M Ű E G Y E T E M   1 7 8 2

Faculty of Mechanical Engineering

Department of Polymer Engineering

Written by:

Gábor Szebényi

Ph.D. student in mechanical engineering on the following topic:

Development of fibre and nanoparticle reinforced hybrid composites

to fulfill the requirements of the PhD degree

BUDAPEST

2011

1. Introduction

The application of glass fibers as reinforcing materials in artificial resins (1938) has revolutionized the field of polymer composites. A further big step ahead occurred with the development of carbon fiber in 1963. The evolution did not stop, newer and newer reinforcing materials (aramid, organic natural fibers, basalt fiber) emerged. Carbon nanotubes, which thanks to their outstanding properties came into focus not only in the field of material science, but also in almost all fields of science, joined this line of reinforcing materials after their discovery in 1991. The tensile strength of a carbon nanotube can reach 60 GPa, its modulus of elasticity 1 TPa and it bears also high ductility. Its electrical conductivity is near to the conductivity of copper and its thermal conductivity is also exceptionally high. While during the first decade after their discovery nanotube research focused mainly on their production technology, nowadays it is possible to investigate their application technologies. Researchers across the globe are constantly trying to utilize their outstanding properties. For example as nanosized circuit elements in electronic devices, as light sources in flat screen displays, for safe hydrogen storage in fuel cells and last but not least as reinforcing and additive materials in materials science. This widespread research is supported by their outstanding mechanical properties and enormous self surface area (SSA). As long as a typical carbon fiber with a diameter of 5-8 μm has a SSA of 0.2 m^2/g, the self surface area of a 2 nm diameter nanotube can reach 1000 m^2/g. One of their drawbacks compared to conventional reinforcing fibers is that the production of continuous fibers is not yet possible.

For the widespread industrial use of nanotube reinforced composites, a high yield, economical production technology is necessary. In the research of the last years numerous experimental production technologies emerged. After the original direct current arc discharge technology CVD (chemical vapor deposition) has been developed, which provided more efficient SWCNT (Single Wall Carbon Nanotube) production. With the upscaling of this technology industrial yield can be reached. In nanotube production the consistent, controlled quality (defined length and diameter range, sufficiently regular structure and purity) is of great importance. These aspects are crucial in composite reinforcement and other, for example electrical applications of nanotubes.

The good connection, permanent adhesion, which provides the load transfer between the reinforcing material and the matrix is a key issue. In its absence the carbon nanotubes function only as fillers. In case of nanotube reinforcement serious problems have to be faced to establish this adhesive connection. Their tendency to aggregate obstructs good adhesion, the nanotubes have a tendency to nest and tangle in the matrix material, lowering the interface, breaking the material consistency, causing stress concentration, which can lead to a weakening effect instead of the reinforcement of the composite. Lot of research is done towards the uniform dispersion of the nanotubes in polymer matrices, up to date the high shear mixing technologies gave the best results, but there are also experiments using solvent dispersed nanotubes mixed with ultrasonic stirrers. Molecular engineering technologies can provide solutions for the improvement of the interfacial adhesion, numerous strongly polar functional groups have been already attached to the walls of the considerably apolar nanotubes, thereby improving the interaction between the fibers and the matrix. These changes in molecular structure can also help to reach uniform dispersion.

The aim of this thesis is to investigate the potential of carbon nanotube reinforcement, especially in case of fiber reinforced thermoset matrix nanocomposites. In my work I intended to combine the accumulated experience in the field of micrometer scale reinforcement and the new opportunities of nanometer scale reinforcement especially in case of complex hybrid polymer composites.

2. Short overview of the related literature, the goal of the thesis

According to the literature survey it can be declared, that the field of carbon nanotube reinforced composites and hybrid composites is a new, active research topic. In the production of nanotubes the original, arc discharge technology, which provided pure, but expensive samples is almost fully superseded by the CVD technology, which has higher yield, and is more economical, but provides samples with more impurities. Besides research facilities, spin-off factories (for example: Nanocyl, Belgium) were founded, after that production began in the far east, mostly China (for example: Shenzhen Nanotech Port, China – 10 metric tons yearly production capacity), and major polymer manufacturers (for example: Bayer, Germany) have also joined the production market of carbon nanotubes. This boom in production caused a fall in raw material prices, instead of the former quantities of some grams, kilogram sized carbon nanotube samples are available for reasonable prizes, making the research of more material demanding applications, like composite reinforcement possible.

Multiple technologies have been developed for the fiber-matrix interfacial adhesion improving functionalization of carbon nanotubes. Most of the technologies utilize a lot of environmentally harmful materials, like potent acids, and their yield is also low. Some articles also report the troublesome control of the process. The present functionalization technologies can also degrade the nanotubes, and hinder their dispersability. According to these results it is essential, that only some producers provide functionalized nanotubes, and the prices are also very high according to the functionalization technology. Research for improving the yield and lowering the cost of functionalization is in progress, but it is still a matter of years before the functionalized nanotubes reach the market. The electron irradiation of the nanocomposite parts can be an alternative to functionalization. In this field only a few publications are available, mostly concentrating on the structural alteration of nanotubes during electron microscope investigations. From the research results the electron beam induced coupling, 3D network forming of nanotubes and bonding of carbohydrates on nanotubes bears great potential in the composite technology aspect.

In the field of dispersion techniques, in case of thermoset matrix ultrasonic and three-roll mill mixing is in the focus of research. The dispersion research started with the use of ultrasonic stirrers, which are available in the laboratory environment and can be effective in case of small mixed portions, but in case of industrial size use an enormous local energy input would be necessary to achieve proper dispersion, which makes this

dispersion technology unfavorable because of the high energy consumption and its reported nanotube fragmenting effect. In the research three roll milling gets increasing attention thanks to its efficiency, economicity, high yield and easy upscalability to industrial levels.

The investigation of the properties of carbon nanotube reinforced composites is also a widely researched area. The casting technology widely used for the production for thermoset resins and nanocomposites also in the industry, the only problems are the usually small specimen size, which does not represent the properties of the real structures and in some cases the extremely low strength matrix materials. The definition of the optimal reinforcing material content, which shows a wide range depending of material combinations and dispersion technologies, can be also a pivotal question. In case of weaker matrix material and effective mixing impressive improvements in mechanical properties can be reached, but we can come across also some publications reporting 5-10 weight% nanotube reinforcement, so the definition of the optimal nanotube content has to have a strong emphasis in the research.

The research in the field of hybrid nanocomposites has also started in the last few decades, but the number of publications is yet low. According to the investigations it looks evident, that nanotube reinforcement can provide outstanding results in matrix dominated properties. For now the optimization of the nanotube content in hybrid systems is almost fully missing from the literature, usually only one or two nanotube contents are used for the experiments. The tests concentrate mainly on the fiber affected tensile and some interlaminar (for example interlaminar shear) properties. Practically no data is available from more demanding test setups (fatigue, fracture mechanics, impact tests).

According the literature survey, the goals of my thesis are:

1. Development of a dispersion technique for the proper dispersion of carbon nanotubes in epoxy resin, which can be upscaled for industrial use.

2. The definition of the optimal reinforcing material content for the matrix/carbon nanotube and matrix/carbon fiber/carbon nanotube composites from a wide nanotube content range.

3. The investigation of the improvement of the carbon nanotube – matrix interfacial adhesion, the development of a method alternative to functionalization.

4. The investigation, analysis of the mechanical properties, especially interlaminar and fatigue properties, of the prepared nanocomposites and hybrid nanocomposites.

3. Methods, tests, and materials used

3.1. Materials

Epoxy resins

In my research I have used a laminating and a low viscosity epoxy resin as the matrix materials of the composites and hybrid composites. During the specimen production I have used the curing cycle, in case of the P+M FM-20 – T-16, bisphenol-A based epoxy resin – amine hardener 4 hours at 60°C, in case of P+M AH-12 – T-58 aliphatic epoxy resin – amine hardener 4 hours at 80°C, provided by the producers in a Heraeus UT20 oven.

Vinylester

In my experiments I have used Cytec Viapal VUP 4652/67 aromatic, epoxy-novolac based, 33.5 volume% styrene content vinylester as an active coupling agent. For the conventionally cured samples before the addition of the initiator I have added 1 weight% Peroxid Chemie CA-12 accelerator to the resin. To initiate the curing I have used 1 weight% Peroxid Chemie MEKP-LA-3 initiator.

Coupling agents

In my experiments I have used BYK ANTI-TERRA-U and BYK DISPEBYK 2050 coupling agents, widely used both by the industry and researchers for the assistance of the dispersion and the improvement of the interfacial adhesion of nanosized fillers with 1:1 coupling agent – nanosized reinforcing material weight ratio.

Nanoparticles

In my experiments I have used Bayer Baytubes BT C150HP multiwalled carbon nanotubes as nanosized reinforcement.

Microsized reinforcing materials

For the production of the hybrid composites I have used Zoltek PX35 FBUD0300 309 g/m^2 surface weight knitted unidirectional carbon fabric consisting of 50k carbon rowings.

3.2. Specimen production technologies

Casting and injecting of specimens

For the production of the specimens not containing microsized reinforcement injection and casting into silicone moulds has been used depending from the resin viscosity. For the removal of trapped air bubbles the filled moulds have been placed under 0.1 bar absolute pressure vacuum for 30 minutes. In the micrographs of the fracture surfaces of the specimens no air bubbles could be observed.

Production of hybrid composites by vacuum bag technology

To produce hybrid composite laminates free of trapped in air bubbles, caused by the increased resin viscosity a specimen production technology utilizing vacuum has been used. This production technology was the vacuum bag technology. The composite laminates were produced by hand layup, and placed in 0.5 bar vacuum bag for 12 hours. The vacuum provided the reproducible production of high fiber content, air bubble free laminates by the constant pressure and the removal of the air bubbles and extra resin. The laminates contained unidirectional reinforcement in all cases, 10 layers in case of DCB specimens, and 6 layers in case of other specimens. The fiber content of the laminates was measured according to EN ISO 3451. In case of specimens for the same test series the fiber contents were in a 2 volume% wide range, all specimens contained 50 volume% $\pm$ 2 volume% fibers.

3.3. Test methods

In this section I present the test methods, equipment and most important parameters used in the experimental part of my research. Where it is not indicated, the tests were performed at room temperature (22$\pm$2^{o}C) at a relative humidity of 46$\pm$2%.

The *tensile tests* were performed according to EN ISO 527-2. EN ISO 3167 type B specimens were used, prepared by injection into silicone moulds. Because of the inhomogeneous deformation and the pullout from the grips I have used Messphysik ME-46 Full Image Videoextensometer for strain measurement, the target markers necessary for the measurement were adhesively bonded to the specimens. The tests

were performed using a Zwick Z020 universal, computer controlled loading frame at 1 mm/min crosshead speed.

The *3-point bending test* of the resin specimens were performed according to EN ISO 178. The specimens were produced according to the standard by injection into silicone moulds. The tests were performed using a Zwick Z020 universal, computer controlled loading frame at 2 mm/min crosshead speed and 64 mm support span.

The *3-point bending test*s of the fiber reinforced composite specimens were performed according to EN ISO 14125. The specimens were cut from the laminates parallel to the fiber direction. The tests were performed using a Zwick Z020 universal, computer controlled loading frame at 2 mm/min crosshead speed and 80 mm support span.

The *interlaminar shear tests* of the fiber reinforced specimens were performed according to ASTM D3846-94 using standard specimens. The specimens were cut from the laminates parallel to the fiber direction. On the opposite sides of the specimens notches reaching the midplane of the specimens have been prepared using a diamond disc cutter, to localize the failure to the interlaminar layer between the middle fabric laminae. The tests were performed using a Zwick Z020 universal, computer controlled loading frame at 1.3 mm/min crosshead speed. To avoid the buckling of the specimens a special support device, described by the standard, has been used. To eliminate friction the specimens were coated with silicone grease.

The *Charpy impact tests* of the resin specimens were performed according to EN ISO 179-2 in an instrumented test setup to achieve higher precision. The standard specimens were produced by injection into silicone moulds. The standard „A" type notches were made using a special cutting disc, having the profile of the notch. The tests were performed on a Ceast Resil Impactor Junior instrumented pendulum equipped with a Ceast DAS 8000 data acquisition system using a 2 J impact energy hammer at 2.9 m/s impact velocity.

The *static mode I. interlaminar crack propagation tests* were performed according to the DCB setup described in ASTM D5528-01. The loading blocks were fixed to the surfaces of the specimens, containing the delamination initiator described by the standard by Sika Sikadur 330 adhesive. A 50 μm thick PET film laminated between the two middle laminae of the laminate has been used as a delamination initiator. Before the start of each test hand precracking was performed to form a natural initial crack front. The static tests were performed using a Zwick Z005 universal, computer controlled loading frame at 5 mm/min crosshead speed. The interlaminar fracture toughness value,

corresponding to the start of crack propagation has been calculated using the 5% deviation method provided by the standard and a newly developed method based on AE crack tracking.

The *cyclic mode I. interlaminar crack propagation tests* were performed using an Instron 8872 servo-hydraulic fatigue tester equipped with a 1 kN Instron Dynacell load cell, at 2 Hz sinusoidal loading in force controlled operation. The peak value of the load was 70 N, the minimum value was 14 N (0.2 load factor). An Instron Fasttrack 8800 control unit was used for data acquisition.

The *interlaminar tensile tests* developed by me were performed on specimens according to ASTM D3846-94 using a Iosipescou shear fixture according to ASTM D5379-05, which provided almost clear interlaminar tensile loading. The specimens were cut from the laminates prepared by vacuum bag technology parallel to the fiber direction, the necessary notches were prepared using a diamond disc cutter. The tests were performed using a Zwick Z020 universal, computer controlled loading frame at 2 mm/min crosshead speed and 8.5 mm support span, to minimize bending loading.

The *dynamic interlaminar shear tests* developed by me were performed using an instrumented dynamic tensile tester described by EN ISO 8256 method A on specimens according to ASTM D3846-94. The specimens were cut from the laminates prepared by vacuum bag technology parallel to the fiber direction, the necessary notches were prepared using a diamond disc cutter. The tests were performed on a Ceast Resil Impactor Junior instrumented pendulum equipped with a Ceast DAS 8000 data acquisition system using a 15 J impact energy hammer and 30 g weight crosshead at 3.7 m/s impact velocity.

The prepared samples and the fracture surfaces of the specimens were investigated using a JEOL JSM-6380LA *scanning electron microscope*. All samples, except the pure nanotubes were gold sputter coated to make the surface electrically conductive. To minimize the loss in detail the coating thickness was minimized. The gold sputter coating was performed using a JEOL FC-1200 fine coater using 20-40 s coating time according to sample.

The *transmission electron microscopy* was performed using a Morgani 268D TEM. The 80 nm thick samples were cut from the specimens using a Leica Ultramicrotome EMUC6 microtome.

The fine structure, composition of the samples was investigated using a TA Instruments µTA 2990 Micro-Thermal Analyzer *atomic force microscope* (AFM) equipped with

Microscopes SFM 1650-00 silicon tip probe in non-contact ant tapping operation on 20 μm x 20 μm and 5 μm x 5 μm surfaces at respectively 30 and 7 μm/s scanning speed and 300 row resolution. To investigate the phase composition of the materials, besides the signals of the internal sensor used for regulation and of the topographic information providing Z-modulation, the phase signal was recorded.

To compare the *viscosities* of the different samples a TA Instruments RA2000 rheometer has been used. The resin samples were investigated in a steady state flow between a temperature controlled flat plate and a rotating, 40 mm diameter disc at a constant 25°C and at a constantly climbing temperature (15°C/min heating rate) in the 25-100°C range. The gap was set to 0.5 mm and 1 mm according to the sample. During the tests 5 min dwell time was used at each point to achieve steady state flow. In the shear rate sweep a 5% deviation between the 10 s mean viscosity values in 3 successive measurements was set before continuing to the next point. To describe the viscosity curve 5 points were registered in each decade of the shear rate.

Fineness of grind tests were performed on the carbon nanotube filled epoxy resins and vinylesters to measure the maximum particle sizes according to EN ISO 1524 using an Elcometer 2020/2 gauge.

Raman spectrometry was performed using a Jobin Yvon LabRam microscope. The excitation was provided by a 532 nm wavelength doubled frequency Nd:YAG and a 785 nm wavelength diode laser using 10x, and 100x magnification objectives. The Raman scattering photons were collected by a CCD detector. The intensities of the Raman spectra were registered in arbitrary units in function of Raman shift. The acquisition times were set to fit the overflow hit value (32000 hits) of the sensor. In case of shorter acquisition times multiple spectra were averaged. The device was calibrated using a silicon crystal after each series and laser changes. Baseline correction was performed on the acquired spectra to exclude the effect of the fluorescent background and help comparability.

4. New scientific results – theses

1ᵗʰ Thesis

I have developed an effective mixing technology for the dispersion of multiwall carbon nanotubes in epoxy resin capable of economical, industry scale use. The technology makes the three roll mill dispersion of nanotubes in low viscosity resins possible. In a mediate step of the technology a high carbon nanotube content, almost solid masterbatch is prepared by three roll milling, which can be thinned to the desired nanotube content. I have defined the necessary roll gap (5 μm) and number of pass-throughs (4 pass-throughs) for the creation of a nanocomposite with properly dispersed nanoparticles on a three roll mill with 120 mm roll diameter, 266, 144, 78 1/min feed, center and apron roll rpm. I have demonstrated that the masterbatch technology is superior to the rival direct high shear mixing alternative in terms of the viscosity, maximum particle size of the nanotube filled resin and the three point bending properties of the composite. I have proven by transmission electron microscope micrographs, that the nanoparticles were effectively dispersed, an actual nanocomposite was prepared. [9, 13, 14]

2ⁿᵈ Thesis

a) I have developed a novel epoxy/vinylester hybrid resin system production technology, in which first the epoxy (EP) is cured using a conventional curing agent, after that the vinylester is cured by electron irradiation. Thanks to the two steps this hybrid resin system can be effectively used to improve the embedding and the interfacial connection of nano- and microsized fillers and reinforcing materials. I have confirmed by Raman spectrometry, that the VE component of the prepared VE/EP hybrid system remains reactive, the number of its unsaturated bonds does not significantly decrease, after the conventional curing cycle of the EP resin. I have demonstrated through Raman spectrometry, that even 25 kGy irradiation dose is enough to cure the VE component of the system. I have examined the functioning and producability of the system in a wide range (1-50 weight%) of vinylester contents. I have proven the electron irradiation initiated decrease between the difference in viscoelastic properties of the VE and EP component by atomic force microscopy (AFM) measurements. [4, 7, 15]

b) I have demonstrated that the developed electron irradiation cured vinylester (VE)/epoxy (EP) system can be effectively used as the matrix of carbon

nanotube/carbon fiber reinforced hybrid composites. I have experimentally proven that the bending and interlaminar shear properties of the developed system surpass the properties of the EP matrix and conventionally prepared VE/EP matrix composites (in case of 50 weight% VE content by 26% in maximum flexural strength, 20% in bending modulus of elasticity, 28% in interlaminar shear strength). I have also demonstrated that the developed system outperforms the performance of the coupling agents (BYK ANTI TERRA-U, BYK DISPERBYK 2050) widely used by the industry in the same mechanical properties (against the samples prepared with the coupling agent with better properties in case of 50 weight% VE content by 19% in maximum flexural strength, 16% in bending modulus of elasticity, 21% in interlaminar shear strength). [4, 7, 15]

3rd Thesis

I have developed a new crack propagation initiation criterion for DCB interlaminar crack propagation tests based on acoustic emission (AE) crack tracking, which has a direct connection to the damage of the material. The theory of the criterion is that the intersection of the x axis and the line fitted to the section between 5% and 20% points of the registered opening displacement-cumulative AE hit number is the crack opening displacement corresponding to the start of crack propagation. I have pointed out that the developed crack propagation start criterion and the AE crack tracking is more appropriate for the evaluation of the interlaminar fracture toughness, than the methods provided by the standard thanks to the exclusion of human subjectivity and the more precise, direct sensing of the start of the crack propagation and the direct physical connection to it. [2, 8]

4Th Thesis

I have demonstrated that the carbon nanotube reinforcement of carbon fiber/epoxy matrix composites can significantly improve the mode I. interlaminar fracture toughness of the composites. The optimal nanotube content in the tested 0.1-1 weight% range was 0.3 weight% according to the test evaluation utilizing acoustic emission crack tracking and crack propagation start criterion. At this nanotube content the interlaminar fracture toughness increased by 33% compared to the conventional composite with no nanotube reinforcement. I have characterized the failure process by evaluating the run of the

acoustic activity and cumulative hit number of the samples. I have also demonstrated that 0.3 weight% carbon nanotube reinforcement can increase the mode I. interlaminar fatigue properties of the composite: in the stable crack propagation section the crack propagation rate decreased by almost 69%, the number of cycles to failure increased to 3.8 times the original value. [2, 8]

5th *Thesis*

I have developed new test methods to evaluate the dynamic interlaminar shear and static interlaminar tensile properties of fibre reinforced polymer composites. Through the developed and standard methods I have demonstrated that carbon nanotube reinforcement improves the static interlaminar tensile (16% at 0.1 weight% nanotube content), shear (21% at 0.5 weight% nanotube content) strength and dynamic interlaminar shear strength (21% at 0.5 weight% nanotube content) of the matrix of polymer composites. [1, 3, 5, 6, 10-12]

5. List of own publications

1. Romhány G., **Szebényi G.**: Preparation of MWCNT reinforced epoxy nanocomposite and examination of its mechanical properties, Plastics, Rubber and Composites, 37, 214-218 (2008). (IF:0,431)

2. Romhány G., **Szebényi G.**: Interlaminar crack propagation in MWCNT/fiber reinforced hybrid composites, Express Polymer Letters, 3, 145-151 (2009). (IF:1,452)

3. Romhány G., **Szebényi G.**: Preparation of MWCNT/carbon fabric reinforced hybrid nanocomposite and examination of its mechanical properties, Materials Science Forum, 589, 269-274 (2008).

4. **Szebényi G.**, Romhány G.: The effect of electron irradiation on the mechanical properties of MWCNT/carbon fiber reinforced hybrid nanocomposites, Materials Science Forum, 659, 91-95 (2010).

5. **Szebényi G.**, Mészáros L., Romhány G.: Többfalú szén nanocsővel erősített epoxi mátrixú nanokompozit előállítása, mechanikai tulajdonságainak elemzése, Anyagvizsgálók Lapja, 17, 20-26 (2007).

6. **Szebényi G.**, Mészáros L., Romhány G.: Többfalú szén nanocső/szénszövet erősítésű hibrid nanokompozit előállítása, mechanikai tulajdonságainak elemzése, Műanyag és Gumi, 44, 312-315 (2007).

7. Romhány G., **Szebényi G.**: Preparation of MWCNT reinforced epoxy nanocomposite with improved interfacial adhesion, Gépészet 2008, 2008. május 29-30., Budapest, Konferencia kiadvány 6 oldal.

8. Romhány G., Niedermann P., **Szebényi G.**: Mechanical properties of MWCNT/fiber reinforced hybrid composites, International Conference on Technical Textiles and Nonwovens, 2008. november 11-13., Delhi, India, Konferencia kiadvány 7 oldal.

9. **Szebényi G.**, Romhány G.: Electric and magnetic field orientation techniques for MWCNT/epoxy nanocomposites, ECCM14, 2010. június 7-10., Budapest, Konferencia kiadvány 5 oldal.

10. **Szebényi G.**, Romhány G.: Szén nanocső és szál erősítésű hibrid nanokompozitok, Erősített műanyagok 2010 Nemzetközi BALATON Konferencia, 2010. május 18-20, Keszthely, Konferencia kiadvány 13 oldal.

11. **Szebényi G.**, Romhány G.: Preparation of MWCNT reinforced epoxy nanocomposite and examination of its mechanical properties, 3rd China-Europe Symposium - Processing and Properties of Reinforced Polymers, 2007. június 11-15., Budapest.

12. **Szebényi G.**, Romhány G.: Preparation of MWCNT/carbon fabric reinforced hybrid nanocomposite and examination of its mechanical properties, VI. Országos Anyagtudományi Konferencia, 2007. október 14-16., Siófok.

13. **Szebényi G.**, Romhány G.: Keverési módszer hatása szén nanocső erősítésű epoxi kompozitok mechanikai tulajdonságaira, Mechanoplast 2009, 2009. március 17-19., Balatonaliga.

14. **Szebényi G.**, Romhány G.: The effect of different dispersion methods on the mechanical properties of MWCNT/carbon fiber/epoxy hybrid composites, 4th China-Europe Symposium - Processing and Properties of Reinforced Polymers, 2009. június 8-12., Guilin, Kína.

15. **Szebényi G.**, Romhány G.: Elektronsugárzás hatása MWCNT/szénszál erősítésű hibrid nanokompozitok mechanikai tulajdonságaira, VII. Országos Anyagtudományi Konferencia, 2009. október 11-13., Balatonkenese.