Rheological and Curing Behavior of Reactive Blending. II. Natural Rubber-*g*-Poly(methyl methacrylate)–Cassava Starch

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ABSTRACT: Graft copolymers of natural rubber (NR) and methyl methacrylate (MMA) were prepared using cumene hydroperoxide and tetraethylene pentamine as redox initiators via the semibatch emulsion polymerization technique. Various molar percentage ratios of NR/MMA were studied in the grafting reaction (i.e., 95/5, 90/10, 80/20, 70/30, and 60/40). The graft copolymer with a 70/30 molar ratio was selected and used to prepare rubber blends with cassava starch. The starch was used at levels of 0, 20, 40, and 60 phr. Another set of rubber blends was prepared for comparison purposes. The NR-*g*-poly(MMA) (PMMA, 75 phr) was blended with 25 phr of NR air dried sheets (ADS) and a given level of the cassava starch. We found that the Mooney viscosity, shear stress, and shear viscosity increased with an increasing concentration of cassava starch. This may be attributed to the chemical interactions between the polar groups of the NR-*g*-PMMA and the cassava starch. The blends were later compounded using a compounding formulation according to ASTM D 3184-89. A similar short delay onset of vulcanization (i.e., approximately 1 min) was observed for the whole set of compounds under study. However, different curing characteristics were observed for the blends of NR-*g*-PMMA–cassava starch and NR-*g*-PMMA–ADS–cassava starch. The NR-*g*-PMMA–cassava starch compounds exhibited two-stage curing characteristics. The curing curve had a slight reversion at a testing time of approximately 8 min. The shear modulus then abruptly increased with an increasing testing time in the range of 20–60 min. The curing curves for NR-*g*-PMMA–ADS–cassava starch blends exhibited a single curing stage with a shear modulus that increased slightly with the testing time was increased from 20 to 60 min. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1453–1463, 2003

Key words: rheological properties; curing behavior; reactive blending; natural rubber-*g*-poly(methyl methacrylate); cassava starch

INTRODUCTION

Graft copolymerization of natural rubber (NR) has been performed using free-radical polymerization in the solution and latex states with various initiator systems, such as benzoyl peroxide, azobisisobutyronitrile, and redox initiators.[1–4] A graft of NR with poly-(methyl methacrylate) (NR-*g*-PMMA) has been produced commercially under the trade name of Heaveaplus MG or MG rubber.[3,5] The applications of MG rubber include adhesives, reinforcing fillers, and impact modifiers for thermoplastics.[4] In recent years, a number of works have focused on the preparation of thermoplastic elastomers from NR and PMMA. The compatibility of NR and PMMA using NR-*g*-PMMA as a compatibilizer is one main topic of interest.[6–8.] NR-*g*-PMMA has also been used as a blend component for NR-*g*-PMMA/NR blends.[9] Various types of starch have been widely used to produce biodegradable blends with polymers, such as low-density polyethylene,[10–13] high-density polyethylene,[14] polypropylene,[13] polystyrene,[13] ethylene–propylene copolymers,[15] and ethylene–vinyl acetate copolymers.[16] Generally, a reactive blending of starch and the polymer was performed by incorporating polar functional groups into hydrocarbon polymer molecules or by using a compatibilizer.[10–12,14–16] However, there was some work done on modifying starch molecules to increase the hydrophobicity.[13,17] Among various types of starch, cassava starch was found to be very useful for preparing reactive blending products with modified NR, which contains polar functional groups, such as epoxidized NR[18] and maleated NR.[19] In the present work NR-*g*-PMMA was synthesized and used to prepare the reactive blending product with cassava starch. The rheological and curing properties of the blends were investigated. Unmodified NR air dried
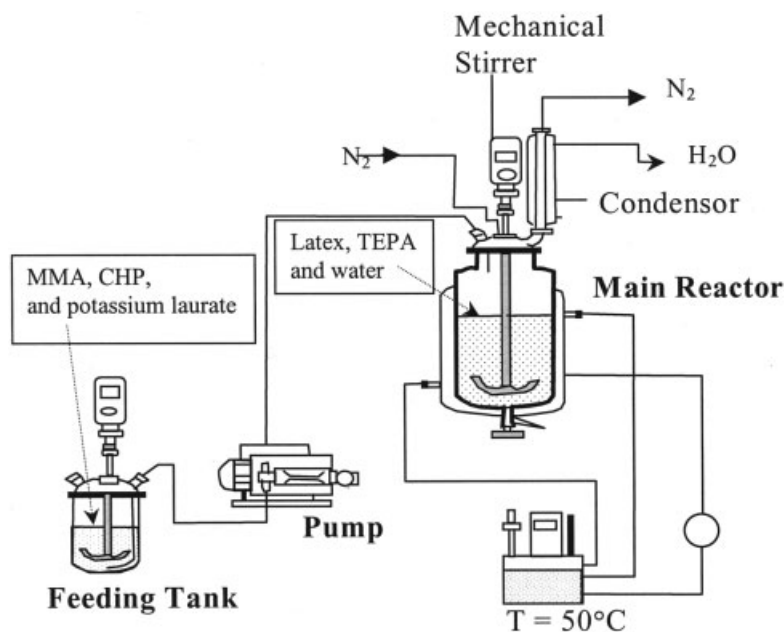
Figure 1 The apparatus used to prepare natural rubber-*g*-poly(methyl methacrylate).

sheets (ADS) were also blended and studied. The results are compared with the results from the pure NR-*g*-PMMA compounds.

EXPERIMENTAL

Materials

The rubber in the study was in the form of high ammonia concentrated latex, which was manufactured by Pattani Industry Co., Ltd. (Pattani, Thailand). The MMA used to prepare the graft copolymers was procured from Merck (Munchen, Germany). Cumene hydroperoxide (CHP) and tetraethylene pentamine (TEPA) were used as redox initiators (Fluka Chemie AG, Buchs, Switzerland). The potassium laurate used to stabilize the latex was prepared from the reaction of potassium hydroxide (Fluka Chemie AG) and lauric acid (Lab Scan Ltd.). Cassava starch was used as a blending ingredient (Thaiwa Co., Ltd., Rayong, Thailand), and sulfur was used as a vulcanizing agent (Ajax Chemical Co., Ltd., Samutprakan, Thailand). Zinc oxide (Global Chemical Co., Ltd., Bangkok, Thailand) and stearic acid were used as activators (Petthai Chemical Co., Ltd., Bangkok), and 2-mercaptobenzothiazole was used as an accelerator (Shanxian Chemical Co., Ltd., Shandong Province, China).

Preparation of NR-*g*-PMMA

The semibatch emulsion polymerization technique with two redox initiators (CHP and TEPA) was used to prepare NR-*g*-PMMA. The apparatus used is schematically illustrated in Figure 1. The NR latex, 2.12 g

of TEPA (85 wt %), and 200 mL of water were added into a main reactor (Fig. 1). The mixture was then thoroughly stirred under a nitrogen atmosphere and a fixed temperature of 50°C. The monomer (MMA), 2.57 g of CHP (70 wt %), 9 g of potassium laurate (30 wt %), and 120 mL of water were incorporated into a feeding tank. The mixture was then stirred and delivered into the main reactor at a flow rate of 2.7 mL/min. Molar percentage ratios of NR/MMA were studied at 95/5, 90/10, 80/20, 70/30, and 60/40. The quantities of the chemicals used are listed in Table I. The reaction was then performed for 3 h. The latex was later coagulated. A Soxhlet extractor was used to wash out the ungrafted NR using petroleum ether and the free PMMA homopolymer using acetone. The presence of the grafted PMMA on the NR backbone was determined using a Perkin–Elmer FTIR spectrometer (model 1600). The grafting efficiency of the graft copolymerization was also characterized.

TABLE I
HA Latex and Methyl Methacrylate Used in Graft Reaction

HA Latex[a]/MMA (mol %)	Weight (g)	
	Latex	MMA
95/5	321	15
90/10	304	30
80/20	270	60
70/30	236	90
60/40	202	120

[a] The moles of natural rubber are calculated based on the molecular weight of an isoprene unit.

Blending of NR-*g*-PMMA and cassava starch

The NR-*g*-PMMA prepared using a 70/30 molar percentage ratio of NR/MMA (i.e., percentage grafting efficiency = 83.42) was used to prepare polymer blends. Two sets of rubber blends were prepared. The first set consisted of blends of graft copolymer and cassava starch (NR-*g*-PMMA–cassava starch). Then 25 phr ADS was incorporated in the second set of blends (NR-*g*-PMMA–ADS–cassava starch). Mixing was performed in an internal mixer (Brabender Plasticorder) at 60°C and a rotor speed of 30 rpm. Premasticating of 100 phr rubber was first performed for 5 min and the mixing was continued for 5 min after incorporation of the cassava starch. Various quantities of cassava starch (0, 20, 40, and 60 phr) were blended.

Chemical interaction of blends using molau test

A Molau solubility test was used to verify the interaction between the blend compositions. Toluene (100 cm^3) was used to dissolve three types of rubber blends (2 g each): NR-*g*-PMMA–cassava starch, NR-*g*-PMMA–ADS–cassava starch, and ADS–cassava starch. The last set of rubber blends was introduced for comparison purposes. Each mixture was then warmed to 50°C and shaken vigorously for 24 h. The mixtures were maintained for 2 months. Changes in the toluene solvent of each sample were observed.

Rheological characterization

A SPRI Mooney viscometer (model AC/684/FD) and a single-bore Rosand capillary rheometer were utilized to characterize the flow properties of the rubber melts. The Mooney viscosity was determined at 120°C, using a large rotor, a preheating time of 1 min, and a testing time of 4 min (ML 1 + 4, 120°C). The shear properties in terms of the shear stress and shear viscosity were also tested at 120°C with shear rates of 10–1500 s^{-1}. The die that was used had a 2-mm diameter, a 32-mm length, and a 180° entrance angle. The equations used to calculate the shear stress, shear viscosity, and shear rate were described in our previous article.[19]

TABLE II
Compounding Formulations

Ingredients	Compound 1 (phr)	Compound 2 (phr)
NR-*g*-PMMA	100	75
ADS	—	25
Zinc oxide	6	6
Sulfhur	3.5	3.5
Stearic acid	0.5	0.5
MBT	0.5	0.5
Cassava starch	0, 20, 40, and 60	0, 20, 40, and 60

TABLE III
Mixing Schedule

Ingredient	Mixing Time (min)
Rubber mastication	5
Cassava starch	5
ZnO	2
Accelerator (MBT)	2
Stearic acid	2
Sulfhur	2
Compound finishing	5

Curing behavior

The NR-*g*-PMMA compounds were prepared using a standard formulation according to ASTM D 3184-89, as shown in Table II. The graft copolymer or graft copolymer mixed with ADS was first masticated using a two-roll mill at 60°C for 5 min. Other ingredients were then mixed according to the time schedule given in Table III. The curing behavior was characterized at 160°C using a Monsanto oscillating disk rheometer (model ODR 2000) at a 1° arc, according to ASTM D 2048-95.

RESULTS AND DISCUSSION

Preparation of NR-*g*-PMMA

Figure 2 shows the IR spectra of NR-*g*-PMMA at various molar percentage ratios of NR/MMA. Characteristic bands 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 the grafted PMMA was characterized using the absorbance ratio of IR peaks at 1732 (—C=O stretch) and 835 cm^{-1} (—C—H stretch on cis C=C bonds), as shown in Figure 3. It was found that the level of —C=O bonds increased with an increasing level of MMA monomers in the grafting reaction. The quantity of grafted PMMA therefore increased with the concentration of MMA used in the grafting reaction. Upon Soxhlet extraction, free-NR and free-PMMA homopolymers were quantified, as shown in Figure 4. We found that ungrafted NR molecules decreased while the PMMA homopolymer increased with an increasing concentration of MMA in the reaction. Figure 5 shows the grafting efficiency, which was calculated as the ratio of the amount of graft copolymer to the amount of dried product coagulum. It was found that the grafting efficiency was decreased with an increasing level of MMA. This was attributed to the abruptly increasing trend of free PMMA homopolymer upon increasing the level of MMA.

Interaction between NR-*g*-PMMA–cassava starch and NR-*g*-PMMA–ADS–cassava starch blends

The Molau test was used to confirm the formation of a chemical interaction between the polar groups on NR-
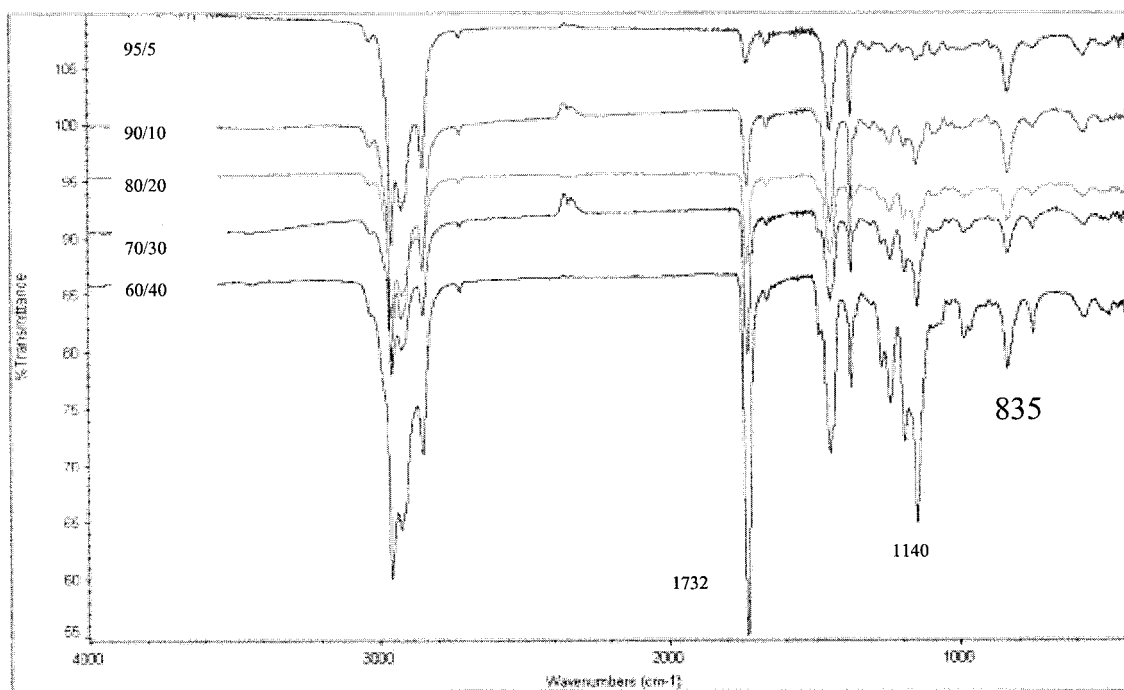
Figure 2 The IR spectra of graft copolymers prepared using various mole ratio of natural rubber and MMA.

g-PMMA and cassava starch. A yellowish gel in the upper fraction of the test tube and a yellowish solution with precipitated white powder (cassava starch) in the bottom fraction were observed for the ADS–cassava starch blends. This system gave negative results in the Molau test. However, in the NR-*g*-PMMA–cassava starch blend, a milky white emulsion was observed, despite the precipitated white powder in the bottom fraction. A similar but lighter milky white emulsion and more precipitated cassava starch powder were observed for the NR-*g*-PMMA–ADS–cassava starch blend. It is therefore concluded that a strong interaction between NR-*g*-PMMA and cassava starch molecules could possibly occur and a partial interaction between NR-*g*-PMMA–ADS–cassava starch components exists.
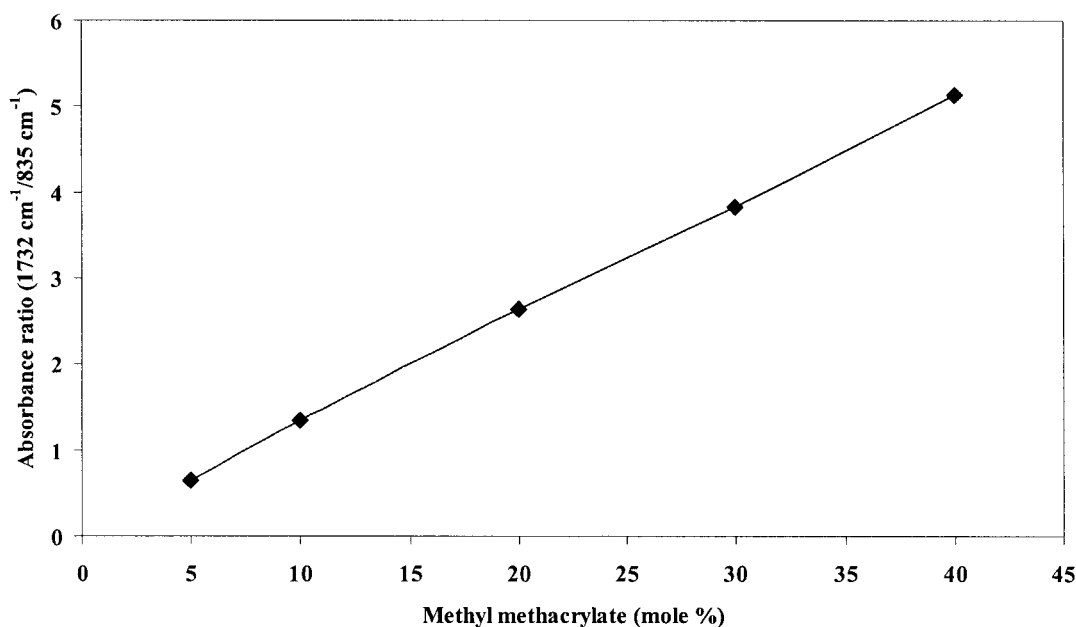
Figure 3 The absorbance ratio of IR peaks at 1732 and 835 cm^{-1} of NR-*g*-PMMA at various levels of added methyl methacrylate.
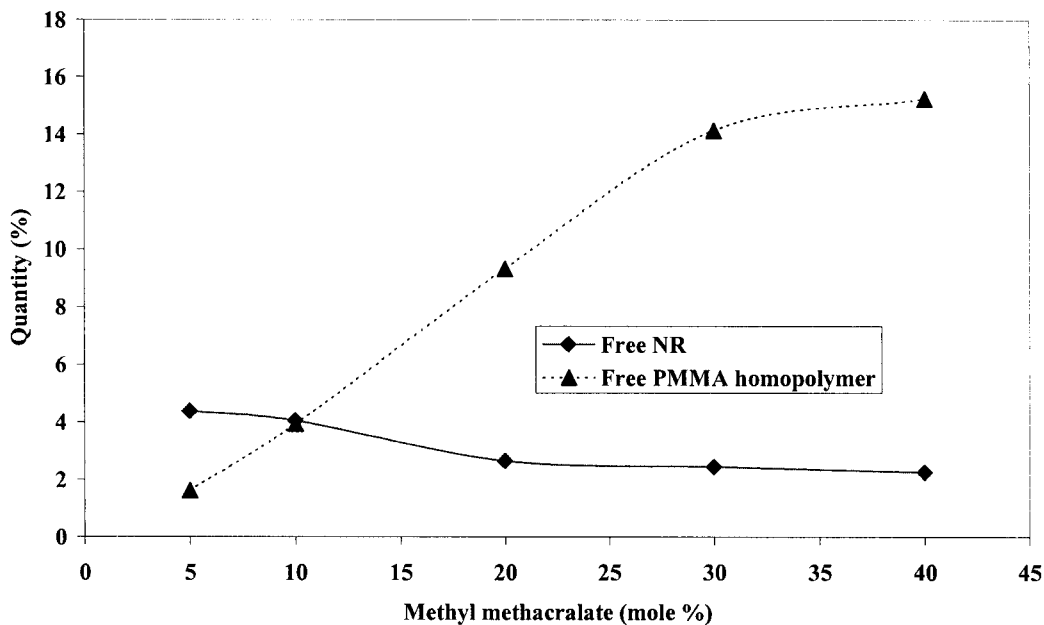
Figure 4 The quantities of free-NR and free-PMMA homopolymer at various levels of added methyl methacrylate.

Rheological properties

Figure 6 shows the Mooney viscosities of blends of pure NR-*g*-PMMA, NR-*g*-PMMA–ADS, and pure ADS at various levels of cassava starch. The Mooney viscosity for all types of polymer blends increased with the increasing concentration of cassava starch. At the same level of starch added, the blend of pure ADS shows the highest Mooney viscosity, while the blend with 25 phr ADS shows a value between those of blends of pure ADS and NR-*g*-PMMA. The level of

interaction was thus quite difficult to observe from the trends of the Mooney viscosities in Figure 6, because the Mooney viscosity of the pure ADS we used was quite high (78) but the Mooney viscosity of pure NR-*g*-PMMA was as low as 56 (ML, 1 + 4, 120°C). The gradient of the plot of the Mooney viscosity versus the level of cassava starch was therefore quantified. This was performed in terms of the difference between an initial Mooney viscosity (i.e., the viscosity of the compound with no starch added) and the viscosities at
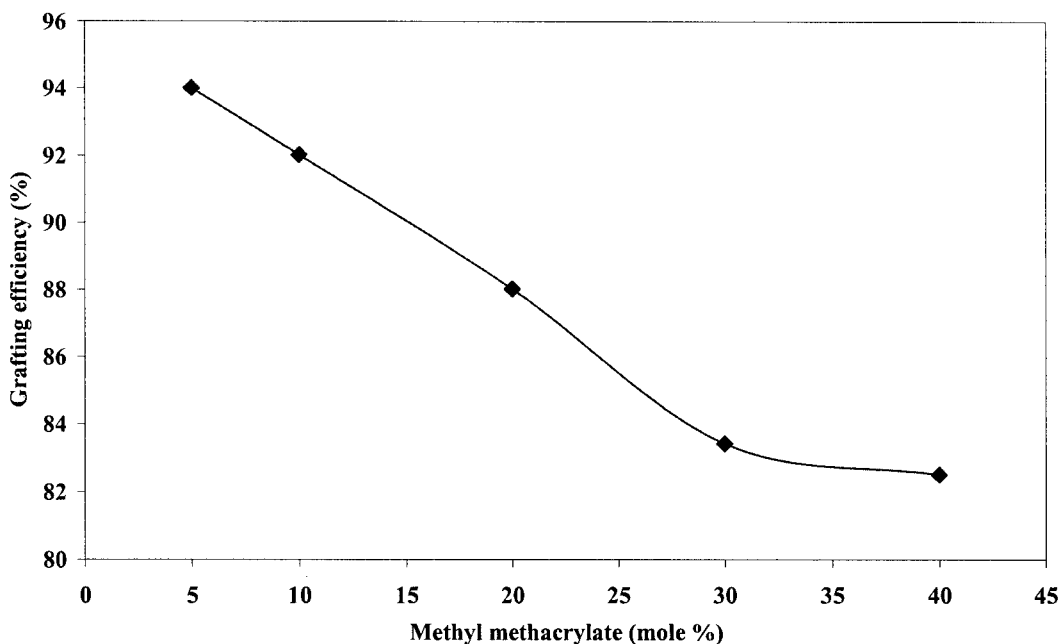

Figure 5 The grafting efficiency of graft copolymerization at various levels of added methyl methacrylate.
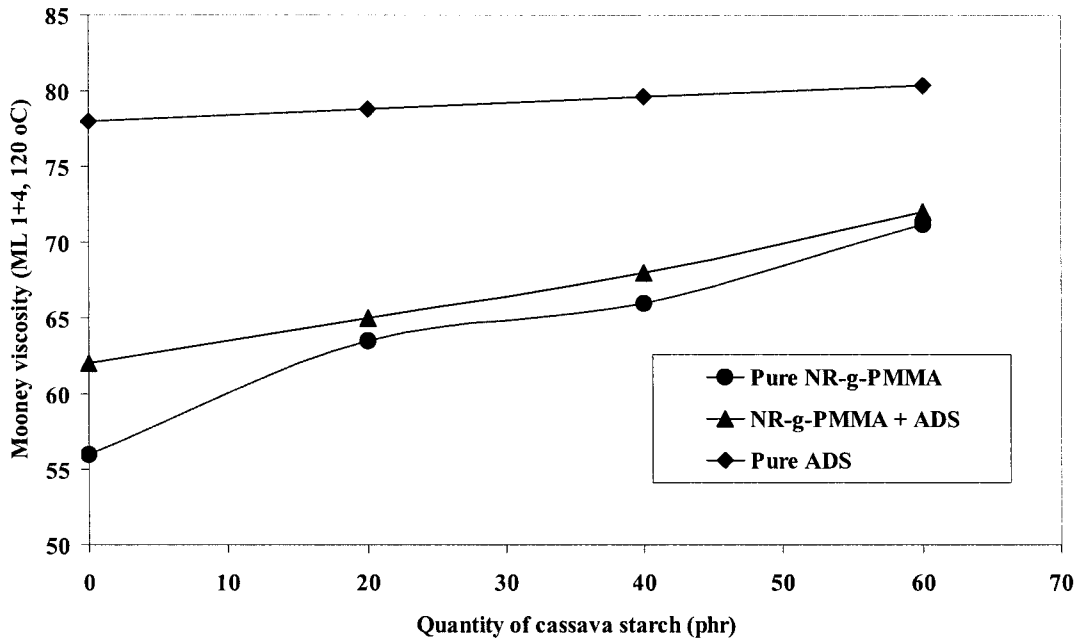
Figure 6 The Mooney viscosity of NR-g-PMMA blends at various quantities of cassava starch. (NR-g-PMMA with 83.42% grafting efficiency synthesized using a 70/30 molar ratio of NR/MMA.

various levels of cassava starch, and the results are shown in Figure 7. The highest value was found for the blend of NR-g-PMMA and cassava starch, and the blend of ADS and cassava starch gave the lowest value. The NR-g-PMMA–ADS–cassava starch exhibits

values between those of blends of pure ADS and NR-g-PMMA. According to the Molau test, ranking the difference in Mooney viscosity may reveal a different level of chemical interaction between the blend components. A strong interaction is believed to occur
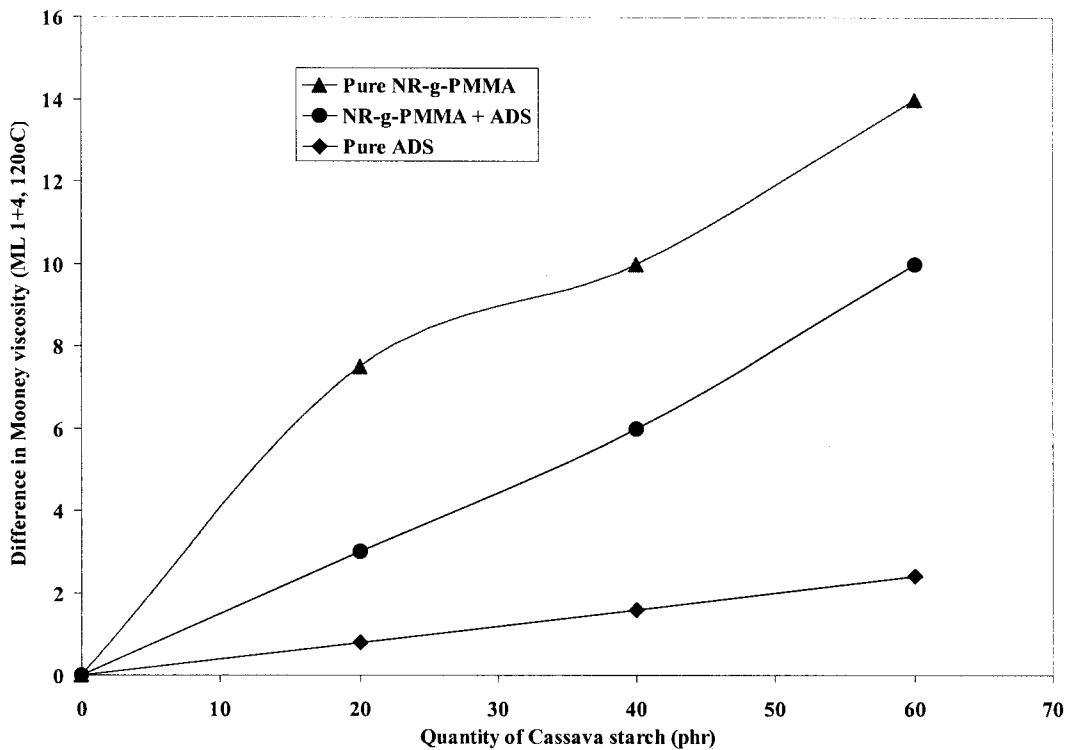

Figure 7 The difference of the Mooney viscosities from their initial values for NR-g-PMMA blends at various quantities of cassava starch.
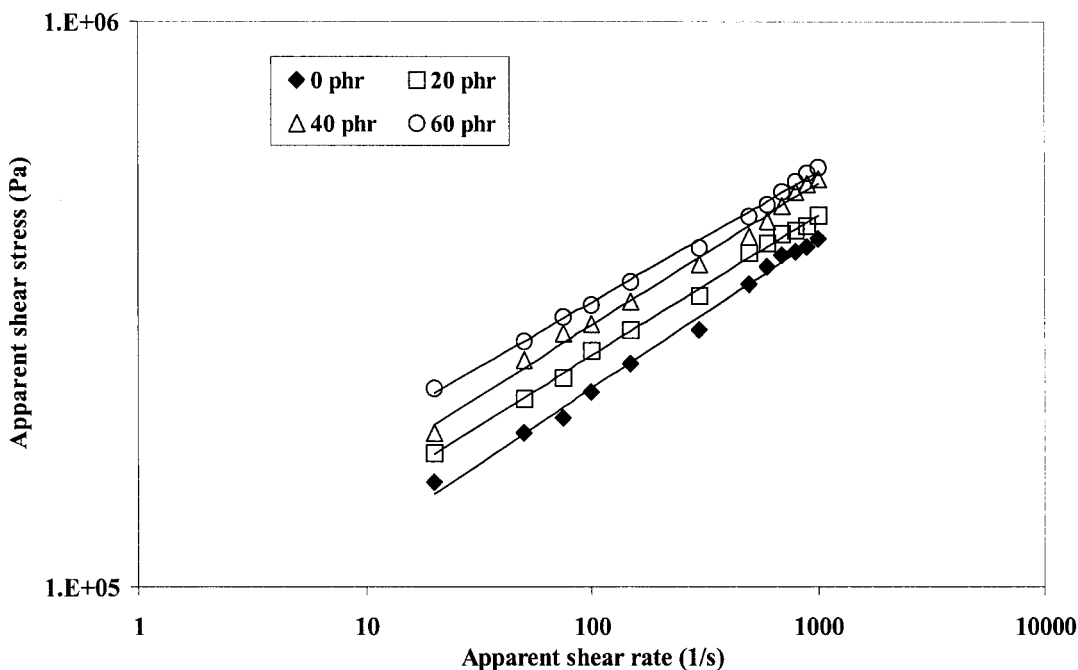
Figure 8 The relationship between the apparent shear stress and apparent shear rate of the NR-g-PMMA graft copolymer blended with various quantities of cassava starch.

between the two types of natural polymers via the polar groups (—C=O and —C—O) in the NR-g-PMMA molecules and the hydroxyl groups in the cassava molecules. Hence, the highest chemical interaction was for the blend of NR-g-PMMA and cassava starch.

The relationship between the apparent shear stress and the apparent shear rate (i.e., flow curve) for the blends of NR-g-PMMA at various levels of cassava starch are plotted logarithmically in Figure 8. The apparent shear stress increased with an increasing shear rate. Furthermore, at the same shear rate level, the apparent shear stress was increased by the increasing concentration of cassava starch. The flow curve was also a straight line. This corresponds to the power law equation proposed by Ostwald[20]:

$$\tau = K(\dot{\gamma})^{n} \qquad (1)$$

where n is the power law or flow behavior index and K is the consistency or viscosity coefficient index.

From the best fit lines on a log–log plot (Fig. 8), one can attain the slope (n) and intercept (K). Plots of the n values versus the concentration of the cassava starch are illustrated in Figure 9. The n value was <1 for all sets of blend compositions. This indicated pseudoplastic (shear thinning) behavior. It was also found that the n values of NR-g-PMMA–cassava starch blends decreased with increasing concentrations of cassava starch. Therefore, the greater pseudoplasticity of the melt for the NR-g-PMMA–cassava starch blends was obvious. In contrast, the power law index for the

NR-g-PMMA–ADS–cassava starch blends increased with increasing concentrations of cassava starch. The flow was therefore less pseudoplastic when increasing the level of cassava starch. The value of n gt; 1 also reflects the deviation of the flow profiles from uniform parabolic patterns (i.e., $n = 1$ for Newtonian flow) to pluglike flow profiles. The blends in the current work exhibited very low n values (i.e., $n \leq 0.27$). Therefore, the highly sheared thinning fluid flowed through the capillary almost as a plug moving at a uniform speed as the melt was sliding down against the channel wall. A lower power law index leads to more pluglike profiles.[21]

The incorporation of cassava starch also increased the apparent shear viscosity, as indicated in Figure 10. However, the apparent shear viscosity was decreased with an increase in the shear rate, exhibiting shear thinning behavior. The increases in the shear stress and shear viscosity might be due to the chemical interaction between the polar functional groups in the grafted PMMA and the hydroxyl groups of the cassava starch molecules. Intermolecular forces are therefore expected to increase upon the increase pf the concentration of cassava starch. To clarify this hypothesis, the differences of the apparent shear stress and shear viscosity between the blend with no starch added and the blend at a 60-phr concentration of starch were quantified. The results for the NR-g-PMMA–cassava starch and NR-g-PMMA–ADS–cassava starch blends are plotted in Figures 11 and 12, respectively. Higher differences were observed in the
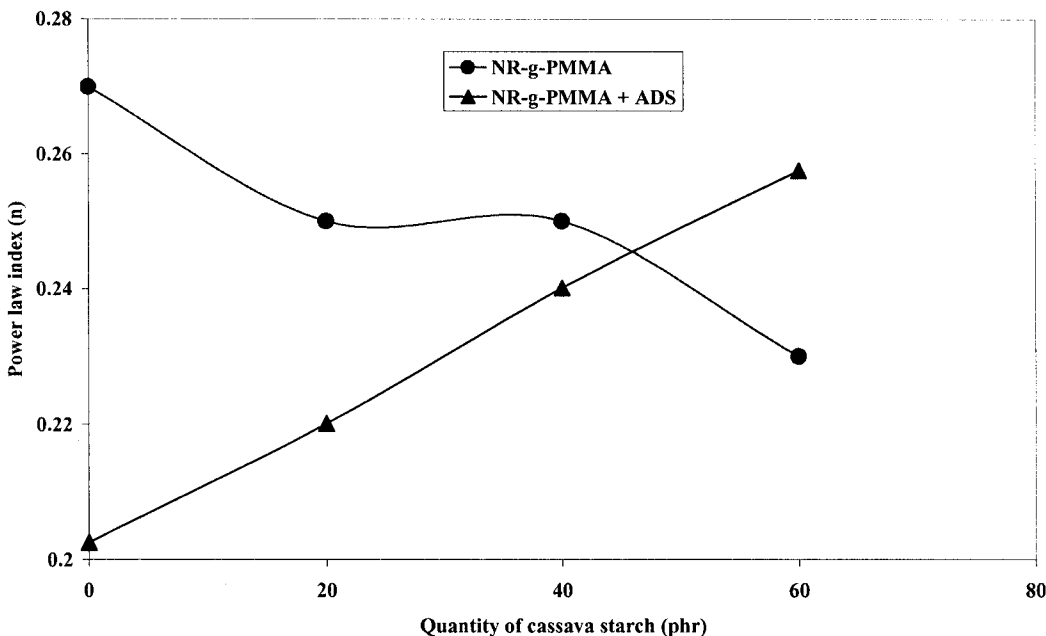
Figure 9 The power law index (*n*) of graft copolymers blended with various quantities of cassava starch.

NR-*g*-PMMA–cassava starch blend than in the NR-*g*-PMMA–ADS–cassava starch one. Therefore, we concluded that the higher chemical interaction between NR-*g*-PMMA and cassava starch was confirmed.

Curing behavior

Figure 13 shows rheometer curves or curing curves from the ODR 2000 for the NR-*g*-PMMA compounds mixed with and without various quantities of cassava starch. The force used to oscillate the disk is proportional to the stiffness or shear modulus of the rubber compounds. A similar delay in the onset of vulcanization of about 1 min was observed. However, different curing behavior for the compounds of NR-*g*-PMMA without and with cassava starch was observed. That is, the single-stage cure characteristic and increasing shear modulus with curing time were ob-

served for the compound without cassava starch (pure NR-*g*-PMMA). However, two curing stages were observed for the curing curves of NR-*g*-PMMA–cassava starch blends. The first curing stage reached a maximum torque at a testing time of approximately 8 min, and reversion was later observed until a curing time of 20 min. The torque was again abruptly increased with the increase of the testing time from 20 to 60 min. Therefore, all curing curves in Figure 13 for the compounds with and without cassava starch were not in equilibrium at the maximum torque. That is, the torque still increased with increasing testing times. Higher stiffness rubber compounds were also observed when increasing the concentration of cassava starch. This may be attributed to the different levels of chemical interaction between the polar groups of the two types of polymers. The reason for the two curing stages of the NR-*g*-PMMA–cassava starch compound
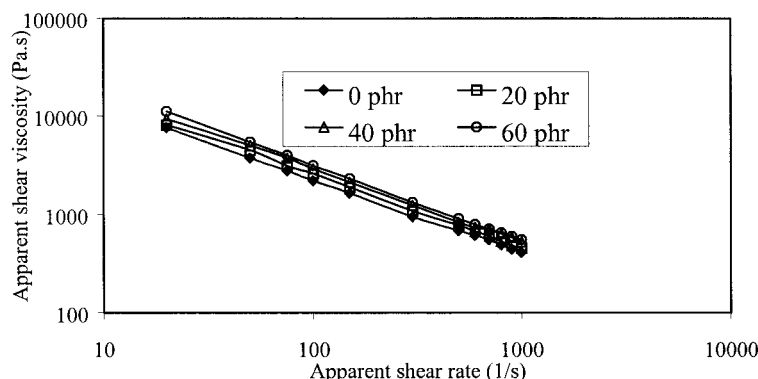

Figure 10 The relationship between the apparent shear viscosity and apparent shear rate of graft copolymers blended with various quantities of cassava starch.
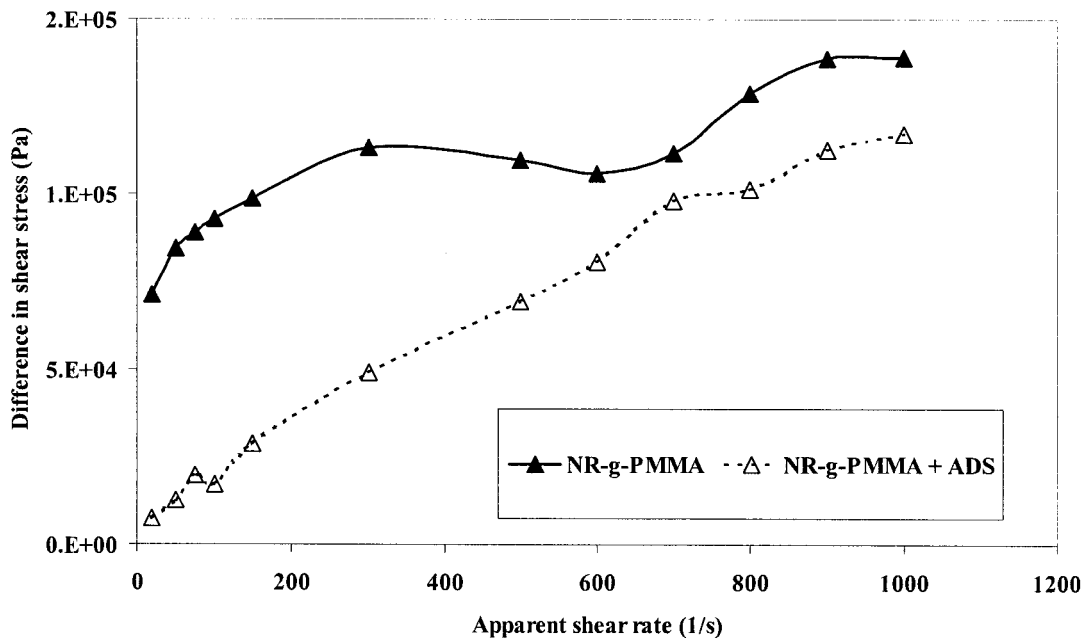
Figure 11 The difference of the apparent shear stress from the initial value: for NR-*g*-PMMA blends at various apparent shear rates and 60 phr cassava starch.

was not clear. However, according to our previous work, we did not observe such curing behaviors for epoxidized NR[18] and maleated NR[19] blended with cassava starch using the same compounding formulation. Single-stage curing characteristics were found for all sets of the compounds under studied. Therefore, two curing stages were observed only in the blend consisting of NR-*g*-PMMA and cassava starch. The incorporation of cassava starch into the NR-*g*-PMMA

may cause the destruction of some new forms of crosslink structures. Therefore, the decreasing trend of the torque was observed in the first stage. Further heat treatment under shear action may cause the formation of new chemical bonds via the vulcanization and chemical interaction between the polar groups of the graft copolymer and cassava starch. An increasing trend of the torque was thus observed for the second stage.
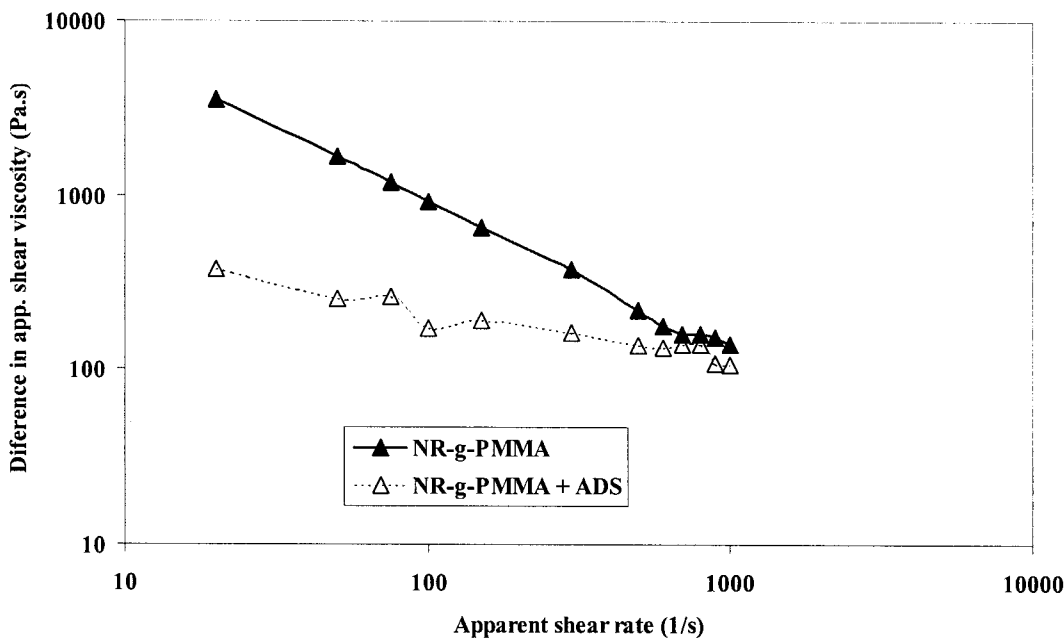

Figure 12 The difference of the apparent shear viscosity from the initial value for NR-*g*-PMMA blends at various apparent shear rates and 60 phr cassava starch.
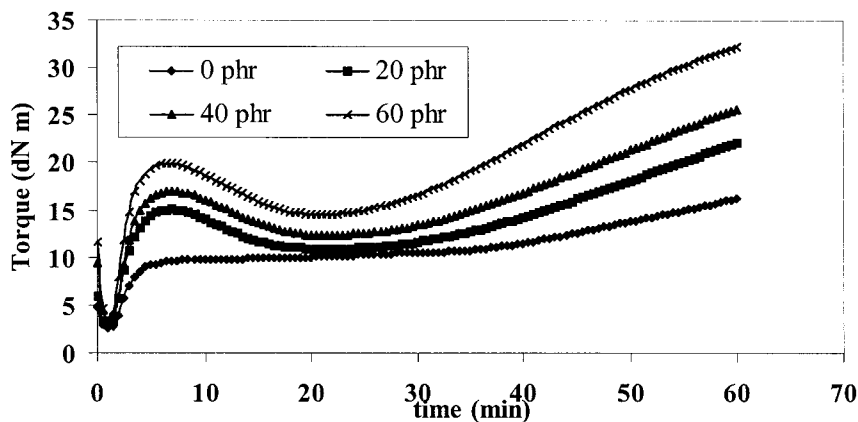
Figure 13 The cure curves of NR-*g*-PMMA at various quantities of cassava starch.

Incorporation of ADS (25 phr) into the compounding formulation (Fig. 14) provided curing curves with a delay in the onset of vulcanization (i.e., approximately 1 min) that are similar to the case in Figure 13. However, a single curing stage (i.e., as a typical curing cure for NR compounds) was observed for the compounds with and without cassava starch. After a testing time of 20 min, the torque increased slightly with increasing testing time. Therefore, these curing curves were also not in equilibrium at the maximum torque. The torque still continued to increase with increasing testing times. Furthermore, higher stiffness rubber compounds were again observed when increasing the concentration of cassava starch. The occurrence of a single curing stage may be attributed to a crosslinking reaction via double bonds in the NR molecules (ADS). This reaction dominated the other reactions. Thus, the destruction of the crosslink structure attributable to the addition of the cassava starch could not be observed.

A comparison of the curing curves at 40 phr cassava starch is shown in Figure 15. All compounds exhibited a similar, short delay in the onset of vulcanization (i.e.,

approximately 1 min) at the beginning stage. The NR-*g*-PMMA–cassava starch compound exhibited a two-stage curing characteristic, while the pure ADS and NR-*g*-PMMA–ADS blended compounds showed single-stage curing curves. The curing curves of both NR-*g*-PMMA and NR-*g*-PMMA–ADS were not in equilibrium at the maximum torque. The highest torque was observed with a 60-min testing time. The curing curve of the ADS blended with 40 phr cassava starch gave maximum torque and a slight reversion, as in the case of the STR 5L compound used in our previous work.[19] The level of stiffness at maximum torque for different types of compounds was ranked as follows: NR-*g*-PMMA–ADS > pure NR-*g*-PMMA > pure ADS. The difference in the stiffness is attributed to the combined influence of the high Mooney viscosity of pure ADS and different levels chemical interaction between the polar functional groups.

CONCLUSIONS

The graft copolymer NR-*g*-PMMA was successfully prepared and used as a blending ingredient with cas-
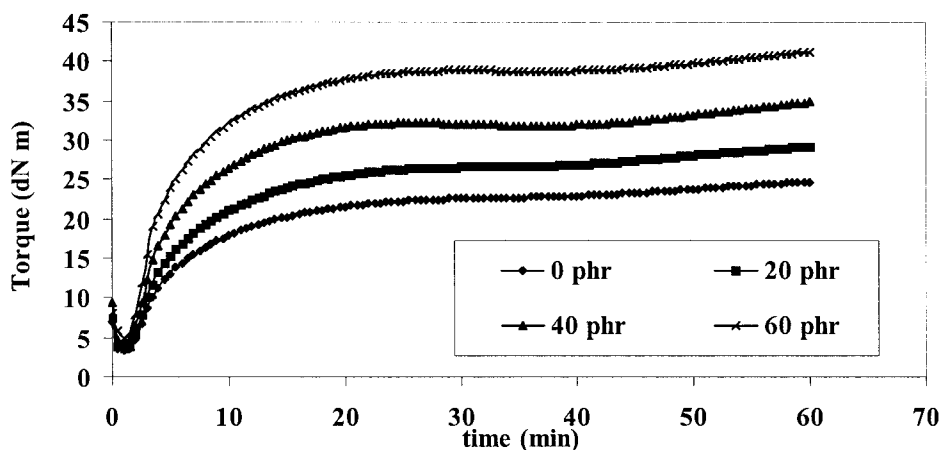

Figure 14 The cure curves of NR-*g*-PMMA and ADS (25 phr) at various quantities of cassava starch.
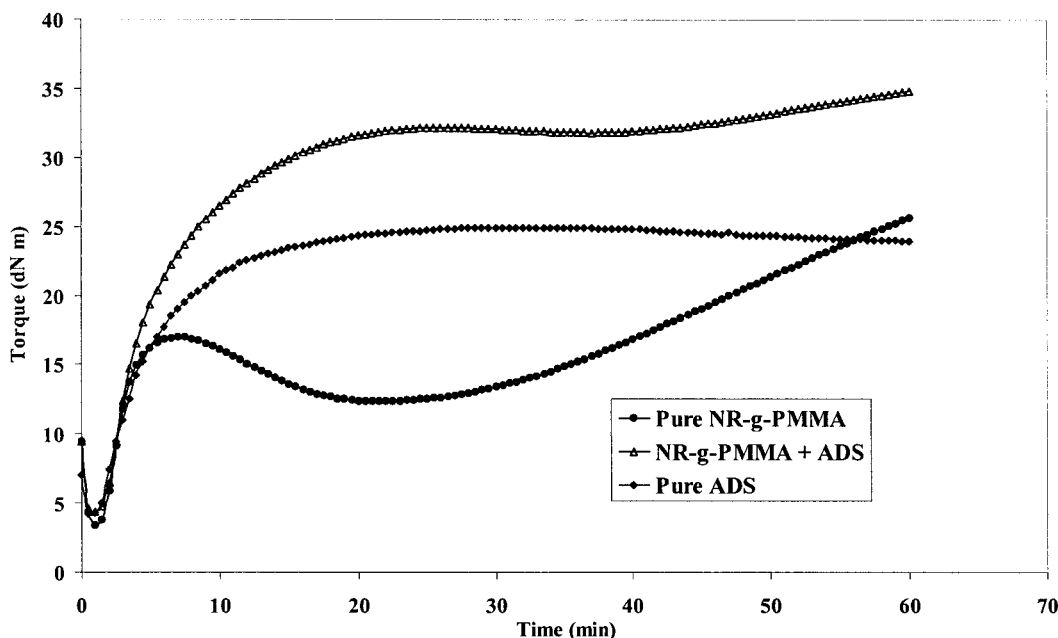
Figure 15 A comparison of the curing curves for NR-*g*-PMMA, NR-*g*-PMMA + ADS (25 phr), and pure ADS at a cassava starch concentration of 40 phr.

sava starch. A strong interaction is believed to occur between the two types of natural polymers via the polar groups (—C=O and —C—O) in grafted PMMA and the hydroxyl groups in the cassava molecules. This is proven by the higher difference in the Mooney viscosity for the NR-*g*PMMA–cassava starch blends than for the NR-*g*-PMMA–ADS–cassava starch blends. Furthermore, the differences in the apparent shear stress and shear viscosity were also found to be higher for the same types of blends. The curing curves for all compounds under study exhibited a similar, short delay in the onset of vulcanization (~1 min) at the beginning stage of the cure. However, different curing behaviors were found for the blends. The NR-*g*-PMMA–cassava starch compounds exhibited two curing stages with the first maximum torque at a testing time of 8 min, and the shear modulus abruptly increased with testing times from 20 to 60 min. For the NR-*g*-PMMA–ADS–cassava starch compounds, the curing curves indicated a single stage and the shear modulus slightly increased with increasing testing time (20–60 min). The curing curves for both NR-*g*-PMMA–cassava starch and NR-*g*-PMMA–ADS–cassava starch compounds were not in equilibrium at the maximum torque. However, the curing curves of ADS–cassava starch compounds provided maximum torque and a slight reversion.

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