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

Sarasanantham, P.[1], Tissera, P.N.[2], Wijesena, R.[2],Karunanayaka, L.[2],

[1] MAS Research & Innovation (Pvt) Ltd, Lot 14, Zone(1), Biyagama Export Processing Zone, Sri Lanka.
E-mail: prageeths@masholdings.com (Sarasanantham P.)
Tel.: +94 -11-4650526 ; Fax: + 94-11-4768010

[2] NANCO (Pvt) Ltd., Lot 14, Zone(1), Biyagama Export Processing Zone, Sri Lanka.E-mail: nadeekat@susnanotec.lk (Tissera P.N.), : wijesenar@gmail.com (Wijesena R.), laleenk@susnanotec.lk (Dr. Laleen karunanayaka)
Tel.: +94 -11-4650500 ; Fax: + 94-11- 4741995

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 65^0C to 152^0C. 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.

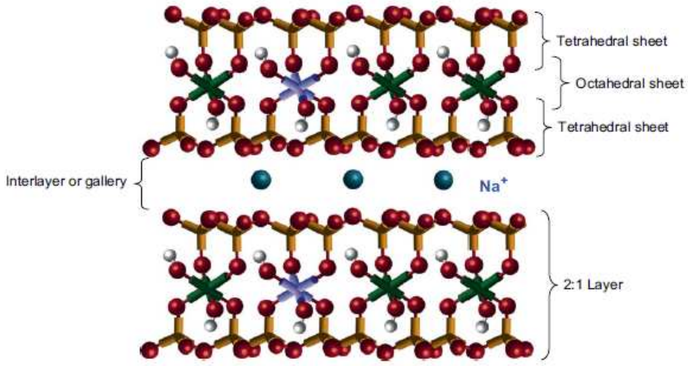

Fig .1: Structure of sodium montmorillonite [10].

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.

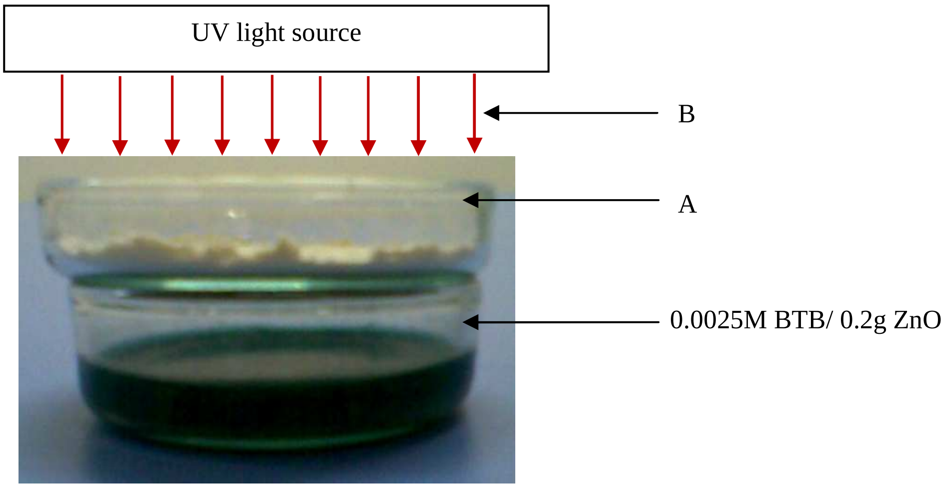

Fig.2: Sample setup for testing

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:

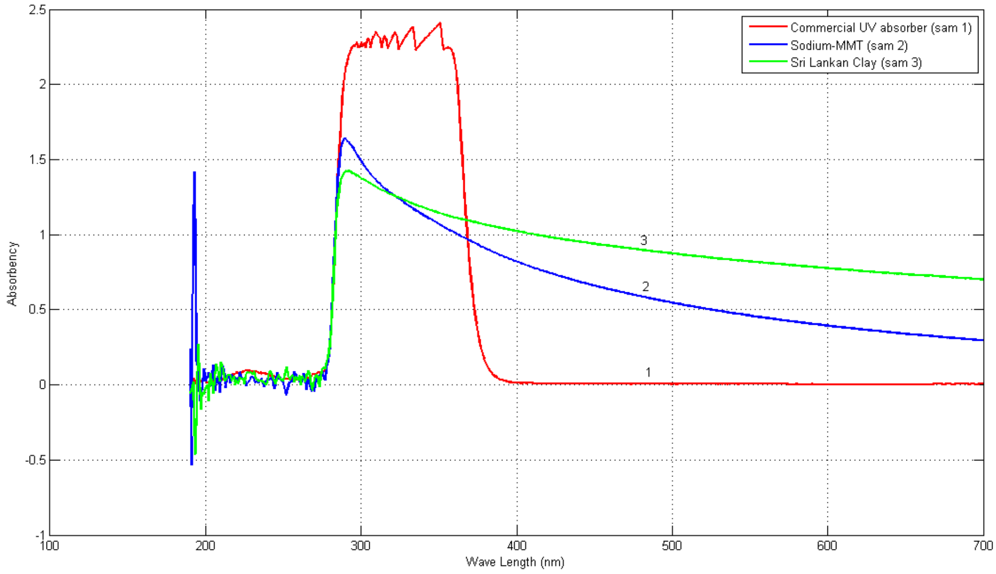

Fig .3: Absorbance behavior of MMT, SL Clay and commercial UV blocker

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.

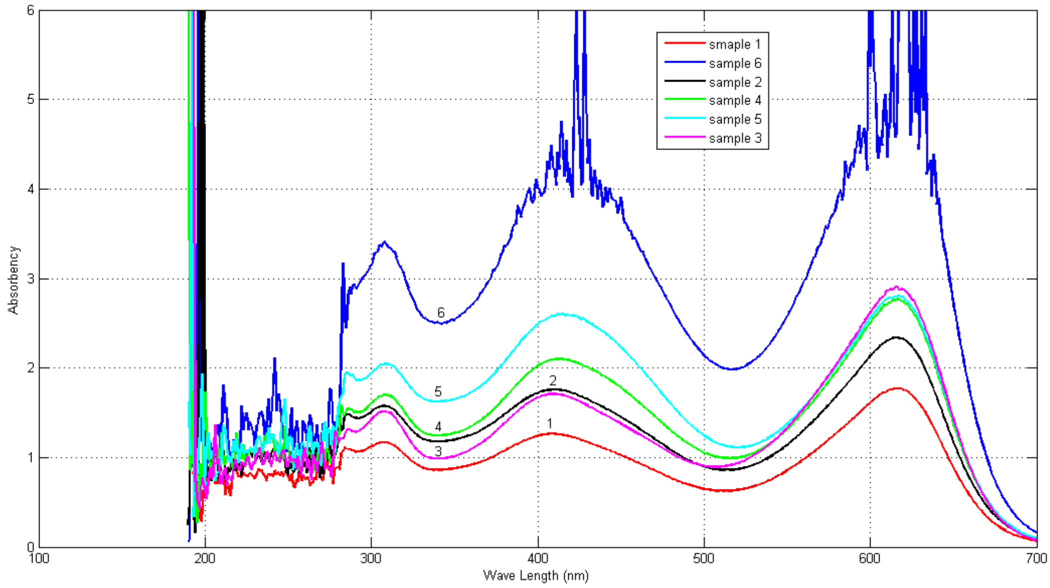

Fig .4: UV blocking behavior of Na-MMT and SL Clay in powder and liquid form

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.

References

[1] Qian L, Juan P. Application of nano technology for high performance textiles, Journal of textile and apparel, volume 4, issue 1, summer 2004.

[2] P. Hinestroza, Journal of textile and apparel technology and management, volume 4, issue 1 summer 2004.

[3] B. Mailhot, S. Morlat, et al, Photodegradation of polypropylene nano composites, Polymer Degradation and stability 82 (2003) pp. 163-167.

[4] H.Qin, S.Zhang, et al, Photo-oxidative degradation of polypropylene/ montmorillonite nano composites, Polymer 46 (2005) pp. 3149-3156.
[5] M. Diagne, M. Gueye, et al, Thermal stability and fire retardant performance of photo-oxidized nanocomposites of polypropylene-graft-maleic anhydride/ clay, Polymer Degradation and stability 89 (2005) pp. 418-426.
[6] Kojima Y.et al. Mechanical properties of nylon 6- clay hybrid. J. Mater. Res, 8(1993) 1185-1189.
[7] Golebiewski J., Galeski A. Thermal stability of nano clay polypropylene composites by simultaneous DSC and TGA. Compos. Sci. Technol., 67(2007) 3442-3447.
[8] K. Hoffmann, K. Kaspar, T. Gambichler, P. Altmeyer, In vitro and in vivo determination of the UV protection factor for lightweight cotton and viscose summer fabrics: A preliminary study, J. Am. Academy of Dermatology 43 (2000) pp. 1009-1016.
[9] H. Van Olphen, An introduction to clay colloid chemistry. New York: Interscience; 1963.
[10] Paul D.R, Robeson L.M, Polymer nano technology:nano composite, Polymer 49 (2008) 3187–3204
[11] P.C Lebaron, Z. Wang, T.J Pinnavaia. Appl Clay Sci 1999; 15: 11–29.
[12] T.J Pinnavaia, G.W Beall. Polymer–clay nano composites. New York: John Wiley & Sons; 2000.
[13] S Yariv, H Cross. Organo-clay complexes and interactions. New York: Marcel Dekker; 2002.
[14] Y Mai, Z Yu. Polymer nano composites. Cambridge: Woodhead; 2006.
[15] Saravanan D, UV protection textile materials, AUTEX Research Journal, Vol. 7, No 1, March 2007.
[16] http://www.coolibar.com/upf-ratings.html. Retrieved on 23rd October 2010.
[17] D. Hanke, K. Hoffman, A. Altmeyer, et al., UV Protection by Textiles, Chemical Fiber International 47 (1997) pp. 130-131.
[18] F. Palacin, Textile finishing protects against UV rays, Textilveredlung 31 (1996) pp. 235-238.
[19] Saravanan D, UV protection textile materials, AUTEX Research Journal, Vol. 7, No 1, March 2007.

Acknowledgements:

The nanoclay research team at SLINTEC in providing with purified SL Clay samples to carry out the testing for this study.