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FEATURE ARTICLE

Polymer nanocomposites: structure, interaction, and functionality

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This feature article discusses the main factors determining the properties of polymer nanocomposites with special attention paid to structure and interactions. Usually more complicated structure develops in nanocomposites than in traditional particulate filled polymers, and that is especially valid for composites prepared from plate-like nanofillers. Besides the usually assumed exfoliated/intercalated morphology, i.e. individual platelets and tactoids, such nanocomposites often contain large particles, and a network structure developing at large extent of exfoliation. Aggregation and orientation are the most important structural phenomena in nanotube or nanofiber reinforced composites, and aggregation is a major problem also in composites prepared with spherical particles. The surface characteristics of nanofillers and interactions are rarely determined or known; the related problems are discussed in the paper in detail. The surface of these reinforcements is modified practically always. The goal of the modification is to improve dispersion and/or adhesion in nanotube and spherical particle reinforced composites, and to help exfoliation in nanocomposites containing platelets. However, modification decreases surface energy often leading to decreased interaction with the matrix. Very limited information exists about interphase formation and the properties of the interphase in nanocomposites, although they must influence properties considerably. The properties of nanocomposites are usually far from the expectations, the main reason being insufficient homogeneity, undefined structure and improper adhesion. In spite of considerable difficulties nanocomposites have great potentials especially in functional applications. Several nanocomposite products are already used in industrial practice demonstrated by a few examples in the article.

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1. Introduction

The general idea of polymer nanocomposites is based on the concept of creating a very large interface between the nano-sized heterogeneities and the polymer matrix. This large interface and the corresponding interphase are supposed to result in exceptional properties not possible to reach with traditional



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particulate filled polymers. Advantages offered by nanocomposites are claimed to be large reinforcement at very small nanoparticle content, but functional properties like decreased flammability or increased conductivity are often mentioned as well. Unfortunately nanocomposites often do not meet the expectations, they possess much worse properties than expected, not exceeding much those of traditional microcomposites. The main reason for the inferior properties is that the basic idea of nanocomposites is often not fulfilled; the large interface cannot be created. The main problems arise mostly from the fact that the homogeneous distribution of the particles in the polymer matrix is extremely difficult to achieve, the structure is not controlled or even known, and interfacial interactions are undefined. The limited degree of exfoliation, *i.e.* the number of individual platelets produced, is a major problem in composites containing plate-like reinforcement that leads to the formation of a complicated structure with several structural units. Aggregation is very difficult to avoid in composites containing fibers, tubes or spherical particles. Even more surprising is that compared to the basic idea behind nanocomposites, interfacial interactions are treated rather superficially, and the available information is limited and very often contradictory.

Nanocomposites can be classified in many ways; in this article we discuss them according to the dimensionality of the nanosized heterogeneity. The size is in the nanometre range in all three dimensions for particles like silica (SiO₂), TiO₂, calcium carbonate (CaCO₃) or polyhedral oligomeric silsesquioxane (POSS). Nanotubes and fibers (carbon nanotubes, CNTs; halloysite) are small in two dimensions, but can be micrometre long, while the individual platelets of layered minerals (montmorillonite, MMT; layered double hydroxide, LDH) are approximately 1 nm thick, but their other two dimensions are usually much larger. Unlike many others, we assume that in spite of particular differences, the general rules of heterogeneous materials apply also for nanocomposites and their properties are determined by the same four factors, *i.e.* component properties, composition, structure and interactions. The properties of both

the matrix and the filler or reinforcement influence composite properties strongly. Larger reinforcement is achieved in a soft matrix than in a stiff polymer, while particle size, size distribution, aspect ratio, specific surface area and surface energy are the most important particle characteristics to be considered. All properties depend on composition and amount of filler added to the polymer. Several structure related phenomena must be considered in nanocomposites, aggregation and orientation of anisotropic particles may occur in all systems, but the structure is much more complex in the case of layered reinforcements. Interactions can be divided into matrix/particle and particle/particle interactions, but they are more complex again in layered silicate or double hydroxide composites because of the presence of surfactants, coupling agents and occasionally other additives. Because of their increased importance in nanocomposites we focus our attention mainly on structure and interfacial interactions. The structure is not characterized properly in a large number of publications, *e.g.* the formation of an intercalated/exfoliated structure is claimed in layered mineral nanocomposites without defining the extent of exfoliation or looking for other structural units. Similarly, interactions are treated in very general terms using expressions like compatibility, miscibility, hydrophobicity, polarity, *etc.*¹⁻⁶ without their definition or quantitative characterization. In our opinion the use of such terms and much of the information published in the literature are misleading thus we discuss them in detail in several sections. We also mention some factors, which are largely neglected during the discussion of nanocomposite preparation, structure and properties. Our views occasionally do not agree with generally accepted beliefs, but we find it important to point out contradictions, to raise doubt, and call attention to questions, which are neglected or not studied in sufficient detail.

2. Nanocomposite structure

The homogeneous distribution of nanoparticles in the polymer matrix is the primary condition of the production of nanocomposites with acceptable properties. Parallel alignment of the reinforcement with the external load as well as good adhesion are further conditions to be met, if the particles are anisotropic (layered silicates, nanotubes) and the composite is used in load-bearing application. Moreover, extensive exfoliation is needed in the case of plate-like reinforcements,⁷⁻¹¹ *i.e.* layered silicate nanocomposites, layered double hydroxides (LDH) or graphene, which is often difficult to achieve. The complexity of structure and the factors determining it change from one nanocomposite to the other, thus the structure is discussed according to the type of reinforcement.

2.1. Plates

The structure of nanocomposites containing plate-like reinforcements (MMT, LDH) differs in two aspects from that prepared with the other two reinforcements discussed here, *i.e.* nanotubes and fibers, and spherical nanocomposites. In order to prepare composites reinforced with plates, the original particles must be exfoliated, separated into individual layers. These composites also may contain several structural entities with different dimensions thus the structure must be considered and



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(particulate filled and short fiber reinforced polymers, blends, nanocomposites), bio-related and biodegradable materials (starch, wood, cellulose acetate, PLA), crystallization, melting and morphology, as well as degradation and stabilization of polymers.

studied in a very wide length scale from the nanometre range to microns. In spite of differences in the chemical structure and consequently the surfactant used, the questions and problems of MMT and LDH composites are very similar and we treat them alike. However, the study of LDH composites has started more recently and less information has been accumulated on them yet, thus most examples are presented on polymer/MMT nanocomposites.

Particle structure. The existence of original particles, *i.e.* large clay entities in the dimension of the original filler added to the polymer, is hardly ever mentioned in studies on nanocomposites.^{12–23} One may deduce from this fact that particles are not present in the composites, *i.e.* they break down to smaller units, into intercalated stacks or into individual platelets during mixing. This is not very surprising since mostly X-ray diffraction (XRD) measurements and transmission electron microscopy (TEM) are used for the characterization of the composites and those do not necessarily detect the presence of large particles. The lower 2θ range of the XRD trace of two polypropylene (PP) composites is presented in Fig. 1. Exfoliation does not take place in the composite containing only organically modified silicate (OMMT). It is dispersed in the matrix as large particles, shown also by the presence of the silicate reflection in the XRD trace (trace a). Exfoliation is facilitated by a coupling agent, maleic anhydride grafted PP (MAPP) in the other composite. The incorporation of 25 vol% MAPP leads to the complete disappearance of the silicate peak (trace b). Based on these results one could claim that the original particles disappeared and the silicate is completely exfoliated.^{10,24–26} However, XRD detects only ordered clay structures,²⁷ and scanning electron microscopy (SEM) done on the etched surfaces of PP/OMMT (Fig. 2a) and PP/OMMT/MAPP (Fig. 2b) composites shows the distinct particulate structure in both cases. Large particles are present in the PP/OMMT composite not containing any functionalized polymer, while the number of large particles decreases drastically on the incorporation of MAPP. A very large amount of smaller particles appears together with one or two larger ones in the 5 to 10 μm range in this composite. As a consequence, we can conclude that in spite of the absence of the silicate reflection in

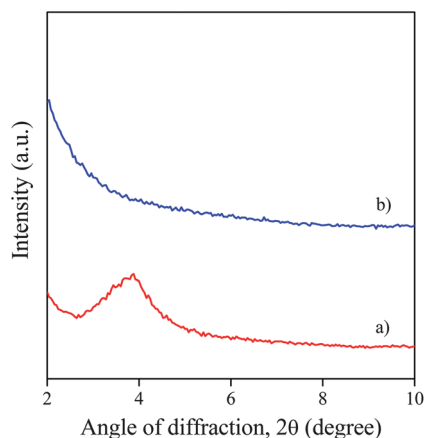


Fig. 1 XRD traces of PP nanocomposites containing 2 vol% silicate (Nanofil 848): (a) PP/OMMT and (b) PP/OMMT/MAPP (25 vol%).

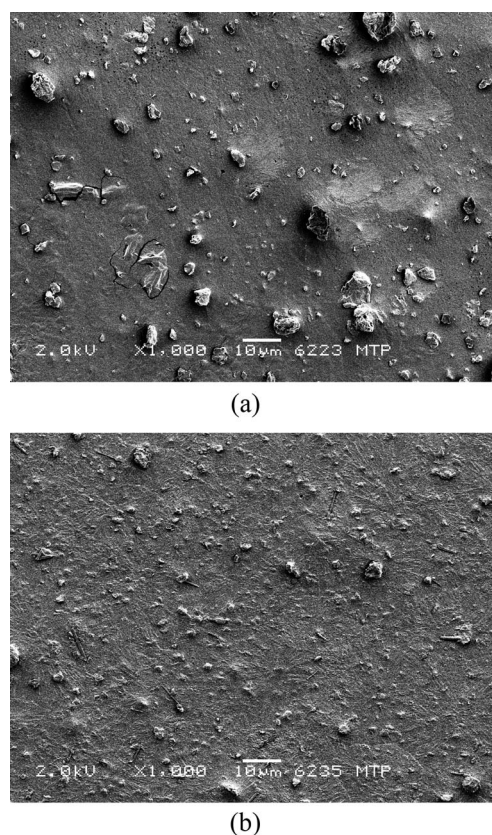


Fig. 2 SEM micrographs taken from the etched surface of PP nanocomposites containing 2 vol% organically modified clay: (a) PP/OMMT and (b) PP/OMMT/MAPP (25 vol%).

the corresponding XRD pattern (Fig. 1, trace b), complete exfoliation has not been achieved, and clay particles in the length scale of microns are also present in the composite. Their amount and size must influence strongly all properties. A similar observation was made by Luduena *et al.*¹⁶ in polycaprolactone/OMMT and Costa *et al.*²⁸ in LDPE/LDH composites.

Gallery structure. The gallery structure of layered minerals is routinely determined by XRD both before compounding and in the composites. The number of reflections and layer distance are determined by the type and amount of surfactant used for modification. The gallery distance is inversely proportional to the position of the silicate reflection recorded at low 2θ angles. Surface modification and the characteristics of the gallery structure are compiled in Table 1 for selected layered minerals. XRD traces are presented in Fig. 3 for five silicates. Large differences can be observed in the number, shape, intensity and location of the silicate reflection. Sodium montmorillonite produces a low intensity reflection at a large 2θ angle (trace a). The position of this peak depends on the water content of the clay, which is usually considerable. The high intensity peak detected at a low 2θ angle for Nanofil 948 as well as the two smaller interference peaks indicate the large gallery distance and a high degree of regularity for this silicate (trace d). Interestingly, Cloisite 20A was modified with the same surfactant, but its XRD pattern differs significantly (see trace c) from that of Nanofil 948. Obviously, besides the type of the surfactant its amount also

Table 1 Surface modification, gallery structure and the dispersion component of surface tension for selected commercial organically modified layered minerals, and two laboratory products modified with *N*-cetyl-pyridinium chloride (CPCIMMT) or trihexyl-tetradecyl-phosphonium chloride (PhoMMT), respectively

Name	Surfactant		Gallery structure			Surface tension, $\gamma_s^d/\text{mJ m}^{-2}$
	Composition	Amount (wt%)	No of peaks	Position, 2θ	Distance/nm	
NaMMT	—	0	1	9.0	1.0	257
CPCIMMT	$\text{C}_6\text{H}_5\text{N}^+(\text{CH}_2)_{15}\text{CH}_3\text{Cl}^-$	22	1	5.0	1.8	32
PhoMMT	$[\text{CH}_3(\text{CH}_2)_{13}]_3\text{P}^+[\text{CH}_3(\text{CH}_2)_5]_3\text{Cl}^-$	27	2	3.8	2.3	38
Nanofil 784	$\text{NH}_2(\text{CH}_2)_{11}\text{COOH}$	20	1	5.2	1.7	48
Nanofil 804	$\text{CH}_3(\text{CH}_2)_{17}\text{NH}^+(\text{C}_2\text{H}_4\text{OH})_2\text{Cl}^-$	30	1	4.9	1.8	36
Nanofil 848	$\text{CH}_3(\text{CH}_2)_{17}\text{NH}_2$	25	1	4.9	1.8	35
Nanofil 919	$\text{CH}_3(\text{CH}_2)_{17}\text{N}^+(\text{CH}_3)_2\text{C}_6\text{H}_5\text{Cl}^-$	35	1	4.4	2.0	32
Nanofil 948	$[\text{CH}_3(\text{CH}_2)_{17}]_2\text{N}^+(\text{CH}_3)_2\text{Cl}^-$	45	3	2.5	3.5	31
Cloisite 20A	$[\text{CH}_3(\text{CH}_2)_{13-17}]_2\text{N}^+(\text{CH}_3)_2\text{Cl}^-$	38	2	3.3	2.7	33
Sorbacid 911NT	—	0	1	11.6	0.8	79
Sorbacid 911T	$\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$	2–4	1	11.6	0.8	26

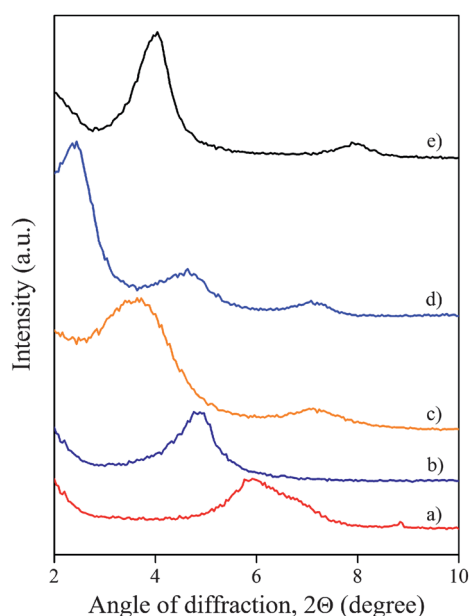


Fig. 3 XRD traces of five silicates: (a) NaMMT, (b) Nanofil 848 (stearyl-amine), (c) Cloisite 20A (distearyl-dimethyl-ammonium chloride), (d) Nanofil 948 (distearyl-dimethyl-ammonium chloride), and (e) PhoMMT (trihexyl-tetradecyl-phosphonium chloride).

influences the gallery structure (see Table 1). The gallery distance of the clay organophilized with stearyl amine is smaller than that of the other two OMMTs indicating a different arrangement of this surfactant in the galleries (trace b). Trace (e) was recorded on a silicate modified with a phosphonium salt. It is very similar to trace (c), although the type and amount of surfactant used for modification are completely different. Although XRD offers valuable information about the gallery structure of layered minerals including graphene, additional information is needed for complete characterization.

Several studies were carried out to investigate the effect of the type and amount of the surfactant on the gallery structure of layered minerals.^{10,29–31} Possible arrangements were shown already by Lagaly^{32,33} and they were confirmed by recent studies.³⁴ The orientation of the surfactant depends mainly on

the ion density of the clay, which is relatively small for MMT,^{33,35,36} and on the type and amount of surfactant used. In montmorillonite usually two surfactant molecules lay parallel to the surface. XRD shows the larger gallery distance when two aliphatic chains are attached to the nitrogen atom of the ammonium salt used as surfactant (see Fig. 3 and Table 1). One of the chains is assumed to be oriented at an angle to the surface in this case. The tilted orientation of the surfactant molecule and larger gallery distance should lead to easier intercalation and exfoliation of this clay in most polymer matrices.

Several groups studied the effect of the chemical structure of the surfactant on exfoliation, composite structure and properties. Reichert *et al.*¹⁰ found in PP/OMMT composites containing also a MAPP coupling agent that large extent of exfoliation cannot be achieved if the length of the aliphatic chain is equal or less than 8; better dispersion was obtained at chain lengths of 12–18 carbon atoms. In PA nanocomposites Fornes and Paul²⁹ showed that surfactants with two long tails are less advantageous than those having a single aliphatic chain attached to the nitrogen atom, smaller head groups lead to increased exfoliation compared to large ammonium cations, and excess surfactant is disadvantageous for exfoliation, structure development and properties. They obtained similar results also in thermoplastic polyurethane matrices.³⁰ Contrary to Fornes and Paul,²⁹ Vaia and Giannelis³¹ found in PS nanocomposites that head groups do not influence intercalation and two long aliphatic chains are more advantageous than one. These apparent contradictions obviously originate from the complex structure of the nanocomposites usually not characterized sufficiently, the insufficient information available and/or supplied (ion exchange capacity of the clay, the amount of surfactant used, its composition, orientation, *etc.*) and from the dissimilar polymers, processing/preparation conditions and characterization methods. These contradictions clearly prove that unambiguous, general correlations have not been established yet among the gallery structure of the silicate, interactions and composite properties.

Exfoliation, platelets. Exfoliation is usually studied by TEM, which is able to detect also individual mineral layers.³⁷ Very few publications present micrographs in which only individual layers are dispersed in the polymer for any matrix and especially for



Fig. 4 TEM micrograph taken from a PP/OMMT/MAPP nanocomposite. Composition: 3 vol% silicate, 20 vol% MAPP.

polyolefins. Usually, intercalated stacks or tactoids with a range of gallery distances form in the composites and such tactoids appear in the micrographs. “Very good” composites with a high



Fig. 5 TEM micrograph showing the peeling off layers from a silicate particle in a PP nanocomposite, changing gallery distance and varying extent of intercalation. Composition: 0.5 vol% silicate, 60 vol% MAPP.

degree of dispersion may contain stacks of silicates with 3 to 10 layers,^{29,38,39} but even this can be achieved only with the proper selection of components and processing conditions. A variety of structural units were detected in PP/OMMT composites. SEM micrographs taken at relatively low magnification proved the presence of larger particles (see Fig. 2). A large tactoid with varying degrees of intercalation is shown in the TEM micrograph of Fig. 4 in a PP/OMMT/MAPP composite. Very large and compact clay particles and individual layers (see bottom of Fig. 4) were also found in the same composite at 3 vol% silicate and 20 vol% MAPP content. A particle is shown in Fig. 5 in the process of intercalation and complete exfoliation at a different composition (0.5 vol% silicate and 60 vol% MAPP). The number of individual layers is also much larger in this micrograph than in Fig. 4. The observed structure, the number of individual platelets and the threshold concentrations for silicate network formation all depend on the amount of MAPP present.⁴⁰ The micrograph indicates that intercalation and exfoliation proceeds simultaneously in the investigated nanocomposites. The structure observed in TEM micrographs obviously depends on the composition (silicate, MAPP), and also on sampling, *i.e.* on the choice of location from which the slice was taken. The evidence presented above proves that a wide range of structural units may be present in PP/silicate, and also in other composites. Similar structures were detected, for example in polyamide/montmorillonite (PA/MMT) composites as well.⁴¹

Network structure. Silicate platelets may interact with each other; face-to-face interaction leads to aggregation, while edge-to-face orientation results in the formation of a network structure. Both phenomena have been observed also in polymer composites.^{10,42,43} The silicate network is usually detected by TEM^{10,44,45} or by the analysis of the linear viscoelastic properties of nanocomposite melts.^{12,24,46} The increase of complex viscosity or G' and/or the appearance of a yield stress in the low frequency range of the spectrum are usually interpreted as network formation.⁴⁷ Moussaif and Groeninckx,⁴⁸ for example, observed a considerable increase of storage modulus with increasing intercalation and/or exfoliation in the low frequency range in poly(vinylidene fluoride)/clay/poly(methyl methacrylate) (PVDF/clay/PMMA) composites and explained the phenomenon with the formation of a silicate network.

A large extent of exfoliation occurs at very small silicate and large MAPP content, and occasionally overlapping of the silicate layers may be observed as a result as shown in Fig. 6. Rheology supplies further proof for network formation. The plotting of the two components of dynamic viscoelastic characteristics against each other, *i.e.* G' vs. G' or η'' vs. η' , yields an arc-shaped curve, if the process can be described with a single relaxation time (Cole–Cole plot).^{49,50} Since a network obviously deforms with different relaxation times than the homogeneous melt, we expect a correlation deviating from a semicircle thus Cole–Cole plots are very convenient for the detection of network formation. The Cole–Cole plots of composites containing 2 vol% silicate and various amounts of MAPP are shown in Fig. 7. The deviation from a skewed semicircle is clearly visible at large MAPP contents. The change in the shape of the plots, which depends on MAPP and silicate content, indicates the appearance of a new relaxation process, probably the formation of the silicate network. The

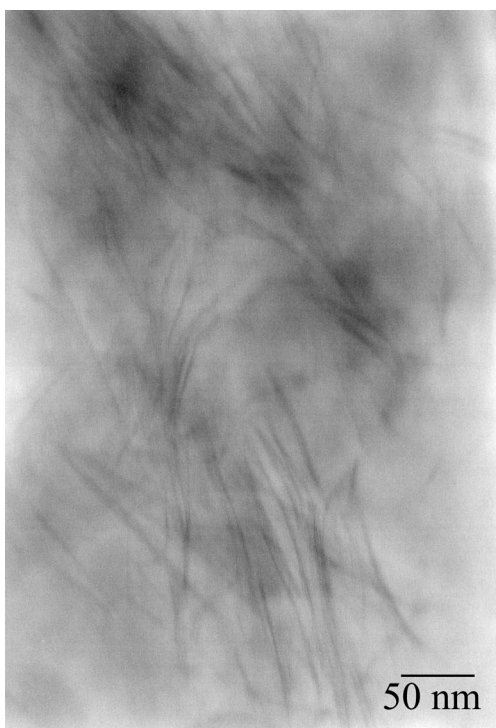


Fig. 6 Interaction of silicate layers in a PP nanocomposite at small clay (0.5 vol%) and large (60 vol%) MAPP content; possible network formation of the silicate sheets.

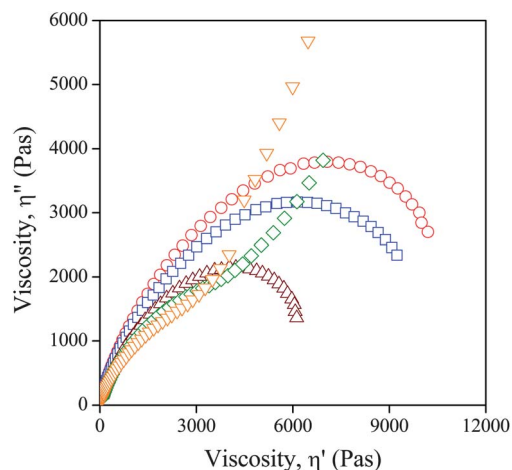


Fig. 7 Cole-Cole plots obtained for PP/OMMT/MAPP nanocomposites at 2.0 vol% clay and various MAPP contents. Symbols: (○) 0, (□) 5, (△) 15, (◇) 25, and (▽) 40 vol% MAPP.

probability of network formation increases with increasing extent of exfoliation. Although TEM, XRD and rheology supply the same qualitative information about structural changes in polymer/layered silicate composites, the quantitative determination of the relative amount of the various structural elements is very difficult with all three of them.^{40,51}

We must also call attention here to the application of various methods for the characterization of the nanocomposite structure. TEM and XRD are used routinely for this purpose, but as shown by the examples presented in previous paragraphs, these two

methods offer information only about certain aspects of the structure. TEM can be used to detect the presence of individual platelets or tactoids, but it does not supply a full picture about the gallery structure or the presence of large particles. SEM must be always used for this latter purpose. XRD characterizes the gallery structure, but not exfoliation, platelets, tactoids or the silicate network. Rheology is the best method for the detection of this latter structural formation, but TEM may be applied as a supporting technique. Only the simultaneous use of several techniques can reveal the complexity of the nanocomposite structure.

2.2. Nanotubes and fibers

Nanotubes and nanofibers have two dimensions in the nanometre range; they are usually micrometre or even millimetre long. They attracted interest mainly because of their exceptional mechanical⁵² and electrical properties.⁵³ Theoretical and experimental investigations proved that carbon nanotubes (CNTs) have Young's modulus in the range of 1.2 TPa, but they are also flexible.⁵⁴ The extremely high stiffness would make these materials ideal reinforcements for composites. Unfortunately, although the fibers have large aspect ratio, the other two conditions of efficient reinforcement, *i.e.* alignment parallel to the direction of the load and good stress transfer, are difficult to satisfy.

Dispersion. The properties of polymer/CNT composites depend on many factors including the technology of preparation and purification, the type and amount of residual contaminations, the structure of the nanotube (single or multiwall), diameter, the length and aspect ratio of the tubes, as well as their association or aggregation (individual tubes, bundles). Numerous methods are used for the preparation of polymer/CNT composites and their main goal is practically always the achievement of homogeneous dispersion. Solvent assisted techniques have several advantages including small scale and efficiency. The nanotubes are first dispersed in the solvent and then the solution of the polymer is added. Unfortunately good dispersion is difficult to achieve even at low CNT content especially for single wall nanotubes. Dispersion is aided by stirring, the use of surfactants, other surface modification techniques including functionalization, and ultrasound assisted homogenization. Although ultrasound efficiently improves dispersion, considerable fiber attrition takes place; the length of the tubes was found to be inversely proportional to the time of ultrasound treatment.⁵⁵ After achieving the necessary dispersion, the polymer is either precipitated from the mixture or a film is cast. *In situ* polymerization is another, but probably not the most convenient method for the preparation of homogeneous CNT composites. First the nanotubes are dispersed in the monomer followed by polymerization. Functionalization of the tubes improves dispersion also in this case. The initiator or catalyst is often deposited onto the surface of the nanotubes before polymerization. Epoxy/CNT nanocomposites are often produced by this approach.^{56,57}

Homogenization by melt mixing is one of the most frequently used techniques for the preparation of CNT composites. The approach has the advantage of using traditional plastic processing technology and equipment, but requires relatively large amounts of material. The technique proved to be generally less efficient than the solvent assisted method and it can be used only at low

nanotube content, since the viscosity of the polymer increases significantly with increasing CNT concentration. The approach was used for the production of composites from polycarbonate (PC),⁵⁸ PA6,⁵⁹ PP⁶⁰ and from several other polymers.^{61,62} Processing technology must be optimized to achieve acceptable dispersion of the nanotubes in the polymer matrix. This is clearly proved by the study of Pegel *et al.*⁶³ who produced PC/CNT nanocomposites using a microcompounder. They found that after 15 min mixing time at 50 rpm, homogeneity characterized by TEM was much better at 250 °C than at 300 °C (see Fig. 8a and b). Further processing experiments showed that the homogeneity of the composites is determined by the relative extent of agglomerate formation and destruction, which depends on the intensity of shearing. However, the possibility to increase shear forces is limited since fiber attrition or even the degradation of the polymer may take place at very large shear rates. The influence of small scale mixing conditions on CNT dispersion was studied extensively by Pötschke *et al.* in PC,⁶⁴ PA⁶⁵ and PLA matrices.⁶²

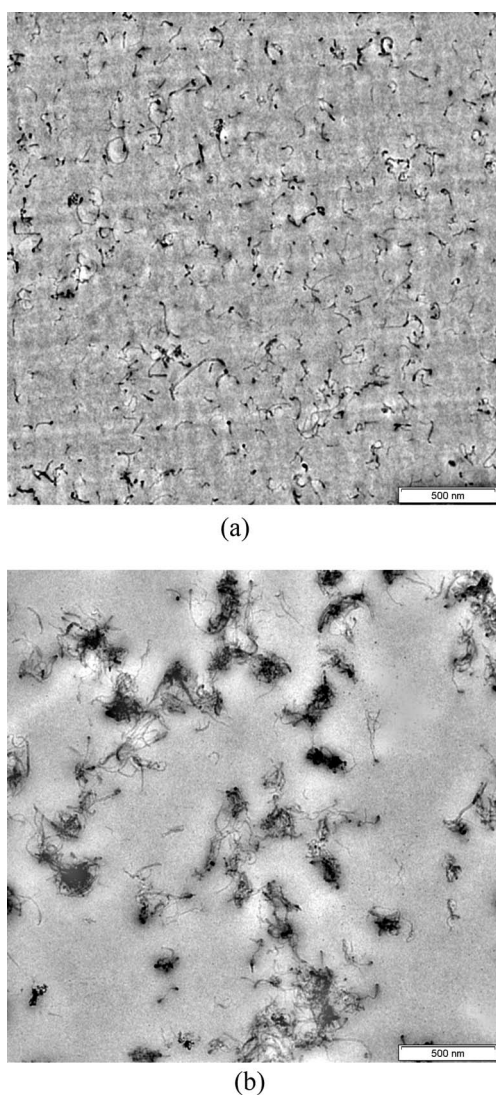


Fig. 8 Aggregation in PC/CNT nanocomposites; effect of processing conditions on dispersion at the rotor speed of 50 rpm. (a) 250 °C and (b) 300 °C.

Orientation. Because of the inherent stiffness of carbon nanotubes,⁶⁶ their use as reinforcement in polymers seems to be obvious, but a large extent of orientation is very difficult to achieve. Orientation of the tubes was attempted in various ways. Raravikar *et al.*⁶⁷ and Feng *et al.*⁶⁸ preoriented the fibers before polymerization to produce PMMA and polyaniline nanocomposites, respectively. In the case of PMMA composites the nanotubes were impregnated with the monomer and then the composite was prepared by *in situ* polymerization, during which the orientation of the tubes did not change significantly. Polymerization can be carried out also in a magnetic field which orientates the tubes into the desired direction. The extent of orientation is influenced significantly by the viscosity of the suspension in this case. The discontinuous technology and the non-conventional method make these techniques rather cumbersome and disadvantageous. More attempts are made to orientate the fibers during processing or by stretching the extruded product,⁶⁹ by fiber spinning from the melt⁷⁰ or by electrospinning.⁷¹ The largest extent of orientation is achieved by the last two methods. Nevertheless, the orientation and dispersion of carbon nanotubes remain the main obstacles before using them routinely as reinforcements in polymer composites. These difficulties are demonstrated well by Table 2 presenting the stiffness of various CNT composites. The increase in modulus is very moderate in most matrices and some of the results seem to be quite strange (7.7 GPa stiffness for TPU⁷² and 0.4 GPa for PA6).⁵⁹

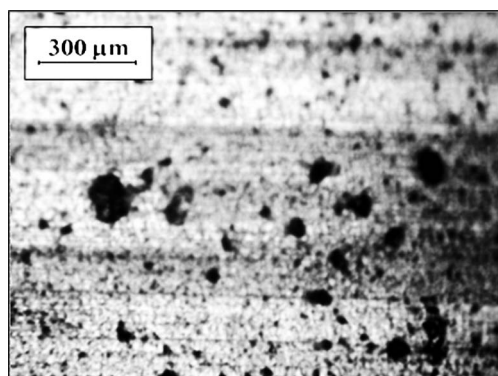
2.3. Spherical nanoparticles

Numerous attempts have been made to distribute spherical nanoparticles in a polymer matrix with the most different methods, since aggregation is the major issue in these composites. The most frequently used approach is the use of traditional thermoplastic or thermoset technologies to homogenize the previously prepared particles into the matrix polymer. Carbon black, precipitated calcium carbonate and silica are the most often used representatives of this class of materials. Interaction and its control is the key to success in the application of these materials, but particle–particle interactions are usually more important than polymer–filler adhesion. It has been shown earlier that the occurrence and extent of aggregation depend on the relative magnitude of adhesion and separating forces.⁷⁶ The ratio of the two forces depends on interfacial adhesion, shear forces and the size of the particles. The aggregation tendency of fillers increases strongly with decreasing particle size. Shear forces can be changed in a limited range thus the main factor to control aggregation is the surface characteristics of the filler. Various treatments and modification techniques are used to control them, like the surface grafting of the silica,^{77,78} but aggregation can be rarely avoided. Aggregation and the importance of controlling surface characteristics are demonstrated by Fig. 9. Unmodified CaCO₃ particles of about 80 nm size form well defined large aggregates in PP, while the size, amount and density of aggregates are much smaller in the composite containing a surface modified filler with approximately the same size.

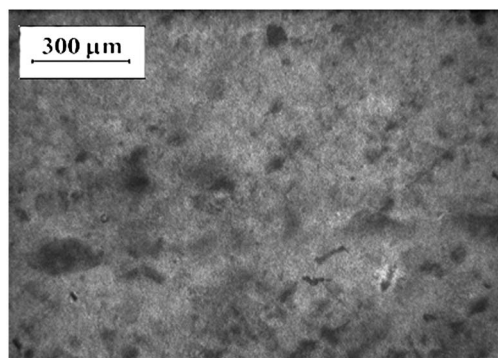
The simultaneous formation of the particles and the polymer matrix, usually in sol–gel technology, seems to have much larger potential. The interest in organic–inorganic hybrids dates back to the 80's and several reviews are available in this field

Table 2 Mechanical properties of selected polymer/carbon nanotube composites at 0.5 wt% CNT content

Composite				
Matrix	Reinforcement	Stiffness/GPa	Tensile strength/MPa	Ref.
Epoxy	—	2.60 ± 0.08	63.8 ± 1.1	73
Epoxy	Carbon black	2.83 ± 0.06	65.3 ± 0.8	73
Epoxy	DWCNT	2.79 ± 0.03	67.7 ± 0.5	73
Epoxy	DWCNT-NH ₂	2.98 ± 0.02	69.1 ± 0.2	73
Epoxy	MWCNT	2.61 ± 0.01	61.5 ± 0.2	73
Epoxy	MWCNT-NH ₂	2.82 ± 0.02	64.3 ± 0.3	73
TPU	—	7.70 ± 1.00	12.4 ± 4.5	72
TPU	SWCNT	14.50 ± 3.40	13.3 ± 4.0	72
PA6	—	0.40 ± 0.04	—	59
PA6	MWCNT	0.77 ± 0.05	—	59
PP	—	0.86	30.8	74
PP	Carbon black	0.89	35.9	74
PP	SWCNT	1.10	32.3	74
PE	—	0.81 ± 0.05	34.1 ± 4.9	75
PE	SWCNT	0.64 ± 0.08	28.9 ± 2.1	75
PE	PE grafted SWCNT	0.80 ± 0.04	33.3 ± 2.5	75
PC	—	1.48 ± 0.04	41.4 ± 1.3	75
PC	MWCNT	1.31 ± 0.07	33.3 ± 1.8	75
PC	Compatibilized MWCNT	2.16 ± 0.07	61.0 ± 2.5	75



(a)



(b)

Fig. 9 Various degrees of aggregation in PP/CaCO₃ composites detected by optical microscopy. (a) Uncoated filler, 20 vol% and (b) coated filler, 25 vol%.

summarizing the technical possibilities, structure, properties and potential applications of these materials.^{79–81} Usually silicate chemistry is used to produce particles of different sizes⁸² or

organic–inorganic networks.⁸³ The size of the particles can be changed from 10 to 500 nm by modifying the conditions of the polymerization, hydrolysis and condensation of the silica precursors.⁸² The homogeneity of the composite is much better in these materials, although depending on chemistry aggregates can form even in this case.⁸²

3. Surface characteristics and interactions

Nanocomposites are expected to have very large interfaces, which are supposed to generate their exceptional properties. The specific surface area of totally exfoliated montmorillonite, for example, is around 750 m² g⁻¹ (ref. 1,84 and 85) and that of graphene was reported to be even larger.¹¹ Limited information is published regarding the surface characteristics of nanofillers, although they are very important since they determine all interactions in the composite, as well as its structure and properties.

3.1. Surface characteristics

With a few exceptions, organically modified silicates are used practically always for the preparation of nanocomposites. Organophilization modifies the surface energy of the silicate drastically. The majority of papers published regarding polymer/layered silicate nanocomposites containing an organically modified silicate claim that surface modification renders the hydrophilic silicate hydrophobic, decreases its polarity, facilitates intercalation and exfoliation, improves wetting and the compatibility of the phases, and results in advantageous properties.^{1,2,10,86} Unfortunately, this explanation does not agree with the fact that nanocomposites cannot be prepared from organically modified silicates and PP without an additional compatibilizer, although both are apolar and hydrophobic.^{10,25,87} Moreover, apart from nanocomposites prepared from polyamide, the properties of most polymer/layered silicate nanocomposites are relatively poor, but they definitely do not

reach the expected values or those predicted on the basis of the principles mentioned above (extensive exfoliation, large interfaces).^{1,9}

It is completely true that the treatment of silicates renders them hydrophobic and decreases their polarity. However, the claim that decreased polarity leads to better compatibility and wetting is not true. Organophilization decreases the surface energy of the silicates leading to the decrease of the strength of interaction between the filler and the polymer.⁸⁸ The interaction of the reinforcement and the polymer, both for neat and organically modified silicates, is an adsorption process. The strength of adsorption can be characterized by the reversible work of adhesion,^{89,90} which considerably decreases upon treatment with an organic substance. Strong polarity of the neat silicate helps adsorption and increases the strength of interaction, while organophilization has the opposite effect. Similarly, the wetting of silicates by polymers is also claimed to improve upon organophilization. Wettability is usually characterized by the thermodynamic quantity

$$S_{mf} = \gamma_f - \gamma_m - \gamma_{mf} \quad (1)$$

where γ_f and γ_m are the surface tension of the filler and the matrix polymer, respectively, γ_{mf} is the interfacial tension and $\gamma_f > \gamma_m$. Accordingly, wettability decreases on organophilization due to the drastic decrease of the surface tension of the filler. In PP/MMT composites the value of S_{mf} is around 160 mJ m^{-2} for neat NaMMT, which decreases to 15 mJ m^{-2} at 100% surface coverage with a long chain aliphatic surfactant.³⁴

The orientation of surfactant molecules influences the distance of the galleries, but the amount used for organophilization and being present in different forms (ionically bonded or attached by dipole interactions) in the galleries is also important in the determination of surface characteristics and behavior. The amount used for surface modification covers a relatively wide range from 20 to 45 wt% corresponding to surface coverages of 90–120% (see Table 1). The analysis of several commercial silicates indicates that they are usually coated near to 100% of their ion exchange capacity leading to monolayer coverage. Inverse gas chromatography (IGC) is frequently used for the surface characterization of particulate fillers^{91–96} and also silicates.⁹⁷ The surface energy of neat NaMMT was found to be quite large, around 260 mJ m^{-2} was measured for its dispersion component at 100°C . Helmy *et al.*⁹⁸ determined a somewhat smaller value (205 mJ m^{-2}) for total surface energy, which is somewhat surprising. The coating of the high energy surface of the silicate with organic compounds, *i.e.* surfactants, leads to the decrease of surface tension.^{99–102} The correlation of surface tension and coverage is plotted in Fig. 10 for a series of silicates. Similar values obtained on calcium carbonate (CaCO_3) are presented for comparison. The character of the correlation is the same in the two cases, but the surface tension of neat NaMMT is much larger than that of CaCO_3 . The surface energies of the coated fillers are very similar, irrespective of the filler type (clay, CaCO_3) or the chemical composition of the surfactant used for treatment. These results prove that organophilization decreases the surface energy which leads to decreased matrix–filler interaction and inferior strength. These observations also agree well with current experience and published results.^{1,9,103}

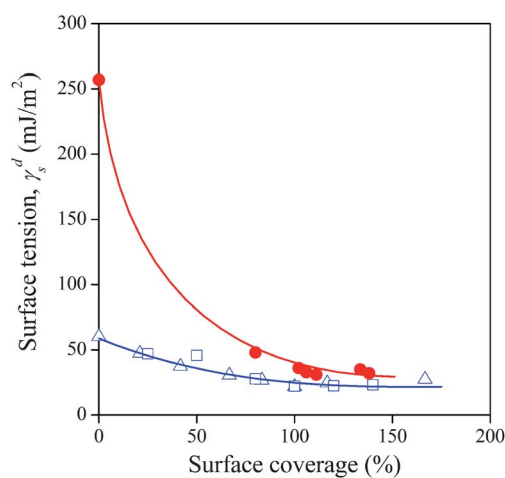


Fig. 10 Effect of surface coverage on the surface tension of layered silicates (●); comparison to CaCO_3 coated with stearic (Δ) and lauric (\square) acid.

3.2. Interactions

The roles of interactions and their modification are relatively simple in nanotube and spherical nanoparticle modified polymers and very similar to other heterogeneous polymer systems in spite of the nanometric dimensions of these reinforcements. However, particle–particle interactions play a much more important role in the case of nanofillers than for traditional reinforcements. Interactions are much more complicated in nanocomposites containing plate-like reinforcements, since they influence exfoliation and structure and the number of possible interactions can be also much larger in them than in composites containing the other two reinforcements.

The thermodynamics of exfoliation and component interactions was considered by several groups. Jang *et al.*¹⁰⁴ used the solubility parameter (δ) approach and showed that the structure can be related to the solubility parameter of the polymer. The δ value of the surfactant has a smaller effect on the structure. Vaia and Giannelis³¹ developed a mean-field lattice model for the description of the thermodynamics of polymer melt intercalation into organically modified layered silicates. The model predicts entropy and internal energy, which change with increasing gallery distance during intercalation. Although the results of static melt intercalation experiments seemed to agree well with the prediction, the terminology and approach are rather confusing. The use of the terms “unfavorable” and “favorable” for disperse and specific interactions as well as the treatment of nanocomposites as blends contradicts the fact that the 500–1000 nm large silicate platelets are 3 to 5 orders of magnitudes larger than lattice sizes in blends and that interaction is an adsorption process in which all interactions are favorable. Balázs *et al.*^{105–107} also proposed various thermodynamic models for the prediction of the intercalation of polymers into organically modified silicates, but their conclusions do not agree with those of Vaia and agree even less with experience.

The interactions developing in layered silicate PA nanocomposites were analyzed by molecular dynamics modeling by Sikdar *et al.*¹⁰⁸ They proved that the strongest interaction forms between the silicate layer and the ammonium ion, but the

backbone of the surfactant also interacts with the silicate rather strongly (Table 3). The various functional groups of the polymer and the surfactant, and the presence of additional components like solvents, additives and compatibilizers, increase the number of possible interactions even more. Obviously, various groups of the components compete for active sites on the silicate surface, and also interact with each other and these competitive interactions determine the extent of exfoliation, the developed structure, polymer/silicate adhesion and finally the properties of the composites.

Two main factors must be considered in composites reinforced with nanofibers or nanotubes: stress transfer and dispersion. Large surface energy resulting in strong interaction is needed for the first, but it results in the aggregation of the fibers. Although experiments directed towards the determination of interfacial fracture energy in multiwalled carbon nanotube reinforced composites indicated the existence of a “relatively” strong interface,¹⁰⁹ whatever that means, interfacial adhesion is usually quite weak in CNT or carbon nanofiber reinforced composites. Carbon nanotubes have a very regular structure almost exclusively consisting of carbon atoms. The surface energy of the tubes is small and the tubes do not contain reactive groups necessary for coupling. This statement is strongly supported by Table 4 listing the surface tension of carbon nanotubes, nanofibers and carbon fibers. Although polar and dispersion components may differ considerably depending on the source, total surface tension is between 30 and 45 mJ m⁻² in each case. This is rather small compared to that of NaMMT, for example, its dispersion component being around 250 mJ m⁻² at 100 °C (see Fig. 10).

The surface of carbon nanotubes is modified by two approaches to control dispersion and improve interactions. Several groups use *surfactants* to facilitate the dispersion of the tubes.^{57,113–115} The surface of the nanotubes is covered with a polymer or a surfactant through physical adsorption. The advantage of the approach is that it improves dispersion, but does not disrupt the conjugated electron system of the tubes. Most often surfactants are added to a water-borne suspension of the nanotubes^{116,117} to create a coating of surfactant micelles around the nanotubes. Anionic, cationic and non-ionic surfactants are equally used; the most often used anionic detergents are sodium dodecyl sulfate (SDS)^{113,118–120} and sodium dodecylbenzene sulfonate (SDBS).^{121,122} Although a surfactant may improve homogenization, it is difficult to see how it can increase the strength of interfacial adhesion between the fiber and the polymer matrix. The surface of nanotubes can be *modified chemically* in order to improve interfacial adhesion. Carbon nanotubes can be modified by direct reaction with the wall of the tubes or by preceding oxidation that creates carboxyl or hydroxyl groups on the surface. Carboxyl groups can be formed

by oxidation in air or oxygen, in concentrated sulfuric or nitric acid, hydrogen peroxide or in a mixture of various acids. The number of functional groups as well as the ratio of –COOH/–OH groups depend on the type and conditions of oxidative treatment, reaction time, and temperature.^{123,124} Carbon nanotubes were successfully functionalized with thiocarboxyl and dithiocarboxyl esters¹²⁵ and they were halogenated with fluor at various temperatures¹²⁶ to facilitate reaction with Grignard reagents or with alkyl lithium.^{127,128} CNT was also reacted directly with nitrenes and carbenes¹²⁹ and aryl groups were also formed on their surface.^{130,131} Polymers are also often grafted to the surface. *Grafting to* has the advantage of using a polymer with well defined molecular weight, polydispersity and structure, but this polymer must be prepared separately and sterical effects decrease grafting efficiency. Nanotubes were successfully modified with PS,¹³² poly(vinyl alcohol) (PVOH),¹³³ PEG¹³⁴ and PLA¹³⁵ in this way. The tubes can be modified also by the *grafting from* approach. In this case larger grafting density can be achieved, but the reaction is more sensitive to the composition of the mixture and to conditions. Nanotubes grafted with PS,¹³⁶ PMMA¹³⁷ and PA6¹³⁸ were prepared with this technique. A list of randomly selected techniques used for the modification of the surface of nanotubes (CNT, halloysite) is compiled in Table 5. Unfortunately, the chemical modification of carbon nanotubes changes their structure, decreases regularity and modifies properties, which usually decreases conductivity. According to Dzenis¹³⁹ nanofibers prepared by electrospinning are superior to nanotubes in many respects, although the way to control interfacial interactions is unclear also in this case.

The methods used for the surface modification of nanotubes can be and are applied also to spherical nanofillers. The surface of the particles is modified either by surfactants or by the proper reactants to introduce functional groups onto the surface of the filler.^{152–156} These groups can react with the polymer during polymerization or cross-linking. This technology may lead to nanocomposites with controlled structure and interfacial adhesion, thus materials with tailor made properties can be produced for the most diverse applications. Polyhedral oligomeric silsesquioxane (POSS) is a modifier having great potential. Sometimes it is regarded as a molecule, while others treat it as a nanofiller. Possible applications are catalysis, precursors to silicates, preparation of copolymers and hybrid networks. Interest and the intensity of research increased further because of the commercial availability of the material. POSS cages can be functionalized by various methods like grafting groups onto preformed clusters or particles, or by the attachment of functional groups during particle formation.^{81,157} Nanocomposites with a wide variety of structures can be formed in this way. POSS can be built into the chains (Fig. 11), can be attached to them by a spacer, can form

Table 3 Interactions acting in PA nanocomposites as determined with molecular dynamics calculations by Sikdar *et al.*¹⁰⁸

Component 1	Component 2	Interacting site	Interaction energy/kcal mol ⁻¹
Clay	Surfactant	Functional group	–330
Clay	Surfactant	Backbone	–217
Clay	Polymer	Backbone	–108
Polymer functional group	Surfactant	Functional group	–143
Polymer functional group	Surfactant	Backbone	–23

Table 4 Surface tension of carbonaceous reinforcements

Reinforcement	Components of surface tension, $\gamma/\text{mJ m}^{-2}$			Ref.
	Dispersion, γ_s^d	Polar, γ_s^p	Total, γ_s	
MWCNT	18.4	26.9	45.3	110
MWCNT	17.6	10.2	27.8	111
Carbon nanofiber	18.4	21.8	40.3	110
Carbon fiber	18.3	27.5	45.9	110
Carbon fiber	35.8	4.5	40.3	112
Pyrolytic carbon black, PCB	20.5	17.6	38.1	96
PCB washed with nitric acid	80.4	25.0	105.4	96
Washed PCB with coupling	141.6	32.6	174.2	96
Commercial carbon black	324.2	52.4	376.6	96

networks, *etc.* Besides POSS, other hybrid organic–inorganic supermolecular assemblies can be also prepared *e.g.* from butyltin oxo-hydroxo nanobuilding blocks and dicarboxylates by the related chemistry.¹⁵⁸ Although the chemistry is not simple, the potential of the approach is large and homogeneity, as well as interactions, can be kept under control relatively easily, at least compared to traditional homogenization technologies.

3.3. Interphase structure and properties

The formation of an interphase in heterogeneous polymers is a well-accepted fact^{159,160} and interphase volume, thickness and characteristics considerably influence composite properties. Large interfaces and a significant interphase volume should form in composites containing fillers or reinforcements with dimensions in the nanometre range. The importance of the interphase was emphasized in composites containing spherical nanoparticles,¹⁶¹ but interphase formation has not been mentioned yet practically at all in layered silicate nanocomposites. The

detection and analysis of the interphase are difficult both by direct and indirect methods. First of all the interphase cannot be present in sufficient amounts to detect it, if the extent of exfoliation is small that happens quite frequently. NMR and dielectric spectroscopy indicated an increase in the mobility of polymers confined in the galleries of layered silicates, and the appearance of a second glass transition temperature lower than that of the bulk material was assigned to the interphase¹⁵⁷ that might explain the less than expected reinforcement in several nanocomposites. These results also indicate that the polymer interacts mainly with the surfactant and not with the silicate surface and only weak interactions form, which do not decrease mobility. The results and conclusions described above are contradicted by the measurements and calculations of Utracki *et al.*^{162–164} The authors prepared various polymer/layered silicate nanocomposites, determined their PVT behavior and applied the Simha–Somcynsky¹⁶⁵ equation of state for the determination of the free (hole) fraction of the materials. The model could be applied only if the adsorption of the polymer was assumed on the

Table 5 Selected surface modification approaches for nanotubes

Nanotube	Method	Modifier	Reference
SWCNT	Surfactant	Anionic (SDBS)	118 and 120
SWCNT	Surfactant	Anionic (SDS)	119
SWCNT	Surfactant	Non-ionic (Triton X-100)	113
SWCNT	Surfactant	Cationic (DTAB)	113
SWCNT	Surfactant	Fluorene-based polymer	140
SWCNT	Surfactant	Amylose	141
MWCNT	—	Thiocarboxylic ester	125
SWCNT	—	Elemental fluorine	126
SWCNT	Grignard synthesis	Alkanes	127
SWCNT	Grafting from	PMMA	128
SWCNT	[2 + 1] cycloaddition	Nitrenes	129
SWCNT	Nucleophilic addition	Carbenes	129
SWCNT	Grafting to, ultrasonication	PMMA	142
SWCNT	Grafting to	Amine-terminated polyimide	143
SWCNT	Grafting to	PEG	134
MWCNT	Grafting to	PLA	135
MWCNT	Grafting from, ATRP	PS	137 and 144
MWCNT	Grafting from, ATRP	PMMA	137 and 144
SWCNT	Grafting from, anionic	PA 6	145
SWCNT	Grafting from, free radical	Poly(4-vinylpyridine)	145
Halloysite	Surfactant	Hexamethylene-tetramine	146
Halloysite	Surfactant	Sorbic acid	147
Halloysite	Surfactant	Quaternary ammonium salt	148
Halloysite	Grafting from	PMMA	149
Halloysite	Grafting	Trimethoxy-silane	150
Halloysite	Grafting	Silane	151

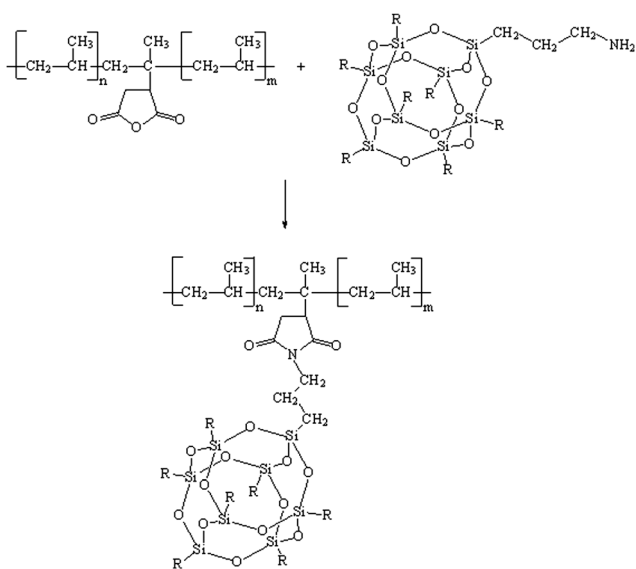


Fig. 11 Modification of PP with amine functionalized POSS cages (after ref. 157).

clay surface resulting in clay platelets covered by a 6 nm layer of a solid like matrix and an interphase of 100–120 nm thickness with changing properties. The results showed that the free volume decreases by 4 to 16% depending on the system studied. Adsorption and the decrease of free volume indicate the formation of a hard interphase. Unfortunately, none of the parameters derived from the model correlated with the actual mechanical properties of the composites.

Recently an attempt was made to determine interphase formation and to characterize interphase properties in PP/MMT composites.⁵¹ Interphase thickness and properties were deduced from the composition dependence of mechanical properties with the help of a model^{166,167} using silicates with different particle sizes. The model yields a parameter (B , see eqn (2) in Section 4.2) which expresses the reinforcing effect of the nanofiller and depends on the specific surface area of the latter as well as on interphase properties (thickness, yield stress). The results obtained proved the formation of an interphase in the PP composites studied, but the determination of its properties was hampered by several factors. First of all, the particle size of the filler changed quite considerably in PP/OMMT composites and even more when a relatively small amount of functionalized polymer (MAPP) was added to the composite to improve adhesion. As a consequence, the estimation of the contact surface between the silicate and the polymer became extremely difficult. In spite of the problems, overall values of interphase properties were obtained using the results of all composites prepared. Plotting the B parameters of all composites against the specific surface area of the fillers used resulted in a straight line (Fig. 12) as predicted by the model. Interphase properties were derived from the parameters (slope, interception) of the line yielding an interphase thickness of 0.23 μm and an interphase yield stress of 51.2 MPa. Unfortunately, these estimates neglected the different interactions developing in composites containing uncoated (NaMMT) and modified (OMMT) silicate, respectively. The correlation indicates that composition (NaMMT, OMMT, MAPP) had a larger effect on

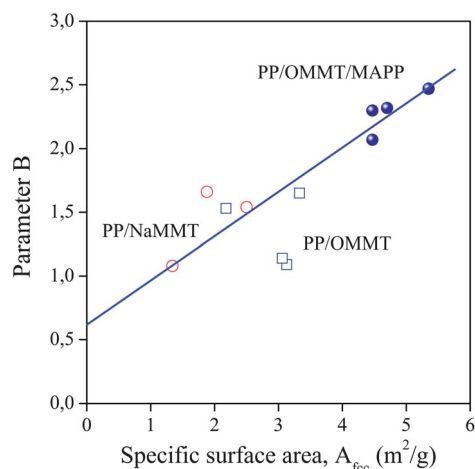


Fig. 12 Parameter B plotted against the specific surface area derived from SEM analysis (A_{fcc}) of PP/silicate composites. Calculation of interphase characteristics. Symbols: (○) PP/NaMMT, (□) PP/OMMT, and (●) PP/OMMT/MAPP (5 vol%).

reinforcement than the surface area of the fillers, at least in the range studied, which further emphasizes the importance of exfoliation and structure in the determination of nanocomposite properties.

4. Composite properties

Review papers and books^{86,157,168–174} offer a detailed account on various properties of polymer nanocomposites prepared from the most diverse matrices and reinforcements. As a consequence, we refrain from the comprehensive listing of papers and discussing property changes merely as a function of composition, but focus more on the effect of structure and interfacial interactions on composite properties.

4.1. Stiffness

Stiffness is the most often measured, modeled and discussed property of nanocomposites.^{7,175–180} The percentage increase in modulus is often used to prove the exceptional properties of this class of materials^{181–184} and also the high degree of exfoliation in nanocomposites prepared with layered reinforcements. The large increase in stiffness is observed in elastomers, indeed, but much more moderate in glassy or crystalline polymers.^{172,185–187} Polyamide is one of the exceptions in which a considerable increase of stiffness can be achieved by silicate modification as shown by Fornes and Paul in their paper.²⁹ Based on data taken from the literature they argue that layered silicates offer exceptional reinforcement at very small filler content. Even larger reinforcement can be achieved by carbon nanotubes with large aspect ratio in PA⁵⁹ (see Fig. 13). However, often serious doubts arise on seeing such results because of the important effect of orientation, which is usually not known, on the one hand, and because sometimes basic values like the stiffness of the matrix do not seem to be correct, on the other hand (small stiffness of PA, see Section 2.2 and Table 2).

Because of its assumed importance, the stiffness of nanocomposites is modeled quite frequently. In their paper Valavala

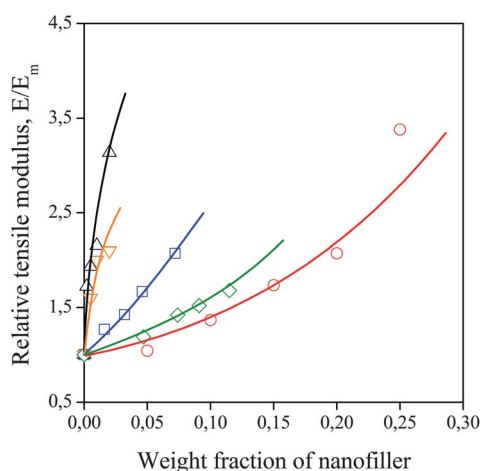


Fig. 13 Reinforcing effect of different nanofillers compared to traditional glass fiber reinforcement in PA composites.²⁹ Symbols: (○) glass fiber,²⁹ (◇) halloysite,¹⁸⁸ (□) layered silicate,²⁹ (▽) layered hydroxide,¹⁸⁹ and (△) MWCNT.⁵⁹

and Odegard¹⁹⁰ compare the theoretical background, advantages and drawbacks of the various approaches used. Usually the composition dependence of stiffness is modeled by continuum mechanical models developed for traditional composites. The Halpin–Tsai¹⁹¹ and the Mori–Tanaka¹⁹² models are used the most frequently,^{7,29,175,177,181,193–195} but other micromechanical models are also applied or developed occasionally.^{175,177,196} Although the papers usually claim good agreement between measured and predicted properties, the general validity of the conclusions is limited for several reasons. Various assumptions are used during the development of these models, like the linear elasticity of the components, homogeneous distribution of the reinforcement in the matrix, its unidirectional alignment, as well as the perfect adhesion of the phases. However, many of the polymers (PA, PP) deform plastically especially around the particles, the distribution of the reinforcement is never as regular as assumed (random close or cubic centered packing), unidirectional alignment cannot be achieved and orientation is difficult to characterize quantitatively, and the adhesion of the phases is never perfect due to the weak adhesion caused by surface modification (see Section 3.2 and Fig. 10). Obviously, most of the assumptions applied are not realistic and the conditions are difficult to satisfy in nanocomposites, thus the validity of the models is questionable.

One encounters enhanced difficulties during modeling in layered silicate nanocomposites because of their complicated structure. Many of the models use various assumptions for the structure and try to account for the structural diversity of layered silicate nanocomposites.^{175,177,193,196} The structure is usually simplified in the calculations, *i.e.* particles and the silicate network are neglected and only individual layers and tactoids are considered. In spite of such simplifications the proper accommodation of the varying degree of exfoliation and changing orientation within the composite into the model present serious difficulties. Fornes and Paul²⁹ proved that very tedious and meticulous procedure is needed to obtain acceptable data for model calculations. Accordingly, most of the modeling efforts are focused around assumptions concerning the structure of the

composite and most output information is related to the structure as well. The resulting characteristics are, for example, the number of platelets per stack or the aspect ratio of the dispersed clay units. However, Osman *et al.*⁷ expressed their doubts about the validity of such estimates based on the argument that the composite modulus depends also on the particle orientation and on the Poisson's ratio of the matrix, and they came to the conclusion that the aspect ratio of the inclusions cannot be estimated from the Halpin–Tsai equation for layered silicate nanocomposites.⁷

4.2. Strength, reinforcement

The basic condition for efficient reinforcement is strong adhesion between the matrix and the reinforcing component. The composition dependence of strength or yield stress gives more accurate information about interfacial interactions and reinforcement in all heterogeneous polymer systems, including nanocomposites, than the modulus.^{42,166,167} The effect of interfacial interaction depends on its strength and on the contact surface between the phases. Although strong interaction is assumed in layered silicate nanocomposites, interaction is usually weak between OMMT and any matrix due to the surface modification of the clay. Weak interaction, however, might be compensated by the large surface, if the degree of exfoliation is sufficiently large. The composition dependence of the tensile yield stress of heterogeneous polymer systems can be described by the simple equation^{88,166,167}

$$\sigma_y = \sigma_{y0} \frac{1 - \varphi}{1 + 2.5\varphi} \exp(B\varphi) \quad (2)$$

where σ_y and σ_{y0} are the yield stress of the composite and the matrix, respectively, φ is the volume fraction of the filler in the composite and B is related to the load carried by the dispersed component, *i.e.* it depends on interaction.^{42,101,166,167,197} The second term $(1 - \varphi)/(1 + 2.5\varphi)$ expresses the effective load-bearing cross-section of the matrix. At zero interaction all the load is carried by the polymer and the load-bearing cross-section decreases with increasing filler content. The same correlation can be used to describe the composition dependence of tensile strength, if the elongation of the composite is small, usually less than 100%.¹⁶⁷ The value of parameter B depends on all factors influencing the load-bearing capacity of the filler, *i.e.* on the strength of interaction and on the size of the contact surface. The effect of these factors on B is expressed as

$$B = (1 + A_f \rho_f l) \ln \frac{\sigma_{yi}}{\sigma_{y0}} \quad (3)$$

where A_f is the specific surface area of the filler (contact surface), ρ_f is its density, while l and σ_{yi} are the thickness and the yield stress of the interphase forming spontaneously in all heterogeneous polymer systems. These two parameters were shown to depend on the strength of matrix–filler interaction.^{198,199} The load carried by the second component depends also on the properties of the matrix (see σ_{y0} in eqn (3)); the extent of reinforcement is larger in a softer than in a stiffer polymer.

If the model is valid, we should obtain a straight line when the natural logarithm of reduced or relative yield stress is plotted against filler content, *i.e.*

$$\ln \sigma_{y\text{rel}} = \ln \frac{\sigma_y}{\sigma_{y0}} \frac{1 + 2.5\varphi}{1 - \varphi} = B\varphi \quad (4)$$

In the representation of eqn (4) the yield stress of composites should fall on a straight line with zero interception and with a slope proportional to the extent of reinforcement (B). PA nanocomposites are undisputedly the reference materials in which layered silicates exert the largest reinforcing effect.^{8,200} Extensive exfoliation and strong reinforcement are almost invariably assumed and expected in PA/layered silicate composites.^{176,201–204} However, if we thoroughly examine and compare published data, we find that the properties of these materials vary in a very wide range and the silicate often has only a moderate reinforcing effect. The tensile yield stress of six materials, including a PA/LDH composite, is plotted against the filler content in Fig. 14, in order to support our statement; the yield stress of the composites covers a very wide range, indeed.

The composition dependence of the yield stress of the composites of Fig. 14 was analyzed by the model presented above. The logarithm of relative yield stress is plotted as a function of silicate content in Fig. 15. Straight lines are obtained in all cases; the deviation from the lines is negligible proving the validity of the approach. The slopes of the lines differ considerably from each other indicating widely differing reinforcing effects. Rather surprisingly very small B values of about 4 or 5 are obtained in some cases even when organically modified MMTs were used, in spite of the general belief that silicates exfoliate in a large extent in PA and properties improve considerably.^{9,26} Although the use of ω -amino acid as surfactant creates strong interaction between the silicate and the matrix,^{206–208} most of the clays were treated with aliphatic amines resulting in weak interaction.^{176,201,202} The results clearly prove again the pitfalls of false generalization assuming that all PA nanocomposites are strong simply because the first composites of the Toyota group^{206–208} showing excellent properties were prepared with an amino acid surfactant. On the other hand, reinforcement seems to be much larger in two of the composites (see $B = 22.9$ and 57.8 , respectively). However, we must mention here that the authors of the silicate composite with

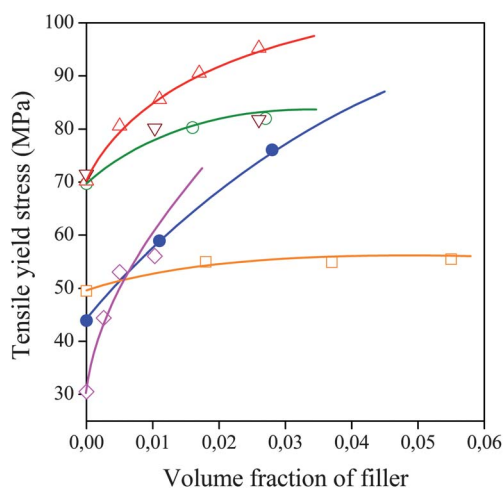


Fig. 14 Wide range of absolute values and different composition dependence of tensile yield stress in PA nanocomposites. Symbols: (□) Liu *et al.*,²⁰² (Δ) Rác *et al.*,²⁰⁴ (○) Fornes *et al.*,¹⁷⁶ (◇) Peng *et al.*,¹⁸⁹ (▽) Hedicke-Höchstötter *et al.*,²⁰⁵ and (●) Shelley.²⁰³

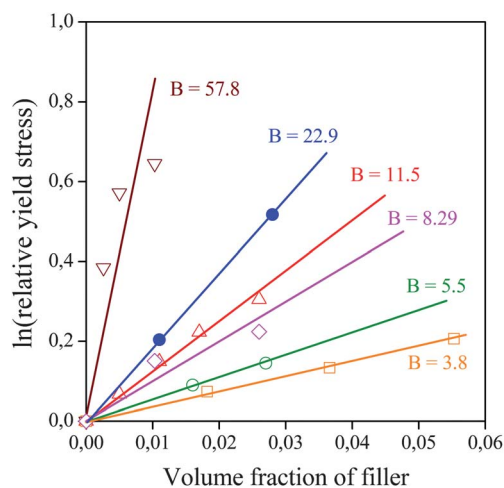


Fig. 15 Relative tensile yield stress of the PA composites of Fig. 14 plotted as a function of silicate content. Symbols are the same as in Fig. 14.

the B value of 22.9^{203} do not supply any information about the composition of their material, on the one hand, while the stress vs. strain traces supplied and the data listed in the corresponding table for the PA/LDH composite with the very large B of 57.8^{189} strongly contradict each other, on the other. The determination of yield stress seems to be the problem in the second case, since a B value of 12 was calculated from the tensile strength. Further information must be obtained about the components, as well as preparation and testing of these composites before the large B values can be accepted at face value.

The determination of B values offers the possibility to estimate also the extent of exfoliation in these composites. We assume that NaMMT does not exfoliate at all, while the specific surface area of the completely exfoliated silicate is known to be about $750 \text{ m}^2 \text{ g}^{-1}$ (ref. 1,84,85). These two cases represent the boundaries for zero and maximum reinforcement. B depends linearly on the specific surface area if all other factors including interaction are the same (see eqn (3)). Using PP/ CaCO_3 composites as reference we obtain the results listed in Table 6. This shows that B values of about 200 should be obtained if exfoliation was complete down to individual silicate layers. The largest B value calculated for the PA/silicate composite of Shelley *et al.*²⁰³ corresponds to a specific surface area of about $90 \text{ m}^2 \text{ g}^{-1}$. This indicates the formation of stacks containing approximately 10 silicate layers on average. This result agrees well with the experience that complete exfoliation is very difficult to achieve and nanocomposites always contain different structural formations including individual silicate platelets, intercalated stacks, and often even large particles.

4.3. Other properties

Compared to stiffness and sometimes to strength, other characteristics of nanocomposites are investigated much less. One of the characteristics mentioned quite frequently in relation to layered silicate nanocomposites is the heat deflection temperature (HDT). This property is closely related to stiffness and changes with composition in a similar way. The introduction of any

Table 6 Estimation of the extent of exfoliation from parameter *B* determined in PP composites

Filler	Parameter <i>B</i>	Specific surface area/m ² g ⁻¹	Extent of exfoliation (%)	Reference
CaCO ₃	1.5	3.3	0	101
NaMMT	1.8	26.0	0	209
OMMT	195 ^a	750	100	1,84 and 85
OMMT	22.9	91.0 ^b	11.7	203

^a Calculated from the published specific surface area assuming complete exfoliation. ^b Calculated from the largest *B* value published.

reinforcement may modify also other characteristics like the appearance of the product (color, surface) or influence the stability of the compound,²⁰² but these are not discussed here.

Cost is an important attribute of every engineering material and it decreases with increasing filler content in traditional composites, but usually increases in nanocomposites. Moreover, decreasing polymer prices and increasing compounding costs make any composite competitive only if technical benefits are utilized to their full extent.

Two properties must be mentioned specifically here. The inherent flammability of plastics is one of their major drawbacks and the use of flame retardants is required today in most applications, especially in construction and transportation. Layered silicates, carbon nanotubes and halloysite were shown to decrease the flammability of plastics. Although they cannot provide the V0 specification of the UL 94 standard for the polymer as a single additive, but they increase flame retardancy considerably in combination with traditional flame retardants.^{210,211} Such flame retarded nanocomposites have found practical application as cable insulation (see Table 7).

Polymers are basically insulators with a surface resistivity of around 10¹⁴ to 10¹⁸ Ω cm. Applications exist which require a certain conductivity, like air ducts in mines, pipes for solvent transport, EMI shielding and some other areas. Conductivity is usually achieved by the introduction of conductive fillers. Traditionally special conductive carbon blacks or metal fillers, particles or flakes are used in such applications, but recently intensive research is going on to use carbon nanofibers, nanotubes or graphene for this purpose.^{171,212–214} Multiwalled carbon nanotubes or some singlewalled CNTs have excellent electrical conductivity which enables their use in electrostatic dissipative

and conductive polymer composites. In order to preserve the conductivity of the tubes in the insulating polymer matrix, they must form a percolation network. Conductivity increases abruptly at the additive content corresponding to the percolation threshold and because of the very high aspect ratio of the tubes this threshold can be reached at much smaller CNT content than for conductive spherical fillers, like for carbon black. This claim is strongly supported by the results of Pötschke *et al.*^{212,213} presented in Fig. 16. The percolation threshold of the special conducting carbon black is around 8 wt% in polycarbonate, while that of single walled nanotube is less than one percent in the same polymer, indeed. A very low percolation threshold, at around 0.04 wt%, was found in melt mixed PA66 composites.²¹⁵ A review on percolation thresholds is given in ref. 216 showing values in the range between 0.0021 and 5 wt% for epoxy composites, and between 0.045 and 15 wt% for thermoplastics. Such small values could not have been reached with graphene yet.²¹⁷

5. Possible applications, functionality

One of the first target areas of most composites prepared with anisotropic particles (fibers, tubes, plates) is their use as load-bearing parts utilizing the large surface area, stiffness and aspect ratio of these reinforcements. Serious obstacles were met during the production of parts with the desired properties for reasons described in previous sections, *i.e.* difficulties with the control of structure, dispersion, orientation, adhesion and last, but not least, price. However GM announced in 2004 that it used 540 000 lbs nanocomposites that year. Recalculation of this large number results in about 250 tons²¹⁸ which is negligible, if we compare it to the capacity of a single PE plant of 400 000 tons per year.

Table 7 Application of nanocomposites in industrial practice; areas and products

Matrix	Nanofiller	Targeted property	Application area, product	Company
PA6	Layered silicate	Stiffness	Automotive, engine room	Toyota, Ube
TPO	Layered silicate	Stiffness, strength	Automotive, body elements	General Motors
Epoxy	Carbon nanotube	Stiffness, strength	Tennis racket	Babolat
Epoxy	Carbon nanotube	Stiffness, strength	Ice hockey stick	Montreal
Various matrices	Multiwalled nanotubes	Electrical conductivity	Antistatic painting	Hyperion Catalysis
Nylon MXD 6	Layered silicate	Barrier property	Food packaging	Nanocor
Not published	Silver particles	Antimicrobial effect	Wound dressing	Beiersdorf, Elastoplast
Not published	Silver particles	Antimicrobial effect	Antibacterial wall paint	Nanovations
Not published	Not published	Decreased gas permeability	Food packaging	InMat, Nanolok
Halogenated polymers	Hydrotalcite	HCl scavenger	PVC products	Akrochem, Süd-Chemie
Polyolefin	Hydrotalcite	Flame retardancy		Akrochem, Süd-Chemie
EVA	Layered silicate	Flame retardancy	Coaxial cable jacketing	Kabelwerk EUPEN AG
PP, TPO, nylon	Halloysite	Stiffness, strength		Naturalnano
Not published	Layered material	Stiffness, strength	Body of wave runners	Nanoxcel, Yamaha
Not published	Carbon nanotube	Conductivity, transparency	Films for display systems	Invisicon, Eikos

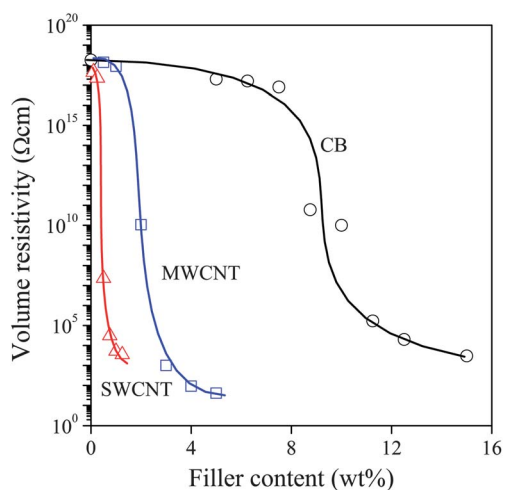


Fig. 16 Comparison of the effect of carbon black (CB), multiwalled (MWCNT) and singlewalled carbon nanotubes (SWCNT) on the conductivity of polycarbonate composites. Data were provided by Petra Pötschke, IPF Dresden, Germany.

Nanocomposites can be used as structural elements in certain areas, but the real potential of these materials is in special, niche application utilizing their functional properties. In previous sections we mentioned already their use as additives in flame retardant packages, or as conductive fillers to render plastics antistatic or conductive. We mention several potential areas in this section like gas permeation and membrane technology, electronics, as well as biomedical and environmental applications.

Gas barrier properties of polymers are claimed to be modified significantly by layered silicates. The general idea is that individual silicate layers with large aspect ratio increase the diffusion path of gases considerably especially if they are oriented parallel to each other. Several groups observed significant decrease in the oxygen permeability of PET/layered silicate nanocomposites produced by *in situ* polymerization.^{219,220} Brule *et al.*²²¹ prepared blown films from PA6/polyolefin/silicate nanocomposites and

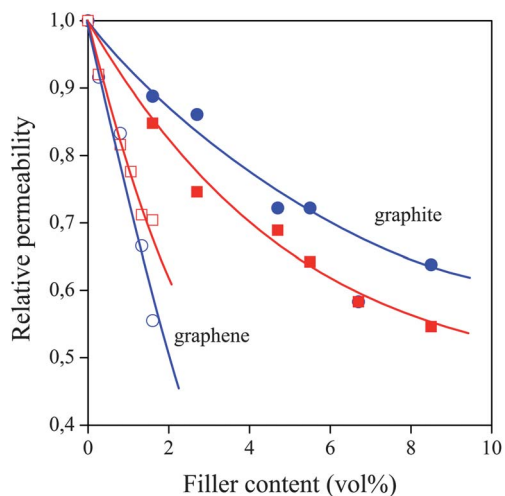


Fig. 17 Reduced relative gas permeability of polycarbonate nanocomposites produced by melt compounding.²²³ Symbols: (○) nitrogen, (□) helium; filled symbols: graphite, empty symbols: graphene.

found that their permeability for styrene decreased in the presence of the silicate. The main field of application for these materials is packaging where the targeted combination of properties is achieved by the preparation of coextruded films. One solution already introduced into practice is the PA6 based Imperm nanocomposite offered by Nanocor for the production of multilayer films, and bottles for packaging of soft drinks.²²² The same principles are used in graphene composites as Fig. 17 shows the permeability of the polymer for various gases decreases considerably in the presence of graphene.²²³ Although the approach seems to work also in this case, practical applications are not known for graphene at the moment.

In the last decades significant progress was made in the production of polymer based membranes. One limiting factor in improving the performance of these membranes is that selectivity decreases with increasing permeation, while productivity decreases with increasing temperature.²²⁴ One way to circumvent these problems is the preparation of nanocomposite membranes, which show improved permeation and selectivity at the same time.^{225–227} Nanocomposite membranes are used already in fuel cells as well. In these cells oxygen is reduced on electrodes containing carbon black and nano-sized platinum particles. The performance of the electrodes could be improved, when carbon nanotubes were used instead of carbon black.²²⁸ The diffusion of methanol is one of the main problems in methanol fuel cells decreasing efficiency considerably. Nanocomposite membranes decrease methanol permeation thus improving the performance of these cells.²²⁹

Another area discussed here is electronics where size reduction requires the use of nanotechnology. The size of active electronic parts is already in the nanometre range in most devices. Both the type and the specific application of nanocomposites are very diverse in this field. Light sensors, photodiodes, super condensers, other sensors, LEDs and transistors are produced from composites containing carbon nanotubes.²³⁸ The electric conductivity of nanotubes is used in various shielding applications as well as in diverse transparent conductive coatings,⁵³ *e.g.* electronic displays are prepared from transparent conductive films containing carbon nanotubes (see Table 7). Sensors are prepared from conjugated polymers and nanoparticles, but metal oxide nanofibers, carbon nanotubes, gold, silver, platinum and palladium nanoparticles are also used in various electronic applications.^{238,239}

Nanotechnology and nanocomposites play an increasing role in many biomedical applications. One important application is the production of networks from nanofibers for cell and tissue growth.²³⁰ Antibacterial effects are achieved with nano-sized silver, silver oxide, or other silver salt containing composites for dendrimer based drugs.²³¹ Gelatin containing hydroxyapatite particles as well as other nanocomposites prepared with this filler are used as prostheses.²³² Controlled drug release and targeted drug delivery are other promising fields in which nanocomposites may play a role in the future. Nanoparticles are used in increasing quantities also in various drug formulations, the particles and tubes are thought to slow down and regulate drug release.^{233–239} Iron oxide particles were used in several experiments targeting controlled drug release, and they were used as MR contrast or immuno-assay materials²⁴⁰ as well. The number of potential applications is probably unlimited also in this field.

Large efforts are done to explore the possible use of nanocomposites in environmental applications, in fact environmental nanotechnology is expected to play an important role in environmental engineering and science in the near future.²⁴¹ A detailed review of the field is offered by a recent paper of Zhao *et al.*²⁴¹ Possible applications include catalytic and redox degradation of contaminants like phenol,^{242,243} trichlorobenzene,^{244,245} nitrobenzene²⁴⁶ and other compounds, biocatalysis, adsorption of pollutants like arsenic^{247–249} and other metallic contaminants (Pb²⁺, Cu²⁺, Zn²⁺),^{250,251} but other applications like pollutant sensing and detection are also envisaged in this field. Although the potential of nanocomposites in environmental protection is great, several outstanding issues (interaction, optimum properties, effect of pollutants on composite properties) need resolution in the future. Moreover, the majority of recent ideas are based on laboratory tests thus industrial production and field application must be solved, which needs further efforts. The potentials of nanocomposites are extremely large in many fields, but progress towards practical applications is slower than expected. Nevertheless, nanocomposites found functional application in several areas; Table 7 gives an overview of selected products used in industrial practice already.

6. Conclusions

The properties of all heterogeneous materials including nanocomposites are determined by the same four factors, *i.e.* component properties, composition, structure and interfacial interactions. On the other hand, usually more complicated structure develops in nanocomposites than in traditional particulate filled polymers, and that is especially valid for composites prepared from plate-like nanofillers. Besides the usually assumed exfoliated/intercalated morphology, *i.e.* individual platelets and tactoids, such nanocomposites may contain also large particles, and a network structure at large extent of exfoliation. Aggregation and orientation are the most important structural phenomena in nanotube or nanofiber reinforced composites, and aggregation is a major problem also in composites prepared with spherical particles. Interfacial interactions should play an increased role in nanocomposites compared to traditional composites because of the assumedly very large interfacial area developing in them. Surprisingly, the surface characteristics of nanofillers and interactions are rarely determined or known. The surface of these reinforcements is modified practically always. The goal of the modification is to improve dispersion and/or adhesion in nanotube and spherical particle reinforced composites, and to help exfoliation in nanocomposites containing platelets. Unfortunately modification decreases the surface energy in most cases leading to decreased interaction with the matrix. Very limited information exists about interphase formation and the properties of the interphase in nanocomposites, although they must influence properties considerably. The properties of nanocomposites are usually far from the expectations, the main reason being insufficient homogeneity, undefined structure and improper adhesion. In spite of considerable difficulties nanocomposites have great potential especially in functional applications. Several nanocomposite products are already used in industrial practice.

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