

# Thermal and Flame Resistance Properties of Natural Rubber-g-poly-(dimethyl(methacryloyloxymethyl)phosphonate)

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**ABSTRACT:** Natural rubber grafted with poly(dimethyl(methacryloyloxymethyl)phosphonate) (i.e., NR-g-PDMMMP) was prepared in latex medium via photopolymerization. Thermal and flame resistance properties of the NR-g-PDMMMP prepared with various levels of grafted PDMMMP or grafting rate (GR) were investigated. Thermal behaviors were investigated by thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC). It was found that the graft copolymer exhibited phase separation with double  $T_g$  values. A shift of  $T_g$ s toward each other was observed with increasing GR, which indicated tendency to become a single phase material. Increasing GRs also caused

increasing heat and flame resistance with increasing degradation temperature and level of char residue. Furthermore, increasing level of limited oxygen index (LOI) and decreasing burning rate were observed with increasing the GR. This is attributed to increasing content of char residue of the phosphorus compound, which acted as the thermal insulation and a barrier of oxygen to transfer to the burning materials. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 255–262, 2010

**Key words:** natural rubber; flame retardant; thermal stability; graft copolymer; poly(dimethyl(methacryloyloxymethyl)phosphonate)

## INTRODUCTION

Natural rubber (NR) is widely used worldwide because of its excellent properties in terms of high elasticity and mechanical strength including high resistance to impact and tear as well as low heat build-up during deformation. However, NR exhibits some drawbacks, for instance low chemical and non-polar solvent resistance because of the hydrophobicity and unsaturation in the molecular chains. Furthermore, NR is prone to burst into flames with fast burning propagation (i.e., high flammability). To improve the flame retardancy of polymers, two types of flame retardant called as “additive and reactive flame retardants” have been used. The additive types are generally incorporated into polymeric material by physical means. The flame-retardant

additives that are commonly used include antimony trioxide, zinc borate, chlorinated paraffin wax, and decabromodiphenyl ether.<sup>1</sup> Typically, the additive flame retardant caused poor compatibility, leaching, and reduction in mechanical properties of polymer. Another approach, the reactive flame retardants involve synthesis of new flame retarding polymers or modification of existing polymers through copolymerization with a flame retarding units in the main chain or as pendent groups along the chain. The modification approach by incorporating the flame-retarding units in the polymer backbone is the most favored route because it imparts permanently flame retardant behavior, and the original physical and mechanical properties of the polymer are maintained.<sup>2</sup>

The various types of halogen compounds have also been used as flame retardant additives of polymeric materials. However, the major growing demand to avoid the generation of toxic and corrosive gases during thermal degradation has led to the development of non-halogen containing flame retardant polymers. These include the utilize of magnesium hydroxide in polyethylene (PE),<sup>3</sup> and ethylene vinyl acetate (EVA),<sup>4</sup> aluminum trihydrate in polyurethane (PU),<sup>5</sup> epoxy resin<sup>6</sup> and polypropylene (PP),<sup>7</sup> as well as antimony oxide in poly(methyl methacrylate) (PMMA).<sup>8</sup>

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Organic phosphorus compounds are also considerably exhibited good flame retardant characteristics in many polymer such as PU foam,<sup>9</sup> epoxy resin<sup>10</sup> poly(ethylene terephthalate) (PET),<sup>11</sup> and acrylonitrile-butadiene-styrene terpolymer (ABS).<sup>12</sup> There have been a number of reports on performance of phosphorus flame retardants prepared by copolymerization of vinyl phosphates onto various commodity polymers. These include PE terephthalate (PET),<sup>13</sup> poly(acrylonitrile) (PAN),<sup>14,15</sup> poly(acrylamide),<sup>16</sup> polystyrene (PS), and poly(methylmethacrylate) (PMMA).<sup>17</sup>

In NR, phosphorus containing flame retardant additives such as antimony-containing polymer of bisphenol-A and triphenyl antimony dinitrate,<sup>18</sup> bromo derivative of phosphorylated cashew nut shell,<sup>19-21</sup> have been used. Phosphorus reagents such as diethyl phosphonate and trichloromethyl phosphonyl dichloride have been incorporated in poly-1,2-butadienes and used as flame retardant additives for NR.<sup>22,23</sup> In addition, chemical modification of NR has been reported by fixing phosphorus atoms onto NR backbone chains with dialkyl or diaryl phosphates and used as a flame-retardant polymer.<sup>24,25</sup>

In the current work, grafting of polymers bearing phosphonate groups was performed by graft copolymerization of NR and dimethyl(hydroxymethyl)phosphonate) in a latex medium. The flame retardant characteristic and thermal properties of the NR grafted with poly(dimethyl(methacryloyloxymethyl)phosphonate) (NR-g-PDMMMP) was then carefully investigated.

## EXPERIMENTAL

### Materials

Analytical grade of triethylamine and common solvents used (i.e., acetone and methanol) were distilled before use. Dichloromethane was also distilled under nitrogen atmosphere. Dimethyl(methacryloyloxymethyl)phosphonate monomer (DMMMP) was prepared in-house using a procedure described elsewhere.<sup>15</sup> Synthesis of *N,N*-diethyldithiocarbamate-functionalized NR (DEDT-NR) used as the photoiniferter was carried out according to our previous work.<sup>26</sup> The reagents used to synthesis the DEDT-NR: sodium *N,N*-diethyldithiocarbamate trihydrate (DEDT-Na) and tetrabutylammonium bromide (TBAB) were supplied by Acros Organics (Geel, Belgium). The reagents used to prepare epoxidized NR latex (i.e., hydrogen peroxide and formic acid) obtained from Acros Organics (Geel, Belgium). NR latex with 60% dried rubber content (DRC), manufactured by Yala latex Co., Yala, Thailand. The non-ionic surfactant, Sinnopal NP 307 used as latex

stabilizer was manufactured by Cognis (Meaux, France). It was used without purification.

### Preparation of NR-g-PDMMMP

Epoxidized NR (ENR) latex was first prepared by performic epoxidation of high ammonia concentrated latex using procedure described elsewhere.<sup>26</sup> Macroinitiators of *N,N*-diethyldithiocarbamate groups (DEDT) in the NR chains (i.e., DEDT-NR) was then created by addition of sodium *N,N*-diethyldithiocarbamate onto epoxidized NR units in a latex medium according to the reaction procedures described elsewhere.<sup>26,27</sup> The graft copolymerization of DMMMP monomer with DEDT-NR was then performed in a latex medium via photopolymerization using ultraviolet radiation with a wavelength of 365 nm. The grafting reaction was performed at room temperature and under nitrogen atmosphere in 250 mL Pyrex reaction kettle equipped with a magnetic stirrer and closed by a screwed stopper with a joint of sealing covered with Teflon. The overall reactions occurred as proposed in a schematic outline of the synthesis route for NR-g-PDMMMP in Scheme 1. In this work, three different levels of DEDT-NR units: 4.0, 7.2, and 12.0 mol % with the molar ratios [monomer]/[DEDT-NR units] = 5, 9, and 15 mol.mol<sup>-1</sup>, respectively were used. The obtained graft copolymer (i.e., NR-g-PDMMMP) was coagulated in methanol, and purified by dissolution/re-precipitation with dichloromethane/methanol and dried at 40°C under vacuum until a constant weight. The product was then Soxhlet extracted with methanol for 24 h to remove PDMMMP homopolymer, which was possibly formed. The residual graft copolymer was recovered by filtration and dried under vacuum at 40°C until a constant weight. The grafting rate (GR) was then determined using the relation as follows:

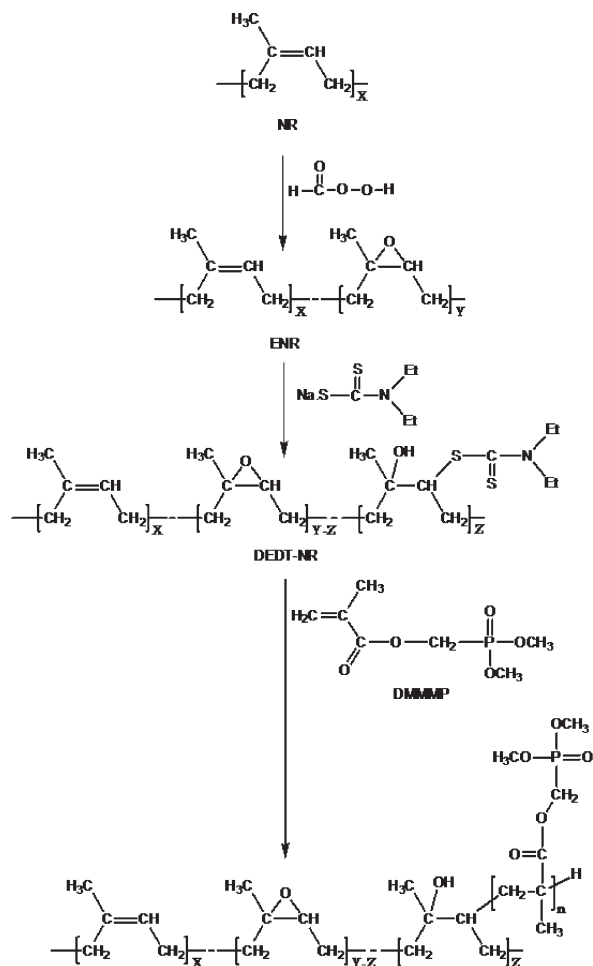
$$\text{Grafting rate} = \frac{W_s - W_t}{W_s} \times 100 \quad (1)$$

where,  $W_s$  is the weight of graft copolymer isolated after extraction with methanol,  $W_t$  is the weight of DEDT-NR before grafting.

### Characterization of NR-g-PDMMMP

#### NMR spectroscopy

<sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P-NMR spectra were recorded on a Bruker DPX 200 Fourier-transform spectrometer, at 200.13 MHz for <sup>1</sup>H, at 50.32 MHz for <sup>13</sup>C, and at 81.01 MHz for <sup>31</sup>P-NMR. Samples were first dissolved in chloroform-D (99.8 % purity, Spectrometrie Spin and Techniques). In <sup>1</sup>H and <sup>13</sup>C-NMR, the chemical shifts ( $\delta$ ) were expressed in terms of ppm,



**Scheme 1** Schematic outline of the synthesis route for NR-g-PDMMMP.

compared with the singlet of tetramethylsilane (TMS) internal standard, whereas the  $^{31}\text{P}$ -NMR spectrum was also expressed in terms of ppm but compared with the phosphoric acid peak external standard.

#### Mooney viscosity

Mooney viscometer, model VISCAL (Tech Pro Co., Cuyahoya Falls, OH) was used to measure Mooney viscosities of pure NR-g-PDMMMP using a fixed rotor speed of 2 rpm at  $100^\circ\text{C}$ . The preheated time was set for 1 min and testing results were recorded at a testing time of 4 min, according to ASTM D5289.

#### Thermal properties

Two techniques of thermal analysis were used to characterize NR-g-PDMMMP samples: differential scanning calorimeter (DSC), and thermogravimetric analysis (TGA). The DSC was performed using the apparatus model Q500, TA Instrument, (New Castle,

DE). Sample (3–10 mg) was first placed in the DSC sample pan and then quenched to  $-80^\circ\text{C}$  with a cooling rate of  $10^\circ\text{C min}^{-1}$ . The sample was heated up to  $100^\circ\text{C}$  with the same rate and held at this temperature for 5 min to remove thermal history. The sample was eventually quenched to  $-80^\circ\text{C}$  with the cooling rate of  $10^\circ\text{C min}^{-1}$  and the transition temperature was recorded.

TGA was performed using TGAQ500, TA instrument. Sample (10–20 mg) was placed in a platinum pan and characterized under nitrogen and oxygen atmosphere with gas flow rate of  $100 \text{ ml}\cdot\text{min}^{-1}$ . The heating rate was set at  $10^\circ\text{C}\cdot\text{min}^{-1}$  for the testing temperature ranges of  $30\text{--}575^\circ\text{C}$ .

#### Limiting oxygen index (LOI)

The LOI values were used to estimate flame retardant properties of the NR-g-PDMMMP. The test was performed according to ASTM D2863–70. The graft copolymer sample with a dimension of  $100 \times 6.5 \times 3 \text{ mm}$  was held vertically in the glass chamber, where flow of oxygen and nitrogen gases could be controlled. The top end of the sample was first ignited and time used to burn 50 mm long of the sample was recorded. The LOI value is defined as the minimum concentration of oxygen in oxygen/nitrogen mixtures necessary to burn the sample over a length of 50 mm. Therefore, LOI values were calculated according to the following relation:

$$\text{LOI}\% = \frac{\text{O}_2}{\text{O}_2 + \text{N}_2} \times 100 \quad (2)$$

where  $\text{O}_2$  and  $\text{N}_2$  are volumes of oxygen, and nitrogen used to burn the sample of 50 mm long, respectively.

#### Burning rate

Burning rate also used to estimate flammability of the NR-g-PDMMMP, according to ISO 3582–1978(E). The test specimen with a dimension of  $50 \times 150 \times 13 \text{ mm}$  was first conditioned at  $27^\circ\text{C}$  and relative humidity of 65% for 24 h. It was then placed horizontally and gaseous hydrocarbon fuel was applied to light one end of the sample. Time for the flame propagated from one end of the sample to the reference mark (i.e., 125 mm far from the end) was measured in terms of burning rate, as a following equation:

$$\text{Burning rate} = \frac{125}{t_b} \quad (3)$$

where  $t_b$  is the time, in seconds, at which the flame reaches the gauge mark.

TABLE I  
Grafting Rates (GR) of NR-g-PDMMMP Obtained at Different Concentrations of DEDT-NR Units and Ratios of [Monomer]/[DEDT-NR Units]

Sample code	DEDT-NR unit (mol %)	[Monomer]/[DEDT-NR units] (mol.mol <sup>-1</sup> )	Reaction time (min)	GR (wt %)
NR-g-PDMMMP 71%	4.0	5	60	71
NR-g-PDMMMP 80%	4.0	5	180	80
NR-g-PDMMMP 89%	7.2	9	180	89
NR-g-PDMMMP 95%	12.0	15	180	95

## RESULT AND DISCUSSION

### Synthesis and characterization of NR-g-PDMMMP

The synthesis of NR-g-PDMMMP was performed in a latex medium based on photopolymerization of dimethyl(methacryloyloxymethyl)phosphonate monomer (DMMMP) with DEDT-NR macroinitiators. The graft copolymerization was initiated using three different levels of *N,N*-diethyldithiocarbamate groups (i.e., 4.0, 7.2, and 12.0 mol %), which previously bound in side position of the NR chains. The aim was to prepare the graft copolymer with various GRs or grafting contents. The NR-g-PDMMMP obtained from a ratio of [monomer]/[DEDT-NR units] = 5 at reaction time of 60 and 180 min are denoted as NR-g-PDMMMP 71% and NR-g-PDMMMP 80%, respectively. This is stated according to the GR results, as shown in Table I. In addition, the graft copolymers obtained from the ratios of [monomer]/[DEDT-NR units] = 9 and 15 at a reaction time of 180 min are denoted as NR-g-PDMMMP 89% and NR-g-PDMMMP 95%, respectively.

Figure 1 shows the <sup>1</sup>H-NMR spectra of NR-g-PDMMMP prepared with various grafting conditions. The signal at  $\delta = 5.14$  ppm ( $H_a$ ) is assigned to the C=C proton in the *cis*-1,4-polyisoprene. The signal at  $\delta = 2.70$  ppm ( $H_b$ ) is attributed to the proton of the remained oxirane rings in the rubber back bone. Furthermore, the signals at  $\delta = 4.40$  ( $H_c$ ) and 3.71 ppm ( $H_d$ ) are related to the methoxylene proton and dimethyl groups of the grafted PDMMMP, respectively. Therefore, the <sup>1</sup>H-NMR results confirmed the presence of the grafted PDMMMP onto NR back bone.

Infrared spectroscopy was also used to characterize the NR-g-PDMMMP, as FTIR spectra shown in Figure 2. The absorption peaks at 1238, 1050, and 958 cm<sup>-1</sup> were observed. They are assigned to the vibrations of -P=O, P-C-O, and P-O-CH<sub>3</sub> in the grafted PDMMMP, respectively. This again confirmed the formation of the NR-g-PDMMMP. The overall reactions used to prepare the NR-g-PDMMMP are shown in Scheme 1.

### Thermal properties

Thermal behavior of pure NR and NR-g-PDMMMP with various GRs was investigated by DSC, as the

results shown in Figure 3. It is seen that NR showed a single glass transition temperature ( $T_g$ ) at approximately to -62.08°C. However, the NR-g-PDMMMP showed double values of  $T_g$  which the low temperature (i.e., in a range of -53.75°C to -40.60°C) corresponding to the glass transition of *cis*-1,4-polyisoprene in NR domains. The transition at higher temperature (i.e., in range of -22.86°C to -22.50°C) corresponded to the transition of dimethylphos-

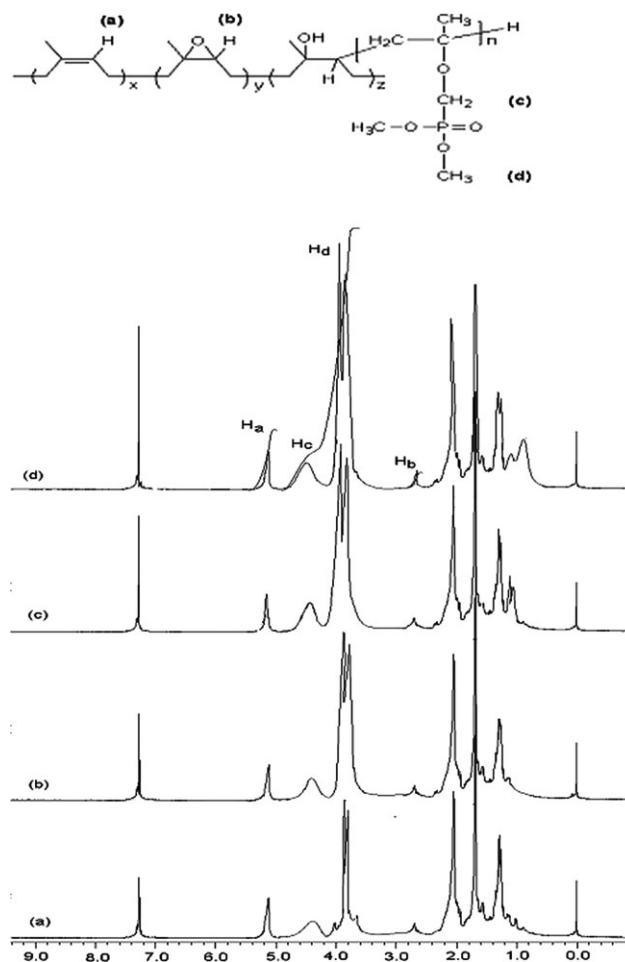
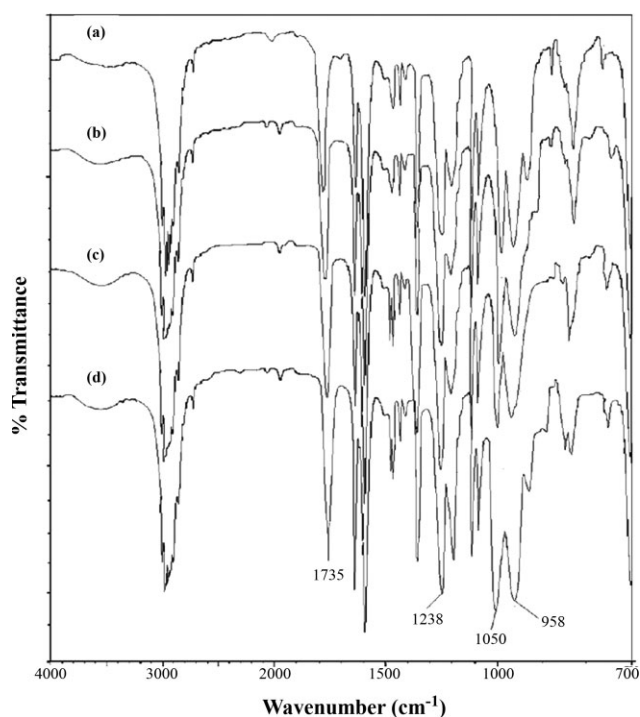


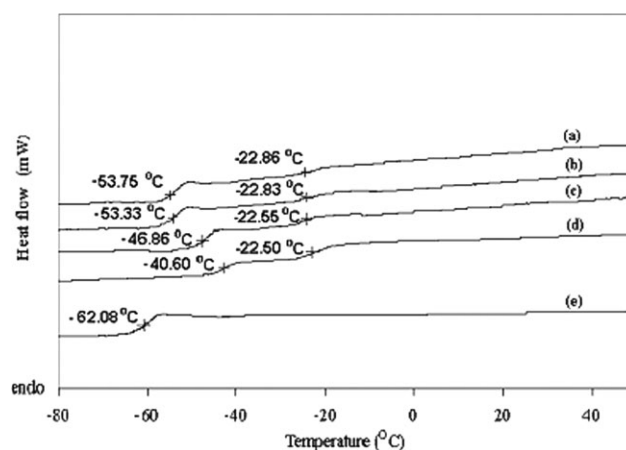
Figure 1 Typical <sup>1</sup>H-NMR spectra of NR-g-PDMMMP with various grafting conditions: (a) 4.0 mol % DEDT-NR with polymerization time = 60 min; (b) 4.0 mol % DEDT-NR with polymerization time = 180 min; (c) 7.2 mol % DEDT-NR with polymerization time = 180 min; and (d) 12.0 mol % DEDT-NR with polymerization time = 180 min.



**Figure 2** Typical infrared spectra of NR-g-PDMMMP with various grafting conditions: (a) 4.0 mol % DEDT-NR with polymerization time = 60 min; (b) 4.0 mol % DEDT-NR with polymerization time = 180 min; (c) 7.2 mol % DEDT-NR with polymerization time = 180 min; and (d) 12.0 mol % DEDT-NR with polymerization time = 180 min.

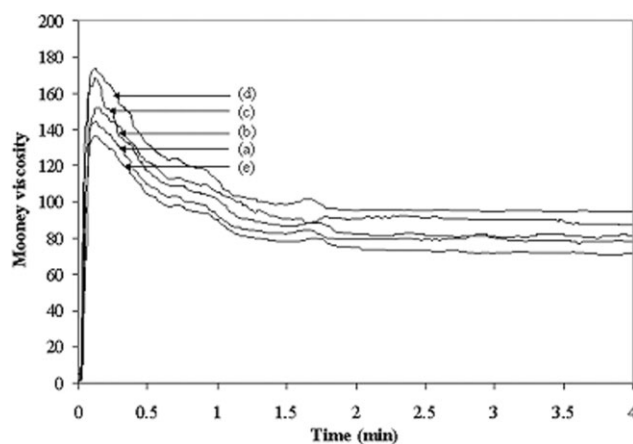
phonate-functionalized grafts. Therefore, in the considered compositions with GR between 71 and 95%, the phase separation occurred. In Figure 3, it is also seen that the  $T_g$  of NR domains increased while the dimethylphosphonate-functionalized graft slight decreased with increasing the GR. This indicates that the material would tend to become homogeneous (i.e., one phase) when GR is increased. It is also seen that the  $T_g$  of NR phase in the NR-g-PDMMMP is higher than that of the  $T_g$  of pure NR. This is attributed to restriction of chain mobility of the graft copolymer because of interaction between the polar functional groups. Higher GR resulted in higher level of dimethylphosphonate-functionalized grafts. Higher chemical interaction and  $T_g$  of the NR domains are consequent. To prove chemical interaction in various types of polymer, Mooney viscosity (MV) was determined, as results shown in Figure 4. It can be seen that the pure NR showed the lowest value of MV (ML, 1 + 4, 100°C). Increasing GR of the graft copolymerization caused increasing values of the Mooney viscosities. This is an evidence of increasing chemical interaction and hence flow resistance of the material. This could correlate well to the restriction of chain mobility during the DSC test, which thereafter caused increasing of  $T_g$  of the rubber phase.

Thermal stabilities of pure NR, PDMMMP homopolymer, and various types of the NR-g-PDMMMP

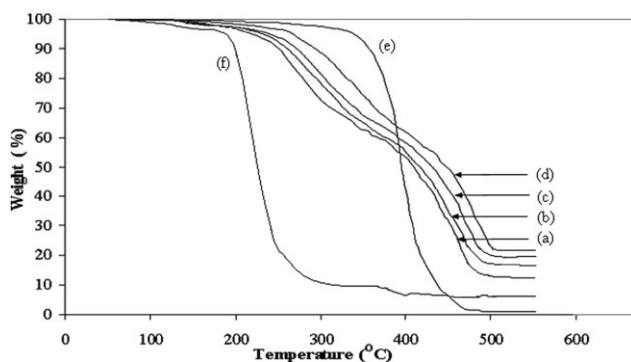


**Figure 3** DSC thermograms of NR-g-PDMMMP with various grafting conditions: (a) 4.0 mol % DEDT-NR with polymerization time = 60 min; (b) 4.0 mol % DEDT-NR with polymerization time = 180 min; (c) 7.2 mol % DEDT-NR with polymerization time = 180 min; (d) 12.0 mol % DEDT-NR with polymerization time = 180 min, and (e) pure NR.

were characterized by TGA technique. Figures 5 and 6 show TGA thermograms obtained under nitrogen and oxygen atmospheres, respectively. In nitrogen atmosphere (Fig. 5), it can be seen that the pure NR and PDMMMP homopolymer exhibited a single step of weight loss with an onset temperature of  $\sim 320$  and  $221^\circ\text{C}$ , respectively (Table II). For NR-g-PDMMMP prepared with various ratios of [monomer]/[DEDT-NR units] and reaction times (i.e., the different GRs), double degradation steps were observed. The first degradation step occurred at onset temperatures in a range of  $258\text{--}276^\circ\text{C}$ , corresponding to a weight loss from 37 to 45%, whereas the second step occurred at onset temperatures from



**Figure 4** MV of NR-g-PDMMMP with various grafting conditions: (a) 4.0 mol % DEDT-NR with polymerization time = 60 min; (b) 4.0 mol % DEDT-NR with polymerization time = 180 min; (c) 7.2 mol % DEDT-NR with polymerization time = 180 min; (d) 12.0 mol % DEDT-NR with polymerization time = 180 min, and (e) pure NR.



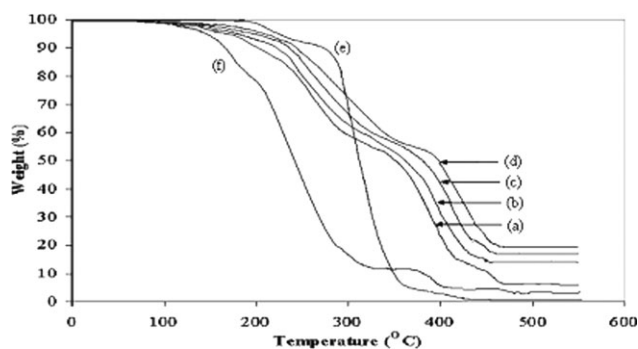
**Figure 5** TGA thermograms under nitrogen atmosphere of NR, PDMMMP, NR-g-PDMMMP with various grafting conditions: (a) 4.0 mol % DEDT-NR with polymerization time = 60 min; (b) 4.0 mol % DEDT-NR with polymerization time = 180 min; (c) 7.2 mol % DEDT-NR with polymerization time = 180 min; (d) 12.0 mol % DEDT-NR with polymerization time = 180 min, (e) pure NR, and (f) PDMMMP.

405 to 445°C, corresponding to a weight loss from 30 to 47% (Table II). The first decomposition step of NR-g-PDMMMP corresponds to the degradation of phosphonate linkages, which occurred at lower degradation temperature than that of the NR backbone. The second decomposition step relates to the degradation of NR component in the graft copolymer. It is clear that this step occurred at higher degradation temperature than that of the pure NR. This proves the ability of dimethylphosphonate-functionalized grafts (i.e., the grafted PDMMMP) to improve thermal stability of NR. This results correlated well with the thermal stability of other types of dimethylphosphonate-functionalized grafts. These include NR-g-poly(dimethyl(acryloyloxymethyl)phosphonate) (NR-g-PDMAMP) and NR-g-poly(dimethyl(methacryloyloxyethyl)phosphonate) (NR-g-PDMMEP).<sup>26</sup> In Figure 5, it is also seen that a shift of the TGA curves and hence the degradation temperature toward higher temperatures was observed with increasing GR of NR-g-PDMMMP. Therefore, the thermal stability of the graft copolymer was improved by increasing level of the grafted PDMMMP onto NR molecules.

Figure 6 shows the degradation behavior of pure NR, PDMMMP homopolymer and various types of NR-g-PDMMMP under oxygen atmosphere. This is to simulate thermal stability of the graft copolymer in commonly used conditions. It is clear that the degradation of various polymers in the oxygen atmosphere occurred at lower temperature. This is attributed to the activity of oxygen as oxidant to accelerate the degradation of the organic compounds. It is seen that the decomposition of pure NR starts at 193°C, but its main decomposition peak

was observed at 260°C. On the other hand, the degradation of PDMMMP homopolymer starts at lower temperature of ~128°C and higher temperature of 175°C. Thermal degradation of the NR-g-PDMMMP in O<sub>2</sub> atmosphere also showed double degradation stages where the stability in oxygen also depends on the GR. That is, the degradation temperature increased with increasing the GR. The onset temperatures for the first degradation step in oxygen varied from 205 to 245°C, corresponding to a weight loss from 39 to 48% for the first degradation stage. The degradation temperatures of the second stage are in a range of 335 to 403°C, corresponding to a weight loss of 49% to 31%. In Table II, it is also seen that the char residue increased with increasing GR of the graft copolymerization from 16 to 25% in nitrogen atmosphere and from 12 to 21% in oxygen atmosphere for the NR-g-PDMMMP with GRs of 71 to 95%, respectively. This clearly proves the increasing tendency of thermal resistance properties of the graft copolymer. Higher content of char residue caused thermally insulated and prevented oxygen to transfer to the burning sample, which thereafter slow down the degradation process.

In Table II, slope of the falling region of the TGA plots was also measured. This is a measure of the rate of the degradation process.<sup>28</sup> It is seen that the slope of the TGA curves of the NR-g-PDMMMP are lower than that of the pure NR. This indicates lower degradation rate of the graft copolymer. It is also seen that the samples observed in O<sub>2</sub> exhibited higher slope values and hence higher degradation rate than observed in N<sub>2</sub> atmosphere. Therefore, higher thermal stability with lower degradation rate of the NR-g-PDMMMP is attributed to the presence of phosphorus atoms.



**Figure 6** TGA thermograms under oxygen atmosphere of NR, PDMMMP, NR-g-PDMMMP with various grafting conditions: (a) 4.0 mol % DEDT-NR with polymerization time = 60 min; (b) 4 mol % DEDT-NR with polymerization time = 180 min; (c) 7.2 mol % DEDT-NR with polymerization time = 180 min; (d) 12.0 mol % DEDT-NR with polymerization time = 180 min, (e) pure NR, and (f) PDMMMP.

**TABLE II**  
TGA Characteristics of Pure NR, PDMMMP, NR-g-PDMMMP With Various Grafting Rates (i.e, 71, 80, 89, and 95%), in Nitrogen and Oxygen

Type of copolymer	Nitrogen atmosphere						Oxygen atmosphere							
	Onset temperature (°C)		Weight loss (%)		Slope values		Char (%)		Onset temperature (°C)		Weight loss (%)		Slope values	
	1st step	2nd step	1st step	2nd step	1st step	2nd step	1st step	2nd step	1st step	2nd step	1st step	2nd step	1st step	2nd step
Pure NR	320	-	99.8	-	0.91	-	0.2	193	260	7	92.9	0.98	-	0.1
PDMMMP	221	-	94	-	0.62	-	6	128	175	12	83	0.75	-	5
NR-g-PDMMMP 71%	258	405	37	47	0.34	0.61	16	205	335	39	49	0.40	0.65	12
NR-g-PDMMMP 80%	262	424	40	40	0.30	0.54	20	220	360	44	39.2	0.38	0.62	16.8
NR-g-PDMMMP 89%	269	440	44	34	0.29	0.48	22	236	383	45	37	0.37	0.58	18
NR-g-PDMMMP 95%	276	445	45	30	0.30	0.45	25	245	403	48	31	0.35	0.53	21

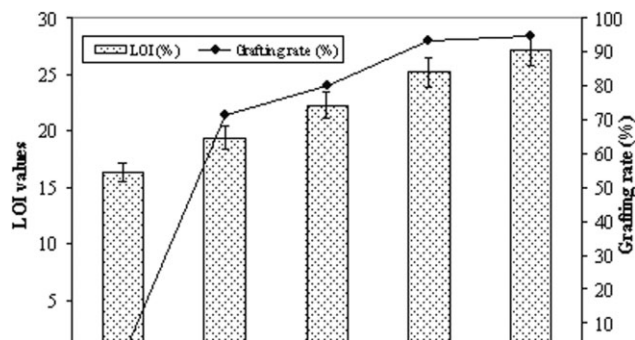
**LOI measurement**

The LOI is defined as the minimum concentration of oxygen in oxygen/nitrogen mixtures, which is necessary to burn the sample with 50 mm long. It has been used to measure flame retardant property of materials. The LOI values of NR and NR-g-PDMMMP with various GRs are shown in Figure 7. It can be seen that the LOI of pure NR is lower than that of the graft copolymer. This indicates lower oxygen needed to burn the pure NR, and hence lower flame retardant property or higher flammability. It is also seen that the LOI of graft copolymer increased with increasing the GRs. This indicates increasing tendency of flame resistance. Therefore, the higher LOI index value was observed, the lower the flammability is consequent.

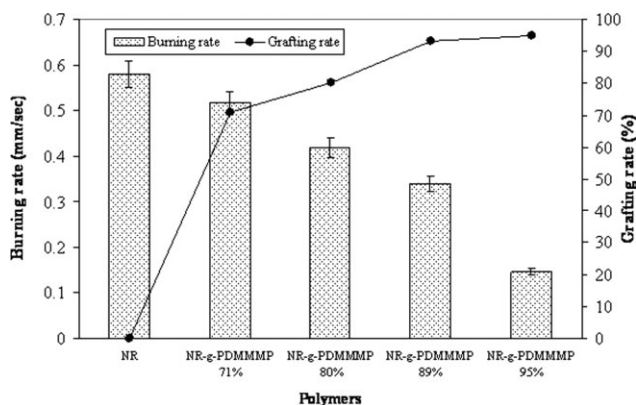
The LOI values and char residue based on the TGA analysis could be correlated (Table II and Fig. 7). It can be seen that pure NR showed the lowest LOI and char residue. Furthermore, the LOI and char residue of NR-g-PDMMMP increased with increasing the GR and hence higher flame retardant properties. This is attributed to the char of phosphorus compounds behaved as thermal insulation to prevent oxygen gas to enter into the flame and thus inhibited combustion. Therefore, higher level of char formed during degradation process caused improvement of flame resistance of the graft copolymer in particular at higher GRs.

**Burning rate**

Burning rate is defined as time required for the flame propagated from one end of the sample to 125 mm of the reference mark. The burning rate of pure NR and NR-g-PDMMMP are shown in Figure 8. It can be seen that the burning rate of the pure NR is the highest. Furthermore, the burning rate of graft copolymer decreased with increasing the GRs. The results correlated well with increasing values of LOI or oxygen needed to burn the sample with a given length as well as with increasing the char



**Figure 7** LOI of pure NR and NR-g-PDMMMP with various grafting rates.



**Figure 8** Burning rate of pure NR and NR-g-PDMMMP with various grafting rates.

residue. Therefore, the grafted polyphosphonate onto NR backbone improved the flame retardant properties of NR. This is attributed to action of phosphorus compound as a char residue to prevent the oxygen to enter into the flame and caused the flame extinguished. Higher level of phosphorus compound (i.e., higher GR) caused higher chemical interaction between the polar functional groups and hence higher flame retardant property as well as higher thermal stability of the NR-g-PDMMMP. Therefore, the NR-g-PDMMMP prepared using DEDT-NR with *N,N*-diethyldithiocarbamate groups at 7.2 and 12.0 mol % (i.e., with the GRs of 89 and 95%, respectively) can be used as thermal insulation materials or flame resistance products.

## CONCLUSION

NR-g-PDMMMP was successfully prepared and characterized by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$ -NMR and FTIR. The MV was also measured to verify the chemical interaction. It was found that the NR-g-PDMMMP exhibited higher MV than that of the pure NR. Also, the MV of graft copolymers increased with increasing GR. This indicates increasing level of chemical interaction between the polar functional groups in the graft copolymer. The DSC results showed that the NR-g-PDMMMP copolymers exhibited two values of  $T_g$ , one corresponded to the glass transition of the *cis* 1,4-polyisoprene, and the other related to the transition of the dimethylphosphonate-functionalized grafts (PDMMMP). It was also found that the  $T_g$  of the rubber phase increased with increasing the GR because of higher chemical interaction and hence lower chain flexibility. TGA results of NR-g-PDMMMP with various GR in nitrogen and oxygen atmospheres showed double degradation steps. The lower degradation temperature was attributed to the decomposition of dimethylphosphonate-functionalized grafts, whereas the higher temperature related to the degradation of

NR backbone. It is clear that the degradation temperature in a second stage was higher than the degradation temperature of the pure NR. This proves thermal stability of NR with the grafted phosphorus-containing monomers along the chains. Furthermore, increasing level of oxygen needed to burn a certain length of the specimen, i.e., LOI as well as decreasing trend of burning rate were observed with increasing the GR which indicated higher flame resistant properties. This is attributed to increasing char residue, which consists of phosphorus compound. This material behave as thermal insulation and a barrier of oxygen to transfer to the burning materials.

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