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# Improvement Properties of EPDM Rubber Using Hybrid Chitin/ Clay Filler for Industrial Products

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THIS work deals to synthesis chitin from Shrimp shells, that were collected from the local market scraped, washed, and ground. Deproteinization and decalcification process were applied on the ground shells to obtain pure chitin that identified and characterized by FTIR spectra, thermogravimetric analysis and scanning electron microscope SEM. The rubber compounds were prepared by incorporation of chitin as biomaterial and the other additive as curative system in ethylene propylene diene monomer (EPDM) rubber matrix using the laboratory two-roll mill. The rheological, rheometric characteristics and the physico-mechanical properties of the prepared rubber vulcanizates before and after exposure to thermal oxidative ageing swelling properties, water uptake and chitin dispersion in rubber were investigated. It is found that the tensile strength of EPDM/chitin vulcanizates was increased as the concentration of chitin increased up to5 phr while the modulus at 50 % elongation and hardness increased with increasing chitin concentration. The samples containing 5 and 10 phr chitin show good thermal stability. Also, the effect of nanoclay concentration (3,5,7 and 10 Phr) as binary filler properties of EPDM rubber were evaluated. It was observed that, the rheological characteristics and the other physico-mechanical properties were improved due to apply nanoclay as binary filler with chitin.

**Keywords:** EPDM, Chitin, Nanoclay, Binary filler, Physico-mechanical properties.

## Introduction

Green compound materials are acquiring notice owing to increase in environmental consciousness and regulations [1]. Up to date polymer/ biofiller composites have attracted many researchers due to their advantages as reducing cost and improving mechanical properties. Eco-friendly polymer composite and biocomposites are considered green composites because of containing either natural polymer matrix or a natural reinforced filler, or a combination of them [2].

Chitin is considered one of the compound full of organic materials and the second natural biopolymer on the earth after cellulose. It is a linear biopolymer and modified polysaccharide [3].

The main source of commercial chitin is shrimp shells. It contains about45% from shrimps [4, 5].

The incorporation of these natural polymers as filler in rubber may help to improve some specific properties for applications in the field of polymer composites. For example, chitin nanowhiskers obtained from crab shells and squid pen were introduced for reinforcing natural rubber matrix [6-9].

Addition of clay to polymer nanocomposites is exhibited high mechanical properties, superior thermal stability, outstanding biodegradability, and excellent gas barrier performances[10]. Incorporation of hybrid two or more component

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fillers can be improved the properties and lower the cost of industrial goods.

The main goal of this work was a trial to extract chitin from locally waste collected shrimp shells to use as biofiller for EPDM rubber and evaluate the rheological characteristics of rubber mixes as well as study the physic-mechanical properties, swelling parameters, the morphological analysis and water uptake of the investigated vulcanizates. Also, study the effect of binary filler system contained nanoclay with chitin on the properties of the investigated EPDM vulcanizates

## Experimental

*Materials*

EPDM of an ethylene content 55% and density of 0.86 g/cm$^3$ was manufactured by Esso Chemi, Germany. Zinc oxide (ZnO) with a specific gravity at 15$^o$C of 5.6, stearic acid whose specific gravity at 15$^o$C is 0.9–0.97, elemental sulfur: with fine pale yellow powder and specific gravity of 2.04–2.06 at room temperature (251±$^o$C), polymerized 2, 2, 4-trimethyl-1,2-dihydroquinoline (TMQ) was used as an antioxidant. Tetramethylthiuram disulfide (TMTD) with a specific gravity of 1.29 1.31 and melting point of 148.5$^o$C, mercaptobenzothiazole disulphide (MBTS)with a specific gravity of 1.5 and melting point of 177-180$^o$C, Sodium –bentonite (product code B3378; Munich, Germany) has a cationic exchange capacity of 88 mequiv/100 g and surface area of 39.3 m$^2$ g$^{-1}$were used.All these materials are supplied by Sigma–Aldrich, Germany.

*Extraction of chitin* [11]

Shrimp shells were collected from the local market (El-Obour, Cairo). Freshly collected shrimp shells were thoroughly scraped and washed, and then ground. The ground shells were used to produce pure chitin by deproteinization and decalcification. Deproteinization was carried out by 10 percent NaOH solution using a material -to- liquor ratio of 1:5 (w/v) at room temperature for 24 hours. After washing with running water, the alkali-treated shells were neutralized with aqueous acetic acid (60%). Decalcification was affected by aqueous hydrochloric acid solution at 25$^o$C for two hours (conc. HCL 0.5g/1g of shell material).

*Preparation of EPDM compounds*

Rubber and their ingredients were mixed in an open two-roll mill at room temperature. The rotors operated at a speed ratio of 1:1.4. All ingredients were mixed with rubber, sulphur and accelerator at the end mixing was added. The recipe of the compounds is described in Table 1. Rubber compounds were vulcanized at 150±1$^o$C in an electrically heated press under a pressure of about 4 Mpa to get vulcanized rubber sheets of 2 mm thickness. The vulcanization time of the sheets corresponds to the optimum cure time $Tc_{90}$ derived from the curing curves data.

*Characterization*

The Fourier transform infrared (FTIR) spectra of samples were reordered on a Jascow (Japan) FTIR 430 series Infrared Spectrophotometer equipped with KBr disks at room temperature in the range of 4000–400 cm$^{-1}$. The surface morphology of the samples was investigated by environmental Scanning Electron Microscope (Quanta FEG-250).

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)were conducted with Shimadzu TGA-50H. The measurements were performed at a heating rate 10 $^o$C/min, from room temperature up to 800 $^o$C and under nitrogen atmosphere. The curing characteristics of the rubber compounds were measured by a Monsanto Oscillating Disc Rheometer (ODR –100 s) at 152$^o$C as per ASTM D-2084-07. From the graphs the minimum torque ($M_L$), maximum torque ($M_H$), optimum cure time ($Tc_{90}$), scorch time ($Ts_2$) and cure rate index $\{CRI = \frac{100}{Tc90 - Ts2}\}$ could be determined.

The physico-mechanical properties of the vulcanizates were evaluated using an Instron Universal Test Machine Model 1425, according to ASTM D412. Tensile strength, elongation at break and modulus of elasticity at 50, 100, and 200 % elongation were measured. The rate of grip separation was 500 mm/min. Thermal oxidative aging was carried out at 90 ± 1 °C in an air circulating oven for different time periods according to ASTM D573-04 (2015). The reported results were the average of minimum five specimens. Hardness was measured using shore Durometer (USA) according to ASTM D 2240 as shore A. Swelling properties of rubber vulcanizates were determined according to the standard method (ASTM D471-06). Test specimens were soaked in toluene at room temperature for 24 hours. The equilibrium swelling in toluene (Q %) could be

**TABLE 1. Rubber formulations [a] and Rheometeric [b] properties [c] of rubber compounds.**

| Sample No. | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Chitin, Phr[d] | 0 | 5 | 10 | 20 | 30 |
| | | | Rheometeric properties | | |
| $M_L$, dN | 10.5 | 11.5 | 12.5 | 15 | 16 |
| $M_H$, dN | 75.5 | 83 | 84 | 86 | 97.5 |
| $M_H$ - $M_L$, dN | 65 | 71.5 | 71.5 | 71 | 71.5 |
| $Tc_{90}$, min | 10 | 10.25 | 9.75 | 9.25 | 9 |
| $Ts_2$, min | 2.5 | 2 | 2 | 1.75 | 1.5 |
| CRI, $min^{-1}$ | 13.13 | 12.12 | 12.9 | 13.13 | 13.13 |
| α | 0.03901 | 0.0993 | 0.1126 | 0.13907 | 0.29139 |

[a] Base recipe:

EPDM, 100; Stearic acid, 1.5; Zinc Oxide, 5; TQM, 1; TMTD, 1.2; MPTS, 0.5; Sulphur, 1.2 ; [b] Minmum torque ($M_L$), maximum torque ($M_H$), optimum cure time ($Tc_{90}$), scorch time ($Ts_2$), cure rate index (CRI), reinforcing factor α( );

[d] Part per hundred parts of rubber

calculated according to the following equation:

$$Q = \frac{\text{Swollen weight} - \text{dried weight}}{\text{orignal weight} - \text{formula weight} \times 100} \quad (1)$$

The crosslinking density (ν), mol/$cm^3$ of EPDM vlucanizates was determined on the basis of solvent-swelling measurements (toluene solvent for 24 h at 25 + 1 °C) using the Flory–Rehner equation [12, 13].

$$\nu = \frac{1}{2Mc} \quad (2)$$

where: Mc is the molecular weight between crosslinks (g/mol)

$$Mc = \frac{-\rho\, Vs\, Vr1/3}{[\ln(1 - Vr) + Vr + \chi\, Vr2]} \quad (3)$$

where: ρ is the density of rubbers (ρ EPDM is 0.86 g/$cm^3$), Vs is the molar volume of the solvent (toluene) =106.35 $cm^3$/mol, χ is the interaction parameter of EPDM rubber, that is 0.49 and Vr is the volume fraction of swollen rubber that can be obtained from the mass and density of rubber samples and the solvent.

Water Uptake Study was performed according to the ASTM D570-95. The vulcanized samples were soaked in a distilled water for different time periods. All specimens were weighed at regular time intervals using electronic balance with an accuracy level of 0.5 mg and the samples were dried using tissue paper before weighing. The water content ($W_c$) of the sample was measured as weight percent. The water uptake was determined according to the following equation:

$$Water\ uptake\ (Wc), \% = \frac{Wt - W0}{W0} \times 100 \quad (4)$$

Where $W_t$ is the weight of specimen at time t and $W_o$ is the initial weight of the sample before placing in water.

## Results and Discussion

*Characterization of extracted chitin*

Figure1 shows the characteristic vibrations bands of the functional chemical groups typical for chitin extracted from shrimp shells. It is clear that OH stretching appears at (3443 $cm^{-1}$), CH, $CH_2$ symmetrical stretching at (2924 $cm^{-1}$) and bending at (1380 and 1423 $cm^{-1}$), and glycosidic bonds symmetric ring-stretching at (901 $cm^{-1}$). Vibrations of C-O groups in ring at (1314 $cm^{-1}$), C-O-C asymmetrical stretching (1159 $cm^{-1}$) and C-OH bending (612 $cm^{-1}$) are characteristic for cellulose. The presence of the peaks at 3264 and1559 $cm^{-1}$characteristics of stretching vibrations of NH and C=O stretching at 1638 $cm^{-1}$ carbonyl present in chitin. NH bending, 1559 $cm^{-1}$ (amide II band), CH bending of $CH_3$ groups at 1380 $cm^{-1}$, CH torsion at 1314 $cm^{-1}$, C-N flexion in secondary amines at 1262 $cm^{-1}$[14, 15]. The type of chitin (α or β) was known by FTIR spectroscopy because of the different hydrogen bonds (Figure 1). The presence of the one peak at 1639 cm-1 characteristics of carbonyl present in anhydrous β –chitin [5].

Thermogravimetric analysis results of chitin such as (TGA, DTG and DSC) are represented in Figure 2. The results showed that the weight loss in 40-90°C , attributed to water evaporation and the second occurred in the range of 220 -420 °C , and could be ascribed to the degradation of molecules of chitin and the weight loss about 82.34%.

The morphological characteristics of extracted chitin were measured using SEM and the results illustrated in Figure 3. It is shown that, pores like structures are presented. Also the diameter of chitin was measured and found ranged from 299–669 nm.

*Characterization of the prepared EPDM vulcanizates*

*Processability characteristics of EPDM/chitin vulcanizates*

The processability of chitin/EPDM mixes can be specified by measuring rheological and curing characteristics such as minimum torque $M_L$, maximum torque $M_H$, scorch time $Ts_2$, optimum time $Tc_{90}$, and CRI as shown in Table 1. It was found that $M_L$ and $M_H$ of the investigated EPDM vulcanizates were increased with increasing chitin concentration. On the other hand the scorch time of all EPDM mixes was decreased with increasing chitin loading but the optimum cure time is slightly decreased. Therefore, the changes in rheometric torque depend on filler loading that describe the filler-EPDM interaction or reinforcement. The reinforcement factor $\alpha_f$ calculated from the rheographs[16, 17] and can be given from the following equation:

$$\alpha f = \frac{\Delta Lmax(filled) - \Delta Lmax(gum)}{\Delta Lmax(gum)} \quad 5$$

where $\Delta L_{max}$(filled) and $\Delta L_{max}$(gum) are the changes in torque during vulcanization for the filled and gum compounds, respectively. From Table 1, it was found that the calculated values of reinforcing factor ($\alpha_f$) increase with increasing chitin concentration.

*Physico-mechanical properties of the EPDM rubber vulcanizates*

It is important to evaluate the physic-mechanical properties of the investigated EPDM vulcanizates containing chitin as biofiller. The physico-mechanical properties such as tensile strength, elongation at break, and modulus at 50 % elongations of the investigated EPDM vulcanizates are measured and collected in Table 2. Also, the stress-strain curves for the prepared EPDM/ chitin rubber vulcanizates are shown in Figure 4. From Table 2 it is shown that, by incorporating chitin into EPDM rubber, firstly tensile strength increased at 5phr, after that the tensile strength slightly decreased. The improvement of tensile strength at low concentration 5 Phr loading chitin attributed to the good dispersion of chitin particles through EPDM rubber chain matrix and good interaction between them. The elongation at break was decreased according to increasing chitin loading on EPDM vulcanizate. The decrease in elongation at break is due to the over load of chitin that reduce and restrict the EPDM chains mobility and consequently reduce the flexibility of chains. This tested data was confirmed with the results of some scientific researchers [18-21]. The results of modulus at 50% elongation exhibited an increase in their values for all the investigated vulcanizates compared to unfilled one. This observation indicated that the incorporation of an extracted chitin into EPDM rubber matrix improve the stiffness of its vulcanizate. Similar trends of moduli were observed in natural rubber composites [22, 23].Also, it is obvious that, the increasing chitin concentration led to increase hardness values of EPDM vulcanizates (Table 2). Also, the presence of high concentration of chitin in EPDM rubber reduces elasticity of the rubber chains, which leads to obtain more rigid rubber vulcanizates than that in case of low chitin concentration.

*Physico-mechanical properties after thermal oxidative ageing*

Rubber products during exploitation are exposed to different environmental factors leading to their degradation. Increased temperature initiate aging of the vulcanizates, so it is interesting to investigate, how these materials react while introduced for this type of process. The rubber vulcanizates are subjected to thermal oxidative ageing up to seven days at 90°C. Figure 5a-c shows the effect of ageing time on tensile strength, elongation at break and modulus at $M_{50}$% elongation ($M_{50}$%) for all of the prepared vulcanizates. It is clear that, the values of tensile strength increased after 24 h for all samples (1-5). According to increasing ageing time, the values of tensile strength decreased for EPDM and EPDM/5phr chitin vulcanizates due to chain scission but increased for samples (3-5)owing to the formation of excessive crosslinking [13, 24]. Also it is found that, the samples containing 5 and 10 phr chitin show thermal stability. The

$M_{50}$% values increase after ageing up to seven day (Figure 5c). These may be attributed to increasing the stiffness of the rubber matrix.

*Swelling characteristics*

Crosslinking density was determined from the data of swelling behaviour in toluene. It is considered one of the most important structural parameters characterizing the investigated crosslinked EPDM / chitin rubber vulcanizates. The effect of chitin content on equilibrium swelling Q, volume fraction of rubber $V_r$, molecular weight between the crosslink points Mc, and crosslink density ν of EPDM / chitin vulcanizates was determined and collected in Table 3. It was found that, the Q and Mc values were decreased and ν is increased with increasing chitin content in the vulcanizates [24]. This behaviour indicates a strong interaction between chains of EPDM rubber matrix and consequently lead to strong physical crosslinks. Also, increasing chitin concentration leads to reduction of the rubber chains molecules movements and causes difficult penetration of toluene through the rubber matrix [25].

*Water uptake*

The results of water uptake percent of the vulcanized EPDM/ chitin vulcanizates as a function of the time are illustrated in Figure (6). It was found that the equilibrium water content in EPDM/ chitin filled vulcanizates (samples 2-5) was higher than that of unfilled EPDM (samples 1). The values of water uptake percent were highly increased with increasing the immersion time until reached to saturation point. The higher initial water uptake percent of the investigated vulcanizates can be explained by the diffusion phenomenon [26]. The sample having 20 phr chitin exhibited higher water uptake than the other vulcanizates. This is owing to the hydrophilicity due to presence of hydroxyl group in chitin, which is able to form hydrogen bonds between chitin and water [27].Moreover, it is observed, the steady state was around 324 days for all EPDM/ chitin vulcanizates. After this state the water was begin to eliminate from all vulcanizates.

*Morphology*

Figure 7a-d shows the surface morphology of the unfilled EPDM and filled EPDM. It was observed that smooth and compatible surface for the vulcanizate without chitin. The surface texture of chitin filled EPDM at concentration of (5,10 and 20 phr) chitin illustrated that, no clear trend for the behavior and dispersion of chitin. The compatibility was not so good at highest concentration. There was some filler agglomeration

**TABLE 2. Physico-mechanical properties of chitin/EPDM rubber vulcanizates**

| Sample No. | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Chitin, Phr[b] | 0 | 5 | 10 | 20 | 30 |
| T.S,Mpa | 1.91 | 2.1 | 1.72 | 1.65 | 1.6 |
| Elong. at break, % | 152 | 143 | 90 | 75 | 51 |
| $M_{50}$, Mpa | 1.10 | 1.3 | 1.45 | 1.55 | 1.6 |
| Hardness, shore A | 63 | 66 | 73 | 75 | 77 |

**TABLE 3 Results of the swelling measurements of the chitin/rubber biocomposites**

| Sample No. | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| **Q** (%) | 183.97 | 176.55 | 152.68 | 152.52 | 140.28 |
| $\mathbf{V_r}$ | 0.35 | 0.36 | 0.396 | 0.396 | 0.416 |
| $\mathbf{M_c}$ (g/mol) | 2288 | 2102 | 1568 | 1564 | 1327 |
| **ν** x $10^{-4}$ (mol/$cm^3$) | 2.19 | 2.38 | 3.189 | 3.19 | 3.77 |

Q, equilibrium swelling; $V_r$, volume fraction of rubber; Mc, molecular weight between the crosslink points; ν, crosslink density

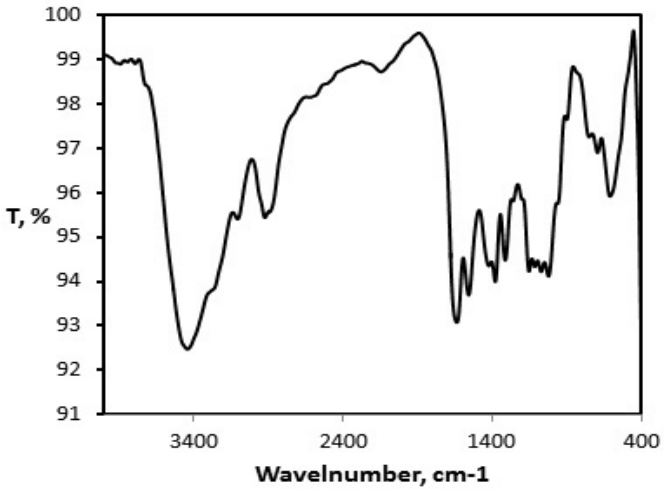


**Figure 1 FTIR spectra of chitin.**

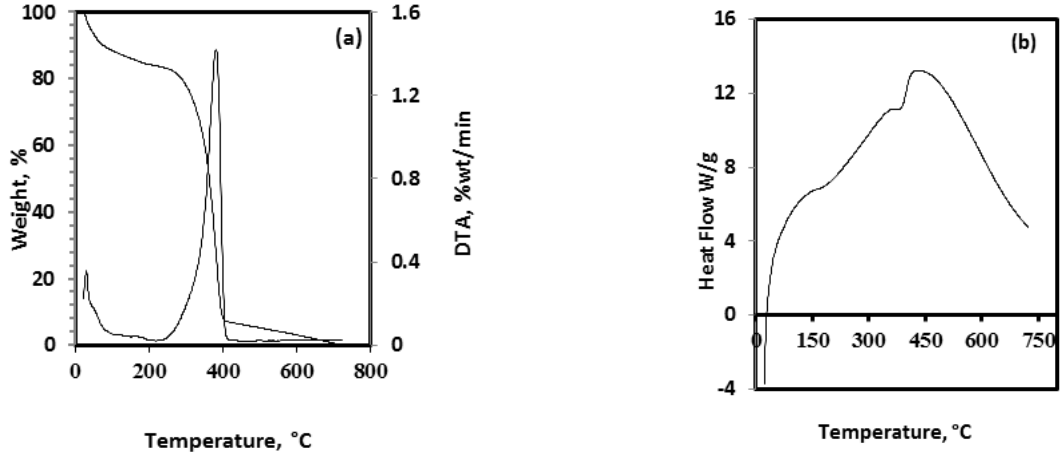


**Figure 2 TGA, DTG and DSC results of chitin.**

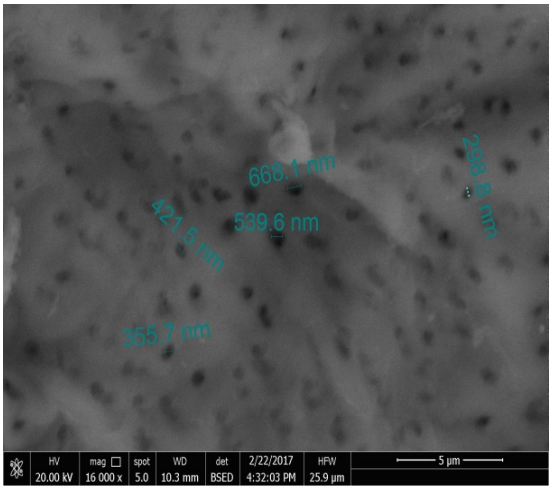


**Figure 3 SEM micrographs of chitin.**

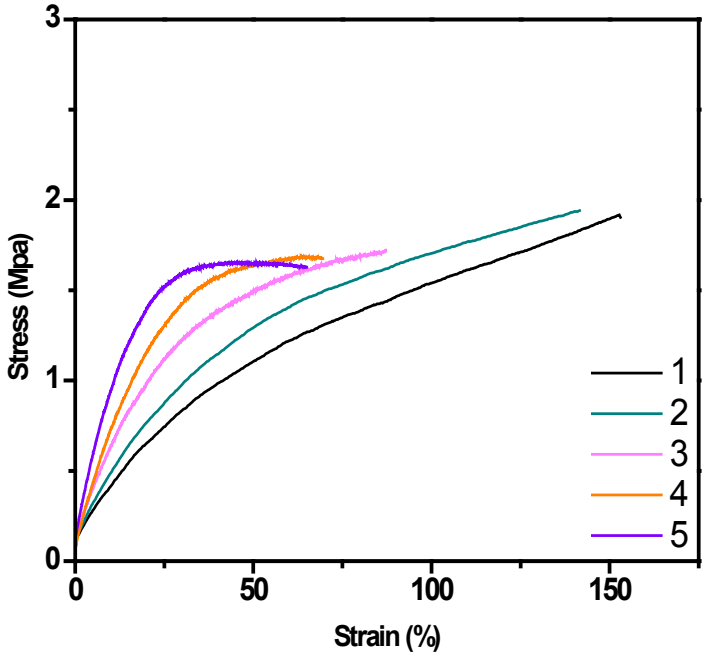


**Figure 4 Stress–strain curves of chitin/ EPDM rubber vulcanizates.**

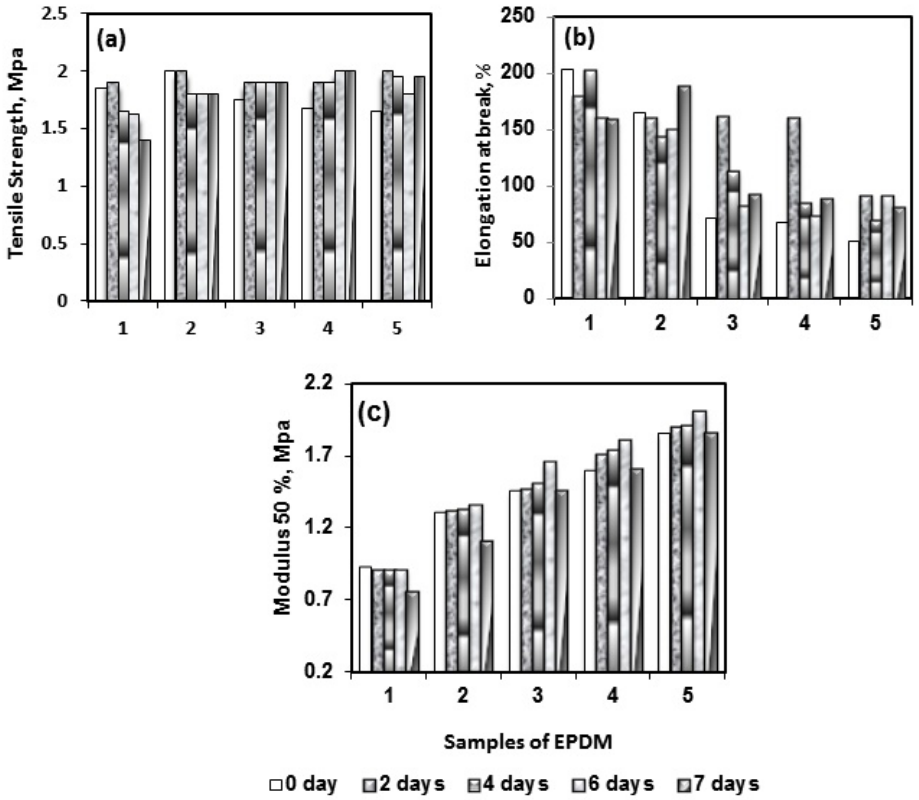


**Figure 5 Physico-mechanical properties of a) tensile strength, b) elongation at break, c) modulus at 50 % elongation versus ageing time for EPDM/ chitin rubber vulcanizates.**

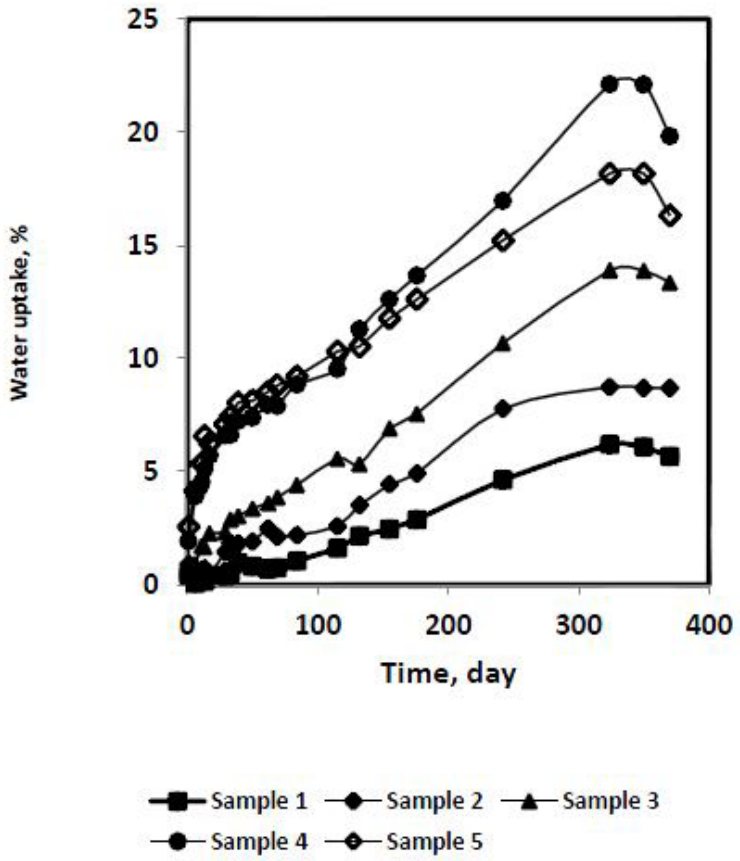


**Figure 6 Effect of chitin loading on water uptake of of EPDM rubber vulcanizates.**

by increasing chitin concentration(Figure 7c, d*)*.This may be attributed to poor interfacial interaction between chitin and chain of EPDM matrix, which led to void formation.

*Effect of nanoclay concentration on the properties of EPDM/chitin vulcanizates*

This section deals to study binary system of filler as nanoclay and chitin to improve the properties of EPDM rubber. Different concentration of nanoclay (3,5,7&10 phr) were incorporated in EPDM/chitin (5&10 phr) mixes. The curing characteristics, physic-mechanical properties of the vulcanizates before and after thermal oxidative ageing, swelling properties, water uptake and morphology of EPDM/chitin (5&10 phr) vulcanizates were measured and the results collected in Table (4,5) and represented Figures (8-11).

*Curing characteristics*

Table 4 shows the curing characteristics of EPDM/chitin/nanoclay hybrid biocomposites of different clay loading. It was noticed that $M_L$ increased as amount of clay increased. This increasing of $M_L$ due to increase in the viscosity of rubber composite and decrease the flow-ability which associated with the processing. On the other hand, $M_H$ showed the contradict trend, as decreased upon increasing the amount of clay loading. Increasing amount of clay in the prepared vulcanizates reduces $Tc_{90}$ and increases $Ts_2$and CRI. This may be owing to polarity of silicate layers of clay which help to hydrogen bond formation and thus accelerated the curing process at low concentration of nanclay.

*Physico-mechanical properties*

Table 5 shows the effect of nanoclay concentrations (3, 5, 7&10 phr) on the Physico-mechanical properties of EPDM/chitin (5&10 phr)/nanoclay vulcanizates. The stress-strain curves for the prepared EPDM rubber vulcanizates with chitin are shown in Figure 8, 9.The tensile strength and elongation at break of rubber vulcanizates are increased with nanoclay loading. Remarkably, the modulus at 50 and100%

**TABLE 4. Rubber formulations and, Rheometeric properties of the chitin/nanoclay/EPDM rubber compounds**

| Sample No. | 2 | 6 | 7 | 8 | 9 | 3 | 10 | 11 | 12 | 13 |
|---|---|---|---|---|---|---|---|---|---|---|
| Chitin, Phr[b] | 5 | 5 | 5 | 5 | 5 | 10 | 10 | 10 | 10 | 10 |
| Nanoclay | 0 | 3 | 5 | 7 | 10 | 0 | 3 | 5 | 7 | 10 |
| | | | | Rheometeric properties | | | | | | |
| $M_L$, dN | 11.5 | 18 | 18.5 | 19 | 22 | 12.5 | 19 | 19.5 | 20 | 22 |
| $M_H$, dN | 83 | 38 | 34 | 32 | 51 | 84 | 48 | 59 | 75 | 78 |
| $Tc_{90}$, min | 10.25 | 7.75 | 7.75 | 7.75 | 8 | 9.75 | 7.75 | 7.75 | 8.75 | 8.25 |
| $Ts_2$, min | 2 | 3.5 | 3.5 | 3.5 | 3.25 | 2 | 4.25 | 3.5 | 3.25 | 3.25 |
| CRI, $min^{-1}$ | 12.12 | 23.29 | 23.29 | 23.29 | 21.05 | 12.9 | 28.57 | 23.53 | 18.18 | 20 |

( b Part per hundred parts of rubber).

**TABLE 5 Physico-mechanical properties of the chitin/nanoclay/EPDM vulcanizates**

| Sample No. | 2 | 6 | 7 | 8 | 9 | 3 | 10 | 11 | 12 | 13 |
|---|---|---|---|---|---|---|---|---|---|---|
| T.S, Mpa | 2.1 | 2.22 | 2.21 | 2.3 | 2.33 | 1.72 | 1.98 | 2.15 | 2.18 | 2.06 |
| Elong. at break, % | 143 | 225 | 236 | 255 | 259 | 90 | 210 | 209 | 212 | 213 |
| $M_{50}$, Mpa | 1.3 | 1.13 | 1.13 | 1.14 | 1.39 | 1.45 | 1.27 | 1.34 | 1.37 | 1.29 |
| $M_{100}$, Mpa | 1.75 | 1.58 | 1.6 | 1.62 | 1.65 | - | 1.64 | 1.76 | 1.76 | 1.68 |
| Hardness, shore A | 66 | 68 | 70 | 70 | 71 | 73 | 76.5 | 77 | 77 | 75 |

**TABLE 6 Results of the swelling measurements of the chitin/rubber/nanoclay biocomposites**

| Sample No. | 2 | 6 | 7 | 8 | 9 | 3 | 10 | 11 | 12 | 13 |
|---|---|---|---|---|---|---|---|---|---|---|
| Q, % | 176.55 | 184.6 | 183.7 | 180.26 | 176.86 | 152.68 | 186 | 179.19 | 179.37 | 180 |
| Vr | 0.36 | 0.351 | 0.352 | 0.357 | 0.361 | 0.396 | 0.349 | 0.358 | 0.358 | 0.357 |
| $M_c$ (g/mol) | 2102 | 2314 | 2289 | 2187 | 2109 | 1568 | 2340 | 2162 | 2169 | 2187 |
| **v** x $10^{-4}$ (mol/$cm^3$) | 2.38 | 2.16 | 2.18 | 2.29 | 2.39 | 3.189 | 2.14 | 2.31 | 2.31 | 2.29 |

elongation values for EPMM vulcanizates filled with chitin (5&10 phr) decreased with addition of clay. These results conformed to the data obtained from the torque differences as tabulated in Table 4. Also, it observed that, the values of hardness increased as the nanoclay concentration increased in the prepared EPDM/chitin vulcanizates. On the other hand, hardness values of rubber vulcanizates increases with adding nanoclay to EPDM/chitin (5&10 phr) vulcanizates

*Physico-mechanical properties after thermal oxidative ageing*

The thermal resistance of the EPDM/chitin (5&10 phr)/clay (3,5,7&10 phr vulcanizates was studied through ageing process at 90° C and time up to 7 days. The data obtained represented in Figures (10,11).The values of the tensile strength and elongation at break increased but modulus at different elongation showed different behavior for all the EPDM vulcanizates containing nanoclay after thermal oxidative ageing. This may be

attributed to the formation of some additional crosslinks between chitin, clay and EPDM [28]. So, the optimum concentration of applied binary filler is (5,10 phr chitin and 3, 5 phr nanoclay).

*Swelling properties*

The effect of nanoclay loading on swelling properties (Q, Mc and )ν of rubber vulcanizates were determined and tabulated in Table 6. The addition of nanoclay (3, 5,7and 10 phr) on EPDM/ chitin (5&10 phr) vulcanizates leads to increase Q and Mc values and decrease crosslinking density value. This may be attributed to the barrier properties of silicate layers of nanoclay.

*Water uptake*

Figure 12(a,b) represents the relation between the water uptake values of EPDM/ chitin (5 and 10 Phr) with nanoclayconcentrations (3,5,7 and 10 Phr). It is observed that, the values of water uptake were increased with incorporation of high concentration of nanoclay and highly increased with increasing the immersion time until reached to saturation point (324day) in case of EPDM/ chitin (5 phr) system (Figure 12a). But in case of EPDM/chitin (10 phr) system shows different behavior, the swelling percent decreased after the incorporation of low concentration of nanoclay and then increased as clay concentration increased (7,10phr) (Figure 12b).

*Morphology*

The final properties of the investigated rubber composites are directly related to the dispersion of filler particles into the rubber matrix [29]. Therefore it is necessary to investigate the prepared vulcanizates surface morphology as well as the selective dispersion of the binary filler (chitin/nanoclay) particles into the investigated vulcanizates**.** Figure 13 illustrated the SEM

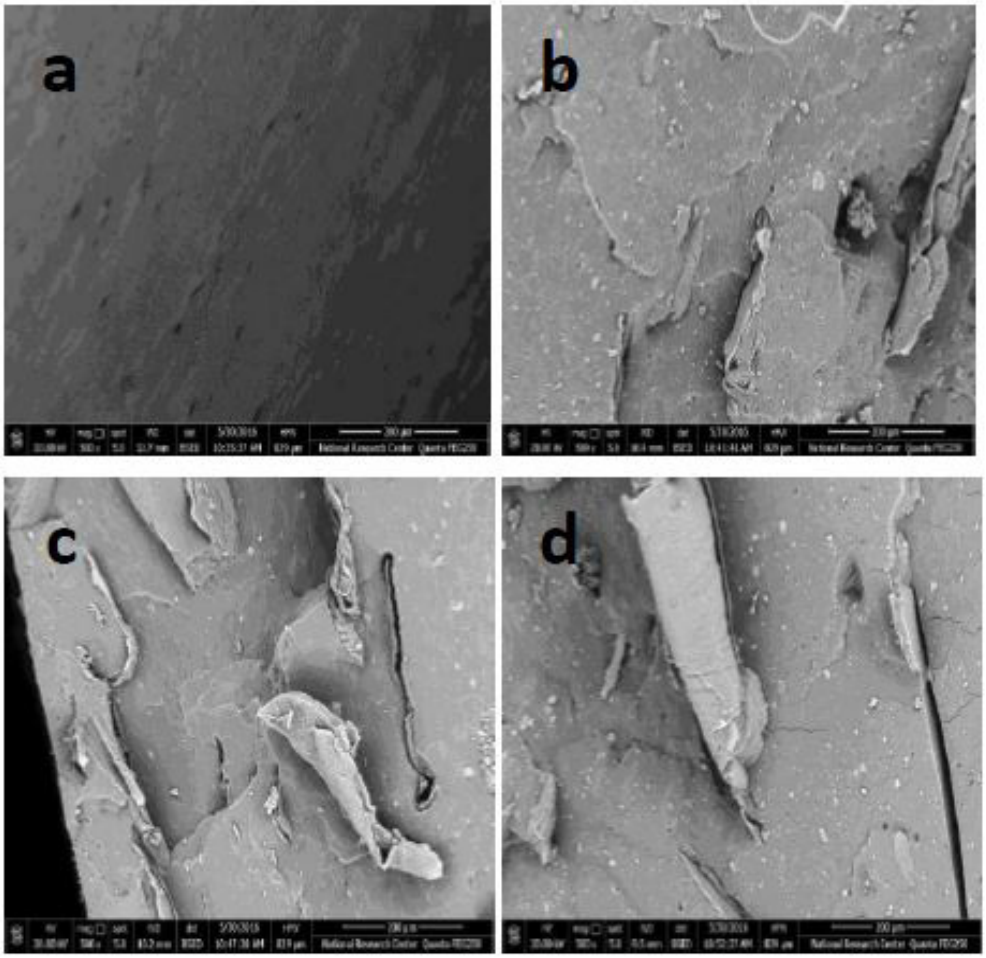


**Figure 7 SEM micrographs for EPDM/ chitin rubber vulcanizates a) 5, b) 10 and c) 20 phr loading ratio of chitin.**

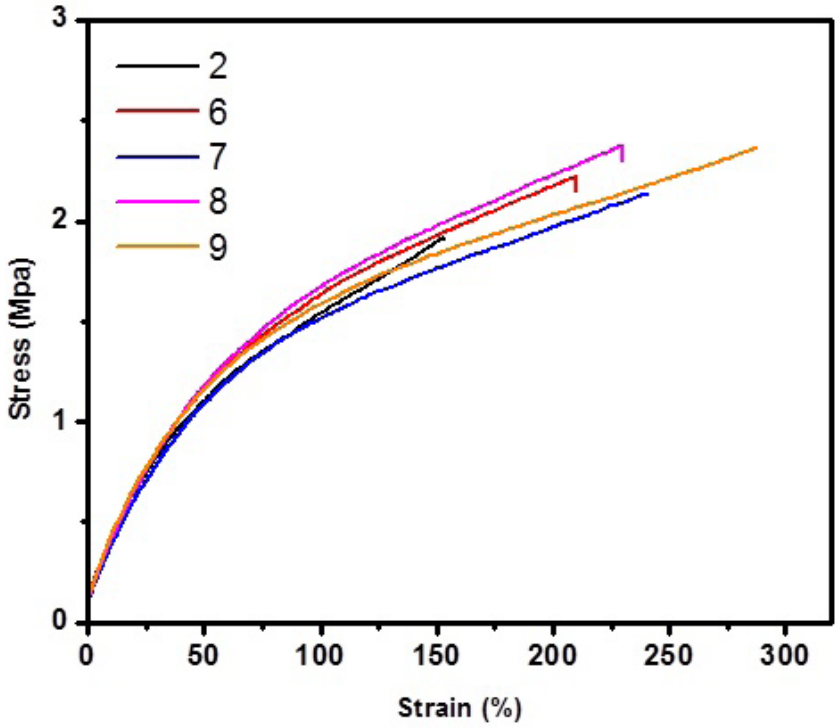


**Figure 8 Stress–strain curves of chitin (5 phr) / EPDM rubber vulcanizates loading with different concentrations of nanoclay (3,5,7,and10 Phr).**

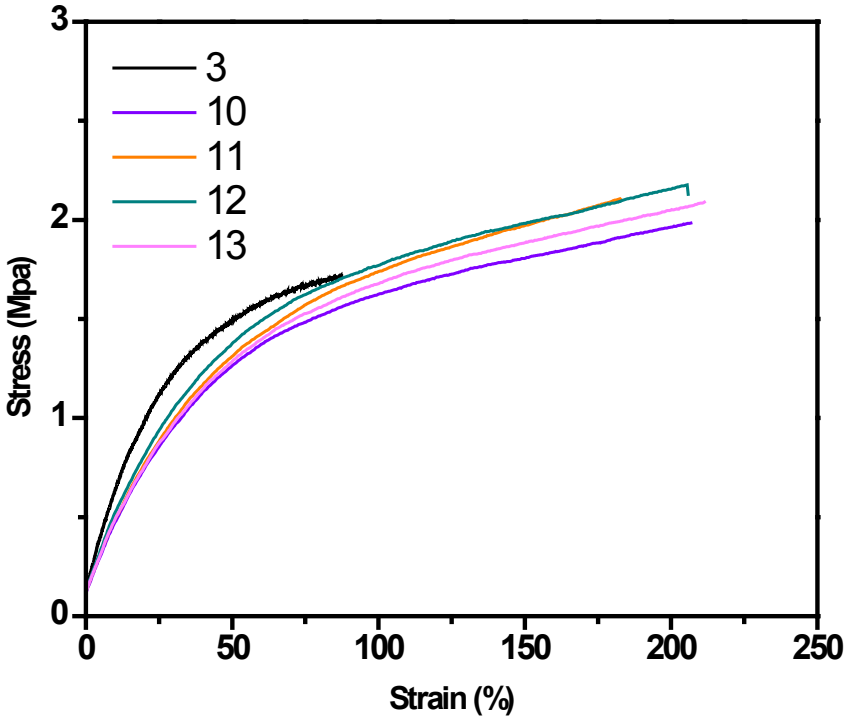


**Figure 9 Stress–strain curves of chitin (10 phr) / EPDM rubber vulcanizates loading with different concentrations of nanoclay (3,5,7,and10 Phr).**

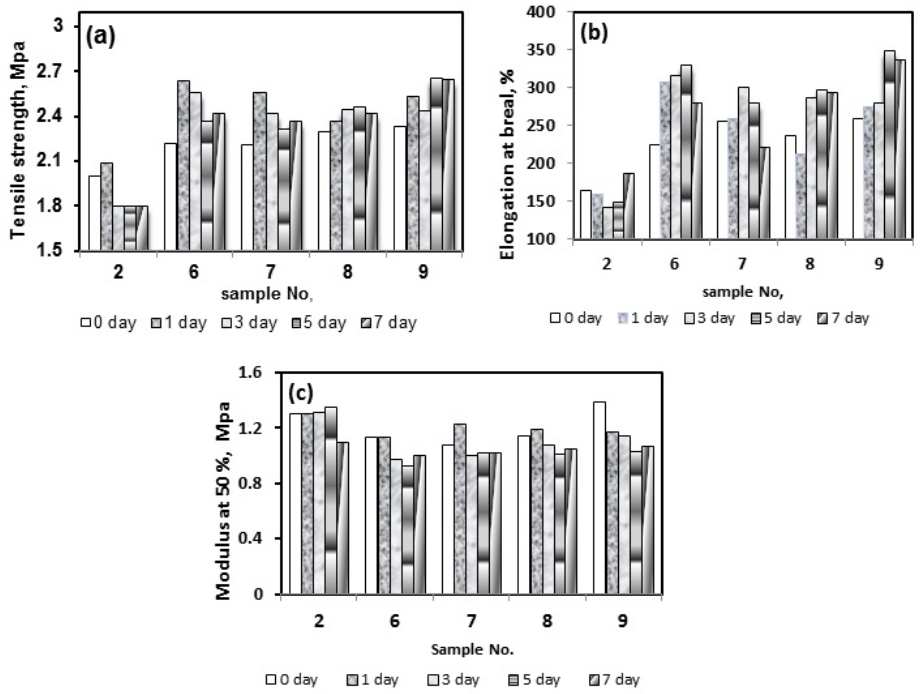


**Figure 10 Physico-mechanical properties of a) tensile strength, b) elongation at break, c) modulus at 50 % elongation versus ageing time for EPDM/ chitin(5 phr) / nanoclay (3,5,7, and 10phr) rubber vulcanizates.**

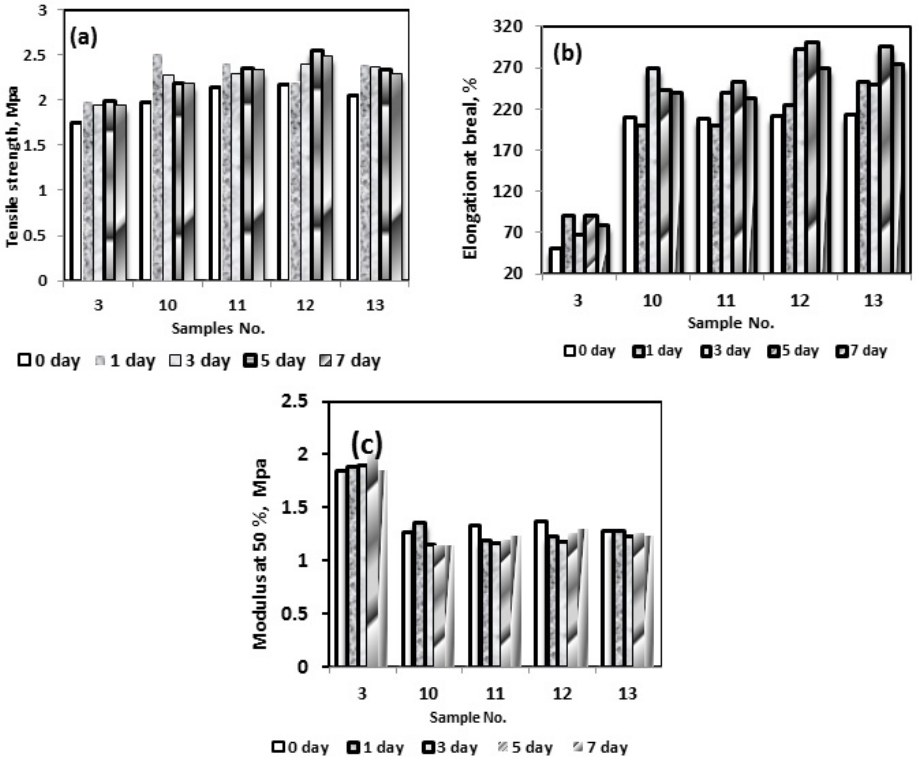


**Figure 11 Figure Physico-mechanical properties of a) tensile strength, b) elongation at break, c) modulus at 50 % elongation versus ageing time for EPDM/ chitin(5 phr) / nanoclay (3,5,7, and 10phr) rubber vulcanizates.**

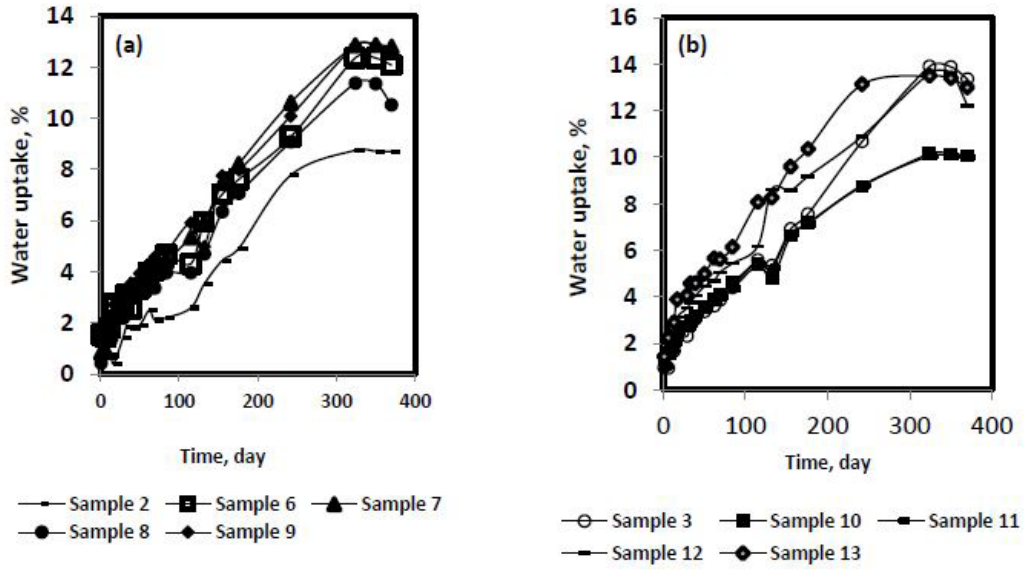


**Figure 12 Effect of nanoclay loading on water uptake of a) EPDM/ chitin(5 phr), b) of EPDM/ chitin (10phr) rubber vulcanizates.**

micrographs of tensile fractured of EPDM/chitin (5,10phr) loaded with 5 and 10 phr nanoclay. It is observed that nanoclay layers may improve surface morphology; it can help to good dispersion and clogging the voids in all surfaces of the investigated biocomposites. There are no pore like structure or bubble type on the surface of vulcanizates.

## Conclusions

1. FT-IR analysis indicated that the type of chitin was found to be as anhydrous β -chitin.

2. Tensile strength of EPDM / chitin vulcanizates was increased as the concentration of chitin 5 phr while modulus at 50% elongation and hardness increased with increasing chitin concentration.

3. Elongation at break was decreased steadily with increasing chitin concentration.

4. The water uptake percent of the investigated vulcanizates was increased at concentration of chitin up to 20 phr.

5. The water uptake steady state was around 324 days for all EPDM/chitin/nanoclay vulcanizates.

6. The properties of the investigated of EPDM biocomposites were enhanced as applying binary hybrid filler system composed of chitin and small amount of nanoclay.

7. The optimum concentration of binary filler for the investigated EPDM was (5,10) chitin and 3 phr nanoclay to improve the properties of EPDM rubber for industrial products.

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