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Effect of Compatibilizer on the Dynamic Mechanical and Electrical Properties of Kaolin Clay Reinforced EPDM Rubber

(Kesan Pengserasi Terhadap Sifat Mekanik dan Elektrik Dinamik Kaolin Bertetulang Getah EPDM)

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ABSTRACT

Industrial pollution issue and dark colour of carbon black, clay based non black filler are getting more importance for reinforcing elastomer. EPDM-Kaolin composites with various maleated EPDM concentration have been prepared by mixing on a two roll mill. The rheometry data showed the optimum cure time increases with increasing compatibilizer concentration without decreasing torque value indicating that acidic functional groups comes from compatibilizer could retard cure rate and increase the optimum cure time rather than change in the ultimate cure state. As the filler concentration increases, the edge to edge and face to edge interaction between filler and EPDM increases and the free volume between EPDM molecules is reduced, the storage modulus increases. Moreover, the dynamic mechanical analysis also showed the increase in glass transition temperature with increase in filler concentration due to the inter-tubular diffusion of EPDM inside the clay. It was also observed that with increasing filler concentration, the resistivity and dielectric strength decreases and moreover with increasing compatibilizer concentration the resistivity decreases due to better dispersion of filler helps to build conduction path. The morphological study also revealed that homogeneity of filler dispersion increases with increase in compatibilizer concentration.

Keywords: Dielectric constant; dielectric strength; EPDM; kaolin; resistivity

ABSTRAK

Isu pencemaran perindustrian dan warna gelap karbon hitam, tanah liat berasaskan pengisi bukan hitam semakin lebih penting untuk mengukuhkan elastomer. EPDM-Kaolin komposit dengan pelbagai kepekatan EPDM telah disediakan dengan mencampurkan dalam pengisar dua rol. Data menunjukkan peningkatan masa awet optimum dengan kepekatan pengserasi tanpa mengurangkan nilai tork yang menunjukkan bahawa asid kumpulan berfungsi daripada pengserasi boleh membantut kadar awetan dan meningkatkan masa penyembuhan optimum merubah keadaan penyembuhan. Apabila kepekatan pengisi meningkatkan interaksi tepi ke tepi dan antara muka pengisi dan EPDM bertambah dan isi padu bebas antara molekul EPDM dikurangkan dan penyimpanan modulus bertambah. Selain itu analisis mekanik dinamik juga menunjukkan peningkatan dalam suhu peralihan kaca dengan peningkatan kepekatan pengisi disebabkan resapan antara tiub EPDM di dalam tanah liat. Dengan peningkatan kepekatan pengisi, kerintangan dan kekuatan dielektrik berkurangan dengan kepekatan pengserasi yang meningkat, kerintangan berkurangan disebabkan penyebaran pengisi yang lebih baik membantu untuk membina rangkaian pengaliran. Kajian morfologi juga mendedahkan bahawa kehomogenan penyebaran pengisi meningkat dengan peningkatan dalam kepekatan pengserasi.

Kata kunci: EPDM; kaolin; kekuatan dielektrik; kerintangan; pemalar dielektrik

INTRODUCTION

Ethylene-propylene-diene rubber (EPDM) is one of the most important synthetic rubbers on market for both general purpose and special applications. Because of its saturated backbone it possesses excellent resistance to heat and oxidation. Ghosh and Chakraborty (2000) and Zonghuanet et al. (2009) showed in their work that the non-polar structure makes EPDM with excellent electrical resistivity and resistance to polar solvents. The main reason for reinforcing rubbers is to improve the mechanical and thermal properties as well as reducing the cost and sometimes weight of the compounds. Carbon black is a typical reinforcing material in rubbers. However, due to pollution issues and dark colour of the carbon black, several researchers have focused on the development of other reinforcements in rubber composites during the last few years. Arroyo et al. (2003), Ismail and Chia (1998) and Ray and Okamoto (2003) worked on EPDM based rubber compound using the non black filler. It has been shown that the silicate layers of the clay can be dispersed at the molecular level in a polymer matrix with the polymer existing between the silicate layers.

In recent years these type of composite have attracted great interest of many researchers since they frequently exhibit unexpected hybrid properties synergistically derived from the two compounds (Usuki et al. 2002).

Incorporation of filler to EPDM changes its electrical character due to change in conductivity of the system. Moreover, due to saturated backbone and lack of polarity of EPDM, compatibility of inorganic filler and rubber is poor. Manjhi and Sarkhel (2010) have discussed the incorporation of maleic anhydride grafted ethylene propylene diene monomer (MAH-g-EPDM) as compatibiliser to EPDM-kaolin [$Al_2Si_2O_5(OH)_4$] composite system which enhances the filler-matrix bonding and hence the distribution of filler. Thus, the present study deals with the effects of the compatibiliser concentration on dynamic mechanical and electrical properties of kaolin reinforced EPDM rubber.

TABLE 1. Compound formulation

Ingredient	Phr
EPDM	100/90/80/70
+	+
m-EPDM	0/10/20/30
Renacit	0.25
Stearic Acid	2
Kaolin	0/5/10/20
TMTD	1.5
ZnO	3
Sulphur	2.5

MATERIALS AND METHODS

MATERIALS

The EPDM rubber (Nordel 4570) and maleated EPDM purchased from DuPont (Dow Elastomers, USA) had an ethylene content of 50%, diene content of 4.9%. The elastomer had a Mooney viscisity of 70 × 10^{-1} Pa s (ML_{1+4} at 125°C), a weight average molecular weight of 210000 g/moL and less than 1% crystallinity (differential scanning calorimetry at 10°C/min), zinc oxide (Titan Biotech Ltd.) and sulfur (E. Merck, Darmstadt, Germany) were of laboratory reagent grade, accelerator tetra methyl thiuram disulphenamide (TMTD), Renacit, stearic acid were obtained from CDH (India) Ltd. The kaolin clay of laboratory grade was supplied by Titan Biotech Ltd, India.

COMPOUNDING

The compounding was done according to the formulation given in Table 1. Sixteen batches were made by using EPDM rubber as base polymer with kaolin clay and variable compatibilizer (mEPDM) concentration. The mixing was carried out in a laboratory two-roll mill (15.24 cm by 38.1 cm) at a friction ratio of 1:1.4, a front and back roll speed of 24 and 33 rpm, respectively, at room temperature. Care was taken for complete dispersion of filler and at the same time was allocated for all the mix to ensure the same level of polymer–filler interaction. The compounds were identified according to the amount of filler content and compatibilizer concentration (Table 2). All the compounds were cured at their respective equivalents of their rheometric optimum cure times at 170°C in an electrically heated hydraulic press. The average thickness of the moulded sheet were 2.0±0.1 mm.

CHARACTERIZATION

The rheometer data have been obtained in a oscillating disc rheometer. The test piece of rubber compound was contained in a sealed test cavity under positive pressure and at a temperature of 170°C. A rotor (biconical disc) was embedded in the test piece and is oscillated through small specified rotary amplitude, ±3° arc. This action exerts shear strain on the test and the torque (force) required to

TABLE 2. Sample code

Sl. No	Sample code	EPDM (phr)	m-EPDM (phr)	Kaolin clay (phr)
1	mEP0-K0	100	0	0
2	mEP0-K5	100	0	5
3	mEP0-K10	100	0	10
4	mEP0-K20	100	0	20
5	mEP10-K0	90	10	0
6	mEP10-K5	90	10	5
7	mEP10-K10	90	10	10
8	mEP10-K20	90	10	20
9	mEP20-K0	80	20	0
10	mEP20-K5	80	20	5
11	mEP20-K10	80	20	10
12	mEP20-K20	80	20	20
13	mEP30-K0	70	30	0
14	mEP30-K5	70	30	5
15	mEP30-K10	70	30	10
16	mEP30-K20	70	30	20

oscillate the disc depends upon stiffness (shear modulus) of the rubber compound. The stiffness of the specimen increases when crosslinks are formed during cure. As the curing starts, the torque increases proportionately. Depending upon the type of compound, the slope of the rising torque varies.

The dielectric strength was determined by the ASTM D149-97a. The voltage on a circular sample of diameter 100 mm was increased from zero until dielectric failure of the test specimen occurred. The power rating of this test was 1 kV/s. The formula followed were $E=V/d$, where V is the voltage, d is the thickness of sample, E stands for electric field intensity and increases with the increase of voltage. When the sample was percolated at some critical voltage, the electric field intensity calculated by such voltage referred to dielectric strength. The capacitance was measured by using the impedance analyser, Alpha ATB, Novocontrol Tech, Germany, ASTM D150-98. The resistivity of EPDM filler with kaolin was measured by conventional four probe technique in which the electrodes were separated by 1 mm. The four probes were slightly pressed on the EPDM samples to ensure good contact. The electrical property measurements were all performed at room temperature.

The dynamic mechanical properties were measured in a DMAQ800, TA instrument USA, according to multifrequency stress method in a dual cantilever system at frequency 10Hz from -70°C to 150°C at a heating rate of 5°C/min. The storage modulus (E') and loss tangent (tanδ) were measured for each sample. To study the morphology of cured sample, tensile fracture sample was taken and coated with platinum and analyzed with a scanning electron microscope (JSM 5000, JEOL, Tokyo, Japan).

RESULTS AND DISCUSSION

The rheographs and cure characteristics of EPDM with kaolin clay with 20% compatibiliser are shown in Figure 1. From the data it was observed that the initially torque decreases due to the softening of the rubber caused by heating. Then, the torque increases as the vulcanization proceed which leads to the formation of crosslinking bond. It is clearly observed that the ultimate cure state of the vulcanisate indicated by maximum torque (M_H) increases with increasing filler concentration for all the concentration of compatibilizer (m-EPDM). The increase in filler concentration reduces the mobility of the elastomer chain hence increased the torque. The addition of compatibiliser increased the maximum torque value which indicated that the addition of mEPDM helps better filler matrix interaction through hydrogen bonding. Modification of composite in presence of compatibiliser, m-EPDM, introduced acidic carboxyl groups which would helps sulfur decomposes into ions instead of radical. But only radical can initiate and participate in vulcanization, so the presence of carboxyl group could reduce the radical number and finally retard the cure rate and increase the optimum cure time. But with the increasing compatibiliser concentration, it will not reduce the torque value indicating that acidic functional groups comes from the compatibiliser could retard the cure rate and increase the optimum cure time rather than change in the ultimate cure state.

Electrons usually transport more easily on the inorganic filler surfaces than in the polymer. Hence, the addition of kaolin not only reinforces the composites mechanically, but also improves the electrical conductivity of filled rubber. It is noted in Figure 2 that the surface

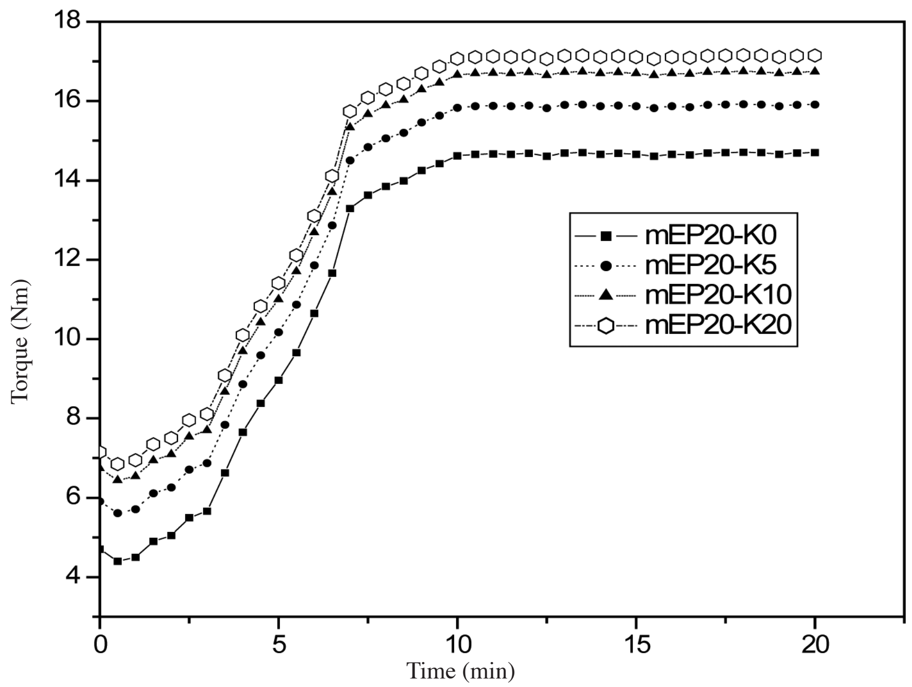

FIGURE 1. Cure curve of EPDM with 20% compatibiliser

resistivity of EPDM filled with kaolin is considerably lower than those of unfilled EPDM. The low resistivity indicated that EPDM with kaolin is suitable to be used in conductive applications. The application of conductive EPDM rubbers includes the electromagnetic shielding, electronic key-press, graphic arts and sensors. Electrical conductivity of filled EPDM has been extensively researched for some time. Three generally accepted mechanisms that account for the electrical conduction through composites filled with carbon black includes the conduction path theory, electron tunneling theory and electric field radiation theory. A significant factor influencing the electrical conduction mechanisms is the percolation limit. The percolation limit is the value of loading at which conduction paths begin to form. The percolation limit of kaolin varies with the surface area. Kaolin filler having a large surface area has a low percolation limit. From the figure it was also observed that with the increasing filler concentration, the resistivity decreases and moreover with increasing compatibiliser, the resistivity also decreases due to better dispersion of filler helps to build conduction path.

The effect of the kaolin and compatibiliser on dielectric strength was examined. The results are displayed in Figure 3. The dielectric strength is influenced mainly by the surface area of the filler. As the filler concentration increases, surface area also increases and results in low resistivity. This is due to the large surface area which leads to a short aggregate distance. The kaolin filler probably form easily into a conducting network in EPDM/kaolin composite. Consequently, the voltage required to puncture the EPDM sample is the lowest. In addition, it has been reported that dielectric strength is partially associated with the degree of crosslinking. It was observed that the dielectric strength in the non-crosslinked samples is higher than in the crosslinked samples. As the compatibiliser concentration increases the crosslinking density of the sample increases which leads to decrease in dielectric strength.

The dielectric constants of EPDM/kaolin composites were determined at room temperature over the 0 Hz to 10^6 Hz frequency range. The variation of dielectric constant with frequency is illustrated in Figure 4. The dielectric constant decreases slightly with increasing frequency. Apparently, the addition of filler induces a considerable decrease in the dielectric constant. The dielectric constant is associated with the mobility of polymer chains. The lower dielectric constant of EPDM/kaolin composites indicates a high degree of crosslinking and higher reinforcement due to both entanglement and chemical bonding.

Dynamic mechanical analysis was carried out to evaluate the extent of filler–matrix interaction of the EPDM/Kaolin composite. Figures 5 and 6 show the effect of kaolin filler on storage modulus and tanδ on EPDM composites as a function of temperature. Figure 5 shows that the addition of kaolin increases the storage modulus. The storage modulus is the highest in case of composite containing 20% of kaolin filler. These results indicated that with increase in filler concentration, a strong interfacial action between rubber and filler was established which lead to the increment in the storage modulus. The mentioned results can be related to the formations of bonds between polymer chains through cross-linking process due to the restricted movement of polymer chains. Figure 6 shows that the addition of filler results in reduction of tanδ. The decrease in tanδ is the most obvious in case of composite due to restricted motion of the polymer chain as it arised due to the strong interfacial bonding between rubber matrix and the filler. The results also revealed that the T_g of the composite compared with the neat polymer is mostly unchanged.

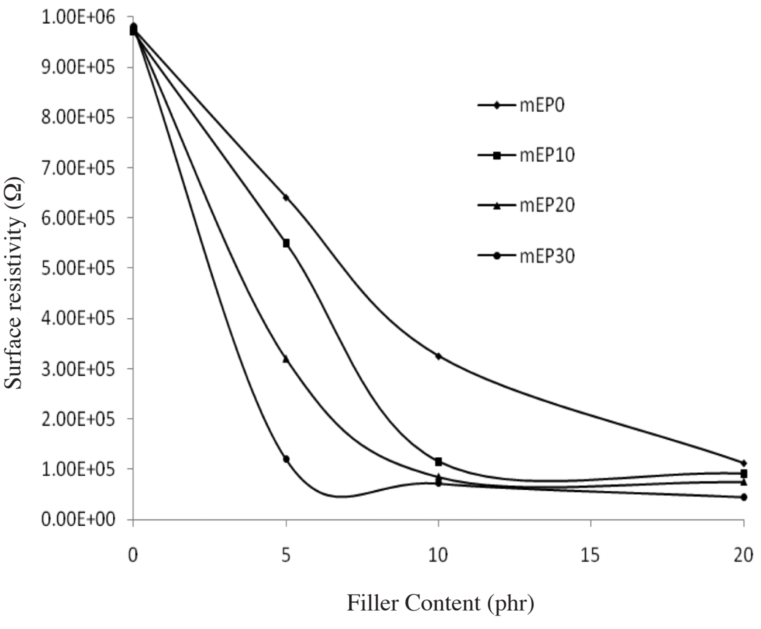

FIGURE 2. Effect of filler content on surface resistivity of Kaolin-EPDM composite

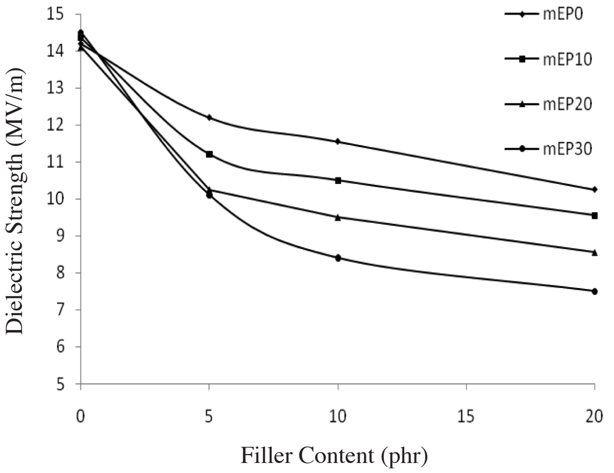

FIGURE 3. Effect of filler content on dielectric strength of Kaolin-EPDM composite

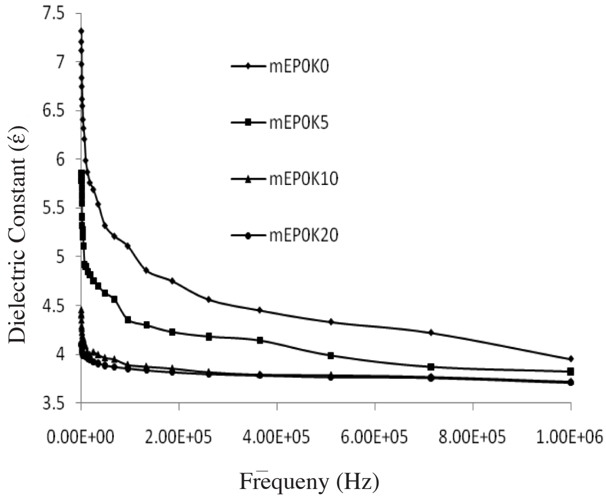

FIGURE 4. Effect of filler content on dielectric constant of Kaolin-EPDM composite

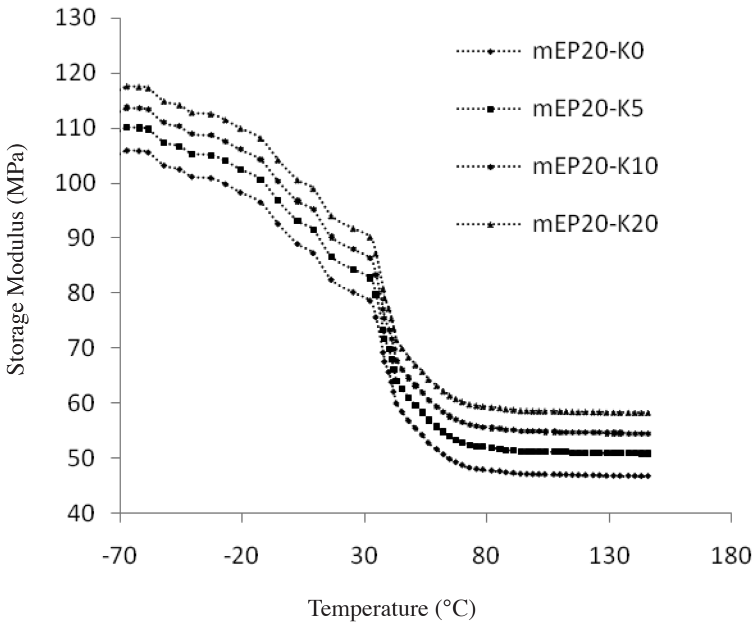

FIGURE 5. Effect of temperature on storage modulus of Kaolin-EPDM composite

Scanning electron microscope micrographs showed the effect of compatibilizer on the filler dispersion. The scanning electron micrographs reveals that the maleated EPDM helps the filler distribution in the major rubber phase. Figure 7 shows that the composite containing 10% compatibilizer with different amount of filler concentration. It was also observed from the figure that the 10% filler containing composite shows well distribution of it. Moreover it was also observed from the SEM micrographs that filler were agglomerated when concentration of filler increased beyond 10%. This indicated that for higher filler concentration (>10%), compatibiliser may not be sufficient for better dispersion.

CONCLUSION

This study revealed that the optimum cure time increased with increasing compatibilizer concentration without decreasing torque value indicating that acidic functional groups comes from compatibilizer could retard the cure rate and increased the optimum cure time rather than change in the ultimate cure state. As the concentration of filler increases the edge to edge and face to edge interaction between filler and EPDM increased and the free volume between EPDM molecules was reduced, leading to less solvent swelling increasing crosslinking density. The results obtained showed that with the increasing filler concentration, the modulus and elongation at break

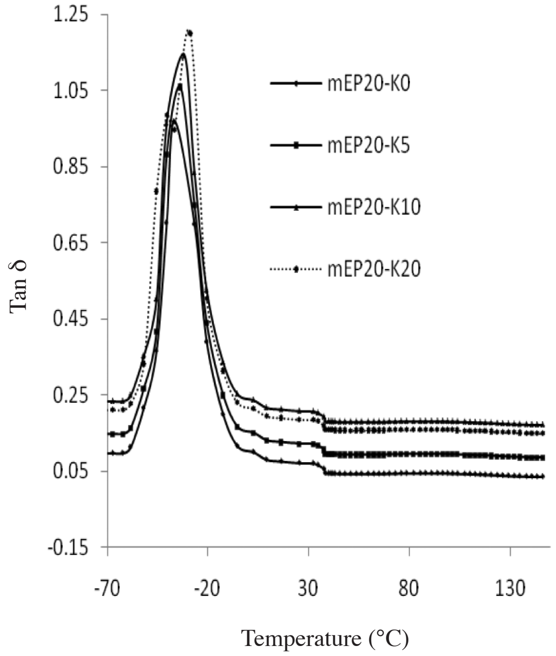

FIGURE 6. Effect of temperature on Tanδ of Kaolin-EPDM composite

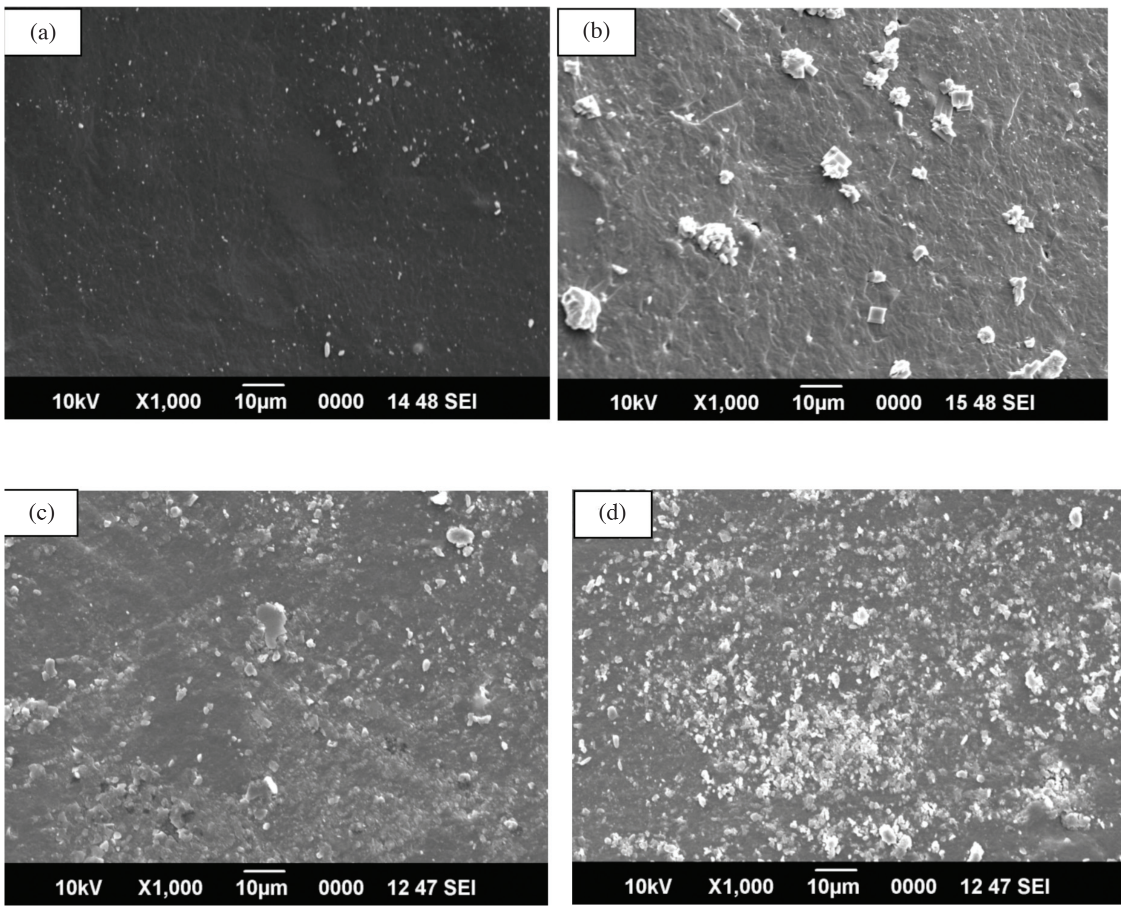

FIGURE 7. Scanning electron micrographs of (a) 0, (b) 5, (c) 10 and (d) 20% kaolin content sample of 10% m-EPDM and 90%EPDM (mEP10)

increased due to the inter-tubular diffusion of EPDM inside the clay. It was observed that the increasing filler concentration resistivity decreased. Moreover 20% compatibiliser concentration may bring the optimum properties in terms of filler dispersion, resistivity, modulus and crosslinking density.

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