

Enhancing Mechanical and Thermal Properties of NBR/Nano-Silica by Proper Loading of Organoclay

Fatemeh Arabgol¹

¹Department of Chemical and Materials Engineering, Buein Zahra Technical University, Buein Zahra, Qazvin, Iran
Box: 3451866391, Islamic Republic of Iran
f.arabgol@bzte.ac.ir

Abstract – Nowadays, elastomeric heat insulators have been widely used in sealing applications in an aggressive environment, cryogenic or high temperatures. Nitrile rubber (NBR) is of interest in this field due to its good resistance and resilience. Although it has good resistance in the modest temperature (at the range of about -50°C to $+120^{\circ}\text{C}$), its performance is influenced by temperature. Therefore, researchers are attracted to improving both thermal and mechanical properties due to the increasing application of this kind of flexible heat insulator at high temperatures in various industries. The nanocomposite matrixes based on NBR-organoclay (Cloisite 30B) were prepared via the solution method. Nano-silica (20 phr) was added to the matrix by two-roll milling and after achieving a good uniformity, then all the other ingredients were mixed and the nanocomposite samples obtained. The morphology of the samples was characterized by XRD. The mechanical properties such as tensile, hardness, and compressibility of the samples were reported. The thermal properties of the nanocomposite insulators were investigated by thermogravimetric analysis (TGA). A flame test was applied for measuring the mechanical erosion of the nanocomposite insulators at higher temperatures. The results were shown that both improved mechanical and thermal properties of this kind of heat insulator can be obtained by about 12 ± 2 wt% of organoclay loading.

Keywords: nitrile, organoclay, nano-silica, thermal, mechanical, compression set, insulator

1. Introduction

Recently, fumed silica has been widely used to enhance the mechanical and thermal properties of rubber [1]. The influence of adding 15 phr the fumed silica or silica aerogel or both of them in nitrile rubber have been investigated in nitrile rubber and has been investigated [2, 3]. Moreover, an increase in the electrical insulating properties of NBR-silica (15-20 phr) nanocomposite based on NBR has been shown the proper electrical insulation properties at 15 phr [4]. It has been investigated that the prepared coated fabrics with 15 wt% of the spherical nano-SiO₂ have increased their thermal protection performance due to improving their radiant reflectivity [5]. Physico-mechanical and thermal properties of hydrogenated NBR containing nano-silica have been studied with respect to the characterization of the dispersion and interaction parameters of the rubber with nano fillers were characterized with the help of XRD and SEM [6]. Clay as another nano particle van enhanced both mechanical and thermal properties or rubbers [7]. The researches have shown that among different kinds of clays, Cloisite 30B have been provided better the tensile strength and modulus at 100% strain than Cloisite Na⁺ and other investigated organoclays [8]. The physico-mechanical properties and thermo-oxidative aging of nitrile butadiene rubber-nanoclay composites with maleic acid anhydride as compatibilizer was studied [9].

In this research, the effect of inclusion both aerosil and different amounts of organoclay (Cloisite 30B) up to 15 wt% on the mechanical properties of nanocomposites, hardness, and compressibility were investigated. Also, the thermal properties of nanocomposite samples were studied in addition to their mechanical erosion at high temperatures. The proper loading of organoclay was obtained to achieve both thermal and mechanical properties of this nanocomposite.

2. Material and Methods

2.1. Materials

Nitrile rubber containing 34 percent acrylonitrile with a specific gravity of 0.98 and Mooney viscosity (ML₁₊₄, 100 °C) was supplied from Kumho company, Korea. The samples were prepared in two stages: the first stage, mixing the organoclay (O-MMT), (Cloisite 30B, Southern Clay, USA) at different levels (0, 5, 10, and 15 wt%) with NBR via dissolving in methyl ethyl ketone (MEK) by mechanical stirrer (IKA, Japan) at a speed of 500 rpm for 12 hours and then

were dried in a vacuum oven at 65 °C. The second stage is the preparation of the elastomeric nanocomposite samples by two roll milling (Brabender OHG 835800, Germany). First of all, aerosil 200 with a specific surface area of 200 m²/g (Degussa, Germany) at a constant level equal to 15 phr (~8 wt%) were added to the elastomeric compound obtained from the first stage. Also, an aerosil-free counterpart compound, which was considered as a reference sample named "NBR-compound", was prepared at the same compositions of other gradients with no organo-clay. Neat nitrile rubber was named "NBR Neat" which implies as received rubber without any additives. All the other ingredients such as Coumarone resin (Japan) and novolac powder (IP502) (Rezitan Co., Iran) as tackifying agents, di-octyl phthalate (DOP oil) (Iran) as a plasticizer to reduce the mixing energy, flame retardant such as magnesium hydroxide (MDH) (Merck Co., Germany), Firebreak ® ZB (Zibo Wuwei Industrial Co., LTD, China), stearic acid and zinc oxide (Iran) as activators, *N*-isopropyl-*N'*-phenyl-*p*-phenylenediamine (IPPD 4010) (China) as antioxidant were mixed by high shear two roll mill with a small nip gap, respectively, according to standard ASTM D3187. Once a homogeneous rubber compound was obtained and cooled up to room temperature, the vulcanization agents included sulphur (Germany) as curing agent, vulkacit M (2-mercaptobenzothiazole), and vulkacit D (dibenzothiazyl) (Germany) as curing accelerators were mixed with rubber-clay compound by using two roll mills until achieving good mixing. Finally, the compound was vulcanized at 160 °C for 30 min in a heated press machine under a pressure of 30 bar producing a proper sheet with 2 mm thickness for dumbbell cutting. The cylindrical shape samples with the height of 30 mm and diameter of 10 mm were prepared to investigate high-temperature mechanical erosion.

2.2. Methods

The morphology of the nanocomposites was elucidated using a Philips X'Pert Netherlands X-ray diffractometer with CoK_α radiation ($\lambda = 1.79 \text{ \AA}$), 40 kV power, and 30 mA current. The angular step size was 0.02° with a step time equal to 1 s. The interlayer spacing can be calculated according to the Bragg equation due to the ordered stacking of platelets and characteristic diffraction peak can be observed. The diffraction peak position will be the same if the interlayer spacing remains unchanged. Expanding interlayer implies that polymer chains intercalate in the basal spacing of the silicate layers of the clay. So, the peak position will shift to a lower angle.

A Taiwan Gotech testing machines Inc. rheometer was used for determination the curing characteristics of the samples at 160 °C by measuring the cure time (t_{90}) and the scorch time according to ASTM D 2084.

The densities of the samples at room temperature are calculated by dividing the mass by the respective volume. The mass is measured by digital laboratory balance (AND, USA) with an accuracy of $\pm 0.0001\text{g}$, and the volume is measured by Archimedes method using pycnometer according to ASTM D-4018. Mechanical properties (the ultimate tensile strength, elongation at the break, and modulus at 100%, 200%, and 300% strains) were determined by a U.K. Instron tensile tester at room temperature and a crosshead speed of 500 mm/min according to ASTM D412. The hardness of the samples is determined by shore A, Zwick, Germany, using a cylindrical sample with a diameter of 12.6 mm and a height of 6 mm according to ASTM D 2240. An average of 5 points measuring has been reported for each sample. The compression set of the samples was performed according to ASTM D395.

Thermal gravimetry analysis (TGA) was performed by a U.K. PL-STA 1500 system to evaluate the thermal stability and thermal decomposition kinetics of the samples. The specimens were heated from room temperature to 800 °C at a heating rate of 10 °C/min under inert conditions (Ar). Samples were analyzed in triplicate to eliminate errors. One-dimensional heat flux equal to 2500 kW m⁻², with a vertical distance between the flame and the sample surface, 15 mm was passed through the samples for 15 s. The surface of the insulator has been mechanically eroded by outputting the produced pyrolysis gases and also the volume shrinkage. The mechanical eroded surface of the samples was calculated from the difference between initial and eroded heights divided by the time duration of the test. The height of the cylindrical sample before and after the flame test was directly measured by a micrometer (with an accuracy of $\pm 0.001 \text{ mm}$). Surface temperature (heated surface), T_w , was measured by pyrometer and was almost constant during the flame test.

The burnt surface of the samples after the exposure to the flame was analyzed by field emission scanning electron microscope (FESEM) with a field emission gun operating normally at 15 kV acceleration voltages (Hitachi S4160, Japan) and also visual inspection.

3. Results and Discussions

The mechanical and thermal properties of the samples have been presented and discussed below, in addition to the microstructures of the nanocomposite samples.

3.1. Morphology

The morphology of nanocomposites is characterized by X-Ray diffraction analysis in comparison to neat O-MMT (Cloisite 30B). As it was shown in Fig. 1, there is a shift in the 2θ value towards the higher side, which indicates nitrile rubber penetrated between the gallery spacing of silicate layers of the clay in all samples. So, the intercalated structures were achieved in all samples.

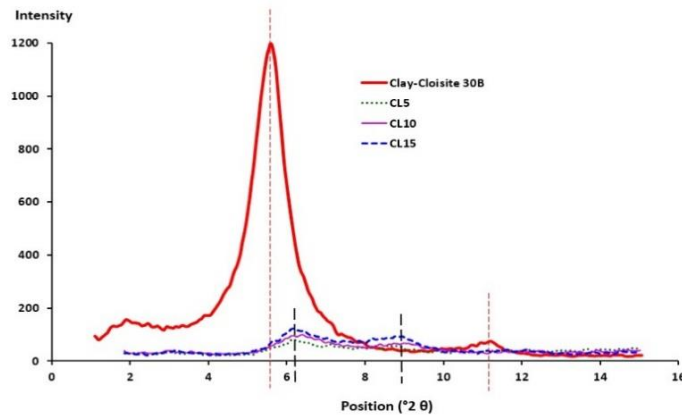


Fig. 1: XRD of Cloisite 30B and nanocomposite samples.

3.2. Mechanical Properties

In Fig. 2, the stress-strain curves of the samples containing 0, 5, 10, and 15 wt% organoclay are plotted (dashed lines) compared to the aerosil-free counterpart sample (solid line) as the reference sample.

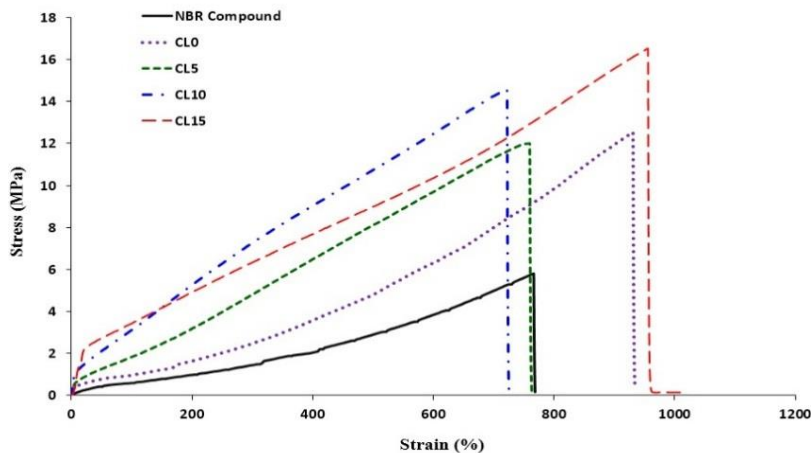


Fig. 2: Stress-strain properties of the samples.

As it is shown in Fig. 2, according to the stress-strain curve, adding aerosil significantly increased the tensile strength of the sample from 5.1 MPa for the aerosil-free sample (the reference one) to 11.0 MPa for the sample containing 20 phr aerosil. The same increasing trend was observed for the elongation at the break of these samples. The tensile strength and elongation at the break were first reduced slightly and then significantly increased by increasing organoclay. Furthermore,

the mechanical behaviour of the samples a little changed toward plastic behaviour due to the more stiffness of organoclay compared to the nitrile rubber. The mechanical data of all the samples have been tabulated in Table 1.

Table 1: Mechanical properties of the samples.

Sample Code	Elongation @ Break	Strength (MPa)	Toughness (kJ)
Reference Sample	757.9±22.4	5.1±0.4	14.7±0.5
CL0	896.1±47.5	11.0±1.6	25.4±0.7
CL5	675.2±66.8	10.9±0.9	20.7±0.6
CL10	685.1±60.9	14.1±10.	37.1±0.8
CL15	889.0±64.3	15.6±0.9	45.9±0.9

As shown in Fig 3, by about 14 wt% organoclay loading an insulator with both high strength and elongation at the break was achieved.

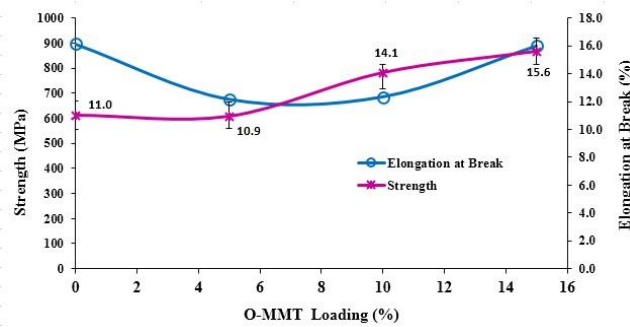


Fig. 3: Variation of the strength and elongation at the break with increasing the organoclay loading.

The modulus at 100% strain of all samples containing different amounts of organoclay (0, 5, 10, and 15 wt%) of the sample was increased (Fig. 4). Because of the more stiffness of silicate layer respected to the flexible nitrile rubber. The modulus at 200% strain of the sample containing 10 wt% of organoclay is slightly more than that of the sample containing 15 wt% organoclay. The increase was more sharply observed for the sample containing around 10 wt% organoclay for the modulus at 300% strain.

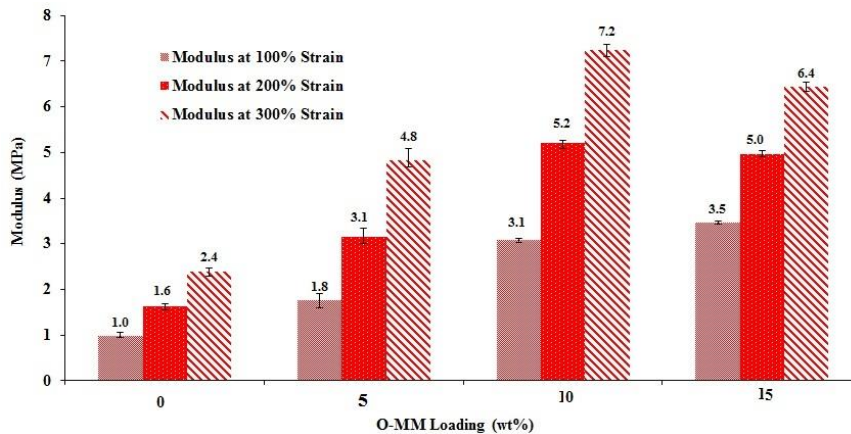


Fig. 4: Modulus at 100%, 200%, and 300% strains of the samples with different loading of organoclay.

The variation of the toughness and modulus at 300% strain by increasing the organoclay loading are plotted in Fig. 5. According to this figure, the proper amount of these two properties was obtained at about 14 wt% of organoclay loading.

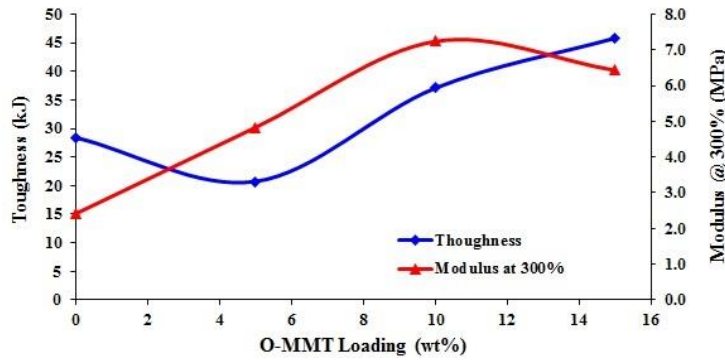


Fig. 5: The variation of the toughness and modulus at 300% strain by increasing the organoclay loading.

As shown in Fig.6, the inclusion of the 8 wt% aerosils enhanced the hardness of the samples from 43 to 50 Shore A at room temperature and 48 to 52 at 100 °C after 70 hours. Moreover, an increasing trend in hardness of nanocomposite samples has been shown by increasing the organoclay from 5 to 10, and 15 wt% compared to the organoclay sample. The hardness of samples was enhanced both at room temperature and after 70 hours at 100 °C, from 50 up to 77 shore A and from 52 up to 79 Shore A, respectively. Restriction in the mobility of rubber chains due to the harder nature of the silica particles and silicate layers of clay rather than the rubber matrix increased the hardness of the samples.

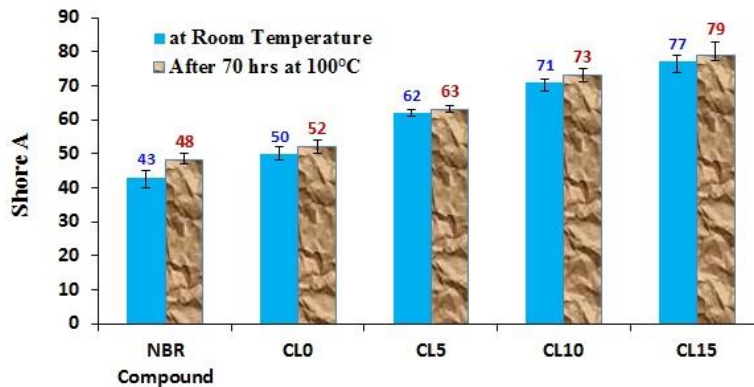


Fig. 6: Hardness of the samples at room temperature and 100 °C after 70 hours.

The compressibility of nanocomposites has been performed by compression set. After removing the applied load, the mobility of the rubber chains was limited as the modulus of the samples increased. It has increased by significantly increasing the organoclay loading due to the plate-shaped nature of silicate in organoclay. The presence of the nano-silica has also slightly increased compressibility from 42 up to 44.8% (Fig.7) due to the restriction of the mobility of the rubber chains. Also, the mobility of the polymer chains decreases while the concentration of organoclay increases. Therefore, the compression set was increased up to 87%.

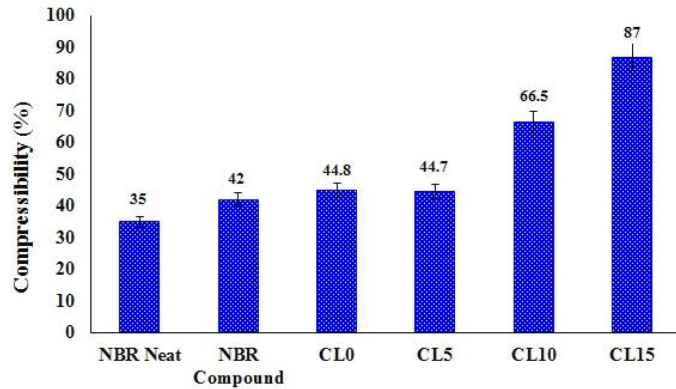


Fig. 7: Compressibility of the samples.

3.3. Thermal Properties

Fig. 8 shows the thermogravimetric analysis of all nanocomposite samples (dashed lines) compared to the neat nitrile rubber (solid line). As it was shown in this figure, degradation of nitrile rubber occurred from 420 °C to 485 °C and in one stage with a char residue amount of 4.3% at 700 °C. Ingredients such as stearic acid, DOP, and so on, which were added to the nitrile rubber were degraded at a lower temperature. So, degradation of NBR compound started from 412-480 °C in two stages with a higher amount of char residue than the nitrile rubber at about 9.5% at 700 °C. Degradation of all the other samples was occurred between 410±5 °C to 480±5 °C with more residue char than NBR compound at about 34±3% at 700 °C.

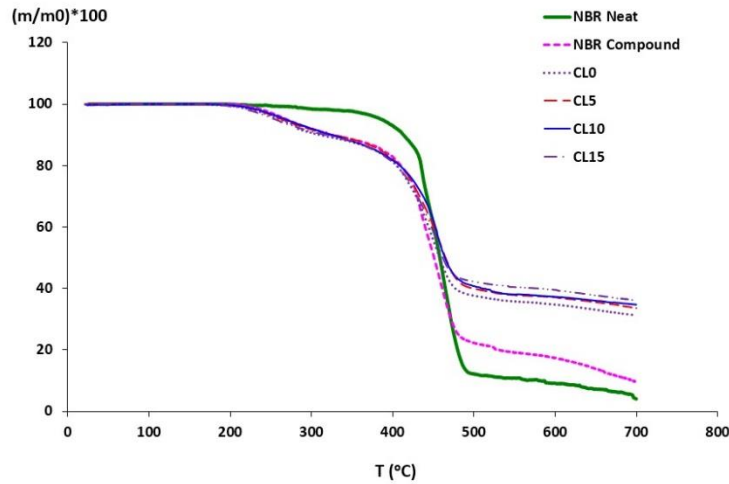


Fig. 8: Thermogravimetric analysis of the samples.

The degradation behaviour of the samples under higher temperatures was investigated using the flame test. It was concluded that at high temperature the residue char acted as a thermal barrier and protected underlayer virgin materials against high temperature.

Finally, selecting the proper amount of organoclay loading must be considered for achieving a light insulator with satisfactory performance. Fig. 9 illustrates the variation of mechanical erosion and insulator density by increasing the organoclay loading. As this figure shows using 13±1 wt% organoclay can provide the proper performance.

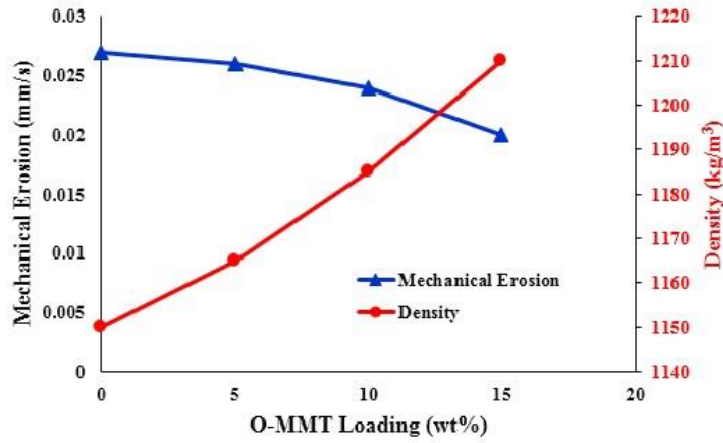


Fig. 9: Variation of the mechanical erosion and the density of the samples by increasing the organoclay loading.

3.3. Microstructure

Fig. 10 shows the scanning electron microscope micrographs of the samples before (as virgin) and after exposure to the flame, i.e. the char surface in high temperature. The microstructure NBR compound as nano silica-free without any organoclay is shown in the above left of Fig.10, the middle above picture is related to the sample having 15 phr nano silica without any organoclay CL0 and the above right picture is related to CL15, in which silicate plate can clearly be seen.

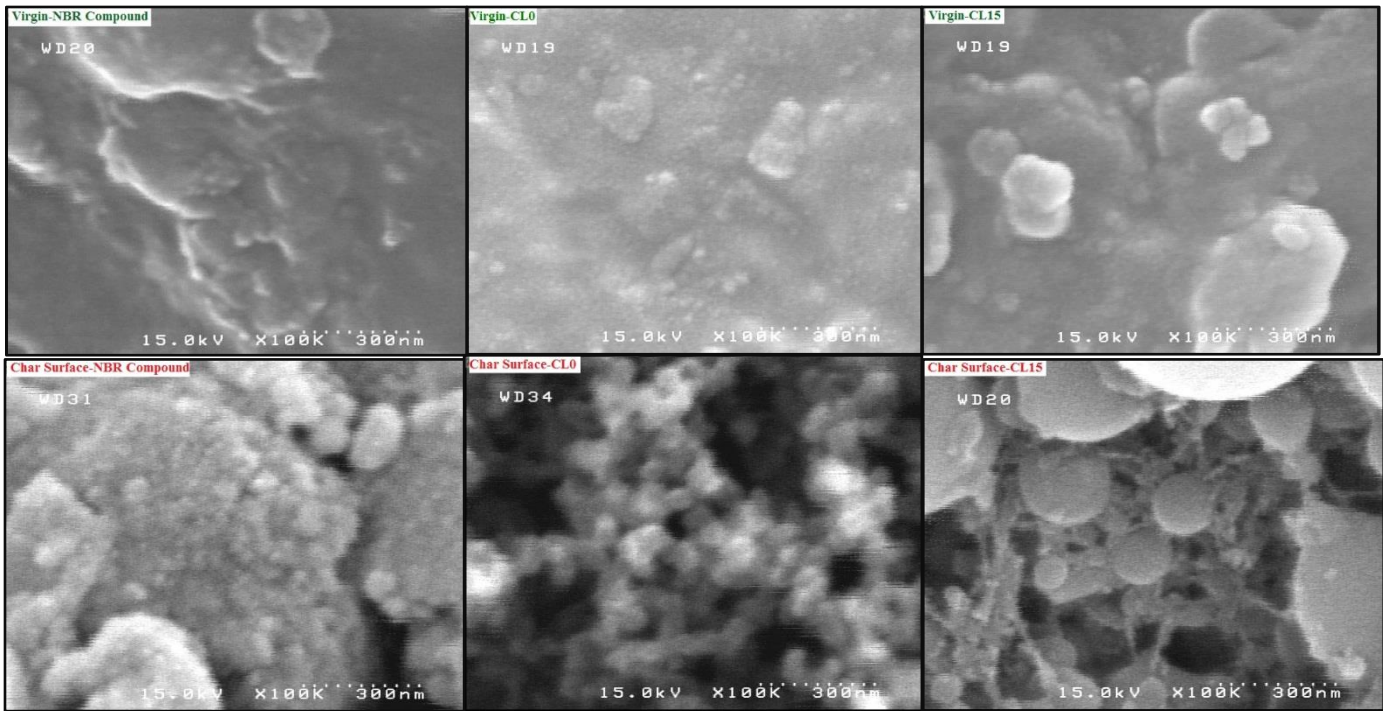


Fig. 10: SEM Variation of the NBR compound, CL0, and CL15 samples before and after flame test.

4. Conclusion

In this research, nanocomposite samples containing both nano-silica and organoclay based on nitrile rubber were prepared by melt method and characterized by XRD and SEM. The effect of inclusion of both aerosil and different amounts of organoclay (Cloisite 30B) up to 15 wt% on the mechanical properties of nanocomposites, hardness, and compressibility, also the thermal properties of nanocomposite samples were studied. The results show that 12 ± 2 wt% of organoclay can provide a light insulator with proper mechanical and thermal performance nanocomposites.

Acknowledgements

The authors would like to thank Iran Nanotechnology Initiative Council (INIC) for the financial support of this work.

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