Soft Rubber Linings Based On Ethylene Propylene Diene and its B lend With Natural and Synthetic Rubbers

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الخلاصــة:
ان الدراسات التي بينت ان مصادر الخامات الموجودة على الارض سوف تستهلك في وقت قريب تقود جميعا الى استنتاج لامناص منه وهو ان العلم والتكنلوجيا لا بد لهما ان يكرسا اهتماما اكثر مما كان عليه في السابق لحفظ المعادن وحمايتها وخاصة الحديد والفولاذ .
لذا وجد ان احد الحلول لهذه المشكلة هو التبطين بالمطاط الطبيعي والصناعي بسبب مقاومتها لتأثير بعض الكيمياويات وخاصة الاحماض والقواعد وذلك لطبيعتها المرنة والمطاطية .
ولتحقيق هذا الهدف تم اختيار الانواع الاتية من المطاط :
١- مطاط الاثلين البروبلين دايين المرن لوحده .
٢- مطاط من الاثلين البروبلين دايين وستايرين بيوتادايين ومطاط طبيعي كخليط مرن .
وتم فلكنة هذه الانواع المطاطية باستخدام مضافات مختلفة ودرست الخواص الفيزيوميكانيكية والخواص الفيزيوكيميائية لجميع النماذج المحضرة ووجد ان افضل النتائج للخواص الفيزيوميكانيكة باستخدام خليط
EPDM/ SBR/ NR بكميات 70 / 15/ 15 Phr . وافضل مقاومة للمواد الكيميائية كانت باستخدام مطاط الاثلين البروبلين دايين المفلكن لوحده .

Abstract;

All studies on minerals stated that some of the earth's raw material resources will soon be exhausted. This leads escapable to the conclusion that science and technology will have to devote more attention that they have done in the past to the protection and conservation of metals especially iron and steel. Rubber lining has been used for severe corrosion protection because; natural and synthetic rubbers have a basic resistance to very corrosive chemicals particularly acids and bases, and rubber materials are both flexible and stretchable.

There fore, in this work the following materials were chose;

1- EPDM alone 2- EPDM blended with NR and / or SBR, to formulation soft rubber.

The vulcanization processes were studied widely together with ingredients. Physico – mechanical and physico – chemical properties were thoroughly studied. And the results show that the optimum value of physico – mechanical properties in using blend of EPDM / SBR / NR (70/15 /15) Phr, and EPDM vulcanized alone gave formulation with good resistance to chemicals.

Introduction;

The corrosion of metal is of great economic importance. Estimates show that a quarter of all the iron and steel produced is destroyed in this way. The prevention of corrosion damage is therefore an economic necessity. It is believed that existing installations of the chemical industry, in which a great variety of corrosion problems is encountered, would decline in value at a rate of a bout 1.5% a year if nothing were done to prevent corrosion (1).

Rubber lining has been used for severe corrosion protection in tank cars for the past 45 to 50 years, even back to the time when tank cars were riveted construction. There are two good reasons for this. First, natural rubber and certain synthetic rubbers have a basic resistance to very corrosive chemicals, particularly acids, second, rubber materials are both flexible and stretchable. These properties, along with low durometer hardness, are essential for the performance of a corrosion protection system in a tank cars are subjected to all kinds of twisting, turning, impact and sudden temperature changes while operating on the roods[2].

The chemical resistance and ability to withstand physical movement make rubber linings the ideal corrosion protection for the interiors of many tank cars [3].

The resistance properties of a rubber lining will depend upon the kind and proportion of raw materials in the recipe of formulation the construction of the lining if it has multiple layers and the method of cure. In general they can be combined to provide excellent acid resistance, abrasion resistance [4].

It is very important that polymeric materials should not interact with medium during service. Evidently, this can be achieved by using strong polar polymers in non – polar media, or non – polar polymers in polar media [5].

In this paper, the rubbers used consist of Ethylene Propylene Diene (EPDM), Styrene Butadiene Rubber (SBR), and Natural Rubber (NR). The hardening agent used consist of sulfur and TMTD and MBTS accelerators. The relation between the types and Phr of rubbers that used either alone or as blends was studied, and the resistance of H_2SO_4 and NaOH at RT and 50 C°.

Materials and Methods

Material;

1- Polysar EPDM (345);

Poly (Ethylene –co- Propylene –co- Diene), is a terpolymer of ethylene, propylene, and a non conjugated diene. The diene is ethylidene norbornene (ENB). The typical ethylene/propylene ratio is 59/41 and the ENB contents are considered (Medium) for EPDM rubber. It has the following characteristic;

Ash content (max. weight %) 0.5,

Volatile matter (max. weight %) 0.75.
Viscosity 1+8 (100C°) 30 – 40.

2 – Styrene Butadiene Rubber SBR

Poly (butadiene - co – styrene) copolymer of styrene 23.5 % and butadiene. It has following characteristic;

Bound styrene (22.5 – 24.5%) Organic acid (5.0 – 7.5%), Ash content (0.4%),Volatile matter at 100C° (0.7), Soap (max. 0.4%).

3 – Natural Rubber SMR – 20

(Cis 1,4 – Poly Isoprene) and has the following characteristics;

Ash content (max. weight %) 0.2, Volatile matter (max. weight %) 1.0, Unmasticated moony viscosity 87.

4 – Carbon Black Type

(HAF, High Abrasion Furnace Carbon Black) Specific gravity (1.78 – 18.2), Fines through 325 mesh 99.9%.

Methods;

The mixing was operated on standard mill, having the following dimensions; roll diameter 150 mm, roll width 450 mm, working width 350 mm. The mill has the facility of roll temperature control. The rubber passes through the rolls twice, at roll opening of 0.2 mm. ± 0.02 mm. Then it bends with mill opening at about 1.5 mm, and ¾ cuts every 1/2 minutes from the alternate side. The roll temperature was adjusted at 50 C° . The weight of blend were checked after mixing to ensure that the loss in weight dose not exceed 0.5 %.

Processing;

The sheets were cuts to slaps, which were compressed in clean polished molds in a press and hold under a pressure of about 250 Kg /Cm^2 [6] for 45 minute. The mold cooled to room temperature and kept overnight until measurement of physico – mechanical properties and other analysis.

Analytical Techniques;

Determination of acetone unextractable material was carried out using the soxelet adopted in ASTM standard [7] . Degree of swelling (α) determined by the gravimetric methods [8]. Tensile strength, elongation and permanent set were measured using Dumbbell shape specimen using ASTM method [9]. Hardness was measured by pressing a cone shape penetrator with flat surface into rubber sample surface under specified load and the resistance to penetration was expressed in hardness units according to shore A scale [9] .

Chemical Resistance;

Standard rubber specimens of rectangular dimensions 25 by 50 by 2.0 ± 0.1 mm. Were cut from the acetone – extracted dried rubber sheets[10]. Two samples of each vulcanized were immersed in 10 ml of 50% H_2SO_4 and 10% NaOH for 72 hrs. at RT and 90 C^{o} . The mass after test was then determined and the change in weight was calculated as percentage change of the original specimen weight.

Result and Discussion;

Effect of Vulcanization System;

The type of vulcanization system used to cure the general purpose and specialty rubbers, largely determines the curing and performance characteristic of the chosen rubbers. The most significant components varied in the vulcanization system are the type and level of organic accelerator and level of elemental sulfur.

The basic objective in the development of vulcanization system is the production of cross links with required physical and chemical properties. Most vulcanization system play a major role in the attainment of required standards of performance by the most economic means of production [(10)]

In this case the accelerator used was a system with consists of TMTD – MBTS. This system is characterized by formation of mono and disulfide cross links [(11)] .

Samples 1,2 in table (1) indicate the using curing system with (TMTD – MBTS and elemental sulfur) give great improvements in vulcanized properties due to effect of TMTD which classified as very fast cure speed [(12)], and this agreed with Imato et al [(13)].

During the development of the use of accelerators in rubber compounding. It became evident that some were "Safer" than others. The term delayed action accelerator was employed to describe an accelerator such as MBTS which was relatively in active below 120 C^{o} [(6)]. For the same reason, mixtures of accelerators were introduced in which the degree of cross linking or the speed cure of one accelerator was boosted by the presence of second one.

It was found that using a mixture of TMTD and MBTS give rise to vulcanized with better physico – mechanical properties MBTS alone irrespective of the difference of total rubber loading and the blending ratio of EPDM with SBR or NR rubbers as shown from table (2).

Effect of Blending Ratio of Rubbers;

EPDM rubber is amorphous terpolymer like other non – crystalline polymers, mechanical properties of the unfilled EPDM are rather than poor, and consequently, reinforcing fillers are added. As compared to other poly diene elastomers (viz., NR, SBR, NBR) EPDM has a very low level of unsaturation, A more important application for EPDM in blends with another rubber is to provide resistant to degradation by heat, light, oxygen, and in, particular ozone [14]

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Blends with NR;

Natural rubber has unique combination of mechanical properties; it has high ability to crystallize when stretched, resulting from its uniform molecular structure. Developments with NR, particularly through blending provide improvements in the performance of the products.

Blends with SBR;

It is also known that when EPDM is replaced by NR or SBR compound up to 30% of the principle elastomer, certain grades of EPDM disperse in the finished compound in the form of extremely small, discrete particles which can be seen only through the electron microscopy.

Table (3) illustrate the function of blending EPDM with various Phr of SBR and NR, keeping all the ingredients constant. The results show that blend of EPDM and SBR, NR, give rise to high tensile strength, hardness, and young modulus, but elongation decreased, as content of SBR is increased and NR Phr decreased, this result agreed with M. A. Mutar [15]. Optimum value of physico – mechanical obtained in using 70 Phr EPDM, 15 Phr SBR, 15 Phr NR.

Chemical Resistance;

The interest in resistance of elastomers to chemicals lies in the volume changes that occur with time and temperature. The change in physical properties as the rubber absorbs chemical solutions acquire low temperature flexibility [5] .

An important characteristic of polymers (plastic or rubber) is their stability to attack by various aggressive media, such as mineral acids and alkaline[16]. In general the rate of attack of polymer molecules by a corrosive depends on the rates of diffusion of the attacking molecules, and the temperature. Polymers are more readily attacked by corrosives at temperature above the glass transition temperature (Tg) and when stiffening groups are not present in the polymer molecules, crystalline polymers are more resistance to liquids than amorphousness [17].

A well – known is that carbon bond with O,S, or N are readily cleaved by acids, basis, and other corrosives material compound with carbon – carbon bonds, since most of these corrosive materials are ionic and/ or highly polar in nature [18] . Since rubber chains are mostly built up from homo chain carbon skeleton, it is easy to identify their stability against normal common chemicals.

The main chains of vulcanized EPDM chains have no double bond and thus are inherently resistant to corrosive material due to their structure and composition [19] .

Sulfuric acid is a corrosive acid and is one of the most important of all industrial chemicals. Concentrated sulfuric acid is also a strong oxidizing agents, finally sulfuric is used as sulfonating agent in organic chemistry. [18] .

The resistance of sulfuric acid 50% and NaOH 10% was tested in two ways;

a) For 72 hrs at room temperature .
b) For 72 hrs at 90 C° .

As can be calculated from numerating data in table (4), the resistance of vulcanizates to chemicals, is good and products have found particular applications where there is contact with strong acid and base. The table which give the weight increase or decrease of different vulcanizates percentages show in change in weight, and EPDM (100 Phr) have strongest resistance to chemicals and EPDM/NR blends have highest weight increase percentage; EPDM/SBR (90/10) blends and EPDM/SBR/NR blends with increasing the phr of SBR have resistance in between the two types.

References;

1- G.P. Bierwagen, J. Coat. Teach. 64 (806), 71 (1992).
2- T. Nguyer, J. B. Hubbard, J. Coat Tech., 63 (794), 43 (1991).
3- F. H. Haines, J. Prot. Coat. Lin. Nov., 42 (1987).
4- R. K. Lewis, J. Prot. Coat. Lin. 26 , 27 (1987).
5- M. Dio, Introduction to Polymer Physics., Clare don press, Oxford,(1996).
6- C. M. Blow, Rubber Technology and manufacture, Butter Worth, London (1977).
7- ASTM Designation. D 297 – 617. April (1967).
8- J. Bares, and J. W. Bill Meyer, Experiments in Polymer Science. Willy New York (1998).
9- Annual Book of ASTM., Standard.
10- A. Whelan, K. S. Los, Developments in Rubber Technology Improving Products Performance, Applied Science Publisher. LTD . London (1979).
11- F. S. Matty, PHD Thesis, University of Baghdad, (2002).
12- M. Morton, Introduction to rubber Technology, Van Nostrand, New York (1973).
13- M. Imato, and 13 Co – authors, Nippon Gomu Kyokaishi, 41, 1095, (1968).
14- U.S. Pat. 3,341, 503 (Sept, 12,1967),J.L. Paige and S.M. Dipalma (to uniroyal, Inc.).
15- M. A. Mutar, PHD Thesis, University of Baghdad (2003).
16- A. Tager, Physical Chemistry of Polymers. Publisher, Moscow, (1972).
17- M. Dio and S.F. Edwards, The theory of Polymer Dynamics, Oxford (1986).
18- M. A. Mutar, F. S. Matty, Ibn Al – Haitham Journal for Pure and Applied Sciences, V 18 N (3), 2005.
19- R.K. Matthan, Rubber Engineering, Mc Graw Hill, New Delhi (1998).

Table (1)

Effect of vulcanization system on physico – mechanical properties of EPDM rubber.

All compounds contain; { Carbon black (HAF) } = 50 Phr, (Sulfur) = 1.5 Phr, (MBTS) = 0.5 Phr, (ZnO) = 5 Phr, (Stearic acid) = 1.5 Phr, (Process oil) = 5 Phr, (Antioxidant) = 1 Phr.

Formulation No.	EPDM Phr	TMTD Phr	Hardness Shore A	Tensile Strength Kg/Cm^2	Elongation %	Young's Modulus Kg/Cm^2
1	100	----	50	48	140	31
2	100	3.0	69.70	105	130	33

Table (2)

Effect of vulcanization system on physico – mechanical properties of EPDM / NR and EPDM / SBR blend rubbers.

All compounds contain; { Carbon black (HAF) } = 50 Phr, (Sulfur) = 1.5 Phr, (MBTS) = 0.5 Phr, (ZnO) = 5 Phr, (Stearic acid) = 1.5 Phr, (Process oil) = 5 Phr, (Antioxidant) = 1 Phr

Formulation No.	EPDM Phr	NR Phr	SBR Phr	TMTD Phr	Hardness Shore A	Tensile Strength Kg/Cm^2	Elongation %	Young's Modulus Kg/Cm^2
3	90	10	----	----	64 – 65	51	185	40
4	90	10	----	3.0	70 – 72	84	165	45
5	90	----	10	----	60 - 61	92	350	26.7
6	90	----	10	3.0	61 - 65	156	275	43

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TMTD; Tetra Methyl Thiuram Disulphide.
MBTS; Dibenzothiazole disulphide.
HAF; High Abrasion Furnace.

Table (3)
Effect of EPDM/NR and EPDM/SBR blend ratio on physico – mechanical
properties of soft vulcanized rubber.

All compounds contain; { Carbon black (HAF) } = 50 Phr, (Sulfur) = 1.5 Phr, (MBTS) = 0.5 Phr, (TMTD) = 3.0, (ZnO) = 5 Phr, (Stearic acid) = 1.5 Phr, (Process oil) = 5 Phr, (Antioxidant) = 1 Phr.

Formulation No.	EPDM Phr	NR Phr	SBR Phr	Hardness Shore A	Tensile Strength Kg/Cm^2	Elongation %	Young's Modulus Kg/Cm^2
7	90	7.5	2.5	62 – 63	82.0	410	38
8	90	5.0	5.0	65 – 67	173.0	232	43
9	90	2.5	7.5	66 – 68	210.0	225	44
10	80	15	5.0	70 – 71	73.44	221	42.8
11	80	10	10	73 – 75	85.30	156	59
12	80	5.0	15	75 – 76	106.0	119	59.7
13	70	20	10	74 – 75	87.70	159	54.7
14	70	10	20	74 – 76	99.70	137	58.6
15	70	15	15	77 - 79	109.0	183	48.3

Table (4)
Chemical resistance of soft vulcanized rubbers;

Formulation No.	Acetone Unextracted %	Swelling Degree(α) % in acetone	Change in weight of tested samples % in			
			H_2SO_4 at RT	H_2SO_4 at 90C°	KOH at RT	KOH at 90 C°
1	98.07	18.24	0.15	1.70	2.51	3.60
2	98.08	18.26	0.11	1.61	2.50	3.45
3	97.44	18.63	0.23	1.86	2.72	3.85
4	97.13	18.14	0.21	1.84	2.71	3.84
5	97.94	18.32	0.19	1.82	2.69	3.66
6	98.12	18.82	0.17	1.78	2.62	3.64
7	97.84	18.29	0.26	1.90	2.83	3.77
8	97.73	18.45	0.22	1.85	2.75	3.73
9	97.68	18.68	0.20	1.84	2.71	3.69
10	97.69	18.34	0.28	2.10	2.87	3.88
11	97.53	18.73	0.25	1.88	2.78	3.76
12	97.64	18.19	0.23	1.84	2.77	3.74
13	97.86	18.17	0.29	1.98	3.23	3.98
14	97.91	18.72	0.26	1.89	3.01	3.90
15	97.99	18.02	0.28	1.91	3.11	3.96