

# Evaluation on the Thermo-Oxidative Degradation of PET using Prodegradant Additives

Ashwinder Chelliah<sup>1</sup>, Malini Subramaniam<sup>1</sup>, Ritu Gupta<sup>2</sup> and Arun Gupta<sup>1\*</sup>

<sup>1</sup>Faculty of Chemical and Natural Resources Engineering, University Malaysia Pahang, Gambang - 26300, Pahang, Malaysia; cashwinder@yahoo.com, malini90@hotmail.com, arun@ump.edu.my

<sup>2</sup>Faculty of Computer System and Software Engineering, University Malaysia Pahang, Gambang - 26300, Pahang, Malaysia; ritugupta.nz@gmail.com

## Abstract

**Objectives:** Transition metal stearates are example of potent pro-degradants reported to work at trace levels. They speed up the oxidative reaction leading to polymeric chain cleavage and reduction in molecular mass causing bio-assimilation of plastic waste. In this paper, attempt to analyze the effect of different loading amounts of cobalt stearate (CS) on the polymeric matrix of polyethylene terephthalate (PET) has been reported. **Methods/Statistical Analysis:** Formulated compounds were melt blended using an extruder and the extrudates were pelletized prior to molding into bone shaped specimens using an injection molding machine for characterization purpose. **Findings:** The effects on the incorporation of CS on the mechanical properties revealed that CS influences its tensile strength and elongation at break (%) at processing stage and studies based on Fourier Transform Infrared Spectroscopy (FTIR) spectra and carbonyl index (CI) measurements indicate that blends' consisting of 0.25CS contributes to thermal degradation of PET. **Application/Improvements:** The outcome of this study would assist in the production of biodegradable materials which could decompose in shorter time frame as well as reduces plastic waste in environment.

**Keywords:** Cobalt Stearate, Polyethylene Terephthalate, Pro-Degradant, Thermo-Oxidation

## 1. Introduction

Polyethylene terephthalate (PET) is linear thermoplastic polyester which is regarded to be a vital thermoplastic entity due to its promising material properties and production demands. Its versatility in applications enables it to be widely incorporated into consumer products such as in packaging, construction, automotive, healthcare and electronics<sup>1</sup>. Interestingly, owing to its flexibility in form and size, high strength-to-weight ratio, durability, transparency and easy process ability, polymeric PET resins has gained much interest in the production of beverage bottles and eventually outpaced the growth of other packaging materials<sup>2,3</sup>. However, following for its short term use in the packaging industry is the creation of inevitable post-consumer waste. Besides, being chemically inert and recalcitrant towards microbial degradation also contrib-

utes in the accumulation of PET waste in ecosystems<sup>4,5</sup>. According to a review by<sup>6</sup>, PET was listed as one of the most abundant plastics visible in solid urban waste.

As a measure to deal with the degradability factor of synthetic polymers, the use of prodegradant additives have been employed<sup>7</sup>. These additives are transition metal ion complexes of carboxylic acids and dithiocarbamates which accelerates the cleavage of long molecular plastic chains due to oxidation reaction and thereby leads to fragmentation of the polymer to facilitate biodegradation process<sup>8</sup>. This process which combines the oxidation and bio assimilation of plastic material by microbial attacks is known as oxo-biodegradation<sup>9</sup>. Transition metal salts which have been widely used are stearate salts of iron, cobalt and manganese<sup>10</sup>. They function to enhance degradation of plastic materials and in return solving the challenges posed by plastic waste towards the environ-

\*Author for correspondence

ment. Previous studies done by Roy et al., indicated that increasing concentration of cobalt stearate additive promotes thermo-oxidative degradation of Low Density Polyethylene (LDPE) films<sup>11</sup>. Not only that, CS is also commonly used as an additive in the growth of commercially available photodegradable polymer<sup>12</sup>. Nevertheless, the effect of incorporating CS additive on the degradation of PET has not been investigated. Therefore, in this work an attempt has been made to evaluate the effects of the addition of CS on the physical and mechanical properties, and thermo-oxidative degradation of PET based on FTIR and scanning emission microscopy (SEM) analysis.

## 2. Materials and Methods

Two commercially available materials namely PET and Cobalt (II) Stearate were used and the designation codes were presented in Table 1.

**Table 1.** Designated Codes

Sample	Loading amount of CS* (%)
PET	0
0.25CS	0.25
0.5 CS	0.5
0.75CS	0.75
1CS	1

\*CS loading based on PET weight basis

### 2.1 Sample Preparation

PET resins were oven dried for 24 hr at 100 °C until the weight of material became constant. After drying, the blends were pre-mixed for few minutes in a sealed plastic bag. The pre-mix was then compounded using a twin screw extruder. The temperature setting was maintained from a range of 265-210 °C throughout the process. Then, the extrudates were pelletized and further dried at 100 °C for 24 hr before moulding them into dumb-bell shapes specimens using an injection molding machine following ASTM D 638 standard.

### 2.2 Sample Characterization

A gas pycnometer under inert helium gas atmosphere was used to measure the density of composite materials. Sets of three cycles were performed for each formulated composite and the average reading was noted for analysis.

Tensile test was carried out using a computer controlled electronic Universal Tensile Machine with a crosshead speed of 5mm/min and load weight of 10kN.

Five specimens from each formulated blends were tested and the average readings for tensile strength and elongation at break (EB) were reported.

Thermo-oxidative test was performed by placing the dumb-bell shaped specimens in an air circulated oven at 70 °C for 600 hr under the exposure of heat<sup>13</sup>. The effect of CS on PET was evaluated by monitoring the changes in FTIR spectroscopy and SEM analysis.

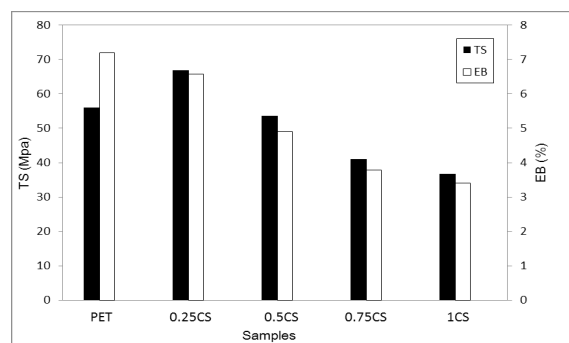
A Fourier transform infra-red (FTIR) spectrometer was employed to analyze the functional groups formed upon heat exposure. Each spectrum were recorded between 4000–400 cm<sup>-1</sup> with 32 scans at an optical resolution of 4 cm<sup>-1</sup>. Results from FTIR analysis were used to determine Carbonyl Index (CI). CI was used as a parameter to characterize the degree of degradation in the composites using baseline method.

$$CI = \frac{(Absorption\ at\ 1712\ cm^{-1})}{(Absorption\ at\ 1408\ cm^{-1})} \quad (1)$$

Morphological analysis of the samples obtained before and after degradation study were observed by using a scanning electron microscope (SEM), at an accelerated voltage of 8-10 kv.

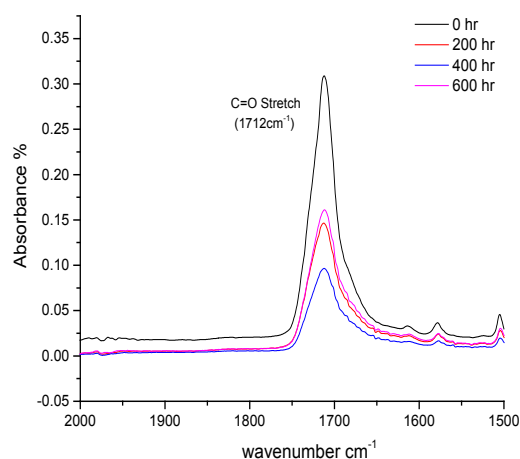
## 3. Results and Discussion

Table 2 presents the effect of CS loading on apparent density of PET. As been illustrated, the density of blends was observed to have a reduced value after blending 0.25CS with PET. This pronounced effect is probably due to the lower density of CS (1.1114 g/cm<sup>3</sup>) compared to PET (1.5665 g/cm<sup>3</sup>). However, increasing loading amount of CS into PET recorded a gradual increment in the apparent density of the blends. The same observation was reported by fellow authors on the degradation study of PP and PE in the presence of CS<sup>7,12</sup>.

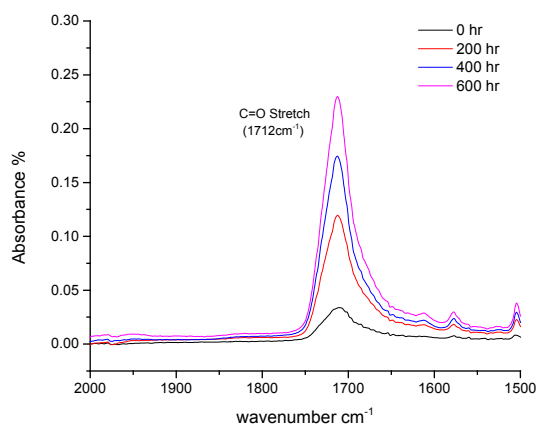


**Figure 1.** Tensile strength (MPa) and elongation at break (%) of PET and PET/CS blend.

The results on the mechanical tests performed with the presence and absence of CS are depicted in Figure 1. From the representative figure, it can be noted that there are appreciable changes which took place with the addition of CS at the processing stage. The tensile strength of 0.25CS shows to possess higher strength in comparison to pure PET. This increment in tensile strength of the blend could be possibly attributed to some reactive interactions taking place between CS additives and PET matrix at the processing temperature, thus aids in promoting to an improved strength of the material. However, increasing loading amount of CS from 0.5% to 1% in PET matrix have resulted in the progressive reduction of tensile strength of about 45%. These trends implies that



(a)

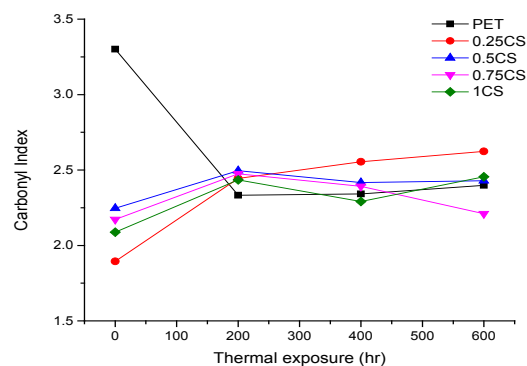


(b)

**Figure 2.** FTIR spectra of (a) PET and (b) 0.25CS before and after 600 hr of thermal exposure.

incorporation of CS exceeding the necessary amount results in poor affinity between the blends and eventually disrupt the mechanical behavior during melt blending. Likewise, a similar trend was noticed for the elongation at break (EB) of the samples as the loading amount of CS was increased. The depreciation of EB values suggest that the blend of samples with increasing amount of CS lacks coherence, thus causing the material to break apart.

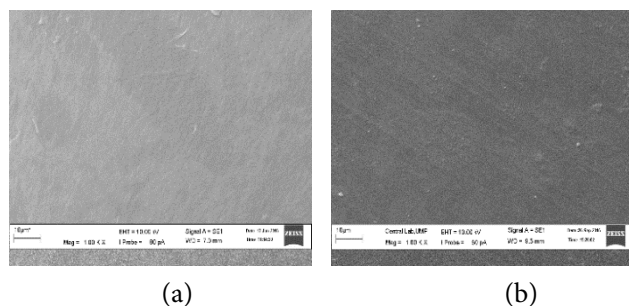
Figure 2 shows the FTIR spectra of (a) PET and (b) 0.25CS before and after thermal exposure, respectively. Structural transformation in the blends were evaluated by monitoring the absorptions regions where receptive bonds to degradation are present ( $2000\text{-}650\text{ cm}^{-1}$ ). As mentioned before, carbonyl groups intrinsic to PET or developed in polymeric chains due to oxidation reaction are located around absorption band of  $1700\text{-}1785\text{ cm}^{-1}$ . From the illustrated figure, it can be seen that the peak intensity at the region of  $1712\text{ cm}^{-1}$  assigned to the C=O stretching of ketone functionality (carbonyl groups) increases gradually and experiences a slight band broadening due to overlapping of stretching bands of carboxylic acid groups ( $1700\text{ cm}^{-1}$ ) and aldehydes and/or esters ( $1710\text{-}1725\text{ cm}^{-1}$ )<sup>14</sup>, as the exposure to thermal effect is prolonged. This growth signifies the beginning of degradation. Anyhow, increased CS loading recorded an uneven growth in peak intensity and does not contribute much to degradation. Comparatively for PET, the peak intensity reduced within the first 200 hr, but begins to build up slightly with very little changes as the exposure time is increased.



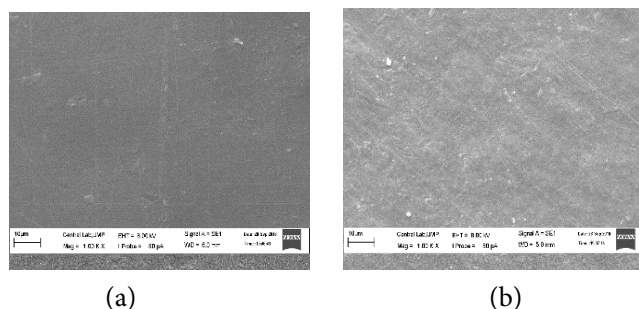
**Figure 3.** Carbonyl indices of PET and PET/CS blends after thermal exposure.

Figure 3 depicts the CI measurement of samples after thermal exposure. As can be noticed, 0.25CS recorded

a proportionate increase with the exposure time corroborating to the changes observed from FTIR spectra, where else PET and samples with 0.5CS, 0.75CS and 1CS are subjected to fluctuating values. The CI of 0.25CS increased from 1.9 to 2.6 after 600 hr of thermal exposure. The increasing CI over the time suggest that loading amount of 0.25% of CS is the optimum amount for degradation to occur slowly in PET during thermo-oxidative aging and increased loading amount of CS does not contribute much to PET degradation.



**Figure 4.** SEM micrographs of PET before and after 600 hr thermal exposure.



**Figure 5.** SEM micrographs of 0.25CS before and after 600 hr thermal exposure.

**Table 2.** Density of samples

Sample	Density ( $\text{gcm}^{-3}$ )	S.deviation
PET	1.5665	0.0018
0.25CS	1.488	0.0006
0.5CS	1.4963	0.0002
0.75CS	1.5042	0.0012
1CS	1.5191	0.001

Figure 4 (a,b) and 5 (a,b) presents micrographs of PET and 0.25CS samples before after 600 hr of thermal exposure at a uniform magnification of 1000x. As depicted in Figure 4(a), the surface of PET is almost smooth with no surface defects. Upon 600 hr of heat aging (Figure 4 (b), it was observed that the surface turned slightly rougher

possibly due to degradation, yet there were no presence of cracks or grooves. This shows that no much change have taken place to pure PET upon thermal exposure.

Comparatively, SEM compilation of 0.25CS samples in Figure 5 (a,b) shows apparent defects upon heat exposure. The sample after 600 hr aging was noticed to develop some grooves and defects, providing evident for degradation taking place.

## 4. Conclusion

The effect of adding varied loading amount of CS on the physical and mechanical properties and thermo-oxidative degradation of PET has been investigated. From the study done, it has been shown that inclusion of CS affects the physical and mechanical properties of PET. Results attained from FTIR analysis, CI measurement and SEM micrograph indicates that CS does promote thermal degradation of PET at an optimum amount of 0.25CS along with a compatibilized effect in the blend.

## 5. Acknowledgement

Authors thank Victorious Step Sdn Bhd for providing the raw materials and financial support to carry out the research study.

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