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Economic Polymer-based Waterproofing Membranes by Incorporation of Wastes to Form Eco-friendly Material

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Abstract

Waste recycling is a way to produce innovative low cost eco-friendly materials to solve environmental problems caused by different types of industrial by-product and polymeric wastes. Natural rubber loaded with different types of waste materials Calcium Hydroxide $Ca(OH)_2$, Calcium Carbonate ($CaCO_3$), Fly Ash (class F) and Waste rubber (WR) by mixing through open mill and then pressed in hot press to obtain low cost eco-friendly waterproofing membranes with desired properties. All samples pass the water penetration test up to 6 bars. The samples water absorption coefficients ranged from (0.1 to 0.3%) for all investigated samples. UV weathering and thermal aging tests were done to the samples while no changes on mechanical properties appeared before and after the tests. Dimensional stability test was done for all samples; a slight dimension change occurs. The mechanical and hardness measurements for all samples were done while good mechanical properties obtained. The price of square meter of 2 mm thickness for all samples was calculated in order to estimate its feasibility. A comparison of our samples with other waterproofing membranes from two famous Egyptian companies was done. Low cost and qualified waterproofing material can be obtained from recycling of some wastes.

Keywords: natural rubber; waste rubber; waterproofing; low cost.

Introduction

Due to several economic and pollution problems and widened consumption and resources depletion, various wastes are existing in huge amounts which is harmful for living organisms i.e. for the environment. These different types of waste should take the concern of scientists and researchers to control it and convert it into eco-friendly or environmentally product that have useful applications for environment [1].

There are a lot of waste types that can be recycled and others that cannot be recycled but can reused such as industrial, commercial, agricultural, rubber waste…., etc. Industrial wastes are the wastes that produced from industries, factories, mining operations and mills [2]. These industrial wastes such as paints, chemical solvents, paper products, metals, industrial by-product and radioactive wastes [3]. In this paper we will reuse the industrial by-product fly ash (class F) and calcium hydroxide as filler for rubber matrix. Calcium carbonate is one of the low cost materials that exist in abundance and only bears the manufacturers the cost [4] of transportation and storage, so using it as filler for rubber matrix will be a good way to obtain a processable low cost highly efficient waterproofing product.

The reusing of rubber tires that no longer suitable for using is an excellent process to get rid of wastes to

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protect the environment from contaminants [5] that consume large spaces in landfill and converting it into new advanced low cost waterproofing product. Reclaiming of waste rubber to be used as a powder in asphalt paving, as extender, or to produce filler to reduce the cost was made by Abbas A. Yehia [6]. The obtained reclaimed polymer can be replaced by 10-30% of the virgin rubber without affecting the basic rubber properties. Recycling of natural rubber (NR) by thermo-mechanical devulcanization occurred and it was revealed that the NR/waste rubber can almost completely recycled with low energy consumption without affecting the quality of the final product [7]. All samples have been subjected to different measurements to study their physical properties such as specific gravity, water absorption, water penetration, UV weathering, thermal aging, dimensional stability, mechanical measurements and hardness shore A.

Experimental work

All materials used in this research come from Alexandria factory for tire manufacture, Egypt. The structure of these materials is as follows:

- Natural rubber (NR), with specific gravity 0.934.
- Zinc oxide (ZnO) as activators with specific gravity 5.55–5.61.
- Stearic acid: melting point 67–69 ^{o} C; specific gravity 0.838.
- Tetramethyl thiuran disulfide (TMTD) as accelerator with specific gravity 1.29–1.31, melting point 1485 ^{o}C and orderless powder.
- Antioxidant N-isopropyl N0-cyclohexyl paraphenylene diamine (IPPD): purple gray flakes have density 1.17 g/cm^3.
- Elemental sulfur (S) with fine pale yellow powder and specific Gravity= 2.04–2.06.
- Naphthenic oil, with specific gravity 0.94–0.96, viscosity80–90 poise at 100^0 C.
- Fillers used in this paper are waste rubber, $CaCO_3$, $Ca(OH)_2$ and fly ash while the three latter fillers were collected from by-product of moisture insulation factory
- Waste rubber were obtained from automobile tire pieces which can easily be obtained from the environment with almost no cost, are shredded and added into natural rubber.

A comparison between two lubricants (processing oil and pre-used car oil) were done. The samples used to perform experimental tests were prepared according to ASTM C11361 with the recipe presented in table 1. Mixing and mastication are conveniently done using two roll mill with 170 mm diameter, 300 mm length, slow roll 18 rpm, and gear ratio 1:2. The mixing operation was executed on two stages. The first one called master batch consist of adding activators, antioxidant, antiozonants, reinforcing agent and processing oil to the natural rubber. The second stage is called the final batch.it consists of the previous master batch, curing agent (sulfur and accelerators). These materials are added at the end of process to prevent pre-vulcanization which may occur due to the elevated temperatures. Vulcanization of the rubber compounds were carried out using an electrically heated uniaxial hot press at 150^0 C and pressure 150 bar for 45 min. samples were prepared by different shapes of moulding according to measurement types.

Table (1): The ratio of natural rubber and the different wastes.

Ingredients	**Concentration (phr)**							
NR	100	100	100	100	100	100	100	100
Ca(OH)2	500	---	---	---	---	---	---	---
CaCO3	---	500	---	---	---	---	---	---
Fly ash(class F)	---	---	500	---	---	---	---	---
WR	---	---	---	500	---	---	---	---
WR	---	---	---	---	1000	---	---	---
WR	---	---	---	---	---	1500	---	---
WR	---	---	---	---	---	---	2000	---
WR	---	---	---	---	---	---	---	3000
Stearic acid	2	2	2	2	2	2	2	2
Zinc Oxide	5	5	5	5	5	5	5	5
Processing Oil	15	15	15	15	20	25	30	35
MBTS	2	2	2	2	2	2	2	2
IPPD(4020)	1	1	1	1	1	1	1	1
Sulphur	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5

*Part per hundred part of rubber by weight

Specific gravity test was conducted according to [ASTM D792-08] [8]. Samples were cut with dimensions (20x 20x3) mm. Dry weight and suspended in water weight were recorded. Water absorption test was conducted according to [ASTM D570] [9,10], Samples were cut with dimensions (100 x 100x2) mm, soaked in water bath for 24h while weighed before and after soaking. Water penetration test was conducted according to [EN: 1928] [11]. The samples were cut 150 mm diameter and connected to the apparatus while subjected to a gradual increase in pressure from 0.6 up to 6 bars. Weathering test was conducted in accordance with the standard specification [ASTM G-154] [12]. This test covers the basic principle for using fluorescent UV light, temperature and humidity intended to reproduce the weathering effects. Dimensional stability test was conducted according to [ASTM D-5147] [13] while the samples were conditioned in an oven maintained at (80±3)℃ for 24 h then reconditioned at room temperature for a minimum of one hour in accordance with [ASTM D-1204] [14]. While the dimensions measured before and after conditioning. Thermal aging test was conducted in accordance with [EN: 1296] [15]. The samples were conditioned in an oven at (70±2)℃ for 4 weeks; the samples were tested mechanically after conditioning. Mechanical measurements (Tensile strength, young's modulus and elongation at break) were measured in tensile testing machine (SHIMADZU AG-X) according to [ASTM D-412-06] [16]. The hardness was determined using Shore A durometer in accordance with [ASTM D 2240-07] [17]. The coverage of square meter per kilogram was calculated for all samples and compared to a data sheet of two products of known insulation factories.

Results and discussion

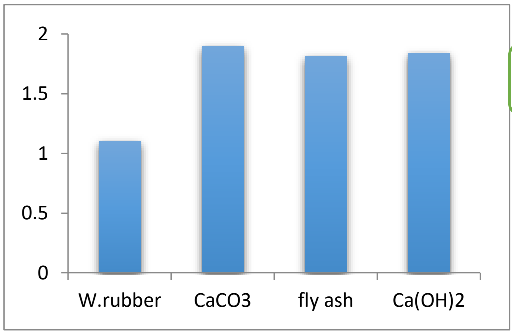
Specific gravity:

Density or specific gravity measurements are significant for industrialization of most today's products, as it's an evidence for formulation process, change in microstructure, composition [18], internal defects [19,20,21], chemical and physical changes [22, 23] that's affect the quality of the final product. Weight reduction of some products is acceptable for product performance and economic savings. A noticeable decrease in density or specific gravity indicates pores existence within the product which doesn't comply with waterproofing products, while density increasing can change the polymer state approaching to crystalline state which is not compatible with waterproofing applications.

The specific gravity (ρ) was calculated according to Eq. (1) [24] for the different filler samples ($Ca(OH)_2$, $CaCO_3$, Fly Ash (class F) and W. rubber) as shown in Fig. (1) and for rubber with different Waste rubber concentrations :

$$\rho = \frac{w_a}{w_a - w_s} \text{ x water specific gravity} \qquad (1)$$

W_a is dry weight, and **W_s** is suspended in water weight.



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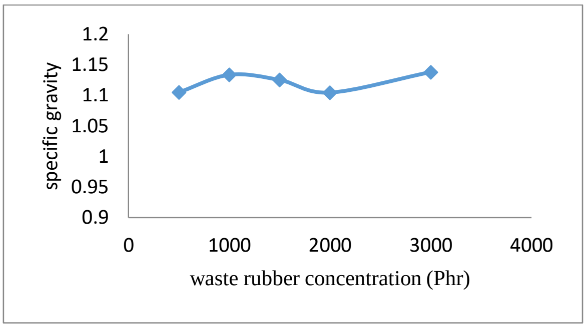


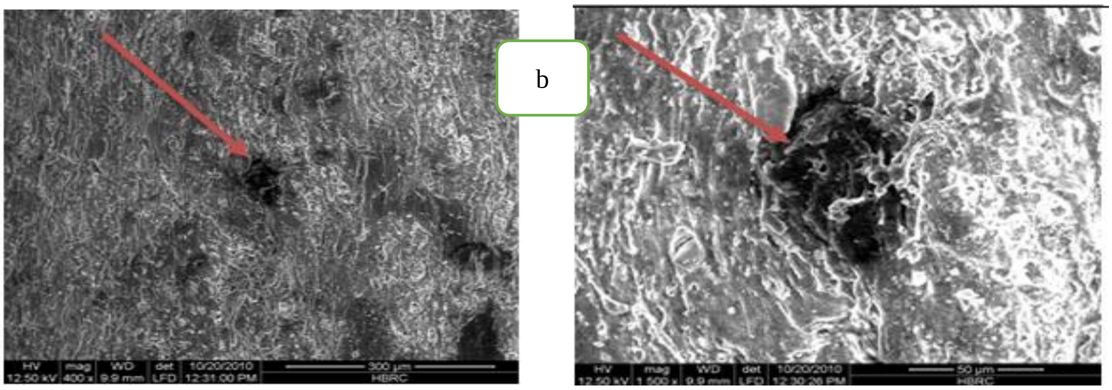


Fig (1) a) Specific gravity for different filler types and different W. rubber concentrations. b) SEM image indicate the air pores.

For membranes applications, the sheets with low specific gravity give more square meters per kilogram of stock so it is preferred to use waste rubber to obtain low cost water proofing sheets. From the above figure it was observed that the specific gravity decreases at 1500 and 2000 Phr which may be attributed to the formation of air pores during preparation which was proved by scanning electron microscope image fig (1) The above calculations show that the lowest specific gravity value is for W. rubber which is in the range of waterproofing membranes [24], while this is a good indication for our applications [25], i.e. this sample is promising for application as waterproofing membranes.

Water absorption measurements:

Water insulation is an important requirement for constructions, as buildings can be insulated by using waterproofing membranes to protect them from breakdown. Large numbers of residential and commercial buildings exposed to damage due to inefficient use of waterproofing sheets, so it is very important to determine the water absorption percent after 24 h immersion as shown in Fig. (2) for the different filler samples and for the rubber with different Waste rubber concentrations (while no effect on water absorption coefficient when waste oil was used), according to ASTM (D570) [10]:

$$\text{water absorption } \% = \frac{m_t - m_0}{m_o} x100 \qquad (2)$$

where, m_0 is the sample mass before immersion, m_t is the sample mass after 24hr. immersion.

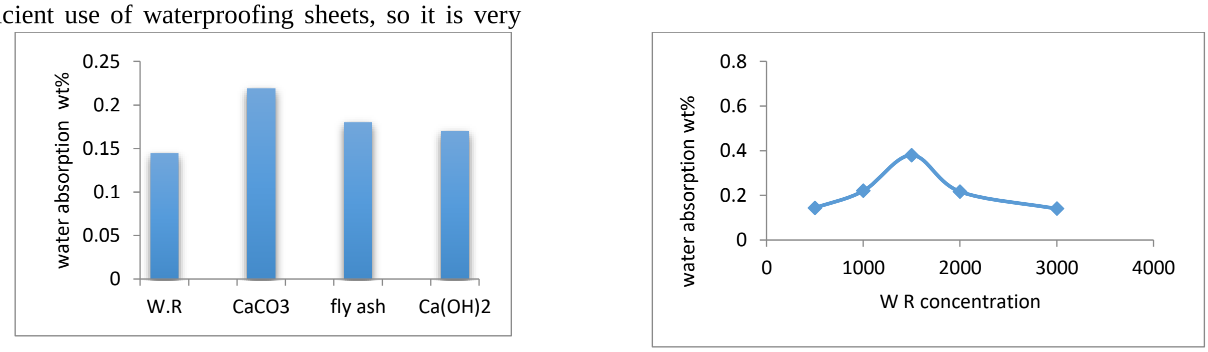


Fig (2) Water absorption % for different filler types and for W. rubber concentrations.

From the above figures it was observed that the water absorption % increases at 1500 and 2000 Phr which may be attributed to the formation of air pores that work as a cavity that absorbs more water than the other samples which was proved by scanning electron microscope image. It is clear that the water absorption wt % for all samples after 24h immersion lies in the range of waterproofing membranes according to the Egyptian code of waterproofing materials [24] which is promising in water insulation sector.

Water tightness measurements:

All the samples were connected to water tightness apparatus and the test were conducted at 0.6, 2, 4, 6 bars pressure (the maximum limit for samples acceptance is 0.6 bar according to the EN standard). All the samples passed the test without any infiltration or cracking.

Weathering measurements:

UV radiation, heat and humidity can cause degradation, cracks or damages for samples that exposed to them, so it is very important for all building materials to be tested to indicate their life time. All samples in this paper were exposed to UV-light (254 nm), 60̊ C and relative humidity 90% for 200 h. All samples pass the test without any observable cracks, damages or degradation due to the using of antioxidants and antiozonants during preparation which qualify these samples for more applications. Mechanical test was done for all samples before and after exposure while no changes on mechanical properties appeared.

Dimensional stability measurements:

Samples were conditioned in an oven for (80) ˚C for 24h. The difference in lengths were calculated and recorded in table (2).

Table (2): The difference in lengths after dimensional stability test.

Sample	∆ L (cm)
Fly Ash (500 Phr)	0.042
$CaCO_3$(500 Phr)	0.103
$Ca(OH)_2$ (500 Phr)	0.027
W. rubber (500 Phr)	0.13
W. rubber(1000 Phr)	0.019
W. rubber(1500 Phr)	0.031
W. rubber(2000 Phr)	0.054
W. rubber(3000 Phr)	0.055

Thermal aging:

Samples were conditioned in an oven at (70) ˚C for 4weeks and examined by mechanical measurements before and after conditioning, while no changes appeared which proves that no cracks or infiltration appeared in the produced samples.

Mechanical properties measurements:

Stress-strain measurement:

Mechanical measurements (tensile stress, young's modulus, hardness, etc.) are important for the evaluation of rubber properties. Cross links or chemical bonds are formed during vulcanization, the higher the number of cross links (cross linking density), the larger the force required stretching the film (tensile stress), the smaller elongation at break, which is indicated in the next figures. Fig. (3(a)) are the stress strain curves for samples with different filler types and samples with different waste rubber concentrations, respectively. Fig. (3(b)) indicate the modulus of elasticity for the two groups. Fig. (3(c)) indicate the elongation at break and (3(d)) indicate the cross linking density for both groups. It is clear from the Fig. (3(a)) that the samples with different filler types show tensile stresses 3.3, 3.4, 5.0 and 6.2 MPa for $CaCO_3$, fly ash, WR and $Ca(OH)_2$, respectively and tensile strength (elastic modulus) 7.5, 9.0, 18.3 and 50.6 for WR (500 Phr), fly ash, $CaCO_3$, $Ca(OH)_2$, respectively which means that the sample with high elastic modulus $Ca(OH)_2$ is stiffer than the sample with lower one. It is obvious from the obtained data that the stiffness decrease with the elastic modulus and cross links decreasing, hence elongation at break should be increased. Fig. (3(a)) show that the tensile stresses are (5.07, 4.4, 6.1, 5.82 and 5.8) MPa and elastic modulus (7.5801, 8.3288, 9.4371, 9, 13.266) for samples containing WR (500, 1000, 1500, 2000. 3000) Phr respectively.

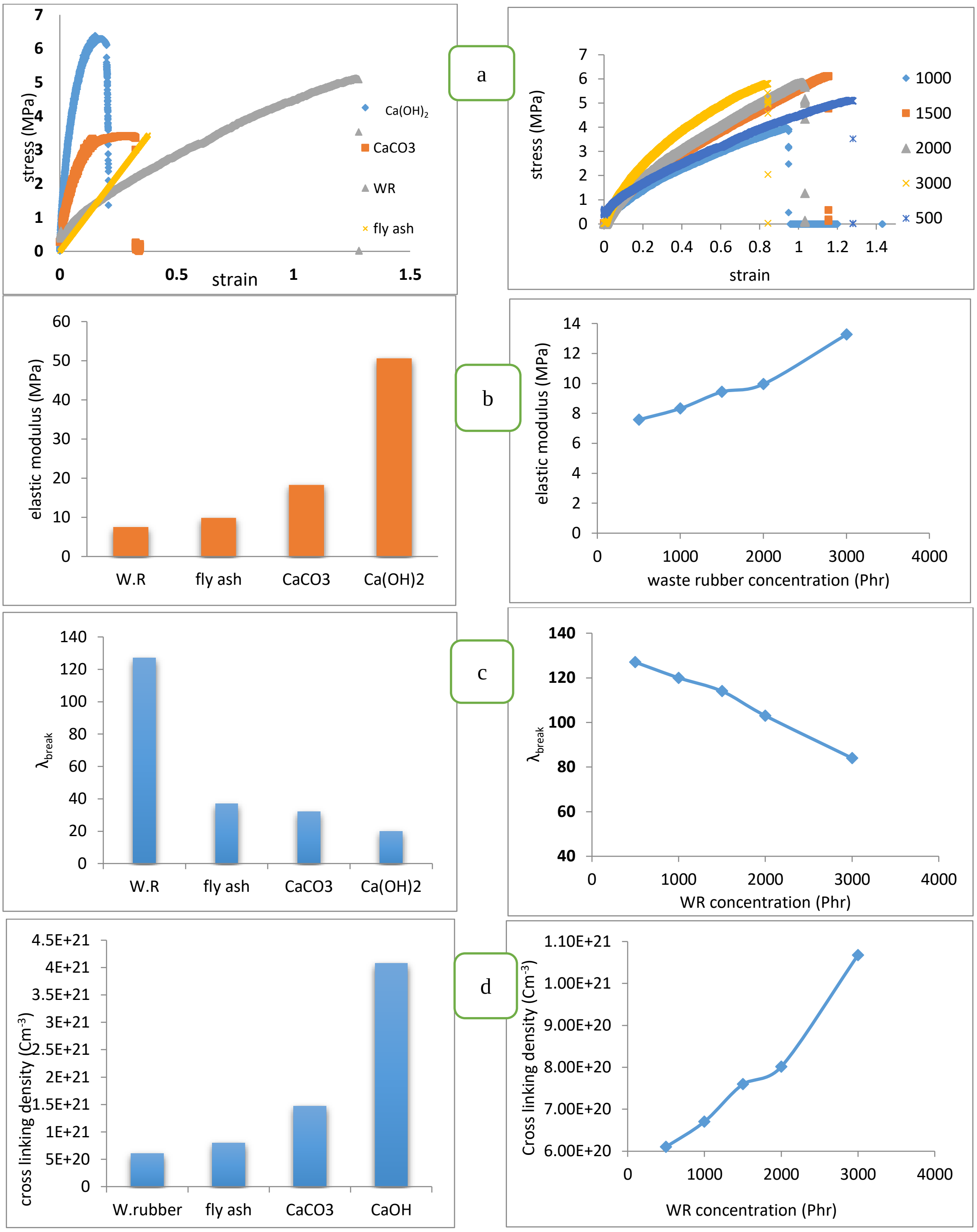
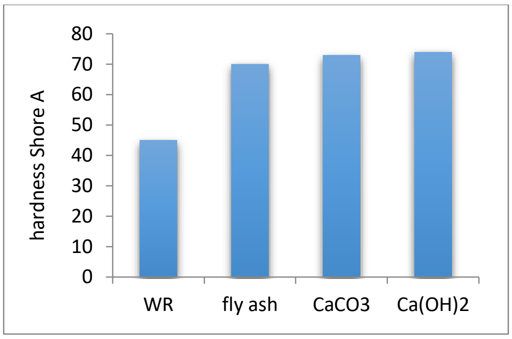


Fig (3) mechanical measurements results (a) Stress Strain curve for the different filler types and the different WR filler. (b) Elastic Modulus for the different filler types and for the WR filler. (c) Elongation at break for the different filler types and for WR filler. (d) Cross linking density for different filler types and for WR filler

From The above results one can recognize that the results of waste rubber containing samples are in the known range of reinforced rubber by some other known fillers [26]. All of the above results may be attributed to C-S-C bonds of the waste rubber that may be broken during grinding and mastication, since some of the C-H bonds which are adjacent to C=C bonds are broken during vulcanization and replaced by sulfur atoms that links with another polymer chain and cross links strongly to form a new physical property to the final product. It was found that no effect on mechanical properties when waste oil was used instead of processing oil.

Hardness measurements:

The resistance of the material to permanent indentation is known as shore hardness which becomes considerable factor when the material is used in applications under pressure. Fig (4) show hardness shore A for the samples of different filler types and the samples of different WR concentrations.



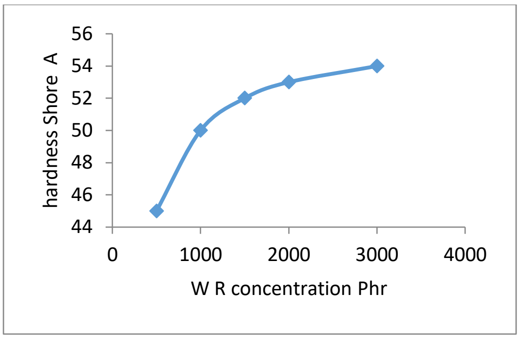


Fig (4) Hardness for different filler types and for WR filler.

From the above figures it is clear that the waste rubber containing samples is less stiff than the other added filler types while with increasing the waste rubber content the stiffness of the material increase which proved obviously by young's modulus and cross linking density that calculated from mechanical measurements, but still in the international hardness rubber scale from 20 up to 90 [17].

Calculation of square meter coverage and cost

The coverage of the square meter per kilogram is a major cost factor. The lower the density of the sample and the less the weight, the higher the coverage (more square meters per kilogram), which helps to obtain a low cost valuable eco-friendly material for water proofing membrane applications.
The square meter coverage per kilogram and the cost of the square meter (when processing oil and waste oil were used) were calculated (table 3).

Table (3): The square meter coverage per kilogram and the cost of the square meter of each waterproofing sheets.

Sample name	Coverage (1mx1mx0.02m) (g)	Price when processing oil used (LE)	Price when waste oil used (LE)
Fly Ash (500 phr)	3223.206	32.1222	-------
$CaCO_3$(500 phr)	4253.14	28.447	-------
$Ca(OH)_2$ (500 phr)	4046.25	26.3205	-------
W. R (500 phr)	2096.92	20.734	19.954
W. R(1000 phr)	2467.34	19.983	19.203
W.R(1500 phr)	2573.19	16.66	15.88
W. R(2000 phr)	2123.4	12.9176	12.0156
W. R(3000 phr)	2088.7	12.0665	10.8765

*LE is the Egyptian pound.

The above results indicate that one can obtain waterproofing membranes with a suitable price by exploiting W. R that has a baleful effect on the environment. In addition to the other fillers (Fly Ash, $CaCO_3$ and $Ca(OH)_2$) results that qualify them to be used in many other applications with reasonable price compared with the other known products.

Comparison between our products with two high quality products:

A comparison between our results and data sheet from two known companies was carried out and listed in table 4, Table (4): A comparison between our results and the data sheets of the companies.

	Our results for (3000Phr) W.R.	Data sheet1	Data sheet 2
Tensile strength (MPa)	5.7	1.1	0.75
Elongation at break (%)	84	45	42
Hardness shore A	54	Doesn't included in the data sheet	Doesn't included in the data sheet
Dimensional stability(cm)	0.055	Doesn't included in the data sheet	0.2
Water absorption (%)	0.14	0.15	0.15
Water tightness (bar)	6	0.6	0.6
Aging due to U.V. radiation	Pass for 200 h of exposure	Doesn't included in the data sheet	pass
Resistance to thermal aging	No damage or cracks were observed after 4 weeks of exposure	4 weeks pass	No sign of deterioration after the test

It is cleared from the data sheet that our product is promising to be used as alternative waterproofing membrane.

Conclusion

Waste recycling can reduce the consumption of national raw materials by using the waste as alternative material. Specific gravity was found in the range of waterproofing membranes. The water absorption % for all samples lies in the range of waterproofing membranes according to the Egyptian code of waterproofing membranes. All the samples passed the water penetration test up to 6 bars. No damages in the samples after 200h exposure to UV weathering test. Tensile strength and elongation at break were obtained for all samples and are suitable for waterproofing applications. Dimensional stability test reveals that samples have maximum changes in dimensions from 0.01 to 0.1 mm which is considered very suitable for waterproofing applications. Resistance to thermal aging test was done and observed after 4 weeks of exposure, while no cracks or damages occur in the samples. Square meter coverage and cost calculations were studied for all samples and showed that some samples are suitable for marketing as waterproofing membranes. A comparison with other two high quality waterproofing product proved the qualification and success of the product to be used in the large scales. Finally, low cost and qualified waterproofing material can be obtained from recycling of some wastes.

1. Conflicts of interest

"There are no conflicts to declare".

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