

Polymer composites, biocomposites and nanocomposites. Production, composition, properties and application fields

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Polymer composites

Many well-defined structures such as metals, ceramics or polymers cannot satisfy all technological demands. Therefore, there is ongoing search for new materials with new, and especially improved properties [1]. Such a task is met by, among others, composite materials that are defined as materials composed of at least two phases, where due to the occurring synergistic effect the material of different properties than properties of the components is formed [2].

The composite material is usually composed of two components, i.e. matrix and filler called also reinforcement or more broadly dispersed phase; sometimes also additional compounds are used, mostly compatibilisers. The matrix, known also as continuous phase, integrates filler particles and allows also to shape products appropriately and determines most of physical and chemical properties of material. The dispersed phase is responsible for additional enhancement of selected material properties. While, the compatibiliser is added to increase interactions between matrix and filler what has significant impact on material cohesion and homogeneity, and as a result on its processing properties and strength.

Due to the type of matrix, one can distinguish following composites: metal matrix composites (MMCs), ceramic matrix composites (CMC) or polymer matrix composites (PMCs). The latter type of composite materials dominates over other in terms of technical applications. The matrix in PMCs might be made of duroplastic or thermoplastic polymers. Duroplasts used as PMC matrix include epoxide resins, polyesters and silicones. Typical thermoplasts used as polymer matrices include polyethylene, polypropylene, poly(vinyl chloride), polystyrene and polycarbonates [3].

Regarding dispersed phase composite materials might be distinguished into:

- particle reinforced composites; dispersed phase includes particles of greater rigidity and hardness than matrix; external loads are transferred both by matrix and filler, while the effective reinforcement is observed when filler content exceeds 20%
- dispersion reinforced composites; the strengthening occurs at microscopic level; external loads are transferred by matrix, while reinforcement is effective when filler content does not exceed 15%
- fiber reinforced composites; filler involve fibers (glass, graphite, carbon or organic fibers) of varying degree of order and different parameters
- structural composites, composed of continuous structures of construction components (e.g. plywood, rods, etc.) [4].

Among various possible types of polymer composite materials, the most important ones are nano- and biocomposites that are recently of great interest due to their unique properties [5].

Polymer nanocomposites

Nanocomposites are composite materials, which contain at least one component of nanometric scale (10^{-9} m). In case of polymer nanocomposites (PNC) this component is usually filler, called then nanofiller. Nanofillers might be classified according to their chemical nature, type of physical structure, but usually they are classified based on the shape of the particles. There are following types of nanofillers: 1D - linear (e.g. carbon nanotubes), 2D - layered (e.g. montmorillonite) and 3D - powder (e.g. silver nanoparticles) [6].

The attractiveness of the nanocomposites is a result of the fact that polymer matrix and nanofiller interact with each other on molecular level. Due to that, nanofiller of dimensions below 100 nm, added in small amount to matrix (usually few percent) might greatly change selected properties of composite material. Production of nanocomposites might be carried out using the same methods that are usually used for typical composites, i.e. in-situ or solvent method or usually by mixing melted polymer matrix. PNCs usually have higher thermal stability, lower gas permeability (higher barrier capacity) and improved mechanical properties, especially increased abrasion resistance in relation to matrix polymer [7, 8].

One of the first nanofillers that achieved technological success was montmorillonite that is layered aluminosilicate from smectite group [9]. This layered nanofiller was used with Nylon 6 - the obtained nanocomposite has shown clear improvement of mechanical and thermal properties [10]. From this moment, the studies started on other aluminosilicates and substances of layer structure using number of polymers as polymer matrices [7, 11 ÷ 13]. Nanocomposites with aluminosilicate fillers are used currently for production of car engine components, in aerospace industry, etc. [9].

The second group of nanofillers are particles of linear structure in form of nanotubes or nanofibers. Currently, carbon nanotubes (CNTs) are usually used - they are composed of graphene layers and have good mechanical and electrical properties [14]. Moreover, it is possible to "control" electric properties of nanocomposite containing CNTs by chemically modifying nanotube surfaces. CNTs have been used in combination with such matrixes as polyethylene, polycarbonate, polystyrene, poly(methyl methacrylate), polylactide as well as polyvinyl alcohol [15 ÷ 17].

Among nanofillers, where all dimensions are below 100 nm, currently there is a great interest in Polyhedral Oligomeric Silsesquioxanes (POSS). These compounds are described by molecular formula $(RSiO_{1.5})_n$, where R can be hydrogen atom, alkyl or aryl group, while n can have value equal to 6, 8, 10, 12 or higher [18]. Moreover, these compounds can take various structures such as disordered network structure, ladder structure, incompletely closed-cage structure or cage structure [19]. The ability to select structure and use almost any R substituent allows to control POSS properties, what definitely increases the attractiveness of these compounds.

POSSs are extensively described in the literature as fillers in such matrices as polyamide, polystyrene, epoxide resins, polyimide,

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polycarbonate or poly(vinyl chloride) [18, 20÷22]. Some of the publications are devoted to nanocomposites, in which matrix is made of polypropylene or polyethylene [23÷27]. However, most of these publications are focused mostly on crystallization process or the morphology of obtained nanocomposites, while just few characterizes influence of POSS on mechanical or thermal properties. M. Joshi et al. [25] have concluded that POSS impact is directly related to its dispersion in matrix. When POSS is dispersed at molecular level, it improves thermal properties of material and may act as typical crystallization nucleating agent [25, 26].

The production and characterization of polyolefin composites with POSSs is also one of the subjects studied by the group of the Division of Chemical Technology and Polymer Chemistry of the Faculty of Chemistry of the Opole University. These works are a result of established cooperation with group of Prof. Bogdan Marciniak from the Department of Organometallic Chemistry of the Faculty of Chemistry of Adam Mickiewicz University in Poznan, who specializes in synthesis of silicon compounds including POSSs. In the previous research, we used compounds of cage structure T8 with various R substituents or optionally with introduced hydroxyl group (Fig. 1).

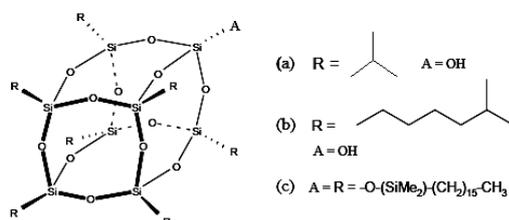


Fig. 2. Structures of compounds (a) POSS1; (b) POSS2 and (c) POSS3

Nanocomposites containing silsesquioxanes of different percentages (up to 10% w/w) were obtained using coextrusion with matrices of polyethylene high-density (PEHD) and polyethylene low-density (PELD).

The carried out studies have shown that the melting point of used nanofiller have great impact on the properties of obtained composite material. Good dispersion in obtained composites was confirmed using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy with EDS detector. The studies of thermal properties using differential scanning calorimetry (DSC) have shown that silsesquioxane nanofiller functions as crystallization nucleating agent of polymer. In case of PELD matrix nanocomposites, addition of silsesquioxane filler in small amount have caused the increase of T_{95} (temperature where 5% of the sample decomposes) even by 20°C in comparison to matrix alone. The POSS content in polyethylene composite have also had significant impact on the mechanical properties of material, mainly impact and tensile strength; and the largest changes were observed when only 1% w/w of filler was added (Tab. 1).

Table I

Selected mechanical properties of composites PELD/POSS

Filler content % w/w	Tensile strength, MPa					Charpy impact strength, kJ/m ²				
	0%	1%	3%	5%	8%	0%	1%	3%	5%	8%
PELD/POSS1	20.3	21.7	-	19.3	18.3	92.2	101.4	-	97.8	93.8
PELD/POSS2	20.3	22.5	21.4	20.4	18.8	92.2	99.2	96.3	98.8	96.0

Addition of POSS to polyethylene matrix have also improved processing ability of material, which manifests by the increase of mass flow rate (MFR) even three times (Fig. 2). Similar impact, is shown by typical internal lubricants used for enhancing processing properties of polymers.

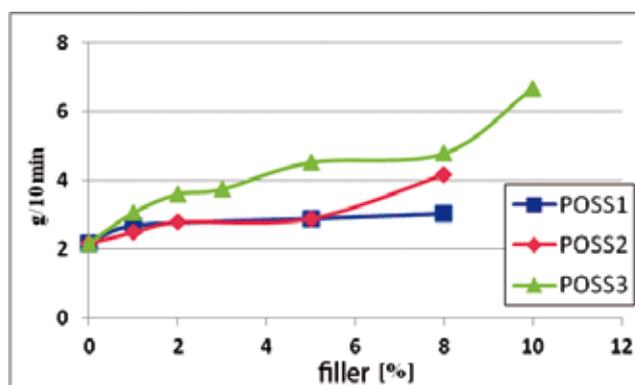


Fig. 3. Impact of PELD/POSS composite composition on MFR value

Bio-composites

In last few decades, the fundamental role in replacing conventional polymer composites in various application is played by composites produced with renewable resource materials. Polymer composites, in which at least one component is biobased or biodegradable, are called biocomposites.

The fundamental benefits from application of biocomposites as alternative material for petroleum-derived products are among others: prevention of an imbalance of supply and demand of products manufactured from non-renewable fossil raw materials [28], sustainable waste management, carbon emission reduction, biodegradability of materials or facilitated recycling process [29, 30].

The polymer composites with plant material content are applied in various fields of economy – especially in automotive industry, where total consumption of plant materials in 2012 in Europe amounted to 80 kt. (Fig. 3) and construction industry. At the same time, the dynamic growth of global biocomposite manufacturing and trade market is observed. This is related not only to increasing demand from industries that are main recipients of these materials, but also due to the fact that application field grows constantly for newly developed and modified (and thus enhanced) materials [29, 31, 32].

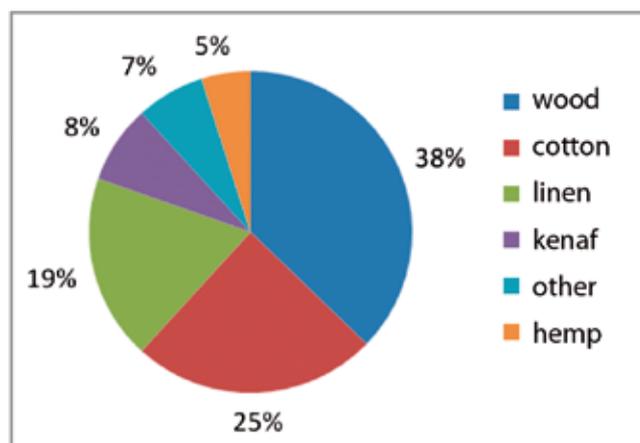


Fig. 4. Consumption of natural fibers for composite production. Data about automotive industry in Europe, 2012 [33]

The extensive research focuses on composites with content of such natural fibers as: kenaf, sisal, jute, flax, hemp, wood flour, ramie, bamboo, cotton fiber or coir [29, 32, 34].

Natural fibers are mostly composed of organic compounds such as cellulose, hemicellulose and lignin. This has fundamental impact on thermal stability of these materials. During manufacturing processes where temperature exceeds 200°C, the thermal degradation of plant materials occurs, what has detrimental impact on material

organoleptic and mechanical properties [35]. Due to that, as the matrix of composites produced with plant material, thermoplastic polymers (PE, PP, PVC, PS) are mostly used as they can be processed in acceptable temperatures. These polymers have also other advantageous properties such as e.g. low viscosity and high mass flow rate [36].

The properties of polymer composites produced with plant materials depends mostly on inter-phase interaction: hydrophobic matrix and hydrophilic filler. The appropriate share of the filler in the matrix is also very important. Very often, it is necessary to use methods, or additives, improving compatibility of composition components [35]. The most commonly used methods include chemical modification, e.g. impregnation of fibers with matrix-compatible polymer [37], graft copolymerisation [38], acetylation, mercerization [39÷41] or physical modification, e.g. corona discharge, thermal and plasma treatment [30]. Such modifications apart from improving adhesion are mostly aimed at limiting water absorption, increasing of dimensional stability and increasing its resistance against environmental factors [42].

In the research conducted by the Division of Chemical Technology and Polymer Chemistry of the Faculty of Chemistry, on development of new type or modification of existing biocomposites thermoplastic materials like PE and PP are mainly used as matrices. These studies are focused on developing composition and characterization of mechanical, rheological and thermal parameters as well as structural analysis of obtained composites with different plant fillers. Additionally, the studies are performed to determine stability of obtained materials subjected to microorganism impact (biodegradation) and natural environment factors, both in outdoor (external) and in simulated, accelerated laboratory tests (tests in xenotest or weatherometer).

The conducted tests of composites filled with wood flour of different type designated as WPC (Wood Polymer Composites) show differences in properties. Differences are determined mainly by the type of used filler, its origin and/or particles size.

The exemplary results in Figure 4 prove that composites containing wood flour Lignocel C-120 and Arbocel C-320, at the share up to 40% does not prove deterioration of mechanical properties. Moreover, application of polyethylene wax as a compatibiliser causes increase of tensile strength of these composites.

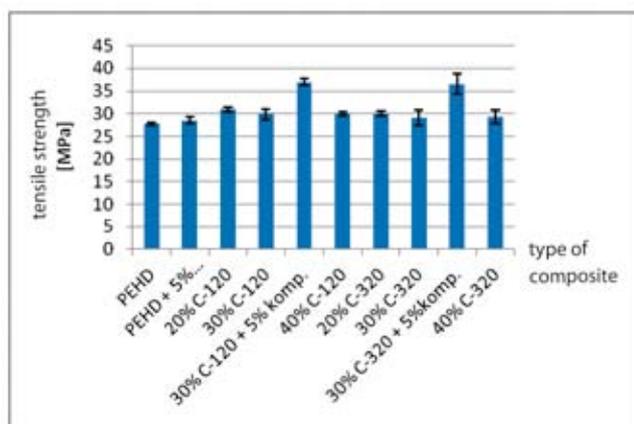


Fig. 5. The comparison of tensile strength for PEHD and selected WPCs of different composition

Summary

The development of new type of polymeric materials and their characteristic allow to expand their application to different fields of industry. Particularly it seems important to search for new competitive fillers (both organic and inorganic), new methods of

fillers modification as well as additives, development of effective technologies for production of uniform composite materials with good or even unique properties. Studies on production and characterization of polyolefinic composites containing different (nano)fillers, both inorganic as well as from renewable plant sources are carried out for many years. The overall description of these works have been presented in this paper.

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