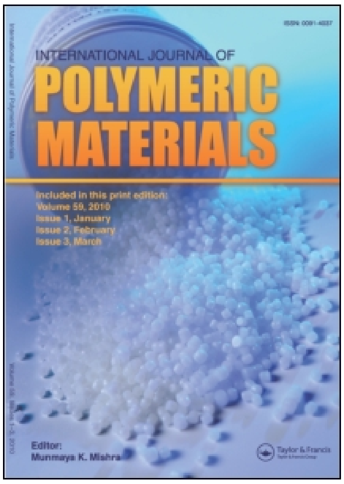

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Effect of Phenol-CNSL Formaldehyde Copolymer on Thermal Ageing of Elastomers

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Cashew nut shell liquid (CNSL) is a cheap agro-byproduct 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, chloroprene, CR and ethylene propylene rubber, EPDM. 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 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 ageing characteristics with respect to tensile strength, modulus, and tear strength.

Keywords: elastomers, phenol-CNSL-formaldehyde polymer, thermal ageing

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

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passes from a predominantly plastic state to a predominantly elastic one because of the formation of intermolecular bridges.

The mechanical properties of crosslinked 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 ageing can be attributed to oxidation processes [1]. Reaction with oxygen causes chain scission and/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 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 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 after ageing 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 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 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 esin 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.

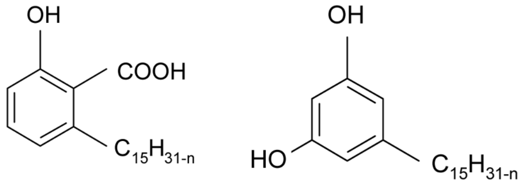
In this investigation, modification of CR and EPDM using a CNSL-based resin has been done to improve ageing characteristics.

CNSL Structure and Composition

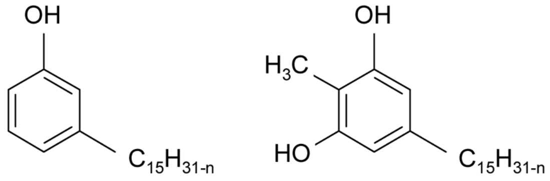
CNSL is a by-product of the cashew industry. It is a naturally occurring phenolic substance. Being an agricultural by-product it has the advantages of low cost and renewable supply, and can replace phenol in many applications. With a need to conserve petrochemicals, increased utilization of this material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



ANACARDIC ACID CARDOL



CARDANOL 2-METHYL CARDOL

FIGURE 1 Components of CNSL.

attempt has been made to separate the components of CNSL. It was used as 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 polymerizable substance, amenable to a variety of polymerization reactions. The

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

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

$(CH_2)_7-CH{=}CH-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2$ n=2

$(CH_2)_7-CH{=}CH-CH_2-CH{=}CH-CH_2-CH_2-CH_2$ n=4

$(CH_2)_7-CH{=}CH-CH_2-CH{=}CH-CH_2-CH{=}CH_2$ n=6

FIGURE 2 Components of side chain.

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 CR and EPDM 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).

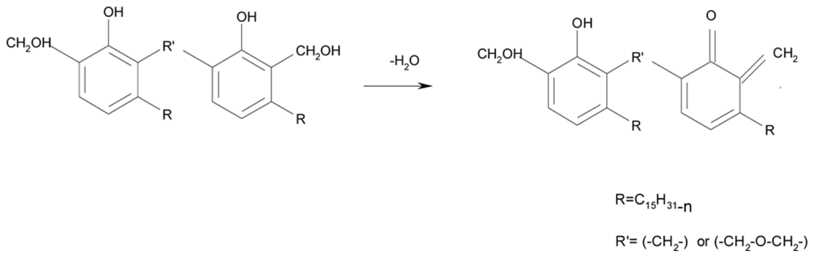


FIGURE 3 Formation of quinone intermediate.

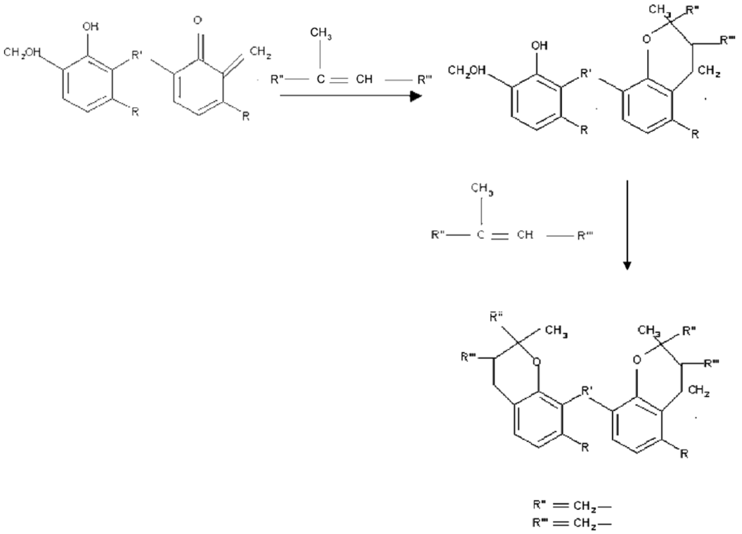


FIGURE 4 Reaction of phenolic resin with elastomers (Chroman mechanism).

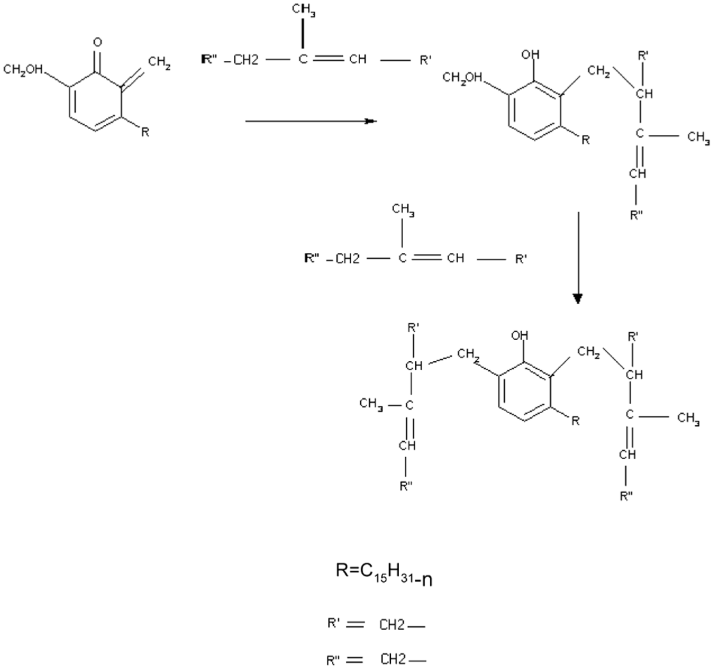


FIGURE 5 Reaction of phenolic resin with elastomers (Allyl hydrogen mechanism).

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 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 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:

$$(CH_2)_6N_4 + H_2O \longrightarrow 6CH_2O + 4NH_3$$

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 CR and EPDM

Materials Used

1. Chloroprene (CR W) was supplied by DuPont, Akron, Ohio.
2. Ethylene Propylene Rubber (EPDM) was supplied by Zenith Rubber and Plastic Works, Mumbai.
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 sulphenamide (MBTS) was supplied by Bayer Chemicals, Mumbai.
8. Carbon black was supplied by Philip carbon Black Limited, Kochi, India.
9. Paraffinic oil was supplied by M/s Hindustan Petroleum Limited, India.
10. Naphthenic oil was supplied by Indian Oil Corporation.

The mixing of the resin and the rubber compound was done on a conventional laboratory size two-roll mill (150 × 300 mm) at a friction ratio of 1:1.25 according to ASTM D 3185-99 [42]. 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 the rate of 5, 10, 15, 20, and 25 phr. The resin had a constant P:F ratio of 1:2.9 and CNSL: P ratio 1:1.

CR was compounded as per ASTM D 3190-00 [43] and EPDM as per ASTM D 3568-03 [44]. Formulation used for compounding CR is shown in Table 1 and for EPDM is shown in Table 2.

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 at 150°C.

For CR, combination of MgO and ZnO were used as curing system and ethylene thiourea as accelerator. Carbon black was used as reinforcing agent and naphthenic oil was used as plasticizer.

TABLE 1 Formulation Used for CR

	R0	R5	R10	R15	R20	R25
CR	100	100	100	100	100	100
MgO	4	4	4	4	4	4
ZnO	5	5	5	5	5	5
Carbon black (HAF)	50	50	50	50	50	50
Naphthenic oil	5	5	5	5	5	5
Ethlene thiourea (NA 22)	0.5	0.5	0.5	0.5	0.5	0.5
Octylated diphenylamine	1	1	1	1	1	1
Resin	0	5	10	15	20	25

For EPDM, sulphur was used as the crosslinking agent and TMTD and MBTS as accelerators. ZnO and stearic acid were added as activators for the vulcanization. Carbon black was used as the reinforcing material. Paraffinic oil was used as plasticizer.

Ageing Studies

Oxidative ageing tests were carried out for ten days as per ASTM D 573-88 [45] 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 [46]. For this, dumbbell-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 [47] using angular specimens punched out from

TABLE 2 Formulation Used for EPDM

	R0	R5	R10	R15	R20	R25
EPDM	100	100	100	100	100	100
ZnO	4	4	4	4	4	4
Stearic acid	2	2	2	2	2	2
S	1	1	1	1	1	1
TMTD	0.5	0.5	0.5	0.5	0.5	0.5
MBTS	2	2	2	2	2	2
Carbon black	50	50	50	50	50	50
Paraffinic oil	5	5	5	5	5	5
Resin	0	5	10	15	20	25

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

Swelling index was measured as per ASTM D 3616-95 [48] and acetone soluble matter as per ASTM D 297-93 (2002) [49].

RESULTS AND DISCUSSION

Effect of Resin on the Ageing Properties of CR

Figures 6–11 show the effect of addition of resin on the properties of CR during ageing. CR is known to have good thermal resistance.

Figure 6 shows the variation of tensile strength with ageing time of CR vulcanizates with different resin contents. There is a marginal increase in tensile strength on addition of resin. It is found that ageing does not affect the tensile strength of CR substantially. Even in the absence of resin there is very little reduction in tensile strength even after 10 days of ageing.

Figure 7 shows that elongation at break falls drastically on continuous ageing. This is normal behavior for crosslinked materials. The samples containing resin has a comparatively lower elongation at break after ageing. This shows stiffening of the network and possible incorporation of the resin into the crosslinked network.

Figure 8 shows that there is initially an increase in tensile modulus on addition of resin. All the samples including the one not containing the resin show an increase in modulus as ageing proceeds. Change in modulus on ageing can be the result of chemical changes like dehydrochlorination and interaction between the rubber and resin.

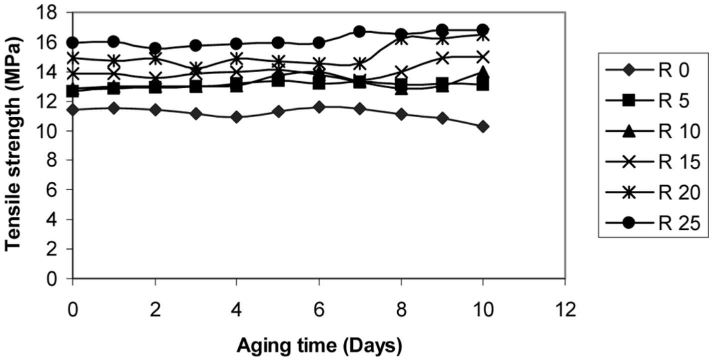


FIGURE 6 Variation of tensile strength with ageing time of CR vulcanizates with different resin contents.

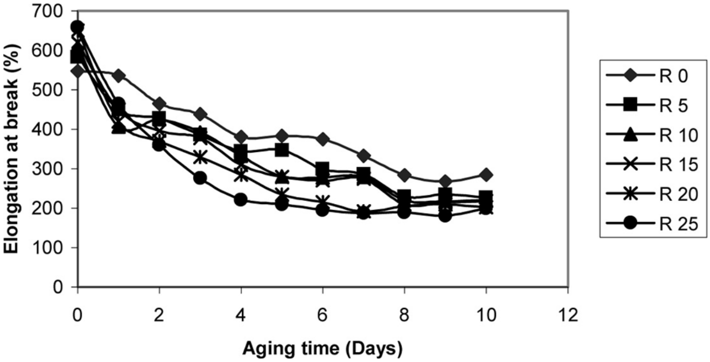


FIGURE 7 Variation of elongation at break with ageing time of CR vulcanizates with different resin contents.

Figure 9 is a plot of tear strength with ageing time. CR containing resin has superior tear strength at all stages of the study. Fall in tear strength with ageing time is very moderate for all cases.

Figure 10 is a plot of swelling index with ageing time. Swelling index decreases as ageing time increases. This indicates continued crosslinking on ageing. The presence of the resin leads to a slight reduction in swelling index. This again points to a greater degree of crosslinking on addition of resin.

Figure 11 is a plot of acetone soluble matter with ageing time. As resin content increases acetone soluble matter content increases. Some amount of uncrosslinked material is introduced by the resin.

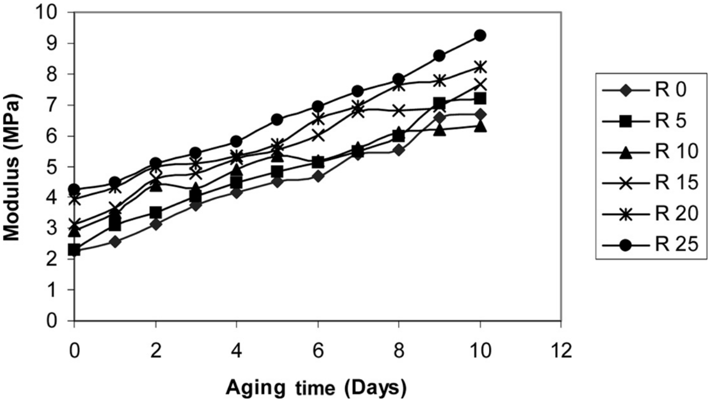


FIGURE 8 Variation of modulus with ageing time of CR vulcanizates with different resin contents.

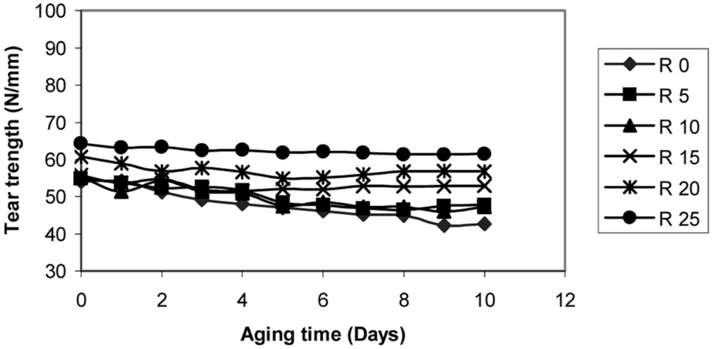


FIGURE 9 Variation of tear strength with ageing time of CR vulcanizates with different resin contents.

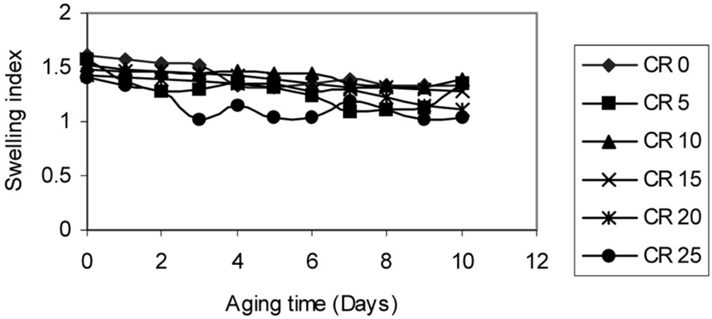


FIGURE 10 Variation of swelling index with ageing time of CR vulcanizates with different resin contents.

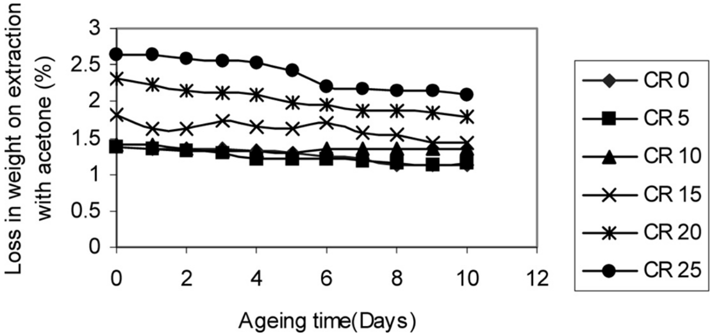


FIGURE 11 Variation of loss in weight on extraction with acetone with ageing time of CR vulcanizates with different resin contents.

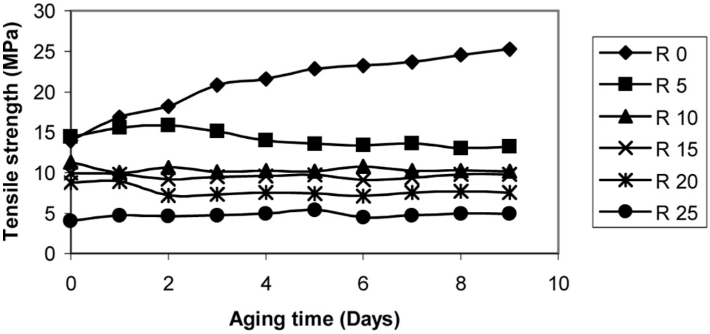


FIGURE 12 Variation of tensile strength with ageing time of EPDM vulcanizates with different resin contents.

Effect of Resin on the Ageing Properties of EPDM

Figures 12–17 show the effect of ageing time on the properties of EPDM containing resin.

Figure 12 shows a slight reduction in tensile strength on addition of resin before ageing. All the samples containing resin show almost constant tensile strength on ageing. EPDM has considerable age resistance. It appears that ageing of the unmodified EPDM leads to introduction of additional crosslinks, resulting in higher tensile strength. The resin is seen to stabilize the tensile strength.

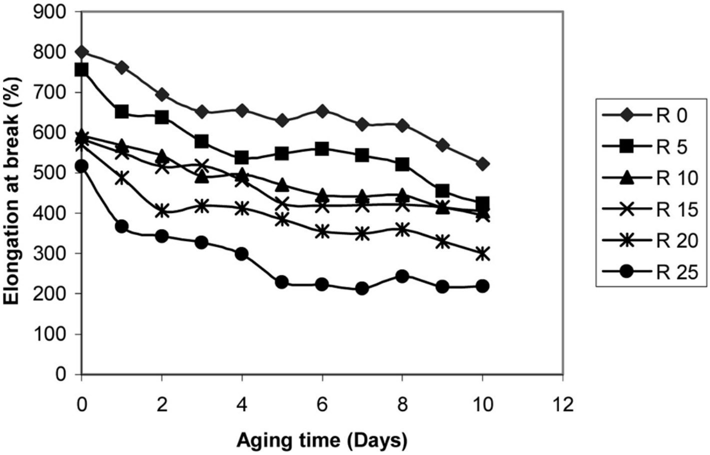


FIGURE 13 Variation of elongation at break with ageing time of EPDM vulcanizates with different resin contents.

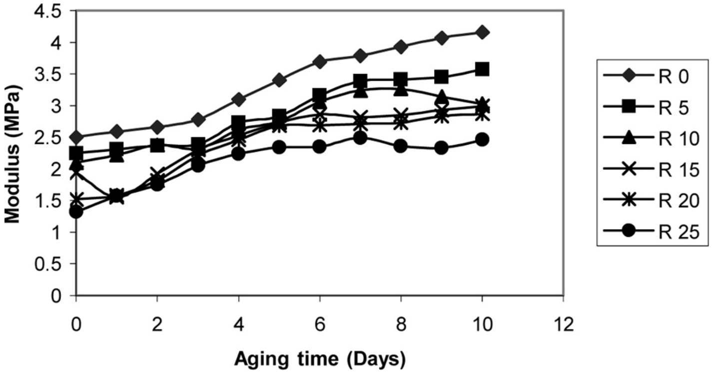


FIGURE 14 Variation of modulus with ageing time of EPDM vulcanizates with different resin contents.

Figure 13 shows a general fall in elongation at break on ageing. The elongation at break for samples containing the resin is less at any stage of the ageing process. The resin causes a stiffening of the network. This may be attributed to either interpenetrating network or the formation of a composite network with intercomponent grafting.

Figure 14 is a plot of tensile modulus versus ageing time of EPDM. There is a general increase in modulus with ageing time. Samples containing resin have a lower modulus at all stages of the study. Hence, a more likely occurance is the formation of an IPN rather than a randomly crosslinked material consisting of rubber and resin.

Figure 15 shows the change in tear strength with ageing time. Samples containing resin in excess of 10% show an increase in tear

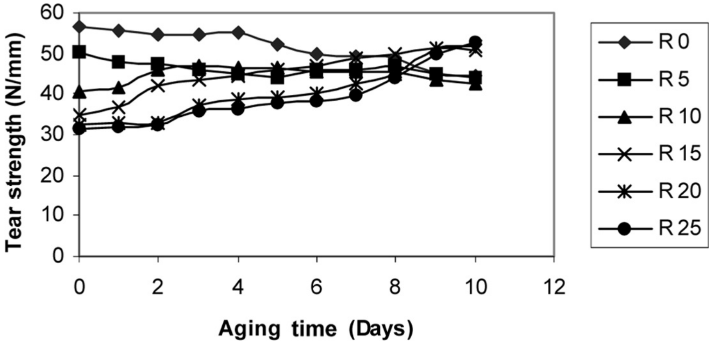


FIGURE 15 Variation of tear strength with ageing time of EPDM vulcanizates with different resin contents.

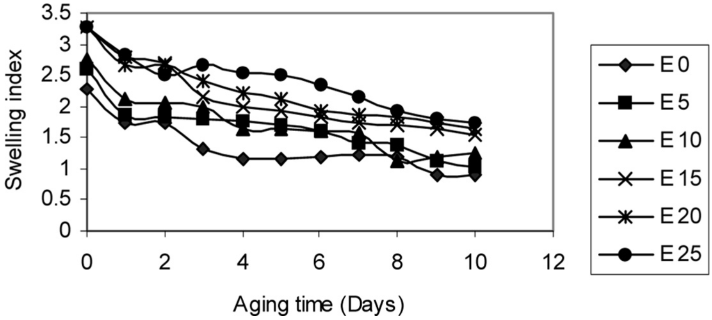


FIGURE 16 Variation of swelling index with ageing time of CR vulcanizates with different resin contents.

strength with ageing time whereas samples with low resin content show a slight fall in tear strength on ageing. At about 8 days of ageing all samples have practically the same tear strength. The tear strength of samples with higher resin content continues to rise even after that.

Figure 16 shows the change in swelling index with ageing time. The fall in swelling index shows that the gel content increases steadily on aging. Because the swelling index is maximum for the samples with higher resin content the more likely explanation is an interpenetrating polymer networks (IPN), which permits penetration by the solvent.

Figure 17 shows the variation in weight loss on extraction with acetone. Although initially there is more loss of material on extraction for samples containing resin, at the end of the ageing peroid all curves converge to the same extent of extractable content. On prolonged ageing the resin and rubber form a highly crosslinked network.

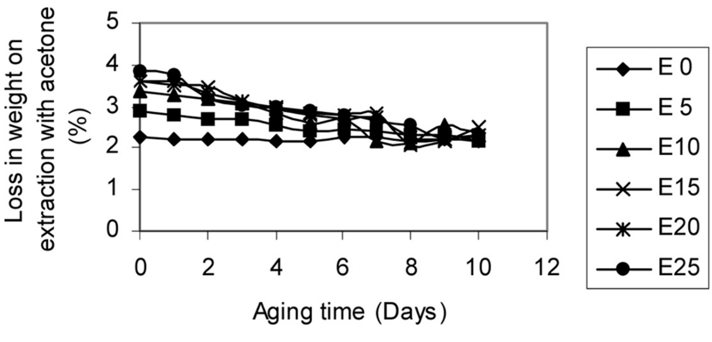


FIGURE 17 Variation of loss in weight on extraction with acetone with ageing time of CR vulcanizates with different resin contents.

CONCLUSIONS

CNSL as well as the copolymer obtained by condensation of phenol and CNSL with hexamethylenetetramine improve the ageing characteristics of CR with respect to retention of tensile strength, modulus, tear strength, and elongation at break.

CR has good inherent resistance to ageing. A marginal increase in tensile strength on addition of resin is retained throughout the ageing period. Tear strength and modulus also show an increase on ageing. The presence of resin does not alter this behavior. The elongation at break reduced on addition of resin and continues to fall on ageing.

Tensile strength, elongation at break, modulus, and tear strength of EPDM are found to decrease on addition of resin. Although the samples show good property retention on ageing, the use of the resin may not be desirable because of the fall in properties on adding it.

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