PMMA degradation protection investigation using ultraviolet additive

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ABSTRACT

Polymethyl methacrylate, PMMA, is one of the most important thermoplastic material which can be used as replacement of glass due to its unmatched properties. But PMMA is prone to UV and thermal degradation. So to overcome this drawback, along with PMMA, UV absorber is incorporated which not only acts as a stabiliser but also inhibits 60% of degradation. It also provides better thermal stability at 70°C. Thus incorporation of UVA prolongs the life span and activity of PMMA. Thus enabling it to be used in commercial preparation. The additive efficiency was confirmed using UV-Vis and FT-IR studies.

Key words: PMMA, degradation, UV light.

INTRODUCTION

Plastic has become an essential material in virtually every aspect of modern life. Recent advances in plastic manufacturing and processing have led to even more applications in which plastics replace other materials such as glass, clay, copper, asbestos-cement, aluminum, iron, paper, wood and concrete pipes in various applications[1]. Construction and industrial films used outdoors for extended periods of time, ranging from some months to a few years, require proper UV light protection in order to meet end-users' requirements. Common applications are stretch films, shrink wraps, heavy-duty bags and pool covers and much more of plastic made items. Plastic generally ages rapidly under the effects of light, oxygen and heat, leading to loss of strength, stiffness of flexibility[2], discoloration[3], scratching and loss of gloss[4].

One of the most commonly used polymers is Polymethyl methacrylate (PMMA) or polymethyl-2-methylpropanoate. It is a synthetic polymer of methyl methacrylate and considered as an important thermoplastic material[5]. PMMA is a very versatile polymer due to its excellent properties such as resistance to strong alkaline or acid solutions and its stability to heat and light[6]. PMMA is a clear plastic, used as a shatterproof replacement for glass and it is lighter than glass. The softness of PMMA leads to get easily scratched compared with glass but it can be made more transparent by heating to 100°C, unlike glass it cannot filter UV (ultraviolet) light. PMMA is an important thermoplastic material. However, PMMA is classified as slow burning, roughly comparable to wood in flammability and ignition characteristics. Therefore, thermal stability and flammability of PMMA is studied extensively[7]. PMMA degrades to lower molecular weight compounds or to the monomer by heating or irradiating with high energy radiation[5]. The photochemistry of PMMA is studied to provide more information on the chemical changes upon UV light exposure in the upper molecular layers of the PMMA surface. PMMA is an important polymer for lithographic applications. In the past, many studies have been performed on the photodegradation of PMMA. Recent interest in the photodegradation of

PMMA comes from the possibility of removing polymeric material in a controlled way by UV-excimer laser ablation. A complete picture of changes introduced by UV-light exposure is still lacking despite of the large number of studies performed on this subject. PMMA starts to degrade upon UV irradiation below ~300 nm. Many degradation studies on PMMA are performed through the analysis of species that desorb from the PMMA surface after irradiation. A recent UV irradiation study on a model compound for PMMA points to a similar photodegradation mechanism[8]. The photolysis of PMMA results in a random scission of the polymer chain backbone by a radical process[9-11]. PMMA depolymerization is favored at 300°C. External sources of radicals and defects in chemical structure make the material more susceptible to this mode of degradation.

Additives in polymers are used to protect polymers from degradation, modify properties, assist in processing, and introduce new properties to material. Many additives have become parts of general formulations developed as much as an art as a science[12-13]. Nevertheless, additives are essential functional ingredients of polymers, and whenever possible, each should be used in optimum amounts for the attainment of high-quality products[14].

Many commercial ultraviolet stabilizers have alkoxyl groups on carbon 4 of the phenyl group. 2-Alkoxybenzophenones and those with bulky groups on carbon 6 are not useful as stabilizers. Other ultraviolet stabilizers are benzotriazoles, such as 2-(2´-hydroxyphenyl) benzotriazoles; substituted acrylonitriles, such as ethyl-2-cyano-3,3´-diphenyl acrylate; metallic complexes, such as nickel dibutyldithiocarbamate; and pigments, such as carbon black[13,15]. Since the effect of ultraviolet radiation on synthetic polymers is similar to its effect on the human skin, it is not surprising that ultraviolet stabilizers such as phenyl salicylate have been used for many years in sun tanning lotions. Phenyl salicylate rearranges in the presence of high-energy radiation to form a 2,2'-dihydroxybenzophenone. The latter and other 2-hydroxybenzophenone act as energy-transfer agents, i.e., they absorb energy to form chelates which release energy at longer wavelengths by the formation of quinone derivatives.

We often classify the types of light or UV stabilizers we make according to their action mode. UV absorbers (UVAs) that act by shielding the polymer from ultraviolet light[16] or hindered amine light stabilizers (HALS) that act by scavenging the radical intermediates formed in the photo-oxidation process[17]. Hindered Amine Light Stabilizers (HALS) are extremely efficient stabilizers against light-induced degradation of most polymers[18]. They do not absorb UV radiation, but act to inhibit degradation of the polymer, thus extending its durability. Significant levels of stabilization are achieved at relatively low concentrations[12]. UVAs have the property to convert the energy absorbed from UV light into heat, via a mechanism called keto-enol tautomerism. This heat can then dissipate through the substrate[19-20].

In this study, attempts are made to find a UVA to prevent or delay polymer degradation by using new additive, thus prolonging polymer life spans. The additive efficiency will be confirmed using UV spectroscopy and Infrared Spectroscopy (FT-IR) methods.

MATERIAL AND METHODS

Materials and Chemicals
Chloroform (BDH), and toluene (BDH) were used as solvents

N-(4-bromophenyl-[(1)-(4-bromophenyl) methylene] amine (A) synthesized in organic lab of the Chemistry department at KAU [21] and *Oxybenzone* (commercial name: Uvinol) $C_{14}H_{12}O_3$ (B) obtained from the supplier were used as UV-absorbent. Their structures are as follow: Polymethyl methacrylate (Aldrich 28036, M.W. 15000)

UV Spectra were recorded with a Shimadzu UV-240 spectrophotometer. The light source was an Entela (MODEL UVGL – 58) 115V ~ 60 Hz which emitted radiation with single wavelength at 366 nm. The distance between light source and polymer samples was about 30 cm. The Electrical heater was a BINDER GmbH Bergstr 14 D-78532 Tuttlingen. Infrared spectra were recorded using IR Spectrophotometer instrument manufactured by Perkin Elmer model No. spectrum RXIFT-IR

(A)   (B)
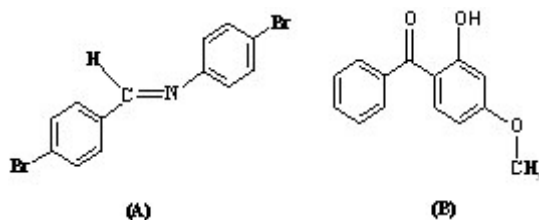
Preparation of (PMMA) solution

Polymethylmethacrylate (PMMA), laboratory grade, was dissolved in chloroform (BDH) at room temperature (0.01M). UV-absorber (UVA) N-(4–bromophenyl-[(1)-(4-bromophenyl)methylene] amine was dissolved in chloroform (BDH) at room temperature (10^{-3} M). Various concentrations of PMMA in the range 1×10^{-6}-1×10^{-1} M by mixing appropriate volumes of the above solutions. Some droplets of each concentration were put on individual glass slides separately and left for a few minutes at room temperature inside fume cupboard until the solvent evaporated. Then absorbance of every film was measured using spectroscopy method in the range of 200-500 nm. From previous measurements, 1×10^{-2} M of PMMA/chloroform was found to be the best concentration. Various concentrations were prepared by mixing PMMA and UV-absorber solutions at room temperature. A few droplets of each concentration for the mixture solution were put on slide, and left until the solvent evaporated[22]. A suitable concentration was chosen (0.5m of UVA in PMMA) for studying and comparing its behavior with that of untreated PMMA.

Ultraviolet spectroscopy

The behavior of both the polymers including and not including UVA were investigated by:

a.   Exposing the samples to UV light (366 nm). Absorbance of these samples was recorded before the exposure and every 2-3 days throughout the exposure period.

b.   storing the samples at 70ºC temperature for 19 days, where measurement of absorbance using UV spectrophotometer were taken at the interval of 2-3 days throughout the storing period.

c.   Uvinol $C_{14}H_{12}O_3$ (Commercial Additive) was added to PMMA (conc. of Uvinol was 0.5 molal in PMMA) for studying the behavior of PMMA/Uvinol (0.5m) samples against UV light and heat.

Fourier transform infrared (FT-IR)

Investigating the behavior of PMMA including and not including UVA was performed using KBr-discs by measuring the absorbance using IR spectrophotometer. The absorbance of the samples was measured before exposing the samples to the UV-light, and then after exposing the samples to UV-light every 2-3 days.

The carbonyl index results, as obtained by IR spectroscopy, showed changes in chemical structure of polymers under UV exposures[23-24].

RESULTS AND DISCUSSION

UV spectroscopy
UV-light effect

Exposure to ultraviolet light is a major cause of PMMA degradation during weathering. Ultraviolet absorbers (UVAs) often are added to block UV light and thereby improve performance. To be effective, the UVAs must absorb light in wavelength range that causes the degradation and harmlessly dissipate the energy. However, the UVAs themselves are subject to loss from migration, volatility, and photochemical decomposition.

Fig. 1 shows the relationship between wavelength and concentration of UVA in PMMA at single wavelength (~ 305 nm). ë$_{max}$ was selected as single wavelength throughout UV range (200-500 nm) where maximum absorbance lies for the material, i.e., 305 nm (see Fig. 2).

From Fig. 1 we can divide absorbance behavior versus UVA concentration into three regions:

a.   Low concentration region, (< 0.2 molal). In this region the absorbance is directly proportional, but yet does not approach to its optimum absorbance value.

b.   Intermediate concentration region, (~ 0.2-0.6 molal); absorbance values reaches to its maxima, and the whole range can be considered as an optimum level.

c.   High concentration region, (> 0.6 molal); in this region the absorbance decreases by

increasing the concentration which may be due to the production of aggregated UVA molecules at high level of concentration.

By plotting absorbance versus time at ~ 305 nm (Fig. 3) the absorbance reaches maxima, after 5 days, then starts to decrease. The increase of absorbance with exposure time to UV light was attributed to the scission of ester side-groups and formation of olefins[25]. Then the absorbance decreased which showed that UV light caused the polymer to degrade.

Fig. 4 shows that the absorbance of the samples increased with exposure time to UV radiation until 8 days then the absorbance decreased at 305 nm. This additive acts by

absorbing UV light and dissipating the energy harmlessly as thermal energy thereby reducing the amount of harmful radiation absorbed by the polymer achieving about 60% of inhibition effect. The presence of UVA prolonged the PMMA life and stability before degradation process takes place. Hence, UVA used in this work can be used as a UV stabilizer.

Heat effect

At high temperature PMMA become thermally unstable, leading to degradation to yield a mixture of monomer and polymer. Fig. 5 shows the relationship of absorbance and time (days) when exposed to heat at 70°C for untreated PMMA. In this figure, we observe that the polymer started to degrade by heat after 5 days. It was found that the
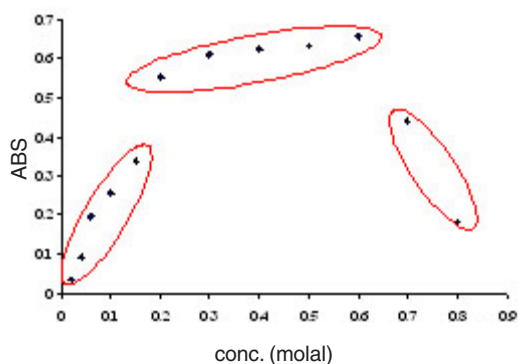

Fig. 1: Relationship between absorbance at 305 nm and concentration of UVA in PMMA films.
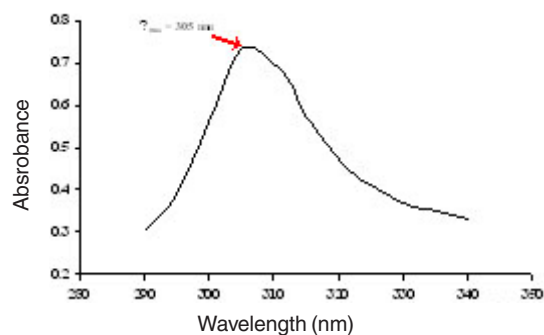

Fig. 2: Relationship between absorbance and wavelength (nm) for PMMA films
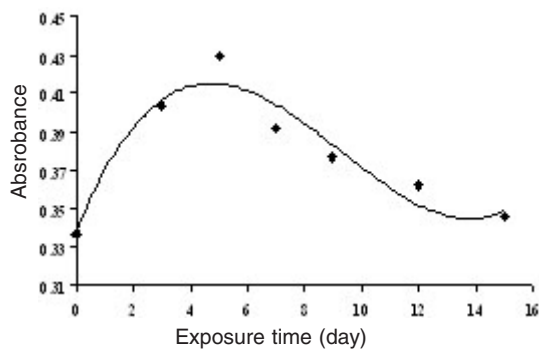

Fig. 3: Relationship between absorbance at 305 nm and time of exposure to UV light for untreated PMMA sample
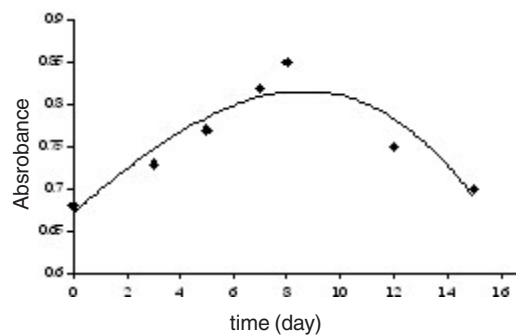

Fig. 4: Relationship between absorbance at 305 nm and time of exposure to UV light for PMMA with 0.5m UVA

treated PMMA samples have better resistance to heat than untreated PMMA samples (Fig.6). Thus, treated PMMA with UVA degraded after 7 days which means that, achieving of about 40% of inhibiting of degradation against heat.

Comparing Figs. 4 & 6 and looking at the percentage outcomes it was found that, UVA played a major role as a resistant to UV light, nevertheless its stability against heat may be considered as a side advantage.

Fig. 7 & 8 show the effect of exposure to UV light and heat, respectively, in PMMA samples in the presence of Uvinol. By comparing the dependence of absorbance with time for PMMA/UVA samples Fig. 4 with that for PMMA/Uvinol Fig. 7, it is obvious that UVA has better performance

against degradation 60% compared to 20% when Uvinol was added to PMMA. On the other hand Uvinol found to show negative effect against heat. This was observed when monitoring the absorption level that began to diminish after 3 days leading to inhibition percentage of -40% when PMMA/Uvinol samples exposed to heat. One may report here that Uvinol has polymer degradation controlling property against light but a negative effect towards heat.

From above, UVA used in this work, beside acting as an effective UV light resistant, it can be used as heat resistant, provided that a particular polymer which is required to be improved, not been treated previously with other additives to avoid any negative effect. Extensive work of thermal analysis for PMMA degradation can be found elsewhere[26].
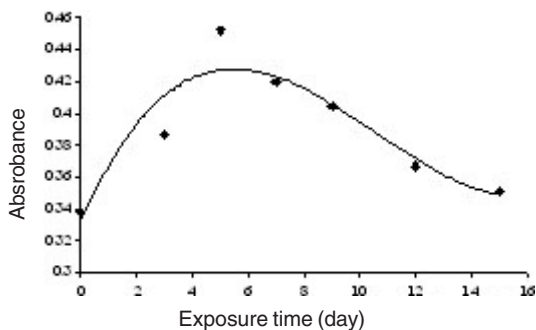

Fig. 5: Relationship between absorbance at 305 nm and time of exposure to heat at 70°C for untreated PMMA
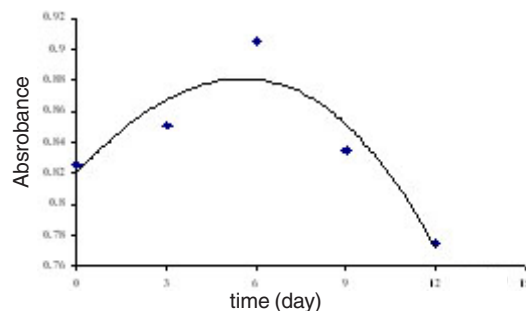

Fig. 6: Relationship between absorbance at 305 nm and time of exposure to heat at 70°C for treated PMMA with 0.5m UVA
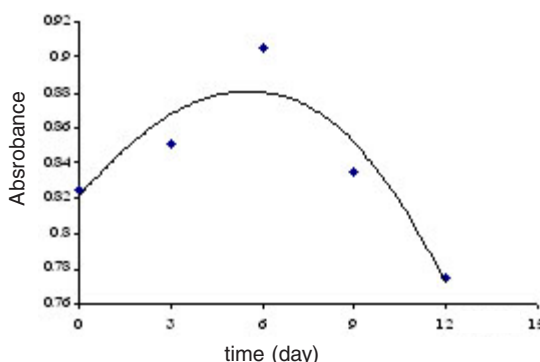

Fig. 7: Relationship between absorbance at 305 nm and time of exposure to UV light for treated PMMA with 0.5 m Uvinol
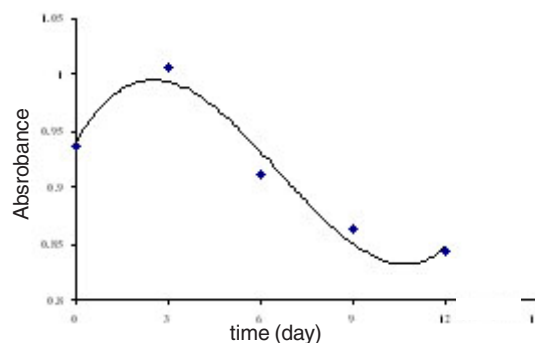

Fig. 8: Relationship between absorbence at 305 nm and time of exposure to heat at 70ºC for treated PMMA with 0.5 m Uvinol.

Fourier transform infrared (FT-IR) spectroscopy

The carbonyl index was calculated from PMMA samples as the ratio of the area under the carbonyl peak (1727-1730 cm^{-1}) to the area under the peak (2933-2950 cm^{-1}).

The (2933-2950 cm^{-1}) peak was taken as a reference in the calculations since it does not vary with the exposure time and it corresponds to -CH$_3$ group.

The PMMA spectrum show a sharp intense peak at 1731 cm^{-1}, which can be attributed to the presence of C=O stretching vibrations. Similar practice was performed by Kim *et al.*[27]. The broad peak ranging from 1260 to 1000 cm^{-1} is due to C–O (ester bond) stretching vibrations. The broad band from 950 to 650 cm^{-1} is due to C–H bending. The broad peak from 3000 to 2900 cm^{-1} is due to the presence of C–H stretching vibrations (Fig. 9). The percentages of inhibition were calculated
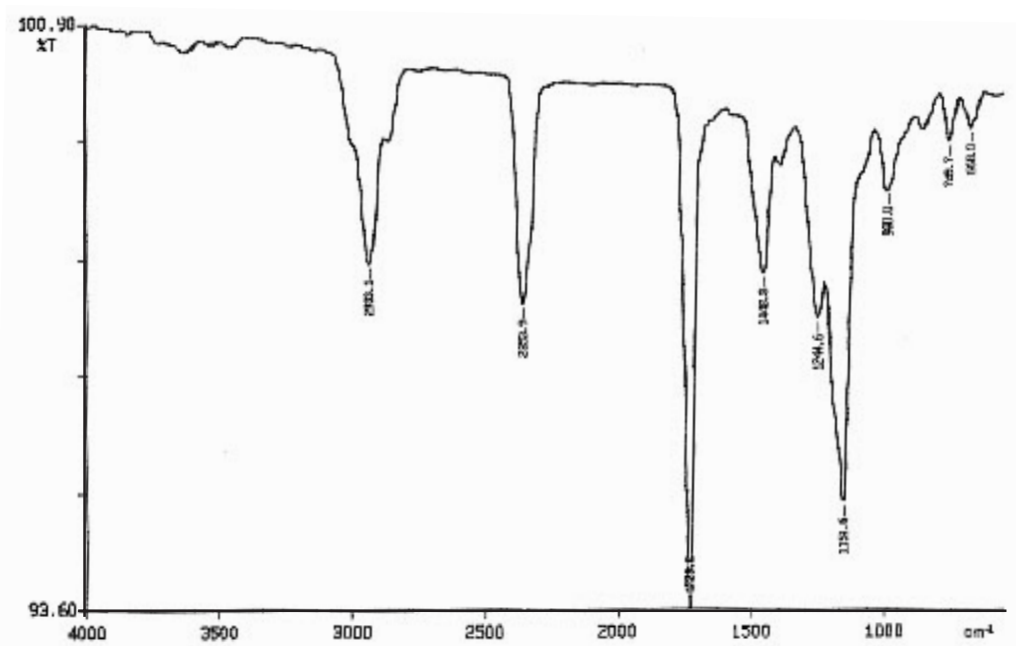

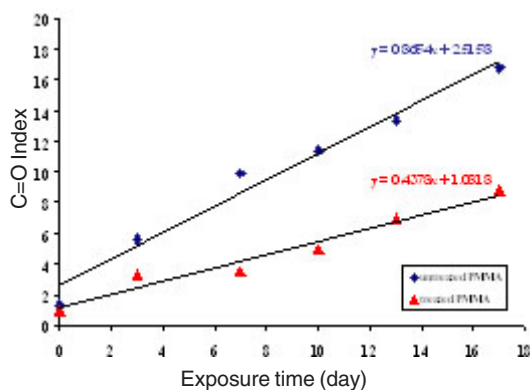**Fig. 9: FTIR specra of PMMA film**

Fig. 10: Carbonyl index as a function of degradation time
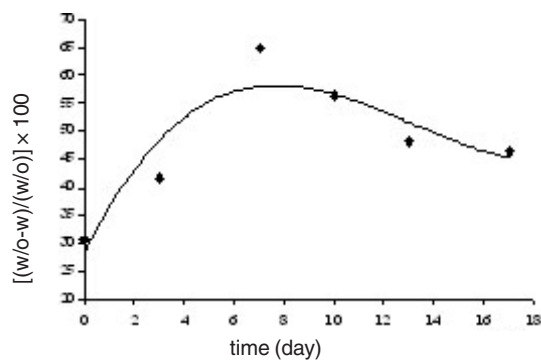

Fig. 11: Inhibition profile as a function of time for UVA/PMMA

through slope values (Fig. 10) for each sample of PMMA either treated or untreated according to the last equation.

Inhibition percentage of 60% was achieved using UV technique, whereas IR technique led to an inhibition percentage of ~ 50%. This difference of about 10% is assumed to be due to technical differences between the two methods, reflecting the possible experimental error in either technique. Moreover, it may be rather difficult to rely on IR as a qualitative technique by its own, but it supports other method's results as a supplement.

When observing UVA behavior in PMMA over time, as depicted in Fig. 11, one may realize that its resistance efficiency against UV light reached up to about ~65%, however after 13 days of exposure time, resistance efficiency declined to reach about ~ 45%.

CONCLUSION

Polymers have versatile and important applications in our life, but they have some problems when exposed to sunlight, for they undergo degradation due to UV light and heat which shortens their service life. In this work, the degradation problem of PMMA has been investigated through the addition of a new additive which is expected to reduce this phenomenon, thus prolonging polymer life span. The ultraviolet absorbent (UVA) additive used in this work was N-(4-bromophenyl-[(1)-(4-bromophenyl) methylene] amine. To establish this investigation (PMMA) was used. The study compared somewhat the degradation level for both polymer untreated samples and the tendency of protection from deterioration in the presence of UVA. This comparison was performed using two methods. Having these results in agreement with that achieved by spectrophotometer methods undoubtedly opens the way for future work. UVA used in this work provided stability advantage against photodegradation to protect the PMMA from getting damaged under UV light. UVA showed to protect laboratory grade polymer from getting damaged if exposed to heat. Univol, commercially available UV light stabilizer showed to protect the sample from degradation up to some extent (20%), however, it accelerates degradation if exposed to heat.

FTIR proved to be more reliable technique in monitoring chemical changes in the polymer, whereas UV spectroscopy method was considered as a supplementary tool to ensure similar trend.

ACKNOWLEDGEMENTS

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