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FRACTURE TOUGHNESS – MICROSTRUCTURE RELATIONSHIPS IN BIODEGRADABLE MEDICAL POLYMERS

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The complete dissertation with the referees' opinion and the minutes of the PhD examination can be inspected at the Dean's Office of the Faculty of Mechanical Engineering of the Budapest University of Technology and Economics

1. INTRODUCTION

The significant rise in musculoskeletal diseases as a result of the increasing number of ageing people combined with the growing rate of osteoporosis contribute to the increased use of orthopedic biomaterials. Revenues in the market of these materials are anticipated to grow from $240 million in 2005 to $609 million by 2012. According to a report by Frost & Sullivan the bone-graft-substitute market is one of the fastest growing sectors of the orthopedic field. In Europe the total bone-graft-substitute market was valued at €27.1 million in 2003. By 2005 this number increased to €41 million and by 2010 to €79 million. The estimated number of bone-grafting procedures is 500,000 annually only in the US, although the number of donors is not more than 20,000. These numbers can double easily on a global basis and indicate the lack of availability of musculoskeletal donor tissue traditionally used in these reconstructions.[1]

During the last three decades, significant advances have been made in the available treatments of skeletal-tissue defects caused by trauma or disease. As an outcome of this, the application of large skeletal allografts, synthetic grafts and total joint replacements has become fairly successful. Unfortunately, there is still a significant failure rate due to mechanical or biological complications. Therefore a new discipline known as tissue engineering has been emerged that combines the concepts of the natural sciences with surgical techniques. The ultimate goal is to develop strategies for the regeneration of musculoskeletal tissue, instead of replacing it. Thereby, scientist will be able to grow living tissue on polymer scaffolds in order to reduce the need for transplants. Since the musculoskeletal system has to withstand functional loads; scaffolds must be able to support the injured tissue during its regeneration temporarily. The synthetic matrix also has to guide cells and help the morphogenesis of the engineered tissue.

Porous scaffolds for bone tissue engineering can be manufactured from metals, ceramics and polymers, as well. The main drawbacks of metallic ones are their high modulus, corrosion and non-degradability. Ceramics are difficult to fabricate and they are too rigid and brittle. Polymers are extraordinarily versatile materials because of the high diversity of molecular and morphological structure. The major difficulty with this class of materials is the relative poor mechanical strength. They have, however, numerous advantages like good biocompatibility, degradability and principally the viscoelasticity. Bone is a viscoelastic material as well, thus polymer based scaffolds can mimic the mechanical properties of bone.

[1] European orthopaedic biomaterials markets - *Report*. Frost & Sullivan, Pub ID: MC1303215 (2006).

The aim of my thesis is to analyze the biodegradability of polymeric scaffolds *in vitro* – which is basically a hydrolysis – regarding the molecular structure, crystallinity as well as the quasi-static mechanical and fracture behavior. Albeit the toughness is of great importance in mechanical engineering applications, the fracture characteristics are often disregarded during *in vitro* degradation experiments in the known literature. Thus I deemed it necessary to perform a comprehensive study concerning the fracture mechanics of biodegradable polymers with special attention to the relationship with their microstructure. Additionally, I plan to investigate feasible solutions for improving the compressive strength and modulus of biocompatible polymers while maintaining adequate biocompatibility and toughness, too.

2. SHORT OVERVIEW OF THE LITERATURE, AIM OF THE STUDY

Based on the literature, it is important to estimate the *in vivo* behavior of biodegradable scaffolds. For this purpose *in vitro* studies are generally used. Albeit several models exist for the characterization of degradation kinetics of long chain polymers; the effect of hydrolysis on the crystallinity of semi-crystalline polymers and on the mechanical performance is far less known. Additionally, the hydrolysis of aliphatic polyesters leads to the embrittlement of the material, thus the characterization of fracture toughness is important. The encapsulated implant fragments lead to post-operative inflammations and if this becomes chronic it can also induce malignant diseases, cancer. Furthermore, materials of sufficient toughness facilitate the manipulation of implants for the surgeons.

However, degradable polymers are usually too weak for bone tissue engineering applications, but some of them possess the toughness of a suitable implant material. In contrast, ceramics are very brittle but they owe high compressive strength and stiffness. The combination of these materials, therefore, could result in good biocompatibility and adequate toughness as well as compressive strength and modulus.

The fracture characterization of tough, ductile polymers requires, however, novel test procedures due to the large plastic regions. Although the EWF method is widely used for the characterization of ductile metals and polymers, further studies are required for its proper implementation and warrant standardization within the ISO. According to the work group of ESIS TC4 the main problem with this method is the poor reproducibility of the results. Although the relationship between the fracture properties and the molecular structure of ductile amorphous polymers is well described, the same could not be stated of semi-crystalline polymers due to the lack of comprehensive studies and suitable model materials. Additionally, the cell-wall-thickness in 3D scaffolds is in the order of several hundred

micrometers, thus the use of EWF method for the determination of plane-stress fracture toughness of scaffold materials is advisable.

Therefore, based on the literature review, the main objectives of my study can be summarized as follows:

— to investigate the effect of porosity on the degradation kinetics in porous scaffolds,
— to analyze the effect of filler content and shape on the fracture toughness as well as on the quasi static tensile and compressive properties,
— to improve the toughness of PLA/PCL blends by manners of reactive compatibilization,
— to explore possible reasons of poor reproducibility during the EWF tests of polymers,
— to investigate the effect of molecular weight and crystallinity on the fracture properties of ductile semi-crystalline polymers,
— to study the effect of hydrolysis on the crystallinity, quasi-static compressive properties and mode I fracture toughness of PCL.

3. MATERIALS AND METHODS

3.1. Applied materials

For the studies four different nominal number average molecular weight (Capa 6250 M_n=25 kDa, Capa 6400 M_n=40 kDa, Capa 6500 M_n=50 kDa and Capa 6800 M_n=80 kDa) PCL were used. The materials were supplied by Perstorp Caprolactones, Perstorp UK Ltd. (Warrington, UK) The poly(D,L-lactide), Natureworks 3051D (M_n≈100 kDa with L-lactic acid/D-lactic acid molar ratio of about 98:2), was obtained from Natureworks LLC (Minnetonka, MN, USA). Prior to use each polymer was dried at 40°C over a day.

Compatibilizers, ethyl ester L-lysine diisocyanate (LDI; $C_{10}H_{14}N_2O_4$; M_n=226 Da) and ethyl ester L-lysnie triisocyanate (LTI; $C_{11}H_{13}N_3O_5$; M_n=267 Da) were purchased from Shanghai Infine Chemicals Co., Ltd (Shanghai, China) and were used as received.

Calcium carbonate was used in two crystal forms. Calcite filler was purchased from Sigma-Aldrich Inc. (St. Louis, MO, USA). The median diameter of spherical particles was determined by microscopic measurements and was 2.3 μm. Aragonite filler in the form of needle-like crystals, called whiskers, was kindly supplied by Bioceramic Department of the Institute of Glass and Ceramics (Warsaw, Poland). The median diameter of crystals was 7.9 μm, the length varied between 30 and 50 μm. The specific surface area of calcite filler was 5.7 m^2/g while that of aragonite was 1.4 m^2/g. The Brunauer-Emmett-Teller (BET) constant was 93 for calcite filler and 18 for aragonite filler suggesting stronger interaction between the calcite particles.

For the hydrolytic degradation tests phosphate buffered saline (PBS) was used. The solution was supplied by Semmelweis University, 1st Department of Pathology and Experimental Cancer Research (Budapest, Hungary) and was prepared according to the ISO 13781:1997 standard. To obtain the PBS 0.2 g/dm^3 potassium chloride, 0.2 g/dm^3 potassium hydrogen phosphate, 1.44 g/dm^3 sodium hydrogen phosphate and 8 g/dm^3 sodium chloride (NaCl) were dissolved in water, while the pH was set to 7.5. Finally 0.16 g/dm^3 Gentamicin was added to the solution as bactericide.

For the preparation of porous scaffolds NaCl with a grain size of 250-500 μm was used.

3.2. Sample preparation

In order to have exact compositions analytical balance (OHAUS Explorer, accuracy of ±0.1 mg; Ohaus Corp., Pine Brook, NJ, USA) was applied to measure the materials prior processing. The neat polymers as well as the compaunds were processed in an internal-mixer

(Brabender PL2000, Brabender GmbH, Duisburg, Germany) at 25 RPM for 15 minutes. The PCL based materials were blended at 100°C while the PLA containing ones at 180°C. Following the homogenization, the mixtures were hot pressed using a COLLIN P-200E-type (Dr. Collin GmbH, Ebersberg, Germany) compression molding machine at 5 MPa pressure and at 100°C temperature for PCL and its composites. For the PLA/PCL blends – uncompatibilized as well as compatibilized ones – the same pressure but elevated temperature (190°C) was used. The molten mixtures were held at the determined temperature for 5 minutes without load, followed by 5 minutes compression at 5 MPa and 10°C/min water-cooling to room temperature.

Type 1BA specimens according to ISO 527-2:1999 were hot-pressed to determine the tensile characteristics. Samples had dumb-bell shape, having a thickness of 2 mm, a clamped length of 55 mm and a width of 5 mm.

The EWF study was performed on double edge-notched tensile specimens. The composite and PCL/PLA blends samples with a width of 30 mm and length of 60 mm (clamped length 40 mm) were machined from sheets with a thickness of 1 mm. The EWF studies of neat PCL were performed on samples with a width of 40 mm, a length (l) of 80 mm (clamped length 40 mm) and a thickness of 0.5 mm. The ligament length (L) varied in both cases between 4 and 12 mm, and at least 25 specimens were tested for each linear regression.

For biocompatibility tests 1.5 mm thick disks having 6 mm diameter were prepared in medical grade stainless steel tool. Cylindrical samples with a diameter of 6 mm and a height of 7 mm were also prepared by compression molding to determine the compressive properties of the samples. These specimens were sterilized at FE-MA Kft. (Budapest, Hungary) by 25 kGy dose β-radiation.

The hydrolytic degradation tests were performed at 37°C in PBS, while the annealed samples were held in a humidity chamber (Memmert HCP 153, Memmert GmbH) at 25°C and RH=50% relative air humidity.

3.3. Test methods

The molecular characteristics of polymers were measured by size exclusion chromatography (SEC) in tetrahydrofuran (THF) at 35°C with a Waters chromatograph (Waters Corp., Milford, MA, USA) equipped with an In-line Degasser, four gel columns (7 μm Ultrastyrolgel columns: 500, 10^3, 10^4, 10^5 Å), a Waters 600 Solvent Delivery System (HPLC pump) and Waters 410 Differential Refractometer detectors. Samples with concentration of 4 g/dm^3 were made of certain polymers by dissolution in distilled THF. After

complete dissolution, samples were filtered through a 1 μm membrane filter, and measured. The measuring parameters were: solvent flow 1 cm^3/min, injection volume 0.1 cm^3, running time 55 minutes. The average molecular weight values of polymers were calculated from their chromatograms on the basis of a polystyrene calibration.

Tensile tests were performed according to ISO 527-1:1999 standard. Both the sample geometry (type 1BA) and the test conditions were set as suggested. The tests were performed at room temperature at 100 mm/min crosshead speed by a Zwick Z020 (Zwick GmbH, Ulm, Germany) universal testing machine. For the determination of each data point five specimens were tested.

The compressive properties of specimens were also measured at ambient conditions (23-25°C, RH=37-45%) at crosshead speed of 2 mm/min by a Zwick Z020 universal testing machine. The test conditions were set and the results were evaluated according to ISO 604:2002 standard. For solid samples five, while for porous ones nine specimens were tested in each data point.

The load-displacement curves of EWF tests were recorded at ambient conditions (23-25°C, RH=40-48%) by a Zwick Z020 universal testing machine at a crosshead speed of 10 mm/min. The numerical integration of curves was accomplished using the trapezoidal rule.

Dynamic mechanical analysis of the polymer sheets was performed on a DMA Q800 (TA Instruments, New Castle, DE, USA) dynamic mechanical analyzer in strain controlled tension mode using a frequency of 1 Hz, an amplitude of 15 μm and a force track of 120%. The properties were measured between -100°C and 100°C with a heating rate of 1 °C/min.

The rheological properties of PCL melts were determined using a plate-plate rheometer (AR2000; TA Instruments, New Castle, DE, USA) at 100°C in the shear-rate range of 0.01 and 5 1/s.

Scanning electron microscopic images were taken of the surface and the crosscut morphology of the specimens by JEOL 6380LA (JEOL Ltd., Tokyo, Japan) instrument. Prior testing JEOL JFC-1200 sputter coater was used to form a thin gold layer on the surface of the specimen.

The specific surface area of the filler was determined using an Autosorb1, (Qantachrome, Boynton Beach, FL, USA) apparatus. Nitrogen was used as adsorbent and the measurement was carried out at liquid nitrogen temperature (~-195°C). The samples were degassed at 10^{-3} Pa vacuum for 24 hours; then a part of the adsorption isotherm of N_2 was measured on the filler. Monomolecular capacity was determined from the linearized form of the equation describing the multilayer, BET II type adsorption of a gas on the filler surface. The

monomolecular capacity is the amount of adsorptive which is necessary to cover a unit surface with a monolayer. The linearized BET equation can be used in the relative pressure range of 0.05-0.35, where 5 points were measured. The linear fit was very good, the correlation coefficient was always larger than 0.99. A parameter can also be determined from the BET measurement, which characterizes the strength of interaction between the components. The specific surface area can be calculated from the monomolecular capacity and from the area occupied by a single gas molecule. In the calculations this latter value was taken as 0.162 nm^2. The standard deviation of the measurement was around 10%.

Wide-angle X-ray diffraction (WAXD) studies were performed to reveal the crystalline characteristics of samples. The patterns were recorded by using an X'pert PRO MPD (PANalytical B.V., Almelo, The Netherlands) X-ray diffractometer equipped with an X'Celerator detector and using Cu K_α radiation.

Differential scanning calorimetry was carried out on the samples by a Mettler-Toledo DSC1 (Mettler-Toledo GmbH, Greifensee, Switzerland). The purge gas was nitrogen (30 ml/min), while liquid nitrogen was used for the cooling. After the measurements the results were evaluated according to ISO 11357-3 standard. The samples were tested between -30°C and 200°C with a heating and cooling rate of 10°C/min.

Human osteosarcomic cells were used to investigate the biocompatibility of PCL matrices. The experiments were performed in 24-well polystyrene culture plates (tissue culture polystyrene, Sarstedt AG & Co., Nürnbrecht, Germany). Prior the cell inoculation the sterile samples were pre-treated with RPMI1640 medium (Sigma-Aldrich Inc.) supplemented with 10% foetal calf serum, 1% antibiotic mixture (Sigma-Aldrich Inc.) in humidified carbon dioxide atmosphere. The cells were seeded at 10^5 cells/ml/well onto sterilized PCL. After two days the medium was changed. For the next seven days the cells were maintained in culture medium at 37°C in a humidified carbon dioxide atmosphere. At the fixed time, the cells were re-suspended by Trypsin-ETA solution (Sigma-Aldrich Inc.) and the cell-growth was determined by cell numbering in Bürker chamber.

4. CONCLUSIONS – THESES

1st Thesis

I have demonstrated during the analyses of the essential work of fracture method (mode I., double edge notched tensile specimens) that the increase of maximum net-section stress (σ_{ns} [MPa]) at small ligament lengths (L<10B, where B [mm] is the specimen thickness) is not solely related to the plane-stress/plane-strain transition. I have shown that the maximum net-section stress can be calculated as a function of ligament length with Equation (T1):

$$\sigma_{ns} = m^* \sigma_u \left(1 + \frac{u}{m^* \sigma_u} \frac{1}{L} \right) \qquad \text{(T1)}$$

where L [mm] is the ligament length, σ_u [MPa] is the yield stress, m^* [-] is a stress state related factor (its value is $1<m^*<1.15$ for isotropic, plastic-rigid materials in plane-stress based on Hill's constraint factor) and u [N/mm] is a factor related to the real material behavior (elastic-plastic material, quasi plane-stress, crack initiation under complex 3D stress state, non-ideal geometric similarity). Due to the $u/m^*\sigma_u$ part of Equation (T1) the stress criterion $\text{Max}(\sigma_{ns})=1.15\sigma_u$ postulating plastic-rigid material behavior cannot be used for the determination of the lower ligament limit (L_{min}) of essential work of fracture tests.

2nd Thesis

I have proven that the ductility level (DL) of the essential work of fracture method (mode I., double edge notched tensile specimens) can be given from the ultimate elongation versus ligament length plots by Equation (T2)

$$DL = e_p \left(1 + \lambda \frac{1}{L} \right) \qquad \text{(T2)}$$

where $\lambda=e_0/e_p$ [mm] is a material dependent constant, e_0 [mm] is the critical crack tip opening displacement, e_p [-] is the half of the crack tip opening angle and L [mm] is the ligament length. e_0 and e_p can be estimated as the ordinate intercept and the slope of the ultimate elongation versus ligament length plot, respectively.

3rd Thesis

I have demonstrated that under given circumstances (T=25°C, RH=40%, mode I., double edge notched tensile specimens) poly(ε-caprolactone) is a good model material for the description of molecular-weight dependence of essential work of fracture parameters in semi-crystalline polymers, since the parameters, that influence the properties of crystalline phase can be either described without significant cross effects (amount and perfection of crystalline phase, spherulite size) or do not change (unit cell). I have shown that the molecular-weight dependence of essential work of fracture parameters can be given after normalization with crystallinity by Equation (T3).

$$w_e=(w_{e0}+a\cdot M_n)\cdot X \qquad \text{(T3)}$$

where w_{e0} [kJ/m^2] is the intrinsic essential work of fracture, a [kJ/kDa·m^2] is a tie molecule density dependent variable, M_n [kDa] is the number average molecular weight and X [-] is the crystallinity. For poly(ε-caprolactone) the constant values (R^2=0.9954) are a=0.713 [kJ/kDa·m^2] and w_{e0}=68.67 [kJ/m^2].

4th Thesis

Based on morphological and fracture mechanical studies I have demonstrated that the biocompatible, but thermodynamically incompatible poly(D,L-lactide) (PLA) (M_n=100 kDa) and poly(ε-caprolactone) (PCL) (M_n=50 kDa) blends (PCL weight ratio between 0 and 1) can be compatibilized with small amounts of lysine di- and triisocyanate (0.5 phr); and the compatibilization results in more finely dispersed second phase and in homogeneous deformation of the matrix and the dispersed phase, as well (T=25°C, RH=40%, v=10 mm/min, mode I., double edge notched tensile specimens). As a result the essential work of fracture values (w_e [kJ/m^2]) increase significantly in compatibilized blends (in the PLA:PCL 1:1 blend the specific essential work of fracture increased by 150% after compatibilization).

5th Thesis

I have demonstrated that in poly(ε-caprolactone) samples (M_n=25-80 kDa) the length of the macromolecule and the crystalline morphology (due to indirect rheological and thermodinamical reasons) influences the plane-stress ductile fracture behavior (mode I., double edge notched tensile specimens) of annealed (T=25°C) samples.

a) I have shown by differential scanning calorimetry and wide angle X-ray diffractometry that the annealing process (studied between 1 and 168 h) increases the crystallinity and the perfection of crystalline lamellae and this, along with the reorganization of chain configurations (that decreases the entanglement density between the amorphous and crystalline phase; the time-constant of this reorganization is related to the third power of the molecular weight), causes the absence of ductile deformation of crystalline phase in the low molecular weight samples (M_n=25 kDa). As a result the crack propagation becomes instable and both the specific essential work of fracture (w_e [kJ/m^2]) and plastic work of fracture (βw_p [MJ/m^3]) values decrease.

b) In materials of higher average molecular weight (M_n=40-80 kDa) the densities of tie molecules and entanglements increase and the time-constant of chain reorganization is larger, too, thus the deformation remains ductile and the crack propagation stable. In these cases the unloosening of crystalline phase is promoted, which was supported by X-ray diffraction measurements. Owing to the more perfect crystalline structure, the specific essential work of fracture (w_e [kJ/m^2]) values increase slightly, while the plastic work of fracture (βw_p [MJ/m^3]) terms do not change significantly.

6th Thesis

I have demonstrated that under given circumstances ($T>T_g$, mode I., quasi plane-stress, double edge notched tensile specimens, v<10 mm/min) the semi-crystalline poly(ε-caprolactone) remains ductile until there is a good connection between the amorphous and crystalline phase and the transferred stress can initiate the plastic deformation of crystallites. If the contact between the two phases deteriorates (hydrolytic degradation of tie molecules and/or entanglements, migration of flexible chain segments above T_g) and the perfection of crystalline phase takes place (secondary crystallization, as a result of increased temperature, 37°C, and water, which can be tracked with DSC by increasing melting temperatures) then the fracture becomes brittle. This has been supported by essential work of fracture tests on hydrolytically degraded poly(ε-caprolactone) samples (sheet thickness of 0.5 mm)

7th Thesis

I have shown during *in vitro* hydrolysis studies of biodegradable poly(ε-caprolactone) that, although the known degradation kinetics models consider the amount of water as constant and geometry independent, while anticipating faster degradation in bulk material because of the autocatalysis of carboxyl groups; the different diffusion lengths and specific surfaces significantly influence the amount of accessible water, and thus the kinetics of hydrolysis in bulk and porous materials. Contrarily to the anticipated autocatalytic effects the degradation of porous poly(ε-caprolactone) is faster (k=7-8·10^{-5} 1/h) than that of bulk materials (k=4,1·10^{-5} 1/h). This has been verified experimentally by size extrusion chromatography, differential scanning calorimetry and quasi-static compression tests on cylindrical samples (Ø6x7 mm, M_n=80 kDa, bulk and porous specimens with porosity of 0.7-0.9).

5. LIST OF OWN PUBLICATIONS

Papers

1. **Tuba F.**: Molecular weight dependence of tensile and fracture properties of poly(ε-caprolactone), Műanyag és Gumi 49(x), xx-xx (2012). – *in Hungarian* (*accepted*)

2. **Tuba F.**, Oláh L., Nagy P.: The role of ultimate elongation in the determination of valid ligament range of essential work of fracture tests, Journal of Materials Science 47(5), 2228-2233 (2012). *doi: 10.1007/s10853-011-6033-3* /IF2010:1.855/

3. **Tuba F.**, Oláh L., Nagy P.: Essential work of fracture study of polymers: a novel criterion for the validation of tested ligament range, Journal of Materials Science 46(24), 7901-7904 (2011). *doi: 10.1007/s10853-011-5778-z* /IF2010:1.855/

4. **Tuba F.**, Oláh L., Nagy P.: Characterization of reactively compatibilized poly(D,L-lactide)/poly(ε-caprolactone) biodegradable blends by essential work of fracture method, Engineering Fracture Mechanics 78(17), 3123-3133 (2011). *doi: 10.1016/j.engfracmech.2011.09.010* /IF2010:1.571/

5. **Tuba F.**, Oláh L., Nagy P.: Characterization of fracture properties of aragonite and calcite filled poly(ε-caprolactone) by essential work of fracture method, Journal of Applied Polymer Science, 120(5), 2587-2595 (2011). *doi: 10.1002/app.33341* /IF2010:1.240/

6. Oláh L., **Tuba F.**: Investigation of calcium carbonates enhanced poly(ε-caprolactone) materials for biomedical applications, Macromolecular Symposia, 296(1), 371-377 (2010). *doi: 10.1002/masy.201051051*

7. Szenti A., **Tuba F.**, Kovács N.K.: Rapid Tooling technologies in the processing of thermoplastic polymers, Materials Science Forum, 659, 97-102 (2010).

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9. Czigány T., Deák T., Al-Gaadi B., Balogh G., Kmetty Á., Sikló B., **Tuba F.**: Hybrid composites – a review, Műanyag és Gumi, 46(12), 471-474 (2009). – *in Hungarian*

10. Tábi T., **Tuba F.**, Oláh L.: Investigation of time-dependent behavior of starch-based, injection molded biodegradable polymer, Materials Science Forum, 589, 281-286 (2008).

11. **Tuba F.**, Oláh L.: Development of polymer based biodegradable scaffolds for bone tissue regeneration, Műanyag és Gumi, 44(4), 171-174 (2007). – *in Hungarian*

Conferences

1. 10th Austrian Polymer Meeting and 2nd Joint Austrian-Slovenian Polymer Meeting 2010, Leoben, Austria, 8-10 September 2010 – **Tuba F.**, Oláh L., Nagy P.: Molecular weight

dependence of essential and non-essential work of fracture of partially crystalline poly(ε-caprolactone)

2. Replast 2010, Balatonfüred, Hungary, 8-9 April 2010 – **Tuba F.**: Biodegradable polymers in waste management (*in Hungarian*)

3. POLYMAT 2009 – International Conference on Polymers and Advanced Materials, Huatulco, Mexico, 22-26 November 2009 – **Tuba F.**, Nagy P., Oláh L., Manero O.: Effect of cold-crystallization on the mechanical properties of poly(D,L-lactide)

4. VII. Hungarian Conference on Materials Science, Balatonkenese, Hungary, 11-13 October 2009 – Szenti A., **Tuba F.**, Kovács N.K.: Rapid Tooling technologies in the processing of thermoplastic polymers

5. 26th Danubia-Adria Symposium on Advances in Experimental Mechanics, Leoben, Austria, 23-26 September 2009 – Oláh L., **Tuba F.**, Borbás L., Hadzima B.: Long-term degradation of polycaprolactone templates

6. European Polymer Congress 2009, Graz, Austria, 12-17 July 2009 – Oláh L., **Tuba F.**: Investigation of calcium carbonate reinforced poly(ε-caprolactone) substrates as bone replacements

7. 25th Danubia-Adria Symposium on Advances in Experimental Mechanics, Ceske Budejovice, Czech Republik, 24-27 September 2008 – **Tuba F.**, Borbás L., Deák Gy., Nagy M., Oláh L., Hadzima B.: Influence of temperature and hydrolysis on the compressive mechanical properties of poly(ε-caprolactone)

8. III. Hungarian Conference on Biomechanics, Budapest, Hungary 4-5 July 2008 – **Tuba F.**, Borbás L., Oláh L., Hadzima B.: Development of polymer based scaffolds for guided tissue regeneration (*in Hungarian*)

9. Gépészet 2008 Conference, Budapest, Hungary, 29-30 May 2008 – **Tuba F.**: Hydrolytic degradation of poly(ε-caprolactone): qualitative study

10. VI. Hungarian Conference on Materials Science, Siófok, Hungary, 14-16 October 2007 – Tábi T., **Tuba F.**, Oláh L.: Investigation of time-dependent behavior of starch-based, injection molded biodegradable polymer

11. MECHANOPLAST 2007, Gyula, Hungary, 20-22 March 2007 – **Tuba F.**, Oláh L.: Development of polymer based biodegradable scaffolds for bone tissue regeneration (*in Hungarian*)