Acetophenone and Benzophenone Derivatives as Catalysts in Photodegradation of PE and PP Films

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Abstract. Due to their versatile functionalization, acetophenone and benzophenone derivatives as plastic additives were synthesized and blended into PE and PP to study rate of degradation under ultraviolet irradiation by monitoring carbonyl index, tensile strength and weight loss. The photolytic reactions of these ketones in benzene solution showed that acetophenone derivatives, especially 3-nitroacetopheone, underwent rapid degradation under the short-wave ultraviolet (254 nm) rather than in the black light (366 nm) while benzophenone derivatives showed small carbonyl index reduction. However, both groups of ketones, in hexane solution or in PE and PP films, primarily lowered the carbonyl index and rised up again except for the bromo derivatives. At 96 hrs of UV irradiation, the tensile strength of the acetophenone-blended PE film reduced only 20% while the tensile strength of the acetophenone-blended PP film decreased dramatically upto 90% and 95% for the benzophenone-blended PP.

Introduction

Recently environmental problems caused by the conventional fuel based plastics have become public major concerns. Many countries applied various policies and managements to overcome these problems e.g. recycle reuse and reduce protocol. However, due to the enormous amount of packaging and household plastics used every day, such attempt was found to be far from succeed. Other modern strategy is to replace the conventional plastics with biodegradable plastics such as modified starches, polylactic acids, polyhydroxyalkanoates and such. However, their prices and applications have always been considerated.

After looking into a natural pathway of auto-oxidative degradation of polyethylene (PE) and polypropylene (PP) which were normally initiated by light or heat (so called photo-oxidative degradation or thermo-oxidative degradation). This step usually is the slow process and becomes the rate determining step because plastics have to combine with oxygen in the air and react to give peroxy compounds which are not stable and can then decompose to carbonyl and free radical intermediates e.g. alkyl radicals or hydroxyl radicals.[1] Moreover, the carbonyl compounds can be photolyzed to more free radicals. The radicals then undergo propagation step in the degradation chain reaction of PE and PP and give more and more of oxygenated carbon skelatons in the plastics in form of hydroxyls, aldehydes, ketones and carboxylic acids [2] which then can be further biodegraded at $\leq$500 Dalton in molecular weight finally resulting carbondioxide and water. [3] In order to jump start the photo-degradation process, the oxygen will be installed in the polymer chain in plastics as the carbonyl additives. Due to their versatile functionalization, acetophenone and benzophenone derivatives as plastic additives were synthesized and blended into PE and PP to study rate of degradation under ultraviolet irradiation by monitoring carbonyl index, tensile strength and weight loss. Our quick start is to introduce highly light absorbing functional group such as the aromatic entities along with carbonyl group in order to enhance molar absorptivity, so called chromophores. Many research groups have introduced the use of carbonyl and other chromophores in the plastic degradation. [4, 5] In this paper, we synthesized acetophenone and benzophenone derivatives and investigated their behaviors under ultraviolet irridiation.

Experimental

Materials

Virgin grade LDPE (IRPC) and PP (IRPC) were used for the preparation of films. Acetophenone (analytical grade), benzophenone (analytical grade), benzene (HPLC grade) and hexanes (HPLC grade) were purchased from Sigma Aldrich. 3-Bromoacetophenone, 3-bromobenzophenone, 3-nitroacetophenone and 3-nitrobenzophenone were synthesized [6, 7] and fully characterized by ^{1}H NMR and IR spectroscopy before uses. {3-Nitroacetophenone: Yield 90%; m.p. 75-77 ^{o}C; IR (KBr) 3092 cm^{-1} (m), 1702 cm^{-1} (s), 1529 cm^{-1}(s), 1353 cm^{-1} (s); ^{1}H NMR (300 MHz, $CDCl_3$) 8.80 ppm (1H, m), 8.40 ppm (1H, m), 8.25 ppm (1H, m), 7.70 ppm (1H, m), 2.56 ppm (3H, s); 3-Nitrobenzophenone: Yield 86%; mp. 80-83 ^{o}C; IR (KBr) 3094 cm^{-1} (m), 1661 cm^{-1} (s), 1522 cm^{-1}(s), 1350 cm^{-1} (s); ^{1}H NMR (300 MHz, $CDCl_3$) 8.63 ppm (1H, s), 8.40 ppm (1H, d), 8.09 ppm (1H, m), 7.70 ppm (3H, m), 7.28 ppm (3H, m); 3-Bromoacetophenone: Yield 86%; IR (KBr) 2935 cm^{-1} (m), 1739 cm^{-1} (s), 608 cm^{-1}(s); ^{1}H NMR 300 MHz ($CDCl_3$) 8.00 ppm (1H, s), 7.70 ppm (2H, m), 7.28 ppm (1H, m), 2.55 ppm (3H, s); 3- Bromobenzophenone: Yield 88%; IR (KBr) 2934 cm^{-1} (m), 1718 cm^{-1} (s), 668 cm^{-1}(s); ^{1}H NMR 300 MHz ($CDCl_3$) 7.80 ppm (1H, s), 7.64 ppm (4H, m), 7.43 ppm (4H, m)}

Study of carbonyl additives in solutions

Acetophenone, benzophenone, 3-bromoacetophenone, 3-bromobenzophenone, 3-nitroacetophenone and 3-nitrobenzophenone were dissolved in both hexane and benzene at 1, 2, 3, and 5% w/v. After vigorously shaken, the solutions then were transferred into 10-ml pyrex sealed tubes and exposed under a 20-watt shortwave UV lamp (254nm) and a 20-watt longwave UV lamp (366 nm) at 30 cm in distance. The solutions then were taken out at 24, 48, 72 and 96 hrs of irradiation to determine carbonyl index using a Perkin Elmer spectrum 2000 FTIR spectrometer. [8]

Study of carbonyl additives in plastic films

Acetophenone and benzophenone were blended into both LDPE and PP at 1, 2, 3, and 5% w/w concentrations using a Twin-Screw Extruder (TSE 16 TC; Intro enterprise Co., Ltd), and then casted to 10-micron thick films using a Chill Roll Cast Film (LE 25-30/C; Labtec Engineering Co., Ltd). The plastic films then were cut to 10x10 cm size and exposed under a 20-watt shortwave UV lamp (254nm) and a 20-watt longwave UV lamp (366nm) at 30 cm in distance. The plastic films then were taken out at 24, 48, 72 and 96 hrs of irradiation to determine carbonyl index using a Perkin Elmer spectrum 2000 FTIR spectrometer, tensile strength using a Universal testing machine (Tensile H5K-T; Calserve Thailand), and % weight loss using a Sartorius BP 2105 Electric balance.

Results and Discussion

In solutions:

After the solutions of acetophenone, benzophenone, 3-bromoacetophenone, 3-bromo benzophenone, 3-nitroacetophenone and 3-nitrobenzophenone in benzene exposed UV irradiation for 24, 48, 72 and 96 hrs, the carbonyl indices were determined.

The investigation of carbonyl index in benzene solution, photolysis or degradation of carbonyl compounds was expected. However, only acetophenone derivatives showed slight reduction of carbonyl index after 24 hrs of irradiation while benzophenone derivatives showed steady carbonyl index through 96 hrs of irradiation as shown in Fig. 1A. This indicated that the acetophenone could reacted with the ultraviolet light and be photolysed generating free radical or such. This corresponded to the pathway of photoinitiator type I. Furthermore, it is important to note that the high energy shortwave ultraviolet showed better interaction with the carbonyl compounds than the long wave ultraviolet.

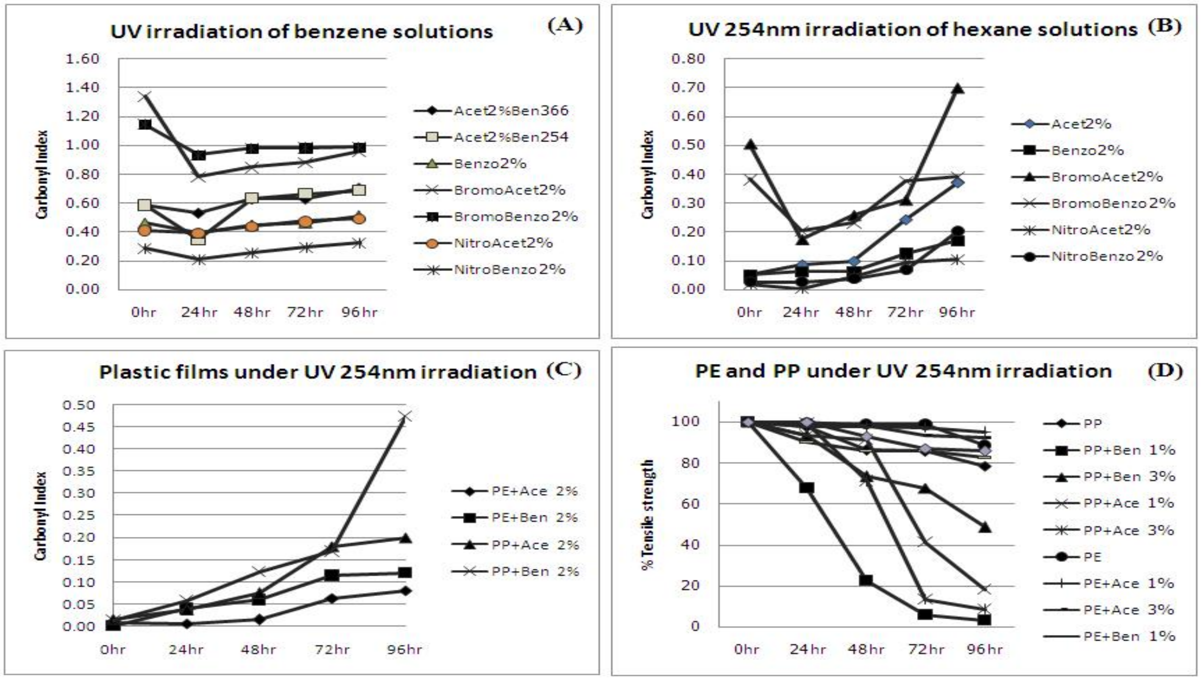

Fig. 1 The percentage of tensile strength reduction of acetophenone- and benzophenone-blended LDPE and PP Films at 1-5% w/w under 96 hrs ultraviolet 254 nm irradiation

The solutions of both 3-bromoacetophenone and 3-bromobenzophenone in benzene exposed under the shortwave ultraviolet showed surprisingly high carbonyl index from the beginning. The carbonyl index of the 3-bromoacetophenone solution tended to lower for two days before rising up again later while the carbonyl index of the 3-bromobenzophenone solution did not change. However, under the longer wave ultraviolet the solutions of both 3-bromoacetophenone and 3-bromobenzophenone showed drastic change of carbonyl index during 96 hrs of irradiation. This may indicate that the bromo derivatives of both ketones could interact very well with the low energy ultraviolet. The nitro derivatives also gave similar results with change at lower attitude. It is possible that this nitro group can somehow stabilize the carbonyls. However, before making a conclusion carbonyl index of these compounds in hexane solution and in plastic films should be investigated thoroughly.

In hexane solution, it is to prove that these carbonyls can generate free radical and/or catalyze the auto-oxidation process in the plastic skeleton by taken up oxygen in the atmosphere. As shown in Fig. 1B, the carbonyl index of the solutions of acetophenone and benzophenone in hexane increased dramatically. Even though, benzophenone did not show photolytic behavior in benzene solution, it also behaved as well as acetophenone. This corresponded to the pathway of photoinitiator type II. Furthermore, the increasing rate of carbonyl index of acetophenone and benzophenone derivatives in hexane became so steep, especially the nitro derivatives.

In PE and PP films:

As predicted, in Fig. 1C, the films of PE blended with acetophenone increased their carbonyl index by 5 times under shortwave ultraviolet irradiation in 96 hrs of irradiation. Also the benzophenone-blended PE films increased their carbonyl index more than 10 times under the same exposure. The result became greater with the films of PP. The 25-time increasing of carbonyl index can be achieved with simple acetophenone and 100-time increasing with benzophenone. These results have proven that carbonyl additives are far more effective than pro-oxidant additives. [9-11]

As shown in Fig. 1D, the tensile strength of the acetophenone-blended and benzophenone-blended PE films decreased by 10–20% after the 96 hrs shortwave ultraviolet irradiation. While in PP film, the acetophenone-blended films showed the dramatic reduction of tensile strength to 90% and the benzophenone-blended films provided rapid drop of tensile strength to 97% at 96 hrs of shortwave ultraviolet irradiation. During this study, brittle or broken PP films can be regularly observed.

The attempt to investigate the films degradation profile using weight loss technique gave only small satisfactory, because the time of ultraviolet exposure is short. However, some progress can be noticed. The acetophenone-blended PE films lose their weight by 0.6% while the benzophenone-blended films lose theirs by 0.5%. In PP films, the acetophenone-blended films showed 0.5% weight loss while the benzophenone-blended films gave 0.8% weight loss.

Conclusions

Acetophenone and benzophenone derivatives (3-bromoacetophenone, 3-bromobenzohenone, 3-nitroacetophenone and 3-nitrobenzopenone) as plastic additives were successfully synthesized. From the investigation of photolytic degradation in solutions, acetophenone derivatives showed the degradation pathway of photoinitiator type I while the benzophenone derivatives catalyzed photo-oxygenation of hydrocarbon chain without photolysis *via* the pathway of photoinitiator type II. Both groups of ketones, in PE and PP films, primarily lowered the carbonyl index and rised up again. After 4 days of irradiation, the tensile strength of the acetophenone-blended PE film reduced by 20% while that of the acetophenone-blended PP film decreased dramatically upto 90% and 95% for the benzophenone-blended PP.

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