# The ethylene propylene diene terpolymers engineering essay

Profession

# INTRODUCTION AND OBJECTIVES

Ethylene-propylene-diene terpolymers ( EPDM ) have been widely used in industrial applications because of their first-class opposition against heat, ozone and weathering, every bit good as their unusual handiness of accepting high burden of fillers [ 1-3 ] . Support in the public presentations of gum elastic compounds, such as tensile strength, resiliency, wear opposition and flex opposition, can be achieved by lading the compounds with particulate fillers. Different classs of C black are the well-known conventional fillers used in EPDM gum elastics compounds [ 4 ] . Increasingly, mineral fillers like silicon oxide and clay have attracted more attending as they cost less and give less wellness jeopardies [ 4 ] . But due to the hapless silica-rubber bonding, the support by silicon oxide has non been to the full exploited [ 4, 5 ] . The handiness of silanised silicon oxide, which is normally obtained by pre-treating silicon oxide with Bi ( 3-triethoxysilylpropyl ) tetrasulphane ( TESPT ) , a yoke agent, adheres silicon oxide to the gum elastic [ 6 ] . Furthermore, it is attractive that the sulphur-bearing bifunctional organosilane can besides assist to bring forth crosslinks between gum elastic ironss with the presence of gas pedals and activators at elevated temperatures, i. e. 140-240A°C [ 5-12 ] . The presence of TESPT improves the remedy procedure in silanised silica-filled EPDM gum elastics with other common vulcanizing systems. Though many research workers have made attempts to look into different remedy systems for EPDM gum elastics [ 3, 4, 13-17 ] , the inquiry on the efficiency of remedy systems for commercial production remains unfastened. That gives the aim of this undertaking which is as following:

Using different remedy systems to crosslink silanised silica-filled EPDM gum elastic ;

Assess efficiency of the remedy systems ;

Choose the most efficient one for bring arounding the gum elastic.

This literature reappraisal foremost introduces the basic background of EPDM gum elastic, including composing, chemical construction and corresponding belongingss and industrial applications in Section 2. Then a brief overview of the preparation of silanised silica-filled EPDM gum elastic compounds is given in Section 3, followed by the elaborate debut of recent plants on fillers and remedy systems for silanised silica-filled EPDM gum elastic in Sections 4, 5 and 6. Finally, the undertaking program will be discussed.

# BASIC BACKGROUND OF EPDM RUBBER

Terpolymerisation of ethene, propene and a non-conjugated diene gives EPDM gum elastic with a concentrated ethylene-propylene anchor and unsaturation site in the side group, introduced by diene monomers [ 17 ] . Generally, ethene and propene monomers are the major constituents in an EPDM, supplying inherently first-class opposition against debasement by heat, visible radiation, O, and, in peculiar, ozone [ 18 ] . The little sum of non-conjugated diene monomers place the reactive unsaturation sites available for sulphur vulcanization or polymer alteration chemicalscience, as the dienes are so structured that merely one of the dual bonds will polymerize [ 19 ] .

Figure 1 EPDM ternonomers

The three co-monomers used in industry are present in Figure 1. Each diene monomer incorporates with a different ability of triping long concatenation ramification or polymer side ironss, hence affect the processing and vulcanization procedure [ 20 ] . The most normally used termononer is ethylidene norborne ( ENB ) as it can integrate easier and has greater responsiveness with sulphur vulcanization [ 19 ] . The chemical construction of EPDM with ENB termonomer is illustrated as follows:

Figure 2 Chemical construction of EPDM

A general sum-up of belongingss of EPDM gum elastic is listed in Table 1 below.

Table 1 Properties of EPDM gum elastics

Polymer Properties

Mooney Viscosity, ML ( 1+4, 125A°C )

5 to 200

Ethylene Content ( wt. % )

45 to 80

Diene Content ( wt. % )

0 to 15

Specific Gravity ( gm/ml )

0. 855 to 0. 88

## Vulcanisate Properties

Hardness ( Shore A Durometer )

30 to 95

Tensile Strength ( MPa )

7 to 21

Compaction Set B, ( % )

20 to 60

Elongation ( % )

100 to 600

Useful Temperature Range ( A°C )

-50 to +160

Tear Resistance

Fair to Good

Abrasion Resistance

Good to Excellent

Resilience

Fair to Good

Electrical Properties

Excellent

EPDM is the fastest turning man-made gum elastic having to its superior ozone and thermic opposition over other diene gum elastics and its burden of fillers and plasticizers to an highly high degree [ 18 ] . EPDM has found widespread applications in [ 18 ] :

Automotive applications, such as seals, hosieries and profiles ;

Construction applications, such as roof sheeting, profiles, and seals ;

Electrical overseas telegrams and jacketing ;

Moulded contraption parts ; besides is

Blended with other gum elastics and thermoplastics.

# EPDM RUBBER FORMULATION

## Fillers for EPDM Rubber

Due to the non-crystallising nature of EPDM gum elastic, support is required for EPDM gum elastic, since the mechanical belongingss of the unfilled gum elastic are rather hapless. Carbon black is the most widely used filler for reenforcing EPDM gum elastics, but silicon oxide, clay, talc and some other mineral fillers are besides used [ 19 ] . Increasingly, more attending is being paid to silica [ 1, 2, 4, 15, 16, 21-25 ] . To accomplish full development of support by reenforcing fillers in EPDM gum elastics, C black and other fillers must be good dispersed. Good support can give EPDM gum elastics with high tensile strength, good tear opposition and improved scratch opposition. Furthermore, a well-mixed batch besides improves the processability for bulge, calendaring and modeling [ 19 ] . The reenforcing fillers and their effects on EPDM gum elastics will be discussed in item in Sections 4 and 5.

## Remedy Systems for EPDM Rubber

As mentioned before, the incorporation of unsaturation sites allows the sulfur vulcanising of EPDM rubber. Sulphur remedy is the most widely used method, busying about 80 % of EPDM applications [ 17 ] . EPDM gum elastic can besides be vulcanised in a peroxide remedy system. Rubber vulcanised by sulfur remedy system can suit more emphasis and exhibit higher elongation at interruption, while the advantage of peroxide remedy over sulphur remedy is the formation of thermo-stable carbon-carbon bonds alternatively of thermo-labile sulphur-sulphur bonds, as the dissociation temperature and energy of sulphur-sulphur bonds is lower than that of carbon-carbon bonds [ 17, 26 ] . Hence higher effectivity of heat opposition of EPDM gum elastic can be obtained by peroxide remedy systems. The treatment of remedy systems for EPDM gum elastics will be unwrapped in Section 6.

## Other Additives

Other normally used additives in EPDM rubber compounds are plasticizers, softeners and treating AIDSs. Naphthenic oils have been the most widely used plasticizers as they have the best compatibility with EPDM gum elastic and lowest cost. Paraffinic oils are normally used for elevated-temperature applications or in colored compounds due to the lower volatility and higher UV stableness. Stearic acid, Zn stearic and other internal lubricators are frequently used as processing AIDSs in EPDM rubber compounds. The presence of tackifier or non is dependent on if there is a demand for presenting tack as EPDM gum elastic compounds are inherently non tacky [ 19 ] .

Different preparations of EPDM rubber compounds consequence in a assortment of applications. A typical formula for C black-filled EPDM gum elastic for sheeting application is shown in Table 2 below. Tiwari and colleagues [ 27 ] studied consequence of different interventions of silicon oxide on silica-filled EPDM gum elastic belongingss and the basic preparation for silanised silica-filled gum elastic is given in Table 3.

Table 2 Typical formula for C black-filled EPDM sheeting [ 19 ]

Components

Amount ( phr )

EPDM A

100

N - 347 black

120

Talc

30

PARAFFINIC oil type 103B

95

Zinc oxide

5

Stearic acid

1

MBTS

2. 2

TMTD

0. 65

TETD

0. 65

Sulfur

0. 75

Table 3 Basic preparation for silanised silica-filled individual EPDM gum elastic

Components

Amount ( phr )

EPDM

100

Silica

50

ZnO

5

Stearic acid

2. 0

Silane ( TESPT )

4

Sulfur

1. 04

N-cyclohexylbenzothiazole-2- sulphonamide ( CBS )

1. 5

Tetramethylthiuram disulphide ( TMTD )

0. 8

Zinc dibenzyldithiocarbamate ( ZBEC )

1. 5

## Fillers USED IN EPDM RUBBER

## Carbon Black: A Conventional Filler

Carbon inkinesss are the most widely used reenforcing fillers in gum elastic industry since the find of their effectivity of bettering the physical and mechanical belongingss of natural elastomers in 1904 [ 12 ] . Different classs of C black have been used in EPDM gum elastics for industrial applications, such as roof sheeting and automotive profiles and many research workers have studied about the mechanical behavior of C black reinforced EPDM gum elastics.

Ghosh and Chakrabarti [ 28 ] reported effects of different sums of C inkinesss on the physical and mechanical belongingss, ageing behavior and conduction of EPDM rubber compounds and the rheological behavior of EPDM gum elastic in bulge processing. Osanaiye [ 29 ] used sinusoidal shear flows to analyze the effects of C black, temperature and shear frequence on dynamic mechanical belongingss of EPDM rubber compounds. The effects of different sums of carry oning C black filler on thaw rheology and relaxation behavior of healing free EPDM gum elastic by cone home base viscosimeter was reported by Ghosh and Chakrabarti [ 30 ] . Abd-El Salam and colleagues [ 31 ] used inactive and dynamic analysis to analyze consequence of different vulcanizing systems on the mechanical belongingss of butyl rubber/

EPDM general furnace black. Cavdar, S. et al [ 3 ] reported a comparative survey on mechanical, thermic, viscoelastic and rheological belongingss of cured C black filled EPDM gum elastic.

There are many more illustrations of research on other facets of C black reinforced EPDM gum elastics. For illustration, conductive gum elastics have been made by adding conductive C inkinesss into EPDM and its blends by Das, N. C. et Al [ 32 ] . The electrical and mechanical belongingss have been studied.

## Silica: A Novel Filler

Recently, man-made silicon oxide is going more popular as reenforcing filler in EPDM gum elastics because they have proved to be every bit effectual as C inkinesss [ 12 ] . Furthermore, silica offers several advantages over C black: in tyre paces, a higher wear opposition and better wet-grip with a lower turn overing opposition can be obtained by utilizing silicon oxide instead than carbon black [ 1 ] . Besides, silica-filled compounds are really suited for light coloring material applications.

## Problem and Treatments

The support of silicon oxide in EPDM gum elastic has non reached the coveted degree because of the hapless silica-EPDM bonding. The surfaces of silicon oxides have siloxane and silanol groups, which make the filler acidic and polar [ 7 ] while EPDM gum elastic is non-polar. When the polar silicon oxide is assorted with non-polar and olefinic hydrocarbon gum elastics, e. g. EPDM, hydrogen-bond interactions between polar siloxane or silanol groups in agglomerates are more likely to happen than the interactions between silicon oxide and rubber [ 1 ] , ensuing in hapless compatibility of hydrocarbon gum elastics with silicon oxide. Furthermore, the acidic silanol groups interact with the basic gas pedals, spread outing the remedy times to an unacceptable degree and take downing the crosslinking denseness [ 5 ] . The polar surface of silicon oxide will besides be given to absorb wet and this influences remedy and belongingss of the cured gum elastic [ 5 ] . Additionally, the viscousness increases with increasing sum of silicon oxide filler and if the viscousness is excessively high, the processability will be reduced and inordinate wear and tear of the processing machine will take topographic point [ 5 ] .

However, the handiness of specific matching agents makes the usage of silicon oxide in EPDM rubber compounds possible. Bifunctional organosilanes are normally used to better the compatibility between silicon oxide and hydrocarbon gum elastics by modifying the surfaces of silicon oxide [ 1 ] .

## Silanes and Silanised Silica

Bifunctional silanes can be used to chemically associate an organic stuff to an inorganic substrate. The rule purpose of utilizing silanes to respond with silica involves cut downing ablating hydrophilicity of silicon oxide and presenting a new organo - functional groups onto the silicon oxide surfaces [ 1 ] . In the instance of sulphur-cured compounds, sulphur-functional silanes perform best and for peroxide-cured compounds, unsaturated silanes such as vinylsilanes are recommended.

In footings of sulphur-cure systems, the usage of Bi ( 3-triethoxysilylpropyl- ) tetrasulphane ( TESPT ) ( Figure 3 ) as a yoke agent is good established, since foremost introduced in 1991 in a practical application in green tyres by Rauline [ 33 ] ..

Figure 3 Chemical construction of TESPT

TESPT possesses ethoxy groups and tetrasulphane groups. The ethoxy groups react with silanol groups on the silicon oxide surfaces via hydrolysis mechanism [ 33 ] , taking to the strong covalent silica-filler bonding. The tetrasulphane groups are no-good reactive and therefore stable rubber-silica bonding can be achieved via sulfur crosslinking. Bis ( 3-triethoxysilylpropyl ) -disulphane ( TESPD ) was subsequently introduced chiefly to get the better of the pro-scorching job of TESPT, as the sulphur-sulphur dissociation energy of TESPD was lower than that of TESPT [ 33 ] .

The silanisation of silicon oxides are normally obtained by two attacks. Silica and silanes are assorted preliminarily at an optimal temperature and reaction clip, or, instead, they can be mixed in situ during the commixture procedure [ 5 ] . The latter is the more normally used method [ 34 ] . A good silanisation is required as it yields best support and reduces compound indurating during storage. A certain sum of $H_2O$ can speed up the silanisation. The optimum wet content is suggested to be around 3-6 % [ 34 ] . The chief influences on the in situ silanisation of silica-silane filled compounds are summarised in Figure 4.

Furthermore, if silicon oxide is used in a blend with, e. g. , C black, relatively more silane is required as silane is less likely to make the silica surface quantitatively in a given commixture clip [ 34 ] . In these instances, silanised silicon oxide obtained by the pre-treatment is advisable.

Optimum silanisation

And

Short commixture times

Release of ethyl alcohol

T a†' and T a†'

Release of ethyl alcohol

Ta†' and ta†'

Good silicon oxide scattering

I·a†' as Ta†"

Complete matching reaction Ta†' and T a†'

Avoid pre-crosslinking

T a†" and T a†"

Fast transit procedures

I·a†" as T a†'

High mobility of the silane ; little size

Best rotor and blending chamber geometry

Figure 4 chief influences on the silanisation reaction [ 34 ]

Apart from sulphur vulcanization, the add-on of vinylsilanes is normally applied to better the mechanical belongingss of peroxide-cured compounds. The general construction of vinylsilanes is shown in Figure 5.

Figure 5 generalized construction of vinylsilanes

In contrast to the reasonably high dose of sulphur-functional silanes in merchandises necessitating high mechanical belongingss, a strong support can be achieved by the incorporation of merely 2 parts by weight Si 225 ( VTEO ) per silicon oxide [ 34 ] . Adding more extremist instigator or activators can ensue in higher crosslink densenesss [ 34 ] .

However, the applications of silanised silicon oxide are largely focused in natural gum elastic ( NR ) , styrene butadiene gum elastic ( SBR ) , and polybutadiene gum elastic ( BR ) . Very few research works has been published on the effects of silane on EPDM gum elastics, but there are still some. Kim [ 33 ] reported consequence of TESPD on the processability and mechanical belongingss of EPDM rubber. Taikum and Luginsland [ 16 ] studied the function of silane-rubber yoke in sulfur, peroxide and metal oxide bring arounding systems for EPDM gum elastic. Das et al [ 4 ] showed that the presence of TEPST increased the content of bound gum elastic in silica-filled EPDM compounds, which was critical to the mechanical belongingss of the gum elastic.

## Other Treatments

Other matching agents

Besides silane, several other matching agents have been employed to modify the silica-EPDM bonding. Das et al [ 4 ] usage Bi diisopropyl thiophosphoryl disuli¬? de ( DIPDIS ) , to modify EPDM rubber alternatively of silicon oxide by two-stage vulcanization technique. The effects of TAC ( Triallyl Cyanorate ) as a yoke agent on hardening and mechanical belongingss of silica-filled EPDM gum elastic were studied by Abtahi and associates [ 1 ] .

Others methods

Tiwari et al [ 23 ] treated the surfaces of silicon oxide by plasma-polymerisation with acetylene monomer and one twelvemonth subsequently, the comparative survey of plasma-thiophene and -acetylene coated silicon oxide in EPDM support was reported [ 27 ] . Tan and Isayev [ 22 ] treated silicon oxide utilizing a coaxal supersonic extruder and investigated the effects on belongingss of ultrasound-treated silicon oxide on filled EPDM gum elastic.

## Other fillers

In most instances, C black and silicon oxide are used to reenforce EPDM gum elastics. Some other sorts of fillers have been added to EPDM rubber matrix and their effects been investigated, affecting montmorillonite ( OMMT ) nanofiller [ 35 ] , nano-zinc oxide [ 36 ] , Sm2O3 [ 26 ] , short cyanuramide fibers [ 37 ] , ash/halloysite [ 38 ] and so on.

# Effects OF FILLERS ON PROPERTIES OF EPDM RUBBER

## Effectss of Carbon Black

As mentioned before, research workers have studied a batch about the effects of adding C black on the mechanical belongingss of EPDM rubber, demoing that the belongingss were improved significantly [ 3, 28-32 ] . Cavdar and associates [ 3 ] reported that the Young 's modulus, Shore A hardness, and compaction force over distortion ranage increased with increasing content of C black, while the elongation at interruption reduced ( Figure 6 ) .

Figure 6 Effectss of C black content on ( a ) mechanical belongingss ; and ( B ) rheological belongingss of EPDM rubber [ 3 ] .

The Young 's modulus was most filler content medium as the value increased aggressively with sum of C black. In footings of rheological belongingss, increasing C black content resulted in higher upper limit torsion and the difference between upper limit and minimal torsion, which corresponded to relative crosslinking denseness. The optimal remedy clip decreased with increasing the filler content.

Considerable research has been done to understand the mechanism of support. Two chief features of active inkinesss are their surface country and sum construction, which determine the inactive and dynamic in-rubber belongingss and therefore do it possible to orient the public presentation of gum elastic merchandises.

# Effectss of Silica

## Effectss of silicon oxide on the mechanical belongingss of EPDM gum elastic

Without silanes

The effectivity of silicon oxide as reenforcing filler in EPDM gum elastic was confirmed by Ichzo and colleagues [ 2 ] who showed that tensile strength had improved by 500 % , tear strength by 400 % and elongation at interruption at 140 % by adding 20 phr of precipitated silicon oxide. They used silicon oxide with different size and demonstrated that an increasing inclination of tensile strength can be achieved when the size of silica atom decreased. The hardness of EPDM gum elastic increased with the filler burden but it was non particle size dependant. They besides found that silicon oxide sums size distribution affected the mechanical belongingss and it deserved more attending.

With silanes

Das [ 4 ] indicated that the Young 's modulus, tensile strength and crosslinking value of silica-filled EPDM gum elastics increased well when 1-2 phr of TESPT was added, while the elongation at interruption decreased, as illustrated in Figure 7 below.

( B )

( a )

( vitamin D )

( degree Celsius )

( degree Fahrenheit )

( vitamin E ) Figure 7 Consequence of TESPT on the mechanical belongingss of EPDM rubber compounds: ( a ) modulus at 100 % elongation ; ( B ) modulus at 300 % elongation ; ( degree Celsius ) tensile strength ; ( vitamin D ) hardness ; ( vitamin E ) elongation at interruption ; ( degree Fahrenheit ) crosslinking value [ 4 ] .

## Consequence of silicon oxide on treating belongings of EPDM gum elastic

As mentioned earlier, adding silicon oxide to EPDM gum elastic will do the processing more hard as the viscousness increases significantly when a large sum of silicon oxide is involved [ 5 ] .

However, the handiness of silanes such as TESPT or TESPD weaken the interaction between silica atoms as the ethoxy groups in silane react with the surfaces of silicon oxide by the silanol groups, taking to a alteration in interfaces between the polymer-polymer, polymer-silica and silica-silica [ 33 ] . Hence, it reduces the viscousness and improves the processability of the gum elastic compounds [ 5 ] . Kim [ 33 ] reported that the add-on of TESPD to silica-filled EPDM gum elastic yielded lower Mooney viscousness, heat coevals and bulge force per unit area build-up through an extruder, which made treating easier.

## Effectss of silicon oxide on thermic belongings of EPDM gum elastic

Madani [ 39 ] studied the thermic belongings of gamma radiation cured silica-filled EPDM via thermohydrometric analysis ( TGA ) and demonstrated that the presence of silicon oxide reduced the rate of debasement and the weight loss of vulcanisates. This was due to the improved adhesion between silicon oxide and EPDM rubber matrix. He besides stated that thermic belongings of silica-filled EPDM gum elastic was determined by the burden of filler, filler size and construction, filler-matrix interactions and processing technique.

## Consequence of silicon oxide on the ageing belongings of EPDM gum elastic

Airplanes et al [ 15, 40 ] used gamma radiation to age unfilled and filled EPDM gum elastics at room temperature and at 80A°C to analyze the influence of silicon oxide on the gum elastic debasement. They evidenced that adding untreated silicon oxide accelerated the polymer stage debasement due to the formation of auxiliary groups triggered by silica irradiation. If silane-treated silicon oxide was presented, the debasement acceleration was delayed.

## Effectss of silicon oxide on the electrical belongings of EPDM gum elastic

Raw EPDM gum elastic is an dielectric with a conduction of about 10-14 S-1 [ 39 ] . It was proved that the add-on of inorganic fillers such as silicon oxide increased the conduction of polymer [ 39 ] . Madani [ 39 ] investigated the fluctuation of dielectric changeless ( ) of some healed EPDM and silica-filled

EPDM gum elastics as a map of frequence and found that was filler content dependant: it increased up to 10 phr, and so decreased with increasing burden. He pointed that the addition was due to the polar groups present on silicon oxide surfaces, and that the lessening was due to the increasing system denseness and the extent of orientation of dipoles.

## Effectss of scattering of silicon oxide on the belongingss of EPDM gum elastic

Filler scattering has a distinguishable consequence on the belongingss of gum elastic compounds. Poor scattering has a negative consequence on gum elastic belongingss by making structural defects [ 5 ] . Polmanteer and Lentz [ 41 ] demonstrated that some belongingss such as tensile strength and tear strength improved as the filler scattering quality increased after they examined consequence of scattering of silicon oxide on the belongingss of some sulphur-cured gum elastics. To obtain a better scattering of fillers in gum elastic compounds, increasing commixture clip is an efficient method, nevertheless, at the cost of take downing the molecular weight of polymer, which leads to the decrease in mechanical belongingss [ 5 ] . The grade of scattering of filler can be examined by microscopy methods, such as negatron microscopy and atomic force microscopy.

# CURE SYSTEMS FOR EPDM RUBBER

## Sulphur Cure systems

Every gum elastic merchandise is vulcanised with its ain specific remedy system, ensuing in assorted belongingss. As already mentioned, the incorporation of pendent unsaturation sites enables that EPDM rubber to be vulcanised by sulphur plus gas pedals. Sulphur remedy is the most widely used vulcanising method for bring arounding EPDM gum elastics, representing about 80 % of the EPDM applications [ 17 ] . Compared with peroxide-cured EPDM gum elastics, sulphur-cured gum elastic compounds are able to suit more emphasis and exhibit higher elongation at interruption.

Basically, three types of sulfur crosslinks are used in elastomers, viz. , monosuphfidic ( C-S-C ) , disulphidic ( C-S2-C ) and polysuphidic ( C-Sn-C ) . The crosslink denseness and the value of Ns are chiefly determined by vulcanizing system and procedure conditions such as remedy temperature and clip. Over the old ages three particular types of remedy systems have been established based on the degree of sulfur and the ratio of accelerator-to-sulphur applied. They are:

Efficient vulcanization ( EV ) systems,

Semi-efficient vulcanization ( SEV ) systems and

Conventional vulcanization ( CONV ) systems.

EV systems are characterised by a high ratio of accelerator-to-sulphur or even sulphurless, but incorporating sulphur-donor alternatively. They are normally used in vulcanisates which require an highly high heat and reversion opposition [ 42 ] . CONV systems are vulcanisation systems with a low ratio of gas pedals to sulfur and they can supply better flex and dynamic belongingss but worse thermal and reversion opposition. A semi-efficient remedy system has an accelerator-to-sulphur ratio in between those of the CONV and EV vulcanization systems. For SEV systems, optimal degrees of mechanical and dynamic belongingss of vulcanisates with intermediate heat, reversion and flex belongingss can be obtained [ 42 ] . The composings of CONV, SEV and EV systems are shown in Table 4.

Table 4 the degrees of gas pedals and sulfur in CONV, SEV and EV systems [ 42 ]

Type

Sulphur ( phr )

Accelerator ( phr )

A/S ratio

CONV

2. 0-3. 5

1. 2-0. 4

0. 1-0. 6

SEV

1. 0-1. 7

2. 5-1. 2

0. 7-2. 5

Electron volt

0. 4-0. 8

5. 0-2. 0

2. 5-12

Increasing accelerator-to-sulphur ratio consequences in increased sum of shorter mono- and disulphidic crosslinks. As the dissociation energy of C-C bonds are larger than that of S-S bonds. Vulcanisates obtained by EV and SEV systems possess a better heat and reversion opposition than those cured by CONV systems. The general influences of the type of vulcanization systems on the construction and belongingss of the vulcanisates are summarised in Table 5.

Table 5 vulcanisate construction and belongingss for different remedy systems

Features

Remedy systems

CONV

SEV

Electron volt

Poly-and disulphidic crosslinks ( % )

95

50

20

Monosulphidic crosslinks ( % )

5

50

80

Cyclic sulfide ( conc. )

High

Medium

Low

Non-sulphidic ( conc. )

High

Medium

Low

Reversion opposition

Low

Medium

High

Heat ageing opposition

Low

Medium

High

Fatigue opposition

High

Medium

Low

Heat construct up

High

Medium

Low

Tear opposition

High

Medium

Low

Compaction set ( % )

High

Medium

Low

Furthermore, nitrosamine free or safe hardening bundles were developed for the replacing of remedy systems which develop nitrosamines during vulcanization. N-nitrosamines formed during vulcanization as condensation merchandises from certain gas pedals and azotic gasses and are carcinogenic [ 43 ] . They are generated from some thiuram and dithiocarbamates gas pedals, which are known as ultra-accelerators and normally used in EPDM gum elastic intensifying [ 43 ] . Traditional ultra-accelerators can be replaced by nitrosamine-free systems, but at disbursal of high costs.

About all imaginable combination of bring arounding ingredients for EPDM rubber compounds have been evaluated over the old ages [ 42 ] . Five typical remedy systems are listed in Table 6. The alternate nitrosamine free or safe remedy systems are suggested in Table 7.

Table 6 Five remedy systems for EPDM rubber [ 42 ]

Systems ( phr )

Advantages

Disadvantages

System 1

Low cost

Blooming

S 1. 5

TMTD 1. 5

2-mercaptobenzothiazole ( MBT ) 0. 5

System 2

Excellent physical belongingss and fast remedy

Scorchy and expensive

S 2. 0

MBT 1. 5

Tellurium diethyl dithiocarbamate ( TDEC ) 0. 8

Dipentamethyl thiuram tetrasulphide ( DPTT ) 0. 8

TMTD 0. 8

System 3

Excellent compaction set and good heat ageing opposition

Bloom and really high cost

S 0. 5

Zinc dibutyldithiocarbamate ( ZDBC ) 3. 0

Zinc dimethyldithiocarbamate ( ZDMC ) 3. 0

4, 4'dithiodimorpholine ( DTDM ) 2. 0

TMTD 3. 0

System 4

Non-blooming

Cure comparatively slow and worse compaction set

S 2. 0

2, 2'-dithiobenzothiaole ( MBTS )

ZDBC 2. 5

TMTD 0. 8

System 5

Zinc O, O-dibutylphosphorodithioate ( ZBPD ) 2. 0

TMTD 1. 0

N-butylbenzothiazole-2-sulfenamide ( TBBS ) 2. 0

S 1. 0

Fast remedy and good physical belongingss

Blooming

Table 7 Some NA free options for the remedy systems above [ 42 ]

Systems

NA free options

## System 1

S 1. 5

S 1. 3

MBT 0. 5

MBT 0. 75

TMTD 1. 5

CBS 3. 8

## System 2

S 2. 0

S 1. 5

MBT 1. 5

ZMBT 2. 0

TDEC 0. 8

ZBEC 0. 5

DPTT 0. 8

ZBPD 2. 0

## System 5

ZBPD 2. 0

ZBPD 2. 5

TMTD 1. 0

0

TBBS 2. 0

TBBS 2. 0

S 1. 0

S 1. 2

Besides, an activator, such as Zn oxide, is normally needed in EPDM remedy systems to maximize the efficiency of gas pedals and chemical adhesion between the filler and gum elastic.

## Silanised Silica: a `` Crosslinking Filler ''

An of import issue must be considered sing the sulphur remedy systems for silanised silica-filled EPDM gum elastic is the fact that the usage of sulphur-functional silanes such as TESPT combine silicon oxide with sulfur into one individual merchandise known as a `` crosslinking filler '' [ 6 ] , such as silanised silicon oxide. It can non merely better the mechanical belongingss of gum elastic, but besides can bring forth crosslinks between the gum elastic ironss at elevated temperatures in the presence of gas pedals due to the sulphur-containing groups. Therefore, the vulcanization procedure can be achieved without elemental sulfur being present [ 6 ] . Research has shown that the mechanical belongingss of some vulcanisates improved significantly in malice of the decrease in the usage of the hardening chemicals [ 6 ] .

It was demonstrated that during the vulcanization procedure the formation of both rubber matrix crosslinking web and silica-rubber yoke web occurred at the same time and did non separate. In the presence of elemental sulfur, the two different crosslinking reactions compete for the added sulfur as the sulphur-functional silanes like TESPT are sulphur acceptor [ 34 ] . Therefore the crosslinking construction and the support are determined by the sums of silane and sulfur. The influence of adding different sums of sulfur and silane on the matrix and silica-rubber yoke webs is shown in Figure 8.

Figure 8 consequence of the sum of ( a ) added sulfur and ( B ) silane ( TSEPT ) on the crosslinking densenesss of matrix and silica-rubber yoke [ 34 ]

It is apparent that increased sum of sulfur enhances the efficiency of the silica-rubber yoke until all the silane is activated. Initially, a little grade of addition in the matrix crosslink denseness is observed, due to the ingestion of free sulfur by the activation of silane. After the full activation of silane, the matrix crosslink denseness additions much faster. With regard to the increasing sum of silane at a changeless sum of sulfur, the entire figure of silica-rubber bonds additions while the degree of the matrix crosslink denseness reduces, owing to the incorporation of sulfur by the silane [ 34 ] . Furthermore, in the instance of TESPD, a disulphide silane, the consequence is more important. Therefore it can be concluded that altering the sum of elemental sulfur and silane consequences in different ratios of the matrix and silica-rubber webs [ 34 ] . Furthermore, mechanical belongingss of silanised silica-filled gum elastic can be predicted because silica-rubber yoke dominates the modulus and hydrophobation lowers hardness values. Some elaborate effects of silane on the mechanical public presentation of silica-filled EPDM gum elastic have been presented in Section 5. 2. 1.

## Peroxide Cure systems

## Overview

Crosslinking with peroxides was foremost introduced in 1915, but did n't pull excessively much attending until the development of to the full saturated ethylene-propylene copolymers ( EPM ) [ 42 ] . Many sorts of elastomers can be vulcanised by peroxide remedy systems expeditiously, including NR, SBR, EPDM, BR, nitrile gum elastic, Silicones and fluorocarbon elastomers [ 42 ] . The unsaturation can better the efficiency of peroxide vulcanization [ 17 ] , due to the higher concentration of allylic Hs [ 42 ] . The comparative efficiency of peroxide crosslinking for different elastomers is:

BR & gt ; NR and SBR & gt ; NBR & gt ; CR & gt ; EPDM

The advantages and disadvantages of peroxide remedy compared to sulfur vulcanization are listed in Table 8 [ 42 ] :

Table 8 Advantages and disadvantage of peroxide remedy compared with sulphur remedy

Advantages

Disadvantages

Thermo-stable C-C bonds alternatively of thermo-labile S-S bonds,

Scorch free storage of compounds,

Simple compound preparation,

Low compaction set even at high remedy temperature,

It is possible to bring around at high temperatures without reversion,

Good electrical belongingss of healed gum elastic,

No stain of compounds.

Low intensifying flexibleness ;

Lack of flexibleness in modulating singe and optimal remedy clip

Inferior tensile, tear and flex public presentation,

Inferior scratch opposition

Higher cost,

Sensitivity to oxygen during vulcanization, Smells of peroxide decomposition merchandises.

## Peroxide remedy of EPDM

Peroxide-cured EPDM gum elastics are being widely used for many old ages. They are normally used in window seals, automotive hosieries, roof sheeting, tanking liner, electrical insularities, steam hosieries, roll coverings moldings and so on [ 42 ] .

## Mechanism of peroxide remedy of EPDM gum elastic

The mechanism of peroxide remedy of EPDM gum elastic and the subsequent practical effects have been reviewed by new wave Duin and colleagues [ 17, 44, 45 ] . In the by and large accepted mechanism of peroxide remedy of EPDM, the major stairss are illustrated in Figure 9.

Figure 9 Mechanism for peroxide remedy of EPDM [ 17, 44, 45 ]

Thermal debasement of the peroxide initiated by procedure triggered a concatenation of free-radical reactions, taking to the formation of primary alkoxy ( ROaˆ? ) or secondary alkyl groups ( Raˆ? ) . Then the abstraction of H-atoms from the EPDM polymer outputs EPDM macro-radicals ( EPDMaˆ? ) . The following measure is the combination of two EPDM macro-radicals, or the incorporation of a macro-radical to an EPDM unsaturation. If a yoke agent, such as vinylsilanes mentioned in Section 4. 2. 1. 1 ( TAC, trimethylolpropane or m-phenylenbis ( maleimide ) ) , is present, the peroxide remedy efficiency can be increased, as they can heighten the H-atoms abstraction and the undermentioned reactions are repressed [ 1, 17 ] :

EPDMaˆ? + ROaˆ? a†’ EPDM - RO ( No crosslinking )

EPDMaˆ? a†’EPDMaˆ? ' + ( I?-Scission )

The issues of the elaborate mechanism of peroxide vulcanization of EPDM gum elastic remain unfastened, chiefly having to the complexness of the system. Several surveies have been conducted to see farther apprehension of the chemical mechanism of peroxide remedy of EPDM [ 46, 47 ] .

## Matching agents for peroxide remedy of silica-filled EPDM gum elastic

As antecedently stated, vinylsilanes are normally incorporated in peroxide remedy systems for silica-filled EPDM gum elastic to better vulcanization efficiency and mechanical public presentation of vulcanisates. The effectivity of TAC as a yoke agent for peroxide vulcanization of silica-filled EPDM gum elastic was investigated by Abtahi et al [ 1 ] and concluded that TAC matching agent improved some belongingss such as tensile strength, scratch and resiliency opposition with a proper preparation. They besides used SEM to hold a deep penetration in the interaction between silica filler and gum elastic in the presence of TAC and found that the grade of support was chiefly affected by the grade of wettability.

## New Developments

Reducing the sulfur content consequences in vulcanisates with better thermal opposition throughout service life, nevertheless, this is at the disbursal of decrease in mechanical public presentations such as dynamic weariness opposition and tear opposition. This via media can be eliminated by utilizing two additives, viz. hexamethylene-1, 6-bisthiosulphate ( HTS ) , a station vulcanization stabilizer and 1, 3-bis ( citraconimidomethyl ) benzine, an anti-reversion agent [ 42 ] .

Vulcanization techniques have effects on EPDM gum elastics. Das [ 4 ] studied the efficiency of one-stage and two-stage sulfur vulcanization techniques of silica- filled EPDM gum elastics and reported that alteration of EPDM gum elastic by two-stage vulcanization technique enhanced the interactions between EPDM rubber and silicon oxide.

Furthermore, assorted remedy systems can besides be employed to heighten the public presentation of vulcanisates.

## Undertaking Plan

The overall purpose of this undertaking is to prove some sulfur and peroxide remedy systems to bring around silanised silica-filled EPDM gum elastic to bring forth a gum elastic with good mechanical belongingss utilizing a suited hardening system. The undertaking programs are:

Prepare silanised silica-filled EPDM gum elastic compounds with peroxide and bring around the gum elastic with gas pedal and activator via the sulfur in the silane ;

Use C black and silanised silicon oxide nanofillers in EPDM gum elastic to measure their effects on the mechanical belongingss of the gum elastic ;

Remedy and step the mechanical belongingss of filled EPDM gum elastic to set up consequence of the bring arounding systems and fillers on the gum elastic belongingss.