Effect of Non-Oiled Sulfur Concentration on the Adhesion Between Nitrile Rubber and Nylon Cord

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ABSTRACT: The effect of non-oiled sulfur concentration on the adhesion between nitrile rubber (NBR) and dipped or undipped Nylon 6,6 cords is discussed. The results show that using undipped cords with NBR (grade 34/50) enhance adhesion. In this article, the crosslink density of different nitrile rubber mixes were estimated to illustrate their effect on adhesion. The resistance to heat aging and ionizing radiation were also studied. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 762–771, 1999

Key words: nitrile rubber; nylon cord; adhesion; sulfur; aging; radiation

INTRODUCTION

Sulfur plays a very important role in the vulcanization process of rubber mixes. This was discussed in detail before.[1,2] It is well known that sulfur may be present in rubber mix in the form of pendant sulfides, mono-, di-, and polysulfides or cyclic mono-, di-, and polysulfides. The state in which sulfur is namely mono-, di-, or polysulfides depends on the sulfur-to-accelerator ratio. High levels of sulfur and low levels of accelerators are called conventional vulcanizing systems. At optimum cure, the vulcanizates contain mostly polysulfidic crosslinks. Low sulfur levels with high accelerator levels, known as efficient vulcanizing systems (EV), will give mainly monosulfidic crosslinks. Semiefficient vulcanizing systems (Semi-EV) have intermediate levels of sulfur and accelerator.

Reinforcement of rubber by textile cords has been discussed by many authors,[3–7] who also discussed factors affecting rubber to cord adhesion. Adhesion is an important factor in using textile materials together with rubber as well as individual properties of each material. The role of adhesion may be (1) to give desirable properties, (2) to improve durability, and (3) maintain the shape of the composite. Tires, belts, and transmission belts are used under severe conditions; therefore, very high levels of adhesion are required. In general, strong adhesion is obtained through adhesive treatment of the textile or through addition of bonding agents to the rubber compounds, or both systems can be used in order to promote adhesion. Hoses and coated fabrics do not require such high adhesion.

Buswell and Meyrick,[8] Rayner,[9] and Albrecht[10] reported that sulfur levels appear to be important with Rayon and Nylon and that adhesion levels increases as sulfur is increased. Meyrick and Watts[11] claimed that the sulfur level is less critical when a direct bonding system is used and that sulfur-less systems gave relatively poor adhesion. The former observations of Meyrick and Watts[11] contradict with Albrecht,[10] who claims that, even when using a direct bonding system, adhesion of nylon is influenced most by the sulfur level.

In this article, the effect of non-oiled sulfur (99% sulfur content and free from naphthenic oil) concentration on the adhesion between NBR 40/50 and 34/50 and Nylon 6,6 cords was exam-

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Table I Specifications of NBR

Product Name	Acrylonitrile Content (%)	Mooney Viscosity ML (1 + 4) 100°C	Density (gm/cm^3)	Stabilizer	Physical Form
Krynac 34/50	33	45 ± 5	0.98	nonstaining	blades
Krynac 40/50	38.5	50 ± 5	0.99	nonstaining	blades

ined. The study also shows the effect of crosslink density of the rubber mix, aging, and radiation on the adhesion.

EXPERIMENTAL

Materials

NBR Compounds

Two grades of NBR were used in this study, Krynac 40/50 and Krynac 34/50, supplied by Polysar Co., France, and denoted as A and B, respectively. These polymers differ in their acrylonitrile content, viscosity, and density. The various properties of both NBR grades are given in Table I, as provided by the producer. In this study, the rubber mixes, based on various non-oiled sulfur concentrations, were prepared on a two-roll mill at a friction ratio of 1 : 1.25. The tricomponent system, consisting of hexamethylene tetramine–Resorcinol–hydrated silica (HRH), was added to the rubber mix in order to promote the adhesion between rubber and textile cord. Curing was carried out at temperature of 153°C and for 10 and 8 min for NBR 40/50 and 34/50, according to the results estimated using the Monsanto Rheometer. The formulations of the two NBR grades are given in Table II.

Textile Cord

Nylon (140/2 tex) was supplied by El Nile Kerdasa Co., Egypt. The cords used were either dipped or undipped. Resorcinol–formaldehyde–latex (RFL) was used as a dipping solution, where the latex is 100% vinyl pyridine.

Adhesion Measurements

H-pullout tests were used to measure adhesion. Dipped and undipped cords were bonded to rubber compounds according to ASTM D2138-83 using a mould capable of producing 30 H-type test

Table II Mix Formulations of NBR 40/50 (Grade A) and NBR 34/50 (Grade B) Containing Different Concentrations of Non-Oiled Sulfur

Mix Symbol → / Ingredients ↓	AS_1 / BS_1	$AS_{1.5}$ / $BS_{1.5}$	AS_2 / BS_2	$AS_{2.5}$ / $BS_{2.5}$	AS_3 / BS_3
Krynac 40/50	100.0	100.0	100.0	100.0	100.0
Stearic acid	1.5	1.5	1.5	1.5	1.5
Zinc oxide	5.0	5.0	5.0	5.0	5.0
GPF–Black	60.0	60.0	60.0	60.0	60.0
Peptizer[a]	10.0	10.0	10.0	10.0	10.0
6PPD	3.0	3.0	3.0	3.0	3.0
Non-oiled sulfur	1.0	1.5	2.0	2.5	3.0
CBS	1.0	1.0	1.0	1.0	1.0
Resorcinol	2.0	2.0	2.0	2.0	2.0
Vulcacil-H[b]	1.2	1.2	1.2	1.2	1.2
Silica	5.0	5.0	5.0	5.0	5.0

Concentrations are in parts per hundred parts of rubber.
[a] Pentachloro thiophenol.
[b] Hexamethylene tetramine.

Table III Mechanical Properties of NBR 40/50 Mixes

Mix Symbol → Mechanical Property ↓	AS_1	$AS_{1.5}$	AS_2	$AS_{2.5}$	AS_3
Tensile strength (MPa)	7.8	11.9	15.4	16.7	24.1
Elongation at break (%)	503.8	449.2	341.6	375.2	314.3
Stress at 100% strain (MPa)	4.1	4.7	4.7	6.3	11.0
Stress at 200% strain (MPa)	5.1	7.0	9.7	11.1	18.8
Stress at 300% strain (MPa)	6.3	9.5	14.1	15.1	23.5
Hardness (Shore-A)	62.8	67.7	73.2	72.7	73.0

pieces. The mould consists of six cavities (170 × 6.4 × 3.2 mm). Through the separating strips were a series of grooves to accommodate the cords. The rubber strips of 6 mm width were placed into the mould cavities, and the cords were placed in the cord slots in contact with the rubber. Each cord was knotted at one end to be secured firmly against the cord slot on one side of the mould, and a tensioning weight of 100 g was attached on the other end of the cord. Further strips of the rubber were placed in the mould cavities on top of the cords, thus sandwiching the cords. The mould was closed, and vulcanization was carried out in a press at a curing temperature of 153°C and for the optimum time estimated. After curing, the pads were stored overnight before being cut and then tested in a tensile tester at a jaw separation of 300 mm/min. The pullout force was expressed in N/cm.

Aging

Aging was carried out according to ASTM D-573-a. Thermal oxidation of the vulcanized rubber–cord assembly was carried out for different time durations in an air-circulating oven at 90°C. The retained values of the adhesion force were determined for various time intervals.

Irradiation Procedure

To study the effect of radiation on the adhesion between cord and rubber, H-shaped samples were exposed to cobalt 60 at a dose rate of 2660 Gy/h. The doses in this study were 2500, 5000, 7500, and 10000 Gy ($1M$ rad = 10^4 Gy). The exposed samples were examined 24 h after irradiation.

Stress–Strain Measurements at Low Strains and Determination of the Crosslink Density of Nitrile Rubber, ν

For these measurements, dumbbell test specimens (30 × 4 × 2 mm) were used, and measurements were made at the central part, 2 cm in length. The thickness and width are measured accurately. Two clamps were designed to grip the sample; the downward clamp has a hook to hold the pan in which different weights were applied. The initial specimen length (l_0) and length (l), corresponding to each force applied (f), were measured accurately using an optical cathetometer. From these results, (f/a_0) were calculated and plotted against ($\lambda - \lambda^{-2}$) where λ is the extension ratio (l/l_0) and a_0 is the cross-sectional area. From these linear relations, the molecular weight between crosslinks M_c and the crosslink density υ were calculated.[12]

Table IV Mechanical Properties of NBR 34/50 Mixes

Mix Symbol → Mechanical Property ↓	BS_1	$BS_{1.5}$	BS_2	$BS_{2.5}$	BS_3
Tensile strength (MPa)	7.2	12.8	19.2	16.2	23.7
Elongation at break (%)	463.6	397.8	452.8	309.0	312.8
Stress at 100% strain (MPa)	4.1	4.9	6.7	6.2	11.3
Stress at 200% strain (MPa)	5.0	7.5	11.2	11.5	18.6
Stress at 300% strain (MPa)	6.0	10.6	15.4	16.0	23.2
Hardness (Shore-A)	55.0	61.4	71.1	67.6	71.7

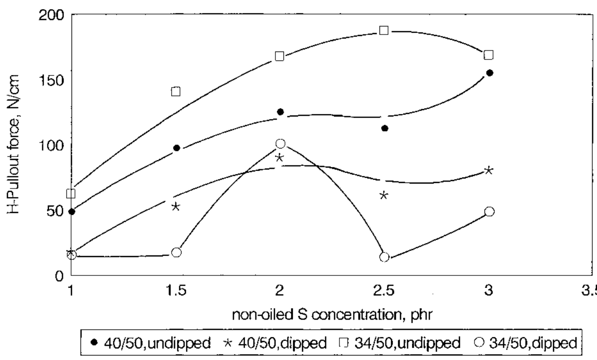


Figure 1 Effect of non-oiled sulfur concentration on adhesion.

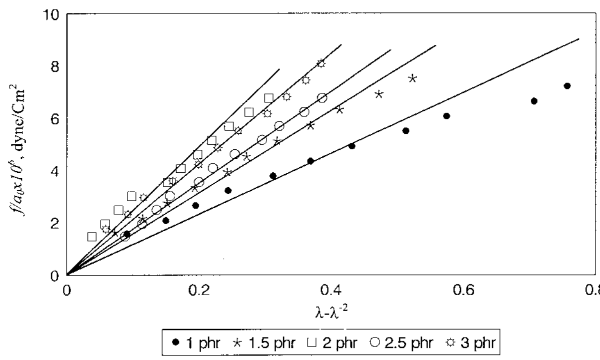


Figure 3 Stress–strain relations for NBR 34/50.

RESULTS AND DISCUSSION

Effect of Non-Oiled Sulfur Concentration on the Adhesion Properties

The mechanical properties of NBR 40/50 and 34/50 mixes are illustrated in Tables III and IV. The relation between the H-pullout force and non-oiled sulfur concentration is shown in Figure 1. The figure shows that 2 phr (part per hundred parts of rubber) non-oiled sulfur is optimum in all cases except in the case of NBR 34/50 bonded to undipped cord, where 2.5-phr non-oiled sulfur is recommended. In all cases, conventional sulfur-curing systems are required to obtain best adhesion results, where polysulfidic crosslinks are mainly formed during the curing process. This may be due to the need of a sufficient amount of sulfur, which is enough for diffusing from the rubber to the cord and covulcanizing both of them together. While mixes containing larger amounts of sulfur form cyclic polysulfidic crosslinks in the rubber mix, that does not contribute to the adhesion process or even in the vulcanization process itself. On the other hand, using small amounts of sulfur (<2 phr) leads to inferior adhesion properties as sulfur will not be enough to covulcanize the rubber with the cord.[1,2]

Effect of Non-Oiled Sulfur Concentration on the Crosslink Density of the Rubber Mix

Figures 2 and 3 illustrate the stress–strain measurements made for NBR 40/50 and 34/50 mixes, respectively, containing different non-oiled sulfur concentrations. The relationship between the crosslink density υ at various concentrations of non-oiled sulfur can be drawn, as shown in Figure 4. From this figure and Figure 1, it is clear that adhesion levels were achieved when the rubber mix possesses the maximum value of crosslink density. Therefore, it can be said that sulfur is apparently involved in a process of covalent bond formation between the rubber mix and either (1) the dip film present on the surface of the cords[3–5,7,11,13–16] or (2) the bare surface of the nylon cords.

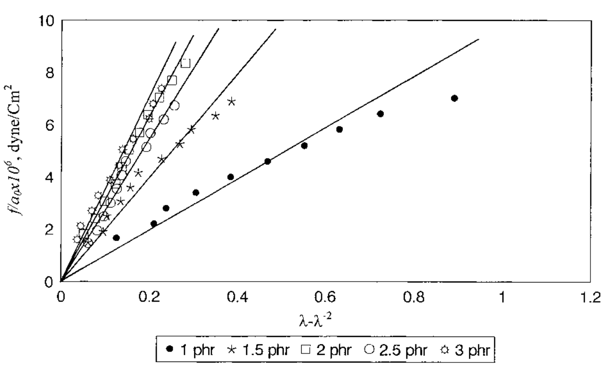


Figure 2 Stress–strain relations for NBR 40/50.

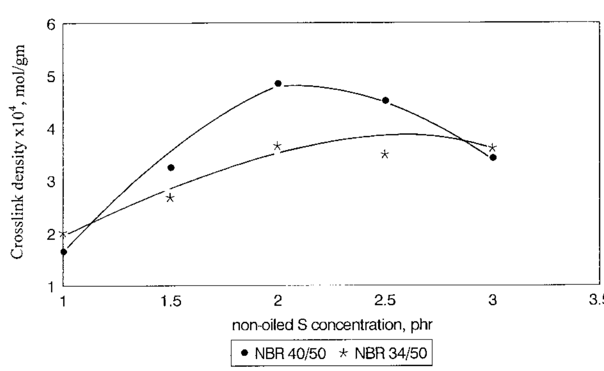
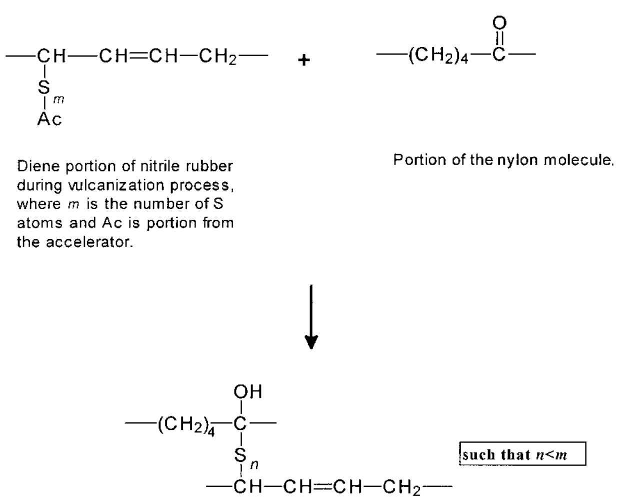


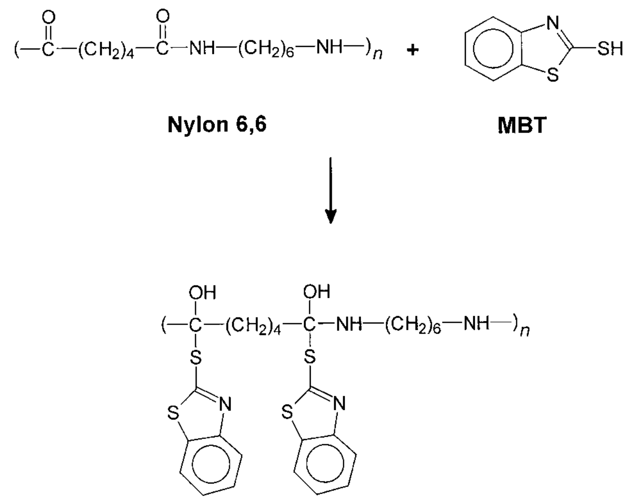
Figure 4 Effect of non-oiled sulfur concentration on the crosslink density of the rubber mix.

Effect of Aging on the Adhesion Properties in Mixes Containing Different Non-Oiled Sulfur Concentrations

Figure 5 illustrates the effect of aging on the adhesion between NBR 40/50 and undipped nylon cords in mixes containing different concentrations of non-oiled sulfur. From the figure, it is clear that mixes containing 1- and 1.5-phr non-oiled sulfur show a remarkable increase in the H-pullout force on early aging stages (<2 days). On further aging, a slight increase in the pullout force is achieved, followed by a state of stability after about 6 days. The achieved pullout force in case of 1-phr non-oiled sulfur is about 600%, while in case of 1.5 phr, it is about 150%. This can be explained by considering the fact that these mixes are vulcanized through a semiefficient vulcanizing system that mainly forms monosulfidic crosslinks as well as pendant sulfides inside the mix.[1,2] Accordingly, the improvement in adhesion can be attributed to the possibility of covalent bond formation between sulfur atoms of the rubber–sulfur–accelerator (rubber–S–Ac) system, as a nucleophile, and the carbonyl groups of the undipped nylon cords during the vulcanization process. This is shown in the following scheme:



This addition reaction is believed to be enhanced thermally during aging; consequently, the adhesion strength is increased. This proposed reaction has been confirmed by reacting a sulfur containing compound like MBT, mercapto benzthiazole, and nylon by dissolving nylon cords in hot glacial acetic acid and adding MBT dissolved in dimethyl formamide (DMF) dropwise with constant stirring until addition is completed. The reaction is illustrated in the following scheme:



The solution was left to cool for 1 h until complete precipitation of the product took place, then the product was filtered, and the precipitate was dried. ^{1}H nuclear magnetic resonance (^{1}H-NMR) and infrared (IR) techniques were used to elucidate the structure of the expected product. Figures 6 and 7 show the ^{1}H-NMR of the pure nylon and the product, respectively, whereas Figures 8 and 9 show their IR spectra. From Figure 7, it is clear that the aromatic signals of MBT appear at 7–7.8 ppm, and the proton of O—H at 1.8 ppm. These signals do not appear in the spectra of pure nylon in Figure 6, which proves the reaction of MBT with carbonyl groups of nylon. These results are supported by the peaks of the IR spectra, where Figure 9 of the product shows both the N—H at 3200 cm^{-1} and the O—H at 3450 cm^{-1}. The latter peak did not appear in Figure 8 of the pure nylon. However, the incomplete disappearance of the carbonyl band at 1624 cm^{-1} can be related to the possibility that the reaction product is still mixed with some unreacted nylon.

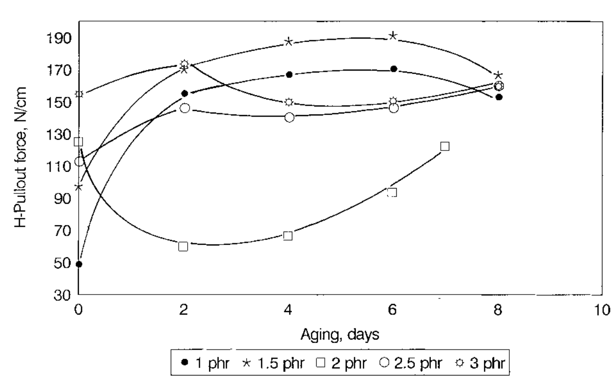


Figure 5 Effect of aging on adhesion between NBR 40/50 and undipped nylon cords.

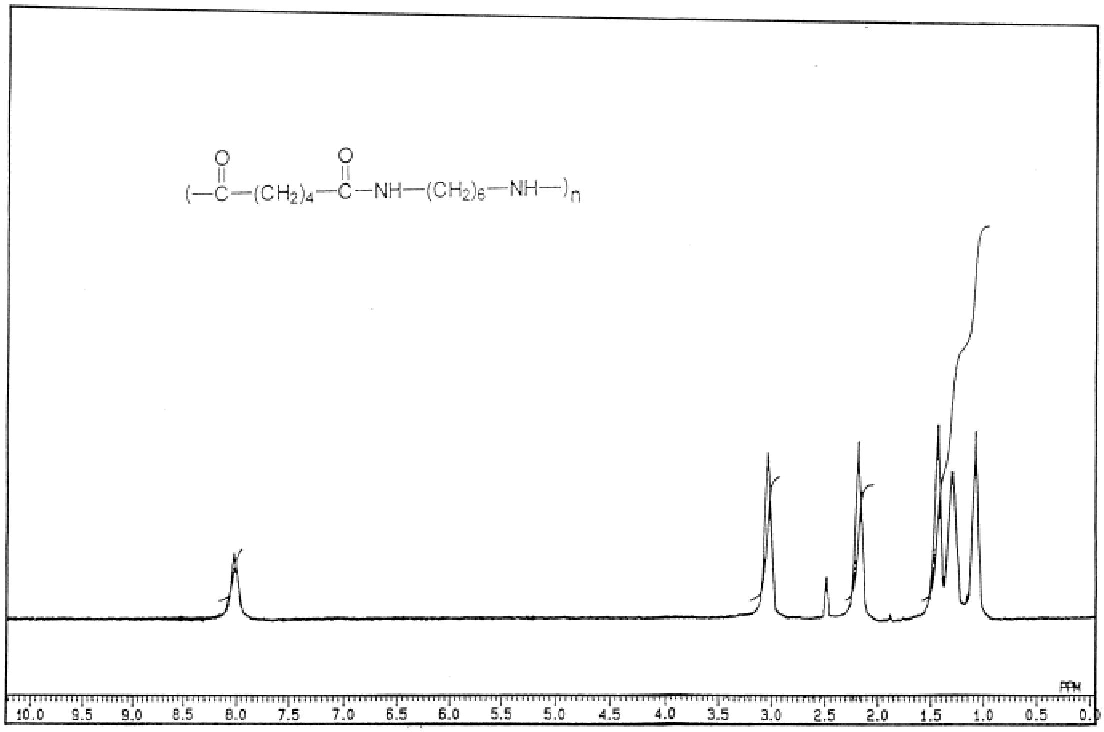


Figure 6 ^{1}H-NMR spectra of nylon.

In case of mixes containing 2-phr non-oiled sulfur, as shown in Figure 5, it is clear that adhesion level decreases on aging, especially after 2 days, where adhesion decreases by 50%. This may be due to the fact that covulcanization had taken place between the rubber and nylon cords through polysulfidic crosslinks. These crosslinks are believed to be weaker bonds than monosulfidic ones and are easily broken during earlier aging stages, leading to a decrease in the adhesion strength. On prolonged aging, the ability of reformation of new types of crosslinks, mono- and disulfidic crosslinks, may have taken place between the rubber mix and the nylon cords, which leads to a gradual increase in adhesion strength. This process may take place through the previous mechanism, where pendant sulfides are formed at least temporary during the break down of the polysulfidic crosslinks. In case of mixes containing 2.5- and 3-phr non-oiled sulfur, an increase in adhesion strength took place after 2 days of aging, and then it leveled. Again, the type of crosslinks in the rubber has a great influence in the adhesion process. In this case, the proportion of sulfur is increased, and there is a possibility of the formation of cyclic sulfides in the rubber mix,[1] which, in this case, did not initially contribute in the adhesion process. These cyclic sulfides may be transformed during the aging process to form mono- and disulfidic crosslinks, causing both the rubber and the cord to covulcanize together. Accordingly, a slight increase in adhesion strength is observed on early aging.

The behavior of NBR 40/50 samples bonded to dipped nylon cords on aging is illustrated in Figure 10. From the figure, it is clear that short aging duration improves adhesion for all mixes. Mixes containing 2-phr non-oiled sulfur reach a maximum adhesion value after 2 days of aging. On further aging, adhesion decreases due to the breakdown of the weak crosslinks; whereas the mixes containing 1-, 1.5-, and 3-phr non-oiled sulfur showed a limited increase in the H-pullout force with a stability after 4 days.

Figures 11 and 12, illustrate the effect of aging on adhesion between NBR 34/50 and undipped and dipped nylon cords, respectively. From Figure 11, it is clear that all mixes show improvement in adhesion during earlier aging stages, followed by stability on further aging. The only case where a decrease in the H-pullout force takes place is for mixes containing 2.5-phr non-oiled sulfur. This is due to the higher proportion of polysulfidic crosslinks.

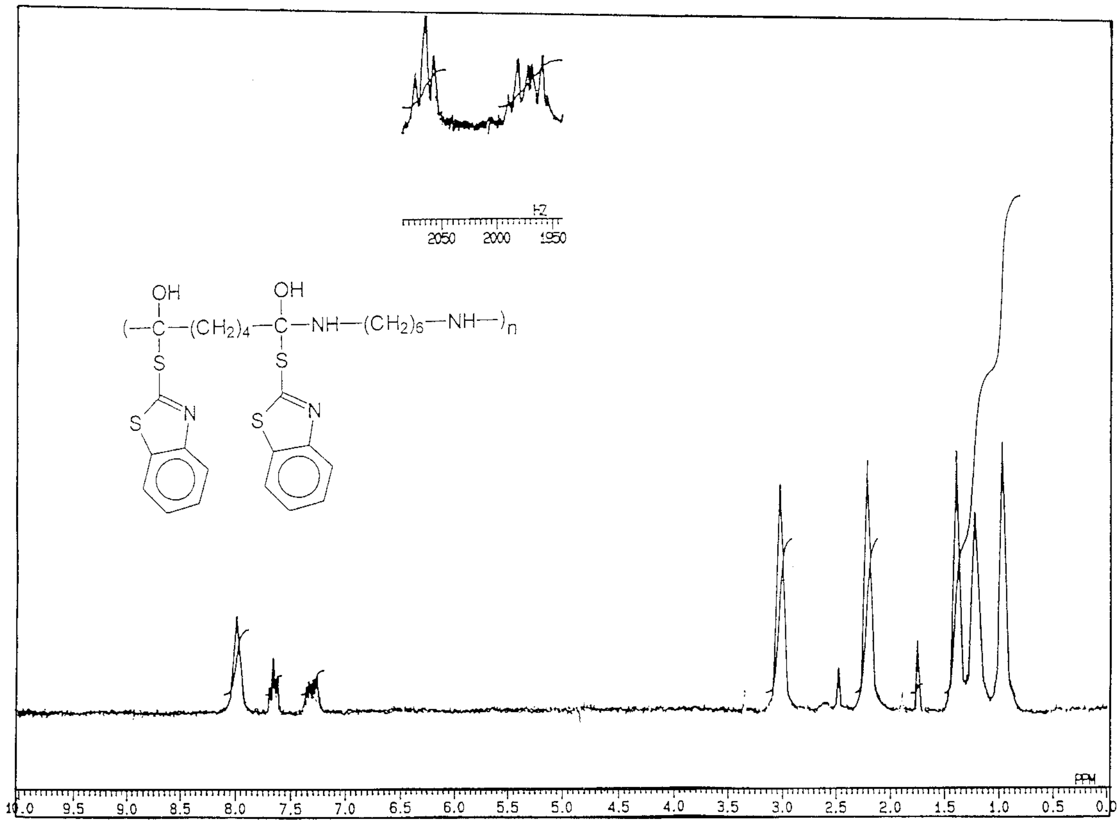


Figure 7 [1]H-NMR spectra of the product (nylon + MBT).

In case of NBR 34/50 bonded to dipped nylon cords, it is clear from Figure 12 that the non-oiled sulfur level is crucial, and mixes containing 1-, 1.5-, and 2.5-phr sulfur show inferior adhesion values and do not improve to any recognizable extent on aging. On the other hand, mixes con-

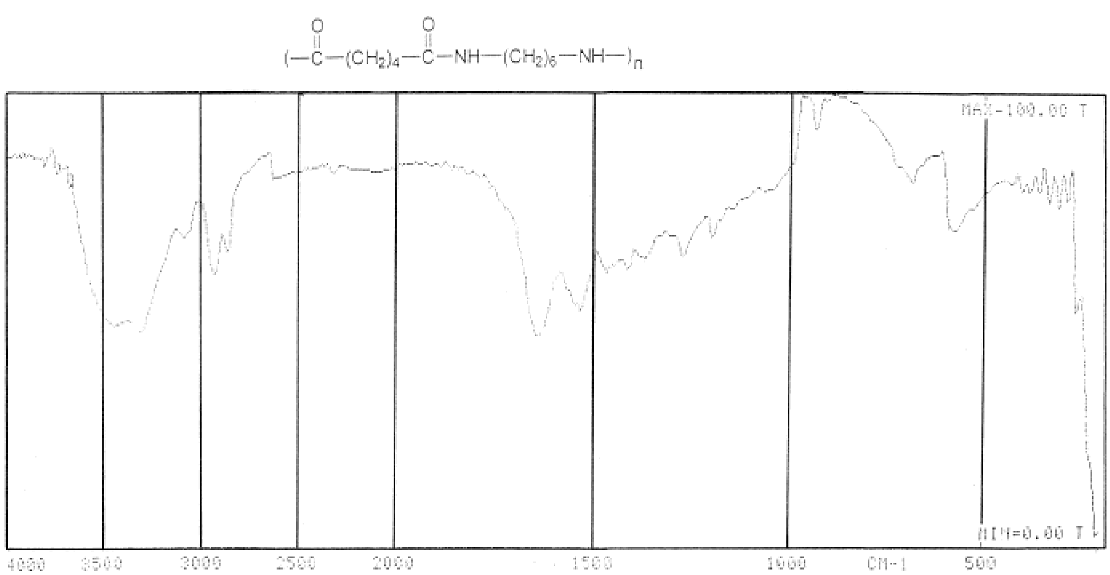
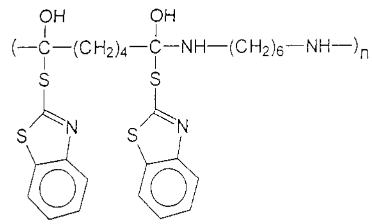


Figure 8 IR spectra of nylon.



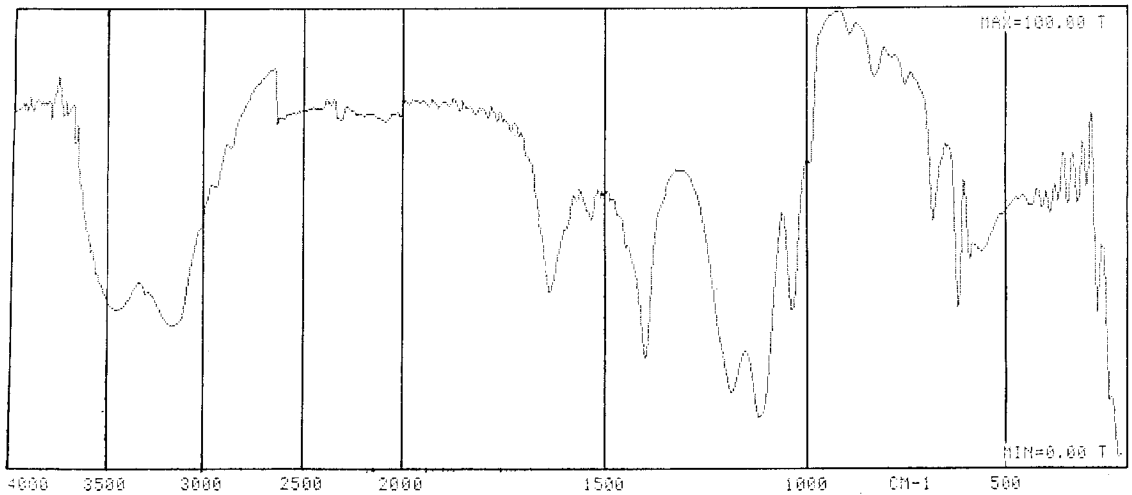


Figure 9 IR spectra of the product (nylon + MBT).

taining 2- and 3-phr non-oiled sulfur show maximum improvement in adhesion after 6 days of aging.

Effect of Radiation on the Adhesion Properties in Mixes Containing Non-Oiled Sulfur Concentration

Figures 13 and 14 show the effect of exposing H-samples of NBR 40/50 containing different non-oiled sulfur concentrations and bonded to undipped and dipped Nylon cords, respectively, to different doses of ionizing radiation. From Figure 13, it is clear that samples containing 2-phr non-oiled sulfur, when exposed to lower doses of ionizing radiation, show a decrease in adhesion values. This may be due to the break down of polysulfidic crosslinks present between the mix and the nylon cord. On further exposure, adhesion shows stability. While in the case of higher non-oiled sulfur concentrations, 2.5 and 3 phr, mixes show very good resistance to γ-radiation without the loss of bond strength.

In the case of NBR 40/50 mixes bonded to dipped nylon cords, as illustrated in Figure 14. It

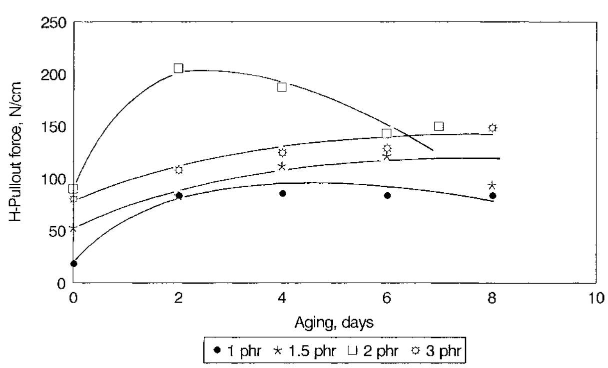


Figure 10 Effect of aging on adhesion between NBR 40/50 and dipped nylon cords.

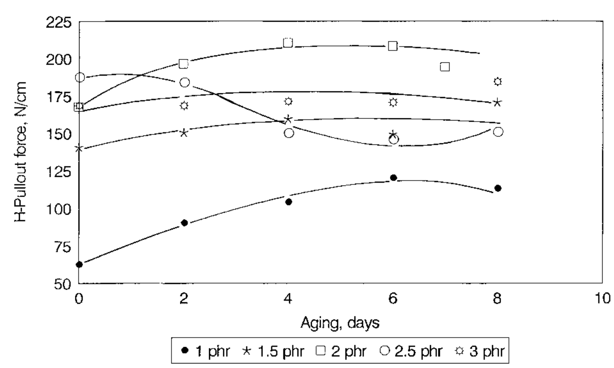


Figure 11 Effect of aging on adhesion between NBR 34/50 and undipped nylon cords.

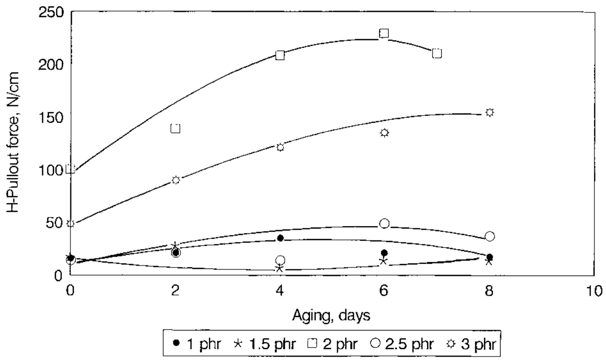


Figure 12 Effect of aging on adhesion between NBR 34/50 and dipped nylon cords.

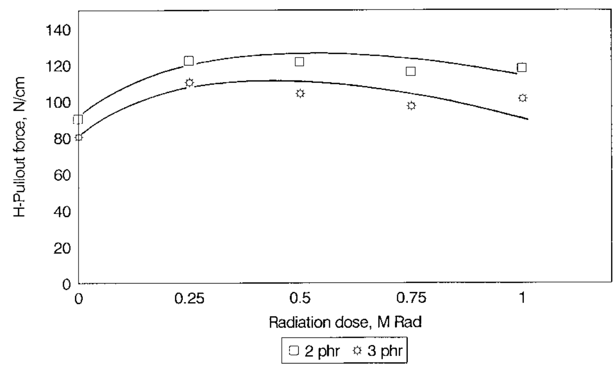


Figure 14 Effect of radiation on adhesion between NBR 40/50 and dipped nylon cords.

is obvious that mixes containing 2- and 3-phr non-oiled sulfur show little improvement in adhesion on exposure to lower radiation doses ($<0.25M$ rad). This may be due to the formation of free radicals in both the rubber and the nylon cord, causing the formation of additional crosslinks.[17,18] On further exposure to γ-radiation ($>0.25M$ rad), no increase in the H-pullout force was recorded.

Figures 15 and 16 illustrate the effect of exposing NBR 34/50 samples bonded to undipped and dipped nylon cords, respectively, to ionizing radiation. It is clear from Figure 15 that all mixes show stability towards exposure to γ-radiation. On using dipped cords with these mixes, as shown in Figure 16, generally the pullout force recorded was comparatively low compared to those recorded for undipped ones. Exposing the rubber-dipped cord product of these mixes to ionizing radiation was aimed to improve these poor pullout force results. But, practically no significant improvement was achieved. This indicates that the type of bonds formed between the NBR 34/50 mixes, and the dipped nylon cords are relatively weaker than those formed with undipped ones.

CONCLUSIONS

Static adhesion tests were carried out on undipped and dipped nylon cords, and two grades of NBR 40/50 and 34/50, using HRH as direct bonding system in the rubber mixes. The results show the following.

1. Generally, nitrile rubber mixes bonded to undipped nylon cords show better adhesion levels than those bonded to dipped ones. The use of 2–2.5-phr sulfur gave high adhesion levels.
2. The crosslink density of the nitrile rubber mixes, depending on the amount of sulfur present in the mix, has a significant effect on the adhesion strength as it controls the

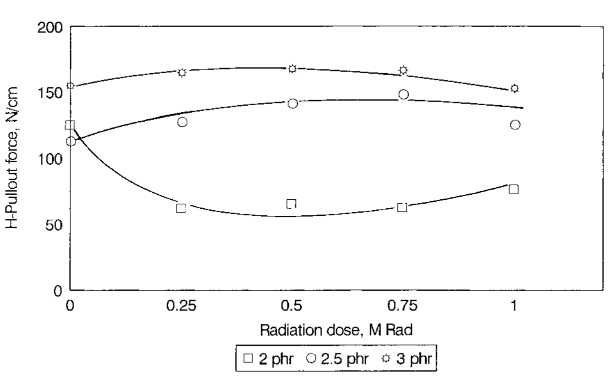


Figure 13 Effect of radiation on adhesion between NBR 40/50 and undipped nylon cords.

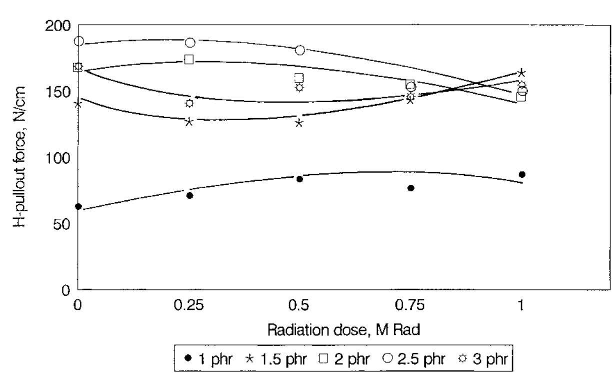


Figure 15 Effect of radiation on adhesion between NBR 34/50 and undipped nylon cords.

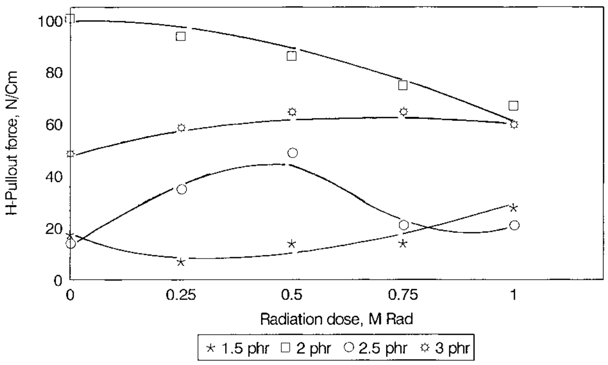


Figure 16 Effect of radiation on adhesion between NBR 34/50 and dipped nylon cords.

ability of successful interaction that takes place between the mix and the cord.

3. The role of sulfur in adhesion is not just in controlling the physical and mechanical properties of the rubber but it also changes the chemical nature of the polymer in a way that either enhances or deteriorates adhesion properties.
4. The results proved that there is a strong ability of covalent bond formation between the sulfur atoms of the rubber–S–accelerator system and the carbonyl groups of the nylon cords.
5. The type of sulfur crosslinks formed between the rubber and the cord during vulcanization has a great influence on the adhesion levels under the effect of heat aging. In most cases, mixes containing 2-phr sulfur show good adhesion levels except that mix of NBR 40/50 with 2-phr sulfur and bonded to undipped nylon cord.
6. NBR 34/50 reinforced by undipped nylon cords and vulcanized using 2.5-phr sulfur possesses higher hardness, higher H-pull-out force, and good stability towards ionizing radiation.

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