

## POLYMERIAL NANOCOMPOSITIONS

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### Abstract

The constant increase in the production and consumption of polymer materials places increasing demands on improving their processing and utility properties. In this respect, the dynamic development of nanotechnology, a science that deals with behavior, properties, and the creation of structures with dimensions approaching atomic size, is a great help. Polymer nanocomposites are nowadays among the highly developing materials. Significant advances in this area are documented not only by the substantial increase in funding for nanocomposite research, but also by the almost exponential increase in the number of scientific publications and patents observed in recent years.

The result is new nanostructured materials, the building units of which are nanoparticles with defined structure and properties. Today, not only polymer nanocomposites are known, but also metallic and ceramic nanocomposites. While polymeric nanocomposites are gradually being used in industrial practice, metal and ceramic nanocomposites have so far only been prepared under laboratory conditions.

**Keywords:** nanocomposites, nanofillers, polymer, structure, carbon fibers.

### 1 Introduction

The first polymer nanocomposites were prepared under laboratory conditions at the end of the seventies. However, the true history of polymer nanocomposites began in the late 1990s, when Toyota introduced the first applications of polyamide-6 (PA6) and montmorillonite nanocomposites in its cars. According to the generally accepted definition, polymeric nanocomposites are polymeric materials containing a filler having at least one dimension less than 100 nanometers. The term 'nanocomposites' is derived from the Greek word 'nano' (dwarf, very small). In terms of structure, polymer nanocomposites, as well as microcomposites, are divided into layered, fibrous and particulate (Fig. 1) [1,8]

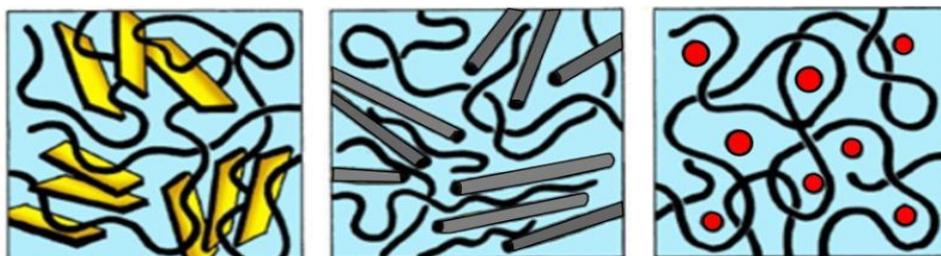


Fig. 1 Polymer nanocomposite distribution [1,8]

### 2 Nanofiller

In this section it is necessary to present in details assumptions and the course of authors' research to such an extent that a reader could repeat those steps to confirm achieved results. In short papers this information should be given as briefly as possible.

A variety of natural and synthetic materials are used as fillers for polymer nanocomposites. In terms of shape, nanofillers are divided into:

- stratified - natural minerals (montmorillonite, talc, hectorite, vermiculite, kaolinite, magadite),
- fibrous - synthetic (carbon nanotubes), natural (halloysite),
- spherical - nanostructured metals (Ag, Al, Ca, Fe, Li, Mg, Ga, Sr) and metal oxides ( $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ).

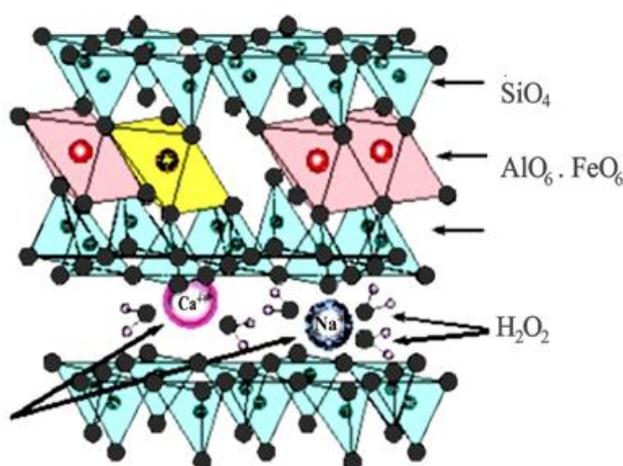
However, the analogy between the shape of particles of micro and nanofills is only apparent. In addition to the dimensions, micro- and nanocomposites differ in many other parameters (Table 1).

**Table 1** Comparison of basic characteristics of micro- and nanofills [1]

Features	Nanofiller	Microfiller
Specific surface ( $\text{m}^2/\text{g}$ )	500-700	5-30
Slenderness ratio (L/d)	500-1000	1-15
Fillers content in the composite (%)	< 5	30-50
Appearance of composites	transparen	opaque

## 2.1 Layered silicates

Layered minerals occur in the form of extremely fine crystals. Their basic structural unit consists of layers (two-network, three-network). From the point of view of industrial use, montmorillonite is the most important of the group of layered silicates (Fig. 2).



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**Fig. 2** Montmorillonite structure diagram [1,9]

The structure of montmorillonite consists of two contiguous nets of central silicon tetrahedrons, between which is located one octahedral node with central aluminum atoms.

Particular interest in montmorillonite stems from the fact that, like other types of layered silicates, it has the ability to expand and absorb large organic molecules into its structure through ion exchange reactions. In addition to increasing the size of the interplanar spaces (from the original approx. 1.6 nm to 2.5 - 4.0 nm), the filler surface character changes from hydrophilic to hydrophobic (organophilic). As modifiers, tertiary and quaternary alkylamines with high carbon numbers ( $\geq 16$ ) are used, but also amino acids, imidazoles, organic silanes and other compounds. Since intercalate intercalations occur during the cation exchange reactions, the expanded mineral structure is referred to as intercalated and organoclay fillers [6,7].

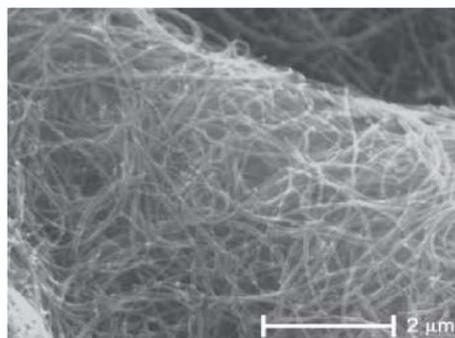
Intercalated nanocomposites are nanocomposites containing a filler, the distance between the individual layers, which is 2 to 3 times higher than the original mineral structure, but the individual layers are not separated from each other.

Exfoliated nanocomposites have individual individual layers [4].

The preparation of the intercalated structure is necessary in the process of preparing polymeric nanocomposites but is not sufficient to achieve a significant improvement in properties. The most important step is to achieve complete separation (exfoliate) of the individual layers and their uniform dispersion in the volume of the polymer matrix. Exfoliated nanocomposites are therefore referred to as polymers containing exfoliated filler [6,7].

## 2.2 Carbon nanotubes

Carbon nanotubes (known as CNT - Carbon NanoTubes) were first prepared in 1991 by Japanese Sumi Iijim. Nanotube walls are created by rolling up a hexagonal graphene layer consisting of carbon atoms (Fig. 3).



*Fig. 3 Carbon nanotubes [7]*

Depending on the method of manufacture, the carbon nanotubes may have one or more walls. Single-walled nanotubes are made up of a single rolled graphene layer, the polyhedron nanotubes (MWNT) consist of a plurality of concentric coaxial graphene rollers inserted into each other. Single-walled nanotubes (SWNTs) differ not only in structure but also in properties (Table 2) compared to multi-walled nanotubes (MWNT).

*Table 2 Comparison of carbon fiber and carbon nanotube properties [1,9]*

<b>C fibers / properties</b>	<b>Tensile modulus (GPa)</b>	<b>Tensile strength (GPa)</b>	<b>Extension (%)</b>	<b>Density [g/cm<sup>3</sup>]</b>
Carbon fibers	270 - 390	2.1	1,5	2,1
Single-wall carbon nanotubes (SWNT)	1000 - 4500	≤ 100	15-23	1,3-1,4
Polystyrene carbon nanotubes (MWNT)	800 -900	≤ 150	-	1,3-1,4

The greatest technological problem in the preparation of polymer nanocomposites is the very poor wettability of carbon nanotubes by the polymer matrix. The functionalization of carbon nanotubes is therefore much more complicated and technologically demanding compared to the modification of carbon fibers. Modification (functionalization) of carbon nanotubes is carried out in a dispersed medium by means of compounds containing functional groups. During functionalization, the modifier adsorbs to the surface of the carbon nanotubes.

Optimally, the modifier will chemically bond to the surface of the carbon nanotubes through weaker Van der Waals bonds or stronger covalent bonds. Since carbon nanotubes are terminated by more reactive fullerene molecules, the attachment of functional groups occurs preferably at their ends [8].

## 3 Properties of polymer nanocomposites

Polymer nanocomposites are characterized by a whole complex of exceptional properties compared to the original polymer matrix. The most important are:

- very good mechanical properties (especially strength, modulus of elasticity, increase of creep resistance),
- very good barrier properties (permeability to gases and air humidity),
- increased heat resistance, increased dimensional stability, non-flammability,
- electrical conductivity,
- transparency, increased scratch resistance.

In addition, polymeric nanocomposites have increased abrasion and scratch resistance, have a smooth surface and are transparent. Their greatest advantage over microcomposites is that the performance is achieved at a substantially lower degree of filling (< 3 - 5 wt.%), i. unlike microcomposites, the density of nanocomposites is virtually the same as the density of the original polymer matrix. A comparison of selected properties of microcomposites and nanocomposites is given in Tab. 3

**Table 3** Comparison of the effect of filler particle size on the mechanical properties of polyamide 6 and montmorillonite composites. Fillers content in the composite = 5 % wt. [1,9]

Composite	Tensile strength (MPa)	Module (GPa)	Tenacity (kJ/m <sup>2</sup> )	Temp. resistance (°C)
Nanocomposite	107	2.6	2.8	145
Mikrocomposite	61	1.0	2.2	89
Original polyamide 6	69	1.1	2.3	65

As in microcomposites, nanocomposites have a decisive influence on the particle size and filler geometry properties. The greater the ratio of filler surface to volume, the greater the effect of the filler on the properties can be expected. In other words, the smaller the particle size of the filler, the greater the improvement in properties can be achieved.

Unlike microcomposites, improving the properties of polymeric nanocomposites is directly related not only to the size, shape, dispersion and orientation of the filler, but also to the size of the surface area.

Due to the extremely high specific surface area (500 - 800 m<sup>2</sup>g<sup>-1</sup>) of nanofillers, the interfacial interface area will increase significantly.

#### 4 Conclusion

Until now, only polymeric nanocomposites based on layered silicates, especially montmorillonite, have been applied (Table 4).

Currently, several types of alkylamine-modified montmorillonites are commercially available not only in the form of powders, but also of concentrates with a polymer matrix in the form of granules.

**Table 4** Anticipated applications of nanofillers [1]

Year	2005	2011
Layered nanofillers	44 %	58 %
Metals, metal oxides	19 %	20 %
Nanoceramics	0	12 %
Carbon nanofibers	0	7%

Polyamide-based nanocomposites are used primarily in the automotive industry, the electrical industry and as packaging materials for food (Table 5).

The first industrial applications of polyamide and montmorillonite-based polymer nanocomposites have already been put into practice by several global automotive companies a few years ago.

**Table 5** Industrial applications of polymeric nanocomposites [1]

Year	2005	2011
Automobile industry	29 %	15 %
Electrotechnical industry	28 %	26 %
Packaging materials for foodstuffs	19 %	28 %
Paints, coatings	14 %	14 %
other	10 %	17 %

Nanocomposites based on polypropylene and polyethylene terephthalate gradually find their application in the food industry as packaging materials for food and beverage bottles, because they have substantially lower gas and water vapor permeability compared to the original polymers.

From an environmental point of view, the possibility of using material recycling, which is not suitable for multilayer polymeric packaging materials currently used, is an undeniable advantage.

Potential applications of polymer nanocomposites based on carbon nanotubes are mainly in the electrical industry and medicine, where it is expected to use their very good electrical and mechanical properties.

Under laboratory conditions, carbon nanotubes have been successfully used to improve the properties of not only fibrous and particulate polymer composites, but also polymer blends.

The use of polymer nanocomposites based on carbon nanotubes has so far been limited not only because of their high cost, but also because of the technological problems associated with the preparation of this type of nanocomposite.

Applications of polymer nanocomposites based on nanostructured metals are envisaged especially in medicine (eg biosensors, prolonged-action drugs) and electrical engineering.

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