Study the photo degradation and biodegradation of p-cresol novolac (polyepoxy) in presence and absence of di-benzoylperoxide

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Abstract

The induced photo degradation of poly epoxy films in air was investigated in the presence and absence of di-benzoylperoxide (BPO)(photosensitizer) by accelerated weathering tester. The addition (0.1 wt%) of BPO to poly epoxy films (25 μm in thickness) increases the photo degradation of the poly epoxy films. The photodegradation rate was followed by increase in carbonyl absorbance of polymers using I.R. spectra.

According to the spectra results, the induced photo degradation mechanisms of poly epoxy films were suggested under the experimental conditions employed using Uv-radiation at λ = 313 nm light intensity 3.49*10⁻⁵ einsteins.dm⁻³.S⁻¹ at temperature 45 °C. The biodegradability of photodegradable polymers has been also studied using different bacteria. This type of bacteria is known to be capable of utilizing the degraded polymers.

Keywords: photo degradation, biodegradation, p-cresol novolac

Introduction

Poly epoxy are among most important thermoset polymers which extensively have used as matrix in various fields such as aerospace and surface coating industries [1], novolac resin is a polymeric additive which can be used as a modifier for poly epoxy. Novolac resin is either easy to produce or low cost and cured novolac shows excellent rigidity, dimensional stability and fire resistance. On the other hand, traditional novolac suffers from brittleness, high shaping pressure and dark color due to the oxidation of phenolic groups [2]. During irradiation of polymeric chains in presence of air, excited chromospheres are formed followed by other processes, such as chain scission, photo oxidation and cross-linking take place [3-9]. The interaction of UV-radiations with polymeric chromospheres in presence of air resulted in the formation free radicals.
There are many sources of biodegradable plastics, from synthetic to natural polymers. Natural polymers are available in large quantities from renewable sources, while synthetic polymers are produced from non-renewable petroleum resources. Biodegradation takes place through the action of enzymes and/or chemical deterioration associated with living organisms. This event occurs in two steps. The first one is the fragmentation of the polymers into lower molecular mass species by means of either abiotic reactions, i.e. oxidation, photodegradation or hydrolysis, or biotic reactions, i.e. degradations by microorganisms. This is followed by bioassimilation of the polymer fragments by microorganisms and their mineralisation. Biodegradability depends not only on the origin of the polymer but also on its chemical structure and the environmental degrading conditions. Mechanisms and estimation techniques of polymer biodegradation have been reviewed [10]. The mechanical behavior of biodegradable materials depends on their chemical composition [11,12], the production, the storage and processing characteristics [13,14], the ageing and the application conditions [15]. The aim of this work study the photodegradation and biodegradation of p-cresol novolac (poly epoxy) in presence and absence of di-benzoyl peroxide.

**Experimental**

**Material**

a- Laboratory di-benzoyl peroxide powder (B.D.H. Ltd A.R.Grade, purity 99%) was used at the test sample.

b- p-cresol novolac (poly epoxy) was prepared as previously method(16).

![Infrared Spectroscopy](image)

**Infrared Spectroscopy (IR)**

A Pye-Unicam SP3-100 infrared spectrophotometer was used to record the IR spectra between (600-4000) cm\(^{-1}\).

**Film preparations**

About 0.1% solution of di-benzoyl peroxide (BPO) (in distilled water) was added to 1% solution of poly epoxy in distilled water. A thickness of about 25 μm was measured by a micrometer type, (2610, Germany). Poly epoxy films with and without
BPO were obtained by casting of solutions into horizontal glass plate (from NaCl salt, 3.41 mm thickness). After solvent evaporation, samples were dried in vacuum for 24 hrs. This was found to be adequate to completely remove of solvent from films.

**Irradiation**

The accelerated weather-o-meter, Q.U.V. tester, (Q-panel company, U.S.A), was used for irradiation of poly epoxy films. The films were positioned (25 μm) apart from the u.v. lamps (eight fluorescent lamps give essentially monochromatic light at λ=313 nm). Temperature of the tester chamber is nearly constant at 45 °C.

**Analysis**

The photo stabilization of the polymer film was followed by I.R spectrophotometer. The absorption spectra (for I.R method) of the film samples were recorded in the wavenumber ranged from 600 to 4000 cm\(^{-1}\). Carbonyl index were calculated by comparison of the I.R absorption peak at 1707 cm\(^{-1}\) for (C=O) group with reference peak at 1500 cm\(^{-1}\) for (-CH\(_2\) ) group for poly epoxy.

**Biodegradation method**

Bacteria type Pseudomonas fluorescens, Pseudomonas viscose, Pseudomonas fragi and Standard bacteria (Bacillus) was grown on irradiated polymers, poly epoxy without and with photosensitizer (BPO), as a sole source of carbon and energy in order to ensure their ability to utilize them. Five milliliters of mineral salt medium (table 1) distributed in 25 mL tube. The tube was sterilized by autoclaving at 120 °C for 15 minutes, then it was taken to the isolated bacteria. All the tubes were inoculated with 1% of fresh culture (18hrs), then 1g/L of polymer was added and incubated with shaking (180 rpm) at 37ºC for two weeks.
Table -1: Mineral Salt Medium for growth bacteria\(^{(17)}\)

| Salt                | Weight (g) |
|---------------------|------------|
| $K_2$HPO$_4$        | 1.170      |
| KH$_2$PO$_4$        | 0.121      |
| MgSO$_4$.7H$_2$O    | 0.121      |
| NH$_4$CL            | 2.140      |
| FeSO$_4$.7H$_2$O    | 0.28       |
| MnSO$_4$.4H$_2$O    | 0.06       |
| H$_3$BO$_3$         | 0.005      |
| ZnSO$_4$.7H$_2$O    | 0.01       |
| CuSO$_4$.5H$_2$O    | 0.061      |
| Co(NO$_3$)$_2$.6H$_2$O | 0.06     |
| NiSO$_4$.7H$_2$O    | 0.00006    |
| Distilled water     | 1000 mL    |

The pH was adjusted to 7.5 by buffer solution ($K_2$HPO$_4$1.17g and KH$_2$PO$_4$0.121g in 100mL).

**Bacteria strains**

The bacteria strain used in this study is:

- Neor: neomycin resistant
- sms: streptomycine resistant

Results and discussion

When the polymer film samples, irradiated with wavelength ($\lambda$=313 nm), The FTIR showed the formation of carbonyl groups absorbance in the wavenumber 1707 cm$^{-1}$, and this band intensity increased exponentially with irradiation time, figure (1), which is expressed in term carbonyl index ($I_{CO}$). In the presence of the di-benzoyl peroxide for different time intervals the photosensitizer increases the formation of carbonyl group in the polymer. The relationship between the carbonyl index ($I_{CO}$) with irradiation time for poly epoxyfilms with and without (0.1 % w/w) of photosensitizers is showed in figure (2).
It has been observed that the carbonyl index greatly decrease with irradiation time for poly epoxy film with di-benzoyl peroxide photosensitizer, where scission of some of the C-C bonds results in the formation of carbonyl end–group (carboxylic) \(^{18}\) is expected to form according to these reactions, scheme (1).
So this photosensitizer is considered as photodegradation inducers as the increase of carbonyl index with this photosensitize is higher than polymer without photosensitize, during the photosensitive of polymer with a BPO, there are crosslinking reactions that occur which effected on analysis physical properties of polymer such as solubility with solvents.

**Biodegradation of polymers**

The bacteria, Pseudomonas fluorescens, Pseudomonas viscose, Pseudomonas fragi and standard bacteria (Bacillus), used in this work, is utilizing aliphatic and aromatic hydrocarbons (such as phenol and n-hexane). In order to ensure that the isolated bacteria was indeed capable to growth in procure of irradiated polymers (as the sole available carbon source), a series of experiments were carried out in which the growth in the polymer environment was compared with that in control (mineral medium free of carbon source). A typical result are shown in table (2)
Table (2): Growth of bacteria on polymers after 300 hours photolysis

| Compounds | Pseudomonas fluorescens | Pseudomonas viscoso | Pseudomonas fragi | standard bacteria (Bacillus) | % loss weight |
|-----------|-------------------------|---------------------|------------------|-----------------------------|--------------|
| 1. Polymer with BPO after irradiated | ++++ (dark green) | +++ (very green) | + (pale green) | - | 50 |
| 2. Polymer with BPO before irradiated | ++ (green) | + (pale green) | + (pale green) | - | 20 |
| 3. Polymer without BPO before irradiated | + (pale green) | + (pale green) | + (pale green) | - | 2 |
| 4. Polymer without BPO after irradiated | ++ (green) | +++ (very green) | ++ (green) | - | 10 |

ASTM rating: (09)

(-) = no visible growth, (+) = 1-30% surface growth, (++ = 30-50% surface growth, (+++ = 50-70% surface growth, (++++) = 70-90% surface growth

It was concluded from such data that these bacteria were indeed capable of a significant amount of growth when the only carbon source present was the polymer. Color changes from colorless solution to green solution indicate to microbial growth. The biodegradation are followed by percentage weight loss of polymer after biodegradation, where the polymer precipitated from bacterial solution by ethanol, then dried under vacuum.

\%

\text{loss weight} = \frac{\text{weight of polymer before biodegradation} - \text{weight of polymer after biodegradation}}{\text{weight of polymer before biodegradation}} \times 100

In general, during UV-irradiation of polymers the concentration of functional groups on the chain ends and inside macromolecules (double bonds and carbonyl groups) increases. It probably makes polymers more susceptible to attack by bacteria in natural environment. It is also well-known that the efficient main chain scission in irradiated polymers causes their mechanical deterioration and breaking on to small
pieces. Thus, the access of oxygen and microorganisms is facilitated to the bulk of such destroyed products. In this way polymers become biodegradable.

From above results, the irradiation polymer contain di-benzoyl peroxide was higher biodegraded with *Pseudomonas fluorescens* than other polymers and polymer without BPO was less biodegraded with all types of bacteria than other polymers, where sensitizer increase photo degradation of polymer. The conclusion of this work that polymer fragments produced by photo degradation of certain plastic molecules indeed attacked and metabolized by soil microorganism.

The use of biodegradation offers a cheap method for recycling nutrients efficiently and, when optimized, at a faster rate than under natural conditions. It would appear to be low in its energy requirements.

**Conclusions**

It can be concluded that addition of small amount (0.1% w/w) of di-benzoyl peroxide effectively influences the photo processes in polymer. It has been found that photo-oxidative degradation of polymer is more efficient in the presence of di-benzoyl peroxide which action as degradation sensitizer for poly epoxy. By using repetitive transfer to mineral media in which the only carbon source is degraded polymer, some of the bacteria isolated are of genera which are known to attack both aliphatic and aromatic hydrocarbons.

These results confirm that polymer fragments produced by photo degradation of certain plastic molecules indeed attacked and metabolized by soil microorganism.

The use of biodegradation offers a cheap method for recycling nutrients efficiently and, when optimized, at a faster rate than under natural conditions. It would appear to be low in its energy requirements.

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