Rheological and Curing Behavior of Reactive Blending. I. Maleated Natural Rubber–Cassava Starch

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ABSTRACT: Maleated natural rubber (MNR) was prepared and used as a blending composition and a compatibilizer for blending of natural rubber (STR 5L) and cassava starch. The melt rheological behavior in terms of Mooney viscosity, apparent shear stress, and shear viscosity at 100°C were quantified. We found that the pure MNR gave the lower apparent shear stress, shear viscosity than did those of the blends with cassava starch. The rheological data of the MNR blends increased with increasing quantity of cassava starch. The highest value was observed for the blend of MNR. The rheological value was as follows: MNR > STR 5L with MNR (as the compatibilizer) > STR 5L compounds. Furthermore, rheological properties increased with increasing the levels of compatibilizer (MNR). The rheological results were described in terms of intermolecular interaction between the polar groups in the natural rubber and cassava starch molecules. Each rubber blend was compounded, and their curing characteristics were studied. The pure MNR compounds exhibited a long delayed onset of vulcanization for approximately 10 min. The retardation was found, because the accelerator (MBT) reacted with the anhydrides in the compound instead of acting as an accelerator. The retardation was not observed for the compound with the cassava starch. The curing curves for all MNRs were not in equilibrium at a maximum torque, while the pure STR 5L compound gave a curing curve with a maximum torque and a slight reversion. The curing curve for the compound with MNR as the compatibilizer was a combination of the curing curves of MNR and STR 5L. That is, the curve was in equilibrium at the maximum torque and the short delayed action. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2803–2813, 2001

Key words: rheological properties; curing behavior; reactive blending; maleated natural rubber, cassava starch

INTRODUCTION

In recent years, the anhydride grafted polymer has been widely studied. The main interest was originated in the graft copolymer as the main compositions in a reactive blend,[1–3] blend compatibilizers[4–11] or as composite matrices.[12] Thermoplastics, such as polyethylene,[1,4,5] polystyrene,[2,3] and polypropylene[6–12] are the main groups of the materials used as backbones of the graft copolymer.

Reactive blends for various types of starch and synthetic polymers are one of main interesting areas. They are used to produce degradable poly-

mers. Compatibility of the two different types of polymer is the main concern for the on-going work. There are many approaches used to improve the blend compatibility. One of which is to prepare graft copolymer of vinyl monomers on the starch backbone,[13] that is, the hydrophobic nature of the starch was increased. An alternative approach is to blend the starch with polymers containing polar functional groups. The special types of the polymer therefore are used as a blend composition or a compatibilizer. Generally, reactive blending of the two polymer takes place by the interaction of the polar functional groups and hydroxyl groups of starch molecules. The physical properties of the blends are therefore improved. There are various types of functional polymer used to prepare polymer blend of starch, for example poly(ethylene-*co*-acrylic acid),[14] styrene maleic anhydride copolymer,[2,3] ethylene maleic anhydride copolymer,[1,4,5] and epoxidized natural rubber (ENR).[15] In this work, natural rubber molecules were modified to be a copolymer of natural rubber–maleic anhydride or a maleated natural rubber (MNR). The graft copolymer was then used to prepare reactive blends of natural rubber and cassava starch. Rheological and curing properties of the blends were then investigated.

EXPERIMENTAL

Materials

The rubber used was the standard Thai natural rubber, STR 5L, manufactured by Thavorn Rubber Industry Co., Ltd., Songkla, Thailand. The maleic anhydride used to prepare maleated natural rubber was manufactured by Riedel-deHaen, Seelze, Germany. The cassava starch used as a blending ingredient was manufactured by Thaiwa Co., Ltd., Rayong, Thailand. The sulphur used as a vulcanizing agent was manufactured by Ajax Chemical Co., Ltd, Samutprakan, Thailand. The zinc oxide used as an activator, was manufactured by Global Chemical Co., Ltd, Bangkok, Thailand. The stearic acid used as an activator was manufactured by Petthai Chemical Co., Ltd. The 2-Mercaptobenzothaizole (MBT) used as an accelerator, manufactured by Shanxian Chemical Co., Ltd, Shandong Province, China.

Preparation of Maleated Natural Rubber

Copolymerization of maleic anhydride and polymer backbone has been normally accomplished using the free radical initiators, such as peroxide[1,16–19] and thermal initiation.[20] The previous work carried out in our laboratory could be claimed that the higher grafted anhydride on the natural molecules was observed for the system without using peroxide.[19] Therefore, the grafting reaction in this work was performed without a chemical initiator, only shearing action was exploited to generate the free radicals.

The graft copolymer of natural rubber and maleic anhydride was prepared by blending natural rubber and maleic anhydride in an internal mixer at 135°C. Small pieces of the natural rubber, STR 5L, were first dried in a vacuum oven at 40°C for 24 h. The internal mixer was then used to masticate STR 5L at 135°C with a rotor speed of 60 rpm for 2 min. A predetermined quantity of maleic anhydride was then incorporated into the internal mixer. The mixing was continued for 10 min at 135°C. The blended product was then dumped out onto the two-roll mill, sheeted out and cut into small pieces. Various quantities of maleic anhydride (i.e., 3, 6, 7, 8, 9, 10, 11, and 12 phr) were each used to prepare a graft copolymer in this work.

The presence of the anhydride group grafted on the natural rubber backbone was determined using a Perkin-Elmer FTIR spectrometer model 1600. However, unreacted maleic anhydride was first removed by the following procedures. Small pieces of the blended product about 3–4 g were dried at 40°C for 24 h. The sample was then dissolved in 400 mL of toluene and refluxed for 6 h. The mixture was then separated by means of filtration. The filtrate was then reprecipitated by adding excess amount of acetone. The precipitant product was then sheeted out and dried in the vacuum oven at 40°C for 24 h. The sample was redissolved in toluene. A thin film was then coated on an NaCl cell surface. After the toluene was evaporated, FTIR spectra were recorded.

Blending of Maleated Natural Rubber and Cassava Starch

MNR and cassava starch were mixed using a two-roll mill at a mixing temperature of 60°C. Mastication of 100 phr of MNR was first performed for 5 min before incorporating the cassava starch. Mixing was then continued for 5 min. The MNR–cassava starch compound was sheeted out and cut into small pieces. Various quantities of cassava starch (i.e., 0, 20, 40, and 60 phr) were each blended. MNR was also used as a compatibilizer

Table I   Compounding Formulations

Ingredients	Compound 1 (phr)	Compound 2 (phr)	Other Compounds (phr)
Maleated NR	100	—	90/75/50/25/10
STR 5L	—	100	10/25/50/75/90
Zinc oxide	6	6	6
Sulphur	3.5	3.5	3.5
Stearic acid	0.5	0.5	0.5
Mercaptobenzothiazole (MBT)	0.5	0.5	0.5
Cassava starch	0, 20, 40, and 60	0, 20, 40, and 60	0, 20, 40, and 60

for a blend of unmodified natural rubber (STR 5L) and cassava starch. The blend was each prepared using the blending ratio of MNR (phr) to STR 5L (phr) of 90 : 10, 75 : 25, 50 : 50, 25 : 75, and 10 : 90, together with various quantities of cassava starch, the same quantity as stated above. The last set of a blend was prepared using 100 phr of STR 5L mixed with various quantities of cassava starch.

Rheological Measurements

Two types of rheological technique were used to characterize the flow properties of rubber melts. They are an SPRI Mooney viscometer (model AC/684/FD) and a Rosand single bore capillary rheometer model RH7. The Mooney viscosities were tested at 100°C using a large rotor, a preheating time of 1 min, and a testing time of 4 min, according to ASTM D1646-89. The result of a typical viscosity was reported as ML(1 + 4, 100°C). Shear properties in terms of shear stress and shear viscosity were measured at a wide range of shear rates using the capillary rheometer. Testing conditions were set at 100°C and the ranges of shear rates of 10 to 1500 s^{-1}. Dimensions of a capillary die used were 2-mm diameter, 32 mm long and a 180° entry angle. Pressure drop across a capillary channel and melt temperature was captured via a data acquisition system. The values of the uncorrected apparent shear stress, apparent shear rate, and apparent shear viscosity were obtained using the derivation of the Poiseuille law for capillary flow[21]:

$$\text{Apparent shear stress (Pa);} \quad \tau = \frac{R\Delta P}{2L} \quad (1)$$

$$\text{Apparent wall shear rate (s}^{-1}\text{);} \quad \dot{\gamma}_{\text{app}} = \frac{4Q}{\pi R^3} \quad (2)$$

$$\text{Apparent shear viscosity (Pa} \cdot \text{s);} \quad \eta_s = \frac{\tau}{\dot{\gamma}_{\text{app}}}, \quad (3)$$

where ΔP is the pressure drop across the channel (Pa), Q is the volumetric flow rate (m^3 s^{-1}), R is the capillary radius (m), L is the length of the capillary (m). The value of R and L used in this work were 0.5 mm and 32 mm, respectively.

Curing Behavior of Reactive Blending Product of Maleated Natural Rubber and Cassava Starch

Maleated natural rubber and cassava starch blends were compounded using a standard formulation according to ASTM D3184-89, as shown in Table I. Natural rubber was first masticated using a two-roll mill at the temperature of 60°C for 5 min. Other compounding ingredients were then mixed according to the time schedule given in Table II. Cassava starch was added into the compound at each level of 0, 20, 40, and 60 phr, respectively. The MNR was also used as the compatibilizer. Each MNR and STR 5L at various weight ratios of 90 : 10, 75 : 25, 50 : 50, 25 : 75, and 10 : 90 was blended. The blends were mixed with cassava starch and compounded followed by the chemicals and the time schedule given in Tables I and II, respectively. Moreover, the compounding

Table II   Mixing Schedule

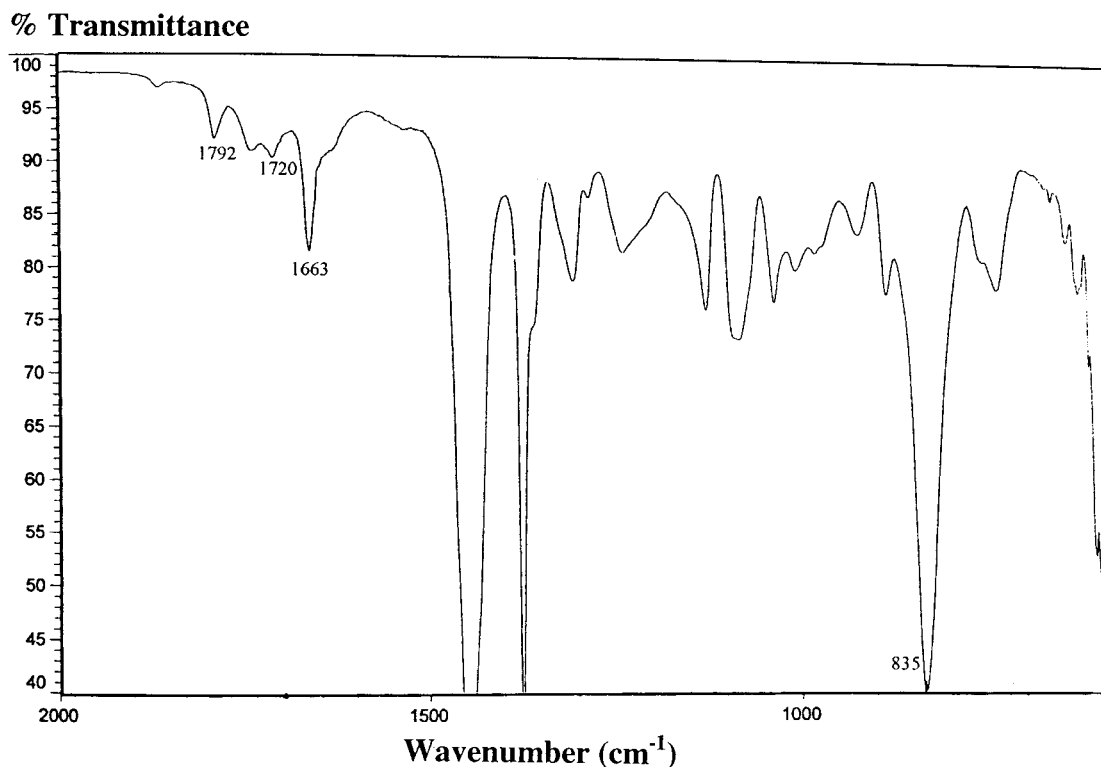| Descriptions	Mixing Time (min)
Rubber mastication	5
Cassava starch	5
ZnO	2
Accelerator (MBT)	2
Stearic acid	2
Sulphur	2
Compound finishing	5

% Transmittance

Figure 1 Infrared spectrum of MNR at a level of maleic anhydride of 6 phr.

of unmodified natural rubber, STR 5L, was also prepared for a comparison. Curing behavior was determined at 160°C using a Monsanto oscillating disk rheometer (Model ODR 2000) at 1° arc, according to ASTM D2084-95.

RESULTS AND DISCUSSION

Preparation of Maleated Natural Rubber

Figure 1 shows the infrared spectrum of maleated natural rubber (MNR), focused on a range of wave numbers of 800 to 2000 cm^{-1}. The anhydride peaks at 1850 and 1780 cm^{-1} disappeared, which indicated that a ring opening reaction of the anhydride group took place at 130°C in the presence of moisture. There was a single peak at 1720 cm^{-1} attributed to the carbonyl group formed by the reaction of the anhydride functional group with moisture. This characteristic peak was unnoticeable when using a nitrogen atmosphere during mixing and blending. The characteristic band of succinic anhydride symmetrical C=O stretch was observed at 1792 cm^{-1}.[22] The level of maleic anhydride grafted was determined using the absorbance ratio of the peaks at 1792 to 835 cm^{-1} (*cis*

C=C), as shown in Figure 2. The highest maleic acid content was observed at 6 phr of maleic anhydride used. Therefore, the natural rubber–maleic anhydride copolymer prepared at 6 phr maleic anhydride was used throughout this work without further purification.

Mooney Viscosity of the Blends

Mooney viscometer is commonly used to assess flow behavior of rubber melt in the rubber industry. The Mooney viscosity is proportional to the true shear viscosity at the very low shear rate (approximately 1 to 2 s^{-1}). Figure 3 shows the Mooney viscosities plotted against various quantities of cassava starch. The Mooney viscosity for all types of rubber blends increased with increasing concentrations of cassava starch. However, at the same concentration of starch added, the blend of MNR shows the highest Mooney viscosity, while the blend of MNR/STR 5L with the MNR as a compatibilizer shows the value between blends of pure STR 5L and MNR. Moreover, the highest gradient of Mooney viscosity curve for the blend of pure MNR was observed, while the blend of STR 5L show the lowest gradient. This may be attributed to the polar nature of anhydride groups pres-
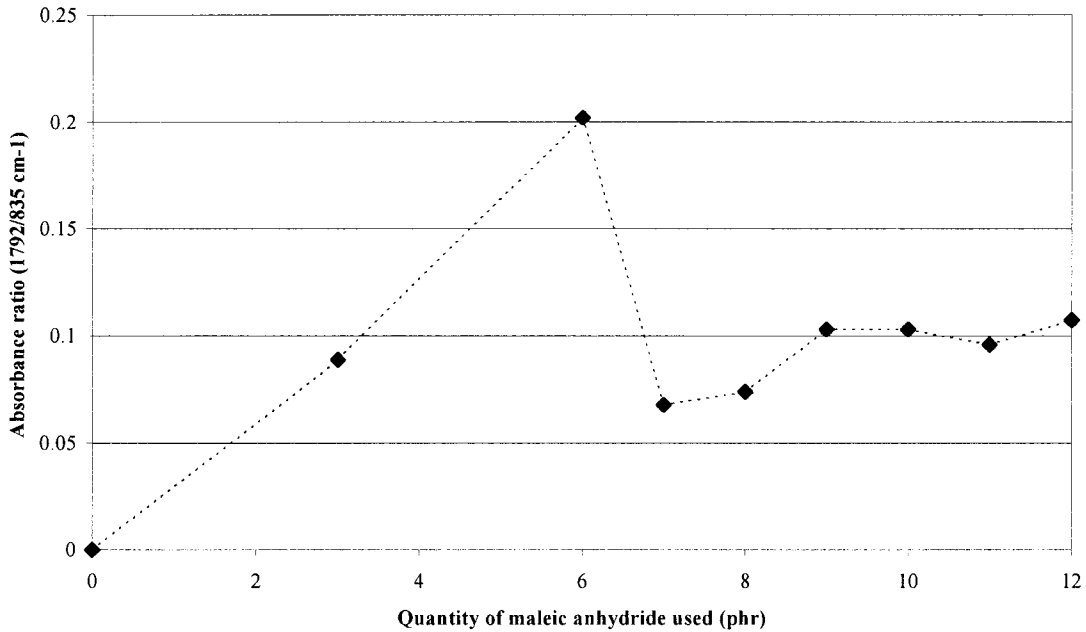
Figure 2 Absorbance ratio of the transmission peaks at 1792 to 835 cm^{-1}.

ence in the MNR molecules and hydroxyl groups in the cassava starch molecules. The formation of intermolecular forces between those polar groups might occur. The blend of pure MNR, therefore, exhibits the highest chemical interaction between those groups, while pure STR 5L shows a poor interaction because of the difference in chemical natures. MNR is apparently used as the compatibilizer for the blends of natural rubber and cassava starch, because the formation of chemical interaction between polar groups in MNR molecules and polar groups in the cassava starch molecules was established. The nonpolar part of MNR molecules was presumably miscible with
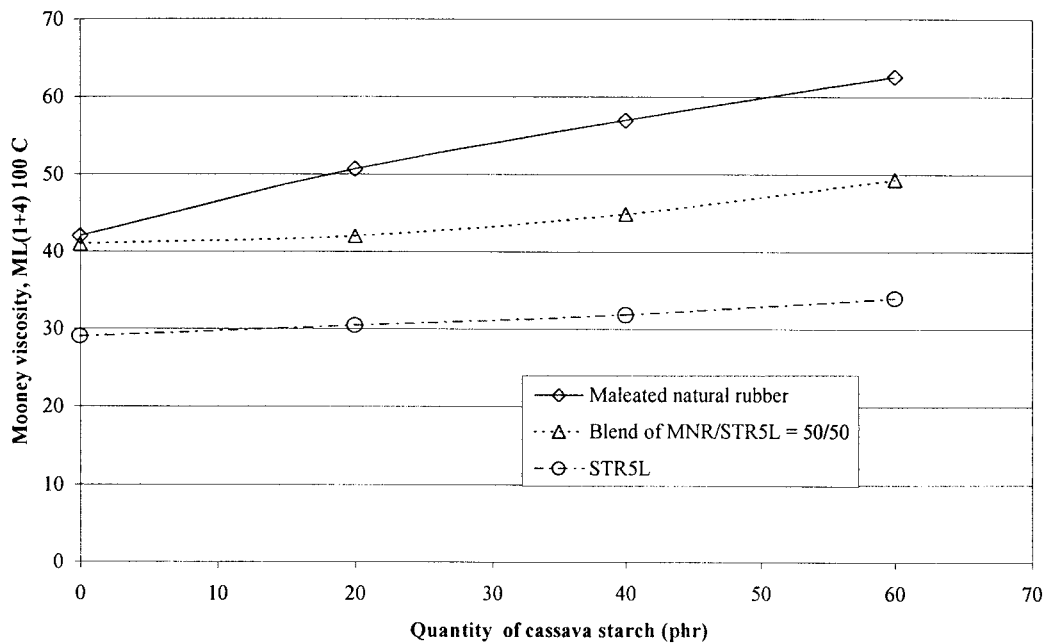

Figure 3 Mooney viscosity of rubber blends for various quantities of cassava starch.
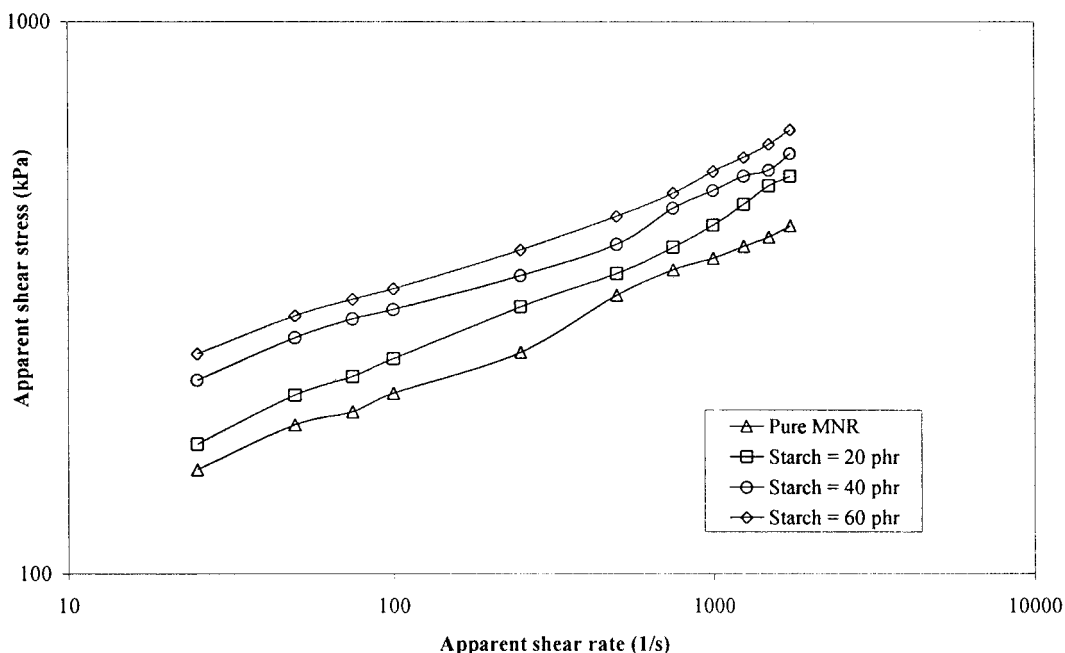
Figure 4 Relationship between apparent shear rate and apparent shear stress of MNR blended with various quantities of cassava starch.

the nonpolar moieties of natural rubber molecules. Therefore, the Mooney viscosity for the blend of STR 5L with ENR as a compatibilizer was higher than those of the blends of pure STR 5L.

Effect of the Apparent Shear Rate on the Apparent Shear Stress and the Apparent Shear Viscosity

Figure 4 compares the effect of apparent shear rate on apparent shear stress for the blends of MNR at various levels of cassava starch, shown as a logarithmic plot. A linear flow curve (a plot of shear rate vs. shear stress) for all sets of test was observed. This corresponds to the power law equation proposed by Ostwald.[23] The apparent shear stress was apparently increased with the apparent shear rate. Moreover, at a given shear rate, the shear stress increased with increasing concentrations of cassava starch. That is, the higher flow curve was found when the increasing concentration of cassava starch was incorporated into the blends. The addition of cassava starch also increased the apparent viscosity, as shown in Figure 5. This implies that a higher pressure was needed during a melt flow in the capillary. The shear thinning behavior of the flow was observed. That is, the apparent viscosity decreased with an increase in the apparent

shear rate indicating a pseudoplastic behavior of the blend. Therefore, the shear stress was required to cause the flow to become smaller when the rate of shear increased. The increase in shear viscosity and shear stress might be due to the chemical interaction between the maleated natural rubber and cassava starch molecules. That is, MNR molecules probably cause the formation of a chemical bonding between the anhydride group and hydroxyl groups of cassava starch molecules. The formation of intermolecular forces is therefore expected to increase upon increasing the concentration of cassava starch. As a consequence, the polymer molecules could not be easily deformed under the shearing action for a capillary flow in the extruder. This observation is in agreement with the result reported earlier on the rheological properties of the polymer blend of epoxidized natural rubber (ENR) and cassava starch.[15]

Figure 6 shows the effect of apparent shear rate on apparent shear stress for the blends of MNR at 40 phr of cassava starch and at various ratios of MNR to STR 5L. The flow behavior according to the power law relationship was also observed. The blend of STR 5L exhibited the lowest flow curve, while the blend of pure MNR gave the highest flow curve. Furthermore, the appar-
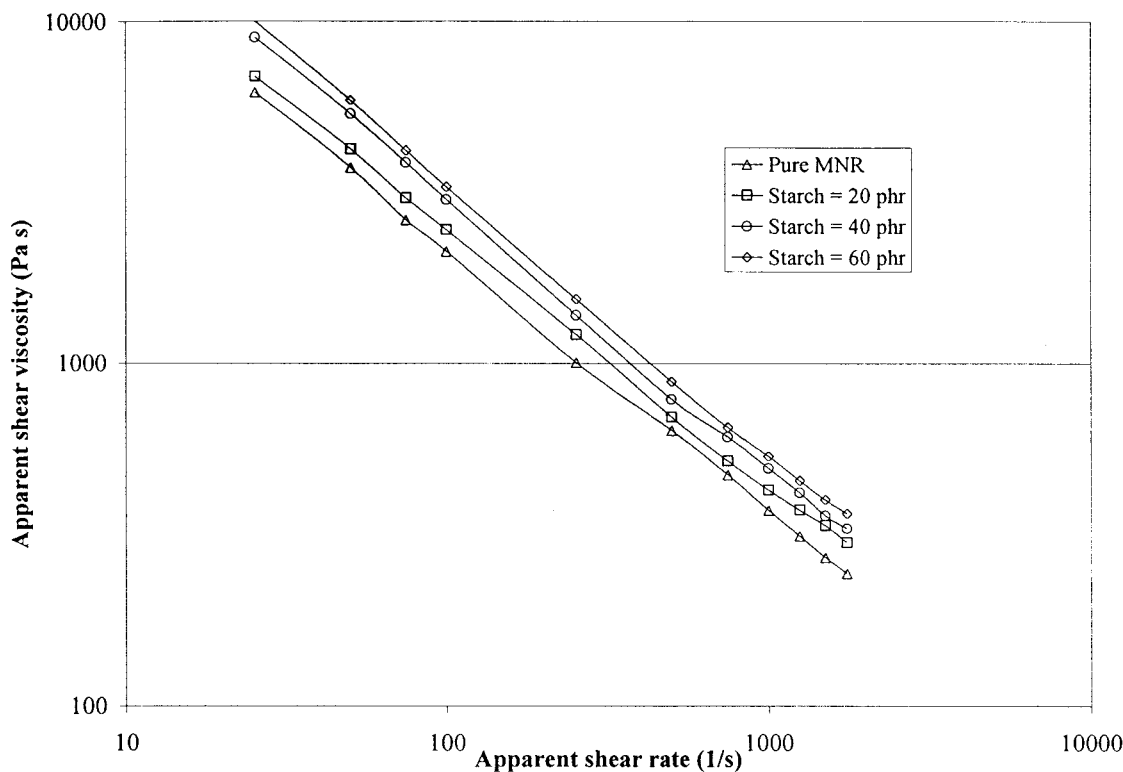
Figure 5   Relationship between apparent shear rate and apparent shear viscosity of MNR blended with various quantities of cassava starch.

ent shear stress increased with increasing the concentrations of MNR as the compatibilizer. That is, the higher flow curve was found for the blend using higher concentrations of MNR. The chemical interaction between the polar groups of MNR and cassava starch molecules might be responsible for different level of shear stresses.

Curing Characteristics

Curing behavior for each set of rubber compound was investigated using Monsanto, oscillating disk rheometer, ODR 2000. Curing curves or rheometer curves were the plots of relationships for the force required to oscillate the disk as a function of time. The force (i.e., in this case a torque) is proportional to the stiffness or shear modulus of the rubber specimen. Figure 7 shows curing curves for the STR 5L compound blended with various quantities of cassava starch. The stiffness of the blends first decreased during the specimen's warm up time, approximately 3 min. The stiffness then abruptly increased due to vulcanization. The curing curve of the STR 5L blended with cassava starch is a curing curve with the maximum torque and a slight reversion at the final stage of the test.

The level of the reversion is seemingly less for the compound of higher cassava starch added. The reversion has been widely accepted that because some crosslink structures were destroyed by a continuous rotor oscillation after the maximum curing.[24] The vulcanization of the STR 5L compounds therefore consists of four reaction phases: the delayed onset of vulcanization (scorch), undervulcanization, optimum vulcanization, and overvulcanization with reversion tendencies. The stiffness of the STR 5L compound also found dependence on the concentrations of cassava starch added in the compounding formulation.

Different curing curves were observed for the MNR compounds as shown in Figure 8. The pure MNR compound exhibited a long delayed onset of vulcanization, that is, the stiffness decreased and became almost constant for approximately 10 min before an increase because of the onset of vulcanization. The intensive retardation for the curing of mercapto-accelerator (such as, MBT) was widely accepted because of the presence of acids or anhydrides in the rubber compound.[13] A reaction between MBT and free maleic anhydride molecules and/or succinic acid (from a ring-open-
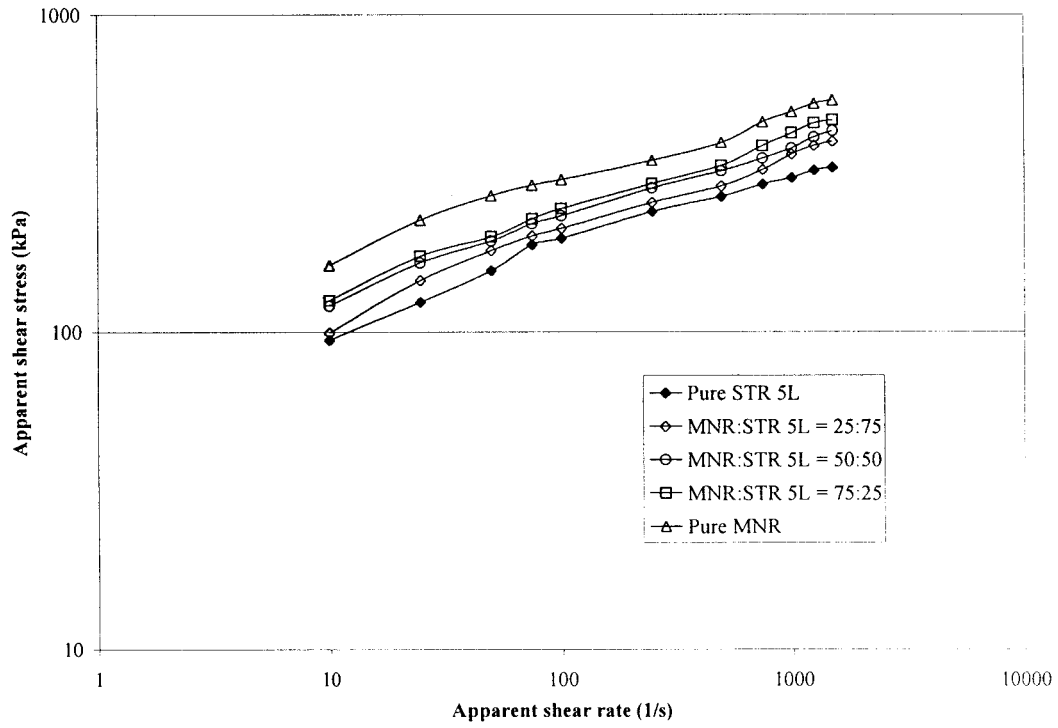
Figure 6 Relationship between apparent shear rate and apparent shear stress of rubber blends at the quantity of starch of 40 phr and different ratios of MNR to STR 5L.
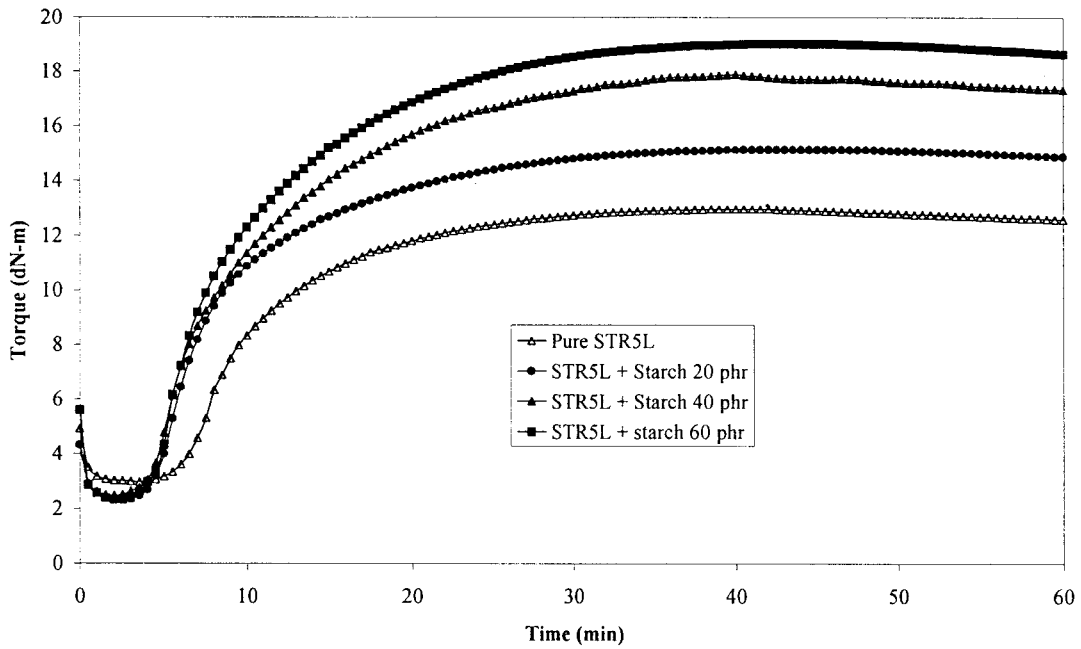

Figure 7 Cure curve of natural rubber (STR 5L) compounds with various quantities of cassava starch.
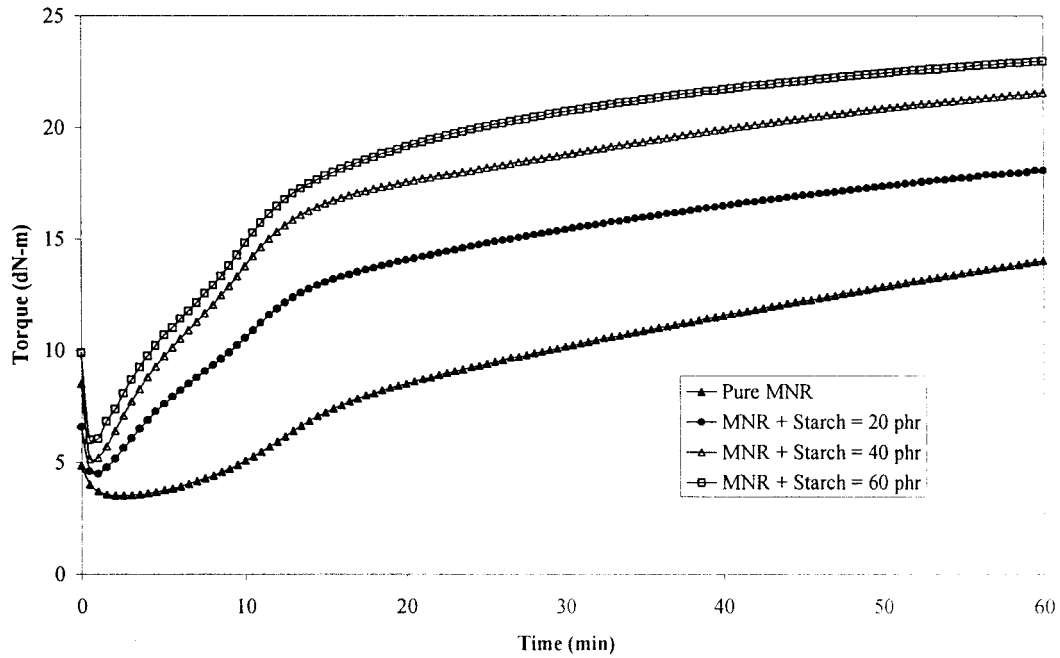
Figure 8 Cure curve of maleated natural rubber (MNR) compounds with various quantities of cassava starch.

ing reaction of the grafted maleic anhydride) was the main reason for the delayed onset of vulcanization. However, incorporation of cassava starch

shortened the delay action time from approximately 1 to 10 min, because some parts of the free maleic anhydride and the grafted succinic acid
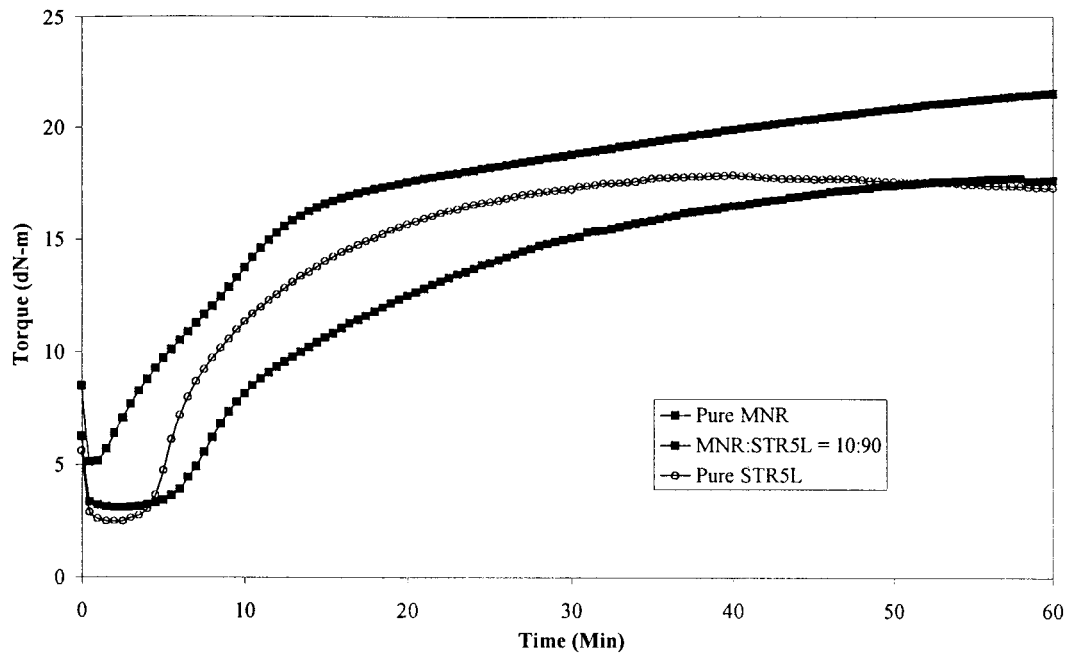

Figure 9 Comparison of the cure curve for MNR, STR5 L, and STR 5L with MNR as the compatibiliser at a level of cassava starch of 40 phr.

reacted with the cassava starch molecules. The MBT, therefore, played a significant role as an accelerator in the valcanization process. Nonetheless, succinic side groups and free maleic anhydride still influenced the curing characteristics of MNR compounds. Consequently, all curing curves in Figure 8 were not in equilibrium at the maximum torque. The stiffness still increased with increasing testing times. The higher stiffness rubber compounds was also observed when increasing the concentrations of cassava starch. This may be attributed to different levels of the chemical interaction between the polar groups of the two types of polymer.

Comparison of curing curves at 40 phr of cassava starch is shown in Figure 9. The compound of MNR exhibited the shortest delayed onset of vulcanization, while the STR 5L and STR 5L with MNR as the compatibilizer (10 phr) gave the similar curing curve at the beginning stage. The curing curve for MNR at 40 phr of cassava starch was not in equilibrium at the maximum torque even the highest torque was observed at the testing time of 60 min. Also, the curing curve of the STR 5L blended with 40 phr of cassava starch gave a maximum torque and a slight reversion, as stated previously. The curing curve of STR 5L with MNR as the compatibilizer (10 phr) exhibited a combination characteristic between the curing curves of MNR and STR 5L compound. It is certain that the curve is in equilibrium at the maximum torque.

CONCLUSION

Natural rubber–maleic anhydride graft copolymer was successfully prepared and used as blending compositions and compatibilizers. The chemical interaction between the polar groups in the NR graft copolymer and cassava molecules is responsible for the characteristics of the Mooney viscosity, apparent shear stress, and shear viscosity of the blends. The Mooney viscosity, apparent shear stress, and shear viscosity of the MNR blended were highest at a given concentration of cassava starch. The blends with MNR as the compatibilizers, at a given level of cassava starch, exhibited the rheological behavior between the blends of pure STR 5L and pure MNR. Curing characteristic was also related to the chemical interaction between the polar groups presence in the compound. The curing curve of pure MNR without cassava starch gave the long delayed onset of vulcanization (10 min), but it was shorten

by adding the cassava starch. The reaction of the accelerator (MBT) with the free maleic anhydrides, and grafted succinic acid were the reason of the long delayed action. The equilibrium at the maximum torque was not observed for the curing of MNR compounds with and without cassava starch. However, the short delayed onset of vulcanization and the equilibrium at the maximum torque were found in the blend of STR 5L with MNR at 10 phr of the compatibilizer. It is concluded that the curing curve was apparently a combination between the curves of the pure STR 5L and pure MNR compounds.

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