

# Thermal Stability, Aging Properties, and Flame Resistance of NR-Based Nanocomposite

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**ABSTRACT:** Polymer/clay nanocomposites have some unique properties due to combination of flame resistance and improved mechanical and thermal stability properties which are important to enhance the material quality and performance. The objective of this work was to investigate the effect of organically modified montmorillonite (org-MMT) on the thermal and flame retardant as well as hardness and mechanical properties of the nanocomposites based on the natural rubber (NR). It was shown that by the addition of 3 wt % of org-MMT to NR, its aging hardness rise was decreased more than 55% and the ignition

time was delayed about 150%. The reduction in heat release rate peak value was equal to 54% compared to the pristine NR. Addition of org-MMT improved the thermal stability of the NR. Furthermore, nanocomposites which were calendared before curing showed much more thermal stability and fire resistance than those which contained similar amount of organoclay. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 855–862, 2011

**Key words:** Nanocomposite; flame resistance; natural rubber; organoclay; thermal aging

## INTRODUCTION

Nanocomposites are a new promising class of materials containing filler with at least one dimension in the nanometer scale. In recent decade, the polymer/clay nanocomposites have been extensively studied because of their excellent properties.<sup>1</sup> These nanocomposites have unique properties when compared to the conventional filled polymers.<sup>2</sup> For example, in these nanocomposites, the mechanical properties such as tensile strength and modulus, flexural strength and modulus, and the heat distortion temperature (HDT) increase noticeably<sup>3</sup> but the gas permeability decreases. Moreover, nanocomposites often exhibit enhanced thermal stability, an important property for high temperature applications and improve flame retardant performance.<sup>4</sup> To meet the wide spread applications in industry, the thermal stability and flame retardant properties of polymeric materials need to be improved.<sup>5</sup>

Blumstein<sup>6</sup> was the first who reported the improved thermal stability of poly(methyl methacrylate) (PMMA) and organically modified montmorillonite (org-MMT) nanocomposites. He showed that

PMMA chains had been inserted between the silicate layers and resisted the thermal degradation under conditions that would otherwise completely degrade the pure PMMA. Blumstein found that the thermal stability of the PMMA that was extracted from the nanocomposite showed better performance than the PMMA which was made by the solution method. He proposed that it might be due to a decrease in the relative amount of terminated double bonds in the PMMA polymerized in the confined environment inside the clay lamellae, when compared to the PMMA prepared in solution.<sup>6</sup>

The first notation about the potential flame retardant properties of a nanocomposite was the application of nylon-6/clay nanocomposite by Fujiwara and Sakamoto.<sup>4</sup> In recent years, there are some reports on thermal stability and flame resistance of polymeric nanocomposites prepared by nanofillers. Morgan and Harris<sup>7</sup> showed that using modified clay improved the characteristics which are related to the thermal stability and flame resistance in nanocomposites based on polypropylene. They showed that the removal of excess organic treatment by soxhlet extraction resulted in improvements in flex modulus, clay dispersion, delayed ignition time, and lowering heat release rate (HRR) during burning.

Styrenebutyl acrylate copolymer (St-BA)/graphite oxide (GO) nanocomposites were prepared by Yuan Hu et al.<sup>5</sup> They carried out differential scanning calorimetry (DSC) measurements and cone calorimetry experiments to evaluate thermal stability and

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flame retardant properties of the aforementioned nanocomposites. The cone calorimetry data showed that the HRR peak was reduced remarkably by 45% in a St-BA/GO nanocomposite with a GO content of only 1 wt %.

Natural rubber (NR) has been widely used in tire technology and laminated rubber bearings for buildings and bridges, etc., due to its unique properties. To meet the ever-increasing applications in industry, its thermal and flame retardant properties need to be improved. Furthermore, increasing the durability of elastomeric products under aging, caused by environmental conditions, is a noticeable concern from material quality control and performance point of views.

Using org-MMT reinforcement to improve the thermal, aging, and flame retardant properties of polymeric matrices is a new way to enhance nanocomposite properties without imposing extensive cost.

In this work a comparative study was conducted on thermal stability, flame resistance, curing characteristics, hardness, and mechanical properties of NR/org-MMT nanocomposites and pristine NR. The effect of nanocomposite morphology, i.e., silicate layers orientation in the elastomeric matrix due to calendaring was also investigated on the hardness and flame resistance of the nanocomposites.

## EXPERIMENTAL

### Materials

NR of SMRL grade was purchased from Guthrie Corp. (M) Bhd., Malaysia.

Org-MMT (cloisite 15A) with 3.15 nm intergallery spacing, ion exchanged by dimethyl dehydrogenated tallow ammonium bromide was provided by Southern Clay Products. Before use, the clay was dried under vacuum at 60°C for 12 h.<sup>8</sup> Other chemicals, obtained from local manufacturers.

### Preparation of NR/org-MMT compounds

NR and 3, 5 or 7 wt % of org-MMT were separately melt-blended using a Brabender Plasticorder (Brabender Weht50). At first, NR was added to the mixing head at 120°C and the rotor speed was set at 60 rpm and allowed to mix until torque establishment. Then the org-MMT was added and the mixture was compounded for 15 min at 120°C and 60 rpm and then cooled to room temperature. Other chemicals, including curing system, introduced in our previous work,<sup>9,10</sup> were added to nanocomposites using Brabender835800 two roll mills at room temperature, until achieving good mixing. NR0, NR3, NR5, NR7 are attributed to the samples containing 0, 3, 5, or

7 wt % of organoclay, respectively. NR0\*, NR3\*, NR5\*, and NR7\* are codes of calendared nanocomposites having the same amount of organoclay.

The nanocomposite compounds were then compression molded at 120°C using an electrically heated hydraulic press according to their curing characteristics.

### Cross-link density measurements

The cross-link density of a vulcanized rubber could be estimated from swelling measurement, using the Flory-Rehner equation or by a mechanical method involving stress-strain measurements.<sup>11</sup>

In this study, the cross-link density of samples was determined by immersing a circular piece of each sample in toluene until equilibrium was reached. Then the sample was taken out and blotted with filter paper and weighed. Measurement method of cross-link density obeyed Flory-Rehner formulation.<sup>11</sup>

### Equipments

X-ray diffraction (XRD) was employed to characterize the nanocomposite morphology using a Philips X'Pert Netherlands apparatus with  $\lambda = 1.5404$  Å. The angular step size was 0.2° with a step time equal to 1 s.

TEM images were recorded on a Phillips CM100 instrument, using an accelerating voltage of 100 kV on ultrathin samples.

The curing characteristics of the samples were determined using a Taiwan Gotech Testing Machines Inc rheometer at 120°C by measuring the cure time ( $t_{90}$ ) and the scorch time according to ASTM D 2705.

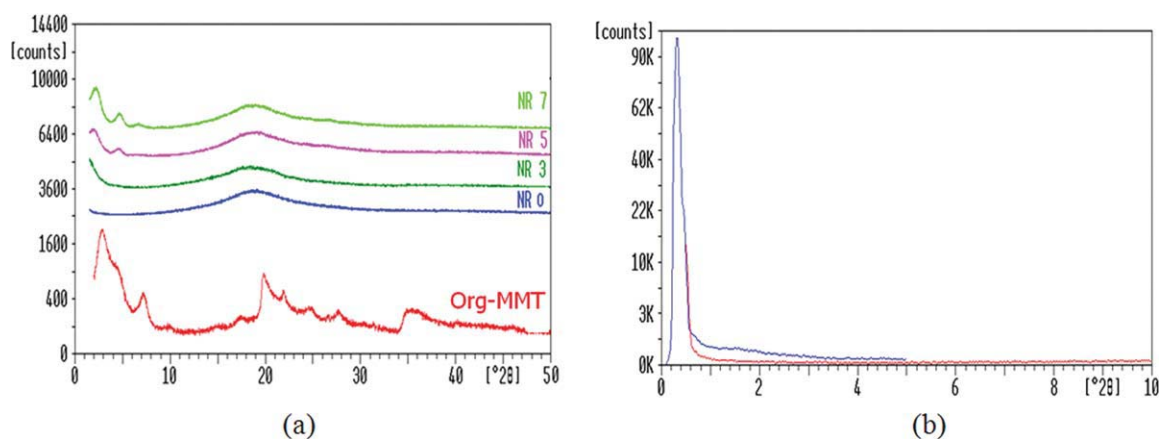
Mechanical properties were determined by a U.K. Instron tensile tester, using dumbbell-shaped specimens which were cut from the sheets according to ASTM D412. Tests were done at room temperature and at a crosshead speed of 500 mm/min.

Hardness properties were analyzed as per ASTM D2240 using a German Zwick Hardness meter.

The samples were aged by keeping in a hot air oven for 7 days at 70°C and the rest at 100°C for similar time, according to ASTM D865.

Thermal gravimetry analysis (TGA) was performed by a U.K. PL-STA 1500 system to evaluate the thermal stability. Samples were heated from room temperature to 700°C at a heating rate of 10°C/min under air. Samples were analyzed in triplicate to eliminate error.

To measure the flame resistance property of nanocomposites, a UK Stanton Redcroft Cone Calorimeter at 50 kW/m<sup>2</sup> heat flux and exhaust flow of 30 L/s using the standardized cone calorimeter procedure (ASTM E 1354-90) was employed. Data collected



**Figure 1** (a) X-ray diffraction patterns of organoclay, pristine rubber and various nanocomposites, and (b) X-ray diffraction patterns of NR3 at low angles. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

were the average of two samples, with an error of 10%.

## RESULTS AND DISCUSSION

### Nanocomposites morphology

It is known that in the formation process of polymer/clay nanocomposite, polymer chains are inserted in the interlayer space of layered silicates and force them keep apart from each other. According to the Bragg's equation, every peak in XRD pattern is related to a distance ( $d$ ), thus the first peak observed in the  $2\theta$  below  $5^\circ$  is attributed to interlayer spacing. The XRD patterns and corresponding data of NR/org-MMT nanocomposites are shown in Figure 1 and Table I, respectively.

As observed, there is a strong peak at the position of  $2.75^\circ$  for org-MMT which corresponds to a  $d$ -spacing of 3.15 nm. After melt mixing with NR, the position of the peak shifts towards the lower angles which means higher  $d$ -spacing for silicate layers.

For NR3 sample, XRD analysis does not show any peak even at very low angles. It means that the morphology of NR3 sample is exfoliated or semi-exfoliated. In NR5 sample (5 wt % of org-MMT), increasing clay content results in stacking layers, therefore separation of layers becomes more difficult, and  $d$ -spacing decreases. But when clay content increases to 7 wt % (NR7 sample), the viscosity of the nanocomposite matrix increases with increasing of clay content; thus the exerted shear stress to the layers increases and makes the clay layers to separate easier.

According to these results, most of the silicate layers in NR5 and NR7 samples are still parallel to each other and intercalation of NR chains merely increases their interlayer spaces.

To investigate the effect of calendaring on the morphology of exfoliated silicate layers, TEM

photomicrographs for NR3 and NR3\* are shown in Figure 2. In both cases TEM images show evidence of complete exfoliation. An orientation direction induced by calendaring which is marked with arrow is evident in the micrographs of Figure 2(b). The appearance of orientation directions for the OMMT particles indicates the particles orientation along calendaring direction of the sheet.

### Properties of nanocomposites

#### Curing and Cross-link Density Characteristics

Scorch time ( $t_s$ ), curing time ( $t_{90}$ ), curing rate index, and cross-link density of nanocomposites are listed in Table II.

The curing rate indexes (CRI) of the compounds are calculated according to eq. (1), as given below.<sup>12</sup>

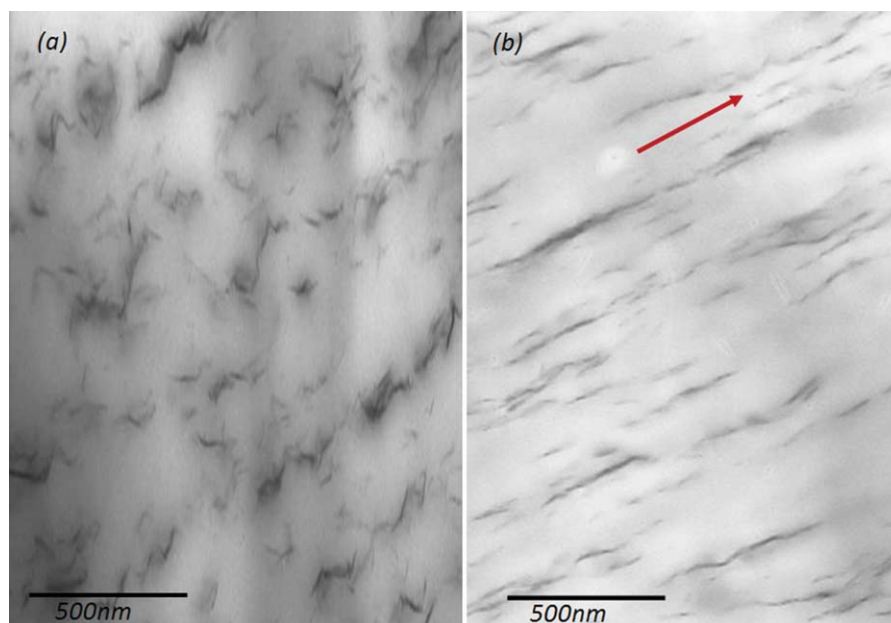
$$\text{CRI} = \frac{1}{t_{90} - t_s} \quad (1)$$

As it is observed, the inclusion of clay lowers the scorch and curing times of nanocomposites in compare to the pristine rubber. The organoclay reduces the scorch time through the accelerating effect of quaternary ammonium salt used in the clay modification. To explain the decrease in curing time ( $t_{90}$ ),

**TABLE I**  
XRD Data for Organoclay, Pristine Rubber and Nanocomposites

Sample code	$2^\circ$	$d$ -spacing (nm)	Morphology
C15A	2.75	3.15	–
NR0	–	–	–
NR3	–	–	Exfoliated
NR5	2.050	4.2059	Intercalated
NR7	1.955	4.5152	Intercalated

Sample codes referred in "Experimental" section.



**Figure 2** Representative TEM images of NR3 (a) and NR3\* (b). Arrow indicates the machine direction in calendaring process. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

one has to consider the cross-link density data in Table II. It is obvious that the presence of silicate layers in the matrix diminishes its cross-link density. By applying temperature, sulfur free radicals are formed and then they attack polymer chains and convert them to macro-radicals. These macro-radicals use sulfur chains to react with each other and form cross-links. If a polymer chain intercalates between two silicate layers, it can hardly find another chain to react with; i.e., silicate layers behave like rigid obstacles that prevent cross-link reactions, therefore the cross-link density decreases. The reduction of these characteristics are affected by two factors; (a) self accelerating effect of modifier which causes scorch time reduction as is suggested by other researchers,<sup>12,13</sup> and (b) less cross-link ability of the rubber which reduces curing time.

Scheme 1 presents the schematic diagram of how silicate layers bringing about the decreases in cross-link densities.

#### Thermal aging

Typical mechanical properties of nanocomposites and thermally aged counterparts have been measured and compared to each other. Table III shows hardness data for pristine rubber and nanocomposite samples at two different aging conditions.

To interpret the reason of hardness rise for nanocomposite samples, one can consider a thin elastomeric sheet; presence of silicate layers increases its shape factor. Shape factor is a geometric function that describes the effect of the geometry on the compression modulus. It is defined as the ratio of the area of loaded surface to the total surface area that is free to bulge as below<sup>14</sup>:

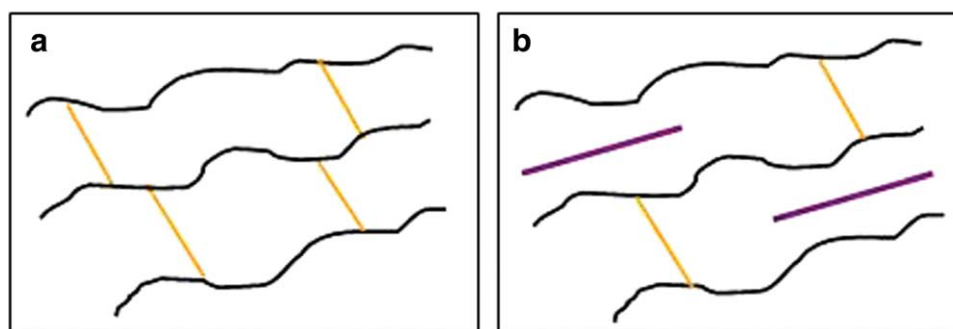
$$S = \frac{A_L}{A_B} \quad (2)$$

It is worth to notify that by adding only 3 wt % of org-MMT, the amount of *hardness rise* for aged

**TABLE II**  
The Main Characteristics of Curing Process and Cross-Link Densities of Pristine Rubber, and Nanocomposites at Two Different Aging Conditions

Sample code	$t_s$ (min.)	$t_{90}$ (min.)	Cure rate index ( $\text{min}^{-1}$ )	Crosslink density ( $v$ ) $\times 10^3$ (g mol/cc)	Crosslink density for aged samples ( $v$ ) $\times 10^3$ (g mol/cc)	
					at 70°C for a week	at 100°C for a week
NR0	11.75	38.93	0.037	2.89	2.98	1.71
NR3	5.48	25.75	0.049	2.69	2.81	1.33
NR5	5.18	24.93	0.051	2.54	2.66	1.2
NR7	3.66	23.82	0.050	2.41	2.49	1.09





**Scheme 1** Schematic diagram of (a) cross-link formation between macromolecules and (b) placement of clay layers between macromolecules and their preventive role against cross-link formation. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

nanocomposite samples decreases more than 55% in compare to the pristine rubber.

It is seen from Table III that the nanocomposite specimens having oriented layered silicates in the calendaring direction exhibit lower *hardness rise* due to aging compared to those have similar amount of org-MMT. It believes that during thermal aging, oriented layered silicates along calendaring direction act as rigid obstacles against plasticizers migration along the transverse direction, i.e., perpendicular to the calendaring direction, so decrease *hardness rise* due to exit of plasticizers. Furthermore, during aging process, the probable residual curative agents which have not been acted during curing process, will likely act and increase the hardness.

Table IV presents the elastic modulus, elongation-at-break and tensile strength data for pristine rubber, nanocomposites, and nanocomposites at two different aging conditions mentioned in the experimental section.

It is observed that at the first aging conditions, elastic modulus increases and this increasing is more significant for pristine rubber due to the same reason which was discussed for hardness changes. However, aging during a week at 100°C causes elastic modulus of samples lowers. The reason is probably the thermal

degradation due to higher aging temperature during the same period of time. Cross-link density values of various samples are presented in Table II. It shows that the cross-link density values of aged samples at 70°C are the same as original samples but they are not similar to those of the aged samples at 100°C. In latter case the cross-link density is less than nonaged counterparts. It means that aging at 70°C does not degrade polymer chemically. It causes merely plasticizers migration in the presence of layered silica. According to the relation between cross-link density  $\nu$  and molecular weight of polymer chains between cross-links ( $M_c$ ),<sup>11</sup> decreasing cross-link density means that the polymer is degraded chemically:

$$\nu = \frac{1}{2M_c} \quad (3)$$

As expected, adding org-MMT decreases elongation-at-break of nanocomposite. It is due to nonelastic nature of clay that affects on the elastic behavior of NR and decreases it. Migration of plasticizers

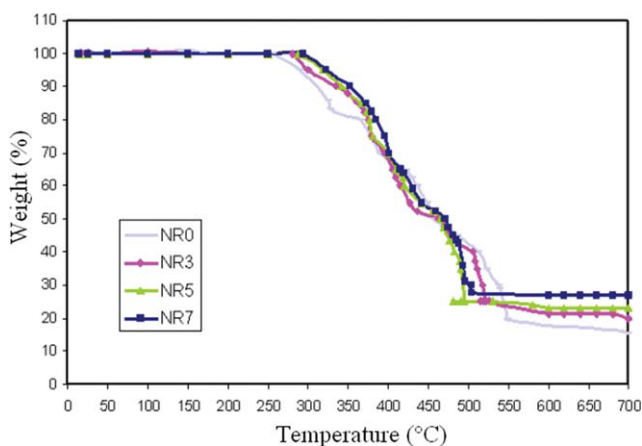
**TABLE III**  
Hardness Data for Pristine Rubber and Various Nanocomposites at Two Different Aging Conditions

Sample code	Hardness (shore A)	Hardness for aged samples (Shore A)	
		At 70°C for a week	At 100°C for a week
NR0	48	53	56
NR3	53.5	56	58.5
NR5	54	57.5	59
NR7	54.6	58	59.3
NR0*	48	53	56
NR3*	54	55.3	58
NR5*	56	57	58.5
NR7*	57.5	59	58.8

\* Indicates the precalendared samples referred in "Experimental" section.

**TABLE IV**  
Elastic Modulus, Elongation-at-Break and Strength Data for Pristine Rubber, Nanocomposites and Nanocomposites at Two Different Aging Conditions

Property	Sample code	Original samples	Aged samples	
			At 70°C for a week	At 100°C for a week
Modulus MPa	NR0	2.98	4.89	1.30
	NR3	4.08	5.03	1.87
	NR5	4.12	5.29	1.97
	NR7	4.22	5.38	2.13
Elongation at break (%)	NR0	576	476	181
	NR3	537	459	177
	NR5	527	454	174
	NR7	477	414	155
Strength MPa	NR0	20.54	18.40	6.90
	NR3	19.51	17.57	6.67
	NR5	18.10	16.57	6.30
	NR7	16.65	15.36	5.93



**Figure 3** TGA analysis of pristine rubber and various nanocomposites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

during aging for a week at 70°C, makes it difficult for macromolecules to slide on and slip among each other, thus elongation-at-break decreases after aging.

There is the same reason for hardness and modulus changes, in case of aged specimens, nanocomposite specimens show fewer changes in elongation-at-break, but for aged samples at 100°C, there is no significant difference between nanocomposite samples and NR0. It is probably because the clay modifier was degraded during the corresponding aging period.

#### Thermal degradation

TGA of polymeric materials measures the weight loss of material when it is heated under a constant heating rate in the presence of air or an inert gas. It gives an idea about the composition and the thermal stability of the material. When a rubber compound is heated, the oily plasticizers migrate to the surface and are removed first, and then the polymer chains will degrade and convert into gaseous products. Further heating will remove all of the organic matter, giving the weight of inorganic part in the compound.

Figure 3 shows the TGA thermogram of weight loss as a function of temperature for NR0, NR3, NR5 and NR7 nanocomposites in the presence of air.

The TGA data are summarized at Table V. In general, major weight losses are observed in the range of 300–500°C for all of the specimens. Evidently, the thermal decomposition of the nanocomposites shifts towards the higher temperature range compared to that of pristine rubber, therefore confirms the enhancement of thermal stability of nanocomposite. It can be seen that the temperature at which 20 and 50 percentage of nanocomposites degradation occurs is increased by 20°C and 15°C, respectively. It is clear that the compounds contained more clay exhibit higher thermal stability. The enhancement in thermal stability of nanocomposites is explained by increasing of heat capacity of rubber via mixing with silicate layers which have higher heat capacity compared to rubber. It is worth bearing in mind that in some cases chemical degradation probably occurs and the silicate layers partially reduce the ease of exit of degraded polymeric chains from the nanocomposite samples compared to oily plasticizers.

#### Flammability

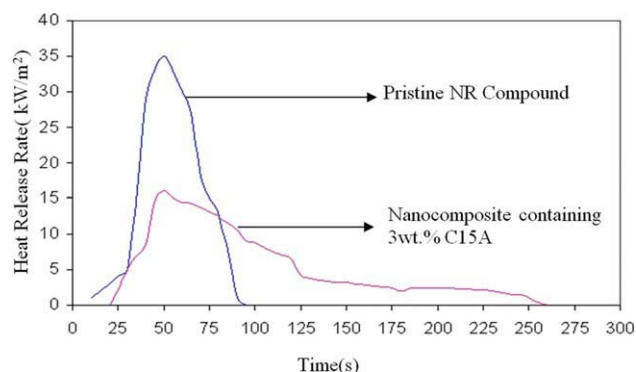
The cone calorimetry technique measures fire-relevant properties such as HRR and ignition time (IT). HRR peak has been found to be the most important parameter to evaluate fire safety.<sup>15</sup> HRR plots of NR0 and NR3 are shown in Figure 4, which are typical for all of the nanocomposites in Table VI.

NR3 nanocomposite has a 54.28% lower HRR peak value than the NR0, but NR5 and NR7 exhibit more than 55% and 58% decrease in HRR peak value, respectively. Comparison of the cone calorimeter data in Table VI reveals that by adding org-MMT, the effective heat of combustion,  $H_c$ , increases significantly.

The primary parameter responsible for the lower HRR of the nanocomposite is mass loss rate (MLR) during combustion. The MLR of the nanocomposite is significantly reduced from the value observed for the pristine rubber. This flame retardant character is traced to the response of a char layer, which develops on the outer surface of the sample during combustion.<sup>16</sup> Indeed, the inorganic part of the org-MMT converts into a uniform ceramic char, which leads to a significantly increase in oxidation resistance. This

**TABLE V**  
TGA Data for Pristine Rubber and Nanocomposites

Sample code	Onset decomposition (°C)	$T_{-20}$ (°C)	$T_{-50}$ (°C)	Maximum weight loss (°C)	wt % residual at 700°C
NR0	252.5	365.11	456.77	326.50	17.75
NR3	290.5	375.18	462.75	377.20	21.19
NR5	303	377.26	465.20	492.45	22.98
NR7	308.7	385.80	470.64	494.91	26.74



**Figure 4** Comparison of the heat release rate (HRR) plots of pristine rubber (NR0) and a typical nanocomposite (NR3) at 50 kW/m<sup>2</sup> heat flux. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

surface-char has a high concentration of org-MMT layers which behaves as an excellent insulator and a mass transport barrier (slowing the oxygen supply as well as the escape of the combustion products during decomposition).<sup>16</sup> Some studies of nylon 6/org-MMT nanocomposites were conducted by Vaia<sup>17</sup> showed fire retardancy enhancement through char formation. The above mentioned results indicate that the finely dispersed layered silicates can behave as a generally applicable anti-flammability additive for commodity polymers.

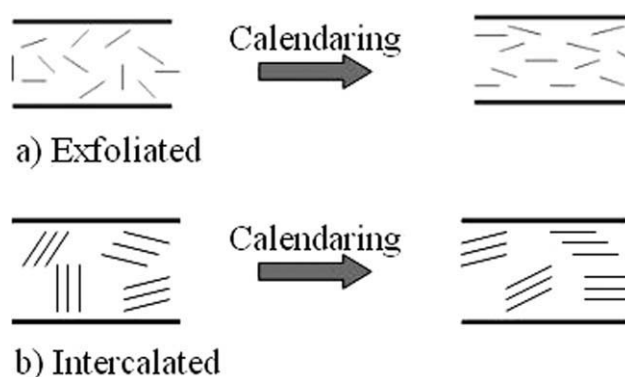
In this work to trace the cause of flame retardant ability of org-MMT, nanocomposite sheets were calendared before molding for flammability test. Each reason was fruitful in the reduction of flammability, either char formation or reduction of fuel charging to the flame. Calendaring which seems to orient nanoclay platelets along machine direction, will synergy this decrease in flammability. It is expected that after calendaring, better char formation occurs and the new orientation of

**TABLE VI**  
Cone Calorimetry Data for Pristine Rubber and Nanocomposites

Sample code	HRR Peak (kW/m <sup>2</sup> )	IT (s)	H <sub>c</sub> (MJ/kg)	MLR (g/s m <sup>2</sup> )
NR0	35	8	1.28	26.9
NR3	16	20	35.5	25.7
NR5	15.5	23	50	24
NR7	14.5	25	73	22.1
NR0*	35	8	1.28	26.9
NR3*	13.8	20	35.5	20.7
NR5*	13.5	23	50	19
NR7*	12	25	73	17.3

H<sub>c</sub>, heat of combustion; MLR, mass loss rate.

\* Indicates the precalendared samples referred in "Experimental" section.



**Scheme 2** Schematic presentation of the effect of calendaring on the organoclay orientation in rubber.

clay platelets causes more obstacles against fuel transportation from bulk to the surface. Flammability tests were done on similar samples that were calendared before molding. Scheme 2 presents layered silicate orientation with exfoliated morphology before and after calendaring.

Table VI presents cone calorimetric data of nanocomposite calendared samples, too. These results approve that layered silicate orientation is effective on increasing flame resistance properties. It is observed that in calendared sheets some characteristics of flammability were reduced noticeably.

## CONCLUSIONS

From this study, the following conclusions can be drawn:

1. The NR/org-MMT nanocomposites were successfully prepared by melt mixing. The structure of prepared nanocomposites was confirmed by XRD and TEM experiments.
2. The present study reveals that in the pristine rubber, adding only 3 wt % of org-MMT decreases the curing time by 33% which is important from saving time and energy point of view.
3. The polymer/layered silicate nanocomposites resulted in a noticeable improvement in thermal stability, i.e. the amount of changes in hardness and elastic modulus of nanocomposites with 3 wt % of org-MMT were 55% and 63%, respectively.
4. The NR3 nanocomposite had a 54.28% lower HRR peak value in compared to NR0. By employing a proper method such as calendaring to induce preferred orientation in raw sheet before curing, HRR peak decreases 60% that means noticeable improvement in flame resistance property.

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