

Degradation of glass polymers due to successive exposure to acid rain and UV radiation

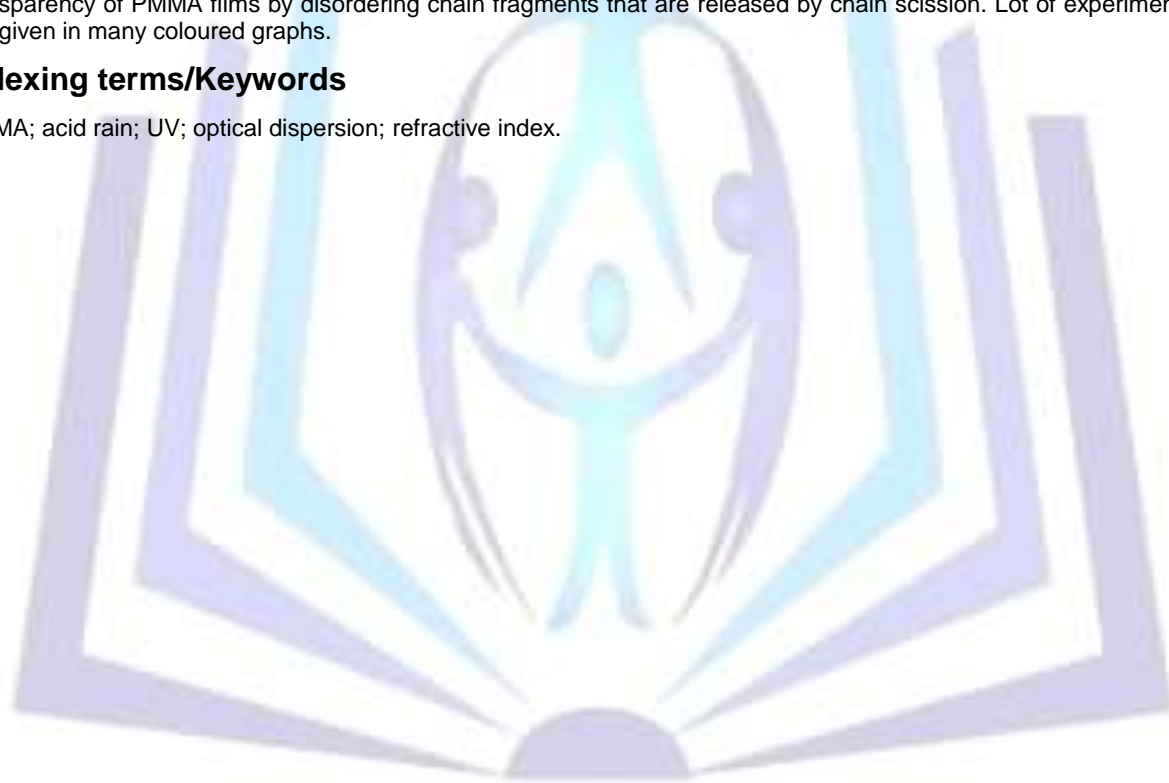
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ABSTRACT

Utilization of polymer products for outdoor applications is continuously increasing. So the stability of polymers against environmental degradation became top of interests for many researchers. The effect of environmental elements on the polymers stability has been studied, but individually. A solution against an environmental element may conflict with a solution against other element. Therefore current study aimed to clarify a sort of these conflicts. Polymethylmethacrylate (PMMA) films as example of glassy polymers are exposed to acid rains and Ultraviolet (UV) radiation in sequenced method for different time intervals. The effects on both structural and optical parameters are deduced from the measurements of Infrared spectra, X-ray diffraction charts, refractive indices and optical dispersion of samples before and after treatments. Chain scission is found to reduce the transparency of the samples. Acid rains are found to enhance the transparency of PMMA films by disordering chain fragments that are released by chain scission. Lot of experimental data are given in many coloured graphs.

Indexing terms/Keywords

PMMA; acid rain; UV; optical dispersion; refractive index.



Council for Innovative Research

Peer Review Research Publishing System

Journal: JOURNAL OF ADVANCES IN PHYSICS

Vol. 11, No. 2

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General view and objective

When sulphur dioxide and nitrogen oxides are emitted into the atmosphere, they come into contact with water where they are chemically converted to acidic compounds of sulphates and nitrates. These strong acids are deposited onto the earth's surface as rain, snow and fog and through dry deposition; the name "acid rain" is commonly used for describing this painful mechanism. Sulphur is released when fossil fuels are burned, mainly for electricity production and industrial processes. Oxides of nitrogen are released during burning of all fossil fuels too, including gasoline and diesel fuel, where the nitrogen in the fuel and atmosphere reacts with oxygen. Acid rain contaminates drinking water, damages buildings, by corroding cement, accelerates plastics degradation, and causes metals to rust.

Of the solar wavelengths, the UV-B component is particularly efficient in bringing about photo-damage in synthetic and naturally occurring materials. This is particularly true of plastics, rubber and wood used in the building and agricultural industries. Solar radiation spectrum ranges over 290-3000 nm and it consists of just less than 10% of UV radiation but it has sufficient energies to dissociate C-C or C-H bonds in polymer. The free radicals produced in this way may then react freely with the atmospheric oxygen and contribute to further degradation of the polymer, which is called photo-oxidation.

The outdoor service life of common plastic materials is limited by their withstanding solar ultraviolet radiation and other environmental conditions like the acid rain. Many researching efforts have been carried out for evaluating the serious effects of solar UV and acid rains individually, although both environmental elements are acting either simultaneously or successively. As a result, several protection solutions are proposed against each individual element regardless the efficiency of this protection solution in presence of the other element. In the current work, a polymer sample is exposed to acid rain and UV radiation in sequenced manner and the net effects were recorded and analysed. This work aims to present more information to increase the efficiency of polymers protection against all environmental conditions on time. Also this work shows practically the difference between the two suggested opinions for the mechanism of crossed effect by multiple environmental elements. First opinion is considered the acid rains and solar UV radiation as the two crossed action environmental elements. This opinion supposed that acid rain reacts and removes the present UV stabilizers from the sample's surface by etching, and hence UV radiation can penetrate to the polymer matrix and degrades it. This opinion is studied in details considering low density polyethylene (LDPE) films which used for greenhouses, samples loaded with all functional additives [1]. The second opinion is studied in the current work. This second opinion supposes that an environmental element may be a catalyst or activation agent for another environmental element. For example, polyethylene is insoluble in xylene solution at room temperature but its solubility is altered by the solar thermal power. Along this idea, films from polymethylmethacrylate (PMMA) have good resistance against diluted acids but if the PMMA samples are irradiated by the solar UV radiation before acid attack, the polymer chemical resistance may be altered. In the first example the solar thermal power is acted as activation agent, and in the second example UV radiation may do the same role.;

Introduction

Plastics have been employed in agriculture and building industry because of their unique properties in comparison with glass, like un-breakability, low price, transparency, flexibility and light weight. The degradation processes of the various types of polymer have specific mechanisms and depend on both the main macromolecular chain nature, structure and on the chemical nature of the branched groups. It is well known, for the oxidation of polyolefin's or rubber (natural and some synthetic types), that hydro-peroxides and the peroxy radicals are intermediates in a long kinetic chain mechanism. In the case of the halogenated polymers the de-hydro-halogenations is the first reaction step followed by the thermal oxidation, while for the polyamides or cellulose the oxidation occurs by hydro-peroxides within a short chain mechanism [2-8].

Despite the relatively low percentage of UV radiation present in the solar spectrum, this is a very damaging radiation for plastics because of the high quantum energy content. The bonds between the atoms in many plastics have dissociation energies that are very similar to the quantum energy present in UV radiation. UV radiation in the region of 300 to 400 nm is therefore capable of breaking the bonds in the plastic to cause rapid degradation of the basic structure of the plastic. For example the $\text{CH}_3 - \text{CH}_3$ molecule can be broken apart by UV radiation of wavelengths greater than 340 nm which contains sufficient energy to break the main bond. The most damaging UV wavelength for a specific plastic depends on the bonds present and the maximum degradation therefore occurs at different wavelengths for different types of plastics [9]. The degradation of polymethylmethacrylate, PMMA, has been studied for many years and it is well known that this material degrades by end chain scission and gives a very high yield of monomer (10). The details of the degradation have only recently been elucidated by Kashiwagi et al (11, 12). Kashiwagi has shown (66) that the degradation is initiated at end chain un-saturations, weak links, such as head-to-head linkages, and also by random scission.

Polymer degradation is a natural phenomenon that cannot be totally stopped. Instead, resin producers seek to stabilize the colour and physical properties of their polymers for a reasonable life span, which varies depending on the end user requirements. Auto-oxidation continues unless countermeasures are taken to halt the process. One way to terminate auto-oxidation is by adding various antioxidants to the resin. Antioxidants (A/O) are a class of chemicals with varying chemical compositions and methods of terminating auto-oxidation. The antioxidant chemicals are additives for specific operation; other additives are widely used for other polymer properties modifications. Additives such as heat stabilizers, light stabilizers, slip agents, plasticizers, and antioxidants represent some of the most common classes of compounds used to tailor polymer properties for specific applications. So, commercial final polymer products should contain some types of additives, these chemical additives may be reacting with some or all environmental elements. In this current work, homo-polymer (virgin PMMA) is used in order to exclude the probability of additives – acids reactions. So, one expects



serious photo degradation of PMMA samples by UV radiation. If other trend could be observed, this will be due to the action of another environmental catalyst.

Experimental measurements:

The materials used in this work are:

- Polymethylmethacrylate (PMMA) granules with ($M_w = 15,000$ from Himedia Chemical Co. RM 1746 – 250G)
- Methylene chloride absolute (99%, from El-Nasr Pharmaceuticals and Chemicals Co., Egypt)
- Commercial high purity and high concentrated sulphuric and nitric acids.

PMMA samples are prepared in thin film format. 5 g of PMMA granules are dissolved in 150 ml methylene chloride at room temperature on a magnetic stirrer. The solution is poured in a glass dish of 18 cm diameter and covered with a filter paper and left until full drying. The film sample is then removed from the dish and is ready for usage. Several samples are prepared by the same method.

1- Sample treatments:

The prepared PMMA films are labelled and divided into four groups plus one piece that is taken as blank sample (denoted later as fresh film) which is not treated at all. Each group is subjected to a specific treatment as following:

- First group: consists of 6 pieces, all pieces are immersed in big basin filled with acid rain simulating solution. After one week one piece is picked out the solution and washed with the tap water and then left to dry in oven at about 40°C for 2 hours. After two weeks the second piece is drawn from the basin and dried too, and so on for the rest of group samples. Samples of this group are denoted as (AR 1-6). Exposure time in acid rain is considered in units of week.
- Second group: consists of 6 pieces, one piece is irradiated by intensive UV radiation for 15 minutes and then drawn out of radiation stream. The next piece is irradiated for 30 minutes, and so on for the rest of this group samples. Samples of this group are denoted as (UV 1-6). Exposure time in UV radiation is considered in units of minutes.
- Third group: consists of 6 pieces, one piece is immersed in the acid rain solution for one week and dried, then it is irradiated by same UV for 15 minutes. Second piece is immersed in the acid rain solution for two weeks and then irradiated by the UV radiation for 30 minutes, and so on for the rest pieces of this group. Samples of this group are denoted as (AR & UV 1-6).
- Forth group: consists of 6 pieces, one is irradiated by the same UV for 15 minutes and then immersed in the acid rain solution for one week and dried. Second piece is irradiated by the UV radiation for 30 minutes, and then immersed in the acid rain solution for two weeks then dried, and so on for other pieces of the group. Samples of this group are denoted as (UV&AR 1-6).

2 – The acid rain simulator

(Schulz, et al, 2000) showed that, the pHs of a real acid rain even at the aggressive environments lied in the range of 3.5-4.5. Acid rain etches the acrylic polymer and strongly damages the surface coating [13]. Another authors said that acid rain is formed when the pH of rain water is below 5.6. As the literature does not provide any exact specification for the chemical content of the acid rain, it is usually assumed to be the mixture of sulphuric acid and nitric acid of pH 4.3 – 4.5 [14]. Therefore a mixture of sulphuric and nitric acids of pH 3.6 was prepared and used in this work as acid rain simulator to represent the aggressive acid rain that is normally characterizing industrial zones and around classical power stations. The pH values were measured by a digital pH-meter model 350 from Jenway Co, with glass probe.

3 – UV source

The used UV radiation source containing three germicidal UV lamps from General Electric Co., model G15T8, 436 mm length, 25.5 mm diameter, 15 W radiation powers and 254 nm characteristic wavelength for 10,000 average useful life. The distance between the light source lamps and samples is (15 cm). Each sample is exposed to this radiation for different periods ranged from 15 to 120 minutes, continuously.

4 – Infrared spectrophotometer

Infrared spectroscopy is a versatile experimental technique and it is relatively easy to obtain spectra from samples in solution or in the liquid, solid or gaseous states. The first dispersive infrared instruments employed prisms made of non-absorbing materials for IR-wavelengths such as sodium chloride. The popularity of prism instruments fell away in the 1960s when the improved technology of grating construction enabled cheap, good quality gratings to be manufactured [15]. In the present work, an instrument model NICOLET- IS10 from Thermo Scientific Co., USA is used. Polymer samples from each sample group were examined after exposure to the selected treatment for detecting the molecular changes, if any.

5 – X – Ray diffraction measurements

X - ray diffraction is a powerful tool for the identification of the crystallization state of solids. The crystallization state includes degree of crystallization, crystal size, crystals type, rate of crystallization and crystal distribution as special case.



The X-ray diffraction charts may provide well information about the macro-molecular orientations. The mean orientation factors (k) may be calculated as the ratio between intensity of crystalline maxima for samples treated and untreated analogues [16]. The x-ray tube that used in the present work was adjusted at the following measurement conditions: Cu target, voltage of 40 kV at 30 mA. (Shimadzu6000, Japan).

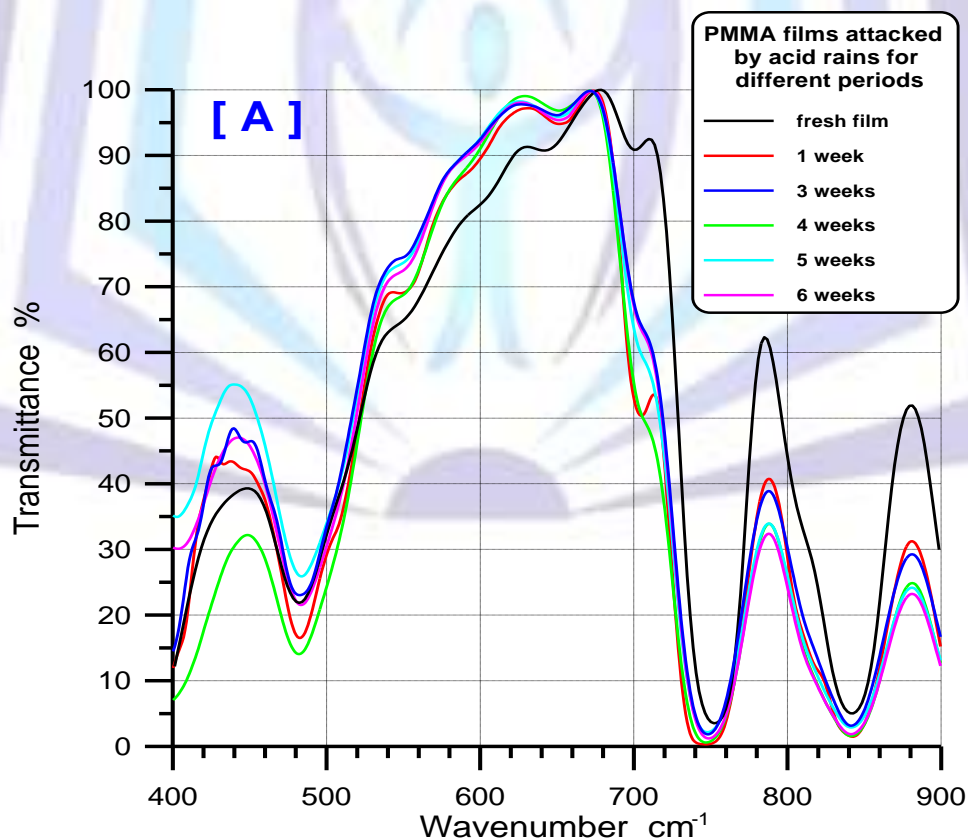
6 . Optical dispersion of glassy polymers:

In general, the carbon-based optical polymers are visible-wavelength materials, absorbing fairly strongly in the ultraviolet and throughout the infrared [17]. The chemistry of carbon-based polymers is markedly different from that of silicate glasses and inorganic crystals in common use as optical materials. Consequently, the refractive properties differ significantly. In practice, those materials which are readily available for purchase exhibit a more limited index range from about 1.42 to 1.65. Optical polymers (OPs) have some key advantages over glass as low cost and weight, high impact resistance and ability to integrate proper mechanical and optical features. They are clear materials that provide excellent light transmission in the visible (VIS) and near-infrared (NIR) regions [18]. Great economies are possible through usage of OPs for reproducing aspheric and other complex geometric surfaces or miniature elements, which are costly to produce in glass [19]. Proper choice of measuring technique depends on the sample shape, size and thickness. Several methods were applied to determine refractive indices n_D of OPs at sixteen wavelengths λ from 435.8 to 1052 nm at 20°C. The used instrument allows measurement of refractive index at 8 discrete wavelengths between 400 and 700 nm. The fully automatic spectral refractometer model ATR-L from Schmidt & Haensch Ltd. The allowed rang of refractive index is 1.33 to 1.7 with a resolution of 0.00001 and accuracy of + 0.0001 at 20°C. The instrument is located in the institute of measurements and standards, Giza, Egypt. The refractometer used in this study measures the refractive index of a transparent samples at the following wavelengths: 404.7 , 435.8 , 486.1 , 546.1 , 589.3 , 632.8 , 656.3 , 706.5 nm.

Dispersion of most of optical polymers (PMMA is among them) is normal and obeys the Cauchy–Schott relation which is valid for transparent media in their region of normal dispersion, Where A ,B..., C are Cauchy's coefficients.

Results and Discussion:

When a material (say polymer) is attacked by acid, the first expectation is occurrence of a chemical reaction. The easier technique to investigate any chemical changes in a material is the IR-spectroscopic analysis. Therefore, PMMA samples that are subjected to the acid rain (AR) were tested; figures 1A-C show the transmittance percent of the AR- group samples at three regions of the spectrum for accurate observation.



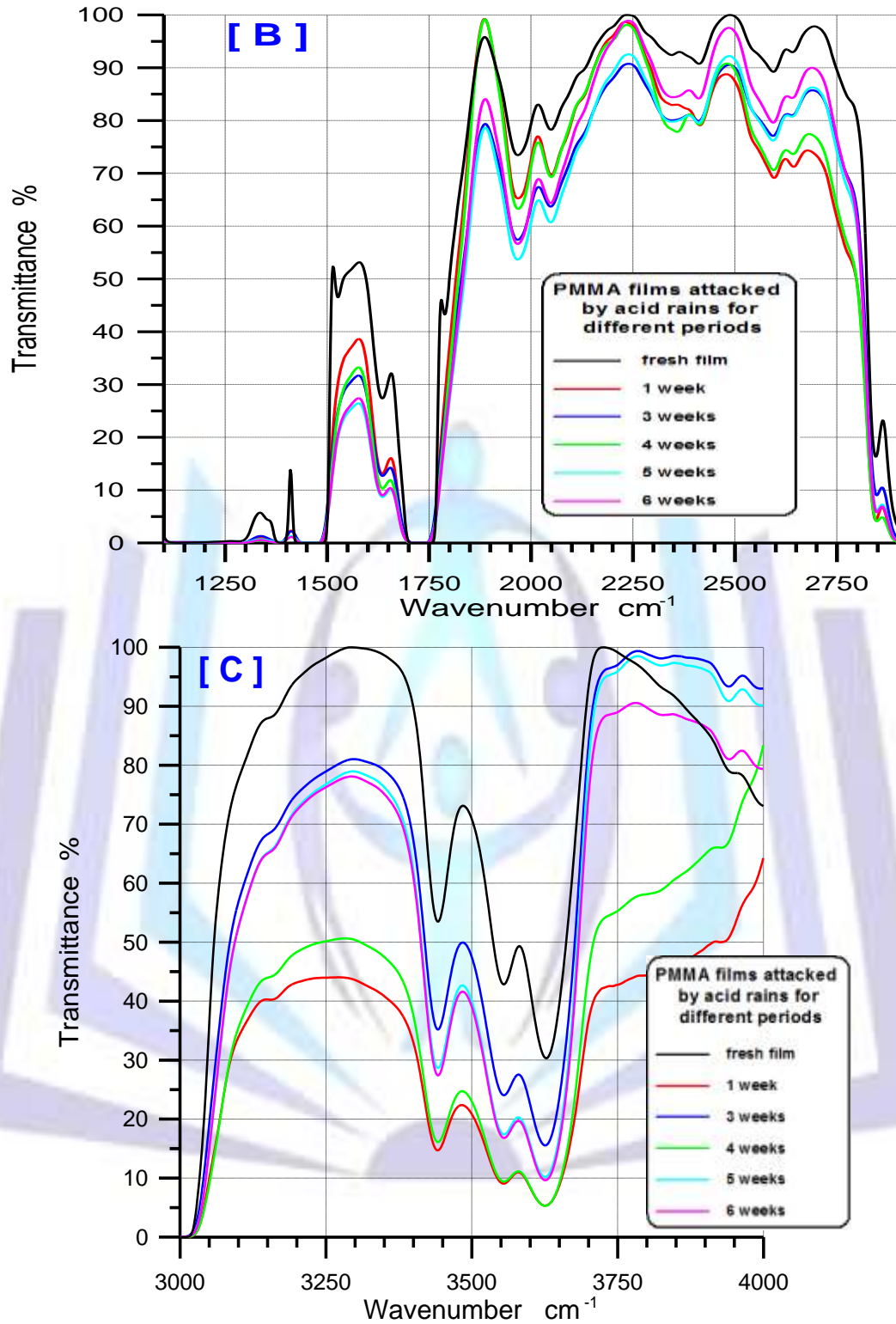


Figure (1A – C): IR-transmission spectrum of PMMA films exposed to acid rain for different time intervals.

Careful checking for these graphs one do not find any marks for formation or dismissing of chemical function bonding. The trend shown in figure 1A means that acid rain increases the transparency of PMMA film only at lower frequencies, while at higher IR frequencies PMMA films appear hazier, figure 1C. The general decrease in transmittance values in figure 1C is, definitely, not due to an increase of the acid treated films thickness than thickness of the untreated film (fresh film), where the same treated films showed more transparency in figure 1A. The IR-spectrum of the UV sample group showed the same behaviour as the previous group, but at high frequencies the samples are hazier than the acid rain treated group, as in figures 2A – 2B.

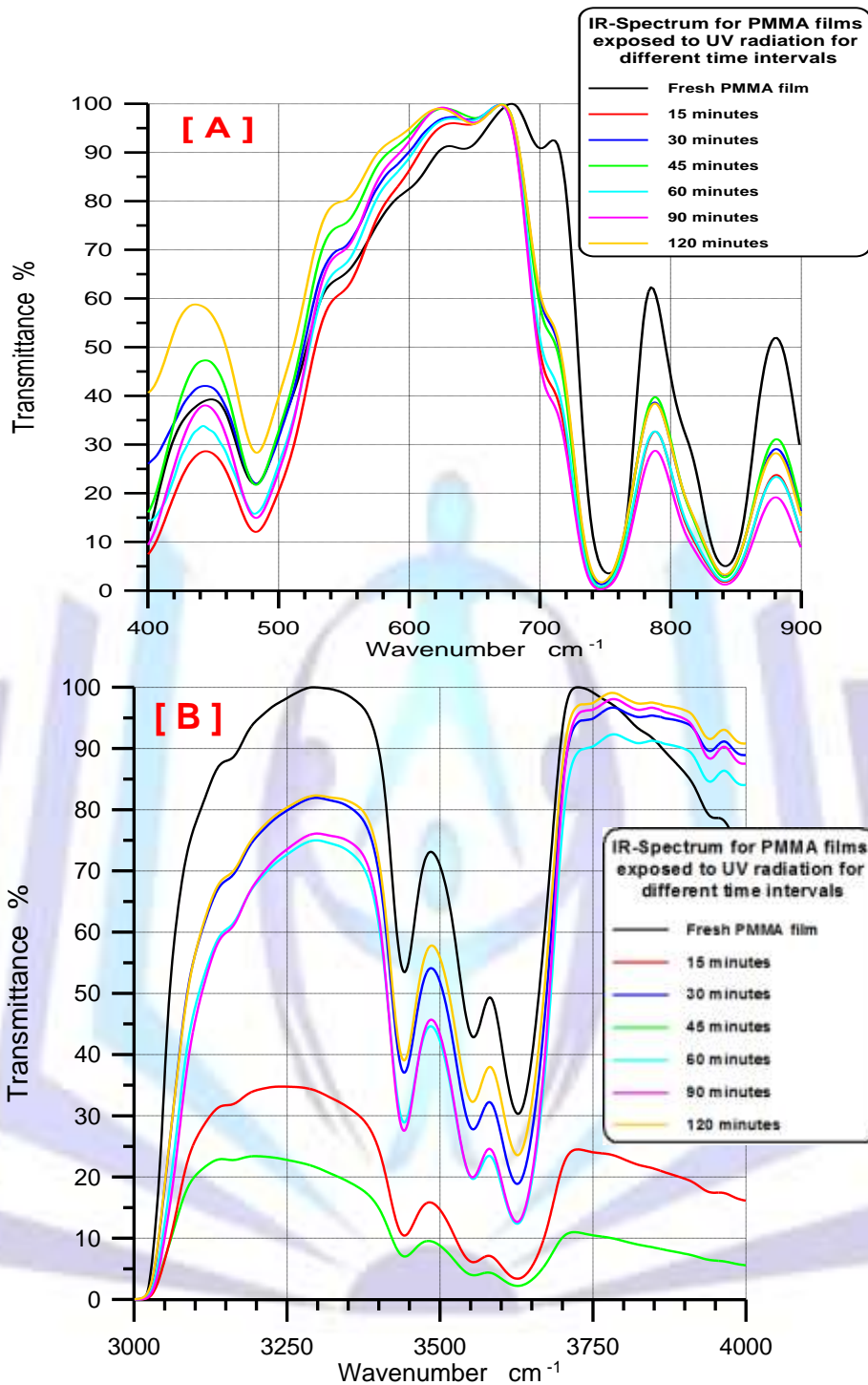


Figure (2A , B): Infrared spectrum of PMMA films after UV irradiationfor different time intervals

The same behaviours shown in figures 1 and 2 are observed for the sample group that exposed to acid rain and then to UV radiation. The question now is what is the source of the sample hazing at higher IR- frequencies? Of course it is not an additional absorption due to the treatments because this great fall in transmittance is not in direct proportionality with the time interval of the treatment. The authors believe that the treatments caused chain scission and these chain fragments consisted scattering centres whose sizes are comparable with certain wavelength range of the IR radiation, at which the radiation is more scattered causing the observed fall of transmittance. As the UV radiation generates a lot of chain fragments at the film surface and inside it, the next acid rain exposure may cause redistribution of these fragments in many bigger colonies and in compact arrangements in such a way that light scattering is no longer probable. Figures 3A, B show this effect of the UV irradiation when followed by acid rain exposure. It is clear that the transmission spectrum of PMMA samples after this treatment became closer to that of the untreated sample, which supports the assumption of chain fragments redistribution.

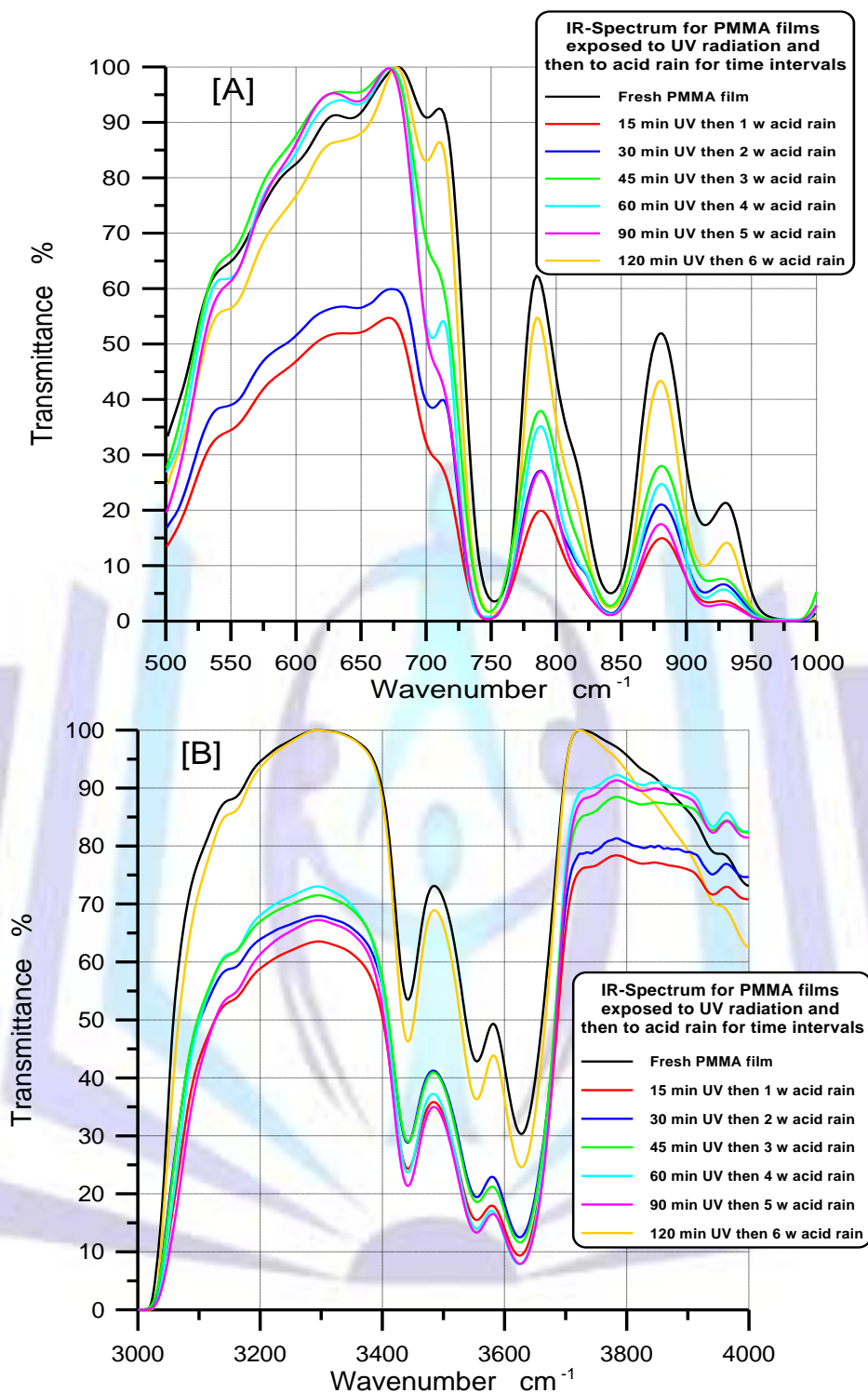


Figure (3A, B): The recovery of PMMA IR-spectrum by acid rain after the chain scission by UV irradiation.

X-ray diffraction helps to confirm studies of macromolecular structures of both polycrystalline and glassy polymers as well. With respect to glassy polymers (like PMMA), X-ray diffraction technique provides researchers with information about the orientations available in the amorphous polymer network. Chain orientation in amorphous region may be long ranged which appears as high round (not sharp) peak in the X-ray diffraction pattern. Medium and short rang orders of chain orientations may appear as faint broad peaks at higher values of 2θ angle. The unoriented amorphous chain structure is appearing as one very broad halo covering most of the 2θ range of the diffraction pattern.

Figure 4 is the X-ray diffraction diagram showing that the fresh (untreated) PMMA sample is an amorphous structure with one long range ordered orientation and two short range ordered orientations. The graph shows also that exposing the oriented amorphous PMMA films to acid rains disordered the short range ordered chains, and

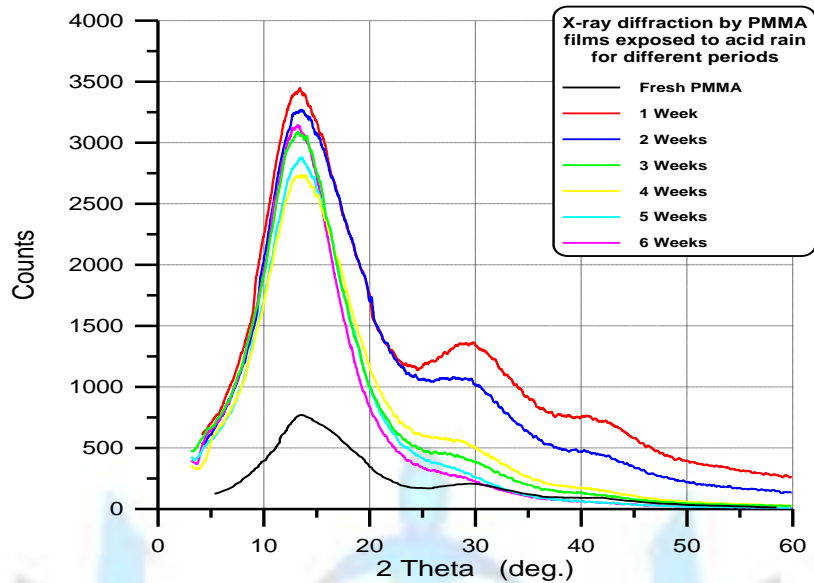


Figure (4): The orientations of amorphous PMMA when exposed to acid rain for different time intervals.

as the exposure time increased as the disordering increases. On contrast, irradiating the PMMA films with UV radiation supports all the ordered ranges in the amorphous structure as shown in figure 5, which increased the haze of irradiated samples.

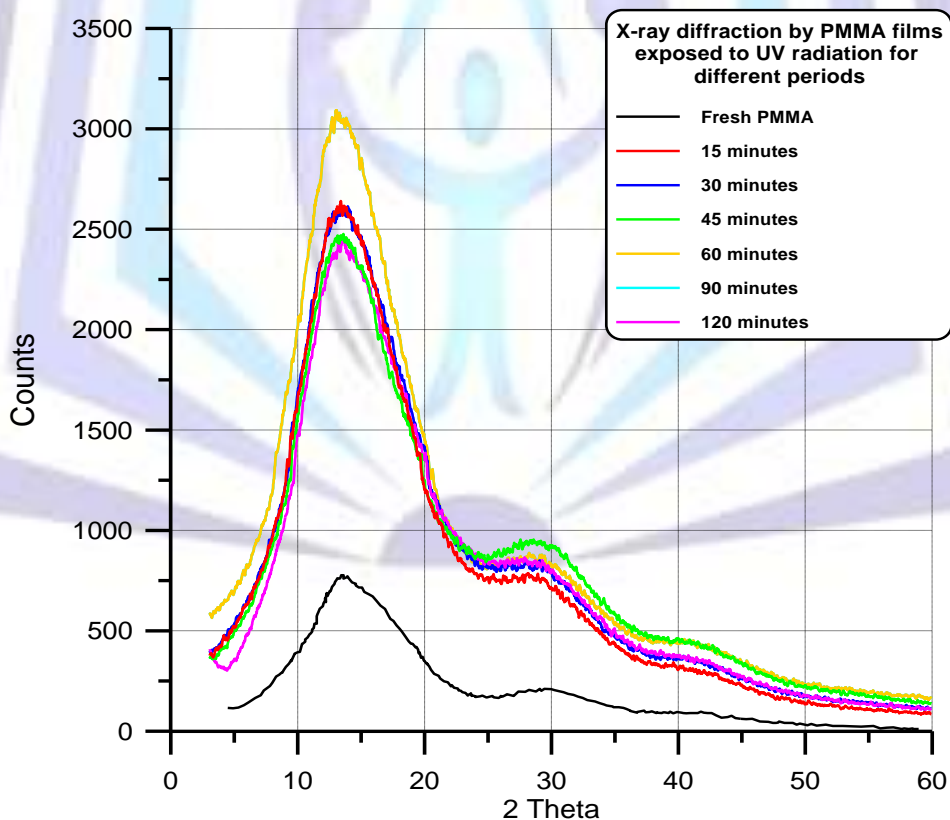


Figure (5): The enhancement of ordered ranges in the amorphous structure of PMMA films due to UV irradiation.

Both effects of UV irradiation followed by acid rains exposure are shown in figure 6, where UV radiation enhances one of the short rang ordered structures, while acid rains disordered the weakest ordered rang.

Amorphous structure of a polymer is the most responsible parameter for the polymer product transparency. Therefore any changes for chains distribution should cause variations in the optical properties of the polymer product. As mentioned

above, exposure to either acid rains or UV or both of them caused remarkably variations in chain orientation, and hence values of some optical constants of PMMA films may show variations after treatment by the environmental elements.

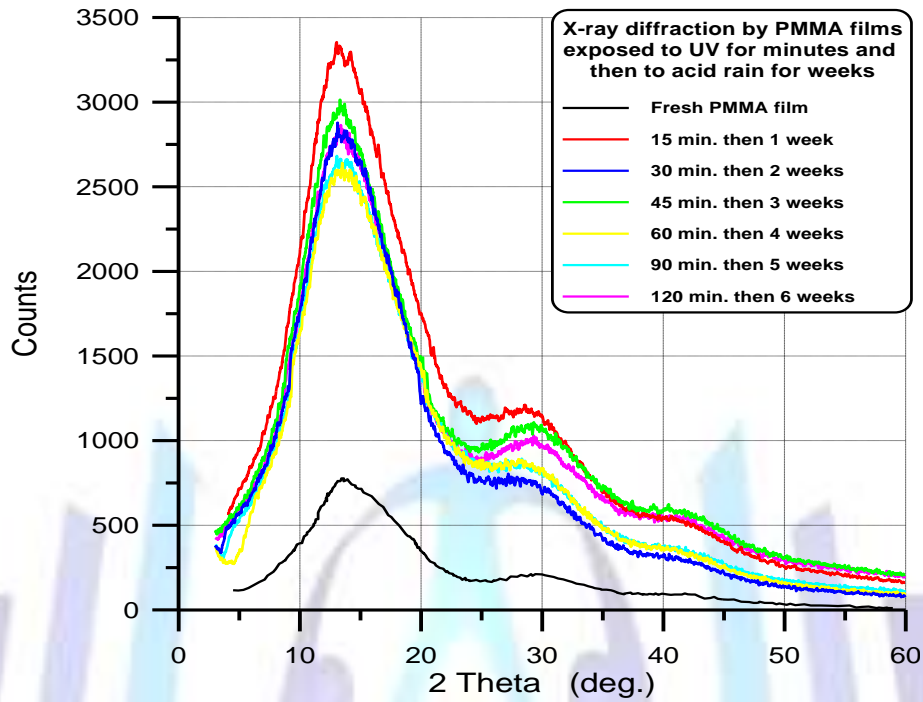


Figure (6): Dual effect of UV radiation and acid rains on the orientations in the amorphous structure of PMMA films.

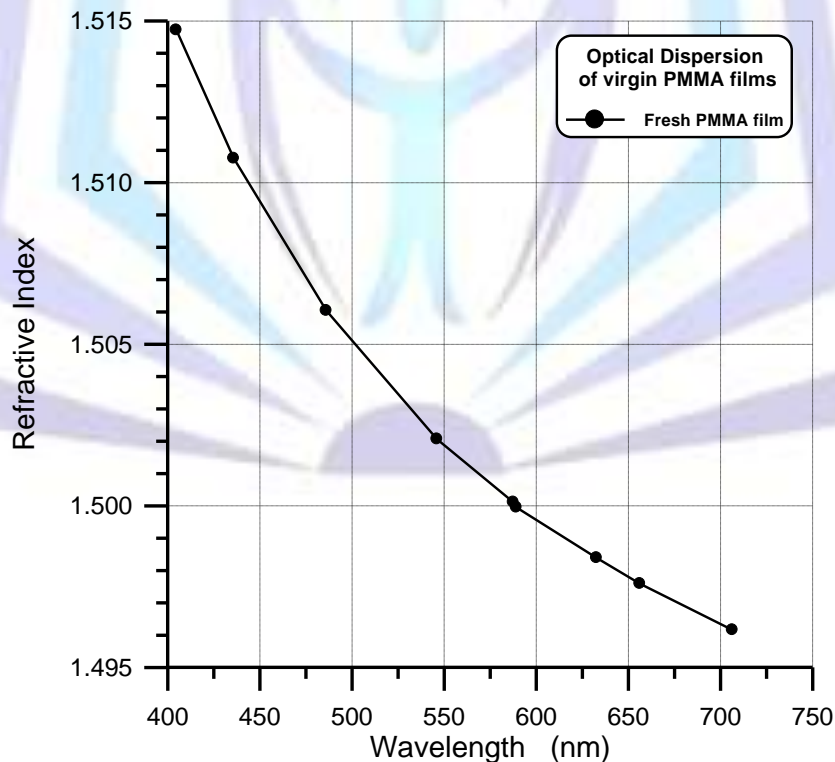


Figure (7): Optical dispersion graph for untreated PMMA films.

From figure 7, it is clear that PMMA obeys the normal dispersion behaviour that is described by Cauchy since long time. Figure 8 shows the excellent agreement of PMMA optical dispersion with Cauchy's equation:

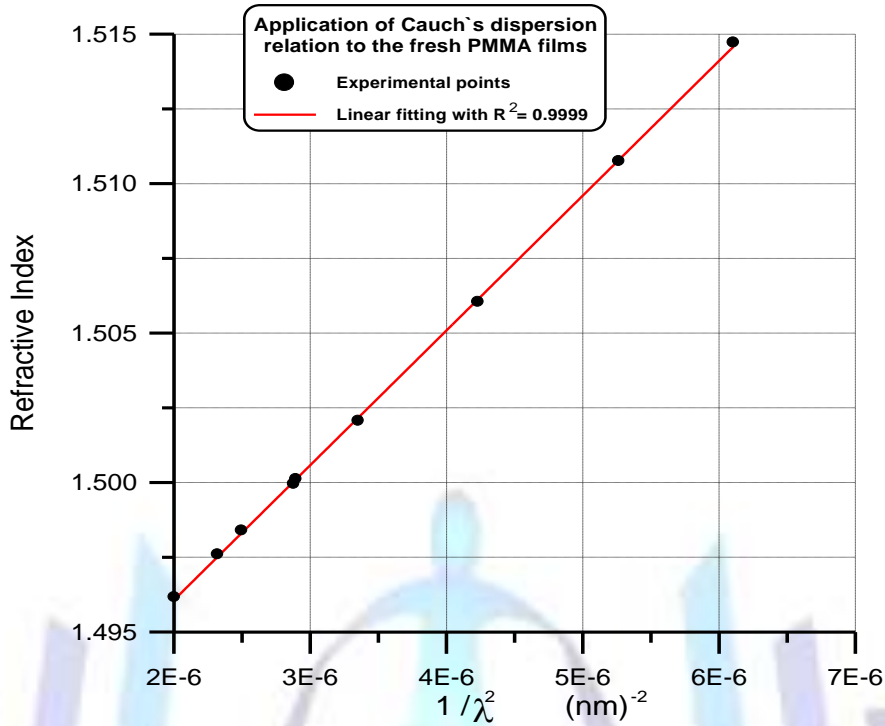


Figure (8): The agreement of PMMA optical constants with Cauchy's equation.

From this graph Cauchy's constants are found as $A = 1.48705$ and $B = 4509.7$

After the extreme treatments by UV and acid rain, the refractive indices of PMMA films are measured and given in figure 9. Sharp and sudden decrease for the refractive indices of treated samples is noted. Such acute changes may be due to unexpected effects during measurements or during sample's treatments. As for effects during treatments, it is unacceptable because treated samples showed reasonable variations according to the applied treatments. As for effects during the index measurements, it is difficult to imagine presence of external effects during the several times of repetition. The only reason behind this acute drop in refractive index of treated PMMA may be a type of interaction between PMMA sample and the immersion liquid which is necessary for the refractive index measurement. If so, then the data shown in figure 9 is example for the fall in index measurement due to interaction of the immersion fluid with the sample.

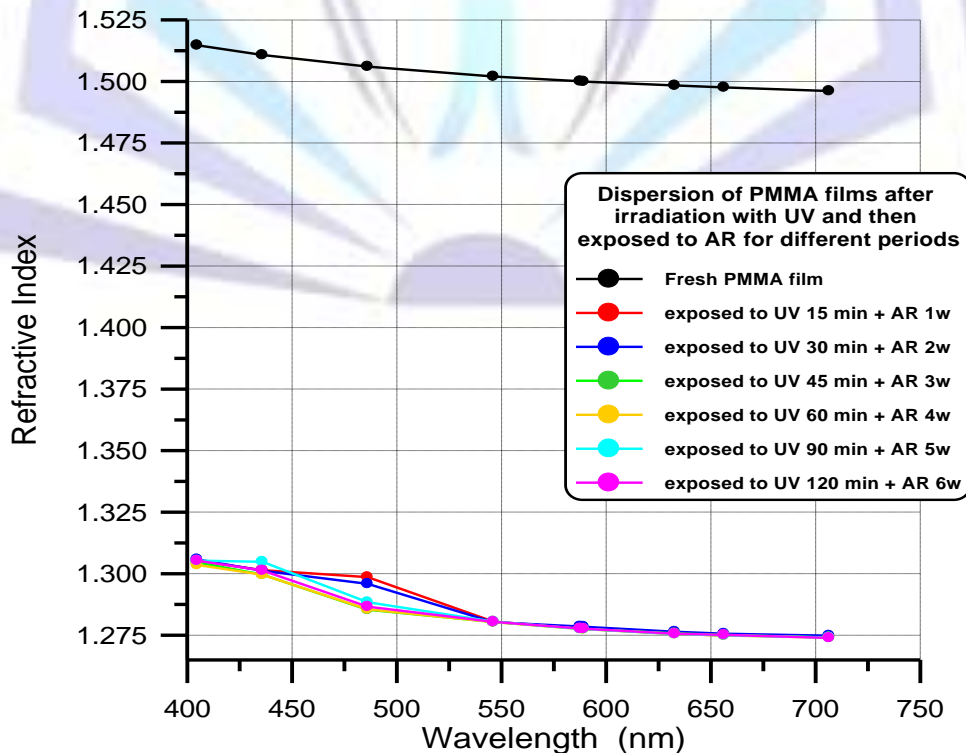


Figure (9): The dispersion of treated PMMA films.



Conclusion

Utilization of polymer products for outdoor applications is continuously increasing. So the stability of polymers against environmental degradation became top of interests for many researchers. The acid rains, UV radiation and heat are the most degrading environmental elements. The effect of these elements on the polymers stability has been studied, but individually. The authors of the current work claim that solutions derived from these individual studies are of limited efficiency, because of their conflicts. The current study clarifies a type of these conflicts. The traditional solution for the UV degradation of polymers is to add certain organic chemical additive to increase the polymer resistance for the UV degradation. Acid rains may react with these chemical additives and restricts their activity against UV radiation, and hence the polymer article becomes unprotected against UV. In case of polymer products that are nearly free from additives, like glassy polymers, some environmental elements may act as catalyst for polymer reaction with other environmental element. This work illustrated that acid rain could recover the damage in transparency that initiated during exposure to UV radiation of the glassy polymer PMMA. The exposure of PMMA films to acid rain causes disorder of the short rang ordered amorphous structure, while exposure to UV enhances the orientation of the ordered regions, but reduces the transparency of the product.

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