

# Dual Filler Effect of Compatibilized Pure and Oil Extended Ethylene Propylene Diene Monomer Nanocomposites

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**Abstract:** Pure and oil extended ethylene propylene diene monomer nanocomposites were prepared using suitable compatibilizer. Since ethylene propylene diene monomer (EPDM) is non-polar, incorporation of organically modified nanoclay may not lead to better dispersion in the rubber matrix. Hence a polar rubber like epoxidized natural rubber (ENR) can be used as a compatibilizer for dispersing nanoclay in the EPDM matrix. ENR - organically modified nanoclay composites (EC) were prepared by solution mixing. The nanoclay used in this study is Cloisite 20A. ENR-nanoclay composites were incorporated in EPDM and oil-extended EPDM (OE-EPDM) matrices along with carbon black. The morphological studies prove that the nanoclay platelets get intercalated in ENR. Low loading of EC in EPDM and OE-EPDM matrices enhances the dispersion of nanoclay forming partially exfoliated platelets. Curing study shows improvement in torque and faster cure time for the compatibilized EPDM and OE-EPDM nanocomposites containing dual filler system compared to pure and single filler (carbon black) containing rubber compounds. Dynamic mechanical thermal analysis shows high storage modulus and lesser damping characteristics for the dual fillers containing EPDM and OE-EPDM compounds. The same compounds show tremendous improvement in mechanical properties. Scanning electron microscopic (SEM) images of tensile fractured single and dual filler containing rubber specimens show rough and tortuous path of fracture, which may be due to physical interaction between filler and rubber.

**Keywords:** Nanoclay, Compatibilizer, EPDM, OE-EPDM, Carbon black.

## 1. INTRODUCTION

Polymer-organoclay nanocomposites were prepared to achieve high degree of dispersion of organoclay aggregates in the polymer matrix. The finely dispersed organoclays yield to very large surface areas, which improves the properties of the polymer. Numerous works have been reported on nanoclay filled thermoplastics and thermosetting polymers. The studies on rubber nanoclay composites constitute in lesser dimension [1-4].

The preparation of polymer-organoclay nanocomposites involves two main faces. Initial face involves the compatibility between polymer and nanoclay. The organically modified nanoclay is polar, hence it may form poor dispersion, while incorporating directly in the non-polar EPDM. In order to overcome this problem, a polar rubber, which is compatible with EPDM, can be used as a compatibilizer. ENR obtained by epoxidation of 1, 4-polyisoprene, depicts higher glass transition temperature and increased polarity. Moreover, ENR is compatible with EPDM [5], and hence it was chosen as a compatibilizer in this study. Nanocomposites based on natural rubber [6-9], nitrile

butadiene rubber [10], styrene butadiene rubber [11], ethylene propylene rubber and OE-EPDM [12] gum compounds were successfully developed using ENR as compatibilizer. In this present study, EPDM and OE-EPDM nanocomposites containing dual fillers (i.e., nanoclay and carbon black) were prepared using ENR as compatibilizer.

The second face is the method used for the preparation of nanocomposites. It includes insitu polymerization intercalation [13], solution intercalation [14], melt intercalation [7], finally co-coagulation of rubber latex and clay aqueous suspension [15]. Incorporation of nanoclay in ENR was done by solution mixing. The obtained ENR-nanoclay composites (EC) were incorporated in EPDM and OE-EPDM in presence of carbon black and the system is sulphur cured. The changes obtained in the morphology, curing characteristics and mechanical properties have been analyzed and compared to their respective controls.

## 2. MATERIALS

Ethylene propylene diene terpolymer used was Royalene 502 [ethylene 63%, propylene 37%, ethylidene norbornene (ENB) 4%].

Oil-extended ethylene propylene diene terpolymer used was Keltan 5531A obtained from DSM Elastomer

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B.V., The Netherlands. (ethylene 63%, Ethylidene norbornene (ENB) 4.5%, paraffinic oil 50 wt.%)

Epoxidized natural rubber containing 50 mol% epoxidic units was supplied from Agricultural Product Processing Research Institute, Zhangjiang, PR China.

Cloisite 20A, a natural montmorillonite modified with a quaternary ammonium salt with cation exchange capacity of 95 mequiv./100 g clay (Southern Clay, Inc, USA), was used as a nanofiller for the preparation of nanocomposites.

Type of carbon black used in the study.

mixture was ultrasonicated for 15 minutes and casted over in a plane glass plate and dried at room temperature.

### 3.2. Compounding

EC was incorporated in EPDM and OE-EPDM matrices. The mixing formulation is shown in Table 1. The compounding was performed in open two-roll mixing mill operated at room temperature. The speed ratio of the rotors was 1:1.4. The rubber compounds were vulcanized in the compression molding machine at 150 °C, according to the optimum cure time obtained from Monsanto Rheometer.

Name	Abbreviation	ASTM Designation	Particle size nm
Intermediate Super Abrasion Furnace	ISAF	N234	24-33

Other compounding ingredients such as sulphur, zinc oxide, stearic acid, *N*-cyclohexyl-2-benzothiazyl sulphenamide (CBS), Tetramethylthiuram disulphide (TMTD) were purchased from Bayer (M) Sdn Bhd Malaysia.

## 3. METHODS

### 3.1. Solution Mixing

ENR was dissolved in toluene. The ratio of the rubber to solvent was 1:3, weight/volume. The rubber solution was continually stirred at room temperature until the rubber gets completely dissolved in the solvent. Subsequently 50 phr of nanoclay (Cloisite 20A) was added to the rubber solution. ENR-nanoclay (EC)

## 4. CHARACTERIZATION TECHNIQUES

### 4.1. Cure Characteristics

The cure characteristics of the rubber compounds were evaluated using Monsanto Rheometer R-100 testing instrument operated at 150 °C with 3° arc at a period of 60 minutes.

### 4.2. X-Ray Diffraction

The crystallographic spacing (*d*) of the nanocomposites was determined using an X-ray diffractometer (Philips PANalytical X'pert PRO) with Cu-K $\alpha$  radiation at a generator voltage of 40 kV and wavelength of 0.154 nm at room temperature. The

**Table 1: Formulation of the Rubber Compounds**

Ingredients	Designation							
	EP	EP1	EP2	EP3	OE	OE1	OE2	OE3
EPDM	100	100	95	90	-	-	-	-
OE-EPDM	-	-	-	-	100	100	95	90
EC <sup>a</sup>	-	-	5	10	-	-	5	10
Carbon black ISAF <sup>b</sup> N234	-	40	40	40	-	40	40	40
Stearic acid	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
CBS <sup>c</sup>	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Zinc oxide	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Process oil	-	2	2	2	-	2	2	2

<sup>a</sup>EC - ENR-Nanoclay composites.

<sup>b</sup>ISAF - Intermediate super abrasion furnace.

<sup>c</sup>CBS - *N*-cyclohexyl-2-benzothiazyl sulphenamide.

calculation was performed using Bragg's law. The range of  $2\theta$  scanning of X-ray intensity employed was  $1.5 - 10^\circ$  with a scanning rate of  $2^\circ\text{min}^{-1}$ .

### 4.3. High Resolution Transmission Electron Microscopy (HR-TEM)

HR-TEM (JEOL 2100) instrument was used to observe the dispersion morphology of nanoclay in ENR (EC), distribution of carbon black in EPDM (EP1) & OE-EPDM (OE1) compounds, nanoclay and carbon black distribution in EPDM compounds (EP2 & EP3), OE-EPDM compounds (OE2 & OE3). The ultra-thin cross-sections of the specimens were prepared using a Leica Ultra Cut UCT ultramicrotome instrument equipped with a diamond knife. The thickness of the HR-TEM specimens were approximately 80 nm and the temperature was maintained at  $-80^\circ\text{C}$  using liquid nitrogen for sample processing. These samples were then placed on the copper grids.

### 4.4. Dynamic Mechanical Thermal Analysis

Dynamic mechanical properties of the compounds are analyzed using a TA Instrument DMA 2980 model in tension mode. The rubber compounds were subjected to sinusoidal displacement of 0.1 % strain at a frequency of 1 Hz between the temperatures ranging from  $-70^\circ\text{C}$  to  $50^\circ\text{C}$  at a heating rate of  $3^\circ\text{C min}^{-1}$ . The storage modulus ( $E'$ ) and loss tangent ( $\tan \delta$ ) of the rubber compounds are analyzed.

### 4.5. Mechanical Testing

Dumbbell and crescent shaped specimens were cut down from the molded slabs for tensile and tear tests. Tensile strength was done according to ASTM D-412-06 and tear strength was determined according to ASTM D-624-00(2007) and the experiment was carried out in a Universal tensile testing machine, Hounsfield HS 10 KS model operated at room temperature at an extension speed of 500 mm/min with an initial gauge length of 25 mm. The values are obtained directly from the digital display at the end of each test.

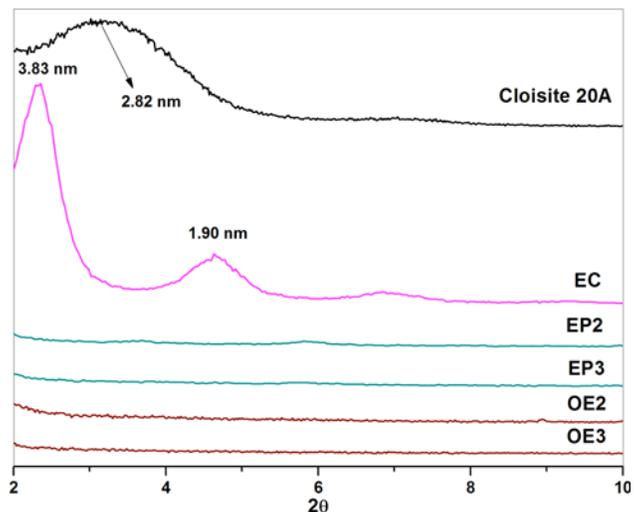
### 4.6. Scanning Electron Microscopy

The morphology of the tensile fractured surface of the rubber compounds was observed through scanning electron microscope (SEM, VEGA TESCAN). Gold coating was done on the samples under vacuum condition to prevent electrostatic charge while examining.

## 5. RESULTS AND DISCUSSIONS

### 5.1. X-Ray Diffraction Analysis

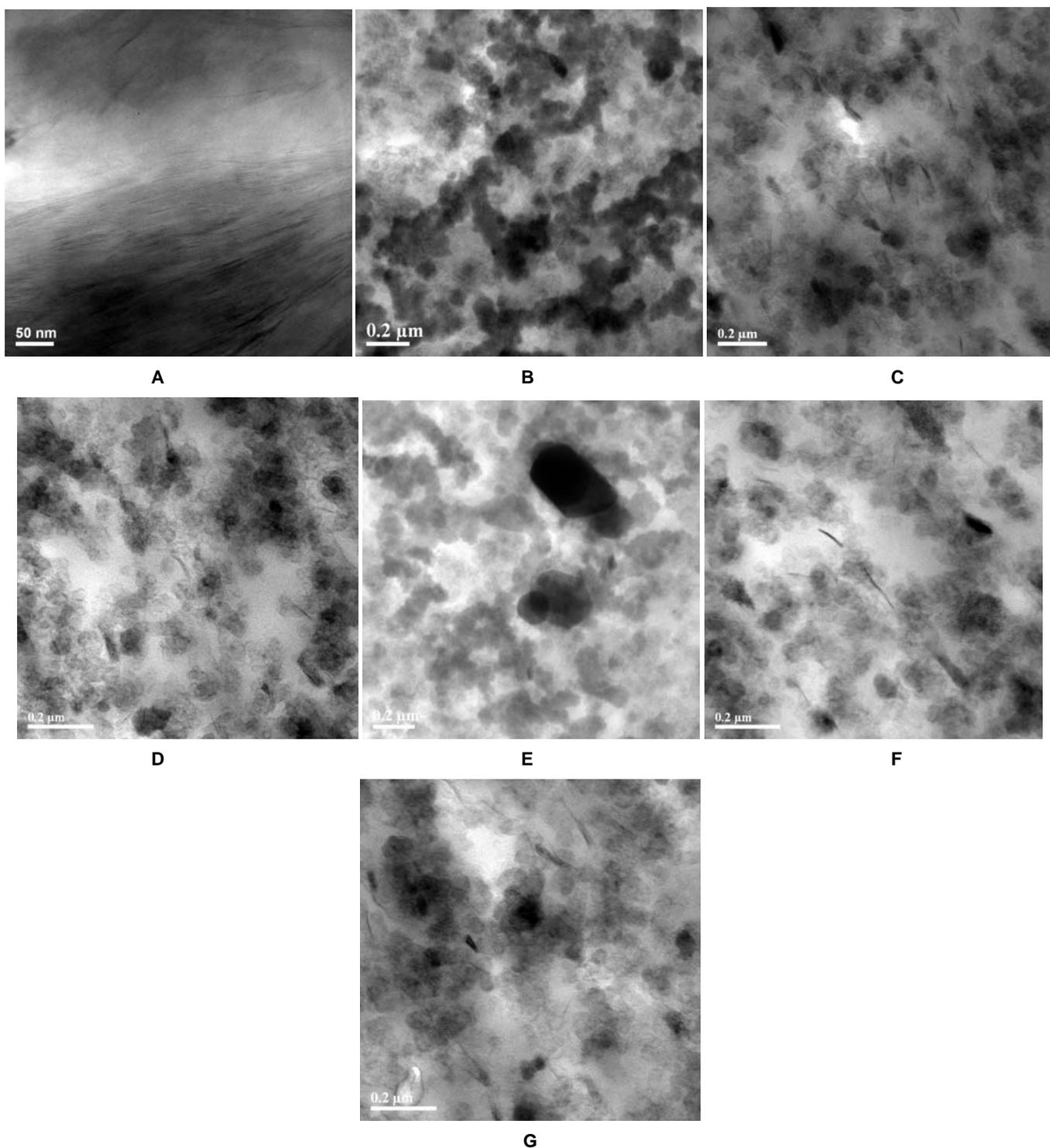
The XRD patterns of the nanocomposites are shown in Figure 1. The nanoclay (Cloisite 20A) shows an intense peak around  $2\theta = 3.144^\circ$ , corresponding to the basal spacing of 2.82 nm ( $d_{001}$ ). The main peak of the nanoclay gets shifted towards the lower angle  $2\theta = 2.31^\circ$ , when nanoclay was incorporated in ENR (EC). The d-spacing increases to 3.83 nm ( $d_{001}$ ). The penetration of ENR chains in between the nanoclay platelets increases the gallery height forming an intercalated structure. However one accompanying peak arises at  $4.65^\circ$  corresponding to the basal spacing of 1.90 nm ( $d_{002}$ ), which diminishes relatively to the main peak [16]. This may be due to some aggregation of nanoclay layers because of higher nanoclay loading (50 phr) in ENR. Loading of EC in bulk EPDM (EP2 & EP3) and OE-EPDM (OE2 & OE3) in presence of carbon black shows absence of nanoclay peaks. The compatibility of ENR and EPDM makes more EPDM chains to penetrate between the nanoclay platelets. The intercalated nanoclay platelets in ENR get partially exfoliated due to the penetration of bulk EPDM and OE-EPDM chains. Moreover, the incorporation of carbon black makes the nanoclay platelets to get disordered. Hence no peaks were observed.



**Figure 1:** XRD of pure nanoclay (cloisite 20A), EC, EP2, EP3, OE2 and OE3.

### 5.2. HR-TEM Analysis

HR-TEM images of the nanocomposites are depicted in Figure 2a-g for EC, EP1, EP2, EP3, OE1, OE2 and OE3 respectively. Nanoclay clusters can be



**Figure 2:** TEM images of (A) EC, (B) EP1, (C) EP2, (D) EP3, (E) OE1, (F) OE2, (G) OE3.

identified from EC image. The dark lines found in the image are the silicate layers. It shows that bulks of nanoclay get intercalated in the ENR. EP1 image (Figure 2b) shows the reinforcement of carbon black in EPDM matrix. Similarly image OE1 (Figure 2e) also shows the scattering of carbon black particles in OE-EPDM. The larger elliptical spots found in the image

denote the presence of zinc oxide in the OE-EPDM matrix. Images EP2 (Figure 2c), EP3 (Figure 2d), OE2 (Figure 2f) and OE3 (Figure 2g) shows the presence of dual fillers (i.e., nanoclay and carbon black) scattered throughout the EPDM and OE-EPDM matrices. The images show the partial exfoliation of nanoclay platelets in the rubber matrix. The distribution of

nanoclay seems to better in EP2 and OE2 due to low loading of nanoclay. Increasing the nanoclay loading in the rubber matrix leads to partial exfoliation as well as agglomeration of nanoclay platelets in EPDM (EP3) and OE-EPDM (OE3) compounds.

### 5.3. Cure Characteristics

The cure characteristics of the rubber compounds are shown in Table 2. Compounds EP1 and OE1 shows improvement in minimum and maximum torque compared to pure EP and OE. The improvement may be due to the reinforcement of carbon black particles in the rubber matrices. The enhancement in maximum torque depends on both the extent of crosslinking and reinforcement of filler particles in the polymer matrix. The torque value further pronounces for the nanoclay and carbon black filled EPDM and OE-EPDM compounds. The increase in nanoclay loading subsequently increases the maximum torque of the rubber compounds. The addition of carbon black in rubber compounds [EP1 and OE1] shows faster scorch and cure time compared to the gum EPDM and OE-EPDM compounds. The possible reasons may be

- (i) The smaller particle size of the ISAF carbon black having high surface area may facilitate the curing reaction [17].
- (ii) The presence of carbon black enhances the formation of  $H_2S$ , which activates most sulphur curing systems by opening the  $S_8$  rings even in the absence of accelerators. It seems that carbon black supports vulcanization reactions without changing their nature substantially [17].

The dual filler [nanoclay and carbon black] containing rubber compounds [EP2, EP3, OE2 & OE3] shows faster scorch and cure time compared to the

unfilled and single filler containing rubber compounds. This may be due to the following reasons

- (i) In addition to carbon black, the loading of organically modified nanoclay which have very high surface area may promote the curing process.
- (ii) The presence of ammonium groups in the organically modified nanoclay may also facilitates the process. The possible formation of Zn complex in which sulfur and ammonium modifier participate may help to enhance rate of cure. The ammonium concentration in the nanoclay enhances the chance of Zn-sulfur-ammonium complex formation in the nanocomposites and consequently faster scorch time and cure time were achieved [18].

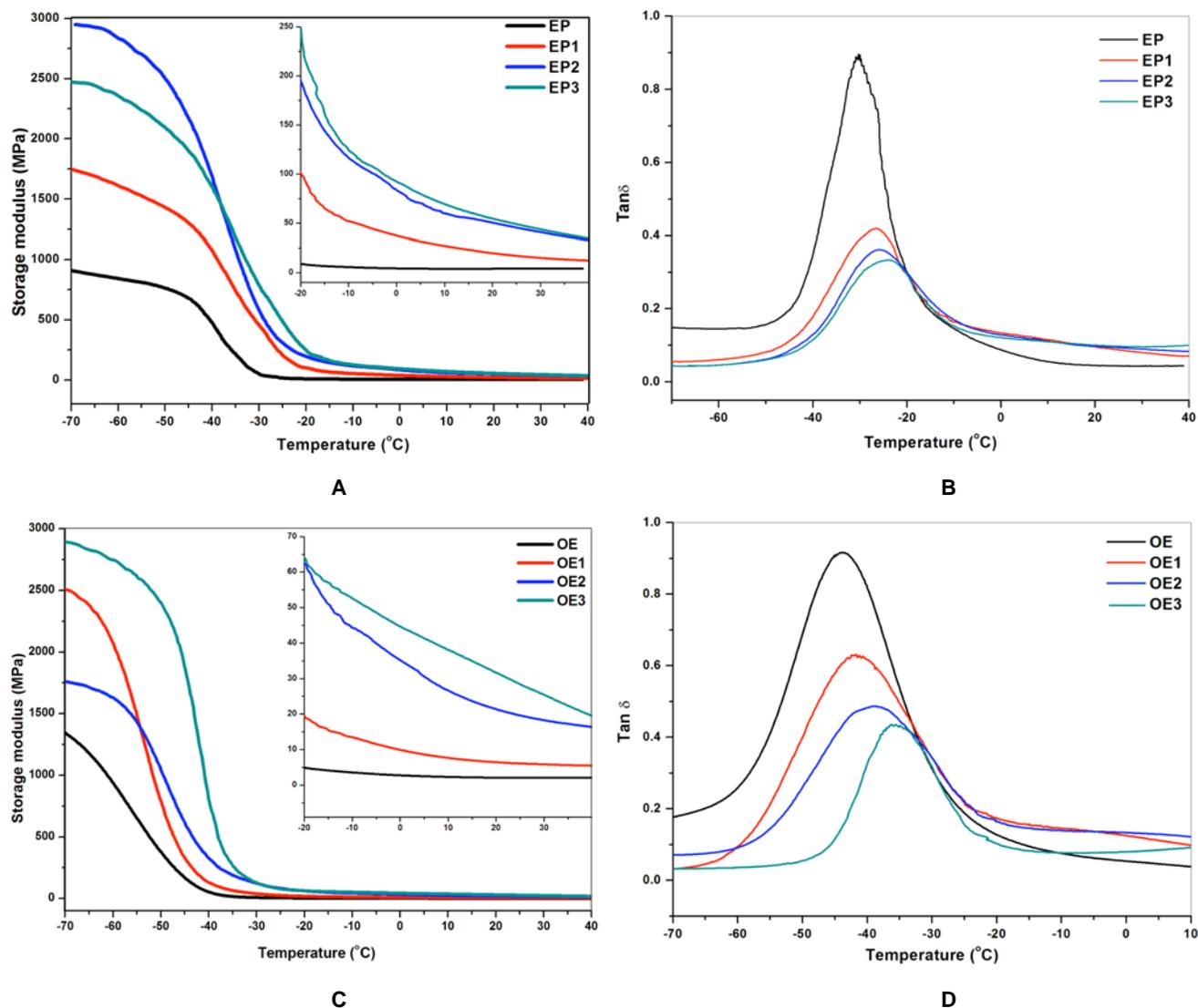
### 5.4. Dynamic Mechanic Thermal Analysis

Figure 3a-d represents the temperature dependence of dynamic storage modulus ( $E'$ ) and loss factor ( $\tan \delta$ ) respectively. The carbon black filled rubber compounds shows enhancement in storage modulus value compared to the gum rubber compounds. At 40 °C, compounds EP1 and OE1 shows 197% and 174% increase in storage modulus. The storage modulus shows remarkable improvement upon incorporation of nanoclay in addition to presence of carbon black in the rubber compounds. Compounds EP2 and EP3 shows 696% and 740% increase in storage modulus. The improvement in storage modulus of OE2 and OE3 are 721% and 877% respectively.

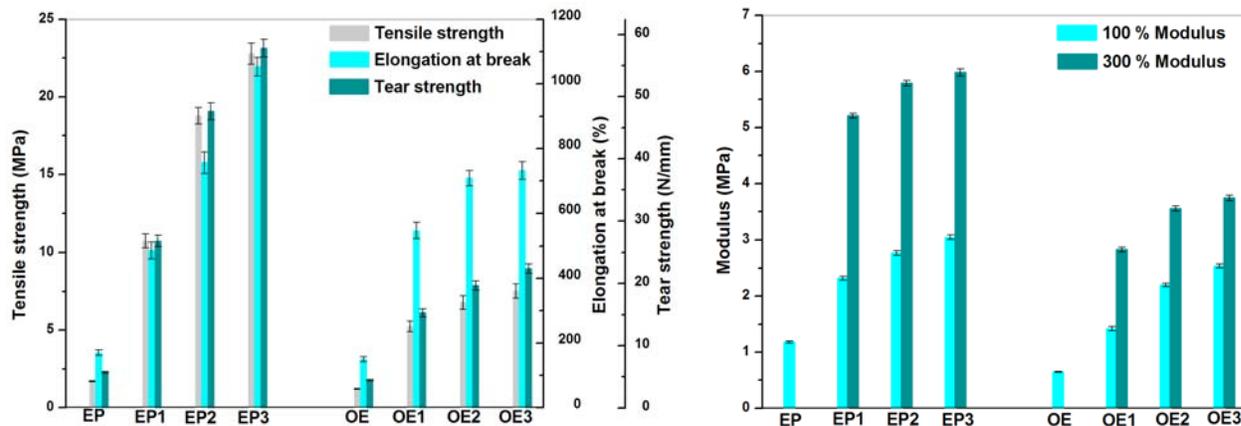
$\tan \delta$  peak decreases due to the loading of carbon black in EPDM and OE-EPDM matrices compared to gum compounds. Incorporation of nanoclay along with carbon black considerably decreases the  $\tan \delta$  peak.

**Table 2: Cure Characteristics of the Rubber Compounds**

Sample code	Min. Torque (dNm)	Max. Torque (dNm)	Torque difference (dNm)	Scorch time (min)	Cure time (min)	Cure rate index
EP	12.0	60.0	48.0	4.30	22.30	5.55
EP1	22.0	82.0	60.0	2.00	13.00	9.09
EP2	22.0	84.0	62.0	2.00	12.00	10.00
EP3	23.0	86.5	63.5	1.30	10.30	11.11
OE	7.0	30.0	23.0	4.00	20.00	6.25
OE1	10.0	38.5	28.5	2.00	13.30	8.85
OE2	10.5	41.0	30.5	1.30	12.00	9.35
OE3	12.0	42.5	30.5	1.30	11.00	10.30



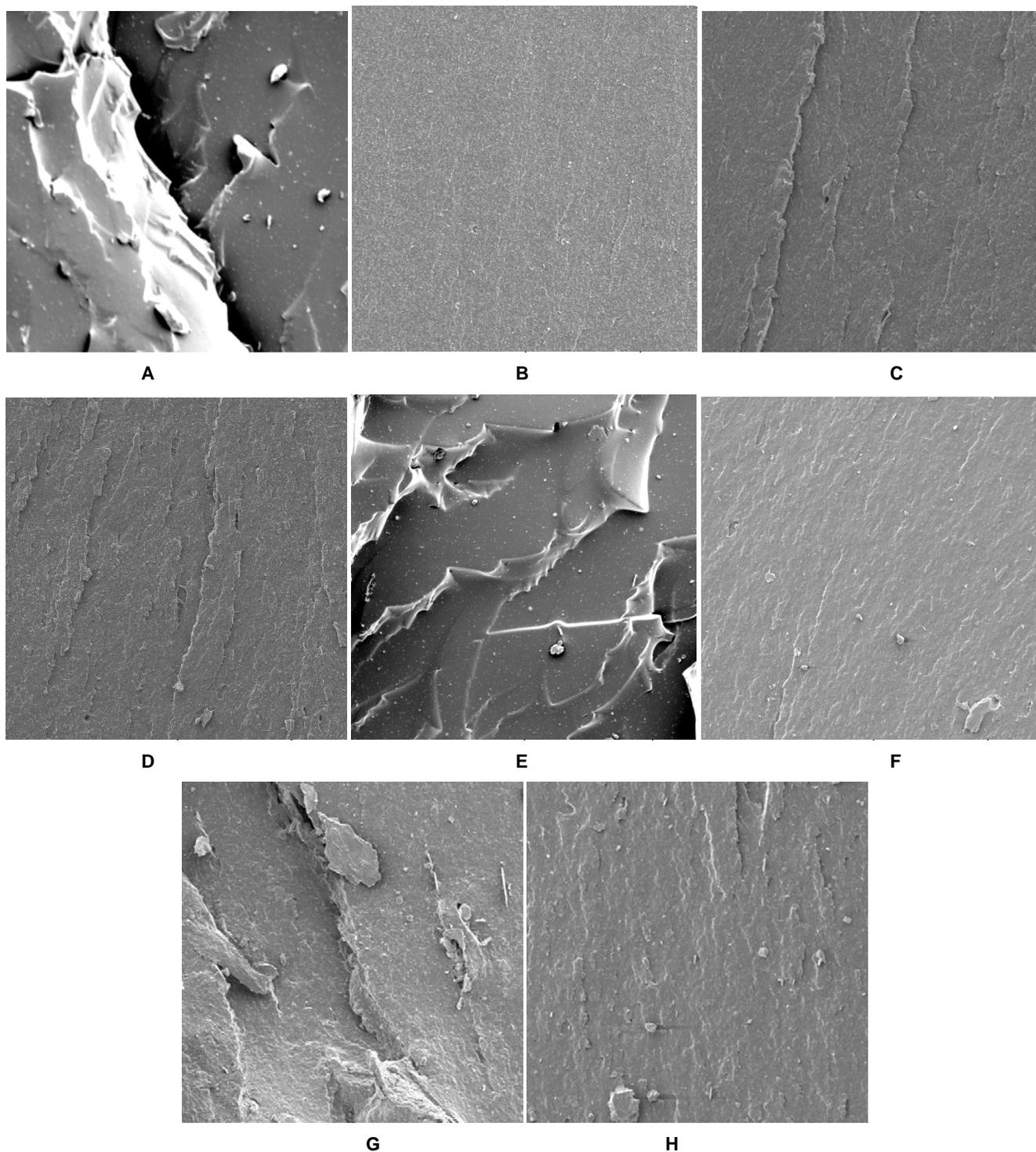
**Figure 3:** (A) Storage modulus OF (B)  $\tan \delta$  of compounds EP, EP1, EP2 AND EP3. (C) Storage modulus of (D)  $\tan \delta$  of compounds OE, OE1, OE2 and OE3.



**Figure 4:** (A) Tensile, elongation and tear strength of rubber compounds (B) Modulus of the rubber compounds.

The decrease in  $\tan \delta$  peak depends on the reinforcing tendency of the nanofiller in the rubber matrix. Restriction in the chain mobility owing to physical and

chemical adsorption of the rubber molecules on the filler surface causes reduction in height of  $\tan \delta$  peak during dynamic mechanical deformation [19]. The



**Figure 5:** Sem images of (A) EP (B) EP1 (C) EP2 (D) EP3 (E) OE (F) OE1 (G) OE2 (H) OE3.

decrease in  $\tan \delta$  peak proves minimum heat buildup and as a result lesser damping characteristics for the nanoclay loaded rubber compounds.

### 5.5. Mechanical Properties

The mechanical properties of the compounds are depicted in Figure 4a & b.

The presence of carbon black in the rubber compounds tremendously increases the mechanical properties. Compound EP1 shows 532% increase in tensile strength and 372% increase in tear strength, OE1 show an improvement of 336% in tensile and 244% tear strength. In addition to carbon black, the presence of nanoclay very well facilitates in improving

the mechanical properties of the rubber compounds. The compound EP2 and EP3 shows an improvement of 1005%, 1240% tensile and 736%, 914% tear strength. Similarly in OE-EPDM batch, compound OE2 and OE3 shows enhancement in tensile strength of 465%, 527% and tear strength of 343%, 400%. The improvement in mechanical properties strongly depends on the reinforcement of filler particles in the rubber matrix. Hence low loading of nanoclay in addition to the presence of carbon black remarkably improves the mechanical properties of the rubber compounds.

### 5.6. Scanning Electron Microscopy

The SEM images of the tensile fracture surface are shown in Figure 5a-h. The single and dual filler incorporated EPDM and OE-EPDM compounds shows highly rough and tortuous path of fracture compared to gum compounds (EP and OE). Incorporation of nanoclay and carbon black in the rubber matrices alters the crack path along their length depending on their orientation in the rubber matrix. The better distribution of filler in the rubber matrices creates more resistance to crack propagation during tensile testing and hence results in higher tensile strength.

## 6. CONCLUSION

The effect of combination of nanoclay and carbon black fillers on the properties of EPDM and OE-EPDM compounds prepared using ENR as compatibilizer has been summarized. The morphology of the nanocomposites analysed from XRD and HR-TEM proves the intercalation of nanoclay platelets in ENR and further incorporation of EC in EPDM and OE-EPDM matrices in presence of carbon black improves the dispersion of the nanoclay platelets forming partial exfoliation. Cure characteristics of the dual filler containing compatibilized EPDM and OE-EPDM compounds show faster scorch time, cure time and increase in maximum torque compared to their respective gum and single filler containing rubber compounds. DMTA results obtained from dual filler systems shows substantial improvement in storage modulus and lesser damping characteristics accompanied with remarkable improvement in mechanical properties. SEM images of tensile fractured surfaces show highly rough and tortuous path of fracture for the single and dual filler containing EPDM and OE-EPDM compounds compared to gum rubbers proving better physical interactions between the filler and rubber.

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