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Studies on Fluorocarbon Elastomer Nanocomposites for Sealing Applications

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Abstract*: The usage of seals in several applications like aircraft engines is mostly made of Fluorocarbon (FKM) elastomer. They are coloured products that enable easier identification based on the applications. In such seals, fillers like carbon black cannot be added to reinforce and improvise the mechanical properties since carbon black does not make it possible to add colours. The properties after ageing are also very critical in sealing application, and they must also be improved. Also, Nanocomposites are the modern and growing trends in the field of polymers that show enormous changes in the properties of the polymers without affecting their basic properties. So, the need for improvisation of FKM seals and the concept of Nanocomposites can be merged to form FKM Nanocomposites with Nano clay and Nano silica as the fillers. The objective of this project is to improve the mechanical properties, better retention of properties after ageing and after fluid interaction of the FKM seals with the aid of Nanofillers. Different proportions of FKM nanocomposites were prepared using modified Nano Kaolin Clay & modified Montmorillonite clay (Cloisite grades). Various mechanical properties like tensile strength, tensile modulus, elongation at break, compression set and tear strength etc., were studied. The test results have shown good improvements while increasing the filler loading. This is helpful to manufacture seals of desired colours thereby avoiding the difficulties faced in the carbon black-filled FKM compounds.*

Keywords: *FKM, Nanocomposites, nanofillers, swelling study, sealing applications*

1. Introduction

Fluorocarbon elastomers (FKM) have become crucial in the seal industry. Due to its wide range of chemical compatibility, temperature range, low compression set, and excellent ageing characteristics, fluorocarbon rubber is the most significant single elastomer developed in recent history. Fluorocarbon elastomers are highly fluorinated carbon-based polymers used in several applications to resist harsh chemical and ozone attacks [1-4]. The working temperature range is considered to be -26°C to +205°C /230°C (-15°F to+400°F/440°F). The modified Fluorocarbon O-rings can be used in aircraft, automobiles and other mechanical devices requiring maximum resistance to elevated temperatures and many fluids. FKM resists mineral oils, greases, aliphatic, aromatic and also special chlorinated hydrocarbons, petrol, diesel fuels, andsilicone oils. It is suitable for high vacuum applications. The filler such as thermal black (N990) is commonly used in fluoroelastomers. For many O-ring applications, fluoroelastomer seals must be specified to have different coloursto avoid mistakes in installing seals in the automotive industry. So, mineral fillers that aid in the colouringof the products i.e., white fillers can be used asalternatives. Nanocomposites are gaining importance in the polymer field as they are the new class of composites with improved mechanical properties, thermal resistance, fire retardancy and solution & gas barrier properties [5-8]. Nanofillers are the ones that make the polymer into a nanocomposite, onto their successful incorporation. Such nanofillers employ better properties than such carbon black fillers. So, a novel technique to fulfil the need for coloured FKM seals through the availability of the nanocomposite systems has led to a new technology of FKM nanocomposites for sealing applications.This project aims at the development of FKM nanocomposites with different nanofillers and testing their compatibility in the production of seals, O-rings and many other sealing devices.

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2. Materialsand methods

2.1 Materials

Tecnoflon FOR5312K is manufactured by Solvay Solexis with a specific gravity of 1.81, Fluorine content 67%, Mooney Viscosity (ML 1+10 @ 120^{o}C)44, and curatives premixed FKM elastomer. Nanomer Kaolin clay is produced by English Clays with a particle size of <100nm. Cloistie 20a &Cloisite 30b (Modified Montmorillonite fillers) is manufactured by Southern Clay products. Similarly, the compounding ingredients Magnesium Oxide (Mg O) is obtained from Star MAGU, Calcium Hydroxide – Rhenofit CF (GE 1890) from Rhenofit, and Struktol WS 280 from Struktol as processing aid.

2.2 Preparation of Nanocomposites

The compounding of FKM with Nanofillers including other ingredients such as calcium hydroxide (Ca $(OH)_2$), magnesium oxide (MgO) was done on a laboratory-sized two-roll mill. Table 1 depicts the compositions of Nanofillers filled with FKM rubber nanocomposites. This compounded rubber was then subjected to rheometric study using a Rheometer to obtain the optimum cure time of the composites. The rubber samples were then cured until their optimum curing time (t90) by a hydraulic press at 170^o C, and then cooled to room temperature and subjected to the post-cure at 230^{o}C for 24h.

Table 1. Formulation for the nanocomposites

S.No	Ingredients	Gum 1	Gum 2 (A)	Nano Montmorillonite Clay		Nano Kaolin Clay		
				NC 5	NC 10	NK 10	NK 15	NK 20
1	FKM	100	100	100	100	100	100	100
2	Mg O	3	6	6	6	6	6	6
3	Ca $(OH)_2$	6	6	6	6	6	6	6
4	Processing aid (Struktol WS 280)	0.5	0.5	0.5	0.5	0.5	0.5	0.5
5	Nano Kaolin clay	-	-	-	-	10	15	20
6	MMT Clay	-	-	5	10	-	-	-

2.3 Experimental part

The cured samples of the composites were subjected to several testing to assess their performance based on their application. The tensile properties were measured with the dumbbell specimens using a Shimadzu Universal Testing Machine (ASTM D412) at a speed of 500 mm/min. Similarly, tear strength was measured according to ASTM D624. The hardness of the samples was measured using a Durometer (Shore – A-type) and the compression set was measured according to ASTM D395 (method B).

3. Results and discussions

The curing or cross-linking of elastomer chains of the FKM is usually done at elevated temperatures. Here, it is done at 170^{o}C and the cure behaviour of the composites of different formulations is studied using an Oscillating Disc Rheometer. From the table, it is evident that on the increment of the Mg O content, there is a dip in the cure rate. And at the same time, the torque levels increase as the compound becomes tough and the curing becomes slower. A similar trend is seen during the increase in the loading of filler content too. The scorch time (ts2) increases when the filler loading is increased (Figure 1), which implies that the filler loading is decelerating the curing of the elastomer. As the filler loading increases, the cure rate decreases and the cure time required becomes longer. It is evident from the data that the tc90 gradually increases as the filler level increases. While comparing the fillers, Montmorillonite clay witnessed a drastic fall in the cure rate even at the lower loading, whereas the Kaolin clay obeys better on loading into the elastomer [9]. The differential torque, i.e., the difference between the minimum and maximum torque developed during cure (Figure 2), is marginally increased with the filler loading. The differential torque is a measure of the extent of the cross-link formation and the filler–matrix interaction. The higher values for the nanocomposites indicate that the matrix is more restrained. For the FKM composites, in addition to thecuring at higher temperatures, it is mandatory to post-cure the composites at the service temperatures for 8-24 h so that, there is an improvement in the mechanical properties. Figure 3 shows the variation in the cure rate as the filler level increases.

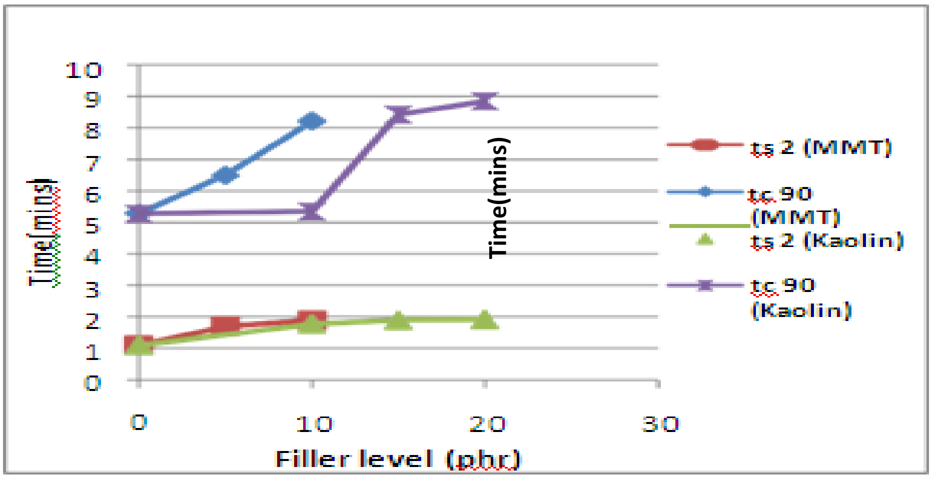

Figure 1. Filler loading (phr)in FKM vs Scorch time (ts2) & Cure time (tc90) (min)

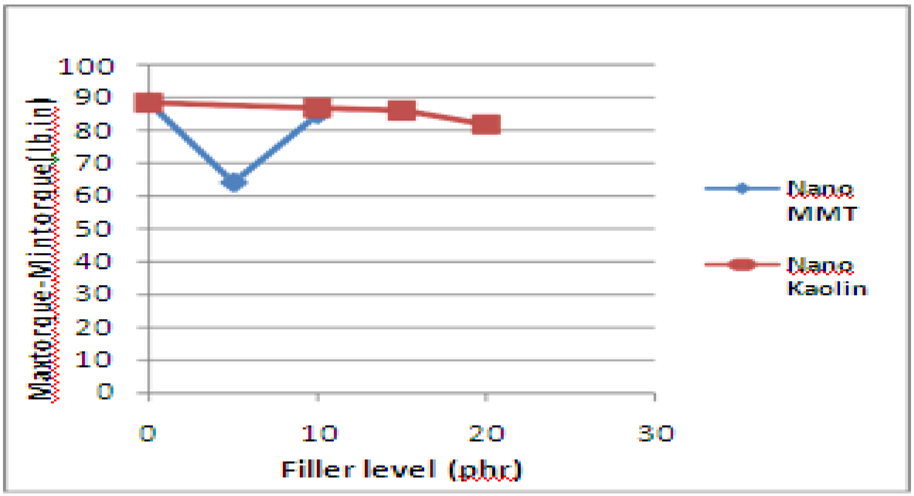

Figure 2. Filler loading (phr) in FKM vs (Max. Torque – Min. Torque)

33.1 Mechanical Properties

As for as this study is concerned, the mechanical properties of the sealing applicationsare the most important considerations for the nanocomposites in the manufacturing of seals. Especially compression set and hardness are the defining properties for seals. Hardness improves as the filler content increases as seen in Figure 4. Montmorillonite sees a better increment at lower filler loading itself, whereas the Kaolin clay improves 1 point per phr loading of the filler. Seals desire a hardness of 70-75 Shore – A. So the filler loading was stopped when the desired properties were attained in the composites.

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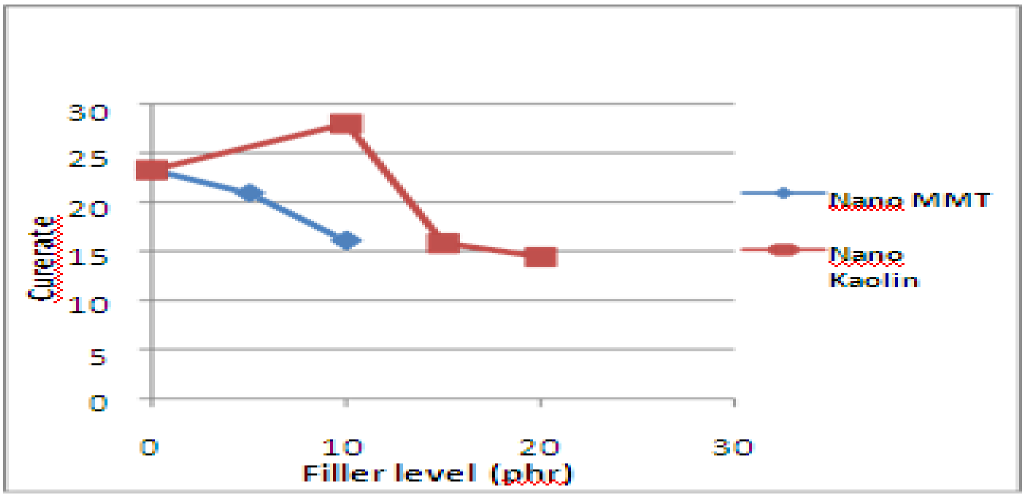

Figure 3. Filler loading (phr) in FKM vs Cure rate

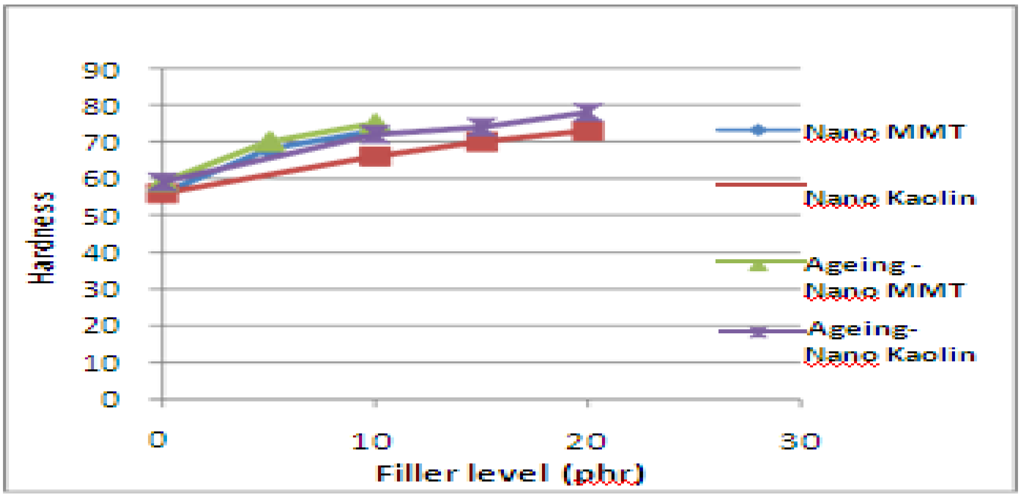

Figure 4. Filler level (phr) in FKM vs Hardness

The tensile strength is also a linear property to the filler loading. Figure 5 shows the gradual increase of the tensile strength, as the filler level increases in the composite. The tensile strength almost doubles on 20 phr loading of the kaolin clay when compared with the gum compound of FKM. This is due to the influence of nanofillers which disperse completely into the matrix. Their higher specific surface area helps them achieve this property which challenges the conventional black fillers. The black fillers provide the same results only at 30-40 phr loading, but the nanofillers achieve it at half of the content. But for nanocomposites, there is a threat to the decline in the mechanical properties at a certain amount of filler loading which denotes the irregular dispersions into the elastomer matrix causing agglomerations. Fortunately, there are no such problems with the nanocomposites here, as there is a rise in the properties with the raise in the filler loading. The elongation at break is an intimate property of filler loading. There is an increment in the strain level with the increase in filler loading which is evident from Figure 6. It is observed to be high for the nanofillers than the normal black fillers. And also, the modulus at 100% & 200% elongation is remarkable as seen in Figure 7 when the filler loading is increased. The nanoclay has a result nearer to that of the FKM compounds with Black fillers.The tear strength, an integral property of the seals is an important consideration for these FKM composites. In Figure 8, the FKM composites see a vital raise in the tear strength as the filler level is increased. But once the filler loading is up to 20 phr, there is a decline in the tear strength which is abnormal. Figure 9 show the Filler level (phr) in FKM vs Compression Set % for different fillers. The reason may be the clogging of the fillers in the elastomer matrix [10].

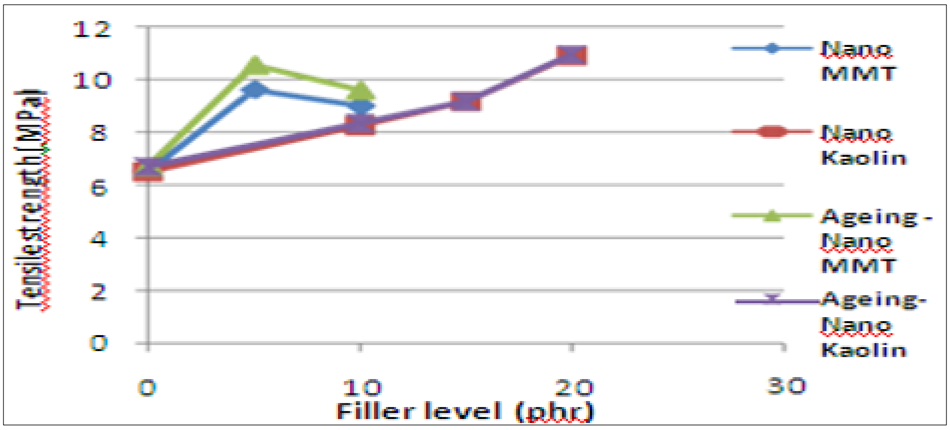

Figure 5. Filler level (phr) in FKM vs Tensile strength

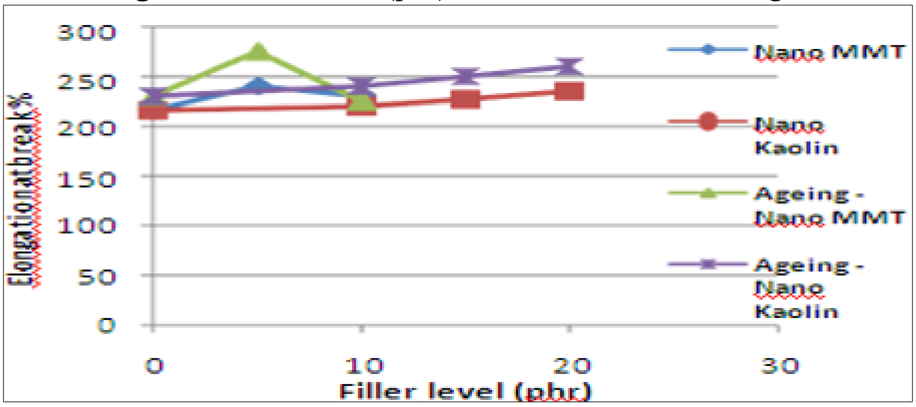

Figure 6. Filler level (phr) in FKM vs Elagonation at break %

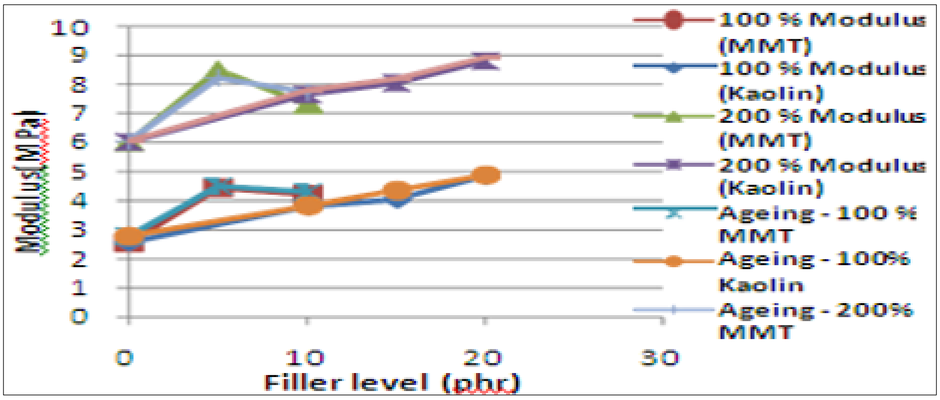

Figure 7. Filler level (phr) in FKM vs Modulus (MPa)

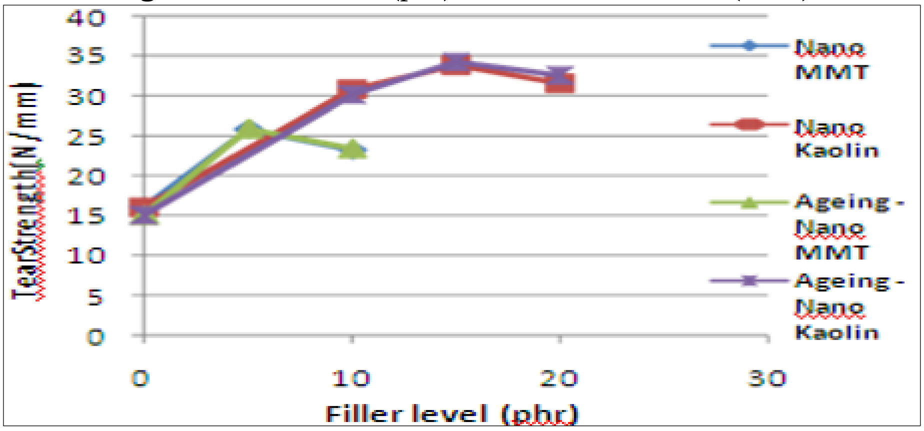

Figure 8. Filler level (phr) in FKM vs Tear strength (N/mm)

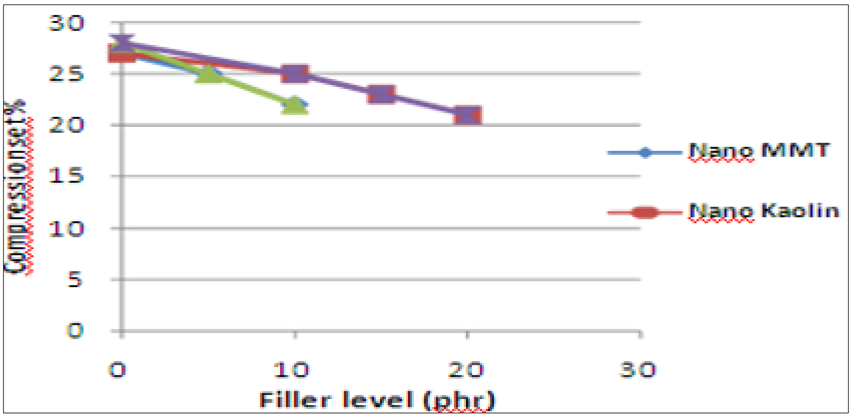

Figure 9. Filler level (phr) in FKM vs Compression Set %

3.2 Analysis and future trends

The detailed analysis of the testing done on the FKM composites are as follows:

Nanofillers are proven to be an alternative to conventional black fillers. These nanofillers on perfect incorporation into the FKM elastomer matrix display the improvement in the mechanical properties which are equivalent to that of the carbon black filled compounds of FKM. A small number of nanofillers say (10 phr) is enough to attain the properties that were achieved by 40 phr of carbon black. Similarly, the swell study proves the ability of the composite and the product made of it to withstand the swelling due to the action of oils and fuels. The nanofillers block the impregnation of the composite to the fluidsupto a certain level and thus make it fit to retard the volume swell. A composite that has a lower swell due to the action of fluid only passes its way to become a seal in future. These nanocomposites are compliant to reduce the volume swell. Almost all the nanocomposites prepared showed a volume swell of less than 4 % as seen in Figure 10, which is found to be an excellent trend. The retention of mechanical properties was excellent and lesser than the acceptable range in terms of 4% as seen in the respective figures. The retention is found to be good for MMT 5 phr and Kaolin 20 phr compounds. So, they were characterized using SEM, whose images are shown in Figure 11 and 12. Life prediction is an important criterion for the seals. The life prediction can be done with the help of a stress relaxometry which predicts life by the evaluation between the Stress and Strain where one of the parameters is kept constant and the other is varied [11-15]. From this study, a clear assessment of the life of the product can be done.

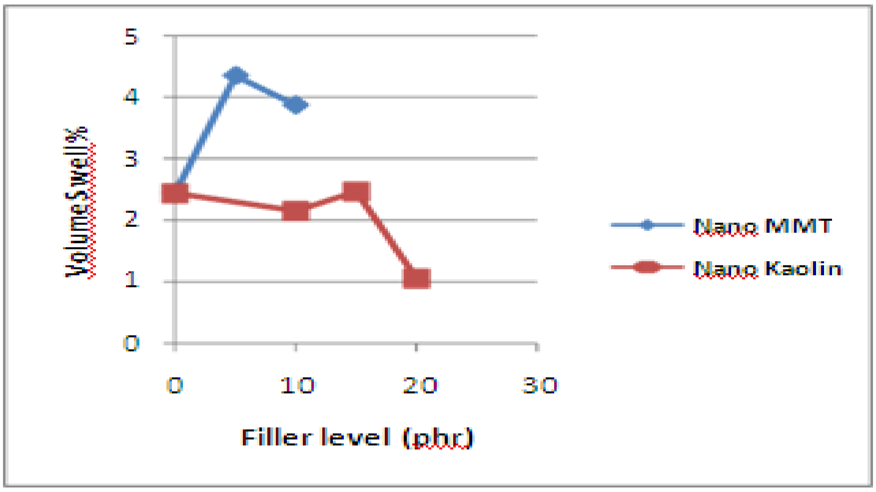

Figure 10. Filler level (phr) in FKM vs Volume Swell %

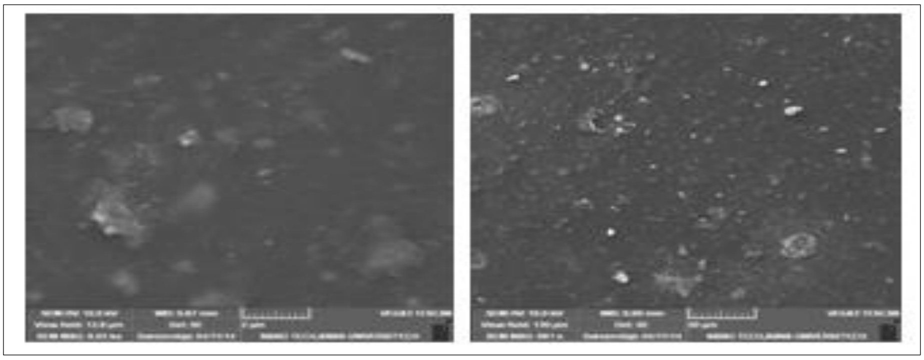

Figure 11. SEM images of compound B (FKM + MMT clay 5 phr)

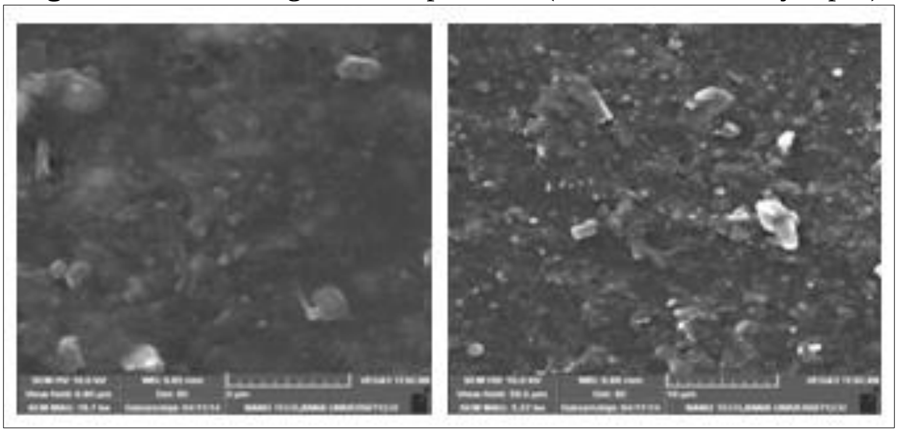

Figure 12. SEM images of compound F (FKM + Kaolin clay 20 phr)

4. Conclusions

FKM nanocomposites were prepared using modified Nano Kaolin Clay and modified Montmorillonite clay (Cloisite grades) with the two-roll mill. The composites were subjected to a cure study to determine the cure time and temperature. Then the specimens for the testing for properties were cut from the cured compounds. The test for mechanical properties like Tensile strength, Tear strength, Hardness, Modulus, Elongation at break, Compression set were done. The test results were proved to be successful with the attainment of improvement in properties on the increase of filler loading. The nanofillers matched the properties of the compounds mixed with carbon black. This leads to the usage of these FKM nanocomposites for the manufacture of seals, O-rings etc., which constitute the sealing systems and are helpful in manufacturing seals of desired colours thereby avoiding the difficulties faced in the carbon black-filled FKM compounds. The higher specific area and the smaller particle sizes of the fillers enable successful incorporation into the rubber. The swell studies can indicate the retention properties due to the effect of fluids. Life prediction by stress relaxation is a future trend to denote the test for seals with these FKMnanocomposites.Thus, nanocomposites become an alternate trend in the field of polymers particularly in the manufacturing of seals with varied mechanical properties.

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