Effect of Phenol-CNSL Formaldehyde on the Thermal Aging of Elastomers-I

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Cashew nut shell liquid (CNSL) is a cheap agro-by-product and renewable resource that consists mainly of substituted phenols. A CNSL-based resin was used in this study to modify the properties of the elastomers Isobutylene-Isoprene Rubber (IIR) and Natural Rubber (NR). The resin was a copolymer obtained by condensing a mixture of phenol and CNSL with hexamethylenetetramine. The effect of the resin on the aging properties of elastomers was studied by following changes in tensile strength, elongation at break, modulus, and tear strength. Comparison of the properties of the aged material containing resin with those of specimens not containing any modifiers shows improved aging characteristics with respect to tensile strength, modulus, and tear strength for IIR.

INTRODUCTION

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

The mechanical properties of cross-linked rubber undergo a marked change on 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 aging can be attributed to oxidation processes [1]. Reaction with oxygen causes chain scission and/or cross-linking. After oxidation a vulcanizate softens or stiffens depending on whether chain scission or cross-linking is more extensive [2–10].

Cross-link shortening with additional cross-link formation, cross-link destruction along with main chain modification and cyclic sulfide formation, S-S bond interchanges, and degradation of the rubber backbone occur during aging [11]. These are due to post-curing phenomena in which free sulfur is used up in forming new cross-links 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 cross-links [12–15]. This leads to a reduction in cross-link density and consequently a loss of mechanical properties. The chemical changes associated with reversion result in cross-link shortening and cross-link destruction.

Because reversion due to aging 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 cross-links and generating mono- and disulfidic cross-links 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 cross-link density and reduce main chain modifications by adding a reactive chemical to the rubber compound to produce thermally stable C-C cross-links. 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 cross-links and the vulcanizates are immune to reversion at higher use temperatures [18–20].

Retention after aging 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 aging due to the post-curing reactions during the aging period [23]. The effect of addition of paraffin oil, vegetable oil, castor oil, and CNSL to natural rubber 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 and neoprene rubbers [25]. CNSL-phenol-formaldehyde resin when incorporated into rubber articles improves their 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 aging characteristics of NBR [29]. Cardol exhibits greater antioxidant activity in rubber compositions than cardanol [30]. The effect of incorporation of phenolic resin on the aging 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 investigation, modification of IIR, and NR using a CNSL-based resin has been done in order to improve aging characteristics.

CNSL Structure and Composition

CNSL is a byproduct 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, which 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, namely, 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 obtained from the cashew processing industry to retain the advantage of low cost.

ANACARDIC ACID   CARDOL

CARDANOL   2-METHYL CARDOL
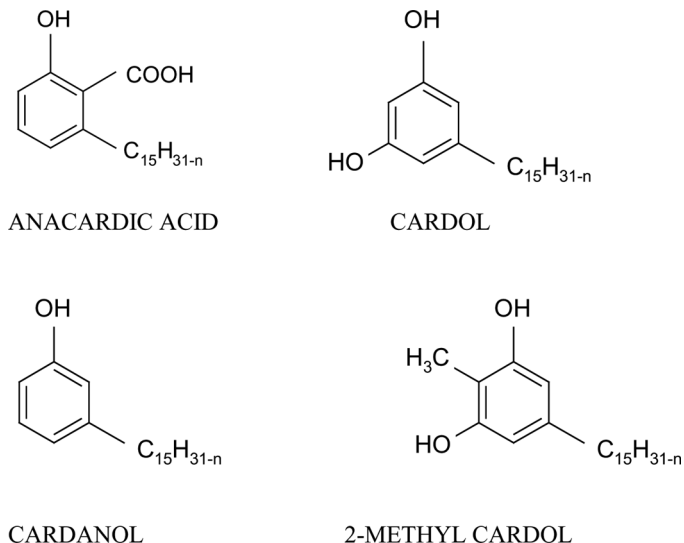
FIGURE 1 Components of CNSL.

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 polymerizable substance, amenable to a variety of polymerization reactions. 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

$C_{15}H_{31}\text{-n} =$

$(CH_2)_7 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$ **n=0**

$(CH_2)_7 - CH=CH - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$ **n=2**

$(CH_2)_7 - CH=CH - CH_2 - CH=CH - CH_2 - CH_2 - CH_3$ **n=4**

$(CH_2)_7 - CH=CH - CH_2 - CH=CH - CH_2 - CH=CH_2$ **n=6**
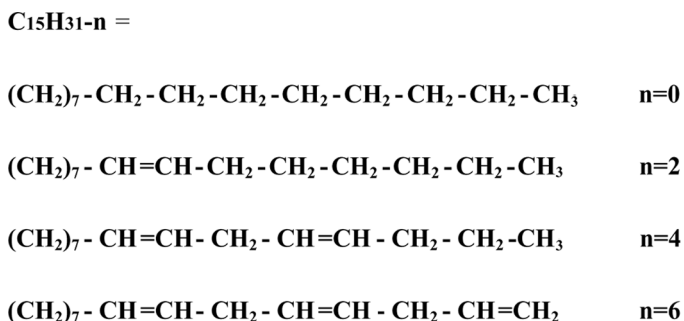
FIGURE 2 Components of side chain.

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 IIR and NR during mastication. The physical properties of the resulting vulcanizates were subsequently determined.
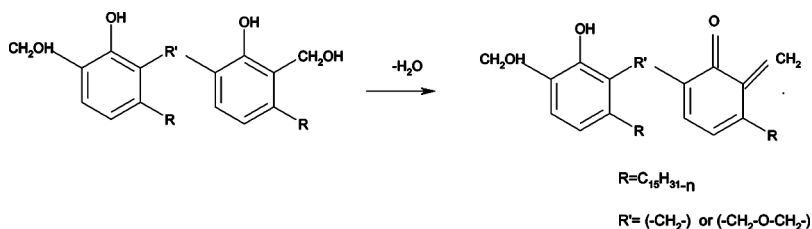
Reaction of Phenolic Resin with Elastomers

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 like this: 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 cross-linked 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).

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

$R' = (-CH_2-)$ or $(-CH_2-O-CH_2-)$

FIGURE 3 Formation of quinone methide.
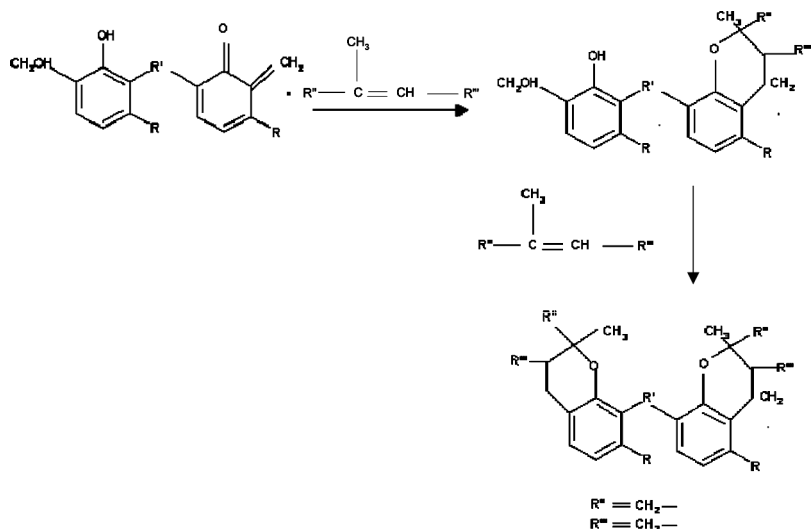
FIGURE 4 Reaction of phenolic resin with elastomers (Chroman mechanism).

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%.

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
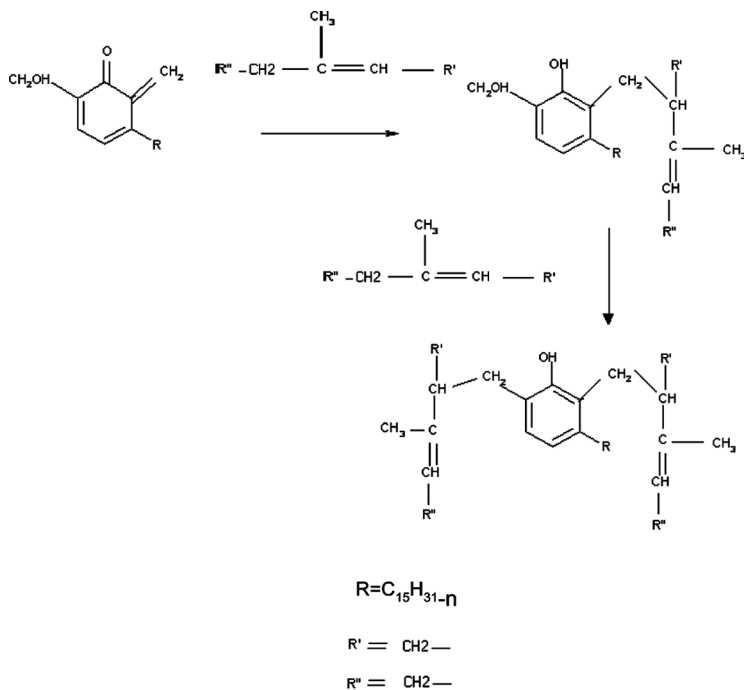
FIGURE 5 Reaction of phenolic resin with elastomers (Allyl hydrogen mechanism).

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 1L RB flask equipped with a stirrer passing through a mercury seal, a water condenser, and a thermometer were 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:

$$(CH_2)_6\, N_4 + H_2O \longrightarrow 6CH_2O + 4NH_3$$
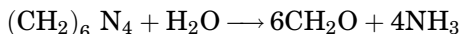
Phenol, CNSL, hexamethylenetetramine and water were weighed out and charged into the flask. The total phenol/formaldehyde (P/F) mole ratios were taken as 1:2.9, 1:2.3, 1:1.7, and 1:1.1. The reaction was carried out at 100°C for 1.5 h with continuous stirring. The semi-solid product was removed from the 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 Elastomers

Materials Used

1. Isobutylene-Isoprene Rubber (IIR) was supplied by Bayer Polymers, India.
2. Natural Rubber (NR)—ISNR-5 was supplied by the Rubber Research Institute of India, Kottayam, Kerala.
3. Zinc Oxide (ZnO) was supplied by M/s Meta Zinc Limited, Mumbai.
4. Stearic acid was supplied by Godrej Soaps (Pvt) Ltd, Mumbai.
5. Sulphur was supplied by the Standard Chemical Company (Pvt) Ltd, Chennai.
6. Tetramethyl thiuram disulphide (TMTD) was supplied by Flexys, Netherlands.
7. Mercaptobenzothiazol disulphide (MBTS) was supplied by Bayer Chemicals, Mumbai.
8. HAF carbon black was obtained from Philip Carbon Black Limited, Kochi, India.

The mixing of the resin and the rubber compound was done on a conventional laboratory size two-roll mill ($150 \times 300\,mm$) at a friction ratio of 1:1.25. The rubber was masticated on a cold mill and the compounding ingredients were added; the resin was added along with the filler. Resin was used at different ratios of 5, 10, 15, 20, and 25 phr. The resin had a constant P:F ratio of 1:2.9 and CNSL:P ratio of 1:1.

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 $30\,cm \times 30\,cm$ platens and $11.76\,Kg_f/cm^2$ at 150°C. IIR was compounded as per ASTM D3188-00 [42] (Table 1) and NR as per ASTM D3184-89 [43] (Table 2). ZnO and stearic acid were added

TABLE 1 Formulation Used for IIR

	R0	R5	R10	R15	R20	R25
IIR	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	1	1	1	1	1	1
MBTS	0.5	0.5	0.5	0.5	0.5	0.5
Carbon black	50	50	50	50	50	50
Paraffinic oil	5	5	5	5	5	5
Resin	0	5	10	15	20	25

as activators for the vulcanization. Sulphur was the cross-linking agent and TMTD and MBTS, the accelerators. Aromatic and paraffinic oils are used as plasticizers and carbon black, the reinforcing agent. Remove styrinated phenol (SP), the antioxidant.

Aging Studies

Oxidative aging tests were carried out for ten days as per ASTM D573-88 [44] using an air oven at 100°C. The physical properties of the specimens before and after aging were determined after every 24 h of aging.

Tensile strength, elongation at break, and modulus of the vulcanizates were determined in accordance with ASTM D412-98 [45]. For this, dumb-bell shaped specimens were punched from vulcanized sheet and the samples were tested on a Zwick tensile testing machine. The crosshead speed was maintained at 500 mm/min.

TABLE 2 Formulation Used for NR

	R0	R5	R10	R15	R20	R25
NR	100	100	100	100	100	100
ZnO	4	4	4	4	4	4
Stearic acid	2	2	2	2	2	2
S	2.5	2.5	2.5	2.5	2.5	2.5
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 (HAF)	50	50	50	50	50	50
Aromatic oil	5	5	5	5	5	5
Resin	0	5	10	15	20	25

Tear resistance of the samples was determined according to ASTM D 624-00 [46] using angular specimens punched out from compression-molded sheets. Throughout the test the speed of the grip was kept at 500 mm/min.

RESULTS AND DISCUSSION

IIR

Figures 6–9 depict the effect of aging time on the properties of IIR containing various amounts of the resin. IIR has a limited number of unsaturation sites and shows good aging characteristics. Even on such a rubber the resin has a very pronounced modifying action.

Referring to Figure 6, before aging there is a decrease in tensile strength on addition of more and more resin. The extent of unsaturation in IIR is not high. Hence there is only limited possibility for interaction between the resin and the elastomer backbone. The tensile strength remains steady on aging in cases where a minimum of 10 phr resin has been added. At high resin contents, say 25 phr, there is a slight increase in tensile strength at later stages of aging. Interaction between isoprene units and resin as per reaction schemes given in Figures 4 and 5 may be responsible for this.

Figure 7 shows the effect of aging time on elongation at break. The presence of the resin is seen to lower the elongation at break, the effect steadily increasing on adding more resin. For higher resin contents there is a steady fall in elongation at break. It is to be concluded that
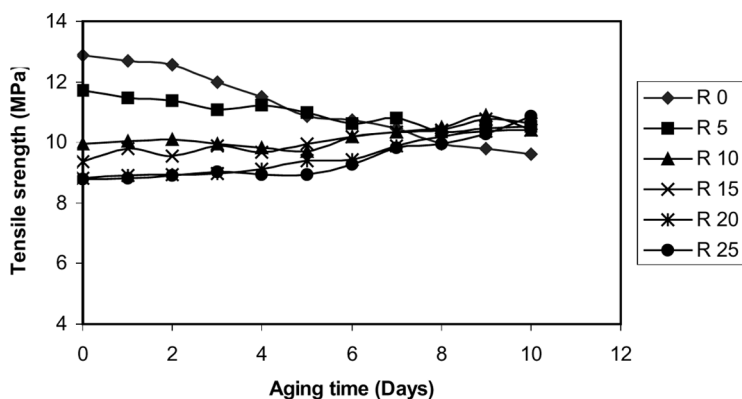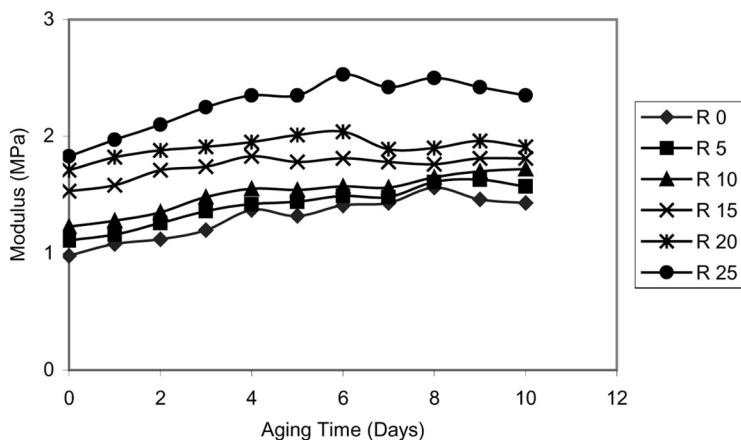

FIGURE 6 Variation of tensile strength with aging time of IIR vulcanizates with different resin contents.
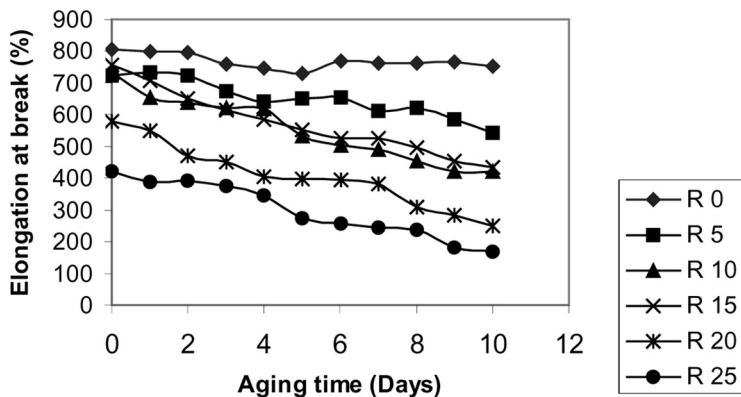
FIGURE 7 Variation of elongation at break with aging time of IIR vulcanizates with different resin contents.

chemical interaction between the resin and rubber increases and intercomponent grafting becomes possible as the resin content increases. This results in some loss of elasticity for samples containing resin as the aging proceeds.

Figure 8 is a plot of tensile modulus of IIR with aging time. Maximum tensile modulus is observed for samples containing the maximum resin (25%). There is a slight increase in modulus as aging proceeds. The magnitude of the modulus almost reaches a constant value at about 7 days and beyond. The slight increase in modulus

FIGURE 8 Variation of modulus with aging time of IIR vulcanizates with different resin contents.
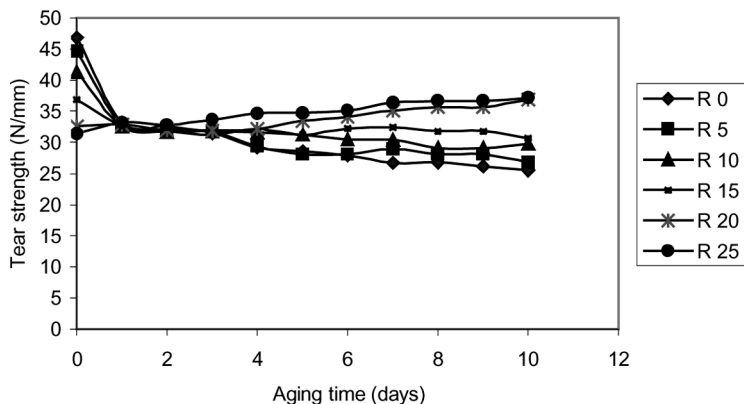
FIGURE 9 Variation of tear strength with aging time of IIR vulcanizates with different resin contents.

during aging suggests the incorporation of the resin into the cross-linked network. The presence of the resin causes stiffening of the chain and leads to a higher modulus.

Figure 9 shows the effect of aging time on tear strength of IIR specimens. The effect of the resin is initially to reduce the tear strength but very soon, after one day of aging, all samples show practically the same tear strength. But beyond that period the tear strength of samples containing the resin shows an increasing trend, the larger the resin content, the higher being the tear strength. Tear strength is one property where the presence of resin substantially improves the aging behavior of IIR.

NR

Figures 10–13 show the effect of aging time on the properties of NR containing resin.

Figure 10 shows the variation of tensile strength with aging time for NR samples. Initially the presence of the resin leads to a high tensile strength. But all the samples show a steep fall in tensile strength on continued aging. At later stages of aging all the curves come closer. NR is known to undergo chain scission on prolonged periods of aging. The extent to which this is prevented by the resin is not substantial.

Figure 11 shows a higher elongation at break for samples containing resin. As in the case of tensile strength, there is a steep fall in
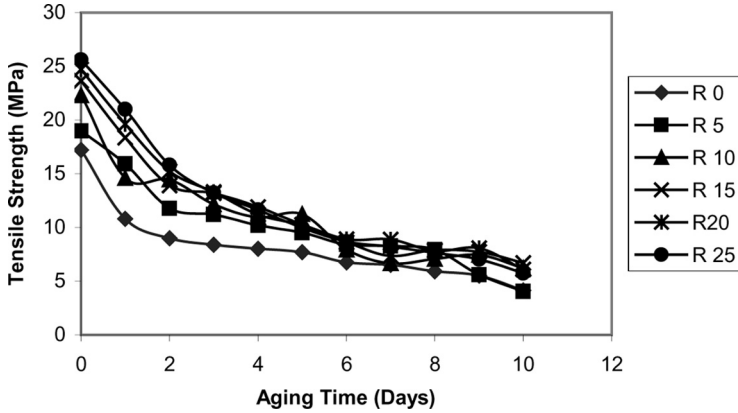
FIGURE 10 Variation of tensile strength with aging time of NR vulcanizates with different resin contents.

elongation at break on aging. The initial high elongation at break of samples containing large amounts of resin falls sharply until at about 8 days of aging time the curves almost overlap each other.

Figure 12 shows the variation of modulus on incorporation of resin. Samples containing high amounts of resin show an increase in modulus on aging whereas those containing little or no resin show a gradual fall in modulus. This can be attributed to the physical presence of resin in the rubber network. For an elastomer with extensive unsaturation like NR the presence of the resin is not sufficient to prevent the deterioration of tensile properties on aging. A reaction between the
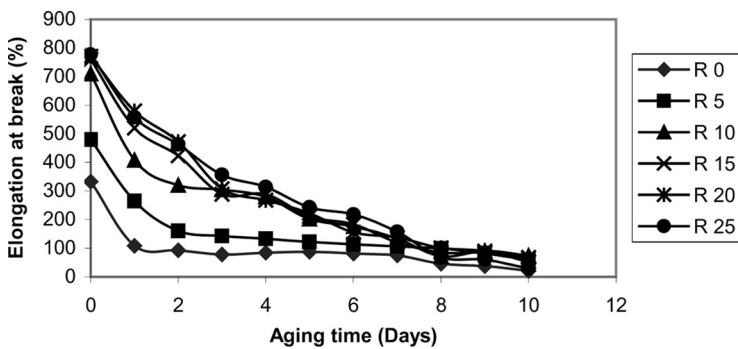
FIGURE 11 Variation of elongation at break with aging time of NR vulcanizates with different resin contents.
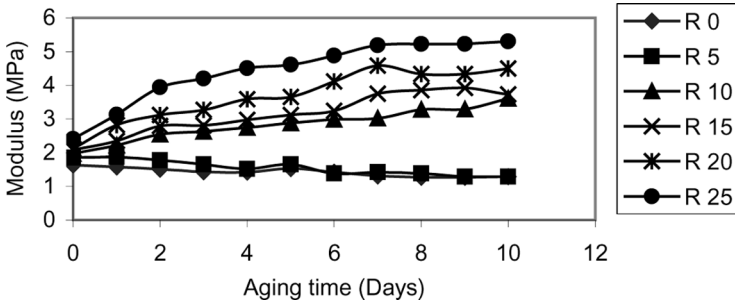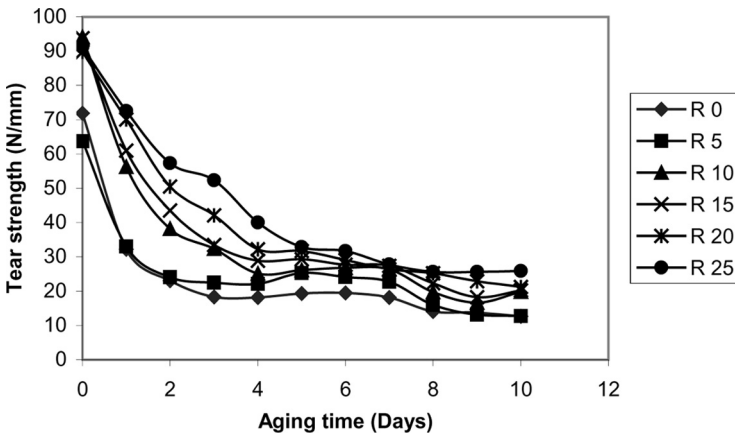
FIGURE 12 Variation of modulus with aging time content of NR vulcanizates with different resin contents.

rubber and the resin is either inadequate or takes place at a few limited sites.

Figure 13 shows the effect of aging time on tear strength. Initially high tear strength is observed for samples with high resin content. But during the later stages of aging the curves come closer. Loss of crystallinity due to the presence of the resin in the network can be the reason for this.

CONCLUSIONS

Copolymer obtained by condensation of phenol and CNSL with hexamethylenetetramine improves the aging characteristics of IIR with

FIGURE 13 Variation of tear strength with aging time content of NR vulcanizates with different resin contents.

respect to retention of tensile strength, modulus, tear strength, and elongation at break. But the effect on tear strength is not encouraging. The resin is effective against aging of IIR, which has only limited sites of unsaturation.

A continuous fall in tensile strength, elongation at break and tear strength in the case of NR is not stopped by the presence of the resin. But initial values of these properties before aging improve marginally on addition of resin. Only the modulus retains/improves the original magnitude on aging. The presence of resin does not alter this behavior. The resin does not improve the aging properties of NR, which has more sites of unsaturation than IIR.

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