

# The Effect of Nanoclay Particles on the Tensile Strength and Flame Retardancy of Polystyrene – Nanoclay Composite

P. Saraeian, K. Ansari, H. R. Tavakoli, E. Soltani

Department of Mechanical Engineering, Najafabad Branch, Islamic Azad university, Isfahan, Iran

---

## ABSTRACT

This study was conducted to evaluate the effect of nanoclay particles on the tensile strength and flame retardancy of polystyrene- nanoclay composite. To conduct the study, first using melt-intercalation method, and a twin-screw extruder was employed to prepare nanocomposite samples from polystyrene with 4, 5 and 6% nanoclay and then nanocomposite granules were injected into a mold using an injection machine. Of the parts thus prepared, tension samples were made and subjected to tensile tests. Further, to ensure proper morphology of nanocomposite, X-ray diffraction (XRD) and transmission electron microscopy (TEM) tests were conducted. Results showed that by increasing nanoclay up to 5%, the tensile strength and modulus of elasticity were increased, while the strength were decreased when 6%, nanoclay was used. Furthermore, the findings of flame retardancy test indicated that there is a decrease in the heat released coupled with an increase in nanoclay proportion during ignition. This work is an applicable study that showed necessity and advantage of nanomaterials like nanoclay to elevate usability of plastics, a cheap and applicable product of industry and nature, via increasing tensile strength and flame retardancy. Furthermore, durability of plastics is one of the important factors to protect healthy nature. Hence, importance of such nanomaterials like nanoclay can be considered as substantial material, in this regard.

**KEYWORDS:** Polystyrene, Nanoclay, Nanocomposite, Tensile Strength, Flame Retardancy.

---

## 1. INTRODUCTION

Nowadays plastics are used increasingly so that most of the materials produced in many industries are made of plastics or affiliate materials. Compared to metals, plastics, among other things, are low in price and costs for formation, require less effort to recycle and are environment-friendlier in nature. However, among other limitations, are their unstable mechanical properties at higher temperatures, lower viscoelasticity compared to metals and much lower flame retardancy. Hence, using plastics in alloys or composites overcomes many drawbacks. However, using composites has their own drawbacks including the fact that reinforcing particles serve to concentrate stress [1]. For this reason, nanomaterials are used to reinforce plastics that have unique properties including the considerably large surface-to-volume ratio and the aspect ratio. Further, a considerably small proportion of these materials increase plastics tensile strength and flame retardancy. In 1974, because of their higher aspect ratio and the thickness of nanometric layers compared to polymer chains, clay layers were introduced as ideal fillers. In 1993, about two decades later, the Toyota research team managed to create a great revolution into the technology of nanocomposites by successfully developing polyamide-6 nanoclay composite. By adding a very small proportion of nanoclay particles, about 4%, to polymer, they managed to raise the tensile modulus by 70% and the tensile strength by 40% [2]. Later, many a researcher conducted extensive studies on the production of nanocomposites using a variety of methods from various materials, exploring the factors affecting them [3, 4, 5]. For instance, nanoclay composite is one result of these studies analyzed by two methods of X-ray diffraction (XRD) and transmission electron microscopy (TEM) [6, 7]. Adding a small proportion of nanoclay albeit can improve some other properties of polymers in many cases [8] like tensile strength of polymers. Although this may add to the brittleness of polymers exposed to impact, increased modulus of elasticity many times its size have also been reported [9]. A current major concern over using polymers is their flammability hazard. Hence, when researchers first learned that nanoclay particles could reduce flammability of polymers, a considerable number of researchers focused their efforts on lowering the flammability of polymers by using nanoclay particles [10, 11]. Additionally, as polystyrene falls within the category of materials used widely in building construction and affiliated industries, decreased flammability of this material has always been a concern. Evidently, this has been tested with other materials and the findings reported [12, 13]. The aim of the present study is to find an appropriate proportion of nanoclay particles to increase tensile strength and flame retardancy of polystyrene – nanoclay composite.

---

\*Corresponding Author: P. Saraeian, Department of Mechanical Engineering, Najafabad Branch, Islamic Azad university, Isfahan, Iran

## 2. MATERIALS AND EQUIPMENT

The materials needed for this study include polystyrene and nanoclay. The polystyrene required for the test was supplied from En-Chuan Company in Taiwan. Also, the nanoclay required for this study was supplied from Southern Clay Company in USA. On the recommendations of this company, Cloisite 15A was selected for polystyrene [5]. Clearly, polystyrene contains a non-polar molecule. It can be said that the molecule is hydrophobic with no affinity to combine with hydrophilic substances. However, nanoclay is a hydrophilic substance. Therefore, it is very difficult to combine these two materials. Hence, as suggested by previous researches, a catalyst was used. Accordingly, poly (methyl methacrylate) was used [4, 14, 15]. Among other, the equipment used in the study, reference can be made to a vacuum oven for drying, Brabender twin-screw extruder with a length-to-diameter ratio screw of 52 and a screw chamber diameter of 25 mm, type DSE25 for mixing nanocomposite, injection machine, injection mold, XRD equipment, TEM and Tensile strength equipment.

### 3. Testing Procedure

The stages in conducting the test for the purpose of this study are drying the nanoclay and polyamide granules in a vacuum oven heated to 80 °C for 12 and 24 hours respectively, mixing the two substances in Brabender twin-screw extruder, preparing nanocomposite granules, injecting nanocomposites, producing standard parts, tensile strength test, XRD test, conducting TEM test to determine the nanocomposite morphology and flammability test which will be discussed in subsequent sections.

#### 3.1. Nanocomposite Granules Preparation

At this stage, polystyrene and nanoclay were stored in a vacuum oven heated to 80 °C for 24 and 12 hours respectively to dry. To mix nanoclay particles and polystyrene, a twin-screw extruder with a length-to-diameter ratio of 25 was used. To obtain nanocomposites with 3, 4 and 5% nanoclay, first 1kg of Master-batch with 10% nanoclay was prepared. In order to improve on nanoclay dispersion, poly (methyl methacrylate) was used as a compatibilizer. The proportions of polystyrene, nanoclay and poly (methyl methacrylate) used in nanocomposites were 900, 100 and 100 grams respectively. Then, to prepare nanocomposites, the samples were diluted with correct quantity of polystyrene. The extruder temperature and equipment RPM were set at 180 °C and 250 respectively.

#### 3.2. Preparation of Nanocomposite Samples

When nanocomposites granules were produced, to prepare parts for the tensile strength test, the granules needed were converted into standard parts. Hence, an injection mold was used to produce parts measuring  $3.4 \times 50 \times 100$  mm. The injection pressure in the machine used for production of parts was set at 30 bars, the injection temperature for nanocomposites with 4% and 5% nanoclay was set at 220 °C and the injection temperature for nanocomposite samples with 6% clay was set at 230 °C.

#### 3.3. Test for Dispersion of Nanoclay Particles in Nanocomposites

In order to ensure correct dispersion of particles in the internal structure of nanocomposite Philips XRD equipment with a wavelength of 1.54 angstroms and a copper electrode measuring the dispersion intensity at angles 1 to 30 degree and a speed of 0.04 degree /second were used. To ensure correctness, first the samples were scanned at low to 30-degree angles and then re-scanned with a higher precision of zero to 5 degrees angles. The findings are presented in the succeeding sections.

#### 3.4. Tensile Strength Test

To measure the tensile strength and modulus of elasticity, samples were prepared from nanocomposite samples per ASTM D 638 standard and then tested using Instron tensile strength test equipment Type 5500 at a recommended speed of 50M/Min. The findings are presented in the subsequent sections

#### 3.5. Flame Retardancy Test

The most essential feature for flammability measurement of materials is the Heat Release Rate (HRR). A cone calorimeter measures and plots this feature every second. The peak of this curve referred to as maximal heat release rate is reported numerically. In a number of reports, apart from this feature, there is another critical parameter obtained by dividing the ignition time into the maximal heat release rate. Accordingly, this feature has been reported for all test materials used in this study. To measure the effect of nanoclay particles on the nanocomposite flame retardancy, a flammability test was conducted using Atlas CONE-2 Type calorimeter at a heat flux of 50 KW/M<sup>2</sup>. The samples thus prepared measure  $100 \times 100$  mm<sup>2</sup> and the findings are reported in the next section.

### 3.6. Scanning electron microscopy (SEM) and TEM Tests

In order to verify the findings from XRD test and ensure correct dispersion of nanoclay particles in the nanocomposite basis a SEM Type XL30 manufactured by Philips, Netherlands was used. Also, layers of the samples as thin as 60 nanometers heated to -160 °C were cut using an OMU3 ultrasonic cutter and then tested for nanocomposite structure using a Philips 120 kv TEM, Type EM 208S.

## 4. RESULTS AND DISCUSSION

### 4.1. The Nanocomposite Tensile Strength

The findings from the tensile strength test are briefly presented in Figure 4 and table 1. To ensure accuracy of the findings, each test was conducted three times. As can be seen, the findings apply to polystyrene nanocomposite with 4, 5 and 6% nanoclay and pure polystyrene. Similarly, reference can be made to an increase in strength by adding the proportion of nanoclay up to 5%. However, when nanoclay reaches 6%, the strength decreases. The cause of reduced ultimate strength at 6% nanoclay might reduce the inter-layer distance, reduce the inter-layer polymer chain and the intra-chain bond which ultimately results in reduced mechanical strength. It should be noted that polystyrene is a highly hydrophobic substance with no affinity to interact with hydrophilic substances. Hence, nanocomposites with 5% nanoclay have maximal strength (27% increases in strength) which with further increase in nanoclay particles result in reduced strength.

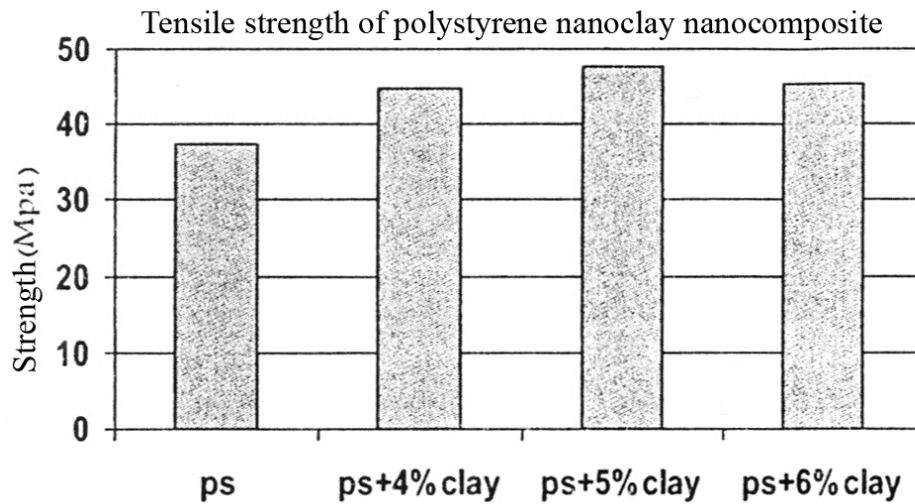


Figure 1 - Ultimate Strength of Nanocomposites Compared

Table 1 - Findings from the Tensile Strength test to measure the strength of nanocomposite

Samples	Tensile Strength, Mpa	Proportion Increase
Pure Polystyrene	37.5	
Nanocomposite with 4% Nanoclay	44.8	19.4%
Nanocomposite with 5% Nanoclay	47.6	26.9%
Nanocomposite with 6% Nanoclay	45.2	20.3%

### 4.2. Nanoclay Particles Dispersed in Nanocomposites

To learn about the structure developed in nanocomposites, in this section, the nanoclay inter-layer distance in the presence of polystyrene is examined using XRD test. Figure 2 displays the XRD findings for polystyrene nanocomposites with various improved nanoclay proportions as well as pure polystyrene and pure nanoclay (Cloisite 15A). The presence of peaks in the figure indicates the presence of nanoclay and the locations where peaks are formed indicates the nanoclay inter-planar distance. The intensity of XRD will not provide precise information on the sample behavior for it heavily depends on the quantity of the test sample. As can be seen from the figure, clay has three distinct peaks at these angles. The first of the above three peaks pertains to an angle of about  $2\theta = 2.75$  indicating an inter-layer distance of 32.1 angstroms. The second peak placed next to the first peak is at  $2\theta = 5.2$  with an inter-layer distance of about 16.98 angstroms. This peak pertains to a set of montmorillonite silicate layers with incomplete corrective operations for the correction time has a significant effect on the inter-layer distances. The

third peak is at  $2\theta = 7.7$  angle with an inter-layer distance of 11.47 angstroms which is due to the clay layers not subjected to corrective operations. Hence, it is more difficult for a polymer chain to find its way into the inter-layer distances and more difficult for it to separate. In table 2, the inter-layer values for nanocomposites have been prepared and inserted.

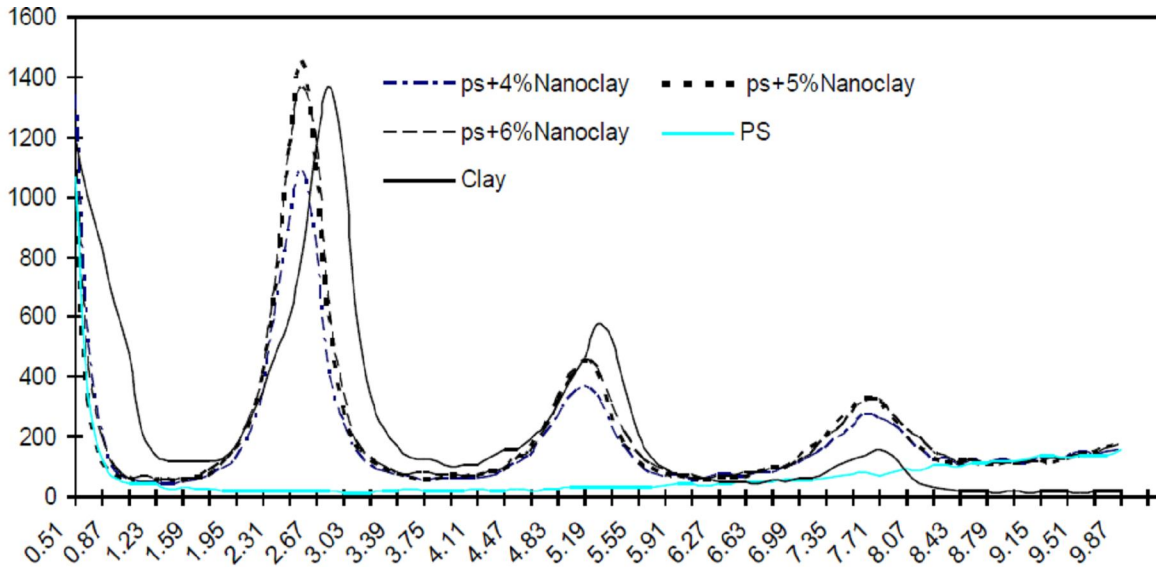


Figure 2 - Findings from XRD Test in nanocomposite and pure polystyrene samples

Table 2 - Values for the angles and inter-layer distances for different nanocomposites

Substance Description	Angle of first peak, degrees	Inter-layer distance, Angstroms	Morphology
Cloisite 15A nanoclay	2.75	30	
Nanocomposite with 4% weight of nanoclay	2.50	35	Inter-layer
Nanocomposite with 5% weight of nanoclay	2.55	34	Inter-layer
Nanocomposite with 6% weight of nanoclay	2.6	33	Inter-layer

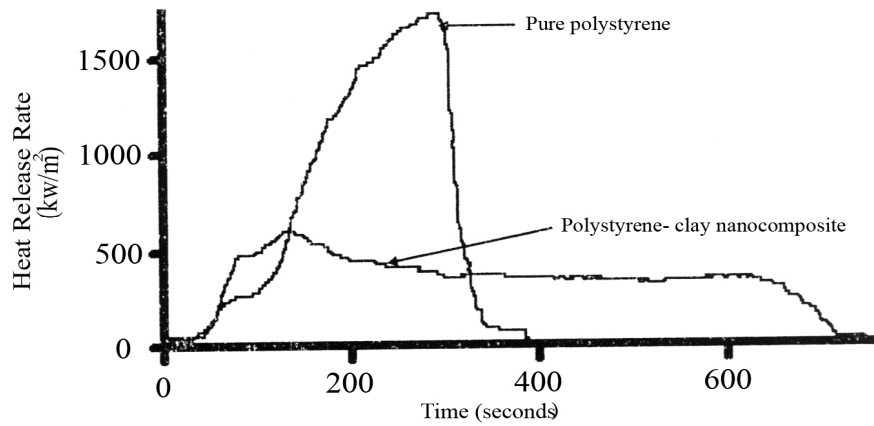
Here, as can be seen, because of its structure, pure polystyrene is absolutely peak-free. However, by adding nanoclay, peaks emerge. Also in nanocomposites with 4% nanoclay, the first peak tends right and when the polymer chain finds its way into the silicate layers, increases the inter-layer distance to about 35 angstroms. Further, in nanocomposites with 5% nanoclay, the inter-layer distance remains unchanged. However, in nanocomposites with 6% nanoclay, the inter-layer distance is approximately reduced and that the nanocomposite structure continues in an inter-layer nature.

### 4.3. Flame Retardancy

In Figure 3, the curves for heat release rate measured in time were plotted on a system of coordinates for nanocomposites with 5% nanoclay as opposed to pure polystyrene. Clearly, a significant reduction was made in polystyrene-clay nanocomposite heat release rate by adding 5% clay to the polymeric carrier. In fact, it can be said that the flammability of polystyrene 5% clay nanocomposite as opposed to pure polystyrene decreased by over 70%. The tests were conducted on three nanocomposite groups. The findings from a cone calorimeter are presented in Table 3.

Table 3 - Data from a cone calorimeter

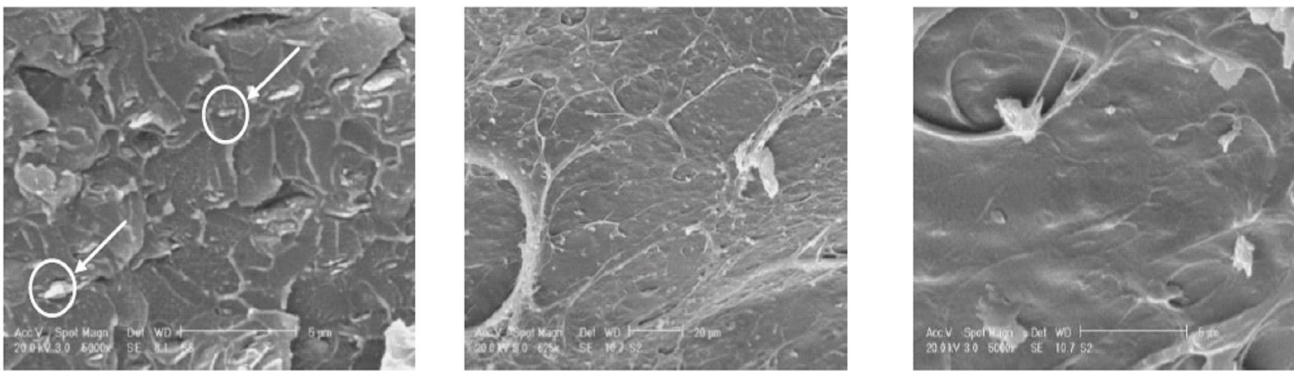
Calorimeter Data	HRR (kw/m <sup>2</sup> )	HRR Reduction %	IT (s)	H <sub>c</sub> (MJ/kg)	SEA (m <sup>2</sup> /kg)	MLR g/sm <sup>2</sup>	IT/HRR (M <sup>2</sup> S) <sup>2</sup> /MJ
Pure Polystyrene	1820	71	25	32.1	1314.12	53.6	13.7
Polystyrene Nanocomposite with 5% nanoclay	527		25	28.2	1723.34	14.6	47.4



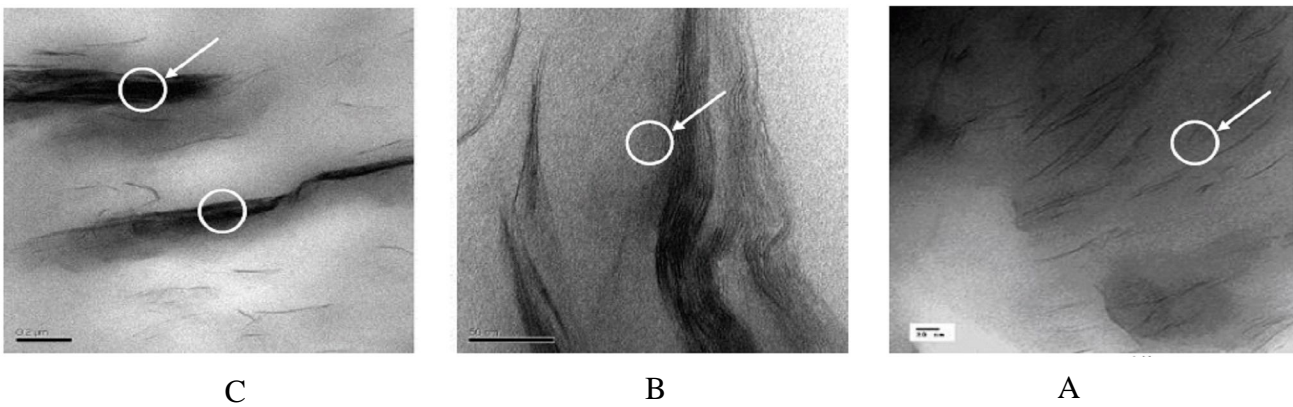
**Figure 3** - Changes in Heat Release Rate expressed in time for pure polystyrene and their nanocomposites

**4.4. Images from SEM and TEM Tests**

The images from SEM and TEM tests are shown in figures 4 and 5 respectively. Figure 4A provides a TEM image of nanocomposite with 4% nanoclay. As can be seen, there is no indication of concentration of particles while in nanocomposites with 6% nanoclay (Figure 4C) there are white spots indicative of concentrated nanoclay particles. These observations completely match the findings from XRD test.



**Figure 4** - Images from SEM: A. 4% Nanocomposite; B. 5% Nanocomposite; C. 6% Nanocomposite



**Figure 5** - Images from TEM: A. 4% Nanocomposite; B. 5% Nanocomposite; C. 6% Nanocomposite

Figure 5A provides TEM images of nanocomposites with 4% nanoclay. As can be seen, the nanoclay particles are completely separated while in Figure 5C, the nanoclay particles fail to fully separate from one another and that the structure is of a nature where the particles are concentrated. Also in Figure 5B, there is a mode between the two previous modes, i.e. the nanoclay particles were neither completely separated from one another such as it is neither in 4% nanocomposite nor in a completely concentrated and non-dispersed mode such as in the 6% mode. Here, it can be seen that the TEM findings approximately match the XRD findings and can plausibly account for the tensile strength test.

## 5. Conclusion

The findings from this study indicate that with an increase in nanoclay proportion of up to 5% the tensile strength increases. However, when nanoclay proportion is increased further, the tensile strength is reduced. This can be taken to be due to a reduction of the nanoclay inter-layer distance and their coming near to each other again. To show how clay layers are positioned in relation to one another and their dispersion pattern in nanocomposites, three methods i.e. XRD, TEM and SEM were used.

With XRD, an increase in inter-layer distance with up to 5% nanoclay and then a decrease in inter-layer distance with 6% nanoclay could be clearly seen. The images obtained from TEM and SEM tests support the findings from XRD. They also clearly show the dispersion of particles in samples containing 4 and 5% nanoclay and their subsequent concentration in nanocomposites with 6% nanoclay. Furthermore, with an increase in nanoclay proportion in polystyrene structure, there is a decrease in the heat release rate. This reduction in the heat release rate can be taken to be due to absorption of heat by nanoclay layers. In general, the results confirm that the tensile strength and the flame retardancy properties of polystyrene – nanoclay composite containing 5% nanoclay are better than polystyrene – nanoclay composite containing 4% or 6% nanoclay .

## Acknowledgments

The authors feel obliged to express their gratitude to the authorities of the Islamic Azad University of Najafabad Branch for their financial support for this study undertaken in a research project registered under # 51504860801004 .

## REFERENCES

1. Suprakas Sinha Ray, Masami Okamoto, 2003. Polymer/layered silicate nanocomposites: a review from preparation to processing, *Prog. Polym. Sci.*, 28 : 1539–1641.
2. Younghoon Kim, 2004. A Study of Polymer/Clay Nanocomposite Formation by Melt- Interaction Process, PhD. Thesis, Akron University.
3. Ray S. Fertig, Mark R. Garnich, 2004. Influence of constituent properties and micro structural parameters on the tensile modulus of a polymer/clay Nanocomposite, *Composites Science and Technology.*, 64 : 2577–2588.
4. N. Sheng, M.C. Boyce, D.M. Parks, G.C. Rutledge, J.I. Abes, R.E. Cohen, 2004. Multiscale micromechanical modeling of polymer/clay nanocomposites and the effective clay particle, *Polymer.*, 45: 487–506.
5. Linjie Zhu, K.A. Narh, 2004. Numerical Simulation of the Tensile Modulus of Nanoclay-Filled Polymer Composites, *Journal of Polymer Science: Part B: Polymer Physics.*, 42: 2391–2406.
6. Zanetti M, et. all, 2001. Combustion Behaviour of EVA-Flurohectorite Nanocomposite, *Polymer Degradation and Stability*, Elsevier ., 74 : 413-417.
7. Gilman J. W., 2000. Flammability Properties of Polymer-Layered- Silicate Nanocomposites, *Polypropylene and Polystyrene Nanocomposites*, *Chemistry of Materials.*, 12: 1866-1873.

8. Lan T., Pinavaya T. J., 1996. Nanolayer Ordering in an Epoxy-Exfoliated Clay Hybrid Composite, *Mat. Res. Soc. Symp. Proc.*, 435: 79-84.
9. J. Wanga, R. Pyrz, 2004. Prediction of the overall modules of layered silicate-reinforced nanocomposites—part I: basic theory and formulas, *Composites Science and Technology.*, 64: 925–934.
10. K.Y. Leea, D.R. Paul, 2005. A model for composites containing three-dimensional ellipsoidal inclusions *Polymer.*, 46 : 9064–90.
11. J. Wuite ,S.Adali, 2005. Deflection and stress behavior of Nanocomposite reinforced beams using a multiscale analysis, *Composite Structures.*, 71 : 388–396.
12. Xiaodong Li, Hongsheng Gao<sup>1</sup>, Wally A Scrivens, Dongling Fe, Vivek Thakur, Michael A Sutton<sup>1</sup>, Anthony, P. Reynolds and Michael L Myrick, 2005. Structural and mechanical characterization of nanoclay-reinforced agarose nanocomposites, institute of physics publishing, *Nanotechnology.*, 16: 2020–2029.
13. G.M. Odegard, T.C. Clancy, T.S. Gates, 2005. Modeling of the Mechanical Properties of Nanoparticle/Polymer Composites; *Polymer.*, 46(2): 553-562.
14. Zeng C, Lee LJ., 2001. Poly (methyl methacrylate) and polystyrene/clay nanocomposites prepared by in situ polymerization. *Macromolec.*, 34(12): 4098.
15. Zeng C, Han X, Lee LJ, Koelling KW, Tomasko DL., 2003. Polymer–clay nanocomposite foams prepared using carbon dioxide. *Adv Mater (Weinheim, Germany).*, 15(20): 1743.