DECLARATION

I hereby declare that the thesis entitled ***"Photodegradation of Polystyrene by Nano Titanium dioxide and Photosensitzers"****, submitted to the University of Calicut in partial fulfillment of the requirement for the award of the Degree of Doctor of Philosophy in Chemistry is a bonafied research work done by me under the supervisions of* ***Dr. Sunil Jose T****, Assistant Professor, Research and Post graduate Department of Chemistry, St.Thomas' College (Autonomous), Thrissur and* ***Dr. Rajesh C****, Assistant Professor, Department of Chemistry, MES Keveeyam College, Valanchery.*

I also declare that the material presented in this thesis is original and does not form the basis for the award of any other degree, diploma or other similar titles of any other university.

Date: 07.12.2020

DINOOP LAL S

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With heartfelt gratitude

DINOOP LAL S

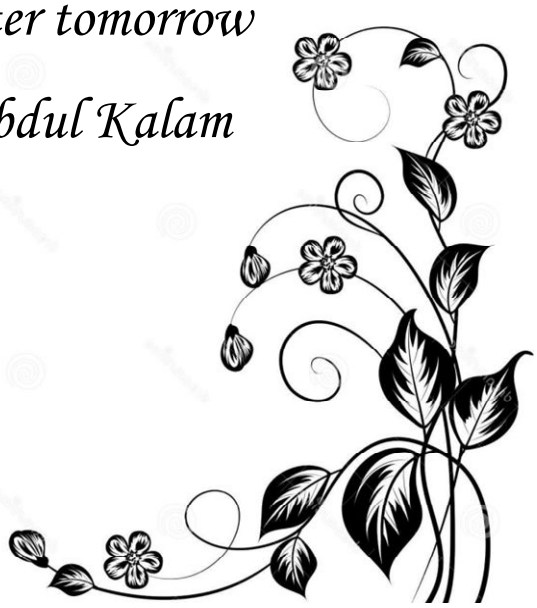
Dedicated to

Our Environment

Celebrating the 100th anniversary of polymer science, let the humanity be more concerned about the potential threats posed by the plastic debris to our environment along with the innovative techniques for the development of future polymer technology.

Let us sacrifice our today so that our children can have a better tomorrow

- A.P.J. Abdul Kalam



Preface

The increasing demand of plastic commodities resulted in their mass production worldwide. The accumulation of the used and thrown away plastics over land and water bodies has contributed to plastic pollution. The past few decades witnessed a steep increase in the total quantity of plastic debris that has affected the eco system badly. Photo degradation is considered as an ecofriendly and cheap method that could be employed for the demolition of such plastic debris. The disadvantage of photo degradation is that, it is a slow process. Application of suitable methods to accelerate the photodegradation process is our research problem. Photodegradation can be enhanced in the presence of photocatalysts. The entire thesis reports the studies conducted in order to accelerate the rate of photodegradation of polystyrene (PS) using different photocatalysts, under controlled ultraviolet (UV) radiation. The mechanical, electrical and thermal properties of the PS-photocatalyst composites are also studied. Nano TiO_2 has been chosen as the core photocatalyst for the degradation of PS considering its efficiency, non-toxicity, photostability, low cost and ease for synthesis. The full-fledged photocatalytic efficiency could not be exhibited by this semiconductor metal oxide due to its faster charge recombination. Modification of TiO_2 using suitable photosensitizers can alter its surface chemistry, resulting in better charge separation, thereby improving its photocatalytic efficiency. In addition to Nano TiO_2, we have also studied the photocatalytic efficiency of ZnO and modified ZnO for the degradation of PS under UV radiation.

The thesis as a whole is divided into eight chapters. A general introduction along with the literature review of PS chemistry, TiO_2, surface modified TiO_2 and ZnO are discussed in chapter 1.

The preparation of PS and PS-photocatalyst composite specimens for their photodegradation studies is explained in chapter 2. PS and PS composite sheets prepared by solvent casting methods were subjected to controlled UV irradiation using a UV tube of power 30 W, emitting UV radiation of wavelength 253 nm. All the specimens were irradiated for a total time period of 1000 hours and monitored at regular intervals of 200 hours, using various analysis techniques. The monitoring techniques included gel permeation chromatography, FTIR and UV spectroscopies, SEM, weight loss measurements etc. Specimens were also moulded for the

determination of electrical and mechanical studies as per ISO standards and these specimens were also subjected to UV irradiation. Electrical properties studied include the break down voltage (BDV) and dielectric constant. The mechanical properties included measurement of tensile and flexural strength. Thermo gravimetric analysis (TGA) of the specimens was also conducted. All these studies were conducted for the non-irradiated as well as UV irradiated PS-composite specimens.

The synthesis and characterization of TiO_2 and ZnO photocatalysts are described in chapter 3. Nano TiO_2 has been synthesized by sonication assisted sol-gel technique. ZnO has been synthesized by three different methods- sonication assisted precipitation, hydrothermal method with uncontrolled hydrolysis and hydrothermal method with controlled hydrolysis. ZnO nanospheres obtained via hydrothermal method with controlled hydrolysis were used as photocatalyst. A comparison of photodegradation of PS in the absence and presence of TiO_2 and ZnO photocatalysts were studied under UV radiation. A possible mechanism was proposed for the UV initiated photodegradation of PS in the presence and absence of TiO_2 and ZnO.

Chapter 4 describes the study of photodegradation of PS in the presence of TiO_2 and ZnO modified by graphene oxide (GO) photocatalyst. The synthesis and characterisation of GO by modified Hummer's method and the preparation of GO-modified TiO_2 and ZnO by sonication assisted hydrothermal method are discussed. Different sets of TiO_2-GO and ZnO-GO composites were prepared with varying percentages of GO. The interaction of GO with TiO_2 or ZnO is investigated. All these photocatalysts were loaded into the PS matrix whose photodegradation was studied.

Chapter 5 deals with the study of photodegradation of PS using polyaniline (PANI) modified TiO_2 and ZnO as photocatalysts. Polyaniline has been synthesised by chemical oxidative polymerization. TiO_2-PANI as well as ZnO-PANI composites were also developed by chemical oxidative polymerization method where insitu polymerization of aniline was done over the surface of dispersed TiO_2 or ZnO particles. The mole percentage of aniline was varied in order to obtain TiO_2-PANI/ ZnO-PANI composites of different composition. The interaction between TiO_2/ZnO with PANI is also investigated.

The role of a few benzophenone derivatives and tryphenylmethane dyes as photosensitizers for the degradation of PS is discussed in chapter 6. The benzophenone derivatives chosen as photosensitizers were 4-methoxybenzophenone 2-hydroxy-4-methoxybenzophenone, 2-chlorobenzophenone, 4-nitrobenzophenone and benzophenone itself. The dye photosensitizers included malachite green and methyl blue. Photodegradation of PS was studied by loading these photosensitizers directly or in coupled state with nano TiO_2. The mechanism of photodegradation of PS in the presence of these photocatalysts is discussed.

Photodegradation of PS catalysed by metal doped TiO_2 is discussed in chapter 7. TiO_2 was doped with Cu, Fe and Ag separately. The mole percentage of the dopant metal used was varied in order to obtain TiO_2-metal photocatalysts of varying composition. The phase change occurred in TiO_2 a result of increasing metal percentages is discussed. The mechanism of improved photocatalytic efficiency of metal doped TiO_2, for the photodegradation of PS is also discussed.

The entire work is summarised in chapter 8. The possible application of PS-composites that depends on the type of photocatalysts loaded is discussed. The significance of the work along with its environmental friendliness and future scope is also discussed.

Abbreviations

PS	Polystyrene
UV	Ultraviolet
GPC	Gel permeation chromatography
UV-DRS	UV-visible diffused reflectance spectroscopy
BDV	Breakdown voltage
PANI	Polyaniline
GO	Graphene oxide
BP	Benzophenone
2HO4MOBP	2-hydroxy-4-methoxybenzophenone
4MOBP	4-methoxybenzophenone
2ClBP	2-chlorobenzophenone
4NBP	4-nitrobenzophenone
MG	Malachite green
MB	Methyl blue

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