

Effect of Chemically Modified Waste Rubber Powder as a Filler in Natural Rubber Vulcanizates

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ABSTRACT: Waste rubber powder (RP) was subjected to chemical modification by using different concentrations of oxidizing agents such as nitric acid and 30% hydrogen peroxide solution. This treatment leads to introducing some functional groups onto the surface of RP. The chemically modified RP was incorporated in natural rubber mixes either alone or in combination with carbon black (HAF). The physicochemical properties of NR vulcanizates obtained

were studied and compared to NR vulcanizates filled with untreated RP. It was found that the chemically modified RP improves tensile strength and aging resistance of NR vulcanizates compared with untreated RP. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 30–36, 2004

Key words: waste rubber powder; reinforcement; filler; vulcanization

INTRODUCTION

Disposal of rubber wastes is a worldwide problem. A potential solution of this disposal problem is recycling of the waste and reusing it in rubber formulations. Although thermoplastic wastes can be recycled easily, recycling of waste rubbers is not so easy, as they are crosslinked and not biodegradable. The main source of rubber waste is worn tires. To eliminate or reduce waste rubber from the environment and to reduce costs of some rubber goods, attempts are being made to reuse waste rubber. There are two main ways to reuse or to consume waste rubber. The first is the incineration or pyrolytic degradation of waste rubber to basic chemicals.^{1,2} The second is grinding the waste rubber to form a granulate or regenerate, both of which are used in the production of technically less demanding rubber goods by mixing the rubber powder with a new rubber.^{3–5}

Worn tires can be shredded and transformed into powder of desired particle size by different techniques.^{6–8} The rubber powder (RP) finds many applications as either asphalt modifier,⁹ toughening agent for thermoplastics and thermosets,^{10–12} or as extender/filler in rubber compounds.^{13–17} The RP is used also in manufacturing of different rubber composites.^{18–20}

Surface modification of rubber powder by use of a proprietary reactive gas atmosphere²¹ and sulphonation²² was attempted. Evaluation of modified RP for recovery of some metal ions as ion exchange resin was conducted.^{22–24} Thus, attempts are being made to increase this proportion²⁵ and trials were made to graft some monomers onto rubber granules^{26,27} and to evaluate the grafted granules in rubber mixtures.

The present article reports the results of studies on the surface modification of RP. This includes surface oxidation of RP by 30% hydrogen peroxide and different concentrations of nitric acid. The chemically modified RP was evaluated as extender/filler in NR mixes.

EXPERIMENTAL

Materials

The rubber used in this investigation was natural rubber (SMR 20). Waste RP of particle size ranges between 125 and 500 μm , produced from the treads of trunk and passenger tires, was kindly provided by MARSO Chemical Co.

Oxidizing agents were as follows: nitric acid, 66% (specific gravity, 1.490); hydrogen peroxide, 30% (specific gravity, 1.110). Compounding ingredients, ZnO, stearic acid, sulfur, high-abrasion furnace carbon black (HAF), and other ingredients were of commercial rubber grade.

Experimental techniques

Surface oxidation

The RP was treated with different concentrations of HNO_3 (10, 20, 30, and 60%) and 30% H_2O_2 . In this

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TABLE I
The Rheometric Characteristics and the Physicomechanical Properties of NR Vulcanizates Loaded with Untreated RP/HAF Combination System

Formula/Code	γ_1	γ_2	γ_3	γ_4	γ_5	γ_6	γ_7
NR	100	100	100	100	100	100	100
ZnO	5	5	5	5	5	5	5.0
Stearic acid	1	1	1	1	1	1	2.0
HAF	50	40	30	20	10	—	—
Untreated RP	—	10	20	30	40	50	—
Processing oil	5	5	5	5	5	5	—
Sulfur	2.0	2.0	2.0	2.0	2.0	2.0	2.0
CBS	1.25	1.25	1.25	1.25	1.25	1.25	1.25
PBN ^a	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Rheometric characteristics at 142°C							
M_L , dNm	3	2	2	1	1	1	2.5
M_H , dNm	70	55	47	41	37	32	61.5
t_{c90} , min	13.5	12.8	12.5	11.6	11.2	11.0	7.0
t_{s2} , min	4.5	4.2	3.8	3.5	3.1	3.1	3.5
CRI, min ⁻¹	11.1	11.6	11.5	12.3	12.3	12.7	28.6
Physicomechanical properties at room temperature							
M 200%, MPa	4.9	4.0	3.8	3.3	2.2	1.3	3.0
TS, MPa	23.7	14.7	12.8	11.0	8.0	5.5	18.5
ϵ , %	550	525	500	480	450	400	650
Q , %	213	220	223	228	231	234	317

^a Phenyl β -naphthyl amine.

treatment, 100 g of the RP was placed in a 500-ml beaker in an ice bath; then, the oxidizing agent was introduced onto the rubber powder dropwise with continuous stirring until complete immersion of the rubber powder. The reaction mixture was heated to 100°C for about 3 h in the case of using nitric acid and to room temperature for H₂O₂ with good stirring. The beaker containing the reaction mixture was covered and then left for 24 h at room temperature. The treated RP was washed thoroughly with distilled water until a neutral solution was obtained. Infrared spectroscopic analysis was carried out by using a Jasco FTIR 300E spectrophotometer. KBr disk technique was applied to detect the change in the fingerprint of RP.

Preparation of rubber mixes and vulcanizates²⁷

All rubber mixes were prepared on a two-roll laboratory mill (diameter, 470 mm; working distance, 300 mm; speed of the slow roll, 24 rpm; gear ratio: 1 : 1.4). The roller temperature was kept at about 50°C during mixing. The compounded rubber was left overnight before vulcanization. The vulcanization was carried out in hydraulic press at 142 ± 2°C under a pressure of about 4 mPa for the optimum cure time t_{c90} .

Tests of rubber mixes and vulcanizates

The following standard methods were used: ASTM D 2084-95 (1998) for determination of rheometric charac-

teristics (M_L , M_H , t_{s2} , t_{c90} , and CRI) by using a Monsanto Rheometer 100, where M_L is the minimum torque (dN m); M_H is the maximum torque (dN m); t_{s2} is the scorch time (min), (i.e., the time to two units of torque increase above the minimum); t_{c90} is the optimum cure time (min) (i.e., the time to 90% of maximum torque developed); CRI is the cure rate Index (i.e., the rate of rubber vulcanization), which is determined as

$$\text{CRI} = 100 / (t_{c90} - t_{s2}), \quad \text{min}^{-1}$$

ASTM D 412-98a (1998) for determination of physicomechanical properties (Modulus M , tensile strength, TS, and ultimate elongation ϵ) by using a tensile testing machine (Zwick 1425). ASTM D 471-97 (1998) for equilibrium swelling (Q) determination in toluene and ASTM D 573-88 (1994) for thermal aging properties.

RESULTS AND DISCUSSION

Evaluation of RP as filler

The untreated rubber powder was examined as filler; thus, it was combined with reinforcing filler HAF in different ratios in NR mixes. The formulations, rheometric characteristics, and physicomechanical properties of the obtained mixes and vulcanizates are given in Table I.

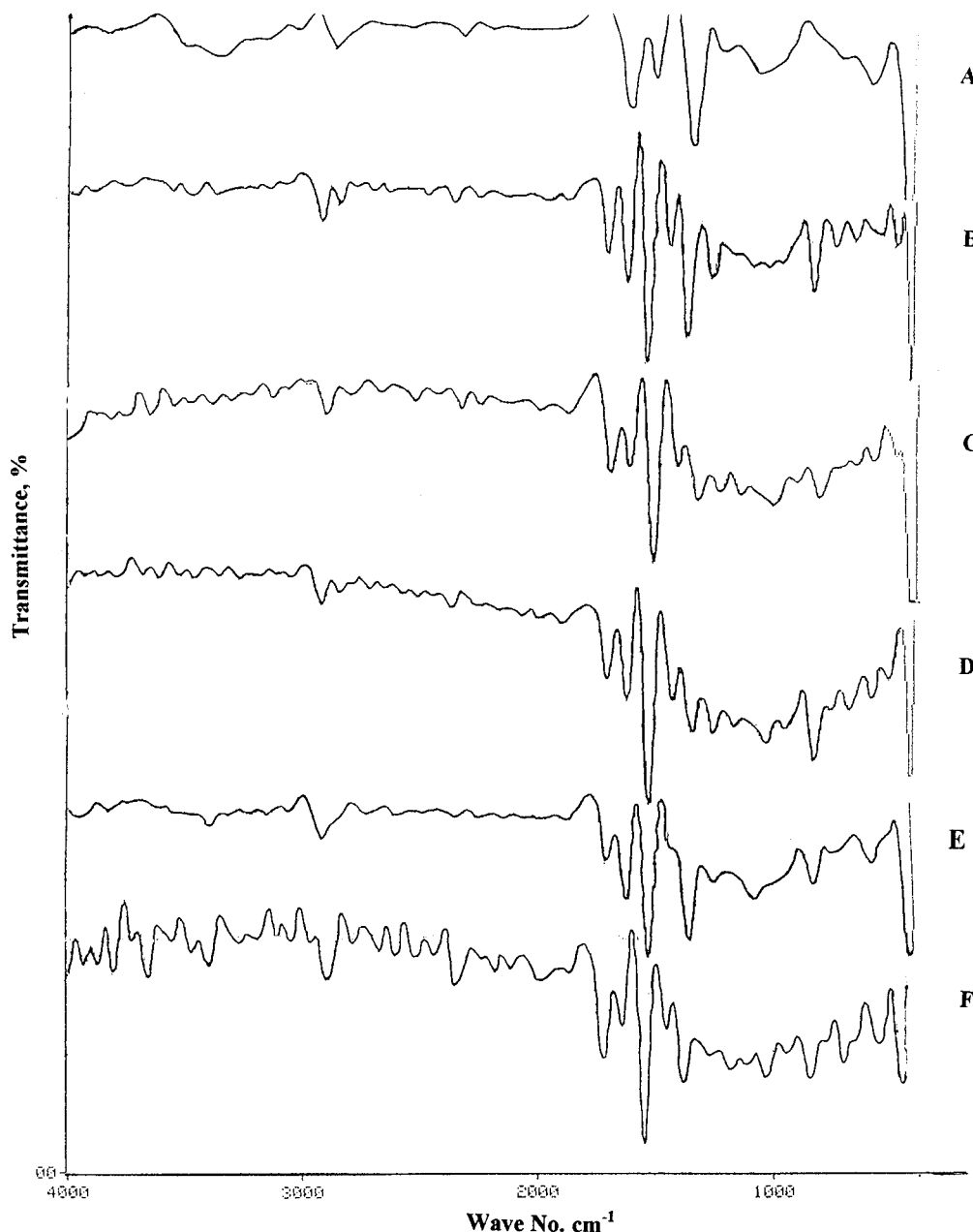


Figure 1 IR spectra of surface oxidized rubber powder. A: blank sample; B: RP oxidized by 10% HNO_3 ; C: RP oxidized by 20% HNO_3 ; D: RP oxidized by 30% HNO_3 ; E: RP oxidized by 60% HNO_3 ; F: RP oxidized by 30% H_2O_2 .

From these results, one can observe that the minimum torque, the maximum torque, the scorch time, and the optimum cure time were decreased, while the cure rate index was increased with an increase in the concentration of RP in NR mixes. The decrease in the minimum torque and the maximum torque can be attributed to the dilution of HAF by an extender such as RP. On the other hand, the decrease in the scorch time and the increase in CRI can be explained on the basis that the RP contains residual curing system such as elemental sulfur and organic accelerators.

The results given in Table I show that the physico-mechanical properties of NR vulcanizates loaded with

untreated RP/HAF combination are lower than that of vulcanizates unloaded or loaded HAF. This behavior can be explained by the fact that the rubber powder has larger particle size (100–500 μm) compared with that of HAF, and consequently, low surface area, and accordingly, the dilution of reinforcing filler HAF with RP is responsible for the decrease in the mechanical properties of the rubber vulcanizates containing them.

The unloaded NR vulcanizates displayed good physico-mechanical properties; this is due to its crystallization during strain. Thus, the formed crystals act as a filler.

On the other hand, it was found that the equilibrium swelling increases as the RP concentration in the rub-

TABLE II
The Rheometric Characteristics and the Physicomechanical Properties of NR Vulcanizates Loaded with RP

Code	γ_8	γ_9	γ_{10}	γ_{11}	γ_{12}	γ_{13}
Oxidizing agent	—			HNO ₃		H ₂ O ₂
Concentration, %	—	10	20	30	60	30
RP, phr	40	40	40	40	40	40
Rheometric characteristics at 142°C						
M_L , dNm	1	1	1	2	2	2
M_{Hr} , dNm	36	30	41	35	28	40
T_{c90} , min	12.5	12.2	12.5	11.8	11.8	11.5
T_{s2} , min	3.5	3.5	3.5	3.2	3.0	3.5
CRI, min ⁻¹	11.1	11.5	11.1	11.6	11.4	12.5
Physicomechanical properties at room temperature						
M 200%, MPa	1.5	1.8	2.4	1.8	1.8	3.0
TS, MPa	5.6	7.4	8.1	7.1	6.8	9.1
ϵ , %	450	450	467	450	400	500
Q, %	225	222	226	223	221	227

ber mixes increases. This can be explained due to the fact that the rubber powder also swells in toluene, whereas HAF black does not swell in such solvent.

The RP can be safely used as a filler in concentrations not exceeding 30 phr in combination with HAF in NR formulations. The obtained vulcanizates have reasonable physicomechanical properties at this level of loading.

Evaluation of treated rubber powder as filler

The IR spectra of the rubber powder treated by either nitric acid or hydrogen peroxide show new bands between 1710 and 1720 cm⁻¹ characteristic of carbonyl groups²⁸ that are absent in the spectrum of the untreated rubber powder, as shown in Figure 1. These functional groups increase the polarity on the surface of the rubber powder, and consequently, may increase its reinforcing efficiency via possible chemical reaction with other suitable function groups present in the reaction medium. For instance, carbonyl or aldehyde or carboxylic groups resulting from rubber powder oxidation may condensate with residual amino groups or inorganic salts forming additional crosslinks. Thus, the treated RP was incorporated alone in NR mixes and compared to those filled with untreated rubber powder. The basic recipe (phr) is (NR, 100; stearic acid, 1; ZnO, 5; RP, 40; processing oil, 5; CBS, 1; S, 2; PBN, 1). The rheometric characteristics and the physicomechanical properties of these vulcanizates are shown in Table II.

From the data obtained in Table II, it was found that the maximum torque (M_H) of the sample filled with treated rubber powder by HNO₃ increases at first and then decreases with increasing acid concentration. This may be due to the deterioration effect of concen-

tration of HNO₃. The other rheometric characteristics M_L and t_{s2} are practically the same for all rubber mixes. The optimum cure time (t_{c90}) is slightly decreased and CRI is increased because of chemical surface treatment of the RP.

On the other hand, the tensile strength of the vulcanizates loaded with treated RP was improved. This improvement can be attributed to the creation of new functional groups because of chemical oxidation and their possible reactions, as mentioned before. Twenty percent of HNO₃ and 30% H₂O₂ gave the highest tensile strength values of the vulcanizates, as shown in Table III.

Evaluation of RP/HAF combination system as reinforcing filler

It was interesting to study the effect of combination of treated RP/HAF as reinforcing filler in NR formulations. It was found from the previous results that the rubber powder treated with 30% H₂O₂ or with 20% HNO₃ has a slight reinforcing effect. Accordingly, the treated RP was combined with HAF in different ratios in NR formulations, as given in Table IV. The rheometric characteristics and physicomechanical properties of these formulations are given in Tables IV and V.

TABLE III
The Improvement % of Tensile Strength of NR Vulcanizates Loaded with Surface Treated RP Alone

Oxidizing agent	Untreated		
	RP	20% HNO ₃	30% H ₂ O ₂
T/S, MPa	5.6	8.1	9.1
Improvement, %	—	44.6	62.5

TABLE IV
The Rheometric Characteristics and the Physicomechanical Properties of NR Vulcanizates Loaded with RP
(treated with 20% HNO₃)/HAF Combination System

Formula/Code	Y_1	Y_{14}	Y_{15}	Y_{16}	Y_{17}	Y_{18}
NR	100	100	100	100	100	100
ZnO	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1
HAF	50	40	30	20	10	—
RP treated with 20% HNO ₃	—	10	20	30	40	50
Processing oil	5	5	5	5	5	5
Sulfur	2	2	2	2	2	2
CBS	1.25	1.25	1.25	1.25	1.25	1.25
PBN	1	1	1	1	1	1
Rheometric characteristics at 142°C						
M_L , dNm	3	3	3	2	2	2
M_H , dNm	70	62	56	48	42	38
t_{C90} , min	13.5	12.2	11.4	11.0	10.5	9.5
t_{S2} , min	4.5	4.5	4.2	4.0	3.7	3.2
CRI, min ⁻¹	11.1	13.0	13.9	14.3	14.7	15.9
Physicomechanical properties at room temperature						
M 200%, MPa	4.9	4.5	4.1	3.4	2.7	1.9
TS, MPa	23.7	15.8	13.7	11.8	10.3	7.7
ϵ_r , %	550	480	465	445	425	400
Q , %	213	218	223	226	227	229

From these results and the results given before in Table I, one can observe that the behavior of the combination of HAF black with treated RP as or with

untreated RP is practically the same. For instance, in both cases the minimum torque, the maximum torque, the optimum cure time, and the scorch time decreased,

TABLE V
The Rheometric Characteristics and the Physicomechanical Properties of NR Vulcanizates Loaded with RP
(treated with 30% H₂O₂)/HAF Combination System

Formula/Code	Y_1	Y_{19}	Y_{20}	Y_{21}	Y_{22}	Y_{23}
NR	100	100	100	100	100	100
ZnO	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1
HAF	50	40	30	20	10	—
RP treated with 30% H ₂ O ₂	—	10	20	30	40	50
Processing oil	5	5	5	5	5	5
Sulfur	2	2	2	2	2	2
CBS	1.25	1.25	1.25	1.25	1.25	1.25
PBN	1	1	1	1	1	1
Rheometric characteristics at 142°C						
M_L , dNm	3	3	2	2	1	1
M_H , dNm	70	64	57	53	48	43
t_{C90} , min	13.5	12.0	11.2	10.6	10.2	9.5
t_{S2} , min	4.5	4.3	4.2	3.8	3.4	3.4
CRI, min ⁻¹	11.1	13.0	14.3	14.7	14.7	16.4
Physicomechanical properties at room temperature						
M 200%, MPa	4.9	4.0	3.8	3.3	2.5	1.7
TS, MPa	23.7	16.5	13.8	12.0	10.5	7.9
ϵ_r , %	550	475	455	435	420	400
Q , %	213	216	221	225	225	227

TABLE VI
The Improvement % of Tensile Strength of NR
Vulcanizates Loaded with RP

Formula	Code		
	Y ₁	Y ₁₈	Y ₂₃
	Untreated RP	20% HNO ₃ treated RP	30% H ₂ O ₂ treated RP
NR	100	100	100
ZnO	5	5	5
Stearic acid	1	1	1
RP	50	50	50
Processing oil	5	5	5
Sulfur	2	2	2
CBS	1.25	1.25	1.25
PBN	1	1	1
Rheometric characteristics at 142°C			
M _L , dNm	1	2	1
M _H , dNm	32	38	43
T _{C90} , min	11	9.5	9.5
T _{S2} , min	3.1	3.2	3.4
CRI min ⁻¹	12.7	15.9	16.4
Physicomechanical properties at room temperature			
M 200%, MPa	1.3	1.9	1.7
TS, MPa	5.5	7.7	7.9
TS improvement, %	—	40	43.6
ε, %	400	400	400
Q, %	234	229	227

while the cure rate index was increased with increasing rubber powder ratio. The only difference lies in the slight improvement in the physicomechanical properties of NR vulcanizates containing HAF combined with treated rubber powder (by either H₂O₂ or HNO₃).

It is also clear that the NR vulcanizates loaded with a combination of HAF and chemically oxidized rubber powder have tensile strength values lower than that loaded with the conventional reinforcing HAF black alone. On the other hand, the elongation at break was not practically affected. This can be attributed to the large difference in the particle size between HAF and RP, as mentioned before. Nevertheless, the tensile strength of the NR vulcanizates filled with a combination of surface-treated RP (20% HNO₃ and 30% H₂O₂) and HAF was slightly improved, as shown in Table VI.

On the basis of the results obtained, it is recommended to use a combination of surface-treated RP with a reinforcing carbon black such as HAF with a ratio depending on the required performance of the rubber article.

Aging of NR vulcanizates loaded with combination of RP/HAF

The rubber vulcanizates loaded with RP (either treated or untreated in combination with HAF) were subjected to thermal oxidative aging in an oven at 90 ± 1°C for different time periods up to 5 days. The physicomechanical properties of the aged samples were determined and the retained values after aging are calculated and represented in Table VII.

From the obtained data, it can be seen that the use of rubber powder as filler in NR vulcanizates slightly impairs the thermal aging resistance of NR vulcanizates. This behavior is expected, because the RP was partially oxidized and further oxidation may proceed during aging. On the other hand, it is observed that the tensile strength, elongation at break, and equilibrium swelling values decrease with increasing aging

TABLE VII
Effect the Surface-Treated Rubber Powder on the Physicomechanical Properties of NR Vulcanizates Before and After Aging

RP/HAF	Untreated RP				20% HNO ₃ Treated RP			30% H ₂ O ₂ Treated RP		
	0/50	10/40	20/30	30/20	10/40	20/30	30/20	10/40	20/30	30/20
M, MPa	4.9	4.0	3.8	3.3	4.5	4.1	3.4	4.0	3.8	3.3
TS, MPa	23.7	14.7	12.8	11.0	15.8	13.7	11.8	16.5	13.8	12.0
ε, %	550	525	500	480	480	465	445	475	455	435
Q, %	213	220	223	228	218	223	226	217	221	225
Mechanical properties after thermal aging at 90°C for 5 days										
M, MPa	7.0	5.8	5.6	4.9	6.4	6.0	5.3	5.8	5.3	4.9
TS, MPa	14.3	8.8	6.8	5.7	9.2	7.0	6.0	9.1	7.6	5.8
ε, %	305	260	240	225	257	240	230	270	250	234
Q, %	198	204	207	211	204	206	210	202	203	206
Retained values (%) after thermal aging at 90°C for 5 days										
TS, %	60.3	59.9	53.1	51.8	58.2	51.1	50.8	55.2	55.1	48.3
ε, %	55.5	49.5	48.0	46.9	53.5	51.6	51.7	56.8	54.9	53.8

time, while the modulus at 200% elongation was increased, indicating further crosslinking of the rubber chains (i.e., the crosslinking density is increased).

Replacing 10–20 phr of HAF by surface-treated powder with H₂O₂ practically is comparable with vulcanizates filled with HAF alone. Such vulcanizates retain 55% of the original tensile strength and elongation at break. This allows for cost reduction of the rubber products.

CONCLUSION

Surface-modified RP can be used as cheap filler in NR mixes without sacrificing the essential physico-mechanical characteristics of the vulcanizates and depending on the performance of the required rubber articles.

The incorporation of RP up to 20 phr in combination with a reinforcing carbon black in NR mixes resulted in vulcanizates that retain at least 50% of their physico-mechanical properties before and after aging.

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