International Journal of Current Engineering and Technology
E-ISSN 2277 – 4106, P-ISSN 2347 – 5161

Research Article

Preparation and Performance Testing of Nano Titanium Dioxide as Fire Retardant of High Density Polyethylene Composite

Ansam Adnan Hashim, Watheq Kareem Salih*, Nozad Anwer Jameel

Materials Research Directorate – Ministry of Science & Technology – Baghdad – Iraq

Accepted 02 July 2016, Available online 11 July 2016, **Vol.6, No.4 (Aug 2016)**

Abstract

Fire retardants are very important class of materials which has importance in saving the persons lives and the properties via reducing the possibility of polymer fires. In this work, High density Polyethylene (HDPE)/titanium dioxide (TiO_2) nano-composite was prepared by melt extrusion to assess the efficiency of nano Titanium dioxide as fire retardant and to detect its effect on melting point of composite. Different weight percentages of nano TiO_2 (0, 2%, 4%, 6%) were used. The Fire retardancy of prepared samples were tested according to standard methods [ASTM D 635, ASTM D4804].The results showed that addition of this kind of nano particles contributed in improving the fire retardancy of high density polyethylene composite for all samples which contained nano TiO_2 . The rate of burning and height of flame were varied according to different additions ratios. The maximum decreases in rate of burning and minimum height of flame was recorded for sample S2 (4%wt. addition) while the addition effect was very limited on melting point. The result clarified the synergic effect of nano titanium dioxide as co-fire retardant of High density polyethylene composites.

Keywords: *HDPE, Nanotechnology, Fire retardant, Titanium dioxide, rate of burning, flame height.*

1. Introduction

It is not a secret that polymer composites and their derivatives have main and outstanding ranking in our everyday demands because of remarkable combined properties, ease formulations and light weight which make them as suitable solutions for many applications in different fields. In spite of these merits, polymer composites have varied defects which lead to important problems and Disastrous results. Flammability of polymers is one of dangerous and serious problems where the economic damages and loses resulted from polymer fire accidents are classified highly cost and deadly accidents not only because of flames but also because of toxicity and corrosivity of accompanied gases and smoke liberated during combustion process.

The major problems arise because most of the polymers on which these materials are based are organic and thus flammable. According international association of fire and rescue service (CTIF) statistics, the annual losses of life and property resulting from fires involving polymeric materials are very huge. In the 31 countries covered by CTIF statistics, fires result in the deaths of some 37 000 persons per annum with at least 10 times that number of associated injuries with a total cost of 1% GDP estimated in terms of property loss and replacement, cost of medical services, etc. These data refer to the 2.3 billion inhabitants living in these countries. Approximating the world's population to over 6 billion, it can be estimated that roughly 6-24 million fires occur in the world annually. These would cause some 100 000 deaths per annum with a cost of about £500 billion. [Horroks & Price ,2001 ; Horroks & Price ,2008]

Consequently, improving the fire retardant behavior of polymers is a major challenge for extending their use to most applications. Safety requirements are currently becoming more and more drastic in terms of polymers' reaction to fire and their fire resistance performances, while various flame retardant additives, such as halogenated additives, are being phased out for their proven or suspected adverse effects on the environment.

The combined challenge thus consists in developing effective and environmentally friendly flame retardant systems for polymer materials. The scientific and technical literatures contain very diverse and efficient strategies for improving polymer fire resistance, which depend primarily on the nature and chemical structure of the polymer concerned, its decomposition mode and the required level of fire safety, and also the global performances of the resulting materials. The development of flame retardant materials and understanding the phenomena that take place during combustion often require close collaboration between

---

*Corresponding author: **Watheq Kareem Salih** several fields of scientific expertise (macromolecular and physical chemistry, physics of mass and heat transfer, rheology, etc.). [Laoutid *et al*.,2009; Visakh & Arao, 2015].

It is significant to note that there is no inclusive fire retardant framework; what works for one polymer in one fire test will probably not work for another polymer in another test, and in most cases, even for the same polymer in another experiment. This point is highlighted to guarantee that the practice to design the fire retardant framework to pass through a test, not to give inclusive fire security. The last goal turned into the objective of the scientific exploration as of late, and it creates the impression that the lower base combustibility of a polymer nano composite is a step in the right trend. Since nano-particles inherently work to bring down the combustion of a polymer matrix, they have been utilized effectively to manufacture fire retardant formulations in two remarkable cases: wire/cable covering

These nano-particles provide an alternative to conventional fire retardants to reduce the flammability of polymer resin. Compared to conventional fire retardants, they are environmentally friendly, highly efficiency, and capable of imparting other polymers properties [Visakh&Arao, 2015].

1.1 fire retardant materials in past and present

A good deal of research work is being carried out on nano-particles and their contribution in the field of plastics. Polymers reinforced with as little as 2 % to 5 % of these particles via melt compounding or in-situ polymerization exhibit dramatic improvements in thermo-mechanical properties, barrier properties and flame retardancy [Döring& Diederichs,2009].
During past decade, the researches were focused on using different materials as fire retardants. They tried their best to make the damages of fires at lowest range .They gave this subject the high priority in their works. But most of these works used the conventional materials at micro- scale. Table 1 is summarized the common types of materials which are used as fire retardants in past decades or in the present time.

Table 1 Traditional fire retardant types

Fire Retardants Types	Mineral Filler Flame Retardants	Hydroxides(Al, Mg) Carbonates (Ca,Mg)
	Phosphorus Flame Retardants	Phosphates phosphinates Ammonium polyphosphate
	Halogenated Flame Retardants	Brominated , Chlorinated, Fluorine and Iodine
	Intumescent Flame Retardants	Mixtures of different additives
	Inorganic Flame Retardants	Zinc Borate ,Stannates, Silicon compounds

But with the huge developments in nanotechnology science, the fire retardant materials witnessed new era in using these novel materials in fire retardancy. So, the focus is concentrated on using nano powder in fire retardant field. Different types of nano-particles have been used to fabricate fire retardant nano-composites. Table 2 is clarified the researches of using nano materials with different types of polymeric nano-composites.

Table 2 Nano particle materials used with different composites

Nano materials	Researchers	Polymer matrix
Nano clay	Jash&Wilkie, (2005)	Poly (methyl metha-acrylate
	Wang *et al* (2008)	phenolic resins
	Zhang *et al.* (2009)	EVA and LDPE
	Frache *et al.* (2011)	Epoxy
	Kumar &Dahiya (2013)	Polypropylene
	Kannan *et al*., (2015)	polyurethane/polypropylene
Carbon nano tube	Wu *et al.* (2010)	Epoxy
	Wesolek&Gieparda (2014)	Polyurethane fabrics
	Yin *et al*., (2015)	Polyamide 6
Elemental Nanoparticles	Lao el. al.,(2008)	Polyamide 11- Alumina nanocomposites
	Rallini *et al.* (2013)	boron carbide nanoparticles/Epoxy
	Wang *et al.* (2008)	boron carbide nanoparticles/ phenolic resin
	Tibiletti *et al* (2011)	Nano alumina /unsaturated polyester
	Ribeiro *et al*.,(2104)	Nano alumina –nano silicon dioxide – nano magnesium hydroxide /unsaturated polyester

1.2 The mechanism of burning of polymers

The burning of plastics and polymers is a procedure containing a multitude of singles steps and essentially started by endothermic heating and pyrolysis. The combustible gasses react with air oxygen and ignite, prompting the exothermic procedures of fire engendering and heat discharge. During heating the high bond restricting and pyrolysis, endothermic procedures happen for defeating energies between induvial atoms (200-400 kJ/mole).

Ignition initiates the exothermic part of processes which override the endothermic pyrolytic reactions. Pyrolysis of polymer is reinforced by thermal feedback (heat release) which fuels the flame at an increasing level .The flame spreads over the decomposed polymer surface. The diffusion flame is supported by extremely high energy H and OH radical which confer a high velocity on the flame front [Troitzch, 1998]. The schematic diagram of combustion process is shown in Figure 1.

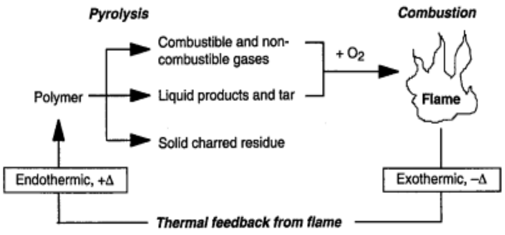

Figure 1 Polymer combustion process mechanism (Zhang, 2004)

1.3 The strategies of fire retardants

The strategies of fire retardants differ from method to another depending on the technique and the principle using in stopping the fires but mainly these strategies can be classified into two main categories. The first one is that block fire physically and the second one that depending on chemical reactions to Stop burning of flammable materials. They are outlined in the following:

1) Physical effect

There are several ways in which the combustion process can be retarded by physical action:

- By cooling. Endothermic reactions cool the material.
- By forming a protective layer. Obstructing the flow of heat and oxygen to the polymer, and of fuel to the vapor phase.
- By dilution. Release of water vapor or carbon dioxide (CO_2) may dilute the radicals in the flame so it goes out.

2) Chemical action

- Reaction in the gas phase. The radical reactions of the flame can be interrupted by a flame retardant. The radical concentration falls below a critical value, and the flame goes out. The processes that release heat are thus stopped, and the system cools down. However, interfering with the flame reactions often results in highly toxic and irritant partially burnt products, including CO, which generally increase the toxicity of the fire gases while reducing fire growth.[Hull & Kandola, 2009, Hull *et al*.,2009]
- Reaction in the solid phase. The flame retardants work by breaking down the polymer so it melts like a liquid and flows away from the flame (just like trying to light candle wax without a wick). Although this] allows materials to pass certain tests, sometimes fire safety is compromised by the production of flammable drops.
- Char formation. Better solid-phase flame retardants are those which cause a layer of carbonaceous char to form on the polymer surface. This can occur, for example, by the fire retardant removing the side chains and thus generating double bonds in the polymer. Ultimately, these form a carbonaceous layer by forming aromatic rings. Char formation usually reduces the formation of smoke and other products of incomplete combustion.
- Intumescence. The incorporation of blowing agents causes swelling behind the surface layer, and provides much better insulation under the protective barrier. The same technology is used for coatings for protecting wooden buildings and steel structures [Hull & Kandola, 2009, Ugal,2015]

Nano titanium dioxide occupied an important role in recent studies through the world because of its special characteristics and unique properties especially in hygienic and solar fields besides other fields.

This work aims to detect the possibility of using nano- titanium dioxide as fire retardant of High-density polyethylene composite and testing the melting point of this composite.

2. Experimental Work

2.1 Material and equipments

2.1.1 Nano Titanium dioxide ($nTiO_2$): The specifications and X-ray pattern of TiO_2 are listed in Table 3 and Figure 2 respectively

Table 2 Nano Titanium dioxide specifications

Titanium Dioxide phase	Anatase
Particle size	< 50 nm
Purity	99.8%
Color	White powder
Manufacturer	Hongwu nanometer company
Country	China

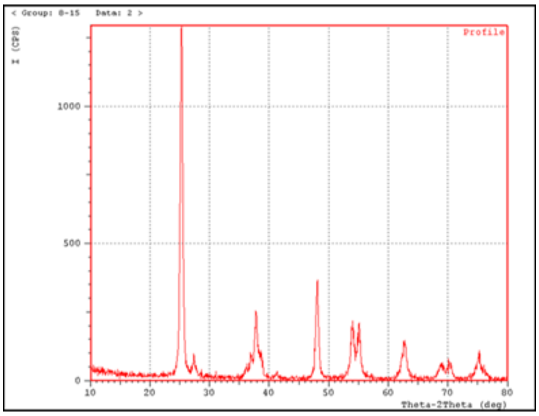

Figure 2 nano TiO_2 XRD Pattern

The XRD test was done via (XRD-600-Shimadtzu – Japan / Cu target -1.5406 A°) to identify the type and phase of $nTiO_2$. The obtained results of the test are identical with ICDD standard card (PDF #21-1272) which is assured the phase is anatase and the system is Tetragonal.

2.1.2 High density polyethylene polymer (HDPE): The properties of this polymer are listed in Table 4

Table 4 Properties of HDPE polymer

Test Method	Value /Unit	Properties
ASTM D1238	8g/10min	Melt flow rate
ASTM D1505	963Kg/m^3	Density
ASTM D638	26MPa	Tensile strength@yield
ASTM D2240	62	Hardness (shore D)
Sabic company / Saudi Arabia		Manufacturer

2.1.3 Extruder machine

A twin screw extruder (model RD11- 100 – 0254 - L/D=20/25/ motor speed 0-40 rpm /China) was used to mold the nTiO_2/HDPE composite.

2.2 Sample Preparation Procedure:

1. The specific ratios of titanium dioxide and HDPE were weighted as described in the Table 5.

Table 5 Samples of HDPE with/ without nano TiO2

Sample code	Materials		
	HDPE (g)	TiO_2 (g)	TiO_2 (wt. %)
S0 [PURE]	200	-	0
S 1 [2% wt]	196	4	2
S 2 [4% wt]	192	8	4
S 3 [6% wt]	188	12	6

2. The samples were prepared according to the procedure which was described in details in [Hashim & Salih, 2016]:

2.3 Tests

1. The rate of burning (RB): Burning rate of nTiO_2/HDPE composites was measured according to the standard method ASTM-D 635- 03. The test was done for three specimens of each sample. The dimensions of specimens were (13mm Width * 100mm Length)
2. Maximum flame height (H):The maximum flame height of prepared sample was done according to standard method UL 94 (ASTM D 4804) .The tests were done for two specimens of each sample. The dimensions of specimens were (10 mm width * 125 mm Length).
3. The time of the first drip was recorded for both burning methods in 1 & 2 (in horizontal and vertical set up of burning) for three specimens for each sample (10 mm W * 125 mm L)
4. Melting point test: this test was done to detect the effect of nTiO_2 addition on melting point property of prepared samples. DSC test was used to find melting point of all samples. The tests were done using DSC (DSC-60 – SHIMADZU) , heating rate 10/min.)

3. Results & Discussion

3.1 Melting point

The results of melting point tests of prepared samples showed that the effect of Titanium dioxide additions on melting point was very limited. The increase was about 1-5 ˚C for all samples.

3.2 Rate of burning (RB)

The rate of burning (mm/ min) is calculated according to the equation 1

$$RB=60\ X/t \qquad (1)$$

Where X= burned length of sample (mm)
t= the time required to burned length (s)
According to the results tabulated in Table 6, RB of prepared samples showed different burning rates which decreased for all samples with additions (S1, S2, S3) compared with the pure sample (S0).

The order of effectivity of decreasing the flame rate showed that sample (S2) which contained 4% addition was the best .

S2 > S3 > S1> S0

Sample S2 revealed a good efficiency in fire retardancy where the rate of burning decreased 33.5% comparing with pure HDPE (S0)

According to ASTM D-635, the behavior samples (S1, S2, and S3) are classified as HB (Horizontal burning)
In all burning experiments, no self-extinguish was noted for all prepared sample. The flame reached to 100 mm reference

3.3 Maximum Height of flame

The tests of the flame maximum height of prepared samples showed the decrease in flame height for those samples which contained nano Titanium dioxide but it is noted that sample S2 has the minimum height among all samples. Table 7 showed the results of this test..The order of flame decreasing was as following

S2 < S3 < S1 < S0

The maximum percentage of decreasing in height of flame was 51.51% for S2 comparing with S0 (without addition) where other samples showed different responses

3. The time of the first drip

The time required for the first drip of melting composite was recorded for vertical and horizontal burning tests. This test gives an indication of thermal behavior and about the needed time to fall the first drop of composite molten where the composite which has a longer time to be best because of its resistance against the melting. Table 8 summarized the of the first drip of all samples.

Table 6 Results of rate of burning test

Sample code	Specimen	Time of first drip T_d (s)	Average time of first drip (s)	Time of 100 mm burning (s)	Average of burning time (s)	Length of burning (X) (mm)	RB (mm)	% decreasing
S0	A1	20	18.667	40	45	100 (X=75)	100	0
	A2	18		45		100 (X=75)		
	A3	18		50		100 (X=75)		
S1	B1	22	22.667	55	60	100 (X=75)	75	25
	B2	24		60		100 (X=75)		
	B3	22		65		100 (X=75)		
S2	C1	22	29	60	67.667	100 (X=75)	66.502	33.498
	C2	34		70		100 (X=75)		
	C3	31		73		100 (X=75)		
S3	D1	20	24.333	40	61.667	100 (X=75)	72.87	27.03
	D2	28		85		100 (X=75)		
	D3	25		60		100 (X=75)		

Table 7 Results of Height of flame test

Sample Code.	Specimen	Height of flame (mm)	Average of height of flame	Height decreasing %
S0	A1	17	16.5	0
	A2	16		
S1	B1	13	12	27.27
	B2	11		
S2	C1	8	8	51.51
	C2	8		
S3	D1	9	10	39.39
	D2	11		

Table 8 Results of first drip test

Horizontal burning				
Sample Code	Specimen	Time of first drip (s)	Average of time of first drip (s)	% improvement
S0	A1	20	22.667	-
	A2	30		
	A3	18		
S1	B1	22	22.667	0
	B2	24		
	B3	22		
S2	C1	20	28.334	25.001
	C2	34		
	C3	31		
S3	D1	20	24.334	7.354
	D2	28		
	D3	25		
Vertical burning				
Sample Code	Specimen	Time of first drip (s)	Average of time of first drip (s)	% improvement
S0	A1	3	3	-
	A2	3		
S1	B1	4	4	33.34
	B2	4		
S2	C1	7	7	133.34
	C2	7		
S3	C1	5	5	66.67
	C2	5		

The addition of nano Titanium dioxide contributed in delay of time of the first drip in both cases (vertical and horizontal burning). The longest time for the first drip was recorded for S2 and the order of tests were as following.

S2< S3 <S1 = S0

The results of three tests in above clarified the role of nano Titanium additions on improving the fire retardant properties of HDPE/n TiO_2. This improvement in three testing results of prepared samples comparing with the pure sample (without an addition of nano particles) can be attributed to the role of nano metal oxide particles in enhancing fire retardancy property. These synergistic effects can be ascribed to physical effects resulting from the arrangement of particles at the surface of the composite during polymer combustion and ablation. The formation of this mineral barrier promotes catalytic effects ascribed to the huge specific surface area of oxide nanoparticles

The nano size of particles empowers the particles to involve the spaces between atoms of polymer and more particles will offer more limitation locales for the polymer chain, and the detachment of the polymer chain will turn out to be very complex and requiring more thermal energy for pyrolysis. The better interfacial connection between the added nanoparticles and polymer chain presented by profound and well dispersion of nanoparticles in the polymer network which leading also to limit movement of the polymer chain.

As the shown in results in above, the sample S2 (4% wt.) was the best among all prepared samples and that can be attributed for good dispersion of nano TiO_2 filler in HDPE matrix because it considers the basic key in specifying the properties of nanocomposites. The homogeneity may be the cause of decreasing the fire retardant of sample S3 (6% wt.) comparing with sample S2. This decreasing can be imputed on agglomeration phenomena between particles which did not treat with organo-surfactant.

Conclusion

Depending on the results in this work, it can be concluded the following:

1. The possibility of using nano TiO_2 as new fire retardant for HDPE composites where the fire retardancy was improved with using nano TiO_2 as filler
2. Sample S2 (4% wt. addition) had maximum value of fire retardancy properties (minimum rate of burning, minimum height of flame and longest the time of first drip)
3. The self-extinguish did not be noted for any of samples in this work so the role of nano TiO_2 needs to improve either with other loadings higher than those in this paper or using other types of nano metal oxides particles like SiO_2 or Al_2O_3 as a co- fire retardant.
4. The effect of nano TIO_2 on melting point of composite was limited

References

Döring M. and Diederichs J. (Eds.) (2009), Innovative Flame Retardants In E&E Applications : Non- halogenated phosphoros, inorganic and nitrogen flame retardants,2nd,Pinfa- *phosphoros,inorganic and nitrogen flame retardants association*, Wilhelm Stober GmbH ,Eggenstein, Germany

Frache, A., Monticelli, O., Nocchetti, M., Tartaglione, G. and Constantino, U. (2011), Thermal properties of epoxy resin nanocomposites based on hydrotalcites,*Polym. Degrad. Stab.* 96, 164-169

Hashim A. A. and Salih W. K. (2016), Anti-bacterial High density Polyethylene/Nano Titanium Dioxide Composite Synthesis and Characterization, International Journal of Scientific & Engineering Research, Volume 7, Issue 2, pp.81-85

Horrocks A R and Price D, (2001), Fire retardant materials, 2nd Ed.,*Woodhead publishing limited,*Cambridge, England,

Horrocks A R and Price D, (2008) ,Advances of Fire retardant materials, *Woodhead publishing limited,*Cambridge, England,

Hull T. R. and Kandola B. K (Eds.), (2009) , Fire Retardancy of Polymers New Strategies and Mechanisms,*The Royal Society of Chemistry*,, UK,

Hull, T. Richard; Stec, Anna A. and Nazare Shonali,(2009), Fire Retardant Effects of Polymer Nanocomposites, *Journal of Nanoscience and Nanotechnology*, Volume 9, Number 7, July 2009, pp. 4478-4486(9)

Jash, P. and Wilkie, C.A.:(2005),Effects of surfactant on the thermal and fire properties Poly (methylmetha-acrylate/nanoclay nanocomposites, *Polym. Degrad. Stab*. 88, 401-406

Kannan, M., Thomas, S. and Joseph, K. (2015), Flame-retardant properties of nanoclay-filled thermoplastic polyurethane/polypropylene *nanocomposites. Journal Of Vinyl & Additive Technology*, Vol 21(3),DOI 10.1002/vnl.21523

Kumar N. and Dahiya J. B.,(2013), Polypropylene-nanoclay composites containing flame retardant additive: Thermal stability and kinetic study in inert atmosphere,*Adv. Mat. Lett.,* 4 (9), 708-713

Lao S. C., . Koo H., Moon T. J. , Hadisujoto B. , Yong1 W., Pilato L. , and Wissler G., (2008), Fire Retardant Intumescent Polyamide 11 Nanocomposites – Further Studies, *The Nineteenth Annual International Solid Freeform Fabrication (SFF) Symposium,* Austin, USA

Laoutid F., Bonnaud L. , Alexandre M.,.Lopez-Cuesta J-M , and Dubois Ph. ,(2009), New prospects in flame retardant polymer materials: from fundamentals to nano-composites, *Materials Sci. Eng.: R: Reports* Vol. 63, (3), 100–125

Rallini M., Natali M., Kenny J. and Torre M, L.(2013), Effect of boron carbide nano-particles on the fire reaction and fire resistance of carbon fiber/epoxy composites,*J. polym*.,54(19) : 5154-5165

Ribeiro M C S, Sousa S P B, Nóvoa P R O, Pereira1 C M and Ferreira A J M, (2014) , Fire retardancy enhancement of unsaturated polyester polymer resin filled with nano and micro particulate oxide additives, *IOP Conf. Series: Materials Science and Engineering* 58 012020

Tibiletti L., Longuet C., Ferry L., Coutelen P., Mas A., Robin J. J. andLópez-Cuesta J. M., (2011) Thermal Degradation and Fire Behavior of Unsaturated Polyester Filled with Metallic Oxides, *Polym. Degrad. Stab.*, Vol. 96(1), 67-75.

Troitzch H. J. (1998), Overview of fire retardants: Fire and Fire Safety, Markets and applications, Mode of action and Main Families,Role in Fire Gasses and Residues , *chemical oggi-chemical today*,Vol 16, p.1-19, Germany

Ugal J. R. (2015), Preparation of Some Haloorganophosphonates(III) Compounds and Using as Flame Retardants for Epoxy and Unsaturated Polyester Resins,*Chemi. Sci. Trans,* 4(2), 516-522

Visakh P.M. and Arao Y.,(Eds.), (2015), Thermal Degradation of Polymer Blends, Composites and Nanocomposites *Springer*, Switzerland

Wang, D.-C., Chang, G.-W. and Chen, Y,(2008), Preparation and thermal stability of boron-containing phenolic resin/clay nanocomposites, *Polym. Degrad. Stab*. 93(1), 125-133

Wesolek D. and Gieparda W. (2014), ,Single- and Mult-iwalled Carbon Nanotubes with Phosphorus Based Flame Retardants for Textiles, *J. Nanomaterials* , vol.2014 , Paper ID 727494,

Wu Q. , Zhu W., Zhang Ch. , Liang Z. and Wang B. , (2010) , Study of fire retardant behavior of carbon nanotube membranes and carbon nanofiber paper in carbon fiber reinforced epoxy composites,*Carbon J.* ,48 1799 – 1806

Yin X. Krifa M. and Joseph H (2015), Flame-Retardant Polyamide 6/Carbon Nanotube Nanofibers: Processing and Characterization, *J. Eng. Fibers and Fabrics,* 10 (3): 1-11,

Zhang H.,(2004), Fire-Safe Polymers And Polymer Composites, *Office of Aviation Research report* ,Washington, USA

Zhang J., Hereida J., Hagena M., Bakirtzisa D., Delichatsiosa M.A ,Finab A., Castrovincib A., Caminob G., Samync F. and Bourbigotc S., (2009,) Effects of nanoclay and fire retardants on fire retardancy of a polymer blend of EVA and LDPE, *Fire Safety J.* , 44 (4), 504–513