



**Radiation Vulcanization of Polymeric Blends Based
on Ethylene Propylene Diene Monomer Rubber/
Waste Materials in Presence of Different Additives**

**Thesis
Submitted to**

**Girls College for Arts, Science & Education
Ain Shams University
(Cairo)**

**For
The Degree of Doctor of Philosophy
In Chemistry
(Physical Chemistry)**

**By
RANIA MOUNIR MOHAMED
(B.Sc. 2005)
(M.Sc. 2011)**

**National Center for Radiation
Research and Technology,
Atomic Energy Authority
2015**

**“Radiation Vulcanization of Polymeric Blends Based on
Ethylene Propylene Diene Monomer Rubber/ Waste
Materials in Presence of Different Additives”**

Thesis Submitted to: Girls College for Arts, Science and Education
Ain Shams University

**In the partial fulfillment for: the Degree of Doctor of Philosophy
in Chemistry**

Submitted by
RANIA MOUNIR MOHAMED

Thesis Supervisors:

Prof. Dr. Abo El Khair B. Mostafa

Prof. of Physical Chemistry,
Chemistry Department
Girls College for Arts, Science and Education
Ain Shams University.

Approved

.....

Prof. Dr. Ahmed A. EL Miligy

Radiation Chemistry Department,
National Center for Radiation Research and Technology.

.....

Prof. Dr. Magda M. Abou Zeid

Radiation Chemistry Department,
National Center for Radiation Research and Technology.

.....

Prof. Dr. Nawal A. Shaltout

Radiation Chemistry Department,
National Center for Radiation Research and Technology.

.....

Ass. Prof. Dr. Maysa A. Mohamed

Radiation Chemistry Department,
National Center for Radiation Research and Technology.

.....

**Head of Chemistry Department
Prof. Dr.**

Date of Examination: / /



Ain Shams University
Girls College for Arts,
Science and Education
Chemistry Department

QUALIFICATION

Student Name : Rania Mounir Mohamed

Scientific Degree : Ph.D.

Department : Chemistry Department

Name of Faculty : Girls College for Arts, Science
And Education

University : Ain Shams University

B.Sc. Graduation Date : May 2005

M.Sc. Graduation Date : July 2011

ACKNOWLEDGEMENT

I am deeply thankful to **Allah**, by the grace of whom the progress and success of this work was possible.

I am especially thankful and grateful to **Prof. Dr. Abo El Khair B. Moustafa**, Prof. of Physical Chemistry, Girls College for Arts, Science & Education, Ain Shams University, for his capable supervision and encouragement.

My deep appreciation goes to **Prof. Dr. Ahmed A. El Miligy**, professor of Radiation Chemistry, National Center for Radiation Research and Technology for his constant help and guidance throughout the course of this work. Continuous supervision that made this work possible.

Deepest gratitude is owed to **Prof Dr. Magda M. Abou Zeid, Professor** of Radiation Chemistry, and National Center for Radiation Research and Technology, for her useful comments and continuous help during the research.

Thanks are also due to **Prof Dr. Nawal A. Shaltout**, Radiation Chemistry, and National Center for Radiation Research and Technology, for suggesting the topic of this work, her sincere guidance, encouragement and continuous supervision that made this work possible.

Thanks are also due to **Ass. Prof Dr. Maysa A. Mohamed**, National Center for Radiation Research and Technology, for her useful comments and continuous help during the research.

I would like also to place on record my great appreciation to all my colleagues who helped me throughout this work.

Acknowledgement is due to National Center for Radiation Research and Technology for offering facilities and support to carrying out this research work.

AIM OF THE WORK

Blending of polymeric materials has proved to be a successful method for preparing new polymeric materials having not only the main properties of the blend components but also new modification as well as specific ones. Hence, the blending technique becomes a desirable one and of commercial interest. Rubbers as polymeric materials are usually solid and therefore the method of mechanical blending has been found to be the most suitable one for preparing blends of rubbers.

Recycling of waste materials (Rice Husk and Ground Tire Rubber) as technique for solving their environmental pollution and using them in various industrial applications, has shown to be an appreciable one.

Ionizing radiation offers possibilities for the process of recycling waste polymers, due to its ability to cause cross-linking and or scission to a wide range of polymeric materials.

This work aims at studying the effect of gamma radiation on polymeric blends based on ethylene propylene diene monomer (EPDM) rubber to produce stable polymeric blends. These blends (EPDM/NBR) are filled at first with waste materials such as rice husk (RH) or ground tire rubber (GTR) as an additive. Different properties of prepared filled blends are followed up, specifically, mechanical, physical, thermal and morphological ones. Improvement of these properties is then aimed by adding together materials of different functional characters such as maleic anhydride (MAH) as a compatibilizer, HAF-carbon black or Hisil as a reinforcing filler and N,N-methylene diacrylamide (MDA) as enhancing polyfunctional monomer.

ABSTRACT

In this investigation, the mechanical blending technique was applied for preparation of elastomeric blend of ethylene propylene diene monomer rubber (EPDM) and nitrile butadiene rubber (NBR) having a fixed ratio of (50/50) by weight. The prepared blend of EPDM/NBR (50/50) was used as a rubber matrix to be loaded with waste materials, namely rice husk (RH) as a natural waste filler and then with ground tire rubber (GTR) as an artificial one. The degree of loading varied from 5 phr to 20 phr. Ionizing radiation, namely, gamma rays were applied for inducing vulcanization of prepared and loaded rubber blends, in the range from 5 kGy to 250 kGy. Different properties of prepared composites were followed up as a function of degree of loading with the waste material and dose of irradiation.

The mechanical properties, namely tensile strength and elongation at break percent of the composites slightly decreased as the filler loading increased over the whole range of irradiation. Tensile modulus and hardness, on the other hand, showed an opposite trend, i.e. the increased. Other properties, namely physical, thermal and morphological confirmed the mechanical ones. Obtained results were affiliated with lack of interface adhesion between the waste materials and the rubber matrix elastomers.

The lack of interface adhesion was improved by filling the composite with a limited content, up to 7 phr, of the compatibilizer, namely, maleic anhydride (MAH). Measurements of different properties was carried out for composite loaded with 10 phr of waste material.

It has been found that the tensile properties were significantly improved with addition of the compatibilizing agent.

Further and significant improvement was attained in properties of prepared later composite by its loading with 40 phr of either HAF-carbon black or Hisil as reinforcing fillers that participates in chemical as well as physical bonding.

Similarly and lastly 8 phr of N, N- methylene diacrylamide (MDA) were loaded as an enhancing polyfunctional monomer, i.e. co-agent Properties obtained showed further improvement due to its participation in gel formation.

CONTENTS

page

CHAPTER I INTRODUCTION

| | | |
|--------|-------------------------------------------------------------|----|
| 1.1. | Classification of polymer blends | 2 |
| 1.1.1. | Elastomer-elastomer blends | 2 |
| 1.1.2. | Elastomer –thermoplastic blends | 3 |
| 1.1.3. | Thermoplastic –thermoplastic blends | 4 |
| 1.2. | Effect of radiations on polymeric materials | 5 |
| 1.2.1. | Sources of radiation | 5 |
| 1.2.2. | Chemical changes of irradiated polymers | 6 |
| 1.2.3. | Cross -linking and degradation | 7 |
| 1.2.4. | Mechanism of radiation reaction | 9 |
| 1.3. | Vulcanization | 11 |
| 1.3.1. | Radiation vulcanization of rubber | 12 |
| 1.3.2. | Other vulcanization methods | 13 |
| 1.4. | Rubber blends vulcanization in presence of additives | 16 |
| 1.4.1. | Fillers | 16 |
| 1.4.2. | Promoters (co -agents) | 19 |
| 1.5. | Properties of EPDM and NBR | 20 |
| 1.5.1. | Ethylene propylene diene monomer (EPDM) | 20 |
| 1.5.2. | Nitrile butadiene rubber (NBR) | 20 |
| 1.6. | Rubber blending | 21 |
| 1.7. | Radiation curing of EPDM/NBR blends. | 22 |
| 1.8. | Rice Husk as natural waste fiber | 22 |

| | | |
|--------|-----------------------------------------------------------------------------|----|
| 1.8.1. | Chemical constituent, structure and properties of raw Rice Husks(RH) | 22 |
| 1.8.2. | Adhesion behavior between elastomers and RH components: | 26 |
| 1.9. | Polymeric waste | 28 |
| 1.9.1. | Waste rubber as landfills | 29 |
| 1.9.2. | Recycled of waste rubber | 29 |
| 1.10. | Applications of recycled/reclaimed rubbers | 30 |
| 1.11. | Effect of gamma radiation on waste rubber | 30 |
| 1.12. | Adhesion behavior between elastomers and GTR components: | 31 |

CHAPTER II

LITERATURE REVIEW

| | | |
|--------|---------------------------------------------------------------------------------------------------|----|
| 2.1. | Classification of polymer blends: | 34 |
| 2.1.1. | Elastomer /elastomer compound | 34 |
| 2.1.2. | Elastomer /thermoplastic compound | 35 |
| 2.1.3. | Thermoplastic-thermoplastic compounds | 37 |
| 2.2. | Blending of Rice husk with virgin polymer | 38 |
| 2.3. | Effect of addition of compatibilizing agents on elastomer/rice husk (RH) composites | 40 |
| 2. 4. | Effect of filler on elastomer /rice husk (RH) composites | 45 |
| 2.5. | Effect of polyfunctional monomer on elastomer/ rice husk (RH) composite | 48 |
| 2.6. | Blending of waste rubber with virgin polymer: | 48 |
| 2.7. | Effect of addition of compatibilizing agents on waste rubber blending with virgin polymer: | 53 |
| 2. 8. | Effect of filler on elastomers /GTR composites | 57 |

| | | |
|------|--------------------------------------------------------------------------|----|
| 2.9. | Effect of polyfunctional monomer on elastomer/ with GTR composite | 59 |
|------|--------------------------------------------------------------------------|----|

CHAPTER III EXPERIMENTAL

| | | |
|----------|---------------------------------------------------------------------------|----|
| 3.1. | Materials | 60 |
| 3.1.1. | Raw rubber | 60 |
| 3.1.2. | Waste materials | 61 |
| 3.1.3. | Additives | 62 |
| 3.2. | Techniques | 64 |
| 3.2.1. | Preparation of samples | 64 |
| 3.2.2. | Irradiation procedure | 65 |
| 3.3. | Measurements | 66 |
| 3.3.1. | Mechanical measurements | 66 |
| 3.3.1.1. | Tensile strength (TS) | 66 |
| 3.3.1.2. | Tensile modulus at 100 % ($M_{100\%}$) | 66 |
| 3.3.1.3. | Elongation at break % ($E_b\%$) | 67 |
| 3.3.1.4. | Hardness | 67 |
| 3.3.2. | Physical Measurements | 67 |
| 3.3.2.1. | Detremination of gel fraction | 67 |
| 3.3.2. | Detremination of swelling number | 68 |
| 3.3.2.3. | Water absorption % | 68 |
| 3.3.2. | Determining of cross-linking density by the Charlesby- Pinner equation | 69 |
| 3.3.3. | Thermal measurement | 70 |
| 3.3.4. | Structure morphology by SEM | 70 |

CHAPTER IV
RESULTS AND DISCUSSIONS
PART ONE

Section 1: Effect of gamma irradiation on the properties of EPDM/NBR (50/50) blend and its composites with different concentrations of rice husk (RH): 71

| | | |
|----------|-----------------------------|----|
| 4.1.1.1. | Mechanical properties | 73 |
| 4.1.1.2. | Physical measurements | 83 |
| 4.1.1.3. | Structure morphology by SEM | 94 |
| 4.1.1.4. | Thermal measurement | 96 |

Section2: Effect of gamma irradiation on the properties of EPDM/NBR (50/50) and filled with 10phr of RH and loaded with different concentrations of Maleic Anhydride (MAH): 108

| | | |
|----------|-----------------------------|-----|
| 4.1.2.1. | Mechanical properties | 109 |
| 4.1.2.2. | Physical Measurements | 121 |
| 4.1.2.3. | Structure morphology by SEM | 132 |
| 4.1.2.4. | Thermal measurement | 134 |

Section3: Effect of gamma irradiation on the properties of EPDM/NBR (50/50) filled with 10phr of RH loaded with 7phr of MAH and loaded with constant concentration (40phr) of Different filler: (HAF-carbon black (N330) and Hisil): 141

| | | |
|----------|-----------------------------|-----|
| 4.1.3.1. | Mechanical properties | 142 |
| 4.1.3.2. | Physical Measurements | 154 |
| 4.1.3.3. | Structure morphology by SEM | 164 |

Section4: Radiation vulcanization of EPDM/NBR (50/50) blend filled with 10phr of RH, loaded with 7phr of MAH, reinforced with 40 phr HAF carbon black and enhanced with 8 phr of MDA as polyfunctional monomer: 167

| | | |
|----------|-----------------------------|-----|
| 4.1.4.1. | Mechanical properties | 168 |
| 4.1.4.2. | Physical measurements | 177 |
| 4.1.4.3. | Structure morphology by SEM | 186 |

PART TWO

Section1: Gamma irradiation induced vulcanization of EPDM/NBR (50/50) blend and its composites with different concentrations of ground tire rubber (GTR): 188

| | | |
|----------|-----------------------------|-----|
| 4.2.1.1. | Mechanical properties | 189 |
| 4.2.1.2. | Physical measurements | 198 |
| 4.2.1.3. | Structure morphology by SEM | 205 |
| 4.2.1.4 | Thermal measurement | 207 |

Section2: Effect of gamma irradiation on the properties of EPDM/NBR (50/50) blend and its composites with 10phr of GTR (ground tire rubber) and different concentrations of maleic anhydride (MAH)): 218

| | | |
|----------|-----------------------------|-----|
| 4.2.2.1. | Mechanical properties | 219 |
| 4.2.2.2. | Physical measurements | 230 |
| 4.2.2.3. | Structure morphology by SEM | 237 |
| 4.2.2.4. | Thermal measurement | 239 |

Section 3 :Effect of gamma irradiation on the properties of EPDM/NBR (50/50) blend filled with 10phr of GTR, loaded with 7phr of MAH and loaded with constant concentration (40phr) of different fillers(HAF-carbon black N330 and Hisil): 245

| | | |
|---------|-----------------------|-----|
| 4.2.3.1 | Mechanical properties | 245 |
| 4.2.3.2 | Physical measurements | 256 |

| | | |
|---------|-----------------------------|-----|
| 4.2.3.3 | Structure morphology by SEM | 263 |
|---------|-----------------------------|-----|

Section 4: Radiation vulcanization of EPDM/NBR (50/50) blend filled with 10 phr of GTR, loaded with 7 phr of MAH reinforced with 40 phr HAF- carbon black and enhanced with 8 phr of MDA as a function of polyfunctional monomer:

| | | |
|---------|-----------------------------|-----|
| 4.2.4.1 | Mechanical properties | 266 |
| 4.2.4.2 | Physical measurements | 274 |
| 4.2.4.3 | Structure morphology by SEM | 279 |

| | |
|-------------------------------|-----|
| SUMMARY AND CONCLUSION | 281 |
|-------------------------------|-----|

| | |
|-------------------|-----|
| REFERENCES | 292 |
|-------------------|-----|

LIST OF TABLES

Page

- Table(1):** the values of (p_0/q_0) and $(1/q_0U)$ of EPDM/NBR (50/50) blend and its composites with different concentrations of RH 93
- Table(2):** Weight loss % at different decomposition temperature for EPDM/NBR (50/50) blend and its composition with different concentrations of Rice Husk for unirradiated and irradiation dose at 150 kGy respectively. 103
- Table(3):** The temperature for different percentage of weight losses of EPDM/NBR (50/50) loaded with 10 phr of RH composites at different irradiation dose up to 250kGy. 107
- Table(4):** The values of (p_0/q_0) and $((1/q_0U)$ of composites filled 10 phr RH, and later composite loaded with different concentrations of MAH 131
- Table(5):** Corresponding decomposition temperatures for different weight losses% of EPDM/NBR (50/50) blend filled with 10 phr RH as well as its composition loaded with 7 phr of maleic anhydride for unirradiated composites. 137