Effects of Rubber Curing Ingredients and Phenolic-Resin on Mechanical, Thermal, and Morphological Characteristics of Rubber/Phenolic-Resin Blends

Babak Derakhshandeh, Akbar Shojaei, Morteza Faghihi

Department of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran 11365-9465, Iran

ABSTRACT: This article examines the physical and mechanical characteristics of mixtures of two different synthetic rubbers, namely styrene-butadiene rubber (SBR) and nitril-butadiene rubber (NBR), with novolac type phenolic-resin (PH). According to Taguchi experimental design method, it is shown that the addition of PH increases the crosslinking density of rubber phase probably due to its curative effects. Thermal analysis of the blends indicates that, contrary to NBR/PH blend, thermal stability of SBR/PH blend is dependent on sulfur content due to predominant polysulfidic crosslinks formed in SBR. Slight shift in glass-transition temperature (T_g) of pure SBR and NBR vulcanizates by the addition of PH suggests that both SBR/PH and NBR/PH are incompatible blends with a partially soluble PH in the rubber phase. Two-phase morphology of the mixtures is also evidenced by scanning electron microscopy. Correlation of the rubber/PH modulus versus PH concentration by Halpin-Tsai model shows a deviation from the model. Presence of PH in the rubber phase is thought to vary the mechanical properties of the rubber phase by changing both the crosslinking density and rigidity of the molecular network of the rubber, leading to misuse of modulus of pure rubber in Halpin-Tsai equation. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 3808–3821, 2008

Key words: morphology; blending; rubber; phenolic-resin; crosslinking

INTRODUCTION

Phenolic-resin (PH) has been the most common polymeric binder that is widely used in the composite friction materials.[1–4] This may be due to its low cost, relatively high heat resistance, i.e., degradation temperature of above 450°C,[5] and suitable processability. However, the widespread use of PH is restricted by its shortcomings such as brittleness and toxicity.[3,6] Thus, it needs to be modified adequately to meet the required properties for specific applications. For instance, PH may be modified with tough polymers such as epoxy resin, silicon oil, and silicon rubber to improve its flexibility.[7,8] Additionally, blends of a suitable rubber and PH have also found applications in friction materials, particularly in frictional braking system of railroad vehicles,[9–11] to achieve a polymeric binder with combined properties of the rubber material and the resin. The content of the resin in such blends could be reached up to 40 wt %. The rubber component of the blend could be natural or synthetic, mainly nitril-butadiene rubber (NBR) and styrene-butadiene rubber (SBR).[9–11] Presence of rubber in the blend makes the friction material conformable and compressible, which are essential in applications such as railroad friction materials to dominate the thermal damages of the friction couple.[12,13]

Literature shows a limited number of studies devoted to the rubber/PH systems.[14–16] In addition, the patents on this subject have provided a few technical details due to proprietary reasons.[9–11] Kosfeld and Borowitz[14,15] studied dynamic mechanical and viscoelastic properties of blends of PH with NBR and SBR with full range of the resin content, i.e., 0–100 vol %. There exists only one recent article on the rubber/PH blends to be used specifically as binder of friction material in which the role of heating on the properties of NBR and PH mixtures has been investigated.[16]

It is well known that the mechanical and thermal properties of a rubber vulcanizate are significantly dominated by the rubber curing ingredients including sulfur, accelerator, and activator.[17] It has been also claimed that increasing concentration of zinc oxide (activator of sulfur vulcanizing system) increases the wear rate of friction materials containing the SBR/PH as polymer matrix.[11] Therefore, it is expected that the type and composition of rubber curing ingredients contribute to the final properties of rubber/PH systems as well. The role of rubber curing ingredients on the properties of NBR and SBR vulcanizates has been extensively studied long

time ago. However, such study for blends of the rubber and PH has not been addressed earlier.

Investigation of compositional parameters in rubber/PH blends by one-factor-at-a-time method, i.e., varying only one parameter while keeping all others constants, is very complicated task and requires performing a large number of experiments. To reduce the size of experiments, several experimental design methods have been presented.[18] Among them, Taguchi's method has found great successes in designing and optimizing the engineering systems, so that the literature indicates a number of studies in this regard.[19–23] This method has also been used successfully to optimize the fillers composition of the friction materials.[24] Generally, the Taguchi method can be utilized to obtain various information about the system under investigation such as average factor effect, relative influence of factors (contribution of factor to a result), possible interaction between factors (influence of levels of one factor on the effect of another) and optimum condition. These can be achieved by laying out the experiments based on appropriate orthogonal array and performing appropriate statistical calculations to the results.[25]

This article deals with the mixtures of two different synthetic rubbers consisting of SBR and NBR with novolac type PH, which can be used as organic binder of the composite friction materials particularly for railroad brakes. Special attention is given to acquire further understanding concerning the influence of the constituents of the blend including the rubber vulcanizing ingredients and the resin content. To reduce the size of experiments, Taguchi's experimental design method is utilized to investigate the compositional parameters of the blends. The morphological characteristics of the blend are also examined by using dynamic and static mechanical analysis and scanning electron microscopy (SEM).

EXPERIMENTAL PROCEDURE AND ANALYSIS

Materials

The polymer materials used in this study include SBR (SBR1502, styrene content of 23%, density of 0.97 g/cm^3; BIPC, Iran), NBR (Europrene N 33.45, acrylonitril content of 33%, density of 0.98 g/cm^3, Mooney viscosity 45, Enichem, Italy) and PH (Novolac IP502, hexamehylenetetramine content 10 wt %, density of 1.28 g/cm^3; Rezitan, Iran). The curing ingredients of both SBR and NBR consist of sulfur, dibenzothiazyl disulfide (MBTS), zinc oxide (ZnO), and stearic acid which are of commercial grades supplied from local companies. Industrial grades of toluene and acetone are used as solvents in swelling experiments.

Design of experiments

Taguchi method

In this study, experimental design method based on the Taguchi approach is utilized to investigate individually the influence of each component, known as factor, on the properties of the rubber/PH mixtures. The Taguchi technique helps us to investigate all of these factors simultaneously by laying out small number of experiments according to an appropriate orthogonal array, depending on the number of factors and their levels.

As will be discussed later in this study, mixing of both NBR and SBR with PH leads to a two-phase blend, containing cured PH phase dispersed within the vulcanized rubber matrix. Properties of the rubber/PH blends are expected to be a function of properties of individual phases, i.e., rubber and resin phases. On the other hand, physical and mechanical properties of rubber phase are dominated by microstructure of the crosslinks network, namely crosslinking density and polysulfidity of the sulfur linkages produced between rubber chains. In addition to sulfur content, other curing ingredients such as accelerator and activator can also play a noticeable role on the crosslinks network of the rubber phase. Accordingly, five factors including concentrations of PH, sulfur, MBTS, ZnO, and stearic acid in terms of phr (part per hundred parts by weight of rubber) are selected in this study. Since all of these factors can be changed independently, they are known as control factor not noise factor. To take into consideration any possible nonlinear influence of the factors upon the results, each factor is studied at four levels within a defined range including sulfur in 2–10 phr, MBTS in 1–5 phr, ZnO in 2–10 phr, stearic acid in 1–5 phr, and PH in 0–40 phr. For 5 four-level factors without considering the outer array for noise factor, modified L$_{16}$ orthogonal array, L$_{16}$ (4^5) or M$_{16}$, is suggested by the Taguchi methodology.[25] According to M$_{16}$ array, 16 compounds are required for each rubber/PH blend, as detailed in Table I, to examine the total compositional parameters. As indicated, each composition is designated by a number ranging from 1 to 16. For instance, SBR-8 is relevant to a blend containing SBR whose composition is given in Table I with code 8.

Analysis of the results

All the 16 compounds for each rubber/PH mixture are subjected to different physical and mechanical tests, and the results are used to extract the role of each ingredient on the properties of the blend. The primary goal of using Taguchi method in this study is to determine (1) the trend of influence of the factors and (2) contribution of each factor on the

Compound no.	Sulfur	MBTS	ZnO	Stearic acid	PH
1	2	1	2	1	0
2	2	2.25	4.5	2.25	12.5
3	2	3.5	7	3.5	25
4	2	4.75	9.5	4.75	37.5
5	4.5	1	7	2.25	37.5
6	4.5	2.25	9.5	1	25
7	4.5	3.5	2	4.75	12.5
8	4.5	4.75	4.5	3.5	0
9	7	1	9.5	3.5	12.5
10	7	2.25	7	4.75	0
11	7	3.5	4.5	1	37.5
12	7	4.75	2	2.25	25
13	9.5	1	4.5	4.75	25
14	9.5	2.25	2	3.5	37.5
15	9.5	3.5	9.5	2.25	0
16	9.5	4.75	7	1	12.5

The levels of ingredients are given in terms of phr.

properties of the blends by performing a few number of experiments. The trend of influence of a factor can be determined by calculating the average effect of a factor at a level. This latter one is obtained by simple statistical calculation as follows[25]:

$$A_i = \frac{\sum_{j=1}^{n} y_i^j}{n} \qquad (1)$$

where A_i is the average effect of factor A at level i, y_i^j represents the j-th observation (result) of factor A at level i, and n stands for total number of observations for factor A. By plotting the average factor effect against the corresponding factor level, an average plot is obtained from which the trend of influence of a factor on the result is extracted. The relative influence of factors (contribution) on the result can also be obtained by somewhat more rigorous statistical calculations known as analysis of variance (ANOVA), see the details in Ref. 25. In this study, calculations of both ANOVA and average factor-level effect are performed by using QT4 software.[25]

Preparation of compounds

The compounds are prepared by a laboratory scale two-roll mill. The rubbers are first masticated at temperature around 50°C for 5 min. Then the masticated rubbers are mixed further with PH and other ingredients for around additional 25 min. The obtained compounds are cured into a sheet using compression molding at 150°C for 1 h under a pressure of 3.5 MPa in accordance to ASTM D-3182. The samples

required for mechanical and physical tests are cut from the cured sheets.

Thermal analysis

Differential scanning calorimeter (DSC, Pyris 1, Perkin–Elmer) is used to investigate the thermal events occurred during the heating of the cured compounds. To do this, DSC analysis is performed at a heating rate of 20°C/min under the nitrogen with flow rate of 200 mL/min. Figure 1 shows the DSC thermogram of typical compounds. As seen, there is an endothermic peak in the graphs. This peak corresponds to the maximum rate of mass loss of the compounds, and in this study, it is taken as their thermal stability.

Mechanical testing

The stress–strain (σ–ε) properties of the cured dumbbell-shaped specimens are determined at room temperature according to ASTM D412 by using an Instron tensile testing machine, operated at a crosshead speed of 60 mm/min. The tensile strength and elongation at break are extracted directly from the σ-ε curves, while the young's modulus is calculated from the initial slope of the curve, namely slope of the curve within strain range of 0–2%. Dynamic mechanical properties of the mixtures are determined by a dynamic mechanical thermal analyzer (DMTA-Triton, Tritic Technology, England) at a frequency of 1 Hz and temperature range from −150 to 180°C with a heating rate of 3°C/min. The DMTA records the variation of storage modulus (E') and loss tangent (tan δ) with temperature.
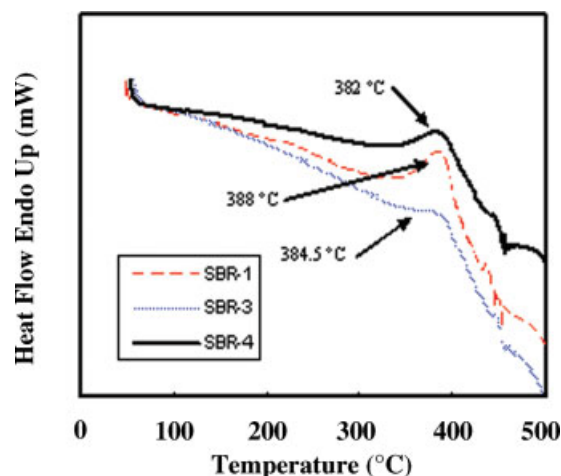

Figure 1 DSC thermograms of typical compounds. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Experimental Results for SBR/PH and NBR/PH Blends

Compound no.	Elongation (%)		Modulus (MPa)		Swelling coefficient (mL/g)	
	NBR	SBR	NBR	SBR	NBR	SBR
1	653 ± 35	766 ± 29	1.9 ± 0.2	1.8 ± 1	2.3 ± 0.5	4.4 ± 0.1
2	346 ± 14	215 ± 62	2.5 ± 0.4	3.4 ± 1.1	2.3 ± 0.1	3.8 ± 0.1
3	256 ± 42	139 ± 27	4.4 ± 0.5	5.9 ± 1.1	2 ± 0.1	3.8 ± 0.1
4	257 ± 23	224 ± 83	5.8 ± 1.7	6.1 ± 0.9	1.8 ± 0.1	
5	151 ± 18	145 ± 29	5.8 ± 1.1	6.1 ± 1.4	1.6 ± 0.1	3.5 ± 0.05
6	194 ± 15	97 ± 14	5.8 ± 1.1	5.3 ± 1.4	1.3 ± 0.1	3 ± 0.1
7	252 ± 13	143 ± 17	2.5 ± 0.6	3.3 ± 0.4	1.5 ± 0.2	3.4 ± 0.05
8	262 ± 20	223 ± 30	1.4 ± 0.7	2.2 ± 0.2	1.6 ± 0.2	3.2 ± 0.03
9	158 ± 14	142 ± 15	3.4 ± 0.4	4.9 ± 0.6	1.3 ± 0.1	2.5 ± 0.07
10	201 ± 25	152 ± 30	2.4 ± 0.1	2.3 ±.05	1.5 ± 0.2	2.4 ± 0.05
11	93 ± 14	102 ± 11	11 ± 1.7	8.4 ± 1.4	1.5 ± 0.9	2.9 ± 0.07
12	141 ± 16	122 ± 19	7.4 ± 0.5	5.5 ± 1.1	1.6 ± 0.2	2.6 ± 0.09
13	124 ± 18	104 ± 18	7.7 ± 1.9	6 ± 1.3	1.4 ± 0.3	2.3 ± 0.08
14	124 ± 19	105 ± 3	11.6 ± 2.2	9.3 ± 1.2	1.3 ± 0.1	2 ± 0.06
15	183 ± 14	120 ± 21	3.9 ± 0.7	3.3 ± 0.5	1.5 ± 0.2	1.9 ± 0.07
16	158 ± 19	113 ± 19	4.7 ± 0.9	3.8 ± 1	1.3 ± 0.2	1.7 ± 0.09

Morphology

The morphology of the blends is characterized by means of a Philips XL30 SEM. To do this, the samples are fractured in liquid nitrogen, and then the fractured cross sections and surface of samples which are sputter-coated with gold layer are used to investigate the phase morphology.

Swelling

The vulcanized samples are first subjected to extraction process using acetone for around 120 h to remove the residual soluble components after vulcanization. The extracted samples are vacuum-dried under 60°C for 2 h and then the dried specimens are weighed. After drying the samples, they are dipped into toluene at room temperature for 120 h. The swollen samples are removed from the solvents and wiped off using tissue and weighed. The swelling coefficient, Q, is obtained using the following relation[26]:

$$Q = \frac{m_S - m_D}{m_D} \times \frac{1}{\rho_l} \qquad (2)$$

where m_S and m_D are the weights of swollen and the dry extracted sample, respectively, and ρ_l is the density of the swelling solvent.

Crosslinking density of the rubber phase can be calculated by the Flory-Rehner relation expressed as follows[26]:

$$M_C = \frac{\rho_r V_S \left(\frac{v_r}{2} - v_r^{1/3} \right)}{[\ln(1 - v_r) + v_r + \chi v_r^2]} \qquad (3)$$

where v_r denotes the equilibrium volume fraction of the rubber in swollen vulcanized rubber which is

estimated here based on the swelling measurements, ρ_r the density of the rubber, V_S the molar volume of solvent, and, χ the polymer solvent interaction parameter. In eq. (3), M_C is the average molecular weight between two crosslinks per primary rubber chains which is an indication of the crosslinking density. The lower the M_C value, the higher crosslinking density is achieved. The interaction parameter reported for SBR-toluene system is 0.39,[26] while for NBR-toluene it is calculated using the following expression[27]:

$$\chi = 0.35 + \frac{V_S}{RT}(\delta_S - \delta_r)^2 \qquad (4)$$

where δ_r and δ_S are the solubility parameters of the rubber and solvent, respectively. Taking $\delta_r = 9.4$ (cal/cm^3)$^{0.5}$ for NBR and $\delta_S = 8.9$ (cal/cm^3)$^{0.5}$ for toluene,[27] interaction parameter for NBR-toluene systems becomes 0.46. The measured average values of density for SBR and NBR vulcanizates are ~ 1 g/cm^3. The density and molar volume of toluene at 20°C are 0.867 g/cm^3 and 106.3 cm^3/mol, respectively.[28]

RESULTS AND DISCUSSION

Compositional effects on the properties of the rubber/PH blends

Table II summarizes the results of experimental measurements performed for 16 compounds of each rubber/PH blends indicated in Table I. These results are used to estimate the influence of each component on the swelling, thermal and mechanical properties of the blends based on Taguchi's analysis. It should be pointed out that all of the plots obtained in this

study based on statistical calculations represent only the trend of influence of each factor upon the result, not the exact value of the result at a given level of a factor.

Swelling characteristics

Knowledge of the swelling behavior of crosslinked polymer can provide further insight into the cross-links microstructure, particularly for two-phase systems. Figure 2 shows the variations of the swelling coefficient against concentration of rubber curing ingredients and PH for both SBR/PH and NBR/PH blends. From Figure 2(a), it is observed that sulfur is the most important parameter influencing the swelling coefficient of the SBR/PH blends. As the swelling coefficient of the rubber phase is dominated by the crosslinking density,[27–29] this result suggests that increasing the sulfur content within the range of 2–10 phr increases strongly the crosslinking density of the SBR. Comparing Figure 2(a,b), it is found that the extent of swelling and variation of swelling coefficient of NBR/PH are less than those of SBR/PH, but the sulfur has still higher influence with respect to the other curing ingredients. This observation suggests that the crosslinking density of the NBR does not vary significantly as much as the SBR.

Figure 2(c) shows that the swelling coefficient decreases by increasing the resin content. On the other hand, the maximum extent of reduction in swelling coefficient of both rubbers within the resin content of 0–40 phr is approximately the same, i.e., extent of reduction is about 0.5 mL/g for both rubbers. This behavior can be explained by the fact that the rubber component is responsible for swelling of the rubber/PH blends. Because, PH is a highly crosslinked thermoset and can not be swelled anymore. This explanation is confirmed by performing separately swelling experiment for cured PH so as to no swelling effect appears. In fact, the swelling of PH is negligible and it acts as rigid filler. So incorporation of PH decreases the content of rubber component in the blend, leading to reduction of the swelling coefficient of the blends, accordingly.

Table III presents the contribution of the components of the blend (relative importance of the factors) on the swelling coefficient. It is found that sulfur is the only dominant parameters on the swelling coefficient of the SBR/PH blends. However, for the NBR/PH, sulfur and PH have almost the similar importance. This could be attributed to lower extent of swelling of the NBR vulcanizate due to its higher crosslink density, as discussed earlier. On the other hand, contribution of other curing ingredients, namely MBTS, ZnO, and strearic acid in SBR/PH blend is negligible, while these factors slightly affect the NBR/PH blend. Slight influence of accelerator
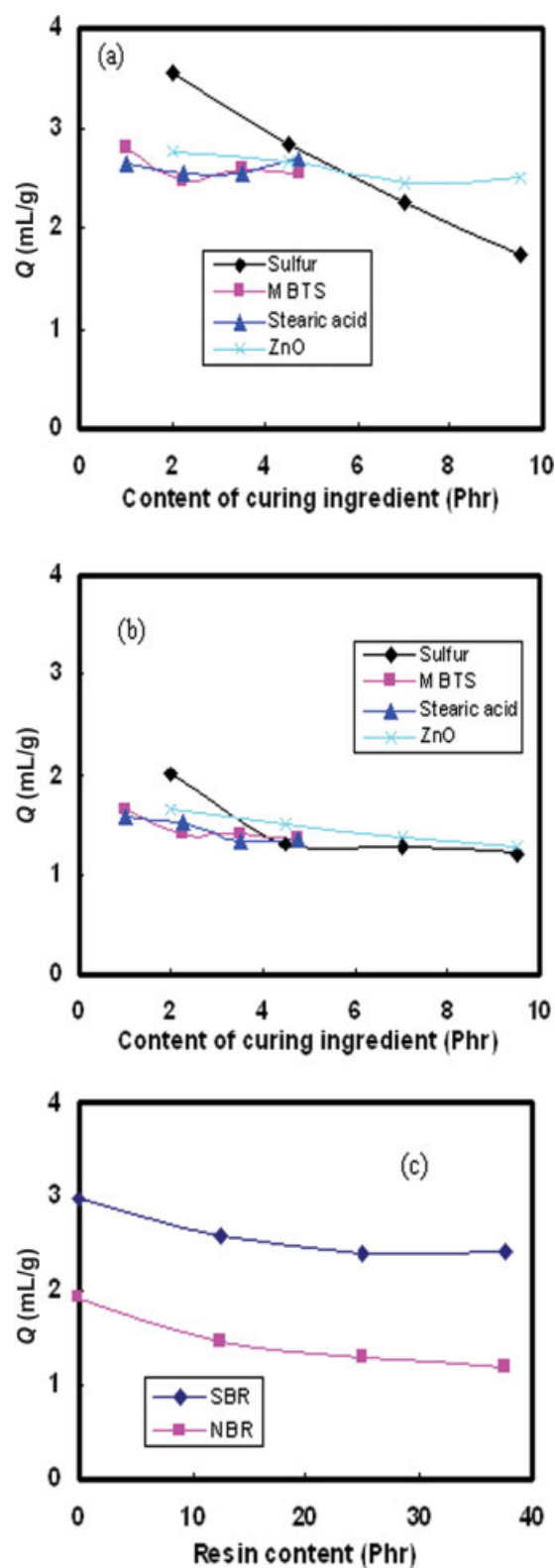

Figure 2 Average effect of components on the swelling coefficient of blends obtained by Taguchi's analysis; (a) effect of curing ingredients on SBR/PH, (b) effect of curing ingredients on NBR/PH blends, and (c) effect of PH on SBR and NBR blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Factor	Contribution to the swelling coefficient (%)		Contribution to the modulus (%)		Contribution to the thermal stability (%)	
	NBR	SBR	NBR	SBR	NBR	SBR
PH	35	9.6	68	84	18	3.7
Sulfur	47	84	23	8	22	86
MBTS	5	2.6	1.7	2.7	4	4
ZnO	8	3	4.8	0.8	30	2.8
Stearic acid	5	0.8	2.5	4.5	26	3.5

and activator is thought to be due to their effects on vulcanization process during development of the crosslinks as reported in the literature.[17,29,30]

As mentioned earlier, swelling of the rubber/PH blends is relevant to the rubber phase. Therefore, crosslinking density of the rubber phase in the blend can be calculated by the Flory-Rehner equation, eq. (3), based on the swelling data. Figure 3 illustrates the variation of M_C with the concentration of rubber curing ingredients. It is found that M_C for SBR is greater than that of the NBR, indicating its lower crosslinking density as compared with NBR; and it reduces mainly by increasing the sulfur content. For SBR, M_C reduces almost from 8000 to 2000 g/mol when the sulfur content varies within 2–10 phr. Variation of M_C for NBR within the same range of sulfur content is between 1500 and 3000 g/mol. These values of M_C for both rubbers stand within the expected range as described in the literature.[26] The higher value of M_C for SBR compared to NBR could be attributed to its chemical structure. In SBR, presence of such large side group as benzene causes a molecular spatial hindrance to produce more sulfur linkages between two polymer chains, resulting in higher value of M_C. According to this explanation, it should be expected to form more polysulfidic crosslinks in SBR, i.e., longer sulfur linkages, between two polymeric chains to overcome the hindrance effect. This characteristic will be examined later in this work using the thermal behavior of the blends. Figure 3 also shows that the value of M_C approximately levels off after 4 phr sulfur content for NBR. A possible explanation for this behavior could be that the molecular weight between two crosslinks after 4 phr sulfur is small enough, i.e., around 1500 g/mol, and two neighbor crosslinks are so close, so as to beyond that new crosslinks could not be formed easily.

Figure 3(c) shows that crosslinking density of the rubber phase increases slightly by increasing the resin content. This observation may be explained by dissolution of small amount of the resin in the rubber phase. This partial solubility of the resin will be examined further by the dynamic and static mechanical experiments carried out in this study. It seems that the dissolved PH participates in the crosslinks network developed during vulcanization of the rubbers in addition to the sulfur linkages.[17,30] This crosslink could be made by reaction of resin and rubber chains through methylene bridging, particularly in presence of hexamethylenetetramine.[31]

Thermal properties

Thermal stability of the blends obtained by DSC thermograms is employed in QT4 software for performing the statistical analysis, and the results are presented in Figure 4 and Table III. Overall degradation temperature of the blends, shown in Figure 4, stands within 370–385°C for different compounds. This temperature range is similar to the degradation temperature of the neat rubber vulcanizate. These results suggest that the degradation temperature of the rubber/resin blend is dominated by the rubber component. Camino et al.[16] reported that the weight loss of NBR, degradation of NBR obtained by thermogravimetric analysis, begins at about 350°C, which is in agreement with the results obtained in this study. They[16] also came into the same conclusion about the mixture of NBR and novolac PH, that the degradation temperature is dominated by NBR.

The results illustrated in Figure 4-c indicate that the resin content has a negligible effect on the degradation temperature of the rubber/resin blends. It is shown that the rubber curing ingredients has a minor effect on the degradation temperature of the NBR blends. However, for SBR blends, the sulfur content is found to be the most effective parameters influencing the degradation temperature. As shown in Figure 4(a), degradation temperature decreases almost from 385 to 372°C by increasing the sulfur content from 2 to 10 phr. This is probably attributable to the structure of the sulfur linkage produced in the SBR network which could be mainly polysulfidic. This explanation is in agreement with the swelling characteristics of the SBR compounds in which
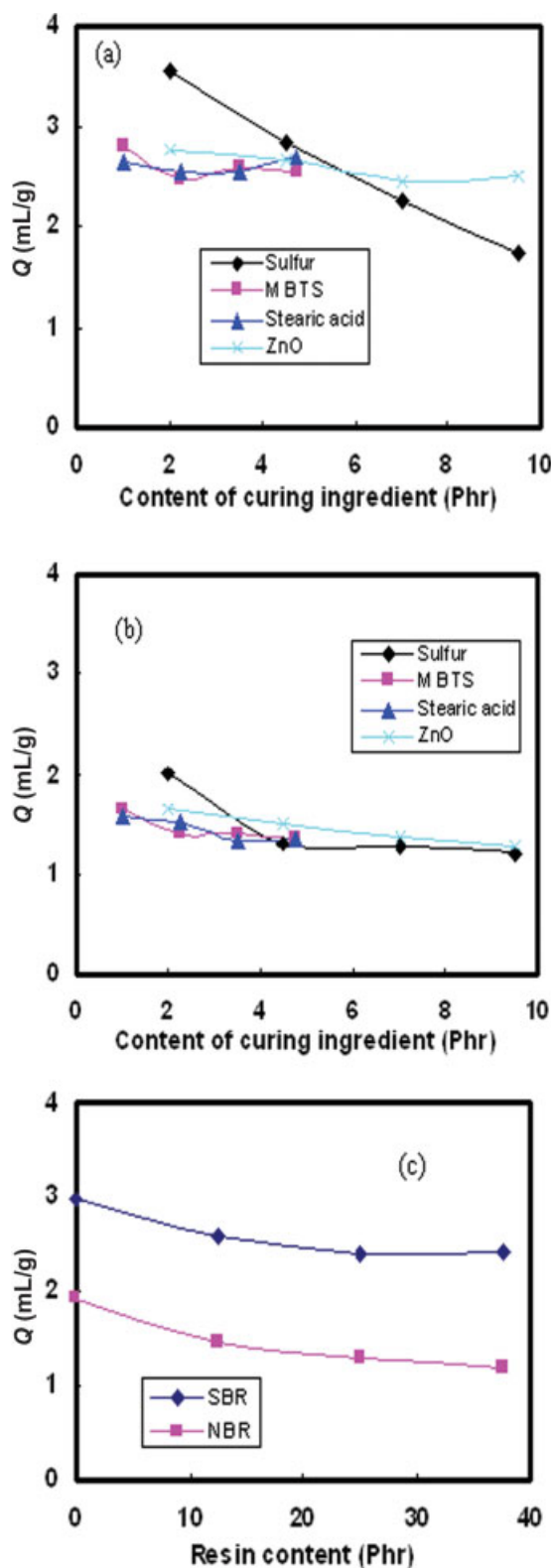
Figure 3 Average effect of components on the M_c; (a) effect of curing ingredients on SBR/PH, (b) effect of curing ingredients on NBR/PH blends, and (c) effect of PH on SBR and NBR blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
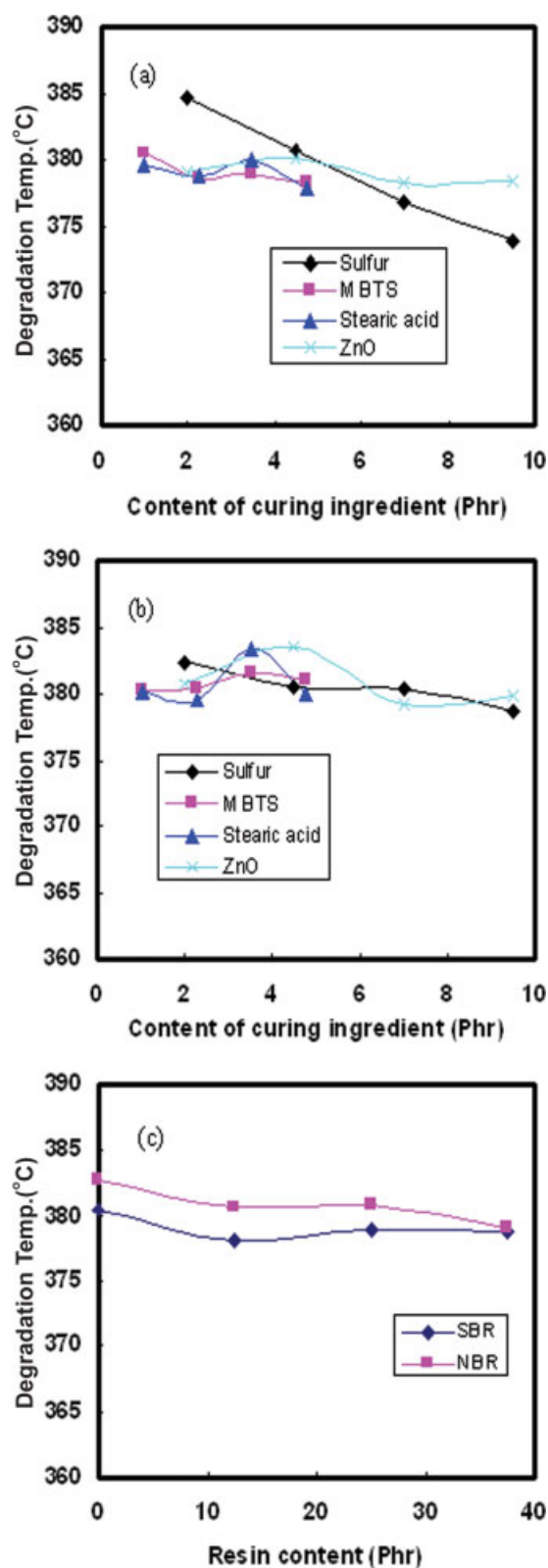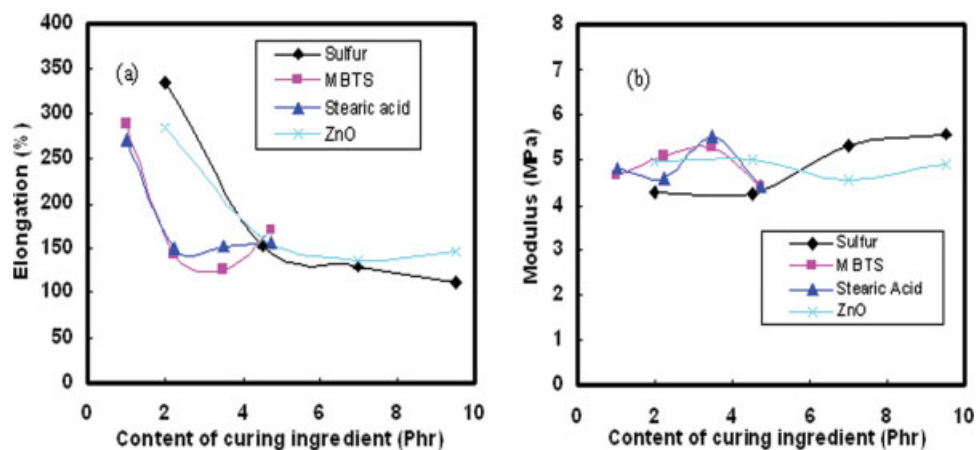
Figure 4 Average effect of components on the thermal stability of blends obtained by Taguchi's analysis; (a) effect of curing agents on SBR/PH, (b) effect of curing agents on NBR/PH blends, and (c) effect of PH on SBR and NBR blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 5 Average effect of rubber curing ingredients on the mechanical properties of SBR/PH blends predicted based on Taguchi's analysis; (a) elongation at break and (b) Young's modulus. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the polysulfidic linkages are thought to be dominant due to hindrance effect of benzene side group. The higher the sulfur content, the more polysulfidic linkages are produced. It is well known that polysulfidic bonds have low thermal stability, leading to the thermal decomposition of the vulcanized rubber at lower temperatures.[29,30]

Mechanical properties

Figures 5–7 depict the variation of mechanical properties of the blends with concentration of the rubber curing ingredients and the resin content. The results show that all of these components influence the mechanical properties. However, from Table III for Young's modulus, it can be found that the contribution of PH is much more pronounced with respect to other components, namely rubber curing ingredients. In addition, from Figure 7, it is shown that by

increasing the resin content, the modulus increases and elongation at break decreases continuously. Since the PH has very high modulus and low elongation at break when compared with both SBR and NBR, see Table IV, these effects of PH are completely expected. We will show in the next section that addition of PH into the rubber material leads to a two-phase system in which the PH component forms a dispersed phase. This resembles a composite material filled with rigid filler, resulting in higher modulus and lower elongation. Moreover, presence of PH in the rubber phase due to the partial solubility of the resin, as pointed out in the swelling characteristics, is thought to increase the stiffness of the rubber phase due to the rigidity of the PH chains and its contribution to the crosslinking density of the rubber phase.

Among the curing ingredients, the sulfur content is expectedly shown to be the significant parameter
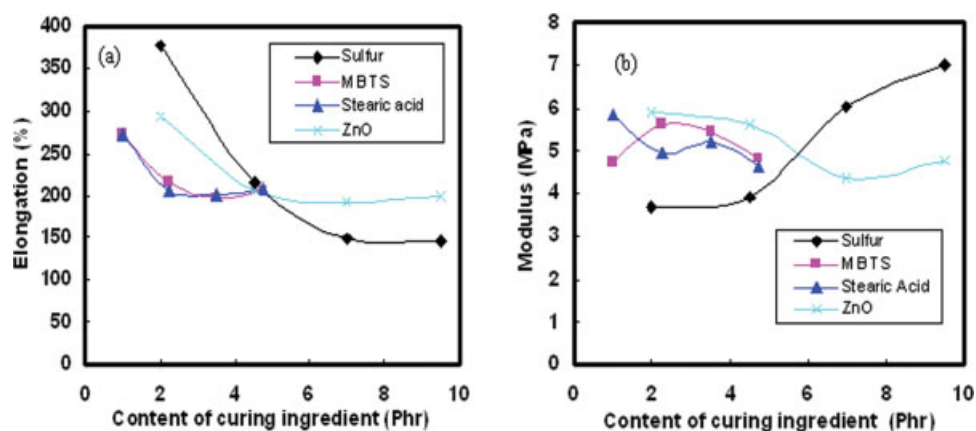

Figure 6 Average effect of rubber curing ingredients on the mechanical properties of NBR/PH blends predicted based on Taguchi's analysis; (a) elongation at break and (b) Young's modulus. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
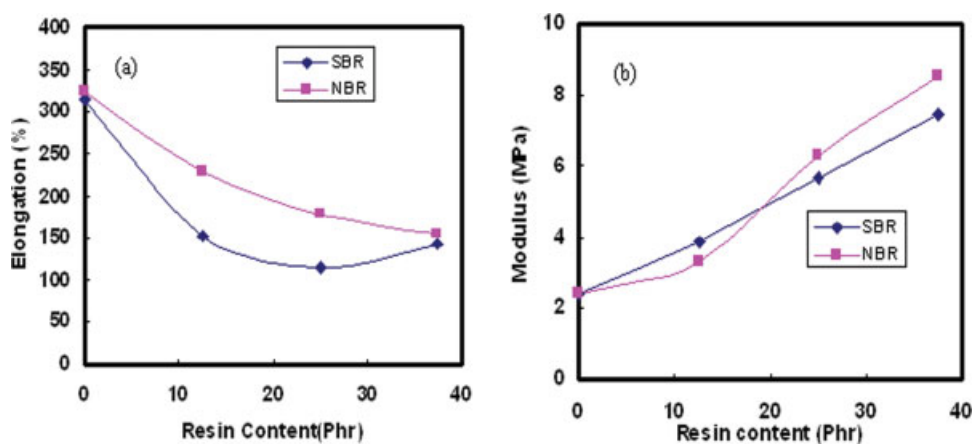
Figure 7 Average effect of resin content on the mechanical properties of the blends predicted based on Taguchi's analysis; (a) elongation at break and (b) Young's modulus. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

influencing the mechanical properties. This behavior can be associated to the alteration of the network structure of the vulcanized rubber. As mentioned in the preceding section, higher crosslinking density for both rubbers is achieved by increasing the sulfur content. It is well known that the higher crosslinking density restricts the mobility of the chain segments further, leading to improved mechanical behavior of the vulcanizates.[26] As observed in the swelling behavior of both rubbers, enhancement of crosslinking density of SBR is much more pronounced when compared with NBR (see Fig. 3), while the variation of modulus for NBR is slightly greater than that of SBR. In agreement with the swelling data and thermal stability of the SBR/PH blend, longer sulfur linkage of SBR vulcanizates could be possibly responsible for this behavior. Because, longer crosslinks increase the mobility of chain segments of the macromolecules and moderates the role of higher enhancement of crosslinking density.

From Table III, it is shown that MBTS, ZnO, and stearic acid also have minor influence on Young's modulus of the blend. As mentioned in the swelling data, this behavior is due to their slight effect upon the structure of the crosslinks.

Morphological investigation

Dynamic mechanical analysis

The dynamic mechanical analysis is performed for the blends of both rubbers with varying amount of PH, ranging from 0 to 23 vol %. In all of these blends, the concentration of rubber curing ingredients is kept constant, i.e., sulfur 2 phr, MBTS 2 phr, stearic acid 2 phr, and zinc oxide 5 phr. Figure 8 illustrates the storage modulus (E') of the blends versus temperature in the range of -150 to $150°C$.

As expected, the storage modulus of the blends above the transition temperature, where a sharp decrease in E' is observed, increases by increasing the PH concentration. This is attributed to the higher stiffness of the PH chains.

Plots of tan δ versus temperature for the blends are given in Figure 9. It is observed that there is a sharp peak at $-18.6°C$ for pure NBR vulcanizate (NBR-1) and at $-38.9°C$ for pure SBR vulcanizate (SBR-1). Indeed, these temperatures indicate the glass transition temperature (T_g) of the rubbers, which are consistent with the reported values in the literature.[14,15,32] Additionally, from Figure 9, the T_g of pure PH is found to be $138°C$. It is shown that the maximum value of tan δ (tan δ_{max}) for pure rubber vulcanizate decreases from 1.2 to 0.45 for SBR/PH and from 1.19 to 0.54 for NBR/PH blends containing 23% by volume of PH. It is well known that the higher mechanical losses which are related to high energy input required for the segmental motion of the macromolecular chains, lead to greater value of tan δ_{max}. For the rubber/PH blends studied here, presence of hard PH segments may possibly restrict the movement of the soft rubber segments, resulting in lower value of tan δ_{max}.

The plots of tan δ, shown in Figure 9, demonstrate that addition of PH to the rubbers shifts slightly the

TABLE IV
Young's Modulus of Phenolic Resin and Rubbers at Two Levels of Sulfur Content

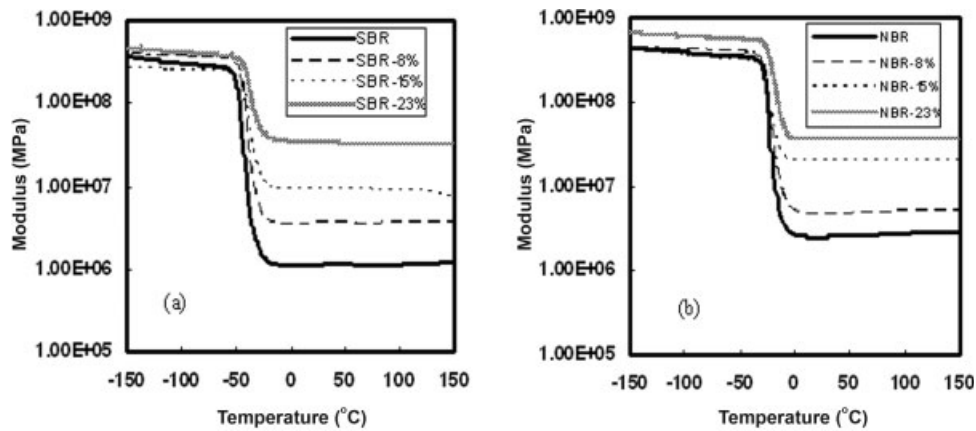| Material	Modulus (MPa)	Elongation at break (%)
PH	5,100 ± 250	1
SBR (2 phr sulfur)	1.82 ± 0.15	320.6 ± 80
SBR (7 phr sulfur)	2.75 ± 0.2	122.75 ± 55
NBR (2 phr sulfur)	1.87 ± 0.1	347.5 ± 32
NBR (7 phr sulfur)	2.9 ± 0.2	141.75 ± 40

Figure 8 Plots of storage modulus versus temperature; (a) SBR/PH and (b) NBR/PH blends.

tan δ_{max} of both rubbers, namely less than 5°C. On the other hand, no separate peak due to the PH component is observed in the blends. Such an observation has been reported by Samui et al.[32] for NBR/PH blends as well. Inward shift of T_g can be an indication of solubility of the PH in the rubber phase.[26] The extent of solubility can be estimated by the rule of mixture, i.e., $T_g = \sum_{i=1}^{2} T_{g_i} \phi_i$.[26] According to this rule and T_g values of the blends, shown in Figure 9, volume fraction of dissolved PH in the rubber phase is found to be around 0.03 for a mixture containing 23 vol % PH. This shows that only small amount of PH is dissolved in the rubber phase, and mixing of the rubbers with PH leads essentially to an incompatible blend and a two-phase system. The incompatibility is expected, because PH is highly polar material due to —OH group, while NBR has a few and SBR has no polar group. The slight dissolution of PH in the rubber phase observed by DMTA supports the enhancement of crosslinking density of the rubber vulcanizate due to the presence of PH in rubber phase as discussed in swelling characteristics of

the blends. Higher shift in T_g of SBR when compared with NBR may be associated to slightly higher dissolution of PH in SBR

Halpin-Tsai relationship for rubber/PH blends

It is well known that the mechanical properties of a polymer blend are governed by microstructure of the dispersed phase and properties of individual phases.[33,34] Hence, as a further evidence to the microstructural behavior of the rubber/PH blends, modulus of these blends is investigated by varying the amount of PH in the blend ranging between 0 and 25 vol %, while concentration of the rubber curing ingredients is kept constant, i.e., sulfur 2 phr, MBTS 2 phr, stearic acid 2 phr and zinc oxide 5 phr. To take into consideration the role of sulfur content on the morphological behavior, variation of blend modulus with the PH concentration is also investigated at higher sulfur content, i.e., 7 phr, while the concentration of other curing ingredients is the same as earlier.
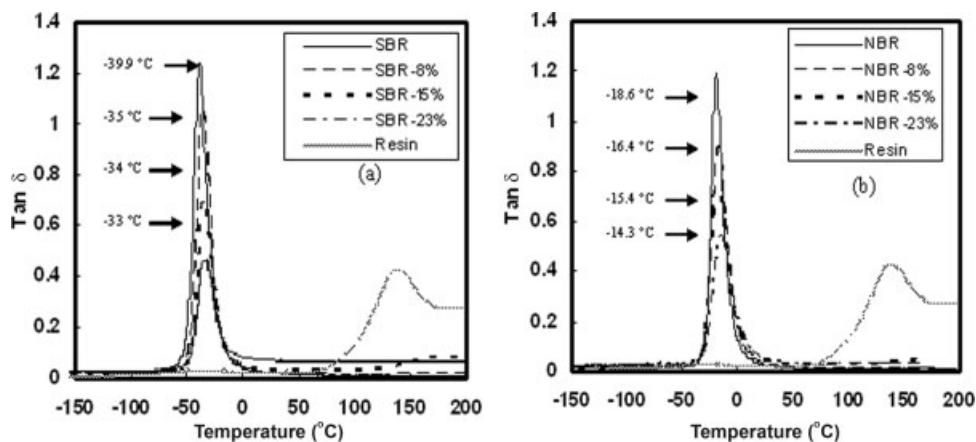

Figure 9 Plots of tan δ versus temperature; (a) SBR/PH and (b) NBR/PH blends.

Table IV presents the modulus and elongation at break of PH and pure rubber vulcanizates at two levels of sulfur content obtained from static tensile tests. It is expectedly realized that increasing the sulfur content increases the modulus of both SBR and NBR vulcanizates approximately up to 60%. Furthermore, it is found that the modulus ratio of the resin to the rubber is so great, i.e., greater than 2000, so as to the dispersed resin can be regarded as rigid filler.

Halpin-Tsai equation is one of the most versatile and widely used semiempirical equations for the polymeric composites and blends. In this study, this model is used to correlate the mechanical behavior of the rubber/PH blends. Halpin-Tsai equation in which the rubber forms the continuous phase is expressed as follows[33]:

$$\frac{E_b}{E_r} = \frac{1 + AB\phi_p}{1 - B\psi\phi_p} \quad (5)$$

where subscripts b, r, and p stand for blend, rubber, and PH, respectively, E represents the Young's modulus, ϕ is the volume fraction, and A, B, and ψ are the model parameters which may be given as follows[33]:

$$\begin{cases} A = k_E - 1 \\ B = \frac{(E_p/E_r)-1}{(E_p/E_r)+A} \approx 1 \\ \psi = 1 + \frac{1-\phi_m}{\phi_m^2}\phi_p \end{cases} \quad (6)$$

in which ϕ_m is the maximum packing fraction of the dispersed phase which can be considered to be about 0.63,[33] and k_E is the generalized Einstein coefficient. To calculate the modulus of the blend by eq. (5), Einstein's coefficient k_E should be known. Theoretical value of k_E is 2.5 which is given by the original Einstein equation expressed as follows[33]:

$$\frac{E_b}{E_r} = 1 + k_E\phi_p. \quad (7)$$

This equation is valid for composite systems having only spherical rigid particles in very low concentrations. In actual situations, morphology of the dispersed phase may deviate from the ideal case. Therefore, the theoretical value of k_E may be inappropriate in such cases. In this study, the value of k_E is determined from experimental data based on the Einstein equation from the slope of E_b/E_r versus ϕ_p. As Einstein's equation is valid for a very low concentration, k_E is extracted from a set of blends with low concentrations of PH, namely up to 3 vol %. k_E values obtained in this way are 6.16 and 8.4 for SBR/PH with 2 and 7 phr sulfur, respectively, and 6.24 and 8.36 for NBR/PH with 2 and 7 phr sulfur,

respectively. In all cases, regression coefficient is so close to one, namely greater than 0.99, indicating the linearity of the curve in this range of PH concentration. It is observed that the empirical values of k_E are higher than that of the theoretical one. This probably could be due to agglomeration of the resin particles within the rubber matrix. It has also been reported that the agglomeration of particles as well as state of agglomeration increase the suspension viscosity and Einstein's coefficient in comparison with the completely dispersed systems.[33] For a suspension viscosity including agglomeration of particle with random packing, a value of 6.76 has been reported for k_E.[35] It is also found that the values of k_E are the same for both SBR and NBR compounds at the same sulfur content; however, it increases by increasing the sulfur content from around 6.3 to 8.3. It seems that the sulfur content increases the affinity of the particles to form more agglomeration, which could be a consequence of decreasing the surface energy of the rubber phase. Such an observation has been addressed in the literature for blend of ethylene–propylene–diene rubber/propylene that a reduction in surface energy has been observed at high extent of crosslinking density.[36] This has been attributed to the reduction of the flexibility of both induced and permanent dipoles attached to the rubber segments within the vulcanized network.[36]

Modulus of the rubber/PH blends

Figure 10 shows the modulus of the blends as a function of volume fraction of PH obtained by the experimental measurements and estimated values using Halpin-Tsai equation. It is observed that the variation of the modulus with resin content for both rubbers can be well described by Halpin-Tsai equation at low resin content. After a certain value of resin content, $\sim$ 15 vol %, moduli indicate a deviation from eq. (5) and the results show a sharp increase, particularly at higher resin content. This observation suggests much more contribution of the PH upon the modulus of the blends at higher volume fraction. There could be some possibilities for this behavior. One possibility could be the alteration of the phase morphology of the blend and converting to cocontinuous morphology. Because, in such cases, the PH can play considerable role on the modulus of the blends.[34,35] However, this explanation is somewhat questionable, because the volume fraction of 0.15 seems to be too low for the rubber/PH blend to become cocontinuous. Only partial cocontinuity due to the tendency of the PH-dispersed phase for agglomeration may be a reasonable explanation for the mechanical behavior of the blend mentioned earlier.
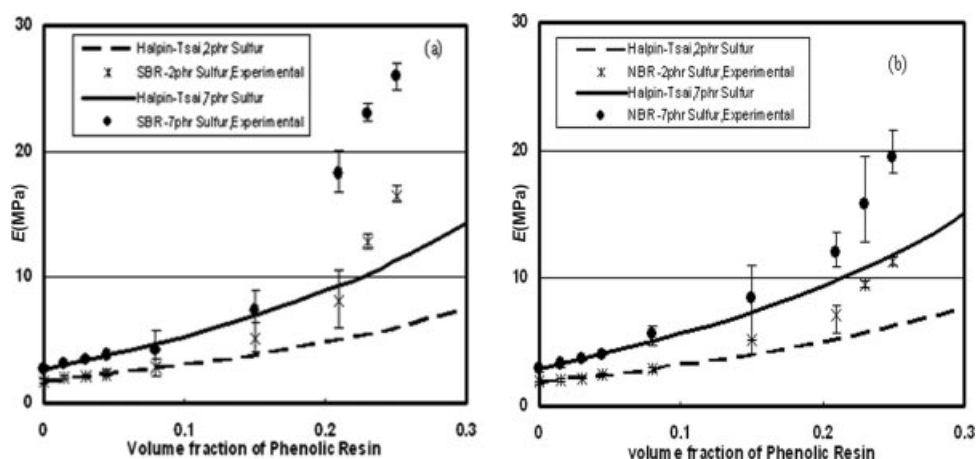
Figure 10 Modulus of blends as a function of resin content; (a) SBR/PH (b) NBR/PH.

Another possibility for deviation from eq. (5) could be the change of the mechanical properties of the rubber phase as a consequence of the addition of the resin. This explanation is most probable than the morphology inversion mentioned earlier and is completely consistent with swelling characteristic and dynamic mechanical behavior of the blends. As mentioned, addition of the resin to the rubber phase increases the crosslinking density of the rubber vulcanizates, resulting in higher modulus of the rubber phase than that of pure rubber vulcanizates. On the other hand, presence of PH in the rubber phase due to its partial solubility, as examined by dynamic mechanical tests, increases the rigidity of the molecular chains, leading to higher stiffness of the rubber phase in the blends. These evidences indicate that the modulus of the rubber phase in the blend is different than that of the pure rubber vulcanizates used in the Halpin-Tsai equation. Consequently, the misuse of the modulus of the rubber in Halpin-Tsai

equation could be responsible for the severe deviation from the model prediction.

From Figure 10, it is shown that effect of PH on enhancement of modulus of SBR/PH blend at high volume fraction of PH is much more pronounced than that of NBR/PH blend. This can be attributed to slightly higher solubility of the PH in SBR, as illustrated in dynamic mechanical tests, resulting in higher enhancement of modulus of SBR. Although the difference between solubility of PH in SBR and NBR is too small, but even very small amount of PH can have observable influence on the modulus of the rubber phase due to very high modulus of PH and its curative effect.

SEM observations

The blends of both rubbers with PH at different volume fractions are depicted in Figures 11 and 12. The SEM micrographs show dispersion of the PH
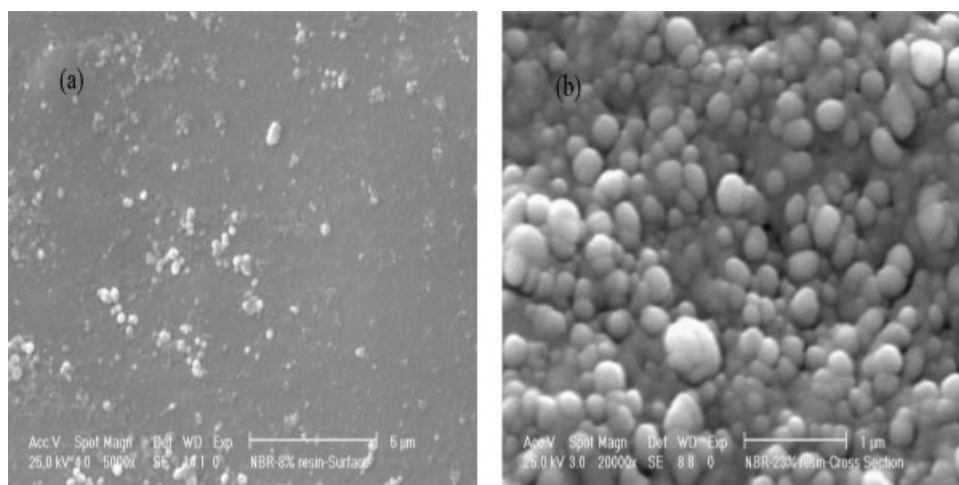

Figure 11 SEM micrographs of NBR/PH blends containing different volume percents of PH; (a) 8% and (b) 23%.
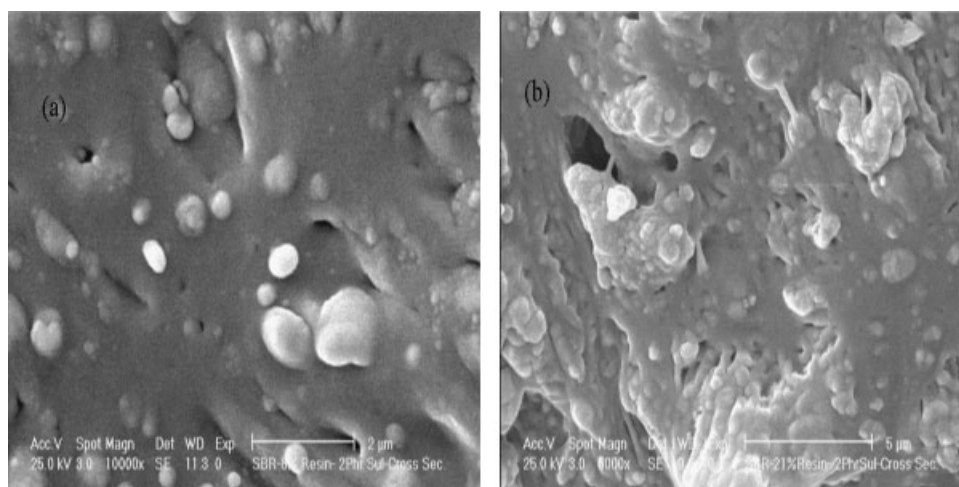
Figure 12 SEM micrographs of SBR/PH blends containing different volume percents of PH; (a) 8% and (b) 21%.

particles within the rubber matrix. The dispersed phase is almost spherical and indicates a good adhesion with the matrix, because no interfacial debonding is observed in the SEM micrographs of the fractured surfaces. However, it can be shown that the PH particles tend to form agglomeration even at low volume fraction of PH. This observation is in complete agreement with the higher value of k_E mentioned earlier in the mechanical properties of the blends. It is also seen that the matrix-dispersed type of microstructure is dominant, although a compact dispersed morphology is observed at high volume fraction of PH.

CONCLUSIONS

Thermal, mechanical, and microstructural characteristics of NBR/PH and SBR/PH blends are investigated in this study. It is shown that the glass-transition of both rubbers is shifted slightly at various compositions of rubber/PH mixtures, showing partial solubility of the PH in the rubber phase. However, these mixtures are incompatible blends and, as evidenced by SEM micrographs, exhibit two-phase microstructures in which rigid spherical particles of PH are embedded in a soft rubber matrix. The results obtained based on Taguchi's analysis show that sulfur has a dominant effect on the crosslinks structure of the vulcananized rubber, although other curing ingredients including accelerator and activator influence the crosslinks network more or less. Moreover, it is shown that crosslinking density of the rubber phase in the blend is also affected by PH. Soluble part of the resin phase, as supported by dynamic mechanical analysis, is shown to be responsible for alteration of crosslinking density of the rubber phase due to curative role of PH. On the other hand, presence of the rigid PH chains in the cross-

link network of the rubber restricts the molecular motion and makes the rubber phase to be stiffer than that of pure rubber vulcanizates. Deviation of the blend modulus versus PH content from Halpin-Tsai model is known as a further evidence for the role of PH on the rubber phase.

Crosslinking density of the SBR is found to be lower than that of NBR at a certain curing agent. This is attributed to the hindrance effect of benzene side group of SBR which prevents more crosslinks to be formed in the polymeric chains. Additionally, thermal stability of SBR blends decreases noticeably by increasing the sulfur content when compared with that of NBR/PH. This is probably due to the formation of more polysulfidic crosslinks in SBR vulcanizates.

References

1. Jacko, M. G.; Rhee, S. K. In Encyclopedia of Composite Materials and Components; Grayson, M., Ed.; Wiley, 1983, 144.
2. Bijwe, J. Polym Compos 1997, 18, 378.
3. Chan, D.; Stachowiak, G. W. Proc Inst Mech Eng Part D: J Automobile Eng 2004, 218, 953.
4. Jacko, M. G.; Tsang, P. H. S.; Rhee, S. K. Wear 1984, 100, 503.
5. Yensik, M. A. U.S. Pat. 5,529,666 (1996).
6. Knop, A.; Pilato, L. A. Phenolic Resins, Chemistry, Applications and Performance; Springer-Verlag: Berlin, 1985.
7. Tsang, P. H.; Coyle, J. P.; Liu, T.; VanderPoorte, J. G. U.S. Pat. 4,537,823 (1985).
8. Kane, J. F.; Mowrer, N. R. U.S. Pat. 5,736,619 (1998).
9. Adelmann, J. C. U.S. Pat. 3,959,194 (1976).
10. Littlefield, J. B. U.S. Pat. 4,313,869 (1982).
11. Eschen, F. W. U.S. Pat. 3,832,325 (1974).
12. Gibson, P. A. In Seminar Publication on Railway Traction and Braking; Institute of Mechanical Engineers, 1996; p 75.
13. Haddadi, E.; Abbasi, F.; Shojaei, A. J Appl Polym Sci 2005, 95, 1181.

14. Borowitz, J.; Kosfeld, R. Rheol Acta 1981, 20, 370 (in German).
15. Kosfeld, R.; Borowitz, J. Rheol Acta 1979, 18, 51–61 (in German).
16. Camino, G.; Alba, E.; Buonfico, P.; Vikoulov, V. J App Polym Sci 2001, 82, 1346.
17. Coran, A. Y. J Appl Polym Sci 2003, 87, 24.
18. Montgomery, D. C. Design and Analysis of Experiments; Wiley: New York, 1997.
19. Liu, S. J.; Chen, C. F. Plast Rubber Compos 2000, 29, 411.
20. Abbasi, F.; Mirzadeh, H.; Katbab, A. A. J Appl Polym Sci 2002, 85, 1825.
21. Kim, S. J; Kim, K. S.; Jang, H. J Mater Process Tech 2003, 136, 202.
22. Chen, D.-C.; Chen, C.-F. J Mater Process Tech 2006, 177, 104.
23. Yang, C.; Hung, S. W. Int J Adv Manuf Tech 2004, 24, 353.
24. Kim, Y. H.; Lee, J. J.; Nisitani, H. Int J Mod Phys B 2003, 17, 1845.
25. Roy, R. K. Design of Experiments Using the Taguchi Approach; Wiley: New York, 2001.
26. Sperling, L. H. Introduction to Physical Polymer Science, 4th ed; Wiley-Interscience: New York, 2006.
27. Rodriguez, F. Principles of Polymer Systems, 2nd ed; McGraw-Hill International Book: London, 1985.
28. Brandrup, J.; Immergut, E. H.; Grulke, E. A. Polymer Handbook; Wiley-Interscience: New York, 1999.
29. Morrell, S. H. In Rubber Technology and Manufacture; Blow, C. M., Ed.; Second Butterworth & Co Ltd: London, 1975; Chapter 5.
30. Hofmann, W. Rubber Technology Handbook; Hanser Publishers: Germany, 1988.
31. Odian, G. Principles of Polymerization; Wiley: New York, 1981.
32. Samui, A. B.; Suryavanshi, U. G.; Patri, M.; Chakraborty, B. C.; Deb, P. C. J Appl Polym Sci 1998, 68, 255.
33. Nielsen, L. E.; Landel, R. F. Mechanical Properties of Polymers and Composites, 2nd ed; Marcel Dekker: New York, 1994.
34. Nielsen, L. E. Predicting the Properties of Mixtures: Mixture Rules in Science and Engineering; Marcel Dekker: New York, 1978.
35. Lewis, T. B.; Nielsen, L. E. Trans Soc Rheol 1968, 12, 421.
36. Goharpey, F.; Katbab, A. A.; Nazockdast, H. J Appl Polym Sci 2001, 81, 2531.