MJPAS Vol. 1, No. 1 (2023) 40-53

Mustansiriyah Journal of Pure and Applied Sciences
https://mjpas.uomustansiriyah.edu.iq
Print ISSN: 2957-9910 Online ISSN: 2957-9929

Influence of Weathering on Physical Properties and Sun Light Transmitted through PMMA/ Safranin Films for Greenhouse Applications

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A B S T R A C T

The effect of weathering on physical properties of pure Poly methyl Methacrylate (PMMA) film and PMMA/ Safranin (S) films for Greenhouse applications has been studied. The solution casting method was used to prepare pure PMMA and PMMA/S films with dye solution (18ml), The concentration of Safranin solution was (1×10^{-4} mole/liter).

Weathering process will be done for these samples at different exposure sun light times (76, 152 and 228) h. Weathering affected on maximum absorption wavelength of Safranin to shift to lower wavelength (520nm) and decrease the absorbance. Also, the optical energy gap will decrease for pure PMMA from (5eV) to (4.8eV) and PMMA/S (18ml) from (5.02eV) to (4.82eV). FTIR results showed that there is no chemical interaction occurs between Safranin and PMMA Polymer, only physical interaction will be occurred. After weathering, the peaks in FTIR spectra shifted slightly and transmitted decreases with increasing the weathering time. These will confidently photostability of these films under weathering conditions and possibility to use them in greenhouse application. It can be concluded that the PMMA /S (18ml) film is better in green house applications in terms of absorption, energy gap and Sun light transmittance, where it is the highest possible transmitted from (10 A.M.) to (3 P.M.).

Keywords: *Safranin Dye, Polymethylmethacrylate, Weathering, Sun Light*.

1. Introduction

Polymer refers to a large molecule that contains a number of monomers are considered relatively modern materials. Polymer composites have recently piqued scientists' interest due to their numerous and extraordinary features, including ease of fabrication, weathering flexibility, light weight, and excellent optical and mechanical capabilities [1, 2]. Organic solar cells, thermal and photo solar collectors, and greenhouses are only a few examples of current polymer composite applications. An appropriate polymeric film for

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covering the greenhouse is required to create a good climate for greenhouse operations such as planting, drying vegetables and fruits, and desalination [3]. Poly (methyl methacrylate) (PMMA) is a transparent thermoplastic polymer made from the methyl methacrylate monomer. PMMA could be regarded a light alternative to glass because of its transparency, attractiveness, and scratch resistance. It's also known as acrylic glass [4]. PMMA polymeric composites are well-known for their utility in technical applications. PMMA is inherently transparent and colorless, with a high transmission of visible light [5].

Basic Red 2 (BR2), commonly known as Safranin-O, is an organic dye that belongs to the Quinone–Imine class. Natural plant pigments are used to make organic colors. This means they're constructed out of organic components like seeds, herbs, or other natural things. In histology and cytology, this dye is utilized. It's typically used to differentiate bacteria and make them more visible. For example, it's frequently employed as a metachromatic technique for yellow-staining cartilages. Even minor amounts of this dye in wastewater will have an impact on marine life [6, 7].

Ultraviolet radiation, UV light, is a type of electromagnetic radiation. It is accompanied by X-rays and Gamma rays and has a higher energy than visible light. UVA (320-400nm), UVB (280-320nm), and UVC (100-280nm) are the three types of UV radiation. Determining the intensity of UV radiation in relation to stratospheric ozone, clouds, altitude, and sun height (time of day and year), as well as reflection, is one of the most difficult parts of evaluating the effects of UV rays on polymers. The complexity of the effects might be rather significant. UV of any kind can cause a photochemical reaction within the polymer structure, which can be advantageous or detrimental to the substance [8].

One strategy to improve agricultural productivity is to employ greenhouses. Greenhouses use temperature and irrigation systems that are automatically controlled to allow farmers to grow vegetables and fruits all year. Greenhouses can help farmers increase yields and improve their livelihoods, as well as reduce spoilage and improve food security. Greenhouses reduce water losses in plants by up to 30% by minimizing evapotranspiration, as well as providing insect and weather protection [9].

The structure of the plastic alters with exposure to a range of mechanical and chemical weathering processes in the environment, making it simpler to break down into smaller and smaller particles. Furthermore, it is currently thought that chemical additives used in the manufacturing process are contributing to the build-up of chemicals in the environment. As a result, plastics and their degradation products may endanger the existence of organisms at all levels of the food chain. Despite this, plastics are thought to have a negligible environmental impact due to their huge molecular weight [10].

Many studies have looked at the physical properties of PMMA films and Safranin dye doped with PMMA or other types of polymers, with interested results and applications [11-15]. The aim of this research is to investigate the influence of weathering on optical properties and Fourier Transform Infrared (FTIR) spectra for pure PMMA and PMMA/ Safranin films. Also, measure the transmitted sun light from these samples after weathering.

2. Theoretical Part

As light passes from one medium to another (for example, from air to a solid substance), some of the energy is transmitted through the medium, some is absorbed and some is reflected at the interface between the two media.

The diminishing ratio of incident light energy in the length unit to wave propagation within the medium is the absorption coefficient, which changes with incident photon energy and is a property of certain materials. The photon is transmitted if the incident photon energy is less than the energy distance, and the thin film transmittance (T) is provided by the relationship [16].

$$T = (1-R)^2 e^{-\alpha x} \quad (1)$$

Where: R: Reflectance and x: Thin film thickness

In the fundamental absorption area, the absorption coefficient (α cm^{-1}) is calculated using Lambert's law [17]

$$I = I_{oe^{-\alpha x}} \quad (2)$$

Where (I_o) and (I) are the intensity of the incident and transmitted light, respectively.

If $\left(\frac{I}{I_o}\right) = T$ then,

$$\left(\frac{1}{T}\right) = e^{\alpha x} \quad (3)$$

So that $\ln(\frac{1}{T}) = \alpha x,\ 2.303 * \log_{10}(\frac{1}{T}) = \alpha x$ (4)

$$A = \log_{10}(\frac{1}{T}) \quad (5)$$

Where: A: Absorbance, So that the absorption coefficient written as [18]:

$$\alpha = \frac{(2.303 * A)}{x} \quad (6)$$

In the examination of optical characteristics, direct and indirect electronic transitions can be distinguished based on the lower position point in the conduction band and the upper position point in the valance band.

The prohibited energy gap (E_g) and the photon energy gap (hv) have a substantial relationship, as seen in the equation below [19, 20]:

$$\alpha h\nu = B(h\nu - E_g)^r \quad (7)$$

Where B: Constant depending on properties of conduction and valance bands, r: constant its value depends on the transition nature, where *r=1/2* for allowed direct transitions, *r=3/2* for forbidden direct transitions. For allowed and forbidden indirect transitions; *r= (2, 3*), respectively.

3. Experimental Work

Safranin dye made in the company (DC Panreac Quimica Company/ Barcelona Spain), and the chemical formula ($C_{20}H_{19}ClN_4$) with a molecular weight of (350.84 g/mole).

Because of its excellent optical qualities, the polymer poly methyl methacrylate (PMMA) has been chosen as the host material for Safranin. PMMA made in the company (Sabic) with the chemical formula $[C_5O_2H_8]_n$ and a molecular weight of (200000 g/mole).

The PMMA film was made by dissolving (0.3 g) of PMMA in (10 ml) of chloroform, and the method of preparation films was solution casting method [21]. The PMMA solution was aggressively shaken with a magnetic stirrer until the polymer was completely dissolved, then placed into a clean glass petri dish with a diameter (7 cm). Pure PMMA films were obtained after one day of drying at ambient temperature (20–23 ^{o}C). Safranin solution has a concentration of (1×10^{-4} mole/liter) and is made by dissolving a certain amount of dye powder (in g) in a given volume (V in ml) of Chloroform using the following equation (8) [22].

$$m = \frac{C \times V \times M_w}{1000} \quad (8)$$

S dye solution (18) ml was added to PMMA solution (0.3 g) using Chloroform (10 ml) to make PMMA/S films. The mixture was then vigorously agitated with a magnetic stirrer until the S/PMMA solution was homogeneous. Pour the solution into a clean glass petri dish and allow for one day at room temperature (20-23^{o}C) to obtain homogeneous films. The thickness of as-prepared films was measured using a digital micrometer with a measurement accuracy of (0.001 mm) over a range of (0-150 mm) (Type Tesha). Thickness of PMMA polymer films is about (0.049 mm) and PMMA/S film measuring around (0.0576 mm). Infrared spectroscopy (FTIR) of Fourier transformation was conducted for all films using (Bruker-Tensor 27 with ATR unit). The UV-Vis spectrophotometer (Type T70/T80) is a device that measures the absorption and transmission spectra in the wavelength range of (200-1100 nm).

The effect of weathering (exposure to sun light) on the prepared samples has been studied for the time period from 13/1/2021 to 16/1/2021 and for specific hours is (76h.). Direct Sun Light is characterized by very intensity.

Table 1. The temperature for (76h.)

Date	**Temperature(^{o}C)**											
	12A.M	2A.M	4A.M	6A.M	8A.M	10A.M	12P.M	2P.M	4P.M	6P.M	8P.M	10P.M
13/1/2021					12	16	19	21	21	19	18	16
14/1/2021	17	14	13	13	13	16	19	20	20	17	14	19
15/1/2021	13	10	9	9	12	15	19	21	21	17	15	14
16/1/2021	13	12	11	9	13	16	19					

The effect of weathering (exposure to sun light) on the prepared samples has been studied for the time period from 28/1/2021 to 31/1/2021 and for specific hours are (76h.). So the total time period (152 h.) for the same selected samples. The temperature recorded for these days as in Table (2).

Table (2) the temperature for (152h.)

Date	Temperature(^oC)											
	12A.M	2A.M	4A.M	6A.M	8A.M	10A.M	12P.M	2P.M	4P.M	6P.M	8P.M	10P.M
28/1/2021					9	15	20	22	19	18	15	10
29/1/2021	9	7	6	10	11	17	21	22	20	19	16	11
30/1/2021	10	7	8	9	12	18	20	23	20	18	17	12
31/1/2021	11	6	5	8	14	19	16					

Then, the effect of weathering (exposure to sun light) on the prepared samples has been studied for the time period from 27/2/2021 to 2/3/2021 and for specific hours are (76h.). So the total time period (228 h.) for the same selected samples The temperature recorded for these days as in Table (3).

Table (3) the temperature for (228 h.)

Date	Temperature (^oC)											
	12A.M	2A.M	4A.M	6A.M	8A.M	10A.M	12P.M	2P.M	4P.M	6P.M	8P.M	10P.M
27/2/2021					8	13	22	22	20	19	19	10
28/2/2021	10	9	9	9	13	18	21	23	23	20	18	17
1/3/2021	15	10	10	11	12	14	21	23	23	19	18	17
2/3/2021	10	9	10	11	12	16	23					

The illuminance of this light on surface of earth varies by season, time day, location and other parameters. So in this work, the location was specified in the Kut City, Wasit Governorate. The temperatures recorded for these days as in Table (3-1). The illuminance levels can be measure by lux light meter application on Huawei Mate 10 Lite. The transmitted intensity of Sun light through the films denoted by (symbol I) and the illuminance of Sun light denoted by (symbol I_o).

4. Results and Discussions

The absorption spectra of pure PMMA film before and after the weathering process for different weathering times illustrated in Figure (1). It is noticed that the maximum wavelength is located at (275 nm) and it remains constant throughout the weathering process.

While the absorbance increases after 152h. And it will be decreases after 228h. Exposure time, as seen in Table (4).

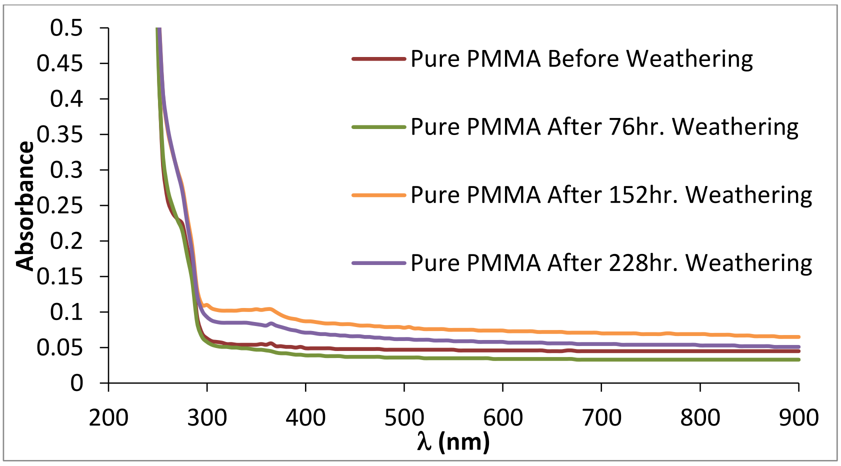

Figure 1. Absorption spectra of pure PMMA films before and after weathering for different exposure times .

Figure (2) shows the energy gap of pure PMMA films after the weathering process. It can be seen that the value of the energy gap decreased with the increase in the hours of the weathering process, as illustrated in Table (4).

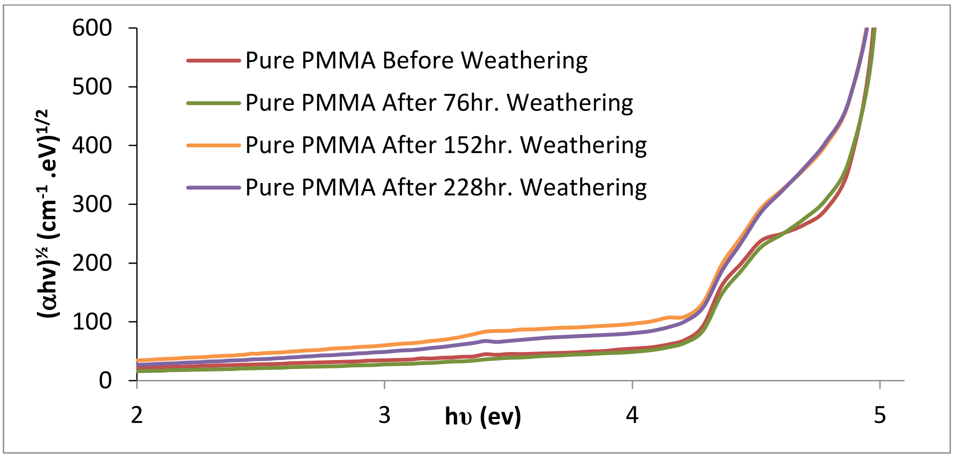

Figure 2. Optical energy gap of pure PMMA film after weathering for different exposure times.

Table 4. Absorption information of pure PMMA after weathering for different exposure times.

Exposure times	**Pure PMMA**		
	λ (nm)	**Abs.**	**E_g (eV)**
Before weathering	275	0.292	5
After (76h.) weathering	275	0.214	4.9
After (152h.) weathering	275	0.276	4.88
After (228h.) weathering	275	0.27	4.86

The absorption spectrum of PMMA/S (18ml) films after weathering demonstrated in Figure (3). Broadband absorption spectrum for Safranin dye before weathering exist, with a maximum wavelength at (530) nm and related intensity (0.472). The π-π* transition is "a type of electronic transition that is characteristic Safranin dye and associated to the charge transfer from the benzene cycle to the pianos moiety. This transition is related to an excitation from the LUMO (the lowest unoccupied molecular orbital) HOMO (the highest occupied molecular orbital) and the HOMO orbital, respectively [16]. After weathering, the maximum absorption wavelength for Safranin (S) dye shift to (520nm), i.e. blue shifting occurred. While absorbance decreases with increasing exposure times, this can be explained by the gradual disappearance of safranin dye from films. While the peaks of the polymer wavelength decreased to (270 nm) after the second period of the weathering process and then returned to decrease in the last period of the weathering process. As for the absorption spectrum, it decreased with the increase of the weathering process hours, except in the period of (152h.). The reason is due to the air temperature and humidity during that period.

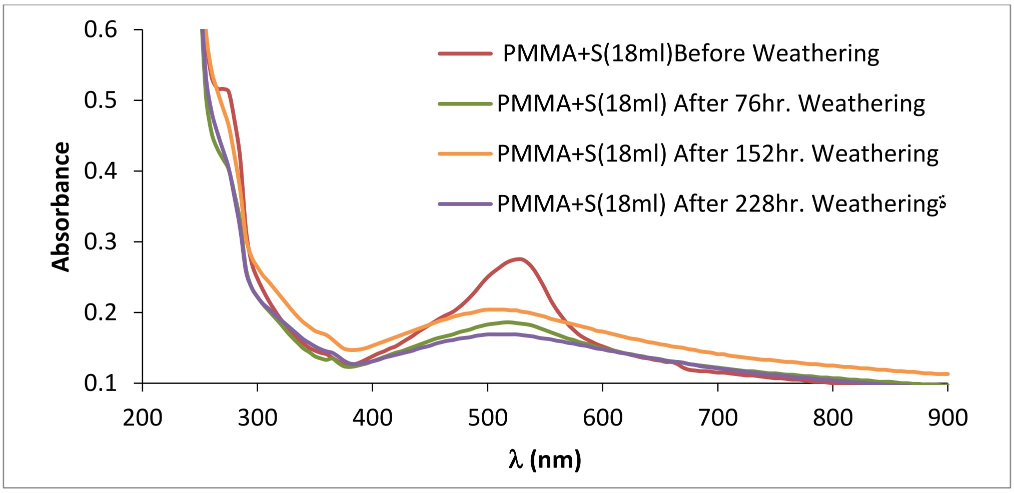

Figure 3. Absorption spectra of PMMA/S (18ml) films after weathering for different exposure times.

The variation of energy gap for PMMA/S(18ml) films after weathering illustrated in Figure (4), It can be seen that the value of the energy gap decreases with the increase in the hours of the weathering process. The Table (5) shows the difference between wavelength, absorption spectrum, and energy gap before and after the weathering process for different exposure times.

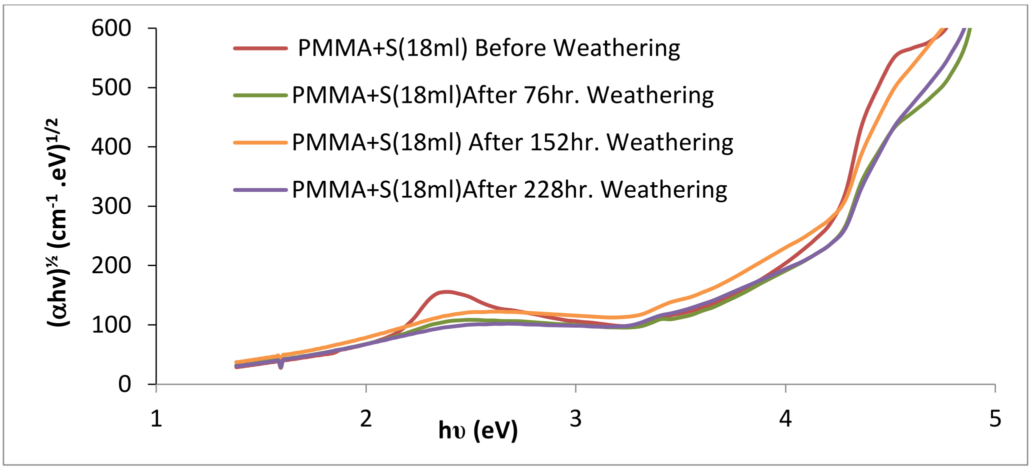

Figure 4. Optical energy gap of PMMA/S(18ml) films after weathering for different exposure times.

Table 5. Absorption information of pure PMMA and PMMA/S(18ml) films after weathering for different exposure times.

Exposure times	**PMMA**		**PMMA/S(18ml)**		
	λ (nm)	**Abs.**	**λ (nm)**	**Abs.**	**E_g (eV)**
Before weathering	275	0.472	530	0.275	5.02
After (76h.) weathering	270	0.43	520	0.186	4.88
After (152h.) weathering	275	0.464	520	0.203	4.84
After (228h.) weathering	270	0.43	520	0.169	4.82

The FTIR spectra of pure PMMA film is shown in Figure (5-A). The transmittance bands for this film have peaks corresponding to C–C appeared at 482.45cm^{-1} and 419.73cm^{-1}. The peaks 1143.36cm^{-1}, 964.72cm^{-1}, 840.74cm^{-1}, 748.71cm^{-1} and 667.39cm^{-1} correspond to the C–O. The peaks 1521.76cm^{-1}, 1435.06cm^{-1} and 1239.26cm^{-1} refers to C=C stretching. The peaks 1718.50cm^{-1} represent C=O bending. The transmittance around 2360.35cm^{-1} characterizes the asymmetric bending vibrations of C–H bond. The explanation of FTIR spectrum of PMMA film matched with Ref. [23].

FTIR spectrum of PMMA/S (18ml) demonstrated in Fiure (5-B). All peaks are in the same position with a slight offset in the vertices as in pure PMMA. With Safranin doping ratios, the transmittance increases. There is no chemical interaction occurs between Safranin and PMMA Polymer, only physical interaction will be occurred.

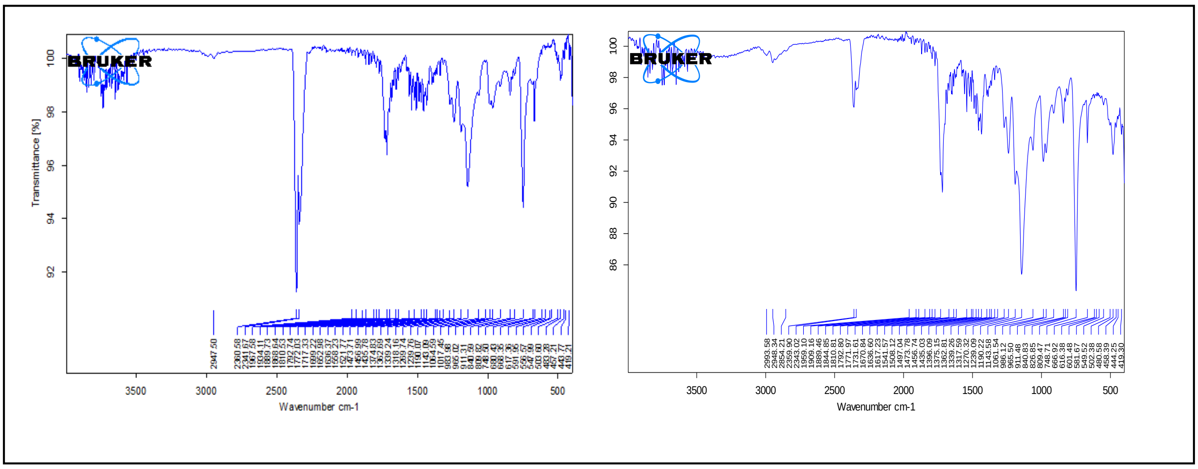

Figure 5. FTIR spectrum for A- pure PMMA film B- PMMA/S(18ml) before weathering

The FTIR spectra of pure PMMA film and PMMA/S (18ml) after 76h, 152h. and 228h. weathering exposure times illustrated in Figures (6 and 7), respectively. The data information for these samples investigated in Table (6).

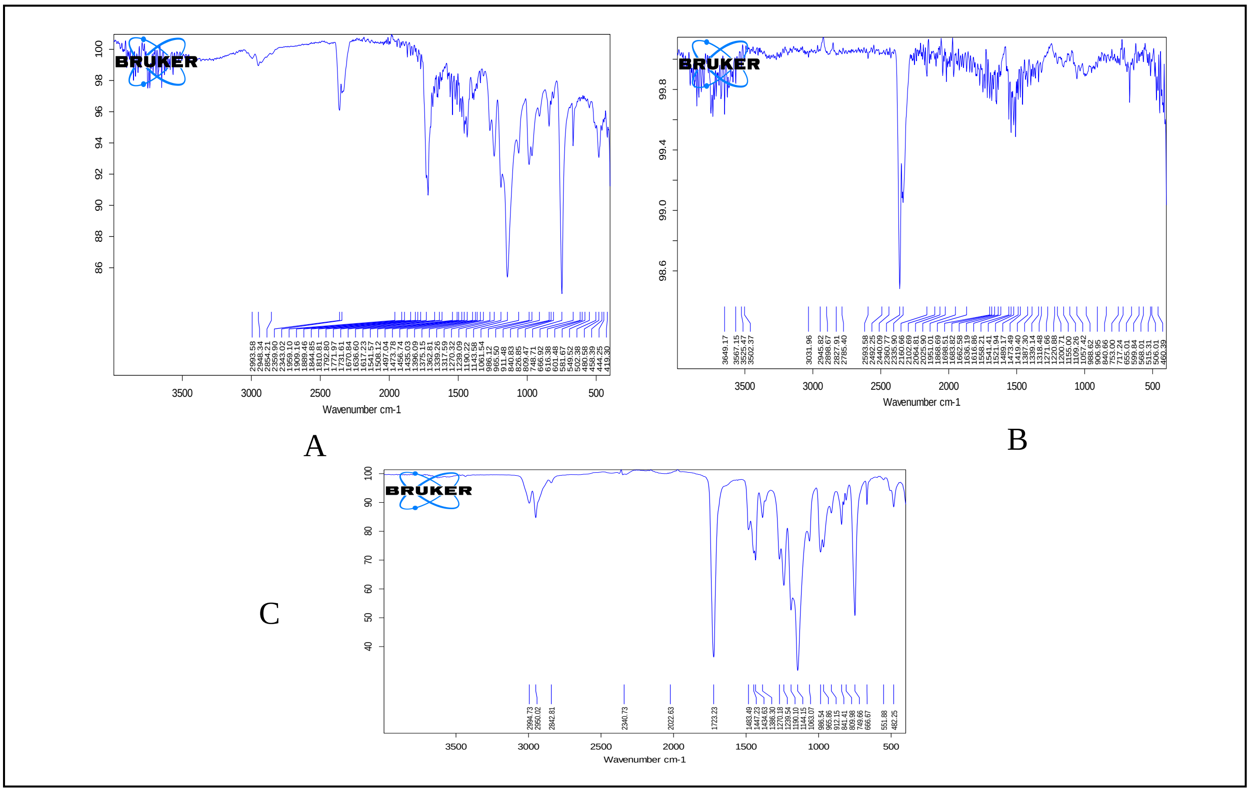

Figure (6) FTIR spectrum for pure PMMA film after weathering A- 76h. B- 152h. C- 228h.

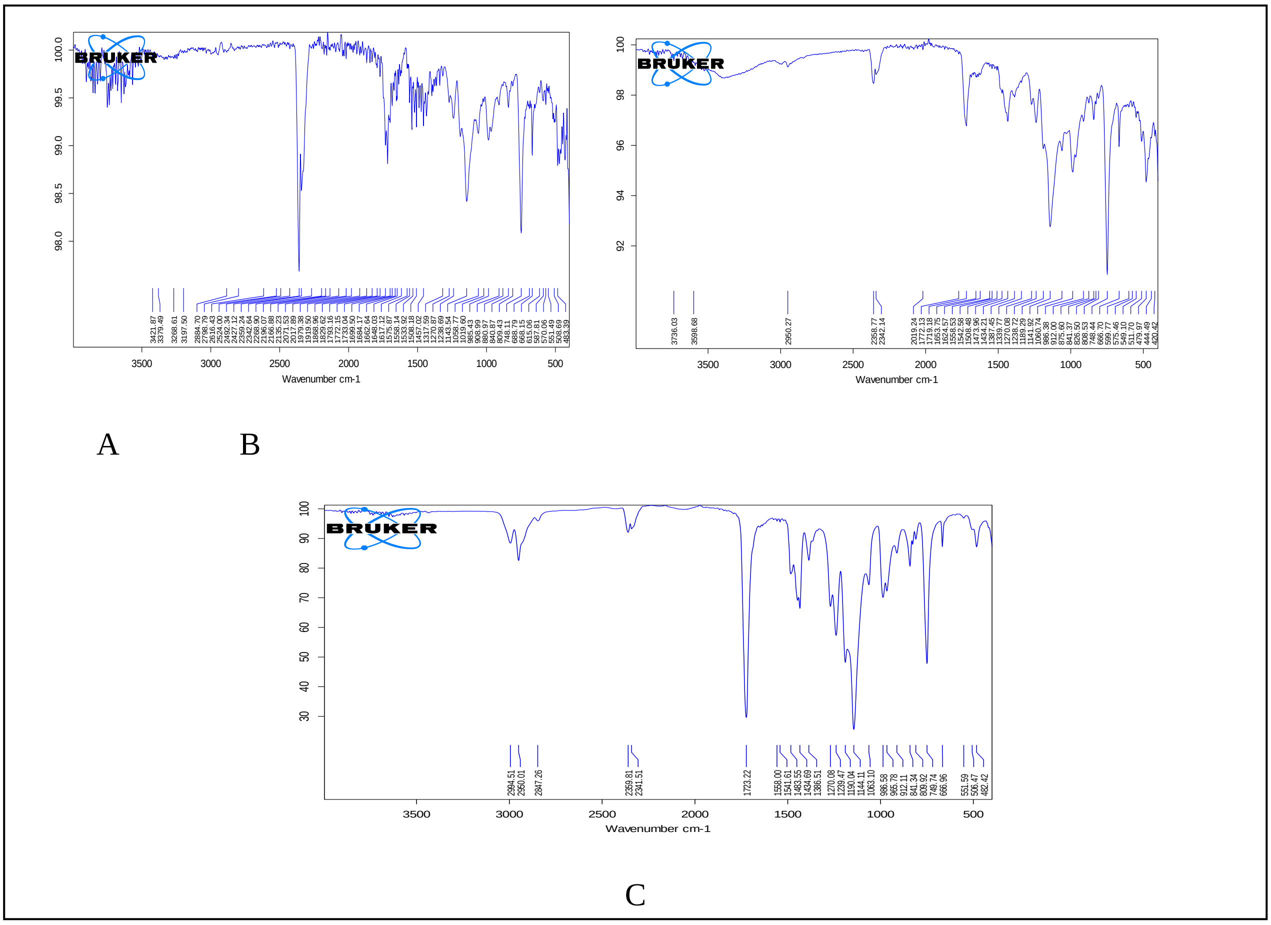

Figure 7. FTIR spectrum for PMMA/ S(18ml) film after weathering A- 76h. B- 152h. C-228h.

Table 6. FTIR characteristics of Pure PMMA and PMMA/S(18ml) films after different exposure times.

Bond	**Pure PMMA**				**PMMA/S(18ml)**			
	Room temperature	**76 h.**	**152 h.**	**228 h.**	**Room temperature**	**76 h.**	**152 h.**	**228 h.**
Out phase bend (400-650) cm^{-1}	482.45 419.73	502.38 419.30	460.39	482.25	457.21 419.21	479.97 420.42	483.39	482.42
C-O stretch(650-1200) cm^{-1}	1143.36 964.72 840.74 748.71 667.39	1143.58 986.12 840.83 748.71 666.92	655.01	1144.15 986.54 841.41 749.66 666.67	1143.09 965.02 840.59 748.50 668.35	1141.92 986.38 841.37 748.44 666.70	1143.54 985.43 748.11 668.15	1144.11 986.58 841.34 749.74 666.96
C=C bending (1200-1700) cm^{-1}	1521.76 1435.06 1239.26	1541.57 1456.74 1435.03 1239.09	1698.51 1662.58 1558.21 1521.94 1473.49	1434.64 1386.30 1239.54	1699.22 1521.77 1473.71 1435.78 1318.16	1434.21 1238.72	1699.50 1648.03 1533.92 1508.18 1457.02	1434.69 1386.51 1239.47

			1318.48 1057.42		1239.76		1270.87	
C=O stretch (1700-2000) cm^{-1}	1718.50	1731.61	………	1723.23	………..	1719.18	……….	1723.22
C-H stretch (2000-3100) cm^{-1}	2360.35	2359.90 2343.02	2360.77 2335.90 2160.66 2025.90	2994.73 2950.02	2360.58 2341.67	2358.77 2342.14	2359.24 2342.64 2017.89	2994.51 2950.01 2359.81
O-H stretch Aliphatic (3100-3600) cm^{-1}	…………	……….	3567.15	………	………….	……….	………	………
Low end stretch Aromatic (3600-4000) cm^{-1}	………….	……….	3649.17	……..	…………	………	………	………

The FTIR spectrum results show that the weathering process in different periods did not effect on the functional groups of PMMA and PMMA/S (18ml) films. The peaks in FTIR spectra shifted slightly and transmitted decreases with increasing the weathering time. This will confidently photostability of these films under weathering conditions and possibility to use them in greenhouse application.

The transmitted Sun light for pure PMMA and PMMA/S (18ml) films before and after weathering for different exposure times(76,152 and 228) h. for one day from 7 o'clock to 5 o'clock demonstrated Figures (8 and 9).

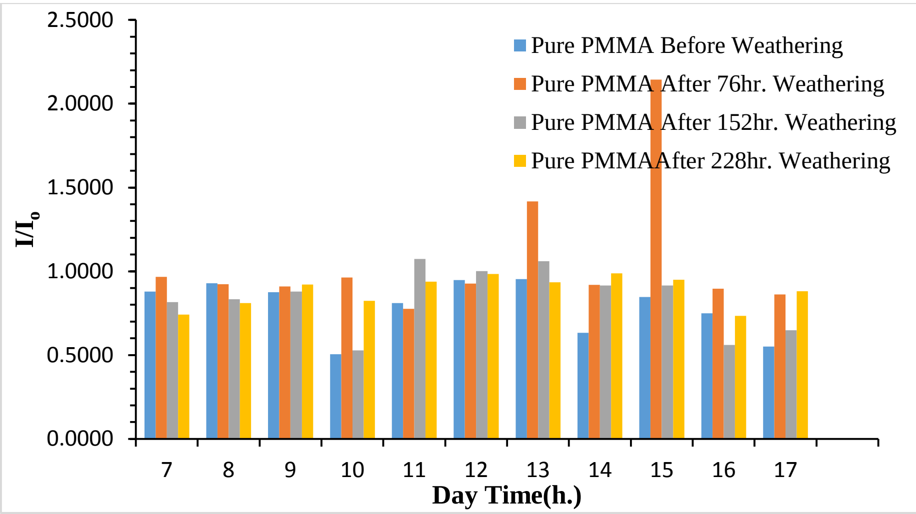

Figure 8. The ratio I/I_o for pure PMMA film after weathering for different exposure times.

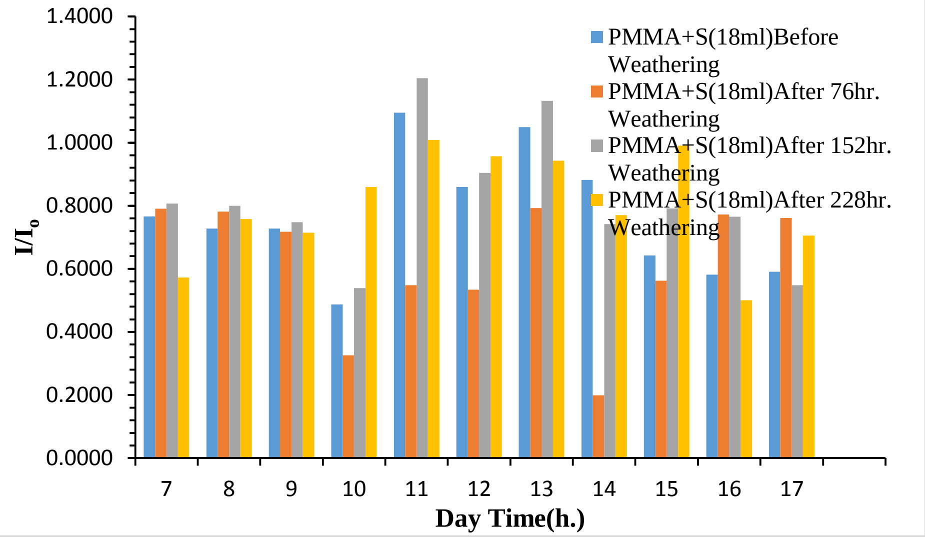

Figure 9. The ratio I/I_o for PMMA/S(18ml) films after weathering for different exposure times.

It can be concluded that the ratio of the transmitted radiation intensity to the intensity of the sun's radiation for PMMA/S(18ml) film after weathering raising as high as possible at (152h.) and then fell back at (228h.). This can be explained by the gradual disappearance of safranin dye. Through these figures, it can be concluded that the PMMA/S (18ml) film is better in green house applications in terms of absorption, energy gap and Sun light transmittance, where it is the highest possible transmitted from (10 A.M.) to (3 P.M.).

5. Conclusions

- Weathering affected the optical properties as it led to a decrease in the wavelength, energy gap and absorption spectrum with an increase in the times exposure of the weathering process.
- The PMMA/S (18ml) film is better in green house applications in terms of absorbance, energy gap and Sun light transmittance.

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