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(54) **Plasticized Carboxylated Nitrile Rubber Vulcanisates**

(57) A carboxylated butadiene-acrylonitrile polymer is compounded with at least one filler and at least one vulcanisation active agent and, as a plasticiser, an epoxidised compound which is not an epoxy resin.

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SPECIFICATION

Improved Carboxylated Nitrile Rubber Vulcanisates

This invention is directed to a process for the production of a plasticised carboxylated butadiene-acrylonitrile rubbery vulcanisate having improved properties.

5 It is well known in the processing of natural and synthetic polymers to add plasticiser, especially during the compounding of the polymer, and that the elastomeric vulcanisates derived from such plasticised polymers have a desirable balance of properties. The chemical form of the plasticisers used may vary from one specific polymer to another — usually a non-polar plasticiser, such as a hydrocarbon oil, is used with non-polar polymers and polar plasticisers are used with polar polymers. 10 Butadiene-acrylonitrile polymers, are well known and constitute one member of the polar polymer group; the plasticisers used with the nitrile polymers are polar materials such as esters, certain resins, phosphate compounds and other like materials. Examples of suitable plasticisers for nitrile polymers include alkyl or alkoxy adipates, phthalates and sebacates, coumarone-indene resins, epoxides of soybean oil, and the alkyl or alkoxy phosphates. Generally, plasticisers would not be added to nitrile 15 polymers when the vulcanisate characteristics are critical with respect to non-extractability and to strength properties. It is well known that, for polymers containing plasticiser, the resulting vulcanisates generally possess somewhat reduced overall strength properties.

Carboxylated nitrile polymers, which are butadiene-acrylonitrile-carboxylated monomer polymers, are well known and have recently been receiving more attention in the rubber industry. Because of the 20 carboxyl groups in the polymer, different methods may be used for vulcanising these polymers which make use of the reaction of carboxyl groups with metal compounds, especially metal oxide compounds. The vulcanisates of carboxylated nitrile polymers have been found to be suitable for certain special uses due to the high strength, hardness and abrasion resistance attainable.

According to the invention a polymeric composition comprises a carboxylated butadiene-acrylonitrile polymer and at least one filler and, as a plasticiser, about 2.5 to 30 parts by weight of an epoxidised hydrocarbyl compound per 100 parts by weight of the polymer. The composition may 25 contain at least one vulcanisation active agent or may be vulcanised.

A process according to the invention for the production of an improved vulcanisate of a carboxylated butadiene-acrylonitrile polymer comprises compounding the polymer with at least one 30 filler and vulcanisation active agent prior to vulcanisation, and also comprises adding to the polymer during the compounding an epoxidised hydrocarbyl compound in an amount ranging from about 2.5 to about 30 parts by weight of epoxidised hydrocarbyl compound per 100 parts by weight of carboxylated butadiene-acrylonitrile polymer.

Carboxylated butadiene-acrylonitrile polymers, generally referred to as carboxylated nitrile 35 polymers, are copolymers of butadiene, acrylonitrile and an unsaturated carboxylic monomer. Suitable unsaturated carboxylic monomers for the carboxylated nitrile polymers used in the present invention include acrylic acid, methacrylic acid, crotonic acid, oleic acid and the like. The polymers may be prepared by the well known emulsion free radical polymerisation process. The acrylonitrile content of the polymer may be from about 20 to about 40, preferably from about 25 to about 35, weight percent 40 of the polymer. The unsaturated carboxylic monomer content of the polymer should be from about 2 to about 10, preferably from about 4 to about 9, weight percent of the polymer. Butadiene forms the balance to 100 percent of the polymer. The molecular weight of the polymer is usually such that the polymer is within the Mooney Viscosity range (ML 1+4 at 100°C) of about 40 to about 80.

The epoxidised hydrocarbyl compound added as plasticiser is a hydrocarbyl compound which has 45 been chemically modified to contain epoxy oxygen groups. The epoxide content of the epoxidised hydrocarbyl compound is usually from about 3 to about 10 percent, expressed as oxirane oxygen. Suitable such epoxidised hydrocarbyl compounds include epoxidised monomeric aliphatic, preferably non-polymerisable, compounds such as epoxidised fatty esters including at least one aliphatic group of at least 12 carbon atoms, preferably epoxidised octyl stearate, epoxidised octyl tallate, epoxidised 50 soybean oil and epoxidised linseed oil. Epoxidised hydrocarbyl compounds useful in the present invention do not include the materials generally known as epoxy resins, such as the reaction product of epichlorohydrin and bisphenol A.

The quantity of epoxidised hydrocarbyl compound added during compounding to the carboxylated nitrile polymer is from about 2.5 to about 30 parts by weight of epoxidised hydrocarbyl 55 compound per 100 parts by weight of carboxylated nitrile polymer. Preferably the amount of epoxidised hydrocarbyl compound added is from about 5 to about 20 parts by weight per 100 parts by weight of carboxylated nitrile polymer. The epoxidised hydrocarbyl compound may also be used in combination with a conventional plasticiser, such as di-octyl phthalate, but then the amount of epoxidised hydrocarbyl compound should be from 5 to about 20 parts by weight and the amount of 60 conventional non-epoxidised plasticiser should be less than about 10 parts by weight and should not exceed the parts by weight of epoxidised hydrocarbyl compound, all parts being per 100 parts by weight of carboxylated nitrile polymer.

Vulcanisation active agents include the well known sulphur and sulphur compounds, organic peroxides, metal oxides and metal peroxides.

When a conventional plasticiser, such as di-octyl phthalate, is added during compounding to a carboxylated nitrile polymer, the Mooney viscosity of the compound is lower than when no plasticiser is present, generally in proportion to the amount of plasticiser added. The vulcanisates obtained from compounds containing a plasticiser such as di-octyl phthalate generally have, in comparison with

5 vulcanisates obtained from compounds containing no plasticiser, lower hardness, lower modulus at both 100% and 300% elongations, usually a lower tensile strength and usually an equivalent or higher compression set. The vulcanisate thus is generally more flexible and usually retains improved flexibility to lower temperatures than vulcanisates not containing plasticiser, but has somewhat reduced strength properties.

10 When an epoxidised hydrocarbyl compound is used as plasticiser for carboxylated nitrile polymers, the compound Mooney Viscosity is lower as the amount of plasticiser is increased, but generally is higher than if an equivalent amount of conventional plasticiser had been used. The corresponding vulcanisates generally have a lower modulus at 100% elongation and a 300% modulus which ranges from marginally lower to higher when compared to vulcanisates containing no plasticiser

15 Vulcanisates containing epoxidised hydrocarbyl compound plasticiser generally have higher tensile strengths than vulcanisates containing conventional plasticiser. Most importantly, the compression set is lower for vulcanisates containing the epoxidised hydrocarbyl compound plasticiser and significantly lower than for vulcanisates containing a conventional plasticiser such as di-octyl phthalate. The reduction in hardness due to the presence of the epoxidised hydrocarbyl compound is found to be

20 about the same as the reduction in hardness when di-octyl phthalate is used as the plasticiser.

Thus, by using the process of the present invention, it is possible to achieve the benefits normally obtained with conventional plasticisers but also, and most importantly and unexpectedly, to achieve significant improvements in the strength and compression set properties of the vulcanisates.

25 The vulcanisates of the present invention may be used in applications where nitrile polymers are used, including O-rings, seals, abrasion resistant rolls, etc.

In the following examples, all parts are parts by weight. The test methods used to determine the vulcanisate properties were all ASTM procedures normally used in the rubber industry. For the compression set measurements the vulcanisates have been cured for twice the time shown and aged for 70 hours at 100°C, except for Example 3 where the vulcanisates were cured for 1.5 times the time

30 shown before aging. In Examples 2, 4 and 5 the compounds were made up using, additionally, the second to ninth components listed in Table 1 in the amounts shown in Table 1.

Example 1

A commercially available carboxylated butadiene-acrylonitrile polymer was compounded with varying amounts of di-octyl phthalate as a known prior art plasticiser and with an epoxidised soybean

35 oil as illustrative of the present invention. The polymer used was Krynac 221 (Krynac is a Registered Trade Mark) which is believed to contain about 7 weight percent of carboxylated monomer and about 28 weight percent of acrylonitrile and which has a Mooney Viscosity (ML 1+4 at 100°C) of about 50. The epoxidised soybean oil used was Paraflex G-62 (Paraplex is a Registered Trade Mark) which contains about 7 weight percent of oxirane oxygen. The details of the compounds and the vulcanisate

40 properties are shown in Table I in which Krynac PA-50 is a mixture of 50 parts of zinc peroxide and 50 parts of a butadiene-acrylonitrile rubber. The compounds were mixed, using conventional procedures, in a laboratory scale internal mixer except for the curatives which were subsequently added on a cool rubber mill.

Table I

Expt. No.	1	2	3	4	5	6	7
Krynac 221 parts	—	—	—	95	—	—	—
Sulphur parts	—	—	—	0.3	—	—	—
Stearic acid parts	—	—	—	1	—	—	—
Polyethylene							
50 AC-617 parts	—	—	—	3	—	—	—
Hisil* 210 parts	—	—	—	25	—	—	—
Hisil* EP parts	—	—	—	25	—	—	—
Krynac PA-50 parts	—	—	—	10	—	—	—
N-Oxydiethylene							
55 benzothiazole							
sulphenamide parts	—	—	—	3	—	—	—
Pennac* TM parts	—	—	—	1	—	—	—
Di-octyl phthalate							
parts	0	5	10	0	0	0	5
60 Paraplex G-62							
parts	0	0	0	5	7.5	10	5
Compound Mooney							
Viscosity							
ML 1+4 at 100°C	101	85	72	97	88	83	82

Table I (cont.)

Cure time at 166°C minutes	8	8	8	11	11	11	11
<i>Vulcanisate Properties</i>							
5 Tensile Strength kg/cm ²	208	226	194	247	234	226	201
100% Modulus kg/cm ²	48	35	30	39	39	40	32
300% Modulus kg/cm ²	135	95	79	132	133	136	107
10 Elongation %	420	570	580	470	440	440	480
Hardness Shore A2	84	75	75	81	80	77	76
Compression Set %	71	80	68	62	55	50	57

* Hisil and Pennac are Registered Trade Marks.

15 Experiments Nos. 1, 2 and 3 are controls and show the expected effects due to the addition of a conventional plasticiser — i.e. reduced compound Mooney, generally lower strength properties and reduced hardness. Experiments Nos. 4, 5 and 6 show the unusual effects due to the addition of epoxidised soybean oil as compared to the di-octyl phthalate plasticiser — i.e. somewhat reduced compound Mooney, slightly reduced 100% modulus, essentially unchanged 300% modulus, higher tensile strength and significantly lower compression set. Experiment No. 7 shows that the addition of a mixture of di-octyl phthalate and epoxidised soybean oil yields a vulcanisate having the high strength properties and lower compression set. 20

Example 2

25 Following the procedure of Example 1, further vulcanisates were prepared and tested. The polymers used were Krynac 211, which is believed to contain about 9 weight percent of carboxylated monomer and about 25 percent of acrylonitrile and has a Mooney Viscosity (ML 1+4 at 100°C) of about 55, and Krynac 221. The data are provided in Table II, in which the high strength properties and lower compression set are readily seen in comparison with the vulcanisates containing di-octyl phthalate. Experiments Nos. 1 and 4 are controls using di-octyl phthalate as the plasticiser and Experiment No. 3 contains no plasticiser. 25

		Table II							
<i>Expt. No.</i>		1	2	3	4	5	6	7	
30	Krynac 211 parts	95	95	—	—	—	—	—	30
	Krynac 221 parts	—	—	95	95	95	95	95	
35	Di-octyl phthalate parts	10	—	—	10	—	—	—	35
	Paraplex G-62 parts	—	10	—	—	10	15	20	
40	Compound Mooney Viscosity ML 1+4 at 100°C	124	143	100	77	92	101	69	40
	Cure time at 166°C minutes	11	11	10	11	12	15	15	
<i>Vulcanisate Properties</i>									
45	Hardness Shore A-2	77	77	81	79	78	77	76	45
	Tensile strength kg/cm ²	190	225	226	197	235	217	196	
	100% Modulus kg/cm ²	52	76	42	32	46	55	44	
50	300% Modulus kg/cm ²	136	210	108	80	140	182	136	50
	Elongation %	425	320	500	600	450	360	400	
	Compression Set %	67	49	64	63	49	38	39	

Example 3

55 Epoxidised soybean oil was evaluated as plasticiser, in comparison with di-octyl phthalate, for carbon black filled vulcanisates in a variety of vulcanisation recipes. The details are shown in Table III, in which Experiment No. 1 is a control. Comparison of Experiments 1 and 2, which are identical except for the plasticiser, shows that the vulcanisate containing epoxidised soybean oil possesses high strength and low compression set properties. 55

Table III

<i>Expt. No.</i>	1	2	3	4	
Krynac 221 parts	—	—	95	—	—
Sulphur parts	0.3	0.3	—	0.3	—
5 Stearic acid parts	—	—	3	—	5
Carbon black (N-660) parts	—	—	60	—	—
Krynac PA-50 parts	—	—	10	—	—
Tetramethyl thiuram monosulphide parts	0.5	0.5	—	—	—
10 N-oxydiethylene benzothiazole sulphenamide parts	—	—	—	3	10
Pennac TM parts	—	—	—	1	—
DI-CUP* 40C parts	—	—	—	—	4
Di-Octyl phthalate parts	15	—	—	—	—
15 Paraplex G-62 parts	—	15	—	15	15
Compound Mooney Viscosity ML+4 at 100°C	51	54	52	51	—
Cure time at 166°C minutes	30	30	30	30	—
<i>Vulcanisate Properties</i>					
20 Hardness shore A-2	79	83	82	84	20
Tensile Strength kg/cm ²	231	246	232	252	—
100% Modulus kg/cm ²	80	130	107	206	—
300% Modulus kg/cm ²	221	—	—	—	—
Elongation %	320	190	260	120	—
25 Compression Set %	40	21	25	13	25

* DIP-CUP is a Registered Trade Mark

Example 4

Using as the carboxylated nitrile rubber Krynac 221 and the procedure of Example 1, further vulcanisates were prepared and tested in which the oxirane oxygen content of the epoxy plasticiser was varied. Plasticiser A is an epoxidised octyl stearate and contains about 3.5 percent of oxirane oxygen, Plasticiser B is an epoxidised soybean oil and contains about 7 percent of oxirane oxygen and Plasticiser C is an epoxidised linseed oil and contains about 9.3 percent of oxirane oxygen. The results are shown in Table IV from which it can be seen that the vulcanisate containing Plasticiser A has a marginal improvement, as compared to the di-octyl phthalate containing vulcanisate in strength properties and an increase in the compression set. The vulcanisates containing Plasticisers B and C both show significant increases in modulus and tensile strength and a significant reduction in compression set.

Table IV

<i>Expt. No.</i>	1	2	3	4	
40 Krynac 221 parts	—	—	95	—	40
Di-octyl phthalate parts	10	—	—	—	—
Plasticiser A parts	—	10	—	—	—
Plasticiser B parts	—	—	10	—	—
Plasticiser C parts	—	—	—	10	—
45 Compound Mooney Viscosity ML 1+4 at 100°C	76	76	95	100	45
Cure time at 166°C	—	—	10 mins.	—	—
<i>Vulcanisation Properties</i>					
50 Hardness Shore A-2	76	76	79	78	—
Tensile Strength kg/cm ²	188	205	209	217	50
100% Modulus kg/cm ²	30	31	41	50	—
300% Modulus kg/cm ²	72	76	122	162	—
Elongation %	560	570	430	380	—
Compression Set %	71	83	54	53	—

55 Example 5

Vulcanisates were prepared and tested using a polymer containing about 25 weight percent of acrylonitrile, about 73 weight percent of butadiene and about 2 weight percent of methacrylic acid. The compounding recipe used was that shown in Example 1. One vulcanisate was prepared which

contained no plasticiser, one vulcanisate contained 10 parts of di-octyl phthalate and one vulcanisate contained 10 parts of Plasticiser B of Example 4, this latter vulcanisate being within the scope of the present invention. The results are shown in Table V.

		Table V			
5	<i>Expt. No.</i>	1	2	3	5
	Di-octyl phthalate parts	—	10	—	
	Plasticiser B parts	—	—	10	
	Compound Mooney Viscosity				
	ML 1+4 at 100°C	96	70	74	
10	Cure time at 166°C				10
	minutes	10	10	10	
	Hardness Shore A-2	69	64	65	
	Tensile Strength kg/cm ²	184	170	181	
	100% Modulus kg/cm ²	32	26	26	
15	300% Modulus kg/cm ²	87	67	66	15
	Elongation %	580	670	690	
	Compression Set %	68	70	65	

Claims

- 20 1. A polymeric composition comprising a carboxylated butadiene-acrylonitrile polymer containing at least one filler and, as a plasticiser, about 2.5 to about 30 parts by weight of epoxidised hydrocarbyl compound per 100 parts by weight of carboxylated butadiene-acrylonitrile polymer. 20
2. A composition according to claim 1 in which the epoxidised compound is an epoxidised fatty ester.
- 25 3. A composition according to claim 1 or claim 2 in which the epoxidised compound contains from 3 to 10% of oxirane oxygen. 25
4. A composition according to any preceding claim in which the epoxidised hydrocarbyl compound is selected from epoxidised octyl stearate, epoxidised octyl tallate, epoxidised soybean oil and epoxidised linseed oil.
- 30 5. A composition according to any preceding claim in which the amount of epoxidised compound is from 5 to 20 parts by weight per 100 parts by weight of carboxylated butadiene-acrylonitrile polymer. 30
- 35 6. A composition according to any preceding claim in which the carboxylated butadiene-acrylonitrile polymer is a copolymer of an unsaturated carboxylic monomer selected from acrylic acid, methacrylic acid, crotonic acid and oleic acid. 35
7. A composition according to any preceding claim in which the carboxylated butadiene-acrylonitrile polymer is a copolymer of 20 to 40 weight percent acrylonitrile, 2 to 10 weight percent unsaturated carboxylic monomer and the balance to 100 weight percent being butadiene.
8. A composition according to claim 7 in which the amount of acrylonitrile is 25 to 35% and the amount of unsaturated carboxylic monomer is 4 to 9 weight percent.
- 40 9. A composition according to any preceding claim including at least one vulcanisation active agent, the composition being vulcanisable. 40
10. A composition according to any of claims 1 to 8 in the form of a vulcanisate.
- 45 11. A process for the production of a vulcanisate according to claim 10, comprising, prior to vulcanisation, compounding the carboxylated butadiene-acrylonitrile polymer with at least one vulcanisation active agent, at least one filler and, as plasticiser, about 2.5 to about 30 parts by weight of epoxidised hydrocarbyl compound per 100 parts by weight of carboxylated butadiene-acrylonitrile polymer. 45