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MULTI-LAYER POLYANILINE ASSEMBLIES IN BENTONITE CLAY

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ABSTRACT

The nanometer scale physical and chemical topography of polymer-layered silicate composites are important in the study and development of nano-structured materials including chemical sensors, photonic devices, and inorganic-organic quantum-well type structures. The properties of such composite materials are often a synergetic combination of the corresponding properties of the host material and the guest polymers. Expandability as well as the capacity for ion exchange of smectite clays such as Bentonite can be exploited in the preparation inorganic/organic host-guest composites. This paper describes the preparation and characterization of a conducting polyaniline-Bentonite composite by the polymerization of anilinium ions within the interlayer space. A procedure for the successive introduction of polyaniline layers was developed. The conductivity of these composites was found to improve with the number of conducting polymer layers incorporated.

Key words: Inorganic/organic host-guest composites, conducting polyaniline, Bentonite

1. INTRODUCTION

Intercalation of electronically conducting polymers into interlayer spaces of layered materials has been a research area of great interest during the recent years[1]. The nanometer scale physical and chemical topography of polymer-layered silicate composites are important in the study and development of nanostructured materials including chemical sensors[2], photonic devices[3], and inorganic-organic quantum-well type assemblies[3,4]. The properties of such composite materials are often a synergetic combination of the corresponding properties of the host material and the guest polymers.

Various techniques used to prepare such intercalated host-guest materials, in general, and conducting polymers in confined environments, in particular, have been reviewed [3]. These include the preparation of polyacetylene, polyaniline, polypyrrole, and polythiophene in templating matrices such as graphite tubes, membranes, zeolites, Langmuir-Blodgett films, pillared clays, porous glass, and lamellar chalcogenides[3,4]. Some researchers have made use of the catalytic properties of ordinary and ion-exchanged clays to polymerize spontaneously monomers of electronically conducting polymers within interlayer spaces of clay particles. Cu(II)-exchanged hectorite thin films have shown to possess remarkable catalytic properties for the spontaneous polymerization of aniline, thiophene and pyrrole[2, 5]. The researchers have claimed that the availability of surface Cu(II) cations *via* defects or faults in the layered silicate structure is crucial to the formation of the subsequent conducting polymer layer. The Fe(III) sites present in Fe(III)-exchanged montmorillonite have been utilized in the preparation of polypyrrole containing montmorillonite composite

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materials[6]. Alternatively, composite materials based on phyllosilicate-type clay and a conducting polymer has been synthesized by polymerizing the respective monomer in a colloidal clay suspension[7]. Photocatalytic polymerization of protonated N-phenyl-p-phenylenediamine using $Ru(bpy)_3^{2+}$ intercalated within hectorite clay has been investigated[8].

In the present study, the expanding nature and ion exchange capabilities of smectite clays, Bentonite in particular, were employed to incorporate polyaniline within interlayer spaces of such clays. Bentonite is a natural material that swells 14 - 16 times upon hydration. Bentonite forms a thick gel in water when the space for free swelling is limited. Further penetration of moisture is thus inhibited. Bentonite has the composition 58.25% SiO_2, 14.27% Al_2O_3, 4.37% Fe_2O_3, 0.5% FeO, 0.36% TiO_2, 2.07% CaO, 3.62% MgO, 0.18% P_2O_5, 0.14% S, 1.2% K_2O, 2.25% Na_2O and 12.19% void. Each crystal of Bentonite has a net negative charge. Thus, it tends to attract cations to its surface. Bentonite clays are generally classified depending on the cations present in majority within the interlayer spaces, for e.g., in sodium bentonite, the majority of cations are Na^+, and in calcium bentonite they are Ca^{2+}, and so on. The cations on the clay can be easily exchanged for other cations. A measure of this capacity is commonly referred to as the cation exchange capacity (CEC) and is usually expressed as milliequivalents of cations per hundred grams of clay. Bentonite used in our work has the cation exchange capacity of 100 milliequivalents per 100 g.

In this publication, we describe the preparation of polyaniline containing Bentonite clays, the technique of film preparation, method used to reload polyaniline within the interlayer spaces of Bentonite, and the properties of the composite materials as characterised by XRD, FTIR spectroscopy, UV-Visible spectroscopy and electronic conductivity measurements.

2. EXPERIMENTAL

30.00 g of Bentonite clay (BDH) was suspended in 500 cm^3 of doubly distilled water and stirred using a magnetic stirrer for 48 hours. The suspension was centrifuged at 5000 rpm, and the clear supernatant was decanted. The resultant slurry was re-dispersed in 500 cm^3 of water and the above procedure repeated until the supernatant was free of any impurity. The slurry thus obtained was stirred for 24 h with either 1.0 mol dm^{-3} HCl (aq) or 1.0 mol dm^{-3} NaCl (aq) solution. The resultant colloidal solution was centrifuged, and the supernatant discarded. The slurry obtained was then stirred with distilled water as above, the suspension centrifuged and the supernatant discarded. This procedure was repeated until the supernatant was free of Cl^- ions [tested using $AgNO_3$ (aq)]. The slurry thus obtained is the Bentonite containing hydrated protons/Na^+ ions within the interlayer spaces of the clay particle (H^+-Bentonite/Na^+-Bentonite).

A small portion of the H^+-Bentonite/ Na^+-Bentonite slurry was re-dispersed in 500 cm^3 of doubly distilled water, and a few drops of the colloidal suspension from the clear top part of the slurry was placed on a clean glass surface and allowed to dry in the ambient laboratory environment. Some of the dried samples were placed in a constant humidity environment (the vapour phase of water saturated with $NaNO_3$), while other some samples were allowed to dry in an oven preheated to 120 °C. XRD Spectra of H^+-Bentonite/Na^+-Bentonite were recorded as a function of aging in the ambient laboratory environment, in the constant humidity environment, as well as after drying at 120 °C for predetermined times. Free-standing thin films of H^+-Bentonite/ Na^+-Bentonite were prepared as follows. A few drops of the slurry, mentioned above, was placed on a thin polythene sheet firmly held on a glass plate by means of a thin layer of water between the glass plate and the polythene sheet. The clay film produced after evaporation of water was peeled off by pulling the polythene sheet against the glass plate. The UV-visible (Hewlett-Packard Diode Array Spectrophotometer), and FTIR (JASCO/FT/IR-410) spectra of these thin clay films were then recorded.

The H^+/ Na^+ ions present in the interlayer spaces of H^+-Bentonite /Na^+-Bentonite were exchanged for various metal ions (Ca^{2+}, Mg^{2+}) and the spectroscopic properties of the ion-exchanged clays were investigated as in the case of H^+-Bentonite. /Na^+-Bentonite The protons of H^+-Bentonite/Na^+-Bentonite were, also, exchanged for anilinium ions by the usual procedure of ion-exchange and the resulting $C_6H_5NH_3^+$-Bentonite were prepared as

films. This new material was extensively characterised by XRD, UV-visible spectroscopy and electronic conductivity measurements. The anilinium ions present within interlayer sites were polymerized using acidified (HCl) aqueous solution of Fe(III) as well as acidified (HCl) aqueous solution of $S_2O_8^{2-}$ as the oxidant. This resulted in a green coloured suspension of clay in water. Subsequent to the polymerization, the suspension was centrifuged and the supernatant decanted. The slurry was then stirred with doubly distilled water, centrifuged and decanted several times until the supernatant was free of chloride ions. The green coloured polyaniline form is known as the emaraldine salt. Films of this Emeraldine salt-Bentonite composite material (EMS1-Bentonite) were prepared as described earlier and its XRD, and UV-Visible spectra were recorded. The polymer present in the clay was then neutralised with NH_4OH to obtain the blue coloured Emeraldine base-Bentonite composite. This material in aqueous suspension was treated with aqueous anilinium chloride in order to insert more anilinium ions. The anilinium ions thus inserted were then polymerized to obtain an intensely green coloured clay suspension composed of Bentonite twice loaded with Emeraldine (EMS2-Bentonite). This material was also purified and characterised as described above. By repeating the neutralisation and reloading of anilinium ions within Bentonite followed by polymerization procedure, Bentonite thrice loaded with Emeraldine salt (EMS3-Bentonite) was also prepared and the materials characterised.

Free standing thin films of $C_6H_5NH_3^+$-Bentonite, EMS1-Bentonite, EMS2-Bentonite, and EMS3-Bentonite as described earlier and their UV-visible and FTIR spectra were recorded. In addition, films of each of these materials were prepared on pre-cleaned glass surfaces for XRD investigation.

3. RESULTS AND DISCUSSION

Figure 1(a) shows the XRD spectra of natural Bentonite film, Na^+ treated Bentonite and anilinium treated Bentonite, dried under ambient laboratory environment for 7 days. The same after heat treating at 150 °C for 2 hrs is shown in figure 1(b). The (001) layer spacings obtained are 15.50 Å, 14.7 Å and 13.32 Å, respectively. When the same samples were oven dried at 150 °C for 2 hours, the (001) layer spacings reduced to 9.96 Å, 9.93 Å and 12.80 Å, respectively.

The first layer spacing (10.0 Å) has been attributed to the presence of dehydrated cations within interlayer spaces[9], and the layer spacing increases up to 13 Å when the cations are surrounded by one water-layer[9]. The presence of two water-layers within interlayer spaces together with cations results in an enhancement of d-spacing up to 16 Å, while three water layers give d-spacing of up to 19 Å [10,11]. However, the above values of d-spacing depend also on the nature of the cations within the interlayer spaces. These Bentonite structures are shown in figure 2. Hence, it can be concluded that the Bentonite samples used in the present work with d-spacing of around 10 Å contain fully dehydrated cations, samples with d-spacings of 13.0 Å contained a single water layer, samples with d-spacings of 15 Å contained two water layers, and samples with d-spacings of 18.0 Å contained three water layers within interlayer spaces[12].

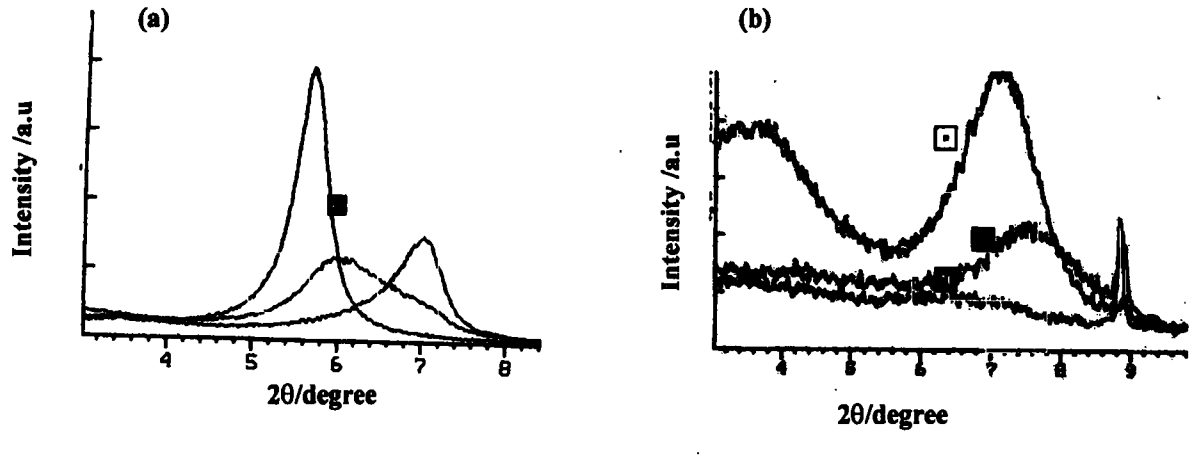

Fig.1 The XRD spectra of natural Bentonite film, Na^+ treated Bentonite and anilinium treated Bentonite, (a) dried under ambient laboratory environment for 7 days, (b) subsequent to 2 hr heat treatment at 150 °C.

We have also observed that when the cations in Bentonite are protons exchanged (Bentonite-H^+), at least one water-layer remains even after drying at 120 °C for several hours (The d-value is 11.61 Å). The d-value of Bentonite-H^+/Na^+-Bentonite is unaffected when exposed to a constant humidity environment for several days. However, it increased to 14.5 Å when placed in the ambient laboratory environment for a long period of time. However, heat-treatment at temperatures above 150 °C removes all water layers and d-spacing decreases to 9.9 Å.

The anilinium exchanged Bentonite (An^+-Bentonite) showed the following d values: 12.5 Å (heat-treated at 130 °C), 13.1 Å (in the constant humidity environment) and 13.1 Å (in the normal laboratory environment), respectively. This suggests that anilinium-exchanged Bentonite particles contain one or two water-layers within its interlayer spaces. When the anilinium ions entrapped within interlayer spaces are polymerized, the d-spacing changes. The d-spacing of Bentonite sample containing polyaniline, dried at 120 °C, is 12.9 Å, and this value is unaffected by the heat treatment up to 175 °C. This indicates that the Bentonite containing polyaniline with an interlayer spacing of 12.9 Å is anhydrous. The Bentonite sample containing polyaniline is green in colour with a surface resistivity of around 15 kΩ cm^{-1}. This material, unlike Na^+/ H^+ or metal ion exchanged Bentonite, does not appear to take up water into its structure. This is probably due to the hydrophobicity of the large polymer chains as opposed to hydrophilicity of inorganic and small organic cations. This observation suggests that when anilinium-exchanged Bentonite is polymerized the polymer is formed within the interlayer. The fact that d-spacing does not decrease below 12.6 Å upon heating confirms this view. As evidenced from UV-visible spectroscopy as well as electronic conductivity measurements, the interlayer polyaniline takes the emaraldine salt form. This material is labeled Bentonite-EMS1.

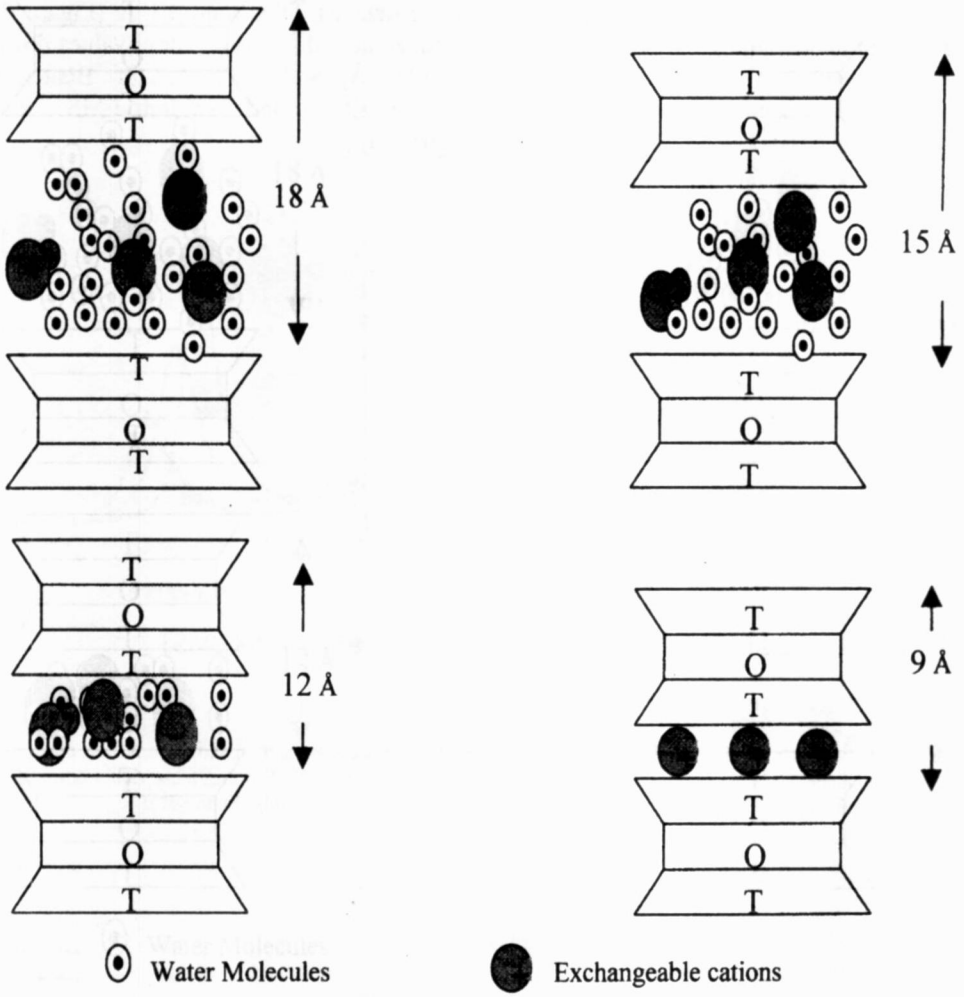

Fig.2 Bentonite samples used in the present work: d-spacing of around 9 Å contain fully dehydrated cations, samples with d-spacings of 12 Å contained a single water layer, samples with d-spacings of 15 Å contained two water layers, and samples with d-spacings of 18 Å contained three water layers within interlayer spaces.

When Bentonite-EMS1 is neutralized by treating with ammonium, the composite material (Bentonite-EMBASE1) becomes blue in colour and electronically insulating. The charge balancing of the clay structure requires the uptake of ammonium ions. When this material is treated with 1 mol dm^{-3} anilinium hydrochloride followed by acidified ferric chloride, the green colour and the electronic conductivity are regenerated. The resulting material, when heat treated at 120 °C has a d-spacing of 13.9. The heat treatment at higher temperatures does not change the d-spacing of this material. This material (Bentonite-EMS2) should, therefore, contain more layers of the polymer within the interlayer spaces of the clay than those present in Bentonite-EMS1.

After reducing the polymer in Bentonite-EMS2 more anilinium ions were incorporated into the interlayer. Subsequent polymerization produced the material labeled as Bentonite-EMS3, which has a higher electronic conductivity, an intense green colour and a d-spacing of 14.8 Å after heat treatment at 120 °C.

The d-spacing of this material is also unaffected by the heat treatment at temperatures higher than 120 °C. Bentonite-EMS1, Bentonite EMS2, and Bentonite EMS3, prepared in the aqueous medium and dried on glass plates in the normal laboratory environment, have d-spacing of around 15 Å (Figure 3a). Heat treatment at 120 °C brings these values down to 12.6 Å, 13.9 Å, and 14.8 Å, for Bentonite-EMS1, Bentonite-EMS2, and Bentonite-EMS3, respectively (Figure 3b).

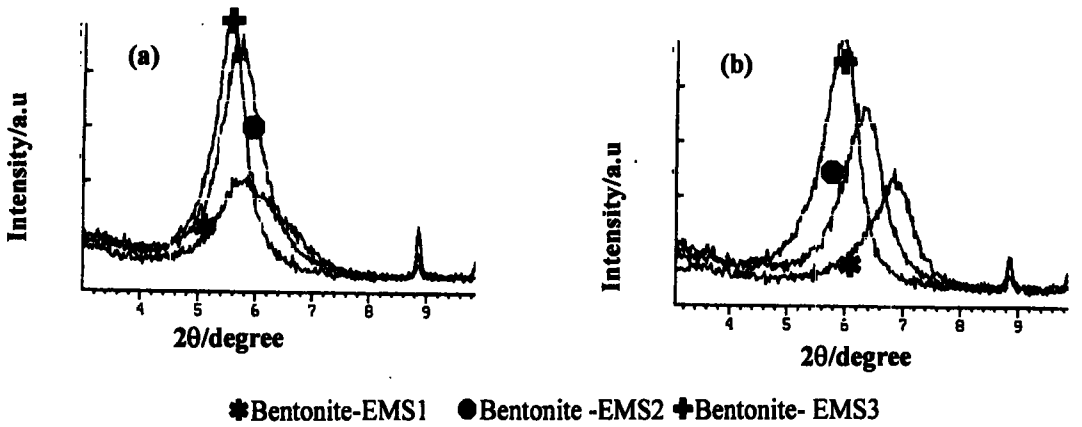

Fig.3 Bentonite-EMS1, Bentonite EMS2, and Bentonite EMS3, prepared in the aqueous medium and dried on lass plates in the normal laboratory environment: d-spacing of around 15 Å (Figure 3a). Heat treatment at 120 °C brings these values down to 12.6 Å, 13.9 Å, and 14.8 Å, for Bentonite-EMS1, Bentonite-EMS2, and Bentonite-EMS3, respectively (Figure 3b).

When these materials are prepared from aqueous solution, they contain layers of water. Heat treatment at 120 °C or above results in the removal of these water layers. The anhydrous polymer, produced by the removal of the layers of water, is resistant to further uptake of water.

The d-spacing versus temperature profiles for ordinary Bentonite, Na^+ treated Bentonite, anilinium treated Bentonite, and Bentonite EMS1 are shown in figure 4 for easy comparison. These experimental results show that multiplayer channels of polyaniline can be incorporated into interlayer spaces of Bentonite by repeating the combined procedure of ion-exchange followed by polymerization. The conductivity of the materials increases with the number of polymer layers incorporated into the inter-layers. The composite materials developed in this work have attributes which make them suitable for application in opto-electronic devices and research is underway to find ways in which these novel materials, developed may be exploited.

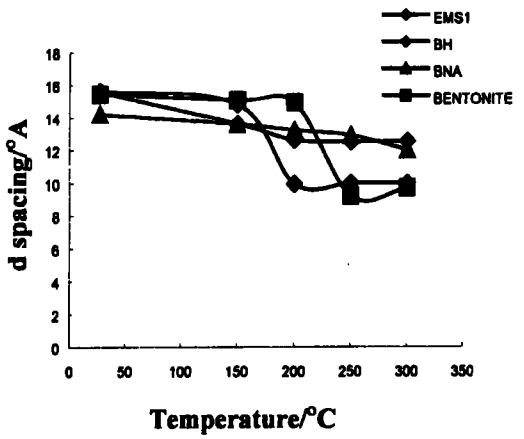

Fig.4 The d-spacing-temperature profiles for ordinary Bentonite, Na^+ treated Bentonite, anilinium treated Bentonite, and Bentonite EMS1.

4. CONCLUSION

In this work the possibility of exchanging inter-layer cationic species of Bentonite clay with anilinium ions was demonstrated. The anilinium ions thus introduced could then be oxydatively polymerized to produce the emaraldine form of polyaniline. This Emaraldine salt-Bentonite composite shows electronic conduction. A procedure was also developed to introduce successive layers of polyaniline in to the inter-layers of Bentonite. Up to three such layers were introduced during this work. The electronic conductivity of the novel composite materials thus prepared showed a significant increase as the number of polyaniline layers within the inter-layer spacing increased. This composite material possesses interesting electronic properties, which make it suitable for novel electronic applications such as opto-electronic devices.

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REFERENCES

1. Emmanuel P. Giannelis,, *Adv. Mater* **8** (1996) 29.
2. Timothy L Porter, Michael E. Hagerman and Michael P Eastman, *Recent Res. Dev. Polym. Sci.* **1** (1997) 1.
3. Daltamir J. Maia, Marco-A. De Paoli, Oswaldo L.Alves, Aldo J. G. Zarbin, Silmara Das Neves, *Quim. Nova* **23** (2000) 204.
4. H. Y. Zhu, E. F. Vansant, J. A. Xia, G. Q. Lu, *Journal of Porous Materials* **4** (1997) 17.
5. M. P. Eastman, M.E. Hagerman, T.L. Porter, R.A. Parnell, J.L. Attuso, M. Bradely, D. Thompson, *Proc. SPIE-Int. Soc. Opt.* (1997) 58.
6. W. Peter Faguy, Wanli Ma, J. Lowe, J. Alan, Wei Ping Pan, Terri Brown, *J. Mater. Chem* **4** (1994) 771.
7. R. M. G. Rajapakse*, D. T. B. Tennakoon and W. M. S. S. Wijesekara, *Proc. Int. Conference on Low cost electronic materials and solar cells,* Colombo, Sri Lanka (4-5 March 1999) 91.
8. Sei Uemura, Masaki Yoshi,; Norihisa Kobayashi,; Takayuki Nakahira, *Polym. J. (Tokyo)* **32** (2000) 987.
9. Ralph E Grim in Clay Mineralogy, McGraw-Hill International Series, Sydney, australia (1968) 235.
10. Duane M. Moore, Robert C. Reynods, JR in X-Ray Diffraction and the Identification and Analysis of Clay Minerals, Oxford University Press, Oxford (1989) 219.
11. Helen J. Bray, Simon A. T. Redfern and Simon M. Clark, *Mineralogical Magazine* **62** (1998) 647.
12. P. Bala, B.K. Samantaray, S.K. Srivastava, *Bull. Mater. Sci.* **23** (2000) 61.