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The Effect of Nano-Composites on the Mechanic and Morphological Characteristics of NBR/PA6 Blends

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Abstract

The present article dealt with studying physical and mechanical properties of binary blend of NBR/PA6. First, samples of NBR/PA6 blends were prepared as control samples then; the effect of Nano-particles on them was studied. The samples mixed with the weight percentages of PA6 (20, 40, and 50) and (2, 4, and 6) percentages of Nano-particles in an internal mixer and experimented after pressing and molding. XRD results showed that increasing Nano-clay particles causes the particles diffusion, the distance between them and the resistance of the samples to be increased, which can be seen through the mechanical results. DSC results showed that increasing NBR and 20 A Cloisite causes crystallization percentage to be decreased because of decreasing polymer and increasing rubber with lower heat resistance. Increasing Nano-clay has no effect on this property. Increasing Nano causes hardness resistance to be compressed and increased and increasing NBR causes this resistance to be decreased because of its elasticity. Furthermore, increasing Nano-particles in impact test can result in decreasing resistance. In tensile samples, increasing Nano-clay with the elasticity of PA6 results in increasing resistance. The objective of this article is to study the effect of increasing Nano-particles of clay on morphology and mechanical properties including tensile strength, Young's modulus and impact resistance of binary blends based on NBR/PA6.

Keywords: acrylonitrile butadiene rubber, poly amid 6, physical and mechanical properties, Nano-composite, binary blend

1.Introduction

Given the special and unique characteristics of PA6 and NBR in terms of having wide spread and variable consumption market along with the reason that these materials are not produced in industrial level in the country, the need to produce their Nano-composites in the country in order to response the costumers of these materials have been felt in recent years. However, rapid progress of technology in different fields causes diverse applications, especially involving Nano, so that there is increasing need to produce composites and special Nano-composites more than ever. Making blends has taken special status because of inflexibility in selecting the materials and the capacity of designing the properties of final products as well as saving costs[1-2]. By making blends we can obtain better products with good components such as higher impact resistance, higher heat deformation, lower viscosity of melting, friendly process and proper price. Over the recent decades, a number of polymers with different structures and applications have been produced and used. In this respect, many methods were used the most important of which is blend making. Polymer blends are of great importance because of inflexibility in selecting the materials and the capacity of designing the properties of final products and saving costs. According to the latest statistic, polymer blends forms 6% of total consumption of polymer blends and, interestingly, average growth of polymer blends is twice as much of casual polymers. Polymer Nano-composites are also new class of composites, which are filled with grain fillers, and at least one dimension of the particles distributed in the polymer has measurements in Nano-meter index. Research on mixed materials based on non-organic and layered compositions, such as clay, has started long ago, but studying Nano-composites took a new life when their unique properties were known[3-5]. Nano-composites are materials with higher performance that present unusual compositional properties and unique design possibilities. With annual growth about 25 %, they have the fastest demand dealing with rubber engineering and the world market of polymer Nano-composites would be amount to 1.2 billion Pound by 2009. They have such capabilities that defined as 21th century materials. Since Nano-clay is used in polymer Nano-composites and considering the properties of Nano-clay including higher capacity of permeability, higher hardness and strength, higher abundance, lower cost and layer structure, make Nano-clay and its Nano-composite properties to be improved through chemical processes and making it compatible with polymer. In this respect, we can refer to some resulted properties as mechanical, thermal and gas permeable properties in sample polymer Nano-composites. This article aimed at studying the effect of increasing Nano-particles of clay on morphology and mechanical properties including tensile strength, Young's modulus and impact resistance of binary blends based on NBR/PA6[6-8].

2.Materials

Chemicals used in this study were mentioned in table 1. The whole materials used in the experiments were of required experimental grade and Nano-composite made based on NBR/PA6/Nano-clay with (20, 40 and 50 % wt.) ratios of acrylonitrile butadiene rubber with weight percentages (2, 4 and 6 % wt.) and commercial name of Cloisite 30B which is a natural treated material. Table 1 shows the properties of the mentioned materials with their commercial names. Table 2 shows the combination the percentage of primary materials based on weight percentage of polyamide 6 with acrylonitrile butadiene rubber and given Nano-particle based on 100 gr per sample. As seen in table 2, there is no weight percentage of Nano-particle in three ones out of the whole samples, which are known as referential samples. They were used to study and compare changes of mechanical and morphological properties of other nine samples having combination of weight percentage of Nano-particle.

Table 1. List of chemical materials used to make Nano-composite

Characteristics	Commercial Name	Materials
Density(g/cm3):1.13 MFI(g/10 min):0.9 Melting Point(C):220	Akulon F130-B LG(koura)	Polyamide 6 (PA6)
Density(g/cm3):0.94 Acrylonitrile (%):34 MoonyViscosity ML(1+4)at 100C:41	Kosyn-KNB 35L Bayer(German)	Acrylonitrile Butadiene Rubber (NBR)
Density(g/cm3):1.98 CEC ‹meq /100 g clay:90 X-Ray Diffraction‹ d-Spacing (A):18.5	Cloisite 30B Southern clay (USA)	Nanoclay

Table 2. Names and weight percentage of the samples based on 100 gr

Nanoclay wt%	NBR wt%	PA6 wt%	Sample code
0	20	80	PN20
0	40	60	PN40
0	50	50	PN50
2	19	79	PN20C2
2	39	59	PN40C2
2	49	49	PN50C2
4	18	78	PN20C4
4	38	58	PN40C4
4	48	48	PN50C4
6	17	77	PN20C6
6	37	57	PN40C6
6	47	47	PN50C6

2.1.Preparing Nano-composite

Since we should use the monophasic process of melting and mixing device volume unit of which was 50 cc in Teacher Training University to develop given Nano-composite, it was required to do a set of calculations before preparing the materials, so that the amount of each three materials can be indicated for each sample. The density of each three materials and their weight percentages were available in table 1, so after calculating, we gained average density of 1.087 g/cm^3 and for next calculations, we used the average density of 1.087 g/cm^3. In continue, considering the volume of internal mixer device and the factor of filling of 0.75, we calculated value of 41.5 gr to each sample preparation in the device. Table 3 shows the values of each three materials (acrylonitrile butadiene rubber, polyamide and Nano-particle) for each twelve samples. After finishing calculations, the values of samples were indicated and prepared to be used. However, before preparing the samples by the device, we should do preparation process on the very materials. Since polyamide 6 and Nano-particle absorb moist, they should be dried in oven for 24 hours with 80^0 heat at vacuum. This experiment was carried out in the laboratory of Shahreza Azad University. Furthermore, parts of acrylonitrile butadiene rubber were made smaller to facilitate the experiment. So far, we are ready to take samples and work with the internal mixer device. Of course, it is worth to note that since acrylonitrile butadiene rubber and polyomide 6 both tend to be polar, we need no fixing materials in this project to make samples and build Nano-composite.

Table 3. The values of each three materials for any Nano-composite

Nanoclay (gr)	NBR(gr)	PA6(gr)	Sample code
0	8.3	33.2	PN20
0	16.6	24.9	PN40
0	20.75	20.75	PN50
0.83	7.885	32.785	PN20C2
0.83	16.185	24.485	PN40C2
0.83	20.335	20.335	PN50C2
1.66	7.47	32.37	PN20C4
1.66	15.77	24.07	PN40C4
1.66	19.92	19.92	PN50C4
2.49	7.055	31.955	PN20C6
2.49	15.355	23.655	PN40C6
2.49	19.505	19.505	PN50C6

3.Results and discussion

3.1. Impact strength test

This test composed of a bar with a clip at one end where the sample placed in it vertically. The bar makes a hit, under controlled conditions on the sample located in the clip. In this state, required energy to break the sample can be considered in advance. The formed sample is usually breached and its crack should be placed upper than the clip, as a result, tension focused around the crack. This is the reason why they usually record lower firmness for cracked samples compared with non-cracked ones. Crack energy in this test defined as Joule. The thickness of the samples 3 mm and their width is 129 mm. Therefore, only one set of dimensions of the sample can be used. As said before, two forms in rectangle shape with crown made and used in impact test. That is, the samples were placed in one jaw of GOTECH device model GT-7045-MD made in Japan, then the weight released from top to hit the sample on the top point of the crown so that crack created. Standard weight of 5.5 was used in this test. The results showed that a hit with thickness of 3 mm and 129 mm width and crown length of 2.5 mm would show desired result only in the samples having acrylonitrile butadiene rubber with 20 % weight percentage with the weight 5.5 Joule. By increasing Nano-clay in the samples reduction of hit can be observed because of tension compaction in the samples with Nano-clay.

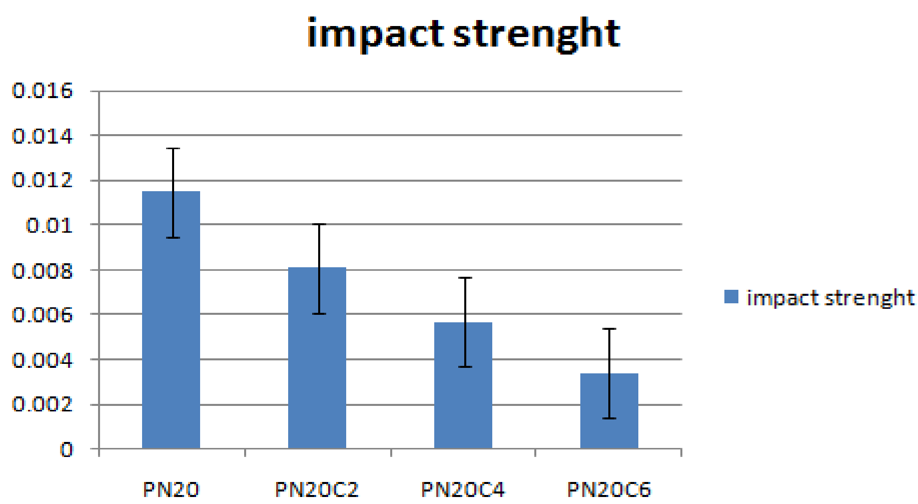

Figure 1. Impact strength test wit NBR 20 % wt. and changing Nano-clay

Table 4. Results of impact strength test

PN20C6	PN2OC4	PN20C2	PN20	Sample
0.21	0.34	0.49	0.69	J
6.73	10.9	15.7	22.11	J/m2

3.2. Hardness test

The firmness of a polymer sample can be evaluated rapidly by hardness test. This test is to indicate resistance against the concavity of a penetrated material (in a spherical, conical, pyramidal shape). A number that gained through one of the applied ways describes the curve. Explaining the results from hardness test of the samples is difficult, since a combined change of unconformity in the shape of elastic and plastic and time depended takes place. There are different methods to indicate hardness each of which may have their own pros and cons. According to the results from the referential samples, in hardness test, by increasing the weight percentage of acrylonitrile butadiene rubber decreasing of hardness can be observed. The graphs show the results of total samples. With the fixed weight percentage of acrylonitrile butadiene rubber in PN 20 sample and the weight percentage of Nano-clay, hardness variable increased a little. However, by increasing the weight percentage of acrylonitrile butadiene rubber with the fixed weight percentage of Nano-clay in PN50C2, PN40C2 and PN20C2 samples, decreasing of hardness can be observed. This indicates that high value of hardness resulted from the relation between polymer and Nano-clay.

Table 5. Results of hardness test

PN50C4	PN50C2	PN50	PN40C6	PN40C4	PN40C2	PN40	PN20C6	PN20C4	PN20C2	PN20	sample
50	49.33	48	59	57.33	57.66	54.66	68.66	68.33	68	68	hardness

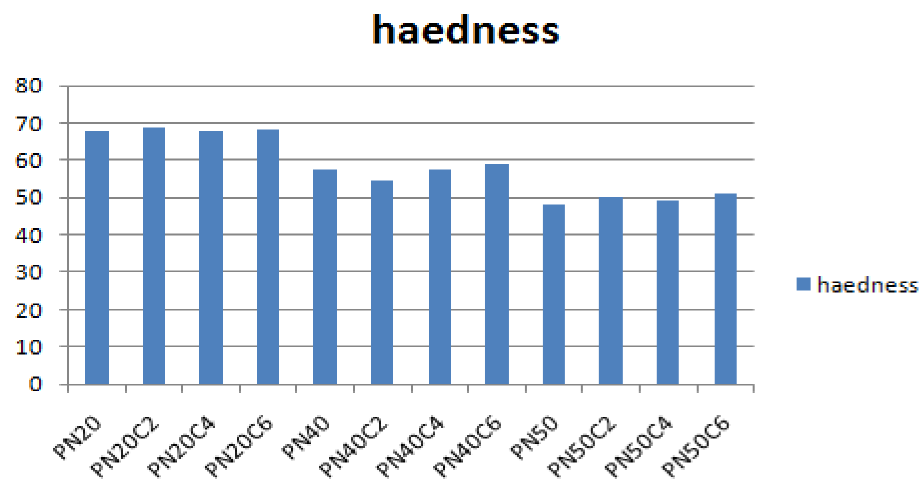

Figure 2. Results of hardness test, according to table 5

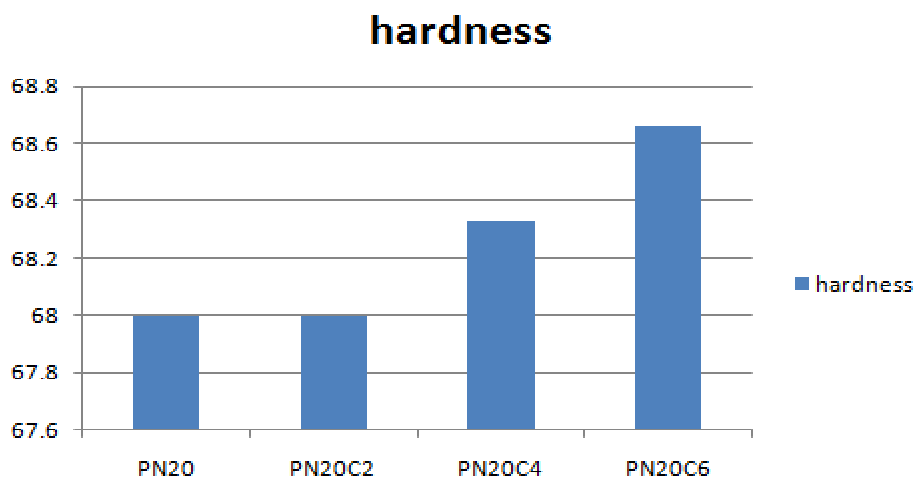

Figure 3. Results of hardness test, related to NBR (20 % wt.) and weight percentage of the variable of Nano-clay.

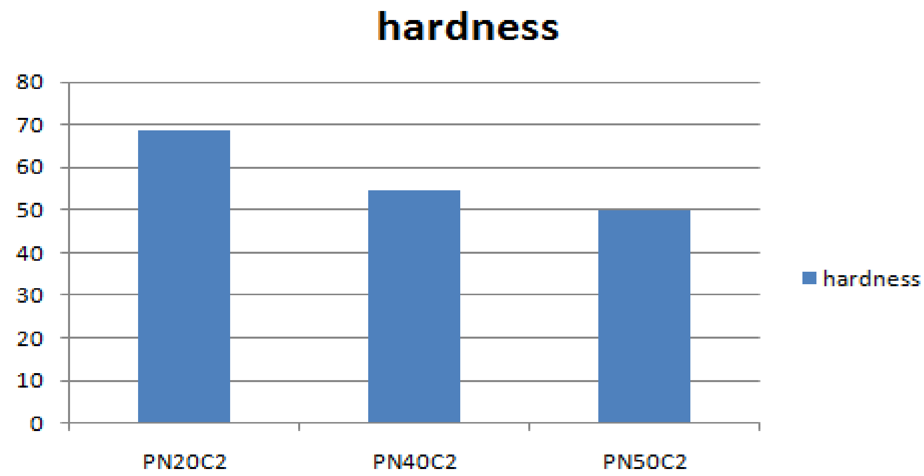

Figure 4. Results of hardness test, for (2 % wt. of Nano-clay).

3.3. Tensile strength test

The capability of different materials to resist against breaking through their tensile strength is one of the most important and applicable properties which can indicates how and to what extent different materials would be utilized. Required tensile force on area unit (PSI or Mpa) to break a material is defined as tensile strength. The simple experiment of traction is a Well-known method to measure this property in polymers, especially in plastics. It worth to note that tensile strength test is suitable to measure quality of plastics but is should not to be used in designing, because in different conditions different results may be obtained. In this area, tensile has a linear relation with strain. Parameter of E is called Young's modulus or elastic which the more it is the harder the experiment material will be. In elastic area, if the practiced tension is omitted the length of the sample will be back to its primary position. At the end of elastic area, change of form can be started when the elastic limit exceeded. The amount of tension, which transition from elastic to plastic area takes place, can be called yield stress, which is an important parameter in designing engineering of a product. This is the first point on tension-strain curve, where increasing in length occurred without increasing of any tension. Slope of the curve on this point is zero. If tension is omitted from the sample in plastic area, changing in elastic form will be omitted as hook line and reach zero but the value of changing in elastic form or the percentage of changing in permanent length will be remained on the piece. If the tension reaches, its highest limitation it may defined as final tensile strength with final strain. Tension of changing elastic form is done steadily up to this point, that is, the cross section area of the sample may change equally on the whole sample. However, after this tension, necking phenomenon occurs on the sample and continues up to break. The tension, which makes the sample to break, is called tension fracture and presented with fo. Multiplying strain by 100 the percent of length change can be obtained. The value of tensile length change for improved polymers is about 5 %. It is worth to note that in tensile-strain test, the sample is stretched in velocity between 0.2 -20 in/min. In this respect, two standards, namely, ASTM D638 and ISO 527 are used. The test of polymer films carries out by ASTM D882 standard and the test of elastomers by ASTM D412. In this tensile test, some dumbbell shaped samples were used. The test was carried out in Industrial University of Esfahan by means of HOUNSFIELD device. The method was that the sample was placed and pressed between two parallel jaws and dragged with 5 mm/min force, as done in ASTM-638 test, until they broke.

Table 6. Results from tensile test for all samples

Tensile strength	Elongation at break	Modulus	Sample
4.5	15.52	5.314	PN20
4	12.52	6.891	PN20C2
3.2	7.32	7.034	PN20C4
3.17	5.9	8.377	PN20C6
3.82	12.85	2.98	PN40
3.66	12.12	3.421	PN40C2
3.42	10.1	3.461	PN40C4
2.98	7.03	3.822	PN40C6
2.	3.197	1.07	PN50
1.8	3.22	1.24	PN50C2
0.95	3.07	1.43	PN50C4
0.4	3.04	1.483	PN50C6

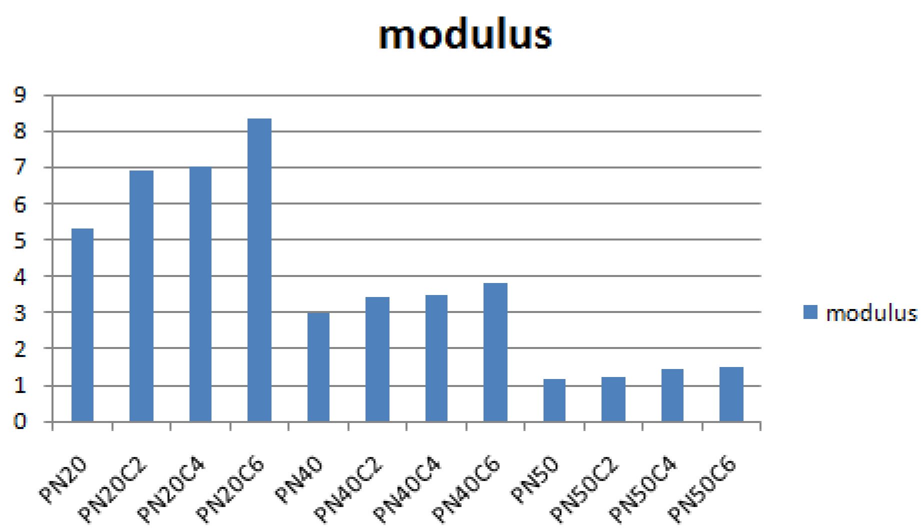

Figure 5. Modulus results from tensile test for all samples

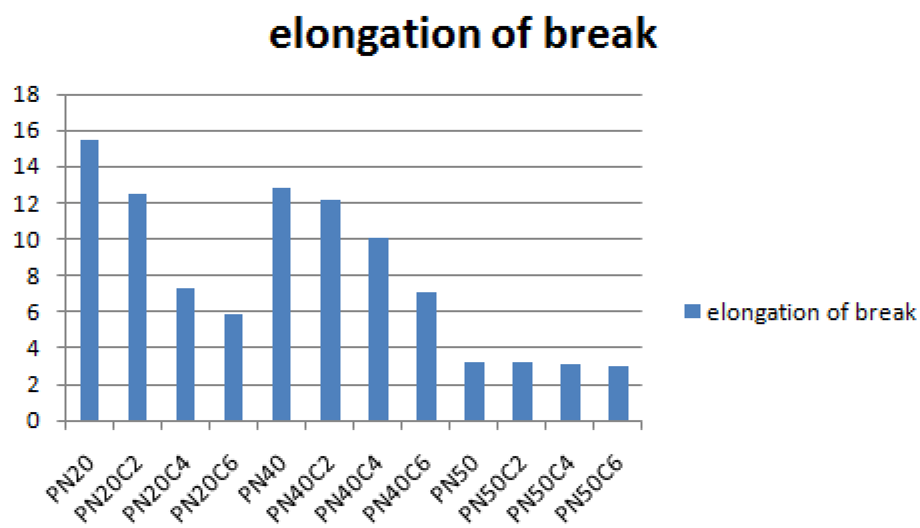

Figure 6. Results of elongation from tensile test for all samples

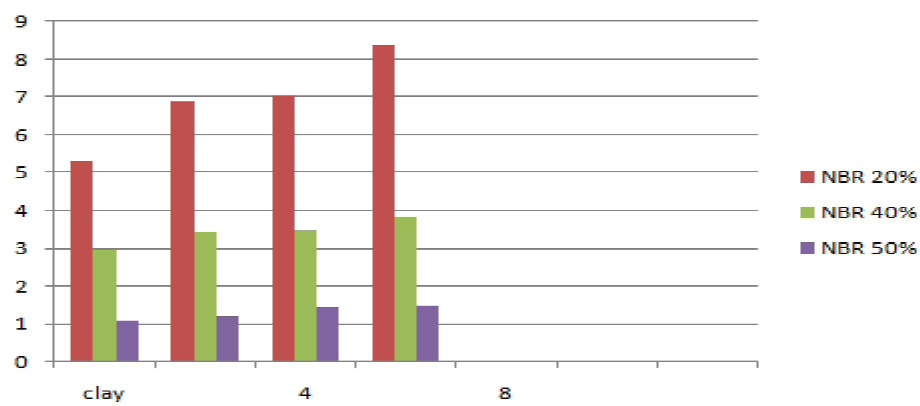

Figure 7. Modulus results with NBR 20, 40 and 50 % wt. with the changes of Nano-clay

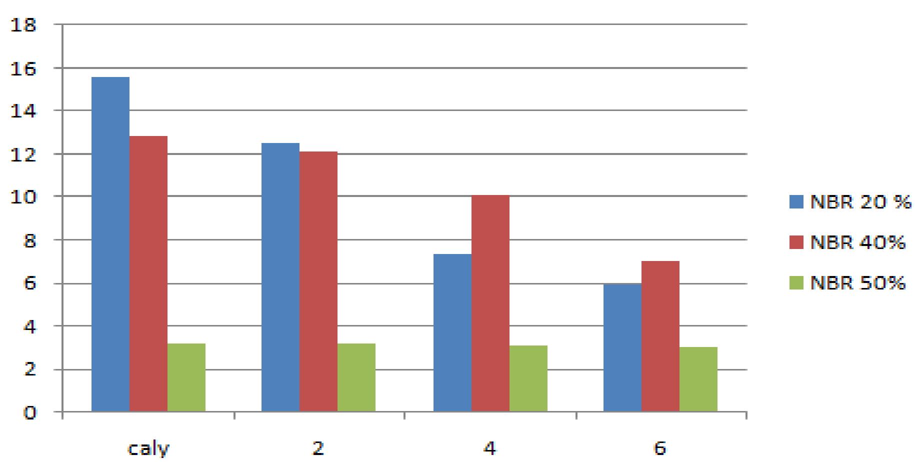

Figure 8. Results of elongation for NBR 20, 40 and 50 % wt. with the changes of Nano-clay

As discussed before, the capacity of materials to resist against breaking resulting from tensile strength is one of the most important and applicable properties which can indicates how and to what extent different materials would be utilized. Required tensile force on area unit (PSI or Mpa) to break a material is defined as tensile strength. The simple experiment of traction is a Well-known method to measure this property in polymers, especially in plastics. It worth to note that tensile strength test is suitable to measure quality of plastics but is should not to be used in designing, because in different conditions different results may be obtained. In this area, tensile has a linear relation with strain. This tensile test was carried out in room temperature with speed of 5 mm/min between the jaws, as shown in the charts above, modulus decreases by increasing the weight percentage of acrylonitrile butadiene rubber in the referential samples. With fixed weight percentage of Nano-clay and increased weight percentage of acrylonitrile butadiene rubber, again we have modulus reduction as well as length. Likewise, with fixed weight percentage of acrylonitrile butadiene rubber, by increasing weight percentage of Nano-clay, we have modulus reduction as well as length. Furthermore, the charts involving modulus and elongation of the samples with different weight percentage of acrylonitrile butadiene rubber and Nano-clay may confirm the mentioned analysis. Table 6 shows that reinforced samples of Nano-clay in all composites and combinations were improved comparing with similar and referential samples, which indicates that layers of the sheets of Nano-clay can be the main factor to improve the strength.

3.4.XRD test

The most important parameter affecting rheological behavior and physical and mechanical properties of polymer Nano-composites is the dispersion value of Nano-particles in matrix. Thus, to study the degree of dispersion, we need some tests the most important of which is dispersion of X ray. We can study the effects of dispersion and distribution of Nano-particles in polymer Nano-composites. The height and form of the resulted picks are the function of structure and percentage of Nano-particles dispersion. Since Nano-particles have different structures, ray dispersion is done through different angles and thereby, picks would be different, too. For XRD test, the referential samples have no picks. However, because of Nano-clay, pick can emerge first, and then two picks can be observed because of increasing weight percentage of Nano-clay in next sample. In addition, these two picks experience length increasing in the last sample with the last percentage of Nano-clay. This shows that the strength of the samples increased because of increasing of volume of the samples and weight percentage of Nano-clay. The results show that breaking tension took place through matrix along the combination then increased, thereby, combined viscosity increased because of increasing content of acrylonitrile butadiene rubber and in turn, the solution process of Nano-soil density can be facilitate, respectively.

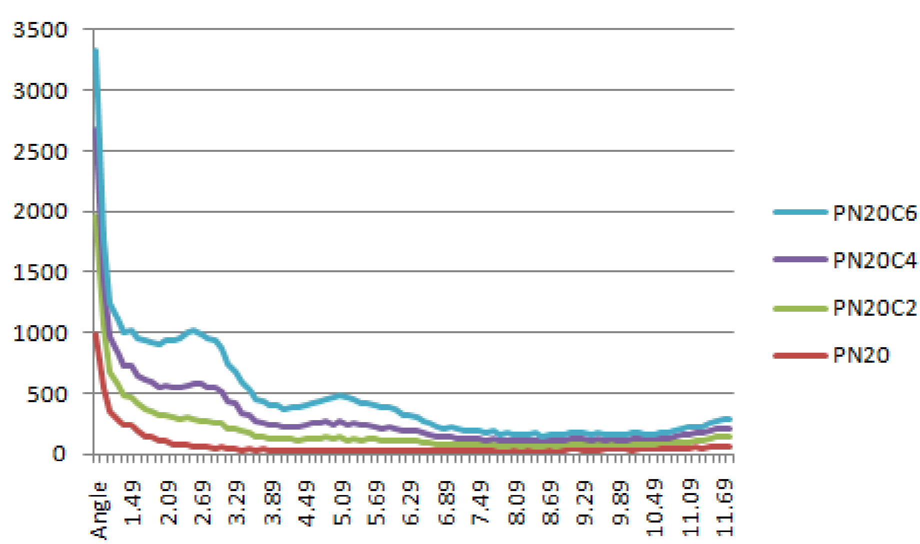

Figure 9. Results of XRD test with 20 % NBR wt. and Nano-clay with variable percentage

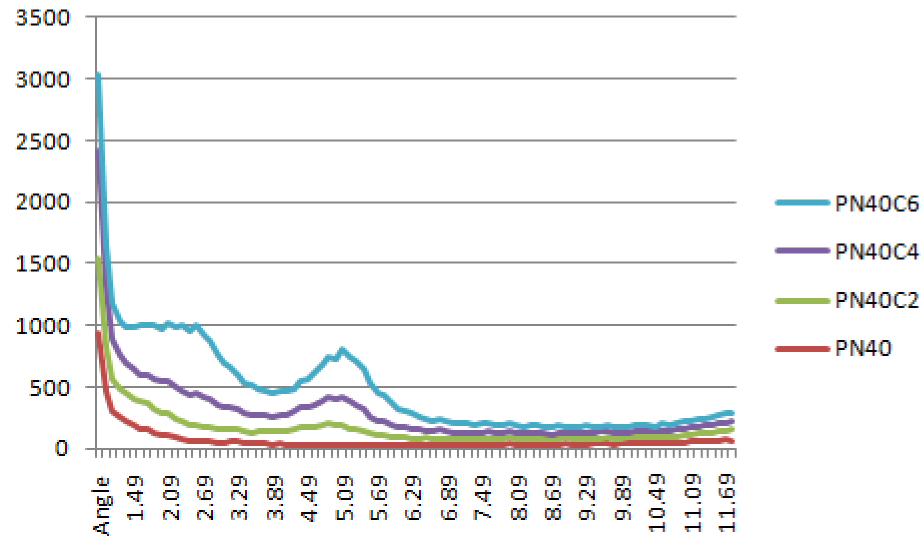

Figure 10. Results of XRD test with 40 % NBR wt. and Nano-clay with variable weight percentage

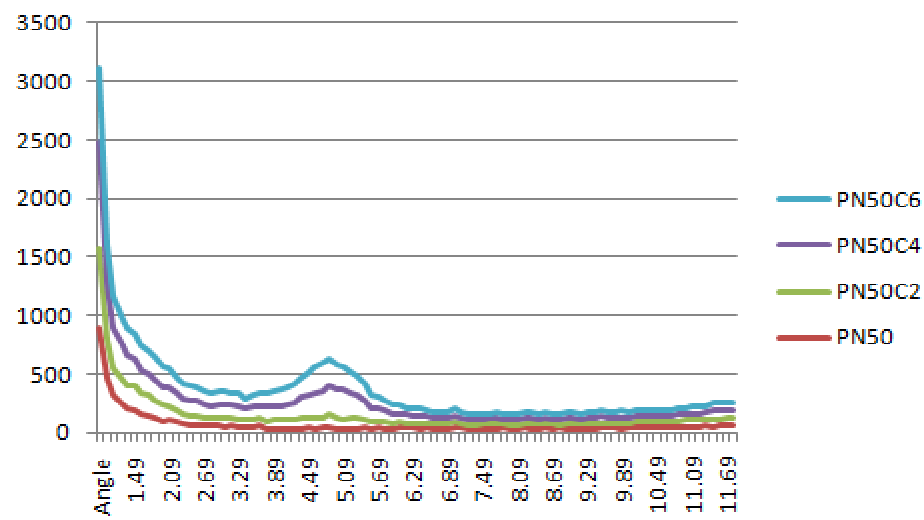

Figure 11. Results of XRD test with 50 % NBR wt. and Nano-clay with variable weight percentage

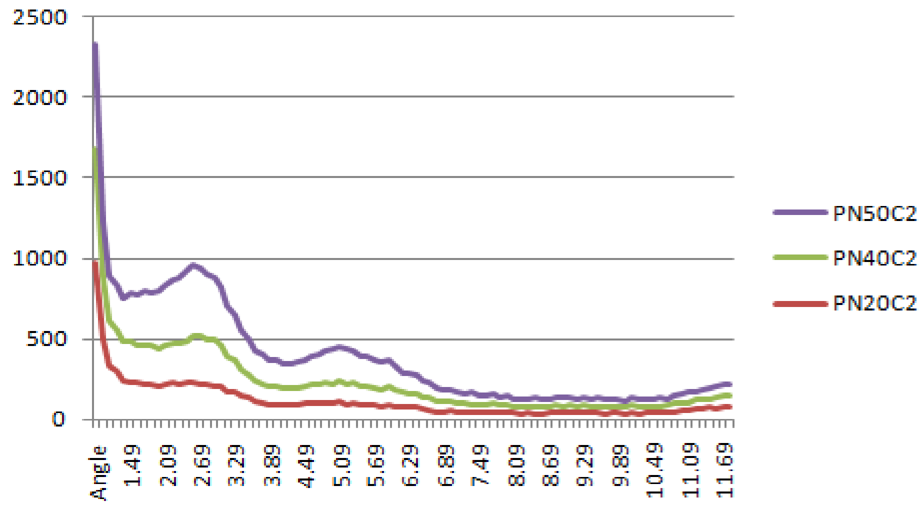

Figure 12. Results of XRD test with 2 % Nano-clay wt. and NBR with variable weight percentage

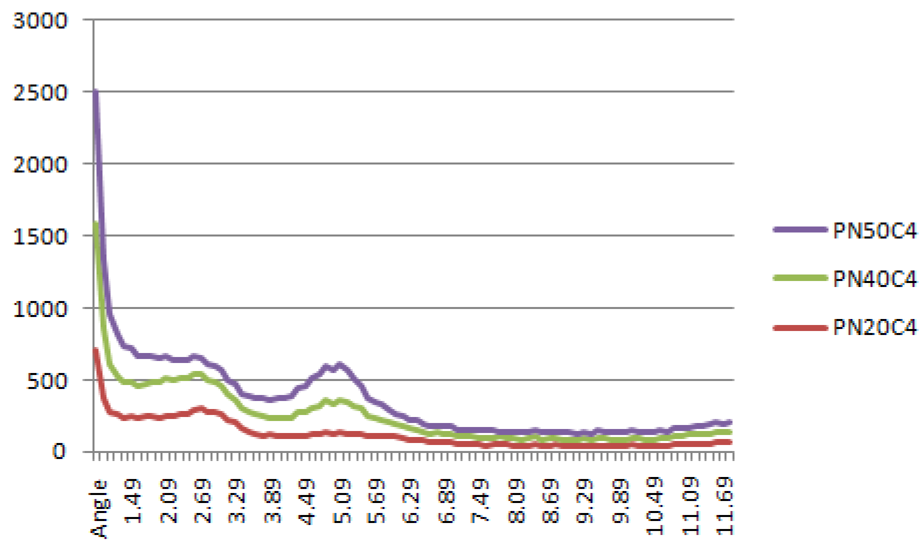

Figure 13. Results of XRD test with 4 % Nano-clay wt. and NBR with variable weight percentage

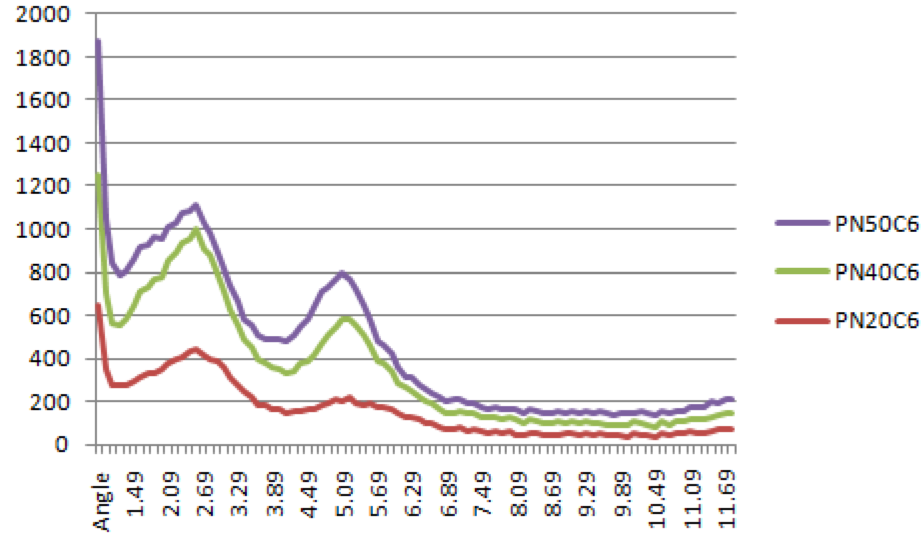

Figure 14. Results of XRD test with 6 % Nano-clay wt. and NBR with variable weight percentage

3.5. DSC test

Crystallization behavior and movement of polymer materials are studied by thermometry of deferential exploration. Moreover, DSC is used to recognize heat exchange of glass, melting point, time and temperature needed to crystallization, percentage of crystallization, fusion heat and responses, specific heat, temperature stability while melting, degree of improvement and response, and kinematics of crystallization of polymer materials. In DSC test temperature and latent heat of fusion reduces by increasing Nano-clay in go or start state and then, reduction in temperature and latent heat of fusion can be observed again by increasing weight percentage of Nano-clay in come back status, which presents reduction of crystallization percentage. This test was carried out in 25 – 245^0 along with go and come back status. Table 7 shows the test results, noticing that the heat of fusion relates to polyimide 6/240. As seen, increasing Nano-clay results in reduction in degree and value of crystallization because of the relation between Nano-clay and polymer matrix. The reduction of tensile strength of Nano-composites of polyimide 6 and acrylonitrile butadiene rubber may cause the reduction of crystallization of Nano-composites.

Table 7. Results of DSC test

SAMPLE	PN20	PN20C2	PN20C6	PN40	PN40C2	PN40C6	PN50	PN50C2	PN50C6
normalized	50.81	41.09	36.34	43.8	34.25	31.24	31.24	28.17	26.97
X%	21	17	15	18	14	13	13	11	11

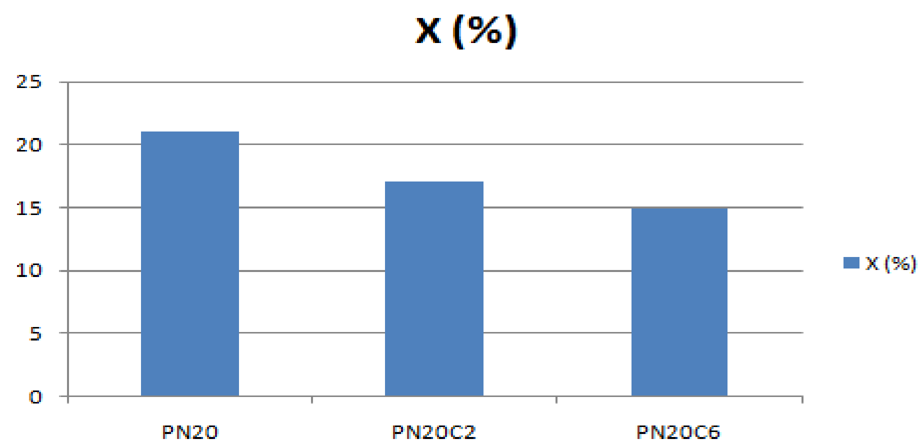

Figure 15. Results of DSC test with NBR 20 % wt. and variable wt. of Nano-clay

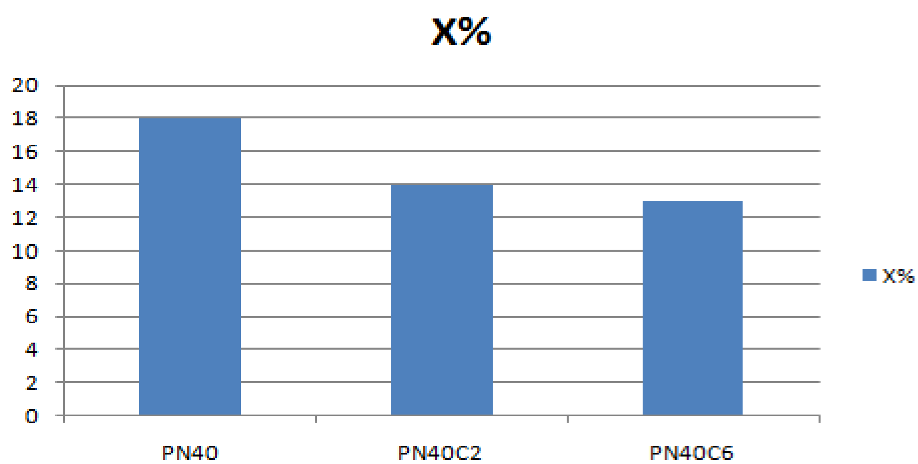

Figure 16. Results of DSC test with NBR 40 % wt. and variable wt. of Nano-clay

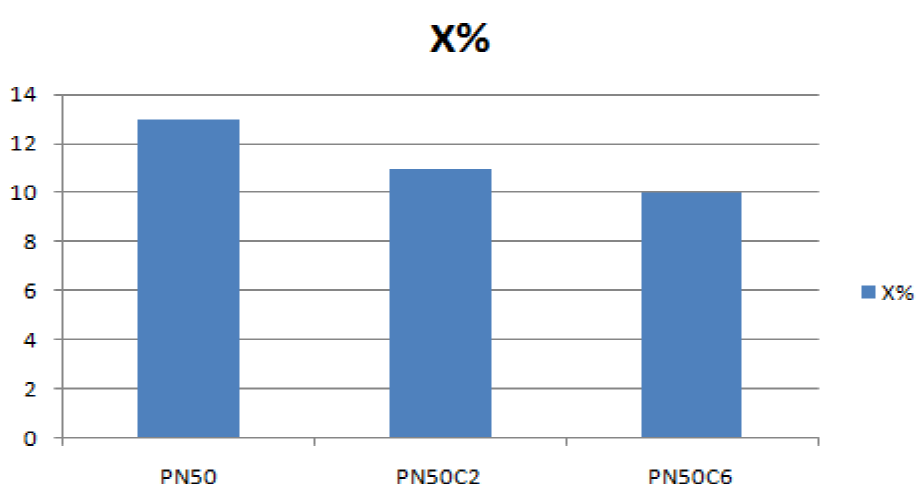

Figure 17. Results of DSC test with NBR 50 % wt. and variable wt. of Nano-clay

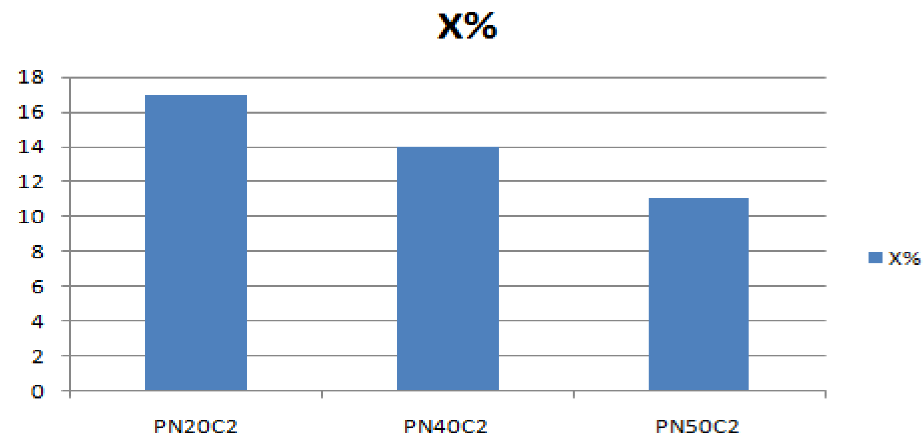

Figure 18. Results of DSC test with Nano-clay 2 % wt. and variable wt. of NBR

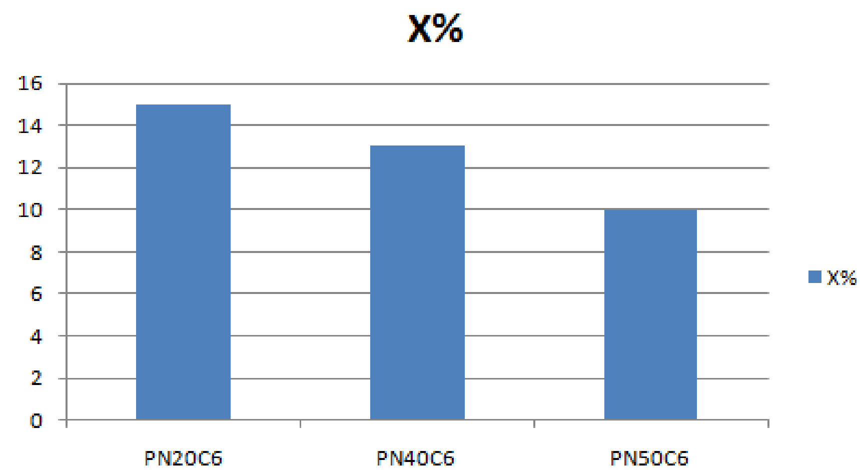

Figure 19. Results of DSC test with Nano-clay 6 % wt. and variable wt. of NBR

4.Conclusion

1. Compound moment vs time during the composition rule of reaction shows evidence concerning composition relation to time. It is obvious that increasing content of acrylonitrile butadiene rubber increases compound moment of Nano-composites, which can be related to higher viscosity of fusion of component of NBR related to PA6. In open moment, it seems that increasing Nano-clay can increase the value of moment because of indirect relation of strong connection between matrix of polymer and Nano-clay.
2. The more Nano-clay increases the more compressed the blend will be and resistance against the entrance of needle will increase. Thus, the hardness will increase a little because of higher hardness in Nano-clay related to the polymer. While carrying out hardness test, increasing weight percentage of NBR vs Nano-clay reduces hardness, which can cause hardness property to be lower because of increasing NBR comparing with matrix.
3. Increasing the content of rubber increases the strength of hit on isotope of NBR/PA6/ Nano-clay samples while increasing the content of Nano-clay reduces the hit strength. The reason for this is increasing of Nano-clay because of the effect of tension density. Increasing of NBR, because of increasing its hit strength, made limitation against testing with the given weight. By increasing Nano-

clay content and relation between silicate layers and matrix of polymer, the mobility of the chain from polymer segments near to the Nano-clay will show limitation.

4. Reduction in strength and tensile resistance of Nano-composites can increase by increasing Nano-clay content. Moreover, tensile strength can increase through increasing the weight percentage of NBR because of tensile strength of NBR in relation to PA6. Reinforced samples of Nano-clay in all composites, in comparison with similar materials, improved dealing with referential samples. This shows that the layered sheet of Nano-clay are the main factor to develop and improve the strength. Nano-clay is harder than the matrix of polymer. The placement and distribution of Nano-clay in polymer causes composite to resist more against modulus tension. In tensile strength test, increasing acrylonitrile butadiene rubber caused the modulus to be decreased and increasing Nano-clay increases it. We can observe that layered sheets of silicate are the main factor to increase the improvement of strength.
5. In mechanical features of NBR/PA6 and their Nano-composites, it seems that the measurement of reinforced samples of Nano-clay in all composites improved in comparison with similar samples with unsaturated blends.
6. In tensile strength, increasing of acrylonitrile butadiene rubber reduces elongation and increasing of Nano-clay causes it to be increased. Increasing of Nano-clay makes Nano-composites to be stronger, which results in strong connection between polymer and Nano-clay.
7. The results of XRD test show that increasing the percent of Nano-clay and the number of its sheets in a fixed volume of Nano-composite matrix may reduce the distance between the sheets, which can be seen on related charts. The reason is that for Nano-clay with lower weight percentage, the strength of picks reduces from left to forth. Furthermore, increasing the density of Nano-clay results in increasing the strength of the pick of XRD, because the strength of the pick presents the strength of sheets in the experimental environment. The reason for increasing of viscosity through increasing matrix is that the strength of picks increased in advance.
8. In DSC test, the degree and value of crystallization decrease by increasing the percentage of Nano-clay and its reason refers to the relation between clay and the matrix of polymer, which reduces crystallization process. This reduction depends on the tensile strength of NBR/PA6. Increasing of acrylonitrile butadiene rubber causes crystallization to be reduced.

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