Fabrication and Characterisation of Polyaniline/Laponite based Semiconducting Organic/Inorganic Hybrid Material

Walt V.K. Wheelwright[*], Sudip Ray, and Ralph P. Cooney

School of Chemical Sciences, The University of Auckland, New Zealand
[*]E-mail: vkol006@aucklanduni.ac.nz

ABSTRACT

Novel organic-inorganic semiconducting hybrid material is developed by chemically grafting polyaniline (PANI) onto an inorganic template, Laponite. The surface active silanol groups of the Laponite sheets were silylated with an aniline functionalised 3-phenylaminopropyltrimethoxysilane (PAPTMOS) coupling agent followed by deposition of PANI onto the silylated surface. The method includes the reaction of Laponite with PAPTMOS dissolved in a very small amount of methanol at 110 °C for 44 h in a vacuum oven, interaction of the silylated product with PANI via *in situ* polymerisation of aniline and one-step isolation process by means of the removal of the non-connected PANI with N-methylpyrrolidinone-diethylamine binary solvent. After isolation and re-doping with methane sulfonic acid the Laponite-PAPTMOS-PANI hybrid becomes electrically conductive. The chemical attachment of PANI with silylated Laponite in the hybrids were characterised by Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, elemental analysis, and scanning electron microscopy.

Keywords: Laponite, silylation, 3-phenylaminopropyltrimethoxysilane, polyaniline, organic-inorganic semiconducting hybrid material

1. INTRODUCTION

In general, the concept behind the fabrication of organic–inorganic type hybrid materials is to successfully connect the individual components i.e., connecting the organic moiety onto the inorganic substrate, where the organic substrate offers the functional properties and the inorganic substrates act as the template or carrier. However, just physically combining an inorganic substrate with a functional organic material may not lead to adequate binding between these two components due to dissimilarities between their surface chemistry. Thus a special class of chemicals known as coupling agents are commonly used which can anchor these individual components effectively through chemical bonding. In this present study, an attempt has been made to functionalise a clay[1] substrate, Laponite (synthetic Hectorite), using a functional conductive polymer, polyaniline (PANI)[2], with the help of a silane coupling agent.

The formula of Laponite is $Na_{0.7}[(Si_8Mg_{5.5}Li_{0.3})O_{20}(OH)_4]\cdot H_2O$. It has many different applications, such as surface coating (decorative, textured, automotive and rust converting coatings), general industrial applications (pigment suspension, grinding pastes, and ceramics), binding products (plasters and fillers, wood adhesives), paper and polymer films (static and antistatic coatings, inert barrier films), household products (detergents, cleaners, and shampoos), personal care products (toothpaste, cosmetics) and many others. Laponite contains Si-OH active groups on the edge of its sheets[3,4] and was used to immobilise Mn(III) salen catalysts in enantio selective epoxidation[5]. The surface of Laponite was also treated with octyltrimethoxysilane to be used as host inorganic matrix for intercalation of an antifungal compound intraconazole[6]. Laponite films were used

as inorganic scaffolds in combination with other materials such as CdSe quantum dots and catalytic surfaces that promote the *in situ* polymerisation of PANI to yield nanocomposites for light emitting diodes and solar cell applications[7].

Some existing and potential applications of pure Laponite and Laponite containing hybrids require a strong binding between the functional organic component, PANI, with this inorganic substrate. One prospective way is to carry out *in situ* polymerisation of aniline on the substrate provided the substrate surface contains aniline moieties. Laponitedoes not contain any aniline functionality, which can be introduced my means of a suitable coupling agent. Silylation of this clay by different coupling agents has been reported earlier. For this current research objective, silylation of Laponite by 3-phenylaminopropyltrimethoxysilane (PAPTMOS) can introduce this aniline functionality[8].

Thus, this paper focuses on the method of silylation of Laponite with PAPTMOS followed by direct deposition of PANI applying a 'low solvent' method that was developed for silylation of silica gel using a very small amount of methanol as solvent. This method has the advantages of both a 'green chemistry' approach and at the same time a simplified procedure[9]. The substituted aniline-functionalised silanised clayis used as an active template for linking the functional polymer by *in situ* polymerisation of aniline monomer.

2. EXPERIMENTAL
2.1 Materials

Laponite RD was supplied by Laporte Industries Ltd. (former Laporte Inorganics)[10,11]. It was thermally pre-treated

before the experimental procedure by heating in a vacuum oven at 120 °C for 24 h. Other reactants supplied by Sigma-Aldrich (PAPTMOS) were of analytical grade reagents and were used as received.

2.2 Silylation Method

1 g of Laponite was mixed in a ceramic crucible with 0.25 mL of 3-phenylaminopropyltrimethoxysilane (PAPTMOS) dissolved in 0.75 mL of methanol. The crucible containing the reaction mixture was covered with a ceramic lid and heated in a vacuum oven at 110 °C for 48 h. After washing with methanol the product was vacuum dried at 60 °C for 24 h.

2.3 Binding of PANI to Silylated Laponite

2.3.1 Binding

0.5 g of Laponite was suspended in 20 mL of 1 M aqueous MSA containing 0.5 g of dissolved aniline stirred magnetically at room temperature. 10 min later 1.37 g of Ammonium peroxydisulfate APS dissolved in 10 mL of water was added dropwise. After additional stirring for 5 h at the same condition the green precipitate was separated by centrifugation and decanting, then washed with water.

2.3.2 Isolation

Conventional (dedoping with aqueous ammonia) and novel (ammonia dedoping stage replaced by one-step binary solvent treatment) approaches were applied at this stage.

(a) Conventional approach: The green product from the silylation stage was magnetically stirred in 30 mL of 3% aqueous ammonia for 5 h. The final dark blue product was separated by centrifugation and decanting and washed with water. It was then washed a few times with NMP and finally with acetone. The product was then dried in vacuum at 40 °C for 24 h.

(b) Novel approach: The green product from the silylation stage was washed by centrifugation and decanting twice with a binary NMP-DEA (30:2.5 v/v) solvent and one time with pure NMP. The dark blue product was washed with water to remove the solvent residue and finally with acetone. The hybrid was vacuum dried at 40 °C for 24 h.

2.3.3 Re-doping

The product isolated in the previous stage was suspended in 20 mL of 1 M aqueous methanesulfonic acid (MSA) while stirring magnetically at room temperature for 14 h. The final dark green product was washed with water, acetone and then dried in vacuum at 50 °C for 24 h.

2.4 Characterisation Methods

Few methods to characterise the samples or to confirm the presence the components in the hybrids were applied.

FTIR spectra were taken in the solid state of analysed samples using a Thermo Electron NICOLET 8700 FT-IR spectrometer with Diamond or Germanium crystal ATR attachment. Germanium crystal ATR was applied for all the PANI containing samples. 64 scans at resolution 4 cm^{-1} were averaged for each sample. The signals were processed using OMNIC software.

Elemental analysis was carried out using Carlo Erba Elemental Analyser EA 1108. The analytical method was based on the complete and instantaneous oxidation of the sample by 'flash combustion' at 1020 °C which converts all organic and inorganic substances into combustion products. The resulting mixture is directed to the chromatographic column where the components (carbon dioxide, water, sulfur dioxide and nitrogen) are separated and detected by a thermal conductivity detector which gives an output signal proportional to the concentration of the individual components of the mixture.

The electrical conductivity of compressed pellets was measured by means of Jandel RM2 instrument (four-point probe measurement technique) at room temperature.

The XPS data were collected on a Kratos Axis Ultra DLD equipped with a hemispherical electron energy analyser. Spectra were excited using monochromatic Al Kα X-rays (1486.69 eV) with the X-ray source operating at 150 W. This instrument illuminates a large area on the surface and then using hybrid magnetic and electrostatic lenses collects photoelectrons from a desired location on the surface. In this case the analysis area was a 300 by 700 µm spot (=hybrid/slot). The measurements were carried out in normal emission geometry. A charge neutralisation system was used to alleviate sample charge build-up, resulting in a shift of approximately 3eV to lower binding energy. Survey scans were collected with 160 eV pass energy, whilst core level scans were collected with pass energy of 20 eV. The analysis chamber was at pressures in the 10^{-9} Torr range throughout the data collection.

SEM was performed using Philips XL30S FEG. Because of charging effects, the samples were prepared on the surface of a carbon film and coated in vacuum with platinum by PVD (physical vapour deposition) method.

3. RESULTS AND DISCUSSION

3.1 Fabrication of the Hybrid Material

The general reaction scheme towards the formation of the hybrid material is shown in Fig. 1. In the silylation stage, only the replacement of one methoxy group is shown. Actually, all three methoxy groups from PAPTMOS can be involved with three surface silanol groups from Laponite. PAPTMOS can react with more than one Laponite unit that has been reported for other silanes[4]. In the stage where Laponite-PAPTMOS hybrid reacts with aniline giving Laponite-PAPTMOS-PANI hybrid, the formation of a by-product, PANI homopolymer chain could also occur (not shown in the Fig. 1). Thus at this stage, a mixture of this hybrid material and PANI homopolymer in the electrically conductive emeraldine salt (ES) form, or doped form of PANI would form. A one-step procedure was applied to remove the homopolymer from the mixture[12]. Thus, the reaction mixture containing both hybrid and homopolymer was washed with N-methylpyrrolidone (NMP)-diethylamine (DEA) binary system with the volume ratio 10:1. In this case the insoluble ES form of PANI is converted by DEA to emeraldine base (EB) form that is soluble in NMP. That solution canbe separated by centrifugation and decanting or by filtration. Only PANI EB homopolymer is removed, because PANI EB from the hybrid remains strongly connected to the Laponite-PAPTMOS part of the hybrid that is insoluble in NMP-DEA. Since this PANI
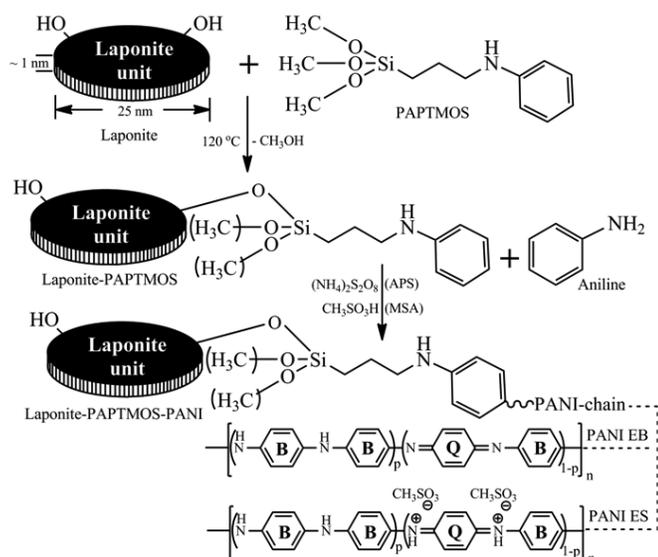
Figure 1. Schematic presentation of binding PANI onto the surface of silylated Laponite(B – benzenoid and Q– quinoid form of the benzene ring in the PANI chain).

EB form is not electrically conductive, re-doping the hybrid material with an acid (MSA) was performed at the final stage.

3.2 Evidence for the Formation of Hybrid Material

3.2.1 Morphological studies

The SEM images shown in Fig. 4 represent some morphological details of the Laponite and Laponite containing products. The surface morphology of the pristine Laponite and Laponite-PAPTMOS hybrid is very similar. The surface topography of PANI (MSA) containing hybrid has a relatively even coating layer of PANI ES conductive form (dark green). This layer consists of PANI aggregates with spherical particles mostly 10 nm to 20 nm and up to 40 nm - 50 nm in diameter.

3.2.2 Elemental Analysis

The results of the elemental analysis of the Laponite-PAPTMOS and PANI EB containing hybrids are shown in Table 1.

The C:N ratio in the silylated Laponite is near to 9:1. This is a characteristic ratio of the PAPTMOS silyl moiety when all the methoxy groups were replaced in the process. The PAPTMOS as a reactant has three more carbon atoms in each

molecule given 12:1 ratio. This means that almost all (96%) of the methoxy groups were participated in the silylation process. The C:N ratio in the PANI EB containing hybrid is lower due to the deposition of PANI EB, where C:N theoretical ratio is 6:1.

3.3 Determination of the Oxidation State of PANI in the Hybrid Materials

The common oxidation states of PANI are represented by different kinds of nitrogen in its chain, being reduced in -NH (amine nitrogen) and oxidised in -N= (imine nitrogen) containing units. Oxidised imine nitrogen can be easily protonated (doped) to form an electrically conductive polarons[13].

3.3.1 FTIR Spectroscopy

The results of the FTIR spectroscopic studies of PAPTMOS and the various silylated products are shown in Fig. 2.
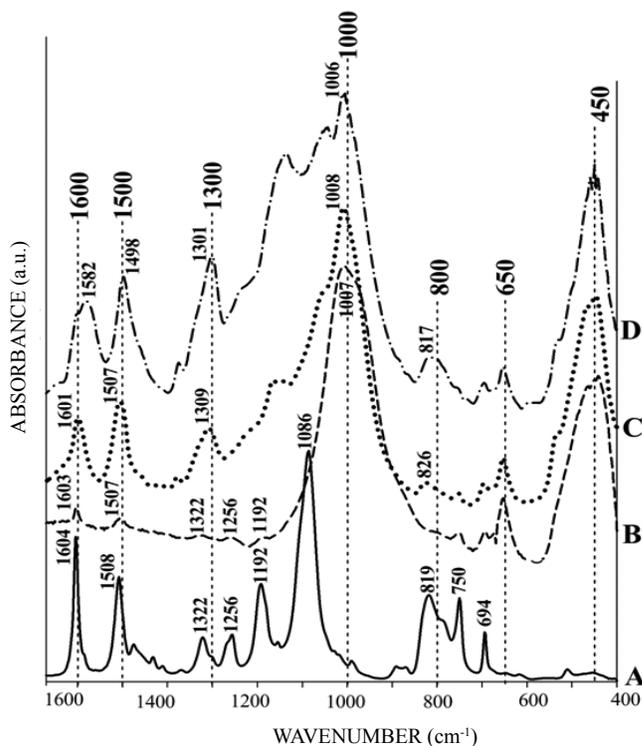

Figure 2. FTIR spectra (mid-wave) of PAPTMOS (A) and the products: (B) Laponite PAPTMOS, (C) Laponite-PAPTMOS-PANI EB, (D) Laponite-PAPTMOS-PANI ES.
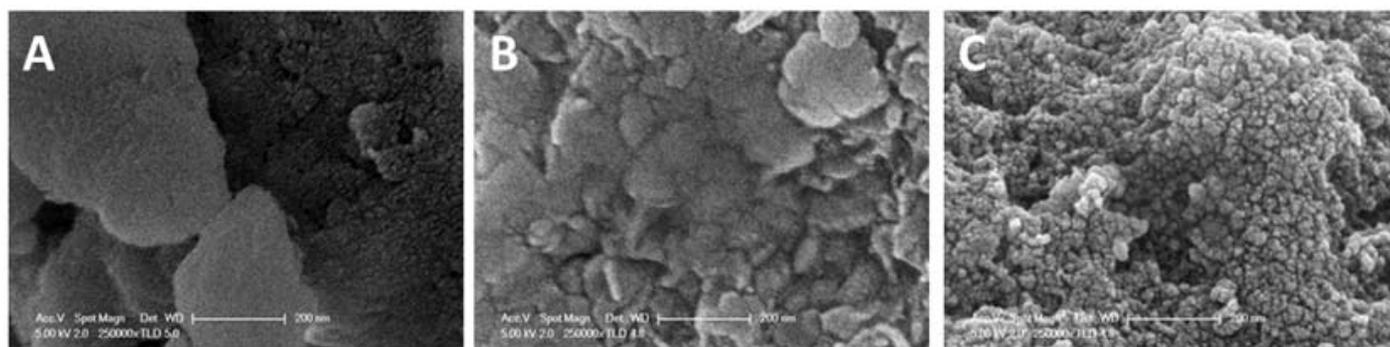

Figure 4. SEM images of Laponite and Laponite containing products (Magnification 250000x): (A) Laponite, (B) Laponite-PAPTMOS, (C) Laponite-PAPTMOS-PANI(MSA).

Table 1.   Elemental analysis data for Laponite containing hybrids

Compound	C, %	H, %	N, %	C:N, atom ratio
Laponite-PAPTMOS	6.17	1.72	0.79	9.12:1
Laponite-PAPTMOS-PANI EB	15.12	2.665	2.72	6.48:1

The most important diagnostic signals of PAPTMOS are the stretching modes of benzene ring at 1604 cm^{-1} and 1508 cm^{-1} respectively (Fig. 2(a) .The appearance of these two peaks in the silane treated Laponite indicates that the clay substrate was successfully silylated (Fig. 2(b).The peaks at 1322 cm^{-1} (δ Si-CH), 1256 cm^{-1} (δ scissoring CH$_3$) and 1192 cm^{-1} (δ C-N in C-NH-B) can be also assigned in the silylated product although their peak intensities are very week. The peak at 1086 cm^{-1} (ν Si-O in plane) and some peaks in the range between818-694 cm^{-1} (ν and δ of Si-O) from PAPTMOS are overlapped by stronger peaks of the silicate part of the Laponite.

After grafting PANI EB to the silylated Laponite, the intensities of signals at 1601 cm^{-1} for ν (N=Q=N) in oxidised unit and 1507 cm^{-1} for ν (N-B-N) in reduced unit are increased, indicating the presence of significant amount of PANI on the surface of Laponite-PAPTMOS-PANI EB product. Shifting of these two peaks towards lower waven umbers at 1582 cm^{-1} and 1498 cm^{-1}respectively indicates and confirms typical conversion of the undoped emeraldine base to the doped emeraldine salt form of PANI. The signals at 1309 cm^{-1} (PANI EB) and 1301 cm^{-1} (PANI ES) due to ν (C-N) in a secondary aromatic amine[14] are also identified. The peaks due to the Laponite substrate, e. g. (around 1000 cm^{-1}, 650 cm^{-1})[15] and 450 cm^{-1}(δ Mg-O)[16],were detected in the hybrid compounds.

3.3.2   XPS

XPS is an important analytical technique to get information on the chemical composition and chemical bonds of solid surfaces[17-19]. A survey *XPS* scan was performed from 0 to 1300 eV binding energy to determine the elements present at the surface of the Laponite containing hybrids. The binding energy scale was calibrated for the peak maximum at 284.6 eV of the C1s. The presence of all the main elements in the Laponite-PAPTMOS hybrid was observed with peak maxima at: O (1s) – 532.2 eV, C1s – 285.2 eV, Si (2p) – 103.2 eV. N1s had the peak maxima at 399.4 eV that is characteristic for amine nitrogen from a PAPTMOS moiety. When deconvoluted, the N1s peak was monocomponent. The similar peaks were also observed in the Laponite-PAPTMOS-PANI ES hybrid. The N1s deconvoluted spectrum of the final electrically conductive product is shown in Fig. 3. Four components were found in that spectra: at 397.5 eV (7.2 At %) for –N= (component 1), at 399.5 eV (70.9 At %) for –NH- (component 2), at 400.7 eV (17.8 At %) for =NH$^+$- (component 3) and at 402.1 eV (4.1 At %) for –NH$_2$$^+$- (component 4). The ionic forms of nitrogen atoms from PANI further confirm the presence of conducting form of PANI in the hybrid material.
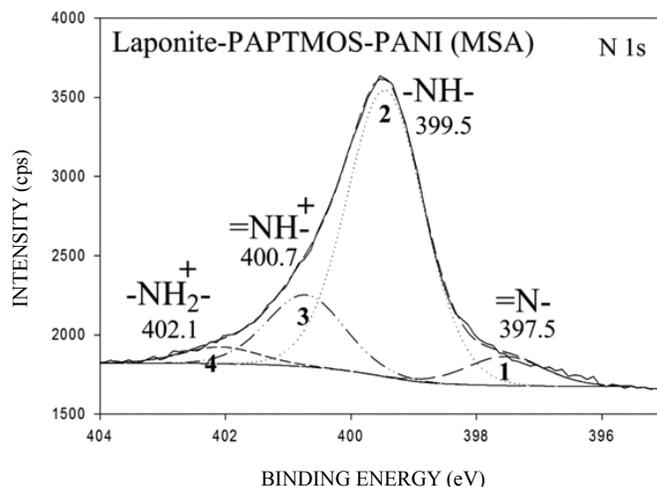

Figure 3.   N1s XPS deconvoluted spectra of Laponite-PAPTMOS-PANI(ES) hybrid.

3.3   Electrical Conductivity

The conductivity of pristine Laponite, Laponite-PAPTMOS and Laponite-PAPTMOS-PANI EB was below the detection limits of the four-probe instrument due to their highly insulating nature. After re-doping the Laponite-PAPTMOS-PANI EB hybrid material, electrical conductivity of Laponite-PAPTMOS-PANI ES was measured, which showed semiconducting behaviour $(1.05\pm0.05)\times10^{-4}$ S·cm^{-1}.

4.   CONCLUSIONS

Laponite was functionalised with a silane containing an aniline moiety (PAPTMOS), subsequently PANI was grafted with the silylated Laponite. Elemental analysis results indicate that almost all of the methoxy groups from the coupling agent were participated in the silylation process. The Laponite-PAPTMOS-PANI hybrid was isolated with NMP-amine solvent. The hybrid compound was re-doped with MSA and was found to be electrically conductive. The studies of oxidation states of different forms of PANI by FTIR spectroscopy and XPS confirmed that insulating Laponite clay can be successfully converted to semiconducting material by binding with conducting polymer like PANI. The method can be applied to other commercially available and industrially important clays to introduce electrically conductive functionality which would be important in the catalysts, adsorbents, in electromagnetic devices, to prepare electrostatic, anticorrosion and maybe antimicrobial coatings and surfaces.

REFERENCES

1.   Chauhan, R.S.; Chaturvedi, R. & Gutch, P.K. Polymer-clay nano composites. *Def. Sci. J.,* 2006, **56**, 649-64.
2.   Kumar, N.; Vadera, S.R.; Singh, J.; Das, G.; Negi, S.C.; Aparna, P. & Tuli, A. Conducting polymers: Emerging commercial materials. *Def. Sci. J.,* 1996, **46**, 91-104.

3. Cummins, H.Z. Liquid, glass, gel: The phases of colloidal Laponite. *J. Non-Cryst. Solids.* 2007, **353**, 3891-905.

4. Herrera, N.N.; Letoffe, J.-M.; Putaux, J.-L.; David, L. & Bourgeat-Lami, E. Aqueous dispersions of silane-functionalized laponite clay platelets. A first step toward the elaboration of water-based polymer/clay nanocomposites. *Langmuir,* 2004, **20**, 1564-71.

5. Das, P.; Silva, A.R.; Carvalho, A.P.; Pires, J. & Freire, C. Enantioselective epoxidation of Alkenes by Jacobsen catalyst anchored onto Aminopropyl-functionalized Laponite, MCM-41 and FSM-16. *Catal. Lett.,* 2009, **129**, 367-75.

6. Park, M.; Shim, I.-K.; Jung, E.-Y. & Choy, J.-H. Modification of external surface of laponite by silane grafting. *J. Phys. Chem. Solids.* 2004, **65**, 499-501.

7. Kehlbeck Joanne, D.; Hagerman Michael, E.; Cohen Brian, D.; Eliseo, J.; Fox, M.; Hoek, W.; Karlin, D.; Leibner, E.; Nagle, E.; Nolan, M.; Schaefer, I.; Toney, A.; Topka, M.; Uluski, R. & Wood, C. Directed self-assembly in laponite/CdSe/polyaniline nanocomposites. *Langmuir.* 2008, **24**, 9727-38.

8. Ruckenstein, E. & Li, Z.F. Surface modification and functionalization through the self-assembled monolayer and graft polymerization. *Adv. Colloid Interface Sci.,* 2005, **113**, 43-63.

9. Wheelwright, W.V.K.; Ray, S. & Easteal, A.J. A novel low solvent method for grafting polyaniline to silylated silica. *Macromol. Symp.,* 2010, **298**, 51-6.

10. Huang, A.Y. & Berg, J.C. High-salt stabilization of Laponite clay particles. *J. Colloid Interface Sci.,* 2006, **296**, 159-64.

11. Mongondry, P.; Tassin, J.F. & Nicolai, T. Revised state diagram of Laponite dispersions. *J. Colloid Interface Sci.,* 2005, **283**, 397-405.

12. Wheelwright, W.V.K.; Ray, S.; Easteal, A.J. & Cooney, R.P. Interfacial interactions of polyaniline grafted alumina hybrid. *Macromol. Symp.,* 2013, *In press*.

13. MacDiarmid, A.G. & Epstein, A.J. Polyanilines: A novel class of conducting polymers. *Faraday Discuss. Chem. Soc.,* 1989, **88**, 317-32.

14. Dmitrieva, E. & Dunsch, L. How linear is 'Linear' Polyaniline? *J. Phys. Chem. B.* 2011, **115**, 6401-11.

15. Bourlinos, A.B.; Jiang, D.D. & Giannelis, E.P. Clay-Organosiloxane hybrids: A route to cross-linked clay particles and clay monoliths. *Chem. Mater.,* 2004, **16**, 2404-10.

16. Palkova, H.; Madejova, J.; Zimowska, M. & Serwicka, E.M. Laponite-derived porous clay heterostructures: II. FTIR study of the structure evolution IR spectra. *Microporous Mesoporous Mater.,* 2009, **127**, 237-44.

17. Banerjee M.; Sachdev P. & Mukherjee G.S. Studies on the Magnetic-nanocomposite of Carbon, Cobalt and Vinyl polymer prepared by ion bean sputtering technique. *J. Sci. Conf. Proc.,* 2009, **1**, 86-92.

18. Banerjee M.; Sachdev P. & Mukherjee G.S. Preparation of PVA/Co/Ag film and evaluation of its magnetic and micro-structural properties. *J. Applied Phys.*, 2012, **111**, 094302.

19. Kovač J. Surface characterization of polymers by XPS and SIMS techniques. *Materials Technologies.*, 2011, **45** 191-197.

CONTRIBUTORS

Dr Walt V. K. Wheelwright received his PhD from The University of Auckland, New Zealand. Presently, he is working in the MBIE Hybrid Polymers Research Group, School of Chemical Sciences of The University of Auckland, responsible for the technical development of the project. His research interests are focused on the preparation and studies of properties and interfacial interactions in the hybrid polymers systems containing an inorganic or bioorganic substrate connected to a conductive component such as polyaniline.

Dr Sudip Ray obtained his PhD from IIT, Kharagpur, India. He is a Research Scientist in the School of Chemical Sciences, University of Auckland, New Zealand and is currently involved in projects on MBIE funded Hybrid Polymers Programme. His current research focus includes polymers for biomedical applications, sustainable packaging. He holds about 100 research publications including journal papers, conference papers, monograph, book chapters and patent.

Prof. Ralph P. Cooney working as a Director, MBIE Anti-microbial hybrid polymers. His interest of research focussed primarily on anti-microbial polymers (hybrid polymers), conducting polymer membranes, actuating micro-pumps, colloids, electro-spun fibres and zeolites/molecular sieves. He has published 250 papers.