Studies on the Effect of mono-alkoxy pyrophophato coupling agent on the Mechanical Properties of Magnesium hydroxide Filled HDPE/Mg$(OH)_2$/TCA - 114 Composites.

Dr. Nabil Abdullah Noman Alkadasi

Abstract:

Effect of treatment of mono-alkoxy pyrophophato coupling agent on mechanical properties of composites made from High Density Polyethylene and Magnesium hydroxide is reported here. The coupling agent in the form of solution (1.5%) was used for treatment of the filler. The treatment resulted in enhancement of mechanical properties of composites when compared with composites containing untreated Magnesium hydroxide. The properties under consideration were tensile strength, modulus at (%) elongation at break, elastic modulus, hardness, etc. Although good reinforcement was observed due to treatment of 1.5% coupling agent, observed was very much remarkable to compared to untreated one. Comparison of properties of composites filled with treated and untreated Magnesium hydroxide established that treatment of Magnesium hydroxide imparts better reinforcing properties. The properties under consideration were tensile strength, (%) elongation at break , elastic modulus, hardness, etc. Tensile strength was improved by 21.43%, elastic modulus was improved by 71.53%, while hardness was improved by 1.01%, at (0.37) volume fraction .

Keywords: Titanate Coupling Agent , Mechanical Properties of Magnesium hydroxide , HDPE/Mg(OH)2/TCA-114 .

Introduction:

Magnesium hydroxide is a low cost inorganic filler used extensively in rubbers and plastics . Although it is economic it does not contribute to reinforce the composites and there are severe limitations on its use. In our efforts to find out economical and yet reinforcing filler a study was undertaken on Magnesium hydroxide earlier. Magnesium hydroxide was treated with various percentage of Titanate coupling agents and was incorporated in High Density Polyethylene [1,4] . Since coupling agents work as molecular bridges at the interface between two dissimilar substrates, it was reasoned that the treatment of coupling agents would convert an ordinary filler into a value added one. The results were quite encouraging and hence the study has been continued for Magnesium hydroxide. In the present work Magnesium hydroxide was treated with Titanate coupling agents (1.5 grams solution) for 100 gram (wt) of [5,8] Magnesium hydroxide. The treated filler (in various percentages) was incorporated in High Density Polyethylene using a melt compounding at 160°C in

ThermoHaake rheomixer with a rotation speed of 60 rpm, and the mixing time is 6 min for each sample. Finally the composites were moulded in sheets form using compression moulding technique at 180^0C. Properties under consideration were tensile strength, elongations, hardness, etc. Comparisons of magnitudes of property reveal that the treatment had a favorable effect on properties of composites. Tensile strength was improved by 21.43%, elastic modulus was improved by 71.53%, while hardness was improved by 1.01%, at (0.37) volume fraction.

Experimental:

Materials:

High-density polyethylene (HDPE, 5502, MFR = 0.35g / 10 min) was from Daelim, Korea. The filler magnesium hydroxide ($Mg(OH)_2$, average particle size=2µm) was obtained from Dalian Yatai Science and Technology New Material Co.Ltd., China, Titanate coupling agent [(TCA114)] was obtained from Anhui Tianchang Organic Chemical Plant is the organotitanium pilot base of Shanghai Institute of Organic Chemistry.

Physical parameters of High Density Polyethylene , titanate coupling agent and constituents of Magnesium oxide are reported in table 1, 2 and 3 respectively.

Table 1. General Characteristics of High Density Polyethylene .

Trade Name	HDPE, 5502 **,** Daelim, Korea
Appearance	White
Specific Gravity (g/cm^3)	0.96
Melt index (g/10 min)	0.05-0.8

Table 2.Physical characterization of Titanate coupling agents (TCA-114)

Chemical Name	mono-alkoxy pyrophophato coupling agent
Typical purity (%)	99
Physical form	Liquid
Color	light yellow viscous liquid
Density	(GB4472-84) D30 About 1.03g/cm3
Flash point (^{0}c)	(GB37-77)open 50
Refractive index	(GB6428-86)ND30 About 1.45
Viscosity (cp)	(GB265-70) 30 About 300mm/s
pH	3
Solubility	Isopropyl alcohol, xylene, Toluene, DOP, Mineral oil, MEK .

Table 3 . General Properties of Magnesium hydroxide .

Name	Magnesium hydroxide
Molecular formula	Mg(OH)
Molar mass (g/mol)	58.33
Appearance	White solid
Melting point (°C)	Decomposes at 623 K (350 °C)
Density (g/cm^3)	2.4
Solubility (g)	0.0012 g in 100 g water
pH	6.5-7

Treatment on Magnesium hydroxide by Titanate Coupling Agent

The coupling agent (1.5g) was mixed [6-14] with isopropyl alcohol (100 ml) to make a solution for applying to filler (100 g) . 1.5 grams of coupling agent was used per 100g of Magnesium hydroxide . The filler (Magnesium hydroxide) was mixed with the solution of coupling agent in isopropyl alcohol with stirring to ensure uniform distribution of the coupling agent, mixing was continued for 30 minutes. The treated filler (Magnesium hydroxide) was then dried at

100 ^{0}C in an oven for about 6 hours to allow complete evaporation of the alcohol.

Preparation of composites:

HDPE/$Mg(OH)_2$/TCA-114 , composites were prepared via melt compounding at 160^{o}C in ThermoHaake rheomixer with a rotation speed of 60 rpm, and the mixing time is 6 min for each sample. The mixed samples were transferred to a mold and preheated at 180^{o}C for 15 min, then pressed at 20MPa and then successively cooled to room temperature while maintaining the pressure to obtain the composites sheets for further measurements. Before mixing, all the components were dried in vacuum oven at 80^{o}C for at least 12 h.

Table 4 . Compounding Recipe For HDPE/$Mg(OH)_2$ /TCA-114 .

Volume fraction	HDPE (Wt – g)	Mg(OH)2 (Wt – g)
0.0	50	0.0
0.04	45	5
0.09	40	10
0.14	35	15
0.21	30	20
0.28	25	25
0.37	20	30

0.48	15	35
Filler (Treated &Untreated)	Variable (0.0 – 0.48 Volume fraction)	
Curing Time (min)	15	
Curing Temp (^{o}C)	180	

Scanning electron microscopy (SEM):

The SEM micrographs of samples were observed by JEOL JSM-5510 scanning electron microscope. The samples are chosen after the tensile test. The content of HDPE/$Mg(OH)_2$ at 0.48 Volume fraction . The surface of the treated and untreated samples was coated with a thin layer of gold to avoid electrostatic charging during examination.

Photographs of representative areas of the sample were taken at 5000X magnifications**.**

Measurement of Mechanical Properties:

Mechanical properties such as tensile strength, elongation at break ,elastic modulus were determined by subjecting dumbbell shaped specimens (in confirmation with ASTM D – 638) to a universal testing machine (Shenzhen Reger Instrument Co. Ltd, China). The sheets from which specimens were cut had been conditioned for 24 hours prior to subjecting to universal testing machine (100 kg load cell), at a crosshead speed of 50 mm/min. Hardness was measured on Machine – LX –A ,produced by Shanghai , Liuzhong meterage , factory.

Results and Discussion:

Treated Magnesium hydroxide composites showed improvement in mechanical properties and the mechanism of adhesion due to titanate coupling agent is proposed for Magnesium hydroxide as filler.

Tensile strength:

The dependence of the tensile strength on volume fraction of magnesium hydroxide is represented in fig 1. It is seen that on increasing the volume fraction of (both treated and untreated) magnesium hydroxide , the tensile strength increases up to a certain value and it declines .The peak values of tensile strength of the composites correspond to 17 MPa and 14 MPa for treated and untreated Magnesium hydroxide composites respectively. It is noteworthy that the tensile strength of composites filled with treated Magnesium hydroxide at 0.37 volume fraction is 1.21 higher than that of untreated Magnesium hydroxide composites.

Elastics Modulus :

Fig 2 shows the dependence of elastics modulus on concentration of treated and untreated filler in HDPE. It is seen that, Elastics Modulus of both treated and untreated $Mg(OH)_2$ -HDPE composite increased linearly on increasing the concentrations of fillers . The elastic modulus of treated magnesium hydroxide at 0.37 volume fraction is about 1.7 times higher than that of untreated magnesium hydroxide .The rate of increment in the property with increasing volume fraction of the filler.

Hardness:

Fig 3 shows the dependence of hardness on concentration of treated and untreated filler in HDPE. It is seen that, hardness of both treated and untreated $Mg(OH)_2$ -HDPE composite increased linearly on increasing the concentrations of fillers, with a constant rate of increment for composites containing treated and untreated filler (separately) as evidenced by constant and identical slopes of the lines (figure 4). The hardness of treated magnesium hydroxide at 0.37 volume fraction is about 1. times higher than that of untreated magnesium hydroxide .The rate of increment in the property with increasing volume fraction of the filler.

SEM of Composites:

The SEM photomicrographs of filler magnesium hydroxide and Titanate coupling agent are shown in plate 1 & 2. It is clear from these photographs that untreated magnesium hydroxide and Titanate coupling agent shows tendency to form agglomerates. SEM of HDPE/$Mg(OH)_2$ /TCA-114 Composites are shown in plates 3 - 5 . Untreated composite fracture shows non -adhesive appearance and formation of agglomerates while treated composites show a very uniform distribution, regular, adhesive appearance indicating further enhancement in polymer–filler attachment.

Conclusions:

The treatment of Magnesium hydroxide with Titanate coupling agent has effected magnitudes of tensile strength and Elastic modulus and Hardness . The filler treatment proved to be beneficial by enhancing polymer – filler adhesion as evidenced by SEM study. Considering the cost of the filler and the improvement in properties, the treatment is advisable.

References:

1. Nabil.A.N.Alkadasi, D.G.Hundiwale, U.R.Kapadi," Effect of Coupling Agent on The Mechanical Properties of Flyash Filled Polybutadiene Rubber" J Appl Poly Sci 91,1322-1328 (2004).

2. Nabil.A.N.Alkadasi, Bhimrao. D. Sarwade, D.G.Hundiwale, U.R.Kapadi, "Studies on Effects silane and titanate coupling agents on the Mechanical Properties of clay Filled Chloroprene Rubber" J Rubber Chem and Review XXXIII, 23-28, Nov-Dec 2003.

3. Nabil.A.N.Alkadasi, D.G.Hundiwale, U.R.Kapadi, "Effect of Bis (3- Triethoxy Silylpropyl) Tetrasulphide (2.0%) on the Mechanical Properties of Flyash Filled Styrene Butadiene Rubber" J Rubber Chem Technol (Accepted Nov-Dec) 2003 .

4. Dr. Nabil .A.N. Alkadasi, " Effects of Silane Coupling Agent on the Mechanical Properties of Talc Filled – Natural Rubber " Rubber Chem. Review, XXXIV, No.5-6 , Jun - Feb. 2005.

5. Salvatore J.Monte,"KEN–REACT " Reference Manual– Titanate, Zirconate and Aluminate Coupling Agents, Publisher American Chemical Society (1995).
6. P.K.Pal and S.K.De ,"Studies of Polymer –Filler Interaction , Network Structure , Physical Properties , and Fracture of Silica and Clay –Filled EPDM Rubber in the presence of a Silane Coupling Agent " ,Rubber Chem Technol 56,736-773 (1983) .
7. S.K. Disawal, D.G.Hundiwale, U.R.Kapadi, " low cost Multichannel DTA Apparatus Specially for Chemical and Pharmaceutical analysis ", AdV.Phar .Tox. 4 (1) 2003,45-49.
8. P.K.Pal. and S.K.De, Studies of Polymer –Filler Interaction, Network Structure, Physical Properties , Filled EPDM Rubber in the presence of a silane coupling Agent" Rubber Chem Technol, **55**,1370 (1983)
9. S. Debnath, S. K. De, and D. Khastgir, " Effects of Silane Coupling Agents on Mica – Filled Styrene – Butadiene Rubber " J Appl Polym Sci, **37**,1449- 1464, (1989).
10. P. Bajaj. And R. Jha. " Effect of Titanate Coupling Agents on Mechanical Properties of Mica –Filled Polypropylene " Polym Eng Sci, **29**, 8, 557 (1989).

11. Nabil .A.N. Alkadasi, Bhimrao D. Sarwade, D.G. Hundiwale, U.R. Kapadi, "Studies on the effect of titanate Coupling Agent (2%) on the Mechanical Properties of clay Filled – Poly butadiene Rubber "Journal of Polymeric Material ,21(2)(2004).

12. P. P.S.N. Chakravrty, and S K DE, "Effect of Clay on Vulcanization Network Structure, and Technical Properties of Natural Rubber in the Presence of Silane Coupling Agents "J Appl Polym Sci, Vol. **28**, 659-683 (1983).

13. I.Kadivec, Z. Susteric, M. Strle, " The Method of Incorporating Organofunctional Silane –Based Agents into Rubber Compounds: Effects on the Properties or on SBR – Based Compound Filled with Synthetic Calcium Silicate " Polym Intren, **33** (4) 381 (1994).

14. H. D.Rozman, Z.A.Mohd. Ishak, " Rubber wood – High –Density Polyethylene Composites: Effect of Filler Size and Coupling Agents on Mechanical Properties " J Appl Polym Sci, **69**,1993 (1998).

15. A.S.Hashim, B.Azahari, " The Effect of Bis (3-Triethoxy Silylpropyl) Tetrasulfide on Silica Reinforcement of Styrene –Butadiene Rubber" Rubber Chem Technol, **71,** 289 -299 (1997).

Fig. 1: Tensile Strength of the Treated & untreated HDPE/$Mg(OH)_2$ /TCA-114 composites.

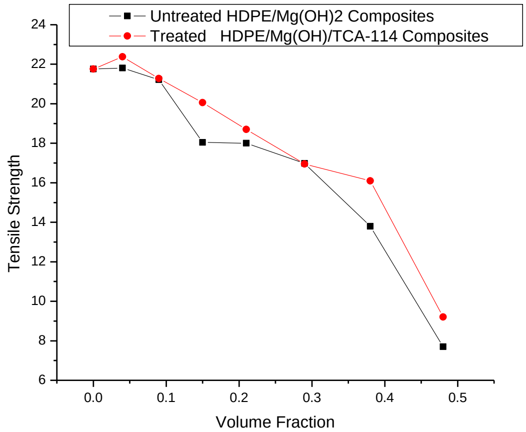

Fig. 2: Elastic Modulus of the Treated & untreated HDPE/$Mg(OH)_2$ /TCA-114 composites.

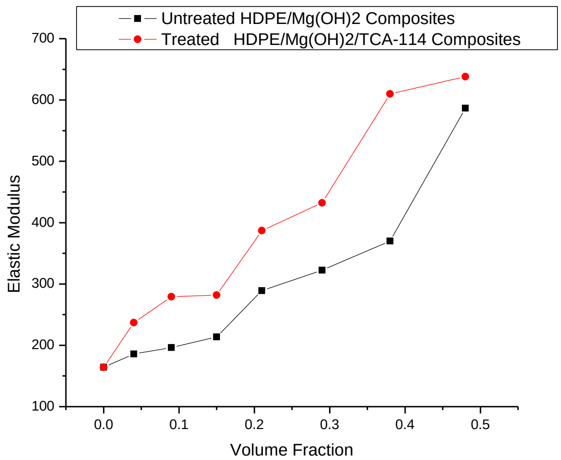

Fig. 3: Hardness of the Treated & untreated HDPE/$Mg(OH)_2$ /TCA-114 composites.

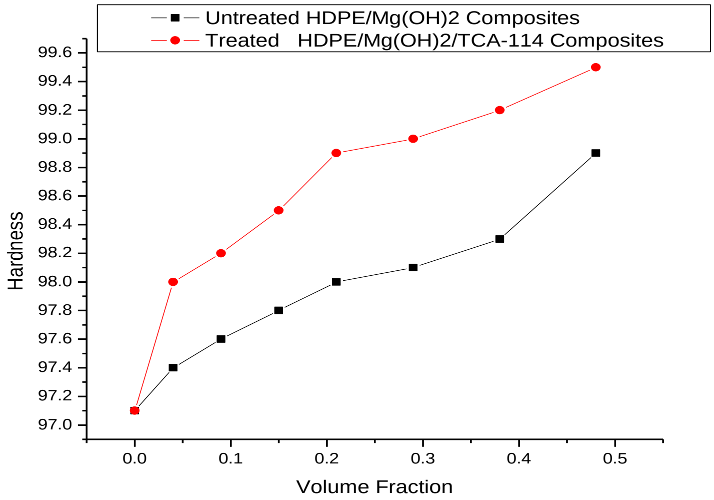

Plate1: SEM of $Mg(OH)_2$ Powder (2µm) .

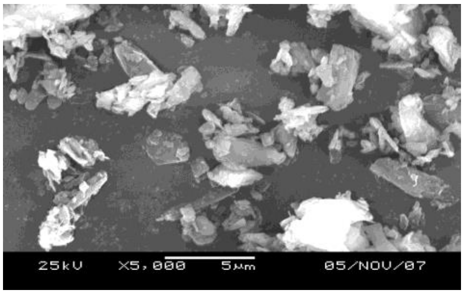

Plate2: SEM of Mg(OH)2/TCA-27 Composites .

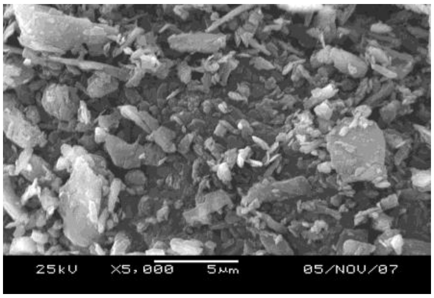

Plate 3: SEM of HDPE Composites .

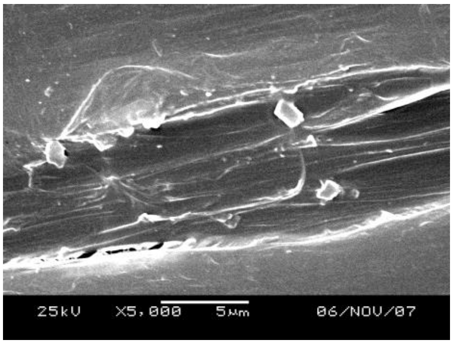

Plate 4 . HDPE/$Mg(OH)_2$

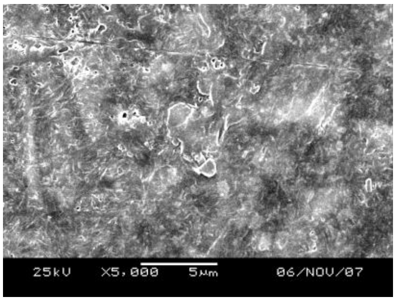

Plate 5 . HDPE/$Mg(OH)_2$/ TCA-114 composites .