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## 1. Introduction

Plastics are used in every segment of our life today from industrial applications to the production of household articles. The ever increasing demand of the public to improve the performance and quality of products as well as to decrease their price results in continuous development work and in constant search for new materials. This tendency is valid also for the plastic industry. Modification of polymers is one of the most often used approaches to produce new materials. Polymers can be modified in many ways. Copolymerization, polymer analogous reactions or plasticization are out of the scope of this work. Here we consider only modifications with a second component introduced in considerable amounts into the matrix polymer forming a new material with heterogeneous structure, i.e. blends and composites. Modified polymers can be classified in several ways, we divide them into three categories, to blends<sup>1</sup>, particulate filled polymers<sup>2</sup>, and to fiber reinforced composites<sup>3</sup>. Although the three classes are often treated separately, the factors determining their properties are exactly the same<sup>4</sup>. This thesis discusses short fibers, which represent a transition between particulate fillers and long fibers. Since the factors determining the properties of the two classes of materials are the same, the question of classification is not very important.

The Laboratory of Plastics and Rubber Technology (LPRT) and the associated Department of Applied Polymer Chemistry and Physics at the Institute of Materials and Environmental Chemistry, HAS, have long tradition in the research and development of heterogeneous polymer systems. The group

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<sup>1</sup> Paul, D. R., Bucknall, C. B.: *Polymer Blends*, Wiley, New York, 2000.

<sup>2</sup> Rothon, R. N.: *Particulate – Filled Polymer Composites*. Rapra Technology, Shrewsbury, 2003.

<sup>3</sup> Pilato, L. A., Michno, M. J.: *Advanced Composite Materials*, Springer-Verlag, Heidelberg, 1994.

<sup>4</sup> Pukanszky, B., in *Polypropylene: Structure, Blends and Composites*, Karger-Kocsis, J. (ed.), Chapman and Hall, London (1995) Vol. 3, pp 1-70.

started with the study of particulate filled polymers many years ago. The research resulted in extensive knowledge on the factors determining composite properties, and to the development of models describing the various phenomena in these materials. Successful research led to extensive cooperation with partners all over the world both in academia and industry. The materials and problems studied changed considerably during the years. Particulate filled polymers gave way to blends, multicomponent materials, carbon fiber reinforced thermosets and to layered silicate nanocomposites. The study of the composition dependence of basic mechanical properties was partly replaced by the investigation of interfacial interactions and experiments directed towards the detailed analysis of micromechanical deformation processes occurring in these materials under the effect of external load. This Thesis is a further step in this process focusing on new materials and questions.

In recent years the interest of the scientific community turned towards new fields. Much research is done on nanocomposites<sup>5</sup>, but considerable interest is focused on bio-related<sup>6</sup> materials derived from renewable resources. These new materials include all kinds of natural polymers and their derivatives like starch, cellulose, cellulose acetate, natural fibers and wood. LPRT is involved in several industrial and European projects on wood fiber reinforced thermoplastic composites. As a consequence, the main goal of this Thesis is to extend knowledge on factors determining the properties of short fiber reinforced composites, to establish structure-property correlations, to study and modify interfacial interactions, to determine or estimate these latter quantitatively, and to identify specific questions related to natural fibers. In the way to achieve these goals, we utilize the knowledge compiled on heterogeneous

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<sup>5</sup> Alexandre, M., Dubois, P., *Mater Sci Eng* **28**, 1-63 (2000)

<sup>6</sup> Blunk, T., Göpferich A., Tessmar, J., *Biomaterials* **24**, 4335 (2003)

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polymers by the group up to now and extend them to the new problems and materials. Although most of the research focuses on natural fiber reinforced materials, some results obtained on carbon fiber reinforced composites are also included into the Thesis. This reflects the shift of interest of the community in materials, but also offers a way to compare different reinforcing components and to generalize our conclusions.

Wood flour, and other natural fillers are used for the production of composites because of their good strength and stiffness, as well as low density<sup>7</sup>. An important aspect is price, since these raw materials obtained from natural, renewable resources are usually cheaper than other fillers and reinforcements. Besides their advantages listed above, natural fillers and fibers have some drawbacks as well thus several problems may be encountered during the production of such composites. One of these is the dependence of the quality of the fibers on season, climate, crop area, etc, and also heat and moisture sensitivity. The transverse strength of the fibers is small and they can easily break or split, if the direction of the load is not right. Probably the most important issue is the interaction of the components, surface modification techniques and their effect on composite properties. Although most sources agree that interfacial interactions are important and even make an attempt to modify them<sup>8</sup>, much controversy surrounds this question. The characterization of surfaces is usually insufficient and interactions are treated in a very qualitative manner. The same applies to the effect of treatment. This is demonstrated well by the evaluation of the treatment of natural fibers with silane compounds<sup>9</sup>. Very often significant improvements in properties are claimed, but these improvements are not specified and they very often do not exist. Silane treatment

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<sup>7</sup> Bledzki, A. K., Gassan, J., *Prog Polym Sci* **24**, 221-274 (1999)

<sup>8</sup> Lu, J. Z., Wu, O., McNabb, H. S. Jr., *Wood Fiber Sci* **32**, 88-104 (2000)

<sup>9</sup> Bledzki, A.K., Reihmane, S., Gassan, J., *J Appl Polym Sci* **59**, 1329-1336 (1996)

demonstrates another problem related to surface modification. Because of the success of this approach for glass fiber reinforced composites, it is assumed to work as wonder for all kinds of materials irrespectively of the matrix or the reinforcement even without specifying the mechanism, the amount of coupling agent used or the goal of the treatment.

Although interactions and surface modification seem to be the most sensitive questions of fiber reinforced composites, other issues exist, which are not investigated and treated according to their importance. The structure of wood flour composites is assumed to be simple, usually the homogeneous distribution of the particles in the matrix is assumed. However, possible aggregation and the orientation of anisotropic wood particles must be also considered in order to interpret experimental results<sup>10</sup>. Micromechanical deformations and the failure mechanism of the composite are also important issues, which are not investigated sufficiently. Very few, if any, papers are available in the open literature, which discuss them<sup>11</sup>. This and the previous paragraph unambiguously show that a large number of questions are still open in relation with the preparation and use of fiber reinforced composites in spite of the fact that intensive research is done on them and that they are extensively used in practice. In this Thesis we focus our attention onto the most important ones and try to extend our knowledge in these areas, and if possible find solutions which may lead to the preparation of better composites.

## 2. Materials and methods

PAN based carbon fibers oxidized in sulfuric acid were characterized by cyclic voltammetry (CV), diffuse reflectance infrared spectroscopy (DRIFT) and X-ray photoelectron spectroscopy (XPS). Interfacial adhesion

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<sup>10</sup> Raj, R. G., Kokta, B. V., *J Appl Polym Sci* **38**, 1987-1996 (1989)

<sup>11</sup> Hristov, V. N., Krumova, M., Michler, G. H., *Macromol Mater Eng* **291**, 677-683 (2006)

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was measured in epoxy microcomposites by fragmentation. PP/wood composites were prepared in a wide composition range from 0 to 80 wt% wood content. Four different approaches were used for the modification of interfacial interactions in polypropylene/wood flour composites: two maleinated polypropylenes (MAPP) with different molecular weight and functionality, two surfactants (stearic acid and cellulose palmitate) and wood was modified chemically (benzylation) as well. The mechanical properties of the composites were characterized by tensile testing, while their fracture resistance was determined with instrumented impact measurements. The strength of interfacial adhesion was estimated quantitatively with model calculations. Micromechanical deformation processes were followed by acoustic emission (AE) and volume strain (VOLS) measurements. Structure was characterized by X-ray diffraction (XRD) and differential scanning calorimetry (DSC) measurements. The progress of benzylation was followed by the measurement of weight increase and by diffuse reflectance infrared spectroscopy (DRIFT). The surface tension of benzylated wood was determined by inverse gas chromatography (IGC). The water absorption of the wood filler and the composites was determined as a function of time. Changes in the viscosity of the melt were followed by the determination of melt flow rate (MFR). The distribution of wood particles and failure mechanism were studied by scanning electron microscopy (SEM).

### **3. New scientific results**

1. We proved by the detailed characterization of the surface of carbon fibers oxidized in sulfuric acid under a wide variety of conditions and by the thorough analysis of the results that the usual approach of characterizing surface activity by the total oxygen content is misleading, since mainly carboxyl groups participate in coupling reactions [1].
2. We observed and proved by the study of the structure and properties of highly filled PP/wood composites that wood particles may aggregate at

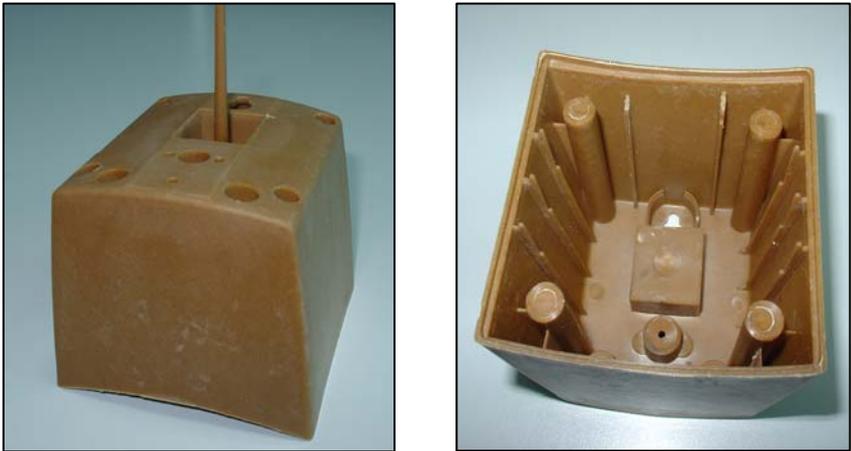
large fiber content purely from geometric reasons in spite of their large size and small surface energy, which otherwise facilitate homogeneous dispersion [2,4].

3. We analyzed the micromechanical processes taking place during the deformation and failure of PP/wood composites with advanced methods and showed for the first time that several processes take place parallel or consecutively in these materials. The matrix polymer deforms mainly by shear yielding. Debonding and fiber pull-out are the dominating processes when interfacial adhesion is poor, while limited debonding occurs and fiber fracture dominates in the presence of an efficient coupling agent [4].
4. We predicted by the detailed analysis of the micromechanical deformation processes occurring in PP/wood composites that the strength of these composites can be increased further only by improving the inherent strength of the wood particles. The prediction was later proved in another project which showed that fiber fracture decreased and the deformation mechanism changed when the size of the wood particles was decreased [4].
5. We could confirm the coupling mechanism of functionalized polymers with the quantitative estimation of interfacial adhesion. We proved that longer chains lead to more entanglements that result in increased deformability and in larger load bearing capacity of the wood fibers [5].
6. We developed a technology for the benzylation of wood, which resulted practically exclusively in the modification of the surface of wood particles. We proved that such a modification decreases the water absorption of the wood drastically, but does not influence significantly other properties [6].
7. We proved by the comparison of three different surface modification approaches (functionalized polymer, surfactants, and chemical modification) that the proper selection of the approach and the level of surface modification leads to considerable improvement in targeted properties, but leaves

unchanged or even deteriorate others. As a consequence, properties must be optimized for good overall performance [7].

#### 4. Perspectives, utilization

Polymer composites reinforced with natural fillers and reinforcements are used mainly in the automotive and building industry, but furniture, household and office appliances are also prepared from them. Using the knowledge obtained in our work on PP/wood composites we developed compounds which can be used for the production of extruded or injection molded articles. The photo of a sound box produced from one of our compounds in international cooperation is presented in Fig. 1.



**Figure 1** Sound box prepared from one of our PP/wood composites.

#### 5. Publications

##### 5.1 *The thesis is based on the following papers*

1. Dányádi, L., Százdí L., Gulyás, J., Bertóti, I., Pukánszky, B.: Surface chemistry and adhesion in carbon fiber reinforced epoxy microcomposites, *Compos Interfaces* **12**(3-4), 243-258 (2005). IF: 0.929, I: 1

2. Dányádi, L., Renner, K., Szabó, Z., Nagy, G., Móczó, J., Pukánszky, B.: Wood flour filled PP composites: adhesion, deformation, failure, *Polym Adv Technol* **17**(11-12), 967-974 (2006). IF: 1.406, I: 5
3. Dominkovics, Z., Dányádi, L., Pukánszky, B.: Faliszt erősítésű PP kompozitok; az erősítőanyag reaktív felületmódosítása, *Műanyag és Gumi*, **43**(12), 517-523 (2006)
4. Dányádi, L., Renner, K., Móczó, J., Pukánszky, B.: Wood flour filled PP composites: Interfacial adhesion and micromechanical deformations, *Polym Eng Sci* **47**(8), 1246-1255 (2007). IF: 1.272, I: 1
5. Dányádi, L., Janecska, T., Szabó, Z., Nagy, G., Móczó, J., Pukánszky, B.: Wood flour filled PP composites: Compatibilization and adhesion, *Compos Sci Technol* **67**(13), 2838-2846 (2007). IF: 2.171, I: 3
6. Dominkovics, Z., Dányádi, L., Pukánszky, B.: Surface modification of wood flour and its effect on the properties of PP/wood composites. *Composites* **A38**(8), 1893-1901 (2007). IF: 1.662, I: 3
7. Dányádi, L., Móczó, J., Pukánszky, B.: Effect of various surface modifications of wood flour on the properties of PP/wood composites-submitted to *Composites Part A* (2008)

## 5.2 Other publications

1. Dányádi, L., Gulyás, J., Pukánszky, B.: Coupling of carbon fibers to polycarbonate: surface chemistry and adhesion, *Compos Interfaces* **10**(1), 61-76 (2003). IF: 0.387, I: 1
2. Dányádi, L., Gulyás, J., Pukánszky, B.: Szénszál reaktív felületkezelése polikarbonát kompozitok készítéséhez: felületi kémia és adhézió, *Műanyag és Gumi* **40**(11), 362-368 (2003), I: 1
3. Mezey, Z., Dányádi, L., Czigány, T., Pukánszky, B.: Sisal szállal erősített polimer kompozitok vizsgálata, *Műanyag és Gumi*, **40**(5), 164-167 (2003)

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4. Dányádi, L., Szabó, Z., Nagy, G., Móczó, J., Pukánszky, B.: Faliszt töltőanyag tartalmú polimer kompozitok, *Műanyag- és Gumiipari Évkönyv*, **4**, 39-42, (2006)

### 5.3 Conference presentations

1. Dányádi, L.: A határfelületen lejátszódó kémiai reakciók vizsgálata polikarbonát/szénszál kompozitokban, Magyar Kémikusok Egyesülete XXIV. Kémiai Előadói Napok, Szeged, Hungary, October 29-31, 2001
2. Mezey, Z., Dányádi, L.: Sisal szálerősítésű polimer kompozitok, MTA Szál- és Rosttechnológiai Bizottságának ülése, Budapest, Hungary, February 24, 2003
3. Dányádi, L., Mezey, Z., Czigány, T., Pukánszky, B.: Természetes szállal erősített polimer kompozitok, MTA Műanyag Munkabizottságának ülése, Budapest, Hungary, April 28, 2003
4. Dányádi, L., Százdi, L., Gulyás, J., Bertóti, I., Pukánszky, B.: Kémiai szerkezet és határfelületi adhézió szénszállal erősített epoxigyanta mikrokompozitokban, MTA Anyagtudományi és Technológiai Komplex Bizottságának ülése, Budapest, Hungary, May 9, 2003
5. Dányádi, L., Móczó, J., Mezey, Z., Czigány, T., Pukánszky, B.: Sisal fiber reinforced polypropylene composites, Eurofillers 2003. Fillers for formulations, Alicante, Spain, September 8-11, 2003 (poster)
6. Mezey, Z., Dányádi, L., Mokoena, M. A., Czigány, T., Pukánszky, B., Luyt, A. S.: Sisal fiber reinforced polymer composites, Narotech 2003, Erfurt, Germany, September 11-12, 2003
7. Mezey, Z., Dányádi, L., Czigány, T., Pukánszky, B.: Investigation of the mechanical properties of sisal fiber reinforced polypropylene composites. 20<sup>th</sup> Danubia-Adria Symposium in Solid Mechanics, Győr, Hungary, September 24-27, 2003

8. Dányádi, L., Százdi, L., Gulyás, J., Bertóti, I., Pukánszky, B.: Surface chemistry and adhesion in carbon fiber reinforced epoxy microcomposites, International conference on Interfaces and Interphases in Multicomponent Materials (IIMM 2003), Balatonfüred, Hungary, October 5-8, 2003
9. Dányádi, L., Szabó, Z., Nagy, G., Pukánszky, B.: Határfelületi kölcsönhatás, szerkezet és tulajdonság farost/polipropilén kompozitokban, MTA DAB Polimer Munkabizottságának ülése, Debrecen, Hungary, April 6, 2004
10. Szabó, Z., Dányádi, L., Nagy, G., Pukánszky, B.: Introduction; The Potentials of Wood Flour Reinforced Thermoplastics, 4<sup>th</sup> „Eureka E! 2819 Ecoplast” meeting, Ljubljana, Slovenia April 15, 2004
11. Dányádi, L., Szabó, Z., Nagy, G., Pukánszky, B.: A határfelületi kölcsönhatások módosítása farost/PP kompozitokban, GTE Műanyag Szakosztály I. Doktorandusz Konferenciája, Budapest, Hungary, June 10, 2004
12. Dányádi, L., Szabó, Z., Nagy, G., Móczó, J., Pukánszky, B.: Structure – property relationships in wood fiber reinforced polypropylene composites. International Symposium on Engineering Plastics (EP’ 2004, Lanzhou), Lanzhou, China August 15-20, 2004 (poster)
13. Szabó, Z., Dányádi, L., Nagy, G., Pukánszky, B.: Correlation between mechanical and acoustic properties of PP/wood composites, 5<sup>th</sup> „Eureka E! 2819 Ecoplast” meeting, Zagreb, Croatia, October 7, 2004
14. Dányádi, L., Pukánszky, B.: A határfelületi kölcsönhatások módosítása polipropilén/faliszt kompozitokban, BME Vegyészmérnöki Kar II. doktoráns konferenciája, Budapest, Hungary, November 24, 2004 (Per. Pol. Chem. Eng., 49/1 (2005), 25-89.)
15. Budapesti Műszaki és Gazdaságtudományi Egyetem, Műanyag- és Gumiipari Tanszék, Tiszai Vegyi Kombinát Rt.: Természetes szálakkal

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- erősített polipropilén kompozit alapanyagok fejlesztése, „EUREKA – COST sikereink”, Budapest, Hungary, March 7, 2005 (poster)
16. Szabó, Z., Dányádi, L., Nagy, G., Pukánszky, B.: Improvement of the Processability of PP/Wood Composites, 6<sup>th</sup> „Eureka E! 2819 Ecoplast” meeting, Guimaraes, Portugal, April 22, 2005
  17. Klébert, Sz., Dányádi, L., Szabó, Z., Nagy, G., Pukánszky, B.: Interfacial interactions in polypropylene/wood flour composites, NaroTech 2005. Exhibition on Renewable Resources with International Symposium, Erfurt, Germany, September 1-2, 2005
  18. Dányádi, L., Szabó, Z., Nagy, G., Pukánszky, B.: Interfacial interactions in polypropylene/wood flour composites, Interfaces’ 05. Achieving Excellence by Technological Innovation, Sopron, Hungary, September 15-17, 2005
  19. Dányádi, L., Szabó, Z., Nagy, G., Pukánszky, B.: Wood flour filled PP composites: interfacial adhesion and processability, Polymers for Advanced Technologies, Budapest, Hungary, September 13-16, 2005
  20. Szabó, Z., Dányádi, L., Nagy, G., Pukánszky, B.: Improvement of the Processability of PP/Wood Composites, 7<sup>th</sup> „Eureka E! 2819 Ecoplast” meeting, Slovenske Konjice, Slovenia, September 30, 2005
  21. Dányádi, L., Pukánszky, B.: Faliszt töltőanyag tartalmú PP kompozitok: adhézió, deformáció, tönkremenetel, BME Vegyészmérnöki Kar III. doktoráns konferenciája, Budapest, Hungary, February 7, 2006
  22. Dányádi, L., Szabó, Z., Janecska, T., Nagy, G., Pukánszky, B.: Faliszttal erősített PP kompozitok, TVK Rt. Éves beszámoló, Tiszaújváros, Hungary, February 10, 2006
  23. Móczó, J., Dányádi, L., Pukánszky, B.: Faliszt töltőanyag tartalmú PP kompozitok: adhézió, deformáció, tönkremenetel, MTA KK AKI Szeminárium, Budapest, Hungary, April 11, 2006

24. Móczó, J., Dányádi, L., Renner, K., Pukánszky, B.: Mikromechanikai deformációs folyamatok faliszt töltőanyagot tartalmazó polimer kompozitokban, Kutatóközponti Tudományos Napok 2006., Budapest, Hungary, May 18-19, 2006
25. Klébert, Sz., Dányádi, L., Renner, K., Móczó, J., Pukánszky, B.: Natural fiber reinforced PP composites, International Scientific Advisory Board at the CRC HAS, Budapest, Hungary, June 7, 2006
26. Dányádi, L., Renner, K., Móczó, J., Pukánszky, B.: Wood flour filled polypropylene composites: Interfacial interactions and micromechanical deformations, 20<sup>th</sup> Bratislava International Conference on Macromolecules, Advanced Polymeric Materials, Bratislava, Slovakia, June 11-15, 2006 (poster)
27. Dányádi, L., Renner, K., Móczó, J., Pukánszky, B.: Mikromechanikai deformációk faliszt erősítésű PP kompozitokban, MTA Természetes Polimerek Munkabizottságának ülése, Budapest, Hungary, November 30, 2006
28. Sudár, A., Dányádi, L., Renner, K., Móczó, J., Pukánszky, B.: Faliszt erősítésű PP kompozitok, MTA Műanyag és Természetes Polimerek Munkabizottságának ülése, Budapest, Hungary, April 12, 2007
29. Móczó, J., Sudár, A., Renner, K., Dányádi, L., Pukánszky, B.: A komponenstulajdonságok és az adhézió hatása heterogén polimer rendszerek deformációs folyamataira, MTA Anyagtudományi Nap, Budapest, Hungary, May 11, 2007
30. Janecska, T., Havas, Zs., Dányádi, L., Móczó, J., Pukánszky, B., Suba, P., Nagy, G.: Effect of coupling agent properties on the rheological characteristics of wood-fiber reinforced PP composites, Eurofillers 2007, Zalakaros, Hungary, August 26-30, 2007 (poster)