

SYNTHESIS OF METALS STEARATE AND THERMAL DEGRADATION  
STUDY OF POLYSTYRENE METALS STEARATE BLENDS

NUHA BINTI AWANG

UNIVERSITI TEKNOLOGI MALAYSIA

SYNTHESIS OF METALS STEARATE AND THERMAL DEGRADATION  
STUDY OF POLYSTYRENE METALS STEARATE BLENDS

NUHA BINTI AWANG

A thesis submitted in fulfilment of the  
requirements for the award of the degree of  
Master of Engineering (Polymer)

Faculty of Chemical Engineering  
Universiti Teknologi Malaysia

APRIL 2013

*To my beloved family and fiance*

## ACKNOWLEDGEMENT

First and foremost, I am very grateful to Allah S.W.T for giving me strength, confidence and patience to endure all problems, obstacles and finally been able to complete this study. I would like to express my special gratitude to my supervisor Dr. Agus Arsad and my co-supervisor Assoc. Prof. Dr. Abdul Razak Rahmat for their valuable advice, encouragement and constant dedication during my period of study.

My sincere thanks are also extended to Prof. Dr. Zainuddin Abd. Manan, Dean of Faculty of Chemical Engineering, Assoc. Prof. Dr. Shahrir Hashim, Head of Polymer Engineering, Assoc. Prof. Dr. Mat Uzir Wahit and all lecturers. I owe my sincere gratitude to Ministry of Higher Education (MOHE) for providing FRGS grant 78552, UTM Research Management Center (RMC), UTM Materials and Manufacturing Research Alliance (MMRA) and Advanced Membrane Technology (AMTEC).

My sincere gratitude to laboratory staffs of Faculty of Chemical Engineering (FKK) namely Mr. Azri, Mr. Nordin, Mr. Aizad, Mr. Nordin, Mr. Suhee and Miss Zainab in giving me help in handling experiments. My loving thanks are due to Mr. Awang, Mrs. Shamsiah and sisters. My special gratitude due to Mohd Fadzhir and friends for loving supports.

## ABSTRACT

Transition metals had been reported to act as effective pro oxidative additive for polymers. This study deals with the synthesis and characterization of three active transition metals complexes such as cobalt stearate, cupric stearate, and ferric stearate. A derivative of active transition metals stearate were synthesized by increasing the pH of metal acetate solution stirred with stearic acid in the presence of sodium hydroxide (NaOH) at 80 °C. The formula for the trimer as prepared is  $[\text{CH}_3(\text{CH}_2)_n\text{COO}]_3\text{M}$  (M= metal). The melting points of the additives were obtained by differential scanning calorimetry (DSC) which resulted 94.33 °C, 99.85 °C and 66.90 °C respectively. Thermogravimetric analysis (TGA) was also conducted to study the thermal stabilities of the additives. The study also involved the investigation of the effect of the oxidative additives on the degradation process of general purpose polystyrene (GPPS). The additives were blended with GPPS with the formulation 0.05-0.20 wt %. Studies on the effects of additives were then carried out by exposing the samples into the oven at 70 °C, 90 °C and 100 °C respectively for 50 hours. The chemical and mechanical changes induced by this exposure were followed by fourier transform infrared spectroscopy (FTIR), melt flow index (MFI), tensile test, TGA and DSC. Surface morphologies of degraded samples were observed by using scanning electron microscopy (SEM). The FTIR result indicates that carbonyl compound had the most significant changes for cobalt stearate at 1756.8-1800  $\text{cm}^{-1}$ . The absorption around band 1756.8  $\text{cm}^{-1}$  which can be assigned to the stretching of C=O functionalities, increased in intensity and broadened substantially, indicating the presence of the most effective oxidation product which is cobalt stearate. The thermo oxidative degradation in presence of metals stearate was found that all the additives effective were at 0.2 wt % according to the following arrangement cobalt> cupric>ferric in 90 °C air exposure.

## ABSTRAK

Siri unsur peralihan telah dilaporkan sebagai bahan tambahan pro-oksida yang berkesan untuk polimer. Kajian ini mengkaji cara sintesis dan pencirian kobalt stearat, kuprik stearat dan ferik stearat. Bahan tambahan pro-oksida disintesis dengan menaikkan pH larutan unsur peralihan asetat yang dicampurkan dengan asid stearik dengan kehadiran natrium hidroksida (NaOH) pada suhu 80 °C. Formula untuk hasil sintesis ialah  $[\text{CH}_3(\text{CH}_2)_n\text{COO}]_M$  (M=unsur peralihan). Takat lebur bahan tambahan pro-oksida dikaji oleh alat pengimbasan pembezaan kalorimetri (DSC) ialah 94.33 °C, 99.85 °C dan 66.9 °C. Analisis gravimetrik haba (TGA) dijalankan untuk mengkaji kestabilan terma bagi bahan tambahan itu. Kajian ini juga melibatkan penyiasatan tentang kesan bahan penambah oksida terhadap proses penguraian polystyrene kegunaan am (GPPS). Bahan tambahan pro-oksida tersebut dicampurkan dengan GPPS dengan formula 0.05-0.20 % jisim. Campuran telah didedahkan di dalam ketuhar pada suhu 70 °C, 90 °C dan 100 °C selama 50 jam. Perubahan sifat dikenalpasti dengan menjalankan ujian spektroskopi jelmaan infra merah (FTIR), indeks aliran leburan (MFI), ujian terikan, TGA dan DSC. Permukaan morfologi dikenalpasti dengan menggunakan teknik mikroskopi imbasan elektron (SEM). Hasil ujian FTIR menunjukkan sebatian karbonil telah menunjukkan perubahan yang jelas bagi kobalt stearat pada 1756.8-1800  $\text{cm}^{-1}$ . Penyerapan gelombang pada 1756.8  $\text{cm}^{-1}$  yang mana ia telah menunjukkan penarikan kumpulan berfungsi C=O, kenaikan pada keamatan dan melebar dengan banyak. Keputusan ini menunjukkan kehadiran bahan tambahan pro-oksida yang paling berkesan iaitu kobalt stearat. Penguraian secara termo oksida dengan logam stearat menunjukkan semua bahan tambahan berkesan pada komposisi 0.20 % jisim megikut susunan berikut kobalt> kuprik> ferik dengan pendedahan sampel pada suhu 90 °C.

## TABLE OF CONTENTS

<b>CHAPTER</b>	<b>TITLE</b>	<b>PAGE</b>
	<b>DECLARATION</b>	ii
	<b>DEDICATION</b>	iii
	<b>ACKNOWLEDGEMENT</b>	iv
	<b>ABSTRACT</b>	v
	<b>ABSTRAK</b>	vi
	<b>TABLE OF CONTENTS</b>	vii
	<b>LIST OF TABLES</b>	xi
	<b>LIST OF FIGURES</b>	xii
	<b>LIST OF SYMBOLS</b>	xiv
	<b>LIST OF ABBREVIATIONS</b>	xv
<b>1</b>	<b>INTRODUCTION</b>	1
	1.1 Research Background	1
	1.2 Problems Statement	6
	1.3 Objectives of the Research	6
	1.4 Scopes of the Study	7
<b>2</b>	<b>LITERATURE REVIEW</b>	10
	2.1 Polystyrene (PS)	10
	2.2 General Purpose Polystyrene (GPPS)	12
	2.3 Physical Properties of GPPS	14
	2.3.1 Density	14
	2.3.2 Durability	14

2.4	Thermal Properties	15
2.4.1	Glass Transition	15
2.4.2	Melting Temperature (T <sub>m</sub> )	15
2.5	Mechanical Properties	16
2.6	Chemical Property	16
2.7	Toxicity (Health and Safety Factors)	17
2.8	Recycling PS	20
2.9	Degradation of Plastic	22
2.9.1	Previous Research on Degradable material	24
2.9.2	Oxidation	26
2.9.2.1	Photo Oxidation on GPPS	27
2.9.2.2	Thermal Oxidation on GPPS	27
2.10	Metals stearate	29
2.10.1	Precipitation (Double Decomposition) Reaction	31
2.10.2	Direct Reaction	32
2.10.3	Fusion Reaction	33
2.10.4	AV Process	33
2.11	The role of Active Transition Metals as Pro-Oxidative Additive	34
2.12	Research on Degradable Plastic Containing Active Transition Metals	37
<b>3</b>	<b>METHODOLOGY</b>	<b>41</b>
3.1	Preparation of Active Transition Metals Pro-Oxidative Additives	43
3.2	Characterization of Metal Stearates Additives	47
3.2.1	Scanning Electron Microscopy (SEM) Micrograph Analysis	47
3.2.2	Solubility Test	47
3.2.3	Thermo Gravimetric Analysis (TGA)	47



3.2.4	Differential Scanning Calorimetric (DSC)	48
3.2.5	Fourier Transform Infrared (FTIR)	48
3.3	General Purpose Polystyrene (GPPS)	49
3.3.1	Formulation	49
3.3.2	Melt Blending (Extrusion Process)	49
3.3.3	Injection Molding	51
3.4	Characterizations of Samples (Polystyrene Blends with Metal Stearates Additives)	52
3.4.1	Setting up Thermo-Oxidative Degradation Testing	53
3.4.2	Melt Flow Index Test (MFI)	53
3.4.3	Thermogravimetry Analysis (TGA)	54
3.4.4	Differential Scanning Calorimetry (DSC)	54
3.4.5	Fourier Transform Infrared Spectroscopy (FTIR)	54
3.4.6	Tensile Test (Elongation at Break)	55
3.4.7	Scanning Electron Microscopy (SEM)	55
<b>4</b>	<b>RESULTS AND DISCUSSION</b>	<b>57</b>
4.1	Synthesis of Metals Pro-Oxidative Additives	57
4.2	Particle Size Definition By Scanning Electron Microscopy (SEM)	59
4.3	Solubility Test	61
4.4	Thermo Gravimetric Analysis (TGA)	62
4.5	Differential Scanning Calorimetric (DSC)	64
4.6	Fourier Transform Infrared (FTIR)	66
4.7	Characterization of General Purpose Polystyrene (GPPS) Blends Metals Stearate	68
4.7.1	Melt Flow Index (MFI)	68
4.7.2	Thermo Gravimetric Analysis (TGA)	69
4.7.2.1	Mechanism of Degradation	72
4.7.3	Differential Scanning Calorimeter (DSC)	73
4.7.4	Fourier Transfer Infrared (FTIR)	77

4.7.5 Tensile Strength (Elongation at Break)	79
4.7.6 Scanning Electron Microscopy (SEM)	82
<b>5 CONCLUSIONS</b>	<b>86</b>
5.1 Conclusions	86
5.2 Suggestions for Further Studies	88
<b>REFERENCES</b>	<b>90</b>
Appendices A-D	101-104

## LIST OF TABLES

TABLE NO.	TITLE	PAGE
1.1	Production and consumption breakdown for main types of styrene based plastics in the late 1999 (Brydson, 1999)	3
2.1	Mechanical properties of polystyrene (Wunsch, 2000)	16
2.2	Physical Properties of PS (Dunn, 2004)	19
3.1	Specification of Stearic Acid	43
3.2	Specification of Sodium Hydroxide (NaOH)	43
3.3	Specification of Metal Acetate	44
3.4	Trials formulation of synthesizing metals stearate	46
3.5	Specification of General purpose polystyrene (GPPS)	49
3.6	Melt bending formulation	50
3.7	Parameter setting for injection moulding	52
4.1	Size of synthesized metal stearates	60
4.2	Degradation temperature of metals stearate	64
4.3	Melting points of metal stearates	66
4.4	Spectra wavelengths for metal stearates	67
4.5	MFI data for GPPS blends metals stearate	68
4.6	Results of thermogravimetric (TG) and derivative thermogravimetric (DTG)	70
4.7	Result of $\Delta H_f$ and $\Delta H_c$ of samples before and after air oven exposure at 90 °C	76
4.8	GPPS blends metals stearate decrease in elongation at break due to 90 °C exposure	80

## LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
1.1	World consumption of polystyrene (www.cmai.com)	2
2.1	Chemical structure of Polystyrene (PS)	11
2.2	PS World Market Demand (www.cmai.com)	12
3.1	Experimental Framework	42
3.2	The experimental setting	42
3.3	Elements of injection moulding	51
4.1 (a)	Cobalt stearate	58
4.1(b)	Ferric stearate	58
4.1(c)	Copper stearate	59
4.2	Copper stearate particles image	60
4.3	The asymmetrical arrangement of metal stearate (cobalt stearate)	61
4.4 (a)	TGA and its derivative curve for copper stearate	63
4.4 (b)	TGA and its derivative curve for cobalt stearate	63
4.4(c)	TGA and its derivative curve for ferric stearate	64
4.5	DSC results of all metal stearates	65
4.6	Result of Fourier Transform Infrared (FTIR)	67
4.7	Comparison TG among GPPS with 0.20 wt/wt% metals stearate	71
4.8	Mechanism of Degradation Reaction of GPPS Blended Metal Stearate (Chiellinia <i>et.al.</i> , 2003)	72
4.9	Syndiotactic structure of GPPS	74
4.10 (a)	DSC scan of heating process before and after air oven exposure at 90 °C	75

4.10 (b)	DSC scan of cooling process before and after air oven exposure at 90 °C	76
4.11 (a)	FTIR spectra for GPPS blends metals stearate before entering air oven	77
4.11 (b)	FTIR spectra for GPPS blends metals stearate after entering air oven at 90 °C	78
4.12	The effect of thermal exposure on percentage of elongation at break	81
4.13 (a)	PCS20 at 70 °C ageing	83
4.13 (b)	PCS20 at 90 °C ageing	83
4.13 (c)	PCS20 at 100 °C ageing	84

**LIST OF SYMBOLS**

$\alpha$	-	Alpha
$\beta$	-	Beta
$^{\circ}$	-	Degree
$^{\circ}\text{C}$	-	Degree Celcius
D	-	Dextro
L	-	Levo
%	-	Percentage
wt %	-	Weight percentage

**LIST OF ABBREVIATIONS**

FTIR	-	Fourier transforms infrared
FUPTPS	-	Formamide and urea-plasticized thermoplastic starch
GPTPS	-	Glycerol-plasticized thermoplastic starch
H <sub>2</sub> O	-	Water
HCl	-	Hydrochloric acid
NaOH	-	Sodium hydroxide
PE	-	Polyethylene
PLA	-	Poly(lactic acid)
PP	-	Polypropylene
PVC	-	Poly(vinyl chloride)
SEM	-	Scanning electron microscope

## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 Research Background**

Plastic provides many benefits such as convenience and durability of applications. However, these same properties have made plastics a major problem in waste production. There are 46 billion pounds of plastic materials had been produced every year but approximately only three per cent of plastics are successfully being recycled ([www.cmai.com](http://www.cmai.com)). The remainders usually become permanent residents in the landfill and most of them are non-degradable (Ren, 2003). It threatens not only our environment but also life on the planet.

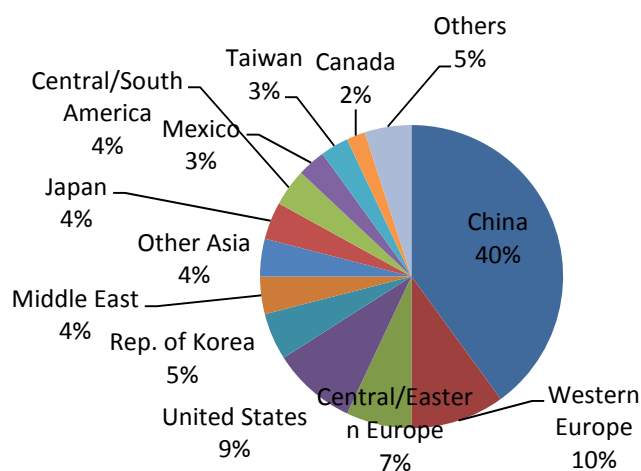
According to Gausepohl and Neibner (2008), polystyrene (PS) is one of the major thermoplastics with a high global demand ranking behind polyethylene, polypropylene and polyvinyl chloride. There are four different types of polystyrene which are general purpose polystyrene (GPPS), impact modified polystyrene (IPS) mostly called HIPS (high impact polystyrene), expandable polystyrene (EPS) and recently syndiotactic polystyrene (sPS).

PS is homopolymer of styrene, member of vinyl with attached benzene ring and random presence of benzene ring creates atactic character in polymer. GPPS



possess good mechanical, thermal and electrical properties but very poor ductility and impact property hence require the modification for potential applications (Srivastava, 2011). GPPS is made by continuous polymerization in bulk (bulk-polymerized polystyrene). The product is made in the form of dyed or undyed stabilized granules with residue monomer content. Suspension polymerization and in-bulk polymerization are the main methods in polystyrene production. The chain length may vary but most commercial products have between 100 and 5000 monomer units per chain (Messey, 2005).

Figure 1.1 shows the world consumption of polystyrene in 2011 surveyed by Chemical Market Associate Inc. (CMAI, 2011). China is the highest ranking consumers of polystyrene. As the time increase, GPPS become one of the highest demanded product which increases from time to time for the packaging and other applications. Due to this situation, the price of GPPS also increases. PS manufacturers are facing higher production costs although the still sluggish demand is likely to prevent any major hike attempts on polymer prices. Higher spot styrene values, which are up by US\$ 45 per ton since the beginning of the month gave signal for higher settlement for the year.



**Figure 1.1:** World consumption of polystyrene (www.cmai.com)

However, the increasing use of plastics in packaging applications has created a serious disposal problem. Burning of these plastic materials is unsatisfactory since it adds to air pollution problems and harmful to human (Taylor, 1977). Therefore, it

has been necessary to add materials to a basic polymer resin in order to make it process able. Additive materials are necessary to lower the average molecular and improve process ability, thus making GPPS the easiest thermoplastic to be degraded.

Table 1.1 shows the production and consumption of styrene based plastic in late 1999. Based on the table, GPPS and HIPS have the highest production in global compared to the others and the most application is packaging.

**Table 1.1:** production and consumption breakdown for main types of styrene based plastics in the late 1999 (Brydson, 1999)

	<b>GPPS and HIPS</b>	<b>XPS</b>	<b>ABS</b>	<b>SAN</b>
<b>Global production (10<sup>6</sup> t)</b>	8.0	1.85	3.0	-
<b>Application breakdown (%)</b>				
<b>Packaging</b>	40	29	-	12
<b>Insulation including refrigerator parts</b>	5	68	-	-
<b>Electricals/Electronics</b>	25	-	24	29
<b>Domestic appliances</b>	10	-	24	28
<b>Automotive</b>	-	-	23	-
<b>Other</b>	20	3	29	31

The usage of PS is getting lots of condemns from environmentalists. PS is non-degradable material, it will last for hundred years without being attacked by natural elements such as oxygen or UV light (Roy *et al.*, 2008). Consequently, many researchers believed that biodegradable food packaging has an excellent potential to be an alternative according to the problem. Raising consumer power and environmental realization, together with the public concerns about the increasing in pre - packaged disposable foods, means that food packagers and manufacturers are drastically subjected to improve their environmental performances. The scenario is also being driven by environmental activists and anti-pollution legislation (e.g., traceability of degradable polymers and compostable).

Therefore, some researchers have proposed to blend PS with starch to produce biodegradable composites. The starch portion in the PS /starch blend will be consumed by microorganisms (Li Ming De, 2000).The leftover skeleton of PS with larger surface area will tend to degrade by environment. However, the skeleton will still need to take several decades to reduce the harmful substance. Within this period, PS will form smaller particles in the soil or water. It will endanger animals lives if accidentally consumed.

Regarding to the above fact, the negatives environmental impact of abundant of plastic wastes had raised worldwide attention especially environmental activists, many solutions have been drawn to curb with the problem. Nevertheless, none of them succeed for example incineration and disposal method this is because incineration will contribute to air pollution due to its high percentage of toxicity and the gases produced spread easily to wind and occupy large volume of surroundings. Disposal method is found irrelevant due to the limited dump site.

In addition to that, incineration method is generally prohibited for PS because harmful gases will be produced during incineration such as carbon monoxide and benzene .Those gases create problem to human welfare after prolonged exposure for example cancer. Other gases that are released from combustion are nitrous oxides, light hydrocarbon, dioxins and sulphur oxides. The gases can cause major health hazards and recycling solution for commingledwaste are irrelevant due to the intensive of energy and expensive. Besides that, petroleum resources are also becoming limited and finite.

Regarding to the above-mentioned statements, with landfillingand incineration, as well as the naturally non-biodegradable PS, researches are being invented to curb with the problem. In 1990; some researchers had found that blending active transition metal pro-oxidative additive is an alternative for fully degradable PS (Brydson, 1999). The rate of degradation depends on the amount of transition metal activation conditions and types as well as the amount in used. However it is also depend on the exposure to the environment. Thermal oxidative

additives are used in polyethylene garbage bag where some of the countries such as Japan, Taiwan, Denmark and Switzerland have fully imposed regulations to use degradable garbage bag (Vlieger, 2005).

The process of degradation in thermo-oxidative degradable plastic had been used widely in late 1990's. Small amounts of active transition metals are being catalyzed with thermo-oxidative degradable plastic which is also an oxidative chain scissoring resulting to oxygenated (carboxylated and hydroxylated) shorter chain molecules that are suitably available for bio mineralization by microorganisms, typically fungi and bacteria ( Taylor and Tobias ,1997).

Thermo-oxidative degradable plastic if either accidentally discarded in the environment or disposed in a landfill will be degraded into oxygenated low molecular weight (MW 5-10.00 atomic mass unit) within 2-12 months referring to the material (polymer resins, oxidants and thickness) and the environment. For example, a PE plastic bag with 2% thermo-oxidative additive of 30  $\mu\text{m}$  thickness degrades within 3 months if it is left exposed and microorganisms in the same way other organic matter is used to generate energy and build biomass. As a result, 150 $\mu\text{m}$  molecules are then biomineralized ("eaten") by the microorganisms (Chiellinia *et al.*, 2003).

Currently, the application of thermal oxidative is very limited only for polyethylene based plastic products. Since the polystyrene are being used widely and generate a lot of non-degradable waste. Thermal oxidative used in polyethylene is lack effective to be applied in polystyrene because of stable benzyl ring structure and thus require higher activate transition metal to attack and chain scissoring the bonds. Hence, it is vitally essential to discover durable plastic alternatives, especially in disposable applications and short term packaging. Besides that, the research has been stimulated by the continuously concerned of the growing public in inventing metal pro-oxidative additives as an alternative to conventional non degradable polymer especially for GPPS. Therefore, the study is believed to find the solution to

alleviate non degradable polystyrene waste problems by synthesizing and characterizing oxidative additives which are from active transition metals

## **1.2 Problems Statement**

The active transition metals pro-oxidative additive degrades the polymer based on several factors such as temperature, moisture, UV light and present of anti-oxidants .The questions that have been identified in this research are as follows:

- 1) How to synthesize ferric stearate, cupric stearate and cobalt stearate?
- 2) What are the effects of thermal ageing (effects of different temperature) on the degradation of GPPS blends active transition metal pro-oxidative additives?
- 3) What is the morphology or surface image of GPPS blends metals stearate after undergoing degradation?

## **1.3 Objectives of the Research**

The purpose of the study is to discover the potential of active transition metals as pro oxidative additives in accelerating the degradation of GPPS. In addition to that, the following objectives are also included in the research:

- 1) To synthesize additives and study the fundamental characteristics of ferric stearate, cupric stearate and cobalt stearate.
- 2) To investigate the degradation of GPPS resulted by addition of different types and amount of active transition metals pro-oxidative additives.

- 3) To study the morphologies of GPPS blends metals stearate after undergoing thermal ageing process at different temperature.

#### **1.4 Scopes of the study**

The study was embarked on the below stages:

- i. Preparation of active transition metals pro-oxidative additives:
  - a. Cobalt, copper and ferric acetate were used as basic substances.
  - b. Cobalt, copper and ferric stearates were synthesized by using sodium hydroxide and stearic acids.
- ii. Characterization of the synthesized pro-oxidative additives using FTIR to investigate the carbonyl index in the additives. TGA and DSC testing was included to characterize thermal stability and melting points of the additives.
- iii. Solubility test had been done by using several types of solvents such as ethanol, n-hexane, cyclohexane, acetone, benzene and toluene.
- iv. Scanning Electron Microscopy (SEM) was applied to define the size of metals stearate particles.
- v. MFI testing with ASTM D1238 was carried out to investigate the change of processing temperature of samples with different formulations before compounding active transition metals pro-oxidative with GPPS in different weight per cent of pro-oxidative additives ( 0.05%-0.20% wt/wt).

- vi. Thermo-oxidative degradation test was setting up by placing the samples into oven at different temperature continuously for a week from 70°C, 90°C and 100°C.
  
- vii. Characterization of active transition metals pro-oxidative additive polystyrene after undergoing thermal ageing process at different temperature:
  - (a) Tensile test was carried out according to ASTM D638 to define the breaking point of GPPS blends pro-oxidative additives after undergoing thermal ageing process.
  
  - (b) Fourier Transform Infrared Spectroscopy (FTIR) was used according to ASTM E1421-04 (2004) to investigate the carbonyl changes in polystyrene.
  
  - (c) Scanning Electron Microscopy (SEM) was applied according to ASTM F1372 -93(2005) to study the breaking sample morphology of GPPS with active transition metals as pro-oxidative additives.
  
  - (d) Thermogravimetry Analysis (TGA) and Differential Scanning Calorimetry (DSC) was handled according to ASTM E1131 -08 and ASTM E1269-05 to study thermal stability of active transition metals pro-oxidative additive GPPS.

## REFERENCES

- Aamodt, K., Abrahantes Quintana, A., Adamová, D., Adare, A. M., Aggarwal, M. and Aglieri Rinella, G.(2011). Suppression of charged particle production at large transverse momentum in central Pb–Pb collisions. *Physics Letters B*, 696(1–2), 30-39.
- Abbas, KB. And Porter, R.S. (1976). Polystyrene degradation induced by stresses resulting from the freezing of its solutions. *Journal of Polymer Science: Polymer Chemistry Edition*, 14(3), 553-564.
- Abrahamson and Lukaski. (1994 ).Degradation of polymers during melt processing. *Polymer Degradation and Stability, Journal of Applied Science* 34, 279–293.
- Achhammer, B. G., Reiney, M. J., Wall, L. A., and Reinhart, F. W. (1952). Study of degradation of polystyrene by means of mass spectrometry. *Journal of Polymer Science*, 8(5), 555-571.
- Acierno, S. and Van Puyvelde, P. (2005). Rheological behavior of polyamide 11 with varying initial moisture content. *Journal of Applied Polymer Science*, 97(2), 666-670.
- Ahlgren, M., and Blomqvist, H. (2005). Influence of bias variation on residual stress and texture in TiAlN PVD coatings. *Surface and Coatings Technology*, 7(2),67-78.
- Ahmad , Swift G. and Gordon. (2007). Biodegradation of thermally oxidised, fragmented low density polyethylenes. *Polymer Degradation and Stability*, 6(2),54-60.
- Ahmad, R., Jilani, G., Arshad, M., Zahir, Z., and Khalid, A. (2007). Bio-conversion of organic wastes for their recycling in agriculture: an overview of perspectives and prospects. *Annals of Microbiology*, 57(4), 471-479.
- Albertsson, AC.and Karlsson, S. (1988). The three stages in degradation of polymers—polyethylene as a model substance. *Journal of Applied Polymer Science*, 35(5), 1289-1302.



- Albertsson, P.-Å. (1995). The structure and function of the chloroplast photosynthetic membrane a model for the domain organization. *Photosynthesis Research*, 46(1), 141-149.
- Albertsson, Sharma N, Chang LP, Chu YL, Ismail H, Ishiaku US, Ishak ZA.A (1994).study on the effect of prooxidant on the thermooxidative degradation behaviour of sago starch filled polyethylene. *Polymer Degradation and Stability*,7(2),89-97.
- Anne Marie, D., George, F. and and Joey , H., (2004). *Encyclopedia of Chemical Technology*. vol. 8. New York: Wiley,145-156.
- Arnaud, M., and Evrard, A. E. (1999). The LX–T relation and intracluster gas fractions of X-ray clusters. *Monthly Notices of the Royal Astronomical Society*, 305(3), 631-640.
- Arnaud,Lin Y., and Gon. (1994) .Study of photooxidative degradation of LDPE film containing cerium carboxylate photosensitiser. *Journal of Applied Polymer Science*,6(3),87-98.
- Arsad, A., Razak Rahm, A., Hassan, A., and Nizam Iska, S. (2010). Mechanical and Rheological Characterization of PA6 and ABS Blends- With and Without Short Glass Fiber. *Journal of Applied Sciences*, 11(13), 2313-2319.
- Avella, M., De Vlieger, J. J., Errico, M. E., Fischer, S., Vacca, P., and Volpe, M. G. (2005). Biodegradable starch/clay nanocomposite films for food packaging applications. *Food Chemistry*, 93(3), 467-474.
- Babbar,K. and Mathur, J.(2003). Biodegradation of thermally-oxidized, fragmented low-density polyethylenes. *Polymer Degradation and Stability*; 81; 341–351
- Bajer, Huang, M. and Ron, J. (2006). Thermal decomposition kinetics of thermotropic poly (oxybenzoate-co-oxynaph-thoate) vectra copolyester. *Polymer Degradation and Stability*, 64, 81–90.
- Barril, X., Brough, P., Drysdale, M., Hubbard, R. E., Massey, A., Surgenor, A., et al. (2005). Structure-based discovery of a new class of Hsp90 inhibitors. *Bioorganic. Medicinal Chemistry Letters*, 15(23), 5187-5191.
- Baur, P. S., Walkinshaw, C. H., Halliwell, R. S., & Scholes, V. E. (1973). Morphology of *Nicotiana tabacum* cells grown in contact with lunar material. *Canadian Journal of Botany*, 51(1), 151-156.

- Beachell, H. C., and Smiley, L. H. (1967). Oxidative degradation of polystyrene. *Journal of Polymer Science Part A-1: Polymer Chemistry*, 5(7), 1635-1643.
- Becker, C., and Gather, U. (2001). The largest nonidentifiable outlier: a comparison of multivariate simultaneous outlier identification rules. *Computational Statistics & Data Analysis*, 36(1), 119-127.
- Bernardin Iii, F. E., and Rutledge, G. C. (2007). Simulation of mechanical properties of oriented glassy polystyrene. *Polymer*, 48(24), 7211-7220.
- Bernardin, Rutledge, K. (2007). Melt Flow Index Values and Molecular Weight Measurements of Commercial Thermoplastics. *Journal Applied of Polymer Science*. Vol 41,161-189.
- Bordes, P., Pollet, E., and Avérous, L. (2009). Nano-biocomposites: Biodegradable polyester/nanoclay systems. *Progress in Polymer Science*, 34(2), 125-155.
- Brydson, J.A., (1999). Polystyrene. *Plastic Materials*. 6<sup>th</sup>. Oxford: Butterworth-Heinemann Ltd,7(3),65-69.
- Calcott, P., and Walls, M. (2005). Waste, recycling, and “Design for Environment”: Roles for markets and policy instruments. *Resource and Energy Economics*, 27(4), 287-305.
- Carniti, P., Gervasini, A., Beltrame, P. L., and Audisio, G. (1989). Evidence of formation of radicals in the polystyrene thermodegradation. *Journal of Polymer Science Part A: Polymer Chemistry*, 27(11), 3865-3873.
- Catia Bastioli (2005). Starch-Based Technology. In Catia Bastioli (Eds.). *Handbook of Biodegradable Polymer*. Crewe, UK: Rapra Technology Limite,3(2),56-67.
- Chauhan, R. S., Gopinath, S., Razdan, P., Delattre, C., Nirmala, G. S., and Natarajan, R. (2008). Thermal decomposition of expanded polystyrene in a pebble bed reactor to get higher liquid fraction yield at low temperatures. *Journal of Applied Science*,5(2),76-98.
- Chiellinia, Susanne and Harris. (2003) Photo-biodegradable plastics: their role in the protection of the environment. *Polymer Degradation and Stability*,29(2),45-67.
- Colom, Landau, M. and Simmon. (2003). Driers and Metallic Soaps. *Encyclopedia of Chemical Technology*. John Wiley & Sons, New York, Volume 8, 432–445.

- David Albertsson AC, Karlson S. (1997). Chemical and morphological changes of environmentally degradable polyethylene films exposed to thermo oxidation. *Polymer Degradation*, 7(3), 178-179.
- De Vlioger J,J (2005). Green plastics for food packaging. Raija Ahvenainen. *Novel Food Packaging Techniques. Finland. Woodhead Publishing* , 5(2), 524-525.
- DeBell, J. M., & Richardson, H. M. (1946). Stimulation of Plastics Technology by German Disclosures. *Industrial & Engineering Chemistry*, 40(4), 651-654.
- Dunn.(2004). New Motivation for the Depolymerisation Products Derived from PET Waste: a Review. *Macromolecule Material Engineering*, 6(2), 567-580.
- Emo Chiellinia, Andrea Cortia, and Graham Swift (2003). Biodegradation of thermally-oxidized, fragmented low-density polyethylenes. *Polymer Degradation and Stability*, (81), 341-351.
- Erlandsson, R., Olsson, L., & Mårtensson, P. (1996). Inequivalent atoms and imaging mechanisms in ac-mode atomic-force microscopy of Si(111)7×7. *Physical Review B*, 54(12), R8309-R8312.
- Erlandsson, Scott G. and Mary, A. (1996). Photo-initiated oxidation of polyethylene effect of photosensitisers. *European Polymer Journal*, 10(1), 123-145.
- Gather. (1995). Recycling of polymer waste: Part I Photo oxidised polypropylene. *Polymer Degradation* 45, 134-137.
- Gausepohl and Neibner. (2008). Structuring a market-oriented federal eco-information policy. *Maryland Law Review*, 5, 14-17.
- Gee.(2007). Study of Photooxidative Degradation of LDPE Film Containing Cerium Carboxylate Photosensitiser. *Journal of Applied Polymer Science*. Vol.63. Page 134-136.
- Goldberg, Jipa S, and Osawa Z.(1976). Chemiluminescence study on the oxidation of several polyolefins -I Thermal induced degradation of additive free polyolefins. *Polymer Degradation and Stability*, 3(7), 65-78.
- Grandjean, P., Bellinger, D., Bergman, Å., Cordier, S., Davey-Smith, G., Eskenazi, B., et al. (2008). The Faroes Statement: Human Health Effects of Developmental Exposure to Chemicals in Our Environment. *Basic & Clinical Pharmacology & Toxicology*, 102(2), 73-75.

- Griffin Kurisu N, Nagashima K, and Nankano K. (1991) The effect of transition metal stearate on the photodegradation of polyethyl-ene. *Journal of Applied Polymer Science*, 4(2),156-167.
- Gul, V. E., Yanovskii, Y. G., Shamraevskaya, T. V., and Litvinenko, O. A. (1993). Correlation of the relaxation and strain-strength properties of elastomers. *Mechanics of Composite Materials*, 28(5), 484-488.
- Halliwell.(2012).Chemical Reactions During the Processing of Stabilized PE: 2. Structure/Property Correlations. *Polymer Degradation and Stability* ,6(3),Page 499-509.
- Harper.(1999). Recycling of polymer waste: Part II Photo-oxidised polypropylene. *Polymer Degradation* ,4(7), 145-156.
- Hou, L., & Yang, G. (2005). Morphology and Thermal Properties of MCPA6/ABS by in situ Polymerization of  $\epsilon$ -Caprolactam. *Macromolecular Chemistry and Physics*, 206(18), 1887-1895.
- Iring, Lofgren EA. Etgar. (1992). Photo oxidative effects on properties and structure of high density polyethylene. *Journal of Applied Polymer*, 6(2),34-45.
- Jakubowicz .(2003.) Chemical and morpho-logical changes of environmentally degradable polyethylene filmsexposed to thermooxidation. *Polymer Degradation and Stability*, 6(3),123-145.
- Jellinek, H. H. G. (1949). Thermal degradation of polystyrene and polyethylene. Part III. *Journal of Polymer Science*, 4(1), 13-36.
- John,K.Citing websites.World Styrene Analysis.Retrieved May13, 2011, from [http:// www.styreneworld.com](http://www.styreneworld.com).
- Kaczmarec, Halina, Sionkowska, Alina, Kaminska, et al. (2001). The influence of transition metal salts on photo-oxidative degradation of poly(ethylene oxide). *Kidlington, Royaumi University: Elsevier*.
- Kelleher, P. G. (1966). Thermal oxidation of thermoplastics. *Journal of Applied Polymer Science*, 10(6), 843-857.
- Khabbaz and Albertsson (2001) Natural and artificial weathering of lowdensity polyethylene (LDPE): Calorimetric analysis. *Journal Applied Polymer Science* , 5(3),145-178.
- Kodera, Y., and McCoy, B. J. (1997). Distribution kinetics of radical mechanisms: Reversible polymer decomposition. *AIChE Journal*, 43(12), 3205-3214.

- Kosal, E., & Niedzlek-Feaver, M. (1997). Female preferences for large, heavy metals (Orthoptera: Acrididae). *Journal of Insect Behavior*, 10(5), 711-725.
- Kosal.(1993). Role of metals and metal deactivators in polymer degradation. *Polymer Degradation and Stability* 3(2), 45-67.
- Lafon, C., Zderic, V., Noble, M. L., Yuen, J. C., Kaczkowski, P. J., Sapozhnikov, O. A., et al. (2005). Gel phantom for use in high-intensity focused ultrasound dosimetry. *Ultrasound in Medicine; Biology*, 31(10), 1383-1389.
- Lang, K. and Gabriel.(2006). Degradable Polymers Principles and Applications. London: Chapman and Hall. Page,7(3), 478-487.
- Li Ming De (2000). U.S. Patent No. 6,090,863, Washington DC: U.S. Patent and Trademark Office.
- Liu, X.-Q., Yang, W., Xie, B.-H., and Yang, M.-B. (2012). Influence of multiwall carbon nanotubes on the morphology, melting, crystallization and mechanical properties of polyamide 6/acrylonitrile-butadiene-styrene blends. *Materials and Design*, 34(0), 355-362.
- Longieras, A., Copinet, A., Bureau, G., and Tighzert, L. (2004). An inert solid medium for simulation of material biodegradation in compost and achievement of carbon balance. *Polymer Degradation and Stability*, 83(2), 187-194.
- Lynn J. Taylor and John W. Tobias (1997). Accelerated Photo-Oxidation of Polyethylene (I). Screening of Degradation-Sensitizing Additives. *Journal of Applied Polymer Science*; 21;1273-1281.
- Majumdar, B., Keskkula, H., and Paul, D. R. (1994). Effect of the nature of the polyamide on the properties and morphology of compatibilized nylon/acrylonitrile-butadiene-styrene blends. *Polymer*, 35(25), 5468-5477.
- Marteen van der Zee (2004). Biodegradability of Polymers- Mechanisms and Evaluation Method. Catio Bastioli. *Handbook of Biodegradable Polymers*. 45-67.
- Massey, M.(2005). Determination of Overall Migration of Constituents of Plastics Materials and Articles Intended to Come in Contact With Foodstuffs- Method of Analysis. *BIS*,4(3), 456-489.
- Massey,M. (2006). Effect of Benzil and Cobalt Stearate on the Aging of LDPE Films. *Polymer Degradation and Stability* (2),567-600.

- McCrum, S., Vora, R.A. and Trivedi, C., (1997). Synthesis and Characterisation of Styrene-maleic Acid Copolymers. *Polymer Degradation and Stability*, 3(2), 111-118.
- McNeill, I. C. (1997). Thermal degradation of polystyrene in different environments. *Die Angewandte Makromolekulare Chemie*, 247(1), 179-195.
- Messey, (2005). Thinking Globally and Acting Locally: St. Paul's Plastic Packaging Ordinance. *Journal of Applied Polymer*, 5(2), 140-151.
- Millan, J., Madruga, E. L., Bert, M., and Guyot, A. (1973). Initial steps of thermal degradation of PVC prepared at various temperatures. *Journal of Polymer Science: Polymer Chemistry Edition*, 11(12), 3299-3307.
- Mitrus, M., Wojtowicz, A., and Moscicki, L. (2010). Biodegradable Polymers and Their Practical Utility: *Wiley-VCH Verlag GmbH & Co. KGaA*. 5(3), 45-67.
- Mo, J., Zhang, Y., Xu, Q., Lamson, J. J., and Zhao, R. (2009). Photocatalytic purification of volatile organic compounds in indoor air: A literature review. *Atmospheric Environment*, 43(14), 2229-2246.
- Mullen, Akcelrud L. and Andy. (1992). Degradation profile of polyethylene after artificial accelerated weathering. *Polymer Degradation and Stability* 3(2), 67-78.
- Nagaoka, H., and Akoh, H. (2008). Decomposition of EPS on the membrane surface and its influence on the fouling mechanism in MBRs. *Journal of Applied Science*. 5(2), 187-190.
- Nakajima, A., Hamada, F., and Shimizu, T. (1966). Change in molecular weight distribution accompanying thermal degradation of isotactic polystyrene. *Die Makromolekulare Chemie*, 90(1), 229-242.
- Newland Bikaris D, Prinos J, Perrier C, Panayiotou C. Thermoanalytical . (1969). study on the effect of EAA and starch on the thermooxidative degradation of LDPE. *Polymer Degradation and Stability*, 6(2), 313-314.
- Osawa et al (1985) Grant MH. Encyclopedia of chemical technology, New York: Wiley, 8(2), 145-178.
- Osawa, Z. (1988). Role of metals and metal-deactivators in polymer degradation. *Journal of Applied Science*. 4(2), 134-145.

- Palmer, J. and Walls,. (2002). Photo-biodegradable Plastics: Their Role in the Protection of the Environment. *Polymer Degradation and Stability*.Vol.29.Page 234-245.
- Pichini, S., Pellegrini, M., Gareri, J., Koren, G., Garcia-Algar, O., Vall, O., et al. (2008). Liquid chromatography–tandem mass spectrometry for fatty acid ethyl esters in meconium: Assessment of prenatal exposure to alcohol in two European cohorts. *Journal of Pharmaceutical and Biomedical Analysis*, 48(3), 927-933.
- Premalal, H. G. B., Ismail, H., and Baharin, A. (2002). Comparison of the mechanical properties of rice husk powder filled polypropylene composites with talc. *Journal of Polymer Science*.3(2),145-150.
- Pushpadess, Demarteau, W. and Enday.(2010).Photodegradation of polyethylene: comparison of various photoinitiators in natural weathering conditions. *Polymer Degradation and Stability* 1992;37:233e45.
- Rabek JF, editor. (1995) Polymer photodegradation. *London: Chapman & Hall*; 1995.3(2),68-78.
- Rabek, J. F., and Rånby, B. (1974). Studies on the photooxidation mechanism of polymers. II. The role of quinones as sensitizers in the photooxidative degradation of polystyrene. *Journal of Polymer Science: Polymer Chemistry Edition*, 12(2), 295-306.
- Randall, S., Harper, D., and Brierley, B. (1999). Ecological and ecophysiological impacts of ferric dosing in reservoirs. *Hydrobiologia*, 395-396(0), 355-364.
- Ren, X. (2003). Biodegradable plastics: a solution or a challenge?.*Journal of Cleaner Production*, 11(1), 27-40.
- Ren,D. (2003). Distribution kinetics for temperature programmed pyrolysis. *Industrial Engineering Chemical Research*, 38, 4531–4537.
- Richardson, K and Savill. (1977). Weather Induced Degradation of Linear Low Density Polyethylene (LLDPE): Mechanical Properties. *Journal of Polymer Engineering*.Page 87-90.
- Robertson, H. (2006). Experiments in Polymer Science. *New York: Wiley-Interscience Publication*,3(2), 305-314.
- Rogers, R. D., Bond, A. H., Bauer, C. B., Zhang, J., and Griffin, S. T. (1996). Metal ion separations in polyethylene glycol-based aqueous biphasic systems: correlation of partitioning behavior with available

- thermodynamic hydration data. *Journal of Chromatography B: Biomedical Sciences and Applications*,6(2),678-679.
- Ross, S., and Evans, D. (2003). The environmental effect of reusing and recycling.*Journal of Applied Science*.3(2),1245-1256.
- Roy, P.K., (2008).Rheological PS Melts Filled with Grafted and Ungrafted Glass Beads. *Journal of Applied Polymer Science*.57(4), 499-508.
- Roy, P.K., Titus, P. Surekha, E. Tulsi, C. Deshmukh, C. Rajagopal (2008). Degradation of abiotically aged LDPE films containing pro-oxidant by bacterial consortium. *Polymer Degradation and Stability*, 93, 1917-1922.
- Roy, Surekha P, Rajagopal C, Chatterjee SN, Choudhary V. (2005).Effect of benzil and cobalt stearate on the aging of LDPE films. *Polymer Degradation and Stability*, 58(2),456-567.
- Roy, Surekha P, Rajagopal C, Choudhary V. (2006) Effect of cobalt carboxylates on the photo-oxidative degradation of low-density polyethylene.Part I. *Polymer Degradation and Stability*, 4(3),45-56.
- Roy,John,K and Lynn. (2007) . Photo-initiated oxidation of polyethylene effect of photosensitisers. *European Polymer Journal*,7(2),67-89.
- Roy.(2007).Thermal Degradation and Oxidative Processes. *In Degradation and stabilization of Polymer*.*Journal of Applied Science Publishers, London*, 82–83.
- Schlemmer, D., Angélica, R. S., and Sales, M. J. A. (2010). Morphological and thermomechanical characterization of thermoplastic starch/montmorillonite nanocomposites. *Composite Structures*, 92(9), 2066-2070.
- Scott .(1990). Importance of weathering factors other than UV radiation and temperature in outdoor exposure. *Polymer Degradation and Stability*, 5(4),56-78.
- Sen, M. and Basfar, A (1998). The effect of UV light on the thermooxidative stability of linear low density polyethylene films crosslinked by ionizing.*Journal of Applied Science*.67,56-89.
- Setnescu, Wang H., Tao X. and Newton E.(1998).Thermal degradation kinetics and lifetime prediction of a luminescent conducting polymer. *Polymer International*, 53, 20–26.



- Shamrevskaya.(1973).Degradation Profile of Polyethylene After Artificial Accelerated Weathering. *Polymer Degradation and Stability*.6(2),Page 456-467.
- Sinclair, B., (2010). Study on the Degradation of LDPE in the Presence of Cobalt Stearate and Benzil. *Journal of Applied Polymer Science*.2(1),Page 99-128.
- Sivalingam, G., Agarwal, N., and Madras, G. (2003). Kinetics of microwave-assisted oxidative degradation of polystyrene in solution. *AIChE Journal*, 49(7), 1821-1826.
- Srivastava. (2011). Harmonizing Food Packaging Regulations: An American and European Dilemma, *47 FOOD & DRUG LJ* 579.
- Stammer, D., Wunsch, C., Giering, R., Eckert, C., Heimbach, P.and Marotzke, J.(2003). Volume, heat, and freshwater transports of the global ocean circulation 1993&#8211;2000, estimated from a general circulation model constrained .*World Ocean Circulation Experiment (WOCE) data. J. Geophys. Res.*, 108(C1), 3007.
- Stankowski, M., Kropidłowska, A., Gazda, M., and Haponiuk, J. (2008). Properties of polyamide 6 and thermoplastic polyurethane blends containing modified montmorillonites. *Journal of Thermal Analysis and Calorimetry*, 94(3), 817-823.
- Taylor, G. E. (1978). Plant and Leaf Resist to Air Pollution. *New Phytologist*, 80(3), 523-534.
- Taylor, Kabamba MS. (1976). Photooxidation of polymers: Part-X:-The photooxidation of an ethyleneepropylene copolymer initiated by benzophenone. *Polymer Degradation and Stability*, 8(4),67-78.
- Taylor, Tibor, K. and Don, H.(1976). Polymer Degradation. *Polymer Degradation and Stability*, 6(5),189-200.
- Taylor,G., (1977). Plant and Leaf Resistance to Gaseous Air Pollution Stress. *New Phytologist*, 80(3), 523-534.
- Taylor. H. and Tobias J., (1997).Plastic Additives and Modifiers.*New York: van Nostrand Reinhold*.5(3),152-156.
- Vlieger,J., (2005).Plasctic Additives Handbook. *Munich:Hanser Publisher*.4(2),45-56.
- Ward,E., Yoon, K. and Fang. (2006). Degradable polymersprinciples & applications. *London: Chapman & Hall*,6(7),567-578.

- Wegner, J., and Patat, F. (1970). Thermal degradation of polystyrene. *Journal of Polymer Science Part C: Polymer Symposia*, 31(1), 121-135.
- White, B., Schmidt, M., Murphy, C., Livingstone, W., O'Toole, D. and Lawler, M., . (2000). Activated protein C inhibits lipopolysaccharide-induced nuclear translocation of nuclear factor  $\kappa$ B (NF- $\kappa$ B) and tumour necrosis factor  $\alpha$  (TNF- $\alpha$ ) production in the THP-1 monocytic cell line. *British Journal of Haematology*, 110(1), 130-134.
- Wingenfeld, L., Freislederer, A., Schulze-Bahr, E., Paul, M., and Bajanowski, T. (2007). Life-threatening hobbies in the youth?: Two autoptic cases suggesting arrhythmogenic right ventricular cardiomyopathy. *Forensic Science International*, 171(1), 89-98.
- Wrzyszczyński, A., Qu, X., Szosland, L., Adamczak, E., Lindén, L. Å., and Rabek, J. F. (1995). Blends of poly(ethylene oxide) with chitosane acetate salt and with dibutylchitin: Structure and morphology. *Polymer Bulletin*, 34(4), 493-500.
- Wunch. (2000). Chemical and Physical Modifications of Alternating Ethyleneecarbon Monoxide Copolymer by Outdoor Exposure. *Polymer Journal*.42(3),56-67.
- [www.baerlocheradditives.com](http://www.baerlocheradditives.com), retrieving date 3<sup>rd</sup> March, 2012.
- [www.cmaiglobal.com/styrene](http://www.cmaiglobal.com/styrene),retrieving date 4<sup>th</sup> March, 2012.
- [www.polystyreneproperties.com](http://www.polystyreneproperties.com), retrieving date 2<sup>nd</sup> October 2011.