A study of physical and mechanical properties of polypropylene Nano composites/modified Nano clay

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Abstract: In this study; physical and mechanical properties of polypropylene Nano composites have been examined using modified Nano clay fillers (Cloisite15A brand) and a ompratiblizer called Maleic Anhydride (MA). In order to 3 levels of %1; %3; and %5 and using X-ray diffraction (XRD) and a Scanning Electron Microscope (SEM); it was examined. Results of (XRD) showed that 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. Testing the mechanical properties showed that tensile and bending strength increased from 1 to 3 percent modified Nano clay by weight; and with an increase in modified Nano clay; the properties decrease. In these Nano composites; the resistance to shock decreases as the amount of modified Nano clay increases.

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Key words: Nano composite; polypropylene; maleic anhydride; modified Nano clay; bending and tensile strength.

Introduction

Today; the significance of polymer Nano composites is obvious to all. These materials having unique properties; have attracted the attention of many scientist and craftsmen[1].Polymer Nano composites are prepared from nanoparticle dispersion in a polymer matrix. The more the compatibility of and interaction between nanoparticles and a polymer is the better properties can be gained from Nano composites[2]. One of the earliest applications of Nano filler production nanotechnology was to improve mechanical properties of composites. Interest in production of composite materials with reinforcements at Nano level has grown quickly in recent years[3,4]. An impact of Nano fillers on composite materials depends on the size of the particles; morphology combination; and their diffraction quality. Nano level clay with a large area ratio helps fabricate good reinforcements and improve all mechanical properties of polymer. Since small quantities of Nano clays are sufficient to improve all properties of composite materials at low costs; they have created an interest; industrially[5,6]. montmorillonites are found in abundance with high purity in nature. And also their chemical structure is so that they could be compatible with organic polymers highly used polymers in polymer-clay Nano composites; we can mention polystyrene; polypropylene; polyethylene; polymethacrylate; etc. in general; layered materials are hydrophilic compounds; and that's why they have a proper compatibility and mixing with different types of polar polymer matrices . However; the layers are difficult to separate due to strong electrostatic forces. Prior to the synthesis of polymer Nano composites; some modifications should be made to these materials[7]. Surface Modification of clay has many advantages; including the possibility of synthesis and penetration of polymers between the layers.[8]

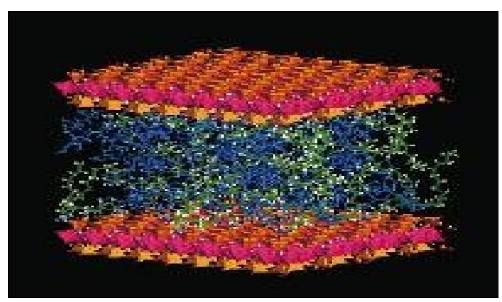


***Fig (1)-modified clay nanoparticles.**

Several researchers have done profound studies on polymer Nano composites of silica layers. Wang et al stated that the influence of Nano clay particles on the properties of composites depends on the form; size; apparent coefficient; type; quantity; and quality of the particles and their adhesion in the area of connection. They also found that addition of small amounts of Nano clay particles improves the Mechanical; thermal properties of composites and stabilizes their dimension. From their studies on the morphological and mechanical-thermal properties of the Nano clay particle-reinforced composites they concluded that these fillers-due to their layered structures-lead to better diffraction of particles in the polymer matrix and finally; they increase tensile modulus; tensile strength; and hardness of composites[9-12]. Foe and Nagoya in a study titled as ((investigating the impact of Nano clay on the mechanical properties of Composites)) stated that only a small amount of monmorillonite matter; having a high apparent coefficient and forming a layered and intercalation structure; could significantly increase the elastic modulus; tensile and bending strength; and also it could lead to an elongation at the fracture point of composites. However; they also conclude that oversized nanoparticles decrease the mechanical strength in composites[13]. Samal et al evaluated the effect of silica layers modified with organic materials on the Mechanical; thermal; and morphological properties of polymer Nano composites. And shock resistance while adding clay to polypropylene matrix improved significantly[14]. 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. In this study; polymer matrix: polypropylene films were used as background material that has the following specification:

Table (1)-specifications of polypropylene used in Nano composite

*materials:

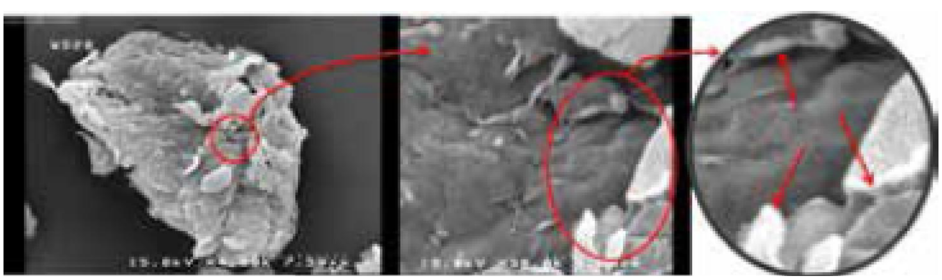
Melt flow index (gr/10min)	Density (gr/cm^3) Amorphous	Density (gr/cm^3) Crystal	Density (gr/cm^3)	Company	Commercial Code
18 – 22	0.85	0.95	0.9	IRAN Bandaremam	Molène V30S

In this study; the Nano-clay powder produced by America's southern-clay company (Cloisite15A brand) was used Cloisite15A clay is a natural form of montmorillonites that has been modified with ammonium salt type Iv .in order to change the hydrophilic property of the clay nanoparticles into organophilic property; and also 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 given in the table below:

Table (2)-chemical structure and properties of modified Nano-clay (Cloisite15A) used in Nano composite.

Beam x-ray Diffraction (d_{001} A°)	Modifier Concentration CEC (Meq/100)	Organic modifier	The Chemical Structure	Commercial Name
31.5	125	2M2HT*	CH3 CH3 - N* - CH3 CH3	Cloisite15A

***2M2HT: dimethyl, dehydrogenated tallow, quaternary ammonium**



FE-SEM image of the modified clay nanoparticles (Fig 2).

Also; maleic Anhydride linked with polypropylene (MAPP) at (4) percent (by weight) was used as the coupling factor (PP-G 101 brand) produced by kimiajavid company (sepahan; Esfahan; Iran).

Methods and devices

To prepare a composite; polypropylene and clay nanoparticles were dried in a vacuum oven for 12 hours at 80 c; so that total possible moisture be removed from their surfaces; and the materials were weighed using a laboratory scale. Polypropylene granules and different of modified clay nanoparticles as much as required by ratios of 1;3; and 5 percent of the filler were added to the polymer melt according to table (1). Melt mixing was conducted in an internal mixer (Hake- Remixed) equipped with roll dual blades. The materials were mixed at 180 c with rotational speed (60 rpm) at 15 min; so that matrix and filler phases are optimally mixed. Then the materials were prepared in the form of granules 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 bending strength; bending modulus; and shock strength were performed on them.

Table (3)-specifications of the prepared composites*

Sample (code)	PP	MA (4%)	Nano-clay cloisite15A
Pure PP	100 g	-	-
(95PP/4mA/1N)	95 g	4 g	1 g (1%)
(93PP/4MA/3N)	93 g	4 g	3 g (3%)
(91PP/4MA/5N)	91 g	4 g	5 g (5%)

In the addition;

Nano-structure of layered clay and morphologhroy 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 A); accelerator voltage (40 KV); and a current of 30 MA. Diffraction spectrum at θ=2 was obtained between 2- 10; and the distance between layers (d...1) was obtained using brag's law .as follows: 2dsinθ=n λ

***scanning electron microscope (SEM):**

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

***device Analysis (mechanical test)**

Tensile test was carried out at room temperature; using MTS device (Model: 10/m). The specimens used were selected with 76*6*36 mm dimensions. Tensile test was performed at the speed of 50 mm/min .tensile; bending modulus and shock strength and the amount for different loading of modified clay nanoparticles were measured in the Nano composite. Dynamic and mechanical analysis (DMTA) of the specimens was out using DMA (triton technology; auk) trite 2000 device. The test was conducted in the frequency of (1) hertz and within a temperature of 110-170 °c at a heating rate of 3° c/min.

Results and Discussion

Morphological studies

Fig (3) shows x-ray diffraction of polypropylene Nano composite filled with modified Nano-clay .it shows that as the amount of Nano-clay increases from 1 to 3 percent; the space between silica layers increases as well. X-ray diffraction peak of the modified Nano clay (Cloisite15A) is created at an angle of 2θ=2/81°; with a space of d_{00}=31/39 nm between the layers which is shifted towards a lower angle (which is related to 2θ=2/37º; with a d_{00}=37/31 space between the layers) as XRD peak increases by 1 to 3 percent in the Nano composite; while with an increase in the amount of Nano clay by 5 percent; the intercalation space reduced due to the concentration and density of the clay masses(d_{00}=35/33, 2θ=2/45°). According to fig(2) and increased space between the clay layers; the Nano composite formed 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.

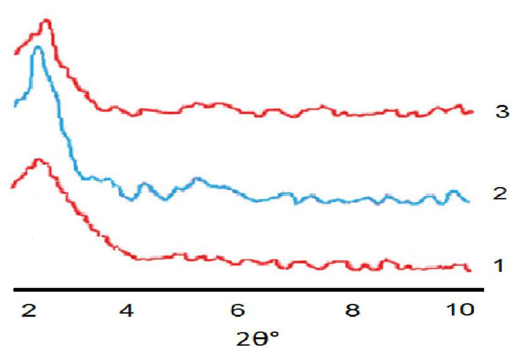


***fig (3)-modified Nano clay 3 (5%); 2(3%); 1(1%) in Nano composite**

Fig (4) shows SEM image of the Nano composite's fracture surface with 3%, 5% by weight) of the modified Nano clay. In fig (4-a); the Nano composite with 3% by weight of the modified Nano clay; the fracture surface shows a constant environment; and the reason is the effectiveness of the clay Nano particles in improving the interaction 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% to 5% (fig 4-b with 5%) will result in the accumulation and Concentration of the clay Nano particles; thus showing ineffectiveness of the clay Nano particles.

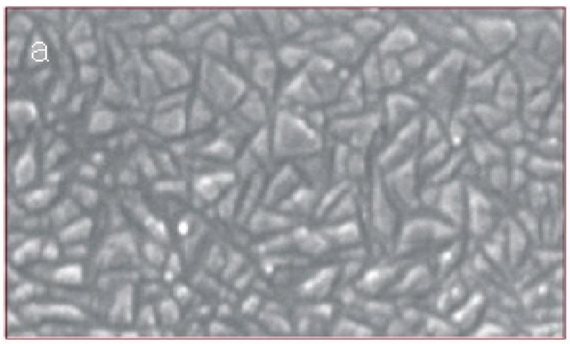


Fig (4): SEM image of a Nano composite (a: %3; and b: %5 modified Nano clay)

*Mechanical properties: there is a close correlation between the mechanical properties of Nano composites and their internal structure. The properties of any plastic reinforced with particles depends on the type of polymer and the reinforcement material used; as well as the array of the particles and the way they are connected to the polymer phase.

Bending strength:

In fig (5); 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 bending strength was obtained in treatments containing three wt. % clay.it seem that bending strength is a function of the amount of clay in the composite. With a 5 WT% increase in the clay; bending strength of composites reduced. Because the modified clay Nano particles reinforce bending 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 reversed. That is why the results show that as the clay's Nano particle percentage increases; bending strength decreases. In fact; it appears that large amounts of the clay Nano particles lead to accumulation which in turn concentrates the stress and reduces bending strength by 3 percent compared to the specimen reduced bending 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's which results in reduced strength in large amounts of Nano particles.

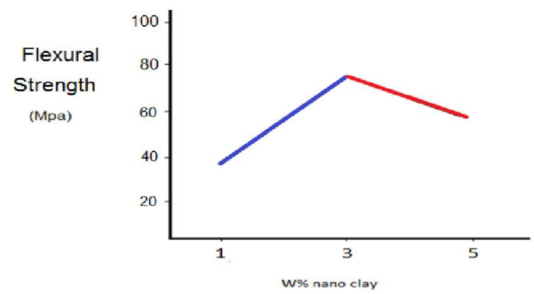


Fig (5): bending strength of a Nano composite with different percentages of the modified Nano clay.

***bending modulus**

Bending modulus shows the adequate force needed to bend the specimen .therefore; more solid objects have a higher bending module .increased clay in a composite improves its bending modulus. As shown in fig(6); in 3 percent by weight of Nano clay;a reinforcing effect can be seen in the properties of polypropylene composite bending 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 to 5 percent; the properties of bending modulus shows a reduction. Not only do the properties of bending 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.

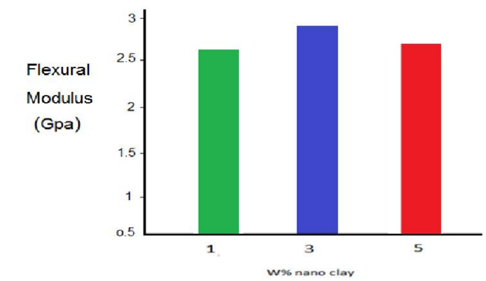


***fig (6): bending modulus of Nano composites with different percentages of the modified Nano clay**

***tensile strength**

Fig (7) 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 percent by weight of modified Nano clay. It is reduced to 5 percent as Nano clay increases.

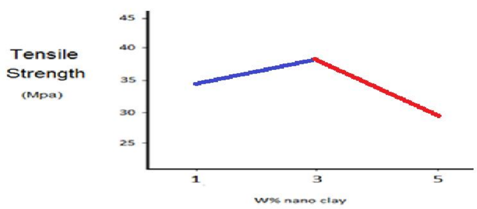


*fig (7): tensile strength of the Nano composite with different percentages of modified Nano clay.

Studies on polypropylene Nano composite-in which maleic Anhydride (MA)is added to clay and thereby reinforces the filler distribution-confirm this.in other words;byadding MA compatiblizer. The modulus improves .this is because of proper distribution of clay Nano particles. 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 when the modulus increases significantly.

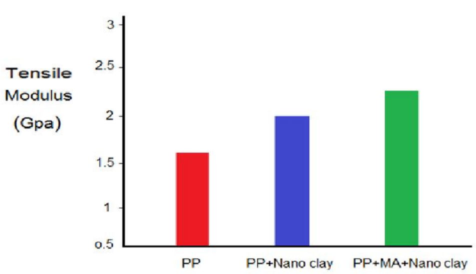


*fig (8)-tensile modulus in different states

shock strength:

This fig(9) shows shock strength of the composite specimens in which clay Nano particles at high weight levels tend to accumulate and these accumulation can easily lead to cracks around them and create the focus of stress and finally result in fracture and reduced shock properties in fact; as Nano clay percentage increases due to the reduction of mobility in chains and possibility of wasting their energy; shock strength is for all three specimens with modified Nano clay .moreover; on increase in the amount of Nano clay results in areas within the polymer matrix which concentrate the stress and initializer the extension of the crack from that area .furthermore; restricted movement of polymer chains near such particles with aspect ratio improves the material resistance against crack development; compared to the common aspheric particles.

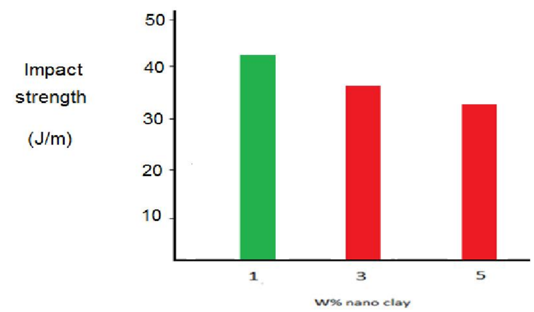


*fig (9): shock strength of the Nano composite with different modified Nano clay.

Conclusion

With an increase in the amount of modified Nano clay by 3 WT%; bending strength; tensile strength; and bending modulus will increase; however; if there is a 5 Wt. %increase; these properties will reduce. Shock strength is rebuked as the amount of modified Nano clay increases. 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 with3 WT% of Nano clay have a larger intercalation space and %5 Nano clay (by weight)compared to specimens (1).and XRD confirms the formation of intercalation structure in the resulting Nano composite.

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