Original Article

Modification of Polypropylene Grid PP552R Using Nanoclay Properties and Study of Modified Polymer Properties

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Abstract

The study of physical, mechanical, and thermal properties provides useful information on the effect of nanoclay and compatibilizer on the polymer matrix as well as the process method. Polypropylene Grid PP552R is production of Shazand Petrochemical Complex that is a homopolymer grid used in textile industry. In this study, to improve the thermal, physical and mechanical properties of this polymer, the effect of nanoclay on it was investigated. In order to improve the dispersion of nanoclay in polymer matrix, 30% nanoclay with a mastercover of malic anhydride PPG-ol was prepared as a polymer-based compatibilizer in a melt mixing kit. Then the master batch at concentrations of 2%, 5% nanoclay was added to the polypropylene. To evaluate the distribution of nanoclay in polymer matrix, XRD and SEM tests were performed. The results showed that intercalated layer structure occurred. The thermal properties of these nanocomposites were tested by DSC and TGA tests, as well as physical and mechanical properties. DSC results show that the temperature of TC increases with increasing nanoclay, which indicates an increase in crystallinity. TGA results showed that the thermal resistance increased with increasing nanoclay. The tensile and bending tests showed that with increasing nano-clay modulus, the tensile strength at the point of submission and failure increased, but the percentage change in length at the point of submission and failure decreased.

Key words: polypropylene nanocomposite, compatibilizer, nanoclay, oligomer, melt mix

INTRODUCTION

Due to the environmental problems and the accumulation of waste from the use of synthetic polymeric products today, a lot of efforts are being made to produce materials that are compatible with nature. Polypropylene / nanoclay nanocomposites are opening up new aspects of the applications of polymer materials. The small increase in nanoparticles in the polymer matrix can significantly increase the material content and increase its use.[1.2] The use of polypropylene nanocomposites has attracted the interest of academics and industry more than ever. The main advantage of nanoparticles in polymer matrix is compared to micro-molecule materials. A smaller amount of nano-materials is needed to create multi-functional properties.[3,4]

To achieve a good polypropylene performance, uniform distribution of fillers in polymer matrix, a strong surface adhesion between nanoclayers and polymer matrixes is required for the synthesis of a nano-polymer filler compound [5, 6] Thermoplastic polypropylene is widely used in sanitary, domestic and automotive coatings, home textiles. Due to the low cost of producing and resistance to chemicals, polypropylene fibers are widely used in the furniture industry and carpet and carpet production. [7,8] Polypropylene having a low melting point between °C180-160 the power of fusion process by nanomaterials improve its properties. By modifying the polypropylene, you can improve the fiber's properties, including color. [9,10] New techniques that are used today to increase the performance of polypropylene fibers to enter new markets. Typical methods for improving the properties of fibers and fabrics do not result in permanent effects, and they lose their function after a while.

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[11] Because of their higher energy levels, nanoparticles have better performance to increase the properties of polypropylene. For this reason research and research on the modification of polypropylene nanocomposite fibers has increased.Generally, the mixing of polymer materials with nanoscale materials increases the thermal stability and strength of the fibers used in various industries. [12, 13] Scanning electron microscopy (SEM) and transmitted electron microscopy (TEM) are a good way to investigate the structure and dispersion of nanoparticles in a polymer matrix. Also, (DSC) and (TGA) are a good description of the thermal stability of nanocomposites in polymer. Tensile, bending, and impact tests have been considered to increase the mechanical properties of polymer nanoparticles. [14,15] In different compositions and concentrations of used nanoparticles in the polypropylene matrix, the correct results are obtained on the shape and surface performance of modified nano fillers and their combinations. Polypropylene Grid PP552R is a homopolymer, which accounts for 90% of annual production of polypropylene based on this grade. This research work provides a thorough understanding of the relationship between properties of polypropylene structure and the analytical methods described. This is in the direction of creating value in petrochemical and customer-centric products.

MATERIALS AND METHODS

Materials
The nanoclay used in this research work is the Closite15A manufactured by ZHESIANG FENCHONG, China country with the DK4 brand. This soil is a natural montmorillonite that has been modified by alkaline ammonium due to its water friendliness and has become an organic friend. The nanoclay properties used in this study in Table 1 and PP-552R and PP-g-MA polypropylene grays are given in Table 2.

Preparation of polypropylene / nanoclay nanocomposites
Preparation of masterbatch
The Master Bach of Nanorro / Malic anhydride were prepared by the melt mixing method, which was performed

Table 1: Features of Closite15A nanoclay

Company	x-ray d001(A)	Special density	Moisture percent	Montmorillonite	2θ
FANCHONG	36	1.7gr/cm³	3%›	98%	7.19

Table 2: Polypropylene properties

Batch No.	Production company	MFI $_{gr/10\ min}$	D $_{gr/cm^3}$
PP	Shazand Petrochemical Co.	30	0.904
PP-g-MA	Aria polymer	17	0.913

in which 30% nanoclay, 5% of the polypropylene graphed with malic anhydride and 65% of the base polymer in the double-strand component BAU TEK L 40 / D 19 at 180 ° C and at 100 rpm of 8 min in the form of fibers from Die. In the water pool, which was controlled by circulating water, the temperature was controlled to an ambient temperature of about 25 ° C and turned into a granule by the mill.

Preparation of nanocomposite
At first, the Master Bach of PP552R was provided with a master bach of PP552R powder with 10gr of calcium stearate and 10g of antioxidant (SIPAX 13215). Polypropylene nanocomposite samples using PP552R direct melt mixing with different weight percent of nanoclay C15 and malic anhydride PP-g-MA in a double-rolled model BAU TEK L40 / D 19 in operating conditions, the temperature is 180 and 100 rpm, 8min. Each sample contains 500 gr of sample with different nanoclay percentages. Weight percentages and preparation formula are given in Table 3. Certain amounts of PP552R and maleic anhydride / nanoclay meanders simultaneously through the feeder and the side feeder enters the compartment compartment after mixing at 8 min at the indicated temperature of the nanocomposite from the nozzle of the end of the compander in the form of a single-strand fiber outside. In a pool of water, controlled by temperature control, the sample was turned into a granule until the temperature of the cold environment and after drying. The tests were performed to analyze the properties of nanocomposites.

DISCUSSION AND RESULTS

Determine the structure
Scanning electron microscopy (SEM)
In order to ensure uniform dispersion of the modified clay in the polymer matrix, a screw electron microscope (SEM) with a PROX model with a magnification range of up to 130,000 times, a KV 10 voltage (Fig. 1)

In SEM, samples are bombarded with a beam of electrons of 100A □ diameter. Due to the collision of electron beams with the sample of electrons excited by the electrons at the time of returning to its original circuit, electrons are emitted from the sample surface and collected and analyzed by a detector. The results of this test show that

Table 3: Percentage of consumables for polypropylene nano-composites production

Sample	Weight percent PP552R	Weight percent PP-g-MA	Weight percent C15A%
PP552R$_1$	100	0	0
PP552R$_2$	93	5	2
PP552R$_3$	90	5	5

polymeric matrices such as nanoparticles, which are a non-polar material, can be dispersed by a compatible device. Dispersing images and non-accumulation of nanoclay in the polymer matrix confirmed.

X-ray diffraction (XRD)

This test is the most common method for measuring the distribution of nanoparticles in polymer nanoparticles. The XRD method is a simple and accessible method for quantitative and qualitative research. The X-ray diffraction (XRD) method has been used to investigate the structure of nanoclay, nanocomposite and the distribution of polymeric chains. This test is based on 2 at an angle between 10 ° to 70 ° with a 40kv 30 mA generator at 25 ° C, using the PHILIPHS model X pert. (fig 2)

Charts show using Bragg's law ($n\lambda = 2\ d\sin_\theta$), where λ is the wavelength of the beam, d is the distance between the

plates and $_\square$ the angle between the incandescent beam and it can be calculated from the distance between the plates (d). With this rule, it is possible to find that the more the courier is in a lower angle, the more spacing the pages. As shown in Fig. 2, in this spectrum, two regions of the nanocomposite are seen to be a part of the nanoclay itself. A polypropylene region is observed in the area of open-angle nanocrystal radiation to a distinct peak in the region of $2_{\theta\ =7.19}$ *, which uses the Bragg formula to distance d = 18.05. In the case of 2% nanocomposites, 5% of the open angle of radiation shifted to a smaller angle, which is $2_{\theta\ =\ 7.13\ and\ 2\theta=7.17}$. The peak of the nanoparticles is less intense. The diffraction curve for the low concentrations indicates the removal of the courier, while indicating the full dispersion of the nanoworld plates in the polymeric bed. At higher concentrations, the desired peak does not disappear but its severity has been reduced to a lower degree. This shows that the PP-g-MA molecules interlocked between nanoclay silicate layers and increased the spacing of nanoclay plates. The graphs indicate that the intercalated layer structure has occurred.

Table 4 shows that with the insertion of polymeric chains, the nanowires of the layers are separated from each other.
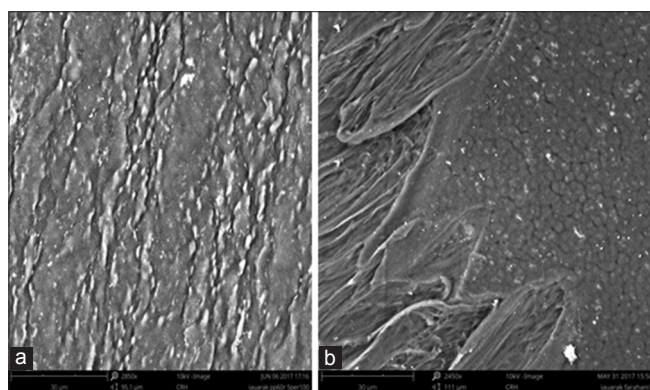

Figure 1-A: SEM Polypropylene with 2% Nanoclay Figure 1- B- SEM Polypropylene with 5% Nanoclase

Table 4: Results of XRD pure polypropylene and nanocomposite with 2%, 5% nanoclay

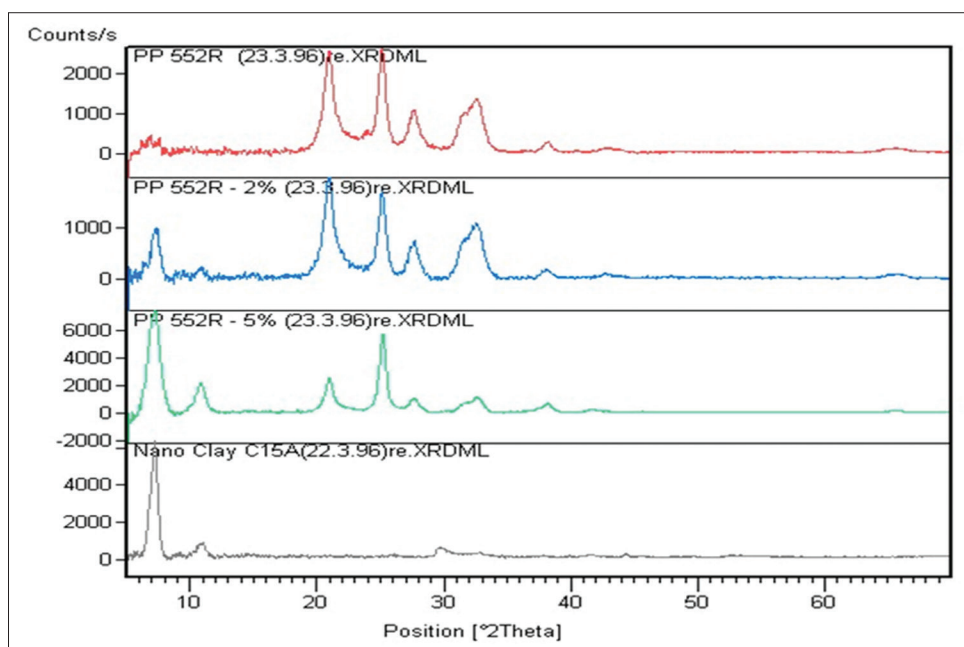| Batch No.	2_θ °	(nm) d	FWHM
Nano Clay	7.19	18.05	1.414
PP552R2	7.17	18.28	2.189
PP552R3	7.13	18.40	3.075

Figure 2: XRD graphs of pure polypropylene and nanocomposite with 2%, 5% nanoclay

Therefore, by increasing the gap between the peaks of the peaks, the curves are transported to lesser 2 θ, which indicates the arrival of polymer chains at intervals between layers. Amorphous materials do not form distinct peaks. In a quantitative analysis of crystalline materials with a regular structure, the specified peaks at angles specifically create. So if size of the particles to be smaller half-maximum (Full width) FWHM is larger, the wider and less intense. Using the Sherer law, you can calculate crystallization size. As a result, peak nanoparticles are less intense and wider than regular ones.

Thermal Properties
Differential Thermometry Analysis (DSC)
Thermal analysis is a thermal technique in which the difference in the heat flow into a material and a reference is measured as a function of temperature. The specimen and reference are heated by separate heaters to keep the temperature equilibrium as the sample temperature is linearly increased or decreased; the difference in the heat flow is measured inside the sample and reference. If the sample process is thermosetting, the pickup will be lowered if the non-heated sample material is heated, in which case the device will transmit more heat to it. Given the fact that the device only records the difference, the courier will be upward. The result of a DSC test is a curve of heat flow versus temperature and time. This flow of heat is either thermally or heat-generating and is shown as a positive or negative peak in the graph. (Fig. 3)

Crystallization and melting behavior of nano-composite and pure polypropylene samples were investigated using dynamic thermometer DSC200 F3 Maia NETZSCH made in Germany. Calibration of the device with indium and silver and measurements in a nitrogen atmosphere at a flow rate of 40 ml/min and an 8mgr concentration at a temperature control of 25 ° C to 230 ° C at a temperature of 10 min for 5 minutes keep and the temperature history and the remaining stresses go away and the specimens were then cooled at the same speed as 25 ° C and again for 5 min at this temperature. Finally, the heating of the samples from 25 ° C to 230 ° C was carried out at the same speed.

The temperature of the crystallization and melting maps was obtained from the second cooling and heating stages, respectively. The crystallinity of the samples using the equation $Xc = [\Delta Hm / \Delta H_{100}]*100$ was calculated in the equation ΔH_{100} enthalpy of fusion polypropylene degree of crystallinity $\Delta H_{100} = 209 J / g) \Delta)$ and ΔHm enthalpy of fusion samples (Table - 5).

DSC analysis shows that nanoclay acts as a agent core for the progression of polypropylene crystallization when nanoclay is added to the polymer. T_c (crystallization start temperature), and (Tm melting temperature) increases the crystallization phase in the final hybrid. As a result of increased crystallization and melting temperature, direct correlation with the increase of nanoclay to polypropylene. The percentage of crystallinity of the sample containing 5% nano-clay has the highest increase compared to pure polymer.

Decomposition of thermo gravimetric (TGA)
Thermogravimetric decomposition (TGA) is thermogravimetric (TGA) decomposition for the thermal behavior of a material against heat. The method of use is such that the sample is placed inside the machine. The device gradually and periodically heat to the material, it analyzes the data and samples the sample at various temperatures, and finally draws a graph. This chart is a two-axis chart that runs a downward path. The vertical axis represents the sample mass and the horizontal axis represents the temperature. The downward trend in the graph reflects the fact that with increasing temperature the sample mass is decreasing. The steady gradient of the graph represents the net content of the material. As the

Table 5: crystallization of pure polypropylene and nanocomposite with 2%, 5% nanoclay

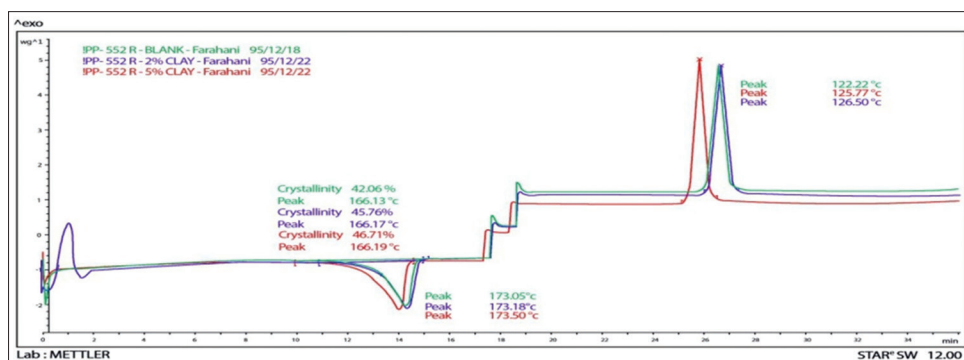| Batch No.	T_c	$X_c\%$	T_m
PP552R$_1$	117.09	42.06	173.05
PP552R$_2$	118.34	45.7	173.18
PP552R$_3$	118.61	46.71	173.50

Figure 3. DSC chart of pure polypropylene and nanocomposite with 2%, 5% nanoclay

temperature rises, we reach a temperature that is no longer horizontal. At this temperature, the degradation of the substance begins, and the gradient goes down, and when the gradient reached zero, the whole sample was destroyed. (Figure 4)

The TGA analysis was used to determine the thermal stability of polypropylene and polypropylene nanocomposites. In this experiment, the samples were heated at a temperature of 20 ° C from a temperature of 30 ° C, and the range of the sample mass loss rate has been evaluated with increasing temperature. The results of this test are shown as thermograms.

The results obtained from this test have been shown as thermogravimetric curves. The temperature of 5 and 10% of the sample degradation (bT⁵□ c. aT⁵ □ c), which is a criterion for the study of thermal stability, is also presented in Table 5. As shown in Fig. 4 and Table 6, the nanosilver weight gain of nanoclay increases the thermal stability of polypropylene / nanoclay nanocomposites compared to polypropylene. In fact, the layered nanocomposite structure reduces the velocity of the evaporative release from the solid phase to the gas phase.

Mechanical Properties
Tensile properties
Mechanical properties are important parameters in the preparation of nanocomposites. The study of

mechanical properties provides useful information on the effect of the nano-compatibilizer and the process of the methods. In general, Malic anhydride shows a sharp decrease in the properties of the resin. Increasing nanoclay to polypropylene improves tensile modulus but reduces elongation at fracture point. The specimens were transformed into 10mm x 4mm x 20mm plates and after drying and rectangular shapes, the shape of the tensile strength tests and the Young's modulus were performed according to the standard ASTM D638 with the INESTERON model 4441 and the 500 Mpa force.(Fig -5)

The measurements of each sample are three times repeated and the values shown are average. Figure 5 shows the tensile stress diagram of the tensile strength variations with the polypropylene and nanoclay compatibilizer at two levels of 5%, 2%. The stretch modulus of nanocomposites as a tensile strength function is shown in Fig. 5. Obviously nanoclay particles increase the hardness of the nanocomposite, especially in the ratio of elongation, with the highest improvement for the combination with 5% nanoclay. The graphs show that Yang's reduction in stretch and yarn modulus show that the sum of nanoclay and malic anhydride has a ductility effect on polymers by adding nanoclay at both mixing surfaces, increasing the elastic elongation modulus.

Adding the compatibilizer improving the bonding between the filler particles and the material increasing the number of hydrogen interactions between the nanoclay and the polypropylene causes the proper distribution of the filler particles in the polymerized matrix thereby increasing the modulus of elasticity. Table 7 shows that the tensile modulus for 423 MPa polypropylene and 474 MPa nanocomposite with 5% nanoclay has a tensile modulus due to the adaptive effect of PP-g-MA. As the nanoclay increases, the tendency to form an amide bond between

Table 6: Thermal stability of pure polypropylene and nanocomposite with 2%, 5% nanoclay

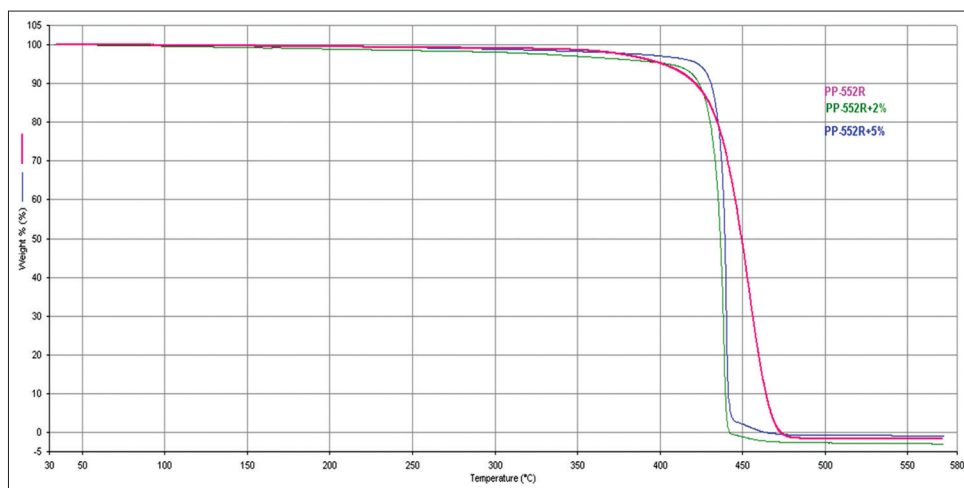| Batch No.	$_aT^5 \,^oC$	$_bT^5 \,^oC$	Remaining weight
PP552R₁	412.75	425.43	1.504%
PP552R₂	423.36	432.53	2.274%
PP552R₃	434.65	442.24	5.223%

Figure 4 - TGA graphs of pure polypropylene and nanocomposite with 2%, 5% nanoclay
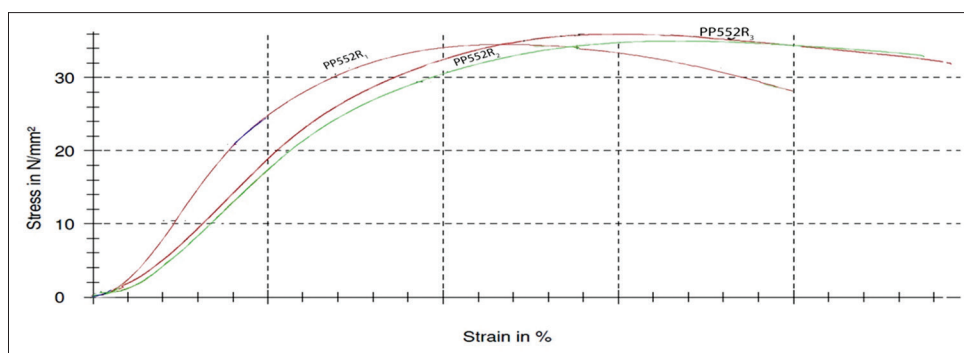
Figure 5 - Young Polypropylene Module and Nanocomposites with 2%, 5% Nanoclay
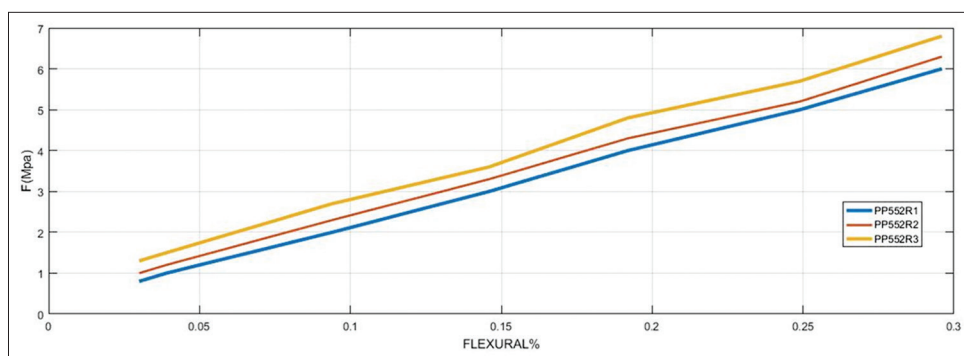

Figure 6 - bending strength curve of pure polypropylene and nanocomposite with 2%, 5% nanoclay

ammonium nuclei of the nano-like friend and MA groups and MA loop reaction increased. The tensile strength of nanocomposite with 2% nanoclay was increased by 0.07% compared to polypropylene and 0.08% nanocomposite with 5% nanoclay. Resistance in the nanocomposite delivery point with 2% nanoclay is 0.23% for polypropylene and 0.29% for nanocomposite with 5% nanoclay. Due to the increase in some mechanical properties, the length increase at fracture points and yields decreased with increasing nanoclay.

Bending Properties

Three-point bending test according to ASTM D790 standard with WIKI PG device, specimen is placed in a rectangular shape on two bases. At 10mm intervals, from each supporting element, the force is applied to the piece and, according to the force of the force, increases, or the piece is broken, or as much as 5% of the thickness of the bending portion. The bending strength obtained in this way is also called the Modulus of Rupture or MOR. (Fig. 6)

When the specimen is exposed to bending, its tensile stress is at its upper surface and at the lower level it produces tensile stress. Here, F is the maximum force applied to polypropylene and nanocomposites. And the most affected nanocomposite with 5% nanoclay.

Table 7: Mechanical properties of pure polypropylene and nanocomposite with 2%, 5% nanoclay

Batch No.	PP552R$_1$	PP552R$_2$	PP552R$_3$
Tensile modulus (MPA)	423	454	474
Tensile strength	33	35.1	35.9
Maximum Tensile strength	32.6	35.2	35.8
Elongation at yield %	17.1	16.3	15.4
Tensile strength at yield	26.8	33.2	34.6
Elongation at break %	29.8	25.1	24.5

Table 8: Results of bending strength testing of polypropylene and nano-composites with 2%, 5% nanoclay

Batch No.	PP552R$_1$			PP552R$_2$			PP552R$_3$		
POINTS	1	2	3	1	2	3	1	2	3
FORCE (MPA)	1	3	6	1.2	4	7	1.5	4.2	7.5
FLACTURAL	0.039	0.14	0.27	0.39	0.14	0.27	0.039	0.14	0.27

Table 8 shows that by increasing the nanoclay due to the formation of more transverse connections by the covalent bond between the polymer chains and the greater penetration of the polymer chains between the silicate plates bring more strength to the nanocomposite. As a
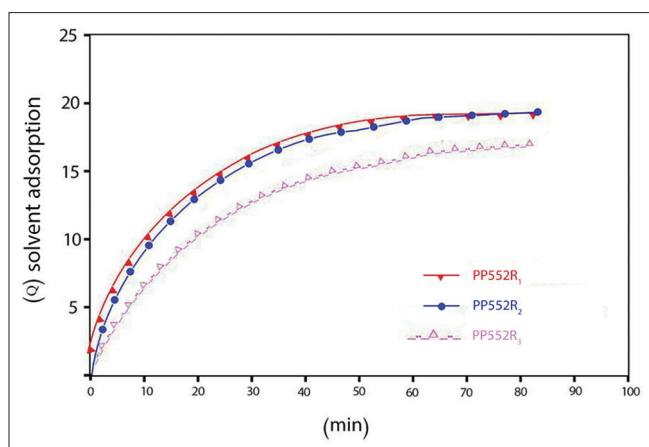
Figure 7- Absorption of pure polypropylene solvent and nanocomposite with 2%, 5% nanoclay

result, the flexural strength improves with the increase of the nanoclay and the malic anhydride compatibilizer.

Solvent adsorption

Stability against solvent adsorption is one of the important parameters in the preparation of nanocomposites. In this test, the samples were converted to 2Cm pieces and placed inside the xylene solvent and every 2 min, once the samples were removed from the solution, weighed by weight and the results were recorded. Stability using the equation calculated. In which polymer mass after solvent adsorption and molar mass of solvent for xylene is 2443.945gr / mol and the polymer's weight before solvent adsorption (Fig. 7)

Based on the results reported in Figure 7, the addition of nanoclay reduced the amount of xylene adsorption in the nanocomposite due to the presence of nanoclay particles between the chains and reduces solvent penetration. As the nanoclay increases, the amount of xylene absorption in the nanocomposite decreases.

CONCLUSION

In these research nanocomposites of PP552R Polypropylene Grade PP/552R of Shazand / Nanocross Petrochemicals with different percentages by molten mixing method using malic anhydride compatibilizer has been investigated. XRD, SEM results show the structure

of polypropylene nanocomposites and malic anhydride if they are well separated in the nanoclay and malic anhydride nanoclay layers and polymer chains penetrate the layers. An appropriate dispersion is created that is interlocked. Tensile strength, Young's modulus, thermal stability, and solvent absorption resistance increased with increasing nanoclay content. One of the advantages of this nanocomposite is to increase the color of the polymer, in spite of its thermal and mechanical resistance, due to the presence of polar compounds which, given its application in the textile industry, can be an advantage.

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