### Effect of Modified Linen Fiber Waste on Physico-Mechanical Properties of Polar and non-Polar Rubber

#### <sup>\*1</sup>A. I. Hussain, <sup>2</sup>A. H. Abdel-Kader and <sup>2</sup>A. A. Ibrahim,

#### <sup>1</sup>Polymers and Pigments Department, <sup>2</sup>Cellulose and Paper Department, National Research Center, Cairo, Egypt \*E-mail: <u>ismaelahmed1@yahoo.com</u>

**Abstract:** The environmental advantages of natural fibers are an important influence, in all worlds. To get rid of linen fiber waste it can be used as filler in rubber. The physico-mechanical properties of natural rubber (NR) as (non-polar rubber) and acrylo-nitrile rubber (NBR) as (polar rubber) vulcanizates loaded with the acetylation modification of linen fiber waste (long & short) were studied. The effect of the fiber content on the physico-mechanical properties of the natural rubber (NR) and acrylo-nitrile rubber (NBR) vulcanizates was also studied before and after aging. Swelling in toluene, motor oil, as well as distilled water was investigated. Also, scanning electron microscope was used in this study to investigate the surface texture of unloaded and loaded rubber vulcanizates with unmodified and modified fiber. The modified linen fiber waste enhanced both of the physico-mechanical properties and the swelling characteristics in different liquids for NR and NBR vulcanizates. [Nature and Science 2010;8(8):82-93]. (ISSN: 1545-0740).

Key Words: Linen fibers waste, Natural rubber vulcanizates, Acrylo-nitrile rubber, Physico-mechanical properties.

#### 1. Introduction

Today there are huge unused quantities of agricultural residues and by-products around the world. Agricultural residues and by-products represent a big renewable source of fibrous raw materials and calls for economic uses. Ignoring these materials and leaving them in the countryside causes fire hazards and enhance spreading of insects, beside the impact on the environment. The environmental advantages of natural fibers  $^{(1, 2)}$  are an important influence, in all worlds. Natural fibers are derived from renewable resources and biodegradable; also do not have a large energy requirement to process, and often from industrial by-products. They are lighter than inorganic reinforcements <sup>(3)</sup>, which can lead to benefits such as fuel savings when their composites are used in transportation applications. Natural fibers can be used to reinforce biodegradable polymers since natural fibers themselves are biodegradable. The disposal of fiber waste has become an environmental issue of growing concern.

Linen fiber waste used in the manufacture of textiles which appear to be some of the oldest in the world, their history goes back many thousands of years. They are highly absorbent and a good conductor of heat, also linen fabric feels cool to the touch. Linen fiber waste is the strongest of the vegetable fibers, with 2 to 3 times the strength of cotton. Linen fiber waste has poor elasticity and does not spring back readily, explaining why it wrinkles so easily. Linen fiber waste is a big problem in linen textile industries. They are by–products waste.

To get rid of linen fiber waste it can be used as

filler in rubber. The performance of the fillers depends on the right combination of reinforcing fillers and extenders. The fillers are generally uniformly distributed through out rubber matrix during mixing process <sup>(4)</sup>. Linen fiber waste is hydrophilic and do not tend to be easily wetted or to bond well with many matrix materials, particularly the commodity thermoplastics. Rubber is used as the base material in a product if it requires rubber-like elasticity <sup>(5)</sup> and flexibility.

In certain cases, rubber products require stiffness along with flexibility, often in specific directions. This can be achieved by reinforcing rubber with long or short fibers to form composites. Short fiber <sup>(6,7)</sup> reinforced rubber composites are more advantageous due to their easy processability and great flexibility in product design. Much research has been performed on such composites containing synthetic fibers such as polyester, nylon, carbon, kevlar, glass and asbestos. Coran and Hamed <sup>(8)</sup> reviewed the reinforcement of elastomers with short fibers. Now studies are in progress to replace the synthetic fibers with natural fibers <sup>(9, 10)</sup> such as wood pulp, jute, sisal, flax, pineapple and oil palm fibers as a means to produce environmentally friendly materials.

Fiber/rubber composites are of tremendous importance both in end-use applications and the area of research and development. These composites exhibit the combined behavior of the soft, elastic rubber matrix and the stiff, strong fibrous reinforcement. The development of fiber/rubber composites has made available polymers that are harder than aluminum and stiffer than steel. Generally short fiber reinforced rubber composites has become popular in industrial fields because of the processing advantages and increase in strength, stiffness, modulus and damping. The design of a short fiber reinforced rubber composite depends on several factors such as the aspect ratio of the fiber, control of fiber orientation and dispersion and existence of a strong interface between fiber and rubber. V.G. Geethamma et al. <sup>(11)</sup> have reported that the efficiency of reinforcement can be increased by surface modification of coir by treating it with an alkali solution and can be enhanced by applying a natural rubber solution to alkali modified fibers.

Also, V.G. Geethamma et al.<sup>(11)</sup> studied the DMA of acetylated short sisal fiber reinforced NR composites. Studies have been made on the effect of a diazide as an adhesion agent on composite of SBR and short PET fibers. DMA of short pineapple fiber reinforced polyethylene and oil palm fiber reinforced phenol formaldehyde resin composites have been conducted in this laboratory. Many studies have been made on the mechanical and dynamic mechanical properties of composites.

The aim of the present study is to evaluate the influence of linen fiber waste (long and short) before and after acetyl <sup>(12, 13)</sup> modification as a reinforcing natural filler on the processing, physico-mechanical properties at normal temperature and after thermal oxidative aging of natural rubber as (non-polar) rubber and acrylo-nitrile butadiene rubber as (polar rubber) vulcanizates. Also, study the influence of the acetyl modification to Linen fiber waste on the swelling of the vulcanizates in toluene, motor oil and distilled water. The importance of utilizing linen fiber waste are of natural origin (by-product), to get rid of this waste by-product (environmental pollutants) and to produce friendly environment material.

#### 2 - Materials and Methods

#### 2.1. Materials:

#### 2.1.1. Rubber:

- a. Natural rubber (NR) "Ribbed smoked sheets Rss-1, Sp.Gr. 0.913", Mooney viscosity ML (1+4) at  $100^{\circ}C = 60-90$ ; glass transition Tg =  $-75^{\circ}C$ .
- b. Acrylo-nitrile butadiene rubber (NBR), acrylonitrile content 33%, Mooney viscosity

a 100 °C 45, specific gravity 1.17, ash content 0.5%. **2.1.2. Fillers:** 

a. High abrasion furnace carbon black N-330 (HAF): Black granulated powder has a particle size of 40 nm and specific gravity 1.78-1.82.

#### 2.1.3. Accelerators:

a. N-cyclohexyl-2-benzothiazole sulphenamide (CBS): Pale grey, non hygro-scopic powder,

melting point 95-100°C and specific gravity. 1.27-1.31.

- 2.1.4. Antioxidants:
- a. [Phenyl- $\beta$ -naphthyl amine (P $\,$  N), specific gravity 1.18-1.24, melting point 105 –106  $^{o}C$  .
- 2.1.5. Plasticizers:
- a. Dibutyl phthalate (DBP), boiling point 220-248 °C and specific gravity 0.983 0.989.
- 2.1.6. Curing agent:
- a. Sulfur: Pale yellow powder of sulfur element purity 99.9%, melting point 112°C, specific gravity 2.04 2.06.
- 2.1.7. Activator:
- a. Zinc oxid, fine powder, purity 99%, specsific gravity 5.6.
- b. Stearic acid, melting point 67-69°C, specific gravity 0.838.

#### 2.1.8. Fibers:

- a. Unmodified linen fiber waste (LFW): lignin 24.6, ash A1.91, pentosan 18.6, hollocellulose 62.0,  $\alpha$ -cellulose 44.2, water retention value162, extractive 3.2, carbon content 42.01, hydrogen content 6.46,
- b. Modified linen fiber waste (MLFW): Acetylation percent 25%

#### 3. Techniques:

#### 3.1. Mixing <sup>(14)</sup>:

All rubber mixes were prepared on a laboratory two-roll mill of 170 mm diameter and 300 mm working distance. The speed of slow roller was 24 rpm with 1:1.4 gear ratio. The compounded rubber was left over night before vulcanization.

#### **3.2. Vulcanization**<sup>(15)</sup>:

Vulcanization was carried out on a heated platinum press under pressure of about 40 kg/cm<sup>2</sup> and temperature of  $162 \pm 1^{\circ}$ C.

#### **3.3. Fiber preparation:**

The fibers cleaned of undesirable foreign matter and pith followed by repeated washing and drying in the oven at 105 °C for 24 hrs. This ensured the removal of unwanted matter present in the fiber. The fibers were then chopped to different lengths of 0.8 mm and 0.5 mm, then partially acetylated and mixed with rubber in different ratios (5-20%).

#### 3.4 Modification of linen by acetylation:

For the preparation of partially acetylated raw material the method which described by Fahmy et al.<sup>(16)</sup> was used. Raw material was first activated by heating with acetic acid at 80°C for 5 min. in liquor ratio 1:10, filtered to 100% pick ratio, then 0.1% perchloric acid in acetic acid was used as a catalyst in liquor ratio 1:8 and filtered after 45 seconds to pick ratio 100%.

The sample was then acetylated at 20°C using an acetylating mixture containing 30% acetic anhydride and 70% acetic acid, liquor ratio of 1:10 was used for the desired time (45min). The sample was then washed with water till neutrality. The acetylated raw material was stabilized by treatment with hot distilled water. The partially acetylated raw material was then air dried, and the acetyl content was then determined according to the modified Eberstadt method<sup>(17)</sup>.

#### **3.5.** Physical testing:

#### 3.5.1. Rheometric characteristics<sup>(18)</sup>:

Minimum torque ( $M_L$ ), maximum torque ( $M_H$ ), curing time: Time at 90% cure ( $t_{c90}$ ), scorch time ( $t_{s2}$ ) and cure rate index (CRI) were determined, using a Monsanto Oscillating Disc Rheometer model-100.

#### **3.5.2.** Physico-mechanical properties<sup>(19)</sup>:

Tensile strength, elongation at break, modulus at 100% strain and Young's modulus were measured at room temperature using on an electric tensile testing machine (Zwick 1425) with crosshead speed 500 rpm, according to ASTM D 412 – 98.

#### 3.5.3. Swelling<sup>(20, 21)</sup>:

Swelling was determined according to (El Nashar) and ASTM D 471 - 98. The samples were immersed in both toluene and distilled water at room temperature for 24 hours and or in motor oil at 100°C for seven days.

The swelling value (S.V.) was calculated as follows:

S. V.=  $[(W_i-W_o)/W_o] \times 100$ where:  $W_0$ = weight before swelling  $W_I$  = weight at time  $t_i$ 

#### **3.5.4.** Thermal oxidative aging <sup>(22)</sup>:

Accelerated aging was carried out in a good aerated electric oven at  $90 \pm 1^{\circ}$ C for different time periods.

#### 3.5.5. Microscopic examination by SEM:

The microscopic examination by scaning electron microscope (SEM) of the surface texture of the rubber vulcanizate samples before and after loading of fillers was inspected in a scanning electron microscope JSM-T20 Japan JEOL. The fracture surfaces were gold coated to avoid electrostatic changing during examination.

#### 3.6. Chemical methods:

#### 3.6.1. Acetyl content determination<sup>(23)</sup>:

Acetyl content or combined acetic acid in cellulose acetate is usually determined by saponification under mild condition. About 0.5 g of the raw material (accurately weighed) was saponified in a stoppered conical flask with 20 ml 0.5N alcoholic potassium hydroxide at 50°C for three hours with occasional shaking. Then 25 ml (excess) of 0.5N sulfuric acid were added to the contents of the conical flask and left to stand for 15 min. The excess sulfuric acid was titrated against 0.5N sodium hydroxide. A parallel blank experiment was also carried out and the acetic acid content was calculated as follows: [a - b] X 3.0026

Where:

(a): the mls of 0.5 N NaOH consumed by the acetate.

W

(b): the mls of 0.5 N NaOH consumed by the blank experiment.

(W): the dry weight of the sample in grams.

The acetyl content can be calculated from the combined acetic acid percent as follows:

The average number of acetyl groups (degree of substitution) per anhydro-D- glucose unit of cellulose (D. S.) can be calculated from the acetyl content.

D. S. = 
$$\frac{3.86 \text{ X acetyl \%}}{102.4 - \text{ acetyl \%}}$$

#### 4- Results and Discussion

Acetyl % = -

In the present study NBR and NR have been loaded with the linen fiber waste (LFW) and modified linen fiber waste (MLFW) at different concentrations and fiber lengths. The rheometric characteristics, physico-mechanical properties at ambient temperature and after oxidative aging, swelling in both toluene, and water at ambient normal temperature for 24 hours, as well as motor oil at 100°C for 7 days have been studied.

#### 4.1. Rheometric characteristics

The effect of addition un-modified and modified linen fiber waste with length 0.8 mm and 0.5 mm in different concentrations to acrylo-nitrile butadiene rubber (NBR) on the maximum torque ( $M_H$ ), minimum torque ( $M_L$ ) optimum cure time ( $t_{C90}$ ), Scorch time ( $t_{S2}$ ) and cure rate index (CRI) is shown in Table (1a and 1b).

	1	2	3	4	5	6	7	8	9
NBR	100	100	100	100	100	100	100	100	100
L un 0.8		5	10	15	20				
L tre 0.8						5	10	15	20
MH (dN.m)	38	40	42	43	45	45	46	46	47
ML (dN.m)	6.23	6.49	6.6	6.7	7	6.3	6.5	7.1	8
TC90(min.)	15.3	14.2	13.3	12.5	12.2	13.15	12.55	12.15	11.3
tS2 (min.)	4.5	4.25	3.55	3.1	2.5	3.5	3.3	3.1	2.55
CRI(min-1)	9.25	10.05	10.25	10.63	10.3	10.36	10.81	11.04	11.42

Table (1a): Rheometric characteristics of NBR loaded rubber with 0.8 mm unmodified and modified linen fiber waste at 162 °C.

Base recipe: Stearic acid 5 (phr); Zinc oxide 4(phr); Oil (DBP) 3(phr); CBS 0.8(phr); P N 1(phr); Sulfur 2(phr), Carbon Black 30(phr),  $(M_L)$  minimum torque,  $(M_H)$  maximum torque,  $(ts_2)$  scorch time,  $(tc_{90})$  optimum cure time, (CRI) cure rate index.

Table (1b): Rheometric characteristics of NBR loaded rubber with 0.5 mm unmodified and modified linen fiber waste at 162 °C.

mounted miter riber waste at 102 °C.									
	10	11	12	13	14	15	16	17	
NBR	50	50	50	50	50	50	50	50	
L un 0.5	5	10	15	20					
L tre 0.5					5	10	15	20	
MH (dN.m)	41	42.4	43	44	43	43.6	44.6	45	
ML (dN.m)	6.76	6.82	6.9	7	6	6.36	6.7	7	
TC90 (min.)	14.2	13.55	13.2	13	15	14.2	14	13.25	
tS2 (min.)	4.25	3.55	3.2	2.5	4.1	3.2	2.55	2.5	
CRI(min-1)	10.05	10	10	9.52	9.17	9.09	8.73	9.3	

Base recipe: Stearic acid 5(phr); Zinc oxide 4(phr); Oil (DBP) 3(phr); CBS 0.8(phr); P N 1(phr); Sulfur 2(phr), Carbon Black 30(phr),  $(M_L)$  minimum torque,  $(M_H)$  maximum torque,  $(ts_2)$  scorch time,  $(tc_{90})$  optimum cure time, (CRI) cure rate index

A Monsanto oscillating disk rheometer model 100 is used with a standard method ASTM D 2084 – 01 for measuring the processing and curing characteristics of the rubber compounds. It is obvious from the table that  $M_{L_{c}}$   $M_{H}$ , and CRI increased as the fiber content increased. While the ts<sub>2</sub>, and t<sub>C90</sub> decreased as the fiber content increased. So, the presence of fibers generates a decrease in viscosity of the mixes.

The increment in torque values with increasing fiber loadings indicates that as more fiber gets into the rubber matrix, the mobility of the macromolecular chains of the rubber reduces resulting in more rigid vulcanizates. The cure time was found to be independent on fiber loading but the gum compound exhibited higher cure time. The reduction in cure time of the filled vulcanizates was attributed to the higher time at the rubber compounds remain on the mill during mixing. As the fiber loading increases, the time of incorporation also increases and consequently generates more heat due to friction. The tables that the formulations containing modified linen fiber wastes had higher  $M_H$  and  $M_L$  than the unmodified linen fiber wastes which indicate to greater dispersibility in rubber matrix.

The effect of addition un-modified and modified linen fiber waste fiber with length 0.8 mm and 0.5 mm in different concentrations to natural rubber (NR) on the maximum torque ( $M_H$ ), minimum torque ( $M_L$ ) optimum cure time ( $t_{C90}$ ), scorch time ( $t_{s_2}$ ) and cure rate index (CRI) is shown in Tables (2a and 2b).

It is obvious from the table that  $M_{H_1}$  tc<sub>90</sub> and ts<sub>2</sub> increased as loaded with linen fiber waste as well as the fiber content increased with respect to the blank.

and mounted men noer waste at 152°C.									
	18	19	20	21	22	23	24	25	26
NR	50	50	50	50	50	50	50	50	50
L un 0.8		5	10	15	20				
L tre 0.8						5	10	15	20
MH (dN.m)	78	87	88.5	89	90	92	92.5	92.5	93
ML (dN.m)	2	2	2	2	2	2	2	2	2
TC90 (min.)	8.5	9.55	9.50	9.40	9.25	9.25	9.15	9.19	9
tS2 (min.)	3.25	3.5	3.55	4	4.2	3.25	3.32	3.4	3.5
CRI(min-1)	19.04	16.52	16.8	18.5	19.8	16.66	17.15	17.27	18.18

Table (2a): Rheometric characteristics of NR loaded rubber with 0.8 mm unmodified and modified linen fiber waste at 152 °C.

Base recipe: Stearic acid 5(phr); Zinc oxide 4(phr); Oil (DBP) 3(phr); CBS 0.8(phr); P N 1(phr); Sulfur 2(phr), Carbon Black 30(phr),  $(M_L)$  minimum torque,  $(M_H)$  maximum torque,  $(ts_2)$  scorch time,  $(tc_{90})$  optimum cure time, (CRI) cure rate index.

Table (2b): Rheometric characteristics of NR loaded rubber with 0.5 mm unmodified and modified linen fiber waste at 152 °C.

mounted mich noer waste at 152 °C.								
	27	28	29	30	31	32	33	34
NR	50	50	50	50	50	50	50	50
L un 0.5	5	10	15	20				
L tre 0.5					5	10	15	20
MH (dN.m)	88	89	90	91	92	92.5	93	94
ML (dN.m)	2	2	2	2	2	2	2	2
TC90 (min.)	9.3	9.25	9.25	9.25	9.25	9.25	9.25	9.25
tS2 (min.)	3.25	3.25	3.2	3.2	4.25	4	3.55	3.5
CRI(min-1)	16.52	16.66	16.52	16.52	20	19	17.54	17.39

Base recipe: Stearic acid 5(phr); Zinc oxide 4(phr); Oil (DBP) 3(phr); CBS 0.8(phr); P N 1(phr); Sulfur 2(phr), Carbon Black 30(phr),  $(M_L)$  minimum torque,  $(M_H)$  maximum torque,  $(ts_2)$  scorch time,  $(tc_{90})$  optimum cure time, (CRI) cure rate index.

It is noticed from the tables that maximum torque  $(M_H)$ , scorch time  $(ts_2)$  and CRI of the NR rubber mixes in case of modified linen fiber waste were higher than the unmodified linen fiber waste. This may be due to the dispersibility of the modified linen fiber waste in the rubber matrix as well as the modification enhances the adhesion between the linen fiber waste and the rubber.

#### 4.2. Effect of changing concentration and fiber length of unmodified and modified linen fiber waste on the physico-mechanical properties of NBR vulcanizates.

It can be seen from Figures (1, 2) that Physico-mechanical properties of the loaded NBR vulcanizates with unmodified and modified linen fiber waste was affected by increasing the fiber concentration.

It is noticed that the unmodified linen fiber waste decreases both of the tensile strength and the

elongation at break more than the modified linen fiber waste. Also, the increasing of the fiber length decreases both of the tensile strength and the elongation at break.

#### 4.3. Effect of changing concentration and fiber length of unmodified and modified linen fiber waste on the physico-mechanical properties of NR vulcanizates.

Figures (3 and 4) represent the variation of the mechanical properties (tensile strength and elongation at break) according to the concentrations of unmodified and modified linen fiber waste which have different fiber lengths. The data illustrated that the properties improved by the addition of modified linen fiber waste with fiber length 0.5 at concentrations 5-10%. But the other concentrations and fiber length of unmodified and modified decreased both of the tensile strength and the elongation at break.

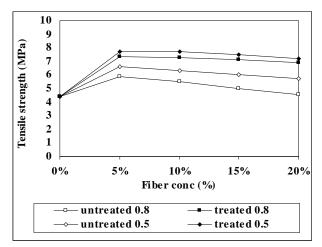


Fig. (1): Effect of fiber loading on tensile strength of NBR

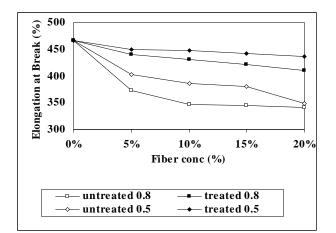


Fig. (2): Effect of fiber loadings on elongation at break of NBR

From the above data it can concluded that the modified linen fiber waste with fiber length 0.5 mm had good mechanical properties more than modified linen fiber waste with fiber length 0.8 mm in both NBR and NR rubber. This means that, the actylation treatment with fine particle size (0.5 mm) increase the dispersibility of the fiber in the non polar rubber matrix which enhances the mechanical properties of NBR and NR. This finding recommends these ratios to possess the most promising mechanical properties; consequently, so, it will be recommended for further investigations.

NBR and NR rubber inherently possess high strength due to strain-induced crystallization. When fibers are incorporated into NBR and NR, the regular arrangement of rubber molecules is disrupted and hence the ability for crystallization is lost. This is the reason why fiber reinforced rubber composites possess lower tensile strength than gum compounds.

# 4.4. Effect of thermal oxidative aging on loaded NBR vulcanizates with unmodified and modified linen fiber waste on the physico-mechanical properties.

The NBR vulcanizates containing different concentrations (low concentration 5% and high concentration 20%) of unmodified and modified linen fiber waste with different fiber lengths (0.5 and 0.8 mm) were subjected to thermal oxidative aging in well ventilated oven at 100°C for different periods up to 7 days.

The physico-mechanical properties of the aged vulcanizates were determined and graphically represented in Figures (5 and 6). The NBR vulcanizates loaded with unmodified and modified linen fiber waste showed decreasing in the tensile strength and elongation at break during aging periods with respect to the blank. The figures showed that the loaded NBR vulcanizates with unmodified fibers decreased more than modified fiber, and all NBR vulcanizates decreased in the same trend of the blank.

These means that the modified linen fiber waste had good aging properties with respect to unmodified linen fiber waste.

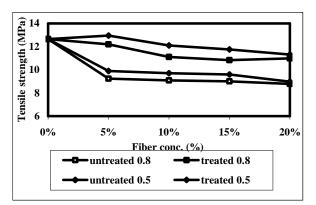


Fig. (3): Effect of fiber loading on tensile strength of NR

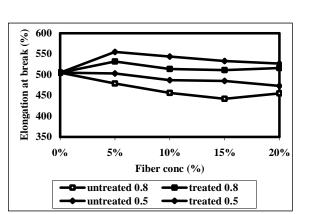


Fig. (4): Effect of fiber loading on elongation at break of NR

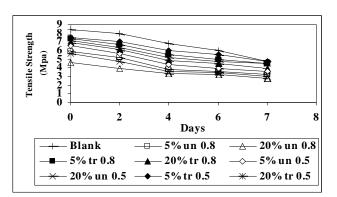


Fig. (5): Effect of fiber loading on the tensile strength of NBR vulcanizates after thermal aging for 7days

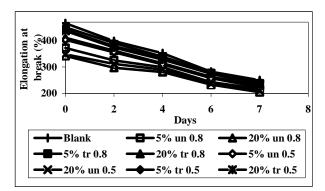


Fig. (6): Effect of fiber loading on the elongation at break of NBR vulcanizates after thermal aging for 7days

## 4.5. Effect of thermal oxidative aging of loaded NR vulcanizates with unmodified and modified linen fiber waste on the physico-mechanical properties.

The NR vulcanizates containing different concentrations (low concentration 5% and high concentration 20%) of unmodified and modified linen fiber waste with different fiber lengths (0.5 and 0.8 mm) were subjected to thermal oxidative aging in well ventilated oven at  $100^{\circ}$ C for different periods up to 7 daysWe can conclude that the modification of the linen fiber waste increases its resistance to thermal oxidative aging of rubber vulcanizates.

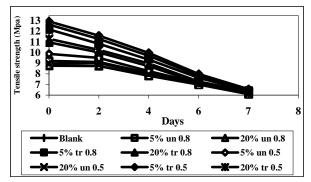


Fig. (7): Effect of fiber loading on the tensile strength of NR vulcanizates after thermal aging for 7day

Figures (7 and 8) represent the effect of thermal oxidative aging on the physico-mechanical properties of the aged vulcanizates. The NR vulcanizates loaded with unmodified and modified of 5% linen fiber waste with 0.5 mm fiber length showed increasing in the tensile strength and elongation at break during aging periods with respect to the blank and the other vulcanizates. The figures showed that the physico-mechanical properties of the loaded NR vulcanizates with unmodified and modified linen fiber waste decreased in the same trend of the blank. Also, it is noticed that the NR vulcanizates affected with thermal oxidative aging more than NBR vulcanizates.

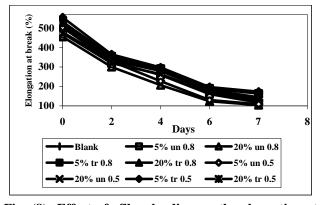


Fig. (8): Effect of fiber loading on the elongation at break of NR vulcanizates after thermal aging for 7days

4.6. Effect of swelling in toluene on loaded NBR and NR vulcanizates with unmodified and modified linen fiber waste.

The test specimen subjected to swelling in toluene at room temperature for 24 hours. The resulting deterioration is determined by measuring the changes in mass, before and after immersion in toluene.

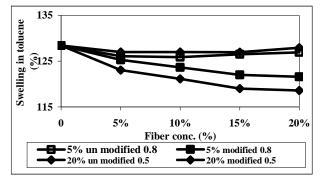


Fig. (9): Effect of fiber loading on the Swelling in toluene of NBR vulcanizates for 24 hours

It is clear from Figures (9 and 10) that the modified linen fiber wastes with fiber length (0.5 and 0.8) increase the resistance of the NBR and NR vulcanizates to swelling in toluene. This may be due to the increasing of polarity by acetylation to the fiber. But it is noticed that the 0.5 mm fiber length increases the resistance more than 0.8 mm fiber length.

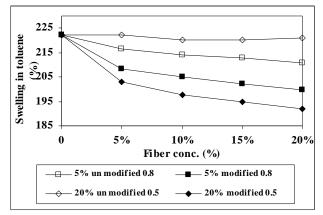


Fig. (10): Effect of fiber loading on the swelling in toluene of NR vulcanizates for 24 hours

### 4.7. Effect of swelling properties in motor oil on loaded NBR and NR vulcanizates with unmodified and modified linen fiber waste.

Oil resistance is the most important property of NBR rubber, thus, it is interesting to study the effect of the investigated unmodified and modified linen fiber waste on the oil resistance of NBR and NR vulcanizates. The prepared samples were immersed in motor oil at 100 °C for different time periods up to 7 days, and the swelling percent was measured and represented in Figures (11 and 12). The obtained data indicated that the addition of the prepared polar modified linen fiber waste to rubber increase the degree of resistance to attack by oil at normal and elevated temperature as expected.

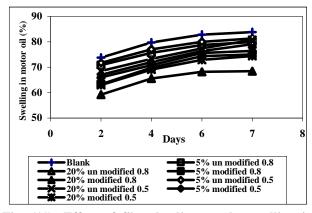


Fig. (11): Effect of fiber loading on the swelling in motor oil of NBR vulcanizates after thermal aging for 7days

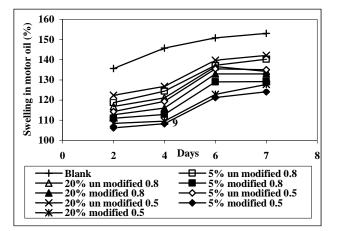


Fig. (12): Effect of fiber loading on the swelling in motor oil of NR vulcanizates after thermal aging for 7days

The above results give the indication that the fiber length affect on the degree of swelling of the NBR and NR vulcanizates as well as the modification of the fiber where the increase in the fiber length increase the oil resistance of the vulcanizates.

## 4.8. Effect of swelling properties in water on loaded NBR and NR vulcanizates with unmodified and modified linen fiber waste.

The penetration of water into rubber is very slow compared with most organic liquids. The loaded fiber may be swelled with water due to their cellular structure. The following tests compare the effect of the modification of linen fiber waste, the fiber length and the concentration of the fiber on the swelling in water.

Figures (13 and 14) represent the effect of the modification of linen fiber waste on the swelling in water of NBR and NR vulcanizates. It is clear from the following figures that the NBR and NR vulcanizates loaded with modified linen fiber waste decrease the swelling in water more than the unmodified especially with fiber length 0.5, while the rubber vulcanizates loaded with unmodified fiber had the highest swelling in water. Also, it is clear from this figure that the swelling in water increase with increasing the concentration of the unmodified and modified fiber. It is noticed that the swelling value of the NR vulcanizates is higher than the swelling value of NBR and the maximum swelling of the loaded NR vulcanizates is lesser than the NBR. This may be due to polarity of the NBR which decrease the swelling properties in water of the vulcanizates.

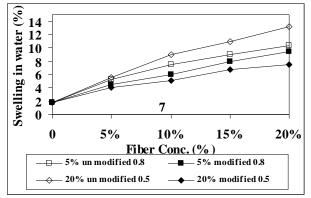


Fig. (13): Effect of fiber loading on the swelling in water of NBR vulcanizates for 24 hours

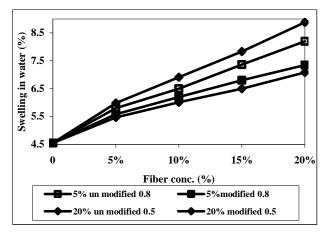
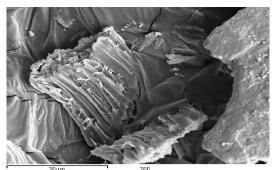


Fig. (14): Effect of fiber loading on the swelling in water of NR vulcanizates for24 hours

#### 4.9. Morphology of blends Using SEM

Scanning electron microscopy (SEM) is a common method to study the surface texture of rubber vulcanizates to show the relation between linen fiber waste and the rubber matrix. Figure (15) shows the (SEM) of the surface topology of unmodified and modified linen fiber waste. The surface topology of unmodified fiber waste shows an uneven surface due to waxy cellular structure of the fiber. The changes in surface topology of modified linen fiber waste are shown in the figure where the acetylation modification decreased the fiber surface and filled the cellular structure of the fiber. This modification enhances the dispersibility of the fiber in the rubber matrix, and increases the compatibility between the fiber and rubber matrix. It is clear that the cellular structure of the fiber which refilled with acetyl group increases the polarity of the fiber and decreases the voids inside the fiber. This may promote the good mechanical and swelling properties of the linen fiber waste of modified fiber with respect to the unmodified fiber.



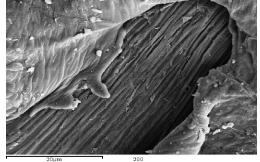
NR unmodified linen fiber waste



NBR unmodified linen fiber waste



NR modified linen fiber waste



NBR modified linen fiber waste

Fig. (15): The SEM of the surface topology of unmodified and modified linen fiber waste

#### 5. Conclusions:

Linen fiber waste is a big problem in flax textile industries. To get rid of linen fiber waste it can be used as filler in rubber. The acetylation modification of linen fiber waste improved its dispersibility in the both polar (NBR) and non polar (NR) rubber matrix. The modified linen fiber waste improved the physico-mechanical properties of natural rubber and acrylo-nitrile rubber vulcanizates with respect to the unmodified one. The effect of modified fiber content on the physico-mechanical properties of the natural rubber (NR) and acrylo-nitrile rubber (NBR) vulcanizates show good properties before and after aging with respect to the unmodified linen fiber waste. The modified linen fiber waste improved swelling properties of the investigated vulcanizates in both of toluene and motor oil, as well as distilled water. Scanning the surface topology of unmodified linen fiber waste with (SEM) shows an uneven surface due to waxy cellular structure of the fiber as well as filling the cellular structure of the modified linen fiber waste.

#### **Corresponding author**

A. I. Hussain Polymers and Pigments Department, National Research Center, Cairo, Egypt E-mail: ismaelahmed1@yahoo.com

#### 6. References

- M. Abdelmouleh, S. Boufi, M.N. Belgacem, A. Dufresne; "Short natural-fibre reinforced polyethylene and natural rubber composites: Effect of silane coupling agents and fibers loading"; Composites Science and Technology, 67, 1627–1639 (2007).
- M. Jacob, S. Thomas, K.T. Varughese; "Mechanical properties of sisal/oil palm hybrid fiber reinforced natural rubber compoites"; Composites Science and Technology, 64, 955–965 (2004).
- Hussain, S. H. El-Sabbagh and I. F. Abadir, "Cement Dust as Filler in NBR Vulcanizates"; J, of Elastomers and Plastics Vol. 35, April (2003).
- 4. H. Ismail, Salmah, M. Nasir; "Dynamic vulcanization of rubber wood-filled

polypropylene/natural rubber blends"; Polymer Testing, 20, 819–823 (2001).

- 5. Hussain and E. A. Abd- El-aal. "Modification of castor oil by isomerization, halogenation and application of some modified products as plasticizer in nitrile rubber formulations"; Journal of Scientific & industrial Research, 60, 383-395(2001).
- S. H. El-Sabbagh; A. I. Hussain and M. A. Abd El-Ghaffar; "Utilization of Maleic Anhydride and Epoxidized Soyabean Oil as Compatibilizers for NBR/EPDM Blends Reinforced with Modified and Unmodified Polypropylene Fibers"; Pigment & Resin Technology, Vol. 34, r 4, PP. 203 – 217 (2005).
- S, Varghese, B. Kuriakose, S. Thomas, A.T. Koshy; "Mechanical and viscoelastic properties of short fiber reinforced natural rubber composites: effects of interfacial adhesion, fiber loading and orientation:; J Adhes Sci Technol;8:235–48, (1994).
- 8. A.Y. Coran, P. I. Hamed, R. B. Seymour, "Additives for plastics", vol. 1. New York, Academic Press; (1978).
- S. Luyt; "Editorial corner a personal view Natural fiber reinforced polymer composites –are short natural fibres really reinforcements or just fillers", EXPRESS Polymer Letters Vol.3, No.6,332, (2009)
- A.A.Ibrahim, F.M.Mobarak and A.H.Abdel-Kader Preparation of fibrous agricultural residues" 7<sup>th</sup> Arab International Conference on Polymer Science & Technology 2005.
- V.G. Geethammaa, G. Kalaprasadb, G. Groeninckxc, S. Thomasd; "Dynamic mechanical behavior of short coir fiber reinforced natural rubber composites"; Composites, Part A 36, 1499–1506 (2005).
- M. J. John, B. F., K.T. Varughese, S. Thomas; "Effect of chemical modification on properties of hybrid fiber biocomposites"; Composites, Part A 39, 352–363 (2008)
- W Zhang, X Zhang, M Liang, C Lu; "Mechano-chemical preparation of surface-acetylated cellulose powder to enhance mechanical properties of cellulose-filler-reinforced NR vulcanizates"; Composites Science and Technology 68, 2479–2484 (2008).
- 14. ASTM D 3182 1989 (2001)
- 15. ASTM D 2084 (2001)
- Y. Fahmy and S. El-kalyoubi.; "Acetylation of paper bulb"; Cellulose Chemical Technology, 613 (1970).

- 17. R. H. Wistler, "Mehods in Carbohydrate Chemistry", Academic Press, Vol. III, Cellulose, New york and London 202, (1963).
- 18. ASTM D-2084-(2001)
- 19. ASTM D 412-(1998)
- Abeer S.A. Reffaee, D.E. El Nashar, S.L. Abd-El-Messieh, K.N. Abd-El Nour; "Electrical and mechanical properties of acrylonitrile rubber and linear low density polyethylene composites in the vicinity of the percolation threshold"; Materials & Design, Volume 30, Issue 9, Pages 3760-3769, October (2009).
- 21. ASTM D 471 (1998)
- 22. ASTM-D573 (1952)
- 23. Genung H. B.; "Interlaboratory Study on Determination of Acetyl in Cellulose Acetate"; Analytical chemistry .24, 400, (1952).

5/5/2010