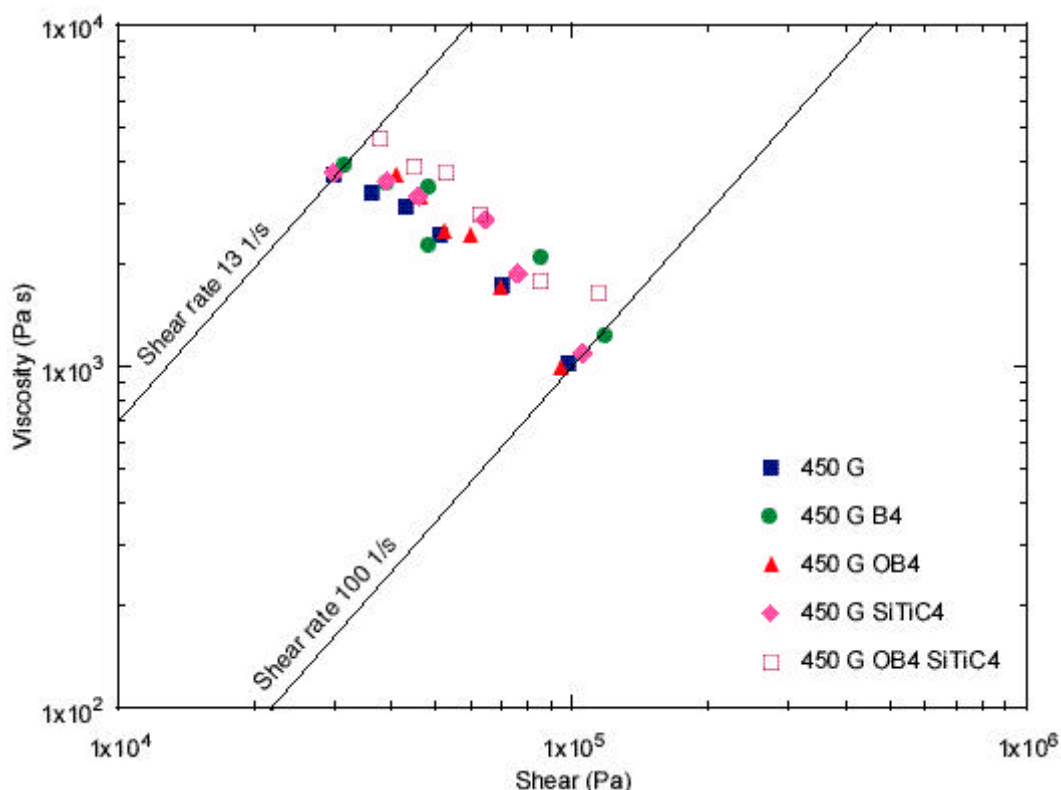


Fig. 1 Viscosity of PEEK 450 nanocomposites at 380 °C. The dependence of the viscosity on the organobentonite fraction is small. 450 G stands for a PEEK standard grade delivered in granule. The reinforcing additives are defined as follows: B – sodium bentonite, OB – organobentonite, SiTiC – silicium-titanium-carbide fibres. The figures following the additive type stand for the incorporated weight fraction.

The nano-structure of the bentonite and organobentonite composites was investigated using TEM. Fig. 2 shows sodium bentonite (a) and organobentonite (b) compounded into PEEK 450 G. The layered structure of the sodium bentonite can be observed. The average interlayer distance between two silicate layers for sodium bentonite is about 1.4 nm. For organobentonite, due to the ion substitution of sodium with octadecylammonium the interlayer distance between two silicate layers could be expanded to about 2.8 nm, showing that the substitution reaction is effective.

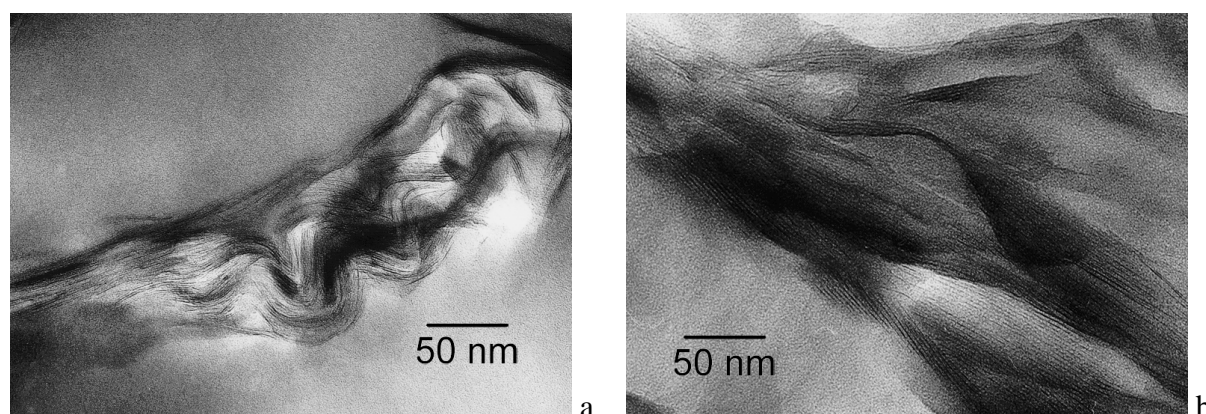


Fig. 2 TEM image of unmodified sodium bentonite and organobentonite compounded into PEEK 450 G at a magnification of 270'000. The interlayer gap measures 1.4 nm and 2.8 nm, respectively.

In Fig. 3 representative SEM micrograph of a tensile testing bar are represented. The overview (Fig. 3a) reveals that voids as well as powder nests were included during compounding and injection moulding. These structure defects induce an early failure of the test bar. The bars had pores and powder nests of an average of 0.4 mm. The size distribution and the location distribution were found to be homogeneous over the full length of the tensile bars.

Different fracture behaviour were observed between the edge (Fig. 3b) and the core (Fig. 3c) of the test bars. The edge was found to exhibit a brittle fracture behaviour whereas the core showed plastic deformations of the matrix. An explanation for this observation could be found in the process of injection moulding. The high temperature difference between the polymer melt and the mould lead to an amorphous shell of the tensile bar, as the partially crystalline PEEK was not given enough time to crystallise.

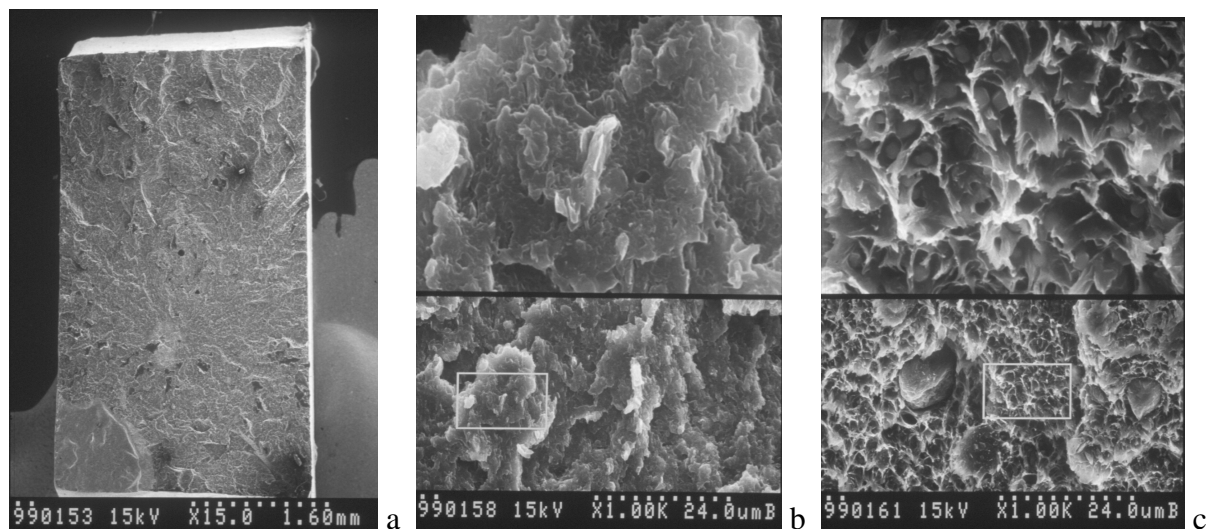


Fig. 3 SEM images of 450 G OB4 nanocomposite. The overview (a) shows porosity as well as powder nests. The two magnified images (b, c) were taken in the edge zone and in the core of the sample, respectively.

Both bentonite and organically modified bentonite (organobentonite) incorporated at 4 wt-% into PEEK 450 G exhibit improved mechanical properties (Fig. 4). However, the mechanical properties of the organobentonite nanocomposite were clearly improved in comparison to the bentonite nanocomposite or to the unreinforced polymer matrix. Increase relative to unreinforced polymer matrix in tensile modulus of 12 % for bentonite and 40 % for organobentonite as well as an improvement of tensile strength of 7 % for bentonite and 21 % for organobentonite were achieved [9, 10].

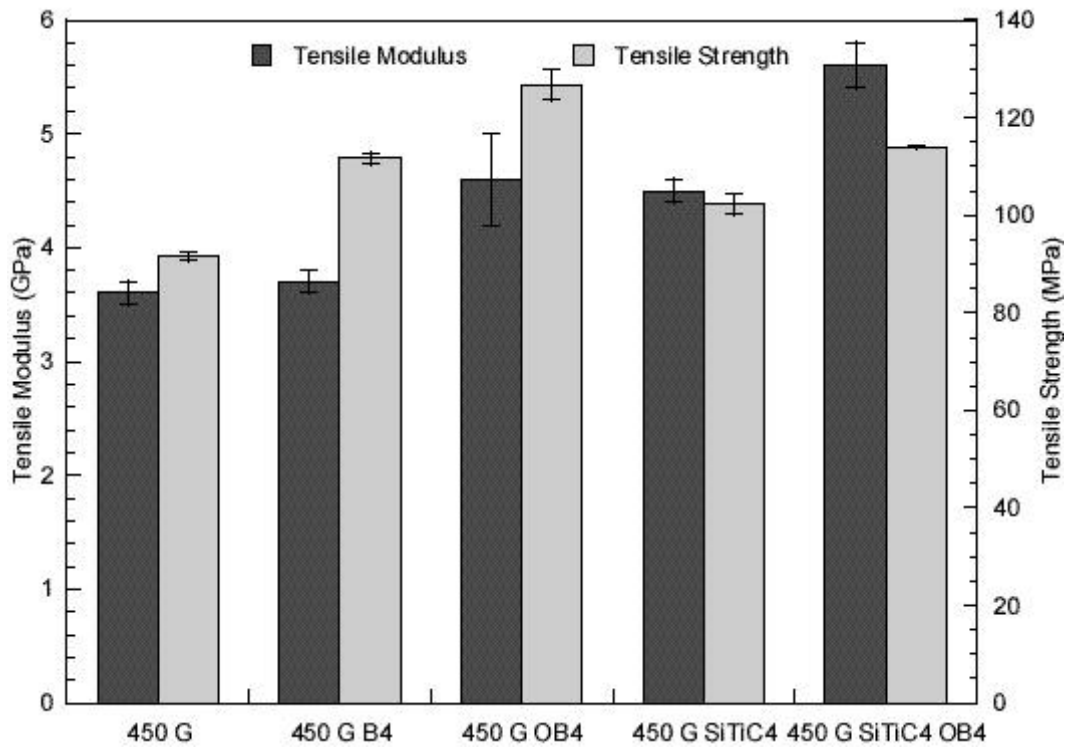


Fig. 4 Tensile modulus and tensile strength of PEEK nanocomposites.

Considering the influence of layered silicate reinforcing additives, it appears that at 4 wt-% all additives exhibit an increase in stiffness and in tensile strength [9, 10]. Comparing PEEK nanocomposites containing unmodified sodium bentonite (450 G B4) and organically modified bentonite (450 G OB4), the modified type proves to better reinforce the polymer matrix. The gain of reinforcement is similar to the one of Si-Ti-C (450 G SiTiC4). The reinforcement of fibre and nano-platelets can be combined, resulting in a composite of further increased elastic modulus (450 G SiTiC4 OB4) containing a total of 8 wt-% reinforcing additives.

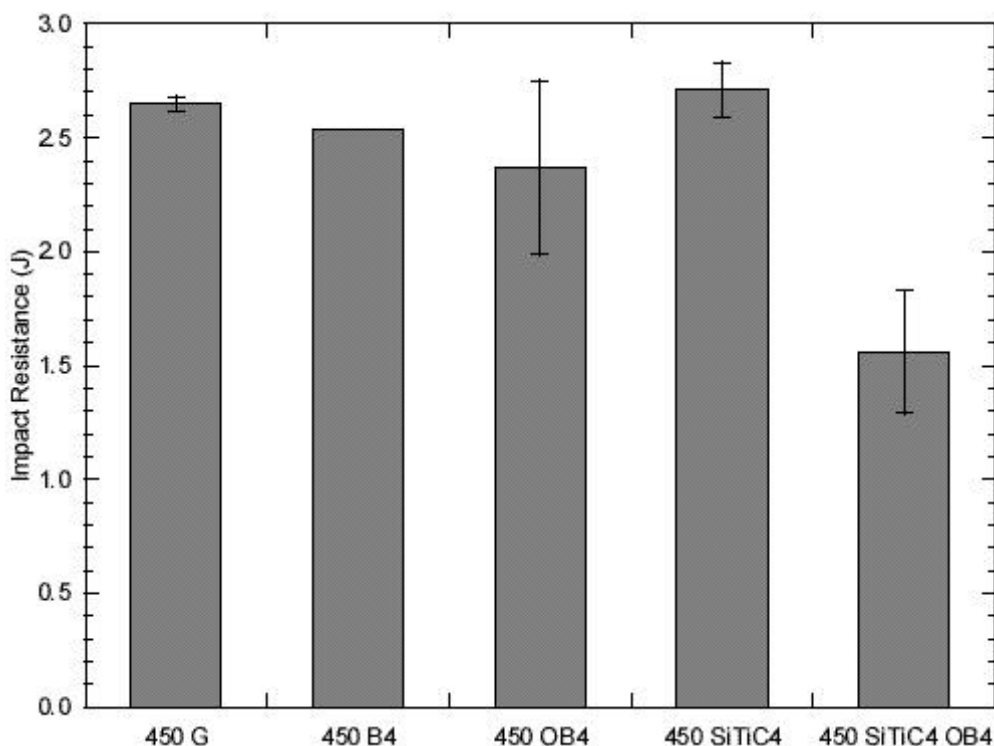


Fig. 5 Izod impact resistance of PEEK nanocomposites.

In Izod impact testing the PEEK nanocomposites performed as expected, showing a slight decrease of impact resistance compared to the fibre-reinforced composite. The combination of nano-platelet and fibre reinforcing agents exhibits a suprisingly low Izod value.

Organobentonite exhibiting superior reinforcement qualities compared to unmodified sodium bentonite, the conclusion can be drawn that the organic modification is effective in delaminating the layered silicate, thus increasing its surface per weight fraction and its contact with polymer chains. Reducing the thickness of silicate layers per particles further increases the strength of the reinforcing additive.

In another study, the problem of void inclusion during processing was further investigated using a vacuum feature for compounding, sucking off trapped air, evaporated solvents and decomposition gases of the organic spacer. This method was shown to be effective also for organobentonite contents up to 15 % [11].

CONCLUSIONS

The direct melt intercalation with shear method was successfully adapted to a technical polymer such as PEEK. For low fractions, i.e. 4 wt-%, the manufactured nanocomposites could compete with fibre-reinforced composites.

Structural analysis of injection moulded nanocomposites showed that the filler distribution in the polymer matrix is still inhomogeneous in the micrometer scale. The homogeneity needs to be optimised in order to exhaust the full potential of such nanocomposite materials systems, thus allowing to increase the organobentonite content up to technical levels known from fibre-reinforced composites.

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