JOURNAL OF Applied Polymer SCIENCE

Influences of the phenolic curative content and blend proportions on the properties of dynamically vulcanized natural rubber/acrylonitrile-butadiene-styrene blends

Pinyo Wongthong,[1] Charoen Nakason,[2] Qinmin Pan,[3] Garry L. Rempel,[4] Suda Kiatkamjornwong[1,5,6]
[1]Program of Petrochemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
[2]Faculty of Science and Industrial Technology, Prince of Songkla University, Surat Thani Campus, Surat Thani 84000, Thailand
[3]Green Polymer and Catalysis Technology Laboratory, Soochow University, Suzhou 215123, People's Republic of China
[4]Department of Chemical Engineering, Faculty of Engineering, University of Waterloo, Ontario N2L3G1, Canada
[5]Department of Imaging and Printing Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
[6]Academy of Science, Royal Society of Thailand, Bangkok 10300, Thailand
Correspondence to: S. Kiatkamjornwong (E-mail: ksuda@chula.ac.th)

ABSTRACT: The vulcanization of natural rubber (NR)-blended acrylonitrile–butadiene–styrene (ABS) was carried out with a phenolic curing agent by a melt-mixing process. The NR compound was first prepared before blending with ABS. The effects of the phenolic curative contents (10, 15, and 20 phr) and blend proportions (NR/ABS ratio = 50 : 50, 60 : 40, and 70 : 30) on the mechanical, dynamic, thermal, and morphological properties of the vulcanized NR/ABS blends were investigated. The tensile strength and hardness of the blends increased with increasing ABS content, whereas the elongation at break decreased. The strength property resulting from the thermoplastic component and the vulcanized NR was an essential component for improving the elasticity of the blends. These blends showed a greater elastic response than the neat ABS. The thermal stability of the blends increased with increasing ABS component. Scanning electron micrographs of the blends showed a two-phase morphology system. The vulcanized 60 : 40 NR/ABS blend with 15-phr phenolic resin showed a uniform styrene-*co*-acrylonitrile phase dispersed in the vulcanized NR phase; it provided better dispersion between the NR and ABS phases, and this resulted in superior elastic properties. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42520.

KEYWORDS: blends; elastomers; mechanical properties; morphology; thermoplastics

Received 23 June 2014; accepted 19 May 2015
DOI: 10.1002/app.42520

INTRODUCTION

The blending of a thermoplastic polymer with an elastomeric polymer to provide new polymeric materials called *thermoplastic elastomers* has created research and industrial topics of considerable interest for many years. The blended product is a valuable material in the polymer industry because it combines the excellent processing characteristics of thermoplastics and the outstanding elastic properties of rubbers. A number of reports have been published on rubber/thermoplastic blends made with either simple blending[1–4] or dynamic vulcanization.[5–22] It has been established that thermoplastic vulcanizates obtained by dynamic vulcanization can show improved mechanical and thermal properties; these are attributed to the unique morphology, in which small and uniform crosslinked rubber particles are finely dispersed in the thermoplastic matrix. Various parameters that influence the morphology of thermoplastic vulcanizates include the vulcanization system,[8–10] compatibilization,[6,8,13] and mixing conditions.[14] Among these, the curative content is one of the most important parameters. However, few articles have reported on the effects of the curative content on the mechanical and morphological properties of these blends.[12,15]

Several crosslinking agents, such as sulfur,[8–10,22] peroxide,[8–10,14,20,21] and mixed sulfur–peroxide[8–10] curing systems, have been normally used to crosslink the rubber phase of rubber/thermoplastic blends. However, thermoplastic vulcanizates containing a sulfur curing agent always give an unpleasant strong odor during the fabrication process. The disadvantage of a peroxide curing system is its tendency to induce a blooming effect and decompose into smelly byproducts. In addition, undesired side reactions, such as disproportionation and chain scission, also occur during the mixing process.[9,14] To overcome these disadvantages, a phenolic curing system has been used. It has been

Table I. Formulations and Mixing Schedule Used for the NR Compound

Ingredient	Quantity (phr)			Mixing time (min)	Cumulative mixing time (min)
	Condition 1	Condition 2	Condition 3		
NR	100	100	100	3	3
Zinc oxide	5	5	5	1	4
Stearic acid	1	1	1	1	5
TMQ	1	1	1	1	6
$SnCl_2{\cdot}2H_2O$	3	3	3	1	7
HRJ-10518	10	15	20	3	10

reported that the phenolic curing agent can overcome the degradation of thermoplastics and the unpleasant smell of the finished products.[10,12]

Synthetic rubbers, such as ethylene–propylene–diene monomer rubber and nitrile–butadiene (BD) rubber, have been reported for blending with thermoplastics and improving the mechanical properties of the blends.[13,15,16] However, these synthetic rubbers are derived from petroleum-based materials, which not only are non-renewable materials but will also be a finite resource in the future. Natural rubber (NR) is an environmentally friendly rubber, and it is derived from a renewable resource. With growing environmental concerns, NR as a green polymer is therefore an interesting material to replace petroleum-based polymers. Because of the excellent elasticity and mechanical properties of NR, it has been widely used for blending with various thermoplastics such as poly(methyl methacrylate),[4] polypropylene (PP),[14] high-density polyethylene (HDPE),[8,12] and nylon 12.[11] Acrylonitrile–butadiene–styrene (ABS) is one of the most important engineering thermoplastic materials. ABS is an interesting polymer for blending with NR because of the superior properties of both constituents. ABS gives high impact strength, chemical resistance, and easy processing characteristics whereas NR provides the outstanding elasticity and mechanical properties. Recently, the use of NR and polystyrene grafted NR as modifiers in ABS has been carried out using a simple blend and it has been reported that the strength properties and thermal stability of the blends were improved.[23] Several reports have described the vulcanization of nitrile–BD rubber/ABS blends and it has been found that superior mechanical properties were obtained.[5,17,18] Studies of mechanical properties of vulcanized NR/ABS blends have also been established.[5] However, the influences of curative content and blend proportions on morphological and the related properties of the vulcanized NR/ABS blends have not as yet been reported in literature.

In this work, vulcanization of NR/ABS blends using a phenolic curing agent by a melt mixing process was carried out. The concentration effect of the phenolic resin on curing characteristics of NR vulcanizates, mechanical and morphological properties of the vulcanized NR/ABS blends was investigated. In addition, the effect of the NR/ABS blend proportions on mechanical, dynamic, thermal and morphological properties of the vulcanized NR/ABS blends was elucidated.

EXPERIMENTAL

Materials

NR (STR 5L) was provided by Yala Latex Industry Co., Ltd. (Thailand). ABS copolymer (SP200) was manufactured by IRPC Public Co., Ltd. (Rayong, Thailand). ABS, with a weight ratio of acrylonitrile (ACN)/BD/styrene (ST) of 24 : 19 : 57, was injection-molding grade with a melt flow index of 17 g/10 min (10-kg loads at 220°C). Hydroxymethylol phenolic resin (HRJ-10518) was manufactured by Schenectady International, Inc. (New York). It contained 6–9% active hydroxymethyl (methylol) groups. Stannous chloride ($SnCl_2{\cdot}2H_2O$) was purchased from Qrec (New Zealand). Stearic acid and zinc oxide were purchased from Loba Chemie (India). 2,2,4-Trimethyl-1,2-dihydroquinoline (TMQ) was provided by Topflight Co., Ltd. (Thailand). Tetrahydrofuran (THF) was manufactured by Labscan (Ireland).

Preparation of the NR Compound and Vulcanized NR/ABS Blends

The NR compound was prepared first before the blending with ABS. The mixing was carried out with an internal mixer (Brabender GmbH & Co. KG, Duisburg, Germany). The capacity of the mixing chamber was 50 cm^3. Mixing was carried out at 50°C with a rotor speed of 60 rpm. The formulations and mixing schedule used for compounding NR at various concentrations of the phenolic resin are shown in Table I. NR was first introduced into the mixing chamber and the other chemical ingredients were then sequentially added. After the mixture was dumped from the mixing chamber, the NR compound was sheeted out with a laboratory mill and left at room temperature for at least 12 h before the blending with ABS. The vulcanization of the NR/ABS blends was carried out with the same internal mixer at 180°C with a rotor speed of 60 rpm. ABS was dried in a hot-air oven at 80°C for at least 5 h. Dried ABS was first mixed in the mixing chamber for 2 min, and this was followed by the mixture of the NR compound. Mixing was further continued for 4 min until a torque plateau was obtained.

Testing and Characterization

The curing characteristics of the NR vulcanizates were characterized with an oscillating disk rheometer (ODR2000, Monsanto) at 180°C for 30 min. The minimum torque (M_L), maximum torque (M_H), scorch time (T_{S1}), and optimum curing time (T_{C90}) were measured on the basis of the curing curve. The curing rate index (CRI) was defined as follows:

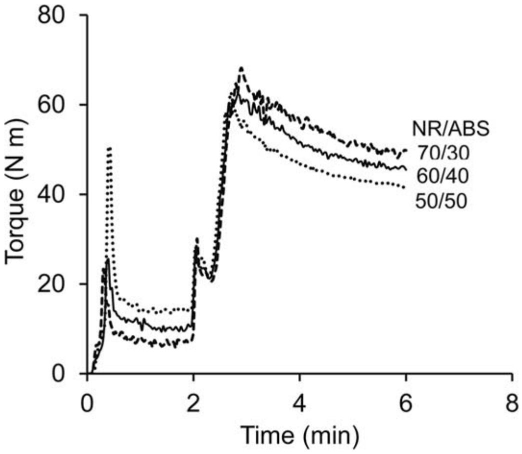

Figure 1. Torque–time curves of the vulcanized NR/ABS blends at blend ratios of 50 : 50, 60 : 40, and 70 : 30 with the NR compound with 15-phr HRJ-10518 at a mixing temperature of 180°C.

$$\mathrm{CRI}=\frac{100}{T_{C90}-T_{S1}} \quad (1)$$

Thin sheets 2 mm thick of the samples for mechanical testing were prepared by compression molding at 180°C for 5 min. The dumbbell-shaped specimens were prepared by the cutting of the molded sheet with a die C, according to ASTM D 412. Tensile testing was performed with a Hounsfield tensometer (H10KS, Hounsfield Test Equipment, United Kingdom) at a crosshead speed of 500 mm/min according to ISO 37. The hardness of the samples was measured with a Shore A durometer according to ASTM D 2240. The Izod impact strength was measured according to ASTM D 256 with a pendulum impact tester (Resil Impactor 21130, Italy). Five specimens of each sample were tested, and the average values plus or minus the standard deviation were reported.

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 6700 spectrometer with a resolution of 4.0 cm^{-1} and 32 scans.

The dynamic properties were investigated with a moving die processability tester (RheoTech MDPT, Tech-Pro, Inc.). The experiment was carried out with a frequency sweep mode at a constant strain of 3% at 180°C.

Thermogravimetric analysis (TGA) was performed on a PerkinElmer STA600 (PerkinElmer, Inc.) at a heating rate of 20°C/min under a nitrogen atmosphere and with a temperature scan range of 30–800°C.

The morphology was investigated via scanning electron microscopy (SEM; JSM-5800 LV, Japan). Molded samples of the blends

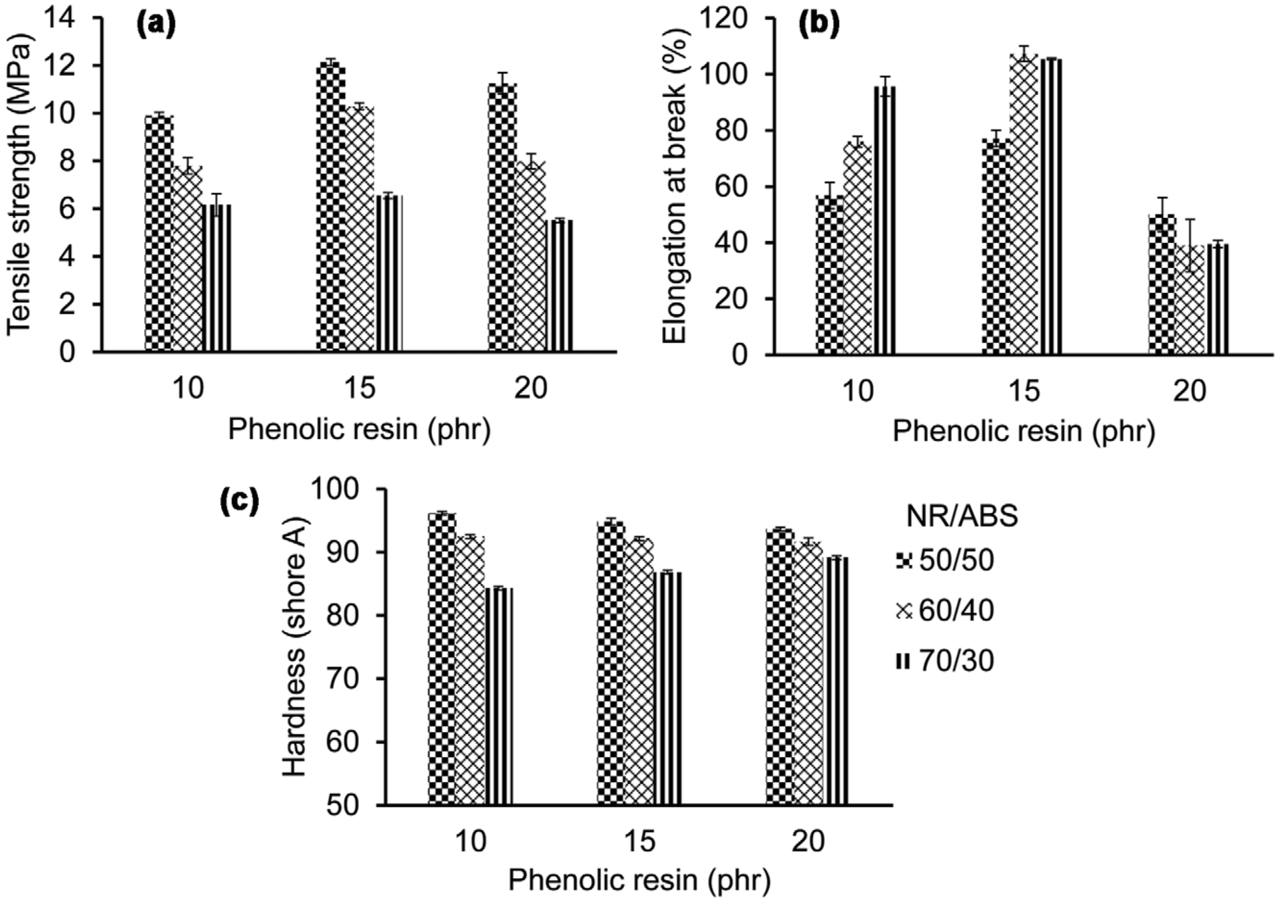

Figure 2. Effect of the phenolic curative content on the mechanical properties of the vulcanized NR/ABS blends at blend ratios of 50 : 50, 60 : 40, and 70 : 30 with the NR compound with 10-, 15-, and 20-phr HRJ-10518 at a mixing temperature of 180°C: (a) tensile strength, (b) elongation at break, and (c) hardness.

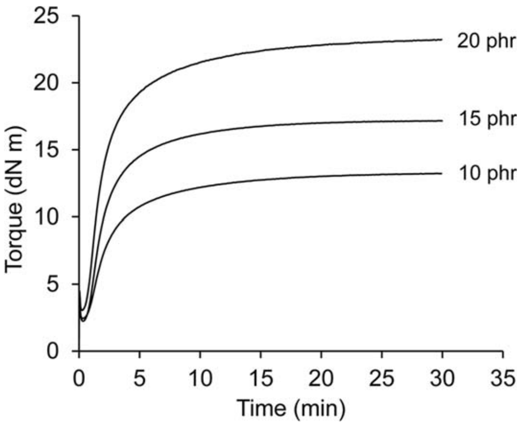

Figure 3. Curing curves of the vulcanization of NR with various phenolic curative contents of 10-, 15-, and 20-phr HRJ-10518 at a curing temperature of 180°C.

were cryogenically cracked in liquid nitrogen to prevent any possibility of phase deformation. The styrene-*co*-acrylonitrile (SAN) phase in ABS was extracted from the blended product with hot THF for 15 min and dried in a vacuum oven at 50°C.[24] The dried samples were later sputter-coated with gold for SEM investigation.

RESULTS AND DISCUSSION

Mixing Torque of the Vulcanized NR/ABS Blends

Torque–time curves of the vulcanized NR/ABS blends at three ratios of 50 : 50, 60 : 40, and 70 : 30 with NR compound with 15-phr HRJ-10518 are shown in Figure 1. In the early stage (before 2 min of ABS processing), the mixing torque rose sharply when the rotor started to work because of the resistance exerted on the rotor by the unmolten ABS. At this stage, the mixing torque increased with increasing content of ABS. This was attributed to the high loading of hard material (ABS), which provided a higher resistance exerted on the rotor and, therefore, resulted in a higher mixing torque. A decrease in torque was later observed because ABS was molten as a result of mechanical shear. When the NR compound was introduced, the mixing torque rose sharply again; this was caused by the resistance of unmolten components and, thereafter, the mixing torque decreased. Then, the mixing torque rose dramatically again because of vulcanization during the melt-mixing process. Mixing was continued further until a torque plateau was obtained. We found that the levels of the final mixing torque increased with increasing content of the NR compound. The 70 : 30 NR/ABS blend gave the highest final mixing torque. This was attributed to the influence of the higher viscosity of the vulcanized NR compared to that of neat ABS. At a higher proportion of NR, a crosslinking reaction of the rubber with the curing agent was more pronounced; this might have been another reason for the increasing trend of the mixing torque.

Effect of the Phenolic Curative Content on the Properties of the Vulcanized NR/ABS Blends

Mechanical Properties. The effect of the phenolic curative content over the range of 10–20 phr HRJ-10518 on the mechanical properties of the NR/ABS vulcanizates at three blend ratios of 50 : 50, 60 : 40, and 70 : 30 is shown in Figure 2. At a given blend proportion, the tensile strength and elongation at break of the blends increased with increasing concentration of phenolic resin up to 15 phr and decreased thereafter. This was attributed to the influence of vulcanization via the phenolic curative molecules, which thereafter resulted in stronger materials. At a given phenolic resin concentration, the hardness of the blends decreased with increasing NR ratio of the blends. This was due to an increase in the NR portion as the soft phase of the blends. However, at a given blend proportion, there was little difference in the hardness between these materials; this indicated that the loading level of the phenolic curative did not play a significant role in the magnitude of the hardness.

To achieve a better understanding of the chemical reaction involved with the vulcanization of NR/ABS blends with phenolic resin, it was essential to know the vulcanization characteristics of the pure NR compounds without any ABS. The curing curves for the vulcanization of NR with various amounts of phenolic resin are shown in Figure 3, and the results are summarized in Table II. M_L is a measure of the stiffness of the nonvulcanized rubber through measurement of the lowest point of the curing curve, whereas M_H is a measure of the stiffness of the fully vulcanized NR at the vulcanization temperature. We found that M_H increased with increasing loading of the phenolic resin. The change in torque ($M_H - M_L$) correlated with the crosslinking efficiency of the curing agent. An increase in $M_H - M_L$ with increasing levels of the phenolic curative was observed. Therefore, the NR compound with 20-phr HRJ-10518 gave the highest value of M_H and $M_H - M_L$. This indicated that the crosslinking density was more pronounced at high concentrations of curing agent. This could be explained by the vulcanization reaction in that the crosslinking reaction occurred through the reactive functional groups of the phenolic resin (i.e., methylol and hydroxyl groups) with the unsaturation in the NR molecules to form the Chroman ring structure,[8] as shown in Figure 4(a). The results obtained indicate that increasing the phenolic concentration allowed more methylol and hydroxyl groups to be available for the reaction; this basically led to a higher extent of crosslinking sites in the NR phase. Decreases in T_{S1} with increasing curing loadings could also be

Table II. Curing Characteristics of NR Vulcanizates at Three Concentrations of the Phenolic Curing Agent

Phenolic resin (phr)	M_L (dN m)	M_H (dN m)	$M_H - M_L$ (dN m)	T_{S1} (min)	T_{C90} (min)	CRI (min^{-1})
10	2.45	13.23	10.78	0.57	9.45	11.26
15	2.25	17.16	14.91	0.49	7.42	14.43
20	3.10	23.22	20.12	0.40	8.55	12.27

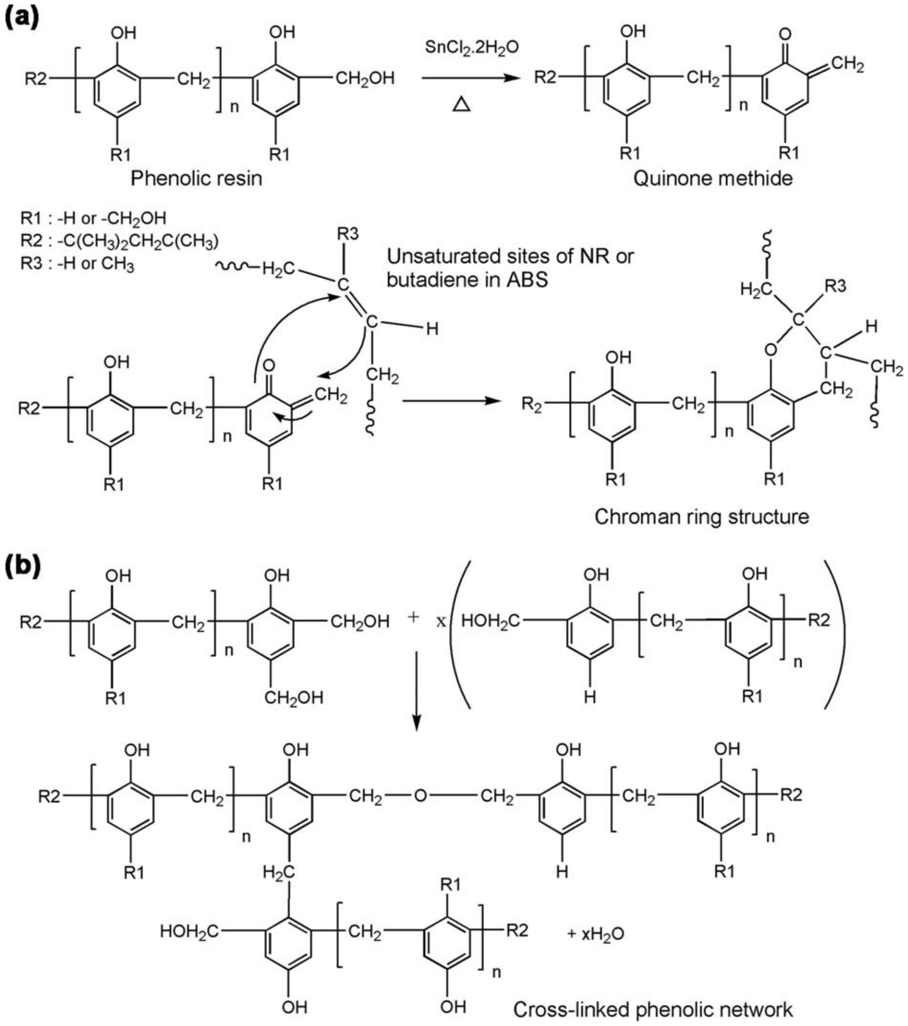

Figure 4. Schematic representations of the proposed (a) crosslinking reaction of NR or BD in ABS with a phenolic resin in the presence of $SnCl_2{\cdot}2H_2O$ and (b) polycondensation reaction of phenolic resin to form a crosslinked phenolic network.

explained by similar reasons. These results were in good agreement with results previously reported in literature.[12,25] CRI is basically a measure of the rate of vulcanization. Among various phenolic curative contents, the amount of 15-phr gave a short T_{S1} and curing time; that is, the highest CRI was obtained.

As shown in Figure 2, the improved tensile strength and elongation at break of the vulcanized NR/ABS blends at higher levels of phenolic curative (i.e., 15-phr HRJ-10518) for a given blend ratio were consistent with the δ torque ($M_H - M_L$) of NR vulcanizates. The higher $M_H - M_L$ generated by the crosslinking reaction through the reactive functional groups of phenolic resin with the double bonds presented in the NR chains, as previously discussed, contributed to the improvement of the mechanical properties of the blends. Similar behavior was observed for vulcanized NR/high-density polyethylene[12] and maleated ethylene propylene rubber/PP[25] blends. It was found that the increased crosslinking density at higher curing loadings resulted in improved tensile strengths and elongations at break of the blends. However, in this study, when the concentration of phenolic resin was greater than 15 phr, a decrease in the mechanical properties of the blends was observed. At a very high loading of 20-phr HRJ-10518, a high curing reaction occurred. In addition, phenolic resins can also self-condense on heating (180°C) to form a crosslinked phenolic network by a polycondensation reaction [Figure 4(b)]. In these crosslinked phenolic polymers, the clusters linked by methylene and dimethylene ether bridges were a hard substance embedded in the blended product; this caused the vulcanized NR/ABS products to become brittle (i.e., to have a low elasticity). As a result, the lowest elongation at break of the blends at three NR/ABS ratios of 50 : 50, 60 : 40, and 70 : 30 was observed when we used the NR compound with 20-phr HRJ-10518. Thus, the NR compound with 15-phr HRJ-10518 was appropriate for blending with ABS. We inevitably observed that the mechanical properties of the blends were influenced by the phenolic curative content. The ABS in this study consisted of three components, ACN, BD, and ST, with a weight ratio of 24 : 19 : 57. During the vulcanization process, the reactive functional groups of the phenolic resin could also interact with the remaining double bonds of 2,3-polybutadiene in the virgin ABS [Figure 4(a)].

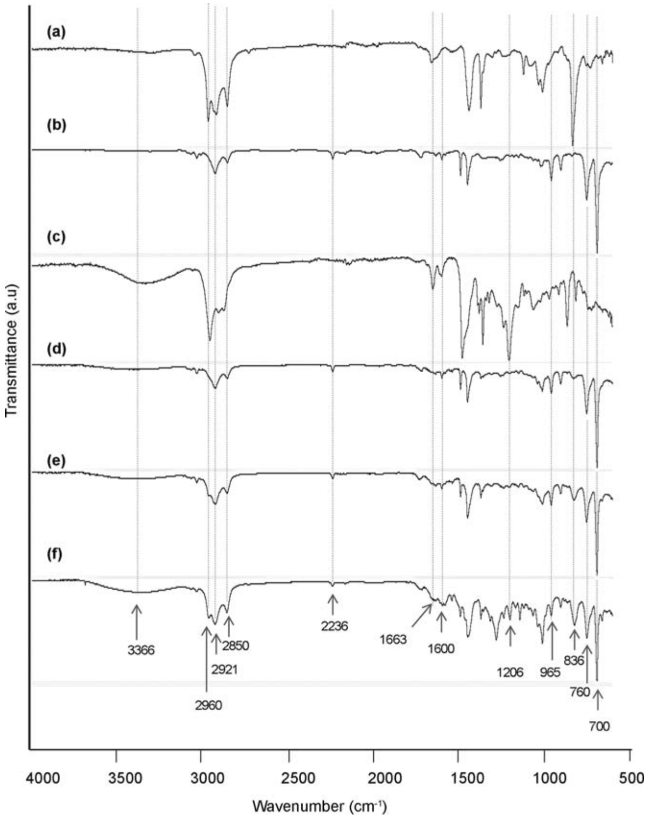

Figure 5. FTIR spectra of (a) NR, (b) ABS, (c) phenolic resin (HRJ-10518), and (d–f) vulcanized NR/ABS blends at ratios of 50 : 50, 60 : 40, and 70 : 30, respectively (all of the blends used an NR compound with 15-phr HRJ-10518 at a mixing temperature of 180°C).

However, for a given blend proportion, the number of unsaturated sites in ABS was much smaller than that within NR. For example, the 70 : 30 NR/ABS blend was composed of 70 wt % NR and 5.7 wt % BD. Thus, the possibility of chemical interaction between the functional groups of the phenolic resin and the double bonds of polybutadiene in ABS was less than that in NR; this suggested that the vulcanization reaction occurs mainly in the NR phase. Therefore, the crosslinking mostly took place in the NR phase. We concluded that the mechanical properties of the blends were influenced by the phenolic resin through the crosslinking reactions, not only by the chemical interactions of the methylol and hydroxyl groups of the phenolic resin with the double bonds in NR (the major component) but also with the remaining double bonds of polybutadiene in the ABS (the minor component). This accounted for the elasticity (elongation) of the vulcanized NR/ABS blends.

FTIR analysis was used to indicate the crosslinking reactions of the blends, as shown in Figure 5. The FTIR spectra of the vulcanized NR/ABS blends showed the combination of NR and ABS absorption peaks and the characteristic absorption peaks relating to phenolic molecules. The peaks for NR appeared at 3026 cm^{-1} (olefinic C—H stretching), 2960–2850 cm^{-1} (aliphatic C—H stretching), 1663 cm^{-1} (C═C stretching), and 836 cm^{-1} (═C—H deformation). The characteristic peaks for ABS appeared at 2236 cm^{-1} (—C≡N stretching of ACN), 1660 and 1600 cm^{-1} (—C═C stretching of ST), 965 cm^{-1} (—C═C stretching of BD), and 760 and 700 cm^{-1} (C—H out-of-plane of polystyrene or monosubstituted benzene; ST). The important characteristic peaks for phenolic molecules appeared at 3366 cm^{-1} (hydrogen bonding of phenol), 1660 and 1600 cm^{-1} (—C═C stretching of aromatic rings of phenol), and 1206 cm^{-1} (—C—O stretching of aromatic rings of phenol).[8] We observed that a small peak at 1663 cm^{-1} was observed for the NR/ABS vulcanizates; this indicated that the unsaturation in the NR molecules were transformed to the saturated NR by the crosslinking reactions. Table III shows the peak height ratios of the IR peaks of the NR, ABS, and NR/ABS vulcanizates. The ACN/NR, BD/NR, and ST/NR ratios of the blends increased with increasing ABS content. The blends with a high proportion of NR, especially the 70 : 30 NR/ABS blend, showed a low peak intensity of BD at 965 cm^{-1}. In addition, the ST/BD ratio of the blends was higher than that of the neat ABS, and it increased with increasing the content of the NR compound. The results indicate that the vulcanization reactions also occurred at the double bonds of polybutadiene in the ABS. The solubility parameter, normally composed of the respective dispersion contribution (δ_d), polar contribution (δ_p), and hydrogen-bonding contribution (δ_h), to make up an overall or total solubility parameter (δ_t). On the basis of the solubility parameters of NR (δ_d, δ_p, and $\delta_h = 16.0$, 4.0, and 6.0 MPa$^{1/2}$, respectively, to give $\delta_t = 17.6$ MPa$^{1/2}$), ABS (δ_d, δ_p, and $\delta_h = 17.6$, 8.6 and 6.4 MPa$^{1/2}$, respectively, to give a $\delta_t = 20.6$ MPa$^{1/2}$), and phenolic resin (δ_d, δ_p, and $\delta_h = 19.8$, 7.2, and 10.8 MPa$^{1/2}$, respectively, to give a $\delta_t = 23.7$ MPa$^{1/2}$).[26,27] The solubility parameter of the phenolic resin was rather close to that of ABS; this indicated that the phenolic resin had a greater affinity to the ABS phase. Thus, BD in the ABS phase was also vulcanized.

Morphological Properties. The morphology of the blends was investigated by SEM, as shown in Figure 6. An NR/ABS blend ratio of 60 : 40 was selected to study the effect of the phenolic curative at different contents of 10-, 15-, and 20-phr HRJ-10518. The SAN phase in ABS was preferentially extracted from the blended products with THF.[24] The SAN phase was etched from the sample surfaces, whereas the vulcanized NR remained undissolved. SEM micrographs of the blends showed a two-phase morphology system (i.e., vulcanized rubber phase and thermoplastic phase). The SAN particles were dispersed in the vulcanized NR matrix for all of the vulcanized NR/ABS blends under study. This was an unexpected result. It has been well established that dynamic vulcanization typically causes the formation of dispersed vulcanized rubber domains in the thermoplastic matrix.[7,12,14,16] However, in our blends, the vulcanized rubber phase was not dispersed particles but a continuous structure; this deviated from the traditional concept of thermoplastic vulcanizates by dynamic vulcanization. This unexpected result might have been due to the complex viscosity of ABS being lower than that of NR at the blending temperature [180°C; see the Dynamic Properties section and Figure 9(c) (shown later)]. The low viscosity of the ABS matrix facilitated the coalescence of the droplets of the NR dispersed phase when

Table III. Peak Heights and Peak Height Ratios of the IR Peaks Obtained from the FTIR Spectra of NR, ABS, and NR/ABS Vulcanizates

Sample	Peak height				Peak height ratio			
	ACN[a]	BD[b]	ST[c]	NR[d]	ACN/NR	BD/NR	ST/NR	ST/BD
NR	—	—	—	69.02	—	—	—	—
ABS[e]	6.20	17.98	80.17	—	—	—	—	4.46
NR/ABS vulcanizates[f]								
50 : 50	5.15	14.98	67.56	4.14	1.24	3.62	16.34	4.51
60 : 40	4.72	13.57	64.25	11.27	0.42	1.20	5.70	4.74
70 : 30	3.33	10.02	58.63	20.42	0.16	0.49	2.87	5.85

[a] Peak height of the ACN group of ABS at 2236 cm^{-1}.
[b] Peak height of the BD group of ABS at 965 cm^{-1}.
[c] Peak height of the ST group of ABS at 700 cm^{-1}.
[d] Peak height of NR at 836 cm^{-1}.
[e] The ACN/BD/ST weight ratio was 24 : 19 : 57.
[f] Vulcanized NR/ABS blends with the NR compound with 15-phr HRJ-10518.

the contact time required for drop coalescence was lower. This might have been due to the fact that when the rubber-melt strength was much higher than that of ABS, the ABS continuous phase with a much lower viscosity may have served as a lubricated phase to help the rotor slip smoothly between the vulcanized NR domains and later formed a crosslinked continuous NR structure. In addition, the high complex viscosity of the vulcanized NR caused the rubber to not elongate and break down into droplets of rubber particles dispersed in the thermoplastic matrix. This was similar to the morphology of the vulcanized polylactide/NR blends.[20,21] We found that the phase morphology of the blends was the droplets of the polylactide domain dispersed in the crosslinked NR phase matrix. Furthermore, the cured rubber-rich 60 : 40 NR/ABS was used in this study. Also, the contents of ACN, BD, and ST in ABS were 24, 19, and 57 wt %, respectively. Therefore, the total content of the rubber phase available for phenolic vulcanization was 67.6 wt %. This might have been one reason for the rubber component becoming the major phase with the dispersed domains of the thermoplastic being mainly the ST and ACN components. A plan to reduce the amount of NR content will be carried out in the future.

During the melt-blending process, the BD component in ABS was simultaneously vulcanized with the NR component and SAN could elongate its molecular chains to give small droplets dispersed in the vulcanized rubber of NR and BD at each blend condition. Figure 7 shows the postulated morphology of the blends. The SAN block formed separate spherical regions, that is, domains dispersed in the continuous vulcanized rubber NR phase, which acted as if it were the matrix. The domains were hard and acted as physical crosslinks in the vulcanized NR. In other words, the vulcanized BD of ABS was in the same phase with NR, whereas SAN was dispersed in the thermoset elastomer of NR. This was similar to the morphology of the styrenic block copolymers.[28] These immiscible vulcanized NR/ABS blends might have been caused by the difference in the molecular weights of NR ($\sim10^6$ g/mol) and ABS ($\sim10^5$ g/mol). An increase in the molecular weight during the curing at a high reaction temperature may have been another reason for the phase separation of the vulcanized NR/ABS blends, that is, reaction-induced phase separation. Among the three conditions, a large amount of the small size, uniformly distributed ABS (SAN) domains were observed for the blend with 15-phr HRJ-10518. On the other hand, nonuniformly vulcanized NR and ABS phases with some irregular structures were observed for the blends with 10- and 20-phr HRJ-10518. These morphologies of the vulcanized NR/ABS blends were consistent with the mechanical properties of the blends, in that the blends with 15-phr HRJ-10518 exhibited a higher tensile strength and elongation at break than those of the blends with 10- and 20-phr HRJ-10518. This change in the mechanical properties of the blends could be related to a result of the morphological changes.[12,15] The well-balanced mechanical properties of the blends with 15-phr HRJ-10518 were attributed to the uniformly crosslinked rubber and plastic phases, which gave a better dispersion between the two phases and thus provided superior mixing properties. Unfortunately, the coalescence of the ABS domains dispersed in the NR matrix was obtained at 20-phr HRJ-10518. The larger dispersed ABS domains with lower interfacial areas gave a poorer dispersion of the vulcanized NR and ABS phases and resulted in a lower mechanical strength. The nonuniformly vulcanized NR and ABS phases might have been caused by different rates of the vulcanization reaction. An increase in the amount of the phenolic curative in the rubber compound caused increasing torque of the curing curves (see Figure 3). Thus, the viscosity of the rubber compound during vulcanization with ABS was also increased. Inevitably, under these conditions, the ABS particles elongated to become coalesced, dispersed domains; this resulted in poorer mechanical properties of the blends with 20-phr HRJ-10518. SEM analysis supported that the mechanical and morphological properties of the vulcanized NR/ABS blends were influenced by the phenolic curative content.

Effects of the Blend Proportions on the Properties of the Vulcanized NR/ABS Blends

Mechanical Properties. Table IV presents the mechanical properties of the neat ABS, vulcanized NR, and vulcanized NR/ABS blends at three blend ratios of 50 : 50, 60 : 40, and 70 : 30. The

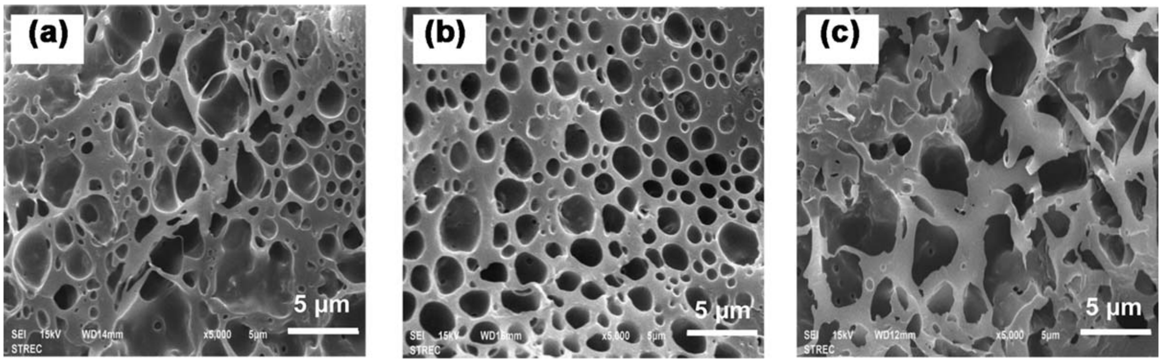

Figure 6. SEM micrographs of the etched, fractured surfaces of the vulcanized NR/ABS blends with various amounts of phenolic resin [(a) 10-, (b) 15-, and (c) 20-phr HRJ-10518] with a fixed 60 : 40 NR/ABS ratio at a mixing temperature of 180°C.

NR compound with 15-phr HRJ-10518 was selected to blend with ABS. We observed that the vulcanized NR had excellent elasticity, whereas the neat ABS provided good tensile strength, hardness, and impact strength but poor elongation. ABS was synthesized by the graft copolymerization of ST and ACN monomers onto polybutadiene. The rubber particles were grafted with SAN, and thus, the properties of ABS depended on the compositions of its constituents. In this study, ABS contained an ACN/BD/ST weight ratio of 24 : 19 : 57. Polystyrene gave the strength and rigidity, whereas the polybutadiene provided the toughness and impact strength. The polar nitrile groups from neighboring chains could attract each other and bind the chains together; this made ABS stronger than pure polystyrene. As shown in Table IV, ABS showed excellent strength and hardness properties and was, thus, a favorable polymer for blending with NR to improve the elongation of the ABS thermoplastic. The results show that the tensile strength and hardness properties of the vulcanized NR/ABS blends increased with increasing ABS content. That is, the strength and hardness of the blends were controlled by the thermoplastic component. On the other hand, the elongation of the blends increased with increasing rubber content and indicated that the vulcanized NR was an essential component for improving the elasticity of the blends. We found that the vulcanized NR exhibited a higher tensile strength than the vulcanized NR/ABS blends because the former was fully crosslinked, whereas the latter was crosslinked only in the NR part. Furthermore, the higher impact strength of the vulcanized 60 : 40 NR/ABS blend compared with that of the vulcanized 50 : 50 NR/ABS blend was obtained. However, the vulcanized 70 : 30 NR/ABS blend was very flexible (unbreakable), and therefore, we could not determine its impact strength. The vulcanized 60 : 40 NR/ABS blend showed well-balanced mechanical properties. These mechanical properties were consistent with the morphology of the blends by SEM analysis; this is discussed in the next section. The obtained results demonstrate that vulcanization of the NR/ABS blends with the phenolic curing agent could provide a new material with superior mechanical properties. These products could be used in protective bumper applications and other appliances where a high impact strength and elasticity are required. It should be noted that the blended product with a high NR content (i.e., 70 : 30 NR/ABS vulcanizate) can be used in the area of soft-touch applications, such as cases for mobile phones.

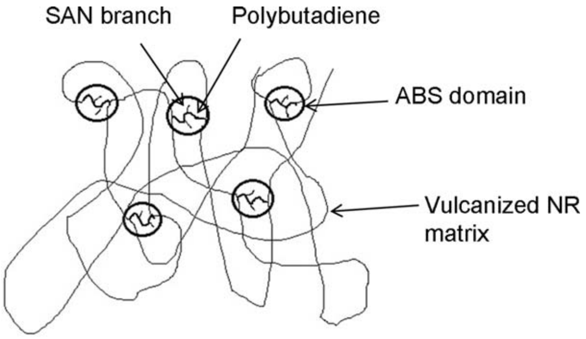

Figure 7. Postulated morphology of the vulcanized NR/ABS blends.

It should be noted that the reasons that the phenolic curing system is used to crosslink the rubber phase of the NR/ABS blends were not only to obtain the superior mechanical properties of the blends but also to overcome the unpleasant odor of the finished products and thermoplastic degradation (i.e., resulting from the sulfur and peroxide curing systems). The results were consistent with those reported previously.[10] We found that the vulcanized epoxidized natural rubber/PP blends with the phenolic curing system exhibited higher mechanical properties than those of the blends obtained by sulfur, peroxide, and mixed sulfur–peroxide curing systems. The phenolic curing system resulted in the absence of PP degradation and, therefore, provided superior properties of the blends.[10]

Morphological Properties. The effects of various NR/ABS ratios of 50 : 50, 60 : 40, and 70 : 30 on the morphology of the blends with NR compound with 15-phr HRJ-10518 were investigated. The etched, fractured surfaces of the vulcanized NR/ABS blends at three blend ratios showed a two-phase morphology system, as presented in Figure 8. Among the three conditions, the finer SAN phases with smaller cavity sizes were observed for the vulcanized 60 : 40 NR/ABS blend. Moreover, the ABS particle size seemed more uniform at a ratio of 60 : 40. Smaller SAN particles provided higher surface areas to promote the dispersion between the NR and ABS phases and, therefore, resulted in superior mixing properties. The nonuniformly vulcanized NR and ABS phases and some irregular structures were observed at a high proportion of NR (i.e., 70 : 30 NR/ABS); presumably, this was due to the incompatibility and partial immiscibility

Table IV. Mechanical Properties of the Neat ABS, Vulcanized NR, and NR/ABS Vulcanizates

Sample	Tensile strength (MPa)	Elongation at break (%)	Hardness (Shore A)	Impact strength (J/m)
ABS[a]	35.0 ± 0.5	25.7 ± 1.5	96.3 ± 0.3	379.8 ± 2.4[c]
Vulcanized NR	16.4 ± 0.8	570.0 ± 9.8	38.3 ± 0.5	—
NR/ABS vulcanizates[b]				
50 : 50	12.1 ± 0.3	77.2 ± 1.9	94.8 ± 0.3	245.9 ± 2.8[d]
60 : 40	10.3 ± 0.2	107.3 ± 2.7	92.2 ± 0.3	313.8 ± 6.7[d]
70 : 30	6.5 ± 0.3	105.4 ± 9.3	86.6 ± 0.6	VF[e]

[a] The ACN/BD/ST weight ratio was 24 : 19 : 57.

[b] Vulcanized NR/ABS blends with the NR compound with 15-phr HRJ-10518.

[c] The failure type was a complete break.

[d] The failure type was a partial break.

[e] Very flexible and unbreakable.

between the two components of rubber and thermoplastic.[23] Also, increasing the rubber proportion in the vulcanized NR/ABS blends caused coalescence of the ABS and vulcanized NR phases. Larger size of the dispersed SAN domains having lower surface areas provided poorer dispersion of the vulcanized NR and ABS phases and resulted in a lower mechanical strength. It was clear that the morphology of the blends was related to the mechanical properties. The results show that the phase morphology of the vulcanized NR/ABS blends was dependent on the blend ratio; this was similar to results previously reported in literature.[8,19] On the basis of the results obtained and as shown in Figures 2, 6 and 8, we concluded that the mechanical and morphological properties of the vulcanized NR/ABS blends were influenced by either the phenolic curative content or the blend proportions.

Dynamic Properties. Figure 9 shows the storage modulus (G'), loss modulus (G''), tan δ, and complex viscosity as a function of the frequency for the neat ABS, vulcanized NR, and vulcanized NR/ABS blends at three ratios of 50 : 50, 60 : 40, and 70 : 30 with the NR compound with 15-phr HRJ-10518. As shown in Figure 9(a), G' increased with increasing frequency. At a given frequency, the vulcanized NR gave the highest and nearly stable G', whereas the neat ABS provided the lowest value and increased with increasing frequency. The vulcanized NR/ABS blends showed intermediate values of G' with a slight increase in their values with increasing frequency. The high G' of the NR vulcanizate was attributed to the formation of stably and chemically crosslinked macromolecular networks of high elasticity. We observed that G' of the blends increased with increasing content of the vulcanized rubber component. This was attributed to a higher content of crosslinked polymers in the blended product. Therefore, the 70 : 30 NR/ABS blend gave the highest G'. Furthermore, G' of the blends was higher than G'' over the frequency range investigated; this indicated that they were more elastic than viscous. Tan δ is a ratio of G'' to G' (i.e., $\tan \delta = G''/G'$). As shown in Figure 9(b), the vulcanized NR showed the lowest tan δ, whereas the highest value was found for the neat ABS. Tan δ of the blends for various blend ratios was lower than 1 as was that of the neat ABS as well, which had frequency dependence. A decrease in tan δ at high loadings of rubber was observed. This means that the blends exhibited a greater elastic response than that of the neat ABS, particularly for the blends with NR/ABS ratios of 60 : 40 and 70 : 30. In other words, ABS behaved in a liquidlike manner under frequency sweep, whereas the vulcanized NR/ABS blends were solidlike materials. The dynamic viscosity as a function of frequency is presented in Figure 9(c). The viscosity decreased with increasing frequency sweeps; this suggested that the vulcanized NR/ABS blends and ABS exhibited shear-thinning behavior (i.e., pseudoplasticity). Similar behavior was observed for the blending of maleated NR with PP.[3] At a given frequency,

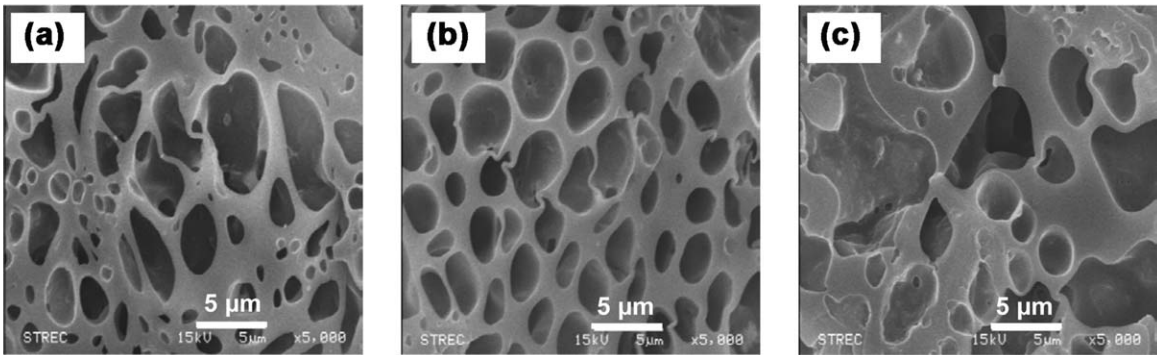

Figure 8. SEM micrographs of the etched, fractured surfaces of the vulcanized NR/ABS blends at various blend ratios [(a) 50 : 50, (b) 60 : 40, and (c) 70 : 30] with the NR compound with 15-phr HRJ-10518 at a mixing temperature of 180°C.

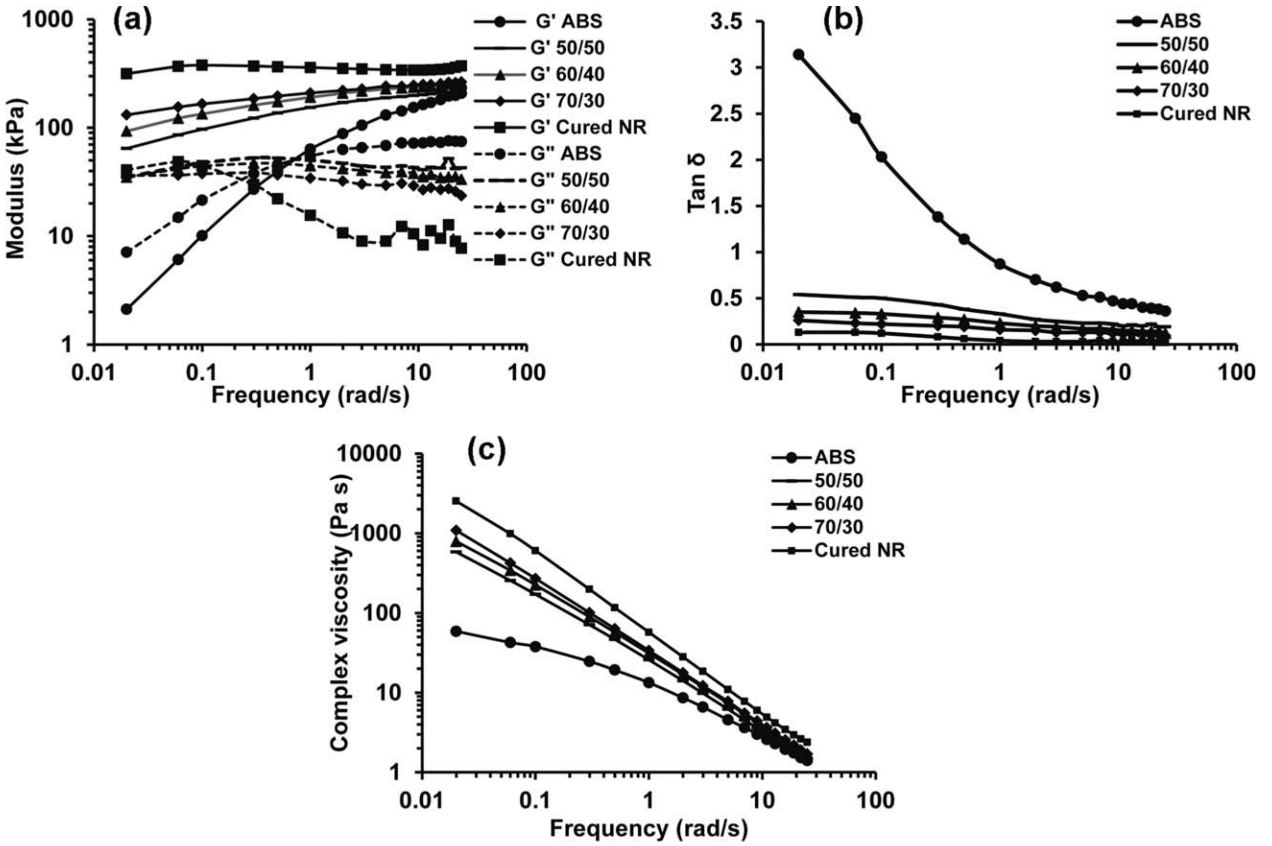

Figure 9. Dependence of the (a) modulus, (b) tan δ, and (c) complex viscosity as a function of the frequency for the neat ABS, vulcanized NR, and vulcanized NR/ABS blends at blend ratios of 50 : 50, 60 : 40, and 70 : 30 with the NR compound with 15-phr HRJ-10518 at a mixing temperature of 180°C.

a higher complex viscosity was observed for the vulcanized NR/ABS blends prepared with a higher content of the rubber. Therefore, the 70 : 30 NR/ABS blend showed the highest complex viscosity, whereas the lowest value was observed at a blend ratio of 50 : 50 because the content of ABS provided a lower complex viscosity. Both NR and ABS were viscoelastic materials, differing in the magnitude of viscous and elastic responses. On the basis of the results obtained, the rheological characteristics of the vulcanized NR/ABS blends (i.e., modulus, tan δ, and complex viscosity) showed intermediate values between the neat NR and ABS. These blends provided a lower tan δ, but the complex viscosity was higher than that of neat ABS. This demonstrated that the rheological properties of the vulcanized NR/ABS blends contributed to the blend component.

Table V. TGA Data for the Neat ABS, NR, and NR/ABS Vulcanizates

Sample	Decomposition temperature (°C)	Char residue at 600°C (wt %)
NR	386.1	0.7
ABS	440.6	0.8
NR/ABS vulcanizates[a]		
50 : 50	418.2	10.8
60 : 40	411.0	11.7
70 : 30	391.2	11.9

[a] Vulcanized NR/ABS blends with the NR compound with 15-phr HRJ-10518.

Thermal Properties. The thermal properties of the ABS, NR, and vulcanized NR/ABS blends at various blend ratios with the NR compound with 15-phr HRJ-10518 are shown in Table V. The decomposition temperature was obtained from the peak maxima of the derivative of the TGA curves. We observed that single decomposition temperatures of the neat NR and ABS were observed at 386 and 441°C, respectively. That is, the thermal stability of thermoplastic was better than that of NR. The vulcanized NR moiety did not melt, but it decomposed before melting under heat. The decomposition temperature of the vulcanized NR/ABS blends increased with increasing content of ABS. That is, the thermoplastic component accounted for the thermal stability of the NR/ABS vulcanizates. The improved thermal stability could be explained by a protective effect; that is, the rubber phase could be protected under thermal conditions by the thermoplastic phase. With regard to the remaining residues, we observed that the neat NR and ABS were almost completely degraded at 600°C; that is, only approximately 0.7–0.8 wt % residues were left. On the other hand, the char residues of the vulcanized NR/ABS blends were 10.8–11.9 wt %; these were higher than that of the neat NR and ABS. The small amount of char residue remaining above 600°C for NR was attributed to the insoluble and intractable materials, which were linked to the cyclized rubber,[1] whereas the residue of ABS could be the ash of partially crosslinked polybutadiene. The higher char residues of the blends might have corresponded to the degradation of the crosslinked rubber in the blends, and/or the degradation of the product of the ACN moieties in the ABS reacted in some manner with the phenolic residue, so as to give hard and glassy particles, which eventually got embedded in the NR during mixing. We observed that the amount of char residue of the three blends was higher than that of the neat NR; this suggested that the thermal stability of the vulcanized NR/ABS blends was better.

CONCLUSIONS

The vulcanization of the NR/ABS blends was successfully carried out with a phenolic curing agent by a melt-mixing process. The results show that the elongation at break of the blends increased with increasing NR content, but the tensile strength and hardness decreased. This indicated that strength and hardness properties of the blends were attributed to the thermoplastic component, and the vulcanized NR was an essential component for improving the elasticity of the blends. An increase in G' of the vulcanized NR/ABS blends with increasing rubber content was observed. This was due to a higher content of crosslinked rubbers in the blended product. These blends showed a greater elastic response than did the neat ABS. We found that the thermal stability of the blends increased with increasing ABS content. SEM micrographs of the blends showed a two-phase morphology system. Compared to the other blend conditions, the vulcanized 60 : 40 NR/ABS blend with an NR compound with 15-phr phenolic curative showed a finer SAN phase dispersed in the vulcanized NR phase; this provided a better dispersion between the two different phases of the blends and, thus, provided superior mixing properties. The results demonstrate that the morphology of the blends was related to the mechanical properties. Therefore, the mechanical properties of the vulcanized NR/ABS blends were mainly controlled by the phase morphology of the blend system. It was clear that the mechanical, dynamic, thermal, and morphological properties of the vulcanized NR/ABS blends were influenced by the phenolic curative content and blend proportions.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the cosupport of the Thailand Research Fund and Chulalongkorn University through the Royal Golden Jubilee Project (contract grant number PHD/0304/2550 to P.W.). Sincere thanks and appreciation go to the Department of Imaging and Printing Technology of Chulalongkorn University for the provision of the research facilities. Sincere thanks also go to Associate Professor Azizon Kaesaman of the Department of Rubber Technology and Polymer Science of the Prince of Songkla University (Pattani Campus) for the rubber blending laboratory facilities.

REFERENCES

1. Asaletha, R.; Kumaran, M. G.; Thomas, S. *Polym. Degrad. Stab.* **1998**, *61*, 431.
2. Mohanty, S.; Nando, G. B.; Vijayan, K.; Neelakanthan, N. R. *Polymer* **1996**, *37*, 5387.
3. Nakason, C.; Saiwari, S.; Kaesaman, A. *Polym. Test.* **2006**, *25*, 413.
4. Oommen, Z.; Thomas, S.; Premalatha, C. K.; Kuriakose, B. *Polymer* **1997**, *38*, 5611.
5. Coran, A. Y.; Patel, R. P. *Rubber Chem. Technol.* **1982**, *55*, 116.
6. Intharapat, P.; Derouet, D.; Nakason, C. *Polym. Adv. Technol.* **2010**, *21*, 310.
7. Mousa, A.; Ishiaku, U. S.; Ishak, Z. A. M. *J. Appl. Polym. Sci.* **1998**, *69*, 1357.
8. Nakason, C.; Nuansomsri, K.; Kaesaman, A.; Kiatkamjornwong, S. *Polym. Test.* **2006**, *25*, 782.
9. Nakason, C.; Wannavilai, P.; Kaesaman, A. *Polym. Test.* **2006**, *25*, 34.
10. Nakason, C.; Worlee, A.; Salaeh, S. *Polym. Test.* **2008**, *27*, 858.
11. Narathichat, M.; Kummerlöwe, C.; Vennemann, N.; Sahakaro, K.; Nakason, C. *Adv. Polym. Technol.* **2012**, *31*, 118.
12. Pechurai, W.; Sahakaro, K.; Nakason, C. *J. Appl. Polym. Sci.* **2009**, *113*, 1232.
13. Shi, Q.; Stagnaro, P.; Cai, C. L.; Yin, J. H.; Costa, G.; Turturro, A. *J. Appl. Polym. Sci.* **2008**, *110*, 3963.
14. Thitithammawong, A.; Nakason, C.; Sahakaro, K.; Noordermeer, J. W. M. *J. Appl. Polym. Sci.* **2007**, *106*, 2204.
15. Vennemann, N.; Bökamp, K.; Bröker, D. *Macromol. Symp.* **2006**, *245*, 641.
16. Wang, Z.; Zhang, X.; Zhang, Y. *Polym. Test.* **2002**, *21*, 577.
17. Wei, D.; Mao, C.; Li, S.; Wang, Z. *J. Macromol. Sci. Phys.* **2014**, *53*, 601.
18. Wei, D.; Zhao, J.; Liu, T.; Wang, Z. *J. Thermoplast. Compos.* **2014**, 1.
19. John, B.; Varughese, K. T.; Oommen, Z.; Potschke, P. *J. Appl. Polym. Sci.* **2003**, *87*, 2083.
20. Yuan, D.; Chen, K.; Xu, C.; Chen, Z.; Chen, Y. *Carbohydr. Polym.* **2014**, *113*, 438.
21. Yuan, D.; Xu, C.; Chen, Z.; Chen, Y. *Polym. Test.* **2014**, *38*, 73.
22. Benmesli, S.; Riahi, F. *Polym. Test.* **2014**, *36*, 54.
23. Pisuttisap, A.; Hinchiranan, N.; Rempel, G. L.; Prasassarakich, P. *J. Appl. Polym. Sci.* **2013**, *129*, 94.
24. Jafari, S. H.; Pötschke, P.; Stephan, M.; Warth, H.; Alberts, H. *Polymer* **2002**, *43*, 6985.
25. Chatterjee, K.; Naskar, K. *Express Polym. Lett.* **2007**, *1*, 527.
26. Hansen, C. M. Hansen Solubility Parameters: A User's Handbook, 2nd ed.; CRC: Boca Raton, FL, **2007**.
27. Andrew, J. T.; Kevin, P. J. Blends of Natural Rubber: Novel Techniques for Blending with Specialty Polymers; Chapman & Hall: London, **1988**.
28. Bhowmick, A. K.; Stephens, H. Handbook of Elastomers, 2nd ed.; CRC: Boca Raton, FL, **2000**.