

Effect of Maleic Anhydride Grafted Ethylene Propylene Diene Monomer (MAH-g-EPDM) on the Properties of Kaolin Reinforced EPDM Rubber

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ABSTRACT: Due to pollution issue and dark color of carbon black, nonblack filler are getting more importance for reinforcing elastomer. EPDM-kaolin composites with variable maleated EPDM concentration have been prepared by mixing on a two roll mill. 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 optimum cure time rather than change in ultimate cure state. As the concentration of filler increases, the edge to edge and face to edge interaction between filler and EPDM increases and the free volume

between EPDM molecules is reduced, leading to less solvent swelling increasing crosslinking density. The results obtained shows that with increasing filler concentration the modulus and elongation at break increases due to the intertubular diffusion of EPDM inside the clay. The morphological study revealed that homogeneity of filler dispersion increases with increase in compatibilizer concentration which support the results obtained from tensile test. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2268–2274, 2011

Key words: EPDM; kaolin; rheometry; cure time; SEM

INTRODUCTION

Ethylene-propylene-diene monomer (EPDM) has been the one of the growing synthetic rubbers on market for both general purpose and special applications. EPDM possesses excellent resistance to heat and oxidation due to its saturated backbone,¹ while the nonpolar structure makes EPDM with excellent electrical resistivity and resistance to polar solvents.^{2,3} Reinforcing fillers generally used for elastomers are carbon black, silica, clay, plastics, and glass fiber. The main reason for reinforcing rubbers is to improve the mechanical and thermal properties as well as reducing cost, and sometimes weight of the compounds. Carbon black is a typical reinforcing material in rubbers. However, due to pollution issues and dark color of the carbon black, several researchers have focused on development of other reinforcements in rubber composites during the last few years.^{4–9} Commonly used fillers for EPDM include carbon black, silica, clay, and fiber.^{10–13} The surface functional groups of filler could influence the cure properties of EPDM and finally affect the

overall properties. Earlier reports observed that channel blacks with lots of oxygen functional groups, which were reported to be acid, would retard cure, while furnace blacks featuring a slightly alkali characteristic because of low oxygen content would accelerate vulcanization.¹⁴ More recently, some studies have reported that by adding a small amount of carbon nanotubes, the thermal stability, flammability, and mechanical properties of polymers were strongly improved.^{15–17} Against the improvement in weight, strength, and thermal properties obtained in polymer layered silicate nanocomposites, the preparation process and organic treatment of nanoclays are complex and costly.¹⁸ Layered silicates need to be exfoliated to separate the layers and obtain the dispersion needed for uniform properties in the nanocomposite materials.¹⁹ Incorporation of filler to EPDM changes its character due to change in polarity of the system. Moreover due to saturated backbone and lack of polarity of EPDM, compatibility of inorganic filler and rubber is poor. The incorporation of maleic anhydride grafted ethylene-propylene-diene monomer (MAH-g-EPDM) as compatibilizer to EPDM-kaolin $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$ composite system enhances the filler-matrix bonding and hence the distribution of filler. Thus, this study deals with the effects of the compatibilizer concentration on mechanical, morphological properties, and cure characteristics of kaolin reinforced EPDM rubber.

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TABLE I
Compound Formulation

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

EXPERIMENTAL

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 viscosity of 70×10^{-1} Pa s ($ML_1 + 4$ at 125°C), a weight average molecular weight of 210,000 g/mol, and less than 1% crystallinity (Differential scanning calorimetry at 10°C/min), Zinc oxide (Titan Biotech, Delhi, India) and sulfur (E. Merck, Darmstadt, Germany) were of laboratory reagent grade, accelerator tetra methyl thiuram disulphenamide, Renacit, stearic acid were obtained from CDH (India). The kaolin clay of laboratory grade was supplied by Titan Biotech, India.

Compounding

Compounding is done according to the formulation given in Table I. Sixteen batches are made by using EPDM rubber as base polymer with kaolin clay and variable compatibilizer (*m*-EPDM) concentration. Mixing was carried out in a laboratory two-roll mill (6 in. by 15 in.) 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 a same time was allocated for all the mix to ensure same level of polymer-filler interaction. The compounds were identified according to the amount of filler content and compatibilizer concentration (Table II). All the compounds were cured at their respective equivalents of their rheometric optimum cure times at 150°C in an electrically heated hydraulic press. The average thickness of the molded sheet were 2.0 ± 0.1 mm.

CHARACTERIZATION

Rheometry

The rheometer data have been obtained in a Future Foundation oscillating disc rheometer. The test piece of rubber compound is contained in a sealed test cavity under positive pressure and at a temperature of 170°C. A rotor (biconical disc) is embedded in the test piece and is oscillated through small specified rotary amplitude, $\pm 3^\circ$ arc. This action exerts shear strain on the test

and the torque (force) required to oscillate the disc depends upon stiffness (shear modulus) of the rubber compound. The stiffness of the specimen increases when crosslinks are formed during cure. The following measurements are taken from the rheograph.

i. Maximum torque (M_H).

As the curing starts, the torque increases proportionately. Depending upon the type of compound, the slope of the rising torque varies. After a while the torque typically attains maximum values and its plateaus out. It is called "plateau curve." If test is continued for sufficient time, there may be continuous fall in the torque, it is called "reverting curve." If the torque shows a continuous rising trend during the period of record, it is called "marching curve." Maximum torque is the highest torque recorded in plateau curve.

ii. Cure rate and optimum cure time.

The cure rate is an essentially a measure of the linear slope of the rising curve. The rate of cure is the rate at which crosslinking and the development of stiffness (modulus) of the compound occur after the scorch point. The rate of cure is an important vulcanization parameter since it determines the time the compound must be cured, i.e., the cure time.

The rate of cure is determined by

$$\text{Cure rate} = \frac{100}{tc_{90} - ts_2}$$

where,

tc_{90} (optimum cure time) = It is the time at which 90% of cure has taken place.

ts_2 = Scorch time for viscosity to rise 2 units above minimum torque.

TABLE II
Sample Code

Sl. no	Sample code	EPDM (phr)	<i>m</i> -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

Fourier transmission infrared spectroscopy (FTIR)

FTIR spectroscopy is a powerful tool to monitor the vibrational energy levels in the region of different molecules. The changes in chemical properties are usually followed by FTIR spectroscopy which is a very sensitive and nondestructive technique. Infrared spectroscopic analysis was carried out using Shimadzu, IR-Prestige Fourier transform infrared spectrophotometer. FTIR spectra were recorded in the range of 400–4000/cm at room temperature. The resolution is 4/cm and the number of scans to record IR spectra is 20. For recording IR spectra, the thin rubber sheet was placed in the transmission cell and the spectra were recorded using DRS mode.

Tensile test

To study the stress-strain behavior of rubber materials, dumbbell-shaped samples were prepared from cured sheets that were subsequently tested for modulus, tensile strength, and elongation according to ASTM D 638 type-IV having a dimension of width—6 mm, thickness—2.5 mm gage length—25 mm using Instron 3366 universal tensile machine. The measurements are taken at 27°C and at a cross-head speed of 300 mm/min.

Crosslink density

Crosslink density is an important parameter since it decides the physical properties of vulcanizate. It virtually gives an idea about the number of crosslinks in the system. It can be defined as the number of crosslinks per unit length/weight of the polymer chain. There is a direct relationship between the small strain modulus (modulus at 100% elongation) and the crosslink density.

$$\text{Crosslink density, } 2M_c^{-1} = \frac{E}{3\rho_r RT}$$

E = modulus at 100% elongation, MPa,

ρ_r = density of rubber, Kg/m³,

R = universal gas constant, KPa m³/Kg mole K,

T = temperature in K,

M_c = molecular weight between crosslink junction.

Hardness

Hardness is a property of considerable importance; it may be defined as the resistance to indentation under conditions that do not puncture the rubber. The hardness test is carried out in a rubber hardness tester (model-shr-markIII, shore A) as per ASTM 2240-00, the scale runs from 0 to 100. The test piece

should have its upper and lower surfaces flat, smooth and parallel to one another. The hardness readings depend on the dimension of the test piece, thickness being the most critical dimension.

SEM

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

Rheometry study in oscillating disc rheometer

The rheographs and cure characteristics of EPDM with kaolin clay with variable concentration of compatibilizer are shown in Figure 1(a,b). The initial decline of torque is ascribing to the softening of the rubber caused by heating. Then torque increases because of the formation of crosslinking bond. It is clearly observed that the ultimate cure state of the vulcanizate indicated by maximum torque (M_H) increases with increasing filler concentration for all concentration of compatibilizer (m -EPDM). The increase in filler concentration reduces the mobility of the elastomer chain hence increases the torque. Moreover, it was observed from the Figure 1(a,b) that the addition of compatibilizer increases the maximum torque value which indicates that the addition of m -EPDM helps better filler-matrix interaction through hydrogen bonding. Modification of composite in presence of compatibilizer, m -EPDM, introduces acidic carboxyl groups which would help sulfur decomposes into ions instead of radical.²⁰ But only radical can initiate and participate in vulcanization, so the presence of carboxyl group could reduce the radical number and finally retard cure rate and increase optimum cure time as observed in Figure 2. But with increasing compatibilizer concentration does not reduce the torque value indicating that acidic functional groups comes from compatibilizer could retard cure rate and increase optimum cure time (Fig. 2) rather than change in ultimate cure state.

Spectroscopy analysis by FTIR

From Figure 3, it is observed the absorbed band to asymmetric and symmetric stretching vibration of methylene at 2919/cm and 2841/cm. In addition, the characteristics peaks at 1705 and 936/cm are assigned to C=O stretching vibration and O=H transforming vibration of —COOH group. Moreover, the sharp peak at 2985/cm assigned to the stretching vibration of the —OH groups.^{21,22} From the above

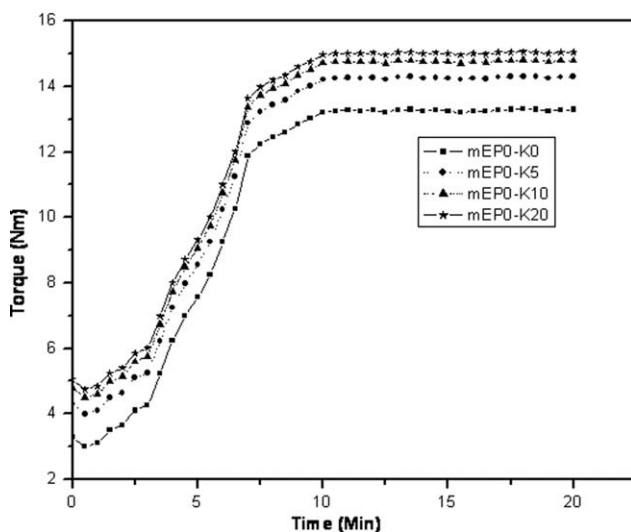
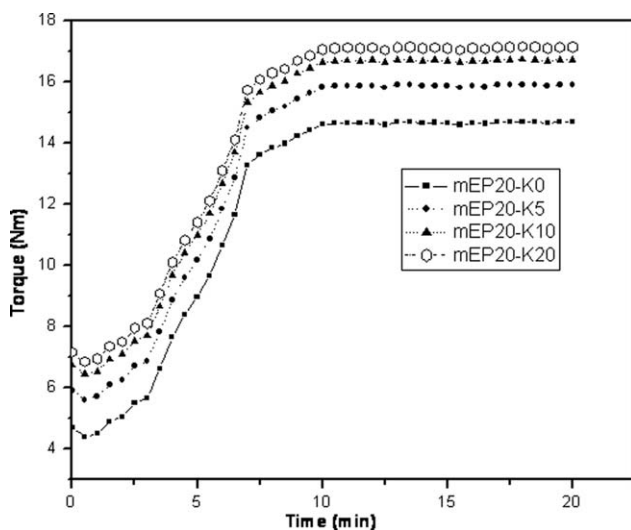


Figure 1 (a) Cure curve of EPDM with compatibilizer. (b) Cure curve of EPDM without compatibilizer.

figure, it is observed that with increasing the filler content the decrease in peak intensity and shifted to higher wavenumber may be due to the reaction between anhydride compatibilizer and the hydroxyl group of filler surface.

Crosslink density

The influence of kaolin loading on crosslinking density of EPDM/kaolin composite is shown in Figure 4. The crosslinking density of the EPDM/clay were increased with addition of filler, and this is probably due to the interfacial and intertubular interaction between EPDM and filler.²³ As the concentration of filler increases the edge to edge and face to edge interaction between filler and EPDM increases and the free volume between EPDM molecules is reduced, leading to less solvent swelling increasing crosslinking density. The increasing crosslinking

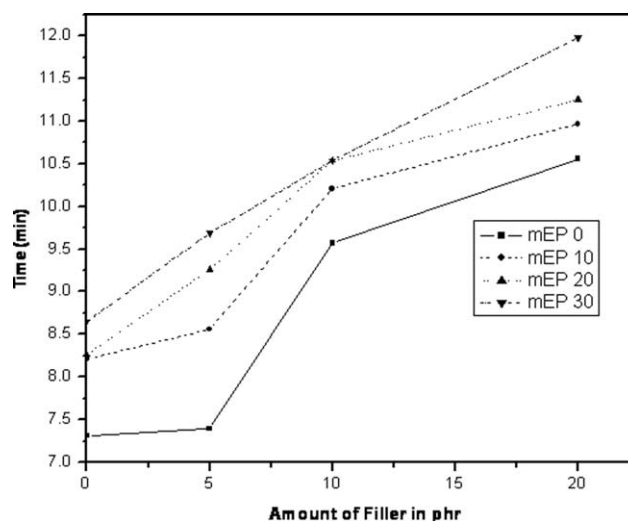


Figure 2 Effect of compatibilizer and filler concentration on optimum cure time.

density decreases molecular mobility therefore lead to higher stiffness as shown in tensile modulus data.

Hardness

The effect of filler loading and compatibilizer concentration on hardness (Shore-A) is shown in Figure 5. The results shows that with increasing the filler concentration, surface hardness increases, and moreover, the hardness also increases with increase in compatibilizer concentration as the filler-matrix interaction increases.

Modulus at 100% elongation and elongation at break

The effect of kaolin clay loading as well as compatibilizer concentration on tensile modulus (i.e., stress at 100% elongation) is shown in Figure 6. The figure showed that increasing trend from 0 to 20 phr kaolin

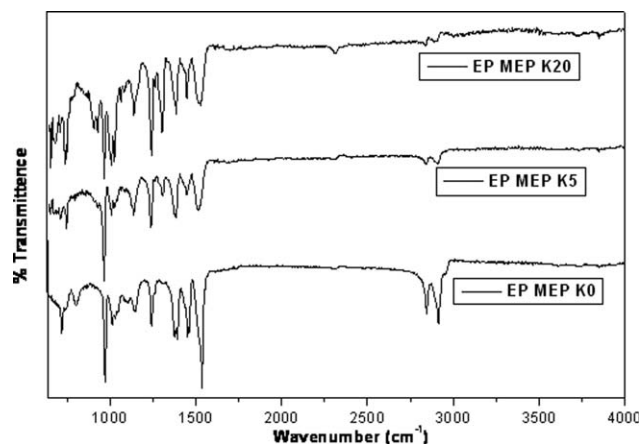


Figure 3 FTIR spectroscopy of filled and unfilled EPDM.

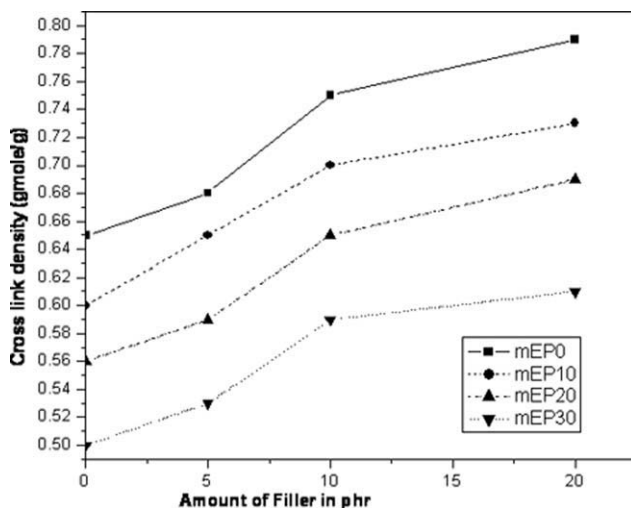


Figure 4 Effect of compatibilizer and filler concentration on crosslink density.

loading increases the modulus which related to the strong interaction between filler EPDM. The reinforcing mechanism is the intertubular diffusion of EPDM inside the clay.²³ Here rubber molecule is trapped between or within aggregates of filler. Therefore, the penetrated rubber inside and between the tubules acts as part of the filler network and increases the stiffness of the EPDM/kaolin composite. Interaction between the *m*-EPDM and kaolin in composite are most likely by Van Der Waals type of bonding due to delocalized electrons on the surface of filler. The oxygen atom on the filler and the anhydride groups on the maleated rubber will interact with each other through the formation of a bridge bonding via a free radical mechanism. The free radicals are formed during the vulcanization reaction which forms a strong interaction between the polymer chains and the fillers through the modifier.

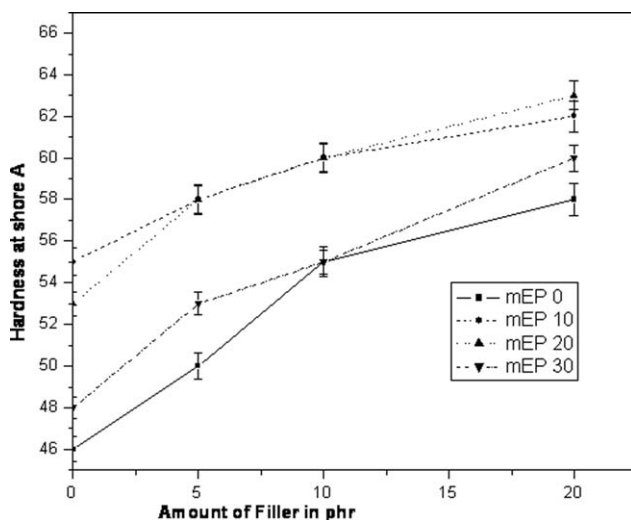


Figure 5 Effect of compatibilizer and filler concentration on Shore-A hardness.

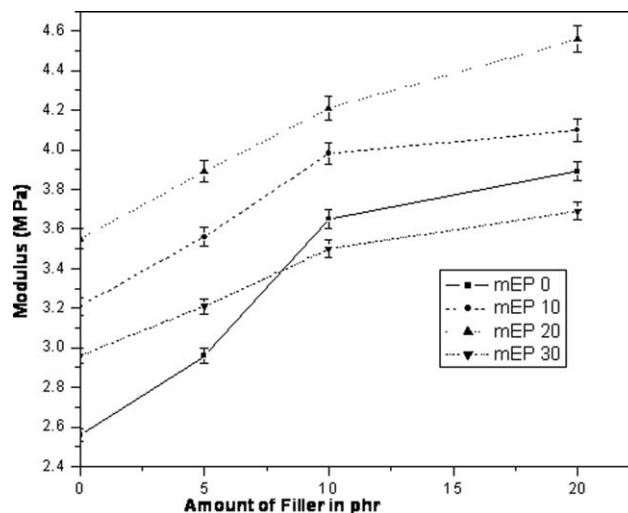


Figure 6 Effect of compatibilizer and filler concentration on 100% modulus.

Moreover the presence of anhydride groups on *m*-EPDM will enhance the degree of nucleophilicity and thus enhance the bonding with the kaolin filler.

Elongation at break of the EPDM-kaolin composite is shown in Figure 7. It was observed that the elongation at break slightly increases with increase in filler loading. These enhancement or no significant change of elongation at break indicates the improve in ductility even after increase in stiffness. The interfacial and inter tubular interaction between filler and polymer as well as homogeneous dispersion of filler at higher compatibilizer concentration are responsible for increasing the stiffness and ductility of the composite.

Scanning electron micrographs

Scanning electron microscope micrographs shows the effect of compatibilizer on the filler dispersion. It

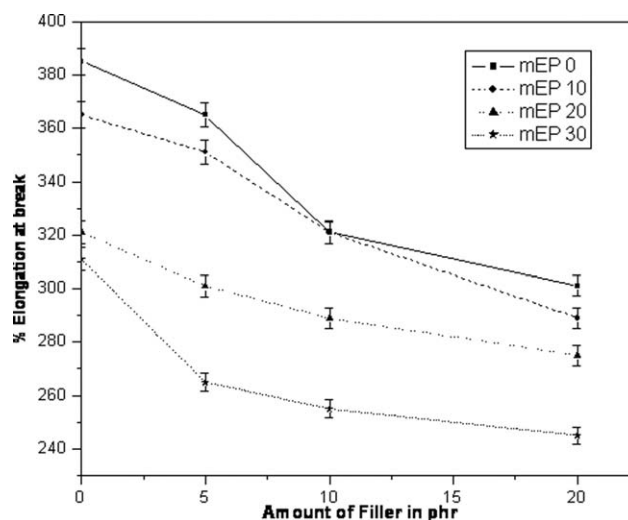


Figure 7 Effect of compatibilizer and filler concentration on elongation at break.

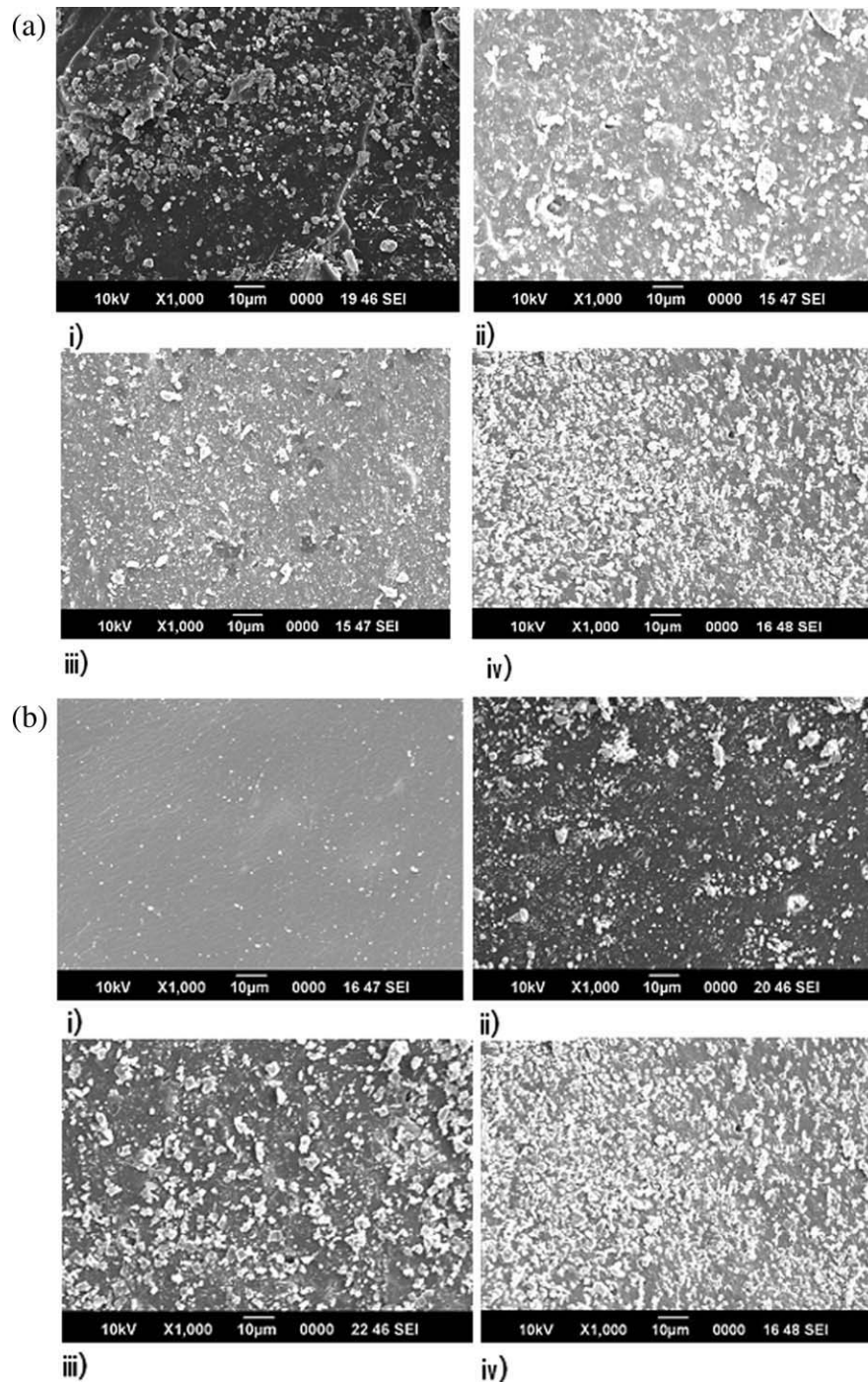


Figure 8 (a) Scanning electron micrographs of composite containing 20 phr filler concentration (i) 0% mEPR, (ii) 10% mEPR, (iii) 20% mEPR, and (iv) 30% mEPR. (b) Scanning electron micrographs of composite containing 30% compatibilizer concentration (i) 0 phr kaolin, (ii) 5 phr kaolin, (iii) 10 phr kaolin, and (iv) 20 phr kaolin.

was observed that with increasing the *m*-EPDM concentration, filler dispersion increases significantly. Figure 8(a) shows that the composite containing no compatibilizer or lower concentration of compatibilizer, the fillers are unevenly distributed and form agglomerate, but with increasing compatibilizer concentration fillers distributed homogeneously and little amount of agglomerate due to establishment of

strong hydrogen bonding between hydroxyl groups of filler surface and carboxyl group of *m*-EPDM. Moreover at a higher compatibilizer concentration (70% EPDM and 30% *m*-EPDM) the dispersion of filler increases with increase in filler concentration (0 to 20%) which may be attributed that at higher filler concentration more shear force generated which may lead to breaks up the filler agglomerate [Fig. 8(b)].

CONCLUSIONS

This study revealed that 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 optimum cure time rather than change in ultimate cure state. As the concentration of filler increases, the edge to edge and face to edge interaction between filler and EPDM increases and the free volume between EPDM molecules is reduced, leading to less solvent swelling increasing crosslinking density. The results obtained shows that with increasing filler concentration the modulus and elongation at break increases due to the intertubular diffusion of EPDM inside the clay. The morphological study revealed that homogeneity of filler dispersion increases with increase in compatibilizer concentration.

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