Rheological, Thermal, and Curing Properties of Natural Rubber-*g*-Poly(methyl methacrylate)

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ABSTRACT: Graft copolymers of NR and PMMA (i.e., NR-*g*-PMMA) were prepared with the bipolar redox initiation system, using various percentages of molar ratios of NR/MMA at 95/5, 90/10, 80/20, 70/30, and 60/40. It was found that the Mooney viscosity, shear stress, and shear viscosity of the NR-*g*-PMMA increased with an increase in the molar ratio of MMA used in the graft copolymerization. This may be attributed to an increasing trend of the chemical interaction between polar functional groups within the grafted PMMA molecules. Furthermore, a decreasing trend of storage moduli was observed with increasing molar ratios of MMA. The glass transition temperature was obtained from the tan δ curves. We found a slightly increasing trend of the T_g's with an increase in molar ratios of MMA used in the grafting reaction. The NR-*g*-PMMA was later compounded using TBBS as an accelerator. With an increase in molar ratios of MMA in the grafting reaction, we observed an increasing trend of minimum torque, maximum torque, cure time, and scorch time, but quite similar levels of torque difference and crosslink density. Furthermore, the tensile strength of the NR-*g*-PMMA gum vulcanizate increased with an increase in molar ratios of MMA, whereas the elongation at break decreased. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1600–1614, 2006

Key words: natural rubber; rheological properties; thermal properties; graft copolymer; poly(methyl methacrylate)

INTRODUCTION

Natural rubber (NR) contains 93–95% *cis*-1,4-polyisoprene.[1] It is an unsaturated elastomer with various good properties, such as high strength, high elongation, and outstanding resilience. However, there are a number of disadvantages of NR such as high sensitivity to heat and oxidation because of the double bonds in its chains. NR also has low tensile strength, tensile modulus, and poor creep characteristics unless highly vulcanized.[2] The disadvantages of NR have limited its application in industry. Various types of chemical modifications have been performed to increase the useful properties of the NR. One of the important modifications to NR is a preparation of graft copolymer of NR with various types of vinyl monomers such as styrene,[3–5] acrylonitrile,[6] stearyl methacrylate/divinyl benzene,[2] dimethylaminoethyl methacrylate,[7] glycidyl methacrylate/styrene,[8] and methyl methacrylate (MMA).[9–16]

The graft copolymerization of NR and MMA has been performed by free-radical polymerization in solution[9,10] or latex states[11–16] with various initiation systems such as benzoyl peroxide,[9] azobis(2-methyl-proprionitrile),[9,13] potassium persulfate,[16] and redox initiators.[11,12,14,15]

In this work, a graft copolymer of NR and MMA was prepared with a semibatch emulsion polymerization technique. A redox initiating system consisting of an initiator (cumene hydroperoxide, CHP) and coinitiator (tetraethylene pentamine, TEPA) was used. This initiation system proved to be very effective for the emulsion polymerization of NR latex. That is, it was not sensitive to oxygen and worked well in the presence of ammonia.[17] Rheological properties of the graft copolymer (NR-*g*-PMMA) were later characterized, using a Mooney viscometer and a capillary rheometer. Dynamic mechanical analysis (DMA) and thermogravimetry (TG) were also used to characterize thermal properties of the graft copolymers. Furthermore, curing and mechanical properties of the NR-*g*-PMMA compounds and vulcanizates were characterized.

EXPERIMENTAL

Materials

The rubber used was low ammonia (LA) concentrated latex, manufactured by Pattani Industry (Pattani,

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Thailand). Methyl methacrylate (MMA) was used as a monomer for the preparation of the graft copolymer of NR and MMA (NR-*g*-PMMA), manufactured by Merck (Muchen, Germany). The CHP and TEPA used as redox initiators were manufactured by Fluka Chemie AG (Buchs, Switzerland). The nonionic surfactant used to stabilize the latex during graft copolymerization was Teric N30 (alkylphenol ethoxylate), manufactured by Huntsman Corp., Australia Pty Ltd (Ascot Vale, Vic, Australia). The zinc oxide used as an activator was manufactured by Global Chemical (Samutprakarn, Thailand). The stearic acid also used as an activator was manufactured by Imperial Chemical (Pathumthani, Thailand). The sulfur used as a vulcanizing agent was manufactured by Ajax Chemical (Samutprakarn, Thailand). The tetramethylenethiuram disulphide (Perkacit, TMTD), *N-tert*-butyl-2-benzothiazolesulphenamide (Santocure, TBBS), 2,2-mercaptobenzothiazole (Perkacit, MBT), and 2,2-dithiobis(benzothiazole) (Percacit, MBTS) used as curing accelerators were manufactured by Flexsys (USA).

Preparation of NR-*g*-PMMA

A semibatch emulsion polymerization technique with bipolar redox initiation system was used to prepare the NR-*g*-PMMA. The redox initiation with CHP and TEPA was performed as described in our previous work.[14] The NR-*g*-PMMA was prepared using various percentages of molar ratios of NR and MMA (i.e., NR/MMA) at 95/5, 90/10, 80/20, 70/30, and 60/40. That is, various concentration of MMA monomer at 5, 10, 20, 30, and 40 mol % were studied. The predetermined quantities of LA latex and distilled water were first added into the main reactor. The mixture was thoroughly stirred, under a nitrogen atmosphere and a fixed temperature of 50°C. The precise quantity of MMA monomer, nonionic surfactant (Teric N30) and distilled water were incorporated into a feeding tank, under continuous mixing by mechanical stirrer. The chemicals in the feeding tank were then delivered into the main reactor, using a fluid delivery pump at a constant flow rate of 5 mL/min. The mixture was allowed to react for 2 h, after all chemicals from the feeding tank were completely delivered into the main reactor. The latex was later coagulated and dried in a vacuum oven for 24 h. The samples were cut into small pieces. The presence of grafted PMMA on the NR backbone was confirmed using a FTIR spectrophotometer, series 1600 (Perkin-Elmer, USA), on a purified form of the graft copolymer. For rheological, thermal, and curing characterization, the graft copolymers were used without purification.

Rheological characterization

Two types of rheological techniques were used to characterize flow properties of the NR-*g*-PMMA. They

were the Mooney viscometer (viscTECH+, shearing disk viscometer) and a single bore Rosand capillary rheometer (model RH7). Mooney viscosities of unmodified NR and various types of NR-*g*-PMMA were quantified at 180°C, using a small rotor with a preheating time of 1 min and a testing time of 4 min. The typical type of the Mooney viscosity was classified as MS (1 + 4), 180°C.

Shear flow properties, in terms of shear stress and shear viscosity at various shear rates, were determined using a capillary rheometer over a wide range of shear rates (5–1600 s^{-1}) at a test temperature of 180°C. Dimensions of the capillary die used were a 2-mm diameter, 32-mm length, and 180° entrance angle with the aspect ratio (L/D) of 16:1. The materials were first preheated in a barrel for 7 min under a pressure of approximately 2–4 MPa to get a compact mass. The excess molten material was automatically purged until no bubbles were observed. The test was then carried out at various shear rates as set by a program via a microprocessor. The pressure drop across the capillary channel and melt temperature were captured via a data acquisition system during the test. Equations used to calculate shear stress, shear viscosity, and shear rate were described in our previous publications.[18,19]

Thermal properties characterization

Two techniques were used to follow the thermal behavior of the NR-*g*-PMMA. They were TG and DMA. The thermogravimetric analysis was carried out in a nitrogen atmosphere, at a heating rate of 20°C/min, in a Shimadzu TGA-50 thermal analyzer. A constant weight of sample was used in all cases. Thermograms were recorded from room temperature to 700°C. The temperature at which the rate of mass loss is at a maximum was determined from the differential thermogravimetry (DTG) curve and called the decomposition temperature (T_d). The DMAs were carried out on a PerkinElmer DMA7 instrument. The experiment was conducted in tension mode. A temperature/time scan was carried out at temperature ranges of −80°C to +150°C at a frequency of 1 Hz. The heating rate was 2°C/min. Liquid nitrogen was used to achieve subambient temperature.

Compounding and cure characterization of NR-*g*-PMMA

The NR-*g*-PMMA prepared with a percentage molar ratio of NR/MMA = 95/10 was selected to compound with various chemicals, as shown in Table I. The influence of various types of accelerators (i.e., TBBS, MBT, MBTS, and TMTD) at the same concentration (i.e., 0.0029 mol/100 g of NR-*g*-PMMA) was first investigated. The NR-*g*-PMMA was premasticated for 5

TABLE I
Compounding Formulation

Ingredients	Quantity (phr)			
	Fl	F2	F3	F4
NR-g-PMMA	100	100	100	100
Stearic acid	0.5	0.5	0.5	0.5
ZnO	6	6	6	6
TBBS	0.7	–	–	–
MBT	–	0.5	–	–
MBTS	–	–	1.0	–
TMTD	–	–	–	0.7
Wingstay L	1	1	1	1
Sulfur	3.5	3.5	3.5	3.5

min, using a two-roll mill maintained at 60°C. Other chemicals were later incorporated according to the mixing schedule shown in Table II. The rubber compounds were sheeted out and conditioned at room temperature in a closed container for 24 h. Curing characteristics were then studied at 160°C, using a Monsanto oscillating disk rheometer (model ODR 2000) at a 1° arc. The scorch time, cure time, and cure rate index [i.e., = 100/(cure time –scorch time)] were calculated based on the ODR curve or curing curve. Furthermore, torques of the curing curves were also quantified.

The most suitable type of accelerator was later selected based on its superior curing characteristics. Various types of NR-g-PMMAs (i.e., prepared with percentage molar ratios of NR/MMA = 95/5, 80/20, 70/30, and 60/40) were again compounded, using the suitable type of accelerator and other chemicals as indicated in Table I, with a mixing schedule shown in Table II. The curing properties were again studied.

Sample preparation and physical testing

The rubber compounds were compression molded into test specimens at 160°C according to the respective cure times determined by ODR 2000. Dumb-bell samples with the length of 115 mm were cut from a 2-mm-thick molded sheet. The tensile testing procedure was carried out according to Test Method A as described in ASTM D412. A Hounsfield tensometer (model H 10KS) operating at 500 mm/min was used to determine the tensile properties in terms of ultimate tensile strength and elongation at break.

Crosslink density

Samples weighing about 0.8 g were cut from cured sheets and immersed in 80 mL of toluene in a dark container for 1 week at room temperature. Swollen samples were blotted with a tissue paper and immediately transferred into a weighing container to determine swollen weight. The swollen samples were later

transferred to a vacuum oven and dried at room temperature for 24 h. The dried weight was then determined. Crosslink density was calculated using the Flory–Rehner equation:[20]

$$\rho_c = \frac{1}{2V_s} \frac{\ln(1 - v_r^0) + v_r^0 + \chi(v_r^0)}{v_r^{0^{1/3}} - \frac{v_r^0}{2}} \tag{1}$$

where ρ_c is the crosslink density (mol/m^3); V_s is the molar volume of toluene (1.069×10^{-4} m^3/mol) at 25°C; v_f^0 is the fraction of rubber in the swollen gel; and χ is the interaction parameter (0.39 for gum NR).

RESULTS AND DISCUSSION

Mooney viscosity

Figure 1 shows the Mooney viscosity of NR-g-PMMA prepared using various molar ratios of NR/MMA compared with the Mooney viscosity of unmodified NR (i.e., at a molar ratio of MMA = 0%). It can be seen that the Mooney viscosity of the graft copolymers was higher than that of the unmodified NR (which was coagulated from the LA latex used as a raw material for a preparation of NR-g-PMMA). This may be attributed to higher chemical interaction between molecules of NR-g-PMMA via polar functional groups (i.e., carbonyl group). Higher torque therefore was needed to deform the NR-g-PMMA melt during the Mooney test. The Mooney viscosity also increased with an increase in the molar ratio of MMA or the concentration of MMA monomer used in the graft copolymerization. This is because of an increase in the grafted PMMA on the NR molecules with increasing concentrations of MMA monomer, as in our earlier findings.[14] As a consequence, higher chemical interaction between polar functional groups of the grafted PMMA was obtained. The force used to move the Mooney viscometer's disc increased with the increase of grafted PMMA content in the graft copolymer molecules.

Shear flow properties of NR-g-PMMA

Plots of apparent shear stress versus apparent shear rate of the NR-g-PMMA prepared with various molar ratios

TABLE II
Mixing Schedule

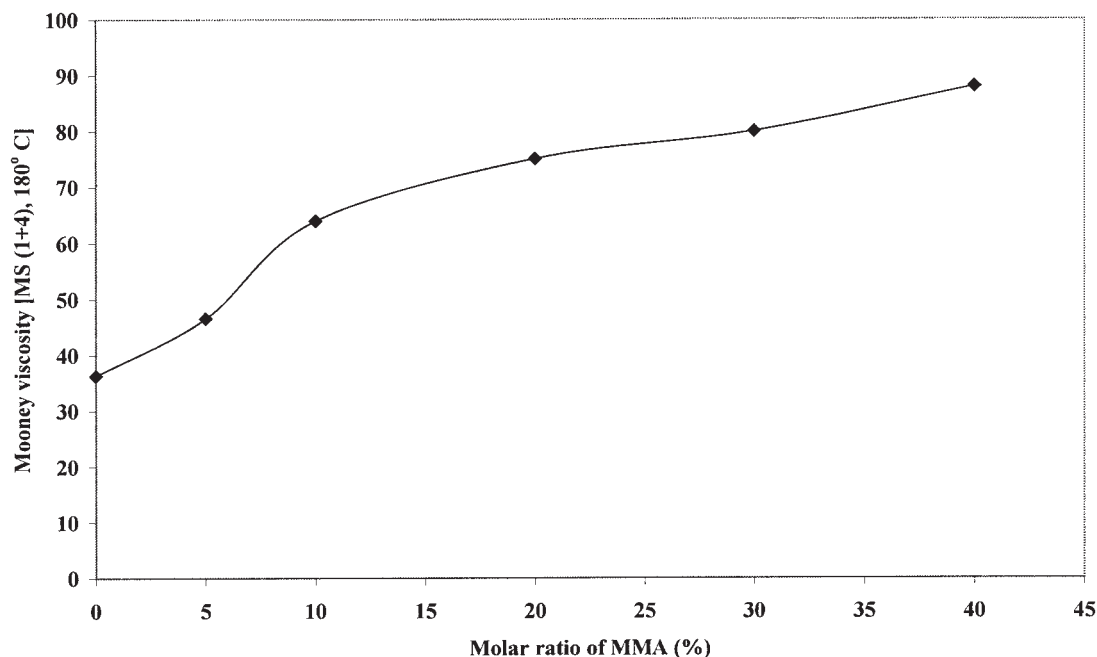| Descriptions	Time (min)
Rubber mastication	5
Stearic acid	1
Zinc oxide	1
Wingstay L	1
Accelerators	2
Sulfur	2
Compound finishing	4

Figure 1 Mooney viscosities for various types of NR-*g*-PMMA compared with that for pure NR.

of NR/MMA compared with the unmodified NR (i.e., pure NR) are shown in Figure 2. It can be seen that the apparent shear stress increased with an increase of shear rate. At the same level of apparent shear rate, the pure NR exhibited the lowest apparent shear stress. Furthermore, the apparent shear stress increased with an increase in MMA concentration used to prepare the NR-*g*-PMMA. That is, among various types of the NR-*g*-PMMA, the graft copolymer prepared with a percentage molar ratio of NR/MMA = 95/5 showed the lowest apparent shear stress, while a molar ratio of NR/MMA = 60/40 exhibited the highest value. The levels of apparent shear stress at a given shear rate for various types of graft copolymer can be ranked according to the percentage of molar ratio of NR/MMA as follows: 95/5 < 90/10 < 80/20 < 70/30 < 60/40. The increasing trend of the apparent shear stress with an increase in molar ratio in NR/MMA was the result of polar functional groups in the NR-*g*-PMMA molecules. Therefore, increasing the concentration of MMA monomer caused an increasing trend of the apparent shear stress and Mooney viscosity (Fig. 1).

Figure 3 shows the plots of apparent shear viscosity versus apparent shear rate for the NR-*g*-PMMA compared with that for pure NR. It was found that the apparent shear viscosity decreased with an increase in apparent shear rate. That is, a shear thinning behavior was observed for all sets of the polymers. Furthermore, the same phenomenon was observed as in the cases of the apparent shear stress and Mooney viscosity. That is, the pure NR exhibited the lowest apparent shear viscosity. Also, the trends of the apparent shear viscosity at a given shear rate increased with an increase in concentration of MMA used in the graft copolymerization. Figure 4 shows the apparent shear viscosity at constant apparent shear rates of 10, 30, and 100 s^{-1}. The results confirm the increasing trend of apparent shear viscosity with the increase in molar ratios of MMA or concentration of MMA used in the graft copolymerization. The increasing levels of grafted PMMA on NR molecules were the reason for the increasing trend.

To clarify the shear thinning behavior of the rubber melts, the power law equation was applied to the relationship between shear rate and shear stress (i.e., in Fig. 2).[21]
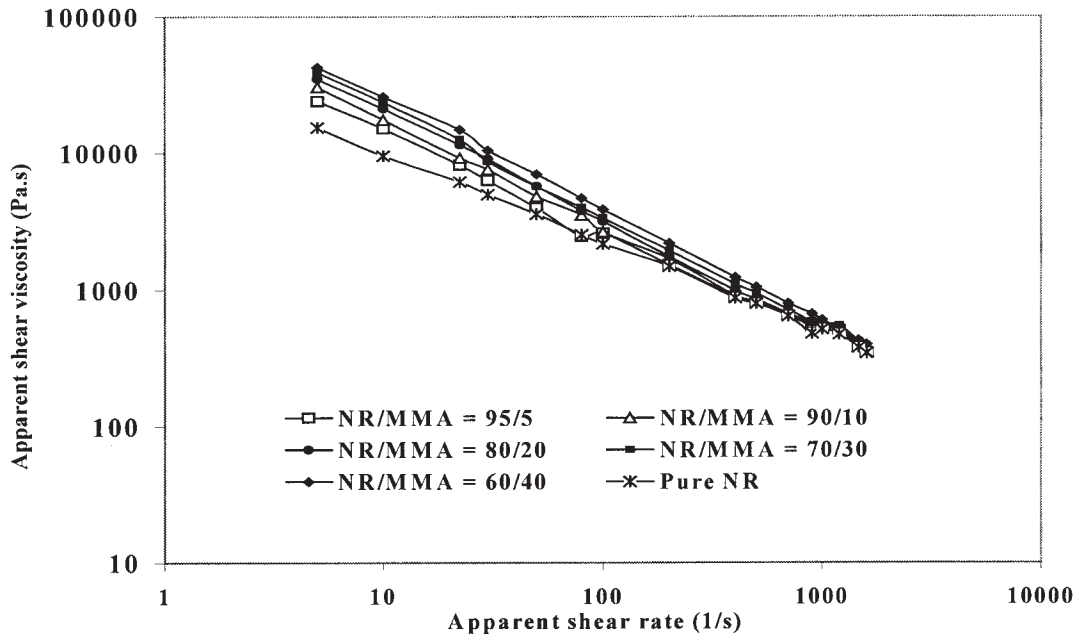

Figure 2 Relationship between apparent shear rate and apparent shear stress for various types or NR-*g*-PMMA compared with that for pure NR.

Figure 3 Relationship between apparent shear rate and apparent shear viscosity for various types of NR-*g*-PMMA compared with that for pure NR.

$$\tau = K(\dot{\gamma})^n \qquad (2)$$

where n is the power law index or the flow behavior index, $\dot{\gamma}$ is the shear rate, τ is the shear stress, and K is the consistency or viscosity coefficient index.

From the linear relation on a log–log scale, we can get the slope (n) and intercept (K), which are plotted in Figure 5. The n value of the pure NR was higher than those of various grades of the graft copolymers. The n values decreased with increasing levels of the grafted
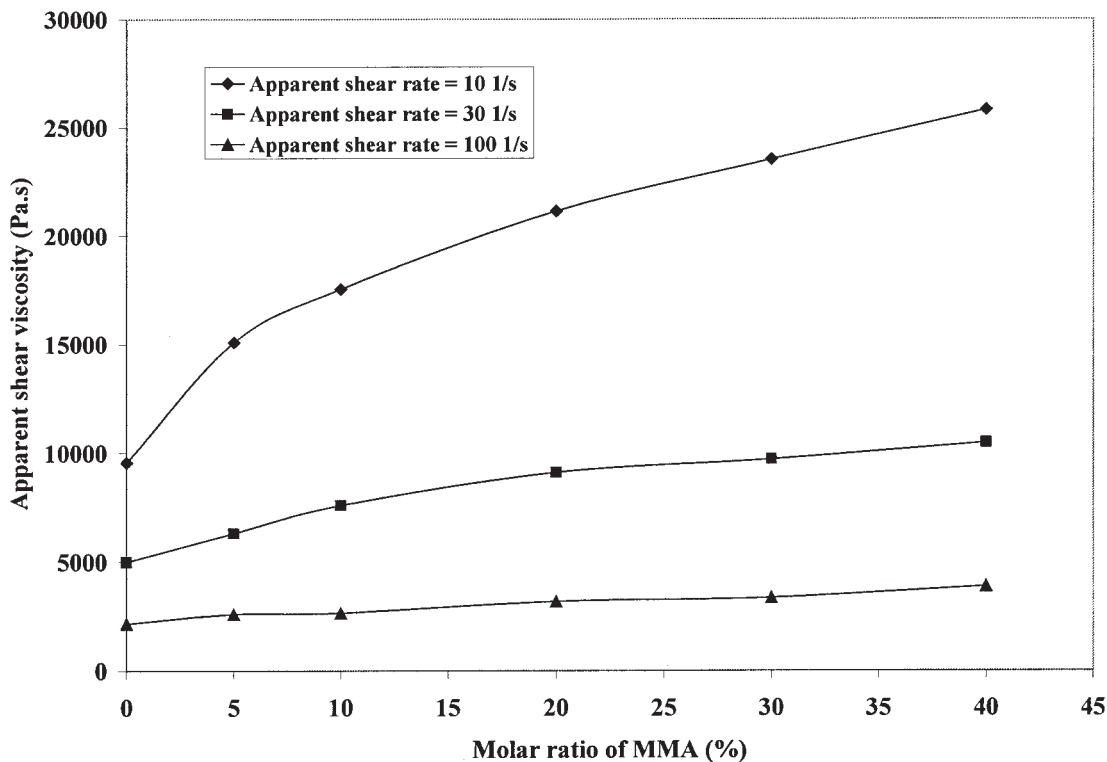
Figure 4 Apparent shear viscosity for various types of NR-*g*-PMMA at constant apparent shear rates of 10, 30, and 100 s^{-1} compared with that for pure NR.
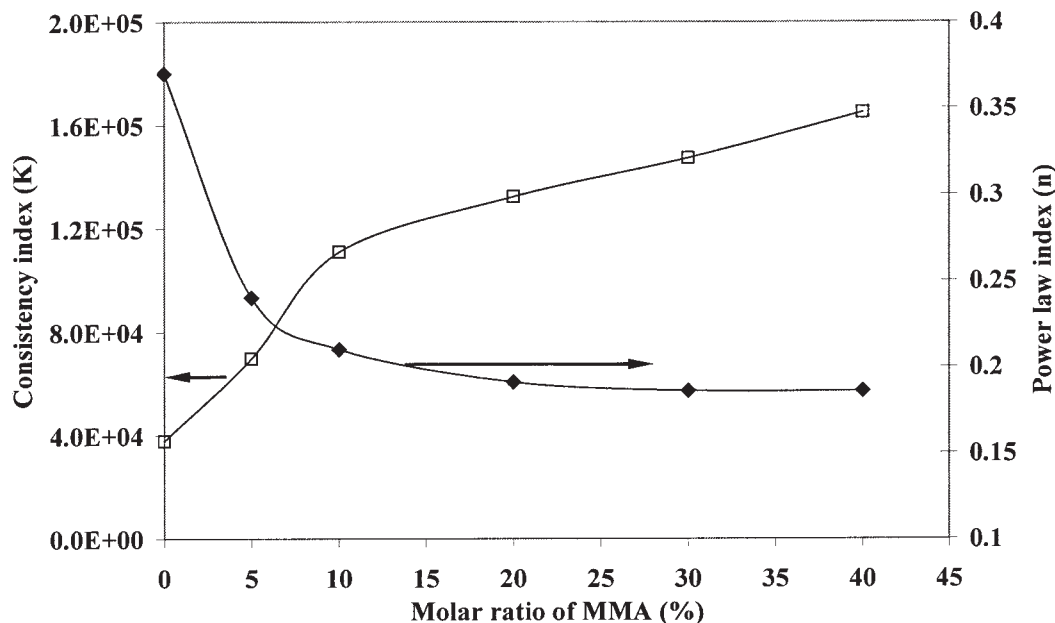
Figure 5   Power law index (*n*) and consistency index (*K*) for various types of NR-*g*-PMMA compared with that for pure NR.

PMMA in the NR-*g*-PMMA molecules. This indicates greater shear thinning in the flow upon increasing the molar ratio of MMA used in the graft copolymerization. The value of *n* also reflects the deviation of the flow profiles from uniform parabolic flow patterns (i.e., *n* = 1 for Newtonian flow) to plug-like flow profiles. The NR-*g*-PMMA exhibited very low *n* values (i.e., *n* < 0.25). Therefore, the highly pseudoplastic fluid flowed through the capillary almost as a plug moving at a uniform speed as the melt was sliding down against the capillary wall. The consistency index, *K*, is also shown in Figure 5. By definition, the consistency is a Newtonian viscosity if *n* = 1 and related to the zero-shear viscosity (i.e., shear viscosity at shear rate of zero) of the flowing rubber melt at a test temperature. It was found that the consistency index increased with the level of grafted PMMA (i.e., increasing the molar ratio of MMA). The trends of consistency index (i.e., zero-shear viscosity) corresponded to the trends of Mooney viscosity (Fig. 1), apparent shear stress (Fig. 2), and apparent shear viscosity (Fig. 3 and 4).

Dynamic mechanical analysis

Thermal transition phenomena of the NR-*g*-PMMA were studied using DMA technique. Figure 6 shows dependence of storage modulus on the temperature for various types of NR-*g*-PMMA compared with that for pure NR. We see that the storage moduli decrease with increase in testing temperature. This is attributed to an increase in mobility of the polymer chains with increasing temperature. The storage modulus at low

temperature of pure NR is greater than those of the graft copolymers. The storage moduli also decreased with an increase in MMA concentration used in the graft copolymerization. As stated earlier, an increase in MMA concentration or a percentage molar ratio of MMA caused an increasing level of chemical interaction between the NR-*g*-PMMA molecules. Also in our previous work,[22] infrared spectroscopy was used to characterize the NR-*g*-PMMA prepared with various percentage molar ratios of NR/MMA. The characteristic bands of infrared spectrum of C=O stretching and C—O stretching were observed at 1732 and 1140 cm^{-1}, respectively. This proves the presence of the grafted PMMA on the NR molecules. The level of grafted PMMA was also quantified using the absorbance ratio of IR peaks at 1732 (—C=O stretch) and 835 cm^{-1} (—C—H out-of-plane-bending on cis C=C bonds). We concluded that the level of —C=O bonds in the graft copolymer molecules increased with an increasing level of MMA monomers in the grafting reaction. Therefore, an increasing trend of chemical interaction within and between the NR-*g*-PMMA molecules is obvious because of increasing levels of polar groups (i.e., —C=O and —C—O) in the molecules. This leads to an increasing trend for a formation of chemical bond such as hydrogen bond. An increase in chain stiffness of the graft copolymer molecules was the consequence. Therefore, the storage moduli decreased with an increase in chain stiffness. The effect of percentage molar ratio of MMA on loss tangent (tan δ) is shown in Figure 7. It can be seen that the tan δ showed a peak around the temperature between −65°C to −50°C, this being known as a transition re-
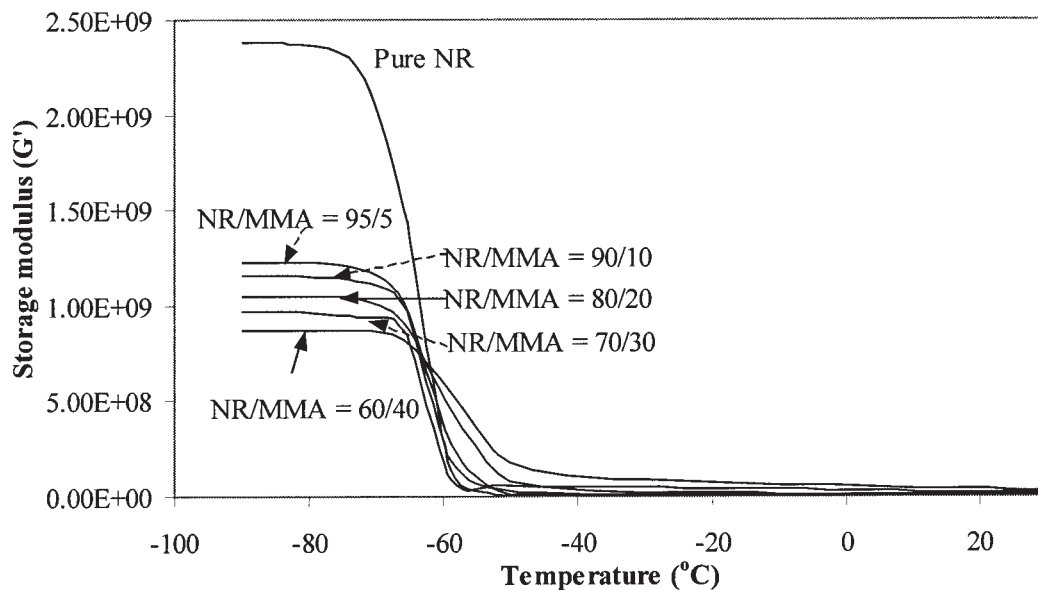
Figure 6   Storage moduli (G') of NR-g-PMMA prepared using various molar ratios of NR/MMA in the graft copolymerization compared with that of pure NR.

gion. The glass transition temperature (T_g) can be quantified at a maximum value of each tan δ curve. The pure NR exhibited the lowest T_g (i.e., −65°C). We also observed the slight shift of the T_g to higher value with an increase in MMA concentration or a percentage molar ratio of MMA used in the graft copolymerization. That is, the T_g's are ordered as follows: NR-g-PMMA with a molar ratio of NR/MMA = 60/40 > 70/30 > 80/20 > 90/10 > 95/5 > pure NR, and the details are given in Table III. This is attributed to an increase in a restriction of molecular chains upon increasing levels of the grafted PMMA in the NR molecule.

Thermal degradation

Thermal degradation of the various types of NR-g-PMMA and unmodified NR (i.e., pure NR) was investigated using TGA. Figure 8 shows the TGA thermograms for various types of rubbers. It can be seen that
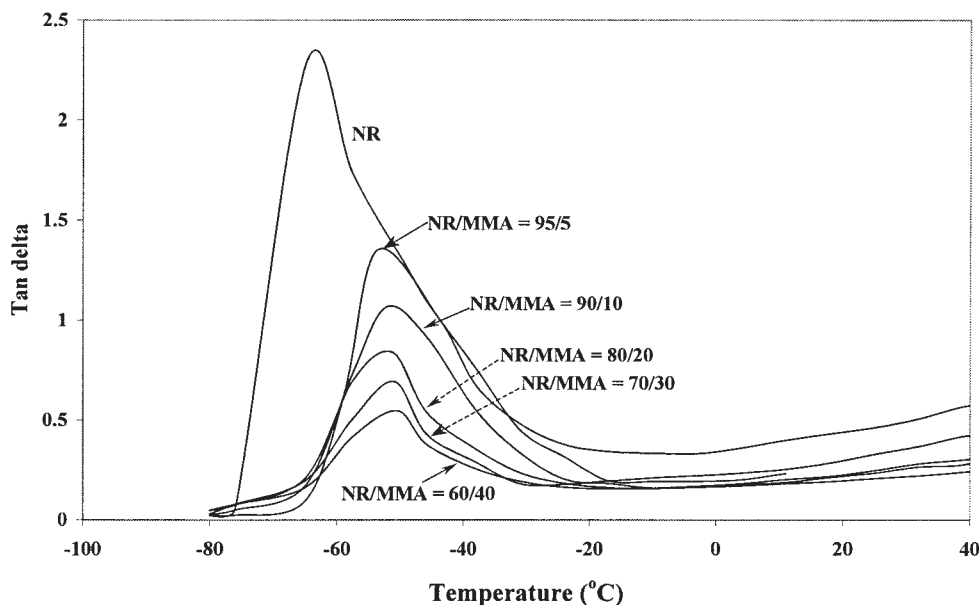

Figure 7   Tan δ of NR-g-PMMA prepared using various molar ratios of NR/MMA in the graft copolymerization compared with that of pure NR.

TABLE III
Glass Transition Temperature (T_g) of NR-*g*-PMMA Prepared Using Various Molar Ratios of NR/MMA in the Graft Copolymerization Compared With Pure NR

Types of polymer	Glass transition temperature (°C)
Pure NR	−65.0
NR/MMA = 95/5	−53.7
NR/MMA 90/10	−52.2
NR/MMA = 80/20	−51.3
NR/MMA = 70/30	−51.0
NR/MMA = 60/40	−50.5

the degradation of pure NR started and completed at the lowest temperature, while the NR-*g*-PMMA prepared using a percentage molar ratio of NR/MMA = 60/40 exhibited the highest temperatures. Therefore, the starting and completing degradation temperature for various types of rubbers are ordered as follows: pure NR < NR-*g*-PMMA (95/5) < NR-*g*-PMMA (90/10) < NR-*g*-PMMA (80/20) < NR-*g*-PMMA (70/30) < NR-*g*-PMMA (60/40). The degradation temperature (T_d) of various types of rubbers was evaluated from the main weight loss obtained from DTG curves (not shown here), and the results given in Figure 9. We found that the pure NR exhibited the lowest decomposition temperature (i.e., at 364.5°C), while various types of NR-*g*-PMMA showed the T_d's at 376.96°C, 377.32°C, 380.63°C, 384.92°C, and 390.96°C for the graft copolymer prepared with the percentage molar ratios of NR/MMA = 95/5, 90/10, 80/20, 70/30, and

60/40, respectively. Therefore, it is clear that the T_d of the pure NR was lower than those of the graft copolymers. Furthermore, the T_d increased with increasing concentrations of MMA monomer used in the graft copolymerization. The increasing trend of T_d with increasing concentrations of MMA can be described as increasing levels of chemical interaction between polar functional groups present in the rubber molecules. Stronger interaction, as observed from increasing levels of the Mooney viscosity (Fig. 1), apparent shear stress (Fig. 2) and apparent shear viscosity (Figs. 3 and 4), upon increasing concentrations of MMA caused increasing decomposition temperatures of the graft copolymers. This may be attributed to the stronger chemical bonds between the molecules with increasing MMA concentration in the grafting reaction. Also, increasing oxygen compounds that exhibited higher resistance to thermal degradation than that of the pure hydrocarbon might be another reason for the increasing trend of T_d's.

Curing properties of NR-*g*-PMMA with a molar ratio of NR/MMA = 90/10

Figure 10 shows curing curves or rheographs (from ODR 2000) of NR-*g*-PMMA prepared from a percentage molar ratio of NR/MMA = 90/10. Curing characteristics of the NR-*g*-PMMA compounds using various types of accelerators (i.e., TBBS, MBTS, MBT, and TMTD) were examined at 160°C for 30 min. Force required to oscillate a rheometer's disc or torque was
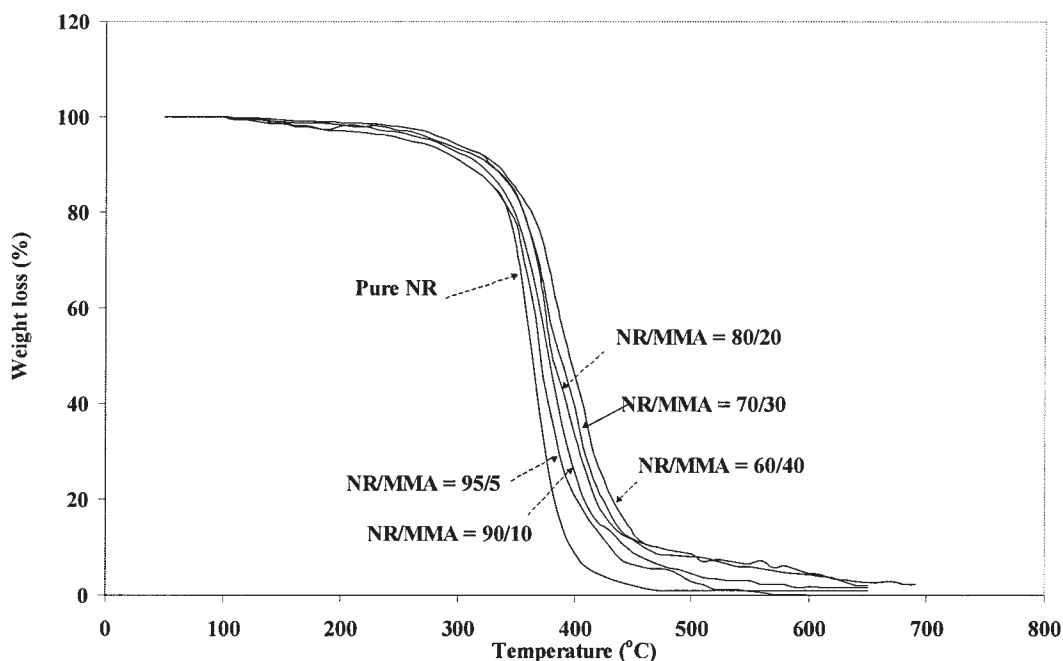

Figure 8 TGA thermograms of NR-*g*-PMMA prepared using various molar ratios of NR/MMA in the graft copolymerization compared with that of pure NR.
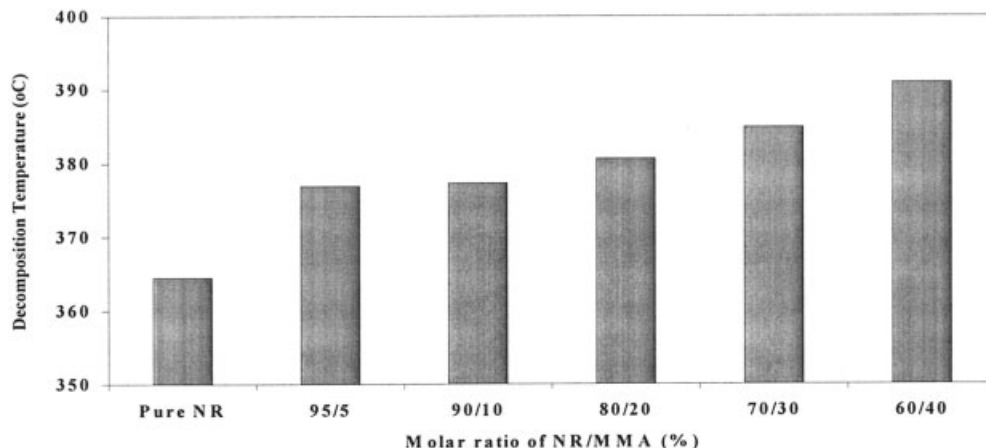
Figure 9 Decomposition temperatures (T_d) of NR-*g*-PMMA prepared using various molar ratios of NR/MMA in the graft copolymerization compared with that of pure NR and PMMA.

recorded as a function of testing time. The torque is normally proportional to the shear modulus or the stiffness of the rubber compounds. In Figure 10, it can be seen that the torques for all sets of experiments first decreased during the specimen warming up time. After ~2 min, the torque increased abruptly, owing to vulcanization of the rubber component. The torques then reached the maximum values (i.e., at 100% vulcanization). The characteristics of the curing curve for the NR-*g*-PMMA compounds using various types of accelerators include a maximum torque and slight reversion. That is, the curing curve was maximized and some crosslinking structures were later destroyed by thermal energy, under the continuous rotor oscillation. Different curing behaviors were observed for the compounds using different types of accelerators. That is, the rubber compound with TBBS exhibited the highest maximum torque (M_H) and torque difference

($M_H - M_L$), while the compound with MBT showed the lowest values (Fig. 11). The torques of the NR-*g*-PMMA compounded with TMTD and MBTS fall between the compounds using TBBS and MBT. Therefore, the M_H and $M_H - M_L$ of various types of NR-*g*-PMMA compounds can be ranked as follows: TBBS > TMTD > MBTS > MBT. It is therefore concluded that the NR-*g*-PMMA compounded with TBBS gave the highest degree of crosslinking, according to its torque difference. The crosslinking density of various types of vulcanizates is shown in Figure 12. We found that the crosslinking density of the gum vulcanizates of NR-*g*-PMMA using various types of accelerators was in agreement with the levels of torque difference.

Figure 13 shows the scorch time (t_{s2}) and cure time (t_{90}) of various types of compounds. It was found that the NR-*g*-PMMA compounded with TBBS showed the lowest cure time and a reasonable scorch time (i.e.,
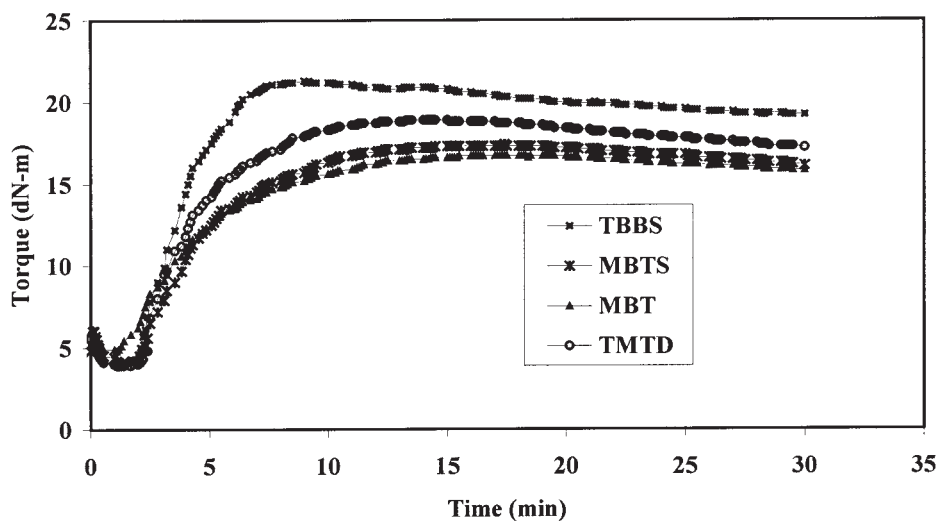

Figure 10 Rheographs of NR-*g*-PMMA with molar ratio of NR/MMA = 90/10, using various types of accelerators.
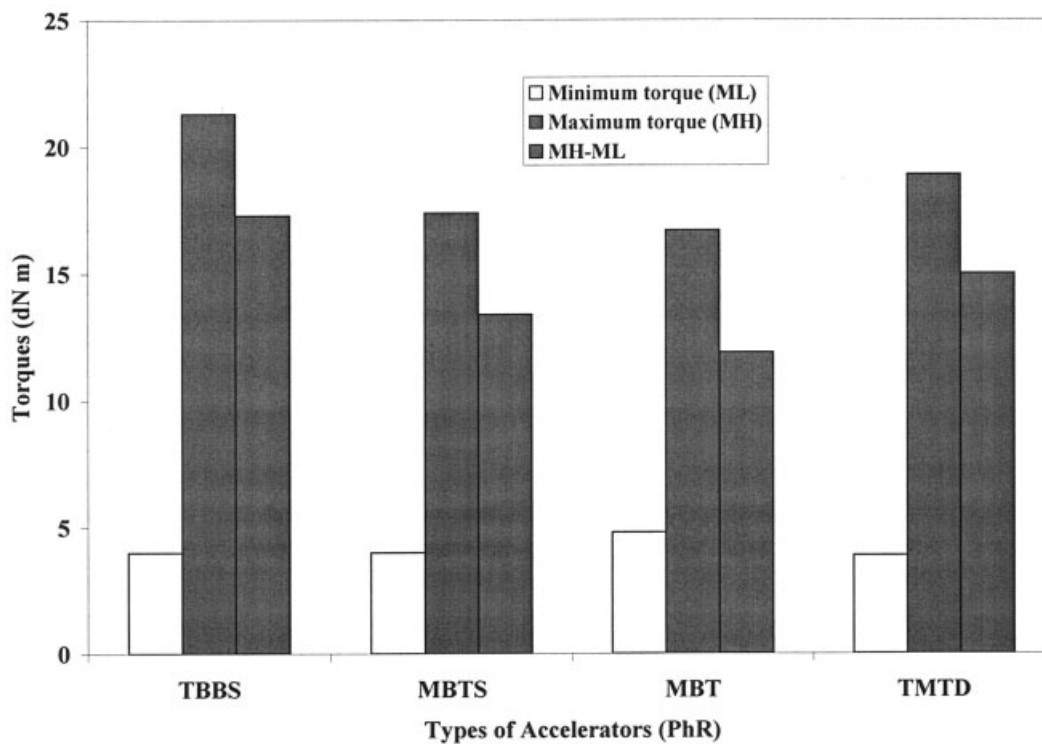
Figure 11 Torque of NR-*g*-PMMA with molar ratio of NR/MMA = 90/10, using various types of accelerators.
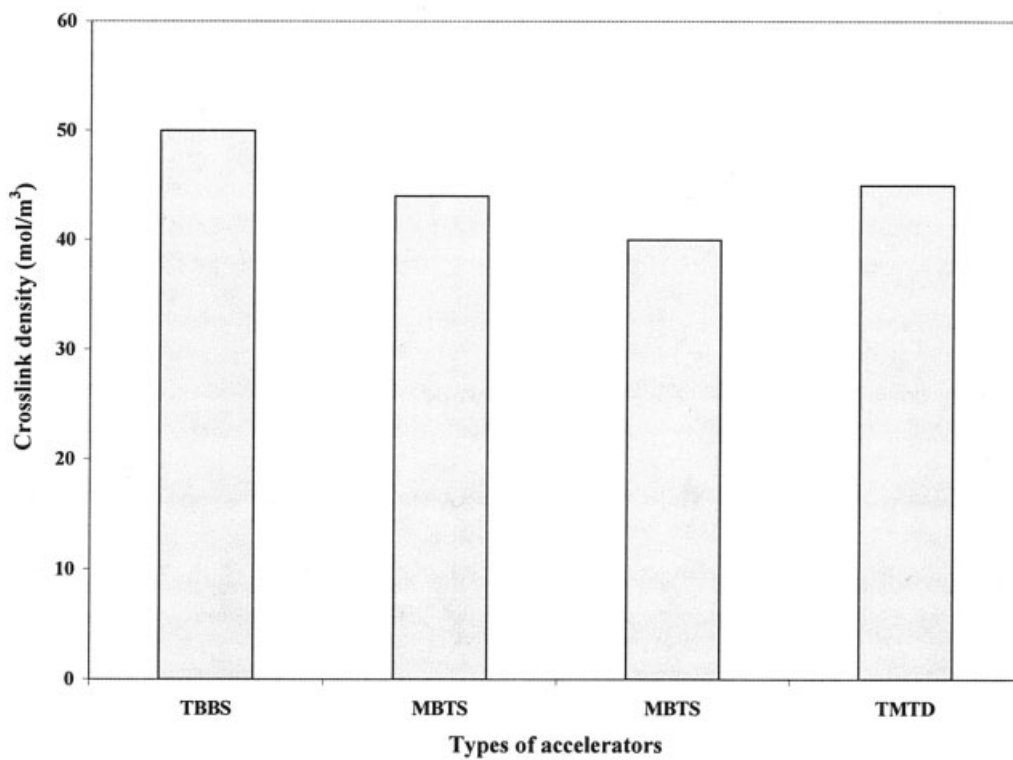

Figure 12 Crosslink density of gum vulcanizate for NR-*g*-PMMA with a percentage molar ratio of NR/MMA = 90/10, using various types of accelerators.
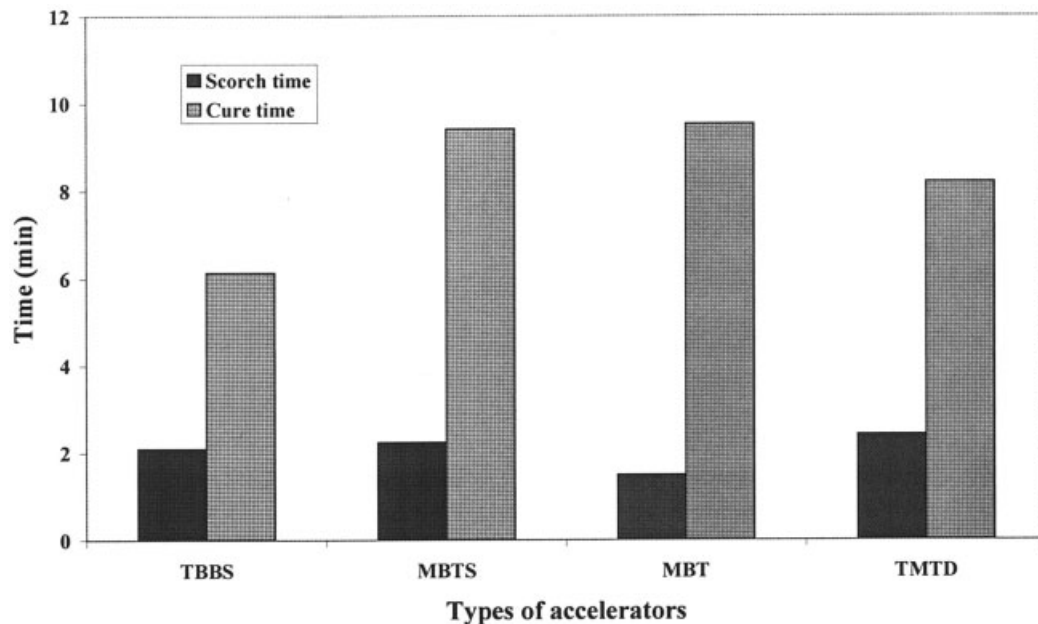
Figure 13 Scorch time and cure time of NR-*g*-PMMA with molar ratio of NR/MMA = 90/10, using various types of accelerators.

long enough to store without a high degree of crosslinking at storage temperature). The cure time of the other types of compounds (i.e., MBT, MBTS, and TMTD compounds) were longer than that of the TBBS compound. Furthermore, the MBTS and TMTD com-

pounds exhibited scorch times similar to the TBBS compound, but the MBT compound showed a shorter scorch time. Figure 14 shows the cure rate index of various types of NR-*g*-PMMA compounds. We found that the TBBS compound showed the highest cure rate
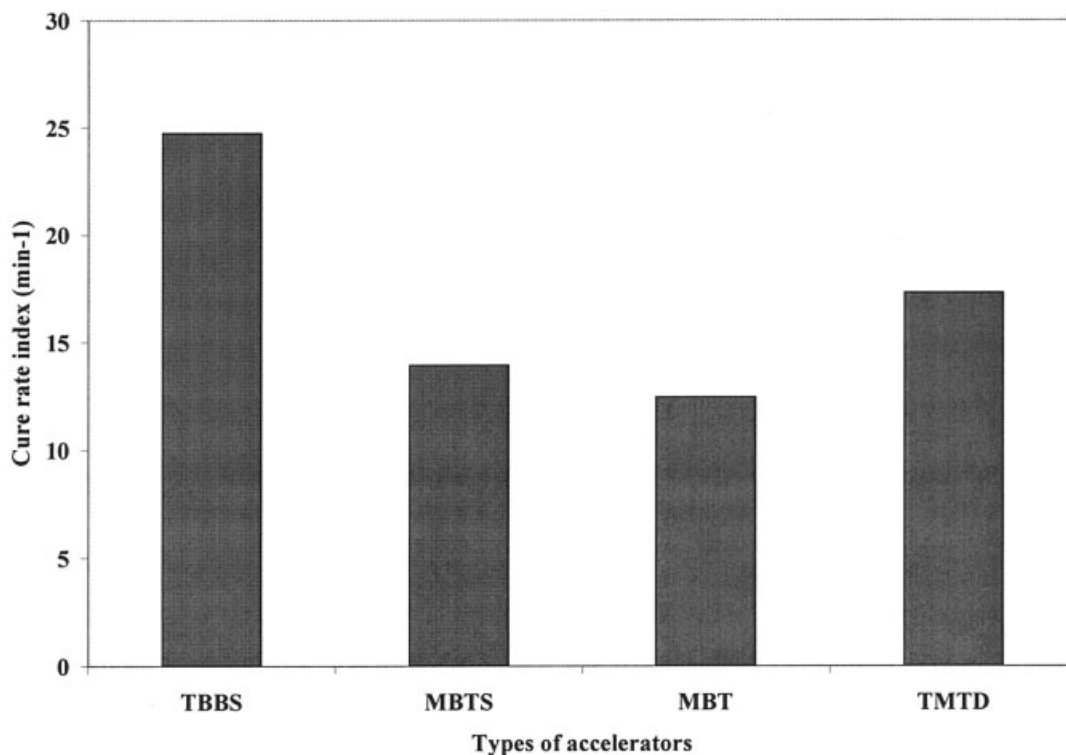

Figure 14 Cure rate index of NR-*g*-PMMA with molar ratio of NR/MMA = 90/10, using various types of accelerators.
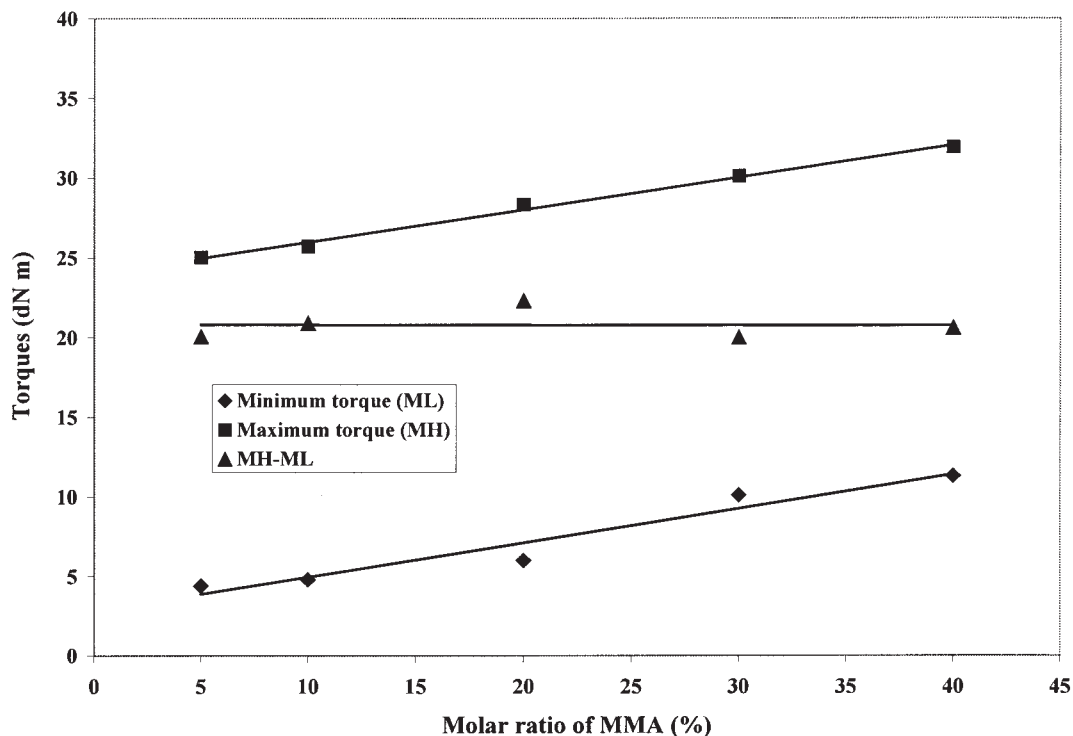
Figure 15 Torque of NR-*g*-PMMA with various molar ratio of NR/MMA used in graft copolymerization.

index or rate of vulcanization, while the MBT compound showed the lowest value. Other compounds were ordered as follow: TBBS > TMTD > MBTS > MBT. Therefore, TBBS was chosen as an accelerator for curing various types of NR-*g*-PMMA (i.e., at the molar ratio of NR/MMA = 95/5, 90/10, 80/20, 70/30, and 60/40) by using the compounding formulation (F1) and mixing schedule as shown in Tables I and II, respectively.

Curing properties of NR-*g*-PMMA with various molar ratios of NR/MMA

Figure 15 shows the influence of molar ratios of MMA used in the graft copolymerization on torques of various types of NR-*g*-PMMA, as obtained from the ODR tests. It can be seen that the minimum (M_L) and maximum (M_H) torques increased with an increase in a percentage molar ratio of MMA monomer. This may be attributed to an increase in chemical interaction, and hence stiffness of the molecules due to an increase in the grafted PMMA with increasing MMA concentration. However, very similar levels of the torque difference (i.e., $M_H - M_L$) were observed. Therefore, the increasing trend of MMA concentration used in the grafting reaction caused increasing trends of stiffness of the rubber vulcanizates but did not have a major affect on the torque difference. The crosslink density of the gum vulcanizate at various levels of molar ratios of MMA monomer was determined. We

found that increasing levels of molar ratios of MMA did not play a major role on the level of crosslink density. That is, a similar level of crosslink density was observed at approximately 50 mol/cm^3. Therefore, the trends of crosslink density corresponded to the trends of torque difference.

Figure 16 shows the influence of a molar ratio of MMA monomer on scorch time and cure time of the NR-*g*-PMMA compounds. We observed an increase in scorch and cure time with increasing levels of MMA concentration used in the grafting reaction. As mentioned earlier, increase in MMA concentration caused an increase in the grafted PMMA in the molecules. Therefore, a higher level of polar functional groups in the NR-*g*-PMMA was obtained. In the compounding procedure, the same concentration of an accelerator (i.e., TBBS) was used to prepare the NR-*g*-PMMA compounds. Some contents of the TBBS might be absorbed by the polar functional groups of the graft copolymer because of their polarities. Therefore, these amounts of accelerator could not perform their function of accelerating the vulcanization process. Hence, a longer time was needed to perform the crosslinking process to reach the optimum curing characteristics. According to our previous observation, we found an increasing trend of ungrafted PMMA or PMMA homopolymer, with an increase in MMA concentration used in the grafting reaction.[14] In this work, the reaction products were compounded without purification
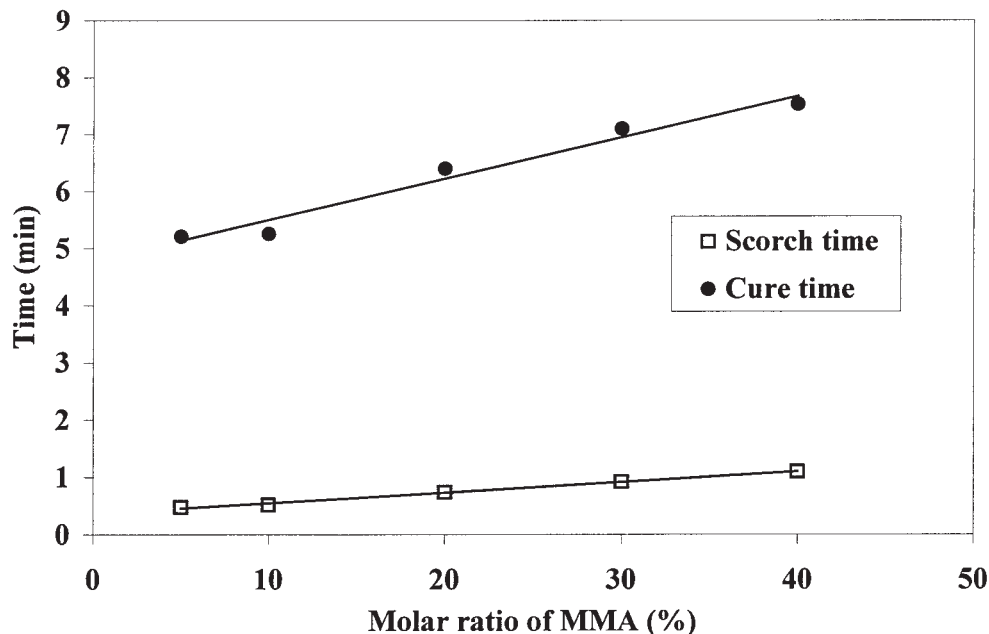
Figure 16   Scorch time and cure time of NR-*g*-PMMA with various molar ratios of NR/MMA used in graft copolymerization.

or separation of any other chemicals that remained in the crude polymer. Therefore, the polar functional groups in the PMMA molecule were capable of absorbing some amount of TBBS because of their polarity. Therefore, a longer time was needed to complete the vulcanization process. Moreover, a lower cure rate was observed with an increase in the molar ratio of MMA monomer used in the graft copolymerization, as shown in Figure 17. This can be attributed to decreased levels of TBBS, which could function as an accelerator upon increasing levels of MMA monomer or increasing levels of polar functional groups in the NR-*g*-PMMA molecules.
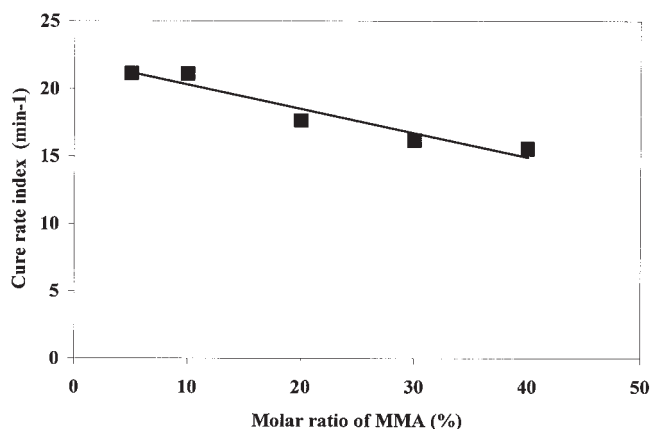

Figure 17   Cure rate index (CRI) of NR-*g*-PMMA with various molar ratios of NR/MMA used in graft copolymerization.

Mechanical properties of NR-*g*-PMMA gum vulcanizates

The influence of molar ratios of MMA used in the grafting reaction on ultimate tensile strength is shown in Figure 18. It can be seen that the tensile strength increased with an increase in the molar ratio of MMA. This can be described as an increasing trend of the grafted PMMA on the molecules. This caused an increasing trend of stiffness of the material. Therefore, higher force was needed to elongate the specimens prepared from NR-*g*-PMMA compounds, using higher molar ratios of MMA. The ultimate elongation or elongation at break (EB) of the NR-*g*-PMMA compounds prepared using various molars ratio of MMA is shown in Figure 19. We found that the NR-*g*-PMMA prepared with a molar ratio of MMA = 95/5 exhibited the highest elongation at break (i.e., 820%), which is similar to the EB of unmodified NR gum vulcanizate. Increasing levels of molar ratio of MMA caused an abruptly decreasing trend of the elongation at break. We found that the elongation at break of NR-*g*-PMMA prepared with molar ratios of MMA = 30 and 40 was very poor. The increasing trend of chain stiffness as an increasing level of the grafted PMMA was the reason for a decreasing trend of elongation at break. Therefore, at higher content of the grafted PMMA, the chain mobility was very much restricted. Rupture of the specimens was therefore observed instead of elongation, when the NR-*g*-PMMA gum vulcanizate using high molar ratios of MMA such as 30% and 40% were used.
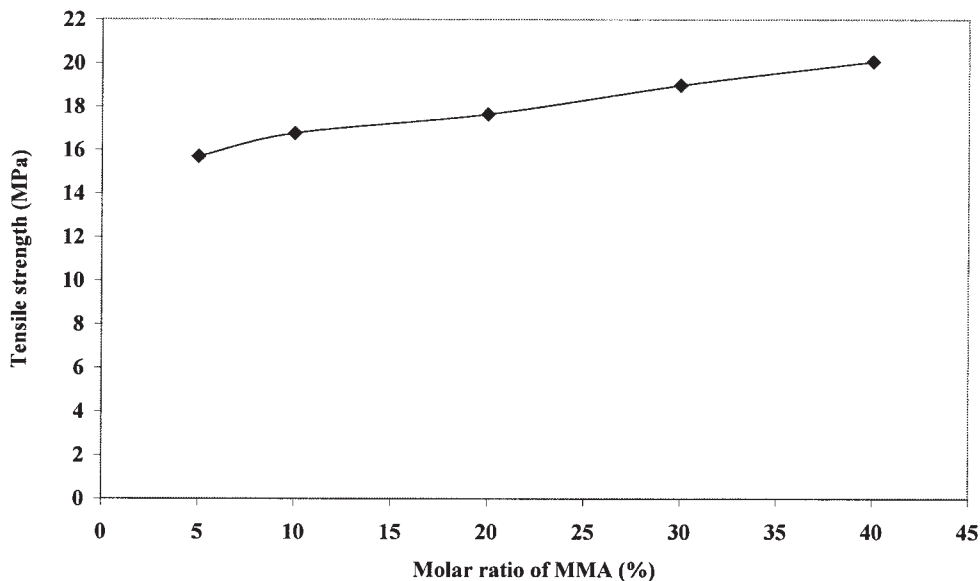
Figure 18 Tensile strength of NR-*g*-PMMA vulcauizates with various molar ratios of NR/MMA used in graft copolymerization.

CONCLUSIONS

Graft copolymers of NR and PMMA (i.e., NR-*g*-PMMA) were prepared using various percentage molar ratios of NR/MMA at 95/5, 90/10, 80/20, 70/30 and 60/40. Rheological properties were characterized. It was found the Mooney viscosity, shear stress, and shear viscosity of the unmodified NR were lower that those of the graft copolymers. Furthermore, we found
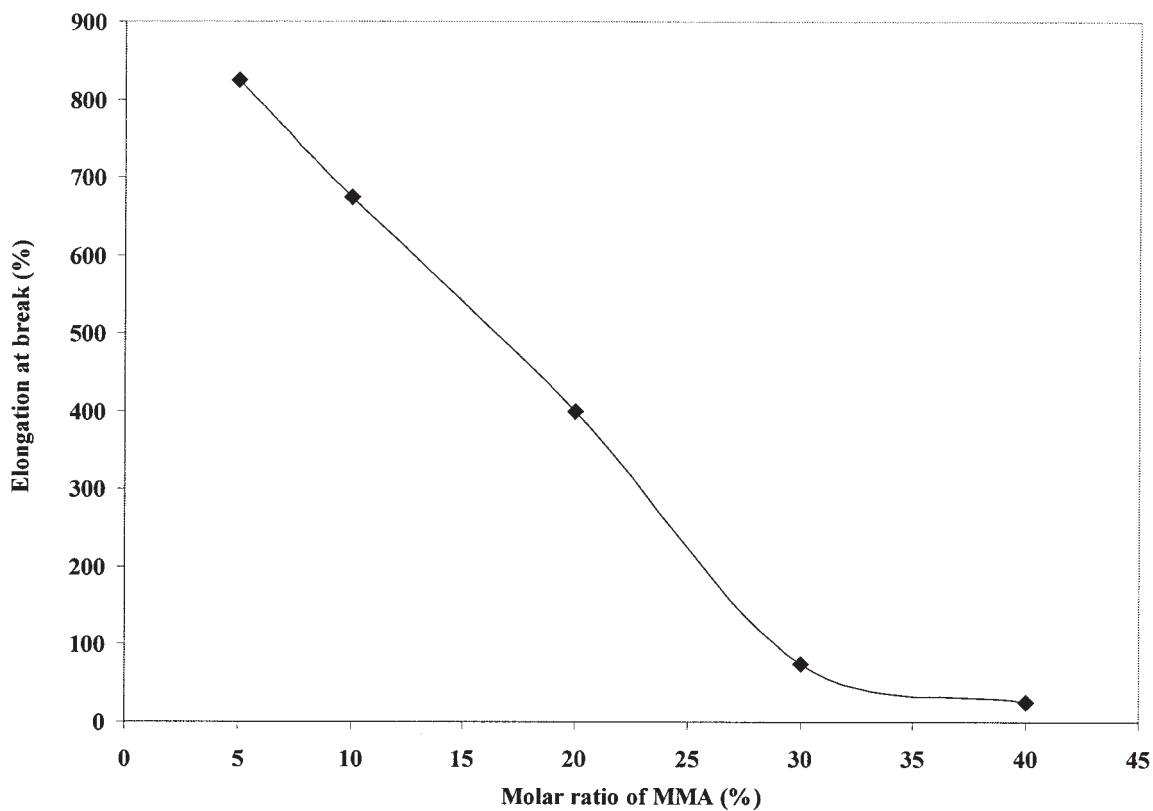

Figure 19 Elongation at break of NR-*g*-PMMA with various molar ratios of NR/MMA used in graft copolymerization.

increasing trends of Mooney viscosity, shear stress and shear viscosity of the NR-g-PMMA with an increase in molar ratio of MMA used in the graft copolymerization. The chemical interaction between polar functional groups in the grafted PMMA was responsible for the increasing trends of rheological properties. The DMA and TGA of the NR-g-PMMA and pure NR were also characterized. We found the pure NR exhibited the highest storage modulus. Also, decreasing trends of storage moduli were observed with increasing molar ratios of MMA. The glass transition temperature was obtained from the tan δ curves. We found a slightly increasing trend of the T_g's with an increase in a molar ratio of MMA used in the grafting reaction. This is because of an increasing level of chain mobility. The decomposition temperature of various types of rubbers was also determined. It was found that the pure NR showed the lowest T_d, while the T_d of graft copolymer increased with an increase in molar ratios of MMA.

The graft copolymer with a percentage molar ratio of NR/MMA = 90/10 was used to study cure characteristics using various types of accelerators (i.e., TBBS, MBT, MBTS, and TMTD). We found that TBBS showed the highest torque difference (i.e., crosslink density), the shortest cure time, and the highest cure rate. Therefore, TBBS was later selected to compound with various types of NR-g-PMMA. We observed the increasing trends of minimum torque, maximum torque, cure time, and scorch time, but quite the same levels of torque difference and crosslink density. The ultimate tensile strength of the gum vulcanizate of NR-g-PMMA increased with an increase in molar ratios of MMA used in the grafting reaction, whereas the elongation at break decreased.

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