International Conference on Sustainable Built Environment

NANCO and University of Melbourne joint research session on Nanotechnology and Sustainable built environment

13-14 December, 2010 at Earls Regency, Kandy, Sri Lanka

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THE UNIVERSITY OF
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Advanced Protective Technology for Engineering Structures

International Conference on Sustainable Built Environments

Special Session on Nanotechnology and Sustainable Built Environment

13th & 14th December, 2010

Earl's Regency Hotel, Kandy,
Sri Lanka

December 2010

Proceedings of the Special Session of the International Conference on:

SUSTAINABLE BUILT ENVIRONEMENTS

NANCO AND UNIVERSITY OF MELBOURNE JOINT RESEARCH SESSION ON NANOTECHNOLOGY AND SUSTAINABLE BUILT ENVIRONMENT

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Conference Chairmen's Message

The building sector needs a new wave of innovation to drive dramatic reductions in environmental impacts while sustaining economic growth and improving social outcomes.

The International Conference on Sustainable Built Environment (ICSBE) –state of the art, brings together academics, students, other researchers and practitioners from Sri Lanka and overseas to exchange ideas and experiences on their recent research in all areas of sustainable built infrastructure. As awareness of climate change, natural disasters, diminishing natural resources and energy costs increases, the demand for sustainable design and construction is increasing at an unprecedented rate. Participants will attend high quality presentations related to those areas by scientists representing both industry and academia. In addition there are special sessions on nanotechnology in construction organised by NANCO and the session on Natural Systems to Control "Water Resources Pollution" and "Water Hazards" Conducted by Saitama University, Japan. There is also the preconference International workshop on "Performance Based Review and Design of Tall Buildings". There are a number of world recognized experts presenting keynote speeches during the conference.

This conference represents a unique opportunity for meeting colleagues and friends, exchanging ideas, and learning about research and development work. The support of Institution of Engineers (IESL) is deeply appreciated. We must also express our sincere thanks to all people who contributed their time and great effort to make the conference possible. Our special thanks go to the organising committee. We would also like to thank all the reviewers of papers, whose reviews have been very important to maintain the quality of the conference.

We are delighted that the Honourable Prime-Minister, Mr. D.M. Jayaratne and Honourable Higher Education Minister, Mr. S. B, Dissanayake have accepted our invitation to open the conference.

The Conference will deliver an awesome volume of information on sustainability initiatives in all building sectors from around the globe, with up to 9 sessions from a diversity of focus groups and organisations presenting their latest findings. We would like to invite participants from all sectors, private and public, to join this important conference from 12th to 14th December. This event promises to be an incredible and rewarding experience.

Conference Chairs

Prof. Priyan Mendis, University of Melbourne, Australia
Prof. Ranjith Dissanayake, University of Peradeniya, Sri Lanka
Prof. Thishan Jayasinghe, University of Moratuwa, Sri Lanka

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Morning Session

PHOTOACTIVE MATERIALS FOR BUILDINGS

De Silva A.P.[1]

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Since the intertwining of light and electron transfer enables life on the planet, it is no surprise that the same phenomenon can serve to empower materials[1] for service in the built environment. The inexpensive generation of electrical power from sunlight in a distributed manner will probably become possible with photoelectrochemical cells embedded in windows. From a chemical viewpoint, **1** can undergo photoinduced electron transfer (PET) with TiO_2 and the resulting $\mathbf{1}^{\cdot+}$ can undergo further electron transfer with electrochemical relay I^-, when the thermodynamic conditions are considered (Fig. 1). However, the efficiency of charge separation following PET in this and related cases is attributable to the nanostructured TiO_2 matrix on which **1** is bound [2]. For instance, the electric current generation efficiency in sunlight is around 1000-fold higher for **1** in nanostructured TiO_2 than on a chosen face of single-crystal TiO_2 in its anatase form[3]. Besides the hugely increased surface area of this matrix (c.f. the single-crystal), it also avoids charge-depletion layers and local electric fields near the particles. Some of these window-cells will probably be adaptable to self-cleaning tasks as well, since photoelectrochemical cells are able to decompose organic compounds via redox processes [4].

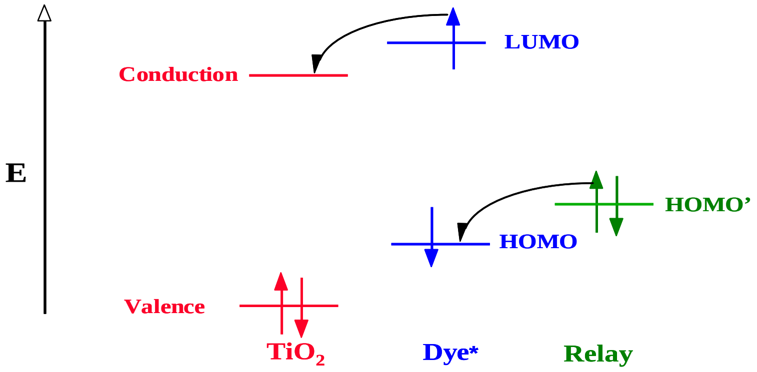
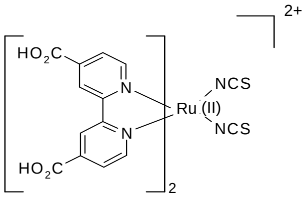


Fig. 1: Energy diagram for the frontier orbitals/bands of a 'TiO_2-dye-electrochemical relay' system which makes up the heart of dye-sensitized photoelectrochemical cells.

When the sun goes down, the conceptual reversal of PET can provide a way of electrical light generation. Organic light-emitting diodes of nanometric thinness and very large area provide an efficient way of approaching this goal, especially those with emitter-layers in each of the primary colours with carefully engineered thicknesses to prevent losses in the internally generated photons before they escape to the outside [5]. The internal space of buildings for work and play can be enhanced with screens on which information may be displayed by adapting the same materials.



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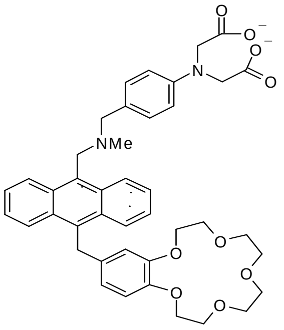

2

Sustainable built environments are particularly useful if people live sustainable lives inside. Detection of health conditions on a do-it-yourself basis will allow concerned people to consult a medical professional for a more thorough evaluation, somewhat like current pregnancy tests. A home equipped with such testing facilities would be a particularly comforting environment to live in. PET can be marshalled to help in this situation too, by being built into sensors and diagnostic systems. These show how medical applications arise from the emulation of computational ideas with molecules. The thermodynamic situations which are encountered during the competition between PET and fluorescence are shown in Figures 2 and 3.

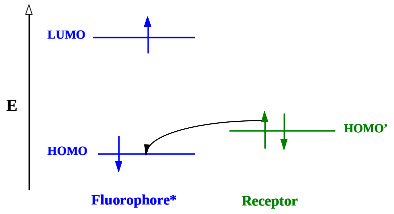

Fig. 2: Energy diagram for the frontier orbitals of a ‘fluorophore-spacer-receptor’ system which makes up the heart of fluorescent PET sensors and logic devices.

For instance, Boolean diagnostic system **2** [6] involves three thermodynamically allowed PET processes arising from each of the receptors - tertiary amine, benzo-15-crown-5-ether, and phenyliminodiacetate targeting H^+, Na^+ and Zn^{2+} respectively. The latter three species form the targets involved in the diagnosis. All three PET processes need to be stopped before the fluorescence output has a chance of being released at a ‘high’ level. As each receptor is bound by its corresponding cation, the PET processes are shut down one by one due to electrostatic attraction between the cation and the transiting electron.

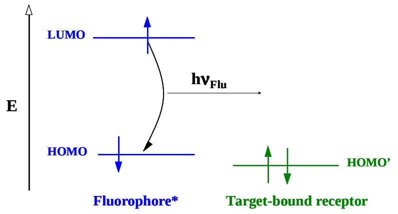

Fig. 3: Energy diagram for the frontier orbitals of a ‘fluorophore-spacer-receptor’ system when the receptor is bound to its target.

The simultaneously ‘high’ concentrations of three biologically important cations are signalled by the emission of a light signal which is easy to see (Fig. 4). In the present context, the adjective ‘high’ means that the cation concentration is large enough to tip the ratio of bound-receptor to free-receptor within **2** to significantly above 1. In chemical design terms, this means that the target concentration is significantly larger than the reciprocal of the receptor-target binding constant. The latter can be chosen to match the target concentration present in the blood, say, of a healthy person. So **2** can be seen to go some way towards easily indicating electrolyte excess and hence, renal dysfunction. The difference with **2** and its cousins [7-9] is that multiple analytes are evaluated simultaneously according to a small, but non-trivial, algorithm. Rudimentary versions of **2**, each responding to a single target are currently used worldwide on a substantial scale [10].

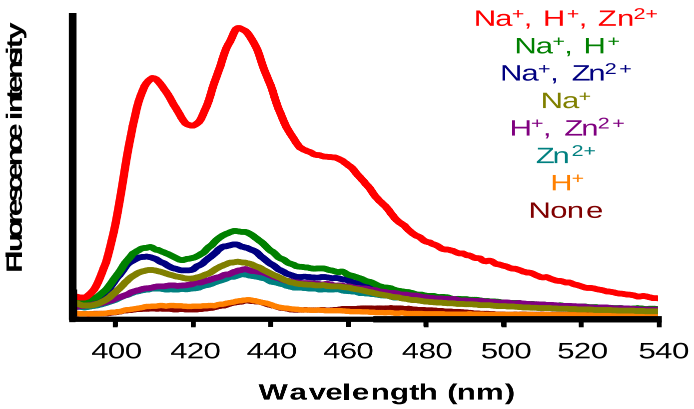

Fig. 4: Fluorescence emission spectra for a 'lab-on-a-molecule' system when it is interrogated with various target combinations.

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MOTION SENSOR APPLICATIONS IN SMART BUILDINGS

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Abstract: Among the many kinds of applications of today's sensor technology, motion detection play a vital role especially for the safety of human being at their day today rituals. In smart buildings, different types of motion sensors are used to monitor parameters which are critical for the safety of its occupants, equipment and also the behavior of any structural changes against environmental changes.

Accelerometers which are connected to the structure of those buildings, for example can capture the vibrations caused by vehicles on highways nearby, trains passing by, etc., and can be programmed to take necessary preventive actions to protect the occupants, equipment inside the building and the structure. Vibration free platforms like the one presented in this paper, will be a suitable solution.
They can also be used to get a feedback of how the buildings were behaved in the disastrous situations.

Keywords: Accelerometer, MEMS, Controller, Control action, Actuator

1 Introduction

Today the concept of smart buildings has marked a new era of the modern building construction industry. They are designed targeting the security and the luxury of the lives of their residents and surroundings and protection of themselves and the properties inside the building at disastrous situations. Smart buildings are equipped with various types of sensors to monitor various parameters of their environment and control systems to perform various tasks according to the requirements of the people inside the buildings and to control the environmental conditions.

Among the different types of parameters which are captured by the sensors inside a building, vibration level is a very important for the guaranteed lifetime of the building as well as the equipment inside the building which are sensitive to vibrations. Importance of concerning on vibration levels is much more highlighted for the building situated near the roads where heavy vehicles are operating and constructed in the areas having a higher probability of earth quakes. Sensitive equipment which are used in the industrial, medical, research and several other types of businesses can get damaged or become malfunctioning due to frequent vibrations coming from the above sources. Development of a vibration free platform is much more important to safeguard such equipment. Accelerometers placed in such locations can be used for monitoring the vibration levels [1].

The accelerometers used for such purposes should be sensitive enough at least along the axis along which the vibrations are sensed. These accelerometers can be fixed to the platforms of the sensitive equipment. Controllers can be designed to compensate those vibrations using applicable actuators.

2 Objectives and Methodology

Objective of the work is to compensate the vibrations created from the heavy vehicles using a combination of active and passive compensators.

This is simulated with the required models of the controllers, spring damped platforms and the actuators fed by typical vibration waveforms.

3 Theory

3.1 Accelerometer

MEMS accelerometers are used to sense the vibration levels. They are designed with a small proof mass suspended by a spring and a damper system [2]. The mass is free to move in between a certain limits.

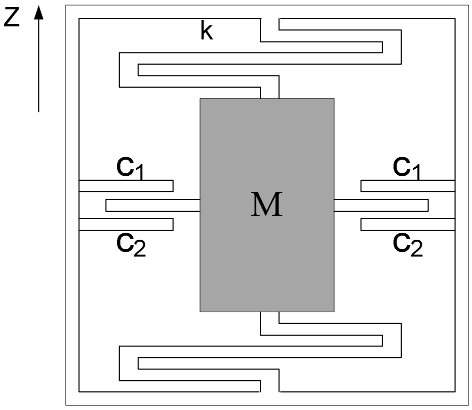

Fig. 1: Structure of a Capacitive MEMS Accelerometer

Capacitors are used to measure the displacement of the spring suspended proof mass of the accelerometer. C1 and C2 capacitance values vary with the displacement of the mass. Following equation explains variation of capacitance with the gap between the capacitor plates in a parallel plate capacitor as in the capacitive MEMS accelerometer.

$$C = \varepsilon \frac{A}{d} \qquad (1)$$

According to the following equation capacitance is inversely promotional to the gap (d) in between the two electrodes. The change of capacitance is measured by the voltage ratio between the two series capacitors (C_1 and C_2).

Acceleration of the proof mass (a) is connected with the displacement (x) according to the following equation. Parameter k represents the spring constant.

$$a = \frac{k}{M} x \qquad (2)$$

4 Results

4.1 Active Compensator Design

A vibration free platform driven by an active compensator with linear actuators is designed to protect the vibration sensitive equipments.

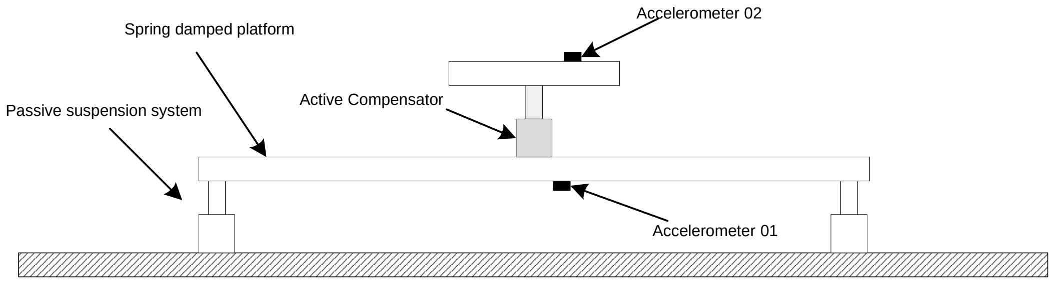

Fig. 2: Structure of the vibration free platform connected to an active compensator and spring-mass damper.

Accelerometers are used to sense the vibrations and feed the signals to the controller of the active compensator. Two accelerometers are fixed as one on the spring-mass damper and another on the vibration free platform as in Fig.2. The spring-mass damper smooth out the vibrations and the controller drives the linear actuator to compensate the damped oscillations of the spring damped platform.

Fig. 3 illustrates the block diagram of the controller.

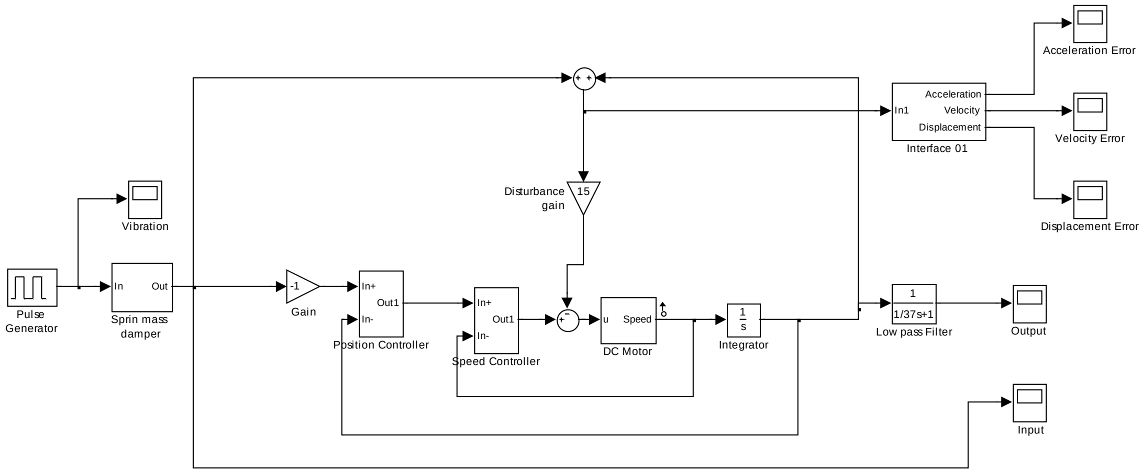

Fig. 3: Controller block diagram.

Output of the feed forward accelerometer placed on the spring damped platform which is used to smooth out the vibrations is inverted and fed as the reference point of the controller. Disturbance input of the system which is obtained from the second accelerometer placed on the vibration free platform is directly fed into the motor to correct the uncompensated movements of the vibration free platform as illustrated on fig. 3.

Fig. 4 illustrates the model of the mass spring damper subsystem [4] which is used to damp out the vibrations before coming to the accelerometer 01. This method cuts off the high frequency components of the vibrations to be matched with the bandwidth of the actuator system as well as reduce the amplitude of the vibration. Fig. 5 illustrates the input and the corresponding output of the spring mass damper subsystem [4].

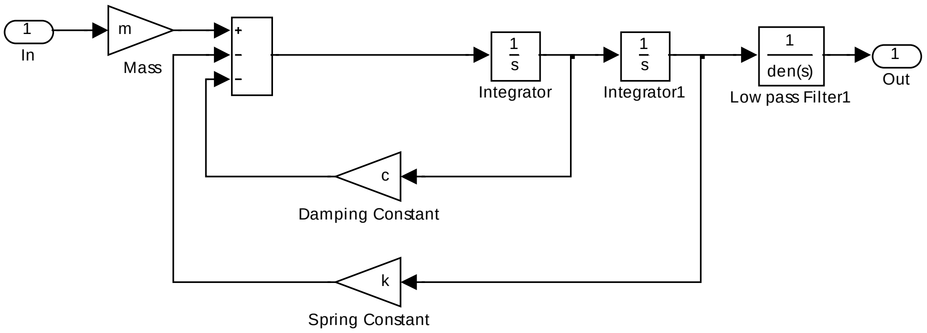

Fig. 4: Spring mass damper subsystem

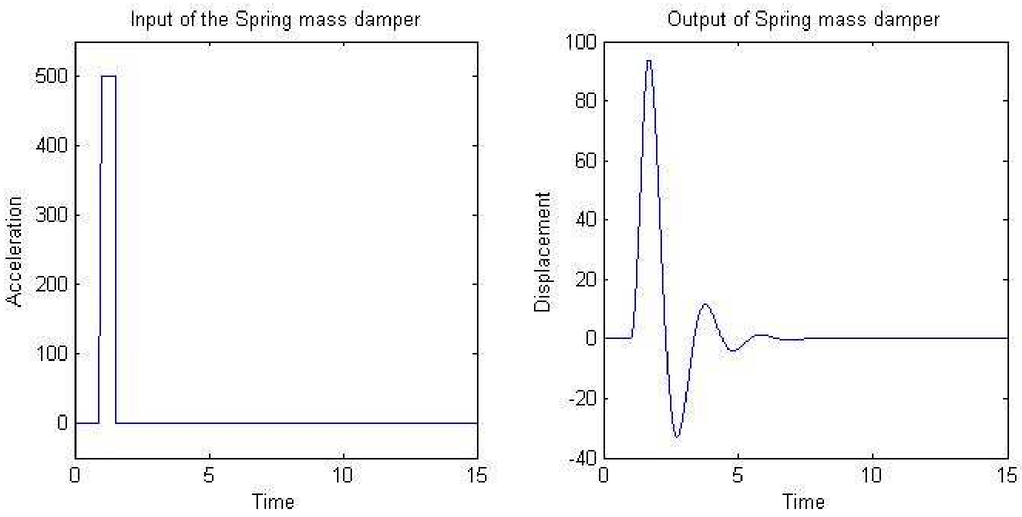

Fig. 5: Input and the corresponding output of the spring mass damper subsystem

Output of the spring mass damper is inverted and fed into the position controller of the system which is a PID controller. A linear encoder is used to sense the displacement of the vibration free platform which is used to generate the feedback of the position controller. Output of the position controller is used as the input to the speed controller.

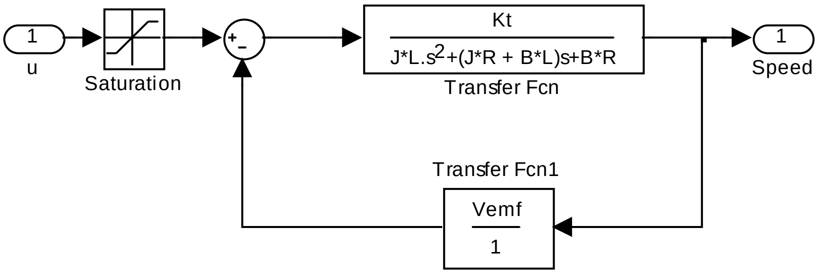

Fig. 6: Motor model

A model of a DC motor [3] is used to drive the vibration free platform. Rotational movement of the motor has to be converted to a linear movement using a rack and pinion gear arrangement and a gear reduction of about 1/5. A disturbance input to the DC motor is generated using the second accelerometer placed on the vibration free platform, which is the error of the compensator. Feeding the disturbance input directly into the motor will increase the performance of the compensator.

Fig. 7 illustrates the input to the controller which is the output of the accelerometer 01 which is placed on the spring damped platform and the control action of the actuator which is converted to a linear motion to compensate the vibration.

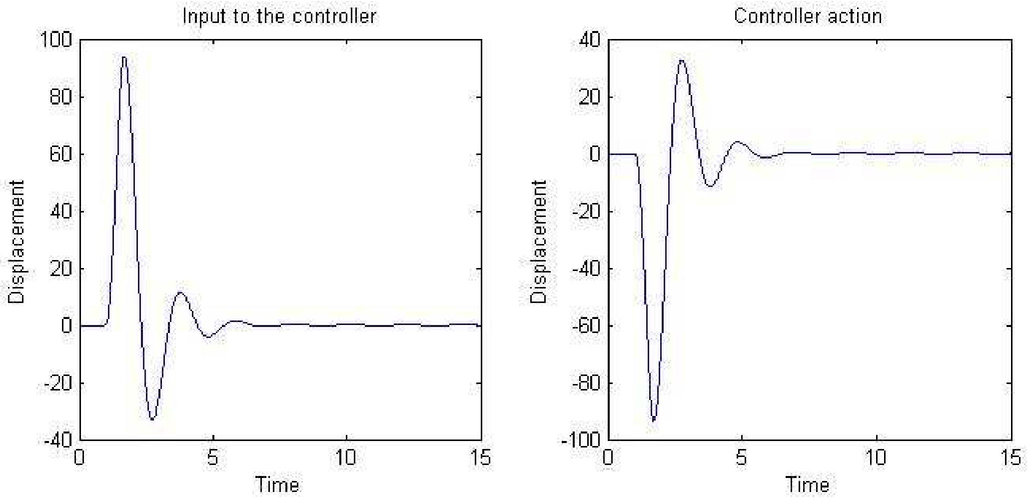

Fig. 7: Input to the controller and corresponding control action

Fig. 8 illustrates the reading of the second accelerometer which is placed on the vibration free platform which detects the uncompensated vibrations sensed on the vibration free platform which is the error of the compensator.

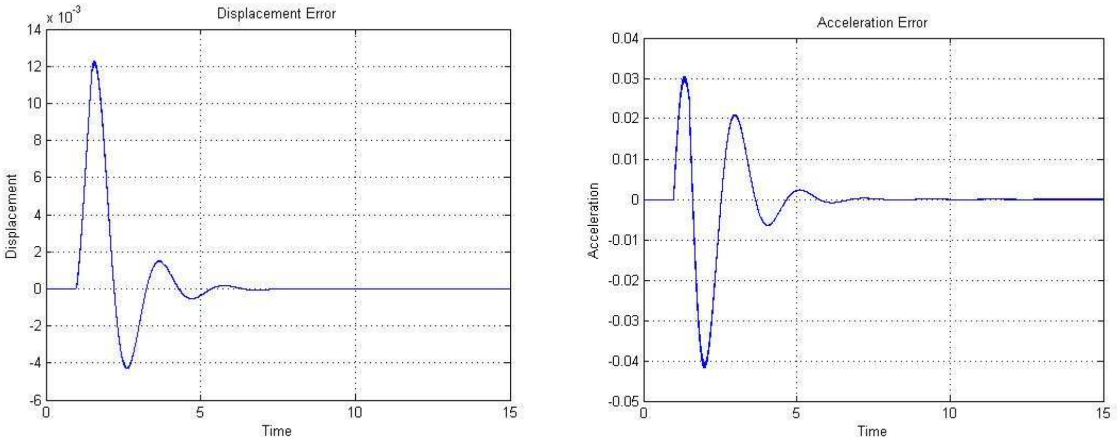

Fig. 8: Movements of the vibration free platform

5 Discussion

According to Fig. 8 the compensation error of the system which is the output of accelerometer 02 is very small compared to the amplitudes of the acceleration waveforms of the input to the controller and the corresponding controller action at Fig. 9. According to Fig. 10 It is clear that the main reason for the control error is a time delay of the control action which might be different with the physically implemented system from the simulation model.

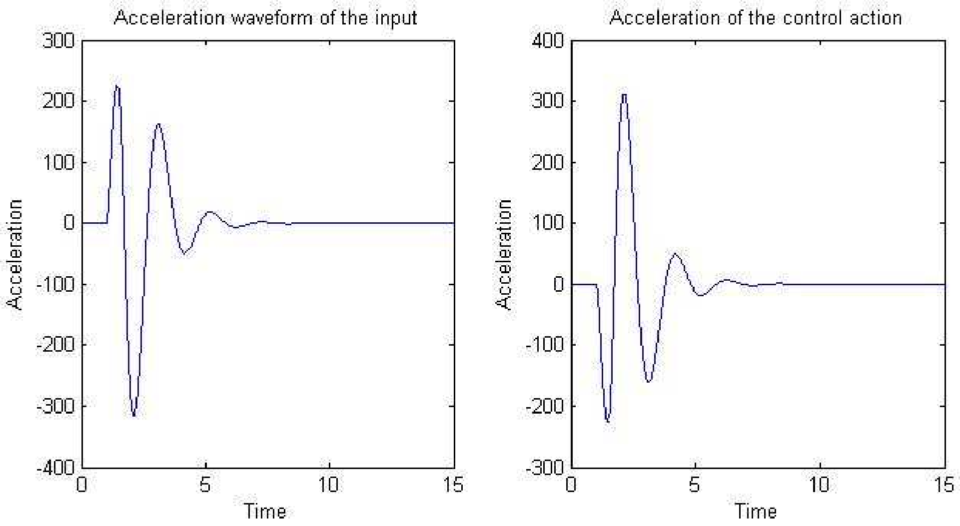

Fig. 9: Acceleration waveforms of the input to the controller and corresponding control action

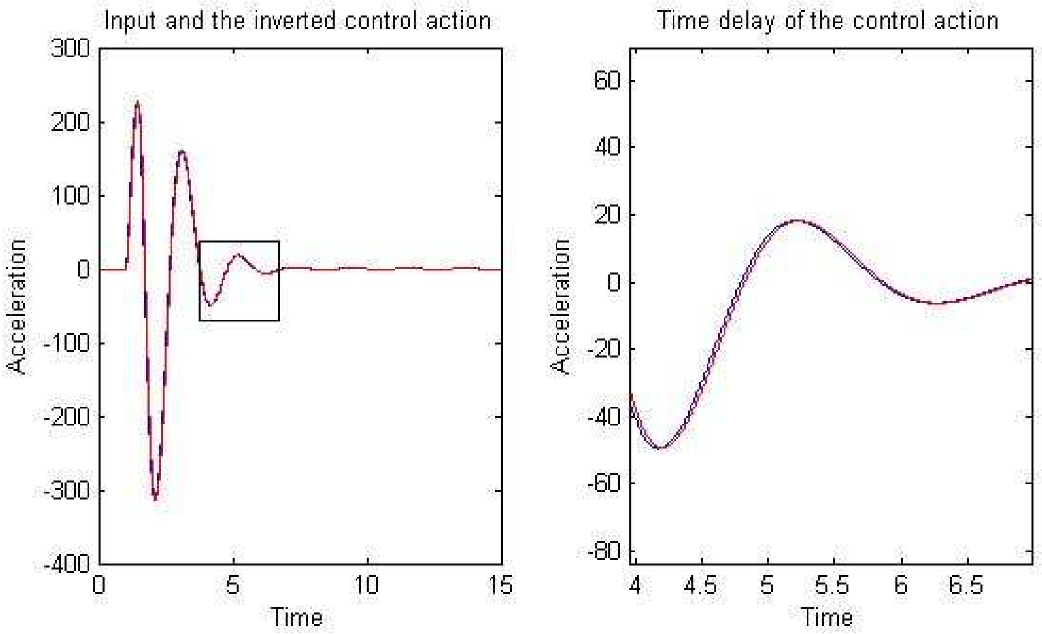

Fig. 10: Time delay of the inverted acceleration waveform of the control action

6 Conclusions

The presented vibration compensation system is highly applicable not only in the area of smart buildings but also in many numbers of applications including automobile, healthcare etc. Considering the smart building applications this is very much effective to protect the vibration and shock sensitive equipments as a vibration free platform for those equipments. This can be scaled up to have several actuators and sensors at different places on a much larger platform to perform the same task.

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DESIGN AND SIMULATION OF MEMS SENSORS WITH INBUILT GSM COMMUNICATION FOR SMART BUILDINGS

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Abstract: Use of MEMS based sensor in building automation is a trend in the present. This is because the inherent behavior of MEMS sensors are being very compact, low powered, sensitive and cheap methods of sensing biological and environmental activities in a smart building. This paper discusses about the use of MEMS based acceleration sensor and a pressure sensor coupled with an inbuilt GSM module in the building automation system, particularly the security applications. The writers have decided about the parameters for the needed sensors and designed the pressure sensor and the acceleration sensors for fabrication accordingly. The conceptual system hardware was tested using commercially available sensors and GSM modules. The applicability and the methods the integrated sensor system can be used for is also discussed. The case study is performed at the premises of The Sri Lankan Institute of Nanotechnology (SLINTEC). The paper contains the design parameters and the electronic systems design data and drawings. It is hoped that this data would be supportive to any person who would design or improve the proposed system.

Keywords: MEMS, Accelerometer, Pressure Sensors, Smart Buildings

1 Introduction

Resent technological advances have revolutionized the standards of living by making the lining environment smarter and interactive with the residents. Smart environments [1] tend to catch the attention of the people because it allows saving of energy, increase of health and security, lowering of maintenance cost and increase of comfort levels for humans.

When smart environments are concerned, smart buildings are the most talked about subject in the field. The essence of the smart building is comprised of advanced and integrated systems for building automation, life support and telecommunications systems. Use of new sensors and communication systems to built sensor networks for smart building installations are becoming more and more popular all over the world. The sensor networks are then connected to an integrated building management system which allows the tenants to manage the building. Fundamental reason for sensor networks is that by integrating the systems the building manager and tenants can do things that simply cannot be done with separate systems. When systems get integrated, communicate and data sharing is easy, provide more functionality and flexibility. In addition, intermigration allows information from one technology system to affect the actions of other systems. For example, if a smoke detector alarm is activated, the access control system changes to emergency mode; the heating, ventilation, and air conditioning systems adjust; the video surveillance camera changes so the affected area can be monitored; and so forth.[2]

Smart security systems are a predominant item in the smart building and management system. Modern homes use Micro Electro Mechanical devices in security systems, ventilation systems, and safety systems. MEMS are mostly used because of their small size and the low power consumption. It is also seen that the response time and the sensitivity is comparatively higher than mechanical only sensors.

In this paper, the use of MEMS acceleration sensors and pressure sensors in security application is presented. The sensor data is processes and sent through wireless communication network to the resident or the building management system. The proposed system can either be incorporated in to the building management system or can be used a separate security system. This separate system is ideal for a resident who does not have a building security system in their buildings but wish to incorporate additional security futures in to the environment they live in or work at.

The proposed system of sensors detects vibrations of floor or the sudden pressure drop inside the room when a person opens the door and enters the room. Then the system notifies to the resident that a human has entered the room. This type of system can be modified for the use for climate control or lighting control as with the system, it is easy to identify if a human has entered the room or not and it is easy to control the lighting of the rooms such as dimming or brightening the room as humans leaving or entering the room or the house. This will in return save the energy usage by the house. With a network of sensors such as these, it is possible to identify where the humans are at a given time. This kind of data would be ideal to model behavioral patterns of the residents in the building and utilize resources accordingly. An example would be to identify the pattern of bathroom usage of the residents. This data can be used to turn the water heater only at times when bathrooms are frequently used such as in the morning and at night.

The paper presents the design specifications and the designs of the sensors. The application circuits of the sensor module and the design specifications are published herewith. The GSM communication system and the software development are also addressed.

2 MEMS based sensor module with inbuilt GSM communication

The objectives of the project is to build a MEMS sensor unit having an acceleration sensor, a pressure sensor and a GSM unit and incorporate the sensor system in to a smart building security system to identify if a person has entered an unoccupied room (breach of security) and relay that information to a mobile phone via the GSM network.

The vibration due to motion of a person can be detected by using an MEMS accelerometer placed on the floor and near windows and entry points. A MEMS pressure sensor can be used for detecting the pressure changes caused by opening and closing of doors in a closed room. Pressure changes inside the room because the change in flow patterns when opening a door or window in a closed room. Because the two sensors are to be near an entry point, the sensors are to be compact and to be unnoticed, minimal number of wires is to come out from the unit. The system built is a single compact unit having a pressure sensor and an acceleration sensor unit. The only wires coming out were the power supply lines.

This system is activated only when the last person left the building. When the system is activated, the system does not expect to detect any movement inside the building, if it detects any movement it considers this as breach of security and immediately alarm the particular party using short message service (SMS).

Commercially available accelerometer and a pressure sensor with a microcontroller are used in the prototype designs to test the validity of the proposed system. A GSM modem is used as the communication equipment.

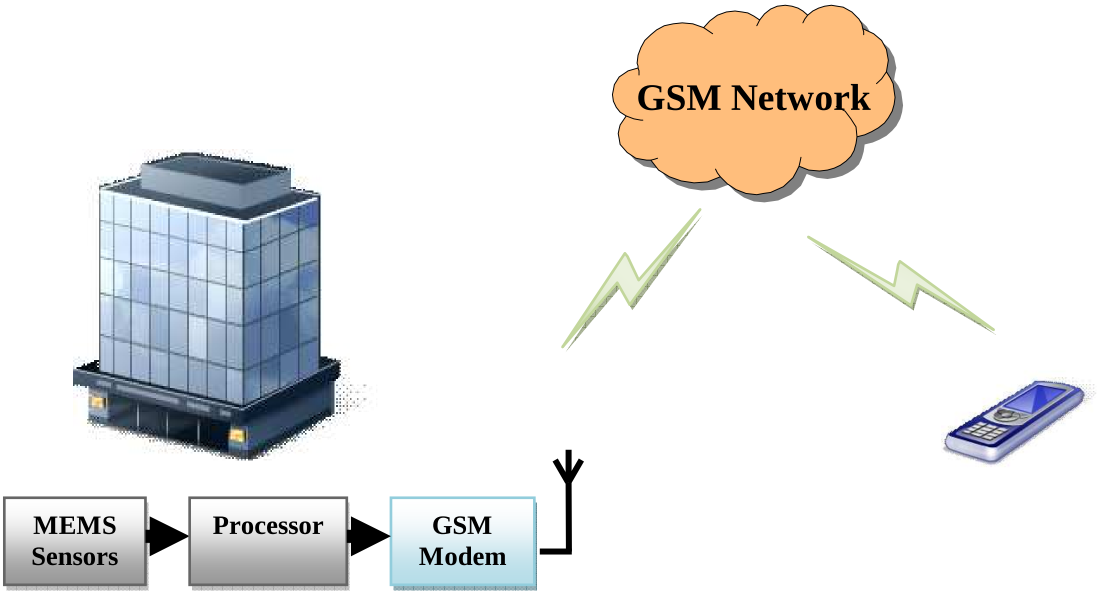

Fig. 1: Schematic diagram of the system

3 Design and Simulation of MEMS based sensors

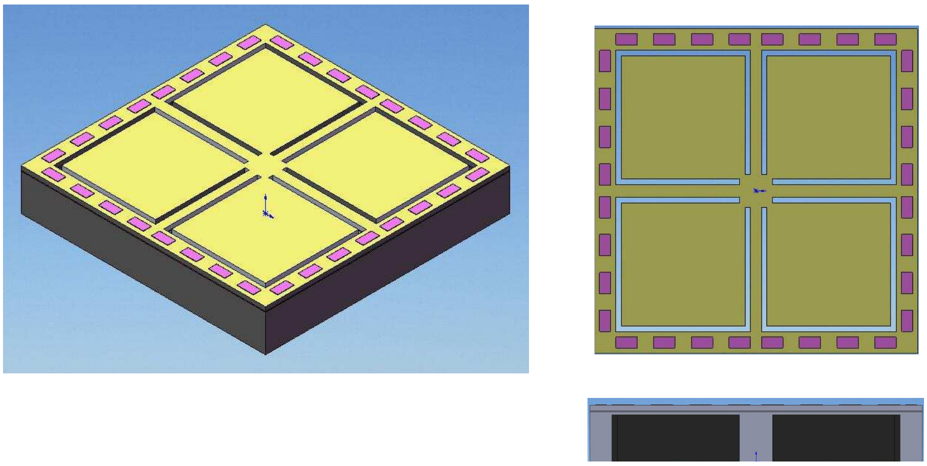

Fig. 2: 3D model of the proposed 3-axis acceleration sensing structure

3.1 Sensing Structure and Working Principle

The working principle of 3-axis acceleration sensor can be explained as follows; when the sensor is under the acceleration, the beam-structure has two kinds of important vibration modes that lead to form two deflection forms. Schematic drawings of deformed shapes of the beam structure are used to describe the working principle of the accelerometer. The first type shown in Fig. 3 (a) is caused by the X- or Y-component of acceleration (AX, Ay). In this case, seismic mass is being twisted around X or Y axes according to applied acceleration. The second type shown in Fig. 3 (b) is caused by the Z-component of the acceleration (Az). Az causes the seismic mass to move vertically up and down. These deflections of the beams as a result of the applied acceleration component on the sensor are generating strain on the crossbeam structure. Finally, stress variations on beam(s) surfaces are produced linearly as a consequence of the strain.

In p-type piezoresistors, the resistivity of diffused layers changes when subjected to strain. This phenomenon has been used as the sensing principle of the 3-axis accelerometer with integrated piezoresistors on a single crystal silicon crossbeam structure. The resistance variations of resistors could be converted into electrical signals by using imbalance of excited Wheatstone bridge circuits.

3.2 Structural analysis

The structural analysis of the sensing chip was done via two steps. Firstly, analytical analysis was done by classical elasticity theory for rough estimation of sensor dimensions based on the required ranges of acceleration, the piezoresistance effect of silicon, the non-buckling condition, and the necessary width of the beam for wiring. Secondly, this model was analyzed by a finite element method (FEM) to investigate more comprehensively the stress field in the structure, to determine the motion of the seismic mass, the resonant frequency of the structure and to refine the specifications of the beam dimensions. The finite element model of the sensing chip was numerically analyzed by using the commercially available ANSYS simulation software. The FEM model of the accelerometer is densely meshed in the beams to better resolve the stress distribution there. Element type, SOLID45 is used for the 3-D modeling of this solid structure. Firstly, the modal analysis was carried out to find the vibration modes of the sensor structure and resonant frequencies. Fig. 4 (a) and (b) show those vibration modes. Secondly, static analysis was performed to find out stress distribution and non buckling conditions of sensor structure. Fig. 4 (a) and (b) show the graphical representation of longitudinal stress distribution on the surface of X-oriented beam structure. Based on the stress distribution results obtained by FEM analysis and the classical elasticity theory, piezoresistors were placed to eliminate the cross-axis sensitivities, and to maximize the sensitivities to various components of acceleration.

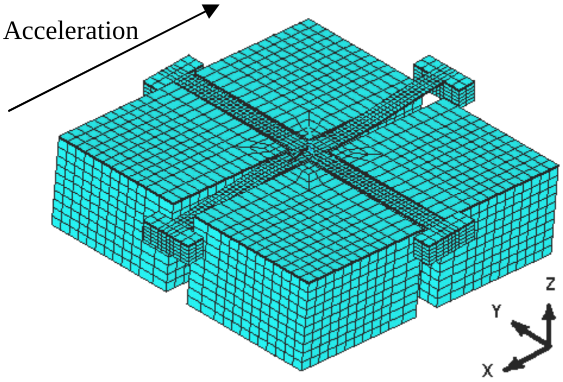

Fig. 3 (a): 1st vibration mode of the sensing structure

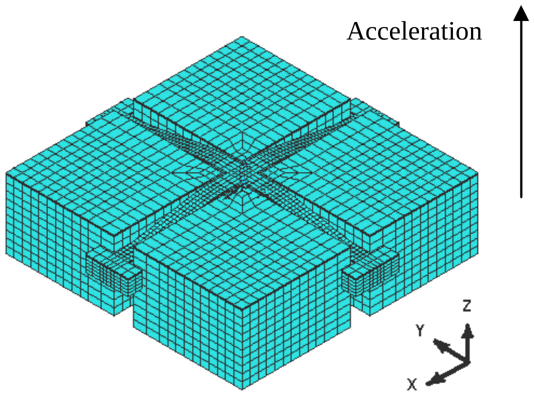

Fig. 3 (b): 2st vibration mode of the sensing structure

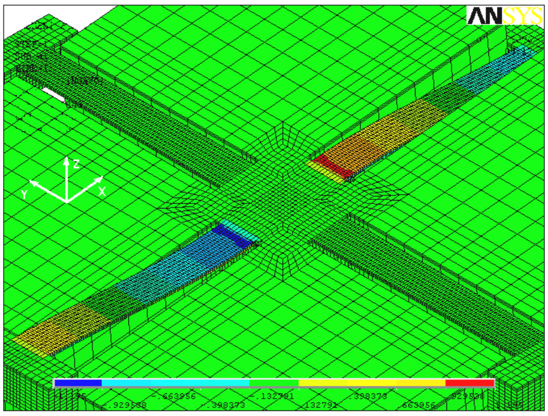

Fig. 4 (a): The stress distribution on surface of X-oriented beam structure under applied acceleration Ax

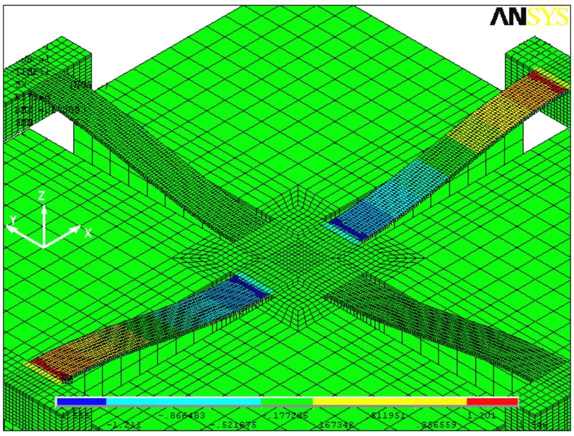

Fig. 4 (b): The stress distribution on surface of X-oriented beam structure under applied acceleration Az

3.3 Measurement Circuits

In most cases, Wheatstone bridges are being used for the measurement of resistance change of piezoresistors on sensors. Identical twelve p-type piezoresistors have been interconnected to form three Wheatstone bridge circuits on the beam structure. Induced voltage under the acceleration can be measured as the output of the sensor. [3]

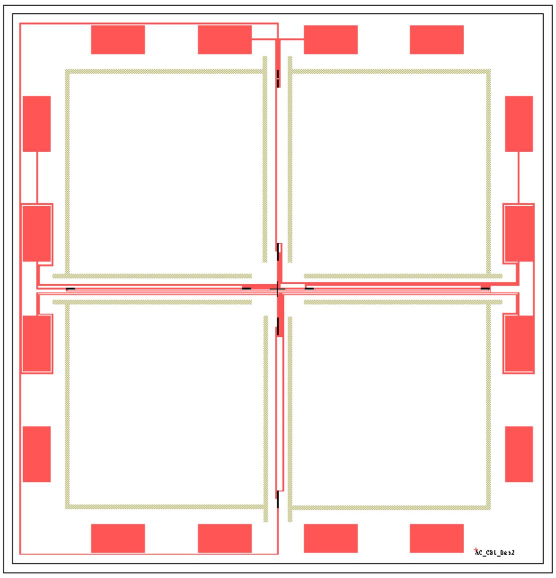

Fig. 5: Mask layout of the sensor (die chip area is 3mmx3mm)

3.4 MEMS Pressure Sensor

Design and Simulation procedure for the MEMS Pressure sensor was same as for the MEMS accelerometer.

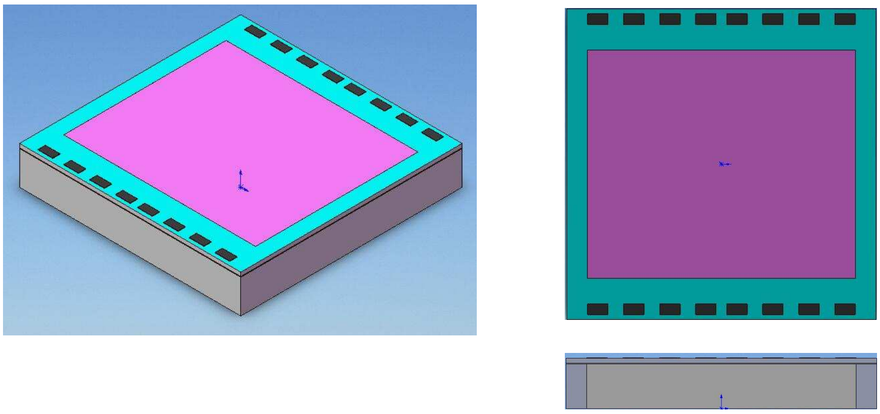

Fig. 6: 3D model of the proposed 3-axis Pressure sensing structure

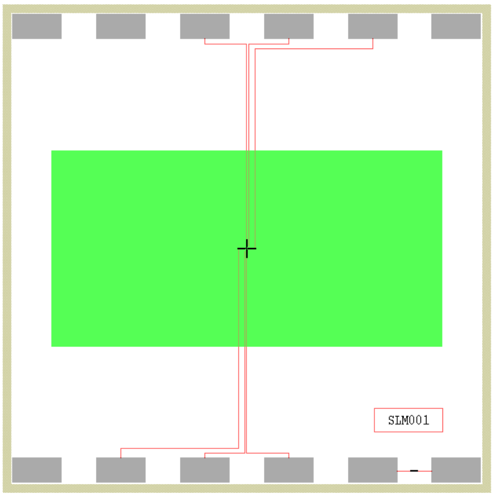

Fig. 7: Mask layout of the Pressure sensor (die chip area is 3mmx3mm*).*

4 Design

4.1 Sensing Mechanism for detecting the breach of security of the room

Vibration data are collected from an accelerometer, fixed on a tile or a plate and put beneath the carpet closer to a door or an entrance to the room. The system can be mounted such a way that it blends with the surroundings. This tile has one degree of freedom in the vertical direction. The amplitude of the tile is about 1mm. The pressure sensor opening is placed such a way that it will detect the pressure differences near the door. When a person walks near the place where the acceleration sensors are placed, they will pick up the vibration. Vibration waveforms can be filtered to identify if a person walked near the place. It also can produce the weight of the person and give characteristics of the persons walking pattern to a some degree of accuracy provided the use of three acceleration sensors near each other and comparing the three sensor data. However this data only is not sufficient to accurately state that a person has entered the room because the acceleration sensor picks up all the vibration signals near the vicinity of the sensor. In a building when a door or a window gets opened air inside the particular room move in a higher velocity, which causes a sudden pressure difference inside the room. This kind of action can be detected by placing a high sensitive pressure sensor inside the entrance. With the acceleration sensor data and the pressure sensor data processed at the same time, it can be concluded that a person has entered the room or passed near the room.

4.2 Electronic Circuit Design

The electronic circuit that was design for this application can be divided into the following major components,

I. MEMS Accelerometer
II. MEMS Pressure Sensor
III. Instrumentation amplifier for signal amplification
IV. Microcontroller with USB interface
V. Voltage regulator
RS232 Level convertor for GSM Modem

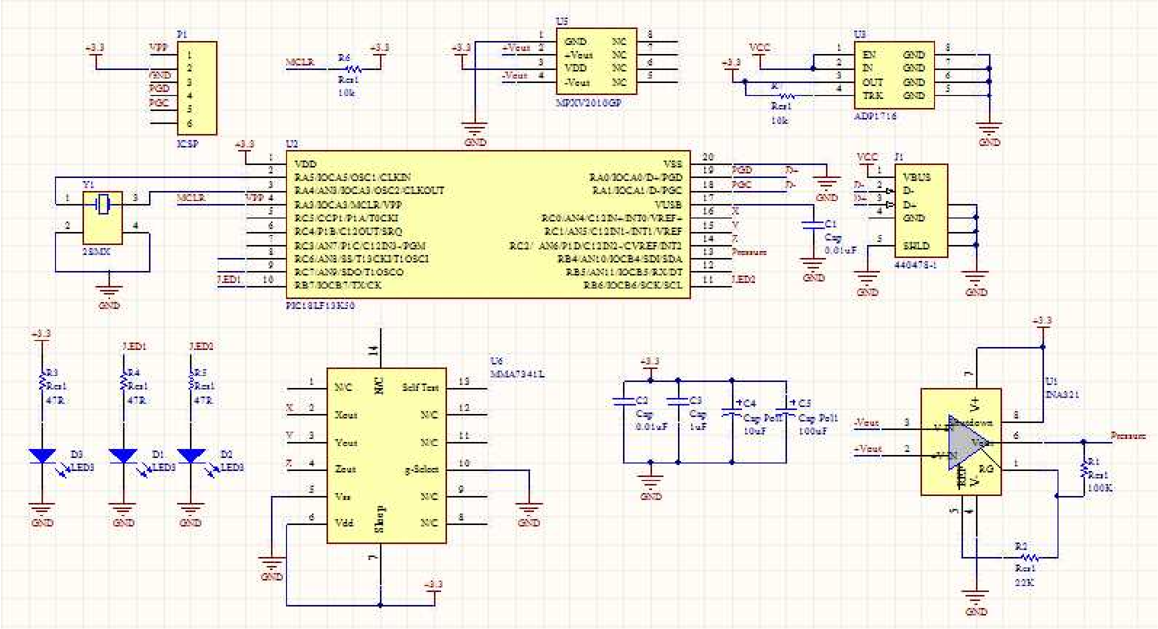

Fig. 8: Schematic diagram of the circuit

Both accelerometer and pressure sensor have very small output voltage value which is not sufficient for the Digital signal processing. Thus the signals had to be amplified. Instrumentation amplifier is used here for signal amplification. In this design we used an INA321 instrumentation amplifier (Texas Instruments) for signal amplification. Commercially available MMA7341 MEMS 3-axis accelerometer (Product of Freescale Corporation) is used for the acceleration sensor. It has a sensitivity of 3g. Commercially available MPXV2010GP MEMS Pressure sensor (Product of Freescale Corporation) is used. It has a sensitivity of 10kPa.

PIC18LF13K50 microcontroller is used for the signal processing. Analog to digital conversion is also performed using the built in analog to digital convertor. Since the GSM modem used in this design has the normal RS232 interface, for the RS232-TTL level conversion a MAX233 chip was used. The USB interface can be used to interface this system to a computer for further signal processing.

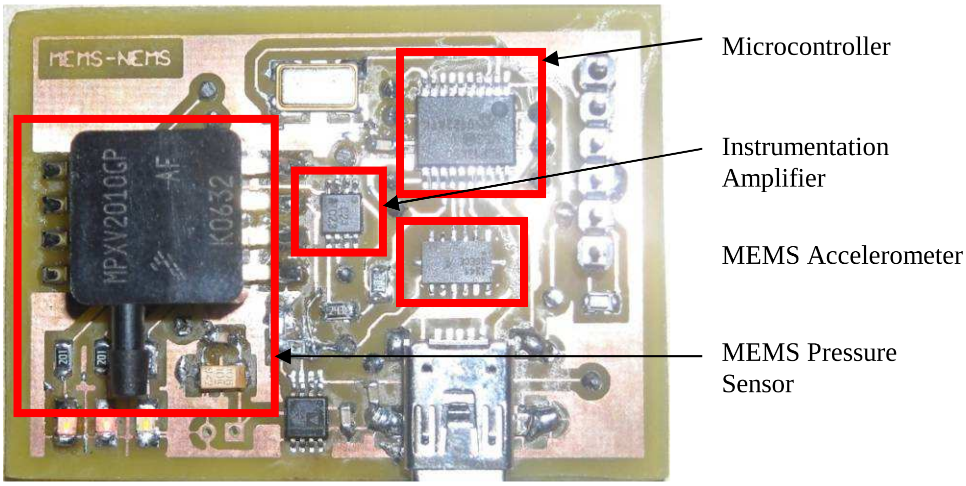

Fig. 9: Hardware circuit module (4.5cm×3.0cm)

4.3 Communication interface

Since GSM communication is very popular nowadays, it has been used to alert the user. SIEMENS mc35i GSM modem is used for the communication which has RS232 interface. Hayes "AT" commands are used to communicate with the modem through RS232. The Hayes command set is a specific command-language originally developed for the Hayes Smartmodem 300 baud modem in 1977. The command set consists of a series of short text strings which combine together to produce complete commands for operations such as dialing, hanging up, and changing the parameters of the connection. Most dialup modems follow the specifications of the Hayes command set. [4]

The following code describes a SMS send and setting up necessary configuration. The code is written in ANSI C language for PIC Microcontrollers.

```
printf("\rAT\r");
delay_ms(1200);
printf("\rAT+CPMS=\"ME\"\r");
delay_ms(1200);
printf("\rATE0\r"); //Disabling Echo feature
delay_ms(1200);
printf("\rAT+CMGF=1\r"); // Entering TEXT mode for SMS
delay_ms(1200);
printf("\rAT+CMGS=0712345678\r");  //send SMS to No 0712345678
delay_ms(2200);
printf ("Test1");
putc(26);
delay_ms(1200);
```

5 Conclusion

In this project we have developed a circuit incorporating a MEMS pressure sensor, an acceleration sensor and a GSM module for smart house security systems. The test codes and circuit designs are presented in this paper. The sensor module is having a compact design and can easily be used in security applications. It is wished that this research carried out would help future engineers to come up with solutions for smart building.

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[4] http://en.wikipedia.org/wiki/Hayes_command_set, visited on 3rd August, 2010

APPLICATION OF NANOMATERIALS IN THE SUSTAINABLE BUILT ENVIRONMENT

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Abstract: Nanotechnology is widely regarded as one of the twenty-first century's key technologies, and its economic importance is sharply on the rise. In the construction industry, nanomaterials has potentials that are already usable today, especially the functional characteristics such as increased tensile strength, self-cleaning capacity, fire resistance, and additives based on nano materials make common materials lighter, more permeable, and more resistant to wear. Nonomaterial are also considered extremely useful for roofs and facades in the built environment. They also expand design possibilities for interior and exterior rooms and spaces. Nano–insulating materials open up new possibilities for ecologically oriented sustainable infrastructure development. It has been demonstrated that nanotechnology has invented products with many unique characteristics which could significantly provide solutions current construction issues and may change the requirement and organization of construction process. This paper examines and documents applicable nanotechnology based products that can improve the sustainable development and overall competitiveness of the construction industry

Keywords: Nano Materials, Concrete, Thermal Insulation, Flame Retardant, Thermal Energy Storage

1. Introduction

Building and construction industry is a prime consumer of world's material and energy resources which accounts nearly for 40%of usage. The industry utilizes natural and synthetic materials which include cement, steel, aggregates, wood, glass, textiles, plastics, foams etc. The current tendency and demand towards more sustainable "green" practices has imposed a tremendous pressure on this material and energy usage in the Building Environment for improvements and conservation (Elvin, 2007). Nanotechnology, the manipulation of matter at the nano scale plays a key role in this matter where it provides answers for current construction related problems. Thus the potential for energy conservation and reduction of resource consumption, waste, toxicity and carbon emissions towards more sustainable "Green Practices" is significant.This paper mainly focuses on better properties concrete, thermal insulation, flame retardant, thermal energy storage, and self cleaning and antimicrobial effect for sustainable built environment.

2. Concrete

Concrete is the most widely used material in the built environment. Concrete mainly consists of cement, aggregates, water and admixtures. Most of the concrete is made up of aggregates which are inert granular materials such as sand, crushed stone or gravel (Tabsh and Abdelfatah, 2009). Cement acts as the main binding phase in concrete. The expansion of the construction industry it is necessary to develop low cost and more efficient types of concrete while maintaining sustainability.

2.1. Incorporating Nano Materials to Concrete- The Present Status

Nano engineering or nano modification to the cement based materials is an active area of research at present(Sanchez and Sobolev, 2010). But, comparing with the other fields, concrete has been slow to catch the emerging enhancements of nano technology. This is mainly due to the lack of basic understanding of concrete at nano level and the lack of broad understanding of what nano modification means to concrete (Garboczi, 2009). The recent developments of the experimental techniques available have facilitated to study the concrete at micro and nano levels. Concrete is a nano-structured multi phased composite material consisting of an amorphous phase, nano meter to micro meter sized crystals and bound water. The reactions within the concrete occur through macro, micro and nano levels (Sanchez and Sobolev, 2010). Therefore, addition of suitable nano particles into concrete can alter many properties of concrete. The effects of adding various nano particles to concrete are described below.

2.1.1. Addition of Nano Silica into Concrete

Nano Silica has been found to increase the strength, flexibility, workability and durability of concrete. The nano Silica particles increase the viscosity of the fluid phase of concrete and fill the voids between cement grains. It reacts with Calcium Hydroxide and results in more Calcium Silicate Hydrate (CSH). Almost all the mechanical and transport properties of concrete are controlled by CSH which is a nano-porus, nano-structured material(Garboczi, 2009). Nano Silica acts as a nucleation site for preparation of CSH which results in high strength than conventional concrete (Sobolev et al., 2009, Hosseini et al., 2009, Vera-Agullo et al., 2009, Sanchez and Sobolev, 2010). Incorporating nano Silica has improved the hydration process of cement (Belkowitz and Armentrout, 2010, Sanchez and Sobolev, 2010). This is mainly due to the large reactive surface area of nano particles.

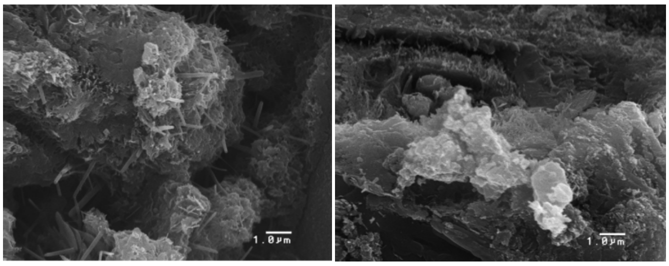

Fig: 1(a) **Fig: 1(b)**

Fig. 1: (a) SEM micrographs of Ordinary Portland Cement Paste and **Fig.1:**(b) Paste containing Nano Silica (Jo et al., 2007)

2.1.2. Addition of Carbon Nano Tubes (CNT) into Concrete

Carbon Nano Tubes (both Single Walled (SWCNTs) and Multi Walled (MWCNTs)) is another material which can be used to enhance the properties of concrete.

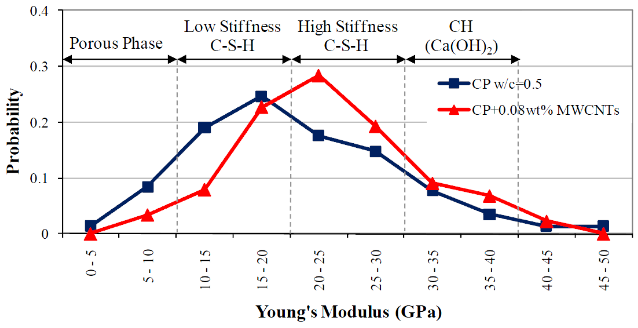

Fig.2: Probability plot of Young’s Modulus of 28 days cement paste(w/c=0.5) and cement paste reinforced with 0.08wt% MWCNTs (Metaxa et al.)

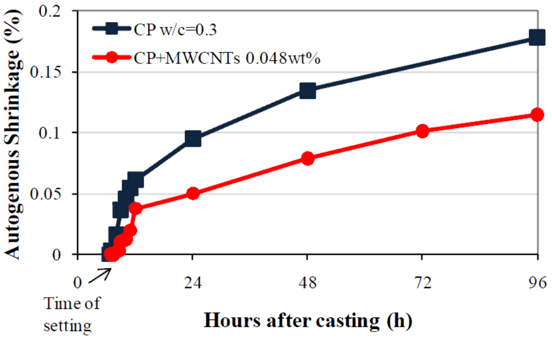

Fig.3: Autogenous shrinkage of cement paste (w/c=0.3) and cement paste reinforced with 0.048wt% MWCNTs (Metaxa et al.)

CNTs display a very high theoretical strength which is 100 times more than that of steel while just having only one sixth of the specific weight of steel(Li et al., 2005). Incorporation of CNTs increases the amount of high stiffness CSH and also reduces the porosity of the CSH phase resulting increase in Young's Modulus, flexural strength, compressive strength and durability and decrease in autogenous shrinkage (Metaxa et al., Li et al., 2005).

2.1.3. Addition of Nano TiO_2 into Concrete

There has been few research carried out to study the effect of nano TiO_2 in concrete mixes. As TiO_2 is an inert material it will not participate in the reaction within the cement paste but the rate as well as the peak of hydration of concrete has shown to be increased as shown in Fig 4 when nano TiO_2 is added due to the heterogeneous nucleation. Nano TiO_2 improves Compressive and Flexural Strengths and enhance the abrasion resistance of concrete (Jayapalan et al., 2009).

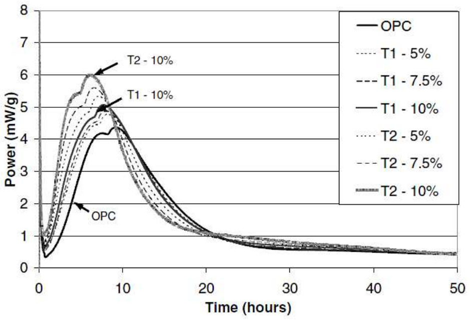

Fig. 4: Rate of Hydration of TiO_2 –blended cements (Jayapalan et al., 2009)

2.1.4. Addition of Nano Fe_2O_3 and Al_2O_3 into Concrete

Partial replacement of cement with nano Fe_2O_3 particles has shown to increase the flexural and compressive strengths of concrete (Nazari et al., 2010a). Another nano material which has been incorporated with concrete is nano Alumina. It has been shown that partial replacement of cement with nanophase Al_2O_3 particles improves the compressive, flexural and split tensile strengths of mortar but decreases its workability and setting time(Nazari et al., 2010b, Nazari et al., 2010c).

2.1.5. Summary of the effects of Nano Materials on Strength of Concrete

A comparison of the percentage increase of flexural and compressive strengths with the addition of nano particles is shown in Figure 5.

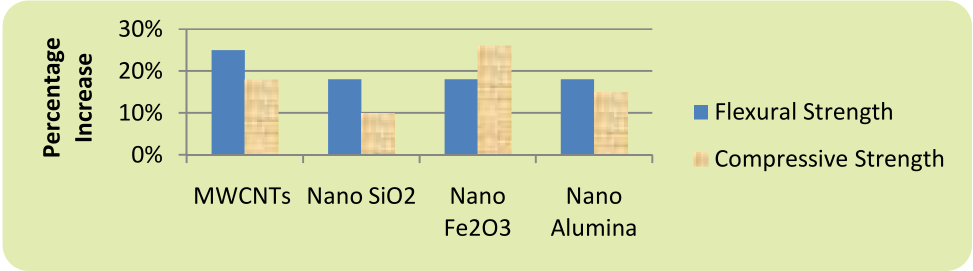

Fig. 5: Percentage increase in Compressive and Flexural Strengths with the addition of nano Particles (Sobolev et al., 2009, Hosseini et al., 2009, Vera-Agullo et al., 2009, Sanchez and Sobolev, 2010), Metaxa et al, Nazari et al., 2010b, Nazari et al., 2010c)

2.1.6. Issues regarding incorporation of Nano Materials into Concrete

It is important to obtain good dispersion of these nano materials to avoid agglomeration and to increase the linkage of nano materials with the binding phase of concrete. Large aggloromates and bundles as seen in Fig 6(a) can be noticed when no dispersing agents are used (Konsta-Gdoutos et al., 2010). Adding an effective superplasticiser, ultrasonification, high speed mixing and chemically functionalizing the surfaces of the nano materials have shown to increase dispersion of nano materials within the matrix phase and enhance the bonding (Kowald and Trettin, 2009, Shah et al., 2009, Sobolev et al., 2009, Cwirzen et al., 2009).

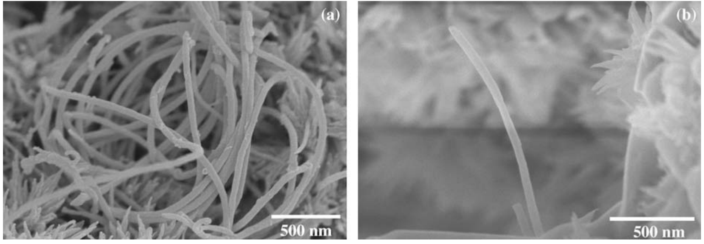

Fig.6: SEM images of cement paste fracture surfaces reinforced with undispersed and dispersed MWCNTs (a) and (b), respectively.(Konsta-Gdoutos et al., 2010)

3. Thermal Insulation

Building insulation will be one of the main focuses, where the demand for more energy efficient buildings is expected to grow significantly in coming years. The presence of glass surfaces and the insulating capacity of the outer cladding are the main reasons for heat loss and gain within the building envelope (Scalisi, 2009). Nanoscale materials provides a far better solution in building insulation due to their high surface-to-volume ratio which enable them to trap still air with in a thin layer of material. The current product range on insulation varies among paints, coatings, thin films or rigid panels.

3.1.Nansulate

Nansulate® coating is a patented insulation technology that incorporates a nanocomposite called Hydro-NM-Oxide, a product of nanotechnology. It’s an excellent insulator due to its low thermal conductivity and the nanomaterial used. Test results for Nansulate® from independent laboratory shows that thermal resistance (1/U) of the wall section coated with Nansulate® was increased by 28.98% (Test Method:UNI EN ISO 8990:1999) (www.nansulate.com).Nansulate can be directly applied to the existing buildings without incurring any post-construction addition, thus creates tremendous energy saving with existing buildings. Nansulate coating thickness on an applied surface is around 200 microns DFT (approximately 3 coat coverage) with very high savings on space reduction (Industrial-nanotech, inc.2010.).

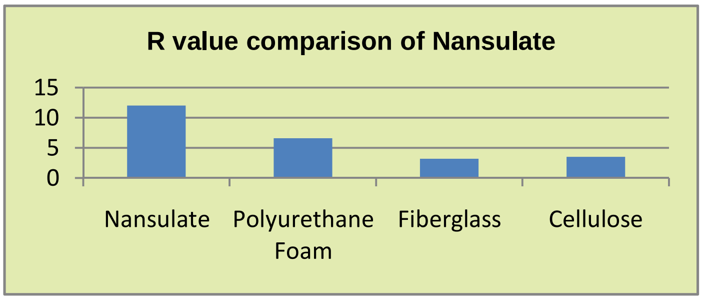

Fig.7: R value (Thermal Resistivity) comparison of Nansulate Shield, especially designed for the construction industry with conventional insulating materials (Elvin, 2007).

3.2. Aerogel

Nanoporous insulation materials like aerogels, an ultra-low density solid provides a superior solution for insulation. The aerogels for thermal insulation used today are most often silica or carbon based with approximately 96% of their volume being air. Silica aerogel is a promising nanocomposite material for applications in buildings because of its high visual transmittance and its low thermal conductivity. Apart from their low thermal conductivity its load bearing capability makes it suitable for evacuated transparent insulation applications

Fig.8: Aerogel, The world's lightest solid (Elvin, 2007).

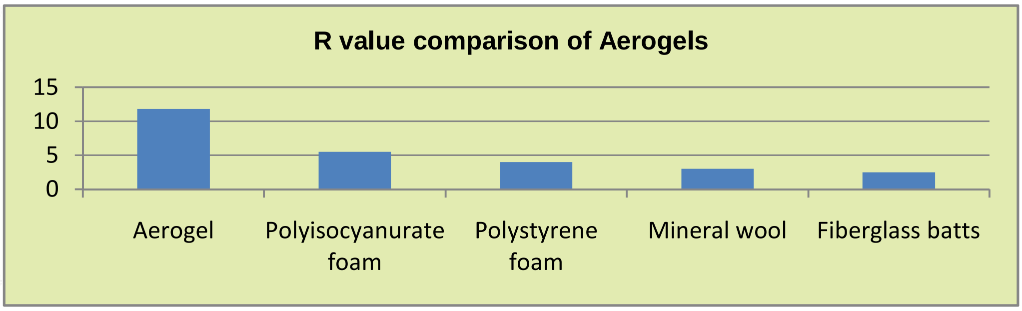

Fig. 9: R value comparison of Aerogels (Elvin, 2007)

4. Flame Retardant

Flame retardant effect can be results as a combination of several kinds of nanocomposites. Due to its low price, many research focused on the production of nanoclay containing composites to achieve these properties but CNT is also heavily used in research for flame retardant materials. The newly developed materials possess properties like reduced flammability, less toxic gases release and less smoke products compared with the traditional flame retardant materials (Zhang, 2005).

4.1.Nanoclay

Research done on polyamide 66/organoclay(nanoclay) (PA66/OMT) nanocomposites shows improved flame retardant properties. The peak HRR (PHRR) is the most important parameter to evaluate fire safety (Zhang, 2005). It shows that pure PA66 burns very fast after ignition and reaches a sharp peak on the HRR curve while the addition of OMT shows a great decline of HRR and the sharp peak tend to be a platform (Song *et al*., 2008).

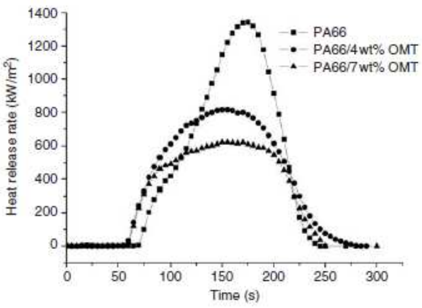

Fig. 10: Comparison of heat Release rates, PA66 and PA66/OMT nanocomposites (Song *et al*., 2008).

4.2.Carbon Nano Tubes

Carbon nanotubes (CNTs) attracted much attention due to their excellent properties as a nanomaterial used for making polymer nanocomposites in recent years (Reim *et al*., 2005). Research done on improving flammability of Ethylene–vinyl acetate (EVA) based composites using Multi wall Carbon Nanotubes shows that the possibility of delaying both the ignition time and reduce the flammability (HRR) of a polymermatrix like EVA by adding a small amount of MWNTs (Peeterbroeck *et al*., 2007).

5. Thermal Energy Storage

5.1.Phase Change Materials

Phase Change Materials (PCMs) are often considered for latent heat thermal energy storage (LHTES) applications. Thermal storage can be part of the building structure due to the advent of PCM implemented in gypsum board, plaster, concrete or other wall covering materials (Castellón *et al.*, 2007*)*. The main drawback that hinders the application of PCMs is their low thermal conductivity (Zeng *et al*., 2009). Paraffin is commonly available PCM material with promising benefits because it has a large latent heat and low cost, and is stable, non-toxic and not corrosive. Research has done to overcome the low thermal conductivity problem of paraffin using exfoliated graphite nanoplatelets (xGnP).

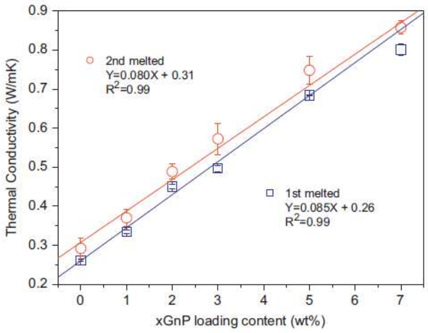

Fig. 11: Thermal conductivity of paraffin/xGnP composite PCMs by melting times (Kim and Drzal, 2008).

6. Self Cleaning and Antimicrobial effect

Need for achieving a cleaner hygienic surface is highly desired in current architectural practices. In a building environment, the primary cleaning actions includes the removal of everyday dirt, dust, or other things that naturally appear on windows or other surfaces in buildings (Ashby *et al*., 2009).

Fig.12: This fabric membrane structure at the Hyatt Regency in Osaka uses a photocatalytic clear coat based on TiO_2, which creates antibacterial effect. (Ashby *et al*., 2009)

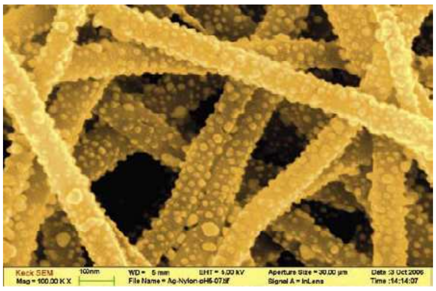

Fig.13: SEM image of nanofibers with silver (Ag) nanoparticles for antibacterial gowns and active surfaces such as carpets and upholstery. (Ashby *et al*., 2009).

Commercials products are available for self-cleaning surfaces with the invention of photocatalytic coatings containing titanium dioxide (TiO2) nanoparticles. These TiO2 particles degrade organic dirt and stains when it is exposed to ultraviolet (UV) light. When the surface is subjected to rain or simple washing hydrophilic action of TiO2 carries out the loosened dirt particles from the surface.

Surfaces which exhibit "antibacterial" properties either kill or inhibit the development of bacteria which causes deleterious effects such as discoloration, staining, or odours (Ashby *et al*., 2009). One such approach is to use copper or silver nanoparticles as a coating on base materials or incorporated directly in the surfaces of the base materials. Apart from the proven history of antibacterial effect of these materials, much larger surface area of nanoparticles helps to provide a sound antibacterial effect.

7. Conclusion

Nanotechnology is a promising field in terms of environmental improvements including energy savings and reduced reliance on non-renewable resources, as well as reduced waste, toxicity and carbon emissions. It's applications in the building industry is expected to show a significant boom in the coming years due to international urge for "more greener" build environment. When considering the built environment, concrete is the main construction material. Better understanding of the properties of concrete at nanoscale can lead to improve the functionality of concrete. The influence of addition of nano particles such as Nano Silica ,nano Al_2O_3, nano TiO_2 and nano Fe_2O_3 in the correct proportions and methods into concrete can increase the mechanical and transport properties, rate of hydration, durability and many other properties. Moreover energy conservation and reducing green house emissions in the building environment can be a reality due to nanomaterials emerging as insulations and energy storage materials. Enhanced insulation material coupled with thermal energy storage properties can reduce the operational energy consumption in a build environment to a great deal. Other applications like self cleaning and antimicrobial surfaces will reduce the resource consumption and lengthen the life cycle of material usage in the industry, thus will drive towards sustainable practices.

As markets are full of uncertainty especially when new technologies are introduced, the application of nanotechnology will also face challenges in terms of material cost, construction industry resistance and public awareness about nanotechnology. But with the outstanding benefits offered by nanotechnology, it will outperform all the obstacles and it's expected that these exciting materials and products that will dramatically change the way future buildings are made and the best is yet to come.

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INTELLIGENT BUILDINGS FOR INTELLIGENT PEOPLE A CONCEPT

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Abstract: The past decade has seen unparalleled evolution in the field of Materials engineering. Largely due to the unique properties seen in materials in the nanoscale relative to their macroscopic counterparts, nanomaterials as an example can be used to enhance tensile strength, insulation and are biomimicable. These properties combined with integrated structural monitoring and diagnostics systems are set to revolutionize the construction industry. Current research shows the inclusion of self healing properties, bringing these endeavors full cycle.

Structural integrity is a key facet of building maintenance which historically has been evaluated on the basis of empirical studies stemming from lifecycle analysis of the concerned structure. The associated costs, lead times and lost revenue due to these activities can be mitigated by using materials which are engineered to report the parameters of concern to building monitoring systems. These systems can be the resultant of nanocomposite materials which are self organizing in nature, in turn forming interrogation capable grids. Dielectric and complex impedance measurements of these grids will be sampled through an analog to digital conversion interface linking the captured data on to the building management system. Alerts can be issued in real time when material boundaries are crossed, indicating impeding structural changes. Constants associated with the nanocomposite materials will set the thresholds for the alerts. The captured raw data would have the ability to monitor parameters such as vibration, stress/stain (piezoelectric materials) and thermal gradients (temperature coefficient of complex impedance).

Furthermore, materials such as TiO2 facilitate photocatalysis, where the free radicals can be used for the oxidization of organic matter resulting in self cleaning surfaces. Anatase titanium dioxide can also be used in the form of a composite addition to cement for Bio mimicking structures to be used to offset our carbon footprint. Although yields of such activities remain low, the research too is in its infancy. By monitoring the redox reactions of these materials in the form mentioned above, it will be possible to observe the conversion efficiency as live “heat map”, resulting in much needed empirical data. Reportedly, the use of TiO2 has been used to control the growth of biological matter. As deterioration of structures due to biological matter is immense, these properties will allow for the control and monitoring of the design and environmental parameters which facilitate their growth.

Macroscopically the construction industry is poised to benefit greatly by these immediate changes that nanotechnology has brought to the materials engineering. Resultant structures would encompass the low carbon footprint which is expected and sought after in the current climate as well as the economic and safety benefits inherent of such activities.

This paper reviews a range of concepts and technologies capable of harmonizing built environment and the state of the art in monitoring and energy capture.

1. Introduction

Individual components of a building can be taken in to consideration due to their placement and thus its inherent potential. The Foundation, Frame, Bulk material, Windows/doors, Floors, Roof and Skin can contribute to 2nd order activities while maintaining its core role through the use of intelligent materials. The 2nd order activities can be identified in two logical and complimentary groups being sensing and energy scavenging. Sensing and Energy scavenging in built environment can be carried out either through the use of intelligent materials which are symbiotic in nature or through the use of components added on to the structure.

2. Concepts and Technology

As an example, an intelligent foundation could implemented either through the use of a ZnO (piezoelectric) coating on the steel bars in the reinforced concrete which would sense the stress strain and sheer components, likewise these properties could also be sensed through the integration of an almost off the shelf optical fibre (Fibre Bragg Grating) sensors which can be mounted on the surface. Geothermal electrical energy generation becomes feasible as the building becomes taller, due to the requirement of a deeper foundation. Further enhancement of the thermal gradient is possible due to the colder environment at higher altitudes enabling faster heat dissipation. Buildings of lower height can also benefit from geothermal energy generation in the form of thermal energy for heating. These vary in terms of economic viability as a 2007 study indicates a break–even price of 0.04-0.10 € per kW·h [i], at a capital expenditure of 2-5 million € per MW of electrical capacity. Expanding on the concept, the ability to capture the heat energy through solar concentrators on the roof and store it for night time use is a further possibility through the use of borehole thermal energy storage. It is a system where an underground structure is used for storing large quantities of solar heat collected in summer for use later in winter. A key concern in power generation, regardless of the source of the energy is providing a consistent output. Hence, the use of an underground heat storage facility would provide a future proof and cost effective mechanism for medium to large scale energy storage.

The structure of a high rise building is predominantly made of steel. Piezoelectric materials mixed composites would allow the building management system to monitor a life stress/strain map of the entire metal structure. The taller the buildings are there exists a slight sway due to the wind factor at the top of the building. These intelligent frames are well placed to monitor the structural rigidity and health of a building during the course of an earthquake, storm or even a manmade disaster such as an explosive device detonating.

Thus situational awareness pertaining to the building would become instantly available to emergency or rescue workers. These material based sensors would allow for early warning for such natural disasters as earthquakes much earlier due to the depth of foundation structure. Likewise costs associated with building maintenance can further be mitigated since real time data is always available. Standard steel based structures can be monitored through the use of Magnetoquasistatic Sensing such as the Meandering Winding Magnetometer. It is inductive sensing using magnetic fields to monitor changes in the properties of magnetic and/or conducting materials such as metals[ii]. A piezoelectric coating or the inclusion of a piezoelectric compound in to the metal structure would allow for power generation due to the inherent sway in larger buildings. This would further complement the carbon footprint of the building. Strategically constructed wind tunnels through a high rise building have been demonstrated to generate significant amounts of electricity. Such activities are currently shifting from the conceptual stages to realization.

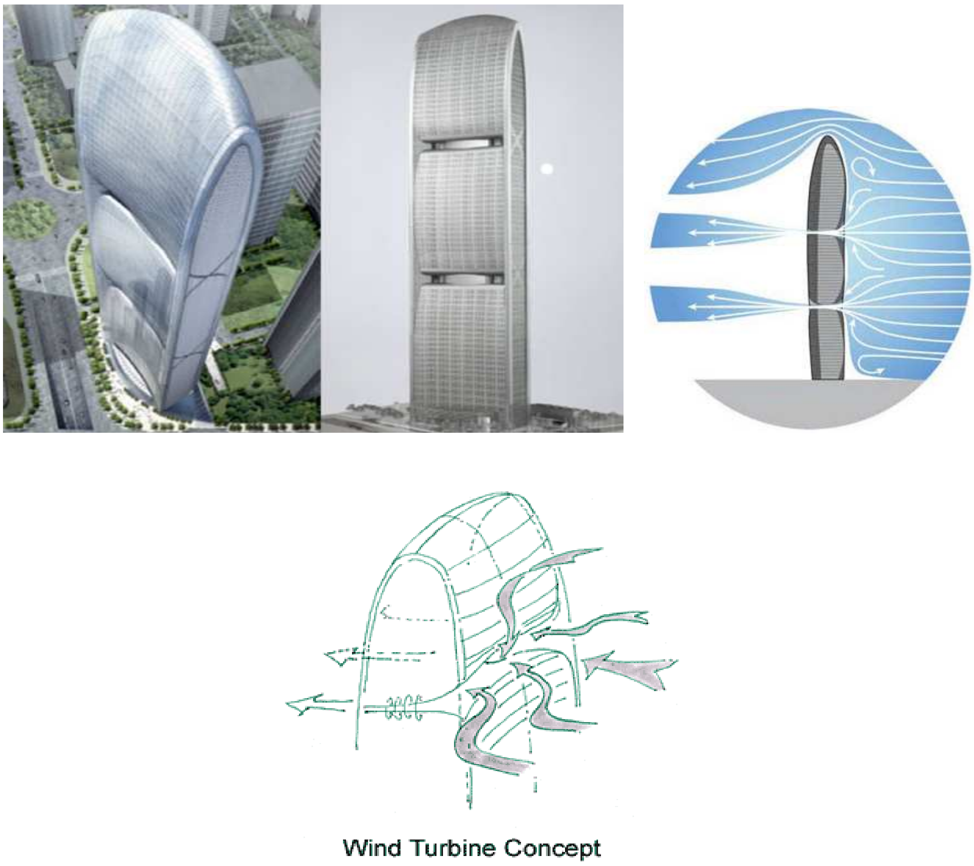

Fig. 1: Pearl River Tower Wind turbine concept (Skidmore, Owings and Merrill)

Bulk building material such as concrete can be modified through conducive fiber compounds for a sensing ability is associated with the reversible change of the electrical resistance of the concrete upon deformation[iii] in the elastic regime. It allows a further aspect in the monitoring of the structural rigidity of the building. Loading due to machinery in large buildings can be analyzed through such sensing mechanism. Since stress is force per unit area, stress relates to force. Hence, the smart concrete can serve as a scale for weighing.

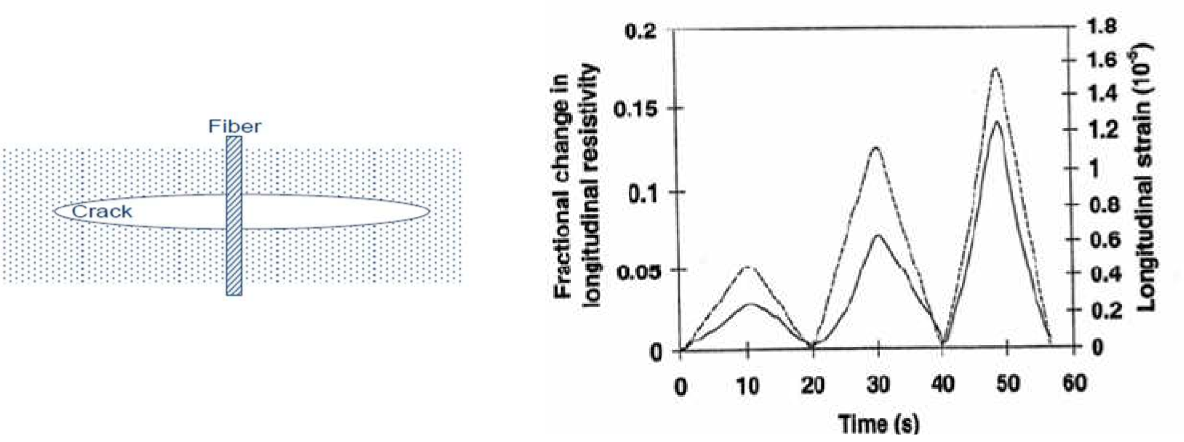

Fig. 2: Smart concrete[iv]

Orifices such as doors and windows can be utilized through the use of nanotechnology based spray on solar cells to generate electricity throughout the day. Such films are at the research stage currently where proofs of concepts have been developed[v]. The use of electrochromic material to automatically attenuate the solar irradiance in to the building can help mitigate air conditioning costs during the summer and heat loss during the winter period. Furthermore liquid crystal displays can be built on to the surface of the windows to allow them to be used as display for the building health data harnessed from the sensors discussed thus far. Another interesting application is the addition of an Organic LED on the surface of each of the outside facing windows of the building to create large scale bill board like structures. The use of transparent electroluminescent materials would convert the simple window in to a multifunctional interface device.

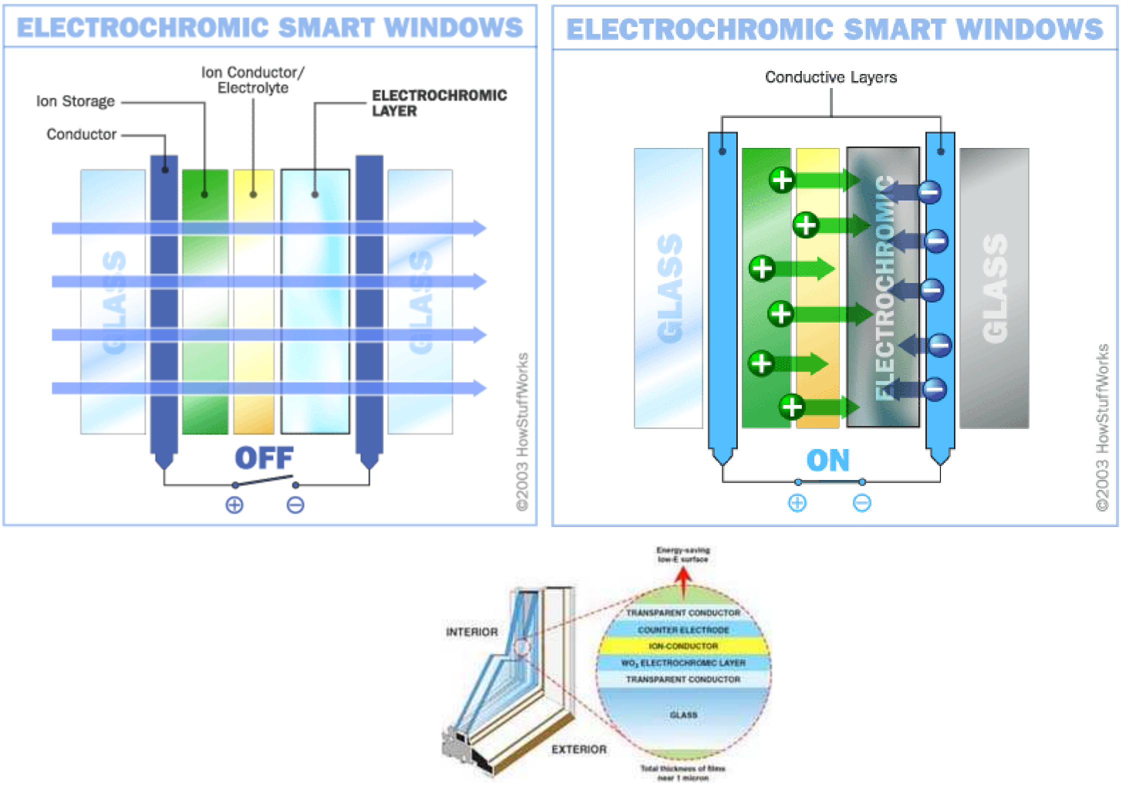

Fig. 3: Electro chromatic window [vi]

Floors are well suited for energy scavenging as it sees continuous use throughout the day in the form of walking which results in vibration energy. Piezoelectric flooring has been demonstrated to be able to harvest this form of energy[vii]. Especially areas which see many visitors such as the entrance or the lounge areas are very well suited to this technology. Concentrated areas of high levels of lateral displacement such as staircases are yet another area were this technology can be implemented. It would also allow for smart cleaning of the building taking in to consideration the level of exposure it has seen to foot traffic.

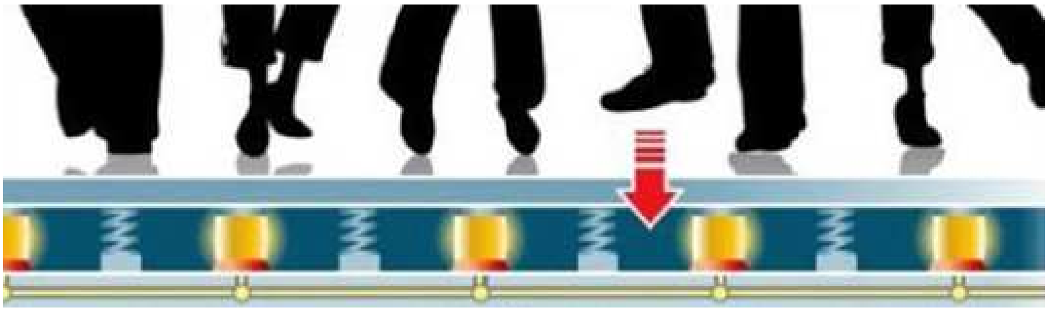

Fig. 4: Piezoelectric floor

The roofing area can be used for solar energy capture at a higher efficiency than the windows of the building. It can be achieved through the use of fresnel lenses (solar concentrators) to greatly enhance the cost effectiveness of solar cell based energy generation. Further maximizing the roof area, the solar cell back plane can be cooled through a heat exchanger which itself will be generating second order energy. Air quality monitoring at gradual elevations would provide valuable data with regards to smog levels and their height above the city. Along with the ability to detect contaminants such as ash from volcanic activity and to map the propagation dynamics.

Paints used in the construction industry are predominantly are based on a TiO_2 filler. TiO2 facilitate photocatalysis, where the free radicals can be used for the oxidization of organic matter resulting in self cleaning surfaces. anatase titanium dioxide can also be used in the form of a composite addition to cement for Bio mimicking structures to be used to offset our carbon footprint.

3. Conclusion

Major breakthroughs in material sciences have allowed us to actively persue green applications in built environment. The benefits are twofold, resultant being self aware and self sustaining buildings. The concepts approached in this paper should be approached at the inception of such projects as it is essentially the bottom up nature which results in a synergy to the structure. Furthermore integration at the scale discussed allow for higher efficiencies in sensing as well as energy generation and conversion. Approaching each element of a building structure has allowed the location and properties inherent to the Foundation, Frame, Bulk material, Windows/doors, Floors, Roof and Skin to be taken in to consideration for relevant enhancement of the overall goal of achieving a intelligent, self sustaining building.

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Afternoon Session

SUSTAINABLE NANOTECHNOLOGY

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1. Introduction

The long-term vision of all nanotechnologists has been the fabrication of a wider range of materials and products with atomic precision. However, experts in the field have had strong differences of opinion on how rapidly this will occur. It is uncontroversial that expanding the scope of atomic precision will dramatically improve high-performance technologies of all kinds, from medicine, sensors, and displays to materials and solar power. Applying Moore’s law it is reasonable to assume all this will happen in the next 15 years or less [1].

Nanotechnology is considered to be the fifth industrial revolution. Unlike any other industrial revolution, its benefits are likely to reach a major portion of the inhabitants of the planet since many nations share a common market driven capitalist economic structure. Experts around the globe agree that we have tipped the scale of population vs. resources, probably for all time, and the balance of resources and their use is no longer in our favor [2]. , in April 2005, the Millennium Ecosystem Assessment carried out by the United Nations [1] indicated that “*...the ability of ecosystems to sustain future generations can no longer be taken for granted.*” In spite of the pervasive economic notion that technology will allow further production gains, accessible global oil production is estimated to have peaked. By 2020 the Middle East will control 83% of global oil supplies, and by 2070, there may be no more cost effective oil supplies available [3,4]. About 75% of the existing prescription drugs in the United States are synthetic [5], and for the remaining 25% derived from nature, they too rely on organic solvents (made from poetroleum) for their extraction and purification. From where will the medicinal agents of the future be derived as the living biomaterials are depleted and the global competition for oil increases on a daily basis? Therefore, we cannot be satisfied scientific discoveries based on non-renewable resources. It is becoming increasingly important to know the outcome of the products of a process at the end of their life time. Today, we are more aware that the innovations we come up with must not destroy the fundamentals that sustain the entire ecosystem including the humans.

2. Nanotechnology and sustainability

It is important to put nanotechnology side by side with sustainability considering the seemingly insurmountable challenges faced by the human race in the coming decades due to population increase and resource depletion. For nanotechnology to make an impact on sustainability, it must come up with solutions to the problems created by technology in general in the last two centuries. Such an analysis makes it easier to understand how nanotechnology could benefit mankind: Nano-scale manufacturing platforms could make geography, raw materials, as well as labour, irrelevant. By employing nanotechnology to build from the bottom-up rather than processing down, the quantity of raw materials required could be sharply reduced. In short, nano-scale technologies are poised to become the strategic platform for global control of materials, food, agriculture and health in the immediate years ahead. With respect to nanotechnology, emerging dictum for the developing world should be: *more from less for more*. Undoubtedly, efficient systems of production and getting more from less is closely related to sustainability.

Nanotechnology can become a sustainable technology only if there is societal acceptance, minimal risk and maximum benefit. Nanotechnology by definition is diverse, enabling, evolving, inter disciplinary and in general generic. Sustainable nanotechnology can be looked at in two ways: producing nanomaterials and products which are not toxic,and producing nano-products that remedy environmental problems. Such an enterprise should at transformations at low temperatures using less energy and renewable inputs wherever possible, and using lifecycle thinking in all design and engineering stages.

In addition to making nanomaterials and products with less impact to the environment, sustainable nanotechnology should strive to make current manufacturing processes for non-nano materials and products more environmentally friendly. For example, nanoscale membranes can help separate useful chemicals from waste. Nanoscale catalysts can drive chemical reactions more efficiently with less waste. Sensors at the nanoscale can be integrated into process control systems, working with nano-enabled information systems.

Secondly, Nanomaterials or products can offer sustainability if they can clean hazardous waste sites, desalinate water, treat pollutants, or sense and monitor environmental pollutants. Furthermore, lightweight nanocomposites can offer fuel savings and material reduction in the transportation sector. Nanotechnology-enabled fuel cells and light-emitting diodes (LEDs) could lead to the conservation of fossil fuels and lead to less environmental pollution. Self-cleaning nanosurface coatings could reduce or eliminate the use of conventional cleaning agents and enhanced battery life could lead to less material use and less waste. Thus, sustainable nanotechnology should take a broad analysis of nanomaterials and products, in order to ensure that unforeseen consequences are minimized and that impacts are anticipated and controlled throughout their full life cycle.

Applications of nanotechnology are enabled by nanomaterials, which have novel optical, electric or magnetic properties. The building blocks of nanotechnology are semiconductors, metals, metal oxides, carbon materials and organics. The emerging commercial growth areas in nanotechnology are nanomaterials and nanomaterials processing, nanobiotechnology, software, nanophotonics, nanoelectronics and nanoinstrumentation. Nanomaterials and nanomaterials processing companies develop the materials and methods to manipulate and manufacture products based on nano materials. Clearly, the raw materials for these industries must come from renewable or non-renewable resources of the planet. Therefore, if the raw materials are not replenished the nanotechnologies will perish before it can yield benefits to successive generations.

Sustainable development of nanotechnology covers several areas. These include:

2.1. Development of "intelligent" materials and reduction of materials use in production;

With nanotechnology, a large set of materials and improved products rely on a change in the physical properties when the feature sizes are shrunk. Nanoparticles, for example, take advantage of their dramatically increased surface area to volume ratio. Their optical properties, e.g. fluorescence, become a function of the particle diameter. These nano-materials or nanocomposite materials made by incorporating nanoparticles into polymers have applications in faster computers, advanced pharmaceuticals, controlled drug delivery, biocompatible materials, nerve and tissue repair, crack proof surface coatings, better skin care and protection, more efficient catalysts, better and smaller sensors, even more efficient telecommunications [6.] Such nanomaterial products, in addition to using lesser raw materials in their production will become an all pervasive technology in the decade to come.

2.2. Development of specific nanotechnologies and new materials for use in water treatment or for energy and transport and agriculture applications;

Only 30% of all freshwater on the planet is not locked up in ice caps or glaciers (not for much longer, though). Of that, some 20% is in areas too remote for humans to access and of the remaining 80% about three-quarters comes at the wrong time and place - in monsoons and floods - and is not always captured for use by people. The remainder is less than 0.08 of 1% of the total water on the planet. The problem is that we don't manage this small quantity very well. Currently, 600 million people face water scarcity. Depending on future rates of population growth, between 2.7 billion and 3.2 billion people may be living in either water-scarce or water-stressed conditions by 2025 [7]. Many areas, especially in developing countries, are seriously contaminated or damaged with consequent impoverishment of natural resources and serious effects on human health. Remediation of contaminated water – the process of removing, reducing or neutralizing water contaminants that threaten human health and/or ecosystem productivity and integrity – is a field of technology that has attracted much interest recently.

Membrane processes are considered key components of advanced water purification and desalination technologies and nanomaterials such as carbon nanotubes, nanoparticles, and dendrimers are contributing to the development of more efficient and cost-effective water filtration processes.

There are two types of nanotechnology membranes that could be effective: nanostructured filters, where either carbon nanotubes or nanocapillary arrays provide the basis for nanofiltration; and nanoreactive membranes, where functionalized nanoparticles aid the filtration process.

In the area of agriculture, in conventional fertilizers the loss of the macronutrient nitrogen to the environment during application is one of the major problems which has not received much attention. Loss of nitrogen exceeding 50 – 60% is due to conversion to water soluble nitrates, gaseous ammonia and incorporation into the soil with the aid of soil microorganisms [8]. Attempts to solve this loss, causing direct and indirect environmental pollution have met with little success. However, application of nanotechnology involving slow release fertilizer can increase the nitrogen utilization efficiency. In an attempt to address this problem, SLINTEC has come up with two slow release fertilizer compositions: In the first solution [9], an inorganic inner nano-core consisting hydroxyapatite nanoparticles which contain the macronutrient phosphorus coated with nitrogen containing urea has been encapsulated within a natural cellulose based outer core [*Gliricidia sepium* (albesia) stem] containing micro/nano porous cavities. In the second project, the fertilizer system is based on urea modified hydroxy apatite nanoparticles intercalated in montmorilonite [10]. The nanocomposites prepared by this processes when applied to aqueous and terrestrial environments releases the macronutrient compound in a slow and sustained manner. The nanocomposite acts as a reservoir for slow and sustained release of nitrogen macronutrient through the soil medium. The soil medium acts as a conduit for providing the pH for release and transport of the macronutrients such as urea to the roots of the plant. Such solution, properly adapted can have a profound impact on energy, the economy and the environment.

2.3. *Development of biosensors for environmental applications;*

Various kinds of nanomaterials such as gold, carbon nanotubes, magnetic nanoparticles and quantum dots are increasingly used as biosensors because of the unique physical, chemical, mechanical, magnetic and optical properties which aid in the enhancement of selectivity and sensitivity of detection [11]. One dimensional nanostructures such as carbon nanotubes are attractive for bioelectronic sensing applications. Of particular importance are electrochemical sensors which are capable of interfacing at the molecular level, applications of enzyme electrodes where direct electron transfer from the enzyme to the electrode surface can open avenues for reagentless biosensors and bioaffinity biosensors such as DNA hybridization biosensors [12].

2.4. *Life Cycle Assessment of the potential benefits, health, safety, and environmental risks associated with nanotechnology-based materials and their processing, and with chemicals processing;*

Life cycle assessment (LCA) of nanoparticles and nano-enabled products are important in finding answers to issues such as [13]:

(a) How do life cycles of products/devices using nanomaterials compare to those made by conventional materials particularly in the area of energy consumption;
(b) What particular phase in the life cycle use the largest amount of energy;
(c) Identification of particular end-of-life management issues specific to nanomaterials such as recovery, reuse and recycling;
(d) Identification eco-toxicity and human toxicity of nanomaterials;

Several types of nanoparticles have shown unintended consequences. For example silver nanoparticles, which are bacteriostatic, may destroy beneficial bacteria which are important for breaking down organic matter in waste treatment plants or farms [14]. Similar concerns have been expressed about TiO_2 and carbonanotubes. Aerosols resulting from nanoparticles and their manipulation, the resulting agglomerates and their degradation aerosols and suspensions should be cleared of any potential harm to humans and the ecosystem. If we rely only on exposure controls, such attempts will fail in the long term. Therefore, research must strive for performance without toxicity with the implicit assumption that innovation is not attractive enough until we reach that point [15]. While conventional technologies may use a compartmentalized model where chemists do the synthesis, epidemiologists and toxicologists document the side effects and find mechanisms of ensuing diseases and hygienists will recommend ways to minimize risk. Because of nanotechnologies complex and emerging nature with high social cost, they must employ a holistic model where risk based and application based research must be integrated thus proactively minimizing health and eco risks.

In the area of using green solutions to nanotechnology based research, SLINTEC has been successful in inventing process for producing a nanocomposite containing exfoliated organically modified montmorillonite clay and maleic anhydride grafted elastomer in a dispersion of natural rubber and inert filler which completely avoids the use of reinforcing and environmentally hazardous carbon black [16].

Public participation with nanotechnologies is often described as ‘upstream’ in nature, reflecting its occurrence before commercialization in real-world applications and before significant social controversy [17]. Thus potential problems are being addressed while research on nanotechnology continues so as not to embrace the controversies that GM foods were subjected to. Risk perception analysis indicates that technology’s acceptability will depend upon people’s perceptions of both benefit and risk, with the balance between the two depending upon the particular technology or the context within which judgments are formed. Nanotechnology survey research in the United States and United Kingdom to date shows two clear findings. The first is that most people know little or nothing about nanotechnologies. Second, notwithstanding this, many feel that nanotechnology’s future benefits will outweigh its risks.

In April 2005, the Project on Emerging Nanotechnologies (PEN) was established as a partnership between the Woodrow Wilson International Center for Scholars and the Pew Charitable Trusts. The main objective of the project is to ensure that as nanotechnologies continue, possible risks are minimized, public and consumer engagement remains strong, and the potential benefits of these technologies are recognized. One of the PEN reports, entitled “Nanotechnology: A Research Strategy for Addressing Risks”, was released in July 2006 [18]. It prioritizes research area needs in order to evaluate risks associated with nanotechnologies. Immediate research needs are sources of exposure, exposure routes and exposure measurement methods. This PEN report also recommends early investment in medium-term and long term-research needs, including risk assessment, life cycle analysis, computational toxicology, nanomaterials release into the environment and ecotoxicology.

In addition to the more direct human and environmental and toxicology issues, some have also suggested that nanotechnologies will raise wider social, ethical and governance issues. These include concerns over long-term unintended consequences, the means by which governments and society might control the technologies, social risks from covert surveillance arising from nano-based sensors and systems, and financial or other detrimental impacts upon the developing world. In the health arena, in particular, longer term developments in nanotechnologies is poised to raise a range of fundamental ethical issues regarding the possibilities for human enhancement, to draw up a demarcating line between ‘enhancement’ and ‘therapy’, and the impacts of these ideas on the identity of individuals [19-21].

In the context of sustainable nanotechnology, the research carried out by the Sri Lanka Institute of Nanotechnology is noteworthy. The nanotechnology initiative in Sri Lanka launched through Nanotechnology Company (NANCO) and the Sri Lanka Institute of Nanotechnology (SLINTEC) is unique because the government and the private sector have invested equally in the project. SLINTEC by definition provides platform research solutions in sustainable nanotechnology to the Sri Lankan industries. In its commitment to the Triple Bottom Line in business, all research projects undertaken by SLINTEC are subjected to a sustainability screen to ensure that research output is in conformity with social sustainability, environmental sustainability and economic sustainability.

Finally, sustainability of nanotechnology will depend on valid questions being asked about the new technology and coming up with scientific answers which will enable society at large shed their confusions and embrace it with reserved acceptance.

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APPLICATION OF NANO INSULATION MATERIALS IN THE SUSTAINABLE BUILT ENVIRONMENT

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Abstract: Nanotechnology is widely being used in the built environment for its advantages in many improved engineering properties of the nano materials. Nano insulating materials open up new possibilities for ecologically oriented sustainable infrastructure development. The most widely used nano material in built environment is for the purpose of insulation to improve the energy efficiency namely in the buildings and dwellings. Nanotechnology has now provided an effective and affordable means to increase energy efficiency in pre-existing buildings as well as new construction by increasing thermal resistance. The major advantage of nano insulation materials is its benefit of translucent coatings which increase the thermal envelope of a building without reducing the square footage. The intrinsic property of nano insulating material is it can be applied to windows to reduce heat transfer from solar radiation due it its thermal resistant property and the translucent property allows diffusing of day light. The nano insulating material has significant advantage in reducing the operational energy aspects of buildings due to its valuable insulating properties.

This paper examines applicable nanotechnology based products that can improve the sustainable development and overall competitiveness of the building industry. The areas of applying nano insulating material in building industry will be mainly focused on the building envelope. The paper also examines the potential advantages of using nanotechnology based insulating material in reducing the life cycle energy, reduction of material usage and enhancing the useable life span. The paper also investigates the operational energy by simulation methodology and compares the reduction of operational energy consumption.

Keywords – Built Environment, Nano Material, Thermal Resistance, Operational Energy, Green House Gas

1. Introduction

The construction and operation of buildings is responsible for significant environmental impacts, predominately through resource consumption, waste production and greenhouse gas emissions. Building insulation will be one of the main focuses, where the demand for more energy efficient buildings is expected to grow significantly in coming years. One of the main problems related to energy consumption in buildings is created by winter heating and summer cooling. The presence of glass surfaces and the insulating capacity of the outer cladding is the main reasons for heat loss and gain within the building envelope (Scalisi, 2009). Insulation is the most effective way to improve the energy efficiency of a home. Insulation of the building envelope helps keep heat in during the winter and keep solar heat away during summer to improve thermal comfort while saving energy. Insulation materials which are used for building insulation include mineral wool, cellulose batting, foam plastics and newly emerged materials like nonomaterial.

Numerous strategies have been adopted in an attempt to improve the operational energy efficiencies with relates building maintenance and to reduce green house gas emissions. Emerging fields like nanotechnology delivers outstanding insulation materials for more efficient, less toxic and environmental friendly insulation. Current applications are in the forms of paints, coatings, thin films or as solid materials. Nansulate® coating is a patented insulation technology that incorporates a nanocomposite called Hydro-NM-Oxide, a product of nanotechnology. It's an excellent insulator due to its low thermal conductivity and the nonomaterial used. It can be directly applied to the existing buildings without incurring any post-construction addition with conventional insulating, thus creates tremendous energy saving with existing buildings. Test results for Nansulate® from independent laboratory shows that thermal flow through the wall section coated with Nansulate® was reduced by 34.80% and thermal resistance (1/U) of the wall section coated with Nansulate® was increased by 28.98% (Test Method:UNI EN ISO 8990:1999 - similar to ASTM C236) (www.nansulate.com).

To reduce life cycle environmental impacts of buildings, their service life should be extended as much as possible (Aye *et al*. 2007). The durability of the structure plays an important role. Application of nanomaterials in to the building envelope will assist in lengthening the service life of building materials, thus reducing the carbon footprint. This study aims to study the impact on operational energy consumption of the building with the application of Nansulate, an insulation product of nanotechnology with compared to conventional cellulose insulation.

2. Methodology

A multi-residential building has been used as a case study to assess the operational energy performance of prefabricated steel construction. This section outlines the case study building that was analysed and the methods used to assess the operational energy requirements associated with both conventional concrete and prefabricated steel construction approaches for this building.

2.1. Case study building

This study involved an assessment of the operational energy associated with a multi-residential building, for two varying construction approaches, a prefabricated modular steel structure and a conventional concrete structure, used for comparative purposes. The building modelled has a gross floor area of 3,943 m^2 with a total of 63 apartments consisting of 58 single-storey and five double-storey apartments. The first six floors of the building each consist of 9 single-storey apartments (Figure 1) and the seventh floor consists of four single-storey and five double-storey apartments. The floor area of the single-storey and double-storey apartments is 63 and 118 m^2, respectively. The ground floor consists of seven tenancies together with other utilities. The ground floor and the sub-structure were not considered in this study. The details of the external/internal walls and the floor/ceiling panels are for each scenario by element is given in Figure 2.

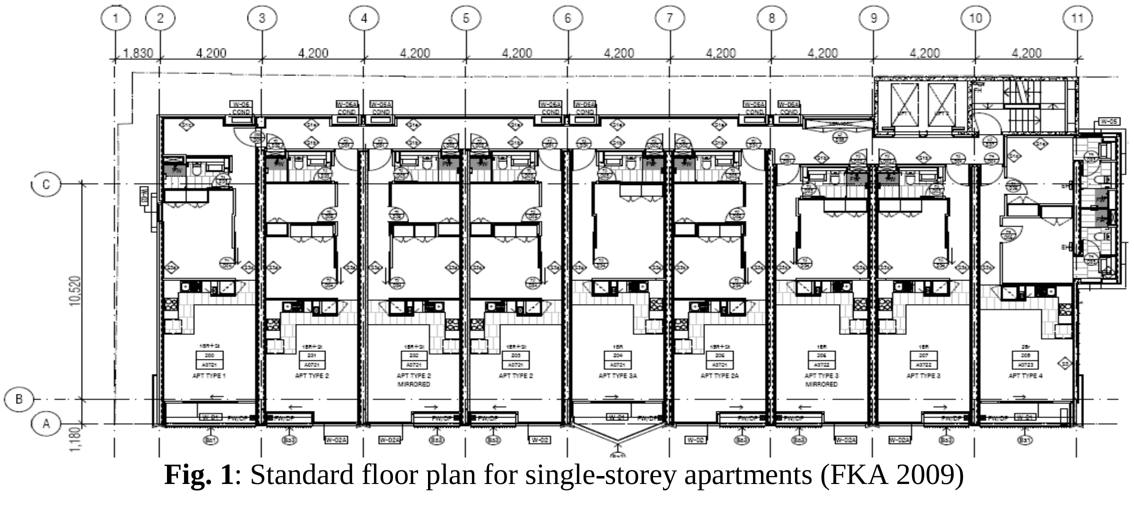


Fig. 1: Standard floor plan for single-storey apartments (FKA 2009)

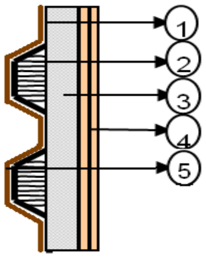
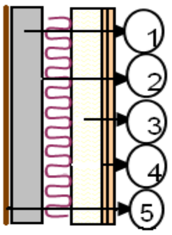
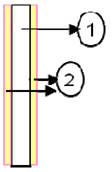
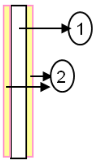
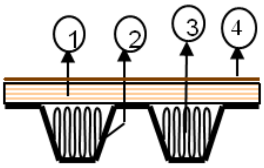
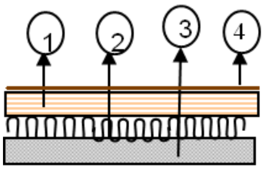
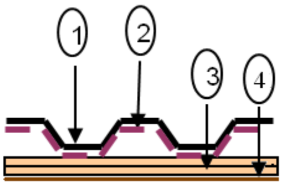
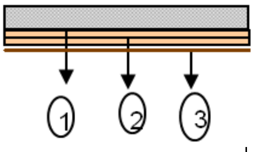
Steel		**Concrete**	
Exterior wall			
	1) 1.6mm thk Corten steel panel 2) 80mm thk Cellulose Insulation 3) 50mm studs 4) Plaster boards(13mm) 5) Nansulate Coating (4mm)		1) Precast Concrete 2) 80mm thk Cellulose Insulation 3) Timber Frame 4)Plaster boards(13mm) 5) Nansulate Coating (4mm)
Internal wall			
	1) Stud wall (50x50x3 SHS) 2) Plaster boards(13mm)		1)Timber frame (50x50 Sections) 2) Plaster boards(13mm)
Floor			
	1) Plywood flooring(19mm) 2) 2.4mm thk Corten steel panel 3) 100mm thk cellulose Insulation 4) Nansulate Coating (4mm)		1) Plywood flooring(19mm) 2) 100mm thk Cellulose Insulation 3) Reinforced Concrete slab (32Mpa) 4) Nansulate Coating (4mm)
Ceiling			
	1) 1.6mm thk Corten steel panel 2) Spray type "Body defender" 3) 16mm thk Plaster Boards 4) Nansulate Coating (4mm)		1)Reinforced Concrete slab (32Mpa) 2) 16mm thk Plaster Boards 3) Nansulate Coating (4mm)

Fig. 2: Details of the main material used in the building for prefabricated steel and concrete structural scenarios, by element

2.2 Operational energy analysis

The operational energy associated with the case study building was calculated using TRNSYS simulation software. Based on the characteristics of the building as well as assumed heating and cooling schedules, TRNSYS was used to simulate the thermal behaviour of the building.

The simulation was performed using the most recent weather data for Melbourne, Australia published by the Australian Bureau of Meteorology The simulation was performed on an hourly basis for a period of one year maintaining a steady temperature range of 20-26 degrees Celsius within the building. The detailed occupational schedules and gains were not considered in this study. The simulation was carried out with and without the nansulate application on the exterior wall, ceiling and floor of the building.

The COP (Coefficient of Performance) values of COP $_{\text{Heating}}$ = 3.0 and COP $_{\text{Cooling}}$ = 2.2 were used in converting the heating and cooling load outputs from the TRNSYS simulation to energy requirements in kWh.

3. Results and Discussion

This section presents the results and discussion of the operational energy analysis of the case study building for both prefabricated steel and concrete construction approaches.

3.1 Operational energy analysis

This section details the annual operational energy requirements associated with the case study building for both concrete and prefabricated steel construction types.

The TRNSYS simulation performed to determine the operational energy required for each Zone to maintain a temperature between 20-26^0 C. The TRNSYS simulation output on temperature control is illustrated in Figure 3.

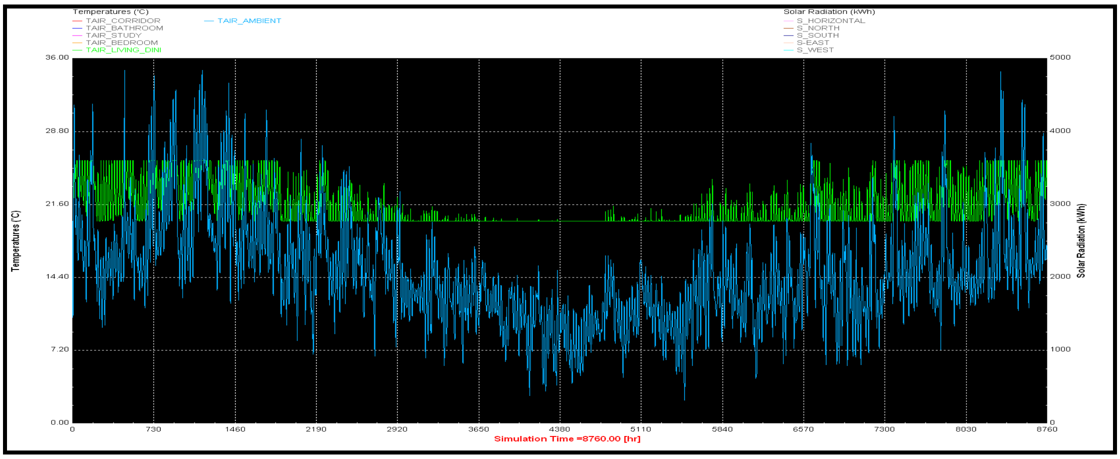


Fig. 3: TRANSYS out put on temperature control between 20-26^0 C vs ambient temperature of Melbourne weather

The simulated monthly distribution patterns of heating and cooling loads for a period of one year is given in Figure 4 and 5, without and with nansulate insulation respectively. All the data was based on Melbourne’s weather data. The heating and cooling load patterns behave similarly for both concrete and prefabricated steel construction types.

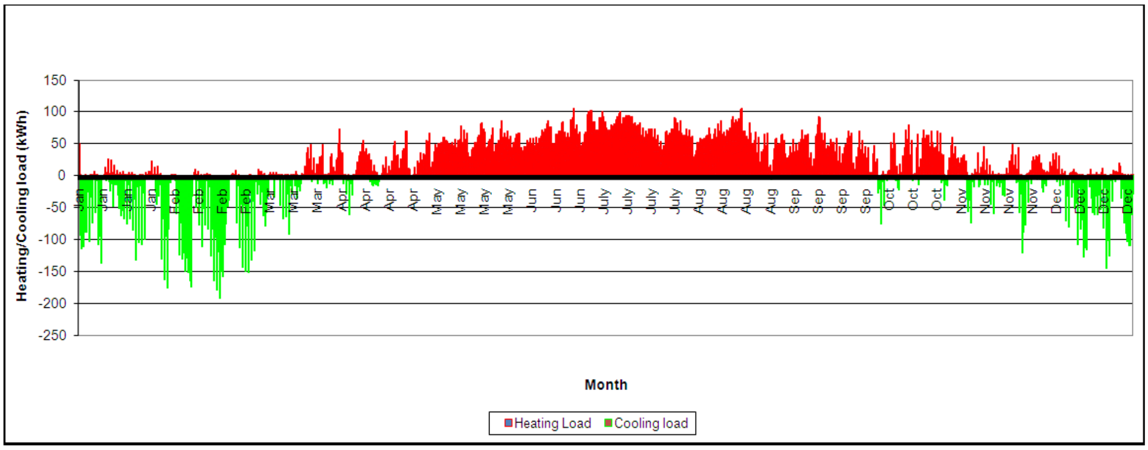


Fig. 4: Heating and cooling load distribution pattern for the case study building- without Nansulate

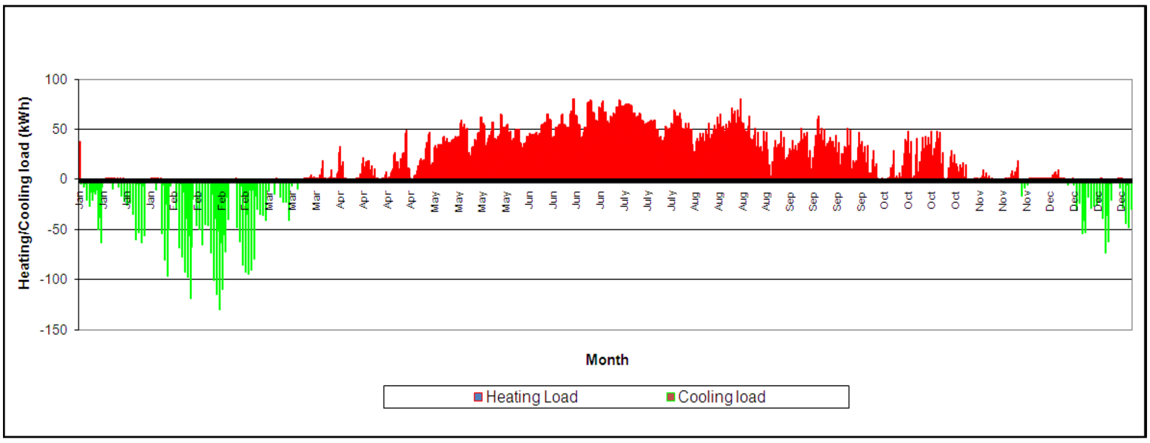


Fig. 5: Heating and cooling load distribution pattern for the case study building- with Nansulate outside

The application of Nansulate in to the exterior of the building shows a saving in the energy consumption through reducing heating and cooling loads. As of figure 4, the heating and cooling loads fluctuate between +100 to -200 without the application of Nansulate. With the application of Nansulate this range reduces up to +80 to -130 as shown in figure 5.

The annual operational energy for the building clearly indicates that for Melbourne the heating energy requirements are much greater than energy requirements for cooling (by at least 180 per cent). There is also a significant difference in operational energy requirements between the concrete and prefabricated steel construction types.

Table 1: Annual operational energy requirements for steel and concrete structural scenarios by square metre of floor area (NLA = 3943m^2)

Structure type	Annual operational energy (kWh/m^2)			Annual operational energy (GJ/m^2)		
	Heating	Cooling	Total	Heating	Cooling	Total
Steel	40.0	12.5	52.5	0.14	0.05	0.19
Concrete	36.8	8.7	45.5	0.13	0.03	0.16

The total operational energy for heating and cooling calculated was 45.5 and 52.5 $kWh/m^2/yr$ for concrete and prefabricated steel respectively (table 1). The difference shown in operational energy due to the difference in the thermal mass of the two construction materials selected. Steel having a high heat storage capacity but it also has a very high rate of thermal conductivity which means that heat is absorbed and released too quickly for any meaningful thermal mass efficiency. Concrete with their high heat capacity and density but moderate thermal conductivity offers a good balance and therefore concrete requires a lower operational energy.

3.2 Insulation with Nansulate

With the application of Nansulate, it is clearly shows that the annual operational energy required for the building is less compared to the cellulose insulation. It is evident that presence of Nansulate without cellulose gives the best energy consumption as illustrated in Table 2.

Table 2: Operational Energy consumed comparison with respect to different insulation options

Insulation Options	Operational Energy over a year					
	Steel			Concrete		
	Heating	Cooling	Total	Heating	Cooling	Total
	(kWh/m^2yr)					
Base with 100mm Cellulose	40.0	12.5	52.5	36.8	8.7	45.5
Base w/o 100mm Cellulose	42.2	12.6	54.8	36.9	5.9	42.8
Nansulate Inside with cellulose	37.4	11.5	48.9	35.8	7.7	43.4
Nansulate Inside no cellulose	39.5	12.2	51.6	36.1	6.7	42.8
Nansulate Outside with cellulose	36.3	10.3	46.6	34.8	6.6	41.4
Nansulate Outside no cellulose	36.6	8.9	45.5	34.7	5.0	39.6

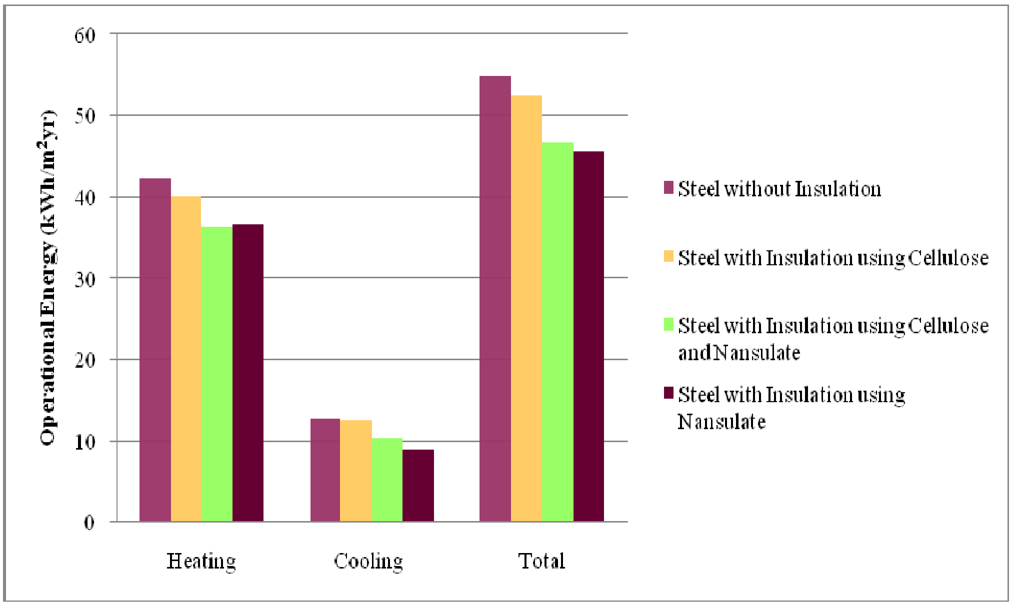


Fig. 6: Operational energy over one year for steel.

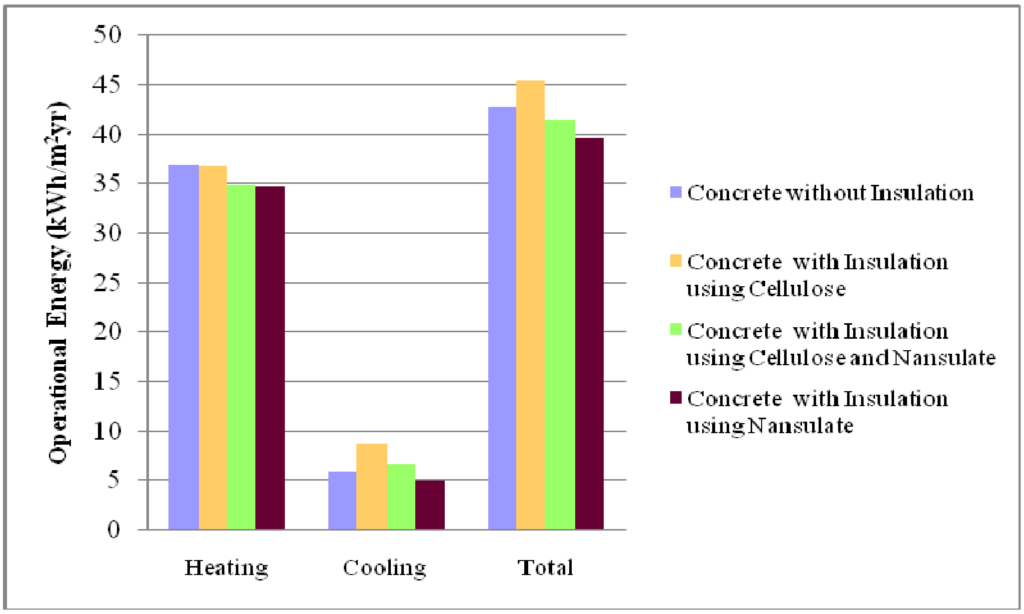


Fig. 7: Operational energy over one year for concrete.

The results in Figure 6 & 7 indicate that the application of Nansulate in the exterior of the building results a significant operational energy reduction compared to conventional insulation material like cellulose resulting saving of 7.47% in operational energy consumption. The removal of cellulose insulation result a saving of 5.9% of the total floor area of the building when Nansulate is applied to the building. The Nansulate insulation coating when applied to the exterior of the walls, it will be less hazardous to the occupants of the building.

4. Conclusion

The study has considered two forms of construction for a multi-residential building, conventional concrete construction and prefabricated steel construction. The results have shown a significant difference in the operational energy requirements associated with the two construction types due to their specific thermal masses. This study has further assessed an operational energy savings of 7.47% with the application of insulation material Nansulate, a product of nanotechnology. With the results obtained from the operational energy analysis through TRANSYS, it was shown that Nansulate provides an effective insulation for both construction methods used against the conventional insulation material cellulose. As the Nansulate coating requires a space of few mm's the results show a saving of 5.9% of the total floor area as a replacement for cellulose.

Further research need to be carried out to determine the impact of thermal mass of concrete on cellulose insulation especially with regards to operational energy required for cooling. The insulation properties of cellulose, high heat capacity and moderate thermal conductivity of concrete needs to be further evaluated on its impact on energy required for cooling of buildings.

As a super insulation product Nansulate provides combined performance qualities of thermal insulation and corrosion prevention which lead to an environmentally safe, water-based coating formulation. Nansulate is a product of nanotechnology that reduces the operational energy consumption of the buildings to a considerably. Thus, it is quite evident that nanotechnology hold a promising results in building insulation applications and the products are yet to come.

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PHOTOCATALYTIC ACTIVITY OF NANO-TiO_2 ON GLASS IN BUILDING ENVELOPE

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Abstract: Titanium dioxide is manufactured by processing naturally occurring titanium containing rutile (TiO_2) or ilmenite ($FeTiO_3$) minerals. Sri Lanka has vast deposits of ilmenite which is the major raw material in TiO_2 production. However, Sri Lanka currently does not produce any type of value added TiO_2 pigments. With the growth of nanotechnology, nano-TiO_2 is now produced worldwide using different methods varying the particle size from 1 nm to 100 nm. Nano-TiO_2 has the tightly controlled particle size that increases both the refractive index and light scattering properties as a result of the uniform particle size distribution and additional surface area. Nano-TiO_2 is particularly interesting in UV resistant surface coatings where it can act as a UV reflector. Because of the higher photocatalytic activity nano-TiO_2 can be used for anti-fogging coatings where nano-TiO_2 incorporated into outdoor building materials can substantially reduce concentrations of airborne pollutants such as volatile organic compounds and nitrogen oxides and as photocatalyst coating which assist in deactivation of bio-contaminants. In this investigation nano-TiO_2 and pigmentary TiO_2 were synthesized using titanyl sulfate precursor, which can easily be produced by Sri Lankan ilmenite with sulfuric acid according to the sulfate process. Synthesized nano-TiO_2 was characterized by X-ray diffraction (XRD), Raman spectroscopy, scanning transmission electron microscopy (STEM) and scanning electron microscopy (SEM) methods. The photocatalytic activity of nano-TiO_2 was assessed by the degradation of bromothymol blue in aqueous solution. Nano-TiO_2 coated on glass showed a higher photocatalytic activity and self cleaning effect that can effectively be used in building envelops.

Keywords: Ilmenite, Nano-TiO_2, Photocatalytic effect, Self cleaning glass

1 Introduction

Titanium dioxide, also known as titanium (IV) oxide or titania, is the naturally occurring oxide of titanium, chemical formula TiO_2. Titanium dioxide has been extensively studied because of its unique properties and wide verity of applications, for example semiconductor electrodes, gas sensors, self cleaning materials and as pigments with enhanced photodegradation activity on visible light [1]. Titanium dioxide has been widely used as a photocatalyst for solar energy conversion and environmental applications because of its low cost, non toxicity and excellent photoactivity. When TiO_2 is irradiated by sunlight with a wavelength less than 387 nm (ultraviolet range), electrons is passed across the band gap into the conduction band, leaving holes in the valence band. These holes have high oxidation power, thus can easily react with adsorbed hydroxide ions to produce hydroxyl radicals, the main oxidizing species which are responsible for the photooxidation of organic compounds [2]. As a new material, nano-sized TiO_2 is of great interest of many scientists in the recent years. Its small size and large specific surface area allow for certain unique unusual physio-chemical properties [1, 2]. Nano- TiO_2 has the tightly controlled particle size that increases both the refractive index and light scattering properties as a result of the uniform particle size distribution and additional surface area. Because of the higher photocatalytic activity, nano-TiO_2 can be used for anti-fogging coatings where nano-TiO_2 incorporated into outdoor building materials can substantially reduce concentrations of airborne pollutants such as volatile organic compounds and nitrogen oxides and as photocatalyst coating which assist in deactivation of bio-contaminants. Recently large number of studies appeared based on the photocatalytic activity of TiO_2 for oxidation of organic chemicals, obviously the most potential environmental friendly process. In general, two methods of application of TiO_2 in photocatalysis have emerged, one as highly dispersed fine particle on porous support materials and suspended fluids in liquid medium and another as their films [3]. However the application of TiO_2 as a film is one of the easiest ways out of those two methods. TiO_2 thin films are prepared by coating the substrate with TiO_2 sol by different techniques such as chemical vapor deposition, chemical spray pyrolysis, electrodeposition and sol-gel methods [3]. Each method has its own advantages and disadvantages. In this present work, we have developed a very simple, efficient and cost-effective method for deposition of thin films of TiO_2 on glass to be used in building envelops. Main objectives of this work is to find the ways of producing nano-TiO_2 and pigmentary TiO_2 by titanyl sulfate precursor which can easily be produced from Sri Lankan ilmenite with sulfuric acid according to the sulfate process [4]. Photocatalytic activity and self cleaning effect of synthesized nano-TiO_2 coated on glasses are also investigated.

2 Material and methods

2.1 Preparation of TiO_2 precursor sol

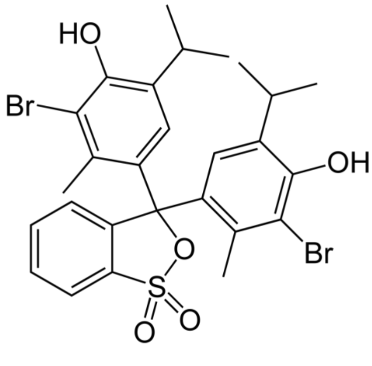
In the preparation of titanium precursor sol, 25 mL of titaniyl sulfate (99.9%, Sigma-Aldrich) was added drop wise to 50 mL of distilled water while stirring at room temperature. Then the pH of the titanium solution was adjusted to pH=3 by adding 3 mol L^{-1} ammonia solution drop wise while stirring to form a white precipitate. The precipitate formed was separated and washed several times to remove NH^{4+} and $SO4^{2-}$. The precipitate was then dispersed in distilled water. This dispersed solution was added drop wise in to 100 mL of 30% H_2O_2 solution while stirring at room temperature. A yellow colored solution with a yellow precipitate was formed indicating the formation of peroxo titanium complex. This solution was stirred for 12 hours at 600 rpm. The precipitated gel was separated by centrifugation at 9000 rpm and washed several times with distilled water. Then precipitated gel was dispersed in 100 mL distilled water and refluxed for 5 hours at 100 °C to obtain TiO_2 sol to be coated as thin film of TiO_2 on glass substrate.

2.2 Preparation of thin film of TiO_2

Glass slides were used as substrates for the deposition of the TiO_2 film. Before the deposition, glass substrates were ultrasonically cleaned using acetone and ethanol respectively. Finally they were thoroughly washed with water and dried. TiO_2 thin film was deposited on substrate by a dip-coating process at room temperature. Substrates were immersed in the TiO_2 sol prepared for 30 minutes and dried at room temperature followed by the drying at 100 °C for 1 hour in an oven. In order to obtain nano-TiO_2 powder, the TiO_2 sol prepared was oven dried at 105 °C and calcined at 800 °C for 1 hour. For comparative study, pigmentary TiO_2 was synthesized using titanyl sulfate solution according to the sulfate process used for the manufacturing of TiO_2 pigment from ilmenite ($FeTiO_3$) [4].

2.3 Photocatalytic decomposition of bromothymol blue on nano-TiO_2 films

The photocatalytic activity of the prepared nano-TiO_2 particles and TiO_2 thin films were evaluated by studying the degradation of bromothymol blue in an aqueous solution under diffused light. One piece of 50 mm × 20 mm glass side having TiO_2 thin films on both sides were dipped in a Petri dish containing the indicator (1.7×10^{-5} mol L^{-1}, 20.00 ml) and exposed to diffused light for 48 hours. Same experiment was carried out by adding 0.5 g of nano-TO_2 powder in to a Petri dish instead of a glass slide. The change in the concentration of bromothymol blue was estimated from the changes in the absorbance in the range of 300 nm to 700 nm using UV-Visible spectrophotometer (SHIMADZU UV-3600, UV-VIS-NIR Spectrophotometer). The maximum absorbance peaks of bromothymol blue are at 428 nm and at 614 nm. The structure of bromothymol blue is shown below.



Bromothymol blue

2.4 Characterization

The crystallinity of the synthesized TiO_2 powder samples were determined by X-ray diffraction (XRD) technique using Brucker D8 Focus X-ray Diffractometer with Cu Kα radiation. The average particle size was estimated by applying the Scherrer equation to the apparent full-width-at-half maximum intensity (FWHM) of the (101) peak of anatase TiO_2 [2], as follows:

$$d= (k\lambda) / (\beta \cos \Theta),$$

where d denotes the average crystallite size, $k = 0.9$, $\lambda = 0.15405$ nm is the X-ray wavelength of Cu-Kα, β is the full-width of the peak measured at the half-maximum intensity (FWHM) and Θ is the Bragg angle of the peak.

Synthesized TiO_2 powder samples were also studied by using UV-Vis absorption spectrum in a wavelength range from 300 nm to 700 nm employing SHIMADZU UV-3600; UV-VIS-NIR Spectrophotometer. FT-Raman spectra of the TiO_2 powder samples were studied using Bruker Vertex80 coupled with Ram-FT module (RAM II) FT-IR Spectrophotometer. For the FT-Raman experiment a CaF_2 beam splitter and InGaAs detector were used with sample illumination by a laser operating at 1064 nm. Scanning Transmission electron microscopy (STEM) at an operating voltage of 30 kV and scanning electron microscopy (SEM) at an operating voltage of 20 kV using Hitachi SU 6600 FE-SEM were carried out to ascertain the particle size and the morphology of TiO_2 powder samples synthesized.

3 Results and discussions

3.1 X-ray diffraction

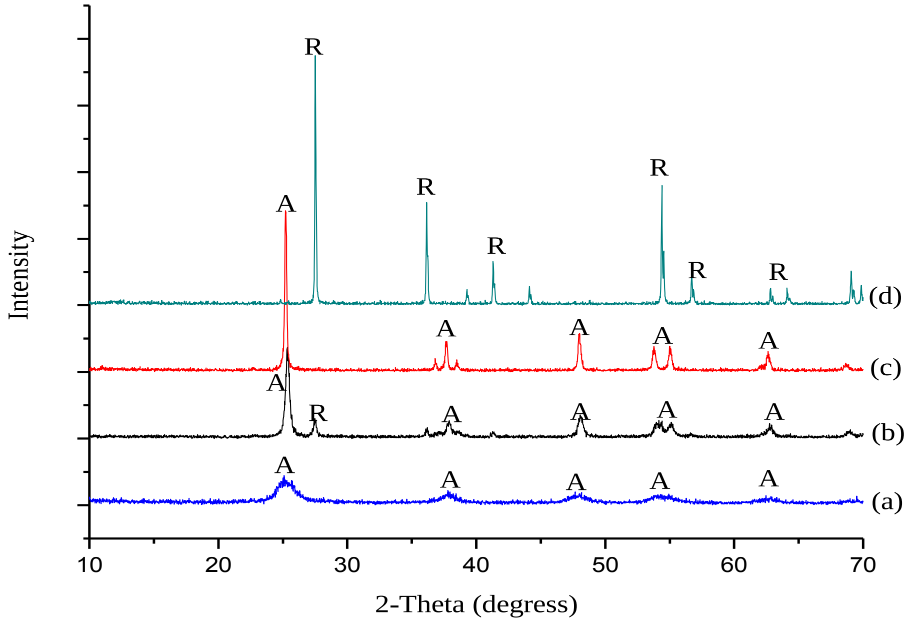


Figure 1: *XRD patterns of the TiO_2 powders: (a) TiO_2 coated on glass, (b) commercial nano-TiO_2, (c) nano-TiO_2 synthesized at 800 °C, (d) pigmentary TiO_2*

The powder XRD patterns of TiO_2 powder samples are shown in Figure 1. The XRD pattern of commercial nano-TiO_2 sample (< 30 nm, Degussa) is given in Figure 1 (b) and it mainly contains the anatase form of TiO_2 with modest amount of rutile. Figure 1 (d) presents the XRD pattern of pigmentary TiO_2 synthesized according to the sulfate process given. The only crystal type found in this pigmentary TiO_2 sample was rutile crystal type. Figure 1 (a) and (c) are X-ray diffraction diagrams of TiO_2 coated on glass surface and nano-TiO_2 synthesized at 800 °C respectively. Higher peak intensity of anatase in Figure 1 (c) shows the increase in the crystallinity due to use of higher temperature in the synthesis process.

The X-ray diffraction pattern of anatase crystal type TiO_2 samples give three major distinctive peaks at 25.3°, 37.9°, 48.0° corresponding to (101), (004) and, (200) crystal planes respectively, where as rutile crystal type TiO_2 samples give three major distinctive peaks at 27.5°, 36.9°, 54.4° corresponding to (110), (004) and, (200) crystal planes respectively.

In general, FWHM of XRD peak corresponds to the crystal size of the materials. When the width is broader, the crystallites exhibit smaller size. The Scherrer equation was used to determine the average particle size of the nano-TiO_2. The average particle size of the nano-TiO_2 coated on the glass and nano-TiO_2 powder synthesized at 800 °C was found to be 10 nm and 60 nm diameters.

3.2 Raman spectroscopy

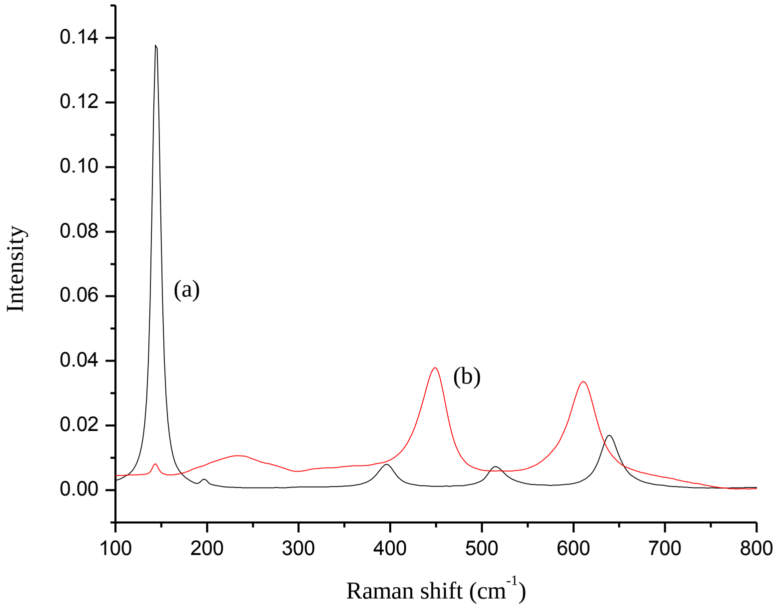


Figure 2: *Raman spectra of the TiO_2 powders: (a) nano-TiO_2 synthesized at 800 °C, (b) pigmentary TiO_2*

Raman spectroscopy can be used to examine the crystal structure of TiO_2 samples as a more sensitive technique compared to X-ray diffraction method for the identification of anatase and rutile crystals in a variety of natural and synthetic materials over a wide range of concentrations [5, 6]. Raman spectra of nano-TiO_2 synthesized at 800 °C and pigmentary TiO_2 synthesized are shown in Figure 2 (a) and (b) respectively. Figure 2 (a) shows Raman shifts at 145, 396, 515, and 639 cm^{-1} for nano-TiO_2 synthesized at 800 °C indicating only anatase crystal phase is present without any impurities. Figure 2 (b) gives Raman shift at 449 and 611cm^{-1} for pigmentary TiO_2 synthesized according to the sulfate process. Pigmentary TiO_2 contained only rutile type crystal according to its Raman spectrum.

Figure 3 (a) and (b) show the Raman spectra of commercial nao-TiO_2 and the TiO_2 coated on glass. Raman spectroscopy results revealed that the TiO_2 coated on the glass slide was only in the anatase crystal form.

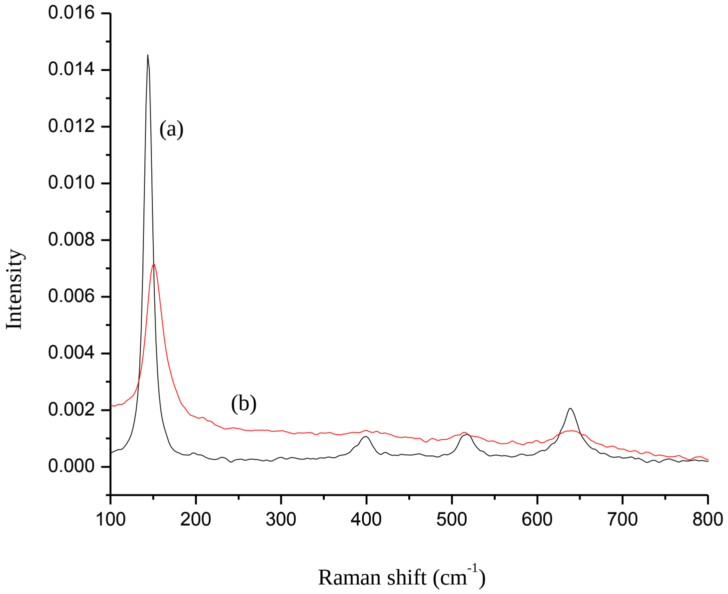


Figure 3: *Raman spectra of the TiO_2 powders: (a) commercial nano-TiO_2, (b) TiO_2 coated on glass*

3.3 UV-visible diffuse reflectance spectroscopy

The UV–visible diffuse reflectance spectra of the TiO_2 samples are shown in Figure 4 (a) and (b). Both commercial nano-TiO_2 and nano-TiO_2 synthesized at 800 °C gave the maximum absorption band at 205 nm wavelength. The spectra show shoulders near 350 nm and bases which approach zero at about 400 nm. The absorption quickly increased above 350 nm due to the absorption of light caused by the excitation of electrons from the valence band to the conduction band of TiO_2.

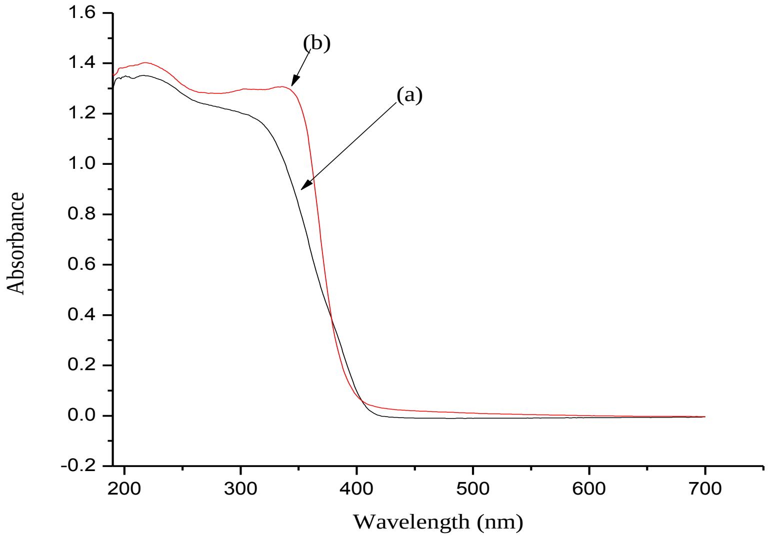


Figure 4: *UV–visible diffuse reflectance* spectra *of the TiO_2 powders: (a) commercial nano-TiO_2 (b) nano-TiO_2 synthesized at 800 °C*

3.4 Surface Morphology

STEM and SEM images of nano-TiO_2 synthesized at 800 °C are shown in Figure 5. Experimental results show the morphological homogeneity with grain size falling mostly in the rage of 20 nm to 60 nm, with soft agglomerates. These spheres consist of many small short rod shaped crystals of TiO_2 crystals due to agglomerations. STEM and SEM images also reveal that particle sizes of nano-TiO_2 synthesized at 800 °C were in agreement to the values determined by using XRD data. In order to investigate nao-TiO2 powder, EDX analysis was also carried out. The EDX analysis shows that nao-TiO_2 synthesized at 800 °C contains only titanium and oxygen elements and there is no impurity in the sample.

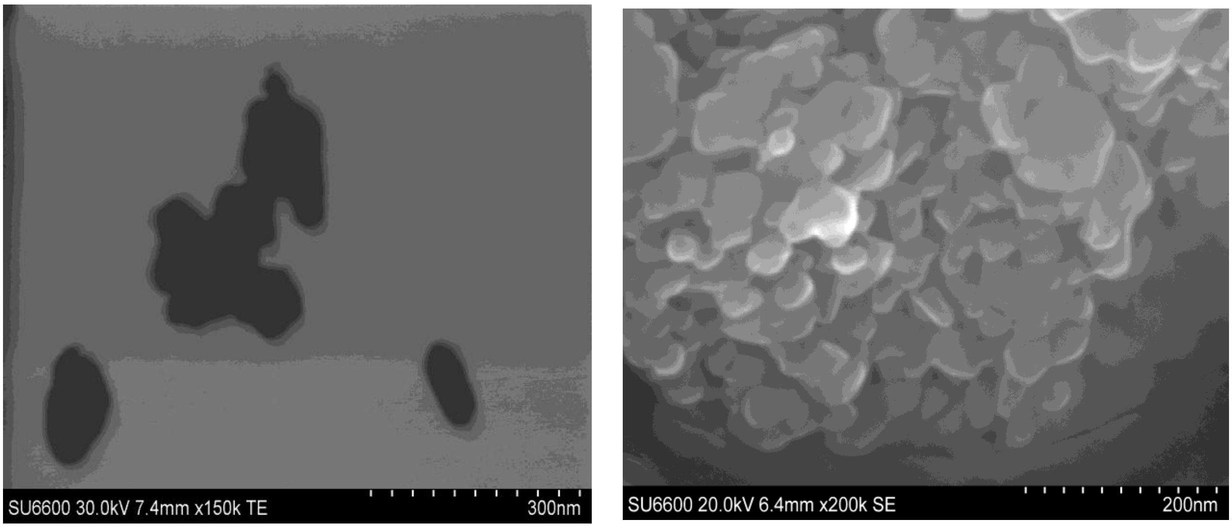


Figure 5: STEM and *SEM images of the nano-TiO_2 synthesized at 800 °C*

3.5 Photocatalytic activity

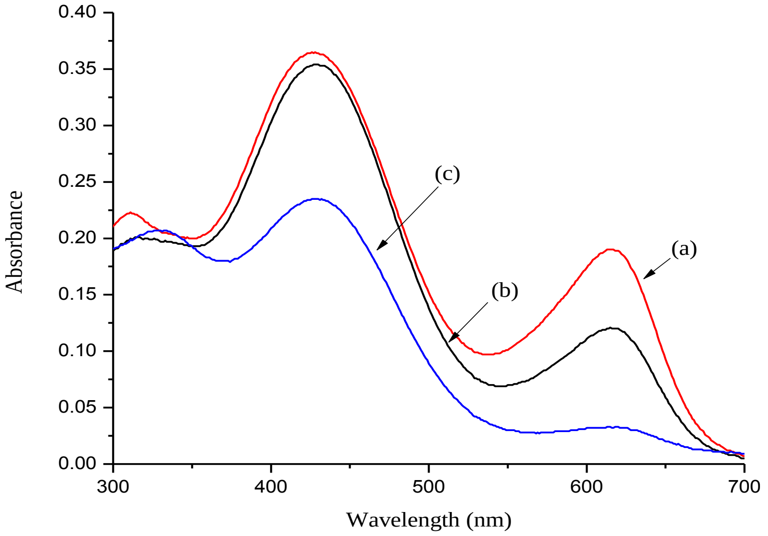


Figure 6: *UV-Vis spectra of reaction product of bromothymol blue solution: (a) with uncoated glass (control), (b) with the TiO_2 coated on glass, (c) with nano-TiO_2 powder after exposing to diffused light for 48 hrs.*

The photocatalytic activity of the thin film TiO_2 was determined by photo-oxidation of bromothymol blue. Figure 6 (a) represents the UV- visible absorption spectrum of bromothymol blue in water (1.7×10^{-5}) after exposing to diffused light for 48 hours with an uncoated glass slide dipped. Figure 6 (b) and (c) are spectra of bromothymol blue in water (1.7×10^{-5}) after exposing to diffused light for 48 hours with a TiO_2-coated glass slide dipped and with 0.5 g of nano-TiO_2 powder respectively.

Figure 6 (b) showed that the reduction of absorbance at 614 nm in bromothymol blue solution was mainly due to the photocatalytic capabilities of TiO_2 thin film coated on glass. Figure 6 (c) shows the significant decrease in absorbance both at 428 nm and 614 nm indicating that most of the bromothymol blue has been photo-oxidized by nano-TiO_2 with diffused light. The maximum percentage of photo-oxidation of bromothymol blue was 82.6% at 614 nm by nano-TiO_2 under diffused light.

5 Conclusions

A simple and inexpensive technique has been established to prepare nanocrytalline TiO_2 powder and thin films from aqueous solution at room temperature. According to XRD analysis the particle size of the nano-TiO_2 particles increased up to 60 nm with an increase in the temperature. Nano-TiO_2 synthesized is in pure anatase form where it shows a higher level of photocatalytic activity. The thin TiO_2 film preparation process involved in research is quite simple and a low temperature route. The photocatalytic activity of nano-TiO_2 was assessed by the degradation of bromothymol blue in aqueous solution. Nano-TiO_2 coated on glass showed a higher photocatalytic activity and self cleaning effect that can effectively be used in building envelops. This method can be implemented on a wide range of applications, involving the deposition of photocatalytic TiO_2 films on low thermally resistant materials, such as plastics. Therefore, value added nano-TiO_2 can easily be produced from Sri Lankan ilmenite ($FeTiO_3$). Nano-TiO_2 coated glass has potential for the effective and efficient photocatalytic and self cleaning effect and in a commercial context may provide savings with respect to both time and energy.

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SRI LANKAN GRAPHITE MAKING THE SPACE ELEVATOR POSSIBLE

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Abstract: A metal catalyst free, low cost process of manufacturing carbon nanotubes (CNT) using Sri Lankan graphite as anode and cathode, in the absence of external cooling, in an inert gas atmosphere is presented in this paper. The CNT yield has been analyzed using High Resolution Transmission Electron Microscopy (HRTEM), Scanning Electron Microscopy (SEM) and Raman spectroscopy.

Keywords: Arc Discharge, Carbon Nanotubes, Graphite

1 Introduction

Graphite is one of the allotropes of carbon and it is an electrical conductor. Carbon nanotubes can be made starting from microcrystalline amorphous carbon or highly crystalline flake graphite or vein graphite. However, the end product depends on the choice of carbon type, the process followed and the conditions applied during the process.

Vein graphite, also known as crystalline vein graphite, Sri Lankan graphite, or Ceylon graphite is a naturally occurring form of solid carbon deposited from a fluid phase, has the highest "degree of crystalline" perfection of all conventional graphite materials. As a result of its high degree of crystallinity, vein graphite is utilized extensively in graphite based products that are used mainly in the electrical applications. However, possibilities of utilizing them in the construction industry are also being looked at and one exciting opportunity is the space elevator concept discussed in "Fountains of Paradise" by Arthur C. Clarke [1].

In the recent past, several methods, such as chemical vapour deposition, arc discharge and laser ablation have been explored to produce CNTs of different characteristics. In the standard process of making carbon nanotubes using electric arc discharge method (Aternating Current or Direct Current), a controlled pressure and inert environment are maintained within the chamber [2]. The parameters such as duration of the electric arc and the discharging current are varied to produce multi walled carbon nanotubes (MWCNT) of various characteristics [3,4]. The process consists of an electric arc generator whose positive terminal is connected to the anode, which supplies the carbon source to make the nanotubes and the negative terminal is connected to the cathode on which the nanotubes are produced and deposited. In the standard arc discharge process, the anode is composed of flake graphite, either in rigid solid state or in powder state whereas the cathode contains either flake graphite or other carbon source. This process produces MWCNT while the cathode has to be modified by adding a small quantity of a transition metal such as iron, nickel or cobalt in order to result in Single Walled Carbon Nanotubes (SWCNT). In the conventional process cathode is water cooled [5,6]. This adds complexity and cost to the process. In addition, it might become necessary to modify the cathode to facilitate this cooling process. As a result, in the standard procedure the SWCNTs are always contaminated with metal particles which require subsequent purification using a chemical or a physical process. Attention must be paid to careful purification without damaging the nanotubes. However, this is a practically difficult and time consuming task.

As SWCNTs are also more expensive to make (SWCNTs cost about $ 500/g and MWCNTs cost about $ 5/g) and the economics of scale may not change until there is a large-scale market and a large scale production capability for SWCNTs. For these reasons, MWCNTs are widely used in applications such as composite materials than its SWCNT counterpart [7].

Hence, it is justified that there exists a growing need for a simple, low-cost method of manufacturing high-quality, CNTs that eliminates the need for extensive cleaning and purification of the CNT product. The objective of this paper is to describe a catalyst free low cost manufacturing process of CNTs from vein graphite using electric arc discharge method, in the absence of external cooling.

2 Experimental

2.1 Apparatus

For the purpose of DC electric arc discharging, a conventional DC power supply working as a current source together with sufficient cable ratings were used. The arcing was done inside a chamber whose interior was purged and filled with argon gas to provide an inert environment, hence to avoid possible firing and oxidation. Figure 1 shows the block diagram of the apparatus designed, fabricated and used for the production of CNT.

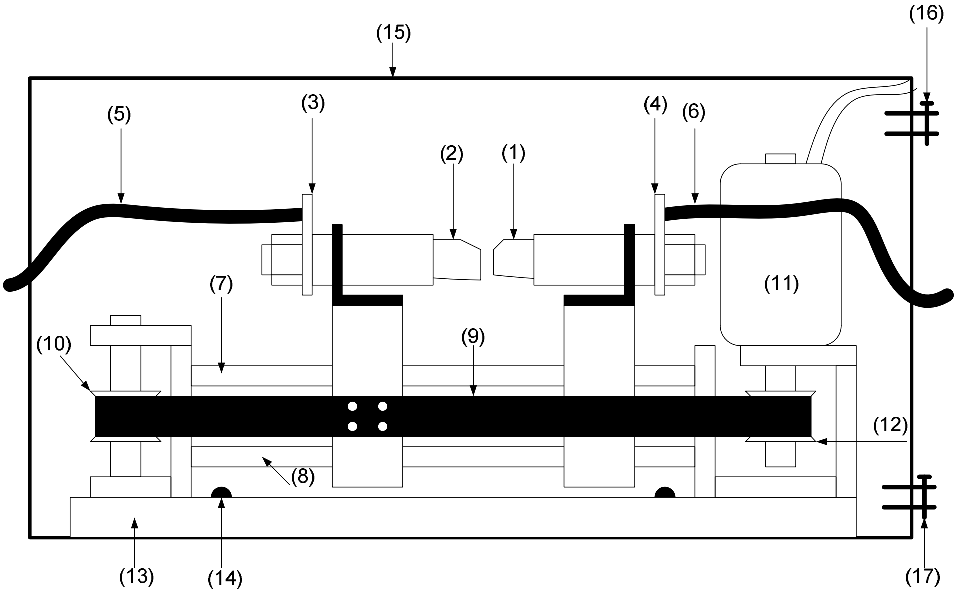

Fig. 1: Block diagram of the apparatus used in the laboratory for CNT production.

The setup shown in Figure 1 contains electrodes comprising a vein graphite cathode (1) and a vein graphite anode (2). Attached to cathode and anode are circular hollow clamps (3) and (4); and jumper cables (5) and (6). Clamp (3) is connected to the positive terminal and clamp (4) is connected to the grounding terminal of a DC arc discharge power source. This discharge power source which is not shown in the diagram can supply 400 A at 100 V. The anode assembly ((2), (3) and (5)) and cathode assembly ((1), (4) and (6)) are connected to the smooth stainless steel guides ((7) and (8)). These smooth stainless steel guides effectively provide for the cathode and anode assemblies to traverse linearly. The two assemblies are connected to a belt drive (9) which is traversed between the two pullies ((10) and (12)). A DC servo motor (11) connects the driving pully (12) and the other pully (10). The anode and cathode assemblies, their guides and the driving mechanisms are mounted securely to a steel frame (13), which is fastened (14) to the vessel (15) to avoid any undesired motion. The gas inlet valve (16) is used to supply Argon (Ar) gas to the vessel, while the outlet valve (17) is used to remove air using a vacuum pump (not shown) and to purge the vessel with argon gas.

2.2 Manufacturing process

The production process of CNT by using DC electric arc discharge method is described in steps as follows:

1. Two vein graphite pieces as received from the mine, are fixed firmly to the anode and the cathode. A linear motion, to bring the electrodes together to initiate the arc and then to separate, the anode and cathode is achieved using a geared mechanism driven by a belt. The entire system is kept inside a 315 l vessel, where there is a window to exchange the electrodes.
2. The vessel window is then closed.
3. The 315 l closed system vessel, in which the manufacturing is carried out, is purged (the pressure inside the vessel drops to -100 mmH_2O) using a vacuum pump.

4. Inert gas argon (Ar) is pumped in to the vessel until the dropped pressure reaches atmospheric pressure.
5. The above two steps are repeated three times to make sure that no active gas remains inside the vessel.
6. The DC power supply is switched on and the electrodes are moved such that the vein graphite pieces connected as anode and cathode come closer and touch each other. The electric arc is initiated at this point.
7. Once the arc is established in two to three seconds, the electrodes have to be moved apart by about 1 mm to 1.5 mm and the plasma is allowed to grow. After about 10 s from the arc initiation, the gap between the vein graphite pieces may be further increased by 1 mm to 2 mm, so that sufficient room exists for the vaporized carbon from the anode to get deposited on the vein graphite pieces of the cathode.
8. The electrodes are allowed cool naturally in the same inert gas vessel. The carbon nanotubes formed from vein graphite by the arc discharge method is allowed to cool naturally by a gradual temperature gradient towards ambient temperature. There is no rapid cooling like in other arc discharge methods. Once the temperature drops to room temperature, the carbon nanotubes formed on the cathode, which will appear as a dark ash colored circle of about 5 mm diameter surrounded by a fully black colored ring, have to be scratched and separated from the electrode.

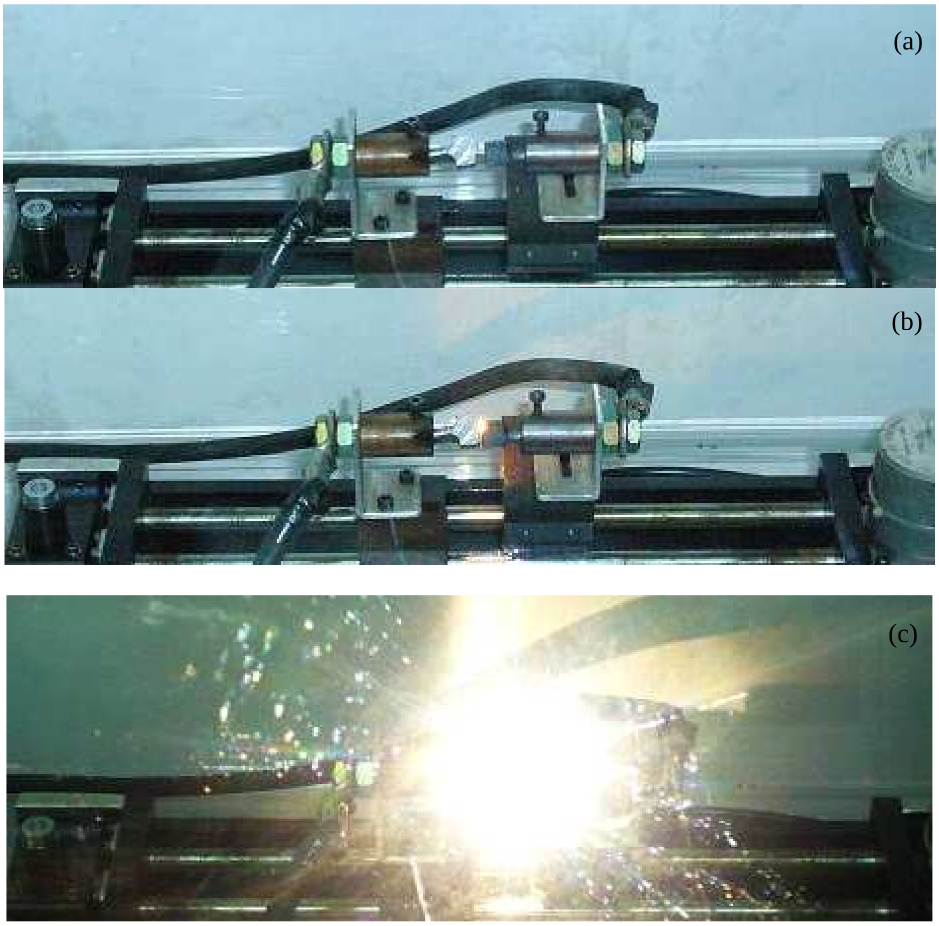

Fig. 2: CNT production by arc discharge – (a) prior to igniting, (b) arc initiation, (c) stabilized plasma.

2.3 Characterization

The particle size and the morphology of the synthesized samples were studied using a SEM, HITACHI SU6600 microscope at the Sri Lanka Institute of Nanotechnology, Sri Lanka. Further, the internal structure of the carbon nanotubes were studied using HRTEM using Jeol 2010F TEM/STEM microscope, where the microscope was operated at 200 keV, corresponding to an electron wavelength of 0.00251 nm. The objective lens had a spherical aberration coefficient of 0.47±0.01 mm and hence a resolution at optimum defocus of 0.19 nm in HRTEM. TEM samples were prepared scratching the surface of the substrate onto holey carbon-coated copper grids.

The presence of SWCNT were confirmed using Raman spectroscopy using Nd:YAG laser beam excitation Bruker, Vertex 80 spectrometer, with a laser beam wavelength 1064 nm, at the Sri Lanka Institute of Nanotechnology, Sri Lanka.

3 Results and discussion

The characteristics of the CNTs produced by the above discussed arc discharge method, were studied specifically using SEM, HRTEM and Raman spectroscopy.

Figure 3a shows a SEM image taken on an as mined raw vein graphite, where the vein structure can be observed as opposed to the structure of flake graphite as shown in the Figure 3b.

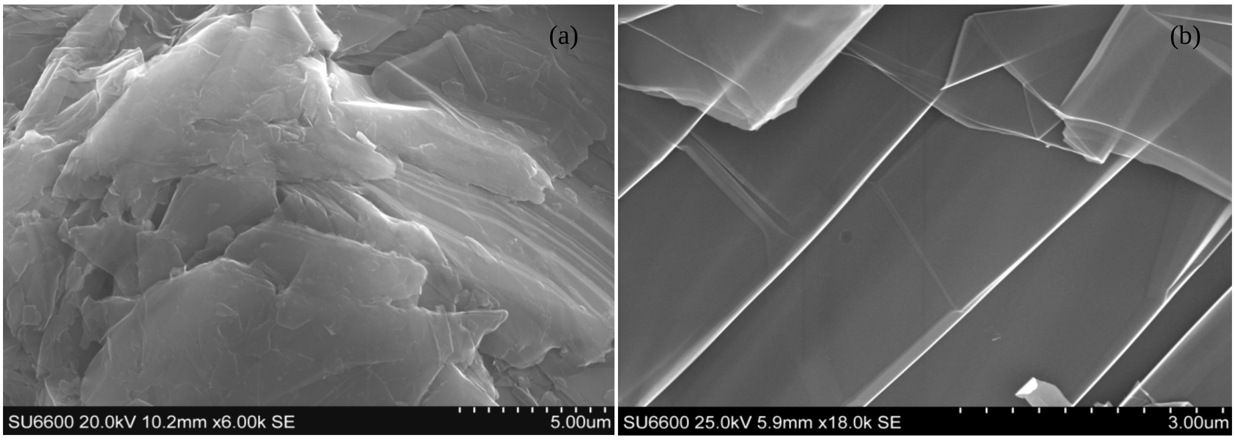

Fig. 3: SEM images of (a) – Vein graphite, (b) – Flake graphite

Figure 4 is an SEM image of an as produced CNT sample, where nests of long straight nanotubes can be observed. As evidenced by the transmission electron microscopic analysis shown in the Figure 5, the carbon soot obtained by arc discharge method contains a mixture of high quality SWCNT with uniform diameter of about 5 nm, MWCNT of with a diameter of 10 nm and carbon nano particles with an average diameter of 15 nm.

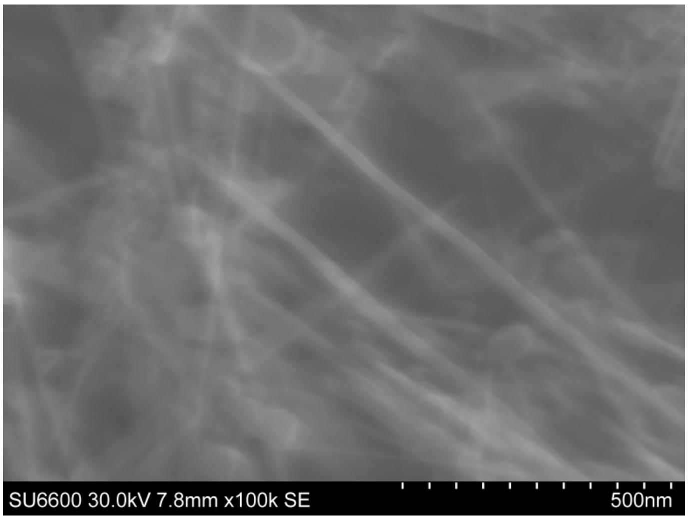

Fig. 4: SEM image of the produced CNTs

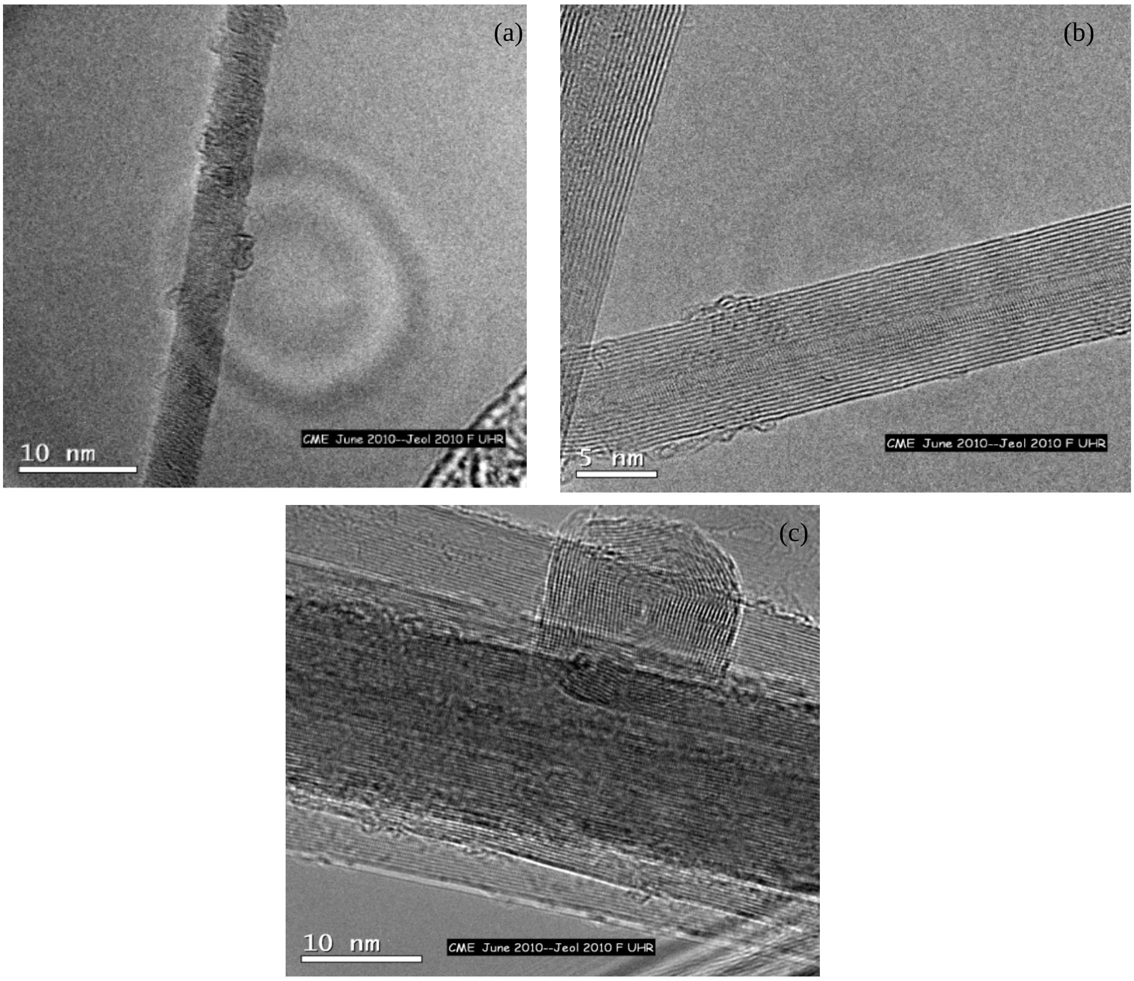

Fig. 5: TEM images of the as produced soot: (a) SWCNT of diameter about 5nm, (b) MWCNT of diameter about 10 nm and (c) Carbon nano onion of average diameter 15 nm.

Raman spectroscopy is one of the most powerful tools that provide the information on unique characteristics of CNTs such as the phonon and electronic structure and the defects. In 2-D vein graphite the only first order Raman peak around 1582 cm^{-1} corresponding to E2g vibrations of SP^2 carbons, is observed while the other transverse out of plane modes are Raman inactive. Comparatively the G-band of the CNTs with a split into many features around 1580 cm^{-1} is observed unambiguously deciding the formation of a 1_D confinement of electronic and phonon states. Furthermore, in Raman spectra of CNTs particularly SWCNTs radial breathing modes (RBM) which are also corresponding to the first order Raman scattering are observed. These characteristic Raman bands are observed below 500 cm^{-1} in the Figure 5. This RBM is a unique phonon mode characteristic of CNTs thus providing direct evidence for the presence of SWCNTs in the product obtained by our catalyst free arc discharge method [8]. The RBM mode in our study, appears as multiple peaks suggesting the possibility of forming SWCNTs with different diameters, which is typical for arch discharge process. This RBM frequency is directly related to the diameter of SWCNTs through $\omega_{RBM}(cm^{-1}) = 248\ cm^{-1}/\ d_t$, where ω_{RBM} is the RBM frequency and d_t is the tube diameter in nanometers [9]. The SWCNT calculated according to this formula varies between 3 nm – 6 nm, which corroborate the diameters observed in TEM images.

In addition, the peak observed around 1330 cm^{-1} corresponds to the sp^2, the local vibration mode of the amorphous carbon. The ratio of the peak height at 1580 cm^{-1} to that at 1330 cm^{-1}reflects the weight ratio of SWCNT to MWCNT in the soot.

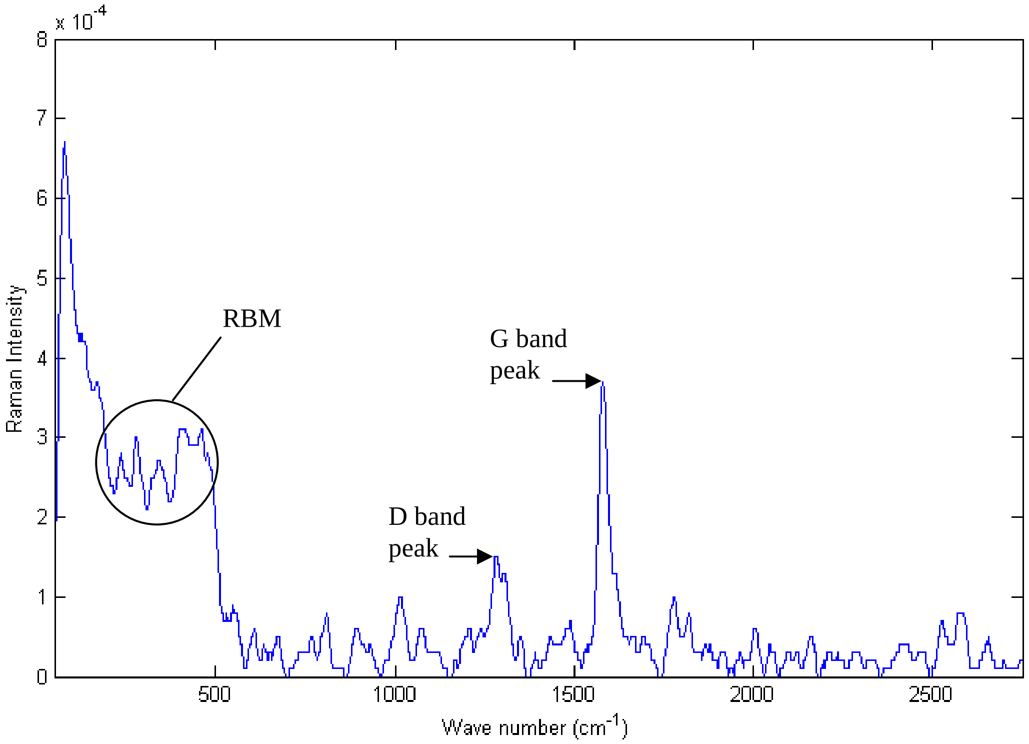

Fig. 6: Raman spectrum of the CNT sample produced by arc discharge method

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DEFLOURINATION OF DRINKING WATER USING LAYERED DOUBLE HYDROXIDES

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Abstract: Safe drinking water is one of the prerequisites for a healthy life. In Sri Lanka 70% of the population satisfy their water needs from ground water and as a result majority of them suffer from water related problems. One of the pertaining problems prevailing in the dry zone of Sri Lanka is the presence of elevated levels of fluoride ions in drinking water leading to many health related problems. Many studies have been carried out to address the issue however little success has been reported up to date. This study focuses on suggesting a nanotechnology based solution to deflourinate drinking water in the dry zone, Sri Lanka, for domestic water tanks or as a region water purification solution. Layered double hydroxides (LDHs) which readily undergo anion exchange reactions have been used as a suitable candidate for deflourination. The study further concentrates on the regeneration of the material after removal of fluoride ions without releasing flouride ions back in to the water cycle.

Keywords: Deflourination, Layered double hydroxides

1 Introduction

An adequate supply of safe drinking water is one of the major prerequisites for a healthy life. Ready access to clean water resources has therefore, become one of the key parameters ensuring that human basic needs are met. About 1 billion people in the world, mostly in developing countries, have no access to potable water while a further 2.6 billion people lacking access to adequate sanitation.[1] Poverty and water are closely linked since it is predominantly the poor who suffers from issues related to water. As a developing country Sri Lanka currently faces a number of water related problems since 70 % of the Sri Lankan population satisfies their water needs from dug wells, deep wells, reservoirs and rivers. [2, 3] One of the pertaining water related problem in the dry zone of Sri Lanka is the presence of elevated levels fluoride ion concentrations as high as 10 ppm in ground water which is well above the WHO recommended levels of 1 ppm. Although fluoride has beneficial effects on teeth at low concentrations in drinking-water, excessive exposure to fluoride in drinking-water, or in combination with exposure to fluoride from other sources, can give rise to a number of adverse effects ranging from mild dental fluorosis to crippling skeletal fluorosis as the level and period of exposure increases.[3] Further, it has been reported that chronic kidney disease (CKD) prevalent in the dry zone of Sri Lanka is directly related to the presence of fluoride ions in drinking water.[3] Although, several studies have been carried out to address the problem of excessive fluoride ions in drinking water in dry zone, little success has been reported so far. Most of the reported fluoride removing methods are based on adsorption, precipitation or adsorption/ion-exchange, electro dialysis and electrochemical processes. [4] There are several projects currently operating along with the awareness programmes among the affected communities to introduce different types of treatment methodologies where safe drinking water scarcity prevails due to high fluoride. The most common approach to remove fluoride in the dry zone of Sri Lanka is the use of brick filters which has a low efficiency. [2] In addition a combination of alum (or aluminium chloride) and lime (or sodium aluminate), together with bleaching powder, are added to high-fluoride water, stirred and left to settle. Fluoride is subsequently removed by flocculation, sedimentation and filtration.

Over the past few decades ‘nano’ a little word with big potential has become rapidly insinuating into the world consciousness. Currently, nanotechnology has not left any field untouched and therefore, this new technology can be harnessed to provide sustainable solutions to water related problems prevailing in Sri Lanka particularly to remove fluoride ions from drinking water.

Layered double hydroxides (LDHs) also known as hydrotalcite like compounds are a class of ionic lamella solids whose layers are positively charged and requires the presence of anions in the inter layer spacing in order to maintain the total charge neutrality. LDHs readily undergo ion-exchange reactions with various anions. High anion exchange capacity and the ability to be regenerated are important factors governing the utility of LDHs as anion exchangers. [5, 6] By utilizing their characteristic ion selectivity, LDHs are expected to find applications in the removal of anion pollutants from liquids particularly for the removal of fluoride ions since the gallery region of an LDH has a high affinity towards fluoride ions. Although, LDHs are rare in nature, they can be readily synthesized by co-precipitating bivalent and trivalent metal salts with a base under controlled conditions in large scales at low cost. [7]

This current study is focused on use of layered double hydroxides as a sustainable method to effectively remove fluoride ions from drinking water in the dry zone of Sri Lanka.

2 Objectives and Methodology

The main objective is to develop a cost effective method of domestic or regional deflourination filter using layered double hydroxides.

1. Layered double hydroxides, a synthetic clay material has been successfully used to remove fluoride ions from drinking water in the dry zone, Sri Lanka.
2. A method for regeneration of the filter after saturation has been proposed.

A cost study was performed to determine the cost effectiveness of the system.

All reagents and chemicals used in this study were purchased from the Sigma Aldrich Company, USA and were of analytical grade and used without further purification. All solutions were prepared using distilled water.

2.1 Characterization techniques

Powder X-ray Diffraction patterns (PXRD) of all synthesized samples were recorded using a Bruker D8 Focus X-ray powder diffractometer, using Cu Kα radiation (λ= 0.154 nm) over a 2θ range of 3-65^o with a step size of 0.02^o and a step time of 1 s.

The chemical nature and molecular bonding of the synthesized samples were determined using Fourier Transform Infra Red Spectroscopy (FTIR), Bruker Vertex80, in a range from 600 to 4000 cm^{-1} using Attenuated Total Reflectance (ATR) technique.

2.2 Synthesis of Mg-Al-hydroxide LDH (Mg-Al-OH)

Hydroxides intercalated Mg-Al- LDH was prepared by the co-precipitation method. Typically, 100 ml of an aqueous solution containing $Mg(NO_3)_2 .6H_2O$ and $Al(NO_3)_3 .9H_2O$, (Mg:Al = 2:1) was prepared and added drop wise to a 50 ml solution containing hydroxide anion (Al: hydroxide = 1:10) under vigorous stirring conditions. During mixing of the metal solutions, the pH of the reaction mixture was maintained at 10 using 2 M NaOH solution. The solution temperature was maintained at 25 ^oC, and the reaction was carried out under N_2 atmosphere. The resulting slurry was aged for 24 hours. The slurry was then filtered, washed three times with distilled water and dried at 100 ^0C.

2.3 Flouride removal from drinking water using Mg-Al-OH-LDH

To test the fluoride removal capability of LDH, a water sample received from the dry zone, Sri Lanka, which contained 8.2 ppm of fluoride ions was used. First, 0.01 g of LDH was placed in a conical flask. Water containing fluoride ion (100 ml) was poured in to the flask and kept it for 24 hours on the magnetic stirrer. Final concentration of the fluoride solution was tested using an ion selective electrode. Amount of fluoride ions intercalated was calculated by the difference between the initial and final fluoride ion concentrations after stirring for 24 hrs with the synthesized Mg-Al-OH-LDH. Same procedure was carried out varying the weight of the Mg-Al-OH-LDH as 0.05 g, 0.1 g, 0.2 g, 0.5 g, 1 g and 2.5 g in order to build the isotherm for adsorbance.

The efficiency of the LDH material was compared with that of the conventional method where brick powder is used as the ion exchange medium.

2.4 Regeneration of the material

Exhausted LDH powder was calcined at 400 °C for three hours. Then the resulting mixed oxide was characterized by PXRD and FTIR. Then it was exposed to 1 M NaOH solution for 24 hours with mechanical stirring and the resulting product was characterized using PXRD and FTIR. The fluoride gas coming out was allowed to absorb into 1 M calcium hydroxide solution.

3 Results and Discussion

The parent LDH was characterized using PXRD and FTIR prior to use as a material for removal of fluoride ions from ground water. As depicted by the PXRD pattern of the material (Figure 1(a)) resulting from the co-precipitation reaction represents a typical LDH, consisting of relatively sharp and intense basal reflections at low 2θ values.

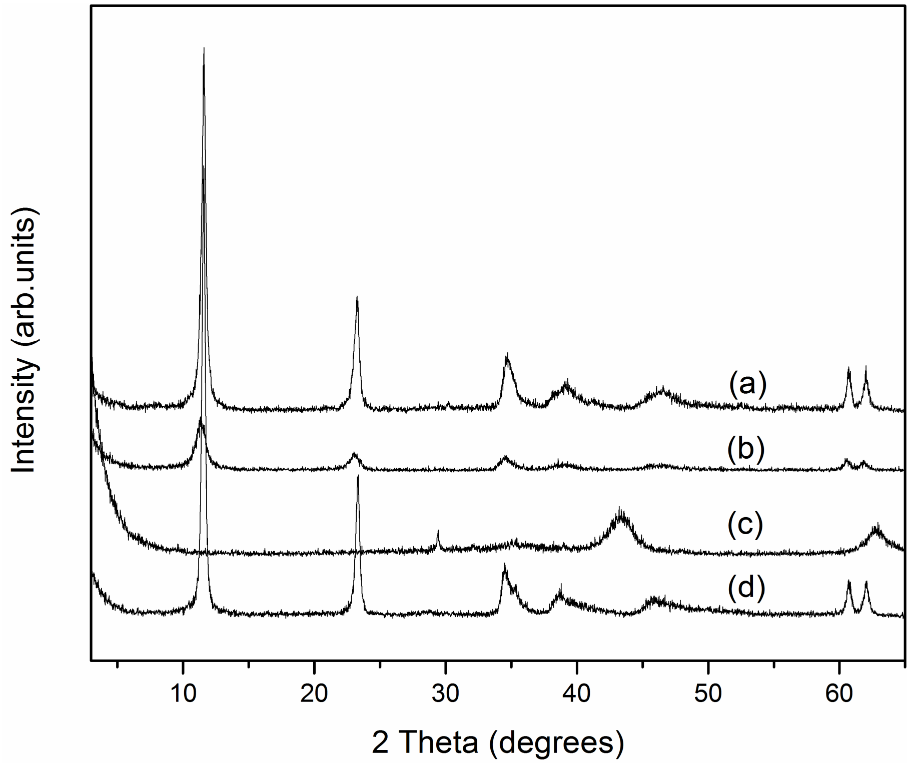


Fig. 1: PXRD patterns of (a) Mg-Al-OH LDH, (b) Mg-Al-F LDH, (c) mixed oxide received after calcination of the Mg-Al-F LDH at 450 ^{0}C, (d) regenerated mixed oxide in the presence of OH ions.

The main diffraction peaks appear at 11.65°, 23.60°, 34.68° and 60.90° 2 theta are in agreement with the previous reports [5] for hydroxyl intercalated LDHs. According to the Fig 1(a) Mg-Al-OH-LDH exhibits an inter layer spacing of 7.61 nm corresponding to the d_{003} diffraction peak. The hydroxide ions were selected as the guest ions for the study since they have minimum effect to the drinking water after ion exchange reactions occur.

The parent LDH was further characterized using FTIR techniques in order to understand the nature of functional groups present before and after exposure to fluoride containing ground water. As shown in FTIR spectra (Fig. 2) the main absorption bands are hydroxide stretching, layer hydroxyl bending motions and the metal-O vibrations of the layers. The very broad band observed around 3500 cm $^{-1}$ is due to the overlapping stretching modes of hydroxyl groups in the brucite layer and interlayer water molecules. Due to the absorption of small amount of carbonate ions into the interlayer space while the synthesis of Mg-Al-OH LDH, a characteristic band is observed at around 1360 cm^{-1} which can be assigned to the carbonate stretching vibrations. The bands below 1000 cm^{-1} are due to M-O vibrations (Mg-O, Al-O) in the brucite layer. [8]

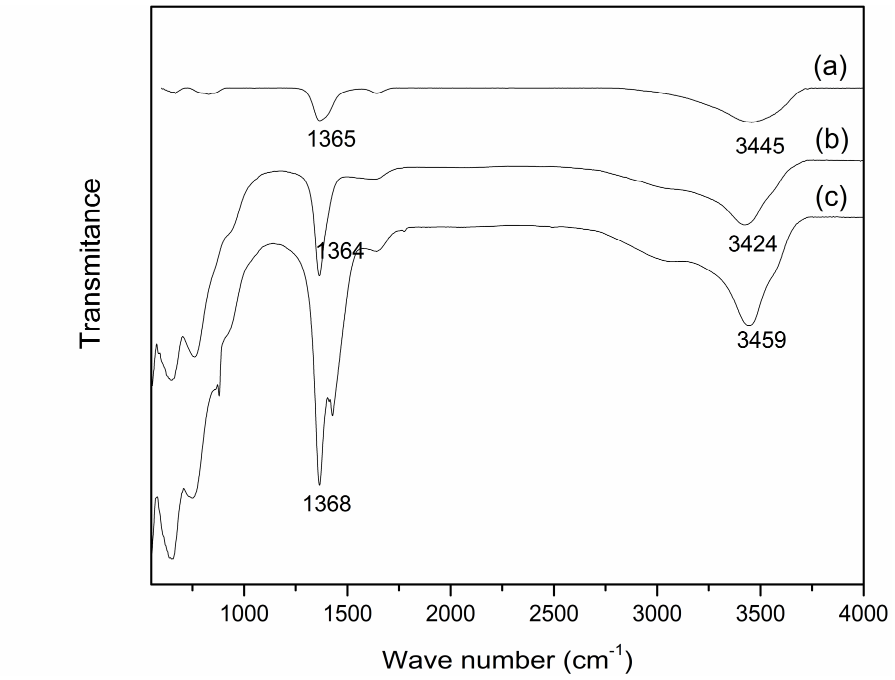


Fig. 2: FTIR spectra of (a) Mg-Al-OH LDH, (b)Mg-Al-F LDH, (c) mixed oxide received after calcinations of the Mg-Al-F LDH at 450 ^{0}C.

Then, the hydroxyl ion intercalated LDH was used to remove the fluoride ions from the drinking water obtained from the dry zone, Sri Lanka. The results after removal of fluoride ions are summarized in table 1. As shown in the table an increased efficiency of removal of fluoride ions from drinking water is observed when LDHs are used as the adsorbant, compared with conventional brick powder. The optimum results were obtained when 2.0 g of LDH were used for 100 ml of contaminated ground water.

Table 1: Flouride ion concentrations after filtering though LDHs and brick powder.

Weight of filter material/ (g)	LDH Flouride concentration (mg/l)	Brick powder Flouride concentration (mg/l)
0	8.04	8.04
0.01	7.80	7.25
0.05	7.57	6.75
0.1	6.63	6.65
0.2	6.54	6.55
0.5	4.57	6.5
1.0	1.80	5.48
2.0	1.05	5.08

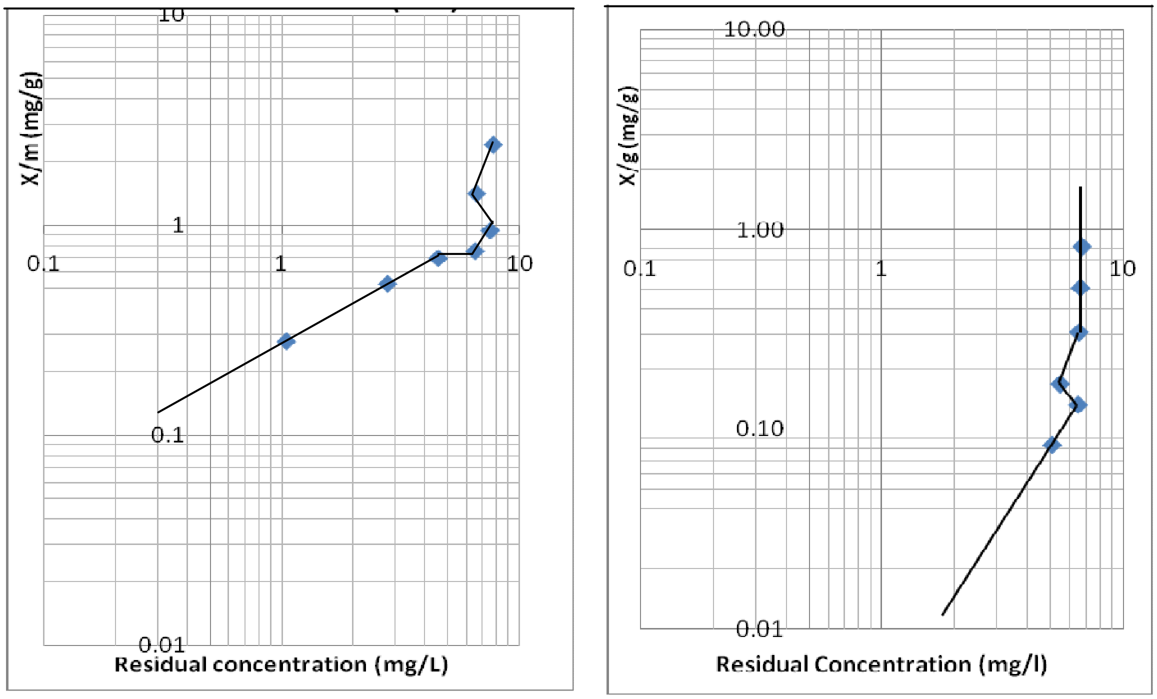
Materials after exposing into the fluoride containing drinking water were characterized by PXRD. According to the figure 1 (b)), the d_{003} basal spacing of the hydroxyl LDH has shifted to 7.79 nm suggesting a successful absorption of fluoride ions into the LDH galleries. Although both fluoride ions and hydroxide ions have similar affinity for the LDH galleries reaction has occurred by replacing the hydroxide ions possibly via a topotactic mechanism.

As shown in the FTIR spectrum (Figure 2(b)) there is a noticeable shift of the O-H stretching vibrations band from 3445 to 3424 cm^{-1} due to adsorption of fluoride ions into interlayer spacing of Mg-Al-OH-LDH (Figure 2 (b)). This characteristic shift appears due to the formation of strong H-bonds between intercalated fluoride ions with OH groups present in the LDH.

The isotherm test with different weights of the LDH samples were carried out and compared with that of conventional brick powder (Fig. 3). As given in the figure the fluoride removal capacity of the LDH is much higher than that of the conventional brick powder. Additionally, multi component adsorbance can be observed for the LDH suggesting that other anions impurities in water also can be removed using LDH material. [9]

After saturation of the LDH galleries with fluoride ions regeneration was carried out through calcination process where fluoride removes as a gas. The evolved fluoride ions were absorbed into a $Ca(OH)_2$ solution where CaF_2 is precipitated from the medium. CaF_2 thus precipitated can be used as an ingredient in the tooth paste industry.

By calcination of Mg-Al-F- LDH, a spinnel like solid solution containing MgO and Al_2O_3 is obtained at 400 ^{0}C and this solid has a strong Lewis basic character and large specific surface area. These spinnels have the ability to recover into the original layered structure, a property known as 'memory effect'. Therefore, it was possible to recover the hydroxyl intercalated LDH by placing the spinnel like mixed oxide with a solution containing hydroxide ions. The regeneration of the Mg-Al-OH LDH was confirmed by comparing the PXRD pattern of the regenerated LDH (Figure 1(d)) and the FTIR spectrum (Figure 2(c)) with the parent material.



(a) (b)

Fig. 3: Adsorption isotherm for (a) Mg-Al-OH LDH and (b) brick powder.

4 Conclusions

Layered double hydroxides have displayed high efficiency in removing fluoride ions from drinking water compared to the methods currently used. LDHs can be used in either regional water purification units or domestic house hold filters. An added advantage of using LDHs would be its superior capability of removing other anions such as carbonate, sulfate which leads to the water hardness.

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Biographical Sketch

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NATURAL RUBBER/LAYERED SILCATE NANOCOMPOSITE FOR BUILDING APPLICATIONS

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Abstract: Polymeric nanocomposite materials with a nano tag are nowadays moving into the market and are beginning to compete with traditional composite materials in various applications. Nanocomposite materials based on a polymeric matrix and nano-scale particles have offered a great opportunity in sustainable construction/green building applications since its potential capability of addressing key components of the sustainable construction: efficient materials and environmental protection.

Natural rubber (NR)/layered silicate (NRLS) nanocomposites have been prepared by melt mixing of NR with organically modified montmorillonite (OMMT) in the presence of functionalized polar additive and other curing chemicals. The resultant nanorubber vulcanizate structures were characterised with X-ray diffraction (XRD) and scanning electron microscopy (SEM). XRD analysis showed that NR molecules diffused into the OMMT gallery in the presence of functionalised polar additive and, as a result, intercalated/exfoliated rubber nanocomposite was formed, the result further confirmed by the analysis of SEM images. The mechanical performances of NRLS nanocomposite material prepared with increasing loading level of OMMT and 90 phr of inert filler (CaCO3) were investigated to evaluate the reinforcing effect of OMMT in the presence of inert filler. The mechanical properties of the NRLS vulcanisate were compared with conventional NR vulcanizate containing carbon black (CB) and CaCO3.

Keywords: Natural rubber, Layered silicate, intercalation, Exfoliation, Polar additive

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1 Introduction

In the recent past, polymeric nanocomposites have emerged as one of the most promising alternative to conventional polymeric composites for various applications such as automotive, packaging, building construction, etc. They are bi-phase material in which inorganic phase is dispersed at nano scale within the range of 1-100 nm within the polymeric matrix [1-2]. Polymeric nanocomposites based on different nanoparticles have received a great attention in the construction industry since it has superior mechanical properties and able to impart different functional properties like flame retardancy, thermal and electrical conductivity in comparison to conventional microcomposites [3-4].

Polymeric nanocomposites based on layered silicates (e.g. montmorillonite clay: belongs to 2:1 layered silicates) have probably received the most attention since it offers an enhanced reinforcement and different functional properties at low loading levels. Generally, polymer-layered silicate nanocomposites (PLSN) are divided into three ideal types: phase-separated conventional micro-composites, intercalated nanocomposites (i.e. polymer molecules intercalate into the clay gallery) and exfoliated nanocomposites (clay particles are separated into individual layers and dispersed homogeneously in the polymeric matrix [5]. Nylon 6/layered silicate nanocomposite was the first investigated polymeric nanocomposite by Toyota Research Group, Japan and it was found that mechanical and thermal properties were improved markedly, at low loading levels, in comparison to unmodified polymer and conventional microcomposites [6-7]. Since then different thermoplastics and elastomer nanocomposites based on layered silicates, especially montmorillonite, have been developed, as an alternative for conventional composites, for various applications [8-9].

Thermoplastic and elastomer composites have increasingly become important as engineering materials and they are greatly used in building and construction applications. For example, construction industry is the second largest user for thermoplastics and its composites [10]. Balanced mechanical properties along with a lighter weight, chemical and thermal stability, and flame retardancy and with ease of processing are few of the key properties of polymeric composites that are explored in structural applications [11]. Efficient design and application of these polymeric materials in built environment are important for sustainable construction.

Natural rubber (NR) is one of the interesting engineering materials which are widely used in building applications such as floorings, as shock absorbing material, gaskets, insulator and sealing applications. However, most of the rubber compounds/products used in building applications contain carbon black (most common filler in rubber industry), as a reinforcing material since NR alone does not provide the required properties. The use of rubber products containing fossil based environmental un-friendly carbon black in building environment does not support the rapidly growing concept of green building/sustainable construction. Layered silicates, especially montmorillonite clay, could be a promising alternative to conventional carbon black. Rubber/layered silicate nanocomposites exhibit not only outstanding mechanical properties, but also show functional properties such as barrier and flame retardant properties, at very low loading levels (i.e. < 10 w/w %) of layered silicates [12].

The objective of this study reported here is to prepare green natural rubber nanocomposites by replacing conventional carbon black with organically modified montmorillonite (OMMT) and to characterize the vulcanisation behaviour and nanocomposite structure. Specific focus is given to evaluate the mechanical and other functional properties of the rubber nanocomposites based on OMMT and inert filler (CaCO3) in view of building applications.

2 Materials and experimental methods

Ribbed smoked sheet (RSS) grade of NR was selected as the rubber matrix in this study. Montmorillonite clay (Cloisite 20A), modified with dimethyl dihydrogenated tallow quaternary ammonium chloride, has been used to prepare natural rubber/layered silicate nanocomposite and was supplied Suthern Clay Products. Industrial grade vulcanizing chemicals such as sulphur, accelerator, antioxidants are also used in the compound formulations.

2.1 Preparation of natural rubber/layered silicate nanocomposite (NRLS) material

NRLS nanocomposites were prepared by the melt mixing of NR and OMMT in the presence of functionalized polar additive as an exfoliating promoter and with other vulcanizing chemicals in a laboratory scale Internal Mixer (Haake Rheomix 600), operating at 60 ^{o}C (set temperature) and with a rotor speed of 80 rpm. Table 1 presents the exact formulations for each NRLS nanocomposite.
Vulcanization parameters of the nanocompounds were determined using Moving Die Rheometer (MDR: Ektron, EKT-2000S) at 150 ^{o}C for 30 min. NRLS nanocomposite vulcanizate sheets of approximately 2 mm thickness were prepared in a hot press at 150 ^{o}C for optimum cure time, t90, derived from rheographs obtained from the analysis of MDR. These vulcanized sheets of NRLS were used to characterise the nanocomposite structure and mechanical properties.

2.2 Characterization of natural rubber/layered silicate (NRLS) nanocomposite material

X-ray diffraction (XRD) analysis was performed with a Bruker D8 diffractometer with Cu Kα radiation to evaluate the nanocomposite structure in terms of intercalation/exfoliation behaviour of OMMT in the NR. XRD diffraofctograms of NRLS nanocomposite vulcanisate sheets by scanning over a 2 θ range from 1 to 10 degrees, at a rate of 0.01/s. The conventional Bragg equation ($n\lambda = 2d \sin\theta$) was used to determine the interlayer spacing of OMMT in the nanocomposite material.

OMMT morphology (dispersion and distribution) within the RLSN material was observed under Scanning Electron Microscope (Hitachi SU 6000), operated at 25 kV.

Table 1: Compositions of NRLS nanocomposite vulcanisates containing different concentration of OMMT

	NR GUM	**NRLS4**	**NRLS8**	**NRLS10**	**NRLS4/ 90**	**NRLS10/ 90**	**NRLS15/ 90**
NR	100	100	100	100	100	100	100
OMMT	-	4	8	10	4	10	15
Polar additive	-	0.46	0.92	1.15	0.46	1.15	1.73
$CaCO_3$	-	-	-	-	90	90	90
ZnO	5	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1	1
IPPD[a]	1	1	1	1	1	1	1
Sulpher	2.5	2.5	2.5	2.5	2.5	2.5	2.5
MBTS[b]	1	1	1	1	1	1	1

[a] *n*-isopropyl *n*-phenyl *n*-phenylenediammine

[b] Mercaptobenzothiazole disulphide

2.3 Mechanical properties of NRLS nanocomposite vulcanisates

Mechanical properties including tensile properties, hardness and rebound resilience of NRLS vulcanisates were analysed to study the effect of OMMT loading levels and CaCO3 on mechanical property performances.

Tensile properties of NRLS vulcanisate prepared by incorporating OMMT and CaCO3 were analysed according to ISO standards, ISO 37: 2005 (E), using Instron 3365 Universal Tensometer. The extension of the samples was measured using an optical extensometer.
Shore A hardness of the NRLS nanocomposite vulcanisate was measured using ASTM standard, D 2240.

3 Results and discussion

Vulcanization curves of NRLS nanocompounds containing different loading levels of OMMT are graphically presented in Figure 1. NRLS nanocompounds (i.e. NRLS4, NRLS8 and NRLS10) have a noticeable higher maximum torque (MH) compared to that of NR-gum compound. These results indicate a higher degree of cross linking and intercalation/exfoliation of OMMT achieved in NRLS nanocompounds. Vulcanisation studies of NRLS nanocompounds further revealed that, as shown in Figure 1, OMMT accelerates the vulcanization process (i.e. increase the cure rate), resulting in reduced the scorch (ts_2) and optimum cure (t_{90}) times. This is attributed to the fact that organic modifier (dimethyl dihrogenated tallow quaternary ammonium) in the OMMT acts as a catalyst during the vulcanization process. However, NRLS4/90 containing 4 phr of OMMT and 90 phr of CaCO3 shows the maximum torque but curing rate does not alter significantly due to the incorporation of $CaCO_3$.

3.1 Characterization of NRLS nanocomposite structure

The NRLS nanocomposite vulcanisates prepared by melt mixing of NR with OMMT in the presence of functionalized polar additive followed by vulcanisation were analyzed with X-ray diffraction technique to evaluate the formation of nanocomposite structure. The exact composition of each NRLS nanocomposite material is shown in Table 1. Figure 2 presents the XRD spectra of pure OMMT and NRLS vulcanisates containing different loading levels of OMMT.

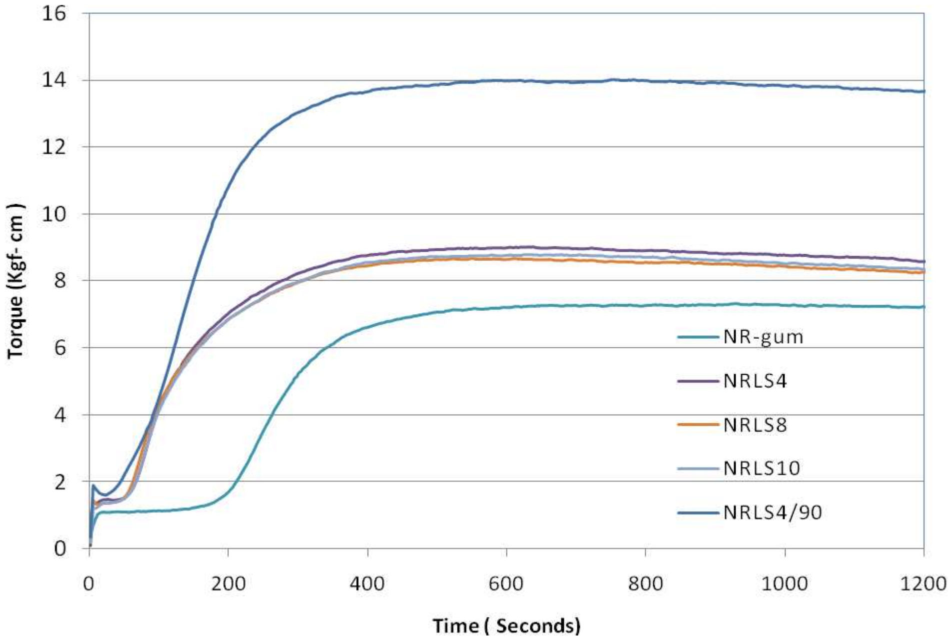

Fig.1: Vulcanisation curves (rheographs) of NR- gum and NRLS nanocompounds at 150 °C

As shown in Figure 2, the characteristic diffraction peak (001) of OMMT is at 2.96 ° of two theta and hence interlayer spacing is 24.5 Å (see Table 2). However, when OMMT is melt mixed with NR in the presence of functionalized polar additive, the diffraction peak of OMMT shifted towards a lower Bragg angle. Table 2 presents the two theta positions of the diffraction peaks and the interlayer spacing for each nanocompound comprising different concentration of OMMT. This could be explained by the polar additives intercalating into the OMMT galleries and, as a result, NR molecules were also likely to diffuse into the OMMT galleries. Hence, interlayer spacing of OMMT was increased, resulting in intercalated NR/OMMT nanocomposite structure For example, interlayer spacing of OMMT in NRLS4 nanocomposite increased from 23.6 Å to 42.0 Å (see table 2).

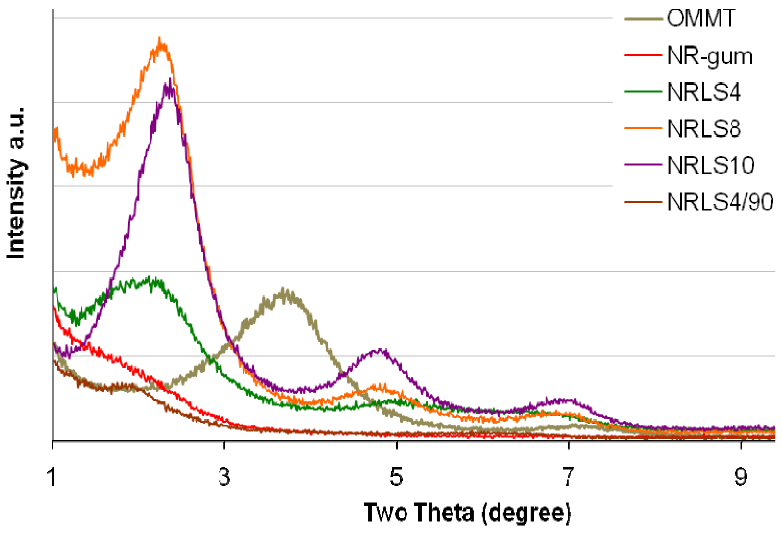

Fig.2: X-ray diffraction spectra of OMMT and NRLS nanocomposites

However, more interestingly, when CaCO3 is incorporated into the formulation (i.e. NRLS4/90) the diffraction peak of OMMT further shifted towards the lower Bragg angle, indicating further intercalation/exfoliation of OMMT during the melt mixing process.

Table 2: Diffraction peak positions and interlayer distances of OMMT in NRLS nanocomposite vulcanisates

NRLS nanocomposite vulcanisate	Two theta (°)	Interlayer spacing (Å)
OMMT	3.73	23.6
NRLS4	2.1	42.0
NRLS8	2.29	38.5
NRLS10	2.37	37.2
NRLS4/90	1.85	47.7

Since XRD data confirms the intercalation of NR molecules into the OMMT galleries, SEM micrographs of NRLS nanocomposite materials were analysed to evaluate the OMMT dispersion within the nanocomposite material. Figure 3 shows the NRLS nanocomposite material containing 4 phr. of OMMT (NRLS4) at a lower magnification (3-a) and a higher magnification (3-b and c). As shown in Figure 3 (a), particulate materials are dispersed uniformly throughout the NR matrix, indicating better compatibility is achieved between OMMT and NR through the functionalised polar additive. On the other hand, high magnification images show the nm size thickness of the OMMT clay stack in the nanocomposite material. It can be clearly seen that these stacks are contained only few individual clay platelets, implying that larger OMMT clay stacks exfoliate/delaminate into smaller stacks during the compounding process.

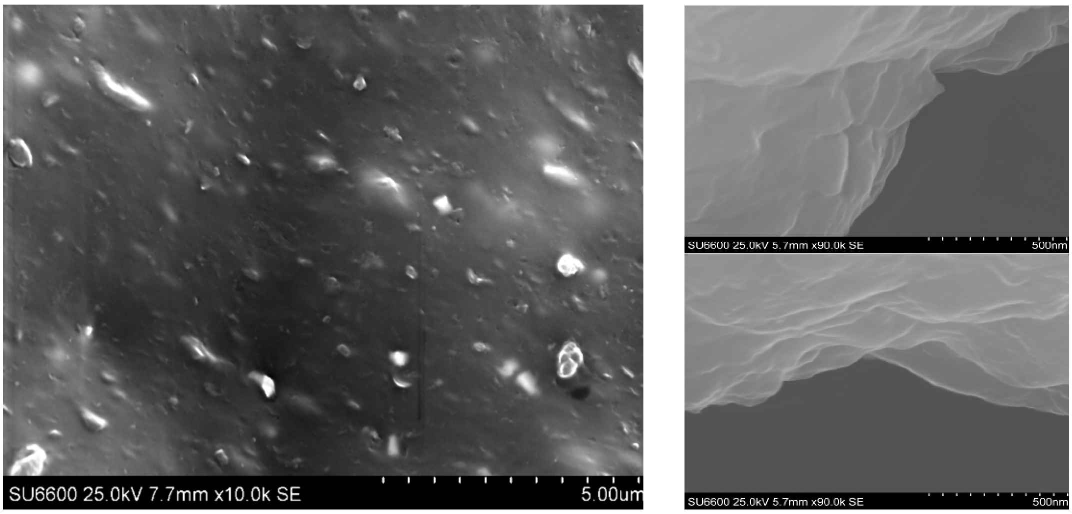

Fig.3: SEM micrographs of NRLS4; (a) dispersability of OMMT in NRLS material at low magnification, 10,000. (b) & (c) thickness of the OMMT stack at a higher magnification

From these X-ray diffraction data and SEM images prove the formation of intercalated/exfoliated OMMT structure with in the NR matrix.

3.2 Mechanical properties of NRLS nanocompoiste vulcanisates

The reinforcing effect of OMMT and the suitability of this new green material (NRLS nanocomposites), which does not contain carbon black, for building applications were evaluated by analysing the mechanical properties of NRLS nanocomposite vulcanisates.

Figure 4 and 5 show the tensile properties (tensile strength and tensile modulus) of NRLS nanocomposite vulcanisates containing OMMT as the only reinforcing material and NRLS/$CaCO_3$ nanocomposite vulcanisates containing 90 phr of CaCO3 as inert filler in addition to OMMT. All NRLS nanocomposites (e.g. NRLS4, NRLS8) containing only OMMT showed a higher tensile strength and modulus with compared to that of NR-gum compound. The improvement of tensile properties of NRLS nanocomposites depends on OMMT aspect ratio, OMMT mechanical properties and the interaction between the NR matrix and the OMMT. As explained in the characterisation of NRLS nanocomposite structure, NR molecules intercalate into the OMMT gallery in the presence of polar additive and, as a result, significantly improve the OMMT exfoliation and subsequent dispersion. Exfoliation of OMMT particles into the nano-meter range, resulting in higher aspect ratio, is the key to improve the tensile properties of NRLS nanocomposite material. However, the tensile NRLS vulcanisates increased rapidly with increasing OMMT content up to 10 phr and, when OMMT content increased beyond 10 phr, the improvement in tensile properties is gradually less. Reduced improvement of tensile properties beyond 10 phr of OMMT could be attributed to that of lower degree of exfoliation at high concentration of OMMT. The lower degree of exfoliation results in a higher number of individual OMMT layers (OMMT platelets) per clay stack and hence decreases the effective length to diameter ratio (aspect ratio).

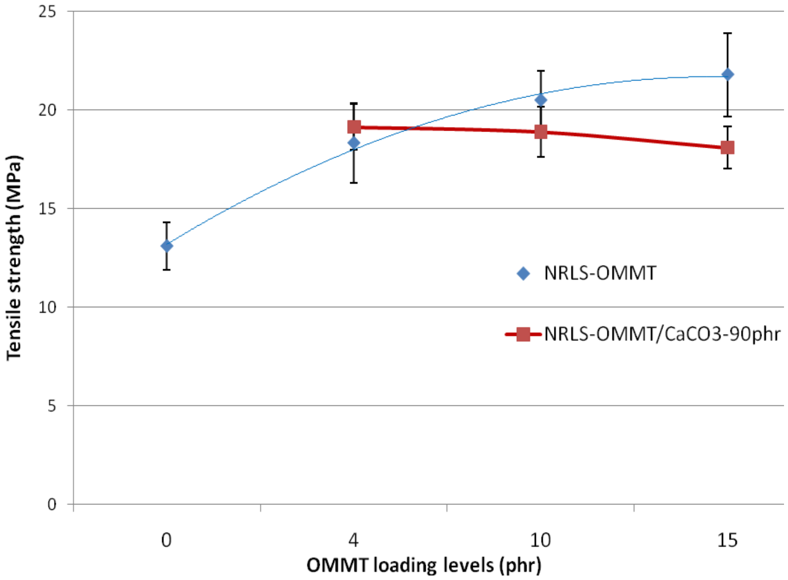

Fig.4: Comparison of tensile strength of nanocomposite vulcanisates of NRLS-OMMT and NRLS-OMMT/$CacCO_3$-90phr).

Generally, incorporation of inert fillers such as $CaCO_3$ deteriorates the reinforcement of rubber compound vulcanisates. However, although the strength characteristics (tensile strength) were slightly reduced by mixing 90 phr of $CaCO_3$ into the NRLS nanocomposites, NRLS/$CaCO_3$ nanocomposites vulcanisates maintained better tensile properties compared to that of NR-gum compound. This would explain that improved reinforcement obtained due to the exfoliation of OMMT does not significantly deteriorate by incorporating $CaCO_3$.

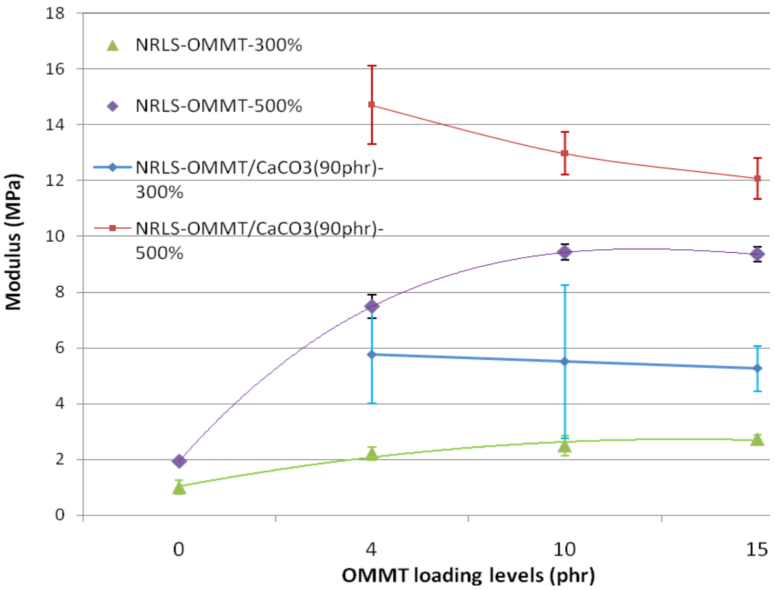

Fig.5: Comparison of tensile modulus nanocomposite vulcanisates of NRLS-OMMT and NRLS-OMMT/$CacCO_3$(90phr).

Table 3 shows the comparison of mechanical properties between the new NR nanocomposite vulcanisate material containing both OMMT and $CaCO_3$ and conventional NR vulcanisate containing carbon black and $CaCO_3$. As shown in Table 3, in comparison to conventional carbon black rubber compound (NRCB30/90), similar mechanical performances (i.e. tensile properties, tear strength and hardness) are achieved in NRLS/$CaCO_3$ nanocomposite vulcanisate containing no carbon black. Characterisation of mechanical properties clearly showed that environmental unfriendly carbon black can be replaced with a lower loading level of OMMT as a reinforcing material and this new elastomeric nanocomposite material would be a potential material for applications in sustainable buildings.

Table 3: Mechanical properties of NRLS/$CaCO_3$ nanocomposite vulcanisate and conventional NR vulcanisate (NRCB30/90)

Compound	Hardness (Shore A)	Tensile strength (MPa)	Modulus-300% (MPa)	Tear strength (KN/m)	Elongation (%)
NR-gum	31.75	13.15	0.99	29.15	726
NRLS4/90	55.92	19.14	5.75	42.01	557
NRLS10/90	57.15	18.90	5.50	37.10	615
NRLS15/90	56.40	18.10	5.26	35.96	618
NRCB30/90[a]	59.50	15.56	5.95	33.35	521

[a] Conventional NR vulcanisate containing 30 phr of carbon black and 90 phr of $CaCO_3$

4 Conclusion

A modified method of preparing natural rubber/layered silicates nanocomposites in the presence of functionalised polar additives and its performances characteristics were presented, in view of replacing conventional NR compound containing carbon black. XRD results revealed that polar additives promote the intercalation on NR molecules into the OMMT galleries whilst SEM images showed the exfoliation of OMMT particles into nano meter scale and subsequent uniform dispersion throughout the NR matrix. Vulcanisation process of NRLS is accelerated by the OMMT due to the presence of amine type organic modifier.

NRLS nanocomposite prepared by incorporating both OMMT and the inert filler ($CaCO_3$) shows good reinforcement and its mechanical performances are as good as with the conventional NR compound. Hence, this new natural rubber nanocomposite material is a potential candidate for green building applications.

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NANOMATERIALS FOR SMART ENERGY SYSTEMS: FROM LED TO SUPERCAPACITORS AND SOLAR CELLS.

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Abstract: It has been forecast that there will be a severe impact on world economics and ecology in future by energy consumption/production that rely on the combustion of fossil fuels. Therefore more sustainable and more environmentally friendly alternative energy/power generation sources are currently under serious consideration. One such alternative is electrochemical energy production. Systems for electrochemical energy storage and conversion include batteries, fuel cells and electric double layer capacitors (EDLCs). Although the energy storage and the conversion mechanisms are different, there are “electrochemical similarities” of these three systems. Electric double layer capacitors, also known as supercapacitors or ultracapacitors, have tremendous potential as high energy high power sources for use in low weight hybrid systems. Commercial applications for such devices include uninterruptible power applications, telecommunication and transportation. The total energy stored in a conventional capacitor is proportional to both the number of charges stored and the potential between the plates. Essentially the former is a function of the size of the electrode while the later is determined by the breakdown of dielectric between the plates. Different voltages, hence energy stored, can be generated when different dielectric materials are used to separate the plates. Materials can be optimized to produce high energy densities for a given size of a capacitor. In contract to conventional capacitors, supercapacitors do not have a conventional dielectric. Instead, two layers of the same substrate and their electrical properties are used in order to effectively separate the charges despite vanishingly thin (on the order of nanometer) physical separation of the layers. Higher energy storage density can be achieved in supercapacitors when nanomaterials or materials with nanoporous structure are used because such materials offer enormous surface to volume ratio.

Activated carbon is a material with unique properties especially in relation to its nanoporosity and can therefore be used in supercapacitors. Sri Lanka is one of the worlds’ best coconut shell based activated carbon producer. Besides, carbon nanotube (CNT, either MWCNT or SWCNT) can also be used in supercapacitors as electrode material where charge storage capacity can be increased to a much higher value. Ceylon vein graphite is a good source for the production of CNT. Further, the use of nano-TiO_2 in conjunction with light absorbing material in cost effective solar cells is a well established process. The charge carrier generation process in solar cells mimics natural photosynthesis (green energy). At present such solar cells have efficiency nearly 11 %. Again Sri Lanka inherits a vast naturally occurring TiO_2 deposit, the range of benefits of which is yet to be explored and harvested to produce nano-TiO_2. Therefore nanomaterials in Sri Lanka has a wide spectrum of application and in this presentation, the opportunities to develop smart energy systems using Sri Lankan nanomaterials will be presented.

Keywords: Sustainable energy, Supercapacitors, Carbon nanotube, Titanium Dioxide, Dye-sensitized Solar Cells, Activated Carbon, anatase-TiO_2, carbon nanotube, graphene.

1. Introduction

"Clean" energy generation and storage is a fascinating area of research. It encompasses many different disciplines varying from biology to physics posing scientifically challenging yet interesting issues. Clean energy generation reinforces the idea of reduction of carbon footprints and gathers momentum to the search of a lasting solution to the world energy crisis. "BP Statistical Review of World Energy" [1] predicts that the petroleum reserve may sufficient to meet the consumption requirements for just over four decades which emphasizes the necessity of coherent research efforts on alternative energy resources for energy generation. Among the alternative energy resources for "clean energy generation", solar energy is far more attractive and important because of its low environmental impact and the abundance. Therefore the research on solar cells has attracted a great deal of interest within the scientific community. Similarly, there is a growing interest to develop new systems/devices for energy storage. In particular, energy storage via capacitors, precisely *via* supercapacitors, has stimulated research efforts in the area of electrochemical energy production. Systems for electrochemical energy storage and conversion include batteries, fuel cells and electric double layer capacitors (EDLCs). Although the energy storage and the conversion mechanisms are different, there are "electrochemical similarities" of these three systems [2].

Electric double layer capacitors, also known as supercapacitors or ultracapacitors, have tremendous potential as high energy high power sources for use in low weight hybrid systems [3-5]. Commercial applications for such devices include uninterruptible power applications, telecommunication and transportation. The total energy stored in a conventional capacitor is proportional to both the number of charges stored and the potential between the plates. Essentially the former is a function of the size of the electrode while the later is determined by the breakdown of dielectric between the plates. Different voltages, hence energy stored, can be generated when different dielectric materials are used to separate the plates. Materials can be optimized to produce high energy densities for a given size of a capacitor. In contrast to conventional capacitors, supercapacitors do not have a conventional dielectric. Instead, two layers of the same substrate and their electrical properties are used in order to effectively separate the charges despite vanishingly thin (on the order of nanometer) physical separation of the layers. Higher energy storage density can be achieved in supercapacitors when nano-materials or materials with nanoporous structure are used because such materials offer enormous surface to volume ratio [6].

Undoubtedly the Si based p-n homojunction solar cells invented in 1941 [7] and developed later by many workers [7, 8] are the most efficient photovoltaic devices to date. Mostly benefiting from the advances in the semiconductor industry, the Si based photovoltaic devices are currently fabricated and have now reached efficiency as high as its theoretical limit [9]. However, the economically intractable production cost of Si based photovoltaic devices has restricted their application in large scale. In the past three decades, a great deal of work has been carried out in the field of cost-effective alternative solar energy generation sources. In particular, sensitized nanostructures based solar cells [10-12] have been the main focus area of research. Commonly referred to as "bulk" junctions or mesoscopic injection or exitonic solar cells, they are formed, for example, from nanocrystalline inorganic oxides, ionic liquids, organic hole conductors or conducting polymer devices. As a result of the use of cost-effective routes and materials in their fabrication process, they offer prospects of low cost fabrication without expensive and energy intensive high temperature high vacuum processes. They can credibly be produced employing flexible substrates and are compatible with a variety of embodiments and appearances to facilitate market entry, both for use in domestic devices as well as in architectural or decorative devices. The mesoscopic injection solar cells operate in an entirely different fashion than conventional Si based p-n homo-junction devices. Mimicking the principles of natural photosynthesis that nature has used successfully over the past 3.5 billion years in solar energy conversion [13], they achieve the separation of light harvesting and charge carrier transport. This unique feature distinguishes them from conventional p-n junction devices where both functions are assumed simultaneously imposing stringent conditions for purity and entailing high materials and production cost.

2. Principles, materials, methods and device fabrication.

In a typical sensitized nanostructures based solar cell, a photo-stable high band gap semiconductor (e.g., TiO_2) is used as the electron harvesting component. By following a well established sol-gel route, a colloidal solution of the semiconductor is first prepared and subsequently deposited after concentrating on a transparent conducting tin oxide (CTO) glass using "doctor blade" technique. Then the film is sintered in an air at 450 ^{0}C in order to create a network of interconnected nanostructures on the electrode. As such nanostructure network generates a high surface/volume to ratio, the photoactive surface area of the electrode become much higher than the geometrical surface area. Larger the photoactive area higher the light absorption cross section and hence the photocurrent. As the high-band gap materials are not sensitive to the visible spectrum, the spectral response of the high-band gap materials are extended to the visible region by using either inorganic (e.g., quantum dots QDs) or organo-metallic (metal-organic based dyes such as the N3 dye) dyes. Here it is essential that we select the dye materials whose light absorption properties are in line with the light emission properties of the Sun. In practice, the dye is anchored to the surface of the semiconductor via a solution based deposition process after which the dye is electronically coupled with the semiconductor. A thin layer of electrolyte containing a redox couple (e.g, I^-/I_3^- redox couple) is sandwiched between the semiconductor and a counter electrode. The counter electrode is usually a conducting tin oxide substrate deposited with Pt islets which is also transparent. The Pt islets deposited on CTO substrate catalyze the electron transfer from the electrode to the one half of the redox couple completing the charge cycle in a short circuit conditions.

However, the presence of a liquid electrolyte to shuttle charge carriers between the two electrodes in this cell has disadvantage that the liquid electrolyte vaporizes due to heat generated in the cell when under constant illumination. In addition, it is not possible to seal the two electrodes effectively as a result of the presence of the liquid electrolyte. These two problems were long standing problems in the field of sensitized nanostructures based solar cells until a group of Sri Lankan scientists (one of the authors (ARK) in this paper involved in this work) who were actively working in the field finds a solution in 1995 [14]. A solid p-type hole transport inorganic material was found to behave in a manner similar to the liquid electrolyte used in the cell paving the way of replacing the liquid in the cell. This was a significant finding in the field as it contained all the necessary ingredients to develop a fully solid state dye-sensitized solar cell by introducing a change to the state of the medium present in the cell. In terms of practical application, the solid form is the “only possible form” for a solar cell. The hole transport material, an inorganic metal halide, Copper (1) iodide, CuI, is a high band gap p-type semiconductor. One of the interesting features of this material is being able to deposit it on the dye coated nanocrystalline surface at an elevated temperature without denaturing the delicate monolyer of the dye. When the hole transport materials is deposited on n-TiO_2 coated with Ru metal based dye, a new type of structure is created where a monolayer of light absorbing material is sandwiched between n-type and p-type high bad gap semiconductor materials. Technically, a hetero-junction is formed consisting of n-TiO_2/dye/p-CuI, the behavior of which is entirely different to that in Si based p-n junction solar cells (i.e., in terms of charge carrier generation and separation). The fascinating feature of such hetero-junction interfaces is the discontinuity of the local band structure at the interface which originates as a result of the bringing of two dissimilar semiconductors with different carrier concentrations in contact [15]. Associated to this intriguing feature, hetero-junction interfaces exhibit interesting and useful electronic properties which are functional in solar cells. Similar to the liquid state solar cells, the organo-metallic dye chemically bonded to the n-type nanostructure via an electronic coupling absorbs photons from the incident light and nanostructure harvests the electrons in solid state dye-sensitized solar cells. However it should be mentioned here that the recent investigation carried out by one of the authors (ARK) at this interface using high flux X-ray absorption techniques at ELETTRA, Synchrotron, Trieste, Italy is seemed to suggest that the N3 dye not only bonds (via carboxylate ligands, -Ti-O-C-) with n-type nanostructured TiO_2 but also with p-type CuI (via Cu-N bond). This envisages the possibility that the dye forms a molecular level bridge between the n-TiO_2 and the p-CuI which could possibly act as a conduit for charge transfer. Nevertheless further studies are needed to evaluate the strength of each bond in order to determine whether the formation of –Cu-N- bond breaks the most important –Ti-O-C- bond as it has been speculated that the –Cu-N- may have an influence on the stability of the –Ti-O-C- bond which is the primary charge transfer channel.

Following the injection of the carriers into the bands, the positive charge left behind in the ground state of the dye is rapidly scavenged by the p-type solid hole transport (HTM) material creating a photocurrent in the cell. The open circuit photovoltage of the cell is determined by the difference in work functions between n-TiO_2 and p-CuI which is over 1eV according to the interface band energy diagram [16]. The sensitized nanostructures based solid state solar cells (i.e., n-semi/dye/p-semi) have shown a remarkable progress since its invention [17] and the progress continues [18].

Solar cells generate energy. Once the energy is generated, there should be a way to store it in order to use it later as required. An attractive way of storing energy lies at the heart of electrochemical energy storage methods. Electrochemical energy storage includes batteries, fuel cells and super-capacitors. Out of these possible routes, supercapacitors or EDLCs has surpassed other devices because they can release burst of stored energy when the need arises. Many electronic devices such as laptops, memory backups, mobiles and communication systems require a burst of energy to start up. A German physicist, Hermann von Helmholtz, first described the concept of EDLC in 1853 [19]. Well over 100 years later, in 1957 General Electric (GE) first patented [20] electrochemical capacitor based on the double-layer capacitance structure. Since then, the field of EDLCs has shown an enormous growth to date. The operating principle of supercapacitors is simple and easy to fabricate.

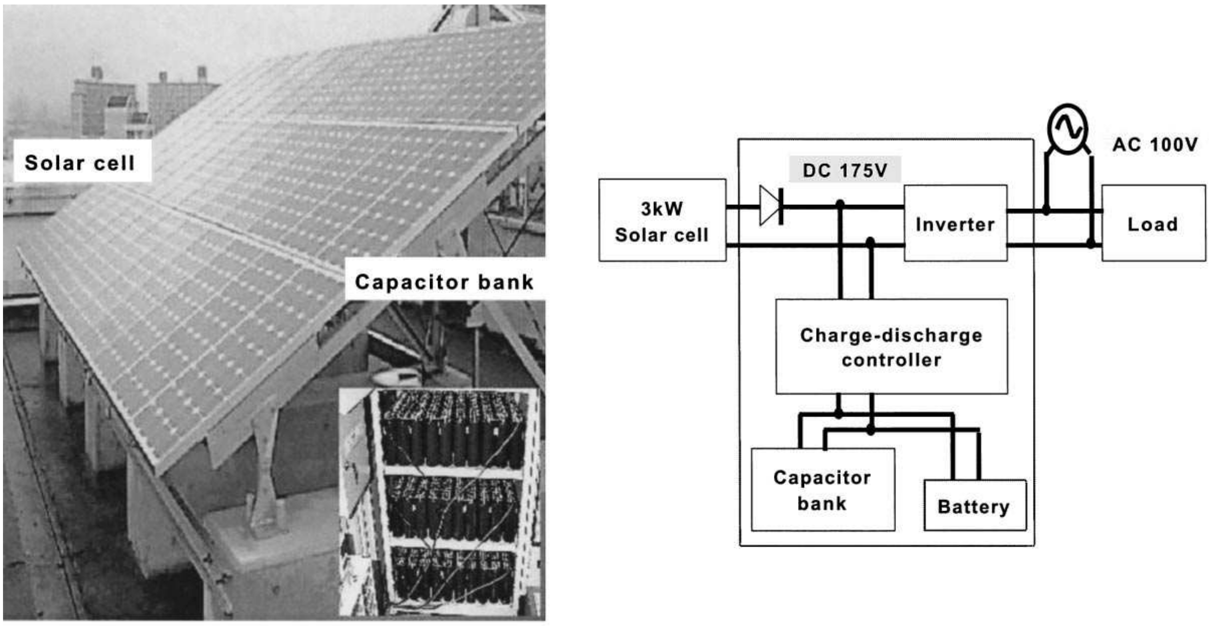
3. Sri Lankan perspectives.

The electrical properties of a super capacitor are determined by the selection of electrode material. Double-layer-charge-storage is a surface process and the surface characteristics greatly influence the capacitance of the cell [21]. Various materials are being used as electrode materials, for example carbon, metal oxides, conducting polymers, hybrid and conducting polymers etc [21]. Carbon has been utilized as high-surface area electrode material ever since the development of double layer capacitor began. Today it is still an attractive material because of its low coat, availability and the long history of use (ref). Carbon electrode can take a number of manufactured forms such as foams, fibers and nanotubes. The use of activated carbon in EDLCs is well established due to its high surface area, e.g., up to 2000 m^2/g. Capacitance up to 5000 F [3] has been reported from commercially available super capacitors produced in USA, Japan and Korea. Research into further develop current numbers using new materials, for example carbon nanotube, are continuing and gaining significant momentum. Besides, dye-sensitized solar cells that use nanocrystalline TiO_2 as the electron harvesting electrode have achieved a remarkable success since its inception. Efficiencies as high as 11.4 % [23] has been achieved with newly developed, thermally stable dyes.

From the point of view of the availability of materials used in these devices, Sri Lanka shows a great promise. The world best coconut shell based activated carbon is produced in SL which can with no doubt go in to develop EDLCs. Vein graphite, one of the naturally occurring forms of graphite which is available only in Sri Lanka in commercial levels is a very good source for making carbon nanotubes to the best of the knowledge of the authors. The vein graphite is also a good resource for making graphite oxide which can be used in nanocomposites, or perhaps even to synthesis the "next generation wonder material graphene" which is expected to be revolutionized the entire electronic industry as Si is reaching its fundamental limits. The significance of graphene has recently been perceived by awarding the highest scientific accolade, the Nobel Prize, for physicists who invented the materials. Moreover, SL has naturally occurring ilmanite ($FeTiO_2$) deposit which can be used to extract titanium dioxide, TiO_2. Credible methodologies have been developed by Sri Lankan scientists who are working in SLINTEC science team at present to convert ilmanite into TiO_2 and then to nano-TiO_2. The use of nano-TiO_2 is multifaceted which includes solar cells, self-cleaning windows, smart clothing, paints, cosmetics, catalysis and many more. Therefore, building a sustainable environment with smart energy systems developed using nanomaterials available in SL is a promising target that has a long range benefits to the Sri Lankan economy.

4. Conclusion

The building environment consumes huge fraction of energy produced in any social system. Therefore the significance of a sustainable built environment in terms of energy is invaluable and scientific and administrative efforts aimed at achieving such an environment should be recognized as a priority issue. The potential of nanotechnology to answer world's current and future burning issues (energy crisis one of them) is great and the scale that one can use the nanotechnology based products spans across a wide a spectrum. When the materials required to develop nanotechnology based devices are liberally available/or the raw materials that can be used to extract such materials are available, the journey to achieve the targets set out in a sustainable built environment is becoming more quicker, easier and also is cost effective. Therefore to build a sustainable built environment, nanomaterials available in Sri Lanka can contribute in a substantial and innovative way. Finally the inquisitive nature of mankind has invented many novel things/methodologies devices in the world up to its development and the quest continues.



(a) Appearance of the system **(b) Construction of the system**

Photo and schematic diagram showing how solar cells and EDLCs could be used in a building environment (Ref. J. Power Sources, 97-98, 2001, 807-811)

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MONTMORILLONITE CLAY NANO PARTCLE EMBEDDED NANO FIBERS FOR UV PROTECTED CURTAINS TO BE USED IN SMART HOUSE WITH NANO TECHNOLOGY

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Abstract: Montmorillonite clay nano particle possess electrical properties, heat, chemical resistance and has the ability of blocking UV light. By reinforcing this clay nano particles to composite fibers will give rise to specific properties such as UV blocking, flame retardant and anti-corrosive behaviors. Electro spinning technology has the ability to produce nano fiber composites containing Montmorillonite nano particles which can be used to produce non woven fabrics or yarns with properties of UV blocking and flame retardant. This nano scale modification to the composite will give rise the ability to extract the improved performance on the end product. Fabrics or nonwovens developed from nano fibers which contain the anti UV and flame retardant properties are more durable and efficient than fabrics coated with anti UV or flame retardant agents. This research was focused on analyzing the UV blocking property of sodium- montmorillonite from Southern Clay, USA and purified clay from Sri Lanka. Testing was carried out to compare and contrast the UV blocking property of Na-MMT and Sri Lankan clay (SL Clay) in powder and liquid form. This research study will also focus in future on extruding Nano fiber composite by mixing the Montmorillonite clay nano particle with polyacrylonitrile (PAN) polymer via electro spinning technology. With the developments of extracting nano clay from Sri Lankan resources will lead to a more efficient and cost effective product to be used in smart houses.

Key words: Electro spinning, Montmorillonite, clay, nanotechnology, nano fiber, Photo catalysis

1. Introduction

1.1 Clay nano particles and its applications on textiles.

Clay nano particles or nano flakes are composed of several anhydrous aluminosilicates. Each type differs in chemical composition and crystal structure. Nano particles of Montmorillonite one of the commonly used clay, have been applied as UV blocker in Nylon composite fibers. The mechanical properties with a clay mass fraction of only 5% exhibit a 40% higher tensile strength, 68% greater tensile modulus, 60% high flexural modulus. In addition, the heat distortion temperature (HDT) increased from 65^{0}C to 152^{0}C. Nano size clay flakes can be arranged densely and alternately than the therefore, the composite material has barrier performance to chemicals or other harmful species [1].

Another function of clay nano particles is to introduce dye attracting sites and creating dye holding space in polypropylene (PP) fibers known as non- dyeable fibers due to its structural compactness and lack of dye attracting sites. Nano particles of montmorillonite modified with quaternary ammonia salt and then mixed with PP before it is extruded at 5% on weight of fiber can lead the non dyeable fiber colored by acid and disperse dye [2]. The improvement of the UV barrier properties of textile fibers with solid nano particles incorporated into the matrix of the PP fibers also requires them to be environmentally durable in their processing and utilization. Photo and thermal degradation, especially of PP nano composites and composite fibers, has been a very attractive area of research in recent years [3-5]. Clay minerals are popular inorganic fillers for the preparation of organic/inorganic nano composites due to their high aspect ratio and good physical properties. For instance, nylon-6/clay nano composite containing just 4.7 *wt*. % of montmorillonite (MMT) exhibited superior mechanical and thermal properties in comparison with pristine nylon-6 [6]. It is also demonstrated that polymeric nano composites containing relatively low amount of clay fillers may exhibit good performance in thermal properties [7], gas permeability and mechanical properties [8]. However, dispersion of clays in polymer matrix is always the key issue. The difficulties such as the hydrophilic features of clays, high van der Waals force between clay lamellae and incompatibility between clays and hydrophobic polymers have to be solved in order to secure satisfactory physical properties of nano composites.

1.2 Sodium Montmorillonite.

The clay known as montmorillonite consists of platelets with an inner octahedral layer sandwiched between two silicate tetrahedral layers [9] as illustrated in Fig. 1.

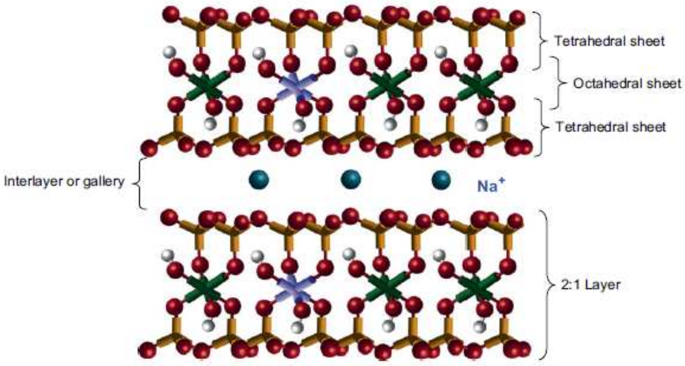

Fig .1: Structure of sodium montmorillonite [10].

The octahedral layer may be thought of as an aluminum oxide sheet where some of the aluminum atoms have been replaced with magnesium; the difference in valences of Al and Mg creates negative charges distributed within the plane of the platelets that are balanced by positive counter ions, typically sodium ions, located between the platelets or in the galleries as shown in Fig. 1. In its natural state, this clay exists as stacks of many platelets. Hydration of the sodium ions causes the galleries to expand and the clay to swell; indeed, these platelets can be fully dispersed in water. The sodium ions can be exchanged with organic cations, such as those from an ammonium salt, to form an organoclay [11-14]. The ammonium cation may have hydrocarbon tails and other groups attached and is referred to as a ‘‘surfactant’’ owing to its amphiphilic nature. The extent of the negative charge of the clay is characterized by the cation exchange capacity, i.e., CEC. The X-ray d-spacing of completely dry sodium montmorillonite is 0.96 nm while the platelet itself is about 0.94 nm thick [11-14]. When the sodium is replaced with much larger organic surfactants, the gallery expands and the X-ray d-spacing may increase by as much as 2 to 3-fold [11].

Ultraviolet rays constitute a very low fraction in the solar spectrum but influence all living organisms and their metabolisms. These radiations can cause a range of effects from simple tanning to highly malignant skin cancers, if unprotected. Sunscreen lotions, clothing and shade structures provide protection from the deleterious effects of ultraviolet radiations. Alterations in the construction parameters of fabrics with appropriate light absorbers and suitable finishing methods can be employed as UV protection fabrics [15].

1.3 Ultraviolet Protection Factor and textiles.

The Ultraviolet Protection Factor (UPF) rating system measures the UV protection provided by textiles. It is very similar to the SPF (Sun Protection Factor) rating system used for sunscreens. A textile with a UPF of 50 only allows 1/50th of the UV radiation falling on the surface of the garment to pass through it. In other words, it blocks 49/50ths or 98% of the UV radiation [16].

The UV radiation of sunlight can be divided into UV-C (100 – 280 nm), UV-B (280 – 315 nm) and UV–A (315–400 nm) components, which denote the effect on living organisms. The human skin has to be protected against UV–B type radiation only, while the most dangerous UV-C type is absorbed by the atmosphere. UV-A radiation is essentially less dangerous than the other two [17]. UV transmittance by textiles consists of both contributions which are transmission through the space between yarns and transmission through fibers. The UPF is affected mainly by the thickness and density of textiles, as well as by dyes, pigments and other compounds in fibers and textiles, such as pectin, wax, water, etc. [18]. Fabric construction is affected by both the fineness and density of the yarn in the warp and weft. Furthermore, the transmission of UV radiation through fibers can be changed by the absorption and reflection of ultraviolet beams. The mass pigmentation of fibers with suitable inorganic pigments, carbon black pigment, or inorganic (nano) filler may provide a permanent improvement of the UV protection of fibers with high fastness in washing [17].

In textiles, UPF is strongly dependent on the chemical structure of the fibers. The nature of the fibers influences the UPFs as they vary in UV transparency [19]. Natural fibers like cotton, silk, and wool have lower degree UVR absorption than synthetic fibers such as PET. Cotton fabric in a grey state provides a higher UPF because the natural pigments, pectin, and waxes act as UV absorbers, while bleached fabrics yields poor UPF (high UV transparency). Raw natural fibers like linen and hemp possess a UPF of 20 and 10 to 15 respectively, and are not perfect UV protectors even with high lignin content. However, the strong absorption of jute is due to the presence of lignin, which acts as a natural absorber. Protein fibers also have mixed effects in allowing UV radiation. Dyed cotton fabrics show higher UPF, and un-dyed, bleached cotton yields very poor UPF values. Wool absorbs strongly in the region of 280 – 400 nm and even beyond 400 nm. Exposure to sunlight damages the quality of silk's color, strength and resiliency in both dry and wet conditions. Mulberry silk is deteriorated to a greater extent than muga silk. Polyester fibers absorb more in the UV-A & UV-B regions than aliphatic polyamide fibers. Bleached silk and bleached PAN show very low UPFs of 9.4 and 3.9 respectively [19].

This research work focus on measuring the UV blocking property of two different types of clay. To measure the UV blocking a simple test has been done with the intension of carrying out a standard UV blocking property measurement for textiles. A Bromothymol blue (BTB) solution was used as a simple indicator with a standard color which at different acid, basic and neutral medium. Zinc Oxide (ZnO) was mixed in a known concentration of BTB solution. Upon exposure to UV light it has been observed that the color of the solution has been totally reduced due to the photo catalytic effect of ZnO. The reduction of color in the BTB solution was due to the degradation of color particles in the solution. The same phenomenon has been used during the study of UV blocking property of clay from Sri Lankan resources and Na-MMT from USA. The BTB/ZnO solution has been screened by the two different types of clay nano particles and BTB/ZnO solution has been analyzed to measure the reduction in the concentration of the color to compare and contrast the UV blocking property of Na-MMT and SL Clay.

2. Materials and sample preparation method:

Na- MMT from southern clay, USA and purified clay from Sri Lanka have been used as the 2 types of main filler materials and commercially available UV blocker which uses in textile applications have been characterized to examine and compare the UV blocking properties of each. Na- MMT and clay from Sri Lankan resources have been dissolved in distilled water to get a uniform dispersion of the clay solution. For the solution preparations two clay samples were mixed with distilled water at a concentration of 1g/1000ml stirred at a rate of 300 rpm under room temperature of 26^0C for 30 minutes to get a uniform dispersion in the solution. The two clay solution and the commercially available UV blocker samples have been tested using UV-VIS-NIR Spectrophotometer to analyze the absorbance. Results obtained for this experiment is discussed using figure 3 in results and discussion section.

To analyze the UV blocking property of clay filler before applying to nano fiber composite a simple experiment has been carried out. A solution of 0.0025M of BTB was prepared, 10ml of 0.0025M BTB has been mixed with 0.2g of ZnO. The samples have been prepared as shown in figure 2 and Table 1. A controlled sample of BTB and ZnO has been maintained without exposure to UV light for comparison purpose. After the exposure to UV light ZnO in each solution was removed using centrifuge method. Absorbance of each samples were measured using UV-VIS-NIR spectrophotometer to compare the UV blocking property of clay. Results obtained for this experiment is discussed using figure 4.

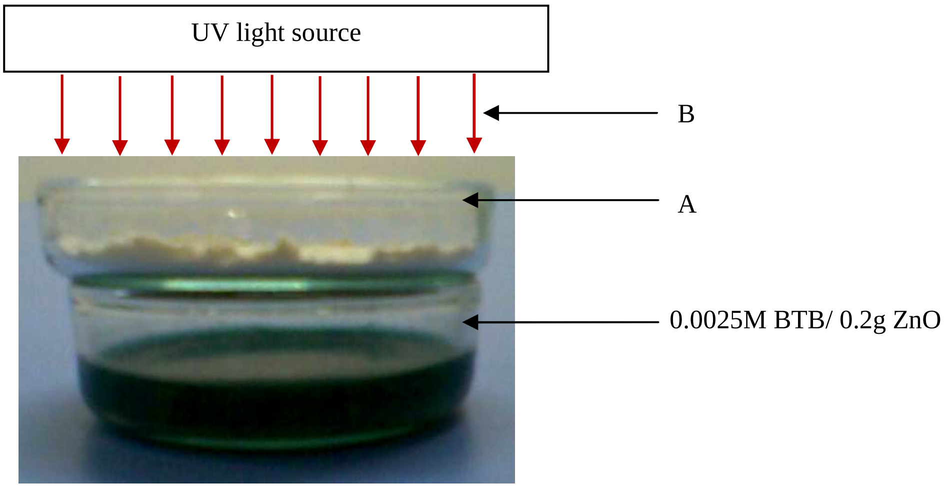

Fig.2: Sample setup for testing

Table 1: *Sample description*

Sample name	A	B
Sample 1	No	No
Sample 2	Na-MMT 1g/1000ml in liquid form to cover the BTB/ZnO solution	UV on for 20 minutes
Sample 3	Na-MMT in solid form to cover the BTB/ZnO solution	UV on for 20 minutes
Sample 4	SL Clay 1g/1000ml in liquid form to cover the BTB/ZnO solution	UV on for 20 minutes
Sample 5	SL clay in solid form to cover the BTB/ZnO solution	UV on for 20 minutes
Sample 6	No	UV on for 20 minutes

3. Results and discussion:

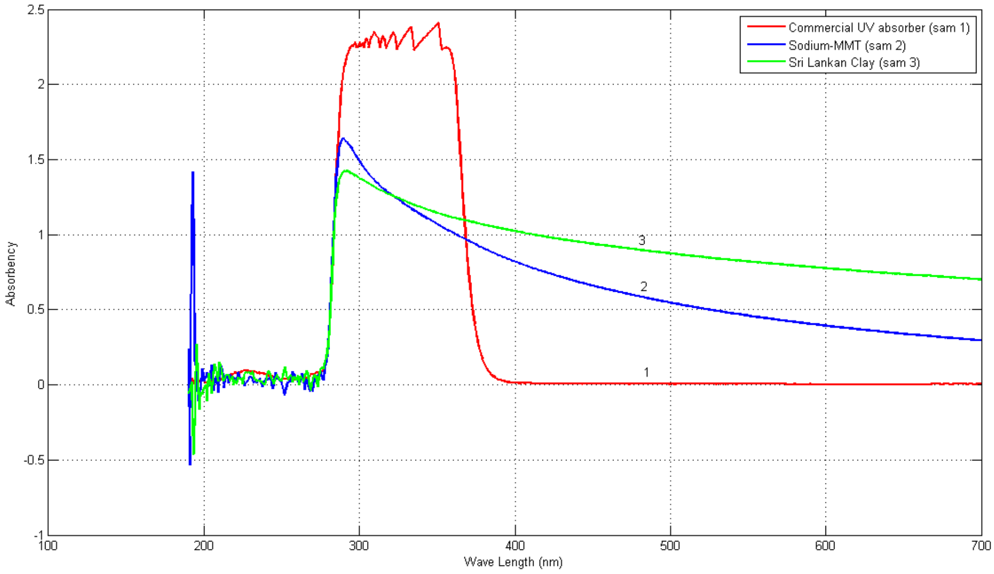

Fig .3: Absorbance behavior of MMT, SL Clay and commercial UV blocker

The benchmark commercial sample shows a very good UV blocking where the absorbance is at the highest level within wavelength range of 272-356 nm (UV- B & UV- A). Commercial UV blocker, Na-MMT, and SL clay shows 2.245, 1.638 and 1.43 absorbance values at 290 nm wave length respectively. Hence compared to Commercial UV blocker Na-MMT showed 27% less UV absorbency while SL clay showed only 36% less.

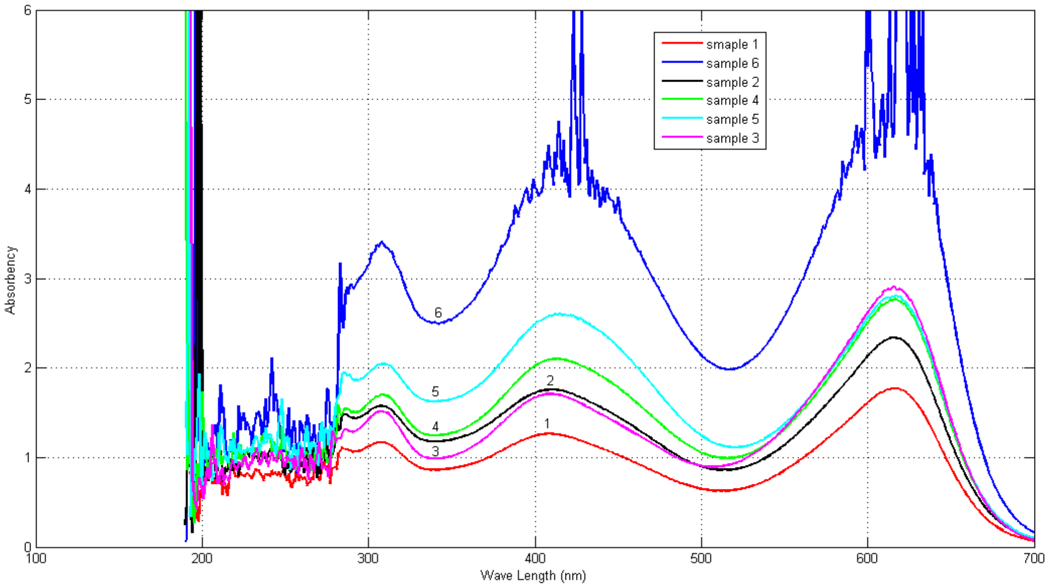

Fig .4: UV blocking behavior of Na-MMT and SL Clay in powder and liquid form

Sample 1 which has been fully exposed to UV showed the minimum absorbance due to the degradation of color concentration due to photo catalytic effect of ZnO. In contrast sample 6 which have not been exposed to UV and were under controlled condition showed the highest absorbency. Compared to control sample 6, samples 2&3 showed least absorbance (less concentration of color) while samples 4&5 showed a better absorbance values than samples 2&3, which lead to the conclusion of SL clay either in powder form or in liquid form has a comparatively higher capability of UV blocking than Na-MMT. Also the results imply that clay particles in solid form shows a good UV blocking compared to clay particles in liquid form.

4. Conclusion:

Purified Sri Lankan Clay particles shows a better UV blocking compared to Na-MMT from southern clay USA. Also this research work will be extended to spin PAN/Clay nano fiber composite to study the UV blocking property of Sri Lankan clay when used in fiber nano composites. Also standard testing for UPF (ultra violet protection factor) will be done for these fiber nano composite to measure the UV blocking property of these.

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