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Noncrystalline L-Phenylalanine-Silica Hybrid Composite Materials for High Selective Reversed Phase Liquid Chromatography

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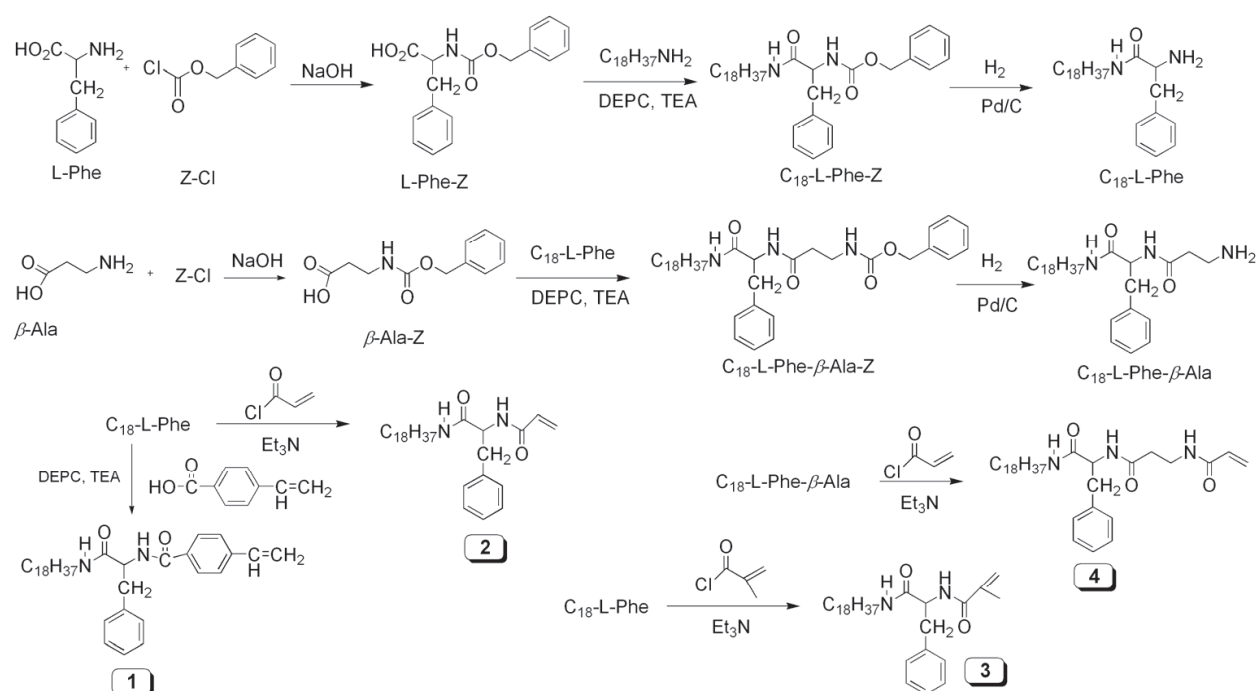
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1. Introduction

Research developments in analytical techniques explore novel silica hybrid materials with interesting and useful functionalities as hybrid inorganic-organic composite materials have attracted increasing attention because of their potential ability to combine the properties of both organic and inorganic materials. There has also been renewed attention in synthetic polypeptides because of their promising application as biodegradable and biomedical polymers, as well as their ability to form highly ordered hierarchical structures through non-covalent forces such as hydrogen bonding. Self-assembling of low molecular compounds have been attractive as a construction tool for nanotechnology because they are essentially generated through three-dimensional network formation from nano-sized one-dimensional fibrillar aggregates, constructed of highly-ordered assemblies like aqueous lipid bilayer membranes. The formation of assemblies from small molecules requires a hierarchically organized aggregation through noncovalent bonds to yield elongated assemblies that further self-organize into fibers that percolate the solution. It is also known that a number of chiral compounds form nano-sized one-dimensional unique aggregates with large curvatures such as nanotubes, nanohelices, and nanoribbons (Terech & Weiss, 1997; Esch & Feringa, 2000; Ihara et al. 2004).

Self-assembly is a “bottom-up approach” in which materials are assembled molecule by molecule to produce supra-molecular structures for appropriate functions (Abdallah & Weiss, 2000; van Esch & Feringa, 2000). For example, molecular self-assembly from solution states often leads to the formation of one-dimensional (1D) solid fibers. This process has attracted attention because 1D fibrous solid, ranging from the submicrometer to nanometer scale, are easily obtained by simple self-assembly through noncovalent interactions. The underlying mechanisms of intermolecular binding interactions include hydrogen bonding, ionic interactions, and π - π stacking in a variety of solvents.^[3] The aggregation or network formation of the fibers in the solvents leads to the occurrence of physical gels in which the molecules that drive physical gelation are called as gelators (Kobayashi et al, 2002). If a functional moiety is introduced into the backbone of a gelator, a new functional 1D object

would be obtained. These aggregates are morphologically interesting and applicable as templates for the creation of peculiar nanostructures, such as inorganic nanomaterials (Suzuki et al., 2006) synthesized by condensation of alkoxy silane or chlorosilane on self-assembled fibrous/helical aggregates (Jung et al. 2000) Equally important that a template method has been also applied to prepare various metal (Hatano et al. 2004) nanomaterials.



Scheme 1. Synthesis scheme for polymerizable octadecyl L-phenylalanine derivatives

Combining organic and inorganic materials on a nanometer/micrometer scale, to create functional hybrid materials is receiving a great deal of attention. Organic modification of inorganic materials such as silicas and/or silicates, not only permits a precise control of surface properties for specific applications, but also can affect their bulk properties. In fact, organic features can introduce flexibility into the framework, while the inorganic components can provide structural, mechanical or thermal stability (Stein et al., 2001; Anwender, 2001; De Vos et al., 2002; Tao et al., 2000). One of the most important classes of composites is the materials obtained by the incorporation of various kinds of polymers of controlled physico-chemical properties into porous inorganic material. The insertion of the polymers into the inorganic host cavities can be obtained carrying out the polymerization process inside the cavities themselves (Cardin, 2002). If the initiator is covalently bound to inner surface of the host the polymer can be synthesized directly inside the host pores (Spange et al., 2001). Applications of hybrid materials in analytical chemistry are not new, particularly in the area of separations science. For example, since the advent of silica as an appropriate chromatography material for separations, several hybrids have been successfully employed, such as the hydrocarbon-silica materials prepared from sol-gel synthesis process. In the fields of separation sciences, sol-gel hybrid materials are often used as alternative stationary phases for liquid chromatography, to improve column efficiency, stability and selectivity. Conventional strategies to introduce functional groups in silica stationary phases for chromatography applications include physisorption and covalent attachment of desired compounds via surface grafting methods to pre-formed silica

materials (Guo & Becker 1995, Crego et al. 1993) These works have led to successful application of organic functionalized silica phases in reversed phase liquid chromatography (RPLC) in particular, those of C8 and C18 phases (Guo & Becker 1995; Crego et al. 1993). In recent years, there has been renewed interest in synthetic polypeptides, because of their potential application as biodegradable and biomedical polymers (Kolk et al. 2000) as well as their feasibility to create highly-ordered hierarchical structures through non-covalent forces such as hydrogen bondings (Li et al. 2003; Hamley et al. 2005). Incorporation of a high degree of amino acid functionality and chirality in polymer chains can enhance the potential to form secondary structures (α -helix and β -sheet) and higher ordered structures (Oishi et al. 2002). These synthetic polymers can be useful as chiral recognition stationary phases for HPLC (Lekchiri et al. 1987) metal ion absorbents, drug-delivery agents, and biocompatible materials (Nagai et al. 2004) Such characteristic self-assembled structures and the potential applications of polymers derived from amino acids have attracted researchers to develop new synthetic routes to prepare a variety of amino acid based polymers using various polymerization techniques. The application of these self-assembling polymeric systems is of great interest to scientists dealing with the preparation of new packing materials for HPLC. Extremely enhanced selectivity was obtained for shape-constrained solutes, e.g., PAHs, aromatic positional isomers, and nucleic acid constituents by using silica-selfassembled dialkyl glutamide derived composite materials. (Rahman et al. 2008) This finding encouraged us to develop polymeric peptide lipid type stationary phases. With this background herein we will discuss four octadecylated L-phenylalanine derived polymerizable monomers as shown in Scheme 1 of those monomer 1 and 4 can aggregate in organic solvents. The polymerization/telomerization of all four monomers are done by both conventional radical polymerization followed by grafting on to inorganic silica particles ("grafting to" method) and also by controlled radical polymerization method ("grafting from" method) as given in scheme 2 to prepare hybrid composite materials. One practical application of these composite materials for separation of toxic PAHs will also be discussed for high selective reversed phase liquid chromatography. The chromatographic performance for the octadecyl L-phenylalanine derived hybrid composites prepared by "grafting to" and "grafting from" method will also be compared.

2. Self-assembling properties of the octadecylated L-phenylalanine derivatives

The monomers were synthesized and characterized by previously reported methods. (Rahman et al. 2008, 2009). The morphological properties of these compounds were studied and the results demonstrated that 1 and 4 can self-assemble in different organic solvents and can form fibrillar aggregation. The FT-IR and ^1H NMR spectroscopies are powerful tools to study hydrogen bonding interactions. Extensive precedent indicates that secondary amide groups (N-H) engaged in the standard amide-amide hydrogen bonds ($\text{C}=\text{O} \cdots \text{H}-\text{N}$) display stretch bands in the range $3370\text{-}3250\text{ cm}^{-1}$ while stretch bands in the range $3500\text{-}3400\text{ cm}^{-1}$ are attributed to "free" secondary amide groups that are not involved in hydrogen bonding. Detailed FT-IR studies of gel state of compound 1 and 4 also shows long alkyl chains in these compounds also played key role as van der Waals interaction among the alkyl chains also plays an important role in the self-assembly of these octadecyl L-phenylalanine derivatives (Rahman et al. 2008). The morphological studies by ^1H NMR and UV aggregation of compounds 1 and 4 and non aggregation of 2 and 3. ^1H -NMR studies of compound 1 in

CDCl_3 at different temperature clearly shows the aggregation of compound 4 at low temperature, however at 70°C the peaks for proton in alkyl chain are very much visible as like as the peaks in solution state. This indicates the aggregation of compound 1 at low temperature which does not exists at higher temperature as high as $60\text{-}70^\circ\text{C}$.

The FTIR, NMR and UV-visible measurements demonstrated that intermolecular hydrogen bonding among the amide moieties, van der Waals interaction between the alkyl chains and p-p interactions of the aromatic groups played the most important role in the self-assembly of these compounds. A possible mechanism for self assembling of octadecylated L-phenylalanine is given in Fig. 2

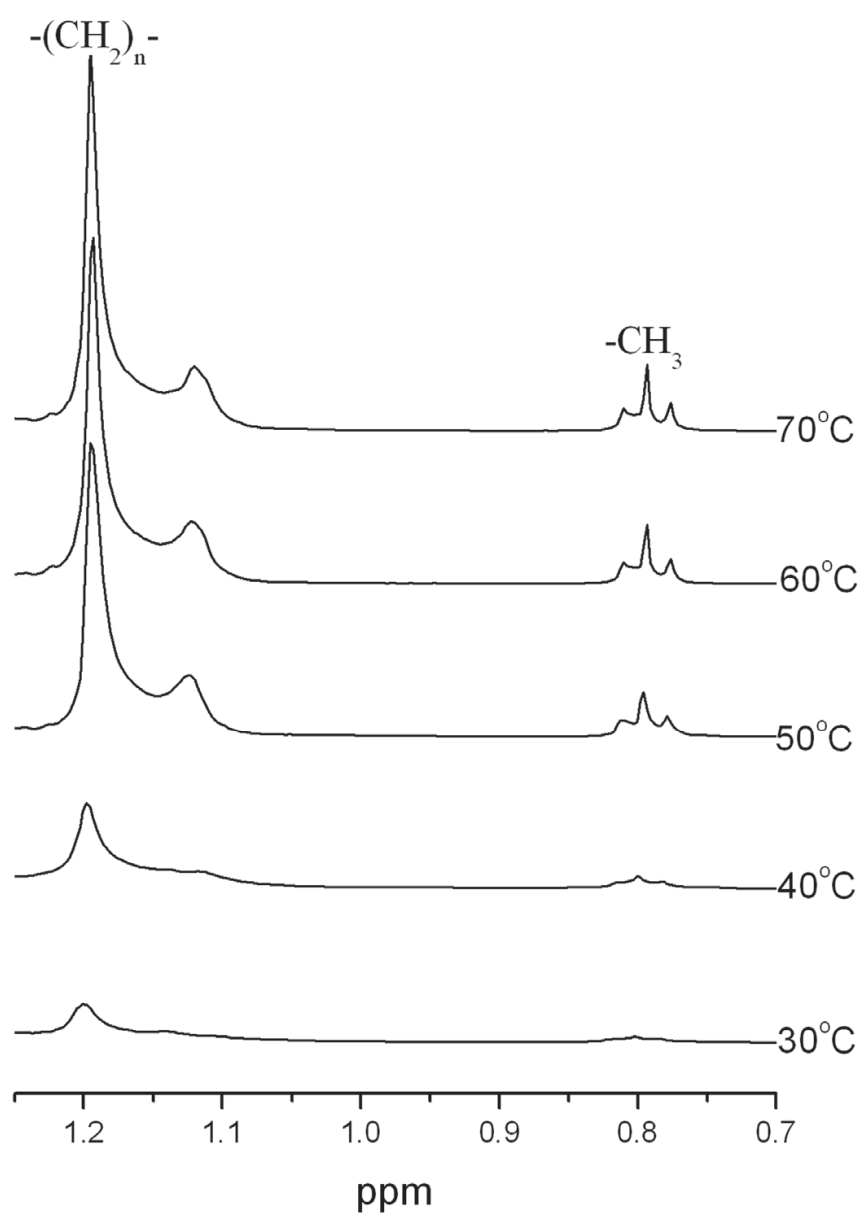


Fig. 1. Partial $^1\text{H-NMR}$ spectra of compound 1 in CDCl_3 at different temperature

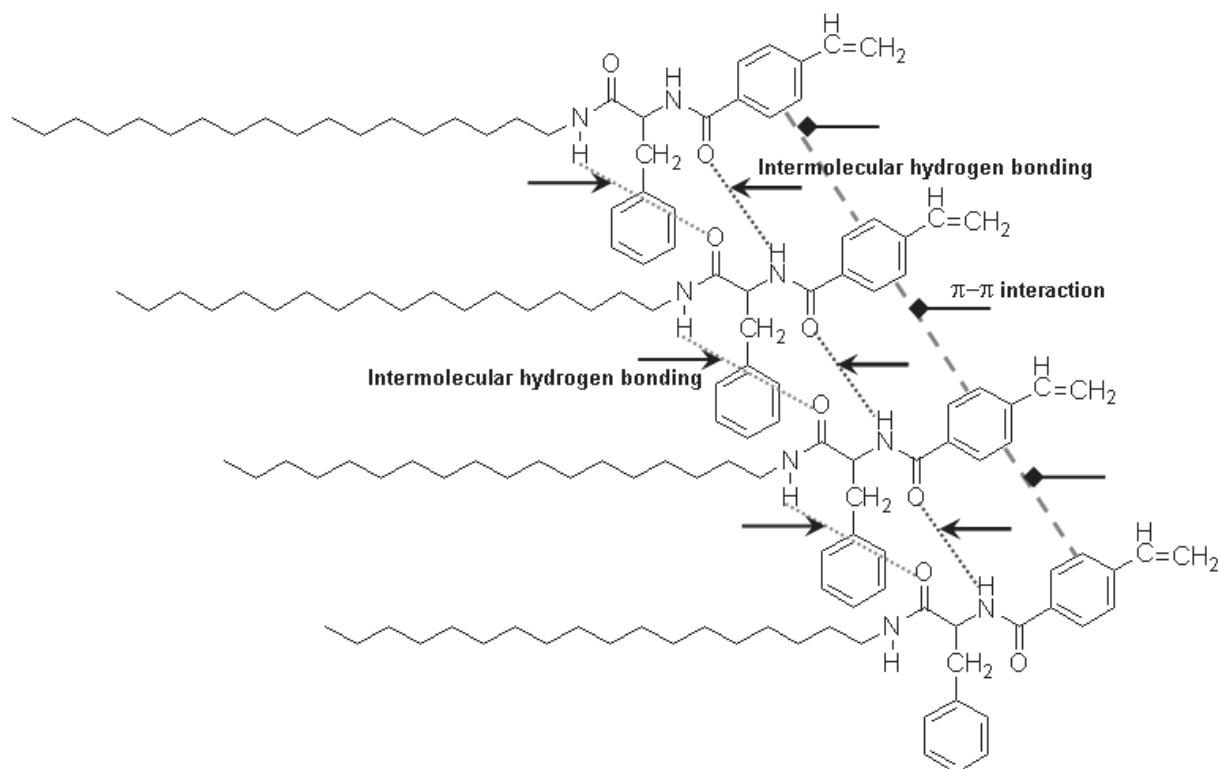


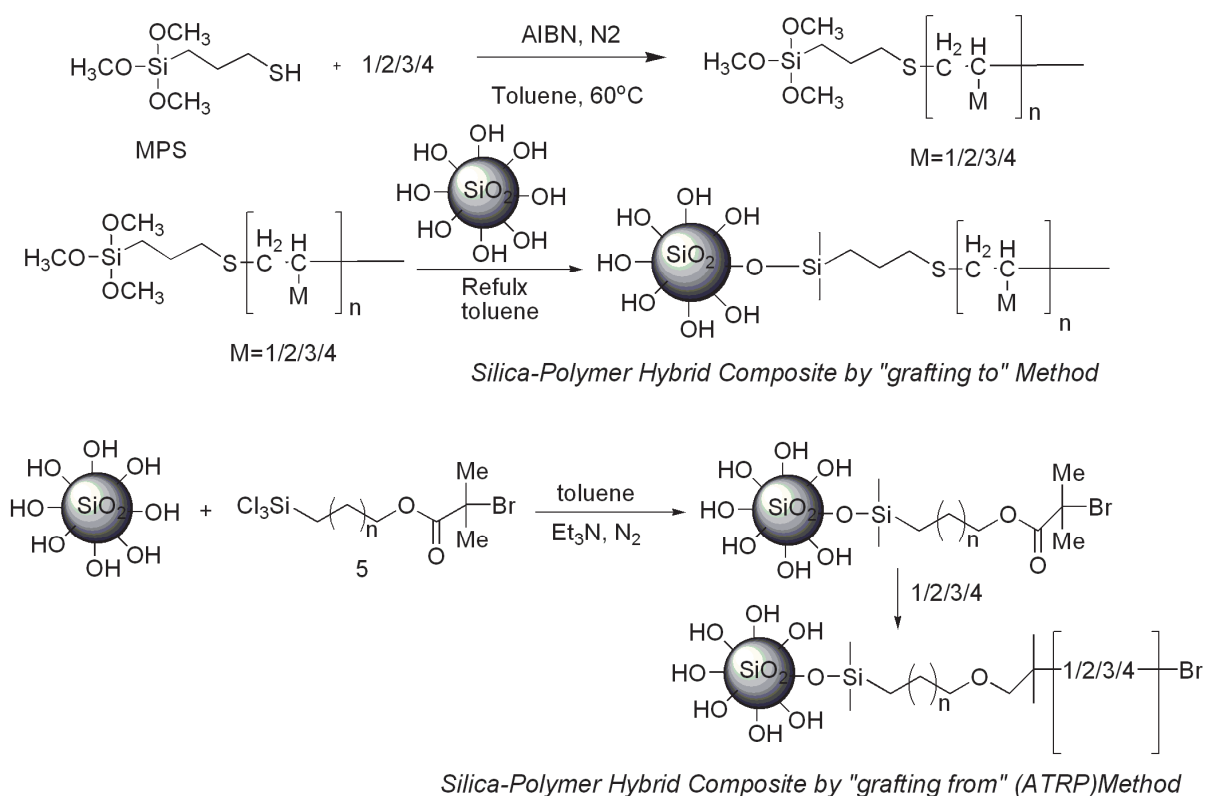
Fig. 2. Mechanism of gelation of compound 1 in different organic solvents

3. Preparation of silica-polymer hybrid composite materials

The surfaces of inorganic materials are functionalized with polymer chains either chemically (through covalent bonding) or physically (by physisorption). Physisorption involves absorption of block copolymers with sticky segments. The non-covalent adsorption makes the adsorption reversible especially during processing and is not a favored technique.

Covalent grafting techniques are preferred to maximize a stable interfacial compatibility between the two phases. Covalent grafting techniques involve either the “grafting to” or “grafting from” methods as shown in Scheme 2. “Grafting-to” involves the reaction of reactive, preformed macromolecules with compatible surface groups. Though experimentally simple, the “grafting to” method has a number of limitations; most notably low grafting densities because of steric crowding of reactive sites by previously attached polymers (Lyatskaya & Balazs 1998). The limitations of physisorption and “grafting to” can be circumvented by the “grafting from” technique. In this process the surface of the particle is modified with an initiator monolayer followed by polymerization under conventional conditions. Using the right system and techniques, one can control the functionality, density and thickness of the polymer brushes. The “grafting from” technique results in significantly higher grafting density because the steric barrier to incoming polymers imposed by the in situ grafted chains does not limit the access of smaller monomer molecules to the active initiation sites ([Pruker & Ruhe, 1993). This polymerization technique is also commonly referred to as surface initiated polymerization (SIP) (Edmondson et al., 2004). Conventional free radical polymerizations are difficult to control and are generally characterized by broad molecular weight distributions, poor control of molecular weight and chain end

functionality, and the inability to synthesize well-defined block copolymers. However, many of these drawbacks can be overcome by using controlled free radical polymerization. The use of surface initiated controlled/living radical polymerization has proven to be a versatile approach for incorporating different types of organic polymers with varied architecture on the silica surfaces. By using this technique, one can manipulate the structure of the resultant polymer shell through changes in grafting density, composition and molar mass. In controlled radical polymerization, the life-time of the growing radical can be controlled resulting in the synthesis of predefined molar mass, polymers with low polydispersity, controlled composition, and functionality. In general controlled/living polymerization can be achieved by stable free radical polymerization, e.g. nitroxide-mediated processes (NMP), metal catalyzed atom transfer radical polymerization (ATRP) and degenerative transfer, e.g. reversible addition-fragmentation chain transfer (RAFT). ATRP Matyjaszewski (Wang and Matyjaszewski 1999) and Sawamoto (Kato et al. 1995) simultaneously reported ATRP in the mid 1990's. The ATRP initiator (typically a α -halo ester or a α -benzyl moiety) is activated in the presence of metals such as Cu, Ru, Fe, and others. The compounds were polymerized by grafting to and grafting from method. Grafting to involves telomerization with silane coupling agent MPS followed by grafting onto silica particles to prepare composite materials. The controlled radical polymerizations were done for monomers 1 and 3 by atom transfer radical polymerization method. The compounds are also polymerized by grafting from via ATRP method. A typical "grafting to" method for compound 1 is 4.0 g (7.32 mmol) of compound 1 was dissolved in 50 ml anhydrous toluene by heating and 0.15 g (0.73 mmol) of 3-mercaptopropyltrimethoxysilane (MPS) and 40 mg AIBN were added into the solution and purged with N_2 gas. The mixture was degassed by three-freeze-pump thaw cycles. It was then placed in oil bath and heated at 60 °C for 24 hrs to complete the polymerization reaction. The reaction mixture was concentrated and dissolved in minimum amount of chloroform and re-precipitated from methanol. The white crystal appeared were filtered washed with methanol several times and dried under vacuum to obtain telomer. For grafting on to silica surface 4.0 g of telomer and 4.0 g silica were taken in a 100 mL three-necked flask and 40 mL dry toluene was added. The suspension was refluxed for 72 hours to complete the grafting process. After filtration the silica particles were washed with hot toluene, methanol, and chloroform repeatedly and finally washed with diethyl ether and dried under vacuum to get telomerized silica-polymer composite materials as shown in scheme 2. To synthesize polymer-grafted silica particles by ATRP method we have synthesized radical polymerization initiator (11-(2-bromo-2-methyl)propionyloxy)undecyltrichlorosilane by previously reported literature. ATRP initiator was grafted onto silica in dry toluene in the presence of triethylamine under nitrogen atmosphere. The reaction between the surface accessible OH group of silica and the anchoring group of the initiator ($-SiCl_3$) resulted in the formation of chemical bond between the silica surface and initiator. ATRP processes have been carried out using Sil-initiator as macroinitiator suspended in the mixture of monomer and toluene in the presence of CuBr and 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA) as catalyst precursors After the ATRP process the prepared composite materials were purified by repeated washing in different solvents to remove the non-grafted polymers from the surface. The grafted hybrid composite materials were characterized by different spectroscopic (DRIFT, NMR) and thermoanalytic methods (TGA).



Scheme 2. Preparation of silica L-phenylalanine composite by different grafting processes

4. Characterization of hybrid-composite materials

Diffuse reflectance fourier transform infrared spectroscopy (DRIFT IR) is a suitable method to study the effectiveness of both immobilization of organic molecules onto silica surface and surface-initiated polymerization. DRIFT IR and FTIR spectra were recorded in the range of 3750-1370 cm^{-1} at room temperature using 4 cm^{-1} resolution and number of scans of 64. Comparison of DRIFT IR spectra of bare silica, ATRP initiator-grafted silica, Silica-grafting from and silica grafting to polymer furthermore FTIR spectrum of telomere are also presented in Figure 3.

The spectra of b and c are nearly identical providing an evidence that fairly high amount of telomere has been grafted onto silica particles. Successful immobilization of ATRP initiator is confirmed by the two strong bands at 2924 cm^{-1} and 2853 cm^{-1} , respectively attributed to the asymmetric and symmetric CH_2 stretching furthermore the band at 1717 cm^{-1} arising from carbonyl group of the ester moiety. Analysis of spectrum e shows a broad band at 1633 cm^{-1} with a shoulder at 1656 cm^{-1} derived from the overlapped amide carbonyl stretching vibrations and a band at 3290 cm^{-1} due to the N-H stretching vibration indicating the presence of polymer on silica surface.

These findings clearly proved that silica particles could be coated using two approaches, namely grafting to technique and grafting from technique (Surface initiated ATRP).

^{29}Si CP/MAS NMR spectroscopy is well suited for assessing the surface reaction of silanes with silica. Resonances for the silica species appears from -90 to -110 ppm. The ^{29}Si CP/MAS NMR spectra of the polymer grafted silica for sil-grafting from polymer and sil-grafting to polymer are shown in Fig. 4. The ^{29}Si CP/ MAS NMR spectrum for bare silica and ATRP initiator grafted silica (sil-initiator) are also included for comparison. The two polymer

grafted silica showed that large extent of silanol groups remain unfunctionalized by both grafting methods.

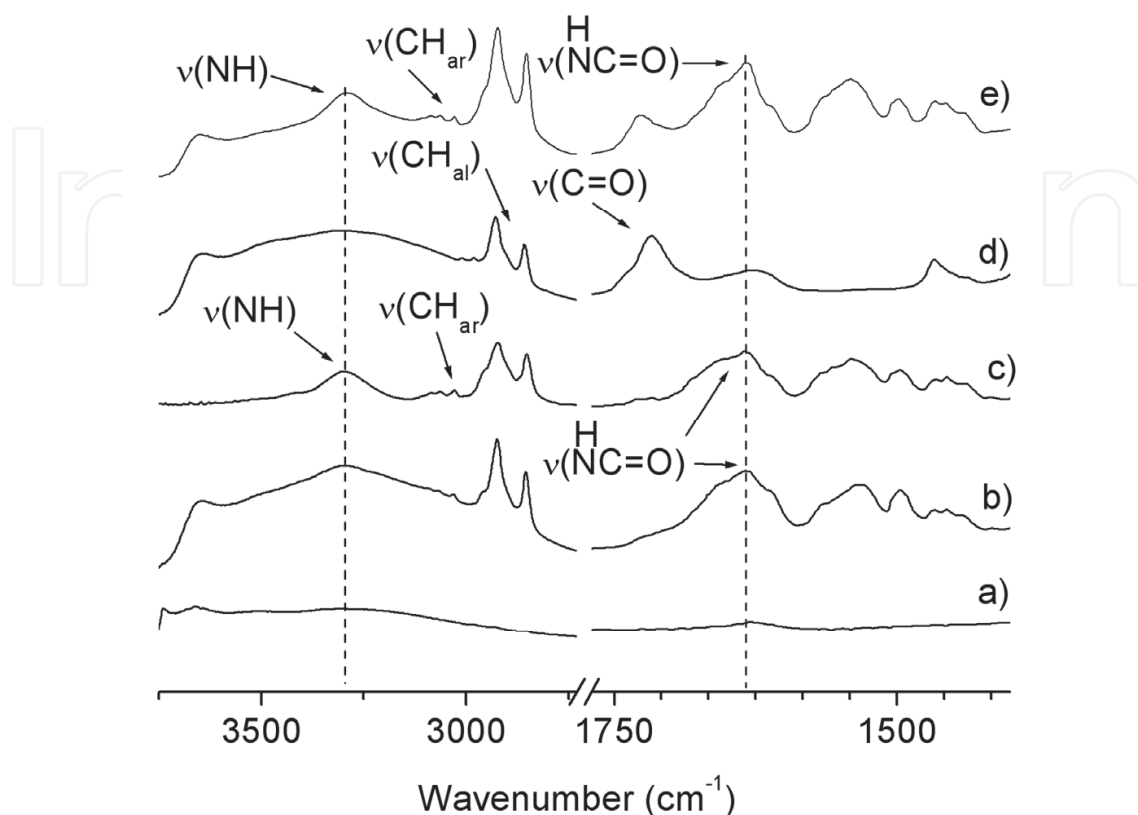


Fig. 3. DRIFT IR spectrum of a) bare silica, b) Sil-grafting to polymer of 1, c) Telomer of 1, d) Sil-ATRP initiator, e) Sil-grafting from polymer of 1.

Figure 4 shows the differentiation between free silanol groups (Q³) and geminal silanol groups (Q²) besides the siloxane groups (Q⁴) that are indicated by signals at -92, -102 and -111 ppm, respectively. In ATRP polymer-grafted silica the signal corresponding to residual geminal silanols (Q²) is not seen while its intensity is very less in ATRP initiator grafted silica (sil-initiator), however this signal is quite intense for d) which was prepared by "grafting to" method. In the spectra after immobilization of ATRP initiator (b) and after polymerization (c) emphasize signals for Tⁿ species that are related to the number of siloxane bonds. When the initiator was reacted with silica surface a large amount of cross-linked T² type silicon species (-57 ppm) was observed while polymer grafting increased cross-linked surface indicating by the appearance of T³ signals (-65 ppm). The disappearance of signal for T¹ in the spectrum (b) and (c) is due to the reaction of the silanol with self-assembling monolayer formed by ATRP initiator. For d) the signal corresponds to T² and T³ are completely absent however, T¹ signal is slightly appeared which indicates that relatively higher amount of silanol groups remain unfunctionalized in d) than c).

In liquid- or suspended-state NMR, only those molecules or parts of molecules are detectable that has very fast rotational motions. Motion must be in such a fast range that it can average out dipolar coupling and chemical shift anisotropy until related NMR peaks becomes narrow enough to be detected. The suspension-state ¹H NMR of sil-grafting from

polymer was measured from 25 to 50 °C. Neither half-height width (line width) of methylene groups nor spin-spin relaxation time (T_2) showed any significant change with temperature (20-50 °C) for both hybrid materials prepared by grafting from and grafting to method. We observed that intensity of the NMR peaks representing terminal methyl and methylene groups of octadecyl moieties increased slightly and detectable when a very high vertical scale was used for graphical presentation. These results indicate that the organic phase on the silica surface is in a solid state at room temperature.

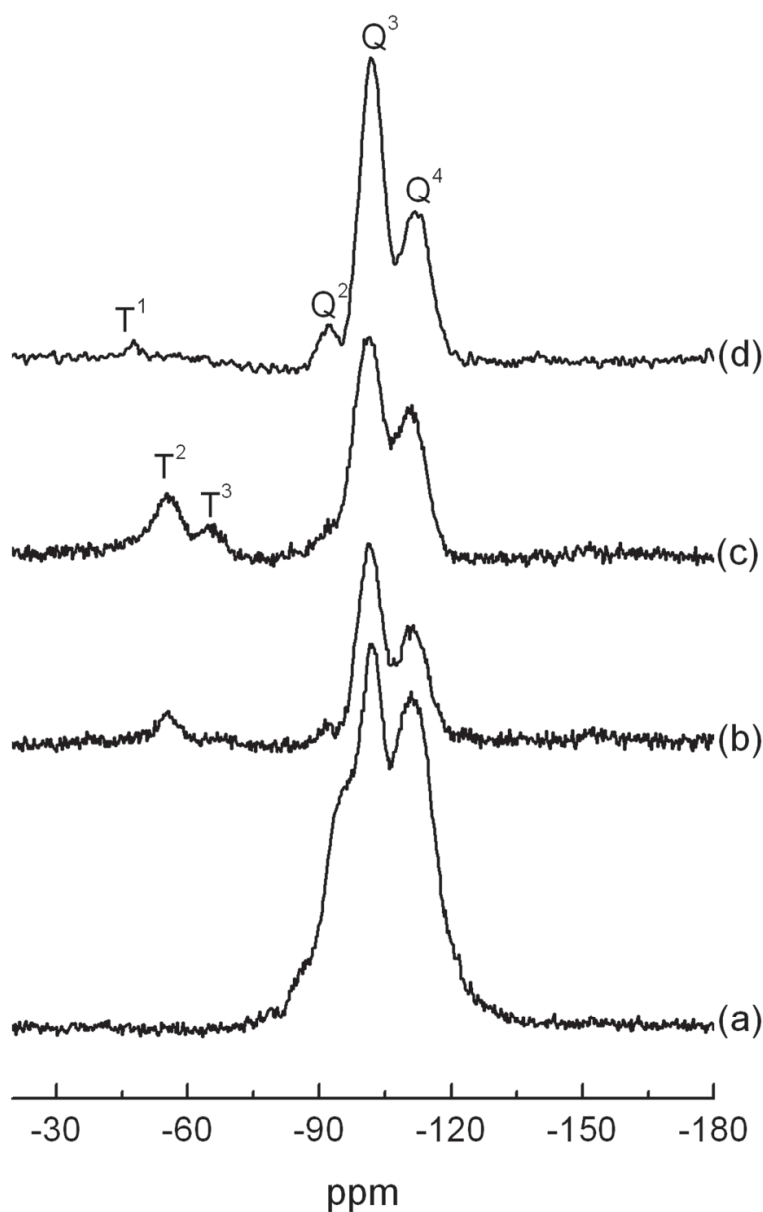


Fig. 4. ^{29}Si CP/MAS NMR spectra (a) bare silica, (b) sil-ATRP initiator, (c) sil-grafting from polymer and (d) sil-grafting to polymer

Under the condition of magic angle spinning and dipolar coupling of protons, the chemical shift of methylene groups in ^{13}C CP/MAS NMR spectroscopy depends largely on the conformation of octadecyl chains. For each central carbon atom in an octadecyl chain with

the *trans* conformation, a chemical shift of around 33 ppm is expected. On the other hand, for conformations with rapid changes between *gauche* and *trans*, a chemical shift of about 30 ppm is expected. Solid-state ^{13}C CP/MAS NMR offers useful information about the chemical composition of the polymer grafted silica in addition, it gives evidence about the conformation and dynamics of immobilized alkyl chains (Grant & Cheney, 1967). Under the condition of magic angle spinning and dipolar coupling of protons, the chemical shift of methylene groups in ^{13}C CP/MAS NMR spectroscopy depends largely on the conformation of alkyl chains - $(\text{CH}_2)_n$. In general, different conformations of the long alkyl moieties are detectable in two signals; for a rigid and ordered *trans* conformation, a chemical shift of around 33 ppm is expected, conversely, for mobile, amorphous and less ordered *gauche* conformations a chemical shift of about 30 ppm is anticipated. ^{13}C CP/MAS NMR spectra for polymer grafted silica were recorded at variable temperature 30 °C to gain insight of the conformational form of the alkyl chain (Fig. 5). The intense signal at 30.1 ppm is attributed due to *gauche* conformation however, the signal at 32.3 ppm due to *trans* conformations are very low. Generally, as the temperature is decreased more *trans* conformations are observed due to the lower mobility and higher rigidity of alkyl chain (Ansarian et al. 2005) The shows the alkyl chains of the grafted polymeric materis exists as *gauche* form which indicates the noncrystalline nature of the polymers also the immobilized alkyl chain stayed mobile, amorphous and less ordered form on silica surface.

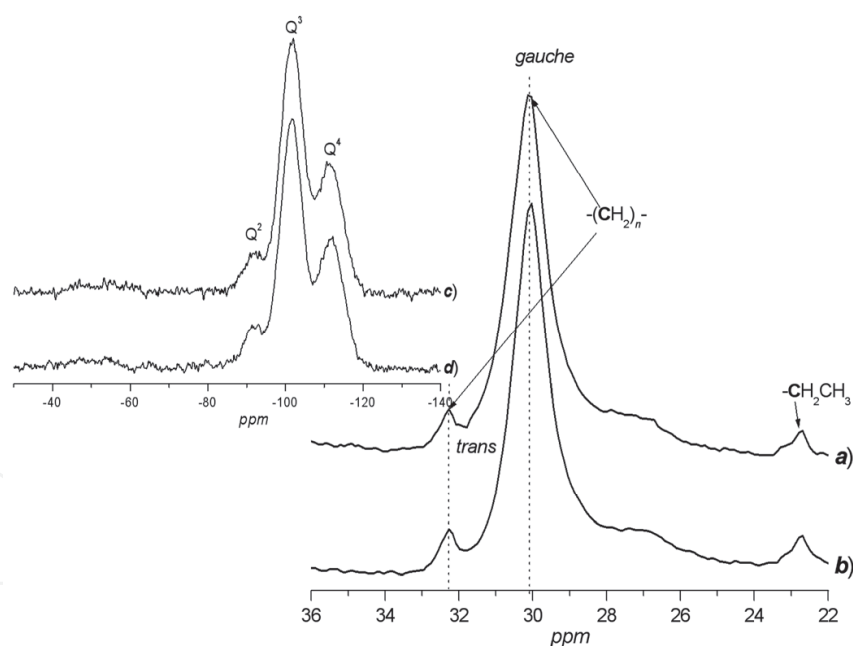


Fig. 5. Partial ^{13}C and ^{29}Si CP MAS NMR spectrum of hybrid composite prepared materials (a) and (c) are for Silica-polymer by “grafting from” method and (b) and (d) are for Silica - polymer by “grafting to” method.

The organic content of the grafted silica particles has been determined by thermogravimetric analysis. TGA runs were conducted at a constant heating rate of 10 °C /min in air using an empty crucible as reference. Heating process was carried out up to 800 °C that has been demonstrated to be sufficiently high to degrade all surface bonded organosilanes. and the resulted thermograms of a) bare silica, b) Sil-ATRP initiator, c) Silica-grafting to polymer d)

silica-grafting from polymer and e) telomere in Fig. 6. All weight retention profiles was observed to reach a plateau at 650 °C confirming that there is no organic material remained on silica at 800 °C. Considering the TGA curve of bare silica particles as reference the weight of the immobilized initiator can be calculated as 9.6 % which was translated to grafting density an average 0.61 initiator per nm². Similarly, the thermogravimetric analysis revealed that 25.5 % ATRP polymer is attached onto silica surface if the weight retention of sil-ATRP initiator was considered as reference at 800 °C. Comparison between the weight retention of bare silica particles and sil-grafting to polymer showed 13.5 % of grafted telomere that is only 53 % of the immobilization obtained by surface initiated ATRP or than that of grafting from process.

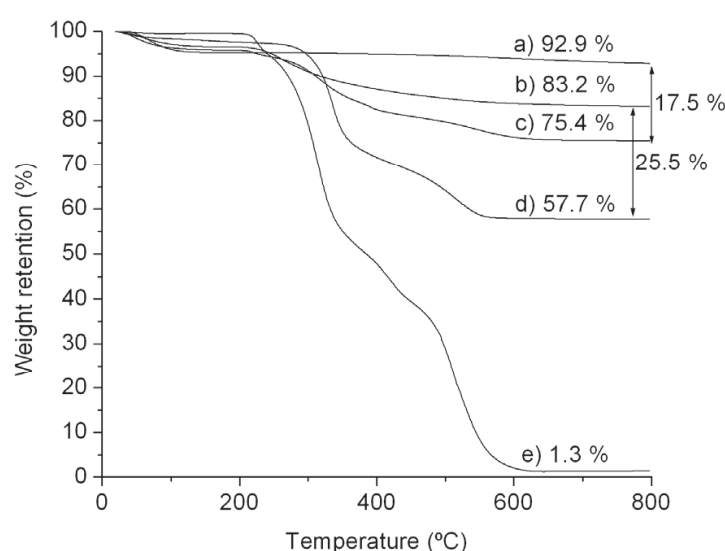


Fig. 4. Thermogravimetric analysis (TGA) data of hybrid composite materials prepared by both “grafting from” and “grafting to” method; a) bare silica, b) Sil-ATRP initiator, c) Silica-grafting to polymer d) silica-grafting from polymer and e) telomer

5. Application of hybrid composites for separation by HPLC

The hybrid composite materials were packed into stainless steel column in order to use stationary phase for high performance liquid chromatography. The chromatographic evaluation was also performed using the Tanaka test mixture containing hydrophobic probes which give information about shape and methylene selectivity, ion-exchange capacities from acidic and neutral media and hydrogen bonding capacities (Tanaka et al. 1989). The chromatogram obtained for monomer 1 by both grafting techniques is shown in Fig. 5 and Fig. 6 and is compared with conventional polymeric ODS column (ODS-p) stationary phase. This characterization protocol is a well-developed approach that is recommended to obtain information about functionality of the silylant reagent, and the methylene selectivity as well as to establish the repeatability and reproducibility of the separation behavior of commercially available stationary phase's ODS-p. The chromatogram showed the separation of two homologous alkylbenzenes as well as planar and nonplanar PAHs.

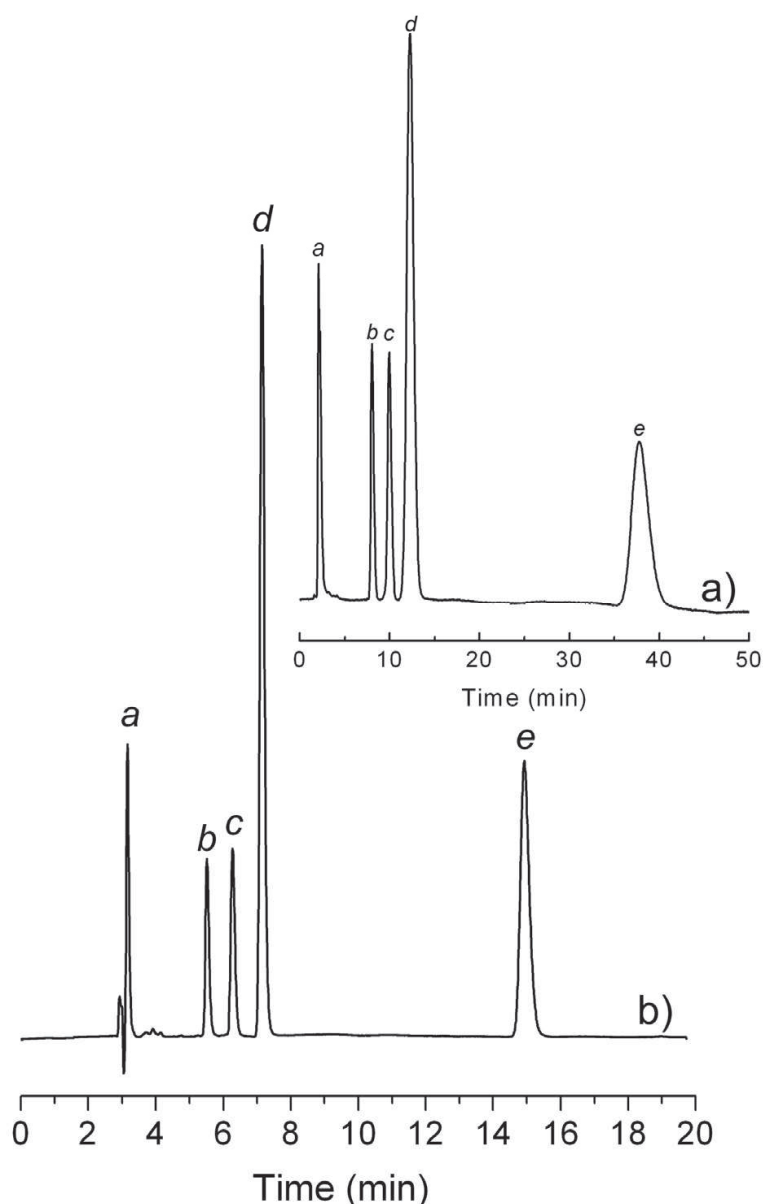


Fig. 5. Chromatogram for Tanaka test mixture for hybrid composite materials obtained from monomer 1 by a) "grafting from" and b) grafting to method. Elutes: a- uracil; b- butylbenzene; c- amylbenzene; d- *o*-terphenyl; e- triphenylene. Mobile phase: methanol: water = 90:10, column temperature 30 °C, flow rate: 1.0 mLmin⁻¹

6. Selectivity for PAHs

The shape selectivity of a given stationary phase can be measured by the separation factor (α) value for pairs of test solutes having the same carbon number but different shape, such as perylene/ 1, 1'-binaphthyl, triphenylene/ *o*-terphenyl, chrysene/ pyrene and *trans*-stilbene/ *cis*-stilbene. On a typical monomeric C₁₈ phase (C₁₈-M) the separation factor $\alpha_{\text{triphenylene/ } o\text{-terphenyl}}$ ranges from 1.0 to 1.7, while the value on a polymeric C₁₈ (C₁₈-P) phase lies between 2.0 to 2.7. Jinno et al.^{56,57} suggested that a separation factor (α) of triphenylene/ *o*-terphenyl ≥ 2.0 is an indication of significant solute planarity recognition.

Table 1 lists some of the α values measured on columns packed with silica-grafting to and silica-grafting from polymer as well as commercial monomer C₁₈ or ODS (Octadecyl silane) phase. It is clear that both the hybrid composite prepared from L-phenylalanine shows selectivity factor α (triphenylene/o-terphenyl) of 3.30-3.20 possesses enhanced shape selectivity for PAHs. The selectivity factor α (perylene/1,1'-binaphthyl) 16.5 and 13.5 on the sil-grafting to and sil-grafting from further exemplifies this extremely high planarity recognition. Interestingly, for the isomeric aromatic pair, chrysene and pyrene, the sil-grafting to phase yielded a selectivity factor of α (chrysene/ pyrene)= 1.55 while sil-grafting from yielded slightly lower value 1.53 demonstrated that on both phases shape recognition includes not only planarity but also the topology of solutes. However all the chromatographic data suggested that the chromatographic performance does not differ for the composite materials prepared by "grafting from" and "grafting to" method.

	separation factor (α)							
	silica- grafting to ^b	silica- grafting to ^c	silica- grafting from ^b	silica- grafting from ^c	C ₁₈ -P ^b	C ₁₈ -P ^c	C ₁₈ -M ^b	C ₁₈ -M ^c
triphenylene/ o- terphenyl	3.30	2.19	3.20	2.84	2.28	2.27	1.29	1.28
chrysene/ pyrene	1.55	1.33	1.52	1.43	1.40	1.40	1.22	1.22
perylene/ 1,1- binaphthyl	13.0	8.10	16.5	14.8	4.5	4.55	2.10	2.12
<i>trans</i> -stilbene/ <i>cis</i> -stilbene	1.58	1.28	1.52	1.41	1.22	1.22	1.06	1.06

mobile phase: ^b methanol/ water (90/10), ^c methanol / acetone / water (70/20/10), column temperature: 30°C and flow rate: 1.00 mLmin⁻¹

Table 1. Separation factors of PAH sample sets on different columns after adding acetone to the mobile phase

7. Conclusion

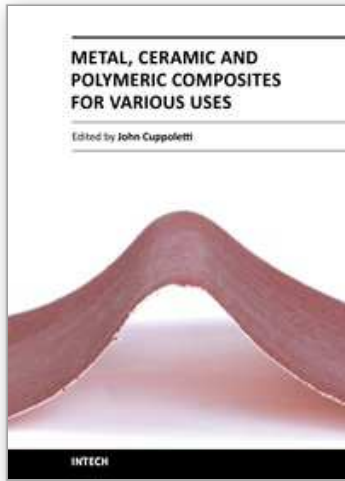
In conclusion we can say, by "grafting from" method significantly higher amounts of polymer can be grafted on to porous silica gels i.e. high grafting density than "grafting to" methods usually enhance the properties of composite materials. In contrast for chromatographic point of view there is no significant differences on selectivity of shape constrained solutes or toxic organic pollutants of different sizes and shapes.

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Composite materials, often shortened to composites, are engineered or naturally occurring materials made from two or more constituent materials with significantly different physical or chemical properties which remain separate and distinct at the macroscopic or microscopic scale within the finished structure. The aim of this book is to provide comprehensive reference and text on composite materials and structures. This book will cover aspects of design, production, manufacturing, exploitation and maintenance of composite materials. The scope of the book covers scientific, technological and practical concepts concerning research, development and realization of composites.

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