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New Trends for Utilization of Rubber Wastes

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Summary: The scrape rubber is difficult to recycle, since it is not thermoplastic material. Consequently, it must be converted into a powder. The scrape rubber powder can be reused via different ways: *a- Reclamation* The reclamation process was studied. This process converts the rubber powder into elastic-plastic materials. The obtained reclaims were introduced into NR formulations. The obtained data reveal that, 10–30% reclaimed rubber can replace virgin NR without scarifying the basic properties of the rubber vulcanizates. In such way we can gain cost reduction. *b- Reuse as filler-extender* The rubber powder was treated with some oxidizing agents and namely HNO_3 and H_2O_2 to modify its surface. The result of such treatment creates some functional groups such as carbonyl groups. The treated rubber powder was used as filler-extender in NR formulations. The treated rubber powder improves the tensile strength of the vulcanizates to some extent (62%). On the other hand, the treated powder was used in combinations with the classical reinforcing carbon black (HAF). The obtained results showed that, 20–40% of HAF can be replaced by the treated powder in NR mixes. The obtained vulcanizates have good physico-mechanical properties. In such way the production cost can be reduced. *c- Utilization of sulfonated rubber powder as ion exchanger* The rubber powder was sulfonated with Sulfuric and chlorosulfonic acids. The sulfonated product was evaluated as ion exchange resin to clear the industrial wastewater from heavy metals. The data showed that the Sodium salt form is more efficient ion exchanger than the acid form. *d- Utilization in pavement* The rubber powder is mixed with asphalt used in road pavement. The performance of asphalt concrete greatly depends on the particle size of the rubber powder used. The fine powder greatly improves the mechanical performance of the road pavement. The rubber powder was chemically modified. It was found that such modification had greatly improved the performance road pavement.

Keywords: aging; asphalt modification; extender; filler; ion exchanger; natural rubber; reclaims; reclamation; recycling; rubber powder; rubber vulcanizate; scrape tires; surface modification

Introduction

The most important use of rubber in tonnage amounts is for tires and inner tubes. All tires of automobiles, trucks, bus, airplanes. etc. is made from rubber due to its unique properties.[1]

The management of rubber wastes is very difficult to municipalities to handle. The whole tires are difficult to landfill, because they tend to float to the surface. Stockpiles of scrap tires are located in many communities, resulting in public health, environmental and aesthetic problems.[2]

Rubber is related to thermo-plastic-elastic materials and is turned to thermosetting on vulcanization during manufacturing as a rubber product or tire. This occurs as a result of the formation of three-dimensional structure due to the presence

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of the so-called vulcanizing system in rubber mixes.[3–5] In this case, it is difficult to recycle rubber waste or refuse it using the general methods used for thermoplastic materials such as polyethylene, polypropylene and other thermoplastics. Thus, recycling of rubber waste is very important problem as such waste is not biodegradable and has its negative impact on environment. Besides, the recycled rubber should be considered as a source of new material with economic impact.[6,7]

It is established that the rubber wastes arise from several millions of wearn out tires collected in stockpiles and from different processing stages and operating unites during tire manufacturing.[7–16]

Consequently, the rubber wastes may be green, scorched and vulcanized rubber. Also the waste may contain metal, rayon or nylon fibers. This waste must be subjected to different methods of treatment such as hydrolysis mechano-chemical reactions or reclamation. The vulcanized waste must be grounded before any treatment.[7]

The present work aims at the recycling of rubber scrap via methods, that may be effective in solving the rubber scrap problem such as: reclamation and utilize the reclaims in rubber mixes or use the chemically modified scrap rubber powder in different useful applications such as as filler-extender, ion exchanger and in road pavement.

Materials and Techniques

Materials

- Natural rubber (NR): grade RSS 1 supplied from TRENCO, Alexandria, Egypt.
- Filler: HAF, High abrasion furnace black, particle size 40–80 nm, surface area about 65–70 m^2/g.
- Scrap rubber powders of particle size 50–500 micron.
- Reclaimed rubber produced by mechano-chemical method.
- The other rubber ingredients were of grades customary used in rubber industry.
- Solvents and Chemicals: All solvents and chemical reagents were of pure grade.

Techniques

Preparation of Rubber Mixes and Vulcanizates

All rubber mixes were prepared on a two roll laboratory mill, (diameter: 470 mm, working distance: 300 mm, speed of the slow roller: 24 r.p.m. and gear ratio: 1:1.4). The roller temperature was kept at about 50–60 °C during mixing. The compounded rubber was left over night before vulcanization. The vulcanization press was operated at 142 ± 2 °C for natural Rubber mixes and 152 ± 2 °C for styrene-butadiene rubber mixes under a pressure of about 4 MPa.

Tests of Rubber Nixes and Vulcanizates

The following standard methods were used:

- ASTM D2084-76T (1972) for determination of rheometric characteristics (t_{S2}, t_{C90}, M_L, M_H and CRI) using a Monsanto Rheometer 100.
- ASTM D412-66T (1967) for determination of physico-mechanical properties using a Zwick tensile testing machine (model-1425).
- ASTM D573 (1952) for determination of thermal aging.
- Equilibrium swelling (Q) was carried out in toluene.[17]
- Indirect tensile strength σ_t and indirect tensile strain[18] are calculated using the following equations:

The indirect ensile strength σ_t is expressed as:

$$\sigma_t = \frac{2P}{\pi\, at}\left[\sin 2\theta - \frac{a}{2r}\right]$$

The indirect tensile strain is given as: $\varepsilon_t = \frac{\delta}{D}$

Where ‘a’ is the width of the loading trips, ‘t’ is the thickness of the specimen, ‘P’ is the maximum failure load, ‘r’ is the radius of the specimen, ‘2’ is the half angle made by the loading strip, ‘D’ is the specimen

Table 1.
Effect of different amines on the sol - gel fractions and Mooney viscosity of the reclaim.

Amine	Aniline			Phenylhydrazine			P-Anisidine		
Conc., phr	1	1.5	2	1	1.5	2	1	1.5	2
Sol fraction, %	49.7	50.7	48.8	51.0	56.0	54.2	48.7	48.7	51.7
Gel fraction, %	50.3	49.3	51.2	49.0	43.2	45.8	53.0	51.3	48.3
Mooney Viscosity at 100 °C									
ML 1 + 4 min	47.8	45.3	46.0	44.0	49.0	40.0	42.0	43.1	44.0
ML 1+ 1.5 min	55.1	51.8	54.7	51.0	58.0	49.0	51.0	52.0	54.0

diameter and ‘δ’ is the total horizontal deformation.

Results and Discussion

Reclamation of Scrape Rubber Powder

Reclamation was carried out by our mechano-chemical method. The optimum condition for obtaining good reclaims can summarized as such: The rubber powder was processed in a Brabender premixer for 30 minutes at constant temperature (150 °C) in presence of some chemicals such as pentachlorothiophenol-amines and softeners such as processing oils. The function of these chemicals is the cleavage of the sulfur crosslinks between rubber chains and the termination of the free radical chains formed as a result of bond cleavage. The function of the softener is to stretch the bond between rubber chains and to reduce the mechanical energy.

It is interesting to reclaim the waste rubber powder in presence of some different amines and metal chlorides, since these systems have the ability to break the sulfur crosslinks between rubber chains.[19,20] The produced reclaims were evaluated by determining the sol-gel fractions and Mooney viscosity. The obtained results are given in Table (1).

From this table one can see that the most powerful reclaiming agent is phenylhydrazine of concentration 1.5 phr, where the sol fraction and Mooney viscosity attain their highest values.

In a series of experiments the efficiency of phenylhydrazine was tried in presence of some metal chlorides and namely $FeCL_2$, $FeCl_3$ and $ZnCl_2$. The optimum concentration of phenylhydrazine (1.5 phr) was used with different concentrations of metal chlorides. The reclaimed rubber was evaluated by determining the sol-gel fractions and Mooney viscosity. The data are given in Table (2).

From this Table one can see that 1.5-phr phenylhydrazine combined with 1 phr $ZnCl_2$ is a very strong reclaiming agent, where the sol fraction attained 63.0%.

Effect of Combination of Pentachlorothiophenol with Phenyhydrazine

0.5 phr Pentachlorothiophenol was combined with different phenylhydrazine concentrations and added to the rubber powder during the reclamation process. The effect

Table 2.
Effect of phenylhydrazine (1.5phr) combined with different concentrations of different metal chlorides on the Sol - Gel fractions and Mooney viscosity of the reclaim.

Metal chloride	$FeCl_2$			$FeCl_3$			$ZnCl_2$		
Conc., phr	1	1.5	2	1	1.5	2	1	1.5	2
Sol fraction, %	56.2	56.1	55.1	56.3	59.1	60.2	63.1	58.1	48.1
Gel fraction, %	43.8	43.9	44.9	43.7	40.9	39.8	37.9	42.2	41.9
Mooney Viscosity at 100 °C									
ML 1 + 4 min	44.1	45.0	44.1	42.5	45.3	45.8	47.7	44.7	42.8
ML 1 + 1.5 min	52.3	54.0	53.2	49.1	56.1	57.2	56.1	55.1	50.7

Table 3.
Effect of Pentachlorothiophenol (0.5 phr) combined with different phenylhydrazine concentrations on the sol-gel fractions and Mooney viscosity of the reclaim.

Phenylhydrazine, phr	1	1.5	2	MARSO	NAROBIN
Sol fraction, %	52.1	59.1	55.2	19.33	20.75
Gel fraction, %	47.9	40.9	44.8	80.67	79.25
Mooney Viscosity at 100 °C					
ML 1+ 4 min	45.7	49.5	43.5	51.7	56.0
ML 1+ 1.5 min	52.0	57.1	51.0	78.8	69.3

of this system on the sol-gel fractions and Mooney viscosity of the reclaim is given in Table (3).

From this table one can see that 0.5 phr Pentachlorothiophenol combined with 1.5 phr phenylhydrazine is a good reclaiming agent, since the sol fraction and Mooney viscosity of the reclaim have the highest values.

From the previous experiments one can conclude that the most efficient reclaiming agent is the combination of phenylhydrazine with $ZnCl_2$.

Utilization of Reclaimed Rubber in NR Mixes

After the reclamation process the obtained reclaim was incorporated in some natural rubber (NR) mixes. Consequently, the NR/Reclaim blends in different ratios are prepared. The rubber formulations, the rheometric characteristics of the rubber mixes and the physico-mechanical properties of NR/Reclaim blend vulcanizates are given in Table (4). From the obtained data, one can replace about 10–30% of NR by the reclaim without sacrificing the essential characteristics of the rubber vulcanizates. These results cost reduction due to the difference in NR and reclaim prices.

Aging of NR/Reclaim Blend Vulcanizates

The NR/Reclaim blend vulcanizates were subjected to thermal oxidative aging in an oven at $90 \pm 1\,^{\circ}C$ for different time periods up to 5 days. The physico-mechanical properties of the aged samples were determined and represented in Tables (5–7), From the obtained data it can be clearly seen that, the tensile strength, elongation at break and swelling decrease with aging time. This indicates further crosslinking of the rubber chains during the period of thermal aging.

Table 4.
The rheometric characteristics and physico-mechanical properties of NR/Reclaim blend vulcanizates.

Ingredients/Code	1	2	3	4	5	6	7	8	9	10	11
NR	100	90	80	70	60	50	40	30	20	10	--
Reclaim	–	10	20	30	40	50	60	70	80	90	100
ZnO	5	5	5	5	5	5	5	5	5	5	5
Stearic acid	1	1	1	1	1	1	1	1	1	1	1
Processing oil	5	5	5	5	5	5	5	5	5	5	5
HAF	30	30	30	30	30	30	30	30	30	30	30
CBS	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25	1.25
Sulfur	2	2	2	2	2	2	2	2	2	2	2
Rheometric characteristics at 142 °C											
M_L, dNm	2	2	3	3	4	6	7	7	10	14	15
M_H, dNm	70	67	66.2	55.5	55.3	54	52.5	50	50	45	35
t_{C90}, min	14.5	14.2	13.5	12.2	11.5	11.0	10.0	9.0	8.7	8.3	8.2
t_{S2}, min	5.5	5.2	4.8	4.5	3.8	3.5	2.7	2.2	2.0	1.75	1.75
CRI min^{-1}	11.1	11.1	11.5	12.9	12.9	13.3	13.6	14.7	14.9	15.3	15.5
Physico-mechanical properties at room temperature.											
T.S., Mpa	17.9	16.9	15.9	14.7	13.4	11.6	7.5	6.7	5.5	4.3	3.1
ε, %	625	562	500	450	417	375	260	214	175	150	100
M 200%, Mpa	5.6	5.2	5.5	5.4	5.5	5.5	6.1	6.1	--	--	--
Q, %	220	225	227	235	240	244	251	253	255	258	258

Table 5.
Tensile strength, (MPa) of NR/Reclaim blend vulcanizates aged at 90 °C.

Code\Time	0-day	1-day	2-days	3-days	4-days	5-days	R.T.S. After 5 days aging
1	17.9	16.2	14.6	12.9	11.4	10.7	56.4
2	16.9	15.2	13.6	12.0	10.6	9.2	54.4
3	15.9	14.3	12.8	11.4	9.9	8.5	53.5
4	14.7	12.9	411.4	9.7	8.4	7.3	49.7
5	13.4	11.7	10.2	8.7	7.7	6.7	50.0
6	11.6	10.2	8.8	7.7	6.8	6.0	51.7
7	7.5	6.6	6.1	5.5	5.1	4.6	61.3
8	6.7	5.9	5.2	4.8	4.6	4.0	59.7
9	5.5	4.8	4.2	3.9	3.5	3.3	60.0
10	4.3	3.8	3.5	3.0	2.8	2.4	55.8
11	3.1	2.8	2.5	2.1	1.8	1.5	48.4

Table 6.
Elongation at break, (%) of NR/Reclaim blend vulcanizates aged at 90 °C.

Code\Time	0-day	1-day	2-days	3-days	4-days	5-days	R.ε After 5 days aging
1	625	555	500	450	400	350	56.0
2	562	480	417	365	320	285	50.7
3	500	425	363	317	275	250	50.0
4	450	380	325	275	233	200	44.4
5	417	352	290	250	210	180	43.2
6	375	314	264	220	176	153	40.8
7	260	210	175	150	125	100	38.5
8	214	178	150	125	100	75	35.1
9	175	150	125	100	75	60	34.3
10	150	122	96	75	57	45	30.0
11	100	75	55	40	30	25	25.0

The obtained data show a further proof that; it is safe to replace the virgin NR 10–30% by the reclaim. These blend vulcanizates can retain a mean value of 50% of the original tensile strength and elongation after aging for a long period (5days) at 90 °C. The change of swelling can confirm these findings.

Evaluation of RP/HAF Combination as Reinforcing Filler

In a previous study,[21] it was found that the NR loaded with 40 phr treated rubber powder with either 20% nitric acid or 30% hydrogen peroxide has improved the tensile strength of the vulcanizates as shown in Table (8).

Table 7.
Equilibrium swelling (%) of NR/Reclaim blend vulcanizates aged at 90 °C.

Code\Time	0-day	1-day	2-days	3-days	4-days	5-days
1	220	214	210	206	201	201
2	225	221	217	211	206	204
3	227	224	218	215	210	210
4	235	230	224	221	215	213
5	240	236	231	226	223	221
6	244	237	230	228	225	225
7	251	245	240	236	234	233
8	253	248	240	237	234	234
9	255	250	247	243	239	237
10	258	254	249	244	241	240
11	258	255	249	246	242	242

Table 8.
The improvement % of tensile strength of NR vulcanizates loaded with surface treated RP alone.

Oxidizing agent	Untreated RP	%20HNO$_3$	%30H$_2$O$_2$
T.S. MPa	5.6	8.1	9.1
Improvement%	–	44.6	62.5

It is interesting to study the effect of combination of RP/HAF as reinforcing filler in NR formulations. The rubber powder that has been treated with 30% H_2O_2 and that treated with 20%, HNO_3. Thus, this rubber powder was combined with HAF in different ratios and incorporated into NR mixes and compared with NR mixes loaded with untreated rubber powder combined with HAF. The physico-mechanical properties are given in Tables (9–11).

On the other hand, The results in Tables (9–11) show that, the physico-mechanical properties of NR vulcanizates loaded with RP/HAF (either treated or untreated) are lower than that vulcanizates filled with HAF alone. On the other hand, the equilibrium swelling was increased. This can be due to the fact that, the rubber powder swells also in Toluene, while HAF black does not swell in such solvents. It is also important to observe that, the NR vulcanizates loaded with the treated RP and HAF have slightly higher mechanical properties than those loaded with untreated RP and HAF.

From these results one can observe some change in the behavior of the chemically modified rubber powder. The tensile strength is improved, but still lower than the classical reinforcing carbon black HAF. This is understandable in the view that the rubber powder has bigger particle size (50–500 micron) than HAF (40–80 nm) and hence the rubber powder has much smaller surface area than the HAF. This means that the surface treatment of the rubber powder with either HNO_3 or H_2O_2 has improved its surface characteristics by creating some functional groups such as CO groups. It is worthy to mention that, the tensile strength of NR vulcanizates filled with HAF and the surface treated powder is slightly improved as can seen from the data given in Table (12).

Table 9.
Physico-mechanical properties of NR vulcanizates loaded with untreated RP/HAF combination system.

Formula/Code	12	13	14	15	16	17
HAF	50	40	30	20	10	–
Untreated RP	–	10	20	30	40	50
T.S., Mpa	23.7	14.7	12.8	11.0	8.0	5.5
ε, %	550	525	500	480	450	400
M 200%, Mpa	4.9	4.0	3.8	3.3	2.2	1.3
Q, %	213	220	223	228	231	234

Table 10.
Physico-mechanical properties of NR vulcanizates loaded with RP (treated with 20% HNO$_3$)/HAF combination system.

Formula/Code	18	19	20	21	22	23
HAF	50	40	30	20	10	–
RP treated with 20% HNO$_3$	–	10	20	30	40	50
T.S., MPa	23.7	15.8	13.7	11.8	10.3	7.7
E, %	550	480	465	445	425	400
M 200%, MPa	4.9	4.5	4.1	3.4	2.7	1.9
Q%	213	218	223	226	227	229

Table 11.
Physico-mechanical properties of NR vulcanizates loaded with RP (treated with 30% H$_2$O$_2$)/HAF combination system.

Formula/Code	24	25	26	27	28	29
HAF	50	40	30	20	10	–
RP treated with 30% H$_2$O$_2$	–	10	20	30	40	50
T.S., MPa	23.7	16.5	13.8	12.0	10.5	7.9
E, %	550	475	455	435	420	400
M 200%, MPa	4.9	4.0	3.8	3.3	2.5	1.7
Q%	213	216	221	225	225	227

On the basis of the obtained results, 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 samples were subjected to thermal oxidative aging in an oven at

Table 12.
The improvement % of tensile strength of NR vulcanizates loaded with RP/HAF combination

Oxidizing agent	%20HNO_3			%30H_2O_2		
RP/HAF	50/0	40/10	20/30	50/0	40/10	20/30
T.S. of Blank (untreated RP), MPa	5.5	14.7	12.8	5.5	14.7	12.8
T.S. of chem. Mod. RP, MPa Improvement, %	7.7	15.8	13.7	7.9	16.5	13.8
	40	7.6	7	43.6	12.3	7.8

Table 13.
Effect the surface treated rubber powder on the physico-mechanical properties of NR vulcanizates before and after aging.

	Untreated RP				20% HNO_3 Treated RP			30%H_2O_2 Treated RP		
RP/HAF	0/50	10/40	20/30	30/20	10/40	20/30	30/20	10/40	20/30	30/20
T.S., 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	345
Q, %	213	220	223	228	218	223	226	216	221	225
Retained Values (%) after Thermal Aging at 90 °C for 5 days.										
T.S., %	60	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

90 ± 1 °C for different time periods up to 5 days. The physico-mechanical properties of the aged samples were determined and represented in Tables (13).

Form the obtained data, the aging of such vulcanizates suffer some changes during aging i.e. the tensile strength decrease, but the elongation at break practically not changed. Also, it is clearly seen from Table (13) that replacing 20–40% phr of HAF by surface treated powder with H_2O_2 practically is comparable with vulcanizates filled with HAF alone. Such vulcanizates retain 55% of the original tensile strength and elongation at break. This makes without doubt the good cost reduction for the rubber products.

The Chemically Modified Rubber Powder as Ion Exchanger

The RP was subjected to react with H_2SO_4 and chlolrosulphonic acid in order to create some sulphonic groups on its surface. The sulphonated RP can be similar to sulfonated crosslinked polystyrene available in the market. The prepared samples were washed good and dried. The elemental analysis was carried out using VARIO EL ELEMENTAR instrument to determine sulfur content. The values of sulfur content of the blank sample and the sulfonated samples are given in Table (14).

From the values of the sulfur content of the sulfonated rubber powder one can observe that, the sample which is sulfonated by chlorosulfonic acid has the highest value of sulfur content i.e., chlorosulfonic acid is more efficient than sulfuric acid. The sulfur content can reach the range of 12.5%, which is a reasonable value.

The ion exchange capacity of sulfonated rubber powder was evaluated with respect to NaCl, $CaCl_2$, $ZnCl_2$, $PbSO_4$, $NiCl_2$, $CrCl_3$, and $CuSO_4$ the obtained results are given in Table (15).

From Table (15) it is seen that, the ion exchange capacity in mg eq per one gram of waste rubber powder ranges from 1.1 mg

Table 14.
Sulfur content of sulfonated rubber powder.

Sample No.	1	2	3	4	5	6
Chemical agent	–	H_2SO_4				H_2SO_3Cl
Temperature. °C	25	100	120	150	180	25
Sulfur content, %	4.79	6.52	7.96	9.26	9.28	12.48

Table 15.
Ion exchange capacity of sulfonated rubber powder (acid form) in mg eq/g.

Type of salt/ Sample No.	1	2	3	4	5	6
NaOH	1.1	3.1	3.5	4.1	4.4	5.2
NaCl	0.9	1.3	1.5	1.6	1.7	2.9
$CaCl_2$	0.9	1.2	1.3	1.6	1.8	2.1
$ZnSO_4$	0.8	1.2	1.2	1.5	1.7	2.0
$PbSO_4$	0.8	1.4	1.6	1.6	1.9	2.2
$NiCl_2$	0.8	1.7	1.8	2.0	2.2	2.4
$CrCl_3$	0.9	1.3	1.3	1.7	2.0	2.3
$CuSO_4$	0.9	1.5	1.7	1.8	2.1	2.8

Table 16.
Ion exchange capacity of sodium salt of sulfonated rubber powder, in mg eq/g.

Sample No.	Dry Form					Wet Form				
Type of salt	2	3	4	5	6	2	3	4	5	6
$CaCl_2$	1.3	1.5	1.7	2.0	2.4	1.3	1.7	1.9	2.2	2.6
$ZnSO_4$	1.3	1.3	1.6	1.9	2.4	1.5	1.6	2.0	2.3	2.8
$PbSO_4$	1.6	1.7	2.1	2.3	2.5	1.8	1.9	2.5	2.6	2.9
$NiCl_2$	1.3	1.3	1.5	1.7	2.0	1.5	1.5	1.6	1.9	2.3
$CrCl_3$	1.5	1.5	1.8	1.9	2.5	1.7	1.7	2.0	2.2	2.8
$CuSO_4$	1.6	1.8	2.1	2.2	3.2	1.8	2.0	2.4	2.9	3.9

eq/g for sample No. 1 and 5.2 mg eq/g for sample No.6 i.e. the ion exchange capacity of sample No. 6 is the highest one, where it contains more sulfonic groups.

The ion exchange capacity of sodium salt of sulfonated rubber powder in both dry and wet form is also studied. The results of evaluations are listed in Table (16). From the results in Table (16) one can see that, the efficiency of the sodium salt of sulfonated rubber powder as ion exchanger is higher than that of the acidic form. Also the ion exchange capacity of the wet form of sodium salt is more than that of the dry form at the same conditions. This can be attributed to the ease of diffusion in the wet powder.

The relation between the time and the amount of Cu^{++}, Zn^{++} and Pb^{++} ions uptake in sulfonated rubber powder containing high concentration of sulfonic groups (sample 6) is shown in Table (17).

From this Table it is shown that, one needs about 12 hours for 2.8 mg eq/g of copper, 2.0 mg eq/g of zinc and 2.2 mg eq/g of lead ions to be taken by the dry form of sample No.6. In contrast one needs about 4-5hours to recover these quantities if the sulfonated rubber samples were water preswelled before the ion exchange capacity measurements. This indicates that, as the hydrophilicity increases the swellability in water and consequently the ion up take increases.

Utilization of Scrape Rubber Powder in Road Pavement

The scrape rubber powder was incorporated in asphalt mixtures. Two mixtures A and B were prepared using asphalt cement (AC-30 asphalt). Mixture A was prepared using a course rubber powder 20 meshes (0.84-mm average particle size) at 5% concentration by weight of asphalt cement. Mixture B was prepared using an 80 meshes (0.18 mm average particle size) at 10% concentration by weight of asphalt cement. The indirect tensile strength and strain were established at room temperature

Table 17.
Metal ions uptake by the acidic form of sulfonated rubber powder (sample No. 6).

Immersion Time, h	Cu^{+2}, mg eq/g		Zn^{+2} mg eq/g		Pb^{+2} mg eq/g	
	Dry form	Wet form	dry form	Wet form	Dry form	Wet form
0.5	1.0	1.2	0.9	1.1	0.9	1.1
1.0	1.3	1.6	1.2	1.4	1.1	1.4
2.0	1.5	2.1	1.4	1.7	1.4	1.6
3.0	1.9	2.5	1.7	2.0	1.6	1.9
4.0	2.5	2.6	1.8	2.4	1.9	2.2
12.0	2.8	3.5	2.0	2.6	2.2	2.8
24.0	3.0	3.5	2.2	2.6	2.5	2.8

Table 18.
Mechanical performance data for two, crumb rubber modified AC-30 asphalt paving mixtures at room temperature (25 °C).

Mechanical Performance	Unmodified Mixture	Mixture A 5% course 20 mesh crumb rubber	Mixture B 10% fine 80 mesh crumb rubber
Indirect tensile Strength, KPa	1,050	970	1,560
Indirect tensile Strain, %	0.56	0.70	0.15

25 °C.These results are shown in Table (18). As it can be seen, the addition of course scrap rubber powder at 5% has slightly decreased the indirect tensile strength and increased the indirect tensile strain, from the unmodified AC-30 asphalt pavement. On the contrary, the use of finer rubber powder at a higher concentration (10%) has substantially increased the indirect tensile strength and decreased the indirect tensile strain as can be seen from Table (18).

Thus, the asphalt modified by fine rubber powder greatly improves the performance of road pavement.

Chemical Modification of Scrap Rubber Powder
The scrap rubber powder was chemically modified and used in paving mixture. The critical value of the fracture resistance **'J_c'** was calculated from the following equation.

$$J_c = -\left(\frac{1}{b}\right)\frac{dU}{da}$$

Where: 'U' is total strain energy to failure, 'b' is specimen thickness, 'a' is the notch depth.

The critical fracture resistance, 'J_c' for the three paving mixtures as obtained from the above equation are given in Table (19).

As can be seen, the chemically modified rubber powder asphalt has a value of 'J_c' which is almost twice that of the other two mixtures. The rubber powder and control asphalt mixtures have similar values of 'J_c', with rubber powder being 20% higher. The higher fracture resistance of the chemically modified rubber powder asphalt mixture is attributed to the chemical modification, which has caused the mixture to become more resistant to crack tip separation.

Conclusion

On the basis of the work done, it can conclude the following:

1- The scrap rubber powder can be reclaimed by the mechano-chemical method. The obtained reclaims are of good quality and can be used in rubber industry.
2- The obtained reclaims can replace 10–30% of the virgin rubber without scarifying the basic properties of the rubber vulcanizates.
3- The surface treated scrap rubber powder improve the physico-mechanical properties of rubber vulcanizates to some extent and can replace 20–40% of the carbon black with scarifying the main properties of the vulcanizates.
4- The sulphonated rubber powder can be used as ion exchanger to clear the industrial water from heavy metals. The efficiency of the sodium salt form is higher than the acid form.

Table 19.
Comparison of the Critical Fracture Resistance for various asphalt mixtures.

	Control	CRA	CMCRA	AR-4000	AC-20	AC-5 +5% SEBS	AC-5 +2% Elvaloy
Critical Fracture Resistance, J_c (kJ/m^2)	0.54	0.65	1.23	0.63	1.03	0.42	0.48
	Current study			Ref. [22]		Ref. [23]	

5- The modified asphalt by fine scrap rubber powder greatly improve the performance of road pavement, especially the chemically modified rubber powder asphalt.

[1] Morton Mourice, "*Rubber Technology*", Publisher New York USA (**1973**).

[2] A. T. Kearney, Scrap Tire Management, October (**1992**).

[3] H. V. Boenig, St. L. Miss oui, "*Structure and properties of Polymer*" Geory Thieme Publishers, stuttgart (**1973**).

[4] Yehia, et al., *J. Appl. Ploym. Science*, **1967**, *45*, 1992.

[5] A. Y. Coran, K. Bostany, P. Hamed, *J. Appl. Polym. Science* **1971**. *15*, 2471.

[6] *Environmental Protection Agency*, Office of Solid Waste USA (**1991**).

[7] A. A. Yehia, et al., Final Report of the project 263-0140. 1 STC, Cairo (**1995**).

[8] V. M. Makarov, M. V. Tupitsian ma, *(USSR) Uch. Zap. Yaroslav. Teckhol. Inst.* **1966**, *9*, 228–2237.

[9] Herbert Hildebrandt *Appl. Oct.* **1963**, *23*, Ger. 1, 244, 309 (Cl.C08cd) July 13, 1967.

[10] Onouchi Yukio, Inagaki Shinji, Okamoto Hiroshi, Furukawa Junji, *Aichi Kegyo Daigaku Kenkyu Hokoku, B.* **1980**, *15*, 43–48.

[11] Hayakawo Rubber Co., Ltd. Jpn. Kokai Tokkyo Koho, JP 82 34,138 (Cl C08J11/00), 24 Feb 1982, Appl. 80/110, 064, 09 Aug 1980.

[12] B. D. Bauman, ACS, Rubber Division Meeting, Chicago, Illinois, April, 20, 1994, paper No.25

[13] T. Y. Yan, *Princeton, NJ 08540 USA. Prepr.- Am. Chem. Soc., Div. Pet. Tem* **1986**, *31*(3-4), 677–685.

[14] Kurita Nobuo, Maruyama Kenklich, Kamimura Tadashi, Jpn. Koki Tokkyo Koho Jp. 0425, 024 [9225,024] 28 Jan. 1992 App. 90/125, 861, 16 May 1990.

[15] Lizefu, Faming Zhuanli Shenqing Gongkai Shuoming CN 1,058,794, 19 Feb. 1992, App. 90, 105, 190 7 Aug. 1990.

[16] J. W. H. Oliver, "Modification of Paving Asphalts by Digestion with scrap rubber" *Australian Research Board* **1980**.

[17] A. Shvarts, i. Kauch, *Rezina* **1957**, *7*, 31. Recent Advances in Recycling and Reuse of Materials and Recent Advances in Recycling and Reuse of Materials and Modified Mixtures Designed using TxDOT Mix Design Method" Transportation Research Board 74th Annual Meeting, paper No. 950356, (1995).

[18] S. Ficker, Reclaiming scrap rubber, *Rubber Age*, **1973**, *104*(8), 53.

[19] Onouchi Yukio, Ingaki Shinji, Okamoto Hiroshi, Furukawa Junji, *Nippon Gomu Kyokaishi*, **1980**, *53*(12), 756–62.

[20] ibid, *Polymer Preprints-Am. Chem. Soc.* **1979**, (20) 943.

[21] 2nd annual report of the project [ID CODE: ENV-001-010. Contact/Agreement No: 15] October 2001.

[22] R. Dongre, M.B. Sharme, D.A. Anderson, "Development of fracture criterion for asphalt mixes at low temperatures," in *Transportation Research Record 1228*, TRB, National Research Council, Washington, DC **1989**, pp. 94–105.

[23] A. Bhurke, E. Shin, L. Drzal, "Fracture Morphology and fracture toughness measurement of polymer modified asphalt concrete", TRB 76th annual meeting Jan 1997, Paper no. 970942.