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Enhanced fire retardancy of polyvinylchloride by combination with graphene and magnesium hydroxide

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Today, many studies are being carried out on fire proofing the materials, especially polymerrs. However, due to the variety of products in the polymer industry and their difference in terms of the type of the primary materials, the method of fire retardancy and intended features for the final product and other issues, the scope of performing these studies has been highly developed. One of the primary materials in this industry is polymer organic materials which contain carbon and hydrogen as the main elements and are destroyed under hear and their ignition has many risks. The purpose of this study was the synthesis of magnesium hydroxide and graphene nanoparticles as polymer filler in order to improve the thermal resistance of PVC (polyvinyl chloride) that is highly used in the industry and their identification was done by FT-IR, SEM, and XRD. Four samples of composite from PVC and $Mg(OH)_2$ with ratios of 10/90, 20/80, 30/70 and 40/60 and four samples of composite from PVC and $Mg(OH)_2$ with ratios of 5/5/90, 10/10/80, 15/15/70 and 20/20/60 were made and their thermal behaviors were studied. The results show that the thermal resistance of polymer, melting point and percentage of residual mass of composite increase with the increase of magnesium hydroxide percent in the composites. Also, adding Graphene to the composites increases thermal resistance and the percentage of their residual mass.

Keywords: Fire Retardancy, Graphene oxide, Poly(vinyl chloride), Nano Mg(OH)2, Nano Composite.

INTRODUCTION

The research and developments on new engineering materials belong to the important fields of material science. One can see the continuous competition between the traditional inorganic engineering materials and polymers. Since polymeric materials (including composites) are promising, due to their economic versatile applicability, they are widely used in many applications, such as housing materials, transport and electrical engineering [1-4]. These commercial polymers are easily flammable. Due to increasing demand for polymers, the development of safe and environmental flame retarded polymers is of great importance. Flame retardants are defined as chemical compounds that modify pyrolysis reactions of polymers or oxidation reactions implied in the combustion by slowing down or by inhibiting them [5].The flame retardant can act in various ways i.e. physically or chemically. Many types of flame retardants are used in consumer products [6-8]. They are mainly phosphorus, antimony, chlorides and bromides, magnesium and boron-containing compounds [5].

Polyvinyl chloride (PVC) is one of the earliest industrialized plastic. Its current output is outranked only by polyethylene, since it exhibits corrosion resistance and good insulation properties for many purposes. PVC is widely used in a number of industries and fields, including construction, furniture, automobile and medical applications. For example, it is mainly applied in cracking resistant sheath of heat resistant wires, cables and electrical cable in electrical industry; used as the steering wheel or the top cover plate in the auto industry; made in all kinds of pipes, plates, sheets and decoration materials for building industry. Polyvinyl chloride can also be processed into pipe, chemical reagent containers products to make a chemical equipment. PVC products are divided into hard ware and software. Software products have very low oxygen index due to the addition of a plasticizer. A way of achieving enhanced flame retardant activity is to add flame retardants, such as magnesium hydroxide, etc. [9, 10].Inorganic compound magnesium hydroxide [$Mg(OH)_2$] as a smoking- and toxic-free additive has been extensively used in halogen-free flame-retardant polymeric materials. However, its fatal disadvantages are low flame-retardant efficiency and thus very large usage amount, which lead the mechanical properties of a flame-retardant polymeric material to drop down

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sharply. The surface modification of magnesium hydroxide in order to increase the compatibility between $Mg(OH)_2$ particles and polymers can enhance the mechanical strength of composites [11].

Graphene is a two-dimensional extended honeycomb network of sp2 hybridized carbon atoms [7].Many methods have been developed to produce large quantities of process able graphene sheets that are separated well from each. One of the most promising methods is to use graphene oxide (GO) synthesized by the oxidation of graphite. With the reduction of GO, most of the properties of graphene are reportedly recovered. Furthermore, GO itself is considered to be a good candidate for use in composite materials that exhibit good electrical and gas-adsorption properties [12].GO has various oxygen functional groups (hydroxyl, epoxide, and carbonyl groups) on its basal plane and edge [13]. The oxygen functional groups of GO can interact with many different functional groups or particles [14]. Recently, GO-based composite materials have been introduced for various applications such as optoelectronic devices and lithium ion batteries [15]. In addition, GO itself and GO-based composites have been considered as new hydrogen storage media due to their large surface-to-volume ratio and intrinsically lightweight. For example, it was proposed that GO has the potential to become an ideal substrate for hydrogen storage [14] and that GO layers can be used as building blocks for potentially useful hydrogen storage materials [15]. As evident from the literature the functionalization of metal nanoparticles on the graphene based surfaces produces new hybrid materials which have potential importance in the areas such as optics, electronics, catalysis and sensors [16].

According to the unique properties of Graphene such as electrical, thermal and electrochemical properties and high specific surface area, the usability of this material has been significantly increased in many functions like sensors, catalysts, energy storage resources and a variety of composites [17].

To reform and improve the properties of composites made of PVC, it is necessary to make some changes in the structure of the proposed types. Thus, in this study, first magnesium hydroxide nanoparticles and graphene oxide nanoparticles were identified as mineral retardants synthesis by XRD, SEM and FT-IR. Then, the composites of PVC were made with different ratio of $Mg(OH)_2$ and DSC-TGA and LOI tests were performed on them. Finally, the composites of PVC were made with different ratios of $Mg(OH)_2$ and graphene oxide and similar to tests were performed on them. Finally, the thermal behaviors of composites with graphene were compared to the composites without graphene.

EXPERIMENTAL

Materials and methods

All materials and solventsused in the synthesis of Nano magnesium hydroxide and Nano graphene oxide were purchased from Sigma Aldrich and Merck and used without any further purification. The melting points (ºC) of the complexes were recorded on a Kruss instrument and TG/DSC curves were obtained from a Diamond TGA PerkinElmer 60 Hz.Poly vinyl chloride (PVC) was obtained from I Tech polymer company Iran (PVC GradeS-7054) with melt mass flow rate (MFR)of 35 g/10 min at 170ºC and 2.16 kg load and density of 1.14 g/cm3.. Infrared spectra were recorded as KBr disks on Tensor 27 Bruker spectrophotometer. The evaluation of graphene oxide and synthesized Nano composites were monitored by powder X-ray diffraction Philips PW 1800 diffractometer with Cu Kα radiation. Atomic force microscopy was carried out on a Denmark Dual scope/Raster scope C26, DME microscope.Scanning electron microscopy measurements was performed on a VEGA\\TESCAN at an accelerating voltage of 15 kV. The LOI values were measured using a ZRY type instrument (made in China) on the sheets of120 · 60 ·3 mm^3 according to ASTM D2863-77 standard.

Synthesis of nano- magnesium hydroxide

To prepare magnesium hydroxide nanoparticles, first 5 g ($MgSO_4.7H_2O$) was solved in 40 ml of deionized water and 5 ml of sodium hydroxide was added to it. Then, the obtained solution was stirred with 1600 rpm for 1 hour in 60 ºC. The obtained solution was passed from Nano filter paper by Buchner funnel and then was rinsed with deionized water in order to completely rinse the Ammonia. The remaining sediment was put in an oven with 105 ºC for 8 hours and finally magnesium hydroxide nanoparticles will be synthesized.

Synthesis of nanographene oxide

Graphene oxide was prepared according to the Staudenmaier method. A reaction flask containing a magnetic stir bar was charged with nitric acid (9 mL) and sulfuric acid (18 mL) and cooled by immersion in an ice bath. The acid mixture was stirred and allowed to cool for 15 min, and graphite (1 g) was added under vigorous stirring to avoid agglomeration. After the graphite powder was well dispersed, potassium chlorate (11 g) was added slowly over 2 h to avoid sudden increases in temperature and allowed to stir at room temperature for appropriate time. On completion of the reaction, the mixture was poured into deionized water (100 mL) and filtered. The graphite oxide was redispersed and washed in a solution of hydrochloric acid (5% w/w). The graphite oxide was then washed repeatedly with deionized water until the pH of the filtrate was neutral and finally vacuum dried. The product had a grayish appearance and was not as shiny as the starting material. The as-obtained graphite oxide was redispersed in deionized water and then exfoliated to generate graphene oxide Nano sheets by ultra sonication.

Preparation of MPs composites

In this study, 4 samples with different percent of magnesium hydroxide and PVC were prepared to study thermal properties that were named as follows.

Table 1. The properties of MPs composite samples

Compounds	Composite
PVC 90% - $Mg(OH)_2$10%	PM-10
PVC80% - $Mg(OH)_2$20%	PM-20
PVC70% - $Mg(OH)_2$30%	PM-30
PVC60% - $Mg(OH)_2$40%	PM-40

To prepare the composite samples, a two-armed mixer device was used and its temperature and speed were adjusted respectively as 200 ºC and 60 rpm and then 7 minutes was considered for the formation of composites.

Preparation of MGPs composites

To study the effect of Graphene nanoparticles in retardaning MPs composite samples, 4 samples of MGPs composite were prepared with different percents of Graphene, magnesium hydroxide and PVC and then were named as follows:

Table 2. The properties of the produced composite samples

Compounds	Composite
PVC90% - - $Mg(OH)_2$5%-Graphene 5%	PMG-10
PVC80% - - $Mg(OH)_2$10%-Graphene 10%	PMG-20
PVC70% - - $Mg(OH)_2$15%-Graphene 15%	PMG-30
PVC60% - - $Mg(OH)_2$20%-Graphene 20%	PMG-40

To prepare these samples, a two-armed mixer device was used and its temperature and speed were adjusted respectively as 200 ºC and 60 rpm and then 10 minutes was considered for the formation of composites.

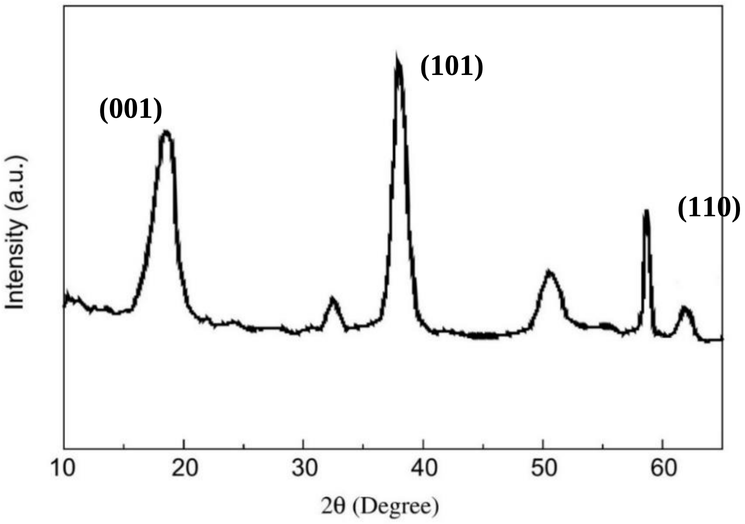
Thermal gravimetric

The tests related to differential thermal analysis were performed by TGA device under ASTM-E1131 standard. Thermal analysis, changes in the sample weight (losing the weight of the sample that is controlled under a heating program) is considered as the basis of thermogravimetry analysis (TG) and test conditions are similar for all produced composites and the temperature increases to 10 centigrade per minute and the temperature range from ambient conditions is to 600 ºC.

Characterization of $Mg(OH)_2$ nanoparticles

The typical powder XRD pattern of $Mg(OH)_2$ nanoparticlesis given in Fig. 1. All diffraction peaks canbe indexed as the hexagonal structure of $Mg(OH)_2$ with the lattice constants comparable to the values of JCPDS7-239. No XRD peaks arising from impurities such as NaCl and MgO were detected. Moreover, the peaks of the samples are significantly broadened. This indicatesthat the $Mg(OH)_2$ particles have a very small grain size,which can be calculated from the broadened XRD peaksby means of Scherrer formula. As a result, the size of 3.77 nm (001), 6.40 nm (101) and 15.11 nm (110) indifferent directions of the crystalline was obtained due toits morphology of thin plate shape or needle-like shape (Table 3).

Scanning electron microscopic analysis (SEM) on magnesium hydroxide nanoparticles was shown in figure 2. As is clear, the magnesium hydroxide nanoparticles have a good and uniform distribution.



.**Fig. 1.** XRD pattern of $Mg(OH)_2$ nanoparticles.

Table 3. Size of $Mg(OH)_2$ particles obtained from the XRD pattern (estimated by Scherrer equation)

Diffraction angle 2θ(deg)	Peak position *d* value (nm)	Miller index (hkl)	Full width at halfmaximum (deg)	Crystallite size (nm)
18.6	0.4765	001	2.157	3.77
38.2	0.2362	101	1.348	6.40
58.6	0.1568	110	0.674	15.11

Characterization of graphene oxide nano sheets (GO)

We employed a mixture of nitric acid, sulfuric acid (1:2) ratio, and potassium chlorate to oxidize the natural graphite powders. During this process, epoxy and hydroxyl groups lie on the surface of each graphene layer, while the carboxyl groups are located near the edges of basal planes of the graphite structure. Simultaneously, carbon hydrolysis occurred and the sp^2 bonds changed to sp^3 bonds. At the same time, NO_3^-, or SO_4^{2-} ions could insert themselves into the graphene layer, inducing an increase in the interlayer spacing.

The FT-IR spectra of GO is presented in Fig. 3. As can be seen, the characteristic peaks of graphene oxide such as the stretching vibration of hydroxyl group (–OH), the stretching vibration of C=O from carboxylic group, the vibration of O=C–O from carboxylate and the vibration of C–O alcohol and C–O–C of epoxy groups centered at 3443, 1735, 1401, 1207 and 1055 cm–1, respectively. Also, the peak at 1629 cm–1 in Fig. 3 is attributed to the vibrations of non-oxidized graphitic domains, in this sample. The oxidation results in an increase in the interlayer spacing of graphite Nano sheets in GO relative to natural graphite, which can be attributed to the intercalation of oxygen-based groups or ions between its layers. Hence, the interlayer distance of graphite can be increased from 3.35 Åof the original graphite to 6-10 Å, depending on water content and the extent of the intercalation process. We monitored the graphite oxidation process by X-ray diffraction. Fig. 4 shows the XRD patterns of the GO. As oxidation proceeds, the intensity of the (002) diffraction line (d-space 3.35 Å at 26.4°) in natural graphite gradually weakened and finally disappeared. Simultaneously, the GO exhibited only one peak at 12.2°. This indicates that the interlayer distance between neighboring graphene layers in GO has increased with oxidation (they are ≈7.22 Å apart), because of the intercalation by oxygen-containing groups and moisture. In during time for 4 days of chemical treatment, the graphite powders were completely oxidized to graphite oxide.

Thermal analysis

The results related to the thermal behavior of MPs composites were shown inTable 4 and the results related to the thermal behavior of MGPs composites were shown in table 5. The temperature of destruction start in MPs composites increased in the first 3 samples with the increase of $Mg(OH)_2$ nanoparticles, but it decreased in PM-40 sample due to the change in physical structure of PVC. In table 4, the highest resistance to keep the physical state of the composite and prevent its destruction is related to PM-90 sample that confirms the effect of $Mg(OH)_2$in retarding the composite. In table 5, there are some MGPs composites that have a difference with MPs composites in the presence of Graphene nanoparticles in the structure of produced composites. One of the most properties of Graphene is the high conductivity of temperature and for this reason, the temperature of destruction start and resistance to keep the physical state of MGPs composites is lower than MPs composites but the thermal resistance of MGPs composites in a temperature over 500 degrees of centigrade is higher than MPs composites.

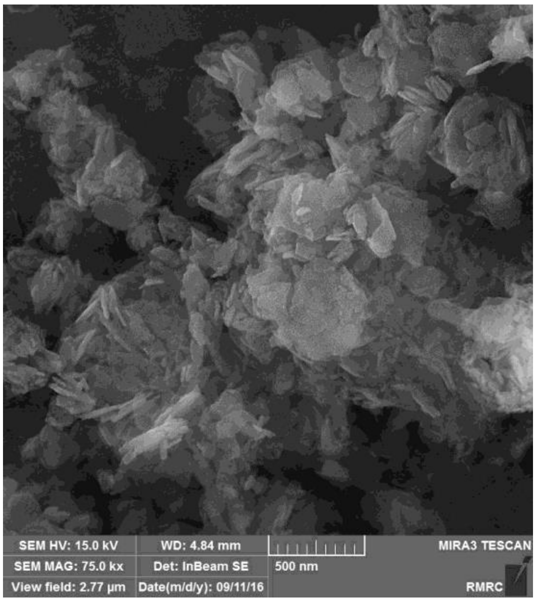


Fig. 2. SEM images of $Mg(OH)_2$ nanoparticles

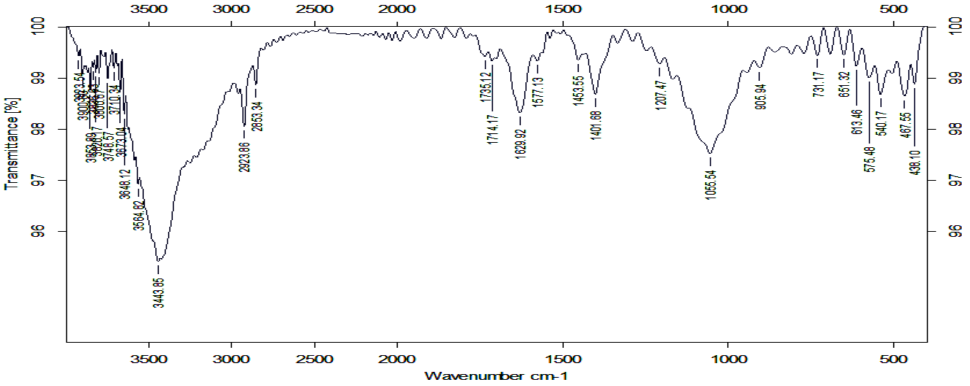


Fig. 3 FT-IR spectra of grapheme oxide

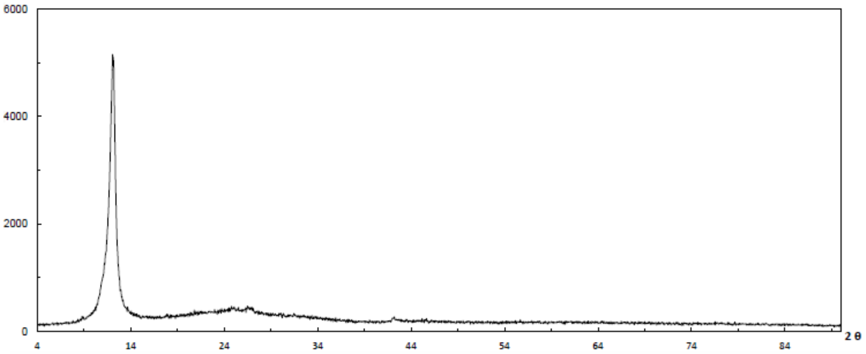


Fig. 4. XRD pattern of graphene oxide

Table 4. Thermal behavior of MPs composites

End Temperature of destruction ºC	Peak Temperature of destruction ºC	First Temperature of destruction ºC	Sample
540	402	255	PM-10
555	403	263	PM-20
570	352	261	PM-30
570	404	200	PM-40

Table 5. Thermal behavior of MGPs composites

End Temperature of destruction ºC	Peak Temperature of destruction ºC	First Temperature of destruction ºC	Sample
550	398	254	PMG-10
557	401	255	PMG-20
568	344	257	PMG-30
600	342	215	PMG-40

The analysis of the remaining percentage of composites

The results related to the remaining percentage of composites after the thermal analysis were shown in Table 6 for MPs composites and in table 7 for MGPs composites. It is obvious that with the increase of the amount of retardants in composite structure, a less percent of them is destroyed. The comparison of tables 6 and 7 shows that a less percent of MGPs composites was destroyed due to hat and its reason is the effect of thermal and mechanical properties of graphene nanoparticles and the improvement of performance in the obtained composites.

Limited Oxygen Index (LOI) analysis

The results of LOI test on MPs composites and MGPs composites were respectively shown in figures 5 and 6. These figures show that with the increase of $Mg(OH)_2$ percent, the minimum amount of oxygen for the ignition of sample has an increasing trend. LOI test of the pure PVC sample was equal to 46.2 that had an increasing trend with the increase of $Mg(OH)_2$ percent to PVC, so that LOI test of PM-40 sample, that 40% of the produced composites contains $Mg(OH)_2$, is 55.8 and has had a 20-percent growth in comparison to pure PVC sample. Figure 6 shows the same increasing trend and the LOI test of P6M-40, that 20% of the produced composites contains $Mg(OH)_2$andanother 20% contains graphene, is 61/8 that has had a 33.7-percent growth in comparison to pure PVC sample.

Table 6. The amount of remaining materials after thermal analysis in MPs composites.

The remaining percentage	Sample
5.42	PM-10
17.17	PM-20
32.31	PM-30
46.24	PM-40

Table 7. The amount of remaining materials after thermal analysis in MGPs composites

The remaining percentage	Sample
3.42	PMG-10
21.13	PMG-20
39.22	PMG-30
55.03	PMG-40

The comparison of Figures 5 and 6 shows the positive effect of Graphene in the improvement of LOI index for MGPs composites and as LOI test of the produced composites is higher; it needs more oxygen for burning. It is obvious that MGPs composites have a better performance than MPs composites.

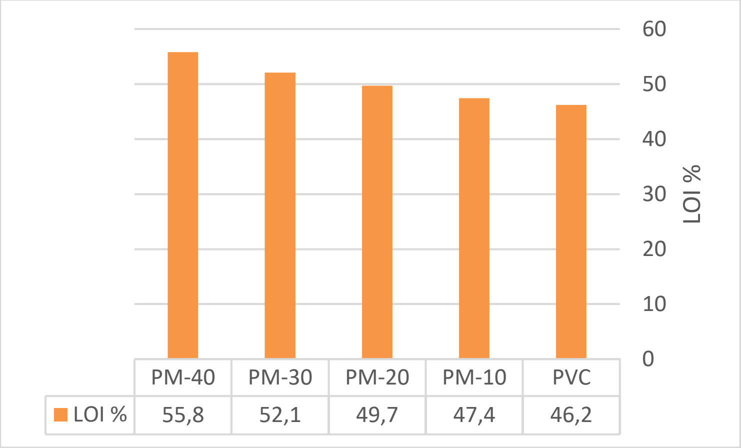


Fig. 5. Limited Oxygen Index (LOI) test for MPs composites

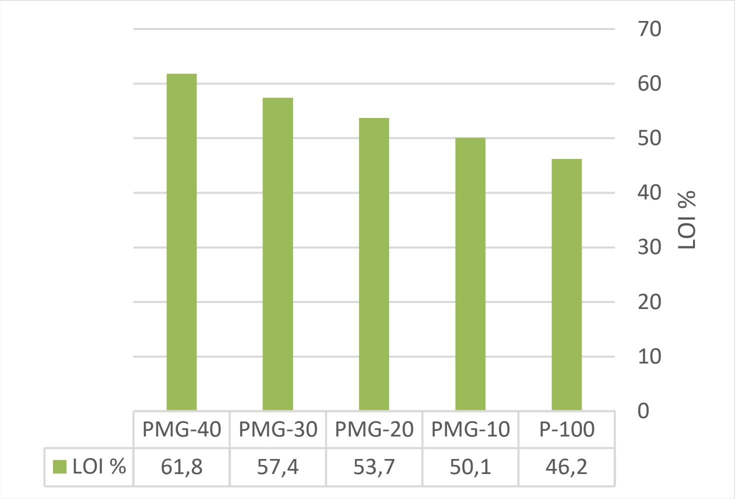


Fig. 6. Limited Oxygen Index (LOI) test for MGPs composites

RESULTS AND DISCUSSION

According to the high importance and use of PVC in different industries, this project attempted to increase the thermal resistance of PVC to fire by using magnesium hydroxide nanoparticles as an additive. Although adding fillers weakens the mechanical and physical properties and behaviors of polymer, according to the obtained results, the resistance of polymer to fire is improved and the amount of leakage from the melt increases. According to the results of TGA and DSC tests, the percent of remaining mass of the materials has an increasing trend with the increase of magnesium hydroxide nanoparticles in the composite. Also, the results of LOI test show that the composites have achieved an appropriate resistance to fire, they do not ignite again and the smoke from the process of burning has reduced. But the thermal behaviors are different in the composites that contain Graphene and magnesium hydroxide. In all samples of MGPs series except PMG-40, the destruction start and destruction peak of composites occurred in a temperature less than MPs composites but the remaining percentage of composites and the results of their LOI test were more desirable than MPs composites and the reason of this occurrence is high capacity and conductivity of Graphene.

Thus, it can be said that among 8 produced composites, PM-20 composite shows desirable results in terms of resistance to fire, and thermal and physical properties .although PMG-40 composite has the highest resistance to heat, due to the high consumption of PVC as the second industrial polymer in the world and high costs of preparing graphene, it will not be economical except specific cases.

REFERENCES

1. X. Almeras, M. Lebras, P. Hornsby, S. Bourbigot, G. Marosi, S. Keszei, *Poly. Degrd Stab.*, **82**, 23 (2003).
2. P. Anna, G. Marosi, S. Bourbigot, M. Lebras, Delobel R. Intumescent flame retardant system of modified rheology. *Polymer Degrad.Stability*, **77,** 243 (2002).
3. S. Bourbigot, M. Lebras, P. Breant, J.M. Tremillon, R. Delobel, *Fire & Mat.*, **20**, 13, (1996).
4. S. Bourbigot, M. Lebras, R. Delobel, R. Decressain, J.P. Amourex, *Faraday Trans*., **92**, 158 (1996).
5. R. Seymour, Additives for Plastics, New York: Academic Press 1978.
6. J. Troitzsch, International Plastics Flammability Handbook. New York: Hanser Pub., 1990.
7. M. Sain, S. Park, F. Suhara, S. Law, *Polym. Degrd. Stab.*, **83**, 337 (2004).
8. S. Zhu, W. Shi, *Poly. Degrd. Stab*. **80**, 217 (2003).
9. Y. Yang, W. Wang, Z. Song, *Ch. Elas*., **13,** 40 (2003).
10. K. Walker, A. Isarov, T. Chen, Fire Performance Synergies of Metal Hydroxides and Metal Molybdates, Antimony-Free Flexible PVC [C], SPE Vinyl Tec, 2010.
11. Z. Wang, B. Qu, W. Fan, P. Huang, *J Appl. Polym. Sci.*, **81**, 214 (2001).
12. S. Stankovich, D. Dikin, G. Dommett, K. Kohlhass, E. Zimney, E. Stach, *Nature*, **44**, 2 (2006).
13. J. Li, L. Vaisman, G. Marom, J. Kim, *Carbo*, **45**, 7, (2007).
14. C. Petit, T. Bandosz, *J. Phys. Chem. C.*, **113**, 3, (2009)
15. A.Lerf, H. He, M. Forster, J. Klinowski, *J. Phys. Chem. B.*, **102**, 4482 (1998).
16. H. He, J. Klinowski, M. Forster, A. Lerf, *Chem. Phys. Lett.* **287**, 56 (1998).
17. Y. Xu, H. Bai, G. Lu, C. Li, G. Shi, *J. Am. Chem. Soc.*, **130**, 585 (2008).