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Research Paper

The Mechanical Properties of PA6/NBR/clay/CaCO$_3$ Hybrid Nanocomposites

Abouzar Haghshenas[1]**, Hamzeh Shahrajabian**[1*]
[1]Department of Mechanical Engineering, Najafabad Branch, Islamic Azad University, Najafabad, Iran
[*]Email of Corresponding Author: h.shahrajabian@pmc.iaun.ac.ir

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Abstract

In this study, polyamide 6 (PA6)/ nitrile butadiene rubber (NBR) based hybrid-nanocomposites reinforced with calcium carbonate and organo-clay as nanofillers in various content of 1, 3 and 5 phr were prepared and characterized. The nanocomposite samples were prepared through the melt processing method in an internal mixer. The effect of rubber phase (NBR) content (10, 30, and 50 wt.%), calcium carbonate content (1, 3, and 5 phr), and organo-clay content (1, 3, and 5) was investigated on morphology and mechanical properties of the nanocomposites. The mechanical properties were evaluated by tensile, flexural, and Charpy impact tests. The results showed that adding the NBR reduces the tensile strength, tensile modulus, flexural strength, and flexural modulus, and increases the impact strength. Introducing the nano-clay and calcium carbonate improves the tensile and flexural strength, tensile and flexural modulus, and decreases the impact strength. The nano-clay content from 1 to 3 phr improved the impact strength.

Keywords

Polyamide 6, Nitrile Butadiene Rubber, Organo-clay, Calcium Carbonate, Mechanical Properties

1. Introduction

The thermoplastic-elastomer materials in a form of blends are developed recently due to the suitable mechanical properties as well as low price [1]. The access to these properties depends on the correct choice of the materials and mixing ratio [2]. Polyamide (PA) polymers have been considered due to very high stiffness and tensile strength, excellent chemical and wear resistance, high melting point temperature, and low friction coefficient [3]. Low impact strength at low temperatures and low strain at breakpoint limit the use of PA. The mixing of the PA with an elastomer such as nitrile rubber (NBR) leads to improve in impact strength and toughness of PA [4]. The PA/NBR prepared by melt mixing possesses very excellent oil resistance at the high temperature [5].

Some researchers developed the PA/NBR blends in different studies. Mehrabzadeh et al. [6] studied the effect of various curing systems on the mechanical and thermal properties of the PA/NBR blends. Chowdhury et al. [7] improved the mechanical properties of PA/NBR by carboxylation of NBR. Kumar et al. [8] investigated the effect of mixing ratio, dynamic vulcanization, and compatibilizer on the rheology of the PA/NBR blends. Cai et al. [9] investigated the influence of acrylonitrile in the content of 34, 39, and 44 wt.% on mechanical properties of the PA/NBR, and concluded that the best tensile strength is obtained when the acrylonitrile content is 34 wt.%.

Although adding NBR to PA improves the toughness of PA, some mechanical characterizes such as stiffness, tensile strength and hardness reduces are reduced. Incorporating the fillers, and cross-linking agents could affect the mechanical, physical, and thermal properties of the polymer blends [2]. The fillers such as carbon black, fiberglass, talk, and calcium carbonate ($CaCO_3$) in high content are used in polymer blends to improve tensile strength, stiffness, thermal stability, and heat distortion temperature. On the other hand, these fillers in high content increase the product weight, and as a result, are not suitable in some applications containing aerospace, and automobile industries [10, 11]. Adding the nano-fillers such as nano clay, nano $CaCO_3$, TiO_2, Al_2O_3, and carbon nanotubes could improve the mechanical, physical, and thermal properties of polymer blends without a considerable increase in weight [12-14]. Nano-fillers make a strong interaction with the polymer matrix compared to micro-sized fillers due to very small dimensions [15]. Mahallati et al. [16] studied the effect of the NBR and nanoclay content on thermal and morphological properties of PLA/NBR blends. Nanoclay reduced the degree of crystallinity of the samples and increased oil resistance and storage modulus of PLA/NBR blends. Paran et al. [17] enhanced the interfacial interaction between PA6 and NBR by incorporating halloysite nanotubes (HNT), and as a result, improved the tensile modulus by 75%. Shemshadi et al. [18] decreased the rubber droplet size in PLA/NBR blend by adding nanoclay. They observed that nanoclay accelerates non-Newtonian behavior of the PLA6/NBR. Paran et al. [19] investigated the effect of HNT on the fracture toughness of PLA6/NBR. The HNTs prevented crack propagation effectively. Nakhaei et al. [20] modeled and optimized the mechanical properties of PLA/NBR/graphene nanocomposites using the response surface method. Their results showed that adding 1.5 wt.% graphenes increased the tensile strength, melting point and crystallization temperature of the PA6/NBR.

In this study, the synergetic effect of nanoclay and $CaCO_3$ nanoparticles on the mechanical and thermal properties of the PLA/NBR blend was investigated. The experiments were done based on Taguchi design of experiment with three factors of NBR, nanoclay, and $CaCO_3$ nanoparticles in three levels. Morphology, mechanical and thermal properties of the samples were investigated by Scanning Electron Microscopy (SEM), tensile, flexural, and Charpy tests, X-Ray Diffraction (XRD), and Differential Scanning Calorimetry (DSC).

2. Material and methods

2.1 Materials

Polyamide 6 with a commercial grade of COPA KN136, a melt flow rate (MFR) of 31.4 gr/10min, a density of 1.14 g/cm^3, and melting point temperature (T_m) of 220 °C was purchased from KOLON Plastics (Korea). Nitrile rubber (NBR) with a commercial grade of KNB 35L, an acrylonitrile content of 34 wt.%, the Mooney viscosity of 41, and a density of 0.98 g/cm^3 was obtained from KUMHO Co. (Korea). The natural montmorillonite nano-clay (Cloisite 30B) with a density of 1.97 g/cm^3 and the d-spacing of 18.5 °A was supplied by Southern Clay Products (USA). $CaCO_3$ nanoparticles with an average diameter of 50 nm and a density of 2.93 g/cm^3 were prepared from Solvay Co. (Belgium).

2.2 Sample Preparation

Before processing the PA6, nano-clay and $CaCO_3$ nanoparticles were dried in a vacuum oven for 24 h at a temperature of 80 °C. The samples were prepared in two steps. In the first step, at the first, the PA6 was fed into an internal mixer, a model of rabender (Germany), at a temperature of 235 °C, rotary speed of 90 rpm to blend effectively for 2 min. After 1.5 min when the torque Vs. time is fixed, the NBR was added into the internal mixer, and mixing was continued for 3 minutes to fix the torque. In the second step, the nanocomposites prepared in the previous step were converted into nanocomposite sheets by compression technique at a temperature of 240 °C and pressure of 40 bar for 4 min. To minimize the number of experiments, the Taguchi design of the experiment (L9 array) was used. Three factors of NBR content, nano-clay content, and CaCO3 content were considered as input parameters. Table 1 shows the levels of the input parameters. The experiments were listed in Table 2.

Table1. The levels of input parameters

Factor \ Level	-1	0	1
NBR (wt.%)	10	20	30
Clay (phr)	1	3	5
CaCO3 (phr)	1	3	5

Table 1. Samples codes and formulation

No.	Sample code	PA (wt.%)	NBR (wt.%)	Clay (phr)	$CaCO_3$ (phr)
1	N10C1Ca1	90	10	1	1
2	N10C3Ca3	90	10	3	3
3	N10C5Ca5	90	10	5	5
4	N30C1Ca3	70	30	1	3
5	N30C3Ca5	70	30	3	5
6	N30C5Ca1	70	30	5	1
7	N50C1Ca5	50	50	1	5
8	N50C3Ca1	50	50	3	1
9	N50C5Ca3	50	50	5	3

2.3 Characterization

The tensile properties of the nanocomposite samples were done based on ASTM D638 with the speed of 3 mm/min at ambient temperature using H25KS tensile machine test (HOUNSFIELD Co.) to determine tensile strength, Young’s modulus, and elongation at the breaking point. The impact strength of the PA6/NBR/Clay/$CaCO_3$ nanocomposites was determined by the Charpy impact test according to ASTM D256 using a Zwick 4100 impact test machine at ambient temperature. Scanning electron microscopy (SEM) was used to examine the morphology of the nanocomposites by the MIRA3 TESCAN (manufactured by Tescan company in the Czech Republic). The X-ray diffraction (XRD) of the nano-clay and nanocomposites was performed by a Phillips X-ray machine with CuKα radiation. The differential scanning calorimetry (DSC) test was carried out to evaluate thermal properties of the nanocomposite samples such as glass transition temperature (T_g), melting point temperature (T_m), crystallization temperature (T_c), and degree of crystallinity ($\%\chi$) using a SANAF DSC analyzer under a nitrogen atmosphere with a heating rate of 10 °C/min from 25 °C to 250 °C.

3. Results and discussion

3.1 XRD analysis

XRD analysis was used to determine the dispersion of nano-clay in the matrix. Figure 1 shows the XRD patterns of the nano-clay and three nanocomposite samples of N10C1Ca1, N10C3Ca3, and N10C5Ca5 containing 1, 3, and 5 phr nan-clay, respectively. A peak at 2ϴ=5.5° is observed in the pattern of nano-clay indicating the interlayer spacing of 13.5 °A approximately. No peak was observed in the XRD pattern of N10C1Ca1 with 1 wt.% nano-clay. This illustrates that the exfoliation structure is achieved in this nanocomposite sample. The XRD pattern of N10C3Ca3 and N10C5Ca5 show a peak at 2ϴ=3.8° and 2ϴ=4.2°, respectively. In these two samples, the nano-clay peak has shifted to a smaller angle indicating the intercalated structure is obtained.

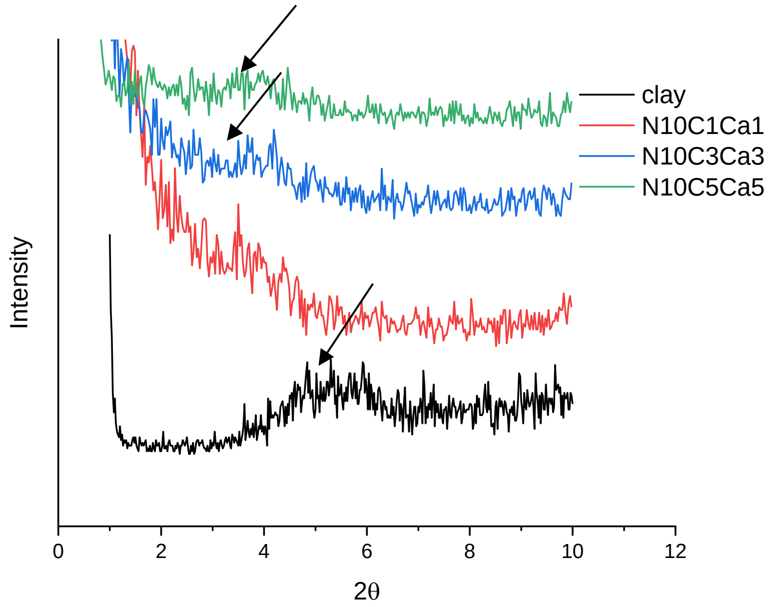
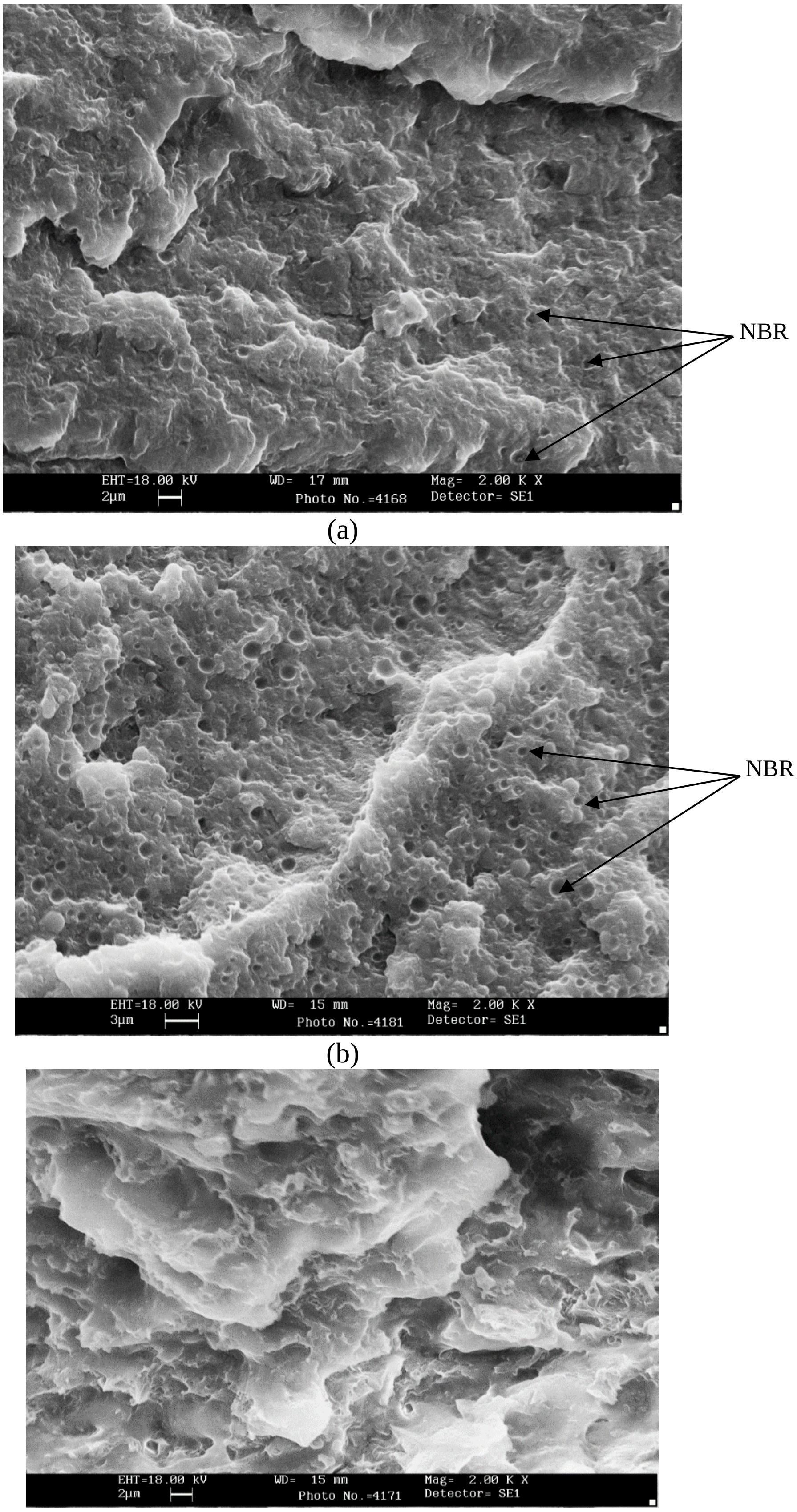


Figure 1. Xrd patterns of the nano-clay, N10C1Ca1, N10C3Ca3 and N10C3Ca3

3.2 Morphology

The SEM images of the N10C3Ca3, N10C5Ca5, and N50C5Ca3 were presented in Figure 2. The NBR droplets have been marked by arrows in the figure. As shown in Figure 2, the NBR droplets are dispersed through PA6 uniformly. In the N10C3Ca3 sample, the dispersed NBR droplets became visible smaller in size compared to the N10C5Ca5 sample. Introducing nanoparticles into the polymer blend can increase the melt viscosity of the PA6, therefore, leads to a reduction in viscosity difference between PA6 and NBR, and as a result, the compatibility improves. The nanoparticle content in N10C5Ca5 is higher compared to N10C3Ca3 leading to nanoparticle agglomeration. Hence, the melt viscosity of the PA6 in the N10C3Ca3 sample can be higher than N10C5Ca5. Figure 2(C) shows the morphology of the N50C5Ca3 containing 50 wt.% NBR. Because of the high loading content of NBR, the NBR droplets are not visible. It can be seen in Figure 2(C), PA6 and NBR phases are blended uniformly.



(a)

(b)

(c)

Figure 2. SEM images of the a) N10C3Ca3, b) N10C5Ca5 and N50C5Ca3

3.3 Mechanical Properties

The tensile test was carried out on the samples at the ambient temperature at the speed of 5 mm/min to obtain mechanical properties such as tensile strength (TS) and elastic modulus (M). The results of the tensile test have been presented in Table 3. Based on the presented data in Table 3, the maximum tensile strength (44 MPa) is obtained for the N10C3Ca3 sample containing 10 wt.% of NBR, 3 phr of nanoclay, and 3 phr of $CaCO_3$, and maximum tensile modulus (2800 MPa) is related to the N10C5Ca5 sample containing 10 wt.% of NBR, 5 phr of nanoclay, and 5 phr of $CaCO_3$. The minimum tensile strength and tensile modulus are for the N10C1Ca5 sample.

Table 2. Tensile properties of the nanocomposite samples

Sample code	TS (MPa	M (MPa)
N10C1Ca1	39	2650
N10C3Ca3	44	2750
N10C5Ca5	37	2800
N10C1Ca3	18.5	1450
N10C3Ca5	23.4	1450
N10C5Ca1	17.15	1900
N10C1Ca5	6.15	500
N10C3Ca1	9.55	600
N10C5Ca3	11.75	1100

The main effect plot for the tensile strength has been shown in Figure 3. The effect of NBR, nano-clay, and $CaCO_3$ content on the TS can be seen in Figure 3. As shown in the figure, by increasing the NBR content, the TS decreases due to the lower tensile strength of NBR compared to PA6. Adding the nanoparticles of nano-clay and $CaCO_3$ up to 3 phr promoted the TS, while the further increase of nanoparticles up to 5 phr the TS has been decreased. This reduction in TS can be due to nanoparticle agglomeration. The nanoparticles have high surface energy due to the high surface to volume ratio, therefore, the nanoparticles tend to absorb each other and form agglomerates. The internal mixer produces high shear stresses to decrease the agglomerates, however, it will be hard to decrease the agglomerates in high nanoparticle loading. The agglomerates can act as the cavities in the polymer matrix and as a result, the mechanical properties decline.

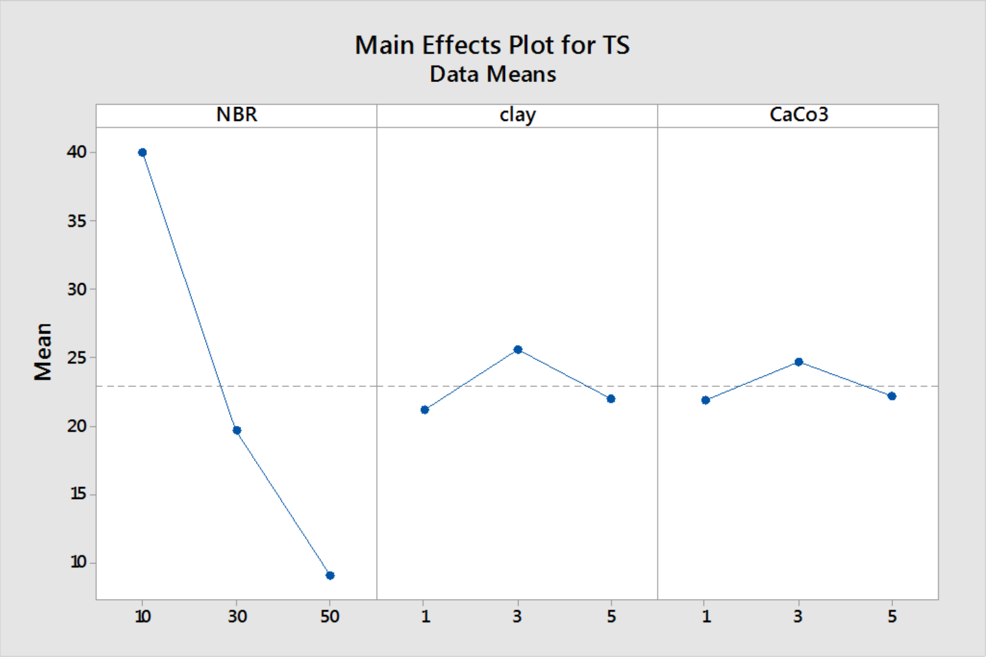


Figure 3. The effect plot for the TS

Figure 4 shows the effect of NBR and nanoparticle loading on tensile modulus. It can be seen, by increasing the NBR content from 10 to 50 wt.%, the tensile modulus decreased significantly because of the lower tensile modulus of NBR compared to PA6. The introducing nano-clay to polymer matrix up to 5 phr improved the tensile modulus. This improvement can be due to the high tensile modulus of nano-clay and good dispersion of these nanoparticles within the polymer matrix. The increase in $CaCO_3$ content up to 3 phr enhanced the tensile modulus, however further increase in $CaCO_3$ content up to 5 phr declined the tensile modulus. This reduction is due to the high surface energy of $CaCO_3$ nanoparticles and their tendency to agglomeration. The clay nanoparticles with planar form are less likely to agglomerate compared to spherical $CaCO_3$ nanoparticles.

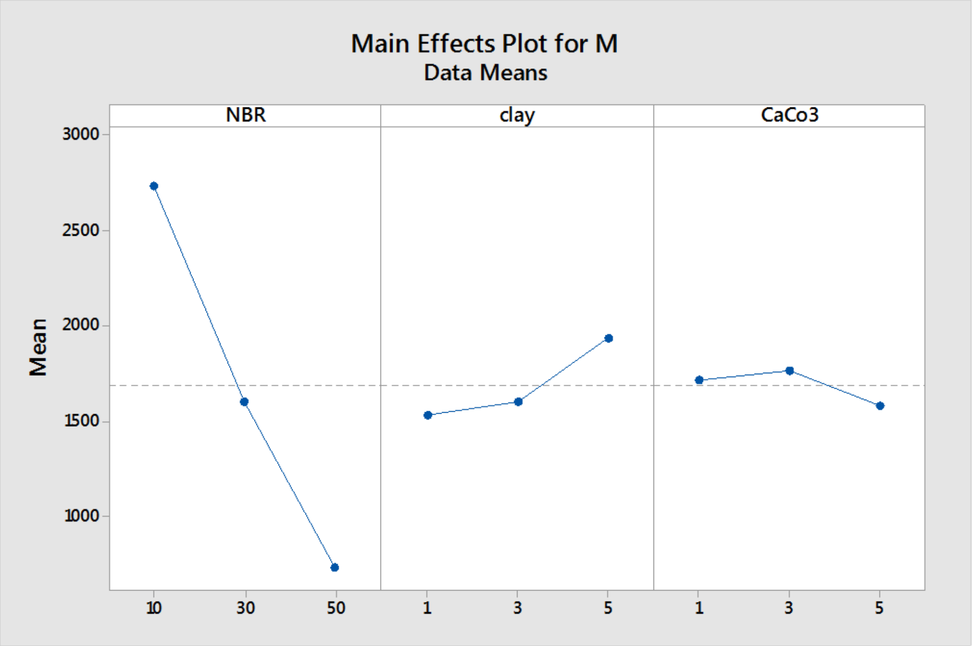


Figure 4. The effect plot for the M

The flexural properties of the nanocomposite samples containing flexural strength (FS) and flexural modulus (FM) have been presented in Table 4. Figures 5 and 6 display the effect of input parameters (NBR, nan-clay, and $CaCO_3$ content) on FS and FM. The maximum FS (87 MPa) and FM (3031 MPa) are obtained in the samples of N10C1Ca1 and N10C3Ca3, respectively and minimum FS (18.16 MPa) and FM (510 MPa) are obtained in the sample of N10C1Ca5. By increasing the NBR content from 10 to 50 wt.%, FS and FM decrease significantly due to lower flexural strength and flexural modulus of NBR compared to PA6. The incorporating nano- clay from 1 to 3 phr into polymer matrix increases FS and further increases up to 5 phr degraded FS, while the $CaCo_3$ nanoparticles declined FS slightly due to nanoparticles agglomeration. The adding clay nanoparticles from 1 to 5 phr into PA6/NBR matrix leads to an increase in FM. The $CaCo_3$ nanoparticles do not have a considerable effect on the FM.

Table 3 Flexural properties of the nanocomposite samples

Sample code	FS (MPa	FM (MPa)
N10C1Ca1	87	2799
N10C3Ca3	84.5	3031
N10C5Ca5	62.25	2807
N10C1Ca3	40.15	1265
N10C3Ca5	47.45	1605
N10C5Ca1	44.4	1761
N10C1Ca5	18.16	510
N10C3Ca1	20.35	666
N10C5Ca3	23.95	991

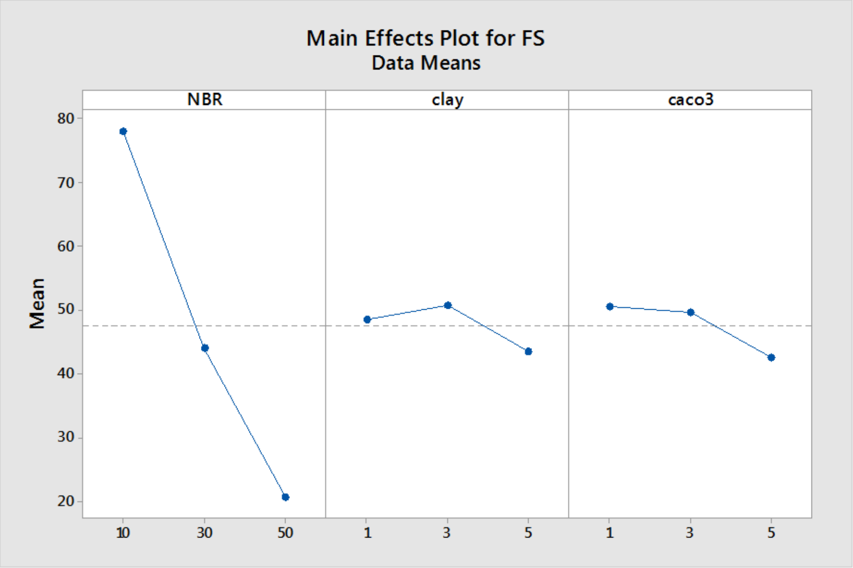


Figure 5. The effect plot for the FS

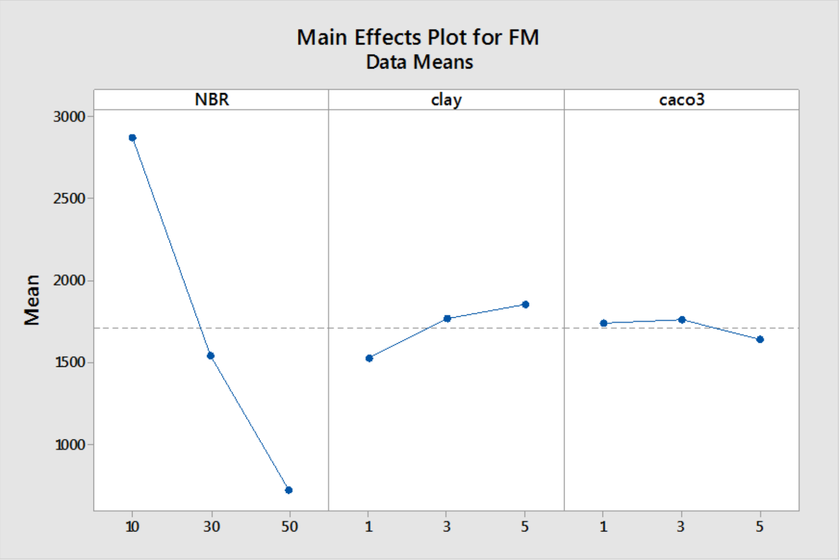


Figure 6. The effect plot for the FM

The results of the Charpy impact test have been presented in Table 5. Figure 7 shows the effect of the parameters (NBR, nano-clay, and $CaCO_3$ content) on impact strength. The results show that an increase in NBR content from 10 to 50 wt.% leads to increase impact strength significantly. On the other hand, by increasing the nanoparticles (nano-clay and $CaCO_3$) content the impact strength declines. The increase in nanoparticle content leads to restrict the polymer chain mobility through the polymer matrix, and therefore reduces the impact strength [21, 22]. As shown in Figure 7, by increasing the nano-clay content from 1 to 3 phr, the impact strength increases. Based on previous studies [23, 24], introducing the nano-clay into PA6/NBR matrix increases the polymer matrix viscosity and consequently reduces the difference between PA6 and NBR phases. On the other hand, the decrease in NBR to PA6 viscosity ratio lads to improve the interaction between NBR and PA6 and more uniform dispersion of NBR droplets on PA6 with smaller size.

Table 4. The Impact strength of the nanocomposite samples

Sample code	IS (kJ/m^2)
N10C1Ca1	6.1
N10C3Ca3	4.3
N10C5Ca5	3.45
N10C1Ca3	8.6
N10C3Ca5	8.45
N10C5Ca1	9.2
N10C1Ca5	20.35
N10C3Ca1	23.22
N10C5Ca3	18.50

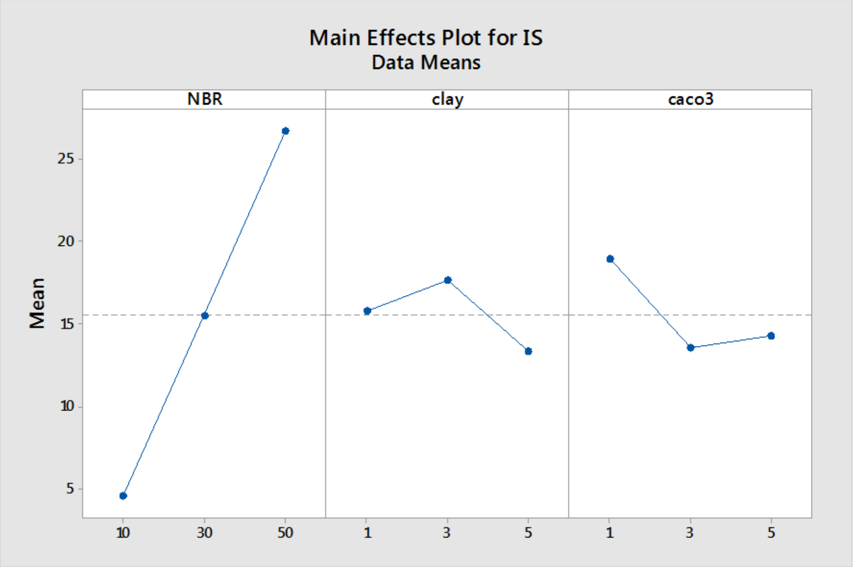


Figure 7. The effect plot for IS

4. Conclusion

In this study, the effect of NBR content (10, 30, and 50), nano-clay content (1, 3, and 5 phr), and $CaCO_3$ content (1, 3, and 5 phr) investigated the mechanical properties of the PA6/NBR blend, and the following results are obtained:

- By adding the nano-clay in the content of 1, 3, and 5 phr, the x-ray diffraction angle shifted from 5.5 for nano-clay to 4.2° for the sample containing 5 phr of nan-clay and 3.8° for the sample containing 3 phr of nan-clay indicating the intercalated structure. For the sample containing 1 phr of nano-clay, no peak was observed indicating the formation of exfoliated structure.
- The increase in NBR content reduced the tensile and flexural strength and tensile and flexural modulus. However, the increase in NBR content increased the impact strength.
- Nano-clay and $CaCO_3$ improved tensile strength and tensile modulus. Introducing the nano-clay into PA6/NBR increased the flexural strength, however, $CaCO_3$ declined the flexural strength. The adding nano-clay from 1 to 3 phr improved impact strength, however, more content of nano-clay up to 5 phr declined the impact strength. The CaCO3 nanoparticle content from 1 to 5 phr decreased the impact strength.

5. References

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