INTRODUCTION

It is a matter of fact that the synthetic polymers are affected by the outdoor weathering conditions and this applies, of course, to the materials of nets and ropes used in the marine environmental techniques [Klust, (1983) and Himmelfarb, (1956)]. The materials of such nets or ropes are usually exposed for extended periods to weathering. This occurs for instance, when they are stored on the deck without any cover or protection. Some stationary fishing nets may stay for weeks or even months above or closely below the water surface.

The term weathering includes rain, air pollution, oxygen, humidity, wind, temperature, dirt setting on the ropes and Solar radiation. The last one has the strongest effect. The strong effect of solar radiation on the synthetic polymers is due to the photochemical degradation which results from the exposure of such materials to sunlight.

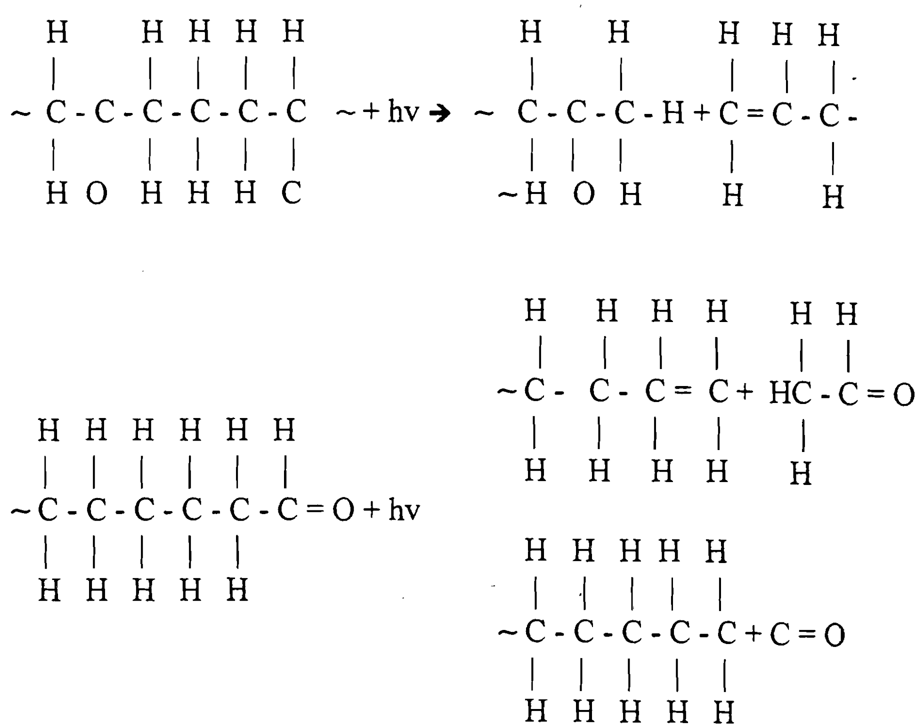
Solar or ultraviolet light as a degradative for polymers :

Vankrelen (1972) stated that, of the electromagnetic energy emitted by the sun, a small portion reaches the earth's surface, namely, rays with a wave - length above 290 nm. On the other hand , x-ray is absorbed in the out most part of the atmosphere. Ultraviolet rays with waves, length up to 290 nm is absorbed also by ozone in the stratosphere. Although the total intensity of radiation is subject to wide variations according to geographical and atmospheric conditions, the overall composition of sunlight is practically constant .

Calvert and Pitts (1965), pointed out that, in the photochemical degradation of a polymer, the energy of activation is supplied by sunlight . Most ordinary chemical reactions involve energies of activation ranging from 15 to 65 k cal/mol. This is energetically equivalent to radiation of wave length between 1900 and 440 nm.. The energies required to break single covalent bonds ranges, with few exceptions, from 40 to 100 k cal/mol, which corresponds to radiation of wave lengths from 710 to 290 nm . This means that the radiation in the near ultraviolet region (300-400 nm) is sufficiently energetic to break most single covalent bonds, except strong bonds such as C-H and O-H .

Seymour (1971) pointed out that sufficient radiation in the 280 to 400 nm range reaches the earth from outer space and affects many organic compounds, specially their physical characteristics. This ultraviolet radiation, in some cases causes yellowing and embrittlement of many organic polymers. The energy in the 280 to 400 nm range (100 to 72 k cal) is sufficient to cleave covalent bonds .

Burguss (1953) concluded that, trace impurities present in commercial polymers may catalyze their photochemical degradation. Such degradation process is related also to the polymer structure. Linear polymers are more resistant than branched chains and the rate of deterioration is proportional to the surface area exposed. Gray and Wright (1965) postulated that the concentration of some carbonyl groups decreases during the ultraviolet irradiation of polymers. Volatile degradation products such as carbon monoxide, water, aldehydes and ketones are also formed. Decomposition of linear polymeric hydrocarbon starts with the carbonyl group as shown by the following equations:



Heskins and Guillet (1968), showed that ultraviolet stabilizers such as 2,4-hydroxy benzophenone absorb energy in the 300 to 400 nm range and or chelates in which the energy is distributed in the system .

Klust (1983) , indicated that, in order to test the resistance of polymers against ultraviolet radiation, the tested material is to be exposed to an artificial light source such as carbon light, the radiation of which contains a high component of ultraviolet . The extent of degradation of a rope sample is usually measured by the loss in its breaking strength .

It is aimed in the present investigation to study the degradation effects of ultraviolet irradiation on the strength and elongation of both mono and multifilament polyamide twines used in the Egyptian marine environmental techniques .

MATERIAL AND METHODS

Monofilament and multifilament polyamide twines, which are commonly used in many techniques in the marine environment of Egypt have been used as test material in the present investigation. The diameter of the tested monofilament materials ranged between 0.12 and 0.50 mm. Denier system was used to describe the linear density of the multifilament materials tested. According to this international system, the linear density of the single yarn is given as the weight (in gm) of 9000 m length of this yarn. The denier of the tested twines ranged between Td 210/2 and Td 210/18.

Irradiation of the tested materials was carried out by the use of Analytical ultraviolet radiation lamp Type VP-60. The lamp power rating is 180 watt, and the steady radiator current is 1.85 Amp. The material was exposed to the ultraviolet light by fixing them at 20 cm distance from the lamp. Ultraviolet filter was placed between the lamp and the irradiated material.

Breaking strength and elongation were measured by Instron Table Model - M tensile strength testing machine. Twenty specimens were tested in each case . The distance between the two clamps of the machine was 50 cm . A research microscope and an eye piece micrometer were used to measure the diameters of the tested twines.

RESULTS AND DISCUSSION

The extent of photochemical degradation of a twine or rope material is usually indicated by the loss in its breaking strength . Some other properties such as elongation or abrasion resistance are expected to decrease as a result of such degradation .

Because of the variations in the strength (intensity) and duration of sun radiation in many tropical or subtropical areas the resistance of rope materials to solar radiation may take an important consideration in the selection of ropes in such areas .

However, the tensile strength of the ropes or nets used in any marine or naval technique is considered to be one of the most important property of such nets or ropes. To achieve high efficiency through out its operation in the marine techniques, the twine strength must be higher than the forces that may be expected to act on it while carrying out these operations .

Table (1) gives the breaking strengths of monofilament polyamide twines of different diameters prior and post exposure to ultraviolet light irradiation. The irradiation of these twines have been carried out for various periods. The shortest was 25 and the longest was 500 hours. Graphical representation of such data is shown in Fig. (1). As indicated from these data the most affected material by the ultraviolet irradiation was the thinnest (0.12 mm diameter) twin. About 50% of its strength was lost after 100 hours of irradiation. Another 20% of the strength were lost on further exposure to ultraviolet light to 400 hours . However the breaking strength of such a twine material decreased from 0.67 kg (as initial breaking strength) to 0.200 kg, which represents only about 30% of its initial strength at the end of the irradiation period of 500 hours.

The second highly affected twine was that having 0.15 mm diameter. The breaking strength of this twine decreased from 1.20 kg to 0.90 kg. The percentage loss in the tensile strength of such twine was only 25% of the original as a result of its exposure to ultraviolet light for a period of 500 hours.

The percentage loss in the tensile strength of the other thicker twines when exposed for 500 hours ranged from 10.2% to 20.9% with the exception of the thickest one (0.50 mm in diameter) which lost only 6.4% of its initial strength as a result of 500 hours irradiation.

Table (1): Breaking strength (kg) of various polyamide monofilament twines after different periods of ultraviolet light irradiation.

Twin diameter (mm)	*Breaking strength after various periods of irradiation*							
	Initial	*25*	*50*	*75*	*100*	*125*	*175*	*500*
0.12	0.67 (100)	0.66 (98.5)	0.50 (74.6)	0.36 (53.7)	0.34 (50.7)	0.30 (44.7)	0.30 (44.7)	0.20 (29.9)
0.15	1.20 (100)	1.20 (100)	1.18 (98.3)	1.12 (93.3)	1.20 (100)	1.03 (85.8)	1.20 (100)	0.90 (75.0)
0.20	1.32 (100)	1.24 (93.9)	1.20 (90.9)	1.14 (86.4)	1.14 (86.4)	1.20 (90.9)	1.20 (90.9)	1.10 (83.3)
0.30	2.78 (100)	2.54 (91.4)	2.50 (89.9)	2.63 (94.6)	2.50 (89.9)	2.51 (90.3)	2.20 (79.1)	2.20 (79.1)
0.35	3.30 (100)	3.10 (93.9)	3.20 (97.0)	2.90 (87.9)	2.75 (83.3)	3.10 (93.9)	2.66 (80.6)	2.70 (81.8)
0.50	6.65 (100)	6.38 (95.9)	6.60 (99.2)	6.60 (99.2)	6.62 (99.5)	6.15 (92.3)	6.05 (91.0)	6.23 (93.6)

(percentages retained strengths are given between brackets)

This may lead us to confirm that thicker twines are more resistant to photochemical degradation than thinner twines when subjected to solar or ultraviolet light irradiation.

In this concern, it has been pointed out by Klust (1983) that, in thinner ropes a higher percentage of the fibers can be affected than in thicker ropes. The effect of sunlight or ultraviolet irradiation on very thick ropes can therefore be in most cases negligible. This is due to the fact that the particularly aggressive ultraviolet radiation component penetrates for only about 1 mm under the surface of the twine.

As for the effect of ultraviolet radiation on the elongation of the polyamide monofilament twines, table (2) shows the total elongation of irradiation twines having different diameters after exposure for various periods of time ranging from 25 to 500 hours.

Table (2):Total elongation percentages of various monofilament polyamide twines after different periods of ultraviolet light irradiation.

Twin diameter	*Breaking strength after various periods of irradiation*							
(mm)	*Initial*	*25*	*50*	*75*	*100*	*125*	*175*	*500*
0.12	16.5 (100)	11.3 (68.5)	8.6 (52.1)	9.7 (58.8)	8.8 (53.3)	9.5 (57.6)	10.8 (65.5)	8.7 (52.7)
0.15	25.3 (100)	20.3 (80.2)	21.6 (85.4)	21.4 (84.6)	20.7 (81.8)	22.0 (86.9)	23.7 (93.7)	21.5 (85.0)
0.20	23.0 (100)	20.3 (88.2)	22.7 (98.7)	21.5 (93.5)	22.0 (95.7)	23.0 (100)	23.0 (100)	21.4 (93.0)
0.30	35.0 (100)	28.7 (82.0)	23.3 (66.7)	31.5 (90.0)	33.2 (94.8)	35.0 (100)	17.3 (74.6)	16.2 (69.8)
0.35	23.2 (100)	22.5 (97.0)	18.5 (79.7)	18.2 (78.4)	15.8 (68.1)	18.5 (79.7)	17.3 (74.6)	16.2 (69.8)
0.50	36.8 (100)	29.5 (80.2)	28.5 (77.4)	30.2 (82.1)	27.8 (75.5)	27.0 (73.4)	25.6 (69.6)	25.0 (67.9)

(Percentages of retained elongation are given between brackets)

The data given in this table indicate that, in general, the elongation of the irradiated twines decreased as a result of the decrease in the tensile strength of these twines. The highly affected twine was the thinnest. The elongation of such a twine decreased from 16.5% to 8.7% as a result of its irradiation for 500 hours. On the other hand, the elongation of the thickest twine in the series decreased from 36.8% to 25% when irradiated for the same period of time. Graphical representation of such data is shown in Figure. (2).

The extent of photochemical degradation of the multifilament polyamide material was examined by subjecting two groups of this material to ultraviolet light. The time of exposure of the first group was 340 hours, while the second group was irradiated for 500 hours, table (3) shows the initial breaking strength of the tested material. The retained breaking strengths of this material after the two periods of ultraviolet exposure are also included. It can be indicated from the data given in this table that most of the twines tested lost about 50% or more of its initial strength as a result of their exposure to ultraviolet light for 340 hours. Further loss in the tensile strength occurred as a result of irradiation for a longer period (500 hours) as indicated in Figure (3). The decrease in the tensile

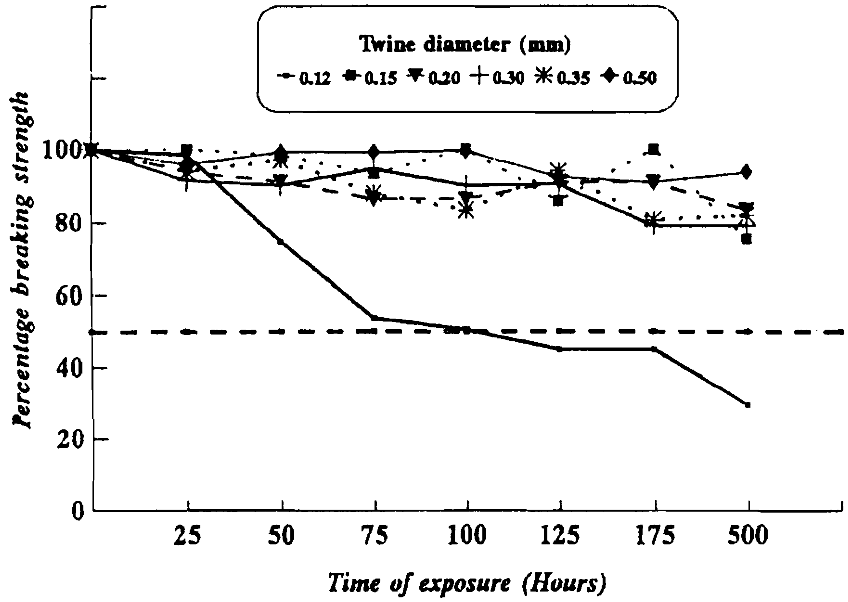


Fig. (1) : Percentage breaking strength of various nylon monofilament materials after exposure to ultraviolet light .

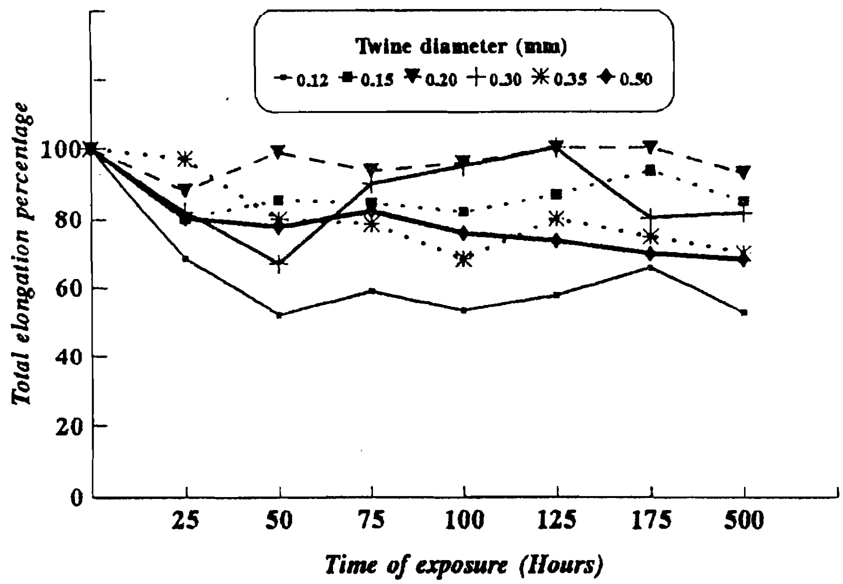


Fig. (2) : Total elongation percentages of various nylon monofilament materials after exposure to ultraviolet light .

strength of the multifilament twines ranged between about 70% to 80% of its initial strength due to its exposure to the ultraviolet light for 500 hours, as for effect on the elongation of the multifilament material tested when on exposure to ultraviolet light, table (3) shows that the elongation of these twines decreased by percentages ranging from 40% to 60% of their initial total elongation when, exposed for 340 hours . Further decrease in the elongation was observed by increasing the time of exposure to 500 hours as shown in Figure. (4) .

Table (3): Breaking strengths (kg) and total elongation of multifilament polyamide twines as s result of ultraviolet irradiation

Denker	***Twin***	***Initial***		***340 hours irradiation***		***500 hours irradiation***	
Td	***diameter (mm)***	***Breaking strength***	***elongation %***	***Breaking strength***	***elongation %***	***Breaking strength***	***elongation %***
210/2	0.24	2.07 (100)	18.0 (100)	1.20 (58.0)	11.0 (61.1)	0.51 (24.6)	7.0 (38.9)
210/3	0.30	3.30 (100)	22.0 (100)	1.50 (45.5)	10.0 (45.5)	0.62 (18.8)	8.0 (36.4)
210/4	0.33	3.80 (100)	22.0 (100)	1.65 (43.4)	9.5 (43.2)	0.90 (23.7)	6.0 (27.3)
210/6	0.40	5.30 (100)	22.7 (100)	2.60 (49.1)	9.5 (41.8)	1.43 (27.0)	6.5 (28.6)
210/9	0.50	9.50 (100)	21.5 (100)	4.15 (43.7)	9.0 (41.9)	2.50 (26.3)	8.0 (37.2)
210/12	0.60	9.90 (100)	17.8 (100)	4.30 (43.4)	12.0 (67.4)	3.10 (31.3)	8.0 (44.9)
210/18	0.75	16.70 (100)	18.5 (100)	5.40 (32.3)	12.5 (67.6)	4.18 (25.0)	10.5 (56.8)

(percentages retained strength and elongation are given between brackets).

Müller (1969) noted that the resistance against light may vary somewhat for the same type of fiber. It is interesting therefore to carry out a comparison between the recorded effects of ultraviolet light on the strength of both the mono and multifilament materials tested in the present study.

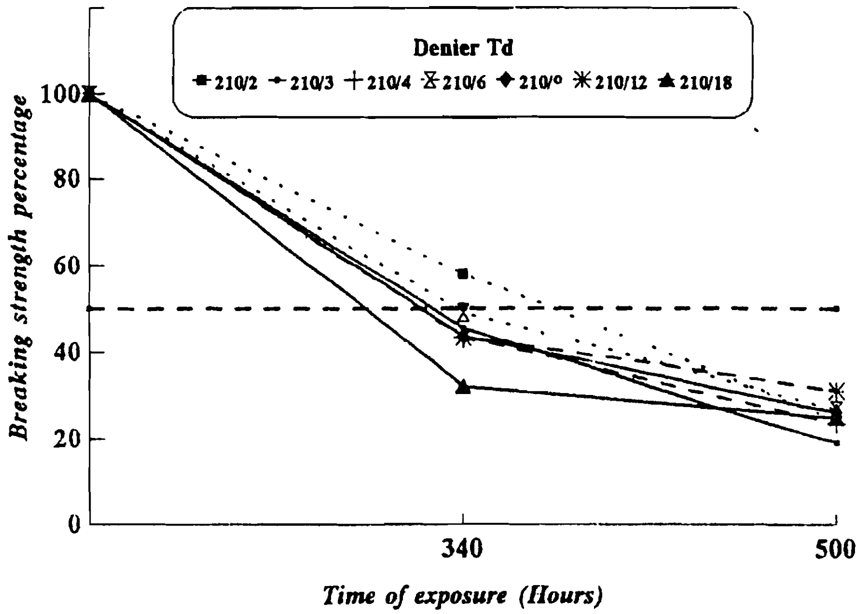


Fig. (3) : Breaking strength percentage of multifilament nylon materials after exposure to ultraviolet light .

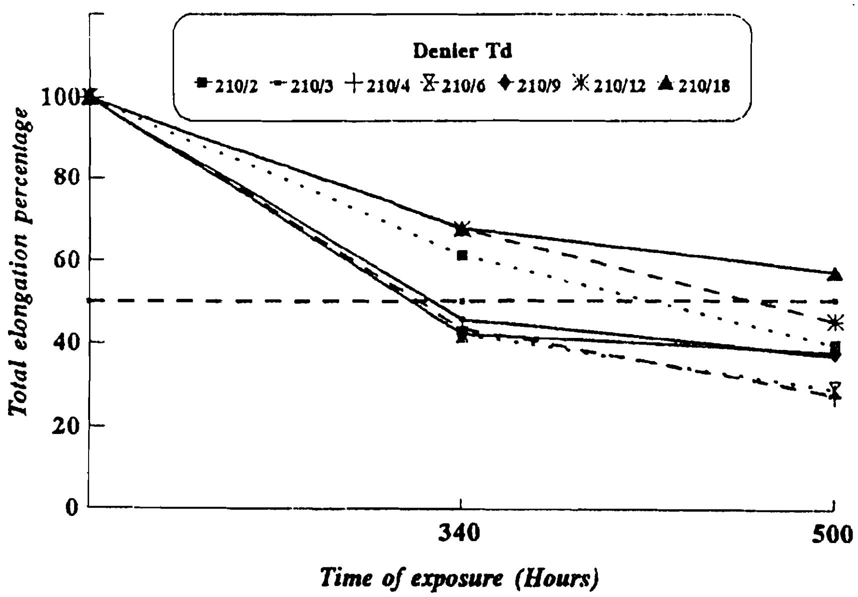


Fig. (4) : Total elongation percentage of multifilament nylon materials after exposure to ultraviolet light .

We conclude, from the previous data and discussions, that the degradation effect of ultraviolet light on the multifilament material was higher than its destructive effect on the monofilament material. In this concern it has been demonstrated by some authors (Gleistein, 1966; Hermann, 1967 and Himmelfarb, 1957) that while the polyamide monofilament material was highly resistant to ultraviolet light, the polyamide multifilament twines had medium resistance to this light. This agrees to a good extent with the data obtained in our study.

Klust (1983), pointed out that the destructive effect of ultraviolet light on synthetic polymers can be reduced by the incorporation of light stabilizers (anti-oxidant and ultraviolet absorbers) into the fibrous substance (polymer) and this treatment is now a common procedure .

However for all fibers types the protection by ultraviolet stabilizers can furtherly be increased by coloring or dyeing. Some synthetic fibers, such as polyamides can be dyed by common techniques either as rope yarns or finished ropes. The chemical industry provides a large choice of organic pigments in many colors and with different radiation protection properties. The best protection is obtained by adding soot to the fibers substance. This black pigment prevents the penetration of light into the fiber. This may be considered as an adequate treatment for the multifilament polyamide materials used in the marine environmental techniques. It is essential, otherwise, to protect the nets and ropes against sunlight, for instance by covering them while being stored for long periods vulnerable to sun light either on the deck or at the stores.

SUMMARY AND CONCLUSIONS

Synthetic polymers widely used for manufacturing nets and ropes that can be used for carrying out various techniques in the marine environment. The photochemical degradation effects of ultraviolet light on both the mono and multifilament polyamide twines have been studied in the present investigated. Loss in the breaking strengths as well as in total elongation of such twines as a result of exposure to ultraviolet light for various periods was considered as a good measure for such degradation.

The following conclusions could be achieved from the present study:

1- The tensile strength of all the twines tested decreased as a result of their exposure to ultraviolet light. The percentage loss in the strength increased by increasing the time of ultraviolet irradiation. This leads us to conclude that higher extent of digression had occurred.

2- The thinner twines of the monofilament material had been affected to a higher extent than the thicker twines. This is due to the idea that the twines diameter may be considered as a limiting factor for the extent of ultraviolet light penetration inside the twine material.

3- The total elongation of all the materials tested as a result of their exposure to the ultraviolet light.

4- The digression effect of the ultraviolet light irradiation was more obvious in case of the multifilament material if compared with its effect on the monofilament material. This could be indicated by the higher rates of decrease or loss in the breaking strengths of the multifilament twines.

5- It is recommended to treat the polyamide materials with light stabilizers to reduce the destructive effect of the ultraviolet light. Otherwise, it is necessary to protect such materials by covering them if left exposed to solar radiation while storing them for long period on the deck of the boats or in the stores.

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