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# Original Research article

# Thermal Degradation and the Morphology of Chlorosulfonated Polyethylene/Nanoclay Nanocomposites

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ARTICLE INFORMATION	ABSTRACT
Received: 23 September 2018 Received in revised: 21 October 2018 Accepted: 24 November 2018 Available online: 01 may 2019	The interaction in the nanoclay is expected to be improved as the result of the amalgamation of hypalon chlorosulfonated polyethylene rubber (CSM) with nanoclay in the presence of compatibilizer agent nature rubber (ENR). Melt intercalation method was also applied to prepare CSM phases. The effect of ENR and nanoclay on the mixture behavior was also detected by scanning electron microscopy (SEM). Thermogravimetric analysis (TGA)
KEYWORDS	contributed to scrutinize the thermal properties of the prepared NR/CSMs.
Nanocomposite Hypalon XRD Thermal degradation Morphology	The outcomes of the X-ray diffraction study are compatible with those of thermal analysis. The results indicated that CSM was infixed into nanoclay. Regarding the fact that the amount of the nanoclay content was lower than 12 wt%, Flynn-Wall-Ozawa (F.W.O) and Kissinger–Akahira–Sunose (K.A.S.), methods were applied to specify the energy of the apparent activation of the nano/hypalon systems holding 3, 6, 9 wt% of nano. The upshots demonstrated that increasing the thermal stability of hypalon was directed into boosting the nanoclay content. This divulges that there is an interplay between nanoclay, ENR and hypalon. Comparing to micro-filled ENR/CSM and ENR/CSM cross linked systems, it is predicted to conclude an enhanced thermal stability, higher values of Tg, better dispersion the nanoclay and more polish without any cracks.

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# **Graphical Abstract**



# Introduction

Thermal stability is mainly dealt with the ability of a material to provide the required properties such as strength, toughness, elasticity, etc., in accelerated temperatures [1]. It is essential to contemplate the decomposition of polymers for the sake of heating in order to design the elastomeric materials with developed properties for specific application. Within the last few years, researchers have highly heeded the elastomers based on different network precursors (i.e, rubber blends) since they are easy to prepare, especially once the individual network precursors are known. The final product firmly relies on the effect of the rubber blending on the thermal stability. New materials with a wide spectrum of properties are brought about by the operation of polymer which are not available in the parent polymers.

So far, various reviews have analyzed the chemical alteration of rubbers through grafting onto a polymer chain, inter-chaining reactions and developing the formation of interpenetrating networks [2]. As polyolefins have been identified as the most widely used class of polymers [3] in the world, they have been combined with various elastomers. They were commercially practiced so as to diminish the low-temperature brittleness and to develop the impact strength [4]. The simultaneous chlorination and chlorosulfonation of polyethylene resulted to achieve ted polyethylene (CSM). CSM is made up of an improved polyethylene rigidity with chloro and sulfonyl chloride side groups. Moreover, cross linking is obtained using various curing methods (e.g., sulfur, peroxides, maleimide, etc.) in order to create a commercial generic hypalon rubber [4]; CSM has been recognized as the most significant and applicable rubber. It is commonly used as a sheath material in electrical cables

practiced in nuclear power facilities. In addition, CSM is put into practice in auto supplies, lifesaving equipment, building materials, etc.

Nanostructured composites have been widely investigated in recent years due to their interesting mechanical, thermal, optical, magnetic and barrier properties for the sake of their layered inorganic solids and organic polymers [5]. Immensely large interface surfaces are responsible for the benefits such as reinforcement with a low nanofiller loading in polymer/clay nanocomposites. It should be considered that some of these improvements could be obtained with conventional fillers only at 20-50% loading. Thus, enormous improvements are brought about by relatively small amounts of plate like clay particles in composite properties in case they are well-dispersed into individual plates [6]. As the type of reaction relies on the interaction between the individual network precursors, it is significant to consider the degree of dispersion occurring during the degradation of the final cross linked materials [7]. CSMs are broadly executed in some areas such as coupling agent, wiring, wire and cable jacketing and single-ply roofing membrane [8, 9]. The CSM may be achieved by solution method, gas-solid method, and solution suspension method. For the time being, Dupont and Jilin petrochemical company are producing CSM using solution method in CCl<sub>4</sub> solvent [10]. Since CCl<sub>4</sub> it is identified as one of the ozone decreasing gases, it has been hampered. Due to literature, no other appropriate solvent has been found to be capable of preparing CSM by solution method in literature. Therefore, the development of CSM has been slowed down.

Nowadays, thermal analysis is conducted by the contribution of commercially available equipment together with remarkable investigations on the thermal behavior of materials. Both thermogravimetry and DSC will provide information about the nature and the extent to which the material is degraded. Tanrattanakul and Petchkaew (2006) studied the blends of CSM with NR. According to their report, such blends could not be mixed, except for NR rich blends (70-80% wt of NR). Furthermore, they concluded that CSM content can make the oil and ozone resistant properties of the blends increase [10]. In case an appropriate compatibilizer like epoxidized natural rubber (NR) was introduced, further improvements in mechanical properties and compatibility of the blends could be achieved. The current research has scrutinized the influence of nanoclay on mechanical properties and thermal stability of matrix blend based on polychloroprene and chlorosulfonated polyethylene (CR/CSM) rubber. There are three types of thermal degradation products. The first type includes components in which the molecular dimensions resemble to monomer through providing the opportunity for the more detailed analyses. The second type holds substances which are volatile at the degradation temperature but non-volatile at ambient temperature. They are mostly the fragments which are larger than the monomer. Their precise

chemical structure was not usually figured out even though they might be adverted to dimeric, trimeric ones and so forth. The third type of substances is identified as the non-volatile residue often remaining insoluble (However, knowledge of the mechanism of degradation reaction combined with spectral data can provide some information about its structure).

The current paper scrutinizes the influence of combining the benefits of augmenting ENR and nanoclay to hypalon in order to evolve improved matrix material and modify the thermal properties. The main purpose of the present study is to pore over the effect of compatibilize reagent and nano-sized concentration on the morphology and thermal properties. As predicted, our study lodged the thermal decomposition of pristine nanocomposite investigated for comparison purpose. Thermogravimetric analysis (TGA) was applied to measure the weight loss and the derivative weight loss of the cured hypalon.

## **Experimental**

#### Material

Chlorosulfonated polyethylene rubber (CSM) with mooney viscosity of 56 [ML(1+4) at 100 °C] (hypalon 40) was purchased from DuPont Co., USA. ENR with the mooney viscosity of ML (1+14) 5140 was purchased from Kumpulan Guthrie Sdn. Bhd., Seremban, Malaysia. The ENR contained 50 mol% epoxidation (denoted further as ENR 50). Magnesium oxide (Rangdineh Pars Co., Iran) and stearic acid (Unichema Co., Malaysia) were used as activators. Montmorillonite modified with octadecyl trimethyl ammonium salt (nanomer I.28E) supplied by Southern Clay Products (Gonzales, TX) Cloisite 30B (C30B), USA was practiced in this study. Sulfur (Tesdak Co. Iran) was used as a vulcanizing agent. Tetramethylthiuram disulfid (TMTD) and mercaptobenzothiazole (MBT) from (Reliance Technochem Co., Thailand) were employed as an accelerator.

#### Compounding

The samples were prepared by a boundary internal mixer (Germany) maintained at 80 °C according to ASTM D-15-627. The mixing time was 20 minutes. Then, the vulcanization agents were added. The specimens were cured and molded at 155 °C in a heated hydraulic press under a pressure of 10 MPa for the optimum cure time. The samples were named either as CSM-*x* or CSM/NR-*x* where *x* denotes the content of Cloisite 30B in phr. The CSM/NR-*x* samples included 3, 6 and 9 Phr NR. All the formulations similarly contained 5 phr MgO, 2 phr St. A, 2 phr TMTD, 0.5 phr MBT, and 1 phr sulfur (Table 1).

Compound	CSPE	Clay	MgO	St.A	TMTD	MBT	Sulfur
Pure CSPE	100	0	5	2	2	0.5	1
CSPE-3	100	3	5	2	2	0.5	1
CSPE-6	100	6	5	2	2	0.5	1
CSPE-9	100	9	5	2	2	0.5	1
CSPE/ER-3	100	3	5	2	2	0.5	1
CSPE/ENR-6	100	6	5	2	2	0.5	1
CSPE/ENR-9	100	9	5	2	2	0.5	1

Table 1. The CSM compounds was cured

## Testing

Tis experiment includes items such as Philips PW1840 X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda$ = 0.154 nm) at a generator voltage of 40 kV and current of 30 mA. The data were collected at the ambient temperature with a scanning speed of 0.02°/s and step size of 0.02°.

The molded compounds were in transmission in the interval of  $2\theta = 1^{\circ} - 12^{\circ}$ , while powder samples were scanned in reflection.

Cambridge apparatus equipped with an energy beam of 15 kV was practiced to implement the scanning electron microscopy (SEM). The prepared samples were cryogenically fissured in liquid nitrogen and then coated *via* gold vapor deposition method using a vacuum sputter before observation.

Regarding the ASTM D6370 under nitrogen atmosphere, the degradation of the nanocomposites was examined by a STA PT1600 thermogravimetric analyzer from Gotech (Germany). The analysis of non-isothermal analysis was done in a temperature ranging from 25 to 500 °C at distinct heating rate (5, 10 and 20 °C/min) for each sample. Nitrogen flow was maintained at 33 mL/min.

# Kinetics of non-isothermal degradation

The following equation (Eq. 1) has been remarked as the basis of all kinetic analyses of nonisothermal data (TGA, DTA) [11].

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = Af(\alpha) \exp((-\frac{E}{RT}))$$
Eq. 1

where  $\alpha$  is the degree of conversion; *A* indicates the pre-exponential factor, *E* stands for the activation energy, *R* shows the gas constant; *T* shows the reaction temperature; *f*( $\alpha$ ) displays the differential conversion function, and  $\beta = \frac{dT}{dt} = \text{const}$  is the linear heating rate.

#### **Isoconversional methods**[12]

The second method holds the isoconversional methods of FWO, Friedman and KAS also known as "model-free" method. This method assumes that the alteration of the heating rate is not affected by

the conversion function  $f(\alpha)$  for all values of  $\alpha$ . It is dealt with measuring the temperatures associated with constant values of  $\alpha$  from experiments at different heating rates  $\beta$ .

**Friedman method (FR) [13]:** The differential isoconversional method suggested by Friedman (FR method) is based on (Eq. 2):

$$ln\beta \frac{d\alpha}{dt} = lnA + lnF(\alpha) - \frac{E}{RT}$$
<sup>(2)</sup>

In (Eq. 2), for  $\alpha$ =const., followed by plotting  $ln \left(\beta \frac{d\alpha}{dt}\right)$  vs. (1/*T*), obtained from the thermograms recorded at several heating rates, a straight line is obtained whose slope allows for evaluation of the activation energy.

### Flynn-Wall-Ozawa method (FWO)

Flynn and Wall and Ozawa independently suggested the isoconversional integral method [14] based on Doyle's approximation [15] of the temperature integral. This method is founded on equations (3) and (4).

$$ln\beta = ln(\frac{AE}{Rg(\alpha)}) - 5.331 - 1.053(\frac{E}{RT})$$
(3)

Where

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$$
(4)

Where in (Eq. 3) for  $\alpha$ =const., the plot of *ln b*v.s. (1/*T*) obtained from the thermograms recorded at several heating rates, should give a straight line whose slope makes it possible to evaluate the activation energy.

#### Kissinger-Akahira-Sunose method (KAS)

(Eq. 5) indicates the conversional integral method due to the Coats-Redfern approximation [16] of the temperature integral.

$$ln(\frac{\beta}{T^2}) = ln(\frac{AR}{Eg(\alpha)}) - \frac{E}{RT}$$
(5)

In (Eq. 5), for  $\alpha$ =const., the plot of  $ln(\beta/T^2)$  vs. (1/T) taken from thermograms recorded at several heating rates results in a straight line whose slope could be practiced to assess the activation energy.

#### **Results and Discussion**

#### Structure of the NR/CSM nanocomposites

Figure 3. illustrates XRD spectra of CSM/nanoclay and (0, 3, 6 and 9 wt%). It is demonstrated that the characteristic peaks related to the layered structure of clay mineral in XRD spectrum will dislodge into lower angles if the intercalation of rubber macromolecules into the nanoclay layers occurs, whereas the diffraction peak is tending to be disappeared in case the layers are properly delaminated. Figure 1. features out that the basal spacing of the CSM-3 was 4.93 nm. The nanoclay pattern revealed a broad intensive peak almost  $2\theta$ =1.79° corresponding to a basal spacing (d<sub>001</sub>) of 4.93 nm, whereas the nanoclay/CSM patterns depicted that the d<sub>001</sub> reflection of the clay moved to lower angles around  $2\theta$ =1° related to a spacing of 8.80 nm. Holistically, it is inferred that the chains of CSM were infixed into the nanoclay. The XRD outcomes substantiate dan intercalated structure [17].



Figure 1. XRD spectra of CSM/nanoclay nanocomposite (0, 3, 6 and 9 wt%) without compatibilizer agent

As the nanoclay raised to 6 wt%, it is featured out that the CSM chains were embedded into the nanoclay more than 3 wt%, but intense peak (peak amount #0) was dwindled up to 9 wt% for the sake of agglomeration in nanoclay (Table 2).

Compound	20	x/nm
Cloisite 30B	-	1.8
CSM-3%	1.79	4.93
CSM-6%	1.73	5.12
CSM-9%	1.07	4.26
CS-ENR-3%	1.00	8.80
CSM-ENR-6%	1.15	7.70
CSM-ENR-9%	1.75	5.02

Table 2. Effect of the nanoclay and compatibilizer agent content on the structure of the CSM nanocomposites

When compatibilizer agent (ENR) is utilized in nanocomposites (Figure 2), it is clear that the XRD peak will be changed into a much smaller angle in the infixed nanocomposites if the intercalation of rubber macromolecules into the nanoclay layers occurs.



Figure 2. XRD spectra of CSM/nanoclay nanocomposite (0, 3, 6 and 9 wt%) with compatibilizer agent

Figure 2. and Table 2. present that nanocomposites display five different specifications of peaks with  $2\theta$  values commencing from 1 to 1.79. Furthermore, this table also illustrates that CSM nanocomposite has scored the highest amount which is 3%. CSM/NR nanocomposite has recorded the lowest amount which is 3%. The results of TEM, SEM and XRD prove the intercalated structure.

# Morphological observation

Figure 3. and 4. show SEM photographs of the nanocomposites. CSM matrix is exhibited in light color and both nanoclay layers and their aggregates are presented in dark lines. Notably, the SEM photographs indicate that the nanoclay layers were homogeneously distributed into the CSM matrix. The infixed and partially delaminated layers coexisted in the nanoclay/CSM nanocomposites. Figure 3b and 3c reveal the fissure surface of 3 and 6 wt% nanoclay dispersed CSM matrix. In comparison to those containing 3 and 6 wt%, the SEM microphotographs of nanocomposite containing 9 wt% are less homogeneous (Figure 3d).

The original layered structure is not divulged by the clay, this is properly distributed in the CSM matrix, specifically in presence of ENR compatibilizer (Figure 4a, b and c). The related structure can be referred to as partially exfoliated and intercalated one [18]. It is considered that the dispersion of the organoclay is far less homogeneous in the uncompatibilized. As the presence of compatibilizer agent in nano-size can improve the dispersion of the nanocomposites, the surface in nano also fills nanocomposites (Figure 4). This result indicates that intercalated nanocomposites are formed.



**Figure 3.** Scanning electron microscopy images of the fractured surface of nanocomposites of **a**: 0 wt%, **b**: 3 wt%, **c**: 6 wt%, and **d**: 9 wt%



**Figure 4.** Scanning electron microscopy images of the fractured surface of nanocomposites of **a**: 3 wt%, **b**: 6 wt%, and **c**: 9 wt% with compatibilizer agent

# Analysis of thermal properties

TGA instruments have been practiced to scrutinize the thermal properties of the modified PE by chlorosulfonation [19–22]. In the current study, c carries out the thermal behaviors of CSM with nanoclay and compatibilizer agent content. Figures 5, 6, 7, 8, 9 and 10 depict TGA curves and the corresponding derivative thermo gravimetric (DTG) curves of CSMs. The degradation of CSM has gone through three weight loss steps. On the TGA curves of CSM, there is a slight weight loss between 170 °C, 240 °C mainly made by the dehydrochlorination of CSM resembling to the decomposition of PVC [23].



Figure 5. Mass loss (TGA%) versus temperature for CSM nanocomposites at the 5 C min<sup>-1</sup>



Figure 6. DTG versus temperature for CSM nanocomposites at the 20 C min<sup>-1</sup>



Figure 7. Mass loss (TGA%) versus temperature for CSM nanocomposites at the 10 C min<sup>-1</sup>



Figure 8. DTG versus temperature for CSM nanocomposites at the 10 C min<sup>-1</sup>



Figure 9. Mass loss (TGA%) versus temperature for CSM nanocomposites at the 20 C min<sup>-1</sup>



Figure 10. DTG versus temperature for CSM nanocomposites at the 20 C min<sup>-1</sup>

It is estimated that the percentage of weight loss was about 35% for raw rubber in the first phase, whereas this percentage was 31% and 27% for nanocomposites with and without compatibilizer, respectively. This shows the enhanced thermal stability of hypalon rubber. Such improvement in thermal stability of hypalon rubber can be associated with the distribution of silicate layers in matrix with higher thermal stability than of polymer. Consequently, it prevents the penetration of oxygen into the polymer mass.

The second weight loss recorded around 420 °C and mainly related to the degradation of dehydrochlorinated residues and the splitting off SO<sub>2</sub>Cl groups of CSM [24]. The second step weight loss beginning at 420 °C was referred to the decomposition of the main chain of CSM (Indeed, the pure hypalon is between 420-460 °C and nanocomposite containing compatibilizer agent is between 435-480 °C) [24]. Moreover, the percentage of weight loss is equal to 48% for both of these nanocomposites in the second phase of degradation. As a result, the percentage of weight loss is almost 53% for raw rubber in this phase.

The third weight loss was made by new network degradation at 500 °C. All these outcomes indicated that the thermal stability of CSM decreased by increasing the chlorine and sulfur content. Considering the two network precursors (rubbers), the degradation behavior of the elastomer insignificantly differs from that of the individual rubber components. It has been reported that the incorporation of a second polymer can improve the thermal stability of one type of polymer. FWO, KAS, and Friedman methods specified the perceptible activation energy for the nanocomposites holding 0, 6 wt% of nanoclay and compatibilizer agent 9 wt% of nanoclay.

Compared to matrix, both initial degradation temperature (Ti) and 50% mass loss temperature (Td50%) monotonously shifted to the higher temperatures by increasing clay loading, indicating a significant improvement of thermal stability. CSM starts to degrade at 260 °C (Td10%) and Td50% occurs at about 448 °C. After incorporation of 6 wt% and 9 wt% GO, Td10% values increased by 20 °C (280 °C) and by 25 °C (285 °C); respectively. Td50% values were also enhanced by 5 °C (452 °C) for 6 wt% clay and by 19 °C (467 °C) for 6 wt% clay loading. The effect of clay has on temperatures corresponding to 10 and 50% weight loss and char residue remaining at 600 °C are given in Table 3.

Sample	Td10% (°C)ª	Td50% (°C) <sup>ь</sup>	RM (%) <sup>c</sup>		
Pure CSM	260	448	10		
CSM-6%	280	452	12.4		
CSM-9%	285	467	18.2		

Table 3. Effect of clay on thermal properties<sup>a</sup> of CSM-Clay

<sup>a</sup> The mass loss temperature observed by TGA at a 5 °C/min heating rate in nitrogen

<sup>b</sup> Tid is the temperature at which initial loss of mass was observed

<sup>c</sup> Residual mass at 600 °C

As the thermal stability of the nanocomposites is increased, the content of nanoclay is enhanced. In fact, the activation energy is grown. High activation energy is dealt with a high temperature sensitivity of the material. It is observed that the rubber amalgamation presented higher activation energy than the pure components. Undoubtedly, blending contributes to better thermal stability [25]. Integral isoconversional methods like KAS, FWO are appropriate for the analysis of TGA curves since they do not require the experimental data to be distinguished in advance. The activation energy taken from models based on a single heating rate reflected less amount in comparison to the ones based on multiple rate.

Both the Friedman technique and the experimental data are practiced to calculate the results of degradation modeling the nanocomposites in three compositions. Two sets of curves are indicated and each one holds the plot of  $ln(d\alpha/dt)$  against 1/T giving the *E* values. The other set is  $ln(1-\alpha)$  against  $10^3$ ( $T^{-1}$ ) [12] giving the *n* values in first two steps (Table 4). It is noted that S1, S2, S3 are pure CSM, CSM-6 wt% nanoclay and CSM/ENR-6 wt% nanoclay, respectively (Figure 11a and b).

Sample	Log A	n	Ea (second)	Ea (first)		
Pure SPE	34.7	1.46	412.5	173.3		
CSPE-6	41.2	1.75	244.4	184.1		
CSPE/ENR-6	44.6	1.93	426.6	210.7		

Table 4. Activation energies and *n* determined by Friedman in first and second steps



Figure 11. DTG versus temperature for CSM nanocomposites by Friedman method

Activation energy (E<sub>a</sub>) calculated from two models varies greatly with conversion. If E<sub>a</sub> does not differ greatly from conversion, it is possible to explain the whole reaction intermission by a single kinetic model even if the actual reaction mechanism is complex. In fact, it is necessary to put into practice various models for this analysis. Table 5 summarizes the outcomes of the analytical methods to compare the kinetic parameters, while two various models including KAS's and FWO's values are mentioned here. As a whole, elastomers have a low thermal stability. The correlation coefficients evidently divulge that the correlation is acceptable in a broad temperature range. All the correlation coefficients are higher than 0.99. Hence, it demonstrates a very suitable correlation of the analysis in the aforementioned temperature range. The thermal stability of the nanocomposites gets increased as the content of nanoclay is accelerated. In consequence, the activation energy is also eked out (plots not shown here) [12]. Results authenticate improved thermal stability of hybrid materials.



Figure 12. KAS plots of nanocomposites at various fixed conversions. A) KAS and B) FWO methods

method	Pure CSPE			CSPE-6				CSPE/ENR-6				
	KAS		FWO		KAS		FWO		KAS		FWO	
Conversion	Ea	r	Ea	r	Ea	r	Ea	r	Ea	r	Ea	R
0/05	144.1	0.990	181.5	0.993	155.1	0.993	194.1	0.998	206.1	0.999	257.1	0.997
0/10	159.7	0.995	201.8	0.996	173.2	0.992	214.3	0.995	235.4	0.999	293.3	0.990
0/15	169.8	0.996	214.6	0.997	189.8	0.996	238.2	0.990	251.7	0.997	312.4	0.995
0/20	182.1	0.997	228.2	0.997	213.9	0.995	258.7	0.994	270.2	0.992	332.7	0.995
0/25	207.4	0.992	255.2	0.996	238.5	0.990	288.4	0.993	-	-	-	-
0/40	-	-	-	-	419.3	0.994	510.5	0.993	456.3	0.995	565.7	0.993
0/45	429.1	0.995	521.7	0.990	443.9	0.997	559.5	0.990	476.1	0.990	590.1	0.997
0/50	381.7	0.990	474.8	0.994	433.1	0.992	547.1	0.995	486.2	0.994	609.3	0.992
0/55	380.5	0.994	475.6	0.998	437.5	0.996	557.1	0.995	475.3	0.995	598.4	0.996
0/60	376.4	0.995	474.4	0.995	436.2	0.995	552.3	0.997	481.8	0.990	610.9	0.995
0/65	370.9	0.996	470.3	0.991	434.8	0.990	552.7	0.991	475.1	0.994	608.8	0.990
0/70	373.7	0.994	476.1	0.994	427.3	0.994	542.5	0.994	478.2	0.993	615.3	0.994
0/75	363.2	0.997	451.7	0.995	431.4	0.999	547.3	0.995	467.2	0.992	600.2	0.993

Table 5. Activation energies determined by FWO and KAS methods

#### Conclusion

The current research probed the effect of chlorosulphonated polyethylene (CSM) rubber, epoxidized natural rubber (ENR) and their blend (ENR/CSM) on morphology and thermal degradation properties of this resin. ENR was blended in nanocomposites. SEM micrographs of the prepared nanocomposites divulged the changes and exchanges during the mixing process and formation of random nanocomposites. Moreover, it has indicated the miscibility and reaction compatibility. TGA curves displayed that the thermal decomposition of the nanocomposites came about in three stages regardless of natural rubber content and nanoclay. The degradation temperature was significantly improved through introducing ENR to CSM nanocomposites. Three different methods have been applied to analyze the TGA and DTG data. Each one of them represented various apparent kinetic parameters. Remarking the ENR and the presence of nanoclay, thermal stability of the nanocomposites gets boosted by increasing the rubber content. Conclusively, it might be the cause of rubber existence counted as a part of blend with lower thermal stability constituent. The activation energy for the degradation of CSM elastomer founded on rubber blend was higher than for pure CSM.

#### References

[1] Janowska G., Rybin´ski, P. J. Therm. Anal. Calorim., 2008, **91**:697

[2] Santhoskumar A.U., Jaya Chitra N. Chem. Method., 2019, 3:83

[3] Gupta S., Chowdhury S.R., Mishra J.K., Das C.K., Patra P.K., Tripathy A.K., Millins W., Banerjee M.S. *Mater. Lett.*, 2000, **46**:125

- [4] Giannelis E.P. Adv. Mater., 1996, 8:29
- [5] Merinska D., Malac Z., Hrnicirik J., Simonik J; Trlica J; Pospisil M; Capkova P; Weiss Z. Antec
- Conferences, 2001, **47**:2166
- [6] Wang Z., Ni H., Bian Y., Zhang M., Zhang H. J. appl. Polym. Sci., 2010, 116:2095
- [7] Jin F.L., Park S.J. J. Mater. Sci. Eng. A., 2008, 478:402
- [8] Tanrattanakul V., Petchkaew A. J. Appl. Polym. Sci., 2006, 99:127
- [9] Kotec J., Kenlar I., Studenovsky M., J. Baldrian., Polymer, 2005, 46:4876
- [10] Zhao R., Cheng S., Shun Y., Huang Y. J. Appl. Polym. Sci., 2001, 81:3582
- [11] Doyle C.D. J. Appl. Polym. Sci., 1962, 6:24.
- [12] Ali-Asgari Dehaghi H., Mazinani S., Zaarei D., Kalaee M., Jabari H., Sedaghat N. J. Therm. Anal.

Calorim., 2013, **114**;184

- [13] Friedman H.L. J. Polym. Sci., 1964, 6:183
- [14] Ozawa T. J. Therm. Anal. Calorim., 1970, 2;301
- [15] Doyle C.D. J. Appl. Polym. Sci., 1962, 6:639
- [16] Callister W.D. *Materials science and engineering: an introduction*. 4th ed. New York: John Wiley Sons Inc; 1997
- [17] Gu Z., Song G., Liu W., Gao J., Dou W., Lu P. J. Appl. Polym. Sci., 2010, 115:3365
- [18] Karger-Kocsis J., Wu C.M. Poly. Eng. Sci., 2004, 44:1083
- [19] Tripathy A.R., Patra P.K., Sinha J.K., Banerji M.S. J. Appl. Polym. Sci., 2002, 83:937
- [20] Varma A.J., Kondapalli P., Deshpande S.V. Polym. Degrad. Stabil., 1999, 63:1
- [21] Chailan J.F., Boiteux G., Chauchard J., Pinel B., Seytre G. Polym. Degrad. Stabil., 1995, 47:397
- [22] Chowdhury S.R., Das C.K. J. Appl. Polym. Sci., 2000, 78:707
- [23] Minsker K.S., Steklova A.M., Zaikov G.E. Polym. Degrad. Stabil., 1990, 28:227
- [24] Serageldin M.A., Wang H. *Thermochem. Acta*, 1988, **125**:247

[25] Markovic' G., Marinovic'-Cincovic' M., Vodnik V., Radovanovic' B., Budinski-Simendic'J., Veljkovic O. *J. Therm. Anal. Calorim.*, 2009, **97**:999

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