Study the Photo-degradation of poly styrene –co-butadiene

in presence of Ni complex and TiO2

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Abstract. In this work, the induced photo-degradation of poly styrene –co-butadiene films in the air has been studied (for 400 hr.) in the presence and absence of TiO2 dye and Ni complex, benzyl bis(benzoylhydrazone) Ni, as a photosensitizer by accelerated weathering tester, which are accomplished with the use of the Ultraviolet radiation at λ = 313nm, intensity of light of 3.490*10⁻⁵ Einstein/dm³.S at 45°Ctemperature. The rate of the photo-degradation has been followed with an increase in the polymers, hydroxyl and carbonyl absorbance of the use of the UV-visible and infrared (IR) spectra respectively and viscometer measurement. The addition of (0.1 wt %) of TiO2 dye and Ni complex to poly styrene –co-butadiene films (25µm thick) improved the photo-degradation of polymer films, and the photo-degradation with Ni complex higher than the photo-degradation of polymer with TiO2 dye where the degradation constant for Ni complex in polymer is higher than TiO2 dye.

Keyword: photo-degradation, poly styrene –co-butadiene, TiO2

1. Introduction

In the few years later, the polymeric materials increased in a fast rate, however, it has been stated that there is a possibility of the rapid photo-degradation of those materials in the case where they undergo exposing to the natural weathering ¹⁻³, which can be considered as one of the serious issues, with environmental and the economic implications, and as a result, a massive amount of efforts has been focused on the understanding of variations occurring at the molecular levels and the kinetics of the degradation. Following a variety of routes, ultra-violet radiation results in a photo-oxidative degradation, resulting in polymer chain breaking, results in radical and decreases molecular weights, which causes decline in the mechanical characteristics and resulting in useless material types, following an arbitrary amount of time ³. Exposures to the ultra-violet radiations could result in significant declining innumerous materials. Damages with the ultra-violet radiations are typically the key reason for discoloring in the pigments and dyes, yellowing of plastics, weathering, sun burnt skin, loss of gloss and mechanical characteristics (e.g. cracking), skin cancer, and some other issues that are related to the ultra-violet light. The manufacturers of plastics, paints, cosmetics, and contact lenses are greatly interested to offer products which stay unchanged for long time periods in light exposure conditions ⁴⁻⁷.
Styrene - Butadiene rubber (SBR) can be defined as a material of commodity, competing with the natural rubber. The elastomeric is commonly utilized in the pneumatic tires. Mainly, this application requires E-SBR, even though the SBR is gaining the popularity. Other utilizations comprise gaskets, shoe heels and soles, and even chewing gums. The latex (i.e. the emulsion) SBR is widely utilized in the coated paper, which is a very cheap resin for binding the pigmented coatings. The titanium di-oxide (TiO₂) can be defined as one of the inexpensive photo-catalysts with sufficient photo stability, non-toxicity and high level of reactivity. In the last few decades, titanium di-oxide has been utilized to accelerate the synthetic polymers’ photo-degradation, one of the promising methods which have resolved the plastic waste disposal issue.

Lately, the researchers investigated the solid-phase photo-catalytic degradations of the polymer-titanium di-oxide nano-composite. Zhao et al. have researched the photo-catalytic degradation of the solid-phase of the poly-ethylene (PE)/TiO₂ nano-composite film. They have discovered that the rate of the degradation of the nano-composite is considerably more rapid and more complete compared to pure PE film in ultra-violet and solar radiations of light. None-the-less, in some titanium di-oxide applications, like the self-cleaning, accurate controlling over photo-catalytic characteristics is important. One of the ways of reaching this objective is coating the titanium dioxide with a layer of carbon.

The behavior of the photo-catalytic degradation of the composite of the PP/TiO₂ in the ultra-violet light has been researched, in addition to that, the impact of the ultra-violet radiation and photo-catalytic degradation on nano-composite mechanical characteristics has been researched. They noticed that with higher content of carbon of the titanium dioxide nano-powders, there’s a lower photo-catalytic degradation. Only in the recent years, a few researches noticed the photo-catalytic characteristics of the carbon-coated titanium dioxide and recognized that its photo-catalytic characteristics strongly depend on the carbon layer thickness.

2. Experimental

2.1 The following materials have been utilized

a- Poly styrene – co- butadiene (“B.D.H. Ltd A.R. Grade , purity 99%”) has been utilized at testing sample.

b- TiO₂ (“B.D.H. Ltd A.R.Grade , purity 99%”) has been utilized at testing sample.
c- Benzyl bis(benzoylhydrazone) Ni, Ni complex, [C_{28}H_{26}N_{4}O_{5}Ni] was prepared and characterization as literature\textsuperscript{21}.

\[ \text{Benzyl bis(benzoylhydrazone) Ni} \]

### 2.2 Ultra-violet visible spectro-photometry (UV):

The spectra of the absorption have been recorded with the use of visible ultra-violet spectro-photometer with the use of Hitachi U2000 and Cary100 conc. for recording the spectra of the absorption in the range of the wave-length from (200nm-600nm).

### 2.3 Infrared spectrometry (IR)

A Pye-Unicam SP\textsubscript{3}-100 infra-red spectro-photometer has been utilized for recording infra-red spectra in the range of (600cm\textsuperscript{-1}-4,000cm\textsuperscript{-1}).

### 2.4 Preparations of the Film

0.10\% solution of TiO\textsubscript{2} dye or Ni complex, benzyl bis(benzoylhydrazone) Ni (in toluene) has been added into 1\% poly styrene – co-butadiene solution in toluene. An approximate 25\(\mu\)m thickness of polymer film has been evaluated with a micrometer type, (2,610, Germany), poly styrene – co-butadiene films with and with out dye and complex have been produced through the casting of the solutions to horizontal glass plate. Following the evaporation of the solvent, the samples have been dried for 24h in vacuum. this has been discovered to be sufficient for the complete removal of the solvent from the films.

### 2.5 Irradiation

The accelerated weather-o-meter, tester of QUV, (“Q-panel company, U.S.A”\textsuperscript{2}), has been utilized to irradiate the films of poly styrene – co-butadiene. The films have been located separated from U.V. lamps (8 fluorescent lamps provide mainly mono-chromatic light at \(\lambda=313\)nm). The tester chamber temperature is almost constant at a temperature of 45\(^{\circ}\)C.
2.6 Analysis

The polymer film photo-degradation has been succeeded with an IR and U.V.-visible spectro-photometer. The spectra of the absorption (for the IR approach) of film samples have been recorded in wave-number in the range between 600cm\(^{-1}\) to 4,000 cm\(^{-1}\). Carbonyl index has been computed through comparing IR peak of absorption at 1,745cm\(^{-1}\) for (C=O) group and 3,364cm\(^{-1}\) for the group of (OH) with a reference peak of 1,430cm\(^{-1}\) for the group of the (-CH\(_2\)) for poly styrene – co-butadiene. The UV-visible spectro-photometer has been utilized for measuring the variation in UV-Visible spectrum throughout the irradiation.

2.7 Determining the relative and specific viscosity

The viscosity has been utilized for following the polymer’s degradation degree. A polymer solution viscosity has been evaluated with a viscometer of Ostwald U-tube. Solutions have been produced through the dissolution of the polymer in a solvent (i.e. toluene) (10g/100mL) and the polymer solution flow times (t) and pure solvent (t\(_o\)), have been respectively evaluated.

The relative viscosity (\(\eta_{rel}\)) given with the flow time ratio of solution (t) to the pure solvent’s flow time (t\(_o\)) has been computed from eq. (1)\(^{22}\)

\[
\eta_{rel} = \frac{t}{t_o} \quad \text{................(1)}
\]

The specific viscosity (\(\eta_{sp}\)), can be defined as the relative viscosity increment of solution over the solvent’s viscosity which is computed as:

\[
\eta_{sp} = \frac{(t - t_o)}{t_o} = \eta_{rel} - 1 \quad \text{................(2)}
\]

The relative viscosity (\(\eta_{red}\)) represented with the (\(\eta_{sp}\)) ratio to the polymer’s concentricity, which was calculated from equation:

\[
\eta_{red} = \frac{\eta_{sp}}{C} \quad \text{..............(3)}
\]
2.8 Photo-degradation rate measurements of polymer films with the use of the UV-visible spectro-photometer

The UV-visible spectro-photometer technique has been utilized for measuring the UV-visible spectrum variations throughout the times of irradiation for copolymers. The absorption spectra were recorded in the wavelength which ranged from 200nm to 600nm and the (λ max) at every peak of absorption has been recorded as well for various times of irradiation.

The constant of the photo-degradation rate for additives (k_d) has been computed using the 1st order eq. 23

\[
\ln (a - x) = \ln a - K_d \times t \quad \ldots \ldots (4)
\]

Where (a) is the additive concentricity prior to the irradiation, (x) is the change in the additive concentricity post the time of irradiation (t), and A₀ is the intensity of absorption of the polymer film which contains the additive prior to the irradiation.

(A_t) is the intensity of the absorption after irradiation time (t), and (A_∞) is the absorption intensity at infinite irradiation time, then

\[
\ln (A_\infty - A_t) = \ln (A_\infty - A_0) - K_d \times t \quad \ldots \ldots (5)
\]

3. Results and discussion

The polymer films’ photo-degradation was researched. The U.V.-visible of poly styrene – co-buta diene films (control) spectra which is irradiated with various intervals of time. 400hrs. after that irradiation, the absorbance increases, the increase rate is considerably higher compared to it in the region of the wave-length of (λ= 300nm-400nm), as shown in figures (1-3), where the increased absorbance results from the formation of the groups of hydroxyl and carbonyl in polymer.

![Figure 1. U.V. –visible spectral change of polymer film without photo-sensitizer](image1)

![Figure 2. U.V. –visible spectral difference of the polymer film with the dye photo-sensitizer](image2)
Figure 3. U.V. –visible spectral difference of the PVC film with complex photo-sensitizer (25μm thick)

There are high growth in the hydroxyl and carbonyl groups absorbance in the wave-numbers 1745 cm\(^{-1}\) and 3364 cm\(^{-1}\) (FT-IR) respectively, and these bands intensity witnesses an exponential increase with the time of the irradiation. Which are expressed in terms carbonyl index (I\(_{CO}\)) and hydroxyl index (I\(_{OH}\)) respectively.

The correlation between the carbonyl index (I\(_{CO}\)) and hydroxyl index (I\(_{OH}\)) with the time of the irradiation is showed in figure (4,5) respectively.

Figure 4. The correlation between the index of the carbonyl and the time of irradiation for the polymer films with and without (0.10%w/w) of the photo-sensitizers

Figure 5. The correlation between the hydroxyl index and the time of the irradiation for the polymer films with and without (0.10%w/w) of photo-sensitizers
It was seen that the index of the carbonyl (I\textsubscript{CO}) with time of the irradiation for the poly styrene – co- butadiene film with complex greatly increases than polymer or dye photosensitizer while hydroxyl index (I\textsubscript{OH}) for poly styrene – co- butadiene film with complex photosensitizer or polymer only increases higher than polymer with dye photosensitizer. This due to decomposition constant for complex in polymer higher than dye in polymer as shows in figures (6) and (7).

The decomposition constant (from figure 3) of copolymer in complex Ni (k\textsubscript{d} = 0.0049hr.) was higher than k\textsubscript{d} value for the same copolymer in TiO\textsubscript{2} dye (k\textsubscript{d} = 0.0015hr.), which is attributed to the

The photo-degradation of copolymers can be followed by the measure of relative, specific and reductive viscosity in toluene solution at 20 °C before and after irradiation with and without photosensitizers using equations (1-3), it has been found that the relative, specific and reductive viscosity of polymers decrease with irradiation time, the relative, specific and reductive viscosity of copolymer without additive is less than that of the copolymer with additive, also viscosity of copolymer with Ni complex is less than copolymer with TiO\textsubscript{2} dye based on the molecular weight of polymers. Tables (1-3) shows the calculated values of the relative, specific and reductive viscosities for the copolymer without and with additives.
Table 1. The calculated values of different viscosity for polymer (without additive)

| Irradiation time (hr.) | Relative viscosity | Specific viscosity | Reductive viscosity (g/mL) |
|------------------------|-------------------|--------------------|---------------------------|
| 0                      | 1.817             | 0.817              | 62.88                     |
| 99                     | 1.799             | 0.799              | 60.31                     |
| 197                    | 2.207             | 1.207              | 52.93                     |
| 344                    | 1.951             | 0.951              | 46.23                     |
| 427                    | 1.676             | 0.676              | 40.55                     |

Table 2. The calculated values of different viscosity for polymer (with dye)

| Irradiation time (hr.) | Relative viscosity | Specific viscosity | Reductive viscosity (g/mL) |
|------------------------|-------------------|--------------------|---------------------------|
| 0                      | 2.660             | 1.660              | 62.20                     |
| 99                     | 2.848             | 1.848              | 59.25                     |
| 197                    | 1.804             | 0.804              | 43.54                     |
| 344                    | 1.575             | 0.575              | 37.43                     |
| 427                    | 1.766             | 0.766              | 35.01                     |

Table 3. The calculated values of different viscosity for polymer (with Ni complex)

| Irradiation time (hr.) | Relative viscosity | Specific viscosity | Reductive viscosity (g/mL) |
|------------------------|-------------------|--------------------|---------------------------|
| 0                      | 2.355             | 1.355              | 62.55                     |
| 99                     | 2.288             | 1.288              | 57.47                     |
| 197                    | 1.910             | 0.910              | 33.56                     |
| 344                    | 1.504             | 0.504              | 28.37                     |
| 427                    | 1.541             | 0.541              | 24.74                     |
The polymer degradation and carbonyl and hydroxyl groups formation is shown in the following mechanism, scheme (1).

Scheme1. Reaction of the photo-degradation of PVC with the existence of O$_2$

It is common that formation of titanium di-oxide has been subjected to the U.V. radiation is capable of creating pairs of electron-hole. Those pairs may be transferred to the titanium di-oxide surface where they are reacting with the absorbed H$_2$O and O$_2$ and as a result, create O$_2$ $\cdot$•, HOO• and OH• $^{24-26}$. Those radicals are capable of reacting with the organic materials and yield in their decomposition and oxidation. Therefore, it looks like the plastic composition with the titanium di-oxide nano-particles is a beneficial way of decomposing the solid polymers in open air $^{27-31}$. UV light and the generated free radical effectively initiate the co-polymer photo-degradation. The radical will abstract hydrogen atom from the chain of the copolymer and this reaction results in photo-degrading the co-polymer.

So these photo-sensitizers (dye and complex) are considered to be inducers of the photo-degradation for the poly styrene – co-butyadiene, due to the carbonyl index and hydroxyl index growth of those photo-sensitizers is greater compared to the polymer without the photo-sensitizers. In addition to that, results have shown that the (complex) acts like better-inducer of the photo-degradation of the polymer, in comparison with other photo-sensitizer (i.e. dye), where the increased in the index of the carbonyl ($I_{co}$) and the index of the hydroxyl are higher than that for polymer(control), these results are in agreement with the literatures$^{32}$. 
Conclusions

It has been concluded that adding small percentage (0.10% w/v) of the low-molecular complexes like the dye and the complex efficiently impacts the photo-processes in the polymer. It was discovered that the degradation of the photo-oxidative polymer is more sufficient in the existence of those sensitizers and complex action is the strongest as the inducer for the co-polymer and dye is less for the co-polymer.

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