Rheological Behavior of Reactive Blending of Epoxidized Natural Rubber with Cassava Starch and Epoxidized Natural Rubber with Natural Rubber and Cassava Starch

C. Nakason,[1] A. Kaesaman,[1] W. Sainamsai,[1] S. Kiatkamjonwong[2]

[1]Department of Rubber Technology and Polymer Science, Faculty of Science and Technology, Prince of Songkla University, Pattani 94000, Thailand
[2]Department of Imaging and Printing Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand

ABSTRACT: Epoxidized natural rubbers (ENR-25 and ENR-45) were prepared using the performic epoxidation method. Two-component (ENR–cassava starch) and three-component (ENR–NR–cassava starch) blends were prepared. ENR-25 and ENR-45 were blended with various quantities of gelatinized cassava starch in the latex state. The pure ENR exhibited lower shear stress and shear viscosity than those of the blends with cassava starch. Furthermore, the shear stress and shear viscosity were increased with an increase in the cassava starch concentration. The chemical interaction between the epoxide groups in the ENR and the hydroxyl groups in the cassava starch molecules might be the reason for the increasing trends of the shear stress and shear viscosity. The blends are classified as compatible blends because of the strong chemical bonding between different phases. SEM micrographs were used to clarify the compatibility. Power law behavior with pluglike flow profiles was observed for all sets of ENR–NR–cassava starch blends. Very low power law index values (<0.34) and highly pseudoplastic fluid behavior were also observed. The log additive rule was applied to plots of zero shear viscosity (consistency index) and the shear viscosity versus the concentration of ENR-25. Positive deviation blending was observed, which indicates compatible blends. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1752–1762, 2004

Key words: rheological properties; reactive blending; epoxidized natural rubber; cassava starch; log additive rule

INTRODUCTION

Epoxidized natural rubber (ENR) is a relatively new type of chemically modified NR. The main objectives for the preparation of ENR are to improve the performance of NR in specific applications and to convert NR into a new material that could diversify its traditional uses. Such ENR vulcanizates are potentially useful materials, which exhibit low gas permeability, high oil resistance, an increased glass-transition temperature (T_g), and improved wet skid resistance.[1,2] Extensive work has been performed using ENR as a reactive blending component based on the polar nature of the epoxide rings. This was carried out using another polar blending component, such as poly(ethylene-co-acrylic acid),[3] polychloroprene,[4,5] poly(vinyl chloride),[6–10] epoxy resin,[11] silica,[12–14] carbon black,[4,14,15] chlorosulfonated polyethylene,[10,16] sulfo-nated ethylene–propylene–diene monomer,[17] or styrene–butadiene rubber.[18,19] Furthermore, the reactive blending of ENR with particulate cassava starch powder was also studied.[20] Reactive blends for various types of starch were investigated for producing biodegradable blends with polymers, such as low density polyethylene,[22–25] high density polyethylene,[25] polypropylene,[25] and poly(ethylene-co-vinyl acetate).[27] The compatibility of the two different types is the main concern of ongoing work. There are a number of approaches used to improve blend compatibility. One of these is to increase the hydrophobic nature of the starch by preparing the graft copolymer of vinyl monomers on the starch backbone.[28] An alternative approach is to blend the starch with polymers containing polar functional groups. Reactive blending of two polymers takes place by the interaction of the polar functional groups and hydroxyl groups of starch molecules. There are various types of functional polymers used to prepare reactive blends of starch, for example, poly(ethylene-co-vinyl acetate),[27] poly(ethylene-co-acrylic acid),[29] styrene maleic anhydride copolymer,[30,31] NR-g-poly(methyl methacrylate),[32] ENR,[20] and maleated NR.[21] The reactive blending of ENR with particulate cassava starch powder was generally performed in the melting state. In this work, NR molecules were modified to be ENR. The ENR was then

used for reactive blending with the gelatinized cassava starch in the latex state. Moreover, three-component blends of ENR–NR– cassava starch were also prepared. The rheology of the blends was investigated later.

EXPERIMENTAL

Materials

High ammonia concentrated NR latex was used as a raw material for the preparation of ENR and a blending component (Pattani Industry Co., Ltd., Pattani, Thailand). The cassava starch used as a blending ingredient was manufactured by Thaiwa Co., Ltd. (Rayong, Thailand). The nonionic surfactant that was used was Emulwin W (aromatic polyglycol, Bayer, Leverkusen, Germany). Formic acid was used as a reactant for the preparation of ENR (Fluka Chemie, Buchs, Switzerland). Hydrogen peroxide was used as a coreactant for the preparation of ENR (Riedel De Haen, Seelze, Germany).

Preparation of ENR

The ENR latex was prepared using high ammonia concentrated NR latex with a dry rubber content (DRC) of approximately 60%. The details for the preparation process of ENR are described elsewhere.[20,33] The latex was first diluted to 20% DRC and stabilized against coagulation by adding 10 wt % of the nonionic surfactant (Emulwin W). Hydrogen peroxide and formic acid were then added to form *in situ* performic acid. The reaction temperature was kept at 50°C. The reaction time was set according to the level of epoxide groups in the ENR products as described in our previous work.[33] Reaction times of 4 and 8 h were selected for the preparation of ENR with epoxide groups of 25 (ENR-25) and 45 mol % (ENR-45), respectively. The level of the epoxide content in the ENR product was later confirmed by IR spectroscopy via a calibration curve.

Preparation of gelatinized cassava starch

We mixed 30 g of cassava starch with 600 mL of distilled water in a 2.5-L reaction kettle. The system was heated at around 85°C for 1 h under a nitrogen atmosphere and agitation to form a pastelike slurry.

Blending of ENR and cassava starch

The ENR–cassava starch blends were prepared in the latex state. The ENR latex (ENR-25 or ENR-45) and the gelatinized starch were mixed in the 2.5-L reaction kettle at 85°C under a nitrogen atmosphere and agitation for 30 min. The mixture was then coagulated by increasing the temperature to approximately 100°C.

TABLE I
Blend Compositions of ENR-25 and NR Latex at Constant Cassava Starch Concentration of 50 phr

Blend code	NR (dry weight)	ENR-25 (dry weight)
A	100	0
B	90	10
C	70	30
D	50	50
E	40	60
F	30	70
G	20	80
H	10	90
I	0	100

Thin sheets were made using a small-scale two-roll mill and thorough washing with distilled water. Then, the sheets were transferred to a hot air oven and left at 50°C for 24 h. The quantity of gelatinized starch in the blends was varied at 10, 30, 50, and 75 phr in the formulation. Three-component ENR–NR– cassava starch blends were also prepared by blending the ENR-25 latex with a given amount of the high ammonia concentration NR latex and a fixed 50-phr quantity of the gelatinized cassava starch. Blending was carried out in a 2.5-L reaction kettle at 85°C under a nitrogen atmosphere and agitation for 30 min. The latices were then coagulated and sheeted out. Later the thin sheets were dried at 50°C for 24 h. Various blend ratios of ENR–NR at a constant 50-phr concentration of gelatinized cassava starch were prepared as shown in Table I.

Rheological characterization

A single-bore Rosand capillary rheometer (model RH7) was utilized to characterize the shear flow properties in terms of the apparent shear stress and apparent shear viscosity. The tests were carried out over a wide range of shear rates (5–1500 s^{-1}) at a test temperature of 125°C. The dimensions of the capillary die were a 2-mm diameter, 32-mm length, and 180° entrance angle with an aspect ratio (length/depth) of 16:1. The materials were first preheated in a barrel for 7 min under a pressure of approximately 2–4 MPa to attain a compact mass. The excess molten material was automatically purged until no bubbles were observed. The test was then carried out with a set of shear rates in 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. The equations used to calculate the shear stress, shear viscosity, and shear rate were described in our previous articles.[20,21,33,34]
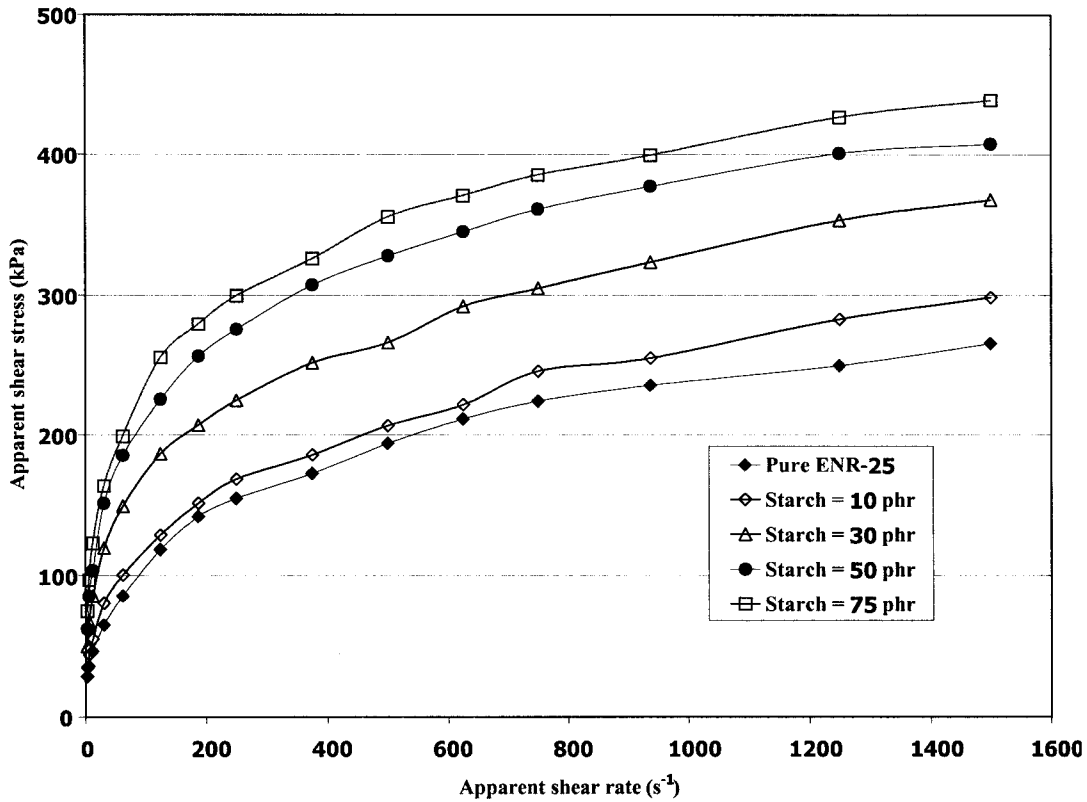
Figure 1 The relationship between the apparent shear stress and apparent shear rate of ENR-25–cassavastarch blends at 125°C.

RESULTS AND DISCUSSION

Shear flow properties of ENR–cassava starch blends

Plots of the apparent shear stress versus the apparent shear rate of pure ENR-25 (Fig. 1) and pure ENR-45 (Fig. 2) are compared with the blends of ENR-25 (Fig. 1) and ENR-45 (Fig. 2) with various concentrations of gelatinized cassava starch (10, 30, 50, and 75 phr). The apparent shear stress was increased with an increase in the apparent shear rate. Furthermore, at a given shear rate, the pure ENR exhibited a lower shear stress
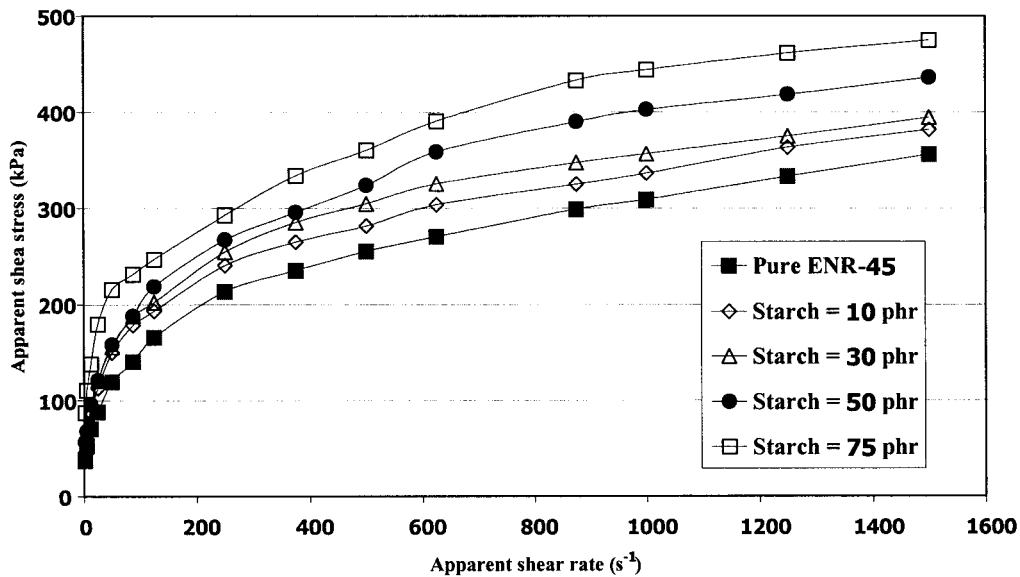

Figure 2 The relationship between the apparent shear stress and apparent shear rate of ENR-45–cassavastarch blends at 125°C.
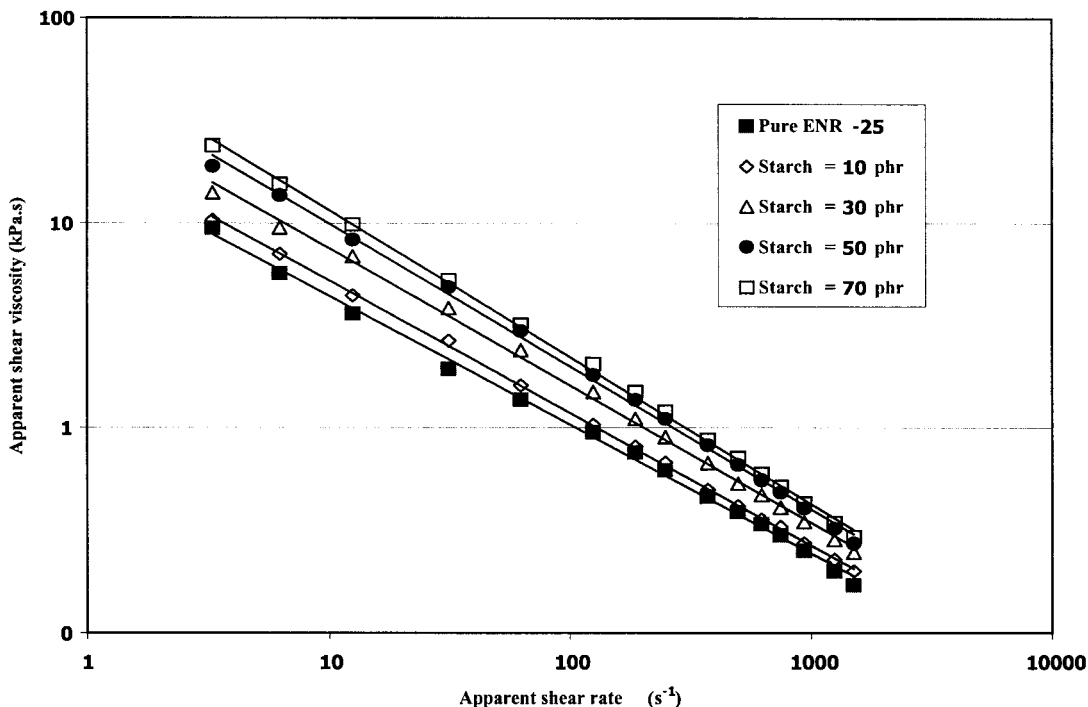
Figure 3 The relationship between the apparent shear viscosity and apparent shear rate of ENR-25–cassava starch blends at 125°C.

than that of the blends. The shear stress also increased with increasing concentrations of cassava starch in all sets of blends. That is, a higher flow curve (on a plot of the shear stress vs. shear rate) was found when an increased concentration of cassava starch was added into the blends. The incorporation of cassava starch

also increased the apparent shear viscosity at a given shear rate, as shown in Figures 3 and 4. This means that a higher viscosity curve (on a plot of the shear viscosity vs. shear rate) was observed upon increasing the concentration of cassava starch in the blends. Furthermore, shear thinning behavior of the flow was
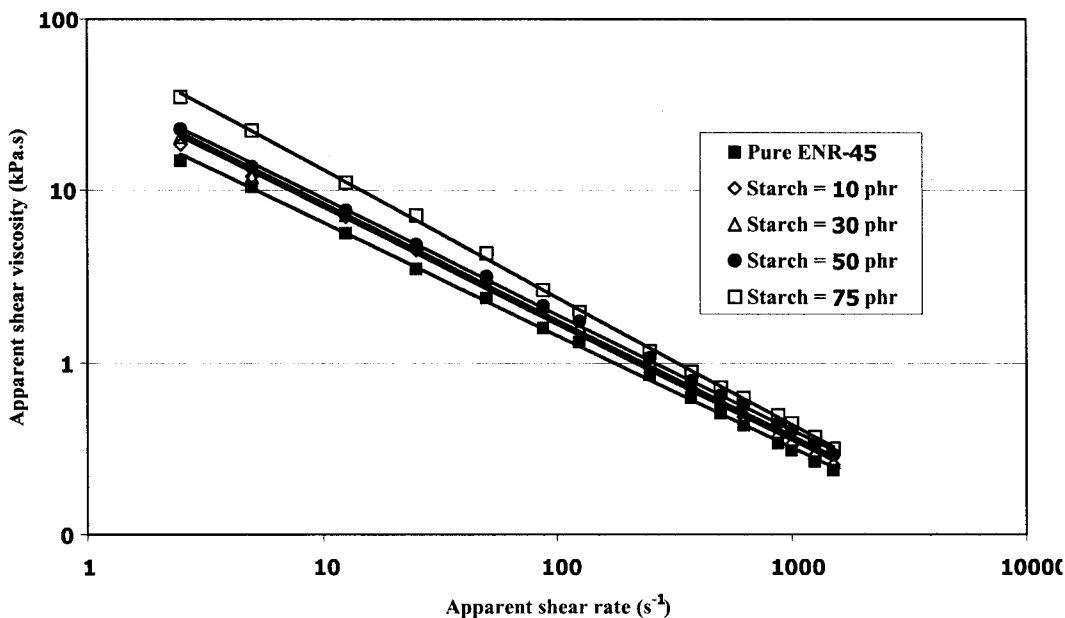

Figure 4 The relationship between the apparent shear viscosity and apparent shear rate of ENR-45–cassava starch blends at 125°C.
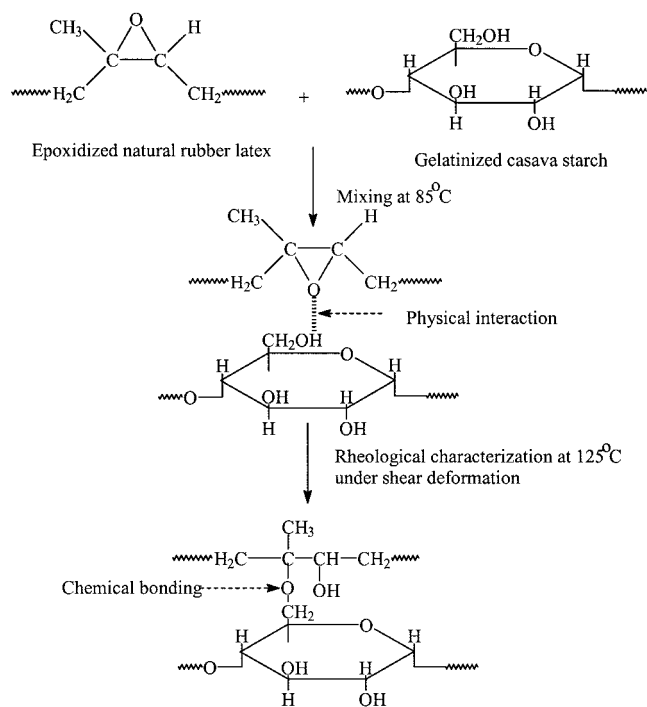
Figure 5 The possible reaction mechanism for the chemical bonding between ENR and gelatinized cassava starch.

observed: the apparent shear viscosity was decreased with an increase in the apparent shear rate. This indicates pseudoplastic (shear thinning) behavior of the blend. Therefore, shear stress was required to cause the flow to become smaller when the rate of shear increased. The increase in shear stress and shear viscosity might be due to the chemical interaction between the ENR and cassava starch molecules. The ENR molecules probably cause the formation of chemical bonding between the epoxide groups and hydroxyl groups of cassava starch molecules. The strength of the intermolecular forces is therefore expected to increase upon increasing the concentration of cassava starch and the level of epoxide groups in the NR molecules. As a consequence, the polymer molecules were not easily deformed under the shearing action of a capillary flow in the rheometer die. This observation is in agreement with the results reported earlier on the rheological properties of polymer blends of ENR[20] and maleated NR[21] with particulate cassava starch powder. A possible reaction mechanism between ENR and gelatinized cassava starch is proposed in Figure 5. Physical interactions between the polar groups of ENR and cassava starch were established during the mixing operation at 85°C after coagulation and drying in a hot air oven. Chemical bonding occurred later during the rheological characterization at the high temperature under shear deformation in the capillary of the rheometer. Therefore, chemical bonding causes the increase in the shear stress and shear

viscosity upon increasing the concentration of the gelatinized cassava starch.

Figures 6 and 7 compare the apparent shear stress and shear viscosity of pure ENR-25, pure ENR-45, and blends at a cassava starch concentration of 30 phr. As expected, at a given shear rate, pure ENR-25 exhibited lower shear stress and shear viscosity that those of pure ENR-45. This is ascribed to the higher epoxide content, which caused higher chemical interactions between the ENR molecules under shear deformation at high temperature. This was proved and described earlier in our previous work.[20] Furthermore, at a given shear rate, the ENR blended with 30 phr cassava starch exhibited higher shear stress and shear viscosity than those of the corresponding pure ENR. The higher flow and viscosity curves were also observed for the blend of ENR-45 and cassava starch. The level of shear stress and shear viscosity therefore depends on the level of epoxide groups in the NR molecules at the fixed concentration of cassava starch used in the blend formulations. This corresponds to the level of chemical interactions of the polar groups in the ENR and cassava starch molecules.

We concluded from the existence of the chemical bonding that the blends of ENR and cassava starch might be compatible or partly compatible blends. This was proven by morphological studies of the pure ENR and ENR–cassava starch blends using the SEM technique, as shown in Figure 8. Compatibilization was found, insofar as no separated white particles of cassava starch could be seen in the electron micrographs.

Shear flow properties of ENR–NR–cassava starch blends

The effects of the apparent shear rate on the apparent shear stress (Fig. 9) and apparent shear viscosity (Fig. 10) for various blend compositions of ENR–NR at a constant 50-phr concentration of gelatinized cassava starch are shown in logarithmic plots. There were straight lines for the flow and viscosity curves for all sets of tests. Furthermore, the flow and viscosity curves for the blends with approximately 10 and 30% ENR contents were lower than the curves for pure ENR (i.e., at ENR = 100%) and pure NR (i.e., ENR = 0%) blends. The highest shear stress and viscosity were found in the ENR ranges of approximately 60–80%. The plots of the apparent shear rate versus the apparent shear stress correspond to the power law equation proposed by Ostwald[35]:

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

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.
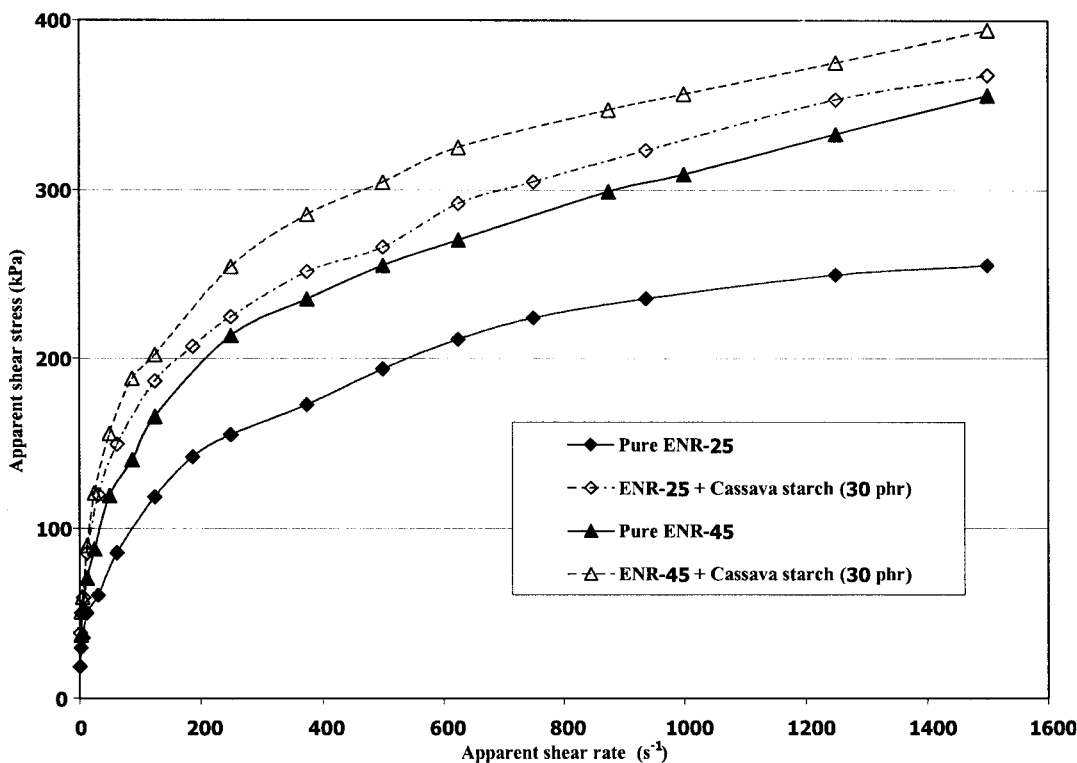
Figure 6 A comparison of the apparent shear stress of pure ENR-25, pure ENR-45, and ENR–cassava starch blends at a cassava concentration of 30 phr.

From the linear relation on a log–log scale, one can attain the slope (n) and intercept (K), which are shown in Table II. Plots of the n and K values against the quantity of ENR-25 in the blend composition are illus-trated in Figures 11 and 12, respectively. The n values of the blends with 10 and 30% ENR-25 were found to be higher than that of the blend of pure NR. However, upon increasing the quantity of ENR-25 above 30 phr,
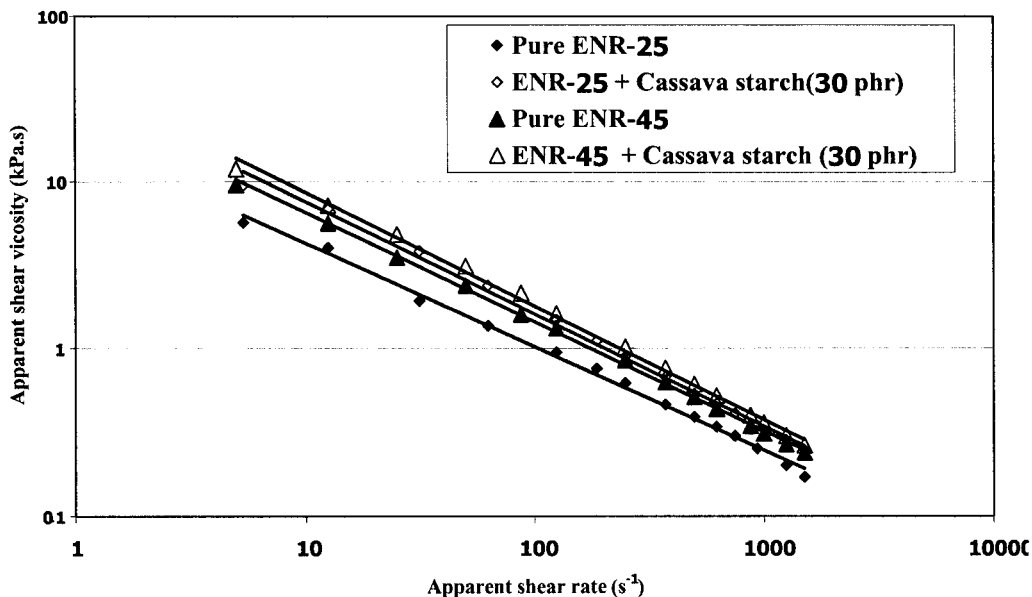

Figure 7 A comparison of the apparent shear viscosity of pure ENR-25, pure ENR-45, and ENR–cassava starch blends at a cassava concentration of 30 phr.
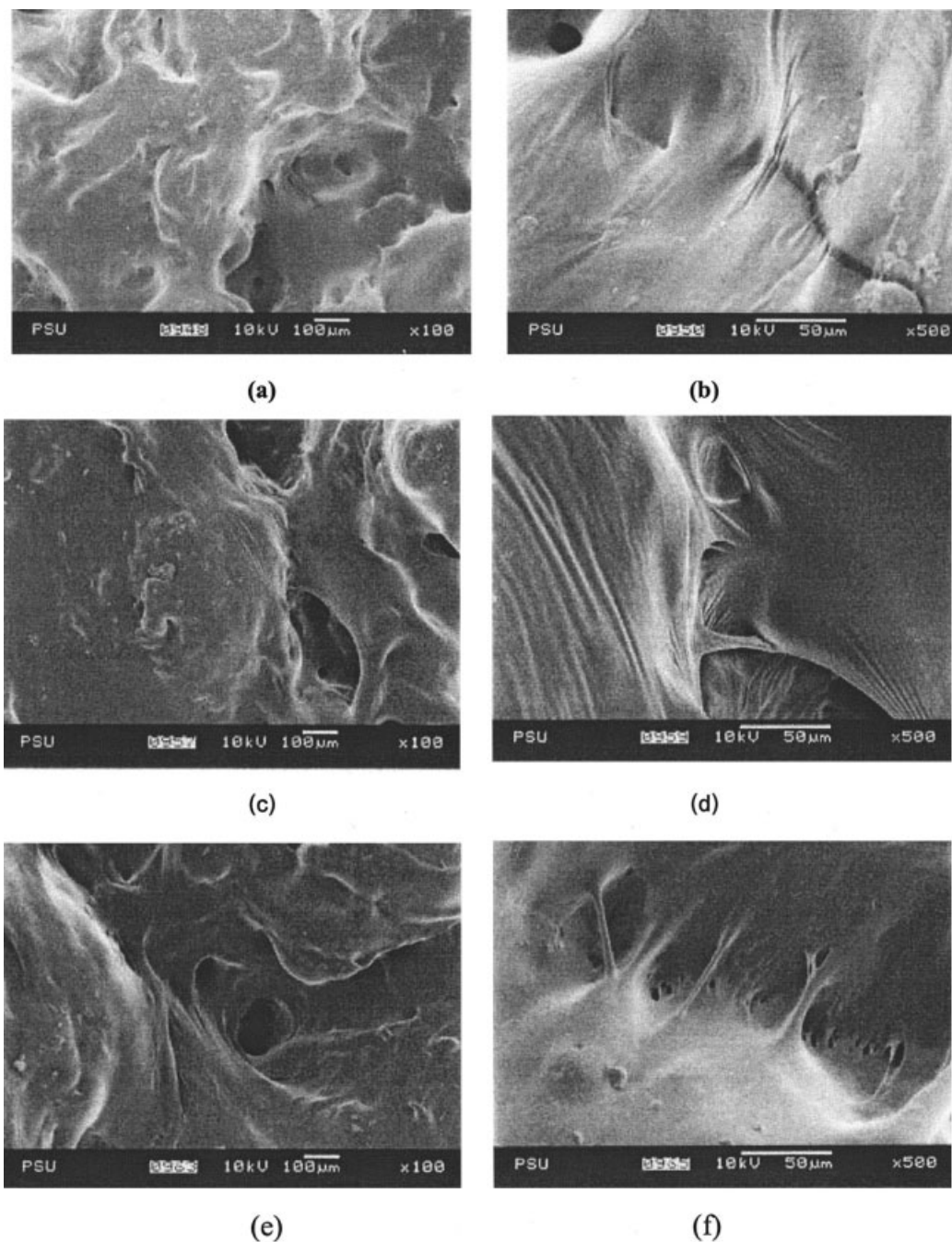
Figure 8   SEM micrographs of (a) pure ENR, (b) pure ENR, (c) ENR with 30 phr cassava starch, (d) ENR with 30 phr cassava starch, (e) ENR with 75 phr cassava starch, and (f) ENR with 75 phr cassava starch. Original magnifications: (a,c,e) × 100; (b,d,f) × 500.

the n value becomes smaller. The n value was found to be quite constant for a level of higher than 50% ENR-25 in the blend composition. For all sets of blends, the power law indices were less than 1.0, which indicates shear thinning or pseudoplastic behavior. We also found that the value of n decreases with an increasing concentration of ENR-25 in the range of 10–50% in the blend formulations. This indicates greater shear thinning in the flow upon increas-

ing the ENR content. 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 blends in this work exhibited very low n values (i.e., $n < 0.34$). Therefore, the highly pseudoplastic fluid flowed through the capillary almost like a plug moving at a uniform speed as the melt was sliding down against the channel wall. The K value is a Newtonian viscosity if $n = 1$. By definition,
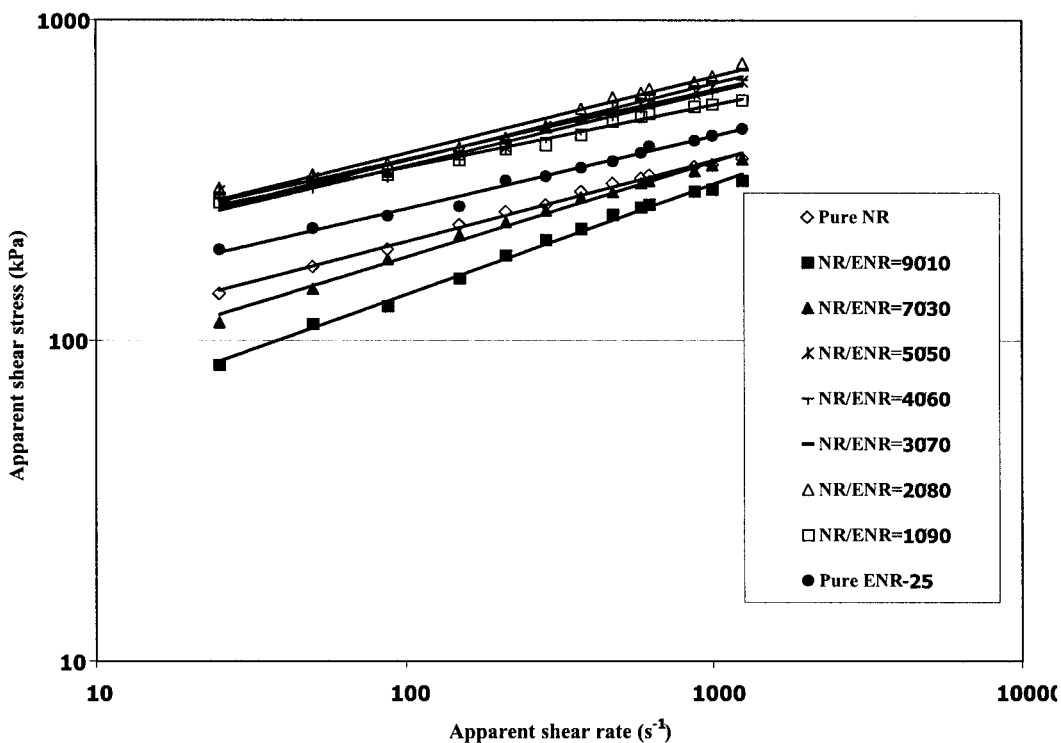
Figure 9 The relationship between the apparent shear stress and apparent shear rate of ENR-25 blended with NR at various blend ratios and at a cassava starch concentration of 50 phr.

the K value is related to the zero-shear viscosity (i.e., the shear viscosity at a shear rate of zero) of the flowing polymer blends at a test temperature (125°C). Excluding the K value for the blend of pure NR and 50 phr gelatinized cassava starch (i.e., at ENR = 0%), the K values of the ENR–NR–cassava starch blends indicate positive deviation blends (PDBs), according to the following log additive rule[36–39]:
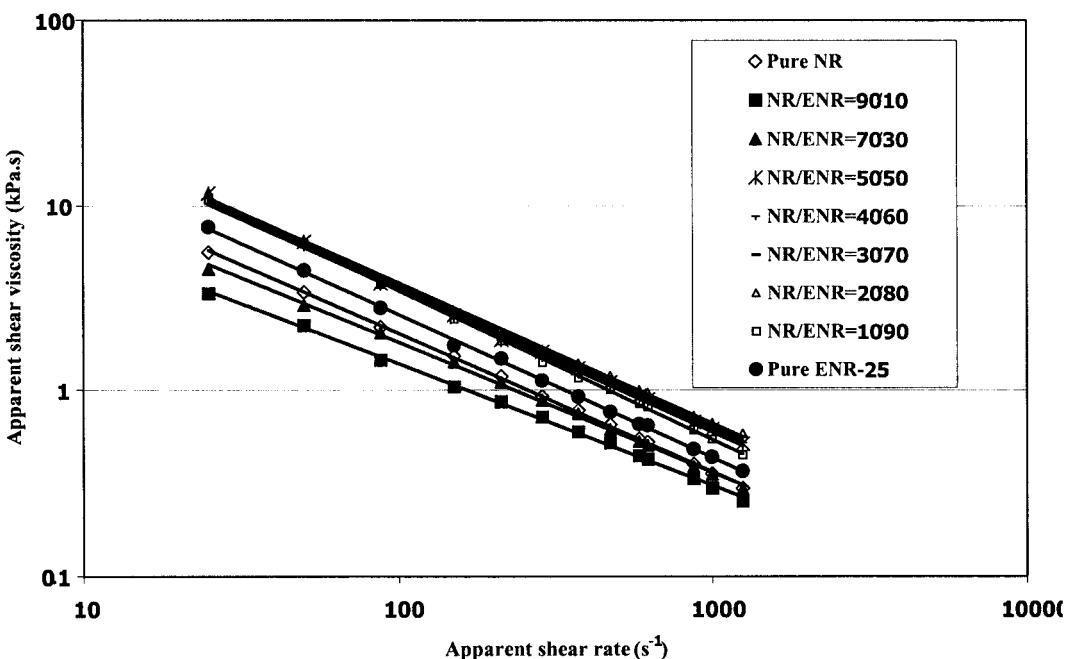

Figure 10 The relationship between the apparent shear viscosity and apparent shear rate of ENR-25 blended with NR at various blend ratios and at a cassava starch concentration of 50 phr.

TABLE II
Power Law Index (*n*) and Consistency Index (*K*) for
Various Blend Compositions

Blend code	n	K (Pa s^n)
A	0.26	76259
B	0.34	28395
C	0.31	41791
D	0.21	144197
E	0.21	133850
F	0.22	132749
G	0.20	163064
H	0.19	143491
I	0.22	96808

$$\log \eta_B = \sum_i w_i \log \eta_i \qquad (2)$$

where η_i and η_B are the viscosities of the *i*th component and the blend, respectively, and w_i is the weight fraction of the *i*th component.

The compatible blends lead to a positive deviation in the rheological properties, such as the viscosity, die swell, and so forth, and are termed PDBs.[37–39] It is therefore concluded that the blends of ENR–NR–cassava starch are compatible blends. However, there are arguments that blends of ENR and NR are incompat-ible.[40] In our previous work we also observed incompatibility for blends of ENR and NR.[20] However, if a third blend component (i.e., cassava starch powder) was incorporated, partly and fully compatible blends were found.

Figure 13 compares the shear viscosities at shear rates of 10, 25, 50, and 200 s^{-1}. According to the log additive rule, PDBs were again observed, particularly at a low shear rate. The results confirmed that the blends of ENR–NR–cassava starch were compatible. The positive deviation of the shear viscosity (Fig. 13) agrees with the plots of the consistency index (Fig. 12). We therefore concluded that the plots of the shear viscosity and zero shear viscosity for the ENR–NR–cassava starch blends could be applied to identify blend compatibility, as was observed for maleated NR–NR–cassava starch blends.[34]

CONCLUSIONS

We successfully prepared ENR-25 and ENR-45 by the performic epoxidation method. These ENRs were later blended with gelatinized cassava starch in the latex state. The shear properties of the blends were characterized at 125°C using a Rosand single-bore capillary rheometer. The pure ENR exhibited lower shear stress and shear viscosity than those of the blends. In addi-
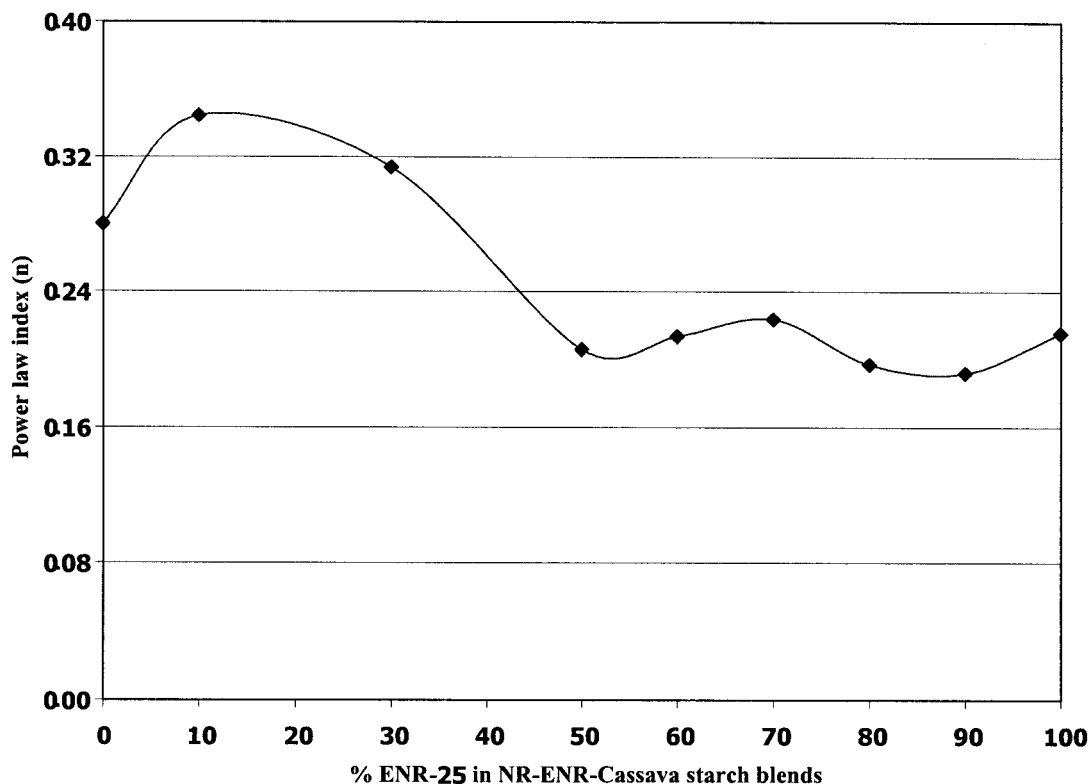

Figure 11 The power law index (*n*) for ENR-25 blended with NR at various blend ratios and at a cassava starch concentration of 50 phr.
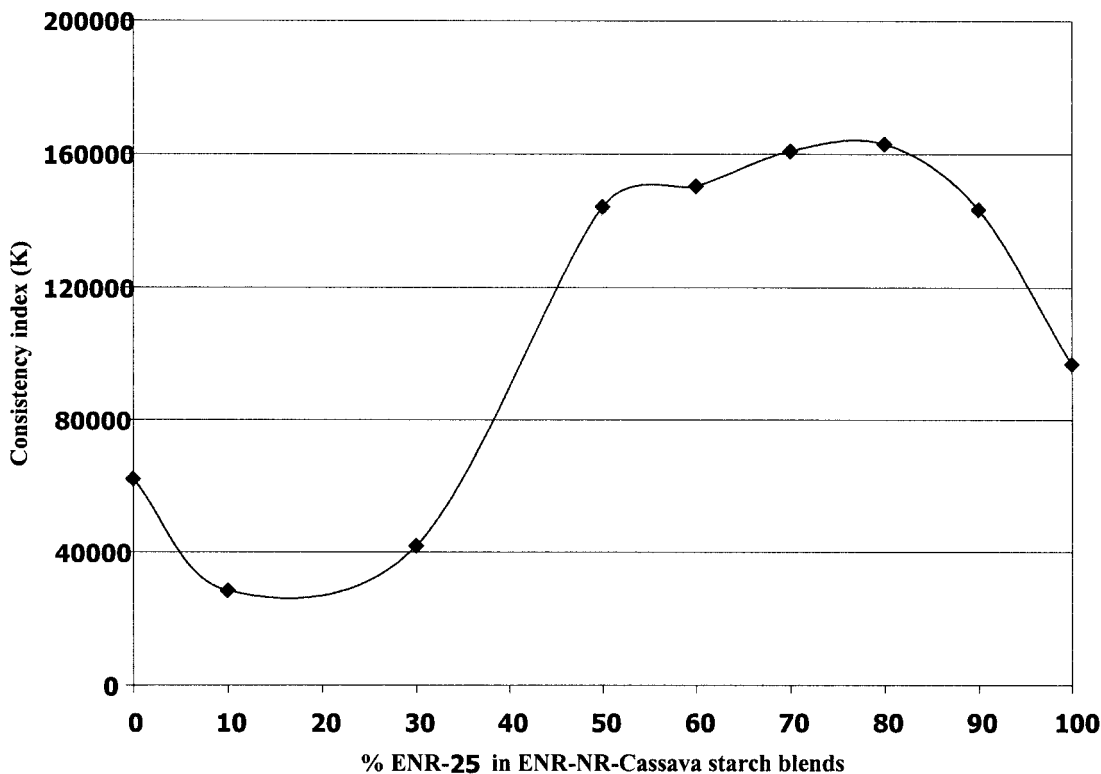
Figure 12 The consistency index (K) for ENR-25 blended with NR at various blend ratios and at a cassava starch concentration of 50 phr.

tion, the shear stress and shear viscosity increased with an increasing concentration of cassava starch in all sets of blends. The increase in shear stress and shear viscosity might be attributable to the chemical interaction between the epoxide group in the ENR and the hydroxyl group in the cassava starch molecules. We concluded from the existence of chemical bonding that the ENR–cassava starch blends are compatible
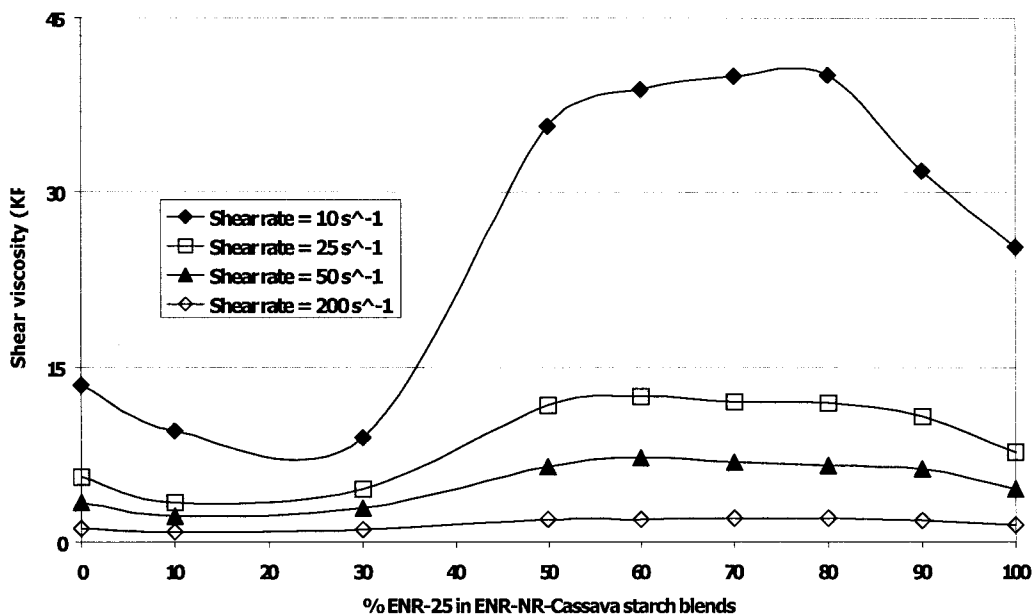

Figure 13 A comparison of the shear viscosity at apparent shear rates of 10, 25, 50, and 200 s^{-1} for ENR-25 blended with NR at various blend ratios and at acassava starch concentration of 50 phr.

blends, and SEM micrographs confirmed the observation. The ENR–NR–cassava starch blends were also prepared. We observed power law behavior for all sets of blends: the flows were pluglike flow profiles with very low n values (i.e., $n < 0.34$) and highly pseudoplastic fluid behavior. The log additive rule was applied to the plots of zero shear viscosity (consistency index, K) and shear viscosity versus the quantity of ENR-25 for the ENR–NR–cassava starch blends, and PDBs were observed. This indicates compatible ENR–NR–cassava starch blends.

References

1. Gelling, I. R. U.K. Pat. 2,113,692 A, 1982.
2. Johnson, T.; Thomas, S. Polymer 1999, 40, 3323.
3. Mohanty, S.; Nando, G. B. Polymer 1999, 38, 1359.
4. Bandyopadhyay, S.; De, P. P.; Tripathy, D. K.; De, S. K. Polymer 1995, 36, 1979.
5. Isamail, H.; Leong, H. C. Polym Test 1995, 20, 1979.
6. Ratnam, C. T.; Zaman, K. Polym Degrad Stab 1999, 65, 99.
7. Mousa, A.; Ishiaku, U. S.; Ishak, Z. A. M. J Appl Polym Sci 1999, 74, 2886.
8. Mousa, A.; Ishiaku, U. S.; Ishak, Z. A. M. Polym Test 2000, 19, 193.
9. Perera, M. C. S.; Ishiaku, U. S.; Ishak, Z. A. M. Polym Degrad Stab 2000, 68, 393.
10. Yamada, N.; Shoji, S.; Sasaki, H.; Nagatani, A.; Yamaguchi, K.; Kohjiya, S.; Huahim, A. S. J Appl Polym Sci 1999, 71, 855.
11. Cizravi, J. C.; Subramaniam, K. Polym Int 1999, 48, 889.
12. Ismail, H.; Chia, H. H. Polym Test 1998, 17, 199.
13. Manna, A. K.; Bhattacharyya, M.; De, P. P.; Tripthy, D. K.; De, S. K.; Peiffer, G. Polymer 1998, 39, 7113.
14. Poh, B. H.; Chen, B. F.; Ding, B. S. J Appl Polym Sci 1996, 60, 1569.
15. Manna, A. K.; De, P. P.; Tripthy, D. K.; De, S. K. J Appl Polym Sci 1998, 70, 723.
16. Roychoudhury, A.; De, P. P. Rubber Chem Technol 1993, 66, 230.
17. Manoi, N. R.; De, P. P.; De, S. K.; Pfeiffer, D. G. J Appl Polym Sci 1994, 53, 361.
18. Isamail, H.; Suzaimah, S. Polym Test 2000, 19, 879.
19. Isamail, H.; Hairunezam, H. M. Eur Polym J 2001, 37, 39.
20. Nakason, C.; Kaesaman, A.; Wongkul, T.; Kiatkamjonwong, S. Plast Rubber Compos 2001, 30, 154.
21. Nakason, C.; Kaesaman, A.; Homsin, S.; Kiatkamjonwong, S. J Appl Polym Sci 2001, 81, 2803.
22. Bikiaris, D.; Panayiotou, C. J Appl Polym Sci 1998, 70, 1503.
23. Bikiaris, D.; Prinos, J.; Koutsopoulos, K.; Vouroutzis, N.; Pavlidou, E.; Frangis, N.; Panayiotou, C. Polym Degrad Stab 1998, 59, 287.
24. Chandra, R.; Rustgi, R. Polym Degrad Stab 1997, 56, 185.
25. Zuchowska, D.; Steller, R.; Meissner, W. Polym Degrad Stab 1998, 60, 471.
26. Kang, B. G.; Yoon, S. H.; Lee, S. H.; Yie, J. E.; Yoon, B. S.; Suh, M. H. J Appl Polym Sci 1996, 60, 1839.
27. Vaidya, U. R.; Bhattacharya, M.; Ramkumar, D.; Hakkarainen, M.; Alberton, A. C.; Karlsson, S. Eur Polym J 1996, 32, 999.
28. Fanta, G. F. In Block and Graft Copolymers; Ceresa, R. J., Ed.; Wiley: New York, 1973; Vol. 1, p 1.
29. Otey, F. H.; Westhoff, R. P.; Doane, W. M. Ind Eng Chem Proc Res Dev 1980, 19, 592.
30. Bhattacharyya, M.; Vaiya, U. R.; Zhang, D.; Narayan, R. J Appl Polym Sci 1995, 57, 539.
31. Vaiya, U. R.; Bhattacharyya, M. J Appl Polym Sci 1994, 52, 617.
32. Nakason, C.; Kaesaman, A.; Eardrod, K.; Kiatkamjonwong, S. J Appl Polym Sci 2003, 89, 1453.
33. Nakason, C.; Sainamsai, W.; Kaesaman, A.; Klinpituksa, P.; Songklanakarin, J. Sci Technol 2001, 23, 415.
34. Nakason, C.; Kaesaman, A.; Samoh, Z.; Homsin, S.; Kiatkamjonwong, S. Polym Test 2002, 21, 449.
35. Han, C. D. Rheology in Polymer Processing; Academic: New York, 1976.
36. Ultracki, L. A. Polym Eng Sci 1982, 22, 96.
37. Kundu, P. P.; Tripathy, D. K. Polymer 1998, 39, 1869.
38. Kundu, P. P.; Tripathy, D. K.; Gupta, B. R. J Appl Polym Sci 1997, 63, 187.
39. Kundu, P. P.; Bhattacharya, A. K.; Tripathy, D. K. J Appl Polym Sci 1997, 63, 1759.
40. Ng, S. C.; Chee, K. K. Rubber Chem Technol 1988, 62, 585.