

# EFFECT OF BLENDING CONDITIONS ON THE PROPERTIES OF EPDM/ORGANOCLAY NANOCOMPOSITES

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## SUMMARY

The effects of blending conditions on the microstructural and mechanical properties of EPDM / organo modified montmorillonite (OMMT) nanocomposites at various clay loadings were investigated. The effects of the processing conditions were manifested in both the morphology and mechanical properties, which showed significant increase when optimized process conditions are applied.

*Keywords: Nanocomposites, Nanoclays, Mechanical properties*

## INTRODUCTION

The materials which can meet difficult conditions with better performance to cost ratio have been demanded by large number of industrial applications. Polymer-layered clay nanocomposites have recently attracted significant research interest due to their improved strength and modulus, better thermal and chemical stabilities and enhancement of flame retardancy [1-3]. The improved properties can be obtained if a relatively better dispersion of clay layers in the polymer matrix can be achieved. A great number of polymer-clay composite systems have been studied based on various matrices such as epoxy resins [4,5], polyimide [6], polystyrene [7,8], polyurethane [9], poly(ethylene terephthalate) [10] and polyolefins [11,12].

Ethylene propylene diene terpolymer (EPDM) is a member of unsaturated polyolefins which is one of the most widely used polymers in industry [3, 13]. It has been extensively applied in applications such as automotive weather-stripping and seals, radiator hoses, electrical insulation, roofing membrane, tubing, belts, house-hold applications and other general-purpose applications and sporting goods [3, 14]. However, it is difficult to disperse the clay layers within EPDM, because EPDM does not have any polar group in its backbone and it is incompatible with polar organophilic clay to prepare products having desired properties [1, 3, 15, 16].

Clay is comprised of layered silicates that have about 1 nm layer thickness with a high surface area and high ion exchange capacity. Because of the layered structure bonded with weak bonding forces, silicate layers may be dispersed in a polymer matrix at the

nanometric level [3, 16-18]. The clay minerals have  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  cations which are hydrated in the interlayer spacing. Homogeneous dispersion the organophobic layered clay mineral in an organic polymer matrix, especially in the absence of high shearing forces, may only be achievable through strategies that promote favorable interactions between the matrix and the clay surfaces. This includes the use of some compatibilizing surfactants. An ion-exchange reaction occurs with the cationic surfactants including primary, secondary, tertiary and quaternary alkyl ammonium cations. Alkyl ammonium cations lower the surface energy of inorganic component and improve the wetting characteristics of the polymer matrix, and result in a larger interlayer spacing [2, 19]. A number of surfactants containing ammonium cations have been studied to modify the clay surfaces. Their influence on the morphology and mechanical properties of the EPDM/OMMT nanocomposites has been reported [20, 21]. Gatos and Karger-Kocsis [21] have been devoted that increasing the polarity of the EPDM has favored the intercalation/exfoliation of the organoclay irrespective to the type of its intercalant (primary or quaternary). They have also investigated the EPDM nanocomposites processed with the EPDMgMA (maleic anhydride grafted ethylene propylene diene terpolymer). They have found that the EPDM based composites with EPDMgMA have better clay dispersions and higher strain values as compared to the EPDM nanocomposites without the EPDMgMA [21].

However, there is no sufficient work reported in the literature on the effects of processing conditions on the properties of EPDM/clay nanocomposites. In this study, the effects of the process parameters on the physical properties of organoclay reinforced EPDM were investigated. The intercalation of organo modified clay was investigated by X-ray diffraction (XRD). The mechanical property evaluation of the nanocomposites was performed by tensile and tear testing.

## **EXPERIMENTAL**

### **Materials**

$\text{Na}^+$  montmorillonite (MMT) clay particles (K-10, Sigma Aldrich) with a cation exchange capacity (CEC) of 120 meq/100 g, and EPDM as polymer matrix (Dutral 4436, having PP content of 28% and oil content of 40%, ENB content of 5,5% and mooney viscosity ML (1+4) at 125°C of 43, Polimeri Europa) were used to prepare nanocomposites. EPDMgMA (Fusabond N MF416D,  $\rho=0,87\text{gr/cm}^3$ , MFI (2800C, 2.16kg)=23 g/10min, Dupont) was used as compatibilizer and Octadecylamine (90%, Sigma Aldrich) was used as surfactant to modify MMT particles. In addition, sulfur, zinc oxide, stearic acid, TMTD (tetramethyl thiuram disulfide) and MBT (mercaptobenzotiazol) were used as vulcanization aids.

### **Modification of Clay**

Organophilic  $\text{Na}^+$ -montmorillonite (OMMT) was prepared from pure  $\text{Na}^+$  montmorillonite (MMT) via an ion-exchange reaction in water with alkylammonium. 40 g  $\text{Na}^+$ -MMT was dispersed in 2500 ml of deionized hot water at 80°C by using a

homogenizer to obtain a suspension solution. 15.5 g (57.5 mmol) octadecylamine and 5.75 ml of concentrated HCl were dissolved in 1000 ml of deionized hot water at 80°C. This solution was poured in the MMT– water solution with vigorous stirring by using the homogenizer for 1 h to yield white precipitate. The precipitate was collected on a filter and washed with deionized hot water until chloride anions were not detected with a 0.1 M AgNO<sub>3</sub> solution, and then it was dried in a vacuum oven at 80°C. OMMT was obtained after grounding and screening with a 325-mesh sieve.

### **Preparation of EPDM/Clay Nanocomposites**

EPDM, organoclay (OMMT) and maleic anhydride grafted EPDM oligomer (EPDMgMA) were prepared by melt-mixing method in a HAAKE Rheometer RC90 (Haake Co., Germany) at 120 and 150°C, a rotor speed of 60 and 90 rpm and mixing time of 10, 15 and 20 min. In the first stage, EPDMgMA was melt-mixed with OMMT using the rheometer. In the second stage, EPDM and the pre-mixture of OMMT / EPDMgMA were melt-blended for 10, 15 and 20 min to prepare the EPDM/OMMT nanocomposites. The EPDM/OMMT blend were sequentially mixed with zinc oxide (5 phr), stearic acid (1 phr), vulcanization accelerator [MBT (0.5 phr) and TMTD (1.5 phr)] and sulphur (1.5 phr) by using a roll mill (Ak Plastic Inc., Turkey) at ambient temperature. Vulcanized EPDM/OMMT was compression molded (140 mm x 140 mm x 2 mm) under a hot press at 160°C for 20 min to obtain rubber sheets.

### **Analysis and Characterization**

To investigate the effect of surface modification on the intercalation of the clay layers, XRD technique was employed. XRD was carried out using Bruker AXS D8 with Cu K $\alpha$  radiation at 40 kV and 40 mA. The diffractograms were scanned in 2 $\theta$  range from 1° to 10° at a rate of 2°/min.

Dispersion of the clay layers in the polymer matrix was investigated by using back-scattered SEM (Phillips XL-30S FEG-SEM) from the fractured surface of the tensile samples. All the sample surfaces were gold-coated by a sputtering apparatus before SEM examination.

The tensile mechanical tests were performed using a Zwick Z020 (Ulm, Germany) universal testing machine at a cross-head speed of 200 mm/min based on type II specimens according to DIN 53504 standard. The tear strength of the nanocomposites was measured using an Instron-4505 universal testing machine at a crosshead speed of 500 mm/min, in accordance to DIN 53507 standard. At least five specimens from each batch were tested.

## **RESULTS AND DISCUSSION**

### **Structure of Clay Layers and Clay Modified Nanocomposites**

Fig. 1 illustrates the XRD patterns of pristine clay (MMT) and organically modified clay (OMMT). MMT exhibits a single peak at 2 $\theta$  of 6, which corresponds to a basal spacing of 14.6 Å, while the modified clay have two different characteristic peaks at 2 $\theta$

of 2.9 and 5.4, which correspond to a basal spacing of 30.9 and 16.3 Å, respectively. This corresponds to a successful organic modification of MMT. During organic modification, the long alkyl chains are intercalated into the galleries of MMT through an ion exchange reaction between Na<sup>+</sup> and the alkyl ammonium cations. Improved intercalation of the long alkyl chains leads to the larger interlayer spacing and the delamination of the clay mineral is enhanced within the polymer matrix. Based on XRD investigations, it was found that the surface modification of the clay particulates results in better intercalation of clay layers with the polymer matrix.

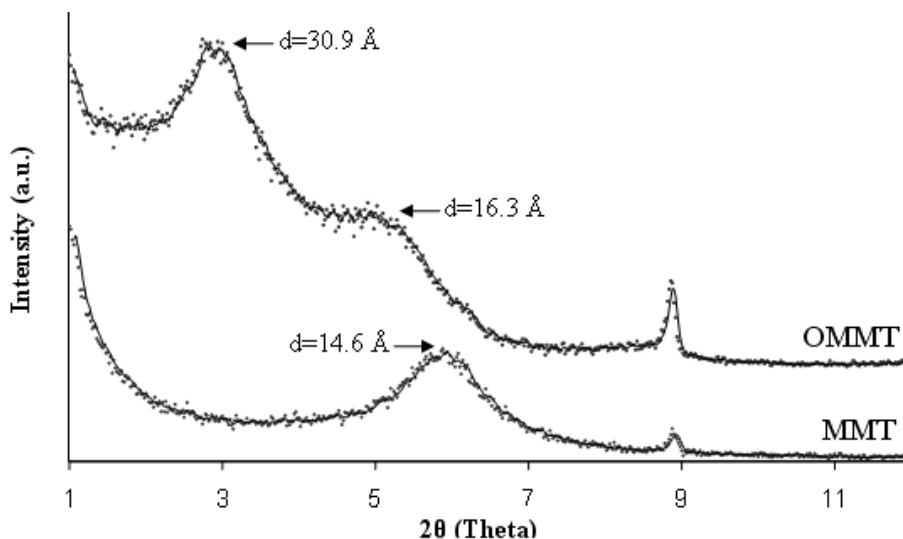


Figure 1. XRD patterns of Na<sup>+</sup>-montmorillonite and organo modified montmorillonite

Fracture surfaces SEM image of neat EPDM after tensile testing is illustrated in Fig. 2. The effects of blending time, temperature and speed on the morphology of the nanocomposite were revealed with SEM fracture surface examination. Fracture surfaces of the nanocomposites with 10 wt. % clay content are shown in Fig. 3. In general, homogenous dispersion of clay particles and vulcanization aids within the EPDM matrix was achieved. In addition to this, no significant effect of blending temperature and rotor speed on the morphology was observed within the range of selected parameters. It was observed that the fracture mode of the neat EPDM was altered due to the addition of OMMT particles. The neat EPDM has a characteristic cross-hatched failure pattern while OMMT/EPDM nanocomposites exhibit a typical line-flow pattern in their own fracture mechanisms.

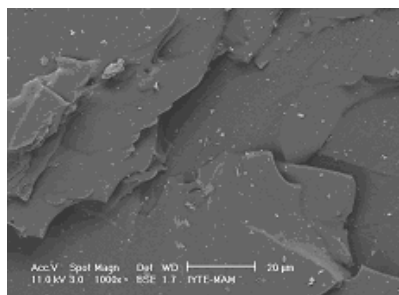


Figure 2. Backscattered SEM fracture surface micrograph of neat EPDM after tensile testing

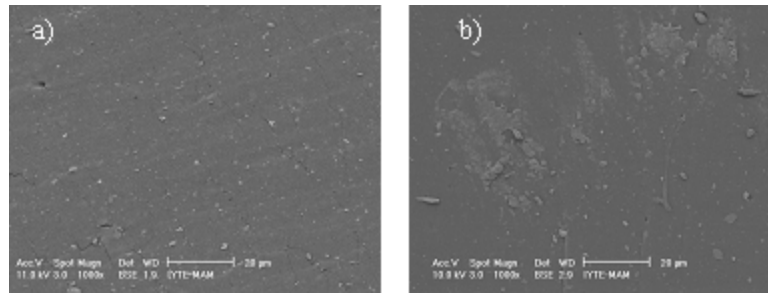


Figure 3. Backscattered SEM fracture surface micrographs of EPDM/ 10 wt. % OMMT nanocomposite blended with a) 60 and b) 90 rpm (Blending temperature and blending time are set to 150°C and 15 min, respectively)

## Mechanical Properties of Nanocomposites

### Effects of Blending Time on the Mechanical Properties

In the first stage, the mechanical properties of neat EPDM and EPDM/OMMT composites were examined by changing the blending time while the blending temperature and rotor speed were fixed at 150°C and 90 rpm, respectively. The average tensile strength of the neat EPDM was measured as 0.97 MPa. The tensile strength of the EPDM increased by 142.1%, and 315.8%, respectively with the addition of 5 and 10 wt. % of OMMT into the polymer matrix for blending time of 10 min (Fig. 4 (a)).

The strength of neat EPDM and EPDM/ 5 wt. % OMMT nanocomposites remained almost constant as a function of blending time. However, for EPDM/ 10 wt. % OMMT nanocomposites an important decrease in the tensile strength values was observed. On the other hand, the plasticization effect of both alkyl ammonium surfactant and EPDMgMA compensates the tensile values as a decrement although the intercalation of EPDM molecules into the clay layers is promoted by longer blending time.

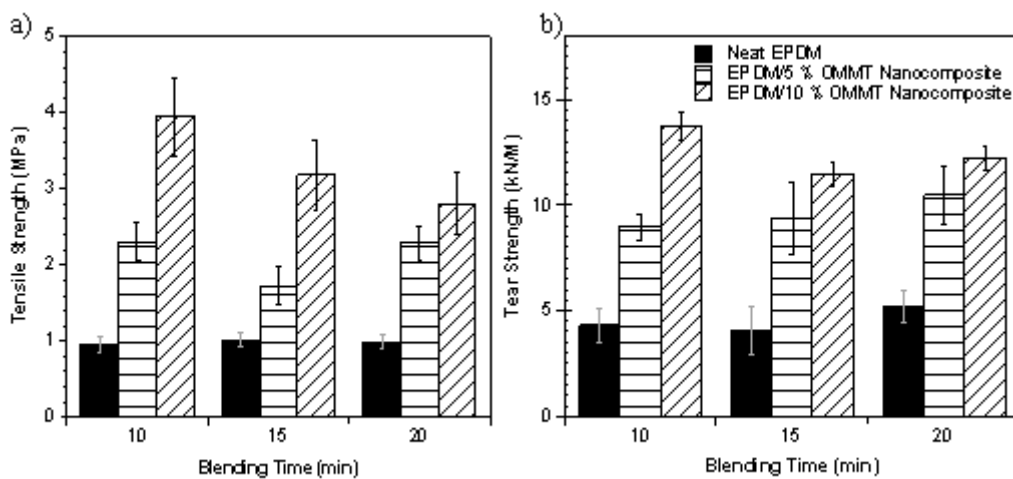


Figure 4. a) Tensile strength and b) tear strength values of neat EPDM and its nanocomposites containing 5 and 10 wt. % of OMMT with respect to various blending times including 10, 15 and 20 min

The same trend seen in strength values was observed when the other mechanical properties of the nanocomposites, such as elongation at break and modulus at 100% elongation are evaluated as summarized in Table 1. In general, the elongation and modulus values improved significantly with the addition of OMMT particles into EPDM. It was also obtained that as the amount of modified clay increase in polymer matrix, the mechanical properties are not always affected positively. The increase in the amount of modified clay increases the amount of surfactant and the compatibilizer which causes a plasticization effect within the structure. As the blending time is increased, the temperature of the nanocomposite system is increased because of the shear forces and friction. That phenomenon also causes the degradation of polymeric molecules indicating a loss in mechanical strength.

Table 1. Effect of mixing time and the OMMT content on elongation at break, modulus at 100% extension and tear strength for neat EPDM and EPDM/OMMT nanocomposites (Standard deviations are given in parenthesis)

Blending Time (min)	10			15			20		
Sample	Neat EPDM	EPDM / 5%OMMT	EPDM / 10%OMMT	Neat EPDM	EPDM / 5%OMMT	EPDM / 10%OMMT	Neat EPDM	EPDM / 5%OMMT	EPDM / 10%OMMT
<b>Elongation at Break (%)</b>	163.87 (±33.37)	240.20 (±20.60)	357.86 (±27.38)	179.80 (±21.27)	182.69 (±17.06)	333.62 (± 34.53)	164.61 (±23.31)	252.43 (±26.23)	284.76 (±29.62)
<b>Modulus at %100 Elongation (MPa)</b>	0.74 (±0.01)	1.13 (±0.02)	1.31 (±0.06)	0.74 (± 0.01)	1.11 (± 0.01)	1.23 (± 0.04)	0.72 (±0.02)	1.12 (±0.04)	1.24 (±0.02)

### Effects of Blending Temperature on the Mechanical Properties

To investigate the effects of blending temperature on the mechanical properties of neat EPDM and its nanocomposites containing 5 and 10 wt. % OMMT, the blending temperature and OMMT content were altered; while the blending speed and time were fixed at 90 rpm and 15 min. The tensile strength of neat EPDM was measured as 0.85 and 0.93 MPa for 120° and 150°C, respectively as shown in Fig. 5 (a). At blending temperature of 120°C, addition of 5 and 10 wt. % of OMMT increases the average tensile strength of neat EPDM by 148 % and 281 %, respectively. On the other hand, as the blending temperature is increased from 120° to 150°C, the tensile strength of neat EPDM and EPDM/OMMT nanocomposites remained almost constant.

Similar to tensile strength values, addition of OMMT into EPDM matrix significantly improves the elongation at break and modulus values as shown in Table 2. For 120°C blending temperature, the average elongation at break and modulus values of neat EPDM is improved by 76.4 %, and 52.7 % for 5 wt. % OMMT addition and by 133.5 % and 77 % for 10 wt. % OMMT addition. The elongation at break values increases due to increased temperature from 120°C to 150°C for neat EPDM. However, for EPDM/5% OMMT nanocomposites, as the temperature of blending increased from 120 °C to 150 °C, elongations at break values were dropped by 18 % and 23.36 %, respectively. For EPDM/10 wt. % OMMT system, the increase of blending temperature resulted with the increase of elongation at break value, while the other mechanical properties remained

almost constant. These results imply that clay layers within EPDM matrix has a strong reinforcement effect that the strength and stiffness values are significantly improved by the presence of clay layers. In addition to improvements on the strength values, the significant improvements on the elongation values imply that the toughness of the EPDM is increased by the incorporation of clay layers with the EPDM matrix.

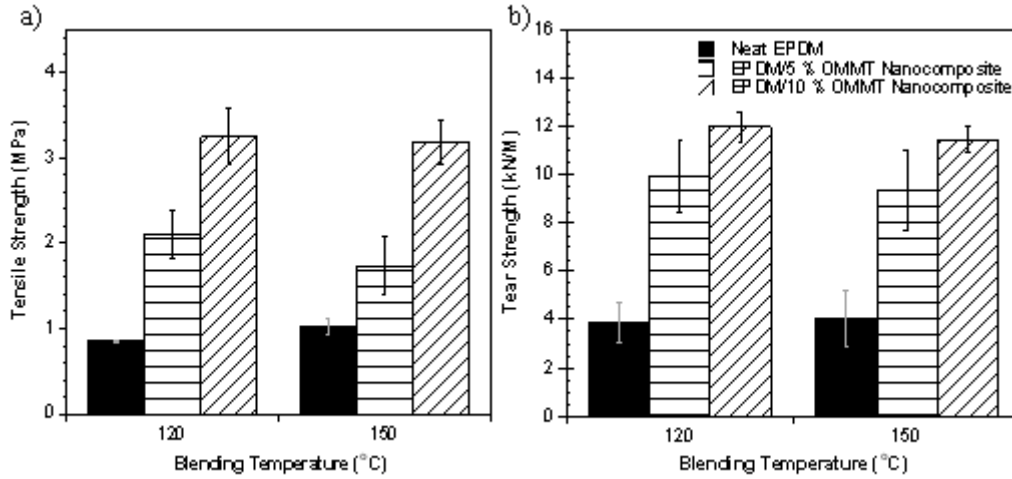


Figure 5. a) Tensile strength and b) tear strength values of neat EPDM and its nanocomposites containing 5 and 10 wt. % of OMMT with respect to various blending temperatures of 120 and 150°C

Table 2. Effect of temperature on elongation at break and modulus at 100% extension for neat EPDM and EPDM/OMMT nanocomposites (Standard deviations are given in parenthesis)

Blending Temperature(°C)	120			150		
	Neat EPDM	EPDM / 5%OMMT	EPDM / 10%OMMT	Neat EPDM	EPDM / 5%OMMT	EPDM / 10%OMMT
<b>Elongation at Break (%)</b>	135.16 (± 7.44)	238.36 (± 27.06)	315.63 (± 27.54 )	179.80 (± 21.27)	182.69 (± 17.06)	333.62 (± 34.53)
<b>Modulus at %100 Elongation (MPa)</b>	0.74 (± 0.02)	1.13 (± 0.03)	1.31 (± 0.03)	0.74 (± 0.01)	1.11 (± 0.01)	1.23 (± 0.03)

### Effects of Blending Speed on the Mechanical Properties

To investigate the effect of blending rotor speed on the properties, blending temperature and time were fixed at 150°C and 15 min, respectively. Increasing the rotor speed increased the tensile strength of neat EPDM and EPDM/10 wt. % OMMT nanocomposites while the tensile strength of EPDM/5 wt. % OMMT nanocomposite decreased (Fig. 6 (a)).

Similar to tensile strength values, addition of OMMT into EPDM matrix significantly improves the elongation at break and modulus values (Table 3). For 60 rpm blending

rotor speed, the average elongation at break and tensile modulus values of neat EPDM (149.17 %, and 0.74 MPa) is improved by 59 %, and 54 % for 5 wt. % OMMT addition and by 76.77 %, and 70.27 % for 10 wt. % OMMT addition. The tensile strength, elongation at break and tensile modulus values increases due to increased rotor speed from 60 rpm to 90 rpm for neat EPDM and EPDM/10% OMMT nanocomposite while tensile modulus values remain almost constant for the same case. These results imply that the shear forces applied on the silicate layers increases due to blending rotor speed. The increased forces improve the intercalation of the silicate layers and results with better dispersion of the silicate layers within the EPDM matrix.

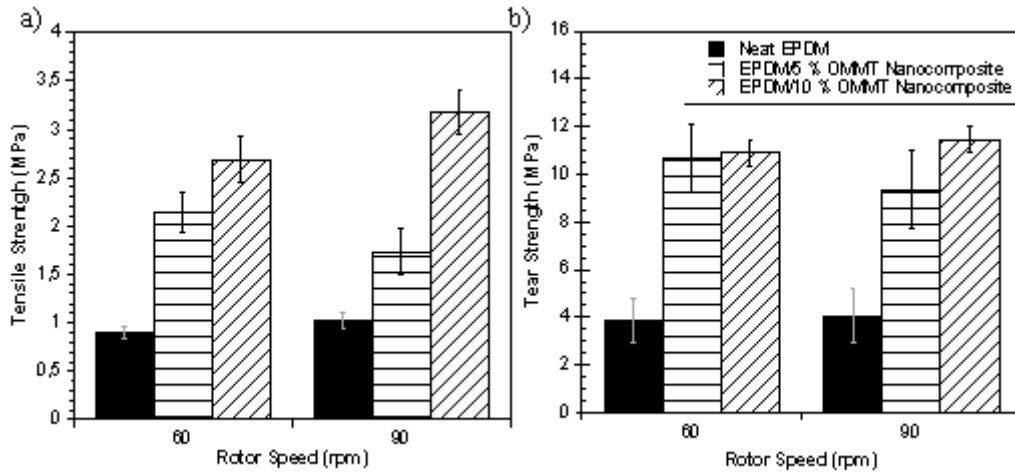


Figure 6. a) Tensile strength and b) tear strength values of neat EPDM and its nanocomposites containing 5 and 10 wt. % of OMMT with respect to blending speeds of 60 and 90 rpm

Table 3. Effect of rotor speed and the OMMT content on elongation at break and modulus at 100% extension for neat EPDM and EPDM/OMMT nanocomposites (Standard deviations are given in parenthesis)

Blending Rotor Speed (rpm)	60			90		
	Neat EPDM	EPDM / 5%OMMT	EPDM / 10%OMMT	Neat EPDM	EPDM / 5%OMMT	EPDM / 10%OMMT
<b>Elongation at Break (%)</b>	149.17 (±15.24)	237.19 (± 22.37)	263.69 (± 20.33)	179.80 (±21.27)	182.69 (± 17.06)	333.62 (± 34.53)
<b>Modulus at %100 Elongation (MPa)</b>	0.74 (± 0.01)	1.14 (± 0.02)	1.26 (± 0.02)	0.74 (± 0.01)	1.11 (± 0.01)	1.23 (± 0.04)

However, for EPDM/5 wt. % OMMT nanocomposite, as the blending rotor speed increased from 60 rpm to 90 rpm, the tensile strength, elongation at break, and tensile modulus at 100% elongation values were dropped by 19.53 %, 30 %, 2.6 %, respectively.



## **Tear Properties of Nanocomposites**

Addition of modified clay layers (OMMT) increased the tear strength values of neat EPDM. By 5 wt. % addition of clay, while the tear strength of neat EPDM was increased about 158.7% at blending temperature of 120°C, it was increased about 130.5% at blending temperature of 150°C. When the rotor speed was 60 rpm, the addition of 5 wt. % clay increased the tear strength of neat EPDM about by 176.9%. Moreover, addition of 10 wt. % OMMT increased this value by 182.9%.

As the tear strength of 5 wt. % OMMT/EPDM nanocomposite increased slightly with time, 10 wt. % OMMT/EPDM nanocomposites showed the same behavior with neat EPDM (Fig. 4 (b)). At high clay contents, the increased amount of surfactant and compatibilizer were resulted with reduced tear strength due to plasticization effect.

When the influence of the blending temperature and blending speed were investigated, there was no significant effect of the blending temperature and speed on the tear strength of neat EPDM and OMMT/EPDM nanocomposites as shown in Fig. 5 (b) and 6 (b), respectively. The tear strength values showed a similar tendency with tensile properties of the nanocomposites.

## **CONCLUSIONS**

This work revealed the effects of clay content and mixing conditions on the microstructure and mechanical behavior of EPDM/OMMT nanocomposites. According to the XRD and SEM results, the clay layers dispersed uniformly in EPDM. The mechanical test results revealed that the addition of OMMT into EPDM matrix significantly improves the tensile strength of the polymer nanocomposites. To compare the effect of different blending times, there was a dramatic decrease in the mechanical properties of EPDM/ 10 wt. % OMMT nanocomposites when increasing blending time. On the other hand, the mechanical properties of neat EPDM and EPDM/ 5 wt. % OMMT nanocomposites remained almost constant. For blending temperatures of 120 and 150°C and rotor speeds of 60 and 90 rpm, the mechanical properties of neat EPDM and EPDM/ 10 wt. % OMMT nanocomposites remained almost constant but for EPDM/ 5 wt. % OMMT nanocomposites, they were slightly decreased. It was found that blending conditions needs to be optimized to obtain the highest performance from the OMMT/EPDM nanocomposites.

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