Ph.D. Thesis

János Gulyás

Interfacial interactions in carbon fiber reinforced composites: surface chemistry and adhesion

Supervisor: Béla Pukánszky, professor, head of department

Budapest University of Technology and Economics
Department of Plastics and Rubber Technology

2002

Introduction

The production of carbon fiber reinforced composites increases all over the world. The use of these materials gradually shifts from traditional areas, like the military and aerospace industry, towards civil applications, pedestrian bridges and other structural elements are produced from them in increasing numbers. In the last few years the production of carbon fiber started also in Hungary, Zoltek Rt. installed a plant with large capacity at Nyergesújfalu. According to the hopes of the company the implementation of the new plant will lead to a further increase in the use of carbon fiber reinforced composites, which, in spite of their excellent properties, remained at a moderate level because of the high price of the fibers. Increasing production and use is achieved by an increase in the type of the matrix polymers as well. New products cannot be designed without the deep knowledge of composite properties. Besides composition the properties of the composites are determined mainly by structure (fiber length and orientation) and interaction.

The success of fiber reinforced polymers originates in the fact that the combination of the two component, the fiber and matrix polymer, results in a new material with properties, which are better than those of the individual components. In the composites the extremely stiff and strong fiber carries the load, while the matrix distributes it among the fibers. The advantages of such a structure can be fully utilized only if the fiber really carries the load, which occurs, indeed, if the fibers are sufficiently long and orientated in the direction of the load. However, stress is obviously transferred only if the adhesion between the fiber and the matrix is strong. Interfacial adhesion of the components can be modified by surface treatment. Commercial coupling technologies are kept secret by the manufacturer or they are protected by patent rights. Our preliminary experiments proved that maximum or even optimum fiber/matrix adhesion cannot be achieved with sized fibers purchased on the market. It became obvious as well, that the use of a fiber having a sizing, which was optimized for a given matrix in another polymer leads to composites with inferior properties, the characteristics of the composites remain below the optimum values.

The most important goal of this study was the investigation of interfacial interactions developing between carbon fibers and various matrices, as well as their modification through the use of appropriate coupling agents. We intended to investigate the type and number of functional groups forming on the surface of carbon fibers during their electrolytic oxidation. We modified the surface composition of the fibers by changing the type of the electrolyte, its concentration, the potential and time of the oxidation in a wide range. The adhesion between the fiber and the matrix was changed through the use of various coupling agents. We wanted to follow the chemical reactions taking place on the surface of the fiber as well as the determination of the character of the chemical bonds formed in these reactions. We looked for a correlation between surface chemistry and the strength of interfacial interaction. In the case of short carbon fiber reinforced composites, which are also very important for practice, the goal of the research was the determination of the correlation between their structure developing during processing and the properties of the produced parts.

Methodology

- A vessel was built for the continuous anodic oxidation of the virgin fiber. Rovings of the fiber was used as anode, while a graphite block was used as cathode. The type and concentration of the electrolyte, the potential of the oxidation and the treatment time were varied in a wide range.

- Surface chemistry of the fiber was followed by diffuse reflectance infrared (DRIFT) and by X-ray photoelectron (XPS) spectroscopy.

- Electrochemical activity of the fiber surface, which is related to its chemical composition, was studied by cyclic voltammetry by using various probe molecules.

- The adhesion between the fiber and the matrix was determined by fragmentation on single fiber micro-composites. We designed and built the apparatus necessary for the execution of the experiments. The length of fiber fragments formed during the tests was determined by optical microscopy.

- The distribution and structure of the coupling agent layer forming on the fiber surface was studied by scanning electron microscopy (SEM).

- Specimens were injection molded from short carbon fiber reinforced polyamide composites under various processing conditions and their properties were characterized by tensile and impact testing.

- The orientation of the fibers in the injection molded specimens was determined by optical microscopy and quantitatively evaluated by image analysis.

New scientific results

- The research directed towards the determination of the role of interfacial interactions developing in carbon fiber reinforced composites as well as the attempts to modify them yielded numerous new results. We found that the conditions of electrolytic oxidation of carbon fibers significantly influence the type and number of functional groups formed on the surface. Type, concentration and potential of oxidation, all influence the composition of the surface. Close correlation was found between the number of certain functional groups formed on the surface during oxidation and interfacial adhesion.

- The results which proved that sodium hydroxide electrolyte adsorbs on the surface of the fiber in an extent depending on the conditions of the oxidation, is important for practice. The adsorption of the electrolyte is strong, it can be removed only with thorough washing. The adsorption of NaOH deteriorates interfacial adhesion, the removal of the adsorbed material significantly improves interaction.

- We found that cyclic voltammetry is an excellent technique for the characterization of the electrochemical activity of carbon fibers. We found close correlation among the peak current detected by cyclic voltammetry, the number of functional groups formed on the fiber surface and interfacial interaction.

- The interaction between the fiber and the matrix can be modified by the application of coupling agents. Experiments carried out with various coupling agents proved that numerous chemical reactions take place on the surface of the fiber. The structure and properties of the coupling agent layer forming on the surface considerably influence the strength of adhesion and the properties of the composites. The coupling agents often take part in complicated polymerization reactions on the surface of the fiber. The structure of the polymer layer depends on the chemical composition of the coupling agent and on the conditions of surface treatment. The obtained results proved that neither a rigid, stiff or a weak layer do not improve interfacial adhesion, both lead to composites with inferior properties.

- In thermoplastic matrices the number of functional groups which makes possible coupling is usually very low. In polycarbonate the coupling agents may enter into chemical reaction only with reactive groups found at the end of the chains. Because of the low number of functional groups, the chain-end –OH groups in polycarbonate, which are available for chemical reactions, interfacial adhesion can be improved by coupling only in a limited extent.

- Besides interfacial interactions composite structure plays also an important role in the determination of properties in short carbon fiber reinforced composites. Fiber orientation and orientation distribution as well as fiber length and its distribution influence the properties of the composites. A skin-core structure develops during the injection molding of a product, fiber orientation differs considerably in the two layers. The thickness of the skin depends on composition and on processing conditions. We found that the stiffness, strength and impact resistance of the composite increases with fiber content at moderate and high concentrations, but a small amount of fiber impact resistance decreases because fibers behave like weak sites in the composite, they initiate fracture. Orientation distribution, which was determined by us in short carbon fiber reinforced polyamide composites differed from that published in the literature. This difference was reflected also in the properties of the composites, which proved again the determining role of structure in these materials.

Publications

1. Molnár, Sz., Rosenberger, S., **Gulyás, J.**, Pukánszky, B.: Structure and impact resistance of short carbon fiber reinforced polyamide 6 composites, **J. Macromol. Sci.-Phys.** B38, 721-735 (1999)

2. Pukánszky, B., **Gulyás, J.**: Interfacial interactions in carbon fiber reinforced epoxy composites, **SPE ANTEC** 57(2), 2650-2655 (1999)

3. **Gulyás, J**., Rosenberger, S., Földes, E., Pukánszky, B.: Chemical modification and adhesion in carbon fiber/epoxy micro-composites; coupling and surface coverage, **Polym. Compos.** 21, 387-395 (2000)

4. **Gulyás, J.**, Földes, E., Pukánszky, B., Lázár, A.: Electrochemical oxidation of carbon fibres; surface chemistry and adhesion, **Composites** 32A, 353-360 (2001)

5. Százdi, L., **Gulyás, J.**, Pukánszky, B.: Anódosan oxidált szénszálak felületi jellemzőinek vizsgálata, **Műanyag és Gumi** 38, 405-410 (2001)

6. Százdi, L**., Gulyás, J.**, Pukánszky, B.: Surface Characterization of electrochemically oxidized carbon fibers: surface properties and interfacial adhesion, **Compos. Interfaces** 9, 219-232 (2002)

7. Százdi, L., **Gulyás, J.**, Pukánszky, B.: Electrochemical oxidation of carbon fibres; adsorption of the electrolyte and its effect on interfacial adhesion, **Composites** (in press)

8. Dányádi, L., **Gulyás, J.**, Pukánszky, B.: Coupling of carbon fibers to polycarbonate: surface chemistry and adhesion, **Compos. Interfaces** (submitted)

9. **Gulyás, J.**, Százdi, L., Pukánszky, B.: Surface chemistry and adhesion of carbon fibers activated by anodic oxidation (in propagation)

Presentations

1. **Gulyás, J.**, Rosenberger, S., Pukánszky, B.: Szál/mátrix kölcsönhatás vizsgálata szénszálerősítésű kompozitokban, **Műanyagok és kompozitok a korrózióvédelemben**, 1998. május 13-15., Sopron

2. **Gulyás, J.**, Rosenberger, S., Földes, E., Pukánszky, B.: Szál/mátrix kölcsönhatás vizsgálata szénszálerősítésű kompozitokban, **KKKI Intézeti Szakmai Napok**, 1999. március 30-31., Budapest

3. **Gulyás, J.**, Meiszel, L., Pukánszky, B.: Structure/property correlations in short carbon fiber reinforced injection molded PA composites, **11th Hugarian-Korean Symposium on Advanced Polymers**, 19-20 April 1999, Budapest

4. Pukánszky, B., **Gulyás, J.**: Interfacial interactions in carbon fiber reinforced epoxy composites, **SPE ANTEC ’99**, 2-6 May 1999, New York

5. **Gulyás, J.**, Pukánszky, B., Lázár, A.: Study of electrochemical oxidation of carbon fibers; surface chemistry and interaction, **IPCM '99**, 8-10 September 1999, Berlin

6. **Gulyás, J.**, Szabolcs, M., Pukánszky, B.: Fracture mechanics study of short carbon fiber reinforced polyamide 6 composites, **2nd ESIS TC4 Conference on Polymers & Composites**, 13-15 September 1999, Switzerland

7. **Gulyás, J.**, Pukánszky, B.: Fröccsöntési paraméterek hatása szénszálerősítésű poliamid kompozitok tulajdonságaira, **Műanyag Kollokvium**, 1999. október 7-8., Lillafüred

8. Százdi, L., **Gulyás, J.**, Pukánszky, B.: Szénszál elektrokémiai oxidációja során lejátszódó folyamatok vizsgálata, **Műanyag Kollokvium**, 2001. május 10-11., Szeged

9. **Gulyás, J.**, Kovács, L., Pukánszky, B.: Coupling of carbon fibers to polycarbonate: surface chemistry and adhesion, **ICCI-VIII**, October 11-14, 2000, Cleveland

10. **Gulyás, J.**, Kovács, L., Pukánszky, B.: Határfelületi kölcsönhatások módosítása és vizsgálata polikarbonát/szénszál kompozitokban, **"A ma diákjai - a jövő tudósai"** konferencia, 2000. november 6., Budapest

11. **Gulyás, J.**, Százdi, L., Pukánszky, B.: Characterization of the surface of carbon fibres activated by anodic oxidation; effect of oxidation conditions, **IPCM 2001**, September 11-14, Arcachon, France

Curriculum vitae

Personal data

Name: János Gulyás

Date of birth: 2nd August 1974

Place of birth: Budapest, Hungary

Education

1988-1992 Petrik Lajos Technical Highschool of Chemistry

1992-1998 Budapest University of Technology and Economics,
Faculty of Chemical Engineering
Dip. Chemical Engineer, Plastic and Rubber Technology Division

1998-1999 Founded researcher of the Varga József Foundation
Budapest University of Technology and Economics,
Faculty of Chemical Engineering

1999-2002 Ph.D. studies at the Budapest University of Technology and Economics, Faculty of Chemical Engineering, Department of Plastic and Rubber Technology

Language skills

- Intermediate level state examination of English Language
- Basic level state examination of German Language

Teaching activities

Laboratory practices:

- Extrusion of polymers
- Composites I-II.
- Injection molding I-II.
- Fiber reinforced polymers
- Investigation of mechanical properties of polymers