



Comparison of Physical and Mechanical Behavior of Polypropylene Nanocomposites Reinforced with Different Percentages of Montmorillonite Modified

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ABSTRACT

In this research, the effect of polypropylene modified montmorillonite (Cloisite15A) evaluation. From maleic anhydride compatibilizer on polypropylene nanoclay was used for compatibility. And the third level of 1.5%, 3.0%, and 4.5%. the results of mechanical tests on the modified nanoclay shows the PP module increases the tensile strength and flexural strength compared to pure polypropylene. And tensile strength from 1.5 to 4.5 wt% nano-clay modified in this study, the effect of modified montmorillonite (Cloisite15A) polypropylene is investigated. These properties showed the largest increase at 3% by weight. To identify these nano-composites ray diffraction X (XRD) and scanning electron microscopy (SEM) were used. XRD studies showed the structure of Nano composites results from an intercalation structure. (SEM) images showed that added PP-g-MA improves the diffusion capability of modified clay in polypropylene matrix and creates a homogenous structure.

Key words: Polypropylene; Nanoclay(Cloisite 15A) ; Nano composite; Flexural and Tensile strength.

INTRODUCTION

One of the earliest applications of Nano filler production Nano technology was to improve mechanical properties of composites. Interest in production of composite materials with reinforcements in Nano level has grown quickly in recent years [1, 2]. Recently there has been a growing interest for the development of polymer/clay Nano composites due to their dramatic improved properties compared to the conventional

filled polymers in a very low fraction of filler addition [3]. Polypropylene is one of lightest and most important Nanoparticles used in polymeric nanocomposites have commodity thermoplastic with a wide variety of been divided into three categories defined in terms of the applications. [4-6].

Apart from its application in plastic number of dimensions of their nanometer size, viz. one industry which has a good share in the market it is

used dimension (platelets), two dimensions (fibers and in textile industry as fibers as well as taps. Growth in the whiskers) and three dimensions (nearly spherical production of polypropylene fiber is the largest among particles). Layered nanoparticles can be exfoliated into a synthetic fibers. The major end-uses of polypropylene dispersion of individual platelets fibers are in special apparel, automotive, home furnishing, One of the most commonly used organically layered industrial and other areas [7,8].

The layered silicates are natural or synthetic minerals consisted of the regular stacks of alumino silicate layers with a high aspect ratio and high surface area. Layered silicates are easily in available and have low cost. The current of the most popular layered silicates used in polymer Nano composites preparation of clays. The preparation of polymer/clay Nano composites with good dispersion of clay layers within the polymer matrix is not possible by physical mixing of polymer and clay particles [9].

The intrinsic incompatibility of hydrophilic clay layers with hydrophobic polymer chains prevents the dispersion of clay Nano layers within polymer matrix and causes to the weak interfacial interactions. Incompatibility and weak interfacial interactions hinders the exfoliation and preparation of dispersed stable Nano composite with improved properties. Modification of clay layers with hydrophobic agents is necessary in order to render the clay layers more compatible with polymer chains [10, 11].

In general, the structures of polymer/clay Nano composites are classified according to the

level of intercalation and exfoliation of polymer chains into the clay galleries. Various parameters including clay nature, organic modifier, and polymer matrix and preparation method are affective on the intercalation and exfoliation level [12]. mechanical properties and therefore fillers are commonly called as reinforcement agents [13-17]. It should be noticed in higher loadings of compatibilizers, they may cause to the some degree of plasticization due to their lower molecular weight, which negatively affect on the modulus of Nano composite .Also the incorporation of clay minerals usually improves the tensile strength of polymers [18-23].

Therefore; given the importance of the issue and a global approach to Nano composites and due to the unknown mechanism of these materials; in recent year; several studies have been conducted on the properties of polymer-clay Nano composites; and applied development of these materials. In the present study; physical and mechanical properties of modified polypropylene Nano composite/Nano clay have been investigated; and the best percentage of modified Nano clay filler (Cloisite15A) with more desirable physical and mechanical properties for industry and mechanical properties for industry and commerce is suggested. Structure of the research is as follows.

EXPERIMENTAL

Materials

In this study; polymer matrix: polypropylene was used as background material that has the following specification ;and the Nano-clay powder that produced by America's southern-clay company (Cloisite15A brand) was used Cloisite15A clay is a natural form of montmorillonites that has been

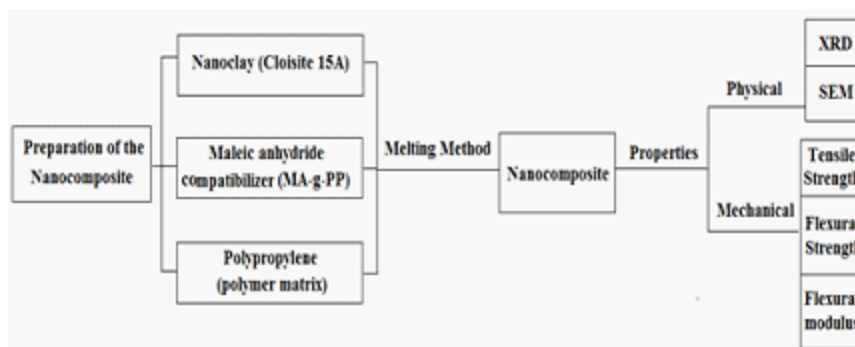


Fig. 1: Structure of the research is as follows

modified with ammonium salt type IV. For changing the hydrophilic property of Nano clay particles to Organophilic property; and to make it reactive with polymer matrix. Furthermore; the modified clay improves the penetration of polymer chains into the clay layers and thus improving the properties of the final product. The specification of the Nano-clay used and its chemical structure is shown in the table below. Also; maleic Anhydride linked with polypropylene (MA-g-PP) at (4) % (by weight) was used as the coupling factor (PP-G101 brand) produced by Kimiajavid Company (Sepahan; Iran).

To prepare a composite; polypropylene and Nano clay particles were dried in a vacuum oven for 12 h, at 90° c; so the total possible moisture be removed from their surfaces; and the materials were weighed and prepared in a laboratory scale. Polypropylene granules and different modified Nano clay particles as much as required by ratios of 1.5%; 3.0%; and 4.5% percent of the filler were added to melting polymer according to table (1). Melt mixing was conducted in an internal mixer

(Hake-Remixer) equipped to roll dual blades. The materials were mixed at 180° C with rotational speed (60 rpm) in 15 min; so the matrix and filler phases were optimally mixed. Then the materials were prepared in the form of granules, by using dual martini extruder (model; WPC - 4815) made by Bornu Pars Company. And using a laboratory hammer mill; the granules were crushed to powder. Next; test specimens were prepared through hot press. Then; mechanical tests including flexural strength; flexural modulus; and tensile strength were performed on them.

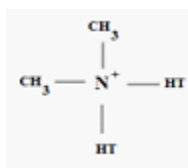
Mechanical testing

Tensile test was carried out at room temperature; by using MTS device (Model: 10/m). The specimens used were selected with 75.5,35 mm dimensions. Tensile test was performed at the speed of 50 mm/min .tensile, bending modulus and the amount for different loading of modified Nano clay particles were measured in the Nano composite.

Table 1: Specifications of polypropylene and Chemical structure and properties of modified Nano-clay (Cloisite15A) used in Nano composite

Specifications of polypropylene					
Density (gr/cm ³) Amorphous	Density (gr/cm ³) Crystal	Density (gr/cm ³)	Melt flow index (gr/10min)	Commercial Code	Company
0.85	0.95	0.90	18 - 22	Moplen V30S	Iran Arak Petrochemical

Chemical Structure and Properties of Modified Nanoclay (Cloisite15A)				
Beam x-ray Diffraction(d ₀₀₁ A°)	ModifierConcentration CEC(Meq/100)	Organic modify	% WeightLoss on Ignition	Commercial Name
31.5	125	2M2HT*	43%	Cloisite15A



*2M2HT: dimethyl, dehydrogenated tallow, quaternary ammonium, and HT is Hydrogenated Tallow (~65% C18; ~30% C16; ~5% C14)

Table 2: Specifications of the prepared Nanocomposites*

Sample	PP	MA-g-PP	Nanoclay (Cloisite15A)
Pure PP	100.0%	—	—
Nanocomposite with 1.5% Nanoclay (A)	98.5%	—	1.5%
Nanocomposite with 1.5% Nanoclay (B)	94.5%	4.0%	1.5%
Nanocomposite with 3.0% Nanoclay (C)	97.0%	—	3.0%
Nanocomposite with 3.0% Nanoclay (D)	93.0%	4.0%	3.0%
Nanocomposite with 4.5% Nanoclay (E)	95.5%	—	4.5%
Nanocomposite with 4.5% Nanoclay (F)	91.5%	4.0%	4.5%

Physical Testing

X-Ray Diffraction

Nano-structure of layered clay and morphology of Nano composites produced are examined through (XRD) test using x-ray diffraction device (model: Advance SiemensD500; made in Germany) with diffraction radiation and wavelength (1.54 \AA); accelerator voltage (40 KV); and a current of 30 mA. Diffraction spectrum at $2\theta=2$ was obtained between $2-10^\circ$; and the distance between layers (d_{001}) was obtained using Bragg's law as follows: $2d\sin\theta = n\lambda$

Scanning electron microscope (SEM)

Scanning electron microscopy studies were carried out using SEM (Hitachi HH-2R). After tensile test, the fracture surfaces of the specimen were sputter coated with gold before analysis; in order to eliminate electron charging.

RESULTS AND DISCUSSION

Mechanical properties

There is a close correlation between the mechanical properties of Nano composites and their internal structure. The properties of any plastic

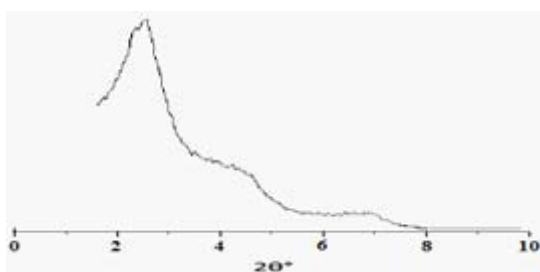


Fig. 2: Modified Nano 3% in Nano composite

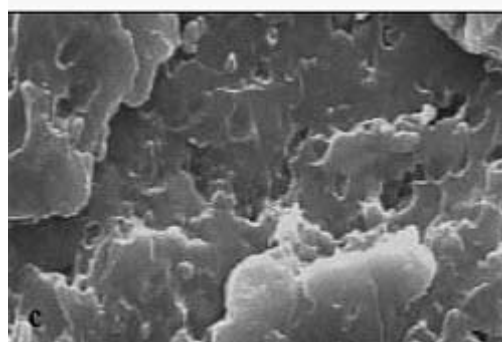
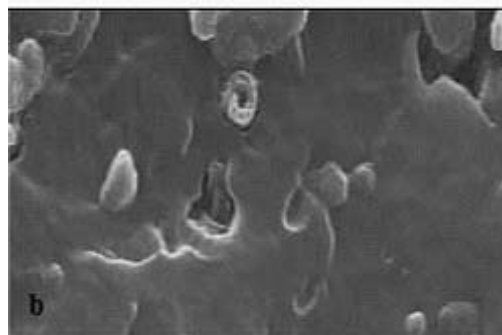
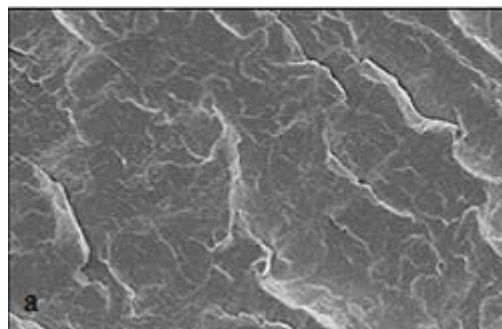


Fig. 3: SEM image of a Nano composite (a:1.5% ; b: 3.0%; and c: %4.5 modified Nano clay)

reinforced with particles depend on the type of polymer and the reinforcement material used; as well as the array and ways of particles are connected to the polymer phase.

Flexural Properties

In fig (4); the impact of the amount of the modified clay on bending strength of the composite specimens is shown. According to this fig (fig 5); the highest Flexural strength was obtained in treatments containing 3 wt. % clay. It seems the Flexural strength is a function of the amount of clay in the composite reduced with a 4.5 WT% increase in the clay; because the modified Nano clay particles reinforce the Flexural strength of the composite. As a result of forming Composite as a result of forming Connections with the polymer matrix However; forming connections with the polymer matrix. However; after a certain level; the increasing process of properties is reduced with an increase

in the clay percentage; and even at times it can be reversed.

That is why the results show that as the Nano clay particle percentage increases; Flexural strength decreases. In fact; it appears that large amounts of the Nano clay particles lead to accumulation which in turn concentrates the stress and reduces Flexural strength by 3 percent compared to the specimen reduced Flexural strength in higher percentages of Nano clay can prevent from balancing allotment of stress and adequate freedom of chains due to the increased inter locking which results in reduced strength in large amounts of Nano particles.

Flexural modulus shows the adequate force needed to bend the specimen .therefore; more solid objects have a higher bending module [18] .increased clay in a composite improves its Flexural

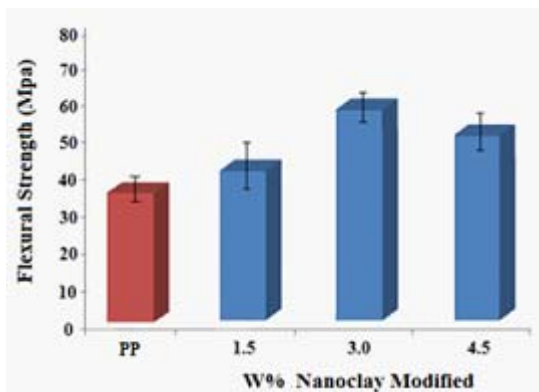


Fig. 4: Flexural strength of a Nano composite with different percentages of the modified Nano clay

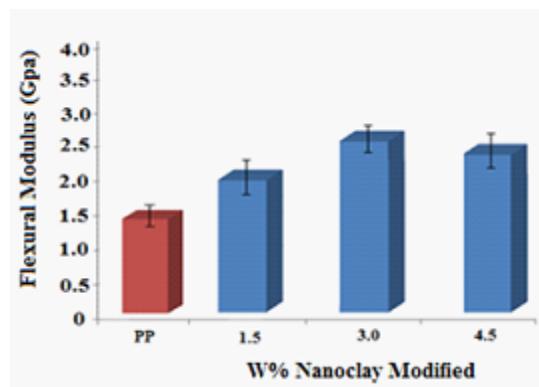


Fig. 5: Flexural modulus of Nano composites with different percentages of the modified Nano clay

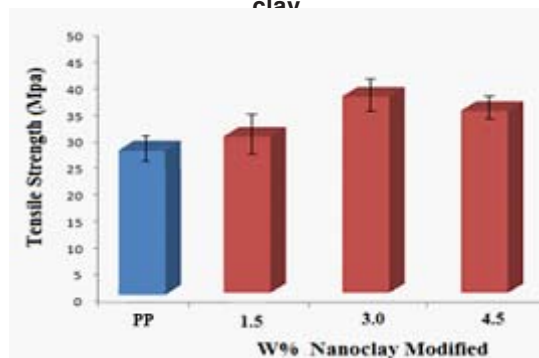


Fig. 6: tensile strength of the Nano composite with different percentages of modified Nano clay

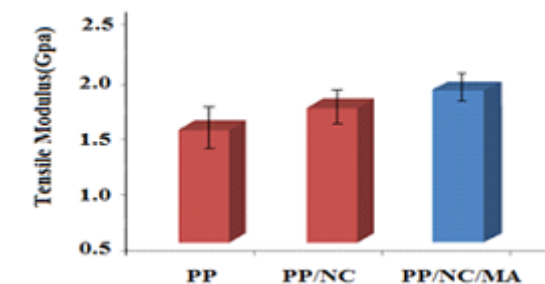


Fig. 7: Tensile modulus in different states

modulus. As shown in fig(5); in 3 percent by weight of Nano clay ;a reinforcing effect can be seen in the properties of polypropylene composite Flexural modulus. In fact; Nano metric particles with high length to diameter ratio are largely in common with the constant phase of the polymer that justifies increased strength of Nano composites .However; as WT% of Nano clay increases from 3.0. To 4.5 percent; the properties of Flexural modulus show a reduction. Not only do the properties of Flexural modulus depend on the properties of the components; but also they are affected by the distribution of clay and interfacial cohesion between Nano clay and the polymer. Results of the published report as well confirm these findings [24].

Tensile Properties

Fig (6) shows the effect of the amount of modified Nano clay on tensile strength and tensile modulus of the specimens of the composite. According to this fig; the highest bending strength is obtained in the specimen with 3.0 percent by weight of modified Nano clay. It is reduced to 4.5 percent as Nano clay increases. Table 4 shows the Findings from the Mechanical properties to measure the strength of nanocomposites.

Studies on polypropylene Nano composite-in which maleic Anhydride (PP-g-MA)is added to clay and thereby reinforces the filler distribution-confirm this. in other words ;by adding MA compatiblizer. The modulus improves .this is because of proper distribution of Nano clay particles. And As inflation and foliation (developing a layered structure) of the polymer increases; layers and the common area between the polymer and the filler

increases as well. This is done when the modulus increases significantly.

Physical Properties

Fig (2) shows x-ray diffraction of polypropylene Nano composite filled with modified Nano-clay. X-ray diffraction peak of the modified Nano clay (Cloisite15A) is created at an angle of $2\theta=2.81^\circ$; with a space of $d_{00}=31.39$ nm between the layers which is shifted towards a lower angle (which is related to $2\theta=2.37^\circ$; with a $d_{001}=37.31$ space between the layers) as XRD peak increases by 1.5 to 3.0 percent in the Nano composite; while with an increase in the amount of Nano clay by 4.5 percent ; the intercalation space reduced due to the concentration and density of the clay masses($d_{001}=35.94$, $2\theta=2.52^\circ$). According to fig (2) and increased space between the clay layers; the Nano composite form is type of intercalation; since the peak related to the crystal area of Nano clay is not disappeared; and it is just reduced towards lower 2θ .in other words; the space between silica layers of Nano clay is increased as a result of the polymer chain permeation; however full separation of the clay layers has not occurred. However; if the structure of the Nano composite is type of exfoliation; due to the collapse of the crystal structure; no peak is left in the curve.

Fig (3) shows SEM image of the Nano fracture surface of composite with 1.5%, 3.0%, 4.5% by weight) of the modified Nano clay. In fig (4-b); the Nano composite with 3.0% by weight of the modified Nano clay; the fracture surface shows a constant environment; and the reason is the effectiveness of the Nano clay particles in improving the interaction

Table 3: Findings from the Mechanical properties to measure the strength of nanocomposites

Sample	Flexural Strength (Mpa)	Proportion increase	Flexural Modulus (Gpa)	Proportion increase	Tensile Strength (Mpa)	Proportion increase
Pure Polypropylene	37.12±1.0	—	1.4±1.0	—	29.65±1.0	—
Nanocomposite 1.5% Nanoclay	44.76±4.0	21.23%	1.9±0.3	35.71%	31.78±4.0	7.18%
Nanocomposite 3.0% Nanoclay	59.18±3.0	59.11%	2.5±0.2	78.57%	38.54±3.0	29.98%
Nanocomposite 4.5% Nanoclay	53.40±4.0	43.56%	2.3±0.3	64.28%	35.11±2.0	18.41%

between Nano clay and polymer. This will increase the strength of the Nano composite; however; an increase in the amount of the modified Nano clay from 3.0% to 4.5% (fig 4-c with 4.5%) will result in the accumulation and Concentration of the Nano clay particles; thus showing ineffectiveness of the Nano clay particles.

With an increase in the amount of modified Nano clay by 3.0 WT%; bending strength; tensile strength; and bending modulus will

increase; however; if there is a 4.5 Wt. % increase; these properties will reduce. Examining the morphology of Nano composites by SEM showed that addition of modified Nano clay will improve the interaction between particles and the matrix; and specimens with 3.0 WT% of Nano clay have a larger intercalation space and %4.5 Nano clay (by weight) compared to specimens (1). and XRD confirms the formation of intercalation structure in the resulting Nano composite.

REFERENCES

1. A.L. Roes, E. Marsili, E. Nieuwlaar, and M.K. Patal, Environmental and Cost Assessment of a Polypropylene Nanocomposite, *Journal of Polymers and the Environment*, **2007**, 15(3), 212-226:
2. I. Kvien, Characterization of Biopolymer Based Nanocomposite, PhD Thesis, Norwegian University of Science and Technology: **2007**.
3. E.T. Thostenson, C. Li, and T.W. Chou, Nanocomposites in context, *Compos. Sci. Technol.*, **2005**, 65, 491-516:
4. M. Modesti, A. Lorenzetti, D. Bon, and S. Besco, Thermal behaviour of compatibilised polypropylene nanocomposite. Effect of processing conditions., *Polym Degrad Stab.*, **2006**, 91(4), 672-680:
5. M.V. Zaragoza, F.J. Vargas, M. Rodriguez, and B.M.H. Martinez, Thermal stability and flammability properties of heterophasic PPEP/ EVA/organoclay nanocomposites, *Polym Degrad Stab*, **2006**, 91, 1319-1325:
6. B. Minisini, and F. Tsobnang, Molecular dynamics study of specific interactions in grafted polypropylene organomodified clay nanocomposite, *Composites Part A: App. Sci. Manufact*, **2005**, 36, 539-544:
7. S. Zhang, A.R. Horrocks, R. Hull, H. Kandola, and B.K. Flammability, degradation and structural characterization of fibre-forming polypropylene containing nanoclay-flame retardant combinations., *Polym Degrad. Stab.*, **2006**, 91, 719-725:
8. L.A. Utracki, Clay-Containing Polymeric Nanocomposites. UK, Rapra Technology Limited, Shropshire. U.K., vol.1: **2004**.
9. S. Pavlidou, and C.D. Papaspyrides, A review on polymer-layered silicate nanocomposites., *Prog. Polym. Sci.*, **2008**, 32, 1119-1198:
10. M.B. Ahmad, W.H. Hoidy, N.A.B. Ibrahim, and E.A.J. Al-Mulla, Modification of montmorillonite by new surfactants., *J. Eng. Appl. Sci.*, **2009**, 4, 3, 184-188:
11. G. Chigwada, D. Wang, D.D. Jiang, and C.A. Wilkie, Styrenic nanocomposites prepared using a novel biphenyl-containing modified clay, *Polym. Degrad. Stab.*, **2006**, 91, 755-762:
12. S.S. Ray, A new possibility for microstructural investigation of clay-based polymer nanocomposite by focused ion beam tomography., *Polymer*, **2010**, 51, 3966-3970:
13. L. Jiang, Y.C. Lam, K.C. Tam, T.H. Chua, G.W. Sim, and L.S. Ang, Strengthening acrylonitrile-butadiene-tyrene (ABS) with nano-sized and micron-sized calcium carbonate., *Polymer*, **2005**, 46, 243-252:
14. G. Gorrasi, M. Tortora, V. Vittoria, E. Pollet, B. Lepoittevin, and M. Alexandre, Vapor barrier properties of polycaprolactone montmorillonite nanocomposites: effect of clay dispersion. *Polymer*, **2003**, 44, 2271-2279.
15. M. Tortora, G. Gorrasi, V. Vittoria, G. Galli, S. Ritrovati, and E. Chiellini, Structural characterization and transport properties of organically modified montmorillonite / polyurethane nanocomposites., *Polymer*,

- 2002** 43 6147–6157.
16. M.A. Osman, J.E.P. Rupp, and U.W. Suter , Effect of non-ionic surfactants on the exfoliation and properties of polyethylene - layered silicate nanocomposites. *Polymer*, **2005** 46 8202-8209.
 17. V. Mittal, Mechanical and gas permeation properties of compatibilized polypropylene – layered silicate nanocomposites., *J. Appl. Polym. Sci.*, **2008** 107 1350-1361.
 18. T.D. Fornes, P.J. Yoon, H. Keskkula, and D.R. Paul, Nylon 6 nanocomposites: the effect of matrix molecular weight., *Polymer*, **2001** 42 9929–9940.
 19. J.S. Shelley, P.T. Mather, and K.L. DeVries , Reinforcement and environmental degradation of nylon 6/clay nanocomposites., *Polymer*, **2002**. 42 5849–5856.
 20. D. Sikdar, D. R. Katti, K. S. Katti, and R. Bhowmik, Insight into Molecular Interactions between Constituents in Polymer Clay Nanocomposites., *Polymer*, Vol. 47., **2006.**, 51.,96-5205.
 21. B. Xu, Q. Zheng, Y. H. Song, and Y. G. Shangguan, Calculating Barrier Properties of Polymer/Clay Nanocomposites: Effects of Clay Layers, *Polymer*, **2006**. 47.,2904-2910.
 22. P. Meneghetti, and S. Qutubuddin, Synthesis, Thermal Properties and Applications of Polymer-Clay Nanocomposites, *Thermochimica Acta*, **2006**. 442 74-77.
 23. G. Scocchi, P. Posocco, A. Danani, S. Prici, and M. Fermeglia, To the Nanoscale, and Beyond: Multiscale Molecular Modeling of Polymer-Clay Nanocomposites, *Fluid Phase Equilibria.*, **2007**. 26(13)66-374.
 24. L. Wan , K. Wang , L. Chen, Y. Zhang, C. He, Preparation, morphology and thermal/mechanical properties of epoxy/nanoclay composite., *Composite Part A: Applied Science and Manufacturing.*, **2005.**, 11 1890-1896.