International Journal of Advance Research in Science and Engineering
Vol. No.5, Special Issue No. (01), February 2016
www.ijarse.com
IJARSE
ISSN 2319 - 8354

GROWING IMPORTANCE OF BIONANOCOMPOSITES

N. Sreenivasulu[1], PothulaLalithaKumari[2], P. Dinesh Sankar Reddy[3]

[123]Department of Chemical Engineering, JNTU College of Engineering, Ananthapuram, (India)

ABSTRACT

The demand for environmental sustainability has resulted in a great interest in finding new materials that are biodegradable and environmentally friendly. Therefore, materials derived from natural resources are now being extensively studied. The properties inherent to the biopolymers, that is, biocompatibility and biodegradability, open new prospects for these hybrid materials withspecial incidence in regenerative medicine and in environmentally friendly materials (green nanocomposites).Research on bionanocomposites can be regarded as a new interdisciplinary field closely related to significant topicssuch as biomineralization processes, bioinspired materials, and biomimetic systems. The upcoming developmentof novel bionanocomposites introducing multifunctionality represents a promising research topic that takesadvantage of the synergistic assembling of biopolymers with inorganic nanometer-sized solids. This article presents importance of a new research field of bionanocomposites where different types of nanomaterials are used as reinforcements in biopolymers.

***Keywords*: Biodegradable, Bionanocomposites, Biopolymers, Reinforcement, Sustainability.**

I. INTRODUCTION

Nanocomposites are composites in which at least one of the phases shows dimensions in the nanometer range (1 nm = 10^{-9}m) [1]. Nanocomposite materials have emerged as suitable alternatives to overcome limitations of micro composites and monolithics, while posing preparation challenges related to the control of elemental composition and stoichiometry in the nanocluster phase. They are reported to be the materials of 21stcentury in the view of possessing design uniqueness and property combinations that are not found in conventional composites. The general understanding of these properties is yet to be reached[2], even though the first inference on them was reported as early as 1992[3].It has been reported that changes in particle properties can be observed when the particle size is less than a particular level, called 'the critical size'(Table 1). Additionally, as dimensions reach the nanometer level, interactions at phase interfaces become largely improved, and this is important to enhance materials properties. In this context, the surface area/volume ratio of reinforcement materials employed in the preparation of nanocomposites is crucial to the understanding of their structure–property relationships. As in the case of microcomposites, Nanocomposite materials can be classified, according to their matrix materials, in three different categories as shown in Table2: Ceramic Matrix Nanocomposites (CMNC), Metal Matrix Nanocomposites (MMNC) andPolymer Matrix Nanocomposites (PMNC) [5].

Properties	**Feature Size (nm) at which changes might be expected**
Catalytic Activity	<5
Making Hard Magnetic Materials Soft	<20
Producing Refractive Index Changes	<50
Producing Super paramagnetism and other electromagnetic phenomena	<100
Producing Strengthening and Toughening	<100
Modifying Hardness and Plasticity	<100

Table 1. Feature sizes for significant changes in properties reported in nanocomposite systems [4].

Class	**Examples**
Metal	Fe-Cr/Al_2O_3, Ni/Al_2O_3, Co/Cr, Fe/MgO, Al/CNT, Mg/CNT
Ceramic	Al_2O_3/ SiO_2, SiO_2/Ni, Al_2O_3/TiO_2, Al_2O_3/SiC, Al_2O_3/CNT
Polymer	Thermoplastic/thermoset, polymer/layered silicates, polyester/TiO_2, polymer/CNT, polymer/layered double hydroxides.

Table 2. Different types of Nanocomposites [5].

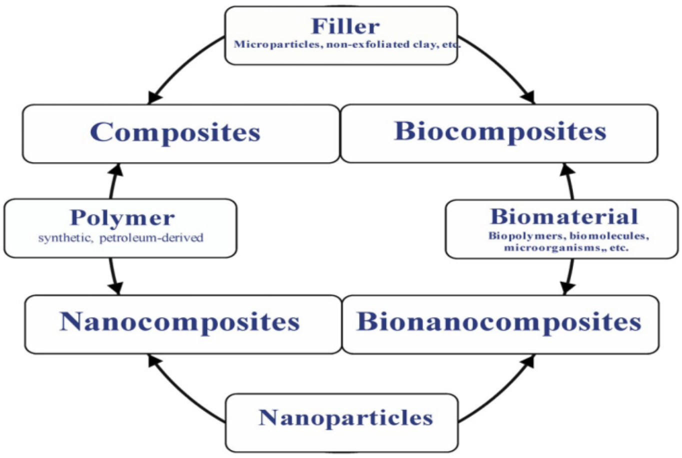

Fig. 1.Main types of composite materials and their constituents [6].

A new generation of hybrid nanostructured materials signifies an emerging field in the frontier between materials science, life science, and nanotechnology [7, 8]. During the last few years, “bionanocomposites” has become a common term.Bionanocomposites represent an emerging group of nanostructured hybrid materials. They are formed by the combination of natural polymers and inorganic solids and show at least one dimension on the nanometer scale. Similar to conventional nanocomposites,which involve synthetic polymers, these bio hybrid materials also exhibitimproved structural and functional properties of great interest for different applications[9].

II. IMPORTANCE OF BIONANOCOMPOSITES

In today's world, bio-nanocomposites are becoming increasingly prevalent owing to the extraordinary properties that they possess. Scientists learn to select suitable matrix (e.g. aliphatic polyesters, polypeptides and proteins, polysaccharides, and polynucleic acids) and fillers (e.g. nanotubes, nanofibers, clay nanoparticles, hydroxyapetite and metal nanoparticles) and alter their chemistry and structure to suit the target field [10].Since the development of nanocomposites two decades ago, materials scientists are making huge efforts in this research area because of the excellent features of these nanohybrids as structural or functional materials, with interesting applications as components in, amongst others, heterogeneous catalysts and optical, magnetic, and electrochemical devices [11].A considerable part of this effort is now being focused on the development of biopolymer based nanocomposites that display the well-known properties of nanocomposites derived from synthetic polymers (improved mechanical properties, higher thermal stability, and gas-barrier properties) [12,13].

In addition to these characteristics, bionanocomposites show the remarkable advantage of exhibiting biocompatibility, biodegradability and, in some cases, functional properties provided by either the biological or inorganic moieties. The great interest towards this research area is supported by the strong increase in the number of scientific publications according to the Institute for Scientific Information (ISI) database (Fig. 2).

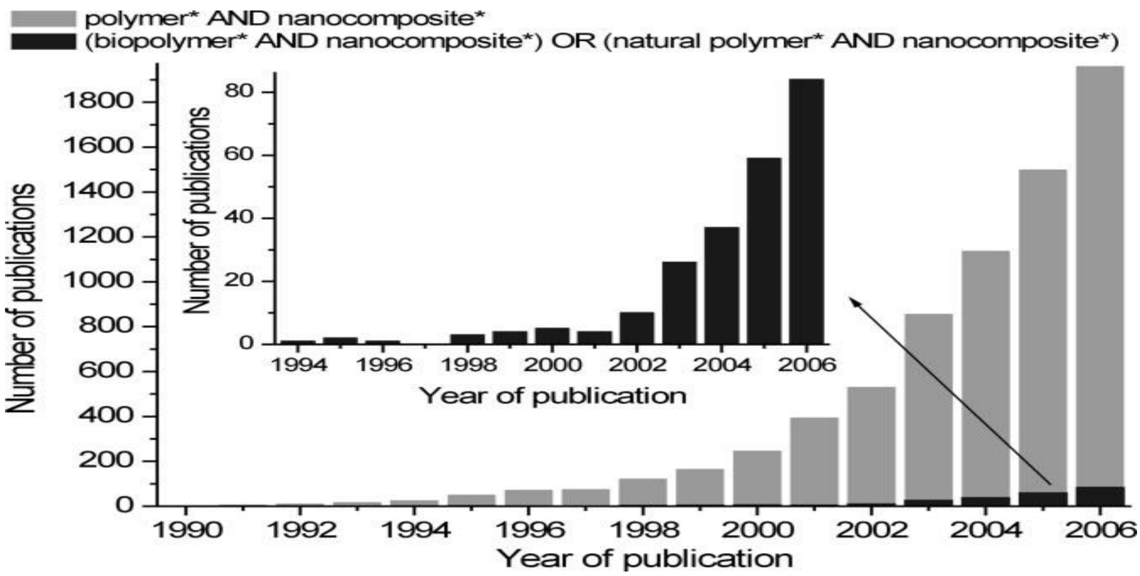

Fig. 2.Number of publications per year related to polymer-based nanocomposites versus biopolymer-based nanocomposites. Data collected from the ISI Web of Knowledge [v3.0]—Web of Science.

2.1 Importance of Green Bionanocomposites

Currently, there is a growing tendency to use environmentally friendly or "green" materials with the aim of replacing non-degradable materials, thereby reducing the environmental pollution that results from large amounts of plastic waste. Environmentally friendly materials with applications in agriculture, the building and food industries, or biomedicine are the main objective of many research groups.Plastics on the basis of synthetic polymers are widely used to make various materials for daily life. Theycan meet any commercial and industrial market requirements, such as low cost, good performance, convenience,durability, high variability in mechanical and other properties, etc. [14,15]. A significant percentage(ca. 40 %) of plastics consumption is used for packaging, which has grown rapidly from thelast decade of the 20th century [16,17]. Because plastics are highly resistant to degradation, humankind isnow being faced with a wealth of non-biodegradable waste, which increases every year. What is more,the synthetic plastics are manufactured from fossil resources that are under a contraction.

The photosynthetically generated biomass transferred into fossil resources (petroleum, natural gas,coal) that took millions of years to form by very slow natural processes. At present, petroleum is themain source for most chemicals and plastics including packaging [14]. The problem is that the fossilresources are not renewable. Fuel, chemicals, and materials are used very quickly in comparison withfossil generation. Furthermore, these resources are exhaustible, being finite in quantity.Increasing consumption of fossil resources has reached such a level that a novel,artificial cycle is created. Its influence on global processes and Earth's environment becomes moreobvious and nowadays is considered as a global environmental problem [18, 19].

Petroleum-derived synthetic plastics are being replaced by biodegradable natural polymers extracted from renewable natural resources, such as starch, cellulose, polylactic acid (PLA), or polycaprolactone, mostly in the production of bioplastics for packaging applications[20]. The possibility of replacing petroleum-derived synthetic polymers by natural, abundant, and low-cost biodegradable products obtained from renewable sources is also the aim of numerous research groups [21-23].Nature is the source of a wide number of bio macromolecules that can be involved in the preparation of these green bionanocomposites, which are most widely employed for this purpose [24]. Their combination with natural inorganic solids, such as clays, provides reinforced bioplastics that offer the advantages of nanocomposites as well as biocompatibility and biodegradability.Neutral polysaccharides, such as starch derived from corn, wheat, rice or potato, and cellulose and its derivatives, are the main biopolymers employed in the development of green nanocomposites [25, 26]. The biodegradable thermoplastic polyester PLA, derived from L-lactic acid produced in the fermentation of cornstarch, is another polymer widely used in the development of reinforced bioplastics, mainly in combination with organically modified silicates.

The biodegradability of reinforced PLA bioplastics strongly depends on the nature of the layered silicate and the organic modifier, making it possible to tailor the material's biodegradability by adding an appropriate organically modified clay as nanofiller (Fig. 3).It has been also stated that a faster hydrolytic degradation takes place for more hydrophilic fillers. New progresses within this field will require investigations concerning the use of alternative biopolymers and also on the methodology, to enhance compatibility with the inorganic moieties. Therefore, it can be expected that the controlled modification of polymers of natural origin, as well as the integration of a wide range of "non-pollutant" nanofillers other than silica and silicate, for example (Lactate dehydrogenase)LDHs, would afford new formulations and improve the mechanical and other properties of the resulting green nanocomposites.

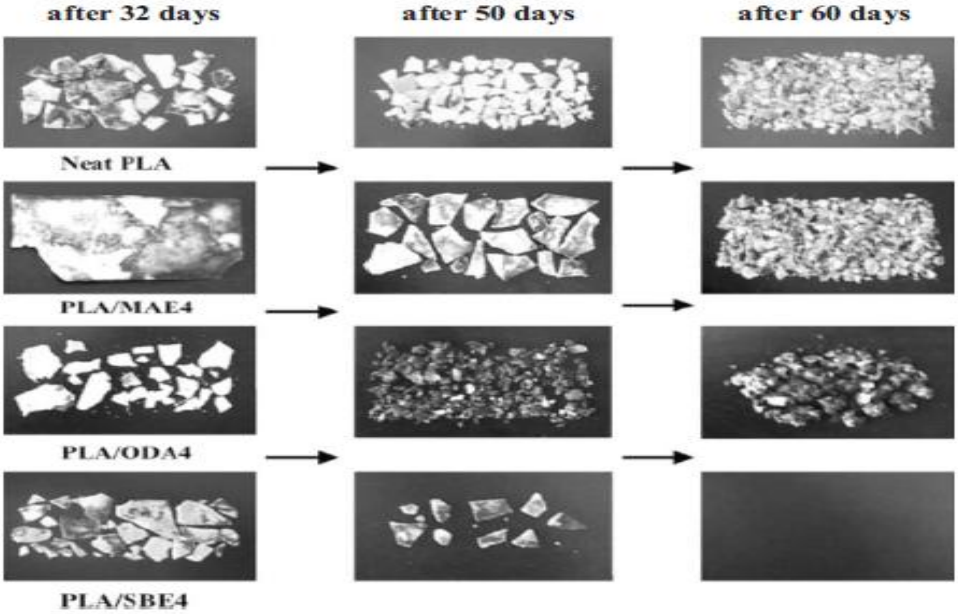

Fig. 3.Biodegradation of neat PLA and several PLA-based bionanocomposites involving organically modified layered silicates. MAE4: dimethyldioctadecyl ammonium cation; ODA4: octadecylammonium cation SBE4: trimethyloctadecylammonium cation. Reproduced from [27].

2.2. Importance of Bionanocomposites in Life Sciences

One of the main applications of bionanocomposites is related to biomedical applications, such as tissue engineering.This fact has led to a wide number of scientific publications on this topic in recent years. However, as recently pointed out by Thomas et al. [28] the development of biomaterials for regenerative medicine can be still considered an emerging field, with tissue engineering, and especially bone implants, being a fast-growing branch of this research area.Biocompatible materials involving biopolymers, such as collagen and PLA, are the most widely studied materials for the regeneration of damaged tissues, acting as artificial supports for cell growth. The requirements for these bioresorbable scaffolds are biocompatibility,suitable mechanical properties to avoid the collapseof the implant, sufficient macroporosity with interconnected pores to allow for the transport of nutrients and metabolic wastes, and controlled biodegradability, because the rate of biodegradation needs to be balanced with the rate at which tissue is regenerated [29, 30].

Most of the works found in literature are devoted to bone repair purposes. A large number of bionanocomposites tested as implants include HAP combined to collagen, a fibrous protein, in order to reproduce the composition, biocompatibility, and mechanical properties of natural bone [31-33].Other biopolymers, such as PLA, [34] alginate, [35] chitosan,[36] seroalbumin,[37] and silk fibroin[38] have also been combined to HAP with the aim of developing suitable scaffolds for the creation of new bone. These implants try to mimic the nanostructure, porosity, and surface roughness of natural bone, as these features seem to facilitate the spreading of osteoblasts and bone regeneration.

Future improvements within this research line could be aimed towards the replacement of HAP in biopolymer-based implants by alternative inorganic, or even organic–inorganic, substrates. Among the few examples that have been studied so far, sepiolite is a magnesium silicate with a microfibrousmorphology that has been successfully combined with biopolymers such as collagen, giving rise to hybrid materials with a high degree of organization [39]. Recently, Al_2O_3–Zr_2O nanoparticles have also been used to reinforce biological matrices such as collagen, enhancing mechanical and thermal properties and leading to hybrid materials with potential use in biomedical and bionic applications [40].Interestingly, the implant could also act as a drug reservoir, working simultaneously as a scaffold for the growth of new tissue and as a dispenser for the controlled release of bioactive compounds. Examples of such innovative applications are the entrapment of a morphogenetic protein to favor tissue regeneration in an HAP–alginate–collagen system (Fig. 4), [41]and the incorporation of a vitamin in a Ca-deficient HAP–chitosan nanocomposite [42].

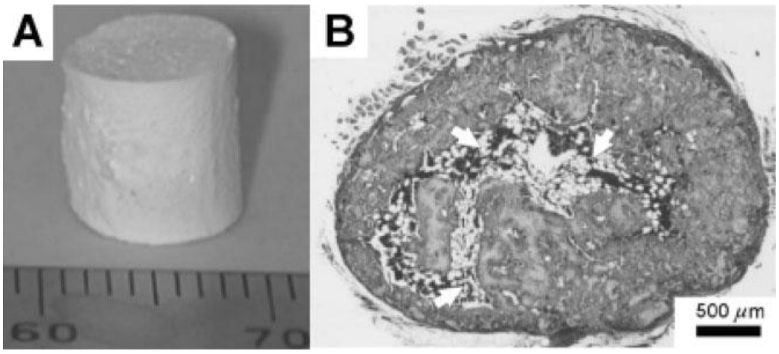

Fig. 4. A) HAP–alginate–collagen implant, and B) HE section of the whole implant loaded with a bone morphogenetic protein, showing bone formation throughout almost the entire implant and bone marrow-like tissue (arrows) 5 weeks after implantation. Reproduced from [41].

Biocompatibility and reduced dimensions are very useful properties for the application of some bionanocomposites as drug delivery systems. Several examples of this application have been reported in the last years, the use of a DNA-loaded LDH as a nonviral vector for gene therapy being one the first works in this topic [43]. Silica-based bionanocomposites processed as nanospheres by means of spray-drying techniques have been also envisaged as a drug delivery system.So far, most efforts were made on HAP and related inorganic solids, but it is expected that ongoing research on biohybrids involving nanoparticulate ceramics of different types, and even metal–ceramic composites, will improve the fracture hardiness and other mechanical properties necessary in, for example, orthopaedic applications. A future goal would involve ternary systems, in which the inorganic moiety is coupled to blends of biopolymers and synthetic polymers. This appears as an attractive route for the preparation of novel bionanocomposites showing good strength behaviors and hierarchical porous order introduced by means of freeze-drying techniques.

2.3 Functional Bionanocomposites

This sectionwill focus on bionanohybrid materials with functionalitiessuited to becoming the active part ofelectrochemical, optical, or photoelectrical devices.Intercalation compounds, resulting from the combinationof several charged polysaccharides with charged inorganiclayered solids such as clay minerals and LDHs, appear as anew class of hybrid materials that show suitable properties foracting as active phases in electrochemical sensors. This newapplication was first reported in 2003, when a chitosan–montmorillonitebionanocomposite exhibiting anion-exchangeability was used to build potentiometric sensors [44].This functional bionanocomposites also possesses excellent mechanical properties that facilitateits application in the construction of electrochemical sensors.The potentiometric evaluation of this device shows amarked selectivity towards monovalent anions, which canoriginate from the special arrangement of the biopolymer inthe clay interlayer space as a nanostructured bi-dimensionalsystem.

Enzymatic biosensors offer numerous advantages, includinggood sensitivity, high specificity, and long-time stability, thatallow re-use of the device in numerous measurements. Theseparameters are closely related to the stable immobilization ofthe biological agent. It is well-known that the encapsulationof enzymes in a confined space prevents irreversible structuraldeformations, preserving their tertiary structure.More recent works have achieved the immobilizationof different enzymes and globular proteins in otherlayered solids such as zirconium phosphate (ZrP), [45]layered calciumniobate ($HCa_2Nb_3O_{10}$, perovskite) [46], manganesetriphosphochalcogenide ($MnPS_3$),[47] and a syntheticmagnesium phyllosilicate,[48] among other examples.Themechanism followed in the preparation of these bionanocompositesinvolves a delamination of the layered solid, usuallyby means of quaternary ammonium salts, followed by the re-stacking of the layers entrapping the biological moiety. These works open the way not only to new activephases for biosensors, but also to nanocontainers and nanoreactorsusing porous solids that entrap this class of functionalbiopolymers. The protective effect of the inorganic matrix and the increasedlong-term stability are the main advantages of enzyme-based bionanocomposites, which appear as new alternativesto the classical methods of immobilization for thedevelopment of improved devices, from biosensors to enzymaticbioreactors. Future trends towards the development of multifunctionalbionanocomposites may include the combinationof active inorganic counterparts present as nanoparticles, providingnew properties to the hybrid systems, with the biopolymersproviding biocompatibility.

III. CONCLUSIONS

Bionanocomposites are hybrid nanostructrured materials based on naturally occurring polymers. In the last decade, they have been the subject of research in many different areas with a wide number of applications, from regenerative medicine to food packaging. Taking into account their common properties, the aim of the present work was to consider them from an interdisciplinary point of view. In fact, bionanocomposites can be integrated in a new field at the frontier of materials science, life sciences, and nanotechnology. Two main reasons have propelled the use of biopolymers in the synthesis of nanocomposites, replacing the commonly employed petroleum-derived polymers. The first one is related to the biodegradability of the obtained materials resulting from the incorporation of these natural polymers, on the other hand, biocompatibility is a crucial property for the application of these biohybrids in food packaging or tissue engineering in regenerative medicine.The future development of novel bionanocomposites with improved properties and multifunctionality can be envisaged as an emerging, open field of research, with plenty of possibilities because of the great abundance and diversity of biopolymers in nature, as well as the advantage of their synergistic combination with inorganic nanosized solids.

REFERENCES

[1] Roy R, Roy RA, Roy DM. Alternative perspectives on “quasi-crystallinity”: non-uniformity and nanocomposites. Materials Letters. 1986; 4(8-9):323-328.

[2] Schmidt D, Shah D, Giannelis EP. New advances in polymer/layered silicate nanocomposites. Current Opinion in Solid State & Materials Science. 2002; 6(3):205-212.

[3] Gleiter H. Materials with ultrafine microstructures: retrospectives and perspectives. Nanostructured Materials. 1992; 1(1):1-19.

[4] Kamigaito O. What can be improved by nanometer composites? Journal of Japan Society of Powder Metalurgy. 1991; 38:315-321.

[5] Pedro Henrique Cury Camargo, KesturGundappaSatyanarayana, Fernando Wypych. Nanocomposites: Synthesis, Structure, Properties and New Application Opportunities. Materials Research, 2009, Vol. 12, No. 1, 1-39.

[6] YuryShchipunov. Bionanocomposites: Green sustainable materials for the near future.Pure Appl. Chem., 2012, Vol. 84, No. 12, pp. 2579–2607.

[7] G. Ozin, A. Arsenault, Nanochemistry: A Chemical Approach to Nanomaterials, Royal Society of Chemistry, Cambridge, UK 2005, Ch. 10.

[8] E. Dujardin, S. Mann, Adv. Mater. 2002, 14, 775.

[9] Margarita Darder, PilarAranda, and Eduardo Ruiz-Hitzky.Bionanocomposites: A New Concept of Ecological, Bioinspired, and Functional Hybrid Materials.Adv. Mater. 2007, 19, 1309–1319.

[10] S. Komarneni, J. Mater. Chem. 1992, 2, 1219.

[11] a) E. Ruiz-Hitzky, Adv. Mater. 1993, 5, 334. b) E. Ruiz-Hitzky, P. Aranda, B. Casal, J. C. Galván, Adv. Mater. 1995, 7, 180. c) Functional Hybrid Materials (Eds: P. Gómez-Romero, C. Sanchez), Wiley-VCH, Weinheim, Germany 2004. d) C. Sanchez, B. Julián, P. Belleville, M. Popall, J. Mater. Chem. 2005, 15, 3559. e) P. Aranda, M. Darder, R. Fernández-Saavedra, M. López-Blanco, E. Ruiz-Hitzky, Thin Solid Films 2006, 495, 104.

[12] M. Alexandre, P. Dubois, Mater. Sci. Eng., R 2000, 28.

[13] E. Ruiz-Hitzky, A. Van Meerbeek, in Handbook of Clay Science (Eds: F. Bergaya, B. K. G. Theng, G. Lagaly), Elsevier, Amsterdam 2006, Ch. 10.3.

[14] J. A. Brydson. Plastics Materials (Butterworth-Heinemann, Oxford, 1999).

[15] D. Rosato, D. Rosato. Plastics Engineered Product Design(Elsevier, Oxford, 2003).

[16] V. A. Fomin, V. V. Guseev. Prog. Rubber Plastics Technol. 17, 186 (2001).

[17] S. Pilla. In Handbook of Bioplastics and Biocomposites Engineering Applications, S. Pilla (Ed.), pp. 1–15, Scrivener, Salem, MA (2011).

[18] K. Sudesh, T. Iwata. CLEAN - Soil, Air, Water, 36, 433 (2008).

[19] D. S. Golomb, J. A. Fay. In Energy, Waste, and the Environment: A Geochemical Perspective. Special Publications 236, R. Giere, P. Stille (Eds.), pp. 153–167, Geological Society, London (2004).

[20] S. Sinha Ray, M. Bousmina, Progr. Mater. Sci. 2005, 50, 962.

[21] J. K. Pandey, A. P. Kumar, M. Misra, A. K. Mohanty, L. T. Drzal, R. P. Singh, J. Nanosci. Nanotechnol. 2005, 5, 497.

[22] L. Yu, K. Dean, L. Li, Prog. Polym. Sci. 2006, 31, 576.

[23] S. Sinha Ray, M. Okamoto, Macromol. Rapid Commun. 2003, 24, 815.

[24] H. M. Park, M. Misra, L. T. Drzal, A. K. Mohanty, Biomacromolecules2004, 5, 2281.

[25] J. K. Pandey, R. P. Singh, Starch 2005, 57, 8.

[26] A. C. Wibowo, M. Misra, H.-M. Park, L. T. Drzal, R. Schalek, A. K. Mohanty, Composites, Part A2006, 37,1428.

[27] S. Sinha Ray, K. Yamada, M. Okamoto, K. Ueda, Macromol. Mater. Eng. 2003, 288, 203.

[28] V. Thomas, D. R. Dean, Y. K. Vohra, Curr. Nanosci. 2006, 2, 155.

[29] V. Thomas, D. R. Dean, Y. K. Vohra, Curr. Nanosci. 2006, 2, 155.

[30] M. S. Widmer, A. G. Mikos, in Frontiers in Tissue Engineering (Eds: C. W. Patrick, Jr., A. G. Mikos, L. V. McIntire, Elsevier, Oxford 1998, Ch. II.5).

[31] P. Fratzl, H. S. Gupta, E. P. Paschalis, P. Roschger, J. Mater. Chem.2004, 14, 2115.

[32] Y. J. Wang, C. R. Yang, X. F. Chen, N. R. Zhao, Adv. Eng. Mater.2006, 8, 97.

[33] S. Yunoki, T. Ikoma, A. Monkawa, K. Ohta, M. Kikuchi, S. Sotome, K. Shinomiya, J. Tanaka, Mater. Lett.2006, 60, 999.

[34] K. J. L. Burg, S. Porter, J. F. Kellam, Biomaterials 2000, 21, 2347.

[35] L. M. Mathieu, T. L. Mueller, P.-E. Bourban, D. P. Pioletti, R. Müller, J.-A. E. Månson, Biomaterials 2006, 27, 905.

[36] A. Tampieri, M. Sandri, E. Landi, G. Celotti, N. Roveri, M. Mattioli- Belmonte, L. Virgili, F. Gabbanelli, G. Biagini, ActaBiomater. 2005, 1, 343.

[37] V. M. Rusu, C.-H. Ng, M. Wilke, B. Tiersch, P. Fratzl, M. G. Peter, Biomaterials 2005, 26, 5414.

[38] A. Sinha, S. Nayar, A. Agrawal, D. Bhattacharyya, P. Ramachandrarao, J. Am. Ceram. Soc. 2003, 86, 357.

[39] N. Olmo, M. A. Lizarbe, J. G. Gavilanes, Biomaterials 1987, 8, 67.

[40] Y. Cao, Y. Zhou, Y. Shan, H. Ju, X. Xue, Adv. Mater. 2006, 18, 1838.

[41] S. Sotome, T. Uemura, M. Kikuchi, J. Chen, S. Itoh, J. Tanaka, T. Tateishi, K. Shinomiya, Mater. Sci. Eng.,C 2004, 24, 341.

[42] T.-Y. Liu, S.-Y. Chen, J.-H. Li, D.-M. Liu, J. Controlled Release 2006,112, 88.

[43] J. H. Choy, S. Y. Kwak, Y. J. Jeong, J. S. Park, Angew. Chem. Int. Ed. 2000, 39, 4042.

[44] M. Darder, M. Colilla, E. Ruiz-Hitzky, Chem. Mater. 2003, 15, 3774.

[45] C. V. Kumar, A. Chaudhari, J. Am. Chem. Soc. 2000, 122, 830.

[46] L. Gao, Q. Gao, Q. Wang, S. Peng, J. Shi, Biomaterials 2005, 26, 5267.

[47] T. Coradin, A. Coupé, J. Livage, J. Mater. Chem. 2003, 13, 705.

[48] A. J. Patil, E. Muthusamy, S. Mann, J. Mater. Chem. 2005, 15, 3838.