The Thermal Properties of Nano Magnesium Hydroxide Blended with LDPE/EVA/Irganox1010 for Insulator Application

Ahmad Aroziki Abdul Aziz, Sakinah Mohd Alauddin, Ruzitah Mohd Salleh, Mohammed Iqbal Shueb

Abstract—This paper illustrates the effect of nano Magnesium Hydroxide (MH) loading on the thermal properties of Low Density Polyethylene (LDPE)/Poly (ethylene-co vinyl acetate) (EVA) nano composite. Thermal studies were conducted, as it understanding is vital for preliminary development of new polymeric systems. Thermal analysis of nanocomposite was conducted using thermo gravimetric analysis (TGA), and differential scanning calorimetry (DSC). Major finding of TGA indicated two main stages of degradation process found at ($350 \pm 25^{o}C$) and ($480 \pm 25^{o}C$) respectively. Nano metal filler expressed better fire resistance as it stand over high degree of temperature. Furthermore, DSC analysis provided a stable glass temperature around 51 ($\pm 1^{o}C$) and captured double melting point at 84 ($\pm 2^{o}C$) and 108 ($\pm 2^{o}C$). This binary melting point reflects the modification of nano filler to the polymer matrix forming melting crystals of folded and extended chain. The percent crystallinity of the samples grew vividly with increasing filler content. Overall, increasing the filler loading improved the degradation temperature and weight loss evidently and a better process and phase stability was captured in DSC.

Keywords—Cable and Wire, LDPE/EVA, Nano MH, Nano Particles, Thermal properties.

I. INTRODUCTION

THEORETICALLY, polymer materials are easily ignited when subjected to heat, producing combustible products that will propagate the fire. Hence, it is desirable to have polymer materials that possess a certain degree of flame retardancy to suppress major fire issues. This can be accomplished by addition of flame retardant fillers, where the most effective are halogen based flame-retardants. However, environmental legislation has restricted their usage due to their corrosiveness, smoke emission and release of toxic gasees during combustion. Therefore more studies and research have been focused on the alternative halogen free flame-retardants, such as aluminum hydroxide, ATH and magnesium hydroxide, MH [1], [3], [4]. Metal hydroxide of magnesium hydroxide possesses decomposition temperature around 320°C. The former will release about 31% water on ignition. Plastic compositions containing magnesium hydroxide can be

processed at much higher temperatures. Basic magnesium carbonate differs in that it decomposes over a broader temperature range and releases carbon dioxide in addition to water [5].

A promising polymer composite for insulating are EVA and LDPE as it widely uses in dielectric insulation in cable communication cables as well as for sheathing. LDPE has extremely low glass transition temperature. Most useful plastics will have relatively high glass transitions (Tg). Generally, its possess very low to medium degree of crystallinity (30 to 50%), which is also responsible for LDPE having a first order melt transition at $137^{o}C$ [6], [9]. These crystalline regions of LDPE provides strength and stiffness to what otherwise would be a rubber-like polymer. LDPE has the basis for its specialty, crosslinkable insulation for medium and high voltage cables. In addition at price, LDPE compounds offer comparable to PVC for flame retardant applications.

Ethylene vinyl acetate (EVA) is the most versatile and widely used thermoplastic polymer in hot melt adhesive formulations. This is mainly due to the acetate functional group, which provides good adhesive strength to polar substrates [7]. The copolymer is also relatively inexpensive. EVA polymers commercially shown vary considerably in percent vinyl acetate and average molecular weight. The higher the percent vinyl acetate (VA) content, the better will be the adhesion with polar adherents [10]. A lower melt index (higher average molecular weight) for an EVA polymer will in general, improve low and high temperature adhesive strengths [8]. Addition of EVA can enhance the ductility of metallic hydroxides filled PE possibly by improving the poor interfacial adhesion between PE and metallic hydroxides [2], [8]. EVA resins are used to build and protect electrical components while delivering the highest levels of performance and reliability in severe operating conditions. The advantages of EVA its ability to be used as an easily peelable, semiconductor layer for field control purposes. EVA also substitutes PVC for low smoke cable compound in the UK.

Hence this paper will give detail thought and definite idea to assess the effect of thermal properties on the flame retardant providing an elementary result regarding on the polymer nanocomposite LDPE, EVA and metal hydroxide.

II. EXPERIMENTAL

A. Material

Ethylene-vinyl acetate copolymer (EVA) contains 18 wt%

Ahmad Aroziki A.A. is with the Universiti Teknologi MARA, UiTM Shah Alam, 41400 Selangor Malaysia (corresponding author to provide phone: +6013-370-7330; e-mail: aroziki_uitm@yahoo.com).

Sakinah M.A. and Ruzitah M.S. are with the Department of Chemical Engineering, Universiti Teknologi MARA, UiTM Shah Alam, 41400 Selangor Malaysia (e-mail: sakinah3676@salam.uitm.edu.my, ruzitah@salam.uitm.edu.my).

Mohammed Iqbal S. is with the Malaysian Nuclear Agency Bangi, 43000 Kajang, Malaysia (e-mail: iqbal@nuclearmalaysia.gov.my).

of vinyl acetate (Exxon's Escorene UL02528) with melt flow index of 2.0g/10 min. A low density polyethylene (LDPE) from Asia Polymer Corporation, Taiwan with density 0.9185 g/cm^3 and melt flow index 8.3 g/10 min, while Nano Magnesium hydroxide (Nano MH) used in this study supplied by Sigma Aldrich, Switzerland, are of an average thickness of 20 nm and length of 90 nm. An Antioxidant Irganox 1010 with a melting point of 115°C supplied by Sigma Aldrich, Switzerland.

B. Preparation of Sample

The LDPE, EVA, nano-MH, and Irganox 1010 were blended together by using an internal mixer at 160°C with a mixing speed of 50 rpm for 10 min. The blended samples were moulded in a compression mould and converted into rectangular sheets (150 × 150 mm) with a thickness of 1.5 mm at 170°C under pressure of 10 MPa for 3 min after 4 min preheating in an electrically heated press. Then the mould was transferred to a cold press and then cooled at the same pressure. The blending ratio of the sample was based on the 100 phr of LDPE with 1:1 ratio of EVA. 0.1 phr of irganox 1010 and the nano MH was varied with 5 different ratios ranging from 0, 5, 10, 15 and 20 phr.

III. TESTING METHOD

A. Thermal Testing

1) Thermogravimetric Analysis

This test was done according to ASTM E1131 using a Courtesy Perkin- Elmer Corporation. The nitrogen gas flow rate was set to 100 cm^3/min to provide the appropriate environments for the test. The test material was placed in the specimen holder and heated and the amount of specimen used for each test range from 15 to 24 mg. Specimens were heated with increasing rate of 10°C/min in air at temperatures ranging from 30 to 1000°C.

2) Differential Scanning Calorimetry

DSC Perkin- Elmer Instruments according to the ASTM D3418 analyzed the nanopolymer composites. The amount of samples used range from 5 to 9 mg. The test was conducted at a temperature range of 30 to 500°C under Nitrogen atmosphere, with a flow rate of 10 cm^3/min and heating rate of 10 ^{o}C/min.

B. Equation

The percent crystallinity calculated using the following equation:

$$\% \text{ Crystallinity} = ([\Delta Hm - \Delta Hc] / \Delta Hm°) \times 100\% \tag{1}$$

where, ΔHm is the heat of melting, and ΔHc is the cold crystallization, that is determined by integrating the areas (J/g) under the respective peaks. The term $\Delta Hm°$ is a reference value and represents the heat of 100% crystalline. $\Delta Hm°$ value used in this case was 293.6 (J/g) of PE [20].

IV. RESULT AND DISCUSSION

TABLE I
ANALYSIS DATA OF TGA

Nano MH ratio	Degradation Temperature (^{o}C)		Total Weight loss (%)
	Stage 1	Stage 2	
0 phr	350.96	479.21	100
5 phr	352.78	478.68	100
10 phr	352.39	476.51	93.83
15 phr	353.11	476.27	93.75
20 phr	355.14	475.80	84.2

From the TGA analysis, it was found that the thermal degradation occurred in two different stages. The first stage (350 ± 25°C) is attributed to the deacetylation process where the evolution of acetic acid occurs due to the decomposition of vinyl acetate groups [11], [12], [14], [17]. All blending ratio of nano MH show same trend of the degradation line. The less steep slope encountered consistently as increasing the amount of nano mh. The loss of acetic acid occurs at an earlier temperature in the virgin composite (0 phr) and the degradation temperature increases with increasing nano MH content, Table I. This suggest that in addition to the auto catalyzed β-elimination of acetic acid, the reaction is depromoted by the presence on nano MH, sufficiently close to the polymer chains depromote such a reaction. This implies that, increasing filler content hinder the deacetylation process.

Once the deacetylation process is finished and the loss of acetic acid is complete the resulting cross-linked polyene material will be formed. The second stage of degradation (480 ± 25°C) Fig. 2 represent these degradation of carbonaceous residue by reacting with the oxygen of the air [3], [11] and [13]. A kinetic analysis could be done projecting the steep of the slope obtained at this stage suppressed the higher activation energy required to degrade the polymeric chain and bonding. A tremendous weight loss occurred with lower nano MH filler content in the matrix. For 0 and 5 phr samples, almost 100 percent of the weight had loss at end of the test while only 84 percent loss for 20 phr sample Table I. The trend of degradation temperature at this stage was difference compared to the first stage. Degradation process exhibits correspond to the filler ratio added with almost 1°C of temperature increase for every ratio in increment. Theoretically, increasing of nano filler ratio provided a loose medium of interaction among monomers resulting in a degradation reaction. In addition, evolved gaseous from oxidization process of carbon toward carbon dioxide gaseous lead to the major of a weight loss. Weight loss occurred due to the volatilization of the residual polymer along both stages of degradation process at temperatures between 370°C and 600°C [15], [19].

TABLE II
ANALYSIS DATA OF DSC

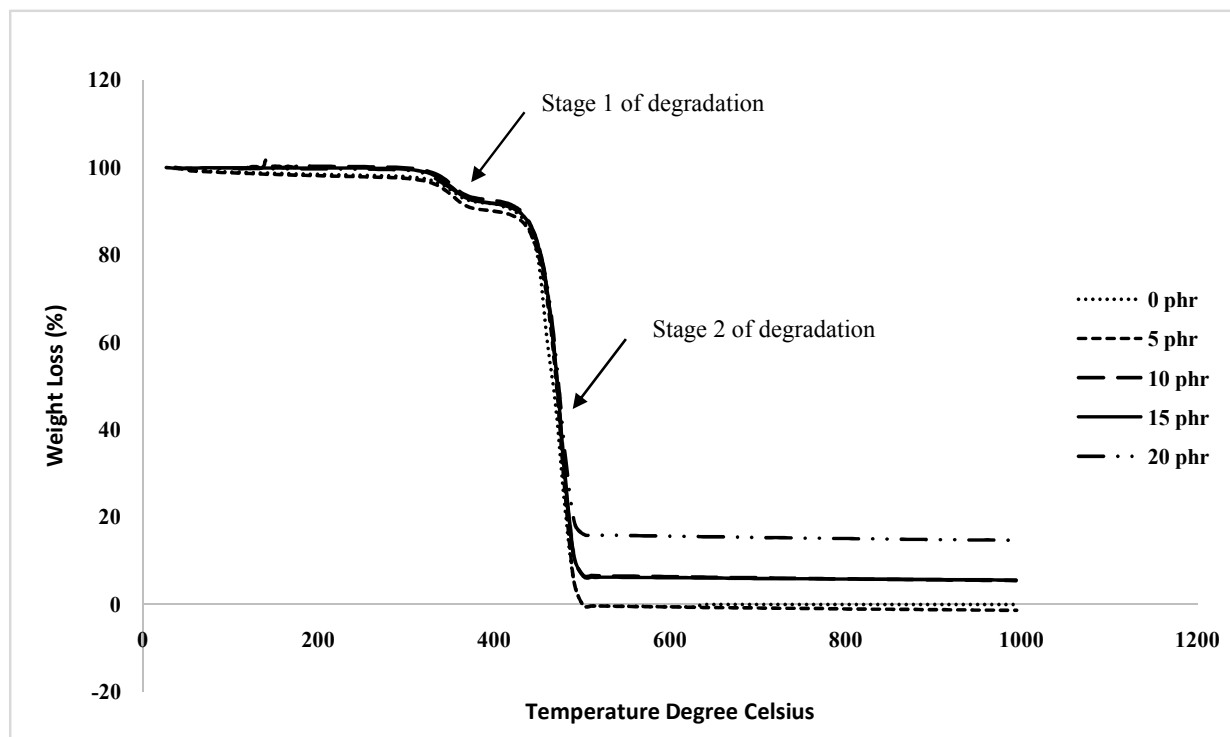| Nano MH ratio	Temperature (^{o}C)			Enthalpy ΔH (J/g)	Crsytallinity X_C (%)
	Tg	Tm$_1$	Tm$_2$		
0 phr	50	83.77	108.22	20.85	7.10
5 phr	50.65	84.40	109.6	21.68	7.38
10 phr	50.82	84.58	108.44	21.53	7.33
15 phr	51.84	84.60	108.81	21.60	7.36
20 phr	51.82	84.77	108.96	22.99	7.83

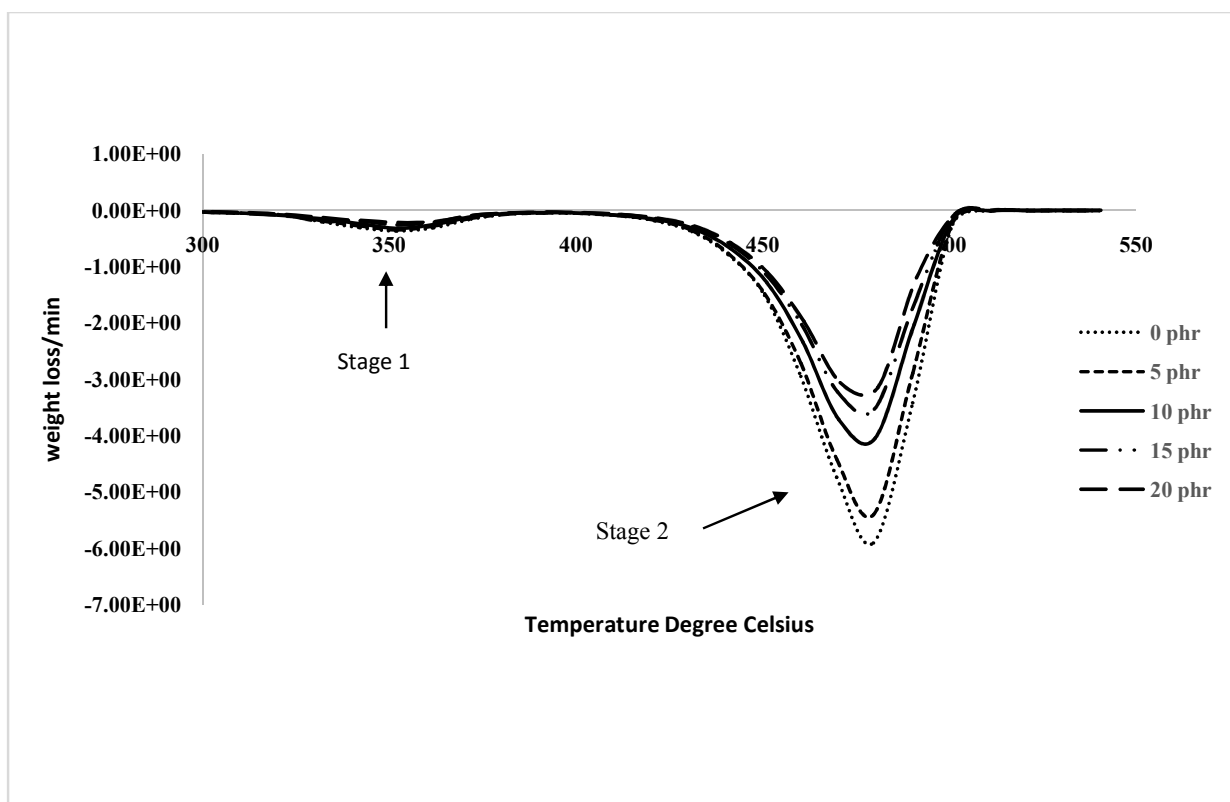Fig. 1 TGA values for Various Nano MH Content Units

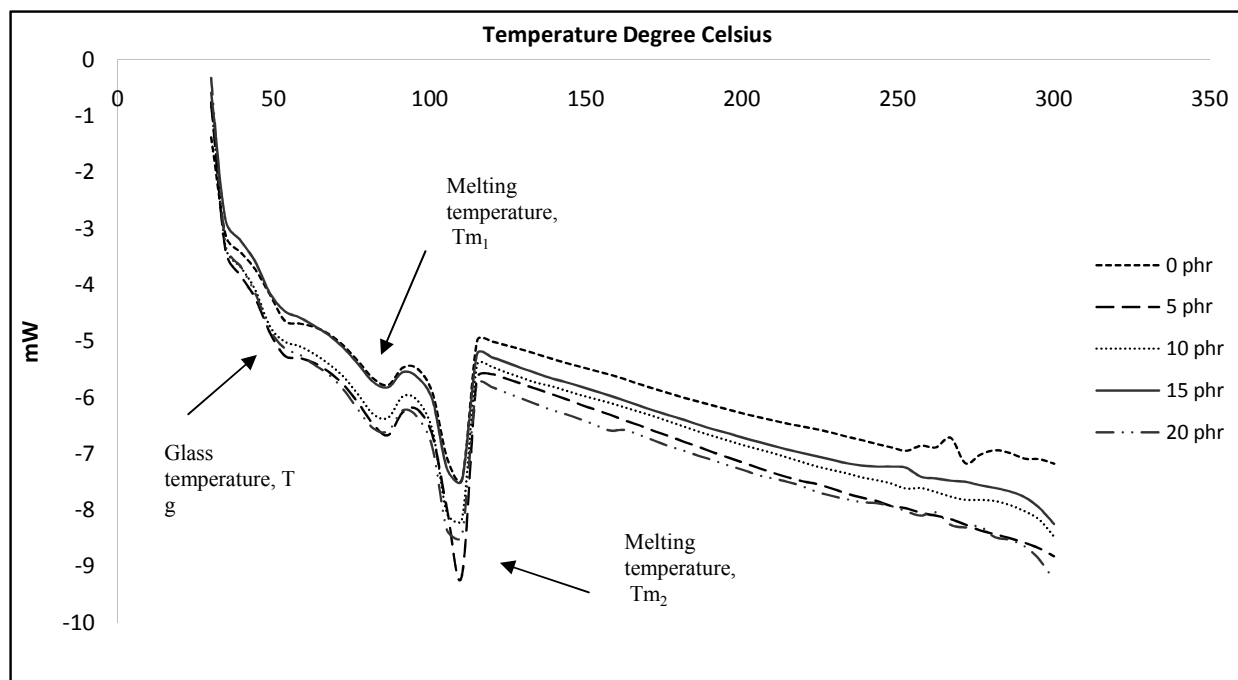Fig. 2 DTA values of TGA for Various Nano MH Content Units

Fig. 3 DSC values for Various Nano MH Content Units

DSC observed a heat of fusion, glass transition and melting temperatures as it undergoes a physical transformation during heating, such as a phase transition, a heat flow or local heat input is established [21]. Polymeric examination Fig. 3 demonstrated that the relaxation endothermic reaction glass transition temperature, Tg, occurred at constant temperature of (51 ± 1°C) for all ratio nanocomposite samples Table. II. This explains the nano MH has no influence in the movement of the monomer to reach a molten rubber like state. Above this temperature, cluster motion of the polymer is reasonably unrestricted by the interaction with neighboring chains with increase local degrees of freedom.

Meanwhile with nano metal increased into the matrix, all reaction regions slightly shifted towards lower peak of temperature. Nano composite exhibits double melting point, Table II. Double melting temperature was recorded as the first occurred due to thinner lamellae at 84 ($\pm 2^{o}$C) but the main temperature more precise of phase changed at 108 ($\pm 2^{o}$C). This phenomenon formed as the polymer to be agreed possesses two different kind of crystalline modification [16]. The higher peak in which Tm_2 point Fig. 3, relate to the melting of the crystal of folded chain termed by imperfect crystals, whereas the lower one correspond to the melting of crystals consist of extended chain [18].

The higher value of enthalpy explained more is heat needed to initialize and complete the phase change. In relation with that, by neglecting the value of cold crystallization since the process showed there was no exothermic peak at all Fig. 3, the percent crystallinity (% Xc) calculated only based on the heat of melting available (1). Increasing in filler ratio from 0 to 20 phr clearly increase the percent crystallinity Table II. This

information of crystallinity helps to observe the overall level of crystalline component in relationship to its amorphous component. The higher the percent crystallinity will provide a more brittle, stiff and tough nano composite material [18]. Corresponded crystallinity result plays an important role in deciding suitable condition required for cable and wire application.

Reduction of almost 1°C occurred across an increment of 0 to 20 phr with 83.77^{o}C to 84.77^{o}C respectively for Tm_1. The same trend observed for Tm_2. Addition of Nano MH exhibit a clear Tm peak whereas the matrix containing less or no presence of Nano MH exhibits no such peak. Sample of 20 phr tend to have more sharp shape of the Tm peak as it get clearer and exit standpoint of further free monomer movement as matter of phase change start to initialize. Apparently the polymer samples were partially crystalline as it suppresses melting peak due to the size of distribution of crystallite [22], [23]. When heated, it melts and the crystallinity is lost and that explained temperature Tm_1 and Tm_2 of the DSC peak, which relates to the loss of the nanostructure bonding, decreased with increasing strain force. These changes were explained in terms of an increase of the stored energy introduced by nano metal which raised the driving force for at intermediate temperatures with reflected the peaks shift slightly to lower [24].

V. CONCLUSION

This study has demonstrated the effect and consequences of thermal properties by adoption of nano particle into LDPE/EVA matrix composite. Process solidity confirmed and well established by taking consideration of important reason provided by analytical of TGA and DSC. Better and steadiness

composite formed as more amount of nano MH coexists to interact and respond in decent way to control the material stability. Furthermore, high degree of temperature resistance of nanocomposite obtained by adopting a metal filler towards the application. A refinement of the particles in this matrix that are in the nano size does significantly enhance their effectiveness for melting point induced and inhibitors. Besides, the DSC percent crystallinity is straightly related to critical properties including optical clarity, toughness, stiffness, creep, barrier resistance, gas permeability, and long term stability due to cable and wire application.

REFERENCES

[1] H. Huang; M. Tian.; L. Liu.; W. Liang.; L. Zhang, Effect of Particle Size on Flame Retardancy of Mg(OH)2-Filled Ethylene Vinyl Acetate Copolymer Composites, Journal of Applied Polymer Science, Vol. 100, 4461– 4469 (2006)

[2] H. L. Ferna´ndez, A. Velasco, J. Chimenos, L. Cuesta, J. Espiell, F. (2007). Thermal stability and flame retardancy of LDPE/EVA blends filled with synthetic hydramagnesite /aluminium hydroxide/ montmorillonite and magnesium hydroxide/aluminium hydroxide / montmorillonite mixtures, Polymer Degradation and Stability. 92: 1082-1087.

[3] L. Qiu, R. Xie, P. Ding, B. Qu, "Preparation and characterization of Mg(OH)2 nanoparticles and flame-retardant property of its nanocomposites with EVA", Anhui, PR China, 2003 pp 391–395

[4] Li, Y.; Qiao, H. Chin Beijing University Chem Tech 2003, 29(3), 48.

[5] Shigeo, M.; Takeshi, I.; Hithoshi, A. J Appl Polym Sci 1980, 25,415.

[6] M.A. Ca´rdenas, D. Garcı´a-Lo´ pez, I. Gobernado-Mitre, J.C. Merino, J.M. Pastor, J. de D. Martı´nez, J. Barbeta, D. Calveras, "Mechanical and fire retardant properties of EVA/clay/ATH nanocomposites – Effect of particle size and surface treatment of ATH filler", Valladolid, Spain, 2008 pp 2032–2037

[7] X. Zhang, F. Guo, J. Chen, G. Wang, H. Liu, "Investigation of interfacial modification for flame retardant ethylene vinyl acetate copolymer/alumina trihydrate nanocomposites", Beijing People's Republic of China, 2005 pp 411- 418

[8] Haurie, L. Ferna´ndez, A. Velasco, J. Chimenos, J. Lopez Cuesta, J. Espiell, F. (2006). Synthetic hydromagnesite as flame retardant. Evaluation of the flame behaviour in a polyethylene matrix, Polymer Degradation and Stability. 91: 989-994.

[9] Marchal, A, Deobel R, Le Bras M, Leroy J-M and price D (1994). Effect of intumescence on polymer degradation. Polymer Degdation and Stability 44:.263- 272.

[10] Mouzheng, F. Baojun. (2004). Synergistic flame retardant mechanism of fumed silica in ethylene-vinyl acetate / magnesium hydroxide blends. Polymer Degradation and Stability.85: 633-639.

[11] Delfosse, L., Baillet . (1989). Combustion of ethylene-Vinyl Acetate

[12] Copolymer Filled with Aluminium and Magnesium Hydroxides. Polymer Degradation and Stability. 23: 337-347.

[13] Maurin, M.B., Pang and Hussain (1992). Thermogravimetric analysis of ethylene-vinyl acetate copolymer with dynamic heating rates. Thermochim Acta 209: 203-207.

[14] Maurin, M.B., Dittert L.W and Hussain (1991). Thermogravimetric analysis of ethylene-vinyl acetate copolymers with Fourier transform infrared analysis of the pyrolysis products. Thermochim Acta 186: 97-102.

[15] Tai, C. M.; Li, R. K. Y. J Appl Polym Sci 2001, 80, 2718.

[16] Carpentier, F. Bourbigot, S. Le Bras, M. Delobel, R. Foulon, M. Polym Degrad Stab 2000, 69, 83.

[17] Cross, M. S. Cusack, P. A. Hornsby, P. R. Polym Degrad Stab 2003, 79, 309.

[18] Yeh, J. Yang, H. Huang, S. Polymer Degrad Stab 1995, 50, 229.

[19] Genovese, A. Shanks, R.A. (2007). Structural and thermal interpretation of the synergy and interactions between the fire retardants magnesium hydroxide and zinc borate, Polymer Degradation and Stability. 92: 2-13.

[20] Rothon, R.N. Hornsby, P.R. (1996). Flame retardant effect of magnesium hydroxide, Polymer.Degradation and.Stablity., 54 (2-3):.383-385.

[21] J. A. Dean: 'The Analytical Chemistry Handbook', 15.1–15.5; 1995, New York. McGraw Hill.

[22] E. Pungor: 'A Practical Guide to Instrumental Analysis', 181–191; 1995, CRC Press, Boca Raton, Florida.

[23] D. A. Skoog, F. J. Holler and T.A. Nieman: 'Principles of Instrumental Analysis', 5th edn, 905–908; 1998, Saunders, Philadelphia, PA, USA.

[24] M. J. Starink: Intl Mater. Rev., 2004, 49, 191-226.