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Effect of EPDM Structure on the Properties of Babylon Tire Black Sidewall Compound

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Abstract

The tire black sidewall is the outer surface that protects the casing against weathering. It is formulated for resistance to weathering, ozone aging, abrasion, tearing and cracking, and for good fatigue life by using blends of natural rubber and cis-1.4- butadiene rubber.

The tire black sidewall uses blends of natural rubber and cis-1.4-butadiene rubber are used to achieve desired physical properties; however, use of these elastomers requires protection against ozone aging in order to maintain desirable properties over the lifetime of the tire. Protection against ozone aging is of particular interest since reaction with these olefinically unsaturated elastomers results in polymer decomposition via chain scission. Ethylene propylene diene terpolymer has proved most effective. However, its use also results in a surface discoloration, and thus it can be used in sidewall compound when the tire appearance is also an important factor.

The best formulations are obtained in the presence of 40,50 phr EPDM to achieve desired physical properties. Improved ozone resistance was obtained by using 40 and 50 phr of EPDM rubber in the compound there is no cracking throughout the life of the black sidewall compound. Blends of NR/BR/ EPDM with up to 50 phr of EPDM rubber afforded adhesion levels greater than that of a natural rubber model sidewall. Compounds containing NR /BR/ EPDM blends with 2 phr of the 6PPD antiozonant provided the best dynamic ozone resistance.

Blending of EPDM with NR and BR enhances the abrasion resistance. However, elongation at break and tear strength values are highest for those compounds having high contents of NR and Butadiene rubber.

الخلاصة

يمثل الجدار الجانب من الإطار السطح الخارجي الذي يحمي الإطار من العوامـل الجويـة. وهـو مصمم لمقاومة تلك العوامل كالظروف الجوية، والتقادم الأوزوني، والقشط، والتمزق، والتشقق، كما يـساعد في الحصول على إجهاد أفضل للإطار باستخدام مزائج من المطاط الطبيعي والمطاط البيوتـاديين-1,4 -cis وللحصول على الخواص الفيزياوية المطلوبة.

على أية حال أن استخدام هذه المطاطات المرنة يتطلب الحماية ضـد التقـادم الأوزونـي وذلـك للمحافظة على الخواص المرغوبة طيلة فترة الحياة. حيث تكتسب تلك الحماية أهمية خاصة لأن التفاعل مـع المطاطات المرنة الغير مشبعة الاوليفينية يؤدي إلى تحلل البوليمر من خلال قص الأواصـر. وقـد أثبـت بوليمر Ethylene propylene diene الثلاثي كفاءة جيدة مقارنة بغيره من البـوليمرات ألا أن اسـتخدامه يؤدي أيضا إلى عدم فقدان لون السطح ولذلك يمكن استخدامه في عجنة جدار الجانب عندما يكـون مظهـر الإطار عاملا هاما أيضا. ويمكن الحصول على أفضل الصبغ بوجود 40،50 phr مـن EPDM للحـصول على الخواص الفيزياوية المرغوبة. كما أمكن تحسين المقاومـة لـلأوزون باسـتخدام 40و phr50 مـن EPDMفي العجنة.

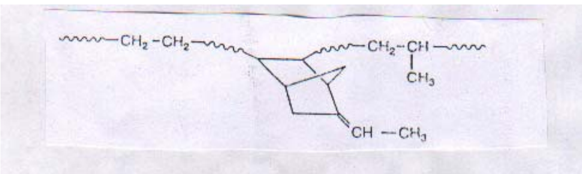
وقد وجد أن مزائج EPDM/NR/BR مع ما يصل إلى phr 50 مـن المطـاط EPDM يعطـي مستويات تماسك أفضل من تلك الموجود في جدار الجانب للمطاط الطبيعي من حيث أن العجنـات الحاويـة على مزائج EPDM/NR/BR مع2 phr من مضاد الاوزنة 6PPD أعطى أفضل مقاومة حركية للأوزون.

ومن جهة أخرى يؤدي مزج EPDM مع NR وBR إلى تحسين مقاومة القشط. ألا أن الاسـتطالة وقوة التمزق تكون هي الأعلى في حالة العجنات التي تحتوي علـى محتويـات عاليـة مـن NR ومطـاط البيوتاديين.

Introduction

The tire is a high performance polymeric composite of many rubbery compon-ents consisting of a tread area which includes the tread, base and cushion compounds; and the casing which includes the bead, carcass plies and belts; and the side wall;inner liner apex and chafer compounds.[1] Each component serves a specific and unique func- tion, synergistically to produce the desired performance. The black sidewall is the outer surface of the tire between its beads that protects the casing against weathering. It is formulated for resistance to weathering, ozone, abrasion, tear, radial, and circumfe-retial cracking, and for good fatigue life[2]. A blend of natural rubber butadiene rubber is generally used in the sidewall along with carbon black, curatives and a high concentration of antidegradants to provide weather resistance[3]. Protection of the tire from ozone aging is of particular interest since the reaction of ozone with elastomers having olefinically unsaturated backbone structures, such as natural rubber and butadiene rubber, results in scission of the polymer chain, as described in the reviews by Rhee, Lattimer and Layer,[4] Layer and Lattimer,[5] and Kuczkowski[6]. The most prevalent approach to achieveing a high- gloos black sidewall over the life of a tire is to use an inherently ozone-resistant, saturated-backbone polymer in blends with a diene rubber. The ozone-resistant polymer must be used in sufficient concentrations and also be sufficiently dispersed to form domaims that effectively block the continuous propagation of an ozone-initiated crack through the diene rubber phase withen the compound. Elastomers such as ethylene-propylene-diene terpolymers, halogented butyl rubbers, or brominated isobutylene-co-para-methylstyrene elastomers have been used in conjunction with natural rubber and/ or butadiene rubber[7].

High unsaturation ethylene-propylene-diene (EPDM) elastomers contain nonconjugated dienes affording carbon-carbon double bonds pendant to the backbone chain of the polymer which is completely saturated. As a result of this chemical struc-ture, EPDM rubber is characterized by its excellent heat, ozone, and weathering resistance; good low temperature flexibility and accepted cure characteristics[8]. EPDM polymers are generally described by ethylene/ propylene ratio, diene type and level, and molecular weight and distribution. Shulman[9] has reviewed some of the uses of EPDM rubber, which include automotive parts (hoses, tubing), weather-strip (sponge, window channel), appliance parts, roof sheeting, and tire white sidewalls.



SCHEME 1 Ethylene-propylene-diene rubber

Sandstrom and Lal[10] reported using EPDM rubber in a natural rubber/ butadie-ne rubber black sidewall composition along with a rubbery aloha-olefin interpolymer and various chemicals. Botzman[11] reported use of an EPDM polymer modified with chlorothio-sulfonmide in order to improve crosslinking with the diene rubber. Von Hellens, Mohammed and Hallman[12] reported that use of a high molecular weight EPDM rubber having an ethylene:propylene weight ratio of 47:26, a 9.5 weight percent ethylene nor- bornene (ENB) content, and being extended with 100 parts by weight of naphthenic oil (EPDM5875) afforded improved compound aged fatigue life, dynamic ozone resistance, and higher resilience while maintaining excellent hot adhesion levels compared to an industrial natural rubber / butadiene rubber control sidewall. Von Hellens, Edwards and Lobos[13] studied the adhesion of EPDM rubber –containing tire black sidewalls to a N550 carbon black –filled natural rubber cacass compound. Use of 10-40 phr of a 100 parts-by—weight oil-extended, high molecular weight and high non-conjugated diene (ENB)-content EPDM rubber (EPDM 5875) in blends with natural rubber and butadiene rubber eliminated the problem of poor adhesion to a carcass compound that was previously associated with use of EPDM rubbers.Neither high molecular weight, nor high non-conjugated diene content alone provided a satisfactory level of adhesion. Gorkina, Goncharova and Nikolaeva[14] studied the same oil-extended, high molecular weight, high non-conjugated diene EPDM rubber (EPDM HMW / NO). They reported difficulties with processing rubber mixes (lower adhesion and cohesion), migration of oil to the surface of mixes, and also limited scope for varying the formulation factors. Use of the experimental non-oil extended, high molecular weight, high non-conjugated diene-content EPDM rubber afforded better compatibility with polyisoprene and resulted in improved crack growth resistance, heat resistance and stability. However, use of this EPDM rubber also gave a lower tear strength compound than that of the standard polyisoprene / polybutadiene (50 / 50) black sidewall.

In this paper, we have studied the use of inherently ozone-resistant polymer
(EPDM) to protect the natural rubber and butadiene rubber of conventional black sidewall compounds has been a successful technique. Ethylene-propylene-diene terp-olymer blended with natural rubber and / or butadiene rubbers have received consider-able attention. Adhesion to carcass compounds, aged fatigue life and dynamic ozone
resistance have been improved using EPDM rubber.Mixing of the elastomer blend is

an important variable in order to minimize the EPDM rubber and diene rubber dom-ains and also to control the carbon black distribution in the natural rubber phase.

Experimental

Materials

The polymers used as a matrix in this study are NR (SMR 20), BR-CIS and POLYSAR EPDM 345 is a terpolymer of ethylene, propylene and a non conjugated diene.The N-(1,3-Dimethylbutyl)-N- phenyl-P-phenylenediamine (6PPD) was used an antiozonant to be compared with EPDM (ozone resistant).

Preparation on of the Rubber Compounds

Eleven rubber compounds with different loading amounts of EPDM were pre-pared. For rubber compounding, we used a laboratory mill: rolls dimensions are: outside diameter 150mm, working distance 300mm, speed of the slow roll 24 rpm and gear ratio 1.4.Compound recipes are summarized in Table 1 . After mixing, the compounds were carefully remilled into flat sheets on a two-roll mill.

Rheocurves were recorded using a Monsanto Rheometer ODR 200 at 160 C°. the t90 time, which denotes the time for 90% cure, and the maximum torque were determined from the rheographs.

When possible, standard ASTM tests were used to determine the cured compound physical properties. Sress / strain properties (tensile strength, elongation at break, modulus values,) were measured at room temperature using a tensometer 10.

Shore A hardness was measured at room temperature by using a Zwick duromatic. Abrasion loss was determined at room temperature by weight difference by an APH40 abrasion tester with rotating sample and rotating drum. Ozone aging of dumbbell specimens was accomplished according to ASTM D-395-82 by using an Orec Environmental Chamber at 40C° with samples undergoing cyclic deformation to 25 % elongation while being exposed to 50 pphm of ozone.Thermal aging of dumbbell specimens was accomplished at 70C° for 7 days. Adhesion to carcass was accomplis-hed at 100 C°.

TABLE 1: RECIPES OF SIDEWALL COMPOUND WITH VARIOUS EPDM LOADING

Ingredients	1 phr	2 phr	3 phr	4 phr	5 phr	6 phr	7 phr	8 phr	9 phr	10 phr	11 phr
NR	50	30	50	60	50	10	-	50	60	50	80
BR-CIS	50	30	10	-	-	50	50	40	20	30	-
EPDM (345)	-	40	40	40	50	40	50	10	20	20	20
Zinc oxide	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	2	2	2	2	2	2	2	2	2	2	2
Sulfur	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3	2.3
MBS[a]	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
6PPD[b]	2.4	-	-	-	-	-	-	-	-	-	-
Aromatic oil	10	10	10	10	10	10	10	10	10	10	10
HAF N326	50	50	50	50	50	50	50	50	50	50	50

a: N-morpholinothio – benzothiazole

b: N- 1,3 dimethylbutyl – N/ phenyl – *p* - phenylenediamine

Results and Discussion

Cure Properties

The levels of the three ingredients (sulfur, zinc oxide,MBS) used to cure the EPDM black sidewall compound were established via statistically designed experiments in order to afford a compound with a T90 cure time at 160 C° of 10-12 minutes, good scorch safety and no reversion. The cure property data of the EPDM elastomer evaluated in this study are shown in Table 2. Inspection of the data shows that there are small variations in these cure properties. Maximum torque values are the highest and scorch values are the lowest for those sidewall compounds having EPDM elastomer.

TABLE 2: SIDEWALL COMPOUND CURE PROPERTIES

Compound	1	2	3	4	5	6	7	8	9	10	11
ML, ib-in	4.93	5.52	4.10	3.90	3.78	5.33	5.86	3.89	3.04	3.54	3.25
MH, ib-in	29.45	31.04	27.12	29.56	27.82	33.31	37.48	28.20	29.65	31.33	24.8
T52[a], min.	1.15	1.14	1.12	1.06	1.02	1.17	1.17	1.06	1.01	1.01	1.00
T50, min	1.80	1.65	1.56	1.46	1.48	1.89	1.97	1.57	1.42	1.46	1.39
T90[b], min.	2.49	2.53	2.65	2.83	1.35	2.87	3.32	2.72	2.92	2.45	2.98

a: Time required for 52% cure .
b: Time required for 90% cure .

Physical Properties of Sidewall Compound Containing EPDM Rubber

Tensile properties. Cured EPDM black sidewall compound physical property data are shown in table 3. Inspection of the data shows large variations in many of the properties. In particular, tensile strength (13.231 -19.571MPa), elongation at break (339-583%) and tear strength(6.895-11.351MPa) values vary widely. Tensile strength values are lowest for those compounds having high EPDM content, see compounds2,3,4,5,6 and 7. However, elongation at break and tear strength values are highest for those compounds having high contents of NR and Butadiene rubber, see compounds 1, 8,9,10 and 11. EPDM rubber in blends with NR and butadiene rubber in black sidewall compounds showed improved resistance in abrasion.

TABLE 3: EPDM SIDEWALL COMPOUNDS PHYSICAL PROPERTIES

Compound	1	2	3	4	5	6	7	8	9	10	11
Hardness, Shore A	56	60	58	59	59	60	61	58	60	58	55
Elongation, %	487	339	410	454	448	388	379	583	546	525	466
Tensile strength, Mpa	17.9	13.99	15.71	16.975	16.415	14.318	13.231	19.571	18.991	18.645	17.524
100 % modulus, Mpa	2.433	2.253	2.310	2.323	2.311	2.289	2.111	2.860	2.793	2.647	2.415
200 % modulus, Mpa	5.446	5.025	5.185	5.421	5.354	5.226	4.446	5.910	5.830	5.720	5.433
300 % modulus, Mpa	9.889	7.356	8.205	9.567	9.471	8.154	7.225	11.323	10.541	10.471	9.779
Tear strength, Mpa	9.638	6.895	7.832	8.283	9.214	7.548	6.658	11.351	10.615	10.587	9.562
Abrasion resistance %	0.266	0.316	0.414	0.461	0.443	0.156	0.921	0.223	0.389	0.276	0.475

Effect of Aging on Sidewall Physical Properties

The effect of aging on the physical properties of sidewall compounds containi-ng different loading of EPDM is illustrated in Table 4. It can be seen that compounds containing EPDM showed characteristically good retention of tensile strength, but rapid loss of extensibility after 7 days of aging. This may be due to the fact that main chains of the EPDM have no double and thus EPDM does not suffer deterioration due to molecular scission even after extended exposure to heat. On further aging, hardness increases and reaches high values after 7 days. This may be related to the increase in the crosslink density. The sources to cause the increase of crosslink density are the formation of new crosslinks between polymer chains. The new crosslinks are formed by the reaction of curing agents remaining in the vulcanizates and the combination reaction of the pendent sulfide groups.

TABLE 4: EFFECT OF AGING ON SIDEWALL PHYSICAL PROPERTIES

Compound	1	3	7	8	9
Aged 7 days at 70 C°					
Hardness, Shore A	66	67	68	69	70
Elongation, %	301	356	373	327	289
Tensile strength, Mpa	13.804	15.207	13.160	17.177	17.794
100 % modulus, Mpa	3.392	2.916	3.343	2.968	2.860
200 % modulus, Mpa	7.899	6.331	7.544	3.310	6.858
300 % modulus, Mpa	13.648	9.982	10.953	11.857	11.768

Effect of EPDM on Dynamic Ozone Resistance and Adhesion to Carcass

Table 5 illustrates the effect of EPDM on dynamic ozone resistance and adhesion to carcass of sidewall compounds containing different loads of EPDM. Ozone resistance depended on the level of the EPDM rubber, ozone resistance also depended on good mixing of the EPDM rubber with natural rubber in order to achieve a polymer domain size of less than one micron, otherwise cracking can be severe. However, improved ozone resistance occurred at the expense of reduced cut growth resistance. Improved ozone resistance was obtained by using 40 and 50 phr of EPDM rubber in the compound there is no cracking throughout the life of the black sidewall compound. The adhesion mechanism involves the creation of radicals when long chains of EPDM rubber and natural rubber are broken down by shear and mechanical work. Grafting between the two elastomer is believed to occur. The graft polymer is thought to act as a compatibilizer[15]. Blends of NR/BR/ EPDM with up to 50 phr of EPDM rubber afforded adhesion levels greater than that of a natural rubber model sidewall.

TABLE 5 : EFFECT OF EPDM ON DYNAMIC OZONE AND ADHESION TO CARCASS OF SIDEWALL COMPOUNDS

Compound	1	2	3	4	5	6	7	8	9	10	11
Dynamic ozone, 50 pphm, 25 % ext., 40C° after 72 continous hours											
Cracking rating[a]	b	OK	OK	OK	OK	OK	OK	S	VS	VS	VS
Adhesion to Carcass @ 100C°											
Adhesion, KN/ m	c	24.6	25.8	26.3	26.9	24.7	26.6	19.6	21.3	20.5	22.2

a OK-no cracks; VS-very slight cracks; S-slight cracks.
b Broke @ 72 hours
c Test simple slipped out of one the grips

Effect of Antiozonant on EPDM-Sidewall Properties

In order to protect the tire black sidewall from cracking, chemically reactive antiozonants are generally added to sidewall formulation at levels tested for effective- ness under both static and dynamic conditions[16]. N-1,3-Dimethylbutyl,-N-phenyl-para-phenylenediamine is presently the most widely used chemical antiozonant. It is known by the name 6PPD. However, para-phenylenediamine antiozonants are highly staining and discoloring materials, and therefore can only be used in limited amounts where tire black sidewall appearance is also an important factor. 6PPD mixed with the natural rubber and butadiene rubber to form a masterbach followed by blending with the EPDM rubber and other ingredients, afforded the most effective processing in order to protect the natural rubber phase. Compounds containing NR /BR/ EPDM blends with 2 phr of the 6PPD antiozonant passed all of the requirements of the tire black sidewall(see Table 6).The presence of 6PPD did not affect adhesion.

TABLE 6: EFFECT OF 6PPD ANTIOZONANT ON EPDM-SIDEWALL PROPERTIES

Compound	8	9	10	11
Dynamic ozone, 50 pphm, 25 % ext., 40C°, after 72 continuous hours				
Crack rating	OK	OK	OK	OK
Adhesion to carcass @ 100C°				
Adhesion, KN/m	20.7	22.5	21.7	23.4

Concolusions

Tire black sidewall compounds are formulated to resist weathering by heat, oxygen, ozone and ultraviolet light, to resist abrasion, tearing, and radial and circumferential cracking, and for fatigue life. In this study, we studied the use of EPDM as ozone-resistant polymer to protect the natural rubber and butadiene of conv- entional black sidewall compounds has been a successful technique. EPDM blended with natural rubber and / or butadiene rubber with different loading of EPDM. EPDM black sidewall compound give rise to good scorch safety and no reversion.

Adhesion to carcass compounds, aged fatigue life, elongation at break, abrasion resistance and dynamic ozone resistance have been improved in presence of EPDM in sidewall compound.

N-1,3- Dimethylbutyl,-N-phenyl-para- phenylenediamine (6PPD) was used as antiozonant.This enhanced the dynamic ozone resistance for compounds containing NR/BR/ EPDM blends with 2 phr of 6PPD passed all of the requirements of the tire black sidewall. The presence of 6PPD did not affect adhesion.

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