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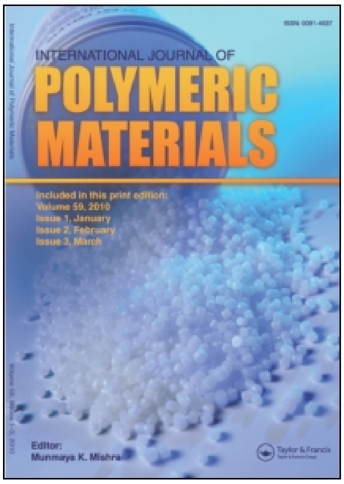

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Effect of Phenol-CNSL-Formaldehyde Copolymer on Thermal Ageing of SBR

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To cite this Article Mary, Lubi C. , Thachil, Eby Thomas and Abraham, Beena T.(2007) 'Effect of Phenol-CNSL-Formaldehyde Copolymer on Thermal Ageing of SBR', International Journal of Polymeric Materials, 56: 2, 147 — 166
To link to this Article: DOI: 10.1080/00914030600758264
URL: http://dx.doi.org/10.1080/00914030600758264

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International Journal of Polymeric Materials, 56:147–166, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 0091-4037 print/1563-5333 online
DOI: 10.1080/00914030600758264

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Cashew nut shell liquid (CNSL) is a cheap and renewable agro by-product that consists mainly of substituted phenols. A CNSL-based resin was used in this study to modify the properties of styrene-butadiene rubber (SBR). The resin was a copolymer obtained by condensing a mixture of phenol and CNSL with hexamethylenetetramine. The effect of the resin on the ageing properties of SBR vulcanizates was studied by following the changes in tensile strength, elongation at break, modulus and tear strength. CNSL directly and CNSL-based resins with different P:F ratios were incorporated into SBR and the physical properties determined. Comparison of the properties of the aged material containing CNSL resin with those of specimens not containing the resin shows improved ageing characteristics with respect to tensile strength, modulus and tear strength.

Keywords: cashew nut shell liquid, hexamine, phenol, styrene-butadiene rubber

INTRODUCTION

The linear molecules of a rubber need to be crosslinked into a network to get the desired physical properties in the final product. The crosslinking agents generally used are sulfur and various accelerators, metal oxides, multifunctional compounds, peroxides, and so on, depending on the nature of the rubber. During crosslinking the rubber passes from a predominantly plastic state to a predominantly elastic one because of the formation of intermolecular bridges.

Received 13 March 2006; in final form 21 April 2006.

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The mechanical properties of crosslinked rubber undergo a marked change on prolonged heating with deterioration in elasticity and strength. The behavior of rubber when exposed to high temperatures is strongly influenced by the presence or absence of oxygen. More than half of the total change observed on ageing can be attributed to oxidation processes [1]. Reaction with oxygen causes chain scission and/or or crosslinking. After oxidation a vulcanizate softens or stiffens depending on whether chain scission or crosslinking is more extensive [2–10].

Crosslink shortening with additional crosslink formation, crosslink destruction along with main chain modification and cyclic sulfide formation, S-S bond interchanges and degradation of the rubber backbone may all occur during ageing [11]. These are due to post-curing phenomena in which free sulfur is used up in forming new crosslinks and the destruction of the weakest polysulfidic linkages.

The phenomenon of reversion or deterioration of properties, in sulfur-based cure systems is due to the decomposition of polysulfidic crosslinks [12–15]. This leads to a reduction in crosslink density and consequently a loss of mechanical properties. The chemical changes associated with reversion result in crosslink shortening and crosslink destruction.

Because reversion due to ageing is an undesirable feature of vulcanizates, various compounding methods have been developed to minimize it. There are three possible approaches to this problem. (I) The established and best-known method to minimize reversion is the efficient cure system. These vulcanization systems reduce reversion by diminishing polysulfidic crosslinks and generating mono and disulfidic crosslinks in the networks [16]. This approach is effective when lowering the sulfur levels does not negatively influence other desirable properties like fatigue, flexural properties, hysteresis, and so on. (II) Another solution to counteract reversion is to compensate for the loss of crosslink density and reduce main chain modifications by adding a reactive chemical to the rubber compound to produce thermally stable C-C crosslinks. This allows rubber compounds to operate under more severe service conditions [17]. (III) The loss in physical properties of sulfur-cured vulcanizates can also be controlled by adding age resistors that are capable of reacting with the agents causing deterioration of elastomers. Thus the service life of sulfur-cured vulcanizates at elevated temperature can be extended by using phenol-formaldehyde resins. These resins can give very thermally stable crosslinks and the vulcanizates are immune to reversion at higher use temperatures [18–20].

Retention after ageing of tensile modulus, tensile strength, and elongation at break of natural rubber vulcanizates containing phosphorylated CNSL (PCNSL), 2-ethyl hexyl diphenyl phosphate, and aromatic oil have been investigated [21,22]. The vulcanizates containing PCNSL showed good retention of tensile properties after ageing due to the post-curing reactions during the ageing period [23]. The effect of addition of paraffin oil, vegetable oil, castor oil, and CNSL to natural rubber (NR) compounds have been compared in terms of the mechanical properties and reported [24]. Polymerized CNSL has been recommended as a substitute for DOP, DBP for nitrile rubber (NBR) and neoprene rubbers [25]. CNSL-phenol-formaldehyde resin, when incorporated into rubber articles improves resistance toward cracking and action of ozone [26]. Sulphur-vulcanized NR containing CNSL possesses greater resistance toward oxidation [27]. CNSL condensed with formaldehyde has been recommended as an effective antioxidant for SBR [28]. CNSL based phenolic resin improves the ageing characteristics of NBR [29]. Cardol exhibits greater antioxidant activity in rubber compositions than cardanol [30]. The effect of incorporation of phenolic resin on the ageing mechanism of NBR has been studied by Cooper [31]. The results show that the resin gets used only gradually subsequent to rubber curing.

In this study, modification of SBR by CNSL and CNSL-based resin has been done to improve ageing characteristics. The modifiers considered were: (1) CNSL obtained as a by-product from cashew processing. (2) A copolymer obtained by condensation of a mixture of phenol and CNSL with formaldehyde.

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CNSL Structure and Composition

CNSL is a by-product of the cashew industry. It is a naturally occurring phenolic substance. Being an agricultural by-product it has the advantages of low cost and renewable supply, and can replace phenol in many applications. With a need to conserve petrochemicals, increased utilization of this material assumes added importance.

Naturally occurring CNSL contains four main components, namely cardanol, cardol, anacardic acid, and 6-methyl cardol [32]. Figure 1 gives the chemical structures of the main components.

Commercial grade CNSL contains hardly any anacardic acid because of decarboxylation during the roasting process that converts anacardic acid to cardanol [33–34]. The roasting process, which is done at 100–300°C, also leads to polymerization, which accounts for there being 7–22% polymeric substances in the oil [35]. The components of CNSL are themselves mixtures of four constituents differing in side chain unsaturation, that is, saturated, monoene, diene, and triene [36–37]. The structures of the side chains occurring in the four major components of CNSL are identical (Figure 2). In this study no attempt has been made to separate the components of CNSL. It is used as

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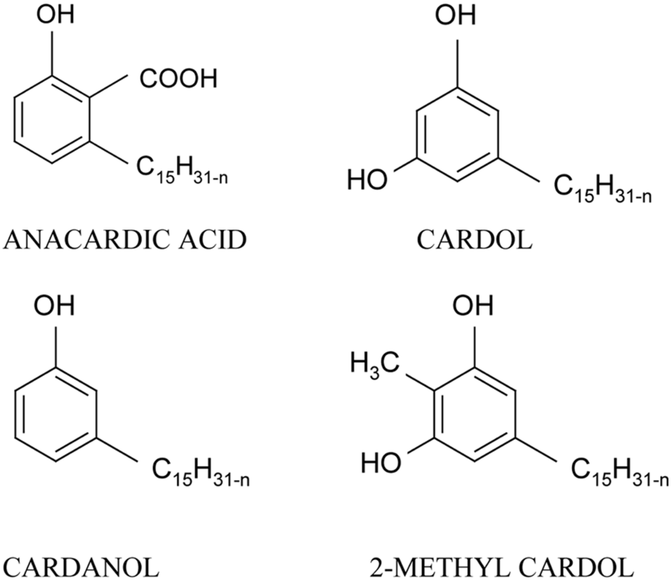

FIGURE 1 Components of CNSL.

obtained from the cashew processing industry to retain the advantage of low cost.

Condensation with Formaldehyde

The phenolic nature of the constituents of CNSL along with varying degrees of unsaturation in the side chain makes it a highly polymerisable substance, amenable to a variety of polymerization reactions.

$C_{15}H_{31}$**-n** =

$(CH_2)_7 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2$ **n=0**

$(CH_2)_7 - CH_2 = CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2$ **n=2**

$(CH_2)_7 - CH_2 = CH_2 - CH_2 - CH_2 = CH_2 - CH_2 - CH_2 - CH_2$ **n=4**

$(CH_2)_7 - CH_2 = CH_2 - CH_2 - CH_2 = CH_2 - CH_2 - CH_2 = CH_2$ **n=6**

FIGURE 2 Components of side chain.

The most obvious and common method of obtaining polymeric materials from CNSL is the condensation reaction with formaldehyde.

The reaction of CNSL with formaldehyde is slow compared to that of phenol with formaldehyde because of the low reactivity of CNSL arising from the steric hindrance caused by the side chain. Pure CNSL-HCHO resin is a brittle substance with inferior mechanical properties compared to phenol-HCHO resins [38]. In this investigation, CNSL-phenol formaldehyde copolymer was first prepared and then incorporated into SBR during mastication. The physical properties of the resulting vulcanizates were subsequently determined.

Reaction of Phenolic Resin with Elastomers

Three types of chemical reactions are possible during the curing of rubber in the presence of phenolic resin—self hardening of phenolic resin, which is a function of both temperature and time during cure, interlinking of phenolic resin with rubber, and vulcanization of rubber.

Resin–rubber interaction may proceed as follows. At high temperature water is eliminated [39] from the resin leading to the formation of quinone methide (Figure 3).

There are two types of mechanisms of resin cure: (1) The chroman mechanism and (2) Allyl hydrogen mechanism [39].

1. The chroman mechanism: Quinone intermediate combines with a rubber double bond in a 1,4-cycloaddition (Diels-Alder type) reaction to give a product with a chroman structure. Subsequent dehydration and a second addition of a molecule of rubber gives the crosslinked product (Figure 4).
2. Allyl hydrogen mechanism: O-methylene quinone abstracts allyl hydrogen from the unsaturated rubber. In this case rubber unsaturation is retained and the double bonds have been shifted (Figure 5).

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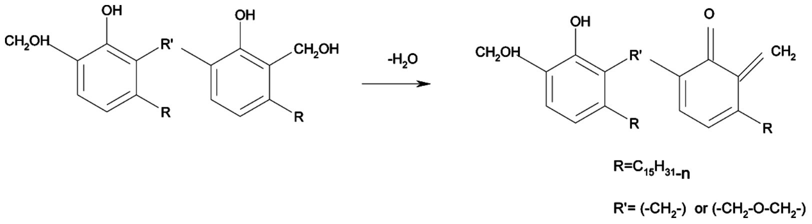

FIGURE 3 Formation of quinone methide.

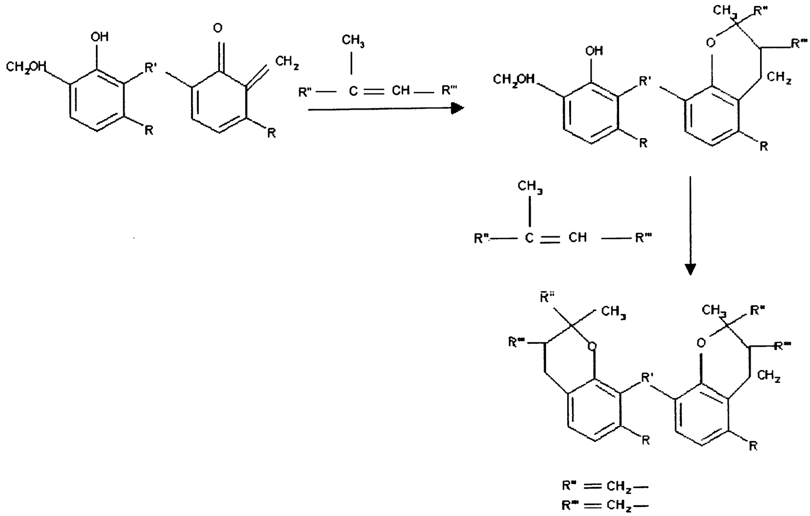

FIGURE 4 Reaction between phenolic resin and elastomer (Chroman mechanism).

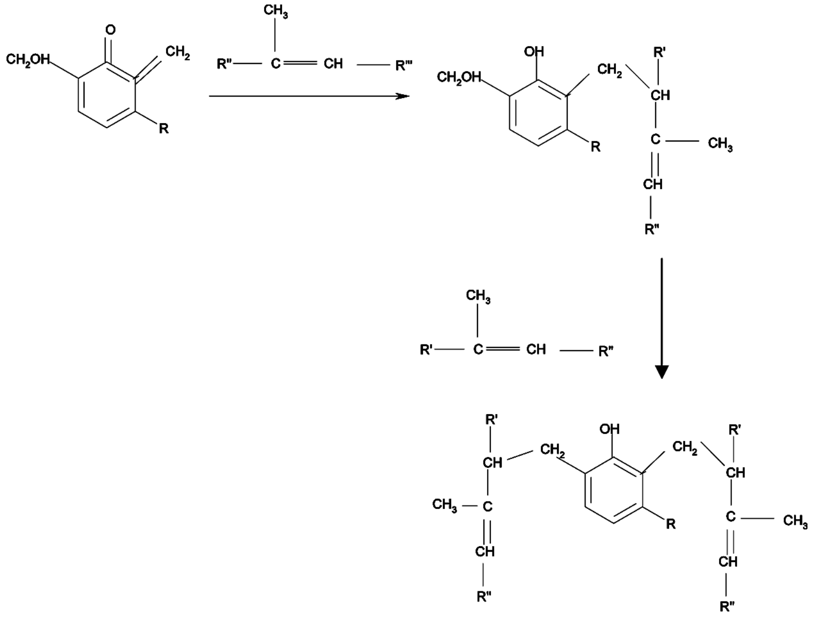

FIGURE 5 Reaction between phenolic resin and elastomer (Allyl hydrogen mechanism).

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EXPERIMENTAL

Raw Materials

Hexamethylenetetramine

Hexamethylenetetramine was supplied by Laboratory and Industrial Chemicals, Cochin, and was of industrial grade. The purity of the sample was estimated by titration against perchloric acid [40]. Purity of hexamine was found to be 94.62%.

Phenol

Phenol of commercial grade was also supplied by Laboratory and Industrial Chemicals, Cochin. Purity was estimated by treating phenol with an excess of potassium bromate and potassium bromide; when bromination of the phenol was complete the unreacted bromine was determined by adding excess potassium iodide and back titrating the liberated iodine with standard sodium thiosulphate [41]. Purity of phenol was found to be 95%.

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CNSL

Refined CNSL conforming to Indian Standard I S: 840 (1964) was supplied by Pierse Leslie Limited, Cochin, in 200 L barrels. The average molecular weight of CNSL was determined by gel permeation chromatography (GPC) using Hewlett Packard (1081 B) equipment. Tetrahydrofuran was used as the solvent.

Number Average molecular weight	−235
Weight Average molecular weight	−506
Z Average molecular weight	−3070

Procedure

A three-necked 1 L RB flask equipped with a stirrer passing through a mercury seal, a water condenser, and a thermometer was employed for the reaction. Heating was by an electric mantle with temperature control. The total number of moles of phenolic substance was computed from knowledge of the average molecular weight of CNSL. Hexamethylenetetramine and water were taken in quantities in accordance with the equation for hydrolysis of hexamethylenetetramine, leading to the liberation of formaldehyde:

$$(CH_2)_6\,N_4 + H_2O \longrightarrow 6CH_2O + 4NH_3$$

Phenol, CNSL, hexamethylenetetramine, and water were weighed out and charged into the flask. The total phenol/formaldehyde (P/F) mole ratios were taken as 1:2.9, 1:2.3, 1:1.7, and 1:1.1. The reaction was carried out at 100°C for 1.5 h with continuous stirring. The semi-solid product was removed from the flask and was then allowed to dry at room temperature for 3 days. The dried product was subsequently ground to a powder and again dried for 24 h.

Compounding and Molding of SBR

Materials Used

1. SBR (Styrene-Butadiene Rubber) was obtained from Apar Polymers Limited, India.
2. Zinc Oxide (ZnO) was supplied by M/s Meta Zinc Limited, Mumbai.
3. Stearic acid was supplied by Godrej Soaps (Pvt) Ltd., Mumbai.
4. Sulphur was supplied by the Standard Chemical Company (Pvt) Ltd., Chennai.
5. Tetramethyl thiuram disulphide (TMTD) was supplied by Flexys, Netherlands.
6. Mercaptobenzothiazol sulphenamide (MBTS) was supplied by Bayer Chemicals, Mumbai.
7. Precipitated silica was obtained from Sameera Chemicals, Kottayam, India.

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The mixing of the resin/CNSL and the rubber compound was done on a conventional laboratory size two-roll mill (150 × 300 mm) at a friction ratio of 1:2.5 according to ASTM D3185-99 [42]. The rubber was masticated on a cold mill and the compounding ingredients were added: the resin was added along with the filler. CNSL and resin were used at the rate of 5, 10, 15, 20, and 25 phr. Resins with P/F ratios of 1:2.9, 1:2.3, 1:1.7, and 1:1.1 were incorporated into the SBR vulcanizates at the rate of 25 phr.

Cure characteristics of the mixes were determined at 150°C on a Goettfert Elastograph (Model 67.85). Vulcanization to optimum cure time was then carried out in an electrically heated hydraulic press with 30 cm × 30 cm platens and 11.76 MPa Pressure at 150°C. The effect of direct addition of CNSL was studied using the formulation given in Table 1 and that of resin was studied using the formulation given in Table 2.

ZnO and stearic acid were added as activators for the vulcanization. Sulphur was the crosslinking agent and TMTD and MBTS, the accelerators. Aromatic oil was used as plasticizer. Carbon black was the reinforcing material and styrenated phenol (SP), the antioxidant.

TABLE 1 Formulation Used for Mixing CNSL Directly

	C0	C5	C10	C15	C20	C25
SBR	100	100	100	100	100	100
ZnO	4	4	4	4	4	4
Stearic acid	2	2	2	2	2	2
S	2	2	2	2	2	2
TMTD	0.2	0.2	0.2	0.2	0.2	0.2
MBTS	0.8	0.8	0.8	0.8	0.8	0.8
Carbon black	50	50	50	50	50	50
Aromatic oil	5	5	5	5	5	5
CNSL	0	5	10	15	20	25

C0- 0 phr CNSL, C5- 5 phr CNSL, C10- 10 phr CNSL, C15- 15 phr CNSL, C20- 20 phr CNSL, C25- 25 phr CNSL.

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Ageing Studies

Oxidative ageing tests were carried out for 10 days as per ASTM D573-88 [43] using an air oven at 100°C. The physical properties of the specimens before and after ageing were determined after 24 h of conditioning at ambient temperature.

Tensile strength, elongation at break, and modulus of the vulcanizates were determined in accordance with ASTM D 412-98 [44]. For this, dumb-bell-shaped specimens were punched from the vulcanized sheet and the samples were tested on a Zwick tensile testing machine. The crosshead speed was maintained at 500 mm/min.

Tear resistance of the samples was determined according to ASTM D 624-00 [45] using angular specimens punched out from

TABLE 2 Formulation Used for Mixing Resin

	R0	R5	R10	R15	R20	R25
SBR	100	100	100	100	100	100
ZnO	4	4	4	4	4	4
Stearic acid	2	2	2	2	2	2
S	2	2	2	2	2	2
TMTD	0.2	0.2	0.2	0.2	0.2	0.2
MBTS	0.8	0.8	0.8	0.8	0.8	0.8
Carbon black	50	50	50	50	50	50
Aromatic oil	5	5	5	5	5	5
Resin	0	5	10	15	20	25

R0- 0 phr resin, R5- 5 phr resin, R10- 10 phr resin, R151- 15 phr resin, R20- 20 phr resin, R25- 25 phr resin.

compression-molded sheets. Throughout the test the speed of the grip was kept at 500 mm/min.

Swelling index was measured as per ASTM D3616-95 [46] and acetone soluble matter as per ASTM D 297–93 (2002) [47].

RESULTS AND DISCUSSION

Effect of CNSL Content

Figure 6 shows the variation in tensile strength with progressive ageing. The immediate effect of adding CNSL is to decrease the tensile strength of the unaged material marginally. This can be attributed to the slow reaction between CNSL and rubber. Tensile strength of vulcanizates without any CNSL and those containing lower than 15% CNSL decreased noticeably with aging time. The presence of CNSL is seen to retard the ageing action at higher percentages of CNSL (like 25%). The antioxidant behavior of CNSL by virtue of the substituted phenol structure may account for this.

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There was a general increase in elongation at break (Figure 7) on addition of CNSL for the unaged material. At initial stages of ageing elongation at break falls for all the samples. Elongation at break decreases soon after due to additional crosslinking and stiffening of rubber chains. But it stabilized after about 2 days of ageing. All the ingredients of CNSL have high boiling points. The plasticizer [48] action of CNSL is hence sustained even after prolonged ageing.

Figure 8 shows the variation in modulus. Modulus of all the samples increased with ageing time. This could have been due to the

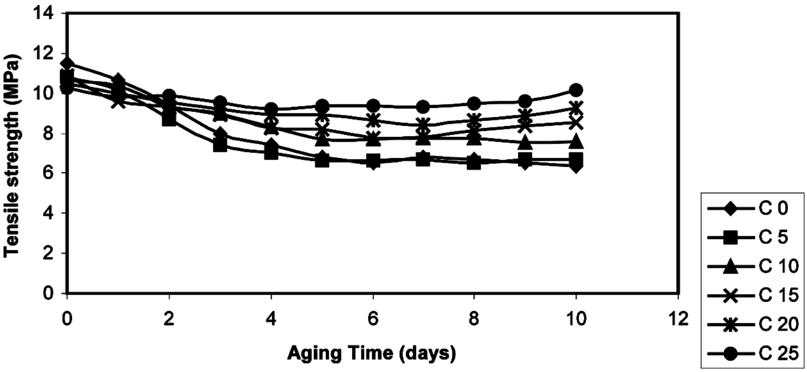

FIGURE 6 Variation of tensile strength with ageing time of SBR vulcanizates with different CNSL contents. (C0- 0 phr CNSL, C5- 5 phr CNSL, C10- 10 phr CNSL, C15- 15 phr CNSL, C20- 20 phr CNSL, C25- 25 phr CNSL.)

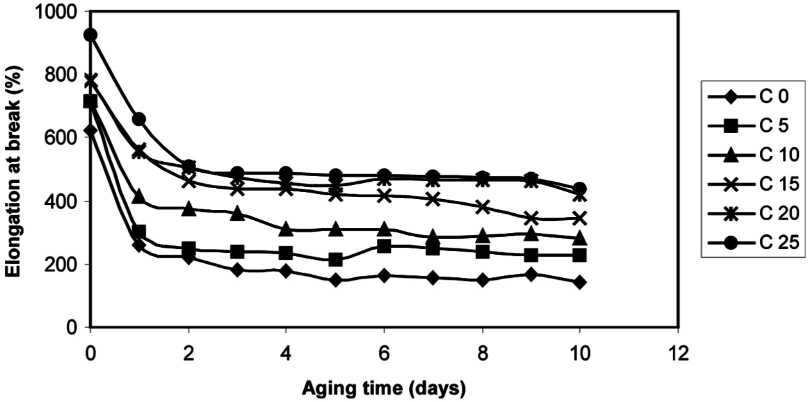

FIGURE 7 Variation of elongation at break with ageing time of SBR vulcanizates with different CNSL contents.

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stiffening of the vulcanizate as ageing time increased. Presence of CNSL decreased the modulus of the vulcanizate.

Figure 9 shows the variation in tear strength. The immediate effect of adding CNSL is to lower the tear strength of unaged vulcanizates. Tear strength of the vulcanizates without any added CNSL and those containing lower amounts of CNSL (0–15 phr) decreased with ageing time in the beginning. Tear strength values largely remained steady on further ageing for all the samples. The presence of CNSL is seen to retard crack generation and propagation. This can be due to additional crosslinking reactions involving rubber and resin.

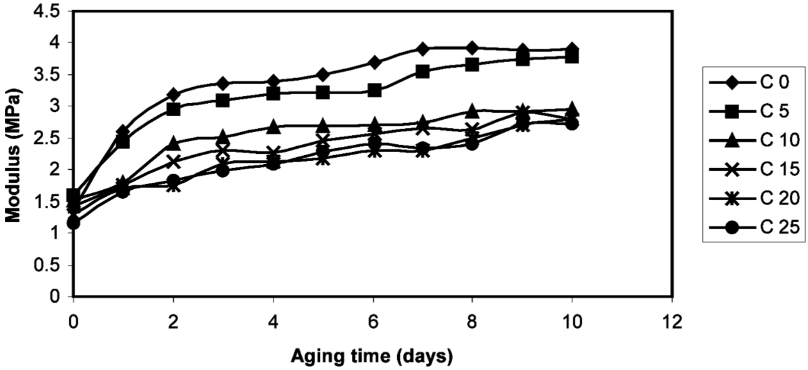

FIGURE 8 Variation of tensile modulus with ageing time of SBR vulcanizates with different CNSL contents.

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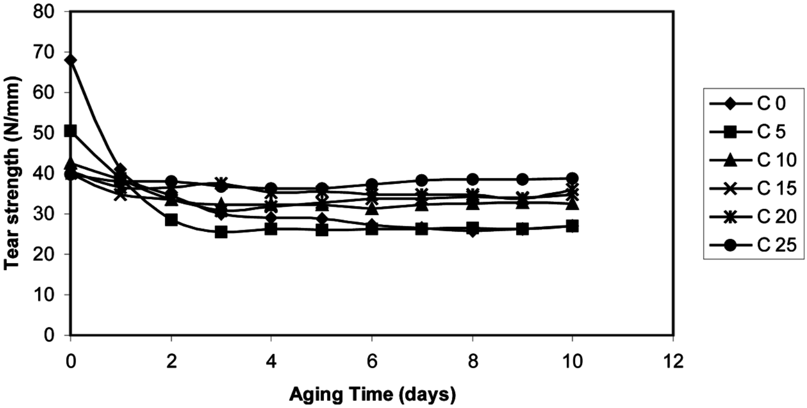

FIGURE 9 Variation of tear strength with ageing time of SBR vulcanizates with different CNSL contents.

Effect of Resin Content

For this part of the study, a P:F ratio of 1:2.9 and CNSL:P ratio of 1:1 was maintained. Figure 10 shows the variation in tensile strength with ageing time of vulcanizates containing different percentages of phenol-CNSL-hexa-resin. The immediate effect of adding the resin is to increase the tensile strength of the unaged vulcanizates. This can be due to additional crosslinking reactions involving rubber and resin. Tensile strength of vulcanizates without any added resin and those containing lower percentages of resin decreases with aging time. Tensile strength of vulcanizates with higher amounts of resin content, on the other hand, increases with ageing time. This indicates additional

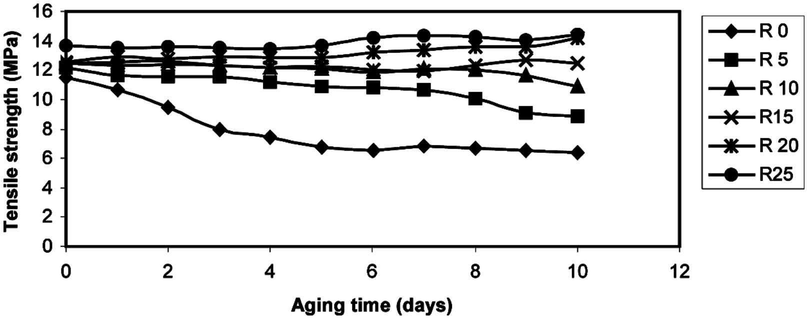

FIGURE 10 Shows the variation of tensile strength with ageing time of SBR vulcanizates with different resin contents. (R0- 0 phr resin, R5- 5 phr resin, R10- 10 phr resin, R15- 15 phr resin, R20- 20 phr resin, R25- 25 phr resin.)

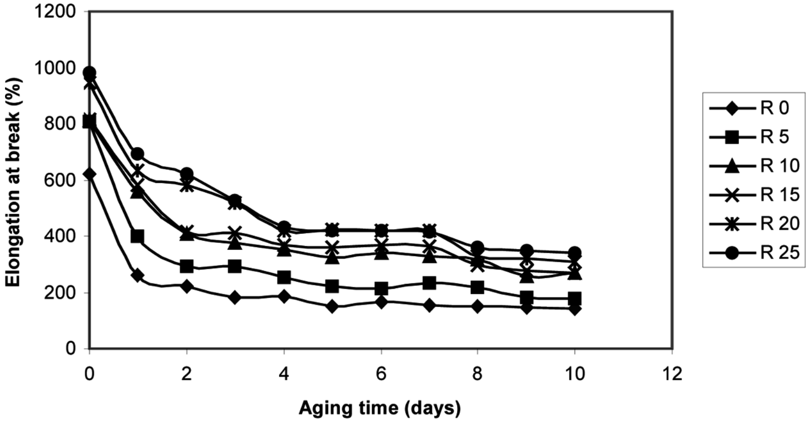

FIGURE 11 Shows the variation of elongation at break with ageing time of SBR vulcanizates with different resin contents.

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network chains resulting from crosslinking between resin and rubber. Samples containing resin maintain higher values of tensile strength at all stages of ageing.

Figure 11 shows the variation in elongation at break with resin content. Addition of resin increased the elongation at break of unaged vulcanizates indicating some plasticizing action. But it decreased with ageing time at initial stages of ageing. After about 2 days the values got more or less stabilized. Crosslinking of the resin and progressive reaction with the rubbers may be responsible for this.

Modulus of all the samples (Figure 12) increased with ageing time. Samples containing higher amounts of resin show higher modulus throughout. This may be the result of crosslinking between resin monomer molecules or interaction between the resin and the SBR chains. The unsaturation present in the butadiene monomer units is a potential site for interaction with the resin.

Figure 13 shows the variation in tear strength with ageing time of vulcanizates containing different amounts of resin. Vulcanizates without any added resin showed a sharp decreasing tendency with ageing time in the beginning. Later, the tear strength of vulcanizates containing higher amounts of resin increased with ageing time. This again points to the progressive reactions in the blend as ageing proceeds.

Figure 14 shows the variation of swelling index. Swelling index decreases as ageing time increases. This indicates increasing levels of crosslinking on ageing, which is along expected lines.

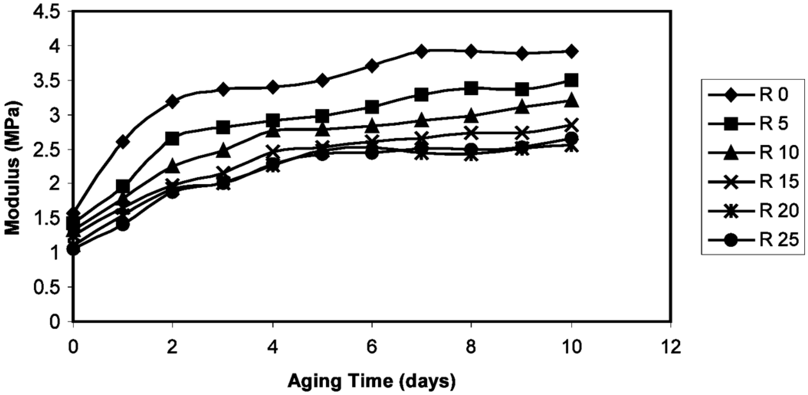

FIGURE 12 Variation of elongation at break with ageing time of SBR vulcanizates with different resin contents.

Figure 15 shows the variation in loss of weight on extraction with acetone. As ageing time increases the matter soluble in acetone decreases. It indicates that more and more resin gets crosslinked or alternatively, gets incorporated into the network as ageing proceeds. The sample not containing resin also shows the presence of low molecular weight extractable matter. At low resin percentage, say 5%, the extractable matter after 10 days of ageing is not very different from that of the sample containing no resin. So at this resin content

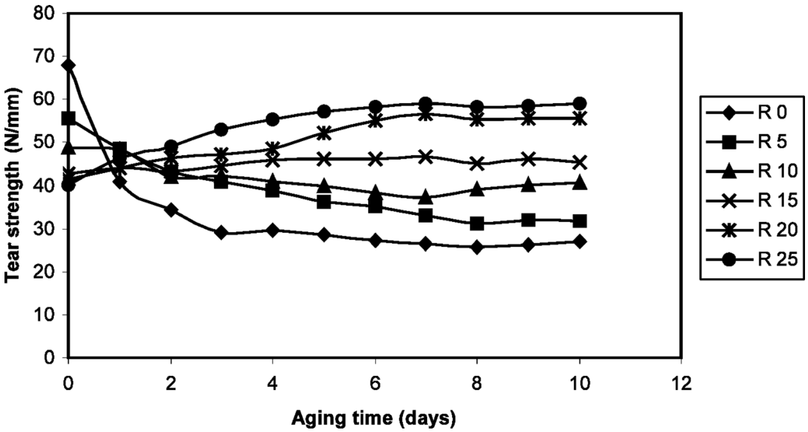

FIGURE 13 Variation of tear strength with ageing time of SBR vulcanizates with different resin contents.

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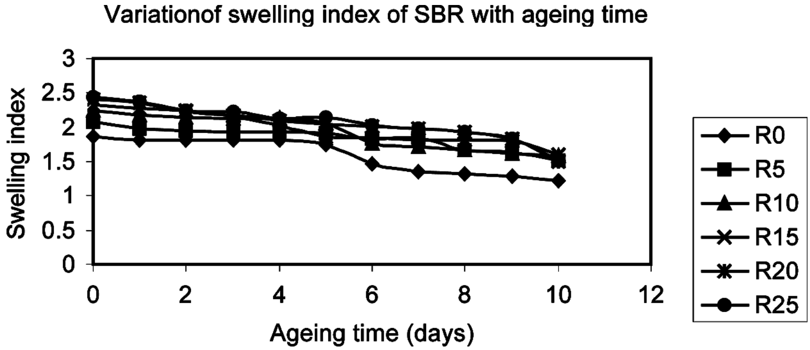

FIGURE 14 Variation of swelling index with ageing time of SBR vulcanizates with different resin contents.

it can be assumed that the resin has fully and inextricably integrated into the rubber.

Effect of P:F Ratio

For this study, a resin with CNSL:P ratio of 1:1 and resin content 25 phr was used.

Figure 16 shows the variation in tensile strength with ageing time of samples with P:F ratios of 1:2.9, 1:2.3, 1:1.7, and 1:1.1. The tensile strength is higher when a resin containing a higher amount of formaldehyde is used. Vulcanizates having resin with P:F ratio of 1:2.9 showed almost constant tensile strength. Such a resin completes its

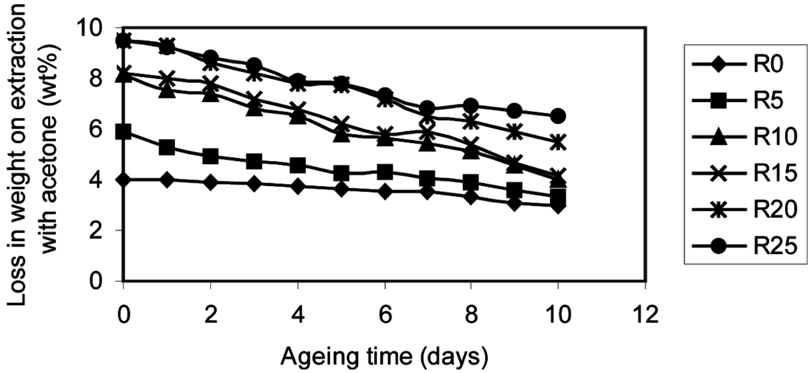

FIGURE 15 Variation of loss in weight on extraction with acetone with ageing time of SBR vulcanizates with different resin contents.

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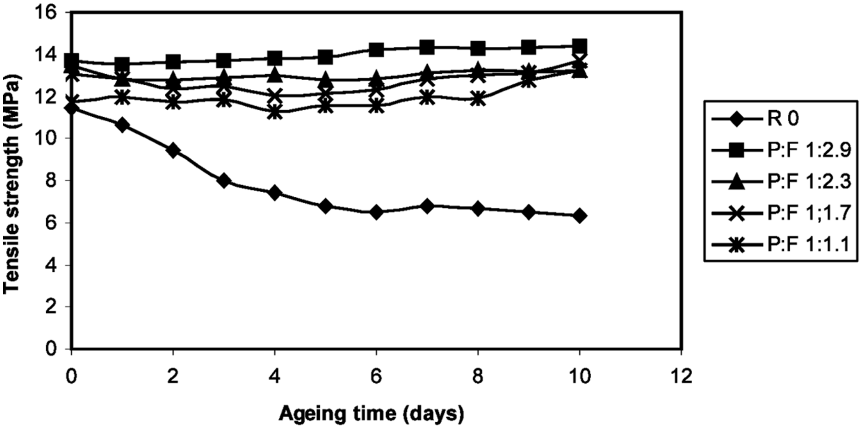

FIGURE 16 Variation of tensile strength with ageing time of SBR vulcanizates with resin having different P:F ratios.

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reaction with rubber at an early stage of ageing and shows high initial tensile strength values. Without the resin, there is rapid fall of tensile strength on ageing.

Figure 17 shows the variation in elongation at break with ageing time of samples with P:F ratios of 1:2.9, 1:2.3, 1:1.7, and 1:1.1. In all cases there is a reduction in elongation at break at the early stages

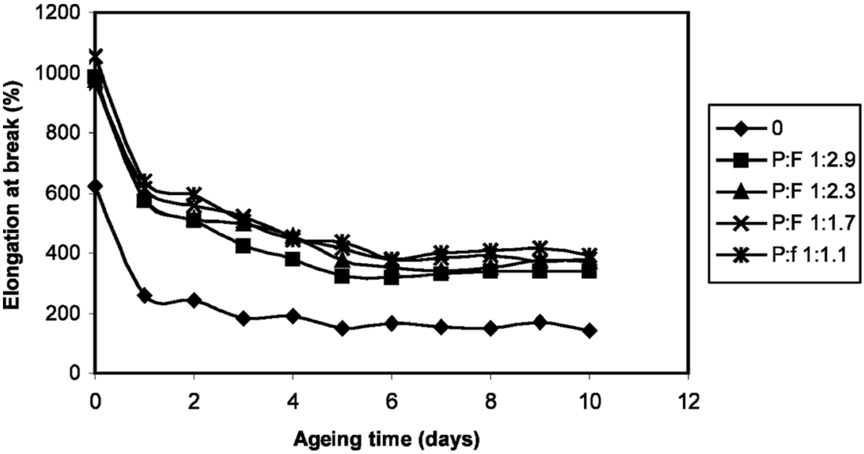

FIGURE 17 Variation of elongation at break with ageing time of SBR vulcanizates with resin having different P:F ratios.

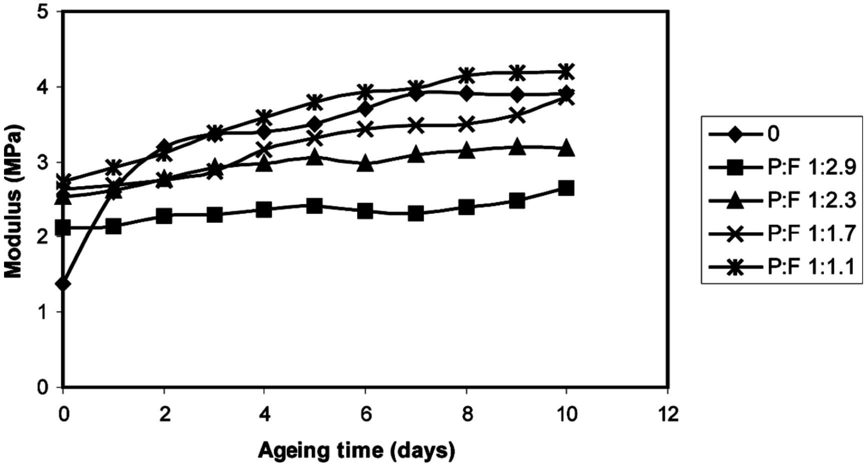

FIGURE 18 Variation of modulus with ageing time of SBR vulcanizates with resin having different P:F ratios.

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of ageing. The presence of the resin leads to greater elongation and a lower formaldehyde content is conducive to higher levels of elongation at break.

As the ageing time increased the modulus (Figure 18) increased for all the samples. This could have been due to the stiffening of the network as ageing proceeds. Vulcanizates containing resin with P:F ratio of 1:2.9 showed the least variation in modulus on addition of resin. The increase in modulus is maximum for a P:F ratio of 1:1.1. At low formaldehyde content (P:F = 1:1.1) the condensate will have

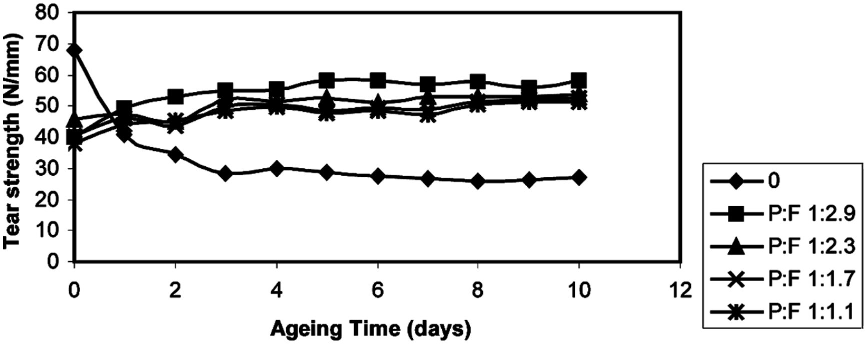

FIGURE 19 Variation of tear strength with ageing time of SBR vulcanizates with resin having different P:F ratios.

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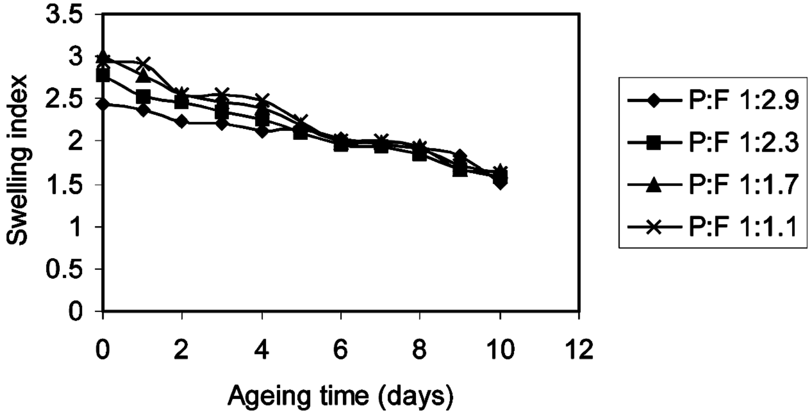

FIGURE 20 Variation of swelling index with ageing time of SBR vulcanizates with resin having different P:F ratios.

more benzene rings per molecule. This may affect the chain flexibility and lead to a higher modulus.

Figure 19 shows the variation in tear strength with ageing time of vulcanizates with different P:F ratios. Tear strength of samples without any resin decreased with ageing time. P:F ratio has very little effect on the contribution of the resin to the tear strength. In the presence of the resin, high values of tear strength are sustained upon ageing.

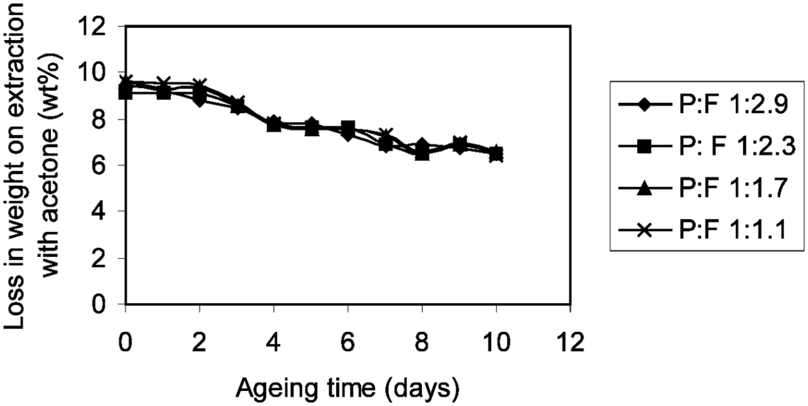

FIGURE 21 Variation of loss in weight on extraction with acetone with ageing time of SBR vulcanizates with resin having different P:F ratios.

Figure 20 shows the variation in swelling index. Swelling index decreases as ageing time increases for all samples, indicating progressive crosslinking. The same level of gel content is indicated for all the samples. Acetone soluble matter (Figure 21) decreases as ageing time increases irrespective of the P:F ratio. Again, high gel contents are indicated as ageing proceeds.

CONCLUSIONS

CNSL as well as the copolymer obtained by condensation of phenol and CNSL with hexamethylenetetramine improve the ageing characteristics of SBR with respect to retention of tensile strength, modulus, tear strength, and elongation at break. Vulcanizates containing resin with a P:F mole ratio 1:2.9 showed the least change in properties on ageing. As the relative amounts of formaldehyde in the resin decreased, the rubber showed increases in tensile strength, tensile modulus, and tear strength on ageing. Although CNSL, when used as such, improves the ageing characteristics of SBR, this effect is more noticeable when the copolymer CNSL-phenol-hexamine is used as the modifier. Considering the low cost of CNSL and its renewable nature this application of CNSL has significance from the conservation point of view.

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REFERENCES

[1] Bevilacqua, E. H., *J. Appl. Polymer Sci.* **10**, 1925, (1966).
[2] Cunnen, J. L., *Rubber Chem. Technol.* **41**, 182 (1968).
[3] Shelton, J. R., *Rubber Chem. Technol.* **G71**, 56 (1983).
[4] Norling, P. M., Lee, T. C. P., and Tobolsky, A. V., *Rubber Chem. Technol.* **38**, 1198 (1965).
[5] Bauman, R. G. and Maron, S. H., *J. Polym. Sci.* **22**, 203 (1956).
[6] Berry, J. P. and Watson, W. F., *J. Polym. Sci.* **18**, 201 (1955).
[7] Keller, R. H., *Rubber Chem. Technol.* **58**, 637 (1985).
[8] Morand, J. L., *Rubber Chem. Technol.* **50**, 373 (1977).
[9] Shelton, J. R., *Rubber Chem. Technol.* **30**, 1251 (1957).
[10] Bevilacqua, E. M. and Wenisch, W. J., *J. Appl. Polm. Sci.* **9**, 267 (1965).
[11] Tobolsky, A. V. (1968). *The Chemistry of Sulfides*, Interscience Publishers, New York.
[12] Bateman, L. (1963). *The Chemistry and Physics of Rubber-like Substances*, Mc Laren and Sons Ltd., London.
[13] Kuran, T. H., *Rubber World* **20**, 192 (1985).
[14] Enrich, F. R. (1978). *Science and Technology of Rubber*, Academic Press, New York.
[15] Slusarski, L. and Janowska, G., *J. Therm. Anal.* **30**, 1105 (1986).
[16] Skinner, T. O. and Awabon, A., *Rubber Age* **99** (11), 76 (1961).
[17] Datte, R. N., Wilbrink, J. H., and Ingham, F. A., *Indian Rubber J.* **8**, 52 (1994).
[18] Searer, J. C., *Rubber Age* **62**, 191 (1947).
[19] Lattimer, R. P., Kinsey, R. A., and Layer, R. W., *Rubber Chem. Technol.* **62**, 107 (1982).

[20] Morton, M. (1995). *Rubber Technology*, Chapman & Hall, New York.

[21] Menon, A. R. R., Pillai, C. K. S., and Nando, G., *Eur. Polym. J.* **34** (7), 923 (1998).

[22] Menon, A. R. R., Pillai, C. K. S., and Nando, G., *J. Applied Polymer Science* **73**, 813 (1999).

[23] Menon, A. R. R., Pillai, C. K. S., and Nando, G. B., *J. Applied Polymer Science* **68**, 1303 (1998).

[24] Kukreja, T. R., Chanhan, R. C., Choe, S., and Kundu, P. P., *J. Applied Polymer Science* **87**, 1574 (2003).

[25] Banarge, B. and Inamdas, C. S., *Rubber India* **30** (4), 13 (1978).

[26] Shinkle, S. D., U.S. Patent 2,648,613 (1953).

[27] Rajapakse, R. A., Gunasena, W. A. S., and Wijekoon, K. B., *Polymer* **20**, 887 (1978).

[28] Fegade, N. B., Sanghvi, Y. B., and Millns, W., *Rubber India* **17**, 3391 (1981).

[29] Lubi, C. M. and Thachil, E. T., *J. of Elastomers and Plastics* **33**, 121 (2001).

[30] Rajapkse, R. A., Anadakumaran, K., Gunasena, W. A. S., and Wijikoon, K. B., *Polymer* **887**, 20 (1979).

[31] Cooper, A. R., *Polymer Engineering and Science* **31** (10), 727 (1991).

[32] Stadeler, A., *Ann. Chem. U. Pharmacie.* **63**, 137 (1847).

[33] Tyman, J. H. P., Wielezynski, D., and Kashani, M. A., *J. Am. Chem. Soc.* **55**, 663 (1978).

[34] Tyman, J. H. P., *J. Chromatog.* **156**, 255 (1978).

[35] Tyman, J. H. P., Tychopoulos, V., and Colenat, B. A., *J. Chromatogr.* **213**, 287 (1981).

[36] Tyman, J. H. P., *Chem. Soc. Rev.* **8**, 499 (1973).

[37] Gedam, P. H. and Sampathkumaran, P. S., *Progress in Organic Coatings* **14**, 115 (1986).

[38] Mahanwar, P. A. and Kale, P. D., *Journal of Applied Polymer Science* **61** (2), 107 (1996).

[39] Knop, A. (1979). *Chemistry and Applications of Phenolic Resins*, Springer Verlag, New York.

[40] Fritz, J., *Anal. Chem.* **1028**, 22 (1950).

[41] Haslam, J. (1965). *Identification and Analysis of Plastics*, Iliffe Books, London.

[42] ASTM D3185-99.

[43] ASTM D573-88.

[44] ASTM D412-98.

[45] ASTM D624-00.

[46] ASTM D3616-95.

[47] ASTM D297-93, 2002.

[48] Pillot, J. P., Dunoques, J., Th. M. D., and Thanah, M. V., *Eur. Polym. J.* **25** (3), 285 (1989).

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