

Utilization of Peanut Shell Powder as a Novel Filler in Natural Rubber

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ABSTRACT: This work focuses on the use of peanut shell powder (PSP) as filler in natural rubber (NR). Peanut, one of the food crops in the world, generates large amounts of waste namely peanut shell. Modified and unmodified PSP-NR composites with varying particle size and dosages were prepared by an open mill mixing technique. The processing characteristics and the curing behavior of the composites were determined by Monsanto Rheometer. The technological performance was done by analyzing the tensile strength, tear strength, and hardness of the vulcanizates. The swelling studies were carried out to observe the crosslink density, rubber-filler interaction, and the reinforcing nature

of the filler on NR. The observed variation in mechanical properties has been supported by the fractography of the composites obtained by Scanning Electron Microscopy. The result of the study shows that the PSP is most effective filler in NR at 10 parts per hundred (phr) loading. Filler reinforcement ability of modified PSP is more when compared with unmodified PSP; therefore, modified PSP-NR composites shows better physicochemical properties. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2322–2334, 2012

Key words: NR-PSP composites; cure characteristics; swelling behavior; crosslink density; mechanical properties

INTRODUCTION

Natural rubber (NR) exhibits outstanding properties such as green strength and tensile strength since it can crystallize spontaneously when it is strained. Rubber composites are mainly used for making ropes, hose, belt, and mats^{1,2} and NR is biodegradable material, which can disintegrate in soil by specific microorganisms.³ It has already been studied as a matrix for biocomposites with chitin whiskers⁴ and cellulose whiskers extracted from *Syngonanthus nitens*⁵ and rachis of palm tree.⁶ Considerable mechanical property improvement has been observed with composites of natural amorphous polymers.^{7,8} A wide variety of particulate fillers have been used in the rubber industry for various purposes, which is dependent on reinforcement, low material cost, and processing ability.⁹ Reinforcement is primarily the enhancement of strength and related properties, like abrasion resistance, hardness, and modulus.^{10,11}

Recently a great deal of attention has been paid to the application of biodegradable polymers such as starch,¹² lignin,¹³ cellulose,¹⁴ and chitin¹⁵ and its

derivatives to replace the conventional petroleum based polymers that cause environmental problems due to its nondegradability. Nowadays, there has been simultaneous and growing interest in developing the use of biobased products that can reduce the dependence on fossil fuel and move to a sustainable material basis.^{16–19} This particular situation provides biocomposites possessing outstanding properties, which have never been found in conventional composites.^{20,21} Therefore, biobased biodegradable composites have become the next generation materials.²² Due to the rapid increase in the cost of raw rubber and other compounding ingredients, most rubber manufactures have made great efforts to reduce the production cost and increase competitiveness.

The environmental conservation is a permanent concern and, in this respect, several studies are being envisaged with an aim to transforming rejects into useful materials, which could be disposed with no damage to the environment, or even better, into reusable goods, and this field is very attractive from both the ecological and economic point of view.^{23,24} The production of peanut, one of the food crops in the world, generates large amounts of waste namely peanut shell. Efforts to find utilization to these materials have resulted mostly in low value or limited applications. In this regard, peanut shell powder (PSP) seems to be an interesting candidate due to its chemical composition. Reports on the application of PSP as filler in polymers have been quite limited. The motivation for such a search is

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reasonable mainly from the ecological stand point. Thus, the use of PSP as a replacement for commercial fillers is of great interest. In this work, PSP is used as alternative filler for NR. The chemical composition of PSP is similar to hard wood, but with higher cellulose content having a bulk density of 0.10 g/cm^3 and moisture content of 25%.

The effects of interaction between the rubber and filler on the adhesion characteristics of elastomer compositions were studied by Kiselev and Vnu-kova.²⁵ When filler is introduced, adhesion interactions between the elastomer and the filler increase with decreasing size of the filler particles. The surface interaction between fillers and rubber molecules or network segments involves a range of bond energies from relatively weak Van der Waals force to very strong chemical bonds. In all cases, physical adsorption undoubtedly occurs to varying degrees depending on particular surface and molecular segments. The filler-polymer related effects are determined by the special structure of the filler in the rubber matrix and its interaction with the polymer. The occluded rubber contributes to this effect. Polymer chains are trapped in the voids of the filler agglomerates and aggregates; they are immobilized and shielded from deformation. They do not contribute to the elastic behavior of the matrix, as their properties resemble the properties of the rigid filler particles rather than the properties of the elastic and flexible free polymer chains. Occluded rubber increases the effective filler loading and thus the strain independent contribution to the modulus.

The treatments to improve fiber-matrix adhesion in composites include chemical modification of fiber (using anhydrides, epoxies, isocyanates, etc.), grafting of polymers into lignocellulosic and use of compatibilizers and coupling agents.²⁶ Various treatments on some lignocellulosic fibers like physical, physicochemical, chemical grafting, etc. to improve their properties were reported by Belgacem and Gandini.²⁷ The main disadvantage of using cellulose as reinforcing filler for composite material is the poor interaction between cellulose particle and polymer matrix.²⁸ Noncompatibility of cellulosic fibers with nonpolar matrices, which are mostly hydrophobic in nature poses problems due to high polarity and hydrophilicity in cellulosic fibers. Therefore, modification of the surface of natural cellulosic fibers is critically to increase the hydrophobicity of the fibers and enhances the adhesion with polymer matrix. Hence, modification of natural fiber surface is used to increase the hydrophobic character or decrease the hydrophilicity of the fibers. The adhesion of cellulose to the matrix can be improved by minimizing the surface tension. Surface modification of cellulosic fibers involves removal of impurities from the fiber surface, ultimately enhances its physi-

cal and chemical properties. Alkaline treatment of cellulosic fibers with sodium hydroxide (NaOH) is a well known method, which has been employed to improve the fiber-matrix interface bonding.²⁹ NaOH removes natural fats and waxes from cellulosic fiber surfaces and thus exposing chemically reactive functional groups such as hydroxyl ($-\text{OH}$) groups. The removal of the surface impurities from the cellulose fibers also improves the surface roughness to the fibers.³⁰ After treatment with NaOH, tensile strength increased due to removal of impurities from rice husk surface, which contain compounds like lignin, hemicellulose, fats, and waxes having chemically reactive functional groups like $-\text{OH}$. Alkali treatment introduces the rough surface on PSP filler that can increase the interfacial interaction between filler and matrix. It was reported that alkali treatment on oil palm fiber was more effective for improving the fiber-matrix adhesion compared to other methods.³¹ The developments in chemical modification and characterization of natural fiber-polymeric composites have been studied by John and Anandjiwala³² and concluded that alkali treatment is the most common and efficient method of chemical modification to treat natural fibers. Herrera-Franco et al.³³ also verified that alkali treatment results in improvement in the interfacial bonding, giving rise to additional sites of mechanical interlocking, thereby promoting more polymer-filler interpenetration at the interface.

This article therefore aims at investigating the feasibility of using unmodified PSP and alkali treated PSP of two different particle sizes (0–45 and 45–90 μm) as filler in NR matrix and evaluation of their physicochemical properties.

EXPERIMENTAL

Materials

NR (ISNR 5) was purchased from Rubber Research Institute, Kottayam, India. Peanut shell was purchased locally and powdered from flour mill. The powder was sieved and the fraction first collecting through 90 μm mesh size sieves and then 45 μm sieve to get the particles of 45–90 μm and 0–45 μm sizes, respectively. NaOH and toluene (Merck) were used as received. Other compounding ingredients such as zinc oxide, stearic acid, sulfur, *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS), and 2,2,4-trimethyl-1,2-dihydroquinoline (TDQ) were of commercial grade and were obtained from local rubber chemical suppliers.

Modification of PSP using NaOH

One gram of PSP (0–45/45–90 μm) was put in 10% 10 mL NaOH solution for 5 h with continuous stirring

TABLE I
Mixing Formulation

Ingredients	Phr ^a
Natural rubber	100
Zinc oxide	5
Stearic acid	2
TDQ ^b	1
Processing oil	1/20th of filler
Filler ^c	0, 10, 20, 30, and 40
CBS ^d	0.8
Sulfur	2.8

^a Parts per hundred of rubber.

^b 2,2,4-Trimethyl-1,2-dihydroquinoline.

^c PSP and alkali treated peanut shell powder of 0–45 and 45–90 micron size.

^d *N*-Cyclohexyl-2-benzothiazyl sulfenamide.

using a mechanical stirrer and was kept for 24 h. Rinsed and washed with water until the water became neutral. The powder was filtered out and was dried in vacuum at 70°C for 24 h for further use.

Chemical modification of the PSP by alkali treatment was monitored using Jasco FTIR spectrometer. The sample for FTIR analysis was prepared as follows: previously dried filler was powdered in a mortar, cooled with liquid nitrogen, and 1 mg of the powder dispersed in anhydrous KBr and was subjected to FTIR analysis.

Preparation of NR-PSP composites

All compounds used were of same composition, except for the amounts of PSP, which were varied from 10–40 phr (parts per hundred). All chemicals were powdered and weighed accurately. Compounding was done in accordance with American Society for Testing and Materials (ASTM) designation D15-627, using a two roll mill at 27°C. Total mixing time has been kept to a minimum to avoid sticking of the rubber compound to the mill rolls. Care was taken to ensure that the mill-roll temperature was not too high, that is exceeding the set temperature, to avoid any cross-linking during mixing. This has been achieved by using cooling. The Nip gap, mill roll speed ratio, time of mixing (12 min) and the sequence of addition of the ingredients were kept the same for all the composites. Table I shows the formulation used in this study. The samples were named as PSP_{45–90} and PSP_{0–45} for unmodified PSP of 45–90 and 0–45 μm sizes, respectively. Similarly alkali treated fillers were named, respectively, as APSP_{45–90} and APSP_{0–45}.

Cure characteristics and vulcanization process

Optimum cure time (t_{90}) for each compound was determined by using Monsanto Moving Die Rheometer (MDR 2000) according to ASTM D 2084-93,

operating at 150°C. After that, the rubber compounds were vulcanized in a hydraulic press to the optimum cure time at the same temperature along the mill grain direction, under a pressure of 6.7 MPa (mold dimension: 150 × 150 × 2 mm³). The various rubber compounds were compression molded at the vulcanization temperature (150°C) according to their respective t_{90} , into test specimens.

Testing of rubber vulcanizates

Equilibrium swelling measurements of the composites were determined in toluene. The vulcanizate with a thickness of 1 mm was cut into rectangular shape weighing about 0.5 g. Then, the sample was dried in a vacuum oven at room temperature. The sample was immersed in 20 mL toluene for 2 days at 27°C. The swollen sample was removed from the toluene and the excess toluene was blotted out. Then, the weight of swollen sample was determined accurately. Swelling ratio, crosslink density, and rubber-filler interactions were measured using this data.

To study the stress-strain behavior of PSP-NR composites, Universal Testing Machine INSTRON-3365 (series IX Automated Materials Testing System 1.38, model-441, Instron Corporation) was used. Tensile properties of the blends were examined according to ASTM D 412-1998, at a crosshead speed of 500 mm/min after conditioning at 27°C. The experimental conditions and equipment for tear measurements were same as that of tensile testing. Tear test was conducted as per ASTM D 624-2000, with the “Die B” crescent shaped test pieces, which were mounted on the Universal Testing Machine with a test speed of 500 mm/min at 27°C. Shore-A-Durometer was used to measure the hardness of the prepared NR-PSP composites according to ASTM D 2240-2004. Density of the prepared NR composites was measured by Electronic Densimeter HD-200 S. A ZWICK DIN Abrader was used to measure the abrasion resistance as per ASTM D-2228 (1994).

Scanning electron microscopy

The morphology of NR-PSP and the modified NR-PSP vulcanizates was studied by a Field Emission Scanning Electron Microscopy (FESEM), Variable Pressure, Hitachi, SU 6600 FESEM. The specimens for SEM were prepared by fracturing the vulcanized blends in their glassy state at liquid nitrogen temperature. The samples were sputtered with gold before examination to prevent charging on the surface.

RESULTS AND DISCUSSION

FTIR spectra

The alkali treatment changes the native cellulose by a process known as alkalization

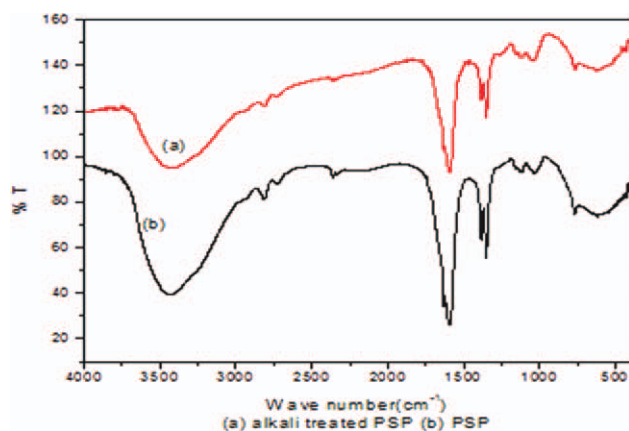
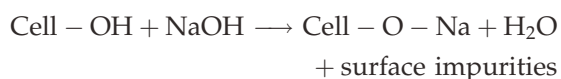


Figure 1 FTIR Spectra of PSP and alkali treated PSP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



IR spectra of PSP and alkali treated PSP (APSP) are shown in Figure 1. From the spectrum, it can be seen that in unmodified PSP a broad peak in the region $3315\text{--}3516\text{ cm}^{-1}$, which is characteristic of the cellulosic $-\text{OH}$ groups. The intensity of this $-\text{OH}$

group is reduced in alkali treated PSP due to the removal of $-\text{OH}$ group by $-\text{ONa}$. Corresponding decrease in the intensity of all other peaks has also been observed in APSP spectrum, which is due to the removal of lignin and impurities after alkali treatment.

Cure characteristics

Figure 2 shows the rheographs of unmodified and alkali treated NR-PSP mixes of $45\text{--}90\text{ }\mu\text{m}$ and $0\text{--}45\text{ }\mu\text{m}$ sizes. The presence of PSP in NR composites increases the rubber compound viscosity. The increment in torque values with increasing filler loadings indicated that as more and more filler dispersed into the rubber matrix, the mobility of the macromolecular chains of the rubber decreased, which ultimately resulted in the rigidity of vulcanizates.

Table II represents the optimum curing time, minimum torque, maximum torque and scorch time of the PSP filled rubber composites. Average values, standard deviation, and 95% confidence interval of three tests are reported. Both scorch time and optimum curing time were found to decrease consistently with increasing filler loading. This clearly indicates that filler increases the rate of curing of

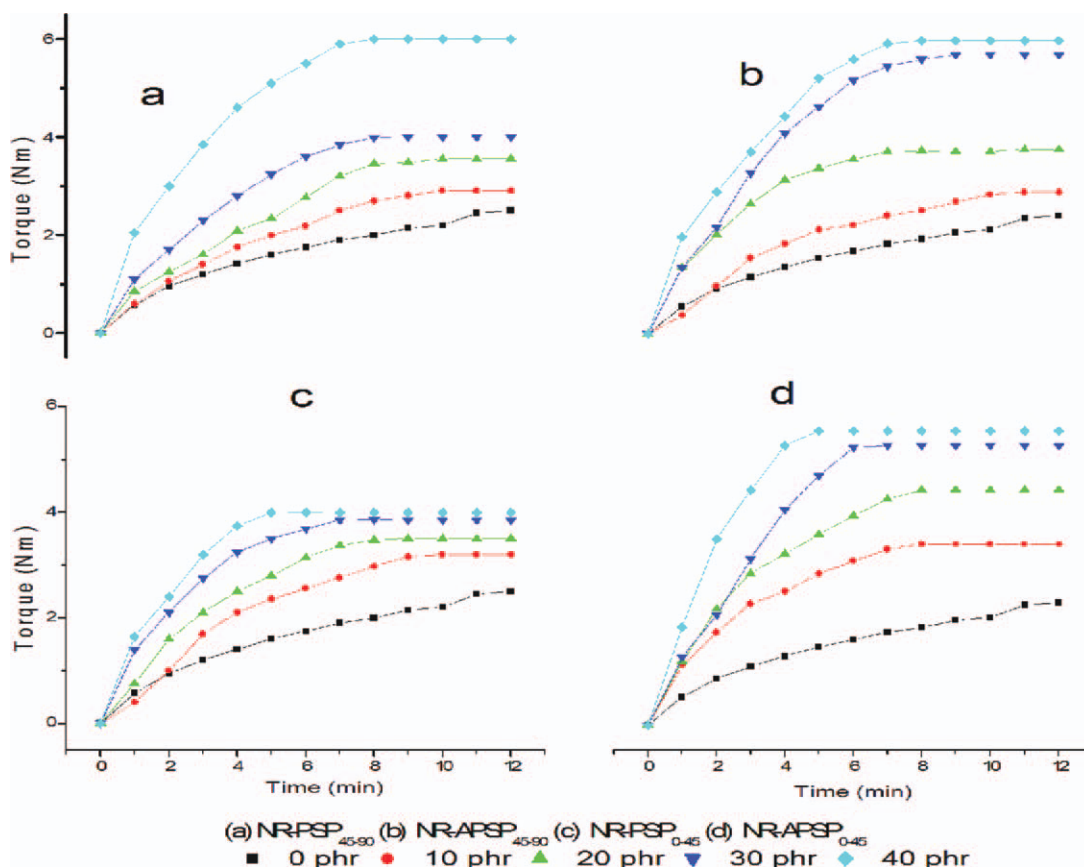


Figure 2 Torque–time curves at different fiber loadings. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Curing Characteristics of PSP-Filled Natural Rubber Composites

Samples	Loading (phr)	Maximum torque (N m)	Minimum torque (N m)	Scorch time (min)	Cure time (min)
NR		2.5 ± 0.8	0.007 ± 0.001	3.33 ± 0.8	11.5 ± 1.4
PSP ₄₅₋₉₀	10	2.9 ± 0.9	0.003 ± 0.001	4.4 ± 1.3	10.13 ± 1.1
	20	3.6 ± 1.1	0.006 ± 0.0012	4.3 ± 1.1	9.99 ± 1
	30	4 ± 0.9	0.009 ± 0.0016	4.1 ± 1	8.57 ± 1.3
	40	6.1 ± 0.77	0.02 ± 0.004	3.9 ± 1.2	8.1 ± 1.6
APSP ₄₅₋₉₀	10	3 ± 0.6	0.009 ± 0.002	4.1 ± 1	10.9 ± 1.1
	20	3.9 ± 0.8	0.012 ± 0.001	2.7 ± 1.1	10.2 ± 1.2
	30	5.9 ± 1.2	0.019 ± 0.001	2.8 ± 0.9	8.6 ± 1
	40	6.2 ± 0.78	0.022 ± 0.008	2.5 ± 1	7.5 ± 0.9
PSP ₀₋₄₅	10	3.2 ± 0.88	0.006 ± 0.007	2.99 ± 1.1	9.5 ± 2.1
	20	3.52 ± 0.1	0.008 ± 0.001	2.66 ± 1.4	8.7 ± 1
	30	3.9 ± 0.7	0.019 ± 0.003	2.55 ± 0.7	8.1 ± 0.9
	40	4 ± 1	0.023 ± 0.002	2.4 ± 0.6	5.1 ± 0.09
APSP ₀₋₄₅	10	3.7 ± 1.2	0.015 ± 0.002	2.23 ± 1	8.1 ± 1.4
	20	4.8 ± 0.9	0.140 ± 0.001	1.99 ± 1.1	7.7 ± 1.7
	30	5.7 ± 0.6	0.166 ± 0.002	1.6 ± 0.9	6.3 ± 1
	40	6 ± 1.1	0.190 ± 0.002	1.44 ± 0.67	5 ± 1

NR-PSP composites. It was reported that, as the filler loading increases, the incorporation time of filler into rubber matrix also increases and consequently generates more heat due to additional friction.³⁴ It was also observed that, at a given loading, both the scorch time and optimum curing time of the PSP₀₋₄₅ filled composites are shorter than those of PSP₄₅₋₉₀ filled composites. Due to the high specific surface area of PSP₀₋₄₅, it imparts the highest viscosity to the composites and, thus, the highest temperature rise during mixing. As it is well known that the specific surface area is inversely proportional to the primary particle size, the results therefore indicate that PSP₀₋₄₅ has the smaller primary particle size, compared with PSP₄₅₋₉₀. Therefore PSPs of 0–45 μm size filled composites possesses the shorter scorch time and optimum curing time. The minimum torque shows a slight increase with increasing filler loading (Table II). This indicates that the processability of the compounds becomes a little more difficult. This increase may be attributed to the agglomeration of filler particles in the NR matrix. At low loading, the chances of forming aggregates are less compared to higher filler loading and hence good dispersion of

the filler is achieved. This is schematically represented in Figure 3.

Maximum torque M_H , as shown in Table II, increases with the increasing of PSP filler loading. At higher loading of PSP, the mobility of macromolecular chains of rubber decreases and resulting in more rigid NR compounds.³⁵ At a given PSP loading, NR compounds with treated PSP filler exhibits higher maximum torques than untreated PSP filler. This observation shows that better rubber-filler interaction was achieved for NR compounds with treated PSP filler.

Calculation of swelling ratio, crosslink density, and rubber-filler interaction from swelling behavior

The crosslink density results are reported in terms of a swelling ratio in toluene according to ASTM D 471, which is defined as:

$$R (\%) = [(w_s - w_i)/w_i] \times 100 \quad (1)$$

where R is the swelling ratio and w_i and w_s are the weights of the test specimen before swelling and

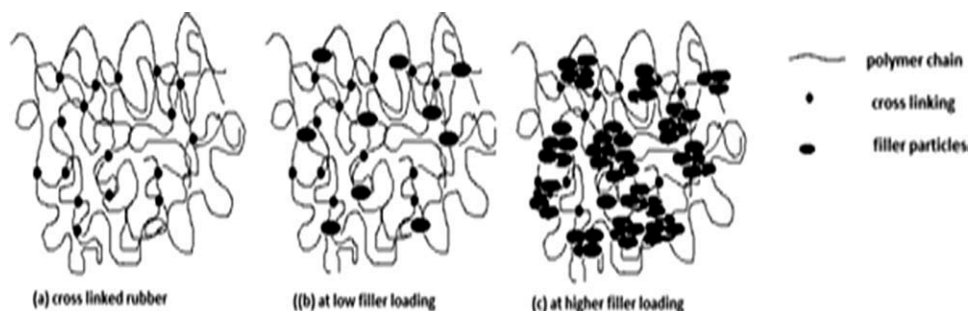


Figure 3 Schematic representation of the unfilled and filled NR composites.

TABLE III
Swelling Ratio (R), Volume Fraction (V_r), and Number of Elastically Active Chain per Unit Volume (n) Obtained From Swelling Data

Samples	Loading (phr)	Density of polymer composites (g/cm^3)	R (%)	V_r	$n \times 10^{-4}$ (mol/cm^3)
NR	0	0.996 ± 0.08	426 ± 12	0.1340 ± 0.001	0.5908 ± 0.02
PSP ₄₅₋₉₀	10	0.999 ± 0.06	371 ± 10	0.1417 ± 0.09	0.6665 ± 0.03
	20	1.123 ± 0.09	336 ± 16	0.1466 ± 0.05	0.7157 ± 0.07
	30	1.212 ± 0.06	322 ± 9	0.1483 ± 0.07	0.7338 ± 0.09
	40	1.326 ± 0.09	$310 \pm$	0.1513 ± 0.03	0.7658 ± 0.1
APSP ₄₅₋₉₀	10	0.858 ± 0.08	354 ± 15	0.1456 ± 0.06	0.7054 ± 0.12
	20	0.968 ± 0.06	352 ± 10	0.1464 ± 0.1	0.7133 ± 0.08
	30	1.023 ± 0.03	317 ± 11	0.1480 ± 0.11	0.7300 ± 0.08
	40	1.135 ± 0.01	293 ± 10	0.1576 ± 0.09	0.8370 ± 0.09
PSP ₀₋₄₅	10	0.921 ± 0.02	352 ± 9	0.1456 ± 0.02	0.7046 ± 0.06
	20	0.988 ± 0.06	327 ± 16	0.1529 ± 0.04	0.7844 ± 0.08
	30	1.124 ± 0.08	290 ± 13	0.1569 ± 0.09	0.8297 ± 0.046
	40	1.25 ± 0.09	280 ± 11	0.1584 ± 0.1	0.8463 ± 0.07
APSP ₀₋₄₅	10	0.748 ± 0.01	361 ± 19	0.1511 ± 0.09	0.7643 ± 0.09
	20	0.939 ± 0.09	303 ± 12	0.1595 ± 0.06	0.8599 ± 0.055
	30	1.01 ± 0.1	289 ± 8	0.1604 ± 0.1	0.8702 ± 0.08
	40	1.124 ± 0.11	246 ± 12	0.1635 ± 0.1	0.9074 ± 0.07

after swelling, respectively. The crosslink density is also calculated based on the Flory–Rehner equation as follows³⁶:

$$-\left[\ln(1 - V_r) + V_r + \chi V_r^2\right] = V_s n \left[V_r^{\frac{1}{3}} - \frac{V_r}{2} \right] \quad (2)$$

where χ is the polymer solvent interaction parameter, V_s is the molar volume of the solvent, n is the number of elastically active chain per unit volume and V_r is the volume fraction of polymer in swollen mass, which is calculated by the equation³⁷

$$V_r = \frac{\frac{w_d - f_{in} w_i}{\rho_r}}{\frac{w_d - f_{in} w_i}{\rho_r} + \frac{w_o^{sol}}{\rho_s}} \quad (3)$$

Here, w_d is the weight of the dried swollen sample after 24 h, f_{in} is the weight fraction of insoluble components, which depends on the sample recipe, ρ_r is the density of polymer composites and ρ_s is the density of solvent, w_o^{sol} is the equilibrium weight of the swelling solvent, $(w_o^{sol}) = w_{24h}^{sol} = w_s - w_d$, where w_s is the weight of the swollen sample. In this work, zinc oxide and filler particles were considered to be insoluble components. These particles do not swell and have to be subtracted to obtain the actual rubber fraction.

The interaction parameter, which is calculated by the equation^{38,39}

$$\chi = \beta + \frac{V_s}{RT} (\delta_s - \delta_p)^2 \quad (4)$$

where β is the lattice constant (0.38), V_s is the molar volume of the solvent, R is the universal gas con-

stant, T is the absolute temperature (300 K), δ_s is the solubility parameter of the solvent and δ_p is the solubility parameter of polymer (δ_s for toluene is 8.9 and δ_p for NR is 8.1). The interaction parameter between NR and toluene in literature is 0.393,⁴⁰ experimental value is 0.4. The molar volume and density of the solvent were taken as $V_s = 106.2$ mL/mol and $\rho_s = 0.87$ g/cm³, respectively.

Table III represents the crosslink density and their 95% confidence intervals represented in terms of the swelling ratio and the number of elastically active chain per unit volume (n) calculated from the Flory–Rehner eq. (2). As can be seen the swelling ratio decreases whereas the number of elastically active chain per unit volume increases consistently with increase in filler loading. These results indicate that crosslink density of elastically active chains per unit volume increases consistently with increasing filler loading. Figure 4 shows the schematic representation of the swelling behavior of unfilled and filled NR-PSP composites. Swelling ratio is inversely proportional to crosslink density. It could also be observed that, at a given loading, APSP₀₋₄₅ yields the rubber composites with the highest degree of crosslinking, compared with PSP₀₋₄₅, APSP₄₅₋₉₀, and PSP₄₅₋₉₀. The crosslink density decreases in the order, APSP₀₋₄₅ > PSP₀₋₄₅ > APSP₄₅₋₉₀ > PSP₄₅₋₉₀. Because, cellulose has a number of hydroxyl groups on its surface, which result in strong filler–filler interactions due to hydrogen bonding, the added cellulose particles became aggregated and formed a coherent gel in the rubber matrix. This physically prevented the rubber from being readily vulcanized and, thus, decreased the crosslink density. This formation of aggregates depends both on the reinforcing ability (in this case hydrophilicity of the PSP filler) and filler particle

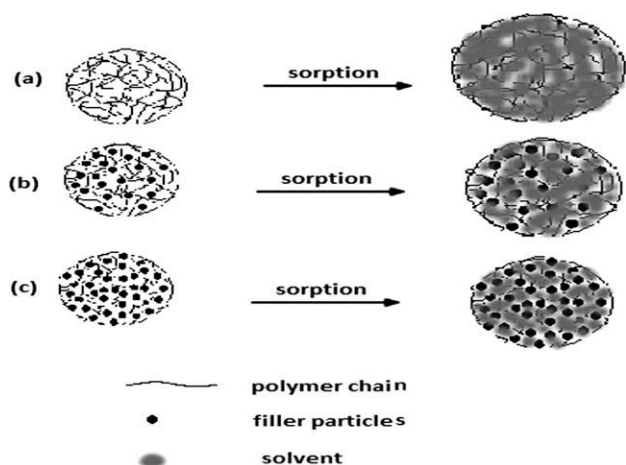


Figure 4 Schematic representation of the swelling behavior of unfilled and filled NR composites. (a) unfilled NR, (b) lower filler loading, and (c) higher filler loading.

size. That's why PSP₄₅₋₉₀ and APSP₄₅₋₉₀ form more aggregates in 40 phr NR composites. This can be clearly manifested from the SEM of NR-PSP composites (40 phr), Figure 12. The results imply that the combined effect of specific surface area and reinforcing ability of the filler are the main factors affecting the crosslink density of the rubber vulcanizate and the alkali treatment enhances the crosslink density compared to unmodified filler.

Rubber-filler interactions

Lorenz and Parks' equation⁴¹ has been applied to study rubber-filler interaction. According to this equation:

$$\frac{Q_f}{Q_g} = ae^{-z} + b \quad (5)$$

where Q is defined as grams of solvent per gram of hydrocarbon and is calculated by

$$Q = \frac{\text{swollen weight} - \text{dried weight}}{\text{original weight} \times 100 / \text{formula weight}}$$

The subscripts f and g in eq. (5) refer to filled and gum vulcanizates, respectively. Z is the ratio by weight of filler to the rubber hydrocarbon in the vulcanizate, while a and b are constants. The higher the Q_f/Q_g values, the lower the extent of the interaction between the filler and the matrix.

From Figure 5, with their 95% confidence interval, it can be seen that the value of Q_f/Q_g for both untreated and treated PSP filled NR compounds increased with the increasing in PSP loading. The higher the Q_f/Q_g value, the lower will be the extent of interaction between rubber and filler. It shows

that NR compounds with higher amount of PSP loading have higher Q_f/Q_g , shows weaker rubber-filler interaction. At a given PSP loading, it can be seen that NR compounds with treated PSP₀₋₄₅ loading has lower Q_f/Q_g ratio than the untreated PSP₀₋₄₅ filled NR compounds. It indicates that treated PSP filled NR compounds have better rubber-filler interaction than untreated PSP filler. Similarly at given PSP loading, both APSP₄₅₋₉₀ and PSP₄₅₋₉₀ have higher Q_f/Q_g ratio than the untreated PSP₀₋₄₅ and APSP₀₋₄₅ filled NR compounds. The NR-PSP composites having minimum Q_f/Q_g are associated with maximum tensile strength, tear strength, abrasion resistance, and crosslink density. This results obtained are similar to the results reported by Jacob et al.³⁵ and supported by the tensile results represented in Table III.

Effect of loading on mechanical properties

Figure 6 displays the representative tensile stress-strain curves for the unmodified and alkali treated NR-PSP composites of 45–90 μm and 0–45 μm sizes. The stress continuously increases with the strain, and the curves show significant yielding after an elongation of 300% that resembles typical uncured elastomeric behavior. For all the uncured composites, discussed within this section, the tensile strength is taken as the maximum stress point in the stress-strain curves and the corresponding values are registered in Table IV.

Table IV shows the effects of filler loading on tensile properties. Average values, standard deviation and 95% confidence interval of three tests are reported. These types of error variation has been

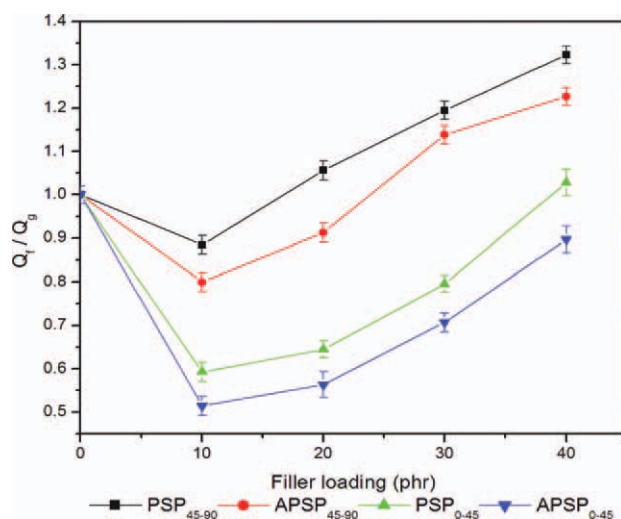


Figure 5 The effect of PSP loading on rubber-filler interaction (Q_f/Q_g) NR-PSP composites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

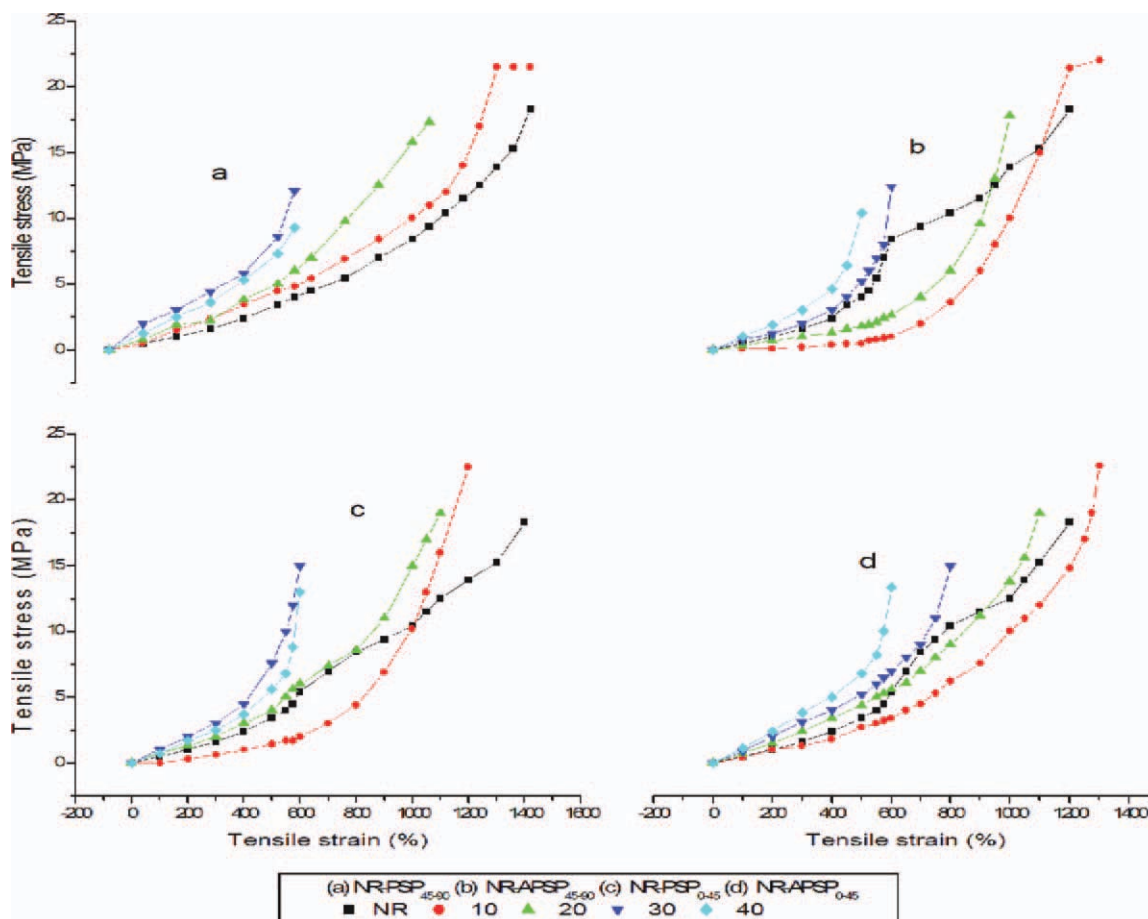


Figure 6 Stress-strain curves of cured NR-PSP composites at varying PSP loading. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

found in the mechanical properties of chemically modified starch reinforced NR composites,⁴² reinforcement of NR with silica/carbon black hybrid filler.⁴³ The tensile strength shows a maximum at 10 phr rubber PSP composites as shown in Table IV. Further increase in filler loading leads to a decrease in tensile strength. This means that the more uniform distribution of filler in NR is in 10 phr loading and this loading provides a large interfacial area of contact, resulting in better interfacial adhesion. It is clear that at 10 phr filler loading, smaller particle size and uniform dispersion of filler in NR compounds contribute to a higher tensile strength. However, when more than 10 phr filler was used, the weak interaction and bonding between the filler particles and the NR matrix is responsible for the deterioration of tensile strength. As the filler concentration increases, agglomeration and hence filler-filler interaction of the PSP filler also increases. It was also found that the degree of reduction from 10 to 40 phr loading was less pronounced for PSP₀₋₄₅ and APSP₀₋₄₅ filled vulcanizate compared with PSP₄₅₋₉₀ and APSP₄₅₋₉₀ filled vulcanizates. As PSP₄₅₋₉₀ and APSP₄₅₋₉₀ possess a very low specific

surface area, when incorporated into rubber compounds it causes severe reduction in the tensile strength, particularly at high loading. The highest value of tensile strength was exhibited by APSP₀₋₄₅ vulcanizates, which is due to the combined effect of high specific surface area of 0-45 μm size filler and more reinforcement of alkali treated filler with NR matrix than PSP₀₋₄₅, PSP₄₅₋₉₀, and APSP₄₅₋₉₀. It was reported that tensile strength of liquid epoxidized NR-rice husk composites increased after alkali treatment of rice husk, which is attributed to the removal of impurities from the rice husk surface like lignin, hemi-cellulose, and fats.⁴⁴

As expected, the elongation at break (EB) tends to reduce with increasing filler loading as shown in Table IV. This is understandable since all fillers used are nondeformable solids and, thus, increasing filler loading gives rise to a reduction in the deformable rubber portion in the composite, widely known as the dilution effect.^{45,46} The increase of PSP filler loading in the NR compounds stiffens and hardens the NR compounds. This will reduce its resilience and toughness, which further leads to lower EB. Comparing the elongations at break at a given PSP-

TABLE IV
Effects of Filler Loading on Tensile Properties

Samples	Loading (phr)	Tensile properties			
		TS (MPa)	EB (%)	M_{100} (MPa)	M_{300} (MPa)
NR		18.3 ± 1.3	1279 ± 20	0.91 ± 0.008	1.52 ± 0.9
PSP ₄₅₋₉₀	10	21.43 ± 1.6	1153 ± 11	0.91 ± 0.07	1.52 ± 0.2
	20	17.18 ± 1.5	936 ± 9	1.14 ± 0.09	1.92 ± 0.8
	30	12.19 ± 1.2	624 ± 17	1.51 ± 0.2	2.4 ± 0.06
	40	9.29 ± 0.8	543 ± 20	1.63 ± 0.03	2.47 ± 0.04
APSP ₄₅₋₉₀	10	21.87 ± 1.7	1186 ± 0.4	1.20 ± 0.007	2.65 ± 0.08
	20	17.51 ± 1.5	981 ± 0.12	1.36 ± 0.9	2.89 ± 1.1
	30	12.26 ± 2.1	577 ± 11	1.45 ± 0.15	3.0 ± 0.06
	40	10.66 ± 1.3	438 ± 18	2.06 ± 0.3	3.05 ± 0.9
PSP ₀₋₄₅	10	22.25 ± 1.7	1184 ± 29	1.01 ± 1.1	1.71 ± 0.03
	20	18.81 ± 1.3	1012 ± 0.3	1.08 ± 0.004	2.28 ± 0.001
	30	14.81 ± 01.8	603 ± 9.9	1.19 ± 0.07	2.31 ± 0.006
	40	12.09 ± 2.2	580 ± 14	1.34 ± 0.03	2.48 ± 0.008
APSP ₀₋₄₅	10	22.31 ± 1.5	1279 ± 12	0.69 ± 0.05	1.03 ± 0.004
	20	19.49 ± 0.6	1102 ± 16	1.3 ± 0.2	2.8 ± 0.02
	30	15.02 ± 1.4	802 ± 22	1.33 ± 0.01	3.6 ± 0.07
	40	13.35 ± 01.7	547 ± 17	1.34 ± 0.4	3.19 ± 0.006

TS, tensile strength; EB, elongation at break; M_{100} , 100% modulus; M_{300} , 300% modulus.

loading, it can be seen that NR compounds with alkali treated PSP₀₋₄₅ loading gives higher EB than untreated PSP₀₋₄₅ and APSP₄₅₋₉₀ and PSP₄₅₋₉₀ filled NR composites. Again, this is due to better interaction between APSP₀₋₄₅ and NR matrix, which will be explained in SEM study.

Variation in tensile modulus, M_{100} (stress at 100% elongation) and M_{300} (stress at 300% elongation), which is a measure of stiffness, is shown Table IV. It can be seen that M_{100} and M_{300} increase slightly with increase in filler loading. This shows that the filler powder behaves like rigid particulates since it has a higher modulus than the NR matrix. As expected, the smaller-sized fillers gave higher M_{300} values than larger filler size.⁴⁷ Figure 7 shows the variation of Young's modulus of NR compounds with untreated and treated PSP loading. The modulus continued to increase with increasing filler content. This is an indication of the material stiffness for NR composites containing fillers. Fillers are known to increase the modulus, provided that the modulus of the filler is higher than that of the polymer matrix. The most important contribution to the elastic modulus arises from polymer-filler interactions; that can be increased when a good dispersion of the filler is possible with polymer, which is the characteristic of the particles and is dependent on the chemical nature of the polymer. As more and more filler particles were introduced into the rubber, the elasticity of the rubber chains decreased, which ultimately resulted in high stiffness. At given filler loading, the APSP₀₋₄₅ filled NR compounds gave the highest modulus, followed by NR compounds filled with APSP₄₅₋₉₀, PSP₀₋₄₅, and then PSP₄₅₋₉₀. Sae-Oui et al.⁴⁵ reported that surface area is the most impor-

tant factor controlling the tensile strength, whereas the surface activity controls the modulus. Other researches⁴⁸⁻⁵⁰ also reported that modulus value increases when the filler loading is increased for NR-jute, SBR-glass and natural rubber-glass composites.

Improvement in tear and abrasion is a measure of enhanced filler reinforcement. The effect of filler loading on the tear strength of the vulcanizate is given in Figure 8. The values are significantly different from each other at the 95% confidence level. It can be seen that the tear strength tends to decrease slowly with increasing PSP loading. The tear strength results show that the maximum value is

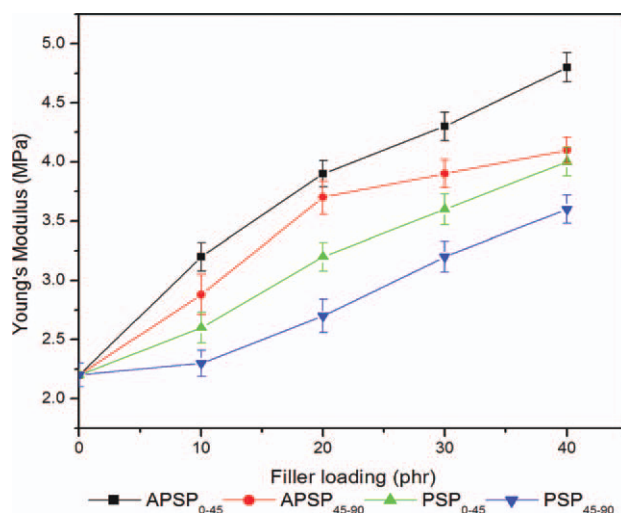


Figure 7 Effect of filler loading on Young's modulus of the rubber vulcanizate. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

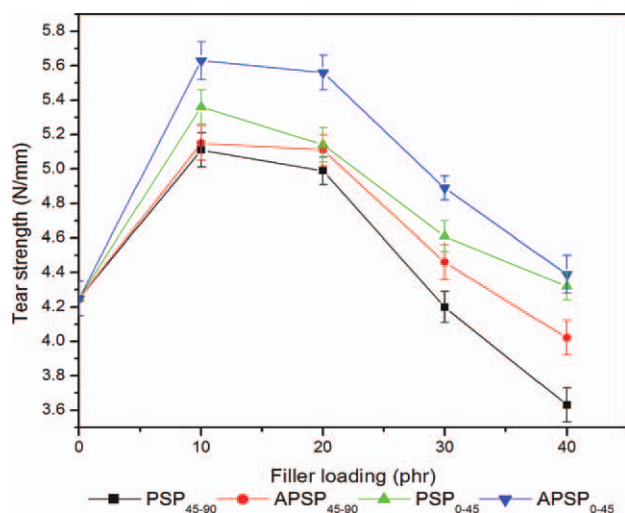


Figure 8 Effect of filler loading on tear strength of the rubber vulcanizate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

achieved with 10 phr followed by 20 phr of the filler. Wanvimon et al. observed similar trend in tear strength, that is, tear strengths decreased with increased loading of the CaCO₃ and limekiln dust NR composites.⁵¹ As the filler loading is increased, eventually a level is reached whereby the filler particles or aggregates are no longer adequately separated or wetted by rubber phase. Thus, the reduction in strength may be due to agglomeration of the filler particles to form a domain that acts like a foreign body or is simply the result of physical contact between adjacent aggregates.⁵² This is clear from the SEM photographs, Figures 11 and 12. Compared with PSP₄₅₋₉₀ composites, APSP₀₋₄₅ and PSP₀₋₄₅ have higher values of tear strength of which the alkali treated NR-PSP composite has higher tear strength than the unmodified PSP composites. The better filler polymer interaction in the case of alkali treated filler is the another reason for higher tear strength. The results imply that the most important factor controlling the tear strength of the filled composites is the specific surface area and reinforcing ability of the filler.

Figure 9 exhibits the effect of filler loading on the hardness of the rubber vulcanizate with the 95% confidence interval. The results reveal that the hardness of the filled vulcanizates increases consistently with increasing filler loading. This is simply due to the fact that the incorporation of more rigid filler particles into rubber reduces the elasticity of the rubber chains and leads to more rigid rubber materials and also due to the combined consequences of (i) an enhancement of crosslink density and (ii) the dilution effect as explained earlier. When the crosslink density increases hardness also increases,⁵³ and as might be expected, at a given filler loading, NR-APSP₀₋₄₅ com-

posite produces a rubber vulcanizate with a higher hardness level followed by PSP₀₋₄₅, APSP₄₅₋₉₀, and PSP₄₅₋₉₀ composites. A plausible explanation for this observation is given by the greater reinforcement ability of APSP₀₋₄₅ due to its higher specific surface area and also by the higher degree of crosslinking achieved for APSP₀₋₄₅ filled vulcanizate.

The abrasion resistance, represented in terms of the abrasive volume loss, of the vulcanizates is illustrated in Figure 10. The values are not significantly different from each other at the 95% confidence level. Clearly, the abrasive volume loss tends to increase consistently with increasing filler loading indicating a reduction in wear resistance. This is due to the increased filler-filler interaction as a result of agglomeration of PSP filler at higher filler loading, and this filler-filler interaction is <0–45 μm sized NR-PSP composites compared with 45–90 μm. Again, the best abrasion resistance was found in APSP₀₋₄₅-filled vulcanizate, followed by, PSP₀₋₄₅, APSP₄₅₋₉₀, and PSP₄₅₋₉₀. This improvement in volume loss of APSP₀₋₄₅ is probably due to the greater surface area and better filler-rubber interfacial adhesion, resulting in an improved abrasion resistance. Moreover, fine particles actually reflect their interface between the filler and the rubber matrix and, hence, provide a better abrasion resistance and adhesion than the coarse ones. Similar results were also reported by Sae-oui et al.⁴⁸

The above results indicate that the PSP fillers do not influence too much on the mechanical properties of NR matrix. According to Leblanc⁵⁴ if the filler particle size is in the order of 10²–10³ nm, it can be classified as semi reinforcing filler. Here, PSP particle size in the 10³ nm range and the PSP filler act as a semi reinforcing filler for NR matrix.

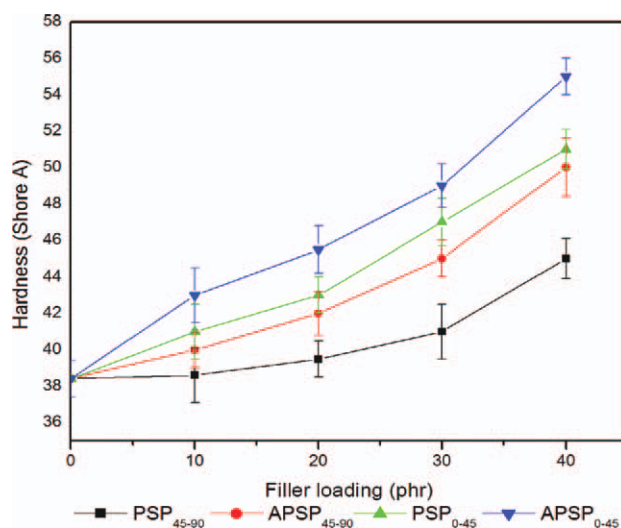


Figure 9 Effect of filler loading on hardness of the rubber vulcanizate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

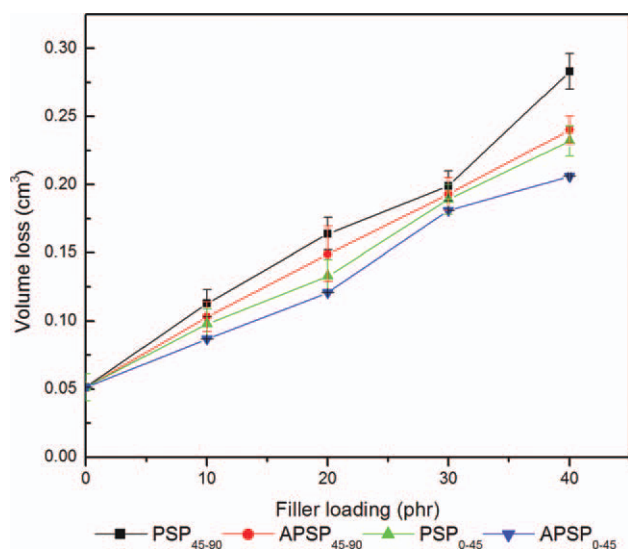


Figure 10 Relationship between abrasion resistance and filler loading. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Scanning electron microscopy

The fracture surfaces of NR vulcanizates filled with 10 phr PSP and alkali treated PSP composites of 45–90 and 0–45 μm particle size are illustrated in Figure 11. Surface of NR compounds with PSP₄₅₋₉₀ and APSP₄₅₋₉₀ [Fig. 11(a,b)] shows holes, this proves that

the rubber matrix and PSP₄₅₋₉₀ and APSP₄₅₋₉₀ have only poor adhesion. Surface impurities such as lignin, pectin, wax, natural oil, and others that cover the PSP surface weaken the adhesion and surface interaction between filler-matrix; this is clearer in the NR-PSP₄₅₋₉₀ composites [Fig. 11(b)]. The PSP₀₋₄₅ and APSP₀₋₄₅, which show more reinforcement with NR matrix are observed in Figure 4(d,e), respectively, and these two have the highest mechanical properties compared with 45–90 μm NR-PSP composites. However, at the same magnification, PSP₄₅₋₉₀ and APSP₄₅₋₉₀ have very poor filler dispersion, because the aggregate of PSP particles can be readily observed in Figure 4(b,c). Compared with the sample having PSP₄₅₋₉₀, APSP₄₅₋₉₀, and PSP₀₋₄₅ better filler dispersion is observed in the sample APSP₀₋₄₅. These results correlate well with the highest physicomechanical properties of APSP₀₋₄₅, showing the greatest filler dispersion in NR matrix.

Figure 12 shows the SEM photographs of NR vulcanizates filled with PSP and alkali treated PSP composites of 40 phr concentration. At high filler loadings (40 phr) the filler distribution in matrix was not good due to the agglomerated filler. This type agglomerations are more in PSP₄₅₋₉₀ and APSP₄₅₋₉₀ [Fig. 12(a,b)]. This clearly indicates that filler matrix miscibility and interactions are weak at 40 phr concentration, resulting in the low values in the Young's

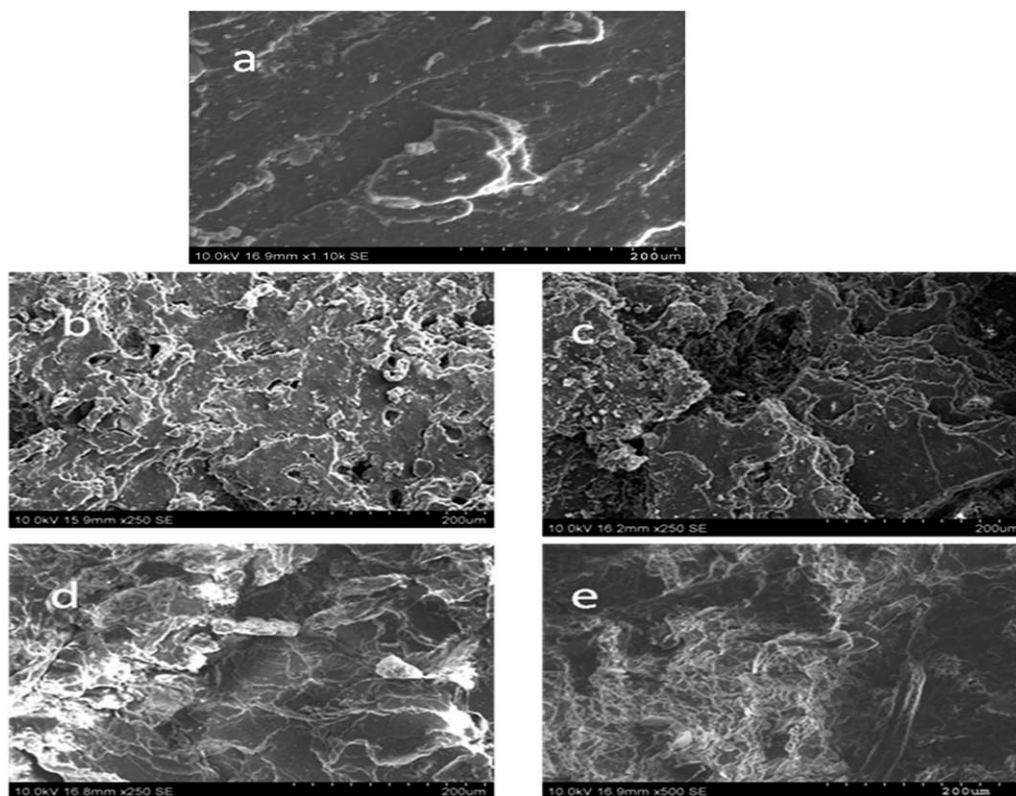


Figure 11 Scanning electron micrographs of NR-PSP composites (10 phr loading). (a) NR, (b) NR-PSP₄₅₋₉₀, (c) NR-APSP₄₅₋₉₀, (d) NR-PSP₀₋₄₅, and (e) NR-APSP₀₋₄₅.

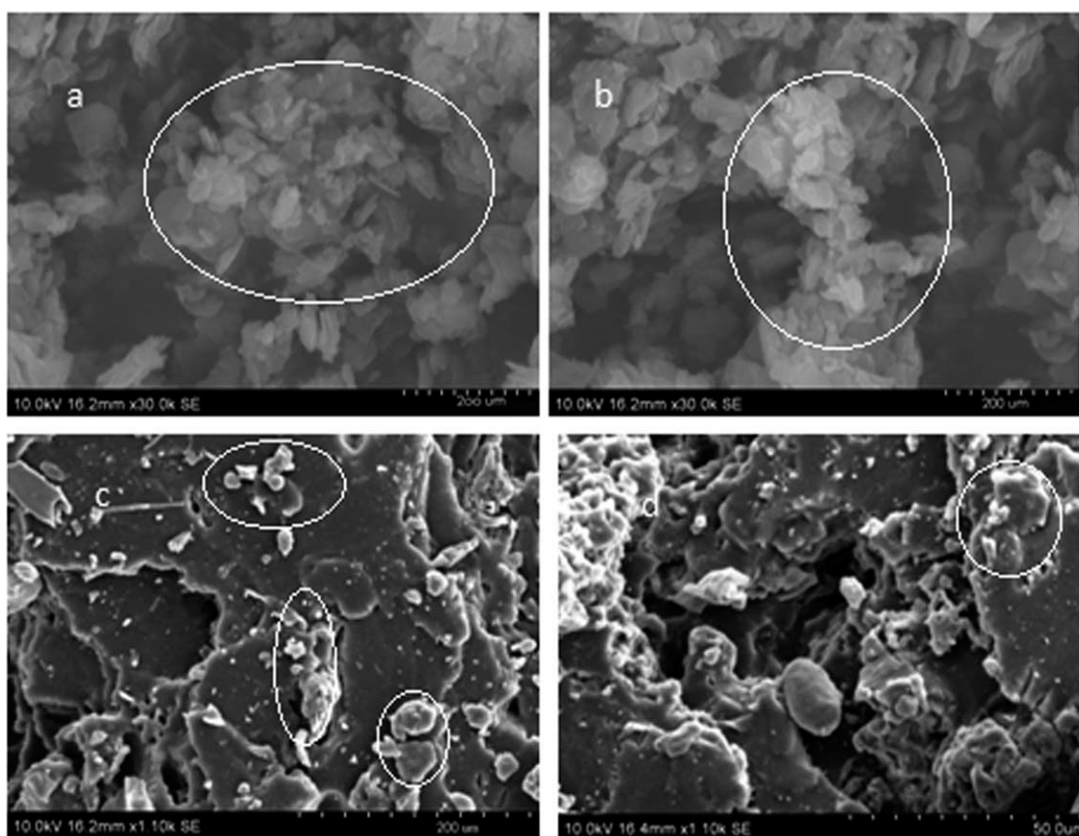


Figure 12 Scanning electron micrographs of NR-PSP composites (40 phr loading). (a) NR-PSP₄₅₋₉₀, (b) NR-APSP₄₅₋₉₀, (c) NR-PSP₀₋₄₅, and (d) NR-APSP₀₋₄₅.

modulus, tensile strength, tear strength, crosslink density, and EB as discussed earlier.

CONCLUSION

In summary, PSP could be used as semi reinforcing filler in the rubber industry. Cure characteristics such as scorch time and cure time of the NR compounds decrease with increasing filler loading but show enhancement in minimum torque and maximum torque. Swelling resistance and crosslink density increase with increasing PSP loading in NR compounds. Mechanical properties such as tensile strength and EB show a decreasing trend with increase in filler loading and the greater the PSP loading, poorer the mechanical properties. The results reveal that the vulcanizates containing 10 phr filler exhibit the better overall mechanical properties. Better rubber-filler interaction has been observed with NR-APSP₀₋₄₅ composites and the rubber-filler interactions decrease with filler loading. However, the composites containing 40 phr of PSP filler give better hardness. Among fillers studied, APSP₀₋₄₅ provides the greatest degree of reinforcement and better physicomechanical properties owing to its higher specific surface area. Among the fillers, the degree of reinforcement could be placed in the following order:

APSP₀₋₄₅ > PSP₀₋₄₅ > APSP₄₅₋₉₀ > PSP₄₅₋₉₀. The SEM photographs also add testimony to these findings.

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