FRACTURE TOUGHNESS – MICROSTRUCTURE RELATIONSHIPS IN BIODEGRADABLE MEDICAL POLYMERS

PhD thesis

Written by:
Ferenc Tuba
MSc in Mechanical Engineering

Supervised by:

Dr. László Oláh
Audi Hungaria Motor Kft.

Dr. Péter Nagy
Associate professor
Department of Polymer Engineering
Budapest University of Technology and Economics

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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ACP</td>
<td>amorphous calcium phosphate</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>calcium carbonate</td>
</tr>
<tr>
<td>DENT</td>
<td>double edge-notched tensile specimen</td>
</tr>
<tr>
<td>DMA</td>
<td>dynamic mechanical analysis</td>
</tr>
<tr>
<td>DNA</td>
<td>deoxyribonucleic acid</td>
</tr>
<tr>
<td>DSC</td>
<td>differential scanning calorimetry</td>
</tr>
<tr>
<td>EPBC</td>
<td>ethylene-propylene block copolymer/poly(ethylene-co-propylene)</td>
</tr>
<tr>
<td>ESIS</td>
<td>European Structural Integrity Society</td>
</tr>
<tr>
<td>EWF</td>
<td>essential work of fracture</td>
</tr>
<tr>
<td>HA</td>
<td>hydroxyapatite</td>
</tr>
<tr>
<td>HIPS</td>
<td>high impact polystyrene</td>
</tr>
<tr>
<td>LDI</td>
<td>ethyl ester L-lysine-diisocyanate</td>
</tr>
<tr>
<td>LEFM</td>
<td>linear elastic fracture mechanics</td>
</tr>
<tr>
<td>LTI</td>
<td>ethyl ester L-lysine-triisocyanate</td>
</tr>
<tr>
<td>NaCl</td>
<td>sodium chloride</td>
</tr>
<tr>
<td>PBS</td>
<td>phosphate buffered saline</td>
</tr>
<tr>
<td>PBT</td>
<td>poly(butylene-terephthalate)</td>
</tr>
<tr>
<td>PC</td>
<td>polycarbonate</td>
</tr>
<tr>
<td>PCL</td>
<td>poly(ε-caprolactone)</td>
</tr>
<tr>
<td>PEEK</td>
<td>poly(ether-ether-ketone)</td>
</tr>
<tr>
<td>PEG</td>
<td>poly(ethylene-glycol)</td>
</tr>
<tr>
<td>PEI</td>
<td>poly(ether-imide)</td>
</tr>
<tr>
<td>PEN</td>
<td>poly(ethylene-naphthalate)</td>
</tr>
<tr>
<td>PET</td>
<td>poly(ethylene-terephthalate)</td>
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<tr>
<td>PETG</td>
<td>poly(ethylene-terephthalate-co-ethylene-glycol)</td>
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<tr>
<td>PGA</td>
<td>poly(glycolic-acid)/Poly(glycolide)</td>
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<tr>
<td>PHB</td>
<td>poly(3-hydroxy-butyrate)</td>
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<tr>
<td>PLA</td>
<td>poly(D,L-lactide)</td>
</tr>
<tr>
<td>PLLA</td>
<td>poly(L-lactide)</td>
</tr>
<tr>
<td>PVC</td>
<td>poly(vinyl-chloride)</td>
</tr>
<tr>
<td>RPT</td>
<td>rapid prototyping</td>
</tr>
</tbody>
</table>
Nomenclature

SEC — size exclusion chromatography
SEM — scanning electron microscopy
THF — tetrahydrofuran
WAXD — wide-angle X-ray diffraction

LIST OF SYMBOLS

*Latin letters*

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<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Description</th>
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<tbody>
<tr>
<td>a</td>
<td>[kJ/kDa·m^2]</td>
<td>tie-molecule dependent variable</td>
</tr>
<tr>
<td>A</td>
<td>[-]</td>
<td>initial crystallinity dependent variable</td>
</tr>
<tr>
<td>B</td>
<td>[mm]</td>
<td>sample thickness</td>
</tr>
<tr>
<td>D</td>
<td>[nm]</td>
<td>size parameter of crystalline domains</td>
</tr>
<tr>
<td>DL</td>
<td>[-]</td>
<td>ductility level</td>
</tr>
<tr>
<td>DL</td>
<td>[-]</td>
<td>average of ductility levels</td>
</tr>
<tr>
<td>e_0</td>
<td>[mm]</td>
<td>experimentally estimated crack opening displacement</td>
</tr>
<tr>
<td>e_p</td>
<td>[-] [rad]</td>
<td>half of the experimentally estimated crack opening angle</td>
</tr>
<tr>
<td>e_u</td>
<td>[mm]</td>
<td>elongation at break</td>
</tr>
<tr>
<td>E</td>
<td>[Pa]</td>
<td>tensile modulus</td>
</tr>
<tr>
<td>E_f</td>
<td>[Pa]</td>
<td>compressive modulus of foam</td>
</tr>
<tr>
<td>E_p</td>
<td>[Pa]</td>
<td>compressive modulus of solid polymer</td>
</tr>
<tr>
<td>F</td>
<td>[N]</td>
<td>load</td>
</tr>
<tr>
<td>G_c</td>
<td>[kJ/m^2]</td>
<td>plane stress fracture toughness (determined from LEFM methods)</td>
</tr>
<tr>
<td>G_{lc}</td>
<td>[kJ/m^2]</td>
<td>mode I plane stress fracture toughness</td>
</tr>
<tr>
<td>k</td>
<td>[1/h]</td>
<td>hydrolysis rate constant</td>
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<tr>
<td>K</td>
<td>[Pa]</td>
<td>foam parameter</td>
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<tr>
<td>K_{lc}</td>
<td>[Pa·m^{1/2}]</td>
<td>mode I critical stress intensity factor</td>
</tr>
<tr>
<td>l</td>
<td>[mm]</td>
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<tr>
<td>L</td>
<td>[mm]</td>
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<tr>
<td>L_{min}</td>
<td>[mm]</td>
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<td>L_{max}</td>
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<td>upper ligament limit</td>
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<tr>
<td>m</td>
<td>[-]</td>
<td>Hill’s factor</td>
</tr>
<tr>
<td>m^*</td>
<td>[-]</td>
<td>experimental estimation of Hill’s factor</td>
</tr>
<tr>
<td>m_i</td>
<td>[-]</td>
<td>estimated value of Hill’s factor for data i</td>
</tr>
<tr>
<td>m_0</td>
<td>[g]</td>
<td>initial dry weight of sample</td>
</tr>
<tr>
<td>Symbol</td>
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<td>Description</td>
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<tr>
<td>--------</td>
<td>------</td>
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</tr>
<tr>
<td>$m_t$</td>
<td>g</td>
<td>dry weight of sample at time $t$</td>
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<tr>
<td>$M_c$</td>
<td>Da</td>
<td>critical molecular weight</td>
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<tr>
<td>$M_n$</td>
<td>Da</td>
<td>number-average molecular weight</td>
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<tr>
<td>$M_{n,0}$</td>
<td>Da</td>
<td>initial number-average molecular weight</td>
</tr>
<tr>
<td>$M_w$</td>
<td>Da</td>
<td>weight-average molecular weight</td>
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<tr>
<td>n</td>
<td>[-]</td>
<td>cell geometry dependent constant of foams</td>
</tr>
<tr>
<td>N</td>
<td>[-]</td>
<td>sample size</td>
</tr>
<tr>
<td>p</td>
<td>[-]</td>
<td>significance level</td>
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<tr>
<td>$P_f$</td>
<td>Pa</td>
<td>property of foam</td>
</tr>
<tr>
<td>$P_p$</td>
<td>Pa</td>
<td>property of solid polymer</td>
</tr>
<tr>
<td>$P_{\text{max}}$</td>
<td>N</td>
<td>maximum load in a DENT specimen</td>
</tr>
<tr>
<td>$R^2$</td>
<td>[-]</td>
<td>correlation coefficient of linear regression</td>
</tr>
<tr>
<td>RH</td>
<td>[%]</td>
<td>relative humidity</td>
</tr>
<tr>
<td>RPM</td>
<td>[1/min]</td>
<td>revolution per minute</td>
</tr>
<tr>
<td>s</td>
<td>mm</td>
<td>displacement</td>
</tr>
<tr>
<td>SD</td>
<td>[kJ/m$^2$]</td>
<td>standard deviation of the linear regression of EWF data</td>
</tr>
<tr>
<td>t</td>
<td>[day]</td>
<td>time</td>
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<tr>
<td>$T_{\text{ccp}}$</td>
<td>[°C]</td>
<td>peak temperature of cold-crystallization</td>
</tr>
<tr>
<td>$T_{\text{end}}$</td>
<td>[°C]</td>
<td>endset of melting/crystallization (extrapolated value)</td>
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<tr>
<td>$T_g$</td>
<td>[°C]</td>
<td>glass transition temperature</td>
</tr>
<tr>
<td>$T_m$</td>
<td>[°C]</td>
<td>melting temperature</td>
</tr>
<tr>
<td>$T_{\text{mp}}$</td>
<td>[°C]</td>
<td>peak temperature of melting</td>
</tr>
<tr>
<td>$T_{\text{mp,PCL}}$</td>
<td>[°C]</td>
<td>peak temperature of melting of PCL</td>
</tr>
<tr>
<td>$T_{\text{mp,PLA}}$</td>
<td>[°C]</td>
<td>peak temperature of melting of PLA</td>
</tr>
<tr>
<td>$T_{\text{on}}$</td>
<td>[°C]</td>
<td>onset of melting/crystallization (extrapolated value)</td>
</tr>
<tr>
<td>u</td>
<td>[N/mm]</td>
<td>ordinate intercept of specific load vs. ligament length plots</td>
</tr>
<tr>
<td>$u_n$</td>
<td>[mm]</td>
<td>elongation at which the centre of the ligament first yields</td>
</tr>
<tr>
<td>v</td>
<td>[mm/min]</td>
<td>test/crosshead speed</td>
</tr>
<tr>
<td>w</td>
<td>[mm]</td>
<td>sample width</td>
</tr>
<tr>
<td>$W_{0.25,f}$</td>
<td>[J]</td>
<td>work consumed for 25% compressive deformation of foam</td>
</tr>
<tr>
<td>$W_{0.25,p}$</td>
<td>[J]</td>
<td>work consumed for 25% compressive deformation of solid polymer</td>
</tr>
<tr>
<td>$w_e$</td>
<td>[kJ/m$^2$]</td>
<td>specific essential work of fracture</td>
</tr>
<tr>
<td>$W_e$</td>
<td>[J]</td>
<td>work spent for the generation of new crack surfaces, “essential”</td>
</tr>
</tbody>
</table>
Nomenclature

\[ w_{e0} \ [kJ/m^2] \] — intrinsic essential work of fracture
\[ w_{e,y} \ [kJ/m^2] \] — yielding related specific essential work of fracture
\[ w_{e,n} \ [kJ/m^2] \] — necking related specific essential work of fracture
\[ w_f \ [kJ/m^2] \] — specific total work of fracture
\[ W_f \ [J] \] — total work of fracture
\[ w_{f,\text{max}} \ [kJ/m^2] \] — maximum specific total work of fracture
\[ w_n \ [kJ/m^2] \] — specific necking related work of fracture
\[ W_n \ [J] \] — necking related work of fracture
\[ w_p \ [MJ/m^3] \] — specific dissipated energy
\[ W_p \ [J] \] — work related to energy dissipation mechanisms
\[ w_{p,y} \ [MJ/m^3] \] — yielding related specific dissipated energy
\[ w_{p,n} \ [MJ/m^3] \] — necking related specific dissipated energy
\[ w_y \ [kJ/m^2] \] — specific yielding related work of fracture
\[ W_y \ [J] \] — yielding related work of fracture
\[ x_p \ [mm] \] — size of the plastic zone
\[ X \ [%] \] — crystallinity
\[ X_{\text{PCL}} \ [%] \] — crystallinity of PCL
\[ X_{\text{PLA}} \ [%] \] — crystallinity of PLA
\[ X_{\text{PLA,init}} \ [%] \] — initial crystallinity of PLA
\[ X_{\text{max}} \ [%] \] — estimated maximal crystallinity of PCL

Greek letters

\[ \alpha \ [\text{rad}] \] — crack tip opening angle
\[ \beta \ [-] \] — geometry dependent correction factor (EWF tests)
\[ \beta_y \ [-] \] — yielding related geometry dependent correction factor
\[ \beta_n \ [-] \] — necking related geometry dependent correction factor
\[ \delta_c \ [\text{mm}] \] — crack tip opening displacement
\[ \Delta H_0 \ [J/g] \] — enthalpy of fusion
\[ \Delta H_{\text{cc}} \ [J/g] \] — enthalpy of cold-crystallization
\[ \Delta H_m \ [J/g] \] — melting enthalpy
\[ \Delta H_{m,\text{PCL}} \ [J/g] \] — melting enthalpy of PCL
\[ \Delta H_{m,\text{PLA}} \ [J/g] \] — melting enthalpy of PCL
\[ \Delta H_{m,\text{PLA,init}} \ [J/g] \] — initial melting enthalpy of PLA
Nomenclature

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<th>Unit</th>
<th>Description</th>
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<td>$\Delta T_{cc}$</td>
<td>°C</td>
<td>temperature range of cold-crystallization</td>
</tr>
<tr>
<td>$\Delta T_m$</td>
<td>°C</td>
<td>temperature range of melting</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>[-] [%]</td>
<td>strain</td>
</tr>
<tr>
<td>$\varepsilon_1$</td>
<td>[-] [%]</td>
<td>lower strain for modulus determination</td>
</tr>
<tr>
<td>$\varepsilon_2$</td>
<td>[-] [%]</td>
<td>upper strain for modulus determination</td>
</tr>
<tr>
<td>$\varepsilon_B$</td>
<td>[-] [%]</td>
<td>strain at break (tensile)</td>
</tr>
<tr>
<td>$\varepsilon_c$</td>
<td>[-] [%]</td>
<td>initiative strain in compressive measurements</td>
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<tr>
<td>$\varepsilon_y$</td>
<td>[-] [%]</td>
<td>strain at yield (tensile)</td>
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<td>$\eta_0$</td>
<td>[Pas]</td>
<td>zero-shear viscosity</td>
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<td>[°]</td>
<td>scattering angle</td>
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<td>$\kappa$</td>
<td>[-]</td>
<td>matrix/filler interaction constant</td>
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<td>$\lambda$</td>
<td>[mm]</td>
<td>length where the steady-state length of fracture process zone is ensured</td>
</tr>
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<td>$\Lambda$</td>
<td>[mm]</td>
<td>wavelength</td>
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<tr>
<td>$\rho$</td>
<td>[mm]</td>
<td>steady-state length of fracture process zone after crack initiation</td>
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<td>$\rho_f$</td>
<td>[kg/m³]</td>
<td>density of foam</td>
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<tr>
<td>$\rho_p$</td>
<td>[kg/m³]</td>
<td>density of polymer</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>[Pa]</td>
<td>slope of specific load vs. ligament length plots</td>
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<tr>
<td>$\sigma_{ext}$</td>
<td>[Pa]</td>
<td>external stress</td>
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<td>[Pa]</td>
<td>average value of the net section stresses (EWF tests)</td>
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<td>[Pa]</td>
<td>net section stress, maximum effective stress (EWF tests)</td>
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<td>$\sigma_u$</td>
<td>[Pa]</td>
<td>tensile yield stress</td>
</tr>
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<td>$\sigma_y$</td>
<td>[Pa]</td>
<td>compressive yield stress</td>
</tr>
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<td>$\sigma_{y,f}$</td>
<td>[Pa]</td>
<td>compressive yield stress of foam</td>
</tr>
<tr>
<td>$\sigma_{y,p}$</td>
<td>[Pa]</td>
<td>compressive yield stress of solid polymer</td>
</tr>
<tr>
<td>$\tau$</td>
<td>[day]</td>
<td>time constant</td>
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<td>$\varphi$</td>
<td>[-]</td>
<td>volume fraction of polymer</td>
</tr>
<tr>
<td>$\Phi$</td>
<td>[-]</td>
<td>volume fraction of filler</td>
</tr>
<tr>
<td>$\psi$</td>
<td>[-]</td>
<td>weight fraction of the studied material</td>
</tr>
<tr>
<td>$\psi_{PCL}$</td>
<td>[-]</td>
<td>weight fraction of PCL</td>
</tr>
<tr>
<td>$\omega$</td>
<td>[rad]</td>
<td>full-width-at-half-maximum of the scattering peak</td>
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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 [1]. According to a report by Frost & Sullivan [2] 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 (Figure 1.1). These numbers can double easily on a global basis and indicate the lack of availability of musculoskeletal donor tissue traditionally used in these reconstructions [3].

![Figure 1.1 US trends in musculoskeletal tissue donors](image)

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 [4]. 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.

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. LITERATURE OVERVIEW

The structure of human body is so complex that the replacement of tissues with man-made materials is almost impossible. In the present clinical practice the implants are able to supply only the main physiological function of tissue. A more ideal situation would be if these synthetic structures could promote the remodeling of living tissue instead of replacing it.

Methods of a multidisciplinary field, called tissue engineering, are attempting to solve this challenge. Langer and Vacanti [5] defined tissue engineering as “an interdisciplinary field which applies the principles of engineering and the life sciences toward the development of biological substitutes that restore, maintain, or improve tissue function”. At the first this definition could sound a bit futuristic but there are already several pre-clinical, clinical or even commercial products available in the market, which fulfill more or less the role of tissue engineering structures. These are either used as simple support materials in body or are combined with cell cultures, stem cells and growth factors to provide man-made grafts for the patients.

Nevertheless, to prepare a suitable scaffold, there are several requirements. According Agrawal et al. [6] musculoskeletal tissue engineering scaffolds should be:
— biocompatible,
— biodegrade, harmonized with the repair or regeneration process,
— highly porous and permeable, to allow proper diffusion while having the correct pore size for the candidate cells,
— strong enough, but not too stiff, to provide the correct microstress environment for cells,
— able to carry biomolecular signals such as growth factors.

The subsequent overview offers only a very brief summary and focuses on the mechanical properties of suitable materials – especially on the fracture mechanical characterization –, on the foaming techniques adequate for guided bone regeneration and on the hydrolytic degradation of polymeric materials. For better understanding, the basics of bone biology are addressed, too. More detailed description for deeper understanding of the various aspects of tissue engineering is available in the cited books [4, 7-10].
2.1. Bone

To develop a suitable implant for guided bone regeneration it is necessary to know the basic biological, chemical and physical nature of bone tissue. However, from an engineering point of view the most important is the mimicking of key aspects of bone structure, composition and mechanical properties. In the following section I will overview the basics of bone biology and construction with an emphasis on structure-property relationships.

2.1.1. Structure and properties of bone tissue

Bone can be considered as a “dynamic, living composite”. Living and dynamic is for its continuous remodeling and composite for its dual polymer-ceramic structure. In this system bone cells are the polymeric matrix. They form approximately one third of bone mass (approx. 40% of volume). The other main component is an inorganic material, the hydroxyapatite (HA) (approx. 40% of volume, as well), which is mineralized in nanoscale around the collagen fibres of cells. Collagen provides toughness for bone, while the mineral component is chiefly responsible for stiffness and modulus. If the organic phase is burned, bone becomes brittle; on the other hand if the inorganic part is solved it will be a very ductile material.

Macroscopically the bone tissue can be divided into two main structural forms. The dense, compact bone is called as cortical, while the porous part is the trabecular or cancellous bone (Figure 2.1). Bone develops by the process of ossification as a specialized connective tissue. During ossification, osteoblasts secrete Type I collagen, and gradually becoming densely fibrous – osteoid. Subsequently hydroxyapatite crystals are deposited in the osteoid (i.e., mineralization), the osteoblasts become enclosed in the matrix, and these cells turn into osteocytes. The third type of bone cells, the multinucleate (typically 6-8 nuclei) osteoclasts are responsible for the bone resorption. In normal adult bone the formation and resorption are balanced, thus the bone mass is maintained [8].

Bone remodelling is controlled not only by metabolic but also by mechanical factors. This idea was first hypothesized by Wolff [11] a century ago, and since then it has been intensely studied and verified. In 1955 Fukada et al. [12] discovered the piezoelectric properties of bone, which resulted in the hypothesis that mechanoelectrical signals influence the bone remodeling. The theory says that remodeling is activated unless an inhibitory signal restrains it, and this signal is provoked by osteocytes. The rate of resorption is elevated when signal generation declines due to the reduced load. When signal transmission is interrupted by
damage due to excessive loading, the rate of bone formation increases. Otherwise, remodeling is maintained at a relatively low level [13].

In bone scaffolds, therefore, it is important to avoid the reduced load of newly formed bone for it results in weaker bone of smaller density due to the unbalance in bone formation and resorption. This can be achieved when the scaffold has similar modulus than the bone.

The musculoskeletal system is very complex. Therefore, it is difficult to determine the exact mechanical properties of the anisotropic, viscoelastic bone tissue. These characteristics depend on age, body-site and density – especially in cancellous bone – health. Table 2.1 summarizes the range of properties of typical human bone. The listed parameters show that bone is not only strong and stiff but also possesses considerable toughness.

<table>
<thead>
<tr>
<th>Table 2.1 Typical properties of cortical and cancellous bone [7, 15, 16]</th>
</tr>
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<tbody>
<tr>
<td>Tensile modulus</td>
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<tr>
<td>Tensile strength</td>
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<tr>
<td>Compressive modulus</td>
</tr>
<tr>
<td>Compressive strength</td>
</tr>
<tr>
<td>Bending strength</td>
</tr>
<tr>
<td>Shear modulus</td>
</tr>
<tr>
<td>Poisson ratio</td>
</tr>
<tr>
<td>Fracture toughness (K_{ic})</td>
</tr>
<tr>
<td>Work of fracture</td>
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</tbody>
</table>
2.1.2. Wound healing in bone tissue

After the implantation of a foreign material the wound healing process involves three phases: inflammation, new tissue formation and tissue remodeling. The inflammatory cells play an important role in the defense against bacteria and they attack any non-immunocompatible materials, implants in living tissue.

In a recent work Eufinger et al. [17] prepared a graded cranial implant (surface approx. 35 cm²), which was composed of an outer compact polylactide-amorphous calcium phosphate (PLLA/PLA/ACP) layer and of an inner porous polylactide-calcium carbonate (PLA/CaCO₃) layer. They found during in vivo tests, that the transition area between skull bone and implant was filled by fibrous connective tissue in 2 months. The implant evoked natural foreign body reactions and the dense, fibrous connective tissue encapsulated the scaffold. After 9 months most of the porous layer degraded, but tissue necrosis and giant cells were detected in the central areas, associated with the remaining implant parts. After 12 months small blood vessels were found around the scaffold, but the implant started to fall into fragments. At the end of the 18 month the newly formed bone reached roughly its 40% on a volume basis, but small (10-30 μm) implant fragments were embedded in newly grown bone.

Bergsma and co-workers [18] also found encapsulated, partially degraded PLLA material in patients even after 6 years of implantation. They presumed that PLLA degrades into particles of high crystallinity and the degradation rate of these fragments is very low. Years after, during the bone remodeling phase, these non-resorbed, embedded particles could cause postoperative inflammatory responses, as observed.

Regarding this topic a recent review from Schafer and Werner [19] could be of interest. This publication analyses the relationship between the wound healing-process and the development of cancer. According to the article a multitude of clinical observations has shown that cancer is frequently the consequence of chronic inflammation in different tissues or organs. During the inflammatory phase numerous inflammatory cells are attracted to the wound site and some of them secrete reactive oxygen containing species. These reactive molecules can directly damage DNA, which could result in the accumulation of mutations in chronic inflammations. Therefore, they are probably responsible for the enhanced frequency of malignant transformation, which is observed in chronically inflamed tissues. The authors stated that it is, and it will be, a major challenge to reduce chronic inflammation and subsequent reactive oxygen species production of chronic wounds.
In tissue engineering applications some polymers release acidic degradation by-products, which can cause strong inflammatory response, as well [20]. If this adverse effect is sustained for a prolonged period, e.g. by an encapsulated highly crystalline polymer fragment in a poorly vascularized tissue site, the inflammation may become chronic and thus the risk of cancer increases.

Therefore, when using scaffolds it is essential to diminish the pH decrease in the surrounding tissue, incorporate antibodies against inflammatory mediators, modify the geometry of devices into less bulky [21] and finally, as far as possible, avoid implant fragmentation.

2.2. Biodegradable materials

Biocompatibility is the key factor of any implant material. This word covers, however, not only the non-toxic feature of implant material but also long-term immune compatibility, chemical and physical conformity and mechanical uniformity compared to the natural tissue.

Metals (stainless steel, cobalt-chrome and titanium alloys) owe high strength, modulus, toughness; but they also have disadvantages like high density, poor \textit{in situ} plasticity and \textit{in vivo} corrosion [9]. Their stability in biological systems often leads to aggressive immune reactions (frustrated phagocytosis) and the fibrous encapsulation of implant is common, too [22]. Additionally, due to their high modulus the stress shielding of bulk metal implants could cause problems, as well [23].

The majority of ceramics (alumina, zirconia, salts of alkali- and alkaline-earth metals) have very good biocompatibility. Additionally, hydroxyapatite is one of the major contents of bone, thus calcium carbonates and phosphates can act as bioactive materials. They have high compressive modulus and hardness, but they are also brittle and difficult to form.

Polymers are very versatile materials. Mostly, they have relatively low strength and modulus, but are easily processible and have good toughness, which ease the \textit{in situ} forming and is important during the implantation process. They degrade \textit{in vivo} and have a viscoelastic nature that is analogous to the natural tissues.

2.2.1. Biodegradable polymers

\textit{Classification}

Even though the application of degradable natural polymer devices (e.g. catgut, silk) had been reported thousands of years ago by Abulcasis [24], the use of synthetic biodegradable polymers started only in the later half of 1960’s. However, during the past two decades many
biodegradable polymers were developed for various medical applications such as temporary prostheses, tissue engineering scaffolds or controlled release drug delivery vehicles. In the literature terms such as biodegradable, bioerodible, bioreorbable and bioabsorbable are often used loosely and confusingly. A possible definition is given by Vert [25], however, in this study I use the word ‘biodegradable’ for materials, which disintegrate in vivo, while the by-products are either incorporated by human body or excreted completely through natural metabolism without any residual side effects.

Biodegradable polymers can be classified in many ways. The basis of classification can be either the chemical structure, the way of synthesis or the mode of degradation [26, 27]. Depending on the mode of degradation in biological environment, polymers can be further classified into hydrolytically and enzymatically degradable ones. Hydrolytically degradable polymers have labile chemical bonds in their backbone. The functional groups susceptible to hydrolysis include esters, orthoesters, anhydrides, carbonates, amides, urethanes, ureas etc. [28]. Furthermore, it should be mentioned that the majority of naturally occurring polymers undergo enzymatic degradation, as well [27].

Biopolymers are polymers formed in nature during the growth cycles of all organisms; hence, they are also referred as natural polymers [26]. The first group of natural occurring degradable polymers includes polysaccharides. In a recent study Barbosa et al. [29] reviewed the applicability of many non-human-origin polysaccharides – cellulose, alginate and chitosan have been chosen as examples – for bone regeneration. The authors stated that despite the disadvantages (e.g. low moduli, strength, thermal and chemical stability, high swelling ability in water, and proneness to microbial and enzymatic degradation) these materials have the ability to overcome some other concerns due to their great versatility.

The other main group of natural, degradable polymers is the polypeptides. Proteins – the major structural components of many tissues – are, for the most part, neither soluble nor meltable without degradation; thus they are applied in their natural form (e.g. fibrous proteins like collagen, wool and silk) [26]. In vivo they undergo through naturally-controlled, enzymatic degradation processes, thus their degradation is well predictable [27].

Collagen is found in every major tissue that requires strength and flexibility, and is the major component of mammalian connective tissue [30]. It has a triple-helix structure, and the rod-like microfibrils are nearly 300 nm long with a molecular weight of about 300,000 Da. Since collagen is the major component of the extracellular matrix and serves as a natural substrate for cell attachment and proliferation; it has been suggested as an ideal matrix
material for tissue engineering and wound dressing applications [27]. However, the general immune incompatibility of such natural materials represents a problem.

Polyhydroxyalkanoate polyesters are natural, biodegradable, biocompatible, thermoplastic materials produced by a wide variety of microorganisms. The molecular weights of these polyesters can range from tens to the hundreds of thousands of Daltons. Poly(3-hydroxybutyrate) (PHB) is highly crystalline and relatively hydrophobic, consequently its in vivo degradation lasts for years. It has high tensile modulus (3.8 GPa) and strength (45 MPa), but it is brittle, its elongation at break is only about 4% [31]. The copolymers prepared from hydroxybutyric and hydroxyvaleric acids are less crystalline and brittle, more readily processible, but they are still fair resistant to hydrolysis [30]. The mechanical properties of these copolymers will be treated later in details.

To summarize, biopolymers are very versatile materials. Some of them has very good biocompatibility, is bioactive, others have long degradation times. Each of these properties could be beneficial in bone tissue engineering applications. On the contrary, their main disadvantage is that these properties extraordinarily depend on environmental conditions (e.g. habitat, nutrient, climate etc.). Synthetic polymers have more predictable nature, thus they can be handled more easily. Consequently, in the next section of this subchapter the main synthetic, biodegradable polymers are briefly overviewed.

Synthetic degradable polymers can be attained either from natural resources or from mineral oil. A wide variety of polymers have been synthesized in the recent years, and the research in organic chemistry continues today, too.

Polyorthoesters and polyanhydrides have advantageous degradation profile for controlled drug delivery systems, but their mechanical performance was found to be poor for load bearing applications [27].

Polyurethanes and poly(ether-urethanes) have been extensively investigated as long-term medical implants, such as cardiac pacemakers and vascular grafts due to their excellent biocompatibility and mechanical properties. Based on the good performance and versatility of stable polyurethanes attempts were made to develop biodegradable ones. Due to the toxicity of common isocyanates – conventional polyurethanes are prepared through the polycondensation reaction of aromatic di- and triisocyanates with alcohols and amines – other biocompatible aliphatic isocyanates have been investigated for the development of biodegradable polyurethanes. A few of them are L-lysine-isocyanates and 1,4-diisocyanatobutane [27].
Another widely investigated group of synthetic, degradable thermoplastic polymers is the linear, aliphatic poly-α-esters. Although all polyesters are degradable because of the reversibility of esterification, only the aliphatic ones can degrade over a time frame required for medical applications. The degradation time varies with the length of aliphatic chains between the ester bonds. The chemical structure of different polyesters is shown on Figure 2.2, while the main thermal and mechanical characteristics are listed in Table 2.2.

### Table 2.2 Thermal and mechanical properties of different polyesters [27, 32, 33]

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Melting temperature, (T_{mp}) [°C]</th>
<th>Glass transition temperature, (T_g) [°C]</th>
<th>Tensile modulus, (E) [GPa]</th>
<th>Tensile strain at break, (\varepsilon_B) [%]</th>
<th>Degradation time* [months]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGA</td>
<td>210-235</td>
<td>35-45</td>
<td>7-12.5</td>
<td>2-20</td>
<td>0.5-1</td>
</tr>
<tr>
<td>PLLA</td>
<td>145-185</td>
<td>53-65</td>
<td>3-3.5</td>
<td>2-30</td>
<td>9-12</td>
</tr>
<tr>
<td>PLA</td>
<td>amorphous</td>
<td>50-60</td>
<td>2</td>
<td>5-240</td>
<td>1-2</td>
</tr>
<tr>
<td>PCL</td>
<td>55-60</td>
<td>-70- -60</td>
<td>0.3-0.5</td>
<td>700-1000</td>
<td>9-15</td>
</tr>
</tbody>
</table>

* half time of the loss of strength, depends on numerous factors

As the glass transition temperatures indicate polyglycolide and polylactides are in glassy state at *in vivo* conditions, therefore – and as a result of short aliphatic chains – they are rigid and brittle materials with high modulus and strength values (Figure 2.2). Polylactide can be attained through the polycondensation of lactic-acid or by ring opening polymerization of lactide. The latter method came into general use, because it is faster and results in higher molecular weight polymers. Additionally, lactide is a chiral molecule and exist in two forms; namely L- and D-lactide. The polymerization of each monomers leads to the formation of semi-crystalline polymers, but the incorporation of a certain amount of D,L-lactide results in the formation of amorphous polymers. These possess lower mechanical strength and modulus, shorter degradation time, but their elongation at break is higher [26, 32].

Poly(ε-caprolactone), in contrast, is an elastomer-like material and possess relative low strength and modulus, but high ductility. It is highly processible, it is soluble in a wide range of organic solvents, has a low melting point, good toughness, while having the ability to form blends with a wide range of polymers. It can be ideal for long time applications, for its degradation rate is fairly slow. Additionally, the weight specific number of ester linkages is the smaller among the listed materials, which results in less dramatic pH decrease and inflammatory response during degradation [34].
According to Hutmacher [32] bone needs at least 4-6 months to reclaim its original mass and mechanical strength. In a recent in vivo study Eufinger and co-workers [17] however observed, that without using growth factors only the half of the original mass of skull bone is regenerated after 18 months. Therefore, the implant has to maintain its mechanical properties for about one year, but should not arrest the physiological stresses for a prolonged time. In this way the formation of new bone could be promoted. If, however, the implant material possesses too high modulus and strength (e.g. metals) it covers these physiological loads and hinders the regeneration according to Wolff’s law [11].

**Degradation mechanisms**

There are two types of polymer degradation. During physical degradation the driving force is a physical effect like temperature, mechanical stress, UV light or other high energy radiation. On the other side, the chemical or bio-chemical degradation has greater importance in biodegradable polymers. These materials generally have hydrolysable bonds in their backbone, which undergo chain scission via hydrolysis or enzyme catalyzed hydrolysis.
The hydrolysis is a complex process. First, water enters the polymer, which is accompanied by swelling. Subsequently, water triggers the chain scission, leading to the creation of oligomers and monomers. The pH inside the material begins to be controlled by the degradation by-products, which in general have acid-base functionality. The acidic groups could lead to autocatalysis that accelerates the chain scission [35, 36]. The degradation also changes the microstructure of the bulk material through the formation of pores. Finally oligomers and monomers are released, leading to the weight loss of polymer device [37]. Summarily, the main steps of hydrolysis are: (i) swelling, (ii) chain scission and finally (iii) mass loss. Swelling is controlled by the diffusion rate of water, while the degradation rate of polymer backbone describes the chain scission. Assuming that the degradation and diffusion rates are uniform inside the polymer, the hydrolytic degradation can be divided into two groups. If the diffusion of water into the polymer is faster than the degradation of polymer bonds, the polymer will undergo bulk (homogeneous) erosion, and the degradation is not confined to the polymer surface. If, however, the degradation of the polymer bonds is faster than the diffusion of water, the water molecules will be consumed during the hydrolysis of bonds on the polymer surface and will be prevented from diffusion into the bulk. This type of degradation is called as surface or heterogeneous degradation [38].

For the mathematical description of hydrolytic degradation of polyesters several theories exist. There are empirical models and theories based on Monte Carlo simulations [39-41]. The advantage of these approaches is that an estimation of the hydrolysis can be made without knowing the mechanism behind it. In one of the first descriptions, Montroll and Simha [42] used a statistical approach. However, this model assumes that all initial molecules have the same molecular weight, which is not true for real polymers. Later Simha [43] developed a random chain scission theory, in which the size distribution of polymers was incorporated, as well. This model describes the chain scission reaction with first order kinetics. It turned out, however, that during the degradation of aliphatic polyesters autocatalytic processes should be taken into account. Pitt and co-workers [44] proposed, therefore, that normal hydrolysis follows first order kinetics in absence of catalytic effects, whereas autocatalytic hydrolysis follows second order kinetics. By considering the concentration of carboxylic acid and ignoring the concentration of ester bonds they derived pseudo-first order kinetics. Lyu et al. [45] assumed that the degradation depends on both the concentration of breaking bonds and water, therefore a second order kinetic equation was proposed. Additionally, the mass loss of polymer is also predicted with a surface process, which could be advantageous for the description of heterogeneous degradation. More recently Antheunis et al. [35, 36] developed a
model that describes the kinetics of hydrolytic degradation and the development of molecular weight distribution based on an autocatalytic chain scission process. This model could be beneficial when the acid concentration of the system is considerable. This eventuates in polymers with carboxyl acid end groups or when the hydrolysis advanced but the mass loss did not start, yet.

In semi-crystalline polymers the crystalline amount can vary over time, which can be deduced from two facts. One is the (re-)crystallization of molecules, oligomers. The chain mobility increases after swelling and the degraded shorter chains also have greater mobility, which may lead to the formation of new crystalline regions. The other effect originates from the different behavior of amorphous and crystalline parts during hydrolysis. In the amorphous phase the diffusion of water is faster, which leads to faster degradation compared to the crystalline regions; thus after the mass loss the overall crystallinity will increase [37].

2.2.2. Bioactive ceramics

Ceramics are frequently used in medicine. Alumina and zirconia are used as hip-joint prostheses and have high compressive modulus, hardness and good wear properties. They are, however, brittle materials, which could result in sudden failure and fragmentation.

As it was discussed earlier, hydroxyapatite is one of the main components of hard tissue. Nevertheless, calcium-phosphates can crystallize in various forms (mono-, di-, tri-, tetra-calcium phosphate, HA) depending on the calcium to phosphate ratio, temperature and presence of water. Each form is very tissue compatible and has been used as fillers in polymeric scaffolds or to make artificial bone and coatings. HA has excellent biocompatibility, it appears to be bioactive (favors tissue growth). In early studies lamellar bone was formed around HA granules after 4 weeks, in vivo [9]. The mechanical properties of calcium-phosphates vary because of their polycrystalline nature. Their compressive moduli values vary from 40 to 120 GPa, while their compressive strength varies between 300 and 900 MPa [9, 10]. These values are, however, one order of magnitude higher than those of cortical bone, which could lead again to stress shielding. Therefore, the use of these materials as reinforcements for weaker polymers could be beneficial.

Calcium carbonate is highly biocompatible, as well. Numerous research groups studied the properties of highly porous corals, which are composed from calcium-carbonate. Guillemin and co-workers [46] found corals to be bioactive. In an in vivo study the implant site was filled at least partially with new bone after 8 weeks. In nature there are three crystalline and one amorphous forms of calcium carbonates present: calcite, aragonite, vaterite and
amorphous calcium carbonate. They are not only bioactive but could also stabilize the pH during the degradation of polyesters [34].

2.3. Toughness of biodegradable polymers, blends and composites

In the recent literature the fracture properties of biodegradable materials are often neglected or treated imperfectly. In most cases the brittleness or ductility is only characterized by the elongation measured during quasi-static tensile tests, or evaluated by linear elastic fracture methods, which are sometimes ineligible due to the viscoelastic-viscoplastic nature of polymers. The following subsection tries to summarize the basic concepts of fracture mechanics and to briefly introduce the common toughness improving methods.

2.3.1. Principles of fracture mechanics

The fracture mechanical concepts originate from the observation that the strength of a real material is far from the estimated ideal. The reasons for this are in general the material-discontinuities like cracks, crazes or non-compatible fillers, impurities. These discontinuities could arise from processing or from environmental effects. The challenge of fracture mechanics is to describe the formation of cracks and their propagation in materials.

Fracture mechanics can be classified from different points of view. Usually it is divided into linear elastic fracture mechanics (LEFM) and nonlinear fracture mechanics. The first describes fracture processes by using linear elasticity and is appropriate for brittle fracture. In contrast, nonlinear fracture mechanics characterizes fracture processes which are dominated by inelastic material behavior (Figure 2.3). Depending on whether the material is ideally elastic-plastic or viscoelastic-viscoplastic, a further partition can be made. The basis of classification can be the loading mode, too. Mode I – crack opening –, mode II – in-plane shear –, mode III – out-of-plane shear – and mixed mode cracks can be differentiated in this way [47].

In linear elastic fracture mechanics the cracked body is regarded as linear elastic in the whole region. The inelastic processes must be restricted to an infinitesimally small region, which can be neglected from a macroscopic point of view. Accordingly, this method is prevalent for the description of brittle fracture.
If a ductile material, which contains a craze, is loaded; plastic flow starts in the crack tip and as a consequence the tip becomes blunted. At the same time the plastic zone grows and results in large-scale yielding. In such situations neither the linear elastic fracture mechanics, nor its parameters and concepts can be applied. There are, however, alternative methods for handling these non-linearities. The first one is the J-integral which corresponds the energy release rate during crack growth in an inelastic body and can be used until the plastic zone at the crack tip remains small, the load is monotonous and the crack growth remains stable [47]. The second is the crack tip opening displacement, which is based on the state of the deformation at a crack tip. In contrast with the previously discussed methods the essential work of fracture (EWF) concept is based on global energetic considerations and deals with the problem of fracture toughness characterization not from initiation, but from the other extreme, the work expended during complete fracture of specimen. This method is used as a practical approach for obtaining fracture toughness data of very ductile materials, where some size requirements of J-integral are difficult to fulfill.

The EWF method was originally developed for the characterization of ductile metals and is valid for polymers under the following application conditions [48] for double edge notched tensile specimens (DENT) under mode I. load:

— the full ligament (cross-sectional area between the notches) has to yield prior to crack propagation,
— the load-displacement curves have to be self-similar,
— the ligament length \((L)\) – full width minus the notch lengths – has to be at least three times greater than the specimen thickness \((B)\) to avoid the plane-strain stress state,
— the ligament length should be maximum the third of specimen width \((w)\) (in this case the fracture process does not reach the specimen edges),
— the specimens have to satisfy the empirical stress criteria; i.e. \(0.9\sigma_m < \sigma_{ns} < 1.1\sigma_m\) for all samples, where the net section stress can be written as \(\sigma_{ns} = P_{\text{max}}/LB\). \(P_{\text{max}}\) is the observed maximum load and \(\sigma_m\) is the mean of \(\sigma_{ns}\).

If the test meets all the previously specified requirements, the total fracture work \((W_f)\) can be calculated using Equation (2.1):

\[
W_f = \int_0^s F(s) \, ds \tag{2.1}
\]

where \(F(s)\) is the load and \(s\) is the displacement. The total fracture work can be divided into the work spent for the generation of new surfaces \((W_e)\) and into the work related to the dissipation mechanisms \((W_p)\). \(W_e\) corresponds to a plane and is therefore a function of area \(LB\), while \(W_p\) dissipates in volume \(L^2B\). Accordingly, (2.1) can be specified and rewritten to Equation (2.2):

\[
w_f = w_e + \beta w_p L \tag{2.2}
\]

where \(w_f = W_f/LB\) is the specific total work of fracture, \(w_e = W_e/LB\) is the specific essential work of fracture, \(w_p = W_p/L^2B\) is the specific plastic work of fracture and \(\beta\) is a geometry dependent factor related to the shape of the plastic zone. The linear regression on the plot of \(w_f\) values versus \(L\) results in \(w_e\) and \(\beta w_p\). According to the literature EWF parameters depend on molecular weight \([49, 50]\), deformation rate \([51]\), temperature, loading mode and aging \([52]\), as well. Karger-Kocsis et al. \([49-51]\) proposed the split of EWF response (Figure 2.4), if the yielding and necking of DENT specimen occur.

![Figure 2.4 Partitioning of load-displacement response [48]](image)

According their model the required total work of fracture can be separated into two terms: (i) the work required to yield the specimen \((W_y)\) and (ii) that to tear the necked ligament area \((W_n)\). Formally (2.2) can be rewritten to Equation (2.3):

\[
w_f = w_e + \beta w_p L = w_y + w_n = w_{e,y} + \beta_y w_{p,y} L + w_{e,n} + \beta_n w_{p,n} L \tag{2.3}
\]
where $w_{cy}$ is the specific essential yielding-related work of fracture, $w_{cn}$ is the specific essential necking work, $w_{py}$ is the energy dissipated during yielding, and $w_{pn}$ is the dissipated work during necking. $\beta_y$ and $\beta_n$ are the geometry factors of the yielding and necking stages, respectively [53]. The advantage of this partitioning is that $w_{cy}$ seemed to be independent of molecular weight [49, 50] and deformation rate [51]; both parameters influenced only the tearing-related parameters. On the other side $w_{cy}$ and $\beta_nw_{pn}$ seemed to be suitable in the predicting of the effect of physically aging [52]. Due to the lack of space further aspects of EWF testing of polymers, blends and composites are not treated here, but they are described in detail in a recent review paper of Bárány et al. [48].

2.3.2. Microstructural and molecular characteristics dependence of essential work of fracture parameters

PCL seems to be a good model material to test the microstructural dependence of EWF parameters in semi-crystalline polymers. Due to its low glass transition temperature ($T_g$≈-60°C [54]) and melting point ($T_m$≈65°C [54]) at ambient conditions it has an elastomeric nature with low Young’s modulus (about 0.4 GPa) and high strain at break (over 200%) [55]. This is advantageous, since in elastomers the presence of flexible chains causes that up to large strains the contribution of energy elastic deformation is negligible compared to the entropy elastic deformation. On the other side, one can only talk of true plastic deformation when there are no frozen in stresses [56]. Well above its glass transition temperature the amorphous phase of PCL has high compliance and in this physical state the entropy elastic and viscoplastic deformations are favored, and the magnitude of frozen in stresses is minimal. In this state of matter the reported problems like the orientation, cold-drawing, physical aging [48, 52] or free-volume decrease [57] of amorphous phase do not interfere with the obtained results. Due to its flexibility, the amorphous network mainly has stress transferring effects, while the load is chiefly carried by the crystalline regions. Additionally, because of the low yield stress – low plastic resistance – the favored deformation mechanism is the shear yielding and plastic deformation of crystallites and the effects of cavitation are negligible [58-60].

The parameters that influence the properties of crystalline phase, among other things, include [61]: molecular structure, molecular weight and its dispersion; crystalline phase and structure; the amount, order and orientation of crystalline fraction; spherulite size; lamellae thickness; chain branching; number and density of tie molecules. Up to the present it is difficult to control only one parameter, since they are strongly interrelated or the resulting structure is unstable.
Mouzakis et al. [62] studied the effect of stereoregularity on the crystallinity and fracture properties of elastomeric polypropylene. It was found that the essential work of fracture increased but the plastic work decreased with decreasing crystallinity. Nevertheless, it should be noted that the molecular characteristics of samples were not presented. Although, it is known that the chain length between the entanglements and therefore the molecular weight has an effect on the fracture parameters as it was previously shown by Karger-Kocsis and Moskala [50] for amorphous polymers. Barry and Delatycki [63] showed in high density polyethylene that the thicker crystalline lamellae and the more ordered crystalline structure results in increased resistance to crack initiation. Conversely, the crack growth resistance decreased with increasing concentration of side chains. Gupta et al. [64] studied the effect of side chain length on the deformation mechanisms of linear low density polyethylenes of similar molecular characteristics and crystallinity. They found that the longer the side chain is the higher the essential work of fracture, which was explained by an anchoring effect of longer molecules. Channel and Clutton [65] studied the effect of molecular weight and chain branching in a series of polyethylenes under impact conditions and found that fracture toughness \( (G_c) \) increases linearly with increasing molecular weight. It was stated that the increase in molecular weight increases the number of tie molecules and the tie molecule density that is accompanied by increased toughness [61].

Additionally, in PCL the contribution of conformational or point defects is less, compared to polyolefins, polyamides or other polyesters due to its lower melting temperature. This is important since these defects can initiate the deformation of crystals [54]. Men et al. [60] also has shown that the critical stress where the crystalline deformation starts is in connection with the intrinsic stability of crystals, which is related to their theoretical equilibrium melting temperature. The low melting temperature of PCL, therefore, also favors the deformation of crystalline regions, observed as yielding, if enough load is transmitted from the amorphous network. Furthermore, the phase transition of crystalline parts also influences the fracture properties as it was reported by Ferrer-Balas et al. [66] for polypropylene. In contrast, PCL has a stable orthorhombic \( (P2_12_12_1) \) crystalline structure with non-planar chain packing conformation in the crystalline lamellae [67, 68], thus these phase transitions has no effect on the fracture behavior either.

### 2.3.3. Micromechanical deformations and failure in semi-crystalline polymers

Since the deformation of polymers during quasi-static or fracture mechanical tests fundamentally differs from that of metals; I deemed it necessary to briefly overview the main
processes. Since in these materials both the amorphous and the crystalline phases are present, only the deformation of semi-crystalline polymers is treated.

The deformation of semi-crystalline polymers prior to yielding is mainly accompanied by the elastic deformation of crystalline regions (e.g. spherulites) and the elastic-inelastic deformation of amorphous phase. After a critical stress is transferred to the spherulites they undergo irreversible deformation [56, 60]. This critical stress value depends on the inherent stability of crystals, which is related to the equilibrium melting temperature of polymers, as it was mentioned earlier. If the stress transferred to spherulites is less than this critical value, then the irreversible deformation of crystallites is absent and the failure propagates on the phase boundary between the crystalline and amorphous region. If the stress is high enough, then the crystalline phase undergo plastic deformation.

The micromechanical deformation of spherulitic crystalline phase, however, also has various subregions [69]. As it is shown in Figure 2.5, the crystalline lamellae first breaks into smaller blocks and those that are diagonally to the loading direction start to rotate and slip. The tearing of tie molecules is the dominant process in the equatorial regions, while in the polar directions the less stable structure promotes the unloosing of lamellar build-up for the deformability of crystalline lamellae is one order smaller in folding direction than perpendicular to it [56].

![Figure 2.5 Schematic deformation mechanisms in spherulites under tensile load [69]](image)

---

**Figure 2.5 Schematic deformation mechanisms in spherulites under tensile load [69]**
The more tie molecules and entanglements are present in the material the higher will be its resistance to crack propagation [48]. On the other hand, if the intrinsic stability of crystalline regions – that is related to the melting temperature and the load transferring capacity of amorphous network, tie molecules [60] – is high or the amorphous phase does not favor the slip and rotation of crystalline blocks – due to small free volume or low temperature and high strain rate – the deformation becomes rigid and brittle. In this case only the tearing of tie molecules counts and the unloosing of crystalline structure does not consume any energy.

2.3.4. Toughening of brittle biodegradable polymers

To overcome the problems resulting from implant fragmentation, the material must have a proper toughness over an appropriate time. Several efforts have been made to improve the toughness of brittle biodegradable polymers like PGA, PLA or PHB. The main methods are, among others, copolymerization, plasticization, blending and reactive copolymerization.

One of the first attempts to solve this problem was the copolymerization. The chain flexibility of these rigid homopolymers can be significantly improved by copolymerization of monomers resulting in low-glass transition temperature polymer segments. In the recent years numerous copolymers were tested and adequate results were attained, as well. For example, a PGA/PCL copolymer is already on market as degradable suture (trade name: Monocryl). Moreover, Pego et al. [70] recently made an attempt to improve the flexibility of poly(D,L-lactide). Copolymers of 1,3-trimethylene carbonate and D,L-lactide were prepared. The tensile modulus, strength at break and elongation at break of neat poly(D,L-lactide) films were 1.9 GPa, 52 MPa and 6%, respectively; while the same properties of neat TMC films were 0.006 GPa, 12 MPa and 830%. The prepared films had a Young’s modulus of 1.5 GPa, while the stress at break was 24 MPa and the elongation at break about 480%. However, the polymerization was quite time consuming, the process lasted three days at 130°C, and there is no information available related to the biocompatibility of the prepared material.

Poly(hydroxyl-butyrate) possesses relative low impact resistance and thermal stability, similarly to polylactide. The conventional processing of this polymer is difficult since its melting temperature is about 175°C, and above 170°C the polymer undergoes a random scission at the ester groups. Its copolymers with hydroxyvalerate have lower melting temperature as well as glass transition temperature and together with the higher elongation at break they are more convenient to handle. The thermal and mechanical characteristics of poly(hydroxybutyrate-co-valerate) copolymers are listed in Table 2.3 [31].
Table 2.3 Thermal and mechanical properties of poly(hydroxybutyrate-co-valerate) copolymers [31]

<table>
<thead>
<tr>
<th>Amount of hydroxyvalerate (mol%)</th>
<th>Melting temperature °C</th>
<th>Glass transition °C</th>
<th>Young’s modulus GPa</th>
<th>Tensile strength MPa</th>
<th>Elongation at break %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>175</td>
<td>9</td>
<td>3.8</td>
<td>45</td>
<td>4</td>
</tr>
<tr>
<td>11</td>
<td>157</td>
<td>2</td>
<td>3.7</td>
<td>38</td>
<td>5</td>
</tr>
<tr>
<td>20</td>
<td>114</td>
<td>-5</td>
<td>1.9</td>
<td>26</td>
<td>27</td>
</tr>
<tr>
<td>28</td>
<td>102</td>
<td>-8</td>
<td>1.5</td>
<td>21</td>
<td>700</td>
</tr>
<tr>
<td>34</td>
<td>97</td>
<td>-9</td>
<td>1.2</td>
<td>18</td>
<td>970</td>
</tr>
</tbody>
</table>

**Plasticization**

Imposing effects can be achieved by plasticization, too. Several authors reported the decrease of glass transition temperature and the increase of elongation at break directly after the addition of low molecular weight oligomers, such as polyglycols [71, 72] and citrate esters [73] to PLA. The main drawback of the application short-chain-length oligomers may be their migration in the polymer system. The migration and phase separation can lead to the deterioration of their advantageous effect over time. Hu and co-workers [74, 75] investigated these aging effects on high molecular weight PLA (M<sub>w</sub> = 160 kDa and 190 kDa, respectively) plasticized with crystalline PEG (M<sub>w</sub> = 8 kDa). Various compositions were prepared, and good correlation was found with the Fox equation up to 30 wt% PEG content, which suggested the miscibility of polymers. They found that the addition of 20 wt% PEG shifted the T<sub>g</sub> from about 60°C below ambient temperature. Parallel to this, the modulus and yield stress decreased with one order of magnitude. During the aging of PLA/PEG 70/30 blend at ambient conditions (23°C, 50% relative humidity) they observed, that the T<sub>g</sub> and modulus increased and the elongation at break decreased over time. They established that the origin of this phenomenon was the crystallization of PEG. The crystallization of PEG enriched the amorphous phase in poly(D,L-lactide) and increased the T<sub>g</sub>. After the T<sub>g</sub> reached the ambient temperature the aging essentially ceased, the reduced molecular diffusivity slowed the crystallization rate dramatically. However, aging resumed if the temperature was raised above T<sub>g</sub>. It was concluded, that aging exhibits under ambient conditions when the PEG content is high enough to shift the T<sub>g</sub> under ambient temperature. Conversely, they stated that the blend with 15 wt% PEG and T<sub>g</sub> about 30°C may be stable over time at ambient conditions. The authors also analysed the effect of stereoregularity and observed that the higher stereoregularity PLA was miscible with PEG only over a smaller composition range. The
PLA/PEG 70/30 blend in this case underwent phase separation at ambient temperature (Figure 2.6).

Other frequently used method to improve the toughness and processability of rigid polymers is the blending of two polymers. This method has the ability to overcome the disadvantages of plasticized systems, i.e. the stability problems.

The polymer pairs can be either miscible or immiscible, however the latter is more common due to the high molecular weight of polymeric materials. The properties of immiscible polymers can be refined by the addition of copolymers or reactive additives. Pötschke et al. [76] categorized the structures obtained after mixing of immiscible polymer pairs into four basic morphology types:

- Matrix-dispersed particles
- Matrix-fibrous structures
- Lamellar structures
- Co-continuous structures

The most common morphology is the matrix-dispersed phase, because the interfacial tension between the incompatible components drives the system toward a minimum surface free energy, which can be attained by spherical structure. The other types are usually not stable and can be achieved only through specific material selection and processing conditions. Despite these difficulties, there is an increasing interest in co-continuous blends. The reason is that this type of morphology can offer better combination of component properties (“hybrid effect”) than the dispersed structures.

**Compatibilization of polylactide-polycaprolactone blends**

In a recent paper Harada and co-workers [77] used various reactive processing agents as compatibilizers in polylactide-polycaprolactone binary blends. These reactive materials could be more cost effective than copolymerization, while similar advantageous effects can be
attained. The authors analyzed the effect of four isocyanates (namely: L-lysine triisocyanate; L-lysine diisocianate; 1,3,5-tris(6-isocyanatoxyethyl)-1,3,5-triazinane-2,4,6-trione and 1,3,5-tris(6-isocyanatoxyethyl)biuret) and of one epoxide (trimethylolpropane triglycidyl ether). They prepared blends containing 80 weight% PLLA and 20 weight% PCL and added 0.5 phr processing agent to each. The samples were injection moulded after mixing in an extruder. The obtained results from unnotched Charpy tests are listed in Table 2.4.

Table 2.4 Charpy (unnotched) impact properties of PLLA/PCL 80/20 blends with 0.5 phr reactive agent [77]

<table>
<thead>
<tr>
<th>Reactive compatibilizing agent</th>
<th>Impact strength [kJ/m²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>17</td>
</tr>
<tr>
<td>L-lysine triisocyanate</td>
<td>64</td>
</tr>
<tr>
<td>L-lysine diisocianate</td>
<td>NB</td>
</tr>
<tr>
<td>1,3,5-tris(6-isocyanatoxyethyl)-1,3,5-triazinane-2,4,6-trione</td>
<td>58</td>
</tr>
<tr>
<td>1,3,5-tris(6-isocyanatoxyethyl)biuret</td>
<td>30</td>
</tr>
<tr>
<td>trimethylolpropane triglycidyl ether</td>
<td>17</td>
</tr>
</tbody>
</table>

According to their results the L-lysine di- and triisocyanates showed the best properties resulting in significantly improved toughness compared to the neat blend. Since the amount of reactive agent was small (0.5 phr) this method is a cost effective way of producing blends with adequate toughness and strength as well as to maintain good biocompatibility [78] – lysine is an amino acid of the human body.

2.4. Properties and fabrication of cellular plastics for bone regeneration

The preparation of highly porous foams with adequate cellular structure and mechanical performance for medical applications raises several difficulties. Due to the special requirements of medicine (e.g.: biocompatibility), there is a restriction related to the adaptable materials and methods, compared to the common foaming techniques. In the following section several scaffold fabrication techniques are introduced and their main advantages and disadvantages are highlighted, too. Additionally the basics of the mechanics of cellular solids are discussed briefly.

Mechanics of cellular plastics

Cellular plastics exhibit unique mechanical characteristics. These properties depend mainly on the cellular structure, i.e. open and closed cell foams. Tissue engineering applications require open cell, interconnected foams, thus throughout the following section these are discussed. The presented concepts are based on the work of Gibson and Ashby [79] and of Hilyard [80].
According to the material properties the closed cell as well as the open cell foams can be further divided into rigid and flexible foams [80]. Rigid foams primarily operate under small strains and are considered as elastic materials. Their property-density relationship is hence relatively easy to describe with Equation (2.4).

\[ P_f = K \cdot \rho_f^n \]  

(2.4)

where \( P_f \) is the property of foam (tensile/compressive modulus, strength), \( K \) and \( n \) are empirically determined constants and \( \rho_f \) is the density of foam. The exponent \( n \) lies between 1 and 2 for rigid foams [80]. An alternative way to express this relationship is in terms of density ratio or volume fraction of polymer (\( \phi \)). Since the enclosed gas phase makes negligible contribution to the mass, the volume fraction can be expressed by Equation (2.5).

\[ \phi = \frac{\rho_f}{\rho_p} \]  

(2.5)

and the respective property-density relationship is Equation (2.6)

\[ P_f = P_p \cdot \phi^n \]  

(2.6)

where \( P_f \) is the property of foam and \( P_p \) is that of bulk polymer. For rigid, elastic foams the value of \( n=2 \) was found [79, 81]. For PCL Oláh [82] found values of \( n \) between 2.40 and 2.51, while Hou et al. [83] found 2.59 for PCL and 2.42 for PLA.

Since polymers are mostly non-linear viscoelastic, rheologically complex materials, these relations can be suitable only under specific conditions (e.g. at low temperatures – below \( T_g \), high deformation speeds). At small strains, however, the deformation mechanisms in flexible foams are essentially the same as those in rigid foams.

**Polymer based scaffold fabrication techniques**

Tissue-engineering scaffolds should have appropriate geometries to direct new tissue formation and mass transport properties for the exchange of biological nutrients and waste. The scaffolds also have to provide temporary mechanical support for the regenerating tissue and they must degrade into biocompatible by-products, preferably on a time scale comparable to the new-tissue-forming. Apart from the properties of the raw material, the major factor determining the final scaffold characteristics is the fabrication technique. The scaffold characteristics can be tailored to the certain application by careful selection of the polymers, the additional components and the fabrication technique. The currently used manufacturing methods can be divided into two major groups. The first group contains the so
called conventional methods while the second one is composed of the computer designed rapid prototyping (RPT) techniques [84].

Each manufacturing method has its own, distinctive advantages and limitations, thus there is no best scaffold fabrication technique available. The key of any bone tissue-engineering applications are the high and interconnected porosity, the adequate pore size for osteoblast migration and nutrient diffusion, the biocompatibility and biodegradability, and finally the sufficient mechanical strength for the period of regeneration [32]. Additionally, to enhance the mechanical properties of scaffolds biodegradable composite materials were developed. A wide range of materials such as hydroxyapatite, calcium-carbonate and calcium-phosphate in either spherical or fibrous form are used in these composites as reinforcement.

RPT techniques build parts by selectively adding materials, layer by layer, as specified by a computer program [85]. Although these methods have an excellent control over geometry and porosity, they did not get in general use yet either due to the relatively high equipment costs, weak connection between the layers or lack of available biodegradable materials.

In conventional methods the control over porosity is not so good, but the material selection and applicability of these methods is easier. Due to the lack of space I would not review all the available scaffold fabrication methods, I only consider that what I will use later on.

Oláh [82] developed a suitable method for preparing scaffold for bone tissue engineering from PCL by melt molding/particulate leaching technique. It was found that above 70% porosity open cell foams can be prepared by using sodium-chloride (particle size between 250 and 500 μm) as porogen. This interconnected structure favors the cell ingrowth and is strong enough to support the cancellous bone. In my thesis, therefore, I will use the same method for scaffold fabrication due to its availability and adequacy.

Oláh et al. [86] also prepared both neat PCL and PCL/CaCO3 composite materials by using solvent casting/particulate leaching technique. By using the needle-like crystal form of calcium carbonate (aragonite) instead of the spherical calcite, a 3–5-fold increase in compression modulus was achieved.

2.5. Critical review 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

In this chapter the experimental materials and the applied analytical techniques will be described.

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 ($M_n \approx 100$ 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-lysine 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 $\mu$m (Figure 3.1 a). Aragonite filler (Figure 3.1 b) 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 $\mu$m, the length varied between 30 and 50 $\mu$m. 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.

![Figure 3.1 Optical micrographs of calcite (a) and aragonite (b) particles](image)
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/dm³ potassium chloride, 0.2 g/dm³ potassium hydrogen phosphate, 1.44 g/dm³ sodium hydrogen phosphate and 8 g/dm³ sodium chloride (NaCl) were dissolved in water, while the pH was set to 7.5. Finally 0.16 g/dm³ 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. Experimental methods

The object of this subchapter is to give an overview of the sample preparation and analytical techniques. The applied equipment will be described briefly, as well.

3.2.1. Sample preparation

In order to have exact compositions, analytical balance (OHAUS Explorer, accuracy of ±0.1 mg; Ohaus Corp., Pine Brook, NJ, USA) and pipette was applied to measure the materials prior processing. The neat polymers as well as the compounds 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 (Figure 3.3). 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
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(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 \(\beta\)-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.

3.2.2. 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 \(\mu m\) 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 \(\mu m\) 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. The initial modulus was calculated according to Hooke’s law from the stress change between \(\varepsilon_1=0.0005\) and \(\varepsilon_2=0.0025\) strains, while the yield point (yield stress) was correlated with the irreversible deformation of crystalline phase (Figure 3.2 a). 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. The modulus was calculated according to Hooke’s law from the stress change between \(\varepsilon_1=0.004\) and \(\varepsilon_2=0.008\) strains – compensated with \(\varepsilon_c\). The yield point was
associated with the knee point of load-displacement curves and the stress and strain values were determined as shown in Figure 3.2 b). For solid samples five, while for porous ones nine specimens were tested in each data point.

Figure 3.2 Scheme for the evaluation of quasi-static tensile (a) and compressive (b) properties

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 (OriginPro software).

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, (Quantachrome, 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 N₂ 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
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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 nm². 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 Kα radiation (λ=0.1542 nm).

Differential scanning calorimetry (DSC) 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 temperature programs were set as follows:

(1) For PCL samples:
   — 1 min isotherm at -30°C
   — Heating to 100°C with a rate of 10°C/min
   — 1 min isotherm at 100°C
   — Cooling to -30°C with a rate of 10°C/min
   — 1 min isotherm at -30°C
   — Heating to 100°C with a rate of 10°C/min

(2) For PCL/PLA blends:
   — 1 min isotherm at 0°C
   — Heating to 200°C with a rate of 10°C/min
   — 1 min isotherm at 200°C
   — Cooling to 0°C with a rate of 10°C/min
   — 1 min isotherm at 0°C
   — Heating to 200°C with a rate of 10°C/min

The crystallinity of polymers was calculated from according to Equation (3.1) and the initial crystallinity – crystallinity before cold crystallization – of PLA from Equation (3.2).
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\[
X[\%] = \frac{\Delta H_m}{\psi \cdot \Delta H_o} \times 100 \quad (3.1)
\]

\[
X[\%] = \frac{\Delta H_m - \Delta H_{cc}}{\psi \cdot \Delta H_o} \times 100 \quad (3.2)
\]

where \( \Delta H_m \) [J/g] is the melting enthalpy, \( \Delta H_{cc} \) [J/g] the cold-crystallization enthalpy, \( \psi \) [-] the weight fraction of the studied material and \( \Delta H_o \) [J/g] the enthalpy of fusion of 100% crystalline polymer. The theoretical values were taken for PLA as \( \Delta H_o = 135 \) J/g [87], while for PCL as \( \Delta H_o = 142.5 \) J/g [88].

Human osteosarcoma 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., Nümbrecht, 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.

3.3. Theory – Determination of essential work of fracture parameters

The essential work of fracture (EWF) concept was introduced by Cotterell and Reddel [89] to determine the fracture toughness when the size of the plastic region is not small compared with the crack length. It is based on the plastic fracture of geometrically similar specimens under plane stress conditions.

If the yielding of entire ligament in thickness (B) eventuates then the work performed to fracture \( (W_f) \) is proportional to the ligament length (L) and can be separated in two components: (i) the essential work performed in the inner fracture process zone \( (W_e) \) and (ii) the non-essential work performed in the screening plastic region \( (W_p) \) [89].

The total work of fracture can be calculated by Equation (3.3).

\[
W_f = \int_0^{\varepsilon_0} F(s) \, ds \quad (3.3)
\]

where \( F(s) \) is the load, \( s \) is the displacement and \( \varepsilon_0 \) is the elongation at break.
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Subsequently, the total fracture work could be written in specific form \( \left( w_f \right) \) as shown in Equation (3.4).

\[
W_f = \frac{W_f}{BL}
\]  \hspace{1cm} (3.4)

If \( w_e \) is the ligament cross-section specific essential work of fracture and \( w_p \) is the specific non-essential work of fracture dissipated in the plastic volume then the total fracture work can be written by Equation (3.5).

\[
W_f = BLw_e + \beta BL^2 w_p
\]  \hspace{1cm} (3.5)

where \( \beta \) is constant, which depends on the shape of the plastic region. Equation (3.5) is valid only in a state of plane-stress and if the yielding of entire ligament precedes the crack propagation. Since the fracture initiates between plane-strain and plane-stress conditions and there is a transition distance after it turns to quasi plane-stress [90], there is a lower limit \( L_{\text{min}} \) to the ligament length that is proportional to sheet thickness. For large ligaments the stress along the ligament, near the centre of sample approaches zero, which results in an unconfined plastic zone and in a not completely yielded ligament. Therefore, the upper limit \( L_{\text{max}} \) is determined by the size of the plastic region \( (x_p) \) – to ensure uncontained yielding – and by the width \( (w) \) of the specimen. Consequently, the valid ligament range can be estimated by Equation (3.6).

\[
(3...5) B < L < \text{Min}(x_p; w/3)
\]  \hspace{1cm} (3.6)

The tests are usually performed on double-edge-notched-tension (DENT) specimens (Figure 3.3), for the transverse stress between the notches is tension and buckling problems are also avoidable [90].

\[\text{Figure 3.3 Sample dimensions of DENT specimens}\]
Based on Irwin’s [91] estimate the size of the plastic region can be approximated by using linear elastic fracture mechanics (LEFM) from Equation (3.7).

\[
x_p = \frac{1}{\pi} \left( \frac{K_{Ic}}{\sigma_u} \right)^2
\]

(3.7)

where \( K_{Ic} \) is the mode I critical stress intensity factor and \( \sigma_u \) is the yield strength. Since the thickness requirements for \( K_{Ic} \) determination are often quite large for the examined materials [92] the size of the plastic region is estimated generally from Equation (3.8).

\[
x_p = \frac{1}{\pi} \frac{E w_{f,\text{max}}}{\sigma_u^2}
\]

(3.8)

where \( E \) is the tensile modulus and \( w_{f,\text{max}} \) is the maximum specific work of fracture recorded. The latter hypothesis assumes that at large ligament lengths \( w_f \) is asymptotic to the plane-stress fracture energy \( (G_c) \). In this case \( K_{Ic}^2 = G_c E \) as estimated from linear elastic fracture mechanics [90].

Since the plane-strain plane-stress transition has also an effect on the maximum net section stress \( (\sigma_{ns}) \) – the maximum load \( (P_{\text{max}}) \) divided by the ligament cross section \( (B\cdot L) \) –, stress criteria were also proposed to validate the test results. Hill [93] has shown that under plane-stress conditions the strain along a neck is zero. In the transition region the stress increases by a modest factor to \( 1.15 \sigma_u \). Based on Hill’s estimate a theoretical stress criterion (Equation 3.9) for the maximum net section stress was proposed by Cotterell et al. [90].

\[
\sigma_u < \sigma_{ns} < 1.15 \sigma_u
\]

(3.9)

This criterion ensures yielding and limits the ligament range at the plane-strain plane-stress transition, when true geometric similarity exists. However, several studies proved that in real materials the absence of ideal geometric similarity results in ambiguities [92, 94-103].

An other stress criterion was suggested in the EWF test protocol by Clutton [104]. This is based on experimental results, uses the mean of the maximum stresses \( (\sigma_m) \) and can be expressed by Equation (3.10).

\[
0.9 \sigma_m < \sigma_{ns} < 1.1 \sigma_m
\]

(3.10)

The problem with this criterion is that it is determined from the results themselves. Therefore it could be used to filter out measurement errors.
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In this work, if not stated else, Equations (3.6), (3.8), (3.10) and the self-similarity requirement of curves are used for data validation. Additionally, the yielding of full ligament is ensured by Equation (3.11).

\[ \sigma_u < \sigma_{ns} \]  \hspace{1cm} (3.11)

The sample size \((N)\) was determined from the study of Pegoretti et al. [105]. They observed that the standard error of the essential work of fracture decreases with sample size (scaling as about \(1/\sqrt{N}\)). According to their paper, a typical sample of 25 specimens results in a dispersion scale of 3-5%, which seems to be adequate for further considerations. Thus a sample size of at least 25 valid specimens was used for the linear regression.

According to the literature [48] the plane stress work of fracture could be also parted to (i) the work required to yield the specimen \((w_y)\) and (ii) the work consumed during crack propagation in the necked ligament area \((w_n)\). If the necking is clearly observable the specific work of fracture could be partitioned. Equation (3.4) and (3.5) could be combined and rewritten to Equation (3.12).

\[ w_f = w_y + w_n = (w_{e,y} + \beta_y w_{p,y} L) + (w_{e,n} + \beta_n w_{p,n} L) \]  \hspace{1cm} (3.12)

where \(w_{e,y}\) is the specific essential yielding-related work of fracture, \(w_{e,n}\) is the specific essential tearing work, \(w_{p,y}\) is the energy dissipated during yielding, and \(w_{p,n}\) is the dissipated work during tearing. \(\beta_y\) and \(\beta_n\) are geometry factors during the yielding and necking stages, respectively. The advantage of this partitioning is that \(w_{e,y}\) seemed to be independent of molecular weight and deformation rate for amorphous polymers; both parameters influenced only the tearing-related terms. On the other hand \(w_{e,y}\) increased with increasing molecular weight between entanglements and also seemed to be an appropriate term to predict the effects of physical aging [48, 52, 53, 106, 107].
4. RESULTS AND DISCUSSION

In this chapter the measurements and observations are interpreted in details. The results are discussed and compared with current theories and literature data. The concluding remarks are presented here, as well.

4.1. In vitro degradation tests

Since the amount of crystalline fraction and therefore the mechanical performance of biodegradable polymers may change with time; in this chapter the influence of hydrolysis on crystallinity and compressive mechanical properties will be analyzed in poly($\varepsilon$-caprolactone) in vitro.

4.1.1. Changes of average molecular weight and crystallinity

The crystallinity of measured samples increased slightly during degradation (Figure 4.1), but no significant lamellae thickening was observed (see Appendix A: Table A1-A4). During hydrolysis the amorphous regions swell, increasing the chain mobility and promoting the recrystallization of the polymer. Additionally, as the degradation progresses the chain length of the molecules in the amorphous phase also decreases, which leads to increased mobility, too [108, 109]. It has to be also mentioned that during the examined time period significant change in the sample weight was not observed (see Appendix A: Figure A1), thus the weight loss of amorphous parts does not influence the crystallinity significantly.

![Figure 4.1 Crystallinity of PCL samples during the degradation](image)

To describe the relationship between time ($t$) and crystallinity ($X$) during degradation a phenomenological expression (Equation 4.1) was used:

$$X(t) = X_{max} \left(1 - Ae^{-\frac{t}{\tau}}\right)$$  \hspace{1cm} (4.1)
where $X_{max}=0.8$ [-] is assumed as the theoretical maximal crystallinity for PCL; estimated from the measurements of Pitt et al. [109]. $A$ [-] is an initial crystallinity related variable, while $\tau$ [day] is the time-constant of the equation. The experimentally determined values are listed in Table 4.1. The constant values increase with increasing average molecular weight indicating the slower crystallization of higher molecular weight samples; i.e. the longer the chain length is the more time is required to its crystallization during the hydrolysis.

<table>
<thead>
<tr>
<th>Material</th>
<th>A [-]</th>
<th>$\tau$ [day]</th>
<th>$R^2$ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capa 6250</td>
<td>0.159</td>
<td>375</td>
<td>0.9100</td>
</tr>
<tr>
<td>Capa 6400</td>
<td>0.208</td>
<td>690</td>
<td>0.7680</td>
</tr>
<tr>
<td>Capa 6500</td>
<td>0.246</td>
<td>840</td>
<td>0.8800</td>
</tr>
<tr>
<td>Capa 6800</td>
<td>0.288</td>
<td>847</td>
<td>0.9440</td>
</tr>
</tbody>
</table>

The crystallinity increase could be explained by the increased chain mobility that originates from the increased temperature (37°C), from the swelling of amorphous domains [35] and the decrease in molecular weight – due to chain scission – also leads to higher crystallinity.

The determination of the amount of crystalline phase is important since during the first phase of degradation only the ester bonds of the amorphous phase are affected, but the size exclusion chromatographic measurements represent an average of molecular weights in crystalline and amorphous fraction, as well. Assuming that in the early stages of the hydrolysis the concentration of water and ester bonds are approximately constant, the autocatalytic effects are negligible and the concentration of formed carboxyl acid end groups is inversely proportional to $M_n$ [110], the first order kinetic reaction can be described with Equation (4.2).

\[
M_n(t) = M_{n,0} e^{-kt}
\]  

(4.2)

where $M_{n,0}$ [kDa] is the initial number average molecular weight at $t=0$ and $k$ [1/h] is the rate constant. The experimentally determined $\ln(M_n)$ versus time plots are shown in Figure 4.2. The determined rate constants for Capa 6250, 6400, 6500 and 6800 samples are $2.55 \cdot 10^{-5}$ 1/h, $2.45 \cdot 10^{-5}$ 1/h, $3.38 \cdot 10^{-5}$ 1/h and $4.13 \cdot 10^{-5}$ 1/h, respectively. Since the molecular structure of the investigated polymers is the same, the deviations between the slopes could originate from the difference in crystallinity and in the number of chain ends. The obtained values are smaller, than those reported by Pitt et al. (7.5 $\cdot$ 10^{-5} 1/h) [44], which could be explained by the different sample geometry (thicker) and termination of polymer chains. In the paper of Pitt et al. [44] the polymer has not been terminated – carboxyl acid end groups were present, which
catalyzed the hydrolysis –, while industrially it is usually terminated with a simple alcohol [111].

4.1.2. The effect of hydrolysis on the compressive mechanical properties

Assuming that the perfection of crystalline phase leads to increasing strength and modulus, while the degradation of molecules causes the deterioration of the same properties, the effects of hydrolysis can be hypothesized as shown on Figure 4.3. The initial slope of the resultant curve and the time, where there is a drop in the mechanical strength and/or modulus depends mainly on the perfection of the crystalline phase, which is linked to the molecular weight as shown in Figure 4.1. The rate constant of hydrolysis is assumed to be independent of molecular weight, only the initial molecular weight influences the change of mechanical performance.
Concerning the compressive modulus significant differences could be observed between the samples of different number average molecular weight. The compressive moduli of Capa 6250 and Capa 6400 specimens did not change significantly during the first year of hydrolysis (Figure 4.4 a, b). However, the moduli of higher number average molecular weight samples – Capa 6500 and Capa 6800, respectively – increased monotonously (Figure 4.4 c, d). The increase in crystallinity and the perfection of crystalline lamellae led to a stiffer structure, which results in higher compressive moduli. On the other side, the degradation led to the scission of short tie molecules in the amorphous phase, which increased the compliance of the samples – decreasing their modulus.

For the formation of stable entanglements there is a critical chain-length, critical molecular weight \( M_c \), which is about 15 kDa for PCL according to Grosvenor et al. [112]. In the investigated materials the \( M_n \) was higher than this \( M_c \) value, which suggests that the polymer network remained entangled during the experiments (see also Appendix A: Figure A2).

In the higher \( M_n \) samples (Figure 4.4 c, d) the tie molecule density is higher due to the longer chains, thus the chain scission did not influence significantly their modulus. Only the
results of higher crystallinity, more perfect crystalline phase are observable. Contrarily, in lower $M_n$ samples (Figure 4.4 a, b) the tie molecule density is smaller and the hydrolysis resulted in increased compliance – albeit the two parallel processes were balanced for the most part of Capa 6250 and Capa 6400 specimens. The hydrolysis of tie molecules dominated the deformation of Capa 6250 only after two years. In this case it is assumed that the practically unlinked spherulites, crystalline lamellae could slip and rotate as uncoupled solids resulting in smaller moduli values.

The crystallinity increase resulted in similar changes in compressive yield stress values, as well (Figure 4.5). A slight increase can be observed until there are enough tie molecules and entanglements to promote the deformation of crystalline structure. However, as the chain scission proceeds the crystalline and amorphous phase become partly unlinked and the deformation of crystallites does not take place everywhere. This led to the decrease of yield stress in Capa 6250 samples (Figure 4.5 a).

![Figure 4.5 Variation of compressive yield strength of (a) 25 kDa, (b) 40 kDa, (c) 50 kDa and (d) 80 kDa PCL samples as a function of hydrolysis time](image)
4.1.3. Effect of porosity on the hydrolytic degradation

Scaffolds in tissue engineering are porous solids. Since the hydrolysis of poly(\(\varepsilon\)-caprolactone) is an autocatalytic homogeneous (bulk) degradation, the thickness of cell walls, i.e. the porosity of scaffold, should have an effect on the diffusion of water and degradation by-products therefore on the degradation rate of the polymer. Additionally, the higher specific surface area of porous material could also lead to faster degradation. In this subsection the effect of porosity is investigated in solid PCL samples (Capa 6800) and in specimens with porosity \((1-\phi)\) of 0.7, 0.8 and 0.9, respectively.

With regard to the average molecular weight faster degradation of porous polymers was observed in any case. However, the higher porosities did not result in significant change of the degradation rate, as it is shown on the plots of Figure 4.6. The determined degradation rates were \(7.25\times10^{-5}\) 1/h, \(7.98\times10^{-5}\) 1/h and \(7.04\times10^{-5}\) 1/h for porosity of 0.7, 0.8 and 0.9, respectively.

![Figure 4.6 Effect of hydrolysis on the number average molecular weight of PCL samples with different porosity](image)

The increase of crystallinity was observed in porous samples, too (Figure 4.7). The amount of crystalline phase was higher in porous specimens compared to solid ones, but the difference in porosity did not cause the variation of measured melting enthalpy values either. The reason of these phenomena could be the faster swelling and chain scission in porous samples, for the diffusion of water was promoted by capillary effects in the interconnected cellular structure. The higher local concentration and diffusion gradient of water facilitated the hydrolysis of the ester groups and the consumed water was also more easily resupplied, which resulted in higher degradation rates and crystallinity.
Results and Discussion

In the literature overview part it was mentioned that power-law relationships could be generally used for the description of different properties of foams [79-83]. In Equation (2.6) one can replace the “P” property by modulus, strength or deformation work values. By plotting the obtained mechanical properties in double logarithmic graphs the constant values can be determined easily. In Figure 4.8 it can be seen that during the first year of degradation the parameters decreased only slightly and can be taken as constant. However, after two years of hydrolysis there was a significant drop in the specific modulus and yield stress values ($E/E_p$ and $\sigma_{y,f}/\sigma_{y,p}$, for foams and solid polymers respectively). This could be either due to the faster degradation of porous samples compared to solid ones or due to the increasing compressive modulus and yield strength of solid specimens (Figure 4.4 and Figure 4.5, respectively). According to the literature the slope of the lines is related to the geometry of pores. Since the cell structure did not change with time (Appendix A: Figure A3), the slight deviation can be interpreted as a measurement error.

Figure 4.7 Crystallinity of PCL samples with different porosity during the hydrolytic degradation

![Figure 4.7](image)

Figure 4.8 Power-law relationship of the compressive modulus (a) and of the yield stress (b) of porous PCL samples as a function of porosity in double logarithmic plots

![Figure 4.8](image)
Results and Discussion

In case of deformation work values (Figure 4.9) similar results were observed, too. However, the data could be interpreted easier, since the measured work values of solid polymer samples \( (W_{0.25,p}) \) decreased monotonously (Appendix A: Figure A4) with time. Therefore, the shift of data points to lower values suggests the faster degradation of porous specimens.

![Figure 4.9 Power-law relationship of the work required for 25% compressive deformation of porous PCL samples as a function of porosity in double logarithmic plots](image)

Summarily, the hydrolysis of PCL leads to the deterioration of average molecular weight and to the increase of crystallinity, due to the swelling and chain scission in the amorphous phase. The previously mentioned effects are more significant in porous samples due to the higher specific surface area and the shorter diffusion lengths. These changes result in the embrittlement of the material, which is disadvantageous for scaffolds in tissue engineering, thus in the following sections attempts are made to increase the toughness of biodegradable implant materials and describe their fracture toughness.

4.2. Poly(ε-caprolactone) based blends and composites of improved performance

The compressive or tensile strength and moduli requirements of load-bearing implants are usually higher than what polymers can sustain. As it was shown in the literature review beneficial effects can be achieved by using inorganic salts as reinforcement. Nevertheless, the raised filler content may demolish the material toughness. Maintaining an adequate toughness, however, is as important as the strength of the scaffold, since the fragmentation of implants during degradation is as long as possible avoidable.
4.2.1. Effect of filler shape on the mechanical performance of bioactive poly(ε-caprolactone)/calcium-carbonate composites

The shape and specific area of reinforcing material is known to have an effect on the mechanical performance. In this subchapter this effect is analyzed in calcite and aragonite filled PCL (Capa 6800) composites.

**Compressive properties**

The most frequent macroscopic mechanical load in human bone is the compression. As mentioned above PCL has good biocompatibility but its mechanical performance is rather limited, therefore mineral filler materials were applied to overcome this problem. Generally, the filler material can increase the modulus of polymers either because of the retained molecular mobility (this was not observed in the present study, see Appendix B: Figure B1) or owing to the higher modulus of the filler and the good adhesion between the matrix and the reinforcement (e.g. described by rule of mixtures).

The compressive strengths and moduli are plotted against the filler content in Figure 4.10. Both compressive modulus and strength increased. The compressive characteristics were enhanced more by calcite than by aragonite. These findings are contradictory to prior observations [86] where the aragonite was superior compared to calcite. This phenomenon can be explained by different processing methods applied in the two studies. At solvent casting/phase separation of scaffolds the aggregation of calcite particles could be more significant, while during melt mixing the shear forces could lead to better dispersion of filler particles. This is important in case of calcite, since the BET constant of this material suggests stronger interaction compared to aragonite.

![Figure 4.10 Compressive modulus (a) and compressive yield stress (b) of PCL/CaCO3 samples as a function of filler content](image-url)
Results and Discussion

Tensile properties

Although the main load in bone tissue is compression, the tensile properties during material characterization cannot be neglected, either. In cell walls of porous bone replacements complex microscopic stresses occur, which are a superposition of compression, tension and bending; therefore each of these characteristics should be known to determine or simulate the expected performance of implant material.

The tensile modulus is plotted versus inorganic filler content on Figure 4.11 a). The tensile modulus of aragonite filled polymers increased linearly, but that of calcite filled samples fit to an exponential curve. This can be explained by the differences in the interphase characteristics originating from the different specific surface area. Both fillers increased the compressive modulus of PCL, significantly; at the highest filler content the upper limit of cancellous bone’s modulus was also achieved.

Figure 4.11 b) indicates the tensile yield characteristics of the samples. Pure PCL deviates from trend in both cases which suggests filler induced material structure or morphology change. It is assumed that the particles induced interfacial crystallization of polymer which resulted in different morphological structure and disparate properties. The yield strength of aragonite filled materials decreased with increasing filler content. In the case of calcite filled polymers the experimental results were different. Pukánszky and Vörös [113] described similar observations. It was assumed that yielding occurs in the filled system when the maximum stress reaches the yield stress of matrix ($\sigma_u$). The external load ($\sigma_{ext}$) necessary to induce yielding is (Equation 4.3):

$$\sigma_{ext} = \sigma_u \frac{1 - \phi}{1 - \kappa \phi}$$

(Figure 4.11) Tensile modulus (a), tensile strength and strain at yield (b) values of PCL/CaCO$_3$ samples as a function of filler content
where $\Phi$ [-] is the volume fraction of filler and $\kappa$ [-] is matrix/filler interaction related constant. In case of composite containing rigid particles adhering to the matrix, a significant part of the load is carried by the particles, and yield stress increases with increasing filler content and $\kappa > 1$. If, however, soft inclusions or voids are present, the entire load is carried by the polymer, and yield stress should decrease with composition; in such cases, $0 \leq \kappa < 1$.

The increasing yield strength of calcite filled materials suggests good adhesion between the particles and the matrix. In case of aragonite slight decrease was observed which suggests inferior interfacial connection between the components. This phenomenon can be explained by the difference in specific surface area, which is for calcite 5.7 m$^2$/g while for aragonite 1.4 m$^2$/g. These values indicate that the applied calcite particles have four times greater specific surface than the aragonite whiskers, and it could be responsible for the different adhesion.

Figure 4.12 indicates the tensile properties at large deformations. The small increase in maximum strain at 10 wt% filler content can be explained by either the previously mentioned structure change of matrix polymer or by toughening effect of rigid particles. The concept of toughening effect of rigid particles was described by Kim and Michler [114]. Rigid particles must debond and create free volume in the blend which is similar to the cavitation mechanism in rubber toughened systems. The formation and growth of voids through debonding results in energy dissipation and the dissipated heat plays an important role for the activation of further plastic deformation [115]. The small filler content (10 wt%) acted in the same way and the dissipated heat slightly increased the deformability and thus the elongation at break of the samples.

![Figure 4.12 Tensile break strength and strain of calcium-carbonate filled PCL samples](image)

The calcite filling of PCL resulted in a brittle material at 50 wt% mineral content. The reason is in connection with the surface properties of the filler. As SEM photographs show
that big aggregates were present in the calcite filled samples (Figure 4.13 a). These aggregates reduced the local cross-section, acted as stress concentrating points and decreased the failure strength and strain of specimens significantly.

In contrast, the failure of aragonite filled composites remained ductile. After processing the aragonite particles were not oriented in the material. During uniaxial tension the local stresses around the cylindrical filler became triaxial and the stress concentration around particles results in local plastic flow and in debonding, forming of voids. During the plastic flow the aragonite needles turned in the direction of flow (Figure 4.13 b) and the local stress decreased due to the smaller interacting surface. The descending stress concentration facilitated the further plastic deformation. Additionally, since the crack propagation is path dependent, the longer aragonite particle created longer crack paths between the just formed microcracks. As a result the small cracks cannot grow to the critical crack size, where the failure would be sudden and brittle.

**Essential work of fracture tests**

As it was mentioned earlier, the toughness of applied materials is evaluated by the essential work of fracture method due to the non-linearities and anelastic deformations. In this subchapter first the application limits of EWF method for particle filled polymer systems are discussed. Next, the obtained work of fracture parameters are discussed for PCL/CaCO$_3$ systems.

In the known literature the conditions of EWF testing are sometimes disregarded [48]. Figure 4.14 shows the major difference between the ductile (PCL) and rigid (PLA) deformation of aliphatic polyesters. Although the self similarity showed up in both cases for wide ligament ranges, the yielding of entire ligament prior to stable crack propagation was not
observed in the polylactide samples. This resulted in a negative slope after linear regression that is one of the indicators that EWF technique is not applicable.

![Figure 4.14 Characteristic load-displacement curves of poly(ε-caprolactone) (a) and polylactide (b) (DENT specimens at \( v = 10 \text{ mm/min} \)].

The major problem with inorganic reinforcement is, that the increasing filler content may also result in less ductile behaviour – the slope of \( \text{wt} \) versus \( L \) plots decreases –, which can make the EWF concept inappropriate [48, 116]. Moreover, when the clear yielding is suppressed the curve-partitioning should not be used either [117]. In this study 10 wt% calcite or aragonite filler content does not affect the yielding behaviour of materials significantly (Figure 4.15), thus the curve partitioning method could be used without any reserve.

![Figure 4.15 Load-displacement curves of 10 wt% aragonite (a) and calcite (b) containing poly(ε-caprolactone) (DENT specimens at \( v = 10 \text{ mm/min} \)].

Due to the more inhomogeneous structure of filled samples the self-similarity of load-displacement curves deteriorated with increasing reinforcement content, especially for calcite reinforced polymers (Figure 4.16). The number of inhomogeneities also increases as a result of aggregation processes (Figure 4.13 a). Figure 4.16 also indicates the lower margin of curve-partitioning EWF approach. At 30 wt% aragonite content the clear drop in load-
Results and Discussion

Displacement curves at yield could be observed as far as the ligament length is more than 4 mm, while at 50 wt% this value increases to 8 mm. The ground for this is the decreasing relative polymer content in the ligament. In these cases the yielding became less observable and the yielding and necking process is hardly severable. In case of calcite filled samples not only the absence of necking but also the worse self-similarity of load displacement curves is observable. After yielding there are instabilities in the crack propagation, which may be related to the aggregation of calcite reinforced samples.

Before calculating linear regression the stress criteria (Equation 3.10 and 3.11) and the size of the plastic zone (Equation 3.8) were analyzed for each material. The results are summarized in Table 4.2. Specimens that did not fulfill the mentioned criteria were left out from further analysis. The higher mean net section stress values ($\sigma_m$) of calcite filled materials again suggests better adhesion between calcite and poly(ε-caprolactone) compared to aragonite reinforced ones. The estimated plastic zone sizes ($x_r$) are higher than the applied ligament ranges thus the plastic zone was confined. The net-section stresses are higher than the yield strength for each material, thus the yielding of entire ligament is ensured.
Table 4.2 Tensile yield strength and mean net section stress values for PCL based composites with the estimated criteria ranges of Equation 3.10 and 3.8

<table>
<thead>
<tr>
<th>PCL/CaCO₃ [wt%/wt%] filler type</th>
<th>σᵤ [MPa]</th>
<th>σₘ [MPa]</th>
<th>0.9-1.1σₘ [MPa]</th>
<th>xᵣ [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0 -</td>
<td>15.9±0.9</td>
<td>19.2</td>
<td>17.3-21.1</td>
<td>66.7</td>
</tr>
<tr>
<td>90/10 calcite</td>
<td>15.5±0.4</td>
<td>19.2</td>
<td>17.3-21.1</td>
<td>74.7</td>
</tr>
<tr>
<td>70/30</td>
<td>17.2±0.5</td>
<td>19.0</td>
<td>17.1-20.9</td>
<td>59.6</td>
</tr>
<tr>
<td>50/50</td>
<td>18.9±0.3</td>
<td>18.2</td>
<td>16.3-19.9</td>
<td>37.6</td>
</tr>
<tr>
<td>90/10 aragonite</td>
<td>15.2±0.7</td>
<td>17.6</td>
<td>15.8-19.3</td>
<td>80.1</td>
</tr>
<tr>
<td>70/30</td>
<td>14.6±0.2</td>
<td>14.9</td>
<td>13.5-16.4</td>
<td>107.9</td>
</tr>
<tr>
<td>50/50</td>
<td>13.9±0.6</td>
<td>12.3</td>
<td>11.0-13.5</td>
<td>91.7</td>
</tr>
</tbody>
</table>

The linear regression fit was good in all cases; the coefficients ($R^2$) were above 0.95. Figure 4.17 shows that $w_n$ and thus $w_f$ scatter more than $w_y$. This can be explained with the present material inhomogeneities and different local instabilities at high deformations. These instabilities can arise from the different stress fields and various cavitation mechanisms around the particles [118]. Until yielding these effects are smaller thus the use of $w_y$ to describe the properties of filled materials could be beneficial.

![Figure 4.17](image)

*Figure 4.17 Total specific work of fracture ($w_f$) and its contributing terms ($w_y$ and $w_n$) as a function of ligament length ($L$) for poly(ε-caprolactone)*

At high filler contents (Figure 4.18), especially for calcite reinforced composites, the results of 12 mm ligament length samples deviated from the linear. This is probably due to edge effects in the specimens, since $w/3=10$ mm. Hence, the results showing this kind of deviation were left out from further analysis. This result shows that although some authors [119] argue the relevance of $L_{max}=w/3$ criterion, in reinforced polymers it is of importance.
Results and Discussion

Figure 4.18 Total specific work of fracture (\(w_f\)) and its contributing terms (\(w_y\) and \(w_n\)) as a function of ligament length (L) of 50 weight% calcite containing poly(\(\varepsilon\)-caprolactone) composites

Figure 4.19 summarizes the obtained essential work of fracture parameters. The yielding related terms remained small and nearly constant, which suggests relatively poor adhesion between the matrix and the filler materials. However, the only exception, the PCL/Calcite 90/10, and the overall better properties of calcite reinforced composites underline the former assumption of better interaction between PCL and calcite spheres before yielding. As it was also mentioned earlier the filler-aggregation (Figure 4.13 a) suppresses this effect at higher particle contents.

Contrarily, the necking related essential work of fracture term (\(w_{e,n}\)) increased. The \(w_{e,n}\) parameter doubled in PCL/Calcite 90/10, PCL/Aragonite 90/10 and PCL/Aragonite 70/30 compared to neat PCL. This means that the formation of new fracture surfaces require more energy during the crack propagation in these composites. This can be associated with the debonding processes between the filler and matrix material.

On Figure 4.19 and Figure 4.20 one can observe that \(w_{e,y}\) and \(\beta_yw_{p,y}\) is independent of filler content. The only exception is again PCL/Calcite 90/10, which suggests that these parameters are indicators of filler-matrix adhesion prior yielding.

Figure 4.19 Specific essential work of fracture (\(w_e\)) and its yielding (\(w_{e,y}\)) and necking (\(w_{e,n}\)) related terms
To investigate the influence of fillers on the crystallinity, DSC measurements were carried out. The results are listed in Table 4.3 and indicate that the incorporation of calcium carbonate fillers only slightly (less than 10%) raise the crystallinity, thus the influence of crystallinity increase on fracture parameters is negligible.

Table 4.3 Thermal properties of PCL and its composites with calcite and aragonite

<table>
<thead>
<tr>
<th>PCL/CaCO₃ [wt%/wt%]</th>
<th>filler type</th>
<th>Tₘ [°C]</th>
<th>ΔHₘₐₜ [J/g]</th>
<th>Xᵦ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>100/0</td>
<td>-</td>
<td>61.4</td>
<td>74.8</td>
<td>53</td>
</tr>
<tr>
<td>90/10</td>
<td>calcite</td>
<td>61.4</td>
<td>81.9</td>
<td>57</td>
</tr>
<tr>
<td>70/30</td>
<td>calcite</td>
<td>61.4</td>
<td>79.0</td>
<td>55</td>
</tr>
<tr>
<td>50/50</td>
<td>calcite</td>
<td>61.4</td>
<td>77.9</td>
<td>55</td>
</tr>
<tr>
<td>90/10</td>
<td>aragonite</td>
<td>61.8</td>
<td>80.3</td>
<td>56</td>
</tr>
<tr>
<td>70/30</td>
<td>aragonite</td>
<td>60.9</td>
<td>76.6</td>
<td>54</td>
</tr>
<tr>
<td>50/50</td>
<td>aragonite</td>
<td>60.1</td>
<td>77.6</td>
<td>55</td>
</tr>
</tbody>
</table>

\(\Delta H_m\) = specific melting enthalpy calculated from nominal composition

\(X_b\) = crystalline fraction were estimated using a heat of fusion for 100% crystalline material of \(\Delta H_f=142.5\ J/g\), given by Crescenzi et al \[88\]

Since the failure mode and the dimensions of plastic zone were similar in each material, the obtained \(\beta_{wp}\) values are comparable. The overall plastic work of fracture (Figure 4.20) decreased with increasing filler content, since the rigid particles with high moduli did not take part in the plastic flow and viscoelastic energy dissipation. The difference between the effect of calcite and aragonite fillers can be explained by the different behaviour during large deformations. Calcite particles behaved as spherical voids (cavitation followed by the collapse of cavitated structure) and the dissipated energy during necking decreased nearly linearly thus they did not interact with the polymer matrix significantly. On the other hand, aragonite whiskers turned in the direction of load (Figure 4.13 b) and the friction during the particle motion, the stress redistribution and local strain rate change and plastic flow could result in higher specific energy values.

Figure 4.20 Specific plastic work of fracture (\(\beta_{wp}\)) and its yielding (\(\beta_{wp,y}\)) and necking (\(\beta_{wp,n}\)) related terms
Biocompatibility tests

In order to confirm that the calcium carbonate filling can improve the biocompatibility; the samples were studied by fluorescent microscope and cell numbering. The fluorescent pictures proved the cell adhesion to the surface (Figure 4.21 b), and the cell numbering showed that if the calcium content is increasing on the surface, the cell growth is increased significantly. In case of calcium carbonate 50 wt% filler content resulted in more than twice as many cells than in case of pure PCL (Figure 4.21 a). It means that not only the strength and modulus, but also the biocompatibility of composites is more advantageous than those of PCL samples.

Figure 4.21 Relative cell number as a function of filler content (a), and cell-adhesion on PCL surface shown by fluorescent microscope (b).
4.2.2. Morphological changes and increased toughness in reactively compatibilized biocompatible poly\(\varepsilon\)-caprolactone/polylactide blends

While PCL has good toughness, other biodegradable aliphatic polyesters, like polylactides, owe higher strength and moduli. These polymers are, however, immiscible and this thermodynamic incompatibility results in poor toughness in their blends. Therefore, the compatibility of the two phases has to be improved by compatibilization. The biocompatibility had been preserved by using biocompatible reactive compatibilizers, namely bi- and trifunctional L-lysine isocyanates (for further information please see Appendix B). The morphology of blends was characterized by scanning electron microscopy (of cryofractured and tested fracture surfaces) and DSC, while the toughness was evaluated by the EWF method.

Morphological analysis of blends

In Figure 4.22 the cryofractured surface of blends is shown. The morphology was phase separated and heterogeneous in blends without compatibilization (Figure 4.22 a, b, c). Upon the whole, in blends where PLA formed the dispersed phase the droplets were bigger (several above 20 \(\mu\)m), while in PLA80/PCL20 material the PCL phase is finely dispersed (below 5 \(\mu\)m). After compatibilization the interfacial adhesion between PLA and PCL (\(M_n=50\) kDa) got better, thus the blend-structure became more homogeneous (Figure 4.22 d, e, f). The LTI or LDI addition retarded the phase separation that is observable in Figure 4.22 e. These stretched inclusions are formed during mixing and could originate from a laced structure. This laced structure was also observed during the phase development of other blend systems; and is unstable unless a chemical or physical freezing of morphology takes place [120]. The compatibilizers slightly promoted the conservation of this laced structure.

The DSC analysis (Table 4.4 and Figure 4.23) showed decreasing melting temperature of PCL (\(T_{mp,PCL}\)) in each blend compared to neat PCL, which is an indicator of less ordered crystalline structure. This was a result of limited molecular mobility after PLA addition. PLA, as a second phase, hindered the growth of crystalline lamellae in the examined materials. The addition of compatibilizers, however, did not generate further changes in the crystalline structure of PCL.
The crystallinity of PCL ($X_{PCL}$, calculated by Equation 3.1) decreased slightly after PLA addition. This result is in correlation with the findings of other authors; Newman et al. [121] also observed similar effects, namely the otherwise fast crystallization kinetics of PCL becomes slower in the presence of increasing amounts of PLA. Moreover, the crystallinity of PCL further decreased after LDI or LTI addition. The grafting reactions resulted in high molecular weight PCL-LTI/LDI-PLA copolymers [77], which are hardly crystallizable and hindered the segment-motion, organization and densification of PCL molecules.
Results and Discussion

The PCL and compatibilizer addition, especially at lower PLA contents, promoted the otherwise slow crystallization of PLA. This was indicated by decreasing cold-crystallization temperatures ($T_{ccp}$) and narrower crystallization ranges ($\Delta T_{cc}$). This observation agreed with the results of Harada and co-workers [77]. The PCL or compatibilizer addition, however, did not affect the melting temperature of PLA ($T_{mp,PLA}$), namely the perfection of PLA crystalline parts. In blends the crystallinity of PLA ($\chi_{PLA}$, calculated by Equation 3.1) significantly increased compared to neat PLA due to the nucleating effect of the second phase. These findings are analogous to the results of Sakai et al. [122], who described the nucleating of poly(L-lactide) in the presence of PCL. The compatibilization, however, did not result in further increase in crystallinity of PLA. On the other hand, the initial crystallinity of PLA ($\chi_{PLA,init}$, calculated by Equation 3.2) was higher in compatibilized blends since the grafted copolymers, as impurities, facilitated the heterogeneous nucleation of PLA similarly to the effect of PCL phase described above.
Table 4.4 Thermal properties of PLA/PCL blends

<table>
<thead>
<tr>
<th>No.</th>
<th>PCL/PLA [wt%/wt%] comp.*</th>
<th>(T_{mp,PCL}[^\circ C])</th>
<th>(T_{mp,PLA}[^\circ C])</th>
<th>(\Delta H_{mp,PCL} [J/g])</th>
<th>(\Delta H_{mp,PLA} [J/g])</th>
<th>(\Delta H_{mp,PLA,init} [J/g])</th>
<th>(X_{PCL} [%])</th>
<th>(X_{PLA} [%])</th>
<th>(X_{PLA,init} [%])</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0/100</td>
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<td>124.0</td>
<td>168.7</td>
<td>-</td>
<td>16.3</td>
<td>5.7</td>
<td>-</td>
<td>7.9</td>
</tr>
<tr>
<td>2</td>
<td>20/80</td>
<td>-</td>
<td>58.9</td>
<td>102.1</td>
<td>167.7</td>
<td>75.5</td>
<td>40.6</td>
<td>5.7</td>
<td>53.0</td>
</tr>
<tr>
<td>3</td>
<td>20/80 LDI</td>
<td>59.1</td>
<td>99.1</td>
<td>167.9</td>
<td>60.5</td>
<td>42.8</td>
<td>9.3</td>
<td>42.5</td>
<td>31.7</td>
</tr>
<tr>
<td>4</td>
<td>20/80 LTI</td>
<td>57.3</td>
<td>98.9</td>
<td>168.2</td>
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<td>8.0</td>
<td>39.3</td>
<td>30.3</td>
</tr>
<tr>
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<td>-</td>
<td>60.3</td>
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<td>75.6</td>
<td>43.6</td>
<td>9.2</td>
<td>53.1</td>
</tr>
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<td>102.5</td>
<td>167.7</td>
<td>63.0</td>
<td>41.6</td>
<td>14.8</td>
<td>44.2</td>
<td>30.8</td>
</tr>
<tr>
<td>7</td>
<td>50/50 LTI</td>
<td>59.1</td>
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<td>167.3</td>
<td>59.8</td>
<td>43.8</td>
<td>17.4</td>
<td>42.0</td>
<td>32.4</td>
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<td>8</td>
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<td>-</td>
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<td>103.2</td>
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<td>69.8</td>
<td>46.0</td>
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<td>9</td>
<td>80/20 LDI</td>
<td>59.9</td>
<td>94.6</td>
<td>166.1</td>
<td>67.8</td>
<td>45.5</td>
<td>21.0</td>
<td>47.5</td>
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<td>80/20 LTI</td>
<td>59.1</td>
<td>95.2</td>
<td>167.2</td>
<td>66.4</td>
<td>44.0</td>
<td>15.5</td>
<td>46.6</td>
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<tr>
<td>11</td>
<td>100/0</td>
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<td>-</td>
<td>77.2</td>
<td>-</td>
<td>54.2</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* the compatibilizer content was 0.5 phr in all cases

Fracture testing of compatibilized PCL/PLA blends

Since PLA at room temperature is in glassy state and is a rigid material, it does not meet all the pre-requisites of EWF procedure. Figure 4.24 shows a typical load-displacement curve of PLA. The yielding of full ligament occurred, but the crack growth was not stable. In PCL and blends, particularly in the compatibilized ones, stable crack propagation took place (Figure 4.24). The results of PLA were, therefore, compared with those of the blends to get a complete insight into the material behavior; but the properties of neat PLA should be treated with reservations.

![Figure 4.24 Load-displacement curves of PLA, PCL and their blends](image-url)
The average of maximum stress in ligament at yield ($\sigma_m$) decreased with increasing PCL content (both the modulus and yield strength of PLA is greater than those of PCL [55]). The $\sigma_m$ values of compatibilized blends plotted on Figure 4.25 can be described with the phenomenological Equation (4.4) ($R^2=0.9989$).

$$\sigma_m = 65.54 \cdot e^{\psi_{\text{PCL}}^{0.3276}} + 16.63,$$

(4.4)

where $\sigma_m$ [MPa] is the average of stress in ligament at yield and $\psi_{\text{PCL}}$ [-] is the weight fraction of PCL. Formally this equation is analogous to models describing the yield strength of heterogeneous blends [123] and filled polymers [124, 125], which suggests $\sigma_m$ to be similar to the conventional yield strength of bulk materials.

According to the rule of mixtures, in homogenous blends at small deformations the tensile properties are linear functions of composition while the exponential change is typical for heterogeneous materials [55, 123-125]. The mixtures of macromolecular materials often exhibit the latter behavior, thus the exponential decrease is one of the indicators of thermodynamical incompatibility. This and the DMA results (Appendix B: Figure B3) underline the incompatibility of PLA/PCL blends, which was also mentioned earlier.

![Figure 4.25 The averages of maximal stress at yield in the ligament of samples](image)

The specific essential work of fracture ($w_e$) values of uncompatibilized blends remained low since the weak interfacial adhesion between the immiscible polymer phases could not prevent the generation of new crack-surfaces (Figure 4.26). The dispersed phase worked as inhomogeneity or void in the matrix and the crack propagated easily on the phase boundary. The only exception was the PLA80/PCL20 blend (Figure 4.22 c), where the dispersed morphology resulted in favorable properties. Although PLA in bulk is a rigid polymer the fine dispersed PCL content promoted the local flow of PLA phase – as it is shown in Figure
4.28 c). This local deformation was also observed in particle-filled systems [126]. The stress concentrating effect of PCL inclusions induced a micro-deformation in matrix but before the tearing of these micro-fibrils the dispersed phase also deformed, which eventually resulted in decreasing stress concentration. This local stress-fluctuation lasted until the collapse of the fibrillar PLA structure. Due to the stress fluctuation in the matrix, the fibrillar PLA phase became more oriented and stronger, thus the formation of new crack-surfaces required more energy (Figure 4.26). These damage mechanisms are similar to the findings of Todo et al. [127], who also found elongated fibrils and PCL spherulites in PLA/PCL blends at 5 wt% PCL content.

Both LDI and LTI addition increased significantly the $w_e$ compared to the uncompatibilized blends (Figure 4.26). This was a result of the grafting-reaction between PLA and PCL which is explained in details in the Appendix B (Figure B2) and in the paper of Harada et al. [77]. The presence of LTI resulted in higher $w_e$ values since this compatibilizer had one more cyanate group compared to LDI; it had more potential to connect PCL or PLA molecules into a branched network. The optimal composition seems to be at around 50 wt% PCL content.

The dissipated energy in the plastic zone ($\beta w_p$) increased with increasing PCL content due to the tough and highly viscous nature of PCL (Figure 4.27; $\beta w_p$ values are shown as the shape and dimensions of the plastic zone and thus the describing factor, $\beta$, was very similar in each tested material). The effect of compatibilizers in case of plastic work of fracture was analogous to the essential work of fracture. $\beta w_p$ increased significantly after compatibilization at 50 wt% PCL content, otherwise the effect remained generally insignificant and matrix dominated. The reasons could be the same as described in previous paragraph. However, LDI
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performed slightly better than LTI, again because of the number of cyanate groups. In this case the more strongly connected LTI containing network hindered the energy dissipative mechanisms in the blends.

![Graph showing specific plastic work of fracture values of the examined blends](image)

*Figure 4.27 Specific plastic work of fracture values of the examined blends*

Fractography

Figure 4.28 shows the effect of compatibilizers on the fracture surface of DENT specimens of different blends. In uncompatibilized blends where PCL is in surplus, spherical PLA droplets could be observed (Figure 4.28. a, b). The stress concentration around the dispersed phase did not deform these inclusions; since the plastic flow of PCL starts at lower stresses than the yield strength of PLA. The flattened ellipsoidal PLA parts on Figure 4.28 b) are a result of processing technique (compression molding). In case of PLA80/PCL20 blends both PCL and PLA phases are deformed (Figure 4.28 c). This dual deformation could be related to the stress fluctuation around the PCL inclusions.

The addition of compatibilizers (Figure 4.28 d, e, f) resulted in all blends in a more homogenous deformation behavior. The phases deformed together, no sharp phase boundary could be found in PLA20/PCL80/LTI and PLA80/PCL20/LTI blends. On Figure 4.28 e) it can be seen that the PLA phase deformed collaterally with PCL after compatibilization. This mechanism, conversely, could not be observed in the PLA50/PCL50 blend, where only the PCL phase took part in the load-bearing process.
Figure 4.28 The effect of compatibilizers on the fracture behavior of PLA/PCL blends: (a) PLA20/PCL80; (b) PLA50/PCL50; (c) PLA80/PCL20; (d) PLA20/PCL80/LTI; (e) PLA50/PCL50/LTI; (f) PLA80/PCL20/LTI (SEM micrographs of the fracture surfaces of DENT specimens)
4.3. Valid ligament range determination for the plane-stress ductile fracture tests of polymers

As it was revealed by Cotterell et al. [90], one of the major sources of error in EWF method is the definition of valid ligament length. For metal films the originally proposed limits seem to be adequate but for polymers the valid data range is more ambiguous (see the report of ESIS TC4 1.2 working group). In this chapter novel hypotheses are investigated based on literature data and measurements on PCL (Capa 6800).

4.3.1. Feasibility of the stress criterion

The increase in net section stress is generally attributed to the plane-strain/plane-stress transition in DENT specimens. The stress criterion of Cotterell [90] as well as that of Clutton [104] is based on this assumption. In this subsection the propriety of these stress criteria is analyzed. They are reconsidered principally for polymers due to the ambiguity between original criteria and experimental results.

By plotting the thickness specific load ($P_{\text{max}}/B$) against the ligament length the results lie on a straight line with a positive intercept. As it was stated by Cotterell and Reddel [89] true geometric similarity occurs when the line passes through the origin. They assumed that crack growth might occur before reaching the maximum load, which resulted in the observed slight deviation. In high yield strength metals the effect of this intercept seems to be negligible, however in materials of lower yield stress it could possibly lead to difficulties during the use of stress criteria.

Ever since several studies and experimental results were released addressing the behavior of metals as well as polymers. As it is shown in Figure 4.29, the plots are linear – implying geometric similarity – and having positive intercept. Since the data were obtained by several research groups [92, 94-102] from wide range of materials the results suggest the potential influence of other, so far disregarded reasons and not measurement errors.

During tests the crack initiates at the notch between plane-strain and plane-stress conditions and there is a transition distance after it turns to quasi plane-stress [90]. In this mixed regime – as it was predicted by Hill [93] – the net-section stress ($\sigma_{ns}$) increases and its value could be given by Equation (4.5).

$$\sigma_{ns} = m\sigma_u$$

(4.5)

where $m$ [-] is the factor determined by Hill [93] and $\sigma_u$ [MPa] is the yield stress. In a plastic-rigid material under plane-stress $m$ is 1.15.
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Figure 4.29 Thickness specific load as a function of ligament length (Note: data were obtained from Refs. [92, 94-102]; results without temperature indicated were measured at ambient conditions; the lines are the least square regression fits)

Usually Equation (4.5) is used to determine the lower ligament threshold of experimental sets. This concept is theoretically correct, but supposes true geometric similarity, plane-stress and plastic-rigid material behavior. Since these are not present the obtained minimal ligament lengths *de facto* do not represent the plane-stress/plane-strain transition. They are only the intersections of the fitted lines (Figure 4.29) and of the line described by Equation (4.5) as it is shown in Table 4.5.

As a result, the presented transition distances from plane-strain to plane-stress are much higher ((30-70)B) than it was observed by Wu and Mai (14B) [103] or even higher than those originally suggested by Cotterell *et al.* [89] for metals ((3-5)B). Additionally, Marchal *et al.* [128] found during statistical analyses that significant non-linearities – transition to mixed region – in the specific work of fracture against ligament length regression could only be observed in the range of (3-5)B for metals and of (6-8)B for polymers. This observation suggests that the presented and commonly used stress criteria are not adequate for the determination of lower ligament limit.
### Table 4.5 Data from the least square regression fits of Figure 4.29 as well as experimental yield stresses and minimal ligament lengths from Refs. [92, 94-102]

<table>
<thead>
<tr>
<th>Material [Ref.]</th>
<th>Data obtained from linear regression</th>
<th>Data obtained from reference paper</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ordinate intercept</td>
<td>Slope</td>
</tr>
<tr>
<td></td>
<td>( u ) ([N/mm])</td>
<td>( \sigma ) ([N/mm^2])</td>
</tr>
<tr>
<td>Copper [102]</td>
<td>154.7</td>
<td>116.0</td>
</tr>
<tr>
<td>PEI [92]</td>
<td>70.8</td>
<td>113.5</td>
</tr>
<tr>
<td>PC [92]</td>
<td>54.0</td>
<td>48.9</td>
</tr>
<tr>
<td>HIPS [98]</td>
<td>19.7</td>
<td>17.1</td>
</tr>
<tr>
<td>PEN at 80°C [95]</td>
<td>118.1</td>
<td>85.1</td>
</tr>
<tr>
<td>PBT [100, 129]</td>
<td>50.1</td>
<td>47.7</td>
</tr>
<tr>
<td>PETG [94]</td>
<td>85.4</td>
<td>48.6</td>
</tr>
<tr>
<td>PET [92, 100]</td>
<td>133.2</td>
<td>103.4</td>
</tr>
<tr>
<td>PVC [96]</td>
<td>55.4</td>
<td>39.3</td>
</tr>
<tr>
<td>PEEK [99]</td>
<td>55.8</td>
<td>62.9</td>
</tr>
<tr>
<td>PEEK at 100°C [99]</td>
<td>23.3</td>
<td>35.4</td>
</tr>
<tr>
<td>EPBC [101]</td>
<td>22.4</td>
<td>27.7</td>
</tr>
<tr>
<td>PCL</td>
<td>15.3</td>
<td>20.0</td>
</tr>
</tbody>
</table>

* calculated as the intersection of fitted lines (Figure 4.29) and Equation (4.5), respectively

As shown in Figure 4.30 a) the slope values are closely related to the yield stress. The only exceptions among the studied materials are the PETG [94], the PEI [92] and the copper [102]. If the slope of the data points is smaller than the yield stress (PETG [94]), then the full ligament yielding is not ensured – or either the yield stress or the net-section stresses were not determined correctly. If, however, the slope is higher than 1.15\( \sigma_\text{u} \), then the plane-stress conditions are not ensured. In case of copper [102] the \( \sigma_\text{ns}/\sigma_\text{u} \) ratio is above 1.5 for all data points, which is much higher than the factor 1.15 suggested by Hill [93].

In Figure 4.30 b) the ordinate intercept values are plotted versus the tensile modulus of the tested materials. The good correlation suggest that the initial elastic deformations are implied in the \( u \) term, therefore it denotes the difference between the plastic-rigid (ideal – Hill’s theory) and elastic-plastic (real) material behavior.

![Figure 4.30 Yield stress versus slope (a) and tensile modulus versus ordinate intercept values (b) of the studied materials](image)

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Thereafter, the observed lines in Figure 4.29 can be described by Equation (4.6).

\[
\frac{P_{\text{max}}}{B} = \sigma_n L = u + m^* \sigma_u L
\]  

(4.6)

where \(u\) [N/mm] is the ordinate intercept of the \(P_{\text{max}}/B\) versus \(L\) linear fits and \(m^*\) [-] is an experimentally determined ratio, which could be given by Equation (4.7).

\[
m^* = \frac{\sigma}{\sigma_u}
\]  

(4.7)

where \(\sigma\) [MPa] is the slope of the \(P_{\text{max}}/B\) versus \(L\) linear fits. If \(1 < m^* < 1.15\) then the EWF method can be used appropriately. If, however, \(m^*\) is out of this range or \(u\) is negative, then further analysis should be made or the EWF method is inapplicable. After rearranging Equation (4.6) the factor can be estimated point by point from Equation (4.8).

\[
m^*_i = \frac{\sigma_n L_i - u}{\sigma_u L_i}
\]  

(4.8)

where \(m^*_i\) [-] is an estimated value of Hill’s factor for data point \(i=1\) to \(N\). Specimens for which \(m^*_i\) is above 1.15 or below 1 should be rejected due to aforementioned reasons. After this treatment the linear fit should be repeated and the \(u\), \(\sigma\) and \(m^*\) values should be recalculated until the criterion \(1 < m^* < 1.15\) is satisfied.

The importance of this treatment is that the deviations from ideal material behavior seem to have an inherent effect on the stress criteria of Cotterell [90] and of Clutton [104], which can be interpreted after the rearrangement of Equation (4.6) for the net section stress by Equation (4.9).

\[
\sigma_n = m^* \sigma_u \left( 1 + \frac{u}{m^* \sigma_u L} \right)
\]  

(4.9)

where the \(u/m^*\sigma_u\) constant is related to the real material behavior – mixed-mode crack initiation, elastic effects, quasi plane-stress conditions, non-ideal plastic deformation etc.

As shown in Equation (4.9) the positive intercept causes, that the measured maximum stress values increase with decreasing ligament length \(L\) independent of stress state changes, which can be misinterpreted as the transition to mixed plane-strain/plane-stress region. This increase results in unnecessarily large \(L_{\text{min}}\) values, albeit the linearity of \(w_f\) values holds. This, however, deteriorates the reproducibility of the measurements, since the confidence interval of linear regression is hyperbolic and the farther we get from the measured data the larger will be the scatter of \(w_c\). Equations (4.6), (4.7) and (4.8) help to avoid this error and facilitate the determination of valid ligament range; for which the linearity of \(w_f\) and \(P\) versus \(L\) holds.
4.3.2. The role of ultimate elongation

In the previous subsection it was shown that during EWF tests the present stress criteria are invalid for ligament range determination in polymers. Additionally, the validity criterions – except the self similarity – do not treat the entire deformation process; they are useful only until the crack initiates. The feasibility of a displacement criterion is tested on PCL, but the final statements are validated on other materials – based on literature data –, too.

**Displacement criterion**

Next, the hypothesis of a displacement criterion is based on the ductility level ($DL$) – first proposed by Martinez *et al.* [130] – that measures the ratio of ultimate elongation ($e_u$) and original ligament length ($DL=e_u/L$) will be presented. By using together with a stress criterion it helps the data validation not until crack initiation but during the entire deformation process (Figure 4.31) and helps the rejection of bad data resulting from instable crack propagation.

![Figure 4.31 Typical load-displacement plot of a DENT specimen with the related criteria](image)

Figure 4.32 shows a series of typical load-displacement curves. As it is observable, the self-similarity holds in a wide ligament range. However, the $DL$ values decreased fairly at higher ligament lengths, while increased at small ligament lengths.

![Figure 4.32 Typical load-displacement curves with respective ligament lengths and DL values](image)
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The analysis of the stress criteria of Cotterell [90] and Clutton [104] (Figure 4.33) shows that the majority of small ligament lengths could be filtered through these methods, i.e. they lie outside of the defined stress range. It can be also noted that the criterion of Cotterell seems to be stricter and narrower compared to the criterion of Clutton for low yield strength polymers. Additionally, it is independent of the scatter of measured values, but requires further tensile tests under different stress conditions.

![Figure 4.33 Stress criterion of Cotterell [90] and Clutton [104] with the related bounds. “Validated data” denote data that have fulfilled the given criterion, while “filtered data” are those that have not](image)

On Figure 4.34 the obtained ductility-levels ($DL$) are shown. The tendency at small ligament lengths and at the common ligament ranges are similar to the findings of Gamez-Perez [131]. However, at ligament lengths higher than $w/3$ the $DL$ values start to decrease. This decreasing tendency is in connection with the asymptotic response assumed by Cotterell [90] and could lead to non-linearities during the regression as it was found by other authors [132, 133]. The original method, however, fails when these non-linearities arise. This observation suggests a simple criterion based on the mean of the $DL$ values (Equation 4.10).

$$0.9 \overline{DL} < DL < 1.1 \overline{DL}$$

(4.10)

where $\overline{DL}$ [-] is the mean of ductility levels.
Although, this criterion is based on test results – and therefore has similar material-dependence and drawbacks, like the stress criterion of Clutton –, it has a possible advantage; namely combined with a stress criterion, this “displacement criterion” allows a data-filtering through the whole fracture process, not just until initiation. Additionally, the problems arise from the non-linearities, incomplete yielding or contained plastic zone formation at large ligament lengths (greater than \( w/3 \)) can be solved in this way. Furthermore, it has a more exact form compared to other arbitrary interpretable requirements, like “self-similarity” or “full ligament yielding”.

Figure 4.35 shows the specific fracture works with the results of different data reducing methods. The first region is connected to the plane-stress/plane-strain transition, while the third region is linked to the asymptotic transition to plane-stress fracture toughness (\( G_c \)). It is also observable that the stress criterion itself only works well at small ligament lengths, but could not handle the errors resulting from greater ligament lengths. For this purpose, the present displacement criterion seems to be more useful.
The incorrect determination of valid ligament lengths – lower and upper bounds – makes the original theory inappropriate and the non-linearities results, therefore, in a significant deviation as it is shown in Table 4.6.

Related to the study of ethylene-propylene copolymer films Williams and Rink [101] proposed a further criterion based on a statistical analysis. They stated that a correlation coefficient ($R^2$) of 0.98 or a standard deviation ($SD$) value of 3 kJ/m$^2$ is required for correct data determination.

In this work the observed $R^2$ values are close to 0.97 and seem to be adequate. However, the standard deviation values are quite high. Even after using Equations (3.10) and (4.10) the $SD$ value is close to 8 kJ/m$^2$. Nevertheless, the goodness of fit could be further improved by rejecting data of high residuals (outside of ±2SD). Next the regression line was recalculated until $R^2$ became higher than 0.98 and no data laid outside the range of 95% confidence limit (±2SD) – see Table 4.6 ‘±2SD’ line. After this final treatment the number of data points slightly decreased ($N$=22), but the calculated $SD/w_e$ ratio complied with the general 0.1 value [101].

The standard deviation, however, remained 6.3 kJ/m$^2$, which is nearly the double of $SD$=3 kJ/m$^2$ found for ethylene-propylene copolymers. This observation supports the statement of Williams and Rink [101], namely the $SD$ value seems to be material specific while the $R^2$ not.

Table 4.6 Essential work of fracture parameters and the goodness-of-fit of linear regressions

<table>
<thead>
<tr>
<th>Data reducing method</th>
<th>Valid data range</th>
<th>$w_e$ [kJ/m$^2$]</th>
<th>$\beta w_e$ [MJ/m$^3$]</th>
<th>$N$ [-]</th>
<th>$R^2$ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equation (3.10) [104]</td>
<td>$0.9\sigma_m&lt;\sigma_m&lt;1.1\sigma_m$</td>
<td>91.3±6.0</td>
<td>12.9±0.5</td>
<td>43</td>
<td>0.9734</td>
</tr>
<tr>
<td>Criterion for metals [48, 89]</td>
<td>5B&lt;L&lt;W/3</td>
<td>68.4±5.8</td>
<td>15.5±0.6</td>
<td>40</td>
<td>0.9667</td>
</tr>
<tr>
<td>Criterion for LLDPE [103]</td>
<td>14B&lt;L&lt;W/3</td>
<td>43.9±9.3</td>
<td>17.9±1.0</td>
<td>32</td>
<td>0.9569</td>
</tr>
<tr>
<td>Equation (3.10) and (4.10)</td>
<td>12B&lt;L&lt;W/3</td>
<td>49.2±6.1</td>
<td>17.5±0.8</td>
<td>29</td>
<td>0.9691</td>
</tr>
<tr>
<td>±2SD [101]</td>
<td>12B&lt;L&lt;W/3</td>
<td>60.8±6.2</td>
<td>16.3±0.6</td>
<td>22</td>
<td>0.9857</td>
</tr>
</tbody>
</table>

Extension of displacement criterion

Next, to generalize the proposed displacement criterion the works of several research groups on various materials [57, 92, 94-102, 131, 134] are reconsidered.

The ductility level terms were calculated for each material from the experimentally observed ultimate elongation values. As it is shown in Figure 4.36 the ductility level is material dependent and the examined materials could be generally sorted into three groups:

(i) metals, polymers of high yield stress and relatively modest $w_e$ and/or $\beta w_p$ values (open symbols);
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(ii) block copolymers of lower yield stress but higher $w_e$ and $\beta w_p$ values (half closed symbols);

(iii) elastomer-like thermoplastic(s) of low modulus, yield stress but high $w_e$ and $\beta w_p$ values (solid symbols).

According to Equation (3.8), in materials of high yield stress and relatively low fracture resistance – and/or modulus – there is higher chance of having contained yield. As it was mentioned earlier this could result in crack propagation prior to full ligament yielding that makes the EWF concept inappropriate.

![Graph](image)

*Figure 4.36 The calculated ductility level values of the examined materials with the estimated ranges*

The advantage of the proposed ductility level criterion is that for polymers it is getting more and more restrictive as the ductility level and the size of the plastic zone decreases (see Table 4.7 and the approximate ranges – from Equation (4.10) – in Figure 4.36). This brings an additional safety in the EWF procedure even if the size of the plastic zone would be estimated incorrectly. Nevertheless, the proposed limits sometimes seem to be too rigorous, thus the broadening of correct data range should be considered (e.g. to $0.85 \, DL$ and $1.15 \, DL$).

The statement of Martinez *et al.* [130] regarding to the applicability of EWF procedure and $DL$ values should be argued, too. The authors stated that “in order to fulfill the EWF
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requirements, $DL$ must be in the range of $0.15<DL<1"$. Although the proposed $DL$ range covers the majority of examined materials there are a few exceptions (Table 4.7). In case of PEN [95, 100] the estimated size of plastic zone is quite small, which could result in contained yield at larger ligament lengths. After rejecting data below 5 mm and above 9 mm the mean $DL$ value increases to 0.17, which seems to be adequate. In case of copper [102] and HIPS [98] such a treatment did not result in higher $DL$ averages. This suggests the inadequacy of EWF method albeit the conventional lower and upper limits held. In case of PCL the studied ligament range was also appropriate and the crack propagated acceptably (Figure 4.32). No “necking” was observed that would make the EWF concept unsuitable. Consequently, the low ($<0.15$) $DL$ values could represent brittle fracture, ductile instability or contained yielding and the evaluation of $DL$ supports the data rejection; but the high values are not definitely resulting from “necking” problems.

As it is shown in Table 4.7 the lower ligament limits calculated from Equation (4.10) are in good agreement with the estimated lower ligament lengths of the selected studies (these are usually determined from stress criteria). The limits fulfilled in all cases the statistically determined lower ligament bound criterion proposed by Marchal et al. [128] – $3B$ for metals and $6B$ for polymers.

<table>
<thead>
<tr>
<th>Material [Ref.]</th>
<th>Lower limit [mm]</th>
<th>Upper limit [mm]</th>
<th>Mean ductility level $(DL)$ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Used in reference</td>
<td>Calculated from Eq. (4.10)</td>
<td>Size of the plastic zone* $(x_p)$</td>
</tr>
<tr>
<td>Copper [102]</td>
<td>10 (100B)</td>
<td>3.5 (35B)</td>
<td>$&gt;100$</td>
</tr>
<tr>
<td>Steel [134]</td>
<td>5.5 (4B)</td>
<td>8 (5B)</td>
<td>$&gt;100$</td>
</tr>
<tr>
<td>HIPS [98]</td>
<td>7 (27B)</td>
<td>5.7 (22B)</td>
<td>15.9</td>
</tr>
<tr>
<td>PEN [95, 100]</td>
<td>5 (40B)</td>
<td>7.2 (38B)</td>
<td>8.4</td>
</tr>
<tr>
<td>PBT [100, 129]</td>
<td>8 (64B)</td>
<td>8.0 (64B)</td>
<td>12.3</td>
</tr>
<tr>
<td>PETG [94]</td>
<td>6 (28B)</td>
<td>5.8 (28B)</td>
<td>20.2</td>
</tr>
<tr>
<td>PET [100]</td>
<td>6 (48B)</td>
<td>5.1 (41B)</td>
<td>9.9</td>
</tr>
<tr>
<td>PVC [96]</td>
<td>6 (15B)</td>
<td>6.3 (16B)</td>
<td>18.2</td>
</tr>
<tr>
<td>PEEK [99]</td>
<td>4 (32B)</td>
<td>5.4 (43B)</td>
<td>10.7</td>
</tr>
<tr>
<td>EPBC [131]</td>
<td>3 (3B)</td>
<td>7.0 (7B)</td>
<td>16.1</td>
</tr>
<tr>
<td>PCL</td>
<td>6 (12B)</td>
<td>4.5 (9B)</td>
<td>66.7</td>
</tr>
</tbody>
</table>

The determination of a valid upper limit seems to be more complex. Arkhireyeva and Hashemi [94-99] found that the plots of $w_f$ versus $L$ remained linear at ligament lengths above $w/3$. They stated that $L_{max}=w/3$ is too restrictive, but at least it is a safe upper bound. Wu et al. [119] also argued the validity of conventional upper limit. They found that the departure from
linearity in the upper region has no relation to the minimum of $w/3$ or $x_p$. In polymers this could be often so, since the yielding is usually accompanied by necking that increases the local stress and stabilizes the plastic region, consequently the yielding remains uncontained and loading dominates unloading. In metals, however there is a large screening plastic region and necking is not observed generally thus $x_p$ influences the yielding. In polymers, therefore, the size of the plastic zone is the advisable upper limit, while in metals the original criterion holds. In this study the upper limits calculated from Equation (4.10) usually agree well with the size of the plastic zone for high yield stress polymers. At lower yield stress values Equation (4.10) seems to be too restrictive. In metals the obtained values are slightly smaller than the values used in the reference papers, which again suggests a shift to safety.

### 4.3.3. Lower ligament limit based on experimental ultimate elongation data

In Figure 4.37 the ultimate elongation against ligament length plots are shown. The previously mentioned three groups can be observed here, as well. The ordinate intercept ($e_0$) was originally interpreted as the critical crack tip opening displacement ($\delta_c$), but Cotterell et al. [90] has shown that it is only equal to $\delta_c$ if the inner fracture process zone is infinitesimally small.

If the elongation at fracture ($e_u$) is a linear function of the ligament length the regression lines can be given by Equation (4.11).

$$e_u = e_0 + e_p L$$  \hspace{1cm} (4.11)

where $e_0$ [mm] is the ordinate intercept and $e_p$ [-] is the plastic contribution factor. If both the length of the fracture process zone and the ligament length at which the centre of ligament first necks are small then $e_0 \approx \delta_c$ and $e_p \approx \alpha/2$ ($\alpha$ is the crack tip opening angle).

Cotterell et al. [90] also showed that for the lower ligament limit there is an alternative validity criterion that can be given by Equation (4.12).

$$L_{\text{min}} > 2\rho$$  \hspace{1cm} (4.12)

where $\rho$ is the steady-state length of fracture process zone after the fracture initiates. Based on Cotterell’s theory $\rho$ could be estimated experimentally from Equation (4.13).

$$\rho = \frac{e_0 - u_n}{2e_p}$$  \hspace{1cm} (4.13)

where $u_n$ [mm] is the elongation at which the centre of the ligament first yields. Pardoen et al. [135] found during the testing of aluminum alloys that Equation (4.12) is more severe than Equation (3.6) for thinner sheet specimens.
Results and Discussion

The term \( u_n \) has generally small value and as such it could be neglected in Equation (4.13). Furthermore, after this neglection the criterion itself becomes more severe. Accordingly, we get an experimentally simply determinable variable \( \lambda \) [mm], which ensures the crack initiation and the formation of steady-state fracture in DENT specimens. This term could be written by Equation (4.14).

\[
\dot{\lambda} = \frac{e_0}{e_p}
\]

and finally Equation (4.12) can be rewritten in the form of Equation (4.15).

\[
L_{\text{min}} > \dot{\lambda}
\]

![Figure 4.37 Plots of the ultimate elongation versus ligament length (Note: the lines are arbitrarily selected least square regression fits of PCL, EPBC and Copper, respectively)](image)

The obtained \( e_0, e_p \) and \( \dot{\lambda} \) values are listed in Table 4.8. By comparing the \( \dot{\lambda} \) values with the \( L_{\text{min}} \) values of Table 4.7 it turns out that for polymers \( \dot{\lambda} \) is closer to the \( L_{\text{min}} \) values obtained from Equation (4.10) than to those used in reference papers, which suggest some relationship between \( DL \) and \( \dot{\lambda} \). The estimated ligament range in case of HIPS and PEN supports the \( DL \) related statement of Martinez et al. [130]; namely the EWF procedure should not be used when \( DL < 0.15 \) due to crack stability problems (the \( \dot{\lambda} \) values of these materials were the
highest). Accordingly, the $DL$ term seems to be a proper expression to characterize the adequateness of EWF method. For polymers, therefore, the modification of lower ligament limit would be advisable to Equation (4.16).

$$L_{\text{min}} = \text{Max}(\lambda; 6…8B) \quad (4.16)$$

In this case $\lambda$ ensures the formation of steady-state fracture process zone, while the term $(6…8)B$ ensures the plane-stress state according to Marchal et al. [128]. Furthermore, the linear regression of ultimate elongation values with high regression coefficients helps the observation and rejection of experimental errors, similarly to the treatment of Williams and Rink [101] for work of fracture.

| Table 4.8 Obtained crack opening displacement parameters |
|---------------------------------|-------------|
| Material | Copper | Steel | HIPS | PEN | PBT | PET | PVC | PEEK | PETG | EPBC | PCL |
| $e_0$ [mm] | 0.25 | 0.63 | 0.44 | 0.64 | 0.93 | 0.62 | 0.89 | 1.05 | 2.04 | 1.23 | 3.69 |
| $e_p$ (rad) | 0.12 | 0.11 | 0.05 | 0.07 | 0.13 | 0.12 | 0.13 | 0.17 | 0.45 | 0.62 | 1.58 |
| $\lambda$ [mm] | 2.1 | 5.7 | 8.8 | 9.1 | 7.2 | 5.2 | 6.8 | 6.2 | 4.5 | 2.0 | 2.3 |

The above mentioned relationship between $DL$ and $\lambda$ could be derived from Equation (4.11) after dividing by the ligament length ($L$) one can get Equation (4.17).

$$\frac{e_{\mu}}{L} = \frac{e_0}{L} + e_p \quad (4.17)$$

Since $DL$ was defined as $e_\mu/L$ after factorization Equation (4.18) gives an expression for the ductility level, which is

$$DL = e_p \left(1 + \lambda \frac{1}{L} \right). \quad (4.18)$$

Thereafter, the $DL$ related material-groups and the shape of $DL$ against $L$ plots can be explained by Equation (4.18), which is formally the same as Equation (4.9). The above mentioned groups are in close relation to the $e_p$ values listed in Table 4.8 and express the “plasticity” of material. The smaller $\lambda$ values (e.g. Copper, EPBC, PCL) resulted in less significant non-linearities in Equation (4.18), which suggested the constancy of $DL$ and was experimentally observed in PCL and EPBC [131]. If Equation (4.11) holds the $DL$ values are asymptotic to $e_p$ at larger ligament lengths. Nevertheless, the disconnection of plastic zones seems to lead to deviations from linear at ligament lengths larger than the size of the plastic zone ($L>x_p$).

Summarily, it was shown that the present stress criteria of EWF method are influenced by the difference between ideal and real material behavior, thus a novel stress criterion was presented. Additionally, an attempt has been made to facilitate the elimination of bad data
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resulting from unstable crack propagation or the missing of steady-state fracture process zone. Based on these results, as a final summary, the valid data of EWF method should fulfill the criteria of Equations (4.6), (4.7), (4.8) and (4.16). Nevertheless, what more important is that the fits of $P_{max}/B$ vs. $L$, $e_u$ vs. $L$ and $w_f$ vs. $L$ data have to be linear with a high correlation coefficient, $R^2>0.98$; and the $L_{min}$ should be as small as possible to diminish the scatter of $w_e$. In my further measurements, therefore, I also use the presented criteria.

4.4. Molecular weight dependence of fracture behavior of semi-crystalline poly($\varepsilon$-caprolactone)

As it was pointed out in a recent review of Bárány et al. [48] the microstructural dependence of fracture mechanical parameters is far less understood for semi-crystalline polymers than for amorphous ones. The strong interrelation between the parameters of crystalline structure usually trammels the independent analysis of structural parameters. Nevertheless, as described earlier, PCL seems to be a good model material. In the following subsections the effect of number average molecular weight and of annealing induced changes on fracture performance will be discussed.

4.4.1. Effect of molecular weight

First the influence of average molecular weight on crystalline structure, crystallinity and lamellar thickness will be examined.

Crystalline structure

The WAXD results (Figure 4.38) show that the PCLs of different molecular weight have the same crystalline structure prior to mechanical testing so the results are comparable and are not influenced by artifacts resulting from different crystalline arrangements.

![WAXD plots of PCLs with different molecular characteristics](image)
Results and Discussion

As it was shown by Skoglund and Fransson [108] PCL crystallizes in spherulitic morphology independent of the crystallization procedure. They also reported that the crystallization is nucleation controlled and the kinetics is slower for higher molecular weight samples. As a result the crystallinity decreases with increasing $M_n$. In Figure 4.39 it is observable that the obtained crystallinity values are in good agreement with the results of Pitt [109] and Skoglund [108]. At high molecular weights the crystallinity tends to $\sim 40\%$, rising to about $\sim 80\%$ as the $M_n$ decreases to $\sim 10$ kDa.

Figure 4.39 Relationship between the crystallinity and the molecular weight of PCL (heat of fusion of 100% crystalline PCL was taken as 142.5 J/g [88], circles data from Pitt [109], triangles data from Skoglund [108]).

Table 4.9 summarizes the melting characteristics of studied polymers. There is no significant difference between the characteristic melting temperatures of samples. According to the Thomson-Gibbs equation [136, 137] the lamellar thickness distribution of crystallites could be estimated from the melting temperatures of DSC endotherms. This observation suggests that there is no significant difference in the crystallite size of the examined samples, either. Only the amount of crystalline regions increases with decreasing molecular weight. The peak temperature of melting ($T_{mp}$) characterizes the order of crystalline phase, which again seems to be independent of number average molecular weight.

<table>
<thead>
<tr>
<th>Name</th>
<th>$M_n$ [kDa]</th>
<th>$T_{on}$ [°C]</th>
<th>$T_{mp}$ [°C]</th>
<th>$T_{end}$ [°C]</th>
<th>$\Delta H_m$ [J/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capa 6250</td>
<td>31.1±0.8</td>
<td>53.6±0.5</td>
<td>57.6±0.6</td>
<td>62.8±0.9</td>
<td>73.1±1.4</td>
</tr>
<tr>
<td>Capa 6400</td>
<td>39.8±1.5</td>
<td>53.3±0.3</td>
<td>57.6±0.4</td>
<td>63.6±1.3</td>
<td>69.7±2.8</td>
</tr>
<tr>
<td>Capa 6500</td>
<td>61.8±4.1</td>
<td>52.0±0.8</td>
<td>58.1±0.7</td>
<td>64.0±1.1</td>
<td>63.4±2.4</td>
</tr>
<tr>
<td>Capa 6800</td>
<td>85.1±8.4</td>
<td>52.2±0.9</td>
<td>59.1±1.9</td>
<td>62.4±1.5</td>
<td>61.9±1.0</td>
</tr>
</tbody>
</table>

To summarize, PCL seems to be a rational model material to investigate the effect of molecular weight induced crystallinity changes on the fracture properties. The change in molecular characteristics influences the amount of crystalline fraction and the number, density.
Results and Discussion

of tie molecules only. The crystalline structure, order and lamellae thickness appear to be independent of examined molecular weight range, while there is no preferred orientation in the crystalline structure due to the sample processing method. Since the crystallization of PCL, according to the literature [108], is nucleation controlled, it is also assumed that the differences in crystallinity mainly originate from the different number of nuclei.

**Mechanical properties**

In PCL the low melting and glass transition temperatures results in highly ductile deformation at ambient conditions; even at higher deformation rates. Due to the relatively slow deformation rate the elongation at break was over 200% during the tensile tests. As it is shown in Table 4.10, the Young’s moduli and yield stress values decrease, while the elongation at yield rises with increasing molecular weight as a result of decreasing crystallinity.

<table>
<thead>
<tr>
<th>Name</th>
<th>$M_n$ [kDa]</th>
<th>$E$ [MPa]</th>
<th>$\sigma_u$ [MPa]</th>
<th>$\varepsilon_u$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capa 6250</td>
<td>31.1±0.8</td>
<td>429±41</td>
<td>16.7±0.7</td>
<td>9.6±0.7</td>
</tr>
<tr>
<td>Capa 6400</td>
<td>39.8±1.5</td>
<td>348±19</td>
<td>14.5±0.1</td>
<td>11.9±0.3</td>
</tr>
<tr>
<td>Capa 6500</td>
<td>61.8±4.1</td>
<td>310±41</td>
<td>13.2±0.4</td>
<td>12.2±1.2</td>
</tr>
<tr>
<td>Capa 6800</td>
<td>85.1±8.4</td>
<td>295±4</td>
<td>12.8±0.2</td>
<td>14.7±0.3</td>
</tr>
</tbody>
</table>

By normalizing the measured tensile properties with crystallinity (Figure 4.40) it is observable that above 40 kDa the normalized tensile moduli and yield stress values are practically independent of molecular weight. This observation suggests that during mechanical tests the influence of the number of entanglements and tie molecules in amorphous regions is negligible compared to the crystalline parts and the stress is mainly carried by the crystalline network. Until yielding the amorphous phase has only a stress transferring and distributing role.

In case of low molecular weight sample (Capa 6250) the shorter tie molecules were more likely pre-tensioned and the crystallites hindered the deformation of one another at small and large strains, too. As a result the tensile parameter values slightly increased.
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Figure 4.40 Normalized tensile properties as a function of number average molecular weight

After yielding, the unloosing of crystalline structure resulted in decreasing crystallinity as it is shown on the WAXD plots of Figure 4.41. The broadening of WAXD peaks also suggests the deformation of crystalline structure and the refinement of crystallite size during the measurements [138] (for details please see Appendix C).

Figure 4.41 WAXD plots of undeformed and deformed PCL samples

Table 4.11 summarizes the obtained work of fracture parameters for different molecular weight PCLs. As a result of enhanced density of tie molecules and entanglements the essential work of fracture terms increase with increasing molecular weight. Additionally, the unloosing and tearing of longer molecules from crystalline lamellae also consumes more energy and raises the essential work of fracture values.

The dissipated energy originates mainly from the various slips and rotations of crystalline blocks and from the unloosing of chain segments. The related work of fracture parameter ($\beta w_p$) has a maximum at about $M_n=40$ kDa. This observation could be explained by a balance in chain-mobility and crystalline build-up. At low molecular weights, the less entangled amorphous network promotes the rotation and slip of crystalline blocks, while the more perfect crystalline build-up, higher crystallinity and shorter tie-molecules hinder it – similarly
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as it was observed during tensile tests. With growing molecular weight the crystallinity drops, while the number and length of tie-molecules increases – these could promote the motion of crystalline blocks. On the other hand, at higher molecular weights the rising entanglement density of amorphous network steadily hinders energy dissipative mechanisms – e.g. hinders the rotation of crystalline lamellae to the favorable position, where they can easily get unloosen (Figure 4.42).

Table 4.11 Effect of molecular weight on fracture parameters and the parameters of linear fit

<table>
<thead>
<tr>
<th>Name</th>
<th>(w_e) [kJ/m²]</th>
<th>(\beta_{wp}) [MJ/m³]</th>
<th>(R^2) [-]</th>
<th>SD [kJ/m²]</th>
<th>(N) [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capa 6250</td>
<td>45.7±3.2</td>
<td>19.9±0.4</td>
<td>0.9901</td>
<td>5.23</td>
<td>25 (22)</td>
</tr>
<tr>
<td>Capa 6400</td>
<td>48.3±4.4</td>
<td>27.6±0.5</td>
<td>0.9951</td>
<td>6.33</td>
<td>25 (17)</td>
</tr>
<tr>
<td>Capa 6500</td>
<td>50.5±5.1</td>
<td>21.9±0.6</td>
<td>0.9891</td>
<td>6.69</td>
<td>25 (19)</td>
</tr>
<tr>
<td>Capa 6800</td>
<td>55.9±2.2</td>
<td>16.5±0.2</td>
<td>0.9955</td>
<td>3.37</td>
<td>25 (24)</td>
</tr>
</tbody>
</table>

*the number of specimens that fulfilled all the validity criteria is in parentheses

After plotting the essential work of fracture values as a function of crystallinity the data lies on a line with positive intercept (\(R^2=0.9670\)). By normalizing the fracture parameters with crystallinity the regression coefficient increases to \(R^2=0.9954\) (Figure 4.43). The correlation can be described with Equation (4.19).

\[
w_e = (w_{e0} + a \cdot M_n) \cdot X \tag{4.19}
\]

where \(w_{e0}\) [kJ/m²] is the intrinsic essential work of fracture, \(a\) [kJ/kDa·m²] is a tie molecule and entanglement density dependent variable, \(M_n\) [kDa] is the number average molecular weight and \(X\) [-] is the crystallinity. For PCL the constant values are \(a=0.713\) [kJ/kDa·m²] and \(w_{e0}=68.67\) [kJ/m²].
4.4.2. Annealing induced changes

**Thermal analysis**

During the cooling of melt to room temperature highly metastable crystals of mixed molecular weight macromolecules were formed. These just formed lamellar, chain folded crystals are usually thin and contain many defects (free chain ends – point defects, large loops and entanglements in amorphous phase –; 3D defects) that results in an excess free enthalpy [139]. Later on, this excess free enthalpy is lowered through a slow reorganization. The three processes that should be considered during the interpretation of the results of thermal analysis are the followings: (i) possible molecular nucleation, (ii) secondary crystallization of amorphous parts and (iii) perfection of poor crystals, change in the shape of crystals towards equilibrium.

As it was demonstrated by Wunderlich [139], molecules that are too short or too long introduce defects and increase the overall free enthalpy thus, if the circumstances permit, they would be rejected by the crystal. Since PCL at room temperature is well above its glass transition temperature in rubbery state, thus the chain segment motions are not frozen in. The reversible fixing and decoupling of flexible chain segments, called as molecular nucleation, could be one of the governing processes in the first hours of annealing. The rejected molecules that are longer than the critical molecular nucleus size could easily complete the crystallization, while the shorter molecules probably form separated extended chain crystals or are transported into the amorphous phase.

As a result the temperature range of melting of low molecular weight PCL (Capa 6250) broadened, a second peak appeared and the originally sharp melting peak became wider due to the newly formed poor crystals (Figure 4.44 a). The secondary crystallization of amorphous parts and amorphous nanophase between crystalline lamellae, along with molecular
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nucleation, increased the overall crystallinity over time. Additionally, the initially rejected or hindered material could also crystallize (Figure 4.44 b; for details please see the Appendix C: Table C1-C4).

The large loops, entanglements, free chain ends and tie molecules represent an excess in free enthalpy (the motion of molecule is restricted as a whole and the decrease in entropy of the molecule cannot be compensated by the heat of crystallization of a shorter molecular segment [54]) thus their number also decrease if the circumstances permit (“reptation”, the time required for the chain to renew its configuration is proportional to $M_n^3$ [140]). Parallel to the previously mentioned processes the perfection of poor crystals also took place. The thin lamellar structure thickened and the surface area of crystals and their free enthalpy decreased, which resulted in increasing melting temperatures and a shift to equilibrium (Appendix C: Table C1-C4). Figure 4.45 shows the scheme of crystals perfection and the changes in the amorphous phase.

![Figure 4.44 Effect of annealing on the non-isothermal DSC traces of Capa 6250 (a) and on the enthalpy of melting of different molecular weight samples (b)](image)

![Figure 4.45 Scheme of the morphology changes during annealing](image)
Tensile testing and fracture characterization

As it was mentioned earlier, the increase in crystallinity and melting temperature indicate the perfection of crystalline structure and the thickening of crystalline lamellae. This more stable crystalline build-up is stiffer and could carry more load before plastic deformation; and as a result the tensile strength and modulus increased with time (Table 4.12). Contrarily, the elongation to yield decreased due to the stiffening of material.

Table 4.12 Effect of annealing on the quasi-static tensile properties of PCL

<table>
<thead>
<tr>
<th>$M_n$ [kDa]</th>
<th>1h</th>
<th>168h</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E$ [MPa]</td>
<td>$\sigma_u$ [MPa]</td>
</tr>
<tr>
<td>31.1±0.8</td>
<td>429±41</td>
<td>16.7±0.7</td>
</tr>
<tr>
<td>39.8±1.5</td>
<td>348±19</td>
<td>14.5±0.1</td>
</tr>
<tr>
<td>61.8±4.1</td>
<td>310±41</td>
<td>13.2±0.4</td>
</tr>
<tr>
<td>85.1±8.4</td>
<td>295±4</td>
<td>12.8±0.2</td>
</tr>
</tbody>
</table>

More significant was, however, the observed change in fracture behavior – especially in case of low average molecular weights. The typical load-displacement plots of Capa 6250 PCL on Figure 4.46 give a clear evidence of the effect of annealing on these characteristics. The crack propagation became unstable as a result of annealing. Karger-Kocsis [106] suggested earlier, based on studies on thermoplastic elastomers, that the improvement of crack resistance in semi-crystalline polymers, blends depends strongly on how efficiently the stress is transferred from the less stiff amorphous phase to the stronger crystalline units, analogously to the fiber reinforced composites.

In this low molecular weight PCL, first there were enough tie molecules, entangled loops to transmit the load from amorphous regions to the crystalline parts. Additionally the crystalline units contained many defects, which lowered the critical stress where the plastic deformation of crystalline lamellae started. In low molecular weight polymers the incorporation of chain ends into crystalline lamellae could also result in structural instability,
as it was shown by Horváth et al. [141] for polypropylene. The load transmitting role of entangled molecules and the structural instability of spherulites induced the plastic deformation of crystallites. The fracture propagated through the crystalline skeleton, and the deformation rate was slow enough to unloose the ordered lamellae, rearrange the molecules and the morphology, retain the stable crack propagation and cause large scale plastic deformation. The transition of lamellar to fibrillar structure occurred (Figure 4.47 a).

As the crystalline lamellae perfected, shifted to their equilibrium shape and the number of incorporated chain ends, entanglements decreased (Figure 4.45), the material itself became more rigid and the crack propagation also turned from stable to unstable with time. These instabilities induced drops in the load response after 12 h indicating deterioration in the contact between the crystalline and amorphous phase.

This phenomenon could be originated from two parallel processes. On the one hand the motion of flexible polymers segments diminished the number of loops and entanglements (caused entropy increase) and thus the transmitted load was reduced (Figure 4.45). On the other hand the stability – melting temperature – of crystallites increased with time, thus higher stresses were required for their deformation [60]. After one week of annealing the crack propagated mainly through the amorphous parts, on the spherulite boundaries, and rounded the crystalline domains. As a result large spherulites remained nearly undeformed, as it is shown on Figure 4.47 b). The amorphous region was, however, in rubbery state and consisted of short molecules with few entanglements, thus the crack propagation became unstable and the failure turned to brittle – the effect of molecular weight on the work of fracture parameters was previously shown by Karger-Kocsis et al. [48, 50] for amorphous polymers; while the entanglement density related zero-shear-viscosity as a function of molecular weight for PCL is shown in Appendix A: Figure A2.
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Figure 4.48 shows the work of fracture versus ligament length values at different annealing-time intervals. The data derived from linear regression is summarized in Table 4.13. During the first 24 h there is adequate correlation, which supports the use of EWF methodology. Nevertheless, in case of 12 h annealing the relatively small sample size led to high standard error and standard deviation values. This is why it would be useful during the EWF studies to indicate not only the $R^2$ and SD values – as it was suggested by Williams and Rink [101] – but also the sample size, the used ligament range and the standard error.

After three days the correlation coefficient decreases steadily and significantly (Table 4.13) due to the unstable crack propagation and decreasing plastic-deformation volume. The results in this case probably converge to the LEFM plane stress fracture toughness ($G_c$). After one week the $w_f$ terms are practically independent of ligament length ($R^2=0.1192$), which also supports the previous assumption.

The essential work of fracture ($w_e$) values decreased significantly after 12 h annealing. This is a result of weaker connection between the amorphous and the crystalline phases. The dissipated energy ($\beta w_p$) dropped, too. As the density of tie molecules, entanglements, incorporated chain ends and other defects decreased due to crystalline perfection, the deformation of crystalline domains became less significant. The transmitted stress was not enough to induce plastic deformation in the crystals, i.e. the stress was less than the “critical network stress” [60] that is required to destruct the crystal blocks and induce the unloosing of crystalline lamellae. As a resulted the plastic deformation related term ($\beta w_p$) also decreased.
Results and Discussion

Table 4.13 Essential work of fracture parameters and the goodness-of-fit of the PCL samples (Capa 6250)

<table>
<thead>
<tr>
<th>Annealing time [h]</th>
<th>$w_e$ [kJ/m$^2$]</th>
<th>$\beta w_p$ [MJ/m$^3$]</th>
<th>$R^2$ [-]</th>
<th>$SD$ [kJ/m$^2$]</th>
<th>$N$ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>45.7±3.2</td>
<td>19.9±0.4</td>
<td>0.9901</td>
<td>5.2</td>
<td>22</td>
</tr>
<tr>
<td>12</td>
<td>26.2±14.9</td>
<td>15.9±1.5</td>
<td>0.9425</td>
<td>7.9</td>
<td>9</td>
</tr>
<tr>
<td>24</td>
<td>19.5±3.7</td>
<td>7.2±0.4</td>
<td>0.9706</td>
<td>3.9</td>
<td>13</td>
</tr>
<tr>
<td>72</td>
<td>15.9±6.3</td>
<td>1.9±0.6</td>
<td>0.5621</td>
<td>4.6</td>
<td>9</td>
</tr>
<tr>
<td>168</td>
<td>15.1±2.2</td>
<td>0.3±0.2</td>
<td>0.1192</td>
<td>1.9</td>
<td>16</td>
</tr>
</tbody>
</table>

The decrease of $w_e$ values were also observed in other studies for polypropylene [66] and poly(vinylidene-fluoride) [142] and was also ascribed to the decrease in the number of tie molecules, entanglements and to the lack in stress-transfer between the ordered zones. However, the effect of annealing on $\beta w_p$ term is more obscure. Ferrer-Balas et al. [66] found increasing values with increasing annealing temperatures in polypropylene. The rise of plastic deformation was attributed to crystal perfection and to a possible “smectic”→”alpha” phase transition [143]. Nevertheless, this phase transition could only occur when the tie molecules could transmit the load from amorphous to ordered phase and the stress is high enough to deform the crystals. In a recent paper Wallner et al. [142] found, however, that neither annealing temperature nor annealing time had an effect on the $\beta w_p$ term of poly(vinylidene-fluoride). A possible explanation of this observation is that the equilibrium melting temperature and thus the predicted “critical network stress” [60] of poly(vinylidene-fluoride) is higher than that of polypropylene. The applied stress either was not high enough to induce phase transition or deformation in crystals or the perfection of crystals did not influence the steady-state deformation processes, only the initiation values. The low equilibrium melting temperature and “critical network stress” of PCL [60] supported the plastic deformation of crystalline parts at first. Later, the number of loops and tie molecules decreased – due to the perfection of crystalline structure – as well as there were fewer entanglements present in the amorphous phase due to the low average molecular weight of the polymer; which finally led to descending plastic deformation.

In case of higher molecular weight samples – $M_n$ ranging between 40 and 80 kDa – the longer chains resulted in increasing entanglement and tie molecule density that could ensure the “critical network stress” for the deformation of PCL spherulites even after annealing – when there were more perfect and strong crystals present. The fracture remained ductile and the crack propagation stable (for details please see Appendix C: Figure C3 and Table C5). Nevertheless, the perfection of crystalline regions (Figure 4.44) led to increasing $w_e$ values (Figure 4.49). The $\beta w_p$ term, contrarily to the behavior of low molecular weight PCL, did not change with annealing time. Thus in relation to the work of Wallner et al. [142] and Ferrer-
Results and Discussion

Balas et al. [66] it can be concluded that the annealing only influences the plastic work of fracture, when

(i) there is a phase transition during annealing or when

(ii) the contact between the amorphous and crystalline phase deteriorates.

In low molecular weight PCL the latter was true, while the phase transition could not take place due to the stable orthorhombic lattice of PCL.

![Figure 4.49 Effect of annealing on the essential work of fracture terms: essential- (a) and plastic work of fracture (b)](image)

The effect of hydrolytic degradation on the fracture behavior

It was shown previously that the annealing of low molecular weight Capa 6250 PCL at room temperature results in ductile-to-brittle transition. During the hydrolytic degradation similar observations have been made (Figure 4.50 a), too. The perfection of crystalline structure was promoted not only by the increased temperature (37°C) but also through the presence of water. Since the plastic deformation was minimal (Appendix C: Table C6) and the yielding was followed by rapid crack propagation, the EWF method seemed to be unsuitable to characterize the effect of hydrolysis on the fracture behavior of low molecular weight PCL. Instead of calculating the EWF parameters by using linear regression, the specific energy to break was determined from Equations (3.3) and (3.4). Due to the negligible plasticity the specific work of fracture values were independent of ligament length. The averages of specific work of fracture are shown on Figure 4.50 b) indicating steadily deterioration of fracture toughness. The small standard deviations on Figure 4.50 b) support the ligament length independency of specific work of fracture. Due to the negligible plasticity and contained yielding these values probably converge to the plane stress fracture \(G_c\) calculated using LEFM concepts.
Results and Discussion

In the Capa 6400 polymer the scission of ester linkages in the amorphous phase resulted in unstable crack propagation – similarly as it was observed during the annealing of Capa 6250 (Figure 4.46). The lack of self-similarity of load-displacement curves (Figure 4.51) prohibited the application of EWF method for this material. Nevertheless, it should be noted that the total fracture energy to break – calculated by Equations (3.3) and (3.4) – became smaller as the hydrolysis proceeded. This can be explained by the scission of polymer chains in amorphous phase that led to decreasing entanglement and tie molecule density. This observation also supports that below a critical average molecular weight there are not enough entanglements and tie molecules present to promote the plastic deformation of crystalline regions.

In case of Capa 6500 and Capa 6800 samples none of the previously mentioned problems were observed during the examined time period (Figure 4.52 a). The tests fulfilled the prerequisites of EWF concept and the tie molecule/entanglement density remained high enough to promote the stable deformation of crystalline spherulites and lamellae. The essential work of fracture ($w_e$) term decreased slightly (Figure 4.52 b) as a result of the
Results and Discussion

hydrolytic deterioration of amorphous phase. However, the plastic work of fracture ($\beta w_p$) was not influenced significantly (see Appendix C: Table C7-C8). Since the hydrolysis starts in the amorphous phase and the crystalline regions are affected only later on, it could be noticed for PCL that

(i) the degradation does not influence significantly the crystalline phase in the first four months of degradation and

(ii) the plastic work of fracture term of semi-crystalline polymers is connected to the energy dissipative mechanisms in spherulites – when the load is high enough to deform the crystalline lamellae.

*Figure 4.52 Effect of hydrolysis on the load displacement plots (a) and essential work of fracture (b) of PCL (Capa 6500 and Capa 6800)*
5. SUMMARY AND OUTLOOK

Biodegradable materials are widely investigated in medicine as orthopedic implants, tissue engineering scaffolds, drug delivery systems etc. For the majority of applications information about the deterioration of molecular structure followed by loss in mechanical strength is needed. Furthermore, present studies and post-operative clinical tests showed that not only the strength and stiffness but also the toughness of biodegradable devices is important. The fragmentation of implants during hydrolytic degradation could result in the encapsulation of small particles and in inflammation years after the operation. The main aims of my study were, therefore, to analyze the hydrolysis induced changes in polymeric biodegradable scaffolds and to characterize the fracture toughness of ductile semi-crystalline PCL as a function of average molecular weight and crystallinity. Additionally, by preparing various blends and composites I improved the strength and modulus of PCL while maintaining its favorable toughness and biocompatibility.

My in vitro hydrolytic degradation tests showed that PCL based implants have appropriate degradation time for tissue regenerative implants, which is independent of porosity. Although, the open cell polymer foam structure led to faster deterioration of molecular network and compressive strength compared to the bulk material, the mechanical properties remained acceptable during the tests. The average molecular weight should be, however, higher than 25 kDa, since in short-chain materials the negative effects of hydrolysis emerge earlier (after 1 year in solid samples).

The modulus and strength of PCL can be increased by reinforcing with calcite spheres or aragonite whiskers, resulting in suitable biodegradable composites. Nevertheless, the filler to matrix volume ratio should not be higher than 1:20 for calcite and 1:7 for aragonite to maintain adequate toughness, as well. The different ratios can be explained by the difference in specific surface area and interaction between particles. In these materials improved biocompatibility was observed by cell numbering, however, further in vivo experiments should be performed to permit the use in medicine [144, 145].

PCL/PLA blends were also prepared to combine the higher strength and modulus of PLA with the toughness of PCL to a tailored material. However, it is known in the literature that these polymers are thermodynamically incompatible. This results in inferior toughness, since the crack easily propagates through the weak interfaces of dispersed structure. To improve the fracture toughness of blends and maintain the biocompatibility of the system L-lysine-isocyanates were used as compatibilizers. Thereafter, the mode I fracture mechanical tests
showed significant increase of the specific work required for the formation of new crack surfaces, especially in blends with a weight ratio of 1:1. Although, each material is biocompatible again further *in vitro* and *in vivo* tests are required to prove the medical applicability of these blends [146].

Based on literature data and my results, investigations have to be done to improve the reproducibility of EWF method and to promote its standardization within ISO. In my thesis I showed that the present stress criteria of EWF method are partly incorrect, since they assume ideal plastic-rigid behavior and the failure of real materials can only be approximated in this manner. Therefore, I presented a novel estimation that contains the theoretical establishments but also treats the real material behavior. Additionally, I introduced a novel displacement criterion that facilitates the evaluation of self-similarity of load-displacement curves and helps the rejection of incorrect data resulting from instable crack propagation [147, 148]. In my opinion these results can contribute to the standardization of EWF procedure, however further theoretical studies and round-robin tests are needed to confirm the propriety of my hypotheses.

In my work PCL also seemed to be a good model material to analyze the microstructural dependence of EWF parameters in semi-crystalline polymers. Since the original theory assumes perfect plasticity the amount of frozen in stresses appear as errors in measurements. However, PCL was tested well above its glass transition temperature thus the partly reversible cold drawing of amorphous phase can be avoided and it has mainly stress transferring role due to its viscous liquid nature. I assumed, therefore, that the toughness of PCL is chiefly governed by the properties and plastic deformation of crystalline phase – which is true plastic deformation. My results showed that there is a good correlation between the essential work of fracture and the number average molecular weight after normalizing by crystallinity. Although, some tendencies are presented further in-depth studies, data mining and theoretical contributions are needed to discover and describe the influence of other parameters on the fracture toughness of semi-crystalline polymers.

### 5.1. Applicability of results

In my opinion parts of my dissertation – stress and displacement criteria – contribute to the standardization of EWF procedure and help to improve the current protocol and the reproducibility of results. Furthermore, my investigations on PCL promote the understanding of the influence of microstructure – molecular weight and crystallinity – on the fracture mechanical parameters in ductile semi-crystalline polymers.
Summary

My *in vitro* degradation studies on solid and porous PCL samples help to understand the hydrolysis of scaffolds and show that the dimensions of implants and therefore the local concentration of water inside of the scaffold and the crystallinity of the material should have taken into account during the modelling of such systems.

I have also shown that the toughness of implant materials have to be evaluated before the *in vivo* application. Adequate results can be achieved by using high molecular weight polymers, compatibilized blends or filled polymers. Nevertheless, in case of reinforced systems the filler content should be low enough to avoid aggregation and the brittle fracture of the implant.

5.2. Further investigations

Concerning the EWF method further round-robin tests and theoretical works are needed to support my novel stress and displacement criteria. Although PCL seems to be a rational model material to analyze the dependence of fracture mechanical performance on microstructural parameters like molecular weight and crystallinity; further in-depth analysis is required to describe the influence of other parameters on the toughness of ductile semi-crystalline polymers.

Based on my *in vitro* degradation tests further experiments and especially further theoretical work should be done to incorporate the effect of changing, time-dependent crystallinity into the existing models. Furthermore, the influence of the scaffold’s dimensions has to be investigated in other polymers to deduce whether the local concentration of water during degradation can be taken as constant (hydrolysis rate vs. diffusion rate of water) or not.

Regarding my blends and composites biocompatibility tests and degradation tests are also needed to prove their biocompatibility and to verify that the degradation kinetics of such systems is appropriate for scaffold materials.
6. 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 \( \sigma_{ns} \) at small ligament lengths \( L<10B \), where \( B \) 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):

\[
\sigma_{ns} = m^* \sigma_u \left(1 + \frac{u}{m^* \sigma_u} \frac{1}{L}\right)
\]

(T1)

where \( L \) is the ligament length, \( \sigma_u \) 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 \( u \) 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)

\[
DL = e_p \left(1 + \frac{1}{\lambda} \frac{1}{L}\right)
\]

(T2)

where \( \lambda=e_0/e_p \) is a material dependent constant, \( e_0 \) is the critical crack tip opening displacement, \( e_p \) is the half of the crack tip opening angle and \( L \) 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 [147, 148].
3rd Thesis
I have demonstrated that under given circumstances (\(T=25^\circ C\), \(RH=40\%, \) mode I., double edge notched tensile specimens) poly(\(\varepsilon\)-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).

\[
\omega_c = (\omega_{\varepsilon0} + a \cdot M_n) \cdot X \tag{T3}
\]

where \(\omega_{\varepsilon0}\) [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(\(\varepsilon\)-caprolactone) the constant values (\(R^2=0.9954\)) are \(a=0.713\) [kJ/kDa·m\(^2\)] and \(\omega_{\varepsilon0}=68.67\) [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(\(\varepsilon\)-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 (\(T=25^\circ C\), \(RH=40\%, \) \(v=10\) mm/min, mode I., double edge notched tensile specimens). As a result the essential work of fracture values (\(\omega_c\) [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) [146].
5th Thesis

I have demonstrated that in poly($\varepsilon$-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^\circ$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 ($\omega_e [kJ/m^2]$) and plastic work of fracture ($\beta \omega_p [MJ/m^3]$) 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 ($\omega_e [kJ/m^2]$) values increase slightly, while the plastic work of fracture ($\beta \omega_p [MJ/m^3]$) 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, \(v<10\ \text{mm/min}\) the semi-crystalline poly(\(\varepsilon\)-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(\(\varepsilon\)-caprolactone) samples (sheet thickness of 0.5 mm)

7th Thesis
I have shown during \textit{in vitro} hydrolysis studies of biodegradable poly(\(\varepsilon\)-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(\(\varepsilon\)-caprolactone) is faster \((k=7-8\cdot10^{-5}\ \text{l/h})\) than that of bulk materials \((k=4,1\cdot10^{-5}\ \text{l/h})\). This has been verified experimentally by size extrusion chromatography, differential scanning calorimetry and quasi-static compression tests on cylindrical samples \((\varnothing6x7\ \text{mm, } M_n=80\ \text{kDa, bulk and porous specimens with porosity of 0.7-0.9)}\).
7. TÉZISEK

1. tézis

A lényegi törésmunka módszer (I. törési mód, két oldalon bemetszett húzó próbatest) alkalmazási kritériumainak vizsgálata során igazoltam, hogy a maximális mérnöki feszültség ($\sigma_{ns}$ [MPa]) növekedése kis ligament hosszoknál ($L<10B$, ahol $B$ [mm] a minta vastagsága) nem kizárólag a síkfeszültség/síkalakváltozás átmenettel van kapcsolatban. Kimutattam, hogy a maximális mérnöki feszültség a (T1) összefüggéssel írható le:

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

ahol $L$ [mm] a ligament hossz, $\sigma_u$ [MPa] a vizsgált anyag folyáshatára, $m^*$ [-] a próbatest feszültségállapotával kapcsolatos tényező (értéke rideg-képlekény, izotróp anyagok esetében, síkfeszültségi állapotban Hill után $1< m^* < 1,15$), $u$ [N/mm] pedig a valós anyagi viselkedéssel (rugalmas-képlekény anyag, kvázi síkfeszültség, repedés-megindulás 3D feszültségek mellett, illetve az ezekből adódó nem ideális geometriai hasonlóság) kapcsolatos tényező.

A (T1) összefüggés $u/m^* \sigma_u$ tagja miatt a rideg-képlekény viselkedést feltételező $\text{Max}(\sigma_{ns}=1,15 \sigma_u)$ kritérium nem alkalmazható a lényegi törésmunka mérések alsó ligament-határának meghatározására ($L_{min}$).

2. tézis

Igazoltam, hogy a lényegi törésmunka módszer (I. törési mód, két oldalon bemetszett húzó próbatest) mérések során a törés jellegét alapvetően leíró képlekényiségi fok ($DL$) a ligamenthossz függvényében ábrázolt maximális nyúlás értékekre illesztett egyenes egyenletéből a (T2) összefüggéssel meghatározható.

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

ahol $\lambda = e_0/e_p$ [mm] anyagjellemző állandó, $e_0$ [mm] a kritikus repedéskinyílási távolság, $e_p$ [-] a repedéskinyílási szög fele és $L$ [mm] a ligament hossza. $e_0$ és $e_p$ paraméterek a ligament hossz – maximális nyúlás görbékől lineáris regresszióval becslhetők [147, 148].
3. tézis
Kimutattam, hogy adott vizsgálati körülmények mellett (\(T=25^\circ C\), \(RH=40\%\), I. törési mód, két oldalon bemetszett húzó próbatest) a poli-\(\varepsilon\)-kaprolakton alkalmas a részben kristályos polimerek lényegi törésmunkájának molekulatömeg-függésének leírására, mivel az egyes befolyásoló paraméterek az átlagos molekulatömeg függvényében kereszthatások nélkül jól leírhatók ( kristályos hányad, kristályos fázis tőkéletessége, szferolitméret) vagy nem változnak ( kristályos módosulat). Kimutattam, hogy a lényegi törésmunka értékek számszerinti átlagos molekulatömegégtől való függése kristályossággal történő normálást követően a (T3) lineáris összefüggéssel adható meg.

\[
w_e = (w_{e0} + a \cdot M_n) \cdot X (T3)
\]

ahol \(X\) [ -] a kristályosság, \(M_n\) [kDa] a számszerinti átlagos molekulatömeg \(w_{e0}\) [kJ/m\(^2\)] anyagra jellemző extrapolált lényegi törésmunka, \(a\) [kJ/kDa\cdot m\(^2\)] pedig a kristályos részeket összekötő moleculák számától, sürűségétől függő állandó. Poli-\(\varepsilon\)-kaprolakton esetében mérések ből (\(R^2=0.9954\)) a következő állandó értékek határozhatók meg: \(a=0.713\) [kJ/kDa\cdot m\(^2\)] és \(w_{e0}=68.67\) [kJ/m\(^2\)].

4. tézis
Szerkezet-, illetve törésmechanikai vizsgálatokkal alátámasztottam, hogy biokompatibilis, de termodinamikailag összeférhetetlen poli-D,L-tejsav (\(M_n=100\) kDa) és poli-\(\varepsilon\)-kaprolakton (\(M_n=50\) kDa) keverékekben (PCL tartalom 0 és 100 tömeggázalék között változtatva) a kis mennyiségben (0,5 tömegrész) alkalmazott két-, illetve háromfunkciós lizin-izocianátokkal való kompatibilizálás az eloszlatott fázis finomodásához, illetve homogén képlékeny deformációjához vezet (I. törési mód, két oldalon bemetszett húzó próbatest, \(T=25^\circ C\), \(RH=40\%\), \(v=10\) mm/perc). A mátrix és a diszperz fázis homogén deformációjának következtében a fajlagos lényegi törésmunka (\(w_e\) [kJ/m\(^2\)]) értékek jelentősen növekedtek (az 1:1 arányú kompatibilizálatlan keverékhez viszonyítva a lizin-triizocianát hatására 150%-al nőtt a lényegi törésmunka) [146].
5. tézis
Kimutattam, hogy poli-ε-kaprolakton mintákban ($M_n=25-80$ kDa) a makromolekulák hossza és a kristályos morfológia (közvetett reológiai és termodinamikai okokból kifolyóan) üvegesedési hőmérséklet fölött és olvadási hőmérséklet alatt ($T=25^\circ C$) történő hőkezelést követően befolyásolja a síkfeszültségi állapotban mért képlékeny törési munka jellemzőit (I. törési mód, két oldalon bemetszett húzó próbatest).

c) Pásztázó kalorimetriai és nagyszögű röntgendiffракciós mérésekkel igazoltam, hogy az idő előrehaladával (1 és 168 óra között vizsgálat) a kristályosság növekszik, a kristályszerkezet tökéletesedik (kristályolvadási csúcshőmérséklet nő), és ez, valamint a lánkconfigurációk újrarendeződése (ami az amorf és kristályos fázis közti áthurkolódások számának csökkenését okozza, és időállandója a molekulatömeg harmadik hatványával arányos) a kis molekulatömegű ($M_n=25$ kDa) mintákban a kristályos részek irreversibilis deformációjának fokozatos elmaradását okozza. Következésképpen a repedésterjedés instabilitása válik, a fajlagos lényegi törésmunka ($\omega_c [kJ/m^2]$) és fajlagos képlékeny törésmunka ($\beta_{wp} [MJ/m^3]$) értékek egyaránt csökkennek.

d) Nagyobb átlagos molekulatömegű minták esetén ($M_n=40-80$ kDa) a több kötő láncmolekula, az amorf fázis jelentősebb áthurkoltsága, valamint a lánkconfigurációk újrarendeződéséhez szükséges hosszabb idő biztosítani tudta a kristályos részek számára azt a feszültségszintet, amely a szférolitok maradó deformációjához szükséges. Ezekben az esetekben a kristályos részek kifűződését, a kristályosság csökkenését röntgendiffракciós mérésekkel bizonyítottam. A tökéletesebb kristályszerkezetek köszönhetően a fajlagos lényegi törésmunka ($\omega_c [kJ/m^2]$) értékek nőttek, míg a fajlagos képlékeny törésmunka ($\beta_{wp} [MJ/m^3]$) értékek nem változtak szignifikánsan.
6. tézis
Kimutattam, hogy részben kristályos poli-ε-kaprolakton (PCL) esetében adott körülmények mellett ($T>T_g$, I. törési mód, kvázi-síkfeszültségi állapot, két oldalon bemetszett húzó próbatest, $v<10$ mm/perc) a polimer képlékenyen törők mindaddig, amíg az amorf és a kristályos fázis között elég erős a kapcsolat ahhoz, hogy meginduljon a kristályos részek maradó deformációja. Ha a két fázis közti kapcsolat romlik (kötő molekulák és/vagy az amorf fázis áthurkolódásainak hidrolitikus bomlása, hajlékony láncszegmensek migrációja $T_g$ felett) és a kristályos részek tökéletesednek (utókristályosodás víz és 37°C hatására, mely a kristályolvadási hőmérséklet növekedésével DSC mérésekkel jól követhető), akkor ridegtörés lép fel. Ezt különböző átlagos molekulatömegű PCL minták (lemezvastagság: 0,5 mm) in vitro hidrolitikus bomlását követően lényegi törésmunka mérésekkel igazoltam.

7. tézis
A biológialag lebomló, szövetépítés vázanyagaként használható poli-ε-kaprolakton (PCL) in vitro hidrolitikus bomlása során kimutattam, hogy annak ellenére, hogy az ismert degradációkinetikai modellek a duzzadást követően a víz koncentrációját állandónak és geometria-függetlennek tekintik, illetve a tömbi anyagban gyorsabb hidrolízist jeleznek előre a karboxilcsoportok autokatalízise miatt, az eltérő diffúziós távolságok és fajlagos felület szignifikánsan befolyásolják a rendelkezésre álló víz mennyiségét, és ebből eredően a bomlás kinetikáját is, tömör, illetve porózus PCL minták hidrolitikus bomlása során. Az autokatalitikus hatások miatt várttal ellentétben a PCL hidrolitikus bomlása gyorsabb nyílt cellás pórusszerkezetű habokban ($k=7,8-10^{-5}$ 1/h), mint tömbi mintákban ($k=4,1-10^{-5}$ 1/h). A fentieket kísérletileg poli-ε-kaprolaktonon (hengeres próbatest: Ø6x7 mm; névleges szám szerinti átlagos molekulatömeg: $M_n=80$ kDa; tömör, illetve 70-90% porozitású nyílt cellás minták) végzett gépermeációs kromatográfiai, pásztázó kalorimetria és kvázistatikus nyomóvizesgálatokkal igazoltam.
8. REFERENCES


References


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APPENDIX A

The mass loss of the samples was calculated after drying according to Equation A.1.

\[
\text{MassLoss} = \frac{m_0 - m_t}{m_0} \cdot 100 \text{ [%]} \tag{A.1}
\]

where \(m_0 \text{ [g]}\) is the initial dry weight and \(m_t \text{ [g]}\) is the dry weight at time \(t\). For each data point at least five specimens were measured.

The mass loss of the samples remained below 1.5% for all samples except for the sample of 70% porosity \((\phi=0.3)\). In these samples the salt leaching was not complete, therefore during the first week of measurements the remnant salt leached out, which resulted in about 8% mass loss. However, after the first week the mass loss of these samples remained constant, too.

![Figure A1 Effect of hydrolysis on the dry weight of samples](image)

According to the Thomson-Gibbs equation [136, 137] the melting temperature of the crystalline lamellae is related to their thickness. In Table A1-A7 the melting ranges are shown. It is observable that the lamellae thickness distribution of the samples during the hydrolysis only slightly changed. Based on the characteristics of the first heating runs some thickening can be noticed, however the second heating plots indicate that this is not related to the molecular weight changes, but merely to the thermal pre-history.
### Table A1 Effect of hydrolysis on the melting characteristics of Capa 6250

<table>
<thead>
<tr>
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<tr>
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<td>69.3</td>
</tr>
<tr>
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<td>69.2</td>
</tr>
<tr>
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<tr>
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### Table A2 Effect of hydrolysis on the melting characteristics of Capa 6400

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<td>69.0</td>
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### Table A3 Effect of hydrolysis on the melting characteristics of Capa 6500

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<td>67.1</td>
</tr>
<tr>
<td>210</td>
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<td>70.5</td>
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<td>70.8</td>
</tr>
<tr>
<td>700</td>
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<td>69.4</td>
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### Table A4 Effect of hydrolysis on the melting characteristics of Capa 6800

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<td>68.0</td>
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<tr>
<td>700</td>
<td>61.1</td>
<td>71.7</td>
</tr>
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### Table A5 Effect of hydrolysis on the melting characteristics of Capa 6800 with a porosity of 0.7

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<td>68.3</td>
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<tr>
<td>150</td>
<td>58.2</td>
<td>69.5</td>
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<tr>
<td>180</td>
<td>60.2</td>
<td>67.6</td>
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<tr>
<td>210</td>
<td>60.5</td>
<td>69.1</td>
</tr>
<tr>
<td>365</td>
<td>60.3</td>
<td>70.1</td>
</tr>
<tr>
<td>700</td>
<td>62.1</td>
<td>71.6</td>
</tr>
</tbody>
</table>


Table A6 Effect of hydrolysis on the melting characteristics of Capa 6800 with a porosity of 0.8

<table>
<thead>
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<th>2nd heating</th>
</tr>
</thead>
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<td>$T_{on}$ [°C]</td>
<td>$T_{mp}$ [°C]</td>
</tr>
<tr>
<td>90</td>
<td>56.5</td>
<td>67.8</td>
</tr>
<tr>
<td>150</td>
<td>58.9</td>
<td>69.1</td>
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<tr>
<td>180</td>
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<td>69.2</td>
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<td>210</td>
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</tr>
<tr>
<td>700</td>
<td>63.1</td>
<td>69.3</td>
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</table>

Table A7 Effect of hydrolysis on the melting characteristics of Capa 6800 with a porosity of 0.9

<table>
<thead>
<tr>
<th>Time [day]</th>
<th>1st heating</th>
<th>2nd heating</th>
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</thead>
<tbody>
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<td>$T_{on}$ [°C]</td>
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<tr>
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<td>59.4</td>
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<tr>
<td>150</td>
<td>59.9</td>
<td>68.4</td>
</tr>
<tr>
<td>180</td>
<td>60.3</td>
<td>68.0</td>
</tr>
<tr>
<td>210</td>
<td>60.8</td>
<td>67.5</td>
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<tr>
<td>365</td>
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<td>68.1</td>
</tr>
<tr>
<td>700</td>
<td>63.6</td>
<td>69.5</td>
</tr>
</tbody>
</table>

Theoretically above the critical molecular weight ($M_c$) the slope of the $\log \eta_0$ versus $\log M_n$ line has an universal value for polymers, which is 3.4 [112]. Based on Equation (A.2) the obtained 3.41 ($R^2=0.98$) is very close to the theoretical approximation.

$$\log \eta_0 = -2.71 + 3.41 \cdot \log M_n,$$

(A.2)

where $\eta_0$ is the apparent zero-shear-viscosity. From Figure A2 it is also observable that the viscosity rises with increasing molecular weight, which is partly a result of increased entanglement density [140].

![Figure A2 Zero-shear-viscosity as a function of number average molecular weight for PCL samples](image)
Appendix

Figure A3 SEM micrographs of porous samples (porosity 0.9) before hydrolysis (a) and after two years (b)

Figure A4 Change in compressive work at 25% deformation of (a) 25 kDa, (b) 40 kDa, (c) 50 kDa and (d) 80 kDa PCL samples as a function of hydrolysis time
APPENDIX B

The peak value of loss moduli in Figure B1 is associated with the glass transition. As the results indicate the incorporation of calcite filler does not cause the increase of $T_g$, which suggests that molecular mobility of PCL was not influenced by the filler material.

![Figure B1 Loss modulus plots of calcium-carbonate filled PCL samples (curves are shifted vertically)](image)

From the proposed reactions, the simplified (ideal) chemical equation for the examined materials is the Equation (B.1).

$$R' - OH + R' - NCO \rightarrow R' - NCO - R' + H_2O \quad (B.1)$$
According to Table B1 and Equation (B.1) the cyanate groups were in surplus in each blend.

<table>
<thead>
<tr>
<th>Table B1 Molar ratio of the reagents in the examined blends</th>
</tr>
</thead>
<tbody>
<tr>
<td>PL A</td>
</tr>
<tr>
<td>PL C L</td>
</tr>
<tr>
<td>Comp.</td>
</tr>
<tr>
<td>R’ -OH</td>
</tr>
<tr>
<td>R’-NCO</td>
</tr>
</tbody>
</table>

From Figure B3 it is observable that the glass transition temperatures of PLA/PCL blends did not change after compatibilization. The peak values do not indicate the miscibility of the polymers either – no shift towards the $T_g$ of PCL was observed. Nevertheless, a small secondary peak can be noticed in the LTI containing blends at about 60-62°C, which can be ascribed to the formation of cross-linked PLA-LTI-PCL molecules. The glass transition temperatures of uncompatibilized PLA50/PCL50 blend and of PLA20/PCL80 blends (Figure B3 c, d) cannot be determined due to the modulus decrease (or rupture) of the specimens after the melting of PCL phase.

![Figure B3 Loss modulus plots of PLA/PCL blends: neat PLA (a), PLA80/PCL20 (b), PLA50/PCL50 (c) and PLA20/PCL80 (d) (curves are shifted vertically)](image-url)
APPENDIX C

The mean lateral dimension of the crystallites of a polycrystalline sample can be estimated from the Scherrer-equation (Equation C.1).

\[ D = \frac{A}{\omega \cos \theta}, \]  

(C.1)

where \( D \) [nm] is a size parameter, \( A \) [nm] is the wavelength, \( \omega \) [-] is the full-width-at-half-maximum and \( \theta \) [°] is the scattering angle. This means that the peak width is inversely proportional to the crystalline domain size, according to Equation (C.2).

\[ D \sim \frac{1}{\omega}. \]  

(C.2)

It should be noted, however, that the inhomogeneous strain, the domain shape and instrumental effects can also contribute to the broadening of the line profile, so Equation (C.2) is only good in first approximation. In Figure C1 the diffractograms of the deformed samples are shown. From Equation (C.2) and from the full-width-at-half-maximum values of reflections of (110) [68] plane at Figure 4.38 and Figure C1 one can calculate the ratio of size parameters (\( D \)).

In Capa 6250 only a slight decrease was observed, which can be attributed to the deformation of the crystalline lattice. In higher molecular weight samples (Capa 6400, Capa 6500 and Capa 6800) the change was more significant. The size parameters were only the third of their initial value, which suggests more intense deformations, crystalline-size-refinement and the unloosing of crystalline domains. This unloosing and size-refinement can be supported by the “amorphization” of the high molecular weight samples (Figure C2).

![Figure C1 Effect of molecular weight on the crystalline structure of the deformed samples](image)

---

**Figure C1** Effect of molecular weight on the crystalline structure of the deformed samples
Figure C2 Photographs of the ligament region of Capa 6250 (a) and Capa 6800 (b)

Table C1 Annealing induced changes in the melting characteristics of $M_n=25$ kDa PCL

<table>
<thead>
<tr>
<th>Annealing time [h]</th>
<th>$T_{on}$ [°C]</th>
<th>$T_{mp}$ [°C]</th>
<th>$T_{end}$ [°C]</th>
<th>$\Delta H_m$ [J/g]</th>
<th>X [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>53.6</td>
<td>57.6</td>
<td>62.8</td>
<td>73.1</td>
<td>53</td>
</tr>
<tr>
<td>1</td>
<td>56.7</td>
<td>61.3</td>
<td>64.6</td>
<td>83.9</td>
<td>60</td>
</tr>
<tr>
<td>12</td>
<td>55.2</td>
<td>61.7</td>
<td>64.8</td>
<td>86.7</td>
<td>62</td>
</tr>
<tr>
<td>24</td>
<td>56.1</td>
<td>62.3</td>
<td>64.6</td>
<td>86.8</td>
<td>62</td>
</tr>
<tr>
<td>168 (1 week)</td>
<td>59.6</td>
<td>63.6</td>
<td>65.6</td>
<td>89.5</td>
<td>66</td>
</tr>
<tr>
<td>1344 (8 weeks)</td>
<td>59.7</td>
<td>64.2</td>
<td>66.7</td>
<td>92.8</td>
<td>66</td>
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<tr>
<td>$\infty$ (as received)</td>
<td>56.5</td>
<td>67.1</td>
<td>72.1</td>
<td>90.9</td>
<td>65</td>
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Table C2 Annealing induced changes in the melting characteristics of $M_n=40$ kDa PCL

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<th>$T_{mp}$ [°C]</th>
<th>$T_{end}$ [°C]</th>
<th>$\Delta H_m$ [J/g]</th>
<th>X [%]</th>
</tr>
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<td>62.7</td>
<td>69.7</td>
<td>51</td>
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<tr>
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<td>57.3</td>
<td>62.1</td>
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<td>62.7</td>
<td>82.4</td>
<td>59</td>
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<tr>
<td>168 (1 week)</td>
<td>55.8</td>
<td>60.2</td>
<td>64.4</td>
<td>83.3</td>
<td>60</td>
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Table C3 Annealing induced changes in the melting characteristics of $M_n=50$ kDa PCL

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<th>$T_{end}$ [°C]</th>
<th>$\Delta H_m$ [J/g]</th>
<th>X [%]</th>
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<td>51.9</td>
<td>58.4</td>
<td>64.6</td>
<td>71.2</td>
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<td>58.5</td>
<td>64.4</td>
<td>75.6</td>
<td>54</td>
</tr>
<tr>
<td>168 (1 week)</td>
<td>54.3</td>
<td>60.4</td>
<td>65.9</td>
<td>77.6</td>
<td>56</td>
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<tr>
<td>$\infty$ (as received)</td>
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<td>66.6</td>
<td>71.5</td>
<td>81.5</td>
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Table C4 Annealing induced changes in the melting characteristics of $M_n=80$ kDa PCL

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<th>$T_{mp}$ [°C]</th>
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<th>$\Delta H_m$ [J/g]</th>
<th>X [%]</th>
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<td>68.1</td>
<td>49</td>
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<td>24</td>
<td>52.5</td>
<td>60.1</td>
<td>64.4</td>
<td>72.0</td>
<td>52</td>
</tr>
<tr>
<td>168 (1 week)</td>
<td>53.9</td>
<td>61.4</td>
<td>65.9</td>
<td>74.8</td>
<td>54</td>
</tr>
<tr>
<td>$\infty$ (as received)</td>
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<td>67.1</td>
<td>71.3</td>
<td>80.9</td>
<td>58</td>
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Appendix

Figure C3 Effect of annealing on the load displacement plots of Capa 6400, Capa 6500 and Capa 6800 (arbitrarily selected DENT specimens, v=10 mm/min)

Table C5 Essential work of fracture parameters and the goodness-of-fit of the PCL samples ($M_n=25-80$ kDa)

<table>
<thead>
<tr>
<th>$M_n$ [kDa]</th>
<th>Annealing time [h]</th>
<th>$w_e$ [kJ/m$^2$]</th>
<th>$\beta w_p$ [MJ/m$^3$]</th>
<th>$R^2$ [-]</th>
<th>SD [kJ/m$^2$]</th>
<th>N [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>31.1±0.8</td>
<td>1</td>
<td>45.7±3.2</td>
<td>19.9±0.4</td>
<td>0.9901</td>
<td>5.2</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>168</td>
<td>15.1±2.2</td>
<td>*Brittle fracture</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39.8±1.5</td>
<td>1</td>
<td>48.4±4.4</td>
<td>27.6±0.5</td>
<td>0.9951</td>
<td>6.3</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>168</td>
<td>52.5±3.7</td>
<td>26.5±0.4</td>
<td>0.9948</td>
<td>5.5</td>
<td>26</td>
</tr>
<tr>
<td>61.8±4.1</td>
<td>1</td>
<td>50.5±5.1</td>
<td>21.9±0.6</td>
<td>0.9891</td>
<td>6.7</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>168</td>
<td>56.8±4.8</td>
<td>22.9±0.6</td>
<td>0.9881</td>
<td>6.3</td>
<td>23</td>
</tr>
<tr>
<td>85.1±8.4</td>
<td>1</td>
<td>55.9±2.2</td>
<td>16.5±0.2</td>
<td>0.9955</td>
<td>3.4</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>168</td>
<td>63.9±3.5</td>
<td>16.4±0.4</td>
<td>0.9882</td>
<td>4.0</td>
<td>23</td>
</tr>
</tbody>
</table>

* Brittle fracture – in case of brittle fracture the EWF parameters cannot be determined satisfactorily since the correlation coefficients are usually small, and the specific work of fracture is constant. In these cases the $w_e$ term denotes the specific work of fracture (Equation 3.4) instead of the specific essential work of fracture

Table C6 Essential work of fracture parameters and the goodness-of-fit of the PCL samples ($M_n=25$ kDa)

<table>
<thead>
<tr>
<th>Time of hydrolysis [months]</th>
<th>$w_e$ [kJ/m$^2$]</th>
<th>$\beta w_p$ [MJ/m$^3$]</th>
<th>$R^2$ [-]</th>
<th>SD [kJ/m$^2$]</th>
<th>N [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>45.7±3.2</td>
<td>19.9±0.4</td>
<td>0.9901</td>
<td>5.2</td>
<td>22</td>
</tr>
<tr>
<td>1</td>
<td>9.6±0.9</td>
<td>*Brittle fracture</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>9.3±0.6</td>
<td>*Brittle fracture</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>3</td>
<td>7.5±0.7</td>
<td>*Brittle fracture</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>6.9±0.8</td>
<td>*Brittle fracture</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Brittle fracture – in case of brittle fracture the EWF parameters cannot be determined satisfactorily since the correlation coefficients are usually small, and the specific work of fracture is constant. In these cases the $w_e$ term denotes the specific work of fracture (Equation 3.4) instead of the specific essential work of fracture

Table C7 Essential work of fracture parameters and the goodness-of-fit of the PCL samples ($M_n=50$ kDa)

<table>
<thead>
<tr>
<th>Time of hydrolysis [months]</th>
<th>$w_e$ [kJ/m$^2$]</th>
<th>$\beta w_p$ [MJ/m$^3$]</th>
<th>$R^2$ [-]</th>
<th>SD [kJ/m$^2$]</th>
<th>N [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>50.5±5.1</td>
<td>21.9±0.6</td>
<td>0.9891</td>
<td>6.7</td>
<td>19</td>
</tr>
<tr>
<td>1</td>
<td>49.9±5.0</td>
<td>19.9±0.6</td>
<td>0.9875</td>
<td>7.2</td>
<td>18</td>
</tr>
<tr>
<td>2</td>
<td>46.6±4.8</td>
<td>19.7±0.5</td>
<td>0.9892</td>
<td>7.1</td>
<td>18</td>
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<tr>
<td>3</td>
<td>45.2±4.8</td>
<td>20.5±0.5</td>
<td>0.9901</td>
<td>7.0</td>
<td>18</td>
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<tr>
<td>4</td>
<td>43.2±3.4</td>
<td>20.7±0.3</td>
<td>0.9948</td>
<td>4.4</td>
<td>21</td>
</tr>
<tr>
<td>Time of hydrolysis [months]</td>
<td>$w_e$ [kJ/m²]</td>
<td>$\beta w_p$ [MJ/m³]</td>
<td>$R^2$ [-]</td>
<td>SD [kJ/m²]</td>
<td>N [-]</td>
</tr>
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</tr>
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<td>16.5±0.2</td>
<td>0.9955</td>
<td>3.4</td>
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<tr>
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<td>16.3±0.5</td>
<td>0.9878</td>
<td>5.7</td>
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</tr>
<tr>
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<td>15.6±0.4</td>
<td>0.9908</td>
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<tr>
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<td>16.8±0.4</td>
<td>0.9899</td>
<td>5.3</td>
<td>18</td>
</tr>
<tr>
<td>4</td>
<td>42.3±4.4</td>
<td>16.5±0.5</td>
<td>0.9833</td>
<td>6.3</td>
<td>23</td>
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</tbody>
</table>