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DEVELOPMENT OF POLYMER MATRIX NANOCOMPOSITES

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1. Introduction

The development of polymer composites used in engineering has got a new impetus form the nanoparticles discovered at the end of the 20th century. At least one dimension of these nanoparticles belongs to the nanometer dimension. In addition to the irregular shaped nanoparticles nanofibers having nanometer diameter and few micrometer length, and platelets having few nanometers thickness but relatively larger width and length, belong to this category. The latter two types are excellent for polymer reinforcement, as due to their extremely high surface/volume ratio, very strong interaction may develop between the matrix and the reinforcement.

Several types of nanoparticles exist. There are various metal oxides, most typical are TiO_2 and Al_2O_3. Fullerenes and layered silicates or plate-like clay minerals also belong to this category. The latter have been applied in polymer technology already for 50 years to improve e.g. solvent resistance or the mechanical properties. In spite of this the structure of polymer systems reinforced by layered silicates was described only in 1976, using a polyamide 6 (PA6) based composite prepared by a technique denoted as *in situ* polymerization. Within a decade Toyota launched composites prepared by a similar technology, so these materials have already been used by the automotive industry. Since then these composites have been used by several other industries (e.g. electronics, mechanical engineering, biomedical engineering), being offered in innumerable versions and grades. Almost all kinds of known polymers have been tried, combined with a wide range of layered silicates.

From the nanoparticles listed above fullerenes exhibit special importance. This new allotrope of carbon opened new ways also in polymer technology. Especially carbon nanotubes attracted a lot of attention. These are typically very small, closed, tube-like structures with 20-100 nm diameter, micrometer length, with one or more walls. The structure composed mostly of closed hexagons is very rigid, therefore its tensile properties are advantageous. The tensile elasticity modulus of nanotubes amounts to 1000 GPa, while the tensile strength of single wall nanotubes is around 50-500 GPa and around 10-60 GPa for multi-wall nanotubes. This value is many times larger than those of the traditional structural materials and reinforcements used in composites.

When preparing polymer matrix nanocomposites one of the biggest obstacles is the aggregation tendency of the nanoparticles. If aggregates remain in the system the

nanoparticles cannot reinforce the system, sometimes even worsen the mechanical properties, as less reinforcing particles are present and aggregates may act as defect centers, in case of failure they are sometimes crack initiators. There are several methods for the proper dispersion of nanoparticles but they are mostly complicated and require great attention. Materials with very advantageous properties can be prepared by the surface treatment of the nanoparticles and by the improvement of the production technologies.

The properties of fiber reinforced composites can be further improved if the matrix is modified by the addition of nanoparticles. Carbon fiber/epoxy resin/nanotube hybrid systems are present already in everyday life, they are mostly used by sport and leisure manufacturers. BMC bike manufacturer in Switzerland uses hybrid systems in the frames of several products. Golf clubs (e.g. Grafalloy Prototype Com NT series) and tennis rackets (e.g. Babolat NS Tour and Drive series) with nanotube reinforcement are available on the market.

In addition to nanoparticles traditional reinforcements have also undergone significant improvement during the past decades. Using better technologies more and more advanced fibers are prepared and new reinforcements appear on the market, perhaps the most promising of them being continuous basalt fiber. Basalt fiber exhibits similar properties to glass fiber, but it has improved heat and chemical resistance and its production is simpler too. If the raw material is of acceptable quality, it is ready for production after a simple cleaning and grinding process. The price of continuous basalt fiber is presently higher than that of glass fiber but, because of the simpler technology and because of the cheap raw material being present abundantly in nature basalt fiber may be a potent competitor of glass fiber in the field of composite applications.

The technology of polymer nanocomposites is a versatile branch of materials science with several new prospects. It seems probable that this family of composites will become a structural material of high importance in the 21st century. The goal of my research was therefore to develop new types of nanocomposites, including the preparation and testing of basalt fiber reinforced hybrid composites containing nanoparticles too.

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

In the literature survey first I presented the variation of surface/volume ratio characteristics of fiber shape reinforcements as a function of diameter and length, where I pointed out that not only long fibers, but also thin lamellar materials (approximately described by discs) are suitable for polymer reinforcement. Afterwards some lamellar and fibrous nanometric fillers are presented, from which montmorillonite and carbon nanotubes are dealt with in some detail. These reinforcements were used in my research, as their mechanical and other physical properties are suitable for being composite reinforcements: they have large specific surface, high strength and tensile modulus.

The most serious problems related to the use of nanoparticles in polymer composites as reinforcements are difficult dispersibility and aggregation tendency – due to the strong inter-particle attractions. In order to eliminate this problem good material pairs must be found, the particles should be surface treated or organophilized and the production technology of the nanocomposite must be properly chosen. A polymer well proven in engineering applications, namely polyamide 6 was chosen for my experiments. From the three methods of nanocomposite fabrication (melt mixing, *in situ* polymerization and solution blending) melt mixing, more closely extrusion was selected because of its easy technical realization potential. Several researchers proved that nanoparticles modify significantly the matrix properties already at a very low concentration, so I added 1 wt% nanofiller in the composites produced.

When studying the literature it turned out that processing parameters may significantly influence the mechanical properties of the nanocomposites. Best nanoparticle dispersion were achieved if large shear forces appeared in the polymer melt, i.e. if the extrusion process was performed at high rpm and various shear elements were used on the screw. The effect of extrusion temperature, however, has not been studied in detail so far.

Aggregation problems similar to those of layered silicates have been encountered when using carbon nanotubes. The use of high shear forces may be expedient to reach proper dispersion here too and it has to be taken into account that multi-walled carbon nanotubes can be dispersed easier. This can be explained by the higher density of multi-walled nanotubes (smaller number of particles in the case of equal filler loading) and by the lower surface/volume ratio, as in this case higher

specific shear force acts on a single nanotube. Based on these arguments I decided to use multi-walled nanotubes in addition to montmorillonite.

When using nanotubes in PA6 composites their effect on the crystalline structure of PA6 has not yet been fully elucidated. Some researchers report a decreasing crystalline ratio, while others observed increased crystallinity. Clarification of this problem needs further research.

As discovered earlier, the surface treatment of the nanoparticles can affect profoundly the reinforcement/matrix interaction. One way of this treatment can be the use of electron irradiation, which may initiate *in situ* polymerization. When using electron irradiation there is a chance that grafted copolymer side chains may be attached to the mineral particle surface by primary bonds. This – in contrast to traditional technologies – may ensure stronger interaction between the matrix and the filler.

There are examples in the literature for preparing glass fiber reinforced hybrid composites containing nano-reinforcements. The use of basalt fiber in hybrid composites has been so far less investigated. The advantageous properties observed in glass fiber reinforced hybrid nanocomposites may also appear when using basalt fibers too.

Based on the literature survey my goal was to develop new nanocomposite production technology allowing a better dispersion of the nanoparticles. I tried to achieve this by optimizing the processing parameters and perhaps by the modification of the surface of the nanopraticles used. My further goal was to produce hybrid composites reinforced by both traditional fibers and nanoparticles. I expected better dispersion of the nanoparticles and synergetic effects, improvement of the ultimate properties from the hybridization. Prepared composites were characterized by their mechanical and morphological properties.

3. Methods, test and materials used

The layered silicate used in the experiments was Nanofil 9 montmorillonite treated by a quaternary ammonium salt, a product of Süd Chemie AG (hereinafter referred to as MMT). 2 hydroxy-ethyl methacrylate (HEMA) of Merck was used for a further modification of MMT. The electron beam initiated polymerization of this monomer was proven in preliminary experiments.

Schulamid 6 MV 13 F produced by Schulman AG was used as matrix material (hereinafter referred to as PA6). BCS 13.6.KV02 grade basalt fiber of Kamenny Vek Ltd. (Ukraine) was used as fibrous reinforcement. The fibers used were chopped fibers produced by continuous fiber spinning technology (nominal diameter was 13 μm, average length was 6 mm).

Multi-walled carbon nanotubes (MWCNT) of Baytubes® C 150 P grade produced by BAYER were used for nanotube reinforcement. According to the manufacturer the nanotubes were not modified by any surface treatment. The average diameter of the nanotubes was 13-16 nm, their length was 1-10 μm.

The electron beam surface treatment of the nanoparticles was performed by a 175 keV Electrocourtain type accelerator made by Energy Science Inc. (ESI) (Woburn, MA, USA). The parameters of the electron beam were as follows: acceleration voltage, U= 175 kV, electron current I = 6 mA, cathode heating P = 350 W, linear velocity of the material under the beam v = 0.5 m/sec. In order to avoid overheating and to achieve complete conversion the treatment was performed in four subsequent intervals. The calculated total dose was D = 150 kGy.

Before processing PA6 containing samples were dried in a Heraeus UT-20 type ventilating oven, according to the datasheet 4 hours at 80ºC.

In the first phase of my experiments materials were produced by a 50 ml Brabender Plasti-Corder 814600 type internal mixer. Mixing was performed at 220ºC at 20 rpm mixing rate. The reinforcement was added when the polymer was in molten state.

Compression molding was performed by a Collin P 200 E type laboratory press. The temperature was raised to 230ºC during compression, pressure was 150 bar. This pressure was maintained for 5 min then the press was cooled by water. 160x100x1 mm frame was used for the compression. Test specimens were cut from the compression molded sheets according to the EN ISO 527-1 standard.

Extrusion was performed on a Brabeder Plasti-Corder PL2100 type twin-screw extruder, at a rate of 1 rpm in each case. The screw diameter was 25 mm, the L/D ratio was 20.

Injection molding was performed by an Arbug Alrrounder 320 C 66-250 type injection molding machine. Injection molded test specimens of 4x10 mm cross section corresponded to the MSZ EN ISO 527-2 standard. Injection molding was performed with identical parameters for each material.

MFI tests were performed with a CEAST Modular Melt Flow 7027.000 type capillary plastometer according to the MSZ EN ISO 1133 standard with the following parameters: capillary length L = 8 mm, capillary diameter r = 1 mm, piston diameter d = 9 mm, load m = 2.16 kg.

Physical properties of the PA6 used as matrix material depend strongly on the temperature and moisture content of the material, therefore the samples were conditioned for at least 48 h prior to the measurements in a MEMMERT HCP 153 type climatic chamber at 25ºC and 50% R.H.

A Phillips type X-ray diffractometer was used to determine the inter-layer distance of MMT equipped with a PW 1730 type generator. Diffraction angles between $2\Theta = 1\text{-}42º$ was scanned, the wavelength was $\lambda = 1.54186$ Å.

Tensile tests were performed by a Zwick Z020 type, computer controlled tensile tester according to the MSZ EN ISO 527-1:1999 standard. Gage length was 30 mm for the compression molded specimens and 110 mm for the injection molded specimens. From the force-elongation curves the tensile strength (σ_M) and the elongation at break (ε_B) values were determined. The elongation at break value was calculated from the crosshead displacement. In order to be able to measure the elongation modulus precisely a video-extensometer was used. The tensile modulus was calculated from the slope fitted to the initial portion of the stress-strain curve. Force control was used during the cyclic tensile test, the rate of load application and removal was 100 N/s. The load was increased stepwise by 100 N in each cycle 30 s rest was applied between the cycles. In this test one sample was used for each material.

Tree point bending tests were performed on a computer controlled, Zwick Z020 type universal tester according to the MSZ EN ISO 178 standard. Span length was 64 mm, the deformation rate was 2 mm/min. As the sample did not break until the limiting deformation prescribed by the standard (6 mm in the case of 4 mm thick specimens), the stress value belonging to the limiting deformation (the limiting flexural stress) was calculated in each case. When determining the flexural modulus – similarly to the tensile test – the initial portion of the flexural curve was taken into account.

The crystalline melting peaks and the crystallinity ratios of the PA6 samples were determined by a Perkin-Elmer DSC-2 equipment. Heating rate was 10 ºC/min, tests were performed in an inert atmosphere, purging the sample by nitrogen, at a volume rate of 30 ml/min. When determining the melting peaks the average of five

parallels were taken into account. When calculating the crystallinity 188 J/g melting heat was assumed for the 100% crystalline PA6 material.

The morphological characteristics and structure of the fracture surface were studied by a JEOL JSM-6380 LA type scanning electron microscope. The surfaces studied were the broken surfaces of the specimens used in the tensile tests. A conducting gold layer was always evaporated onto the surface and the specimens were fixed onto the metal sample holder using an electrically conducting adhesive to avoid the electrostatic charging of the sample. It has to be noted, however, that due to this gold layer the size of the nano-particles seems to be larger as the thickness of the gold coating amounts to several tens of nanometers.

Transmission electron micrographs were taken by a LEO 912 Omega type of equipment. Samples to be studied were prepared by a Leic Ultracut microtome.

4. New scientific results – theses

*1*st *thesis [7]*

It has been demonstrated that in the case of polyamide 6 (PA6) matrix nanocomposites with 1 wt% montmorilonite (MMT) extrusion temperature influences significantly the mechanical and crystalline properties of the materials. It has also been demonstrated that the presence of MMT compensates for the matrix degradation caused by the high temperature extrusion mixing. It has been proved that for these nanocomposites the melting temperature of the crystalline γ-phase increased by 1.6ºC with increasing extrusion temperature, which is caused by the increasing lamella thickness of the crystallites.

*2*nd *thesis [1,2,6]*

A new type of surface treatment was developed for MMT, wherein 2-hydroxyethyl methacrylate (HEMA) monomer was intercalated between the MMT layers (HMMT), then, during the melt mixing an *in situ* polymerization of HEMA occurred, exerting a positive influence on the mechanical properties. Adding 1 wt% HMMT to PA6 during internal mixing, followed by compression molding increased the tensile strength by 38% and the tensile modulus by 127%.

3rd thesis [17]

It has been proved that in the case of short fiber reinforced hybrid composites prepared by extrusion the dispersion of the nanoparticles improves not only because of the apparent viscosity increase caused by the fibers, but also due to higher shear forces caused by the relative displacement of the fibers with respect to each other, leading to stronger de-aggregation and higher reinforcing effect.

4th thesis [11]

Hybrid composites containing 1 wt% HMMT or 1 wt% multi-walled carbon nanotube (MWCNT) (with respect to the PA6 matrix) and 30 wt% basalt fiber were prepared. It has been demonstrated that by a combined application of short basalt fiber and nanoparticles hybrid nanocomposites of advantageous properties can be prepared. With respect to tensile strength, stress belonging to limiting flexural deformation and flexural modulus the joint increase caused by short basalt fibers and nano-reinforcements increased the sum of increments caused by fiber reinforcement and by nano-additives applied alone, i.e. a positive synergistic effect has been achieved.

5th thesis [16]

Using cyclic tests it has been proved that when reinforcing PA6 by 30 wt% basalt fiber (BF) the residual deformation as a function of the cycle number is reduced with respect to the matrix. If HMMT or MWCNT is also present in the system, the failure occurs at higher cycle numbers, at lower residual deformation values. I have introduced the concept of residual deformation compliance (denoted as J_m [1/GPa]), which is described by the slope of the initial portion of the residual deformation cures plotted against the stress load. It has been demonstrated that PA6 composites containing BF are less sensitive to residual deformation than pure PA6, or its versions reinforced by MMT or by MWCNT.

5. List of own publications

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[3]   **Mészáros L.**, Košťáková E., Pokorný P., Romhány G.: Nanotubes' separation by means of ultrasound for nanocomposite materials' production, 13th International Conference: Structure and Structural Mechanics of Textiles, Liberec, Czech Republic, 2006.11.27-2006.11.29. p. 6.

[4]   Szebényi G., **Mészáros L.,** Romhány G.: Többfalú szén nanocsővel erősített epoxi mátrixú nanokompozit előállítása, mechanikai tulajdonságainak elemzése (Preparation of nanocomposites with multi-wall carbon nanotube reinforcement and epoxy matrix, analysis of mechanical properties), Anyagvizsgálók Lapja (Journal of Materials Testing) 17 (2007) 20-26.

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